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Recycling Feldspar Mining Waste as Buffering Agent for Acid Mine Drainage Mitigation

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Abstract: Acid mine drainage (AMD) prevention or remediation is a major issue of the environmental management of sulfide-bearing active and abandoned mining sites, the main sources of acidic waters being wastes and tailings. The present work intends to check a circular economy approach to such issues in the mining region of Sardinia, where environmental pollution, due to AMD, is a major concern. Tests were conducted on basic drainage-producing feldspar mining wastes that could be recycled as buffering agents of sulfide-bearing tailings. Among the sulfide-bearing abandoned mining sites investigated, Furtei epithermal gold deposit tailings are the most polluting and those that can better test the buffering agent efficacy. Buffering test results show that buffering to near-neutral conditions can be attained following steps similar to those of pure calcite buffer. The buffering potential of the recycled waste is due to both the buffer calcite content, which provides short-term buffering, enhanced by feldspar content that can provide long-term buffering. Buffered waters show a dramatic decrease in the concentration of most of the metals present in the leachate, down to conditions that meet the requirements for the discharge of industrial waters according to Italian legislation.

Keywords: acid mine drainage; buffering; feldspar; Sardinia

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Citation: Grieco, G.; Cocomazzi, G.; Naitza, S.; Bussolesi, M.; Deidda, M.L.; Ferrari, E.S.; Destefanis, E. Recycling Feldspar Mining Waste as Buffering Agent for Acid Mine Drainage Mitigation. *Minerals* **2024**, *14*, 552. https://doi.org/10.3390/min14060552

Academic Editor: Manuel Jesús Gázquez

Received: 18 April 2024
Revised: 14 May 2024
Accepted: 23 May 2024
Published: 27 May 2024

1. Introduction

The exploitation of metal deposits has always produced a large number of discards as a result of extraction (wastes) and beneficiation (tailings). Wastes and tailings are the main source of pollution as the materials stored therein can easily release pollutants to the surrounding environment when they interact with atmospheric agents, like surfaces and ground waters. The environmental hazard is highly increased in abandoned mining sites where the waste material was disposed of with less environmental hazard, reducing precautions due to deficiencies in environmental legislation. Moreover, the maintenance of the abandoned sites is often lacking, resulting in the progressive degradation of the facilities implemented for the reduction of the hazard.

The release of pollutants in the environment is highly enhanced in mines where a sulfide-rich ore has been exploited as sulfides react with waters they come in contact with, generating acid mine drainage (AMD) [1–4]. Potentially Toxic Elements (PTE), which are present in high concentrations in sulfide-rich waste materials, are released in high amounts in acidic waters. Finally, as PTE generally increases their solubility with an increase in water acidity, AMD results in the release of highly acidic, PTE-rich, strongly pollutant waters, which can impact both ecosystems and humans [5–8].

AMD processes can be countered by a combination of chemico-physical and biological remediation procedures aimed at reducing acidity and removing contaminants. In wastes and tailings, acidity reduction is mainly reached via chemico-physical procedures while bioremediation is fundamental in removing contaminants, enhancing the removal effect of water neutralization. The present study focuses on a specific procedure aimed to reduce AMD waters to near-neutrality via reaction with basic drainage-producing wastes. This procedure can be used in combination with other remediation practices to mitigate environmental risk at mining sites. Several minerals, when reacting with water, induce an increase in its pH, the most efficient being carbonates. Silicates can also have a buffering capacity but with a lower buffering rate compared to carbonates [9–13].

The most efficient buffering agents are highly basic chemicals such as lime, quicklime, or lye. The present study aims, in a circular economy approach, to investigate the use of mining waste as a buffering agent. The selected waste is a basic drainage-generating washing slime. This choice is related to the real possibility of using it as it is, with no further treatment that could strongly increase the costs of the operation. The results can have wide general interest, as several areas in the world present a close association of basic drainage-generating wastes and sulfide ore mining, where the former could be used as an amendment for the AMD processes.

Sardinia has been, for a long time, a major mining region, and its abundant mineral deposits offer the opportunity to investigate such a circular economy approach to the issue of mitigating environmental hazards by the neutralization of AMD-generating waste materials. Past and present mining activities in this region have produced a variety of wastes and tailings that can cause either basic or acid drainage. The basic drainage-yielding waste material investigated is a dewatered washing sludge dumped, in high amounts, at the feldspar mining site of Florinas, Sardinia, operated by the Italian company Maffei Sarda Silicati. The slime is the result of the de-sliming of the feldspar sands and is a fine-grained, feldspar-rich, carbonate-bearing material. The buffering potential of the feldspar slime for remediation of sulfide-rich wastes and tailings has been investigated in sulfide-rich samples from abandoned mines of Sardinia.

To assess the validity of the chosen approach, it is crucial to investigate both the optimal strategies for buffering acidic environments resulting from AMD as well as the pattern followed by PTEs during the leaching and precipitation processes. The evaluation of the durability and effectiveness over time of such interventions can contribute to the development of sustainable, long-term mitigation strategies.

2. Materials and Methods

Sardinia is the Italian region with the oldest and most important mining history, and the waste materials resulting from present and past mining activities are currently causing a variety of environmental problems [14]. Many of the exploited ores in the island were sulfide-rich, and the abandoned mine sites are now major sources of AMD. A variety of sulfide-rich waste materials from waste rock, tailings, and feed with heterogeneous mineralogy and chemistry were selected for sampling from different abandoned mines of Sardinia. After their minero-chemical characterization through XRD and XRF, a further selection was made. Selected mines Campo Pisano, Furtei, Seddas Moddizzis, and Montevecchio-Telle are all known to produce AMD and a related high environmental hazard. Coordinates of each sample site collection and the typology of the material are reported in Table 1.

Montevecchio-Telle is the pyrite-richest of the exploitation sites of the Montevecchio-Ingurtosu-Gennamari Pb-Zn-Ag mining district, one of the largest in SW Sardinia. Ore bodies are related to a large system of low-temperature quartz-carbonate-sulfide veins hosted in low-grade metamorphic slates and running around the late Variscan Arburèse granitoid pluton [15]. Ore minerals are mainly galena and sphalerite with a gangue of quartz with abundant siderite, ankerite, calcite, and baryte. The mineralization of the

Campo Pisano mine has been defined as SEDEX-type [16]. It is hosted in the dolostones of the basal part of the carbonate sequences of the lower Cambrian Gonnesa Formation. It is distinguished by its high pyrite content, with subordinate sphalerite, galena, and other sulfides in a carbonatic gangue.

Table 1. Location and typology of studied waste materials.

Sample	Mine and Useful Metals	Coordinates	Typology
TL1	Montevecchio-Telle Pb-Zn-Ag	39°32′13.20″ N 08°32′03.94″ E	Tailings
SM1	Seddas Moddizzis Zn	39°16′13.44″ N 08°29′ 26.40″ E	Tailings
CP1	Campo Pisano Pb-Zn	39°17′40.95″ N 08°32′13.64″ E	Waste rock
FS5	Furtei Au	39°32′2.30″ N 08°58′39.30″ E	Feed
FS8	Furtei Au	39°32′13.20″ N 08°32′3.94″ E	Tailings
FS11	Furtei Au	39°16′13.44″ N 08°29′26.40″ E	Tailings

The Seddas Moddizzis mine mainly exploited a supergene Zn-rich ore with a typical "calamine" association of smithsonite, hemimorphite, and hydrozincite, associated with secondary clay minerals and sulfates. The primary ore was a SEDEX-type pyrite-sphalerite-rich one, similar to Campo Pisano, hosted in the same dolostone-limestone lower Cambrian sequence.

The Furtei gold mine consisted of four main sites that exploited a high-sulfidation epithermal deposit [17] connected to the Cenozoic volcanic series of the "Monte Santu Miali Complex" (Upper Oligocene). The mineralization is hosted in andesitic rocks, with pervasive argillic alterations. It includes sulfides and Cu-sulfoarsenides (enargite, luzonite, digenite, chalcopyrite, covellite), tellurides, and Au-Ag. In some areas, sulfides such as pyrite and sphalerite are predominant.

Grain size distribution was determined through sieving with a standard column of eight sieves (4000, 2000, 1000, 500, 250, 125, 63, and 10 µm) and using between 200 and 800 g of material, depending on the grain size.

The evaluation of AMD potential in solid samples has been conducted according to the AMIRA procedure [18], a refinement of the Sobek method [19]. This process involves Acid–Base Account (ABA) tests, and static laboratory procedures aimed at determining the equilibrium between acid-generating and acid-neutralizing processes.

The Acid–Base Account (ABA) tests yield crucial parameters for assessment. The acid potential is quantified as the Maximum Potential Acidity (MPA), expressed in kg H_2SO_4/t, representing the estimated amount of acid released through the complete oxidation of sulfides. The AMIRA standard procedure assumes all sulfur exists as pyrite, potentially leading to an overestimation of AMD risk, particularly when other sulfides, with different acid generation potentials, are present. MPA was determined using total sulfur instead of sulfide sulfur due to the absence (or very low amount) of sulfates according to XRD results.

Conversely, the Acid Neutralizing Capacity (ANC) evaluates the sample buffering capacity, also expressed in kg H_2SO_4/t. The ANC is determined experimentally via titration, following a "fizz test" methodology described by Sobek et al. [19]. A negative ANC value indicates an incapacity for neutralization, reported as 0.00.

The difference between the MPA and ANC, termed the Net Acid-Producing Potential (NAPP), offers insight into the sample acid-generating potential, also expressed in kg H_2SO_4/t. Negative NAPP values suggest adequate ANC to counter acid generation, while positive values indicate potential acid generation.

Buffering tests were conducted on leached samples post-centrifugation (4000 rpm for 4 min using an Eppendorf Centrifuge 5702), following the methodology outlined by Hageman et al. [20].

To ensure that the metal ions precipitate in secondary phases, it is necessary that the neutralization reactions take place completely. For these reactions (the most common is the precipitation of hydroxides) the precipitation rate is rather slow. Therefore, it was decided to conduct preliminary tests, adding a small amount of buffering material by steps, encouraging a faster reaction with a stirrer and measuring the pH for each step. These tests involved incremental additions of 3, 5, or 10 mg into 50 mL solutions, with varying agitation times of 30 min for 3 mg/50 mL and 60 min for 5 and 10 mg/50 mL quantities. For the theoretical determination of the optimal amount of buffering material, see Cocomazzi et. al. [21].

The Synthetic Precipitation Leaching Procedure (SPLP) serves as a critical method outlined by the Environmental Protection Agency (EPA) to assess the potential impact of contaminated soils on groundwater quality [22]. The overarching purpose of SPLP is to simulate and evaluate the leaching behavior of contaminants from soil samples under conditions that mimic natural precipitation. Through this procedure, we can gain insights into the mobility and potential migration of pollutants from soil into groundwater systems. SPLP was used for the samples TL1, CP1, SM1, FS5, FS8, FS11, and FLS (Florinas sludges). The sample must be pulverized to below <1 mm. Then extraction fluid is added to the sample at a solid–liquid ratio of 1:20, for example, 15 g of sample and 300 mL of liquid. The extraction fluid consists of slightly acidified de-ionized water (pH = 5.5) that simulates natural precipitation. Once the fluid is added, the sample is positioned on an end-over-end rotary agitator for 18 h. At the end of this period, the solid is separated from the liquid with a centrifuge used for 3 min with a frequency of 66.66 Hz. Electrical conductance (µS), temperature, and pH of the leaching water obtained are measured and recorded.

Major element whole rock chemistry was determined at the University of Milano-Bicocca through a Panalytical Epsilon3XLE spectrometer. Data were processed with Omnian-standardless software version Epsilon 3x.

Ion concentrations on leaching water samples CP-1 and FS11 and FLS were analyzed using inductively coupled plasma-mass spectroscopy (ICP-MS) by the Romanian laboratory ALS Lab for Be, Cr, Mn, Co, Ni, Cu, Zn, As, Ag, Sb, Cd, Se, Tl, and Pb.

For a qualitative mineralogical analysis of precipitates via X-Ray Powder Diffraction (XRPD), after drying samples at 70 °C, a PANalytical X'Pert-pro (Malvern Panalytical, Worcestershire, UK) was used, at the following operating conditions: 40 kV of voltage; 40 mA of current; Cu anticathode Kα1/Kα2: 1.540510/1.544330 Å. The data were elaborated with the software X'Pert Highscore v.2.3.

3. Results

3.1. Characterization of the Buffering Material

The tested material is a dewatered washing sludge, resulting from the dedusting of feldspar sands mined by Maffei Sarda Silicati for the ceramic industry at Florinas Mine, Sardinia. The mined unit, known as Sabbie Superiori [23] and reported in the geologic maps as Florinas Formation [24], is a Miocenic alluvial to deltaic deposit dated to Serravallian [23]. The dominant lithology consists of coarse- to medium-sized sands poor in clay fraction, whose clasts are mostly feldspar and quartz. Up to 5 m thick calcarenite levels are locally interbedded within the sands. The sands are overlain by the Monte Santo Formation, mostly composed of calcarenites and calcirudites. The dewatered sludge is dumped in a 4000 m^2 tailings dump next to the mining area. Its average chemical composition, according to the accompanying certificate, is reported in Table 1.

The material was provided by the company in a sealed can and was characterized by XRF and XRD. Chemical analysis shows a composition very similar to that certified for Florinas sludges (FLS) with just a slightly lower Ca content, probably due to some variability in the carbonate content due to its presence in the ore body mostly as irregular layers (Table 2).

Table 2. Chemical composition, pH of leachate waters, and Neutralization Potential (NP) of FLS material. L.O.I. is loss of ignition.

	FLS Certificate (wt%)	FLS Analyzed (wt%)
SiO_2	58.6	57.27
TiO_2	0.06	0.08
Al_2O_3	17.8	20.73
Fe_2O_3	0.52	0.65
CaO	7.69	6.67
MgO	0.24	0.32
K_2O	3.52	2.84
Na_2O	0.34	0.38
MnO	N.A [1]	0.01
ZnO	N.A	0.01
L.O.I.	11.1	11.39
Tot	99.85	100.48
pH	-	8.85
ANC	-	149.30 kg/t

[1] Not Analyzed.

According to XRD analysis (Figure 1), the sample mineralogy is dominated by quartz, followed by calcite and plagioclase feldspar. According to the mineralogy of FLS, most of the Ca is hosted in calcite. The contribution of feldspar is very minor, as feldspar in the Sabbie Superiori unit sands is typically low in the anorthite component. The CaO content of feldspar is much lower than that of calcite, and the feldspar amount is lower than the calcite amount. According to CaO content, the calcite content can be estimated, attributing all the detected CaO to calcite, at 11.9 wt%. This is a maximum calcite content that cannot be much higher than the real content.

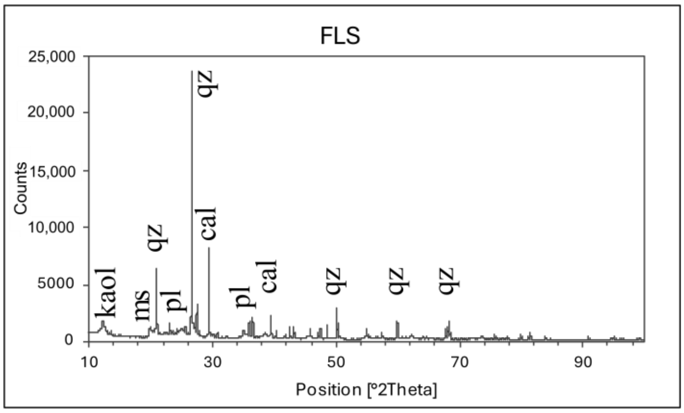

Figure 1. XRD pattern of the Florinas washing sludge FLS; kaol: kaolinite; ms: muscovite; qz: quartz; pl: plagioclase feldspar; cal: calcite.

The buffering potential of FLS, tested following Acid–Base Accounting (ABA) procedure, resulted in an Acid Neutralization Potential (ANC) (Table 2) of 149.30 kg/t.

An SPLP leaching test was conducted on FLS in order to assess its potential to release elements in the water, and the results are shown in Table 3.

FLS shows a strong basic drainage with a pH of the leachate waters of 8.85. The concentrations in the leachate waters reflect the mineralogy of the sample and the solubility of its minerals. High concentrations of Al, Na, and K are due to the dissolution of feldspar and high Ca to the dissolution of calcite; all other analyzed elements show low concentrations.

Table 3. Results of the leaching test on FLS; all values are in μg/L, bdl.

FLS—pH 8.85						
Be	Al	Cr	Mn	Fe	Co	Tl
0.64	9344	3.98	13.73	1150	0.37	bdl [1]
Ni	Cu	Zn	Cd	Sb	Pb	As
2.49	6.84	10.53	0.24	bdl	3.05	bdl
Ag	Na	K	Ca	Mg	Se	S
bdl	480	420	1260	50	bdl	27

[1] below detection limit.

3.2. *Characterization of Sulfide-Rich Mine Wastes and Tailings*

All studied sulfide-rich samples were characterized for grain size, major element, S, Pb, and Zn whole rock chemistry. Two of them, CP1 and FS11, were selected for trace element geochemistry and leaching and buffering tests.

3.2.1. Grain Size

The grain size of the full set of samples is reported in Table 4 and shown in Figure 2.

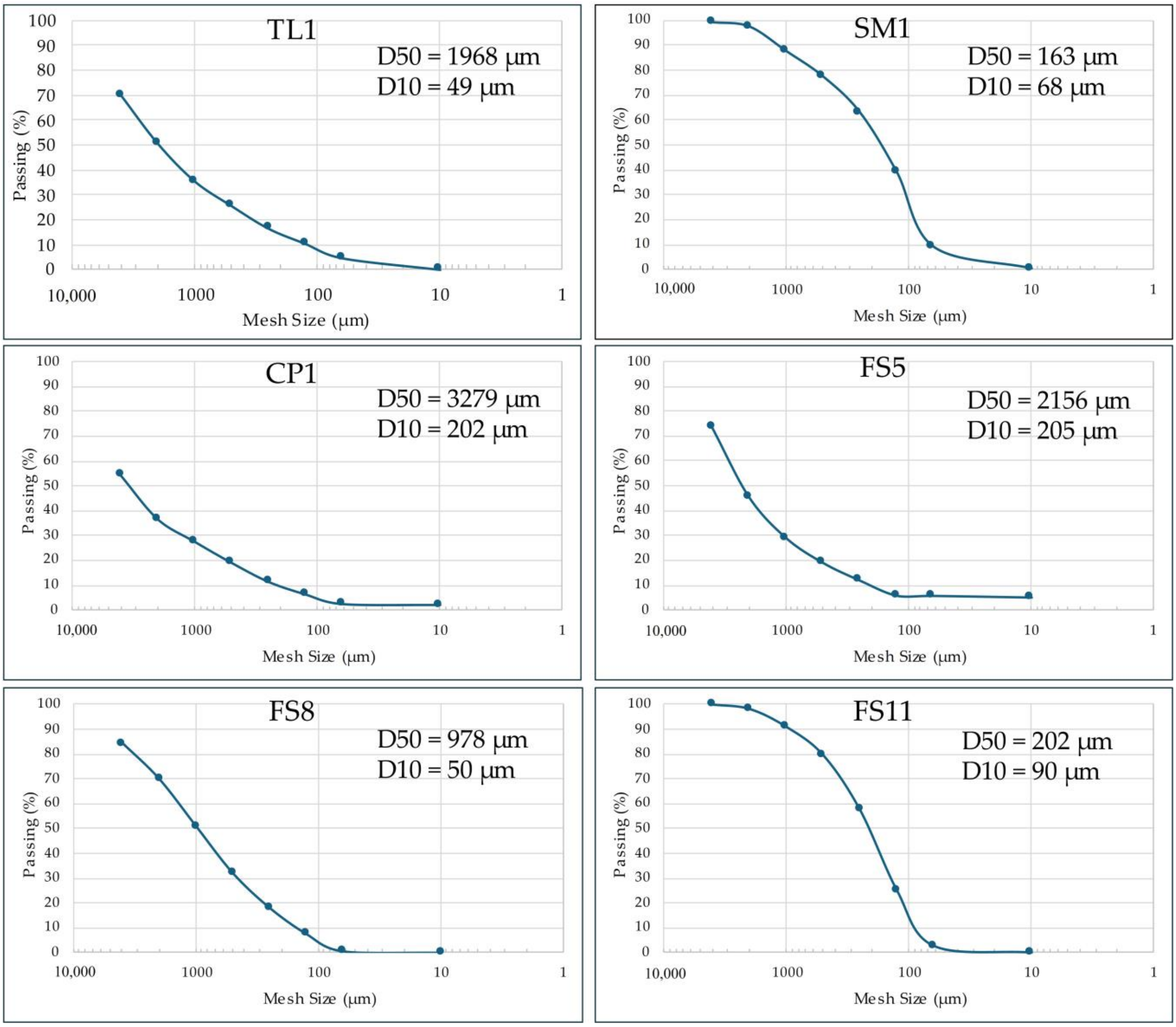

Figure 2. The grain size distribution of the full set of samples; D50 and D10 statistical parameters are also reported.

Table 4. The grain size of sulfur-rich materials; data in wt%.

Mesh Light (μm)	TL1	SM1	CP1	FS5	FS8	FS11
4000	29.86	0.93	45.68	26.27	15.69	0
2000	19.43	1.69	17.65	28.13	14.34	1.72
1000	15.14	9.83	9.08	16.45	18.91	7.17
500	9.91	10.22	8.52	10.05	18.83	11.37
250	9.06	14.46	7.66	7.16	13.95	22.04
125	6.10	24.03	5.06	6.11	10.51	32.39
63	5.73	29.58	3.87	5.05	6.99	22.18
10	4.65	8.70	0.38	0.66	0.64	2.72
Bottom	0.12	0.56	0.10	0.12	0.14	0.41

All samples but CP1 have no fractions coarser than 8 mm and CP1 was cleared of such fractions before grain size analysis.

The waste rock sample CP1 is the coarsest one with a gravel fraction of 63.33 wt%. The SM1 tailings are mainly sandy with such fractions accounting for 78.12 wt% of the sample. FS5 feed sample is 30.03 wt% gravel, mostly sandy and with a low amount of silt. Other tailings are finer but with a wide variety of grain size distributions. The gravel fraction ranges from 1.72 (FS11) to 49.29 (TL1) wt%, and the sandy fraction from 45.94 (TL1) to 95.15 (FS11) wt%. The amount of the finest fraction is always low, never exceeding 10 wt%.

3.2.2. Major Element Whole Rock Chemistry

All samples were analyzed by XRF for major elements, with the addition of sulfur, which is always enriched in the studied materials, and lead and zinc, which are enriched in some of the ores; the results are reported in Table 5.

Table 5. Whole rock chemistry of major elements, S, Pb, and Zn of waste materials (wt%).

Element	TL1	SM1	CP1	FS5	FS8	FS11
SiO_2	70.29	15.55	1.63	44.51	42.92	45.17
TiO_2	0.31	0.14	0.03	0.40	0.48	0.44
Al_2O_3	7.95	2.46	1.40	22.64	23.22	22.70
Fe_2O_3	4.52	18.23	29.74	6.40	6.25	5.97
CaO	0.25	15.50	8.95	0.26	1.15	0.07
MgO	0.43	0.43	3.33	0.32	0.80	0.45
K_2O	1.75	0.59	0.18	1.08	2.30	4.46
Na_2O	0.20	0.16	0.01	0.07	0.18	0.10
S	4.48	12.20	18.59	4.63	4.47	5.33
Zn	0.19	1.41	1.09	nd [2]	nd	nd
Pb	0.05	2.30	0.48	nd	nd	nd
L.O.I. [1]	9.73	30.46	34.42	19.55	18.03	15.32
Tot	100.14	99.44	99.85	99.86	99.81	100.00

[1] L.O.I. is loss of ignition. [2] nd is not detected.

The compositions are strongly variable among different mines: SiO_2 ranges between 1.63 and 70.29 wt%, Al_2O_3 between 1.40 and 23.22, CaO between 0.07 and 15.50 wt%, and Fe_2O_3 between 4.52 and 29.74 wt%. Sulfur shows a quite wide range of concentrations, too, between 4.47 and 18.59 wt%. The three samples from the Furtei mine, on the other hand, are quite homogeneous, even though they came from different areas of the mining site. In general, the variability reflects the different types of ore deposits and the element selection during the beneficiation. The high silica TL1 corresponds to the quartz-dominated gangue of the ore and the enrichment in gangue phases in the tailings. SM1 reflects the mixed gangue of the supergene ore with mainly silicates and sulfates. The Campo Pisano sample is the only waste rock and reflects its carbonatic composition with high CaO and MgO and high L.O.I. and the abundance of pyrite corresponding to high Fe_2O_3 and S contents.

Furtei samples are quite homogeneous, and their compositions reflect the mainly silicatic composition of the gangue.

3.2.3. Mineralogy

The mineralogy of all samples was obtained through XRD analysis. Based on XRD and XRF results, some samples were chosen for further detailed investigations. Results are shown in Figure 3.

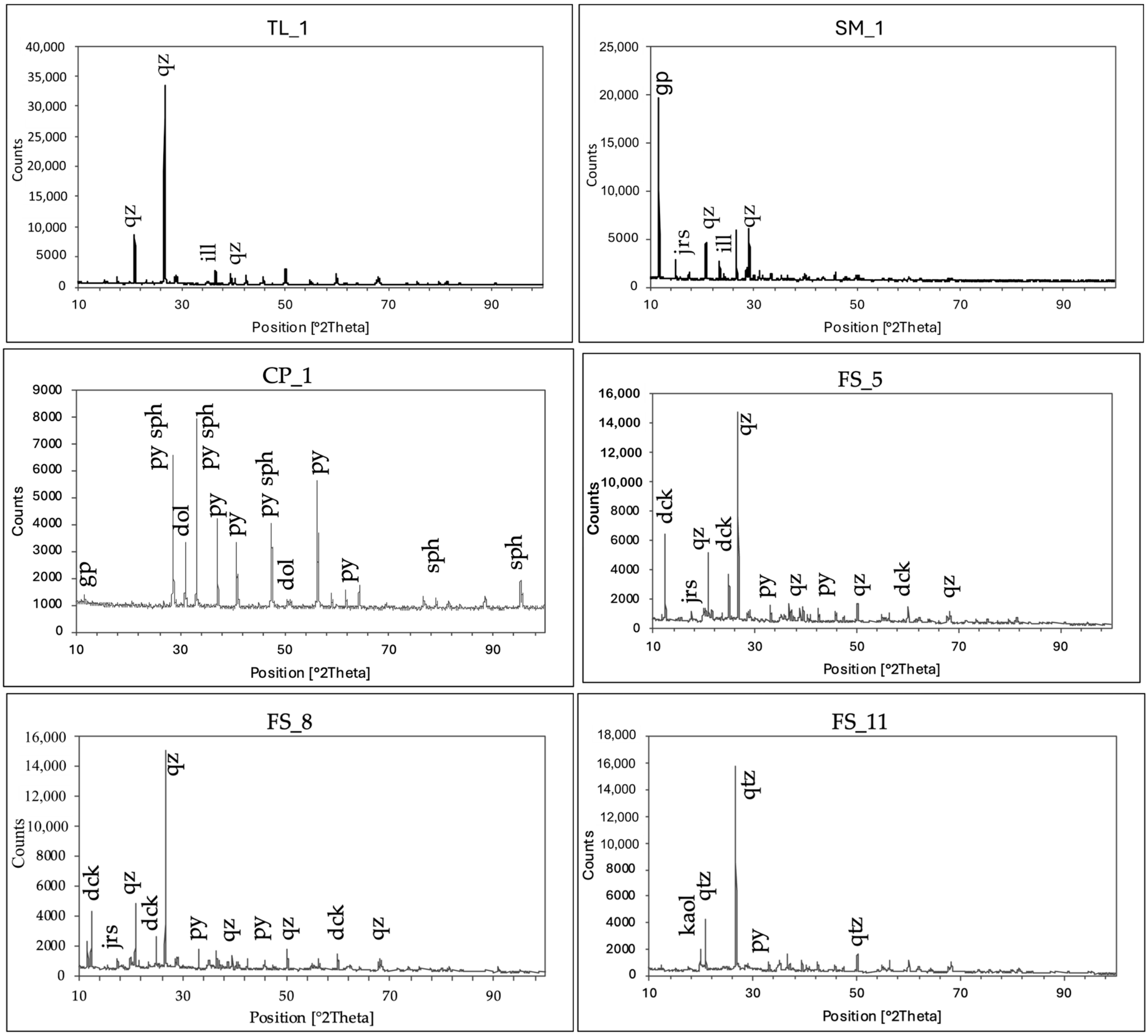

Figure 3. Powder XRD patterns of analyzed samples (qz = quartz; ill = illite; gp = gypsum; jrs = jarosite; py pyrite; sph = sphalerite; dol= dolomite; dck = dickite; kaol = kaolinite).

The Montevecchio-Telle TL-1 sample is dominated by quartz, the main gangue phase of the mineralization, followed by secondary clay mineral and sulfate phases, namely, illite, gypsum, and jarosite, with, possibly, some wollastonite, whose indications are faint. This mineralogy fits well with whole rock chemistry, dominated by SiO_2, and shows that most of the sulfur is present as sulfate that is unable to trigger AMD.

The Seddas Moddizzis SM-1 sample is dominated by clay minerals, reflecting its strong alteration in a surficial environment, followed by quartz and sulfates. Again, the results show that sulfur is predominantly present in a non-AMD-generating form.

The Campo Pisano CP-1 sample shows a different spectrum, characterized by the absence of quartz. The mineralogy is dominated by pyrite, and sphalerite is above the detection limit. Sulfates are present as gypsum but in much lower amounts than sulfides. Dolomite is the only sulfur-free phase detected, enlightening the carbonatic composition of the host rocks. The presence of both sulfides and sulfates is indicative of ongoing AMD processes, and the abundance of sulfides is a strong clue to further acidification.

The three Furtei samples analyzed share a common mineralogy, with just some minor differences. The main detected phase was always quartz deriving from the ore deposit gangue. Pyrite, sulfate, and clay minerals were also detected in all samples with the exception of FS11, where sulfates were not detected. The only other phases are minor amounts of tremolite in sample FS8 and muscovite in sample FS11. The presence of both sulfides and sulfates is again indicative of an ongoing AMD process at Furtei, and, as for Campo Pisano, the abundance of pyrite is a clue of further acidification.

The results led to the selection of the Campo Pisano (CP1) sample and one Furtei (FS11) sample for further investigation and leaching and buffering tests. CP-1 is the highest of all samples in sulfur, most of which, according to XRD data, is in sulfides, and it is liable to produce AMD in spite of the presence of carbonates that could partially buffer acid production. Furtei samples are relatively low in sulfur, but they do not contain carbonates that could buffer AMD. The relative proportion of sulfur as sulfides or sulfates is unknown, but the clues from XRD data indicate the FS11 sample as the one with the highest proportion of sulfides as no sulfates were detected, so the latter, if present, are in low amounts. The Montevecchio-Telle and Seddas Moddizzis samples were discarded because they were both dominated by sulfate sulfur.

The results of this preliminary investigation indicate Campo Pisano and Furtei as the two sites most prone to AMD, and further investigation was restricted to their samples.

3.2.4. Buffering Tests

The sample from Campo Pisano and the three samples from Furtei were leached following the SPLP procedure and then buffered with increasing amounts of FLS sample as described in the analytical methods. The results are reported in Table 6.

Table 6. Step-by-step pH changes during buffering tests. B: amount of buffer material added at each step; RT: reaction time.

		CP-1			FS5			FS8			FS11	
Step	**B (mg)**	**RT (min)**	**pH**	**B (mg)**	**RT (min)**	**pH**	**B (mg)**	**RT (min)**	**pH**	**B (mg)**	**RT (min)**	**pH**
0	0	0	6.02	0	0	2.89	0	0	3.99	0	0	2.71
1	10	30	6.02	10	30	2.94	10	30	4.3	10	30	2.69
2	10	60	6.08	10	60	3.07	10	60	4.38	10	60	2.74
3	10	60	6.11	10	60	3.2	10	60	4.43	10	60	2.78
4	20	60	6.11	20	60	3.22	20	60	4.51	20	60	2.89
5	20	60	6.7	20	60	3.24	20	60	5.1	20	60	2.8
6	30	60	6.72	30	60	3.77	30	60	5.29	30	60	2.77
7	30	60	6.82	30	60	4.01	30	60	5.42	30	60	2.8
8	30	45	6.86	50	45	4.08	30	45	5.74	50	45	3.04
9				50	45	4.15	30	45	6.03	50	45	3.79
10				50	45	4.14	50	45	6.24	50	45	4.03
11				100	60	4.38				100	60	4.18
12				100	60	5.2				100	60	4.38
13				100	60	6.06				100	60	5.1
14										100	60	5.68
15										100	60	6.15

Buffering tests were conducted on Furtei samples leachate waters in incremental steps with the goal of reaching a final water pH higher than 6, close to that of natural rainwaters. Results show that the number of buffering steps and the amount of FLS required increase with decreasing initial pH values. The most acidic waters (FS11) require 780 mg FLS to be added in 15 steps, FS5 waters slightly less acidic require 580 mg in 13 steps, and the least acidic FS8 waters require 280 mg in 10 steps. As CP1 leachate waters have a starting pH of 6.02, the test was conducted in a different way, adding buffer material FLS till the increase in pH was lower than 0.05 for each batch of 30 mg of buffer added three times consecutively. The results show an increase in pH from 6.02 to 6.86 after adding 160 mg of FLS in 8 steps.

3.2.5. Acid–Base Accounting Tests and Geochemical Analyses

CP1 and FS11, the samples from Furtei with the highest AMD, were selected for further investigation. ABA tests were conducted on both samples, and leachate and buffered waters were analyzed for a selection of major and trace elements.

The results of the static ABA tests are reported in Table 7, with the addition of the ANC value of the FLS buffering material already reported in Table 1. The MPA values must be considered indicative, as they were obtained from total sulfur and not from sulfide sulfur, even though sulfates were not detected by XRD analyses in FS11, and only small amounts of gypsum were detected in CP1; hence, the difference between the total and sulfide sulfur MPA results has to be low or even negligible.

Table 7. Results of ABA tests. MPA = Maximum Potential Acidity, ANC = Acid Neutralizing Potential, NAPP = Net Acid Potential Production. All ABA parameters are in kg/t of H_2SO_4 production or buffering capacity.

Sample	CP1	FS11	FLS
S (wt%)	18.59	5.33	
MPA	580.94	166.56	
ANC	152.29	0	149.30
NAPP	428.65	166.56	

The Campo Pisano sample has a very high MPA, due to the abundance of sulfur, which is only partially potentially buffered by the carbonatic gangue responsible for an ANC value that is just about one-fourth of the MPA. The result is a high NAPP of 428.25 kg/t. The Furtei sample has no buffering minerals, and its ANC value is nihil, while its MPA value of 166.56 kg/t reflects its moderate sulfur content and equals the NAPP value.

The distribution of trace elements in the two solid material samples is very different and primarily reflects the geochemistry of the associated ores (Table 8). Campo Pisano shows expected high anomalies in Zn and Pb associated with anomalies in Cd, Ag, Mn, and Tl, all related to SEDEX-type ore deposits. The highest anomalies of the Furtei sample are Cu and As, typical of high-sulfidation deposits.

Trace element contents of leachate waters deriving from the SPLP leaching procedure on CP1 and FS11 are reported in Table 8. The two analyzed samples show quite different behaviors during leaching tests, firstly for the resulting pH of water, which is almost neutral for Campo Pisano (6.02) and highly acidic for Furtei (2.71) (Table 6). The concentration of elements in the water is very different among the two samples, too. In general, the proportions between elements in the leachates closely reflect the same proportions in the solid samples. Campo Pisano water is particularly enriched in Ca and Mg among major elements and Zn, Pb, Cd, Mn, and Tl among trace elements. Furtei leachate water is strongly enriched in Al and Fe among major elements and in Cr, Co, Cu, and As among trace elements. Moreover, for those elements whose concentration is higher in the Furtei water than in the Campo Pisano one, the ratio of the first over the second is much higher than in the solid samples, often of 2 to 4 orders of magnitude, reflecting the much higher solubility of these metals in acidic waters.

Table 8. Selected trace element comparison between solid samples, waters after leaching tests, and after buffering tests.

	Solid Samples (ppm)		Leachate Waters (µg/L)		Buffered Waters (µg/L)	
	CP1	**FS11**	**CP1**	**FS11**	**CP1**	**FS11**
Be	0.06	1.12	<0.5	6.10	<0.5	<0.5
Cr	4	9	<3	53.7	<3	<3
Mn	451	51	3890	1010	4000	1080
Co	4.4	15.8	13.6	467	13.9	68.6
Ni	18.7	7.4	124	303	122	61.5
Cu	149.5	318	<1	17,400	2.60	5.10
Zn	>10,000	142	>25,000	3280	>25,000	89.4
As	47.6	132.5	0.39	1680	0.49	4.24
Ag	77.4	1.14	<1	<1	<1	<1
Sb	6.46	2.78	0.22	0.19	0.22	0.08
Cd	477	0.75	65.8	18.5	67.6	2.43
Se	4	9	<1	49.9	<1	9.40
Tl	32.1	2.1	8.23	0.16	5.09	0.16
Pb	5810	49.5	101	0.57	0.73	0.82
Mg	20,100	2710	95,500	7140	99,800	9310
Ca	64,000	500	488,000	13,800	525,000	997,000
Fe	208,000	41,800	130	25,000	<50	<50
Al	7400	120,000	<10	262,000	<10	29

Buffered waters were, then, analyzed for the same selection of trace elements, and the results are reported in Table 8. CP1 buffered waters do not show any decrease in the metal contents, with the exception of Pb, whose concentration was reduced from 101 mg/L in the leachate to 0.73 µg/L in the buffered waters. The effect of buffering is much more sensible on FS11 waters. Among the analyzed major elements, Al and Fe show a sharp decrease in concentration of several orders of magnitude, while Mg is slightly affected by buffering, and the Ca concentration increased due to the dissolution of calcite from FLS. Among the trace elements, most of them show a sharp decrease in concentration ranging from 2 to 5 orders of magnitude. The only exceptions are Mn and Tl, which are unaffected by buffering, and Pb, which shows a slight increase.

3.2.6. Solid Residues Mineralogy

The solid residue remaining in small amounts after the buffering tests was collected for both samples and analyzed by XRD (Figure 4).

Both solid residue samples do not contain sulfides despite that pyrite was, in CP1, the most abundant phase and, in FS11, still abundant. This confirms the efficacy of the leaching and buffering processes; all sulfides were dissolved, and no sulfides precipitated during buffering. Gypsum is present in both residues, and it is probably the main precipitate phase removing sulfur released in the water during leaching. The other detected phases are probably residues of undissolved minerals from either the waste materials or the FLS buffer.

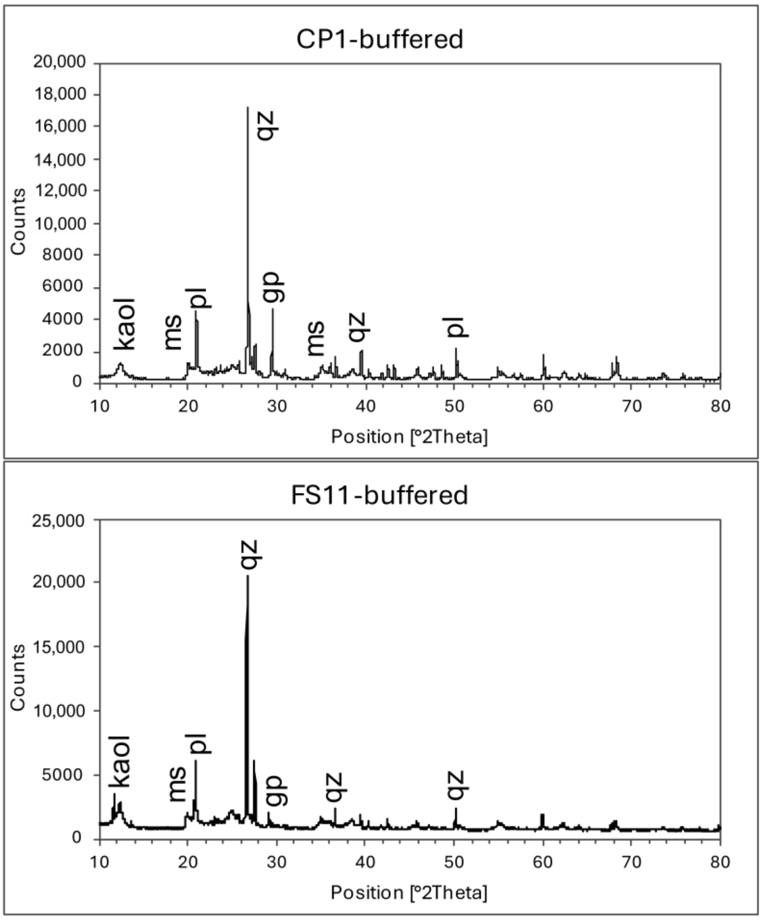

Figure 4. Powder XRD patterns of the solid residues after buffering (kaol = kaolinite; ms = muscovite; pl = plagioclase feldspar; qz = quartz; gp = gypsum).

4. Discussion

Acid mine drainage is a widespread phenomenon in abandoned sulfide-rich mines [2,3,25]. The present study focused on a selection of sulfide-rich waste rocks, tailings, and feed materials from Sardinia, showing that S is a ubiquitous element in different typologies of waste materials. The possibility of ongoing AMD, anyway, depends mainly on three factors: the amount of sulfides in the waste, the presence of buffering minerals, and the lapse of time since the discharge. The samples from the Montevecchio-Telle and Seddas Moddizzis mines are very rich in sulfur, but the XRD data show that their S-bearing phases are secondary sulfates, indicating that AMD certainly occurred but nowadays has been exhausted. This can be explained by the fact that the discharge of the materials occurred over 40 years ago for both mines. As the samples were collected at the surface, this does not mean that all the waste materials at both mines have already exhausted their AMD potential, but they are not suitable for checking the buffering capacity of FLS, the main purpose of the present work. Campo Pisano sample has a very high S content, mostly as sulfides. The sample shows a very high value of NAPP, too, indicating that it could potentially undergo important AMD processes. On the other hand, the leaching test does not result in acidification of water, with a leachate pH around 6. This result can be attributed to the buffering by carbonates, which have a dissolution rate higher than sulfides [9,26] and can promptly buffer acidification. CP1 was selected for further investigation to check the FLS capacity to trigger the precipitation of metal in the conditions of near-neutral drainage.

Furtei samples are all similar in mineralogy and chemistry, showing a moderate amount of sulfur, present as both sulfides and sulfates. The NAPP of sample FS11, according to the ABA test, is 166.56 kg/t, completely due to its sulfur content as the value of ANC is

0. The results are consistent with the younger age of the waste material discharge, the mine having been active for a few years between 1997 and 2008. The AMD processes, here, are ongoing and will last until the complete reaction of all sulfides. The leaching test on FS11 produced strongly acidic waters despite the moderate amount of sulfur, due to the absence of buffering minerals. The sample was, hence, selected for checking the capacity of FLS material to buffer and trigger metal precipitation of strongly acidic waters.

All samples have a grain size distribution fine enough to ensure that the surface reactions between grains and waters occur at a fast enough rate to produce clearly detectable changes within the duration of the leaching and buffering tests. Only CP1 had to be reduced to a fraction below 8 mm to meet this requirement. The samples show quite different grain size distributions within this restricted range. The only waste rock sample (CP1) is the coarsest one, followed by the feed sample, while the tailings samples are much finer.

The choice to select a washing slime as the buffering agent for the tests follows considerations about the real possibility of using it as it is, with no further treatment that could strongly increase the costs of the operation and the fact that the slime is stacked in high amounts at Florinas and other feldspar sands mines in Sardinia at a relatively low distance from the AMD sites and with no need of oversea transportation. The results can have a wide general interest as several areas in the world present close association of feldspar and sulfide ore mining where feldspar slime could be used as an amendment for the AMD processes.

The preliminary characterization of the feldspar washing slime provided positive feedback: it does not contain acid-producing minerals, while it is rich in calcite and hosts also feldspar. The buffering potential of feldspar, even though much lower and with lower reaction rates than calcite, is well known [27–30].

The ABA test provided an ANC of 149.30 kg/t. This value corresponds to a calcite concentration of 152.3 kg/t, according to the following reaction:

$$CaCO_3 + H_2SO_4 - CaSO_4 + H_2CO_3$$

As the calcite content of the FLS sample was estimated to a maximum of 11.9 wt%, corresponding to 119 kg/t, we can argue that the contribution of feldspar to the buffering is close to 33.3 kg/t, which is 22.3% of the total buffering capacity of FLS. Moreover, as the reaction rate of feldspar is lower than that of calcite, the mixture of the two minerals can provide both short- and long-term buffering.

The leaching test on the slime and the analysis of the leachate were conducted to provide information on its buffering capacity and its possible contribution to the pollution. The buffering capacity of the material was confirmed by the strongly basic drainage produced, with a pH of the leachate waters of 8.85. About the potential release of metals in the waters, the test shows a high release in the leachate of Al, Ca, Na, and K, deriving from the dissolution of feldspars and calcite. Particular attention is required for the high concentration of Al, which far exceeds that of natural fresh waters and is well above the lawful limits for releasing waters into the environment. As the material would be used to buffer acid water, the leaching test on FLS does not correspond to the environmental conditions to which it will be subject during the amendment of AMD. These will range from acidic to close to neutrality, as shown by the buffering tests on CP1 and FS11. The solubility of Al is known to be high in highly acid and basic waters, while it is at a minimum in slightly acidic and neutral waters [31–34]. The results of buffering tests on CP1 and FS11 samples confirm that the release of Al from the FLS sludge used for buffering is negligible, and on the contrary, sample FS11, whose leachates had a very high Al concentration of 262.000 μg/L, was buffered by treatment with FLS to 29 μg/L. The presence of relatively high concentrations of Fe in FLS leachate is puzzling, as the Fe content of the material is low and no Fe-bearing phases were detected by XRD analysis. We can argue that Fe comes from a highly soluble phase present in low amounts.

The buffering potential of FLS was confirmed by buffering tests. The AMD-producing samples were first leached following the SPLP procedure. The Campo Pisano sample had, in short time tests such as the SPLP procedure, a strong self-buffering capacity due to its carbonate content, related to the carbonate-hosted SEDEX ore type. This is confirmed by the CP1 ANC value of 152.29 kg/t and by the detection of dolomite in XRD analysis. As a result, the initial pH of CP1 during the buffering test was close to neutrality (6.02). The Furtei sample shows no self-buffering capacity, with an ANC value of 0, due to the absence of carbonate phases, which were not detected by XRD. This is in agreement with the high-sulfidation gold deposit type that, usually, does not contain carbonates. Andini and Gautama [35] found in Lanut epithermal gold deposit ore ANC values of 0 in all samples and MPA values ranging between 110 and 248 kg/t, comparable to the 166.56 kg/t of FS11.

The buffering tests confirm the FLS potential to neutralize waters, as all Furtei samples reached final pH values above 6, and also the CP1 leachate pH, initially around 6, was increased to 6.86 (Figure 5a). The Furtei samples buffering curves clearly draw the plateau described by Nordstrom [31] in his titration simulation of acid mine drainage. In his simulation, the first plateau, at a pH around 3, visible in Furtei samples FS5 and FS11, is due to Fe^{3+} hydrolysis and precipitation, and the second, at a pH around 4 and visible in all Furtei samples, is due to Al hydrolysis and precipitation [31]. At a plateau, the addition of buffering material is compensated by precipitation, without a meaningful increase in pH. The presence of a plateau is an important clue of abundant metal precipitation during buffering. In order to compare the FLS results with the buffering tests conducted with calcite on the similarly acidic mine leachate waters from Fushe Arrez (Albania: samples FA3 and FA5) by Cocomazzi et al. [21], the buffering curves were adjusted to 100% $CaCO_3$, using the FLS $CaCO_3$ content (Figure 5b). In these conditions of equivalent calcium carbonate, FLS is more efficient than the calcite buffer used in Cocomazzi et al. [21]: both FS5 and FS11 require lower amounts of buffer to exceed the pH 6 threshold than FA3, even though the initial pH is lower; FS5, too, requires much less equivalent FLS buffer than FA4, whose initial pH is just slightly lower. The results confirm that feldspar provides a minor but clearly detectable contribution to buffering.

The purpose of treating acidic mine waters with a basic buffer is double: the goal of increasing the water pH to values close to natural waters is coupled with the purpose of triggering metal precipitation and drastically reducing the metal content in the solution. This latter purpose is based on the general reduction in the solubility of the metals typical of AMD waters as the pH value increases [36].

The buffering tests gave very different results for the two samples. CP1 buffered waters show metal contents similar to those of the leachate, with the only exception of Pb and, partially, Fe. The exception of Pb, which decreased its concentration by two orders of magnitude, could be possibly related to its incorporation as a cerussite component in the calcite during its precipitation in buffered waters [37]. When plotted in the diagram proposed by Ficklin et al. (1992) [38] for the classification of AMD waters (Figure 6), the Campo Pisano buffered waters do not show any reduction in the metal contents and remain in the same field, near-neutral and high-metal contents like their leachate waters. The Furtei leachate waters show very high metal contents coupled with very low pH values, and they are plotted in the high-acid and high-metal field of the Ficklin diagram within the field of the waters draining epithermal deposits as described by Plumlee et al. [36]. The leachate can be also compared to the surficial waters from the Furtei mining area analyzed in the works of Cidu et. al. [39,40]. Our leachate falls in the Ficklin diagram close to the upper, more acidic, and higher metal end of the Furtei tailing water field, confirming that the SPLP procedure well simulates the acidification of waters in the mining environment, reproducing the worst conditions at the mine. Other data on Furtei surficial waters show that barren rock waters, which can be considered as a local background, are not affected by AMD, falling in the near-neutral and low-metal field, while the mineralized rock waters underwent very limited acidification, with no increase in metal content. Buffering by FLS shifted back the leachate waters to the field of near-neutral and low-metal waters, very close to the conditions of the mineralized rock waters and hence almost nullifying the

AMD process. The higher concentration in the sum of metals considered in the Ficklin diagram is mainly due to higher contents of Zn and Ni but also with an artificial effect due to the absence of Co in the Cidu et. al. [39,40] analyses. Of all the metals analyzed, only Tl and Pb, whose concentrations were already low in the leachate waters, and Mn are unaffected by buffering with FLS. The Mn concentration remains close to 1 mg/l after buffering. Mn is known to be more soluble than Fe at similar Eh values and is more difficult to oxidize [41–43]. Moreover, Mn usually requires a specific treatment after buffering of AMD waters [44].

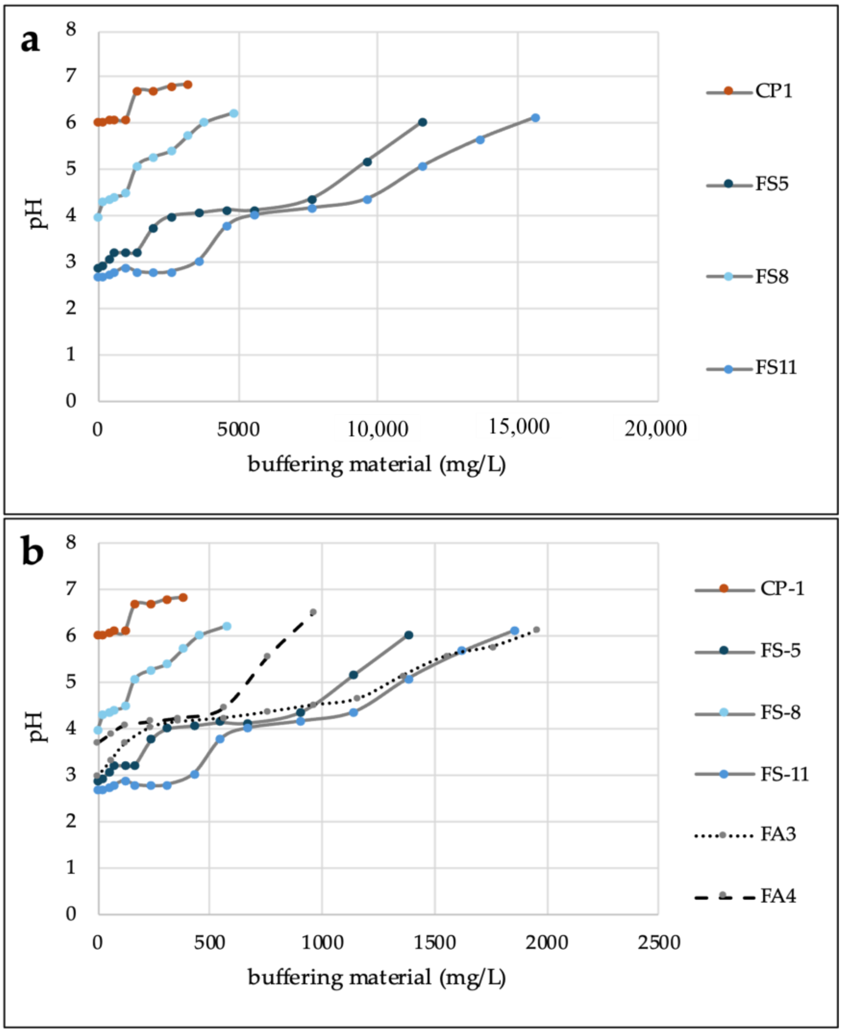

Figure 5. Buffering curves of Campo Pisano and Furtei samples (**a**). The same buffering curves, with the amount of buffering expressed as 100% $CaCO_3$ equivalent, are compared (**b**) with the buffering curves of FA3 and FA4 samples from Fushe Arrez tailing buffering tests (data for Fushe Arrez from [21]).

The concentrations of the analyzed metals in leachates and buffered waters of the FS11 sample were compared in Figure 7 with the threshold values for industrial discharge waters according to Italian environmental legislation. In leachate waters, six metals, Fe, Al, Se, As, Zn, and Cu, show concentrations higher than the thresholds. The pollution is particularly severe for Al, Fe, and Cu, all of which exceed their threshold of more than two orders of magnitude. After buffering, three metals, Mn, Pb, and Tl, do not show any reduction in concentration, but they are below their respective thresholds (Mn and Pb) or are not regulated and show very low concentrations (Tl). All the other metals show a concentration reduction in buffered waters, in most cases of one order of magnitude or more, up to three orders of magnitude for Fe, and four orders of magnitude for Al and Cu, the major pollutants according to the leaching test. What is most important, all the metals, with the only exception of Co, which is very close to the threshold, and whose concentration decreased by almost one order of magnitude with buffering, show concentrations below their respective thresholds in buffered water, confirming that buffering with FLS material is an effective procedure for the treatment of high-acid and high-metal waters, such those present at the Furtei site.

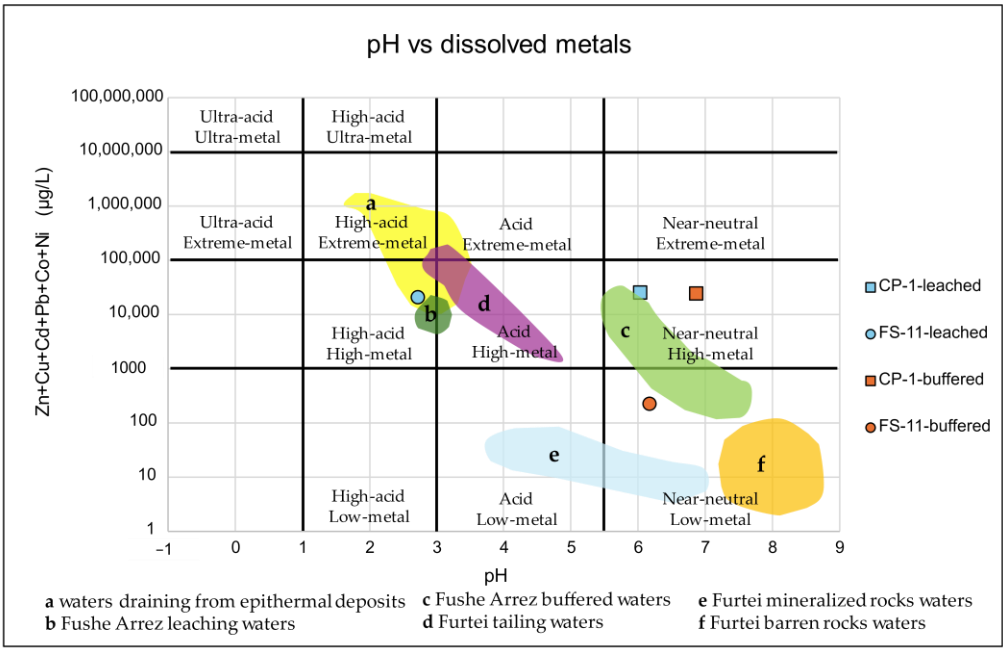

Figure 6. Ficklin diagram where CP1 and FS11 leachates and buffered waters were reported together with the fields for high-sulfidation epithermal deposits, Fushe Arrez leaching and buffered waters, and Furtei buffered tailings, mineralized rocks, and barren rocks waters (data from Plumlee et al. [36]; Cocomazzi et al. [21]; Cidu et al. [39]).

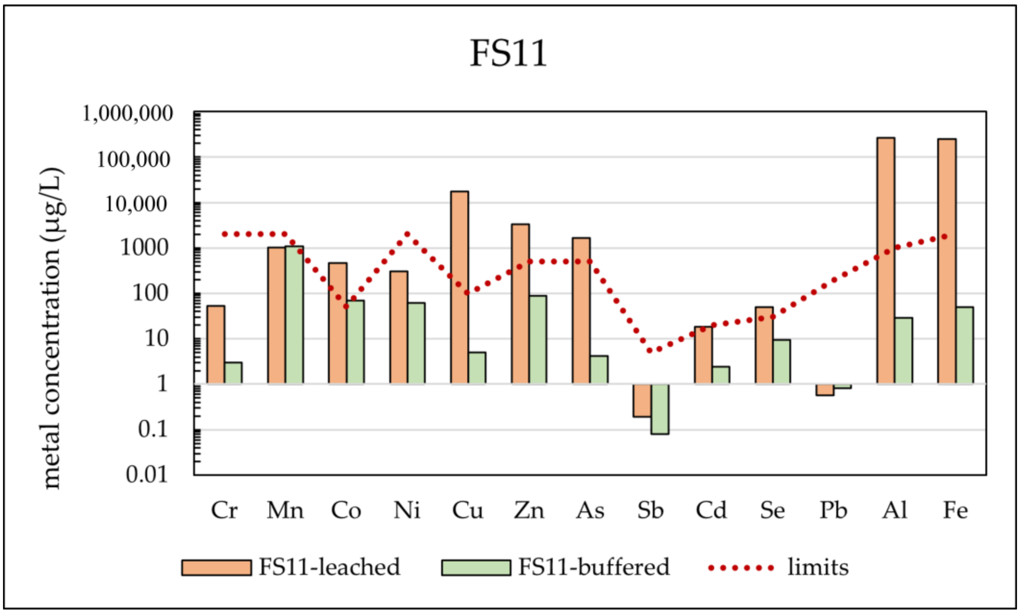

Figure 7. Selected metal concentrations in leachate and buffered FS11 waters. Italian legal limits for industrial discharge waters are shown for comparison (legal limits from [45]).

The mineralogy of the small amount of solid residue collected after buffering is similar for CP1 and FS11. It is a mixture of undissolved FLS mineral quartz, muscovite, and feldspar, with the addition of gypsum deriving from the reaction of carbonate ions with acidic waters. This composition confirms that calcite is quickly dissolved during leaching tests, while the buffering potential of feldspar has probably not been completely expressed due to the short duration of the tests.

5. Conclusions

The treatment of AMD waters is a major concern in the remediation of sulfur-bearing mining sites as the metal content in discharge waters can be several orders of magnitude above the legal thresholds. The treatment with basic substances able to shift the pH to near-neutral conditions, which trigger the widespread precipitation of metals, is a substantial part of the remediation actions aimed at reducing the environmental risk in AMD-affected sites. It can be very efficient in combination with other procedures, especially those based on bioremediation. On the other hand, basic drainage may also occur in carbonate- and feldspar-rich mining sites, leading to the solubilization of metals and the discharge of polluted waters. The present work shows that recycling basic drainage-producing waste materials as an improvement for AMD waters can be a very effective solution to both problems, leading to several advantages:

- Reduction in the amount of waste disposed at feldspar-rich mining sites and subsequent limiting of its basic drainage.
- Neutralization of the discharge waters at the AMD-producing mining site.
- Decrease in metal contents below the thresholds for industrial discharge waters.
- Cost-effectiveness of the recycling approach as opposed to using costly basic products for the amendment of AMD waters.

The present results are of broad interest and possible widespread application, as the validity of the procedure could be assessed for several other couples of acid and basic drainage systems all over the world, where the waste materials of the latter could be used to buffer the AMD-producing materials of the former.

The present study ascertained the scientific validity of the circular economy approach investigated. Further steps are required to define the possibility and conditions to apply the approach to the investigated case study and in other situations. A thorough economic assessment of the cost-effectiveness, comprising technical feasibility, and legal and bureaucratic issues must follow this scientific validity study.

Author Contributions: Conceptualization, G.G. and G.C.; methodology, G.C., E.D. and M.L.D.; validation, S.N. and E.S.F.; formal analysis, G.G., G.C., E.S.F. and M.B.; investigation, G.C.; resources, G.G. and S.N.; data curation, G.C. and M.B.; writing—original draft preparation, G.G.; writing—review and editing, S.N., E.D., E.S.F., M.L.D. and M.B.; visualization, M.B.; supervision, G.G.; project administration, G.G.; funding acquisition, G.G. All authors have read and agreed to the published version of the manuscript.

Funding: Funding for this research was provided by the Italian Ministry of Education (MIUR) (PRIN2017—Mineral reactivity, a key to understand large-scale processes: award No. 2017 L83S77) and "Dipartimenti di Eccellenza 2023–2027—"Le Georisorse per la transizione ecologica e lo sviluppo territoriale".

Data Availability Statement: Dataset available on request from the authors due to the internal policy.

Conflicts of Interest: The authors declare no conflicts of interest.

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