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Release of toxic elements from rocks and mine wastes at the Furtei gold mine (Sardinia, Italy)

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ABSTRACT

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A R T I C L E I N F O

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Keywords: Gold mine Waste rocks Cyanidation tailings Leaching test Water The Furtei gold mine in Sardinia (Italy) exploits a volcanic-hosted high-sulphidation epithermal deposit. Large amounts of materials derived from exploitation are present in open pits, waste rock dumps and cyanidation tailings impoundment. Mineralized rocks in outcrops and waste dumps contain significant amounts of sulphides (mainly pyrite and enargite). These materials have a high potential for acid drainage generation and release of toxic elements (notably Cu and As, but also Al, Ni, Co and Cd) as pointed out by laboratory leaching tests and in agreement with chemical composition of waters draining the mining area, that show pH as low as 2, up to 180 mg/L Cu, up to 5 mg/L As, and up to 788 mg/L Al. On the other hand, leaching solutions and waters interacting with mineral assemblages of the propylitic alteration zone (mainly composed of chlorite, quartz, and calcite, with relic magmatic plagioclase) show higher pH, and lower metal loads. Leachates from cyanidation tailings show variable pH (between 6.2 and 9.7, depending on sulphide content in tailings); cyanide concentration varies between 110 µg/L and about 3 mg/L, whereas contents of toxic elements in leachates are, with the exception of Hg, within the limits of Italian regulations for non-dangerous industrial wastes. Reclamation plans provide for confinement of tailings within specific repositories. This measure should effectively reduce the environmental impact of these materials. Reclamation plans should also include an adequate management of other high-sulphide wastes.

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1. Introduction

Sardinia has been for millennia the main metalliferous region of Italy. Historical mining was carried out in the absence of effective regulations and controls on the environmental impact, and was characterized by disregard of environmental issues, with consequent diffuse contamination (see e.g. Caboi et al., 1999; Cidu and Fanfani, 2002; Frau and Ardau, 2003). On the contrary, in the recently (1997) open gold deposit at Furtei, exploitation was preceded and accompanied by studies on the environmental impact, and plans for reclamation after mine closure (Ciccu and Imolesi, 1996; Madau et al., 1996; Cidu et al., 1997; Da Pelo, 1998; Cidu, 2000; Nicol et al., 2002). The monitoring program conducted by the University of Cagliari upon request of the mining company was mainly addressed to water analysis, whereas solid materials (waste rocks and tailings) received comparatively less attention.

Leaching tests are a time- and cost-saving methods to assess the potential impact of waste materials on the aquatic environment, and represent an important geochemical tool to establish an adequate management of these wastes (e.g. Hageman and Briggs, 2000; Hage and Mudler, 2004). The aim of this study is to estimate, both in the laboratory and in the field, the potential for generation of acid mine drainage and release of toxic elements (especially Cu and As) from natural (mineralized and barren rocks) and mined (waste rocks) materials, and from processing residues (tailings) in the Furtei area. This was accomplished through a mineralogical and geochemical characterization of the different materials, by performing leaching tests on solid materials, and by comparison of experimental results with the chemistry of waters draining the mining area.

2. Study area

The gold deposit at Furtei lies some 40 km North of Cagliari (the capital city of Sardinia), on the eastern border of the Campidano plain, where agriculture activities are extensively developed. Crops occur only outside of the mine property (specifically to the West and to the South-East), whereas livestock is often grazing in areas within the property.

The deposit is linked to calc-alkaline andesitic-basaltic rocks of the Oligo-Miocene volcanic cycle in Sardinia. It shows several typical features of volcanic-hosted high-sulphidation (acid-sulphate) epithermal deposits (as defined, e.g., by Arribas, 1995), specifically, alteration styles, mineral assemblages, relationships of ore bodies with host rocks, and nature of the ore-related fluids (Ruggieri et al., 1997). The

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extensive host rock alteration shows the four typical alteration facies of high-sulphidation deposits: vuggy and massive silica, advanced argillic, argillic, and propylitic. The deposit consists of four main ore bodies: Is Concas, Santu Miali, Su Masoni and Sa Perrima (Fig. 1). In the primary (hypogene) mineralization, the most abundant sulphide is pyrite, followed by Cu–As sulphides (mainly enargite, with minor amounts of luzonite, tennantite and chalcocite). Sphalerite and wurtzite are more abundant at Sa Perrima. Before exploitation, the primary mineralization was covered by an oxidized (supergene) assemblage extending 10–50 m downward. The oxidized cap was mainly composed of Fe oxyhydroxides, and frequently gypsum and jarosite. Several other secondary minerals (mostly Cu–Fe–Al sulphates and arsenates) were observed, mainly in cavities and fissures, and as ephemeral crusts occurring under dry conditions (Da Pelo, 1998 and references therein; Musu et al., 2007a).

The mean rainfall in the area for the period 1922-1992 was $526\pm$ 119 mm/y and the mean annual temperature was 16.5 ± 1 °C. The dry period (rain < 40 mm month⁻¹) usually extends from June to September. In 2003, the rainfall was 546 mm, but the dry period extended from February to August; the rainiest month was October (130 mm).

The area hosts two important reservoirs. The Sa Forada de s'acqua lake lies within the mine concession. It is an artificial basin fed by means of a gallery with water from an upper reservoir (located about 30 km from the study area). Water in the Sa Forada de s'acqua lake is renewed weekly, and is drained to the lower Case Fiume reservoir. From here water is distributed over a large area in southern Sardinia, and used for irrigation and drinking.

The only important water course in the area is the Flumini Mannu. This river flows outside of the mining concession (just West of the area in Fig. 1), but it may occasionally receive the flow of small tributaries draining the mining area. In general, surface drainage in the area consists of ephemeral streamlets, with a flow strongly dependent on rainfall.

Due to the occurrence of argillic and advanced argillic alteration, groundwater circulation in the mining area has been estimated to be very low (hydraulic conductivity: 10^{-7} m/s), with flow directions mostly from East to West (Progemisa, 2003). A shallow phreatic aquifer (depth: <20 m) occurs in the Quaternary alluvial sediments; the water table level may rise to surface during the rainy season and originate ephemeral springs, especially along the Rio S'Alluminu stream. A confined aquifer (depth: 20–130 m) is hosted in the volcanic sequence with intercalated lacustrine calcareous layers. This aquifer has been intercepted by exploration boreholes that showed flow rates in the range of 0.02 to 0.2 L/s.

Gold exploitation began by open pit mining in 1997 for confirmed reserves adding up to 2150 000 metric tons (t) at 2.82 g Au per ton (g/t; Madau et al., 1996). For five years (1997–2001) gold was extracted from the oxidized ore by cyanidation. Upon exhaustion of oxidized ore, sulphide ores were exploited from 2001 to February 2003. Tailings from the cyanidation process and from flotation of the sulphide ore have been disposed of in an impoundment (Fig. 1). Seeps from the impoundment were first observed in 1998; since then, all seeps have been collected in a well and pumped back to the impoundment. After a five year break, operations have been recently resumed at Sa Perrima stope; plans for underground mining are under consideration.

As a consequence of open pit excavations, four pit lakes appeared at Sa Perrima, Is Concas, Santu Miali Cima and Santu Miali Est. They are filled by direct rainfall, and by interception of the groundwater table,



Fig. 1. Schematic map showing the main alteration facies in Tertiary volcanic rocks at Furtei (Sardinia, Italy), and the location of solid and water samples. The main vuggy silica outcrops were in correspondence of Santu Miali and Is Concas open pits. Post mineralization rocks include Miocene limestone and recent alluvial sediments.

the level of which strongly depends in turn on precipitation. Due to intense rock fracturing, especially at Santu Miali, some inflow of deep groundwater cannot be excluded. Remediation actions for pit lakes are in progress; they consist of water pumping to the tailings impoundment, followed by backfilling with mining waste materials. The pit lakes at Santu Miali Cima and Sa Perrima have been completely recovered respectively in 2004 and 2007.

Pre-mining baseline studies carried out in 1994 showed that waters interacting with mineralized rocks were acid (lowest pH: 2.3), had a dominant sulphate-chloride composition, and high levels of contaminants, such as 2000 mg/L Al, 29 mg/L Cu, 11 mg/L Zn, 4 mg/L Ni, 3 mg/L Co, and 0.4 mg/L As (Cidu et al., 1997). Subsequent sampling showed that during exploitation the overall chemistry of waters in the area did not change appreciably with respect to pre-mining conditions, except for seasonal variations as a function of rainfall. In rainy periods, there is a marked dilution effect, with concomitant reduction of dissolved metal load and acidity.

3. Sampling and analytical methods

3.1. Solid samples

A large number of samples of various types of solid materials were collected during repeated visits at the mine, and stored in doubly sealed plastic bags. These samples include: 1) mineralized rocks, defined here as rocks where the presence of sulphides can be detected by eye; they were collected in open pits, in dumps, and at the mill plant; 2) weakly mineralized rocks, i.e. showing no recognizable sulphide mineral under a hand lens; they were collected in outcrops making reference to the previously defined alteration facies, as mapped by Ruggieri et al. (1997) and by the company staff; 3) tailings, picked up directly at the impoundment.

On the basis of a preliminary screening by binocular microscope inspection and/or XRD analysis, fourteen samples were chosen for the leaching tests. Although the inherent heterogeneity of mine materials makes it difficult to demonstrate that the selected samples are really representative of the entire range of solid compositions occurring at the mine scale, we believe that they can be used to provide a reasonably approximation of the geochemical process that are taking place at the Furtei mine as a consequence of exploitation. As it will be shown later on, this assumption is also supported by the results of the leaching tests that are in good agreement with the chemistry of the natural drainages. The location of samples is shown in Fig. 1, and their description is reported in Table 1.

The solid materials exhibit different grain size, from clay to a diameter of 10–15 cm. Rock samples were mechanically crushed and disaggregated, in a ceramic mortar and pestle, to a particle size less than 4–5 mm. For leaching tests all samples were sieved to 2 mm, a common practice for evaluation of weathering effects on mine waste materials (e.g., Smith et al., 2000). As shown in Table 1, for most samples the <2 mm fraction is by far the most abundant. Portions of the 2 mm-sieved samples were prepared as epoxy-mounted sections for SEM-EDX analysis (FEI Quanta 200). Another portion was ground and used for mineralogical analysis by XRD (Panalytical X'PertPro with X'Celerator detector), and for bulk wet chemical analysis.

Microwave digestion of samples was performed with a CEM - MDS 2100 oven by accurately weighing about 0.2 g of each sample into a clean teflon PFA vessel, followed by addition of 2 ml H₂O (MilliQ® ultrapure water), 3 ml H₂O₂ (30% Carlo Erba RPE), 14 ml HNO₃ (68% Carlo Erba Suprapur), and 4 ml HF (50% Carlo Erba Suprapur). The HF was removed by open multiple evaporations to incipient dryness with HNO₃ additions, and the final residue taken up in HNO₃. Solutions were diluted to 100 ml with 1% HNO₃ in volumetric flasks, and transferred to new high density polyethylene (HD-PE) bottles for storage (Jarvis, 1992). One or two reagent blanks and a reference standard SRM2710, prepared in the same way as samples, were

included in each digestion cycle. Duplicate samples were taken for SRM2710 and for several samples. Metals were determined by ICP-AES (ARL-3520B) and ICP-MS (ELAN 5000). Precision of replicate samples was mostly better than 10%. Accuracy was evaluated by replicate analyses of the SRM2710 standard. It was better than 10% for Ca, Mg, Na, K, Fe, Al, Ag, As, Ba, Cd, Co, Cu, Ni, Pb, Rb and Zn, and about 20% for Mn and Cr. Total carbon and sulphur were determined by a combustion infrared spectrophotometer (LECO CS-444 furnace).

3.2. Leaching tests

Leaching experiments were performed on portions of 2 mm-sieved sample, following the protocol UNI 10802/2002. This is a standard release test for industrial wastes (granular and pasty wastes, and sludges) according to Italian regulations (Dlgs 186/2006). Moreover, it represents a good approximation of the interaction of mine materials with rain water. The solid to liquid ratio was modified to 1:20 (instead of 1:10) in order to minimize the possibility of exceeding mineral saturation and to avoid mineral precipitation (e.g. Hageman and Briggs, 2000). Ten g of sample and 200 ml of Milli-Q® ultrapure water (pH=5.6, Eh=0.5 V) were put into a 250 ml wide mouth HD-PE bottle. The bottles were sealed and shaken automatically at 185 rpm for 24 h. The leachates were then filtered through 0.4 µm pore-size polycarbonate filter with an all-plastic filtration assembly. Redox potential (Eh), pH, alkalinity and conductivity were measured immediately upon filtration, and an aliquot of each sample was acidified for complete analyses using the same methods as described in Section 3.3 for waters.

3.3. Waters

Sampling of waters was routinely performed in the framework of a hydrogeochemical monitoring program from 1997 to 2006 (Cidu et al., 1997; Cidu, 2000; Cidu and Da Pelo, unpublished data). The waters considered in this study were sampled in October 2003, immediately after a heavy rain event. These waters are assumed to represent the natural leaching of exposed materials, therefore they will be used for comparison with results of the 24-hours leaching tests. Pit lake waters were sampled close to surface (water depth was about 50 cm). The location of water samples is reported in Fig. 1.

Water samples were filtered in situ through a 0.4 µm pore-size polycarbonate filter with an all-plastic filtration assembly, and acidified upon filtration for metal analyses. At each sampling site, temperature, pH, Eh, alkalinity, and conductivity were measured. The Eh was measured by platinum electrode, and the value corrected against the Zobell's solution (Nordstrom, 1977).

Anions were determined by ion chromatography (IC Dionex DX-120), and cations by ICP-AES and ICP-MS. The ionic balance was always in the range of ±5%; both precision and accuracy were estimated at 10% or better, using randomly duplicate samples and standard reference solution (NIST1643d). Speciation and equilibrium calculations were carried out using the PHREEQC computer program (Parkhurst and Appelo, 1999) and the Wateq4f database as implemented in Da Pelo et al. (2001). Saturation index (SI) is calculated as $\log \frac{IAP}{K}$, where IAP is the product of the activities of the relevant ionic species, and K is the solubility product for the specific mineral.

4. Results

4.1. Composition of solid samples

The mineralogical composition of solid samples is reported in Table 2. The XRD analyses showed that quartz and kaolinite/dickite are the most abundant phases in all samples; Ti-oxides are ubiquitous in trace amounts. Pyrite is abundant in mineralized rocks, whereas weakly

Description of solid samples collected in the Furtei area

Weakly mineralized rocks

- FS3 Brittle red-purple ash-flow deposit highly argillified from advanced argillic alteration zones. No macroscopic evidence of sulphide occurrence. More than 89% of the sample is in the grain size <2 mm and 27% in the range of 63–250 μ m.
- FS4 Brittle white ash flow-deposit with rare limonite from advanced argillic alteration zones. No macroscopic evidence of sulphide occurrence. About 74% of the sample is in the grain size <2 mm and 20% in the range of 63–250 μm.
- FS6 Sample from the strata bound body of sa Perrima, silicified with high crystalline and amorphous iron hydroxides minerals content. No macroscopic evidence of sulphide occurrence. About 20% of the sample is in the grain size <2 mm and 4% in the range of 63–250 μm.
- FS7 Red-purple-brown sample from the strata bound body at sa Perrima, with high content of plastic argillaceous materials. No macroscopic evidence of sulphide occurrence. More than 77% of the sample is in the grain size <2 mm and 21% in the range of 63–250 μ m.

Mineralized rocks

- FS5 Gray sample from the milled sulphide ore pile in the plant. Macroscopic occurrence of sulphide and efflorescence of gypsum About 46% of the sample is in the grain size <2 mm and 11% in the range of 63– 250 µm.</p>
- FS8 Sample from waste rocks dump of Sa Fronti with macroscopic sulphides occurrence. More than 70% of the sample is in the grain size <2 mm and 18% in the range of 63–250 μ m.
- FS9 Gray sample from waste rocks dump of Sa Fronti with macroscopic sulphides occurrence. More than 65% of the sample is in the grain size <2 mm and about 24% in the range of 63–250 μm.
- FS10 Gray sample from waste rocks dump of Su Masoni with macroscopic sulphides and jarosite occurrence. More than 84% of the sample is in the grain size <2 mm and 32% in the range of 63–250 μ m.
- FS11 Gray sample from open pit of Santu Miali with macroscopic sulphides
- occurrence. More than 98% of the sample have grain size ${<}2\,$ mm and 55% in the range of 63–250 $\mu m.$
- FS12 Gray sample from open pit of Is Concas with macroscopic sulphides occurrence. More than 56% of the sample is in the grain size <2 mm and 15% in the range of 63–250 μm.
- FS13 Sample from a yellow highly argillified dump, with jarosite and rare sulphides occurrence. More than 62% of the sample is in the grain size <2 mm and 18% in the range of 63–250 μ m.

Tailings

- FS1 White-gray sample from cyanidation processing of oxidized ore. Grain size ${<}63\ \mu\text{m}.$
- FS2 Gray sample from flotation processing of sulphide ore collected in the impoundment, partly mixed with cyanidation tailings. Grain size <1 mm with more than 70% in the range of 63–250 μm.
- FS22 Gray sample from flotation processing of sulphide ore collected direcly from the spigot. Grain size <2 mm with more than 70% in the range of 63–250 μm.

mineralized rocks contain little or no sulphide minerals. Tailings samples contain minor amounts of montmorillonite and gypsum (XRD detect-

Table 2

Mineralogical composition of solid samples collected in the Furtei area

Table 3

Concentration of major elements (excluding Si) in solid samples collected in the Furtei area

	Ca	Mg	Na	К	С	S	Al	Fe	Mn
					mg/kg				
Weakl	y mineral	lized rock	s						
FS3	4770	2979	6562	3338	<1000	1200	107000	39500	89
FS4	4676	1911	9965	3243	<1000	1600	47000	8500	17
FS6	8068	5627	21513	4831	5300	5500	68000	50500	292
FS7	58350	9995	2325	10115	6700	44800	72000	3700	1475
Miner	alized roc	ks							
FS5	7085	3100	5320	8685	<1000	75700	79000	54500	194
FS8	7635	5324	18268	2102	1800	72000	87000	54000	735
FS9	1868	1748	2271	12799	<1000	83600	89000	59000	86
FS10	10509	5883	4840	23852	3600	29500	81000	42000	1258
FS11	798	2595	2221	30259	<1000	71000	85000	45000	58
FS12	1133	834	2456	4020	<1000	102000	81400	78603	11
FS13	2360	23154	17290	8782	<1000	19500	80000	32000	500
Tailing	ŢS								
FS1	73644	4412	8052	5678	5700	46500	86000	17000	277
FS2	12625	5699	26182	5095	<1000	41500	54000	30500	107
FS22	2826	806	1186	4205	<1000	52600	49800	40328	84

able), traces of enargite and Fe-oxyhydroxides (detected by SEM), and pyrite in variable amounts.

The total concentrations of elements derived by chemical attacks are reported in Table 3 for major components, and in Table 4 for minor elements. All solid samples have high amounts of Al, due to the high quantity of clay minerals (see Table 2). Presumably Na, K and Mg are mostly linked to silicates such as chlorite, illite and montmorillonite, but Na and K are also partly associated to members of the jarosite group. In weakly mineralized rocks, Fe is mostly linked to crystalline and/or amorphous Fe-oxyhydroxides. The comparatively high amounts of Pb in these samples could be explained by adsorption of this metal onto iron oxyhydroxides (see e.g. Lee et al., 2005). High concentrations of S and Ca, as in sample FS7, appear linked to gypsum.

In mineralized rocks, the highest amounts of S and Fe mostly derive from pyrite; Cu, As and Ba are also abundant, due to the presence of enargite and barite (see Table 2). Tailings samples present high concentrations of S, mostly due to sulphide in FS2 and FS22 samples, while gypsum is the dominant sulphur-bearing phase in FS1. The small amounts of C should be ascribed to the presence of minor carbonates; indeed, calcite was positively identified in two samples (Table 2).

	Weakly n	nineralized	rocks		Mineraliz	Mineralized rocks								Tailings		
	FS3	FS4	FS6	FS7	FS5	FS8	FS9	FS10	FS11	FS12	FS13	FS1	FS2	FS22		
Abundant (XRD detectable)	Qz Kao/Dck III/Ms Hm	Qz Kao/Dck III/Ms	Qz Kao/Dck	Qz Kao/Dck Ill/Ms Mm Gy	Qz Kao/Dck Py Mm Gy Jar Cl-chl	Qz Kao/Dck Py Mm Gy	Qz Kao/Dck Py Mm Gy	Qz Kao/Dck Py Ill/Ms Mm Gy Iar	Qz Kao/Dck Py III/Ms	Qz Kao/Dck Py Mm	Qz Kao/Dck Mm Jar Cl-chl	Qz Kao/Dck Mm Gy Cal	Qz Kao/Dck Mm Gy Py	Qz Kao/Dck Gy Py		
Traces(SEM detectable)	Ti-Ox Hfo Zr	Ti-Ox Hfo Zr Bar Jar	Ti-Ox Hfo Bar Jar	Ti-Ox Hfo	Ti-Ox Hfo Bar	Ti-Ox Hfo Bar Jar Enr	Ti-Ox Hfo Bar	Ti-Ox Hfo Bar Cal	Ti-Ox Hfo Sl	Ti-Ox Hfo Zr Bar Enr	Ti-Ox Hfo Enr	Ti-Ox Py Enr Bar	Ti-Ox Na-Jar Goe Bar Enr Sco	Ti-Ox Na-Jar Hfo Enr Goe		

Bar=barite; Cal=calcite; Cl-chl=clinochlore; Enr=enargite; Hfo=amorphous and low crystalline Fe(III)-oxyhydroxides; Goe=goethite; Gy=gypsum; Hm=hematite; III/Ms=illite/ muscovite; Jar=jarosite; Kao/Dck=kaolinite/dickite; Mm=montmorillonite; Na-Jar=natrojarosite; Py=pyrite; Qz=quartz; Sco=scorodite; Sl=sphalerite; Ti-Ox=titanium oxide; Zr=zircon.

Concentration of minor elements in solid samples collected in the Furtei area

	As	Ba	Cd	Со	Cr	Cu	Ni	Pb	Rb	Sr	Zn
						mg/kg					
Weakly	, minera	ulized ro	cks								
FS3	13	337	< 0.5	3	40	25	17	160	17	162	57
FS4	59	177	< 0.5	1	36	56	5	120	7	182	48
FS6	39	329	< 0.5	5	21	44	4	60	15	575	47
FS7	18	78	< 0.5	12	7	14	4	7	45	56	73
Minera	lized ro	cks									
FS5	309	504	< 0.5	23	44	1390	20	110	40	653	60
FS8	99	232	< 0.5	17	27	1031	12	70	72	426	93
FS9	110	363	0.8	25	31	599	22	70	57	639	241
FS10	83	229	0.5	16	14	177	7	40	107	209	118
FS11	141	325	0.6	16	11	335	5	40	158	104	129
FS12	788	569	< 0.5	81	46	3284	33	88	17	590	27
FS13	59	234	< 0.5	3	19	57	8	60	37	137	81
Tailing	s										
FS1	210	384	< 0.5	11	37	196	8	130	28	767	48
FS2	251	448	< 0.5	9	20	615	6	80	19	393	36
FS22	381	811	< 0.5	11	18	690	34	73	18	360	38

4.2. Leachates

The results of leaching experiments are reported in Table 5, whereas the percentage of the leached fraction of each element with respect to the total concentration in the solid is reported in Table 6.

With the exception of FS7, the leachates of weakly mineralized rocks are characterized by slightly acidic pH (5.1–5.9), low total leached solids (TLS) (0.02–0.15 g/L), low concentrations of major components, and low or intermediate concentrations of minor components. Moreover, toxic elements are mostly immobile. These results are clearly related to the low solubility of silicate minerals and the small availability of sulphide minerals. The peculiarity of FS7 leachate is represented by a near-neutral pH (7.6), and high concentrations of Ca, SO₄ and Sr, related to the dissolution of gypsum.

The leachates of mineralized rocks are characterized by acidic pH and high concentrations of SO_4 , Fe, Al, Mn and other minor components (especially As, Cd, Co, Cu, Ni and Zn). Copper is leached up to 80% of the total concentration. The relatively high, albeit variable, percentages of leached As should also be noted. These results

Table 5

Concentration of major and minor components in the le	eachates of solid samples collected in the Furtei area
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	pН	Eh	TLS ^a	Ca	Mg	Na	К	Alk ^b	Cl	SO ₄	NO_3	SiO ₂	Al	Fe	Mn
		mV	g/L							mg/L					
Weakly r	nineralize	d rocks													
FS3	5.1	509	0.15	2.3	6.1	39	2.4	< 0.1	58.4	40	5.2	1.2	0.1	< 0.01	0.012
FS4	5.7	517	0.02	0.1	<0.2	4	<1	< 0.1	4.0	6.8	0.9	0.7	< 0.01	< 0.01	0.001
FS6	5.9	489	0.12	4.7	2.4	22	1.7	< 0.1	30.9	34	2.4	1.4	2.4	1.4	0.1
FS7	7.6	459	1.74	466	23	34	10	15.8	3.3	1186	<0.5	0.9	0.02	0.02	0.002
Mineraliz	zed rocks														
FS5	2.8	679	1.64	45	34	0.9	2.5	< 0.1	8.1	1297	< 0.5	0.60	132	113	9.8
FS8	3.7	632	0.96	154	56	0.8	<1	< 0.1	0.6	725	< 0.5	0.73	4.6	3.7	13.2
FS9	2.6	684	2.04	50	17	0.5	2.2	< 0.1	3.0	1540	< 0.5	0.64	97	322	2.4
FS10	5	546	0.92	162	60	0.9	2.4	5.2	1.1	676	< 0.5	0.94	0.5	1.4	12.0
FS11	2.7	676	101	63	4	<1	<1	< 0.1	2.0	840	< 0.5	0.63	86	69	0.7
FS12	2.6	696	2.60	20	12	11	<1	< 0.1	3.0	1970	< 0.5	0.45	102	482	0.06
FS13	3.3	747	0.39	15	39	<1	<1	< 0.1	0.7	314	< 0.5	1.99	14	3.0	1.1
Tailings															
FS1	97	387	192	421	< 0.2	194	<1	50.0	176	1061	87	122	27	0.28	0.002
FS2	62	451	0.59	27	8	145	14	10.1	49	312	38	2.46	0.02	0.02	0.002
FS2 FS22	6.7	573	0.28	62	7	5.4	1.3	14.5	2.4	187	0.9	1.52	0.06	< 0.01	0.53
	As		Ва	Cd	Со	Cr	Cı	1	Hg	Ni	Pb	Rb	Sr	Zn	CN
								μ	g/L						
Weakly r	nineralize	d rocks													
FS3	<	0.4	22.0	0.25	4.37	0.4		54	<0.5	2.7	2.2	1.8	30	28	<10
FS4	<	0.4	8.30	< 0.08	0.05	<0.4		<7.3	<0.5	< 0.07	< 0.9	<0.9	70	6	<10
FS6		0.8	50.0	1.8	1.80	1.3		98	< 0.5	6.3	2.5	2.7	64	36	<10
FS7	<	0.4	2.66	<0.08	0.40	0.5		<7.3	<0.5	8.0	<0.9	2.0	570	<3	<10
Mineraliz	zed rocks														
FS5	9	0	7.30	11.5	608	47	49	9300	<0.5	330	1.1	<0.9	11	1270	<10
FS8		0.9	1.06	1.7	135	1.9	11	1000	<0.5	80	< 0.9	<0.9	32	840	<10
FS9	27	2	0.01	7.6	512	56	21	1800	< 0.5	505	< 0.9	1.04	19	1800	<10
FS10		0.6	2.44	3.26	58.7	0.7		122	< 0.5	24	< 0.9	3.0	102	168	<10
FS11	17	5	0.70	14.4	226	24	1	3410	< 0.5	65	< 0.9	2.3	2	1352	<10
FS12	1000	0	8.25	1.77	2600	77	66	5940	< 0.5	740	1.3	5.5	63	254	<10
FS13	5	6	0.53	2.24	57.0	2.6		724	<0.5	26	<0.9	<0.9	6	216	<10
Tailings															
FS1	2	6	17.9	< 0.08	46.0	11.4		18.5	< 0.5	7.0	<0.9	16	400	<3	3300
FS2		1.6	14.0	0.2	72.0	< 0.4		30	3	4.0	<0.9	1.8	25	16	1400
FS22	<	0.4	17.0	0.1	11.0	< 0.4		9.3	0.7	5.0	<0.9	1.1	99	7	110

(liquid to solid ratio=20).

^a TLS=total leached solids.

^b ALK=alkalinity expressed as HCO₃.

Leached fraction of each element expressed as percentage of the total concentration in the solid

	Ca	Mg	Na	К	S	Al	Fe	Mn	As	Ва	Cd	Со	Cr	Cu	Ni	Pb	Rb	Sr	Zn
										%									
Weakly	, minerali	zed rocks	;																
FS3	1	4	12	1	22	< 0.1	-	0.3	-	0.1	-	3	< 0.1	4	0.3	< 0.1	0.2	0.4	1
FS4	< 0.1	-	0.8	-	3	-	-	< 0.1	-	0.1	-	0.1	-	-	-	-	-	0.8	0.3
FS6	1	0.9	2.0	0.7	4	0.1	0.1	0.7	< 0.1	0.3	-	0.7	0.1	4	3	0.1	0.4	0.2	2
FS7	16	5	29	2	18	<0.1	<0.1	<0.1	-	0.1	-	0.1	0.1	-	4	-	0.1	20	-
Minera	lized rock	S																	
FS5	13	22	0.3	0.6	11	3	4	100	0.6	< 0.1	-	53	2	71	33	< 0.1	-	< 0.1	42
FS8	40	21	0.1	-	7	0.1	0.1	36	< 0.1	< 0.1	-	16	0.1	21	13	-	-	0.2	18
FS9	54	19	0.4	0.3	12	2	11	56	5	< 0.1	19	41	4	73	45	-	< 0.1	0.1	15
FS10	31	20	0.4	0.2	15	< 0.1	0.1	19	< 0.1	< 0.1	13	7	0.1	1	7	-	0.1	1	3
FS11	16	3	-	-	8	2	3	26	2	< 0.1	48	28	4	80	25	-	< 0.1	< 0.1	21
FS12	35	29	9	-	13	3	12	9	25	< 0.1	-	65	3	41	44	< 0.1	0.7	0.2	19
FS13	13	3	-	-	11	0.4	0.2	4	2	<0.1	-	44	0.3	25	7	-	-	0.1	5
Tailings	5																		
FS1	11	-	48	-	15	0.1	< 0.1	< 0.1	0.2	0.1	-	9	0.6	0.2	2	-	1	1	-
FS2	4	3	11	0.5	5	< 0.1	< 0.1	8	< 0.1	0.1	-	16	-	0.1	1	-	0.2	0.1	0.9
FS22	44	17	9	0.6	2	< 0.1	-	13	-	< 0.1	-	2	-	< 0.1	0.3	-	0.1	0.5	0.4

-: not estimated due to values below detection limits.

reflect the large availability of pyrite, whose oxidation promotes the oxidation of other sulphides, the release of metals, and the formation of soluble secondary minerals.

The leachates of tailings show either alkaline or near-neutral pH: leachates of tailings from cyanidation processing of oxidized ore (FS1) have pH 9.7, whereas tailings from flotation of sulphide ore yield a pH

Table 7

Physical-chemical parameters and concentration of major components dissolved in waters draining the Furtei area

No.	Type ^a	Temp	pН	Eh	TDS ^b	Ca	Mg	Na	К	Alk ^c	Cl	SO ₄	SiO ₂	Al	Fe	Mn	Zn	Sr	
		°C		V	g/L							mg/	L						
Waters dr	aining we	akly miner	alized ro	ocks															
F41	BCN	20	6.5	0.28	5.7	705	179	847	20	422	1124	2378	15	0.7	5	0.5	0.02	7.8	
F16	BCN	20	7.6	0.12	6.8	501	79	1451	22	272	842	3647	8.4	0.1	0.4	4.6	0.03	5.4	
F20	BCN	18	6.9	0.25	4.7	324	59	1038	16	473	1011	1719	12	0.1	3.7	0.2	19	4.9	
F15	BFN	19	5.9	0.37	4.6	497	178	645	16	77	1012	2127	10	1.0	7.0	15	1.2	3.9	
F5	ST	17	7.6	0.41	4.1	406	205	600	16	185	1218	1481	9	0.4	0.5	2	0.03	2.1	
F5bis	ST	16	7.4	0.42	2.3	297	101	277	9	70	622	951	6	0.4	0.7	3	0.02	1.2	
F12	ST	19	7.5	0.43	1.8	204	83	229	11	46	389	811	13	0.2	0.2	5.4	0.20	0.8	
F13	ST	16	7.1	0.37	1.2	158	47	147	8	66	235	575	11	0.7	1.3	0.4	0.03	0.6	
ICRW2	ST	15	7.0	0.44	4.4	525	255	445	14	195	851	2132	12	0.1	0.2	2.1	0.02	1.8	
ICRW3	ST	17	7.6	0.41	3.3	462	121	368	13	223	586	1519	10	0.03	0.1	0.4	0.02	1.5	
F14	SP	16	7.1	0.43	0.8	38	28	149	5	212	131	206	14	0.2	0.2	0.1	0.02	0.2	
F11	Р	16	7.0	0.36	0.7	111	21	47	8	62	67	346	7.1	0.2	0.3	0.3	0.02	0.3	
F52	Р	19	6.8	0.45	3.0	354	135	361	8	23	464	1614	4.1	0.6	0.8	0.8	0.06	1.0	
F34DT	UTI	15	6.7	0.39	4.0	591	126	506	10	90	387	2247	14	0.3	2.1	8.4	2.6	2.9	
F34FT	UTI	17	7.4	0.39	4.9	658	134	634	10	157	781	2466	12	0.1	0.4	11	0.05	3.7	
F9	R	16	7.7	0.45	0.8	170	12	42	9	360	57	62	30	7.5	11	0.5	0.10	0.7	
F30	D	21	8.0	0.42	0.3	44	14	27	3	115	42	73	1.4	0.1	0.1	0.0	0.01	0.2	
Waters dr	aining mir	neralized ro	ocks																
F7	BCN	21	4.2	0.49	5.3	498	152	882	23	6	1160	2484	9	3	32	4	0.69	3.6	
SFRW0	ST	15	3.0	0.75	2.9	108	159	77	7	nr	102	2118	21	66	238	19	1.0	0.3	
SFRW1	ST	18	3.0	0.77	2.7	93	139	23	4	nr	34	2157	37	199	25	5.6	2.5	0.2	
Т0	S	22	3.9	0.53	7.1	564	292	805	15	nr	1136	3965	74	111	93	56	11	1.5	
F3	S	21	2.3	0.73	16.1	416	703	32	<14 ^d	nr	79	12674	118	788	1224	24	6.3	0.4	
F25B	S	24	2.3	0.69	8.8	523	354	862	<14	nr	1015	5483	90	168	203	68	24	0.9	
F50	PL	17	2.5	0.87	10.9	292	228	57	<7	nr	119	8351	40	413	1338	33	8.2	0.4	
F51	PL	19	2.8	0.81	9.0	605	525	813	18	nr	1441	5178	24	91	255	17	4.69	4.1	
F53	PL	19	2.2	0.74	20.2	445	633	296	<14	nr	511	14831	101	645	2563	105	96.9	0.5	
F54	PL	20	2.8	0.76	10.1	526	970	252	<14	nr	350	7400	28	192	260	60	12.0	3.6	
Waters in	teracting v	vith tailing	S																
F25	S	20	6.5	0.24	6.3	622	207	935	24	386	879	3148	22	0.5	25.4	35	0.60	1.8	
F22	TI	18	4.5	0.52	5.9	520	140	1029	22	8	749	3400	28	19.1	3.6	22	2.4	2.2	

^a Type: BCN: borehole confined nappe; BFN: borehole phreatic nappe; ST: streamlet; SP: spring; P: pond; UTI: upstream of tailings impoundment; R: river; D: drain; S: seepage; PL: pit lake; TI: tailings impoundment;

^b TDS: total dissolved solids.

^c Alk: alkalinity expressed as HCO₃; nr: not revealable.

^d <: indicates values below detection limits calculated taking into account the dilution factor.

Concentration of minor elements dissolved in waters draining the Furtei area

No.	As	В	Ba	Cd	Со	Cu	Cr	Hg	Li	Ni	Pb	Rb	CN
							µg/L						
Waters dra	ining weakly 1	nineralized roo	cks										
F41	42	448	10	<1 ^a	1	48	3.5	0.5	624	6	<4	43	nd ^b
F16	2.4	389	25	<1	2	8	2.9	< 0.5	90	5	11	16	<10
F20	11.8	511	8	<1	6	5	4	< 0.5	82	3	<4	16	174
F15	1	446	52	38	99	11	<3	< 0.5	45	36	10	7	<10
F5	2.5	258	95	3.4	22	5	1.8	< 0.5	18	9	<4	4	<10
F5bis	4.2	129	83	2.2	23	49	1	< 0.5	20	9	<4	2	<10
F12	1	179	150	19	33	19	<3	< 0.5	21.6	11	<4	3	<10
F13	1.6	123	96	2.2	3.5	18	0.9	< 0.5	7.4	3.9	3	3	<10
ICRW2	0.6	144	23	<1	4	13	1.7	< 0.5	24	7	<4	3	nd
ICRW3	1.3	261	43	<1	1	15	2	1	17	5	<4	3	nd
F14	0.7	126	9	<1	1	5	1.8	0.6	1	1	<4	1	<10
F11	0.8	47	70	<1	0.7	9	0.6	< 0.5	4.4	1.7	1.07	2	<10
F52	1	98	36	1.5	8	11	<1	< 0.5	16	8	<4	4	nd
F34DT	1.3	231	27	202	212	54	1.2	0.7	37	50	<4	4	12
F34FT	3.4	172	27	2	277	19	1.0	< 0.5	40	16	8	6	1100
F9	1.8	103	325	1	7.8	29	6.6	< 0.5	12	30	19	4	<10
F30	1.3	25	37	<1	0.3	3	1	<0.5	2.2	1.2	<4	1	<10
Waters dra	ining minerali	zed rocks											
F7	27	785	18	<1	9	40	2	< 0.5	2370	6	<4	69	nd
SFRW0	730	95	49	9	495	32400	43	1	118	271	4	3	nd
SFRW1	3.5	43	48	28	317	2179	20	<0.5	225	187	4	2	nd
Т0	< 0.4	380	15	138	826	1462	3.4	0.8	292	190	184	34	5775
F3	175	<200	<39	41	1487	13339	403	0.7	629	2061	<72	<28	nd
F25B	28.5	398	2	225	951	4532	30	1.8	348	269	90	37	14450
F50	5000	20	3	47	2489	180000	116	1	718	779	36	6	nd
F51	270	201	10	56	871	80000	49	< 0.5	637	392	14	27	nd
F53	3411	<3000	53	1667	4255	153577	314	1	816	1754	86	<28	nd
F54	370	200	<50	75	2120	122000	51	<2	439	1200	16	19	nd
Waters inte	eracting with t	ailings											
F25	260	386	19	<1	412	21	3.2	1	71	39	<4	23	32800
F22	1.5	263	21	49	1125	3510	<3	19	448	493	4	25	35700

 $^{\rm a}~<:$ indicates values below detection limits calculated taking into account the dilution factor. $^{\rm b}~$ nd: not determined.



Fig. 2. Piper diagram showing the main chemical composition of the Furtei waters sampled in 2003.



Fig. 3. Modified Ficklin plot (Ficklin et al., 1992) showing metal contents versus pH respectively in leachates of solid materials (a) and in the Furtei waters (b) sampled in 2003. Symbols are the same as in Fig. 1.

of 6.2–6.7. The high Na and NO₃ concentrations are due to the use of alkaline Na-cyanide solutions in the ore processing. This is also testified by high CN^- concentrations, especially in FS1 and FS2 leachates. The dissolution of calcite and gypsum accounts for the high release of Ca, CO₃ (expressed as alkalinity in Table 5a), SO₄ and Sr from FS1. With regard to minor components, all toxic elements are within limits imposed by Italian regulations for leaching tests on industrial wastes¹, except for Hg (up to 3 µg/L against the limit of 1 µg/L). The relatively high As concentration in the FS1 leachate is linked to the high solubility of As at alkaline pH. On the contrary, little As is leached from FS2 and FS22, although these samples contain appreciable amounts of pyrite and enargite, probably because of As sorption onto Fe(III) oxides/hydroxides (e.g., Lee et al., 2005, and references therein).

4.3. Chemical composition of waters

Dissolved concentrations of major and minor components are reported in Tables 7 and 8, respectively. Taking into account the main rock type drained, waters were divided in three groups: 1) waters draining weakly mineralized rocks with low sulphide content, including waters sampled outside of the mining area, draining barren rocks, 2) waters draining high-sulphide mineralized rocks, including the waters in pit lakes (F50, F51, F53), and 3) waters interacting with tailings, including the F25 sample, that receives seepage from the tailings impoundment.

The Piper diagram in Fig. 2 shows the major chemistry of waters considered in this study. The group 1 waters show either a dominant Ca–HCO₃ composition with low salinity, or Na–Ca–SO₄–Cl composition with moderate salinity. They usually have near-neutral to slightly alkaline pH, and low amounts of toxic elements. The group 2 waters show a marked Mg–SO₄ composition, high salinity (TDS up to 20 g/L), low pH (2.9±0.7), and very high concentrations of dissolved Al, As, Cd, Co, Cu, Fe, Mn, Ni and Zn. With respect to Italian regulations for



Fig. 4. Variation of the saturation index (SI) with respect to albite (a), chlorite (b) and calcite (c) versus pH in the Furtei waters sampled in 2003.

¹ As defined in the Annex 3 of Dlgs 186/2006.



Fig. 5. Variation of Al (a), Cu (b), and As (c) concentrations versus pH in the Furtei waters sampled in 2003.

industrial discharges², the elements that exceed the limits to the largest extents are Al (up to 800 times the limit), As (up to 100), and Cu (up to 1800).

The group 3 waters have a dominant Na(Ca)–SO₄ composition, pH values in the range of 4.5 to 6.5, and values of salinity and dissolved metals intermediate between group 1 and group 2 waters. The group 3 waters are characterized by high cyanide concentrations $(34\pm2 \text{ mg/L})$. Other waters in the area have negligible cyanide contents. The only exceptions are the F25B and F34FT samples that receive cyanide leakage from the impoundment. It must be pointed out that all such leakages are collected in a well (sample T0), and

pumped back into the impoundment (Cidu, 2000; Cidu and Da Pelo, unpublished data).

5. Discussion

The results of leaching experiments are a direct consequence of sulphide availability in the solid materials. Mineralized rocks and waste dumps contain significant amounts of pyrite and other sulphide minerals. Pyrite oxidation results in generation of acid solutions, where heavy metals are highly mobile. On the other hand, the low sulphide content of weakly mineralized rocks results in slightly acid, low metal leachates. These results are in good agreement with the chemical composition of waters. Fig. 3 shows the cumulative concentration of dissolved toxic elements (As+Cd+Co+Cu+Ni+Pb+ Zn) versus pH in the leachates (Fig. 3a) and in the waters (Fig. 3b). Pit lakes and water draining sulphide mineralized rocks show the lowest pH and the highest metal contents, similar to what is observed in leachates from mineralized rocks. In spite of the low permeability of rocks in the Furtei area, these waters might slowly infiltrate, and affect the groundwater. In this case, As would represent an element of concern, due to its higher mobility than in surface waters at the lower Eh observed in groundwater (Musu et al., 2007b).

On the other hand, where surface waters interact with mineral assemblages of the propylitic alteration zone (chlorite, quartz, calcite, minor epidote, sericite and pyrite, and subordinate Fe-oxides, with relic magmatic plagioclase: Ruggieri et al., 1997), they show an approach to equilibrium with respect to albite (Fig. 4a), chlorite (Fig. 4b) and calcite (Fig. 4c), as indicated by saturation index (SI) values close to zero. This corresponds to a marked increase in pH concomitant with a decrease in dissolved metals. This behavior is well exemplified by Al and Cu, as can be observed in Fig. 5a and b, respectively, whereas the trend displayed by As (Fig. 5c) is more complex, reflecting the well known mobility of this element as oxyanion at circumneutral pH (e.g., Smedley and Kinniburgh, 2002). The coupled increase in pH and decrease in dissolved metals was previously reported for waters draining the southeastern margin of the exploited area (Riu S'Aluminu creek in Fig. 1; Cidu et al., 1999), and confirms an important buffering capacity of the propylitic assemblage in this type of deposits (see e.g. Plumlee et al., 1995).

In summary, the major threats to the environment of the studied solid materials arise by their pyritic content that generates acidity, and by the presence of Cu–As bearing minerals, mainly enargite. In addition to the release of toxic elements, this mineral can contribute to acid drainage (Plumlee, 1999; Lattanzi et al., 2008). In acid environments, enargite appears comparatively sluggish to react (Lattanzi et al., 2008). However, the presence of bacteria and/or of dissolved ferric iron from pyrite oxidation speeds up enargite dissolution, with



Fig. 6. Variation of CN[−] concentrations and pH in the tailings pond from 1999 to 2003. The sudden drop in CN[−] and pH indicated by the arrow corresponds to the start of sulphide ore processing.

² As defined in Table 4 of Dlgs 152/ 2006.

consequent release of As and Cu to the water. We emphasize that a comparatively slow reaction rate can still result in the release of a harmful amount of contaminants. Musu (2007) determined a rate of As release of 10^{-10} mol m⁻² s⁻¹ during the oxidative dissolution of enargite at pH=4 (HCl), 50 ° C. At this rate, each exposed square meter of enargite surface could release 0.24 g of arsenic in the aqueous environment in one year. This seemingly small amount could potentially contaminate (beyond the 10 µg/L limit for As in drinking waters recommended by World Health Organization) about 24 m³ of initially As-free water. Actually, such a release should be lower at lower temperatures, and delayed by As immobilization in secondary minerals such as scorodite and/or via adsorption onto Fe(III) oxy-hydroxides-sulphates (Musu et al., 2007a,b). The experiments by Musu (2007) were conducted in the absence of ferric iron and/or bacteria, which would enhance the dissolution rate of enargite.

Finally, we consider the potential threat posed by tailings. Tailings leachates are not acidic, and show a relatively low release of contaminants. However, there is no guarantee that this condition will be maintained for long. Indeed, as Fig. 6 shows, there was a marked decrease of pH and CN⁻ in waters at the tailings impoundment. This change occurred when pyrite-bearing flotation tailings, instead of residues from cyanidation of the oxidized ore, began to be discharged into the impoundment (Musu, 2007). Cyanide concentrations in the tailings leachates are also relatively high (up to 3 mg/L CN⁻), and their very dangerous nature is obvious. However, CN⁻ will slowly decompose in some years (especially considering the pH decrease), giving way to less dangerous components, such as NO₃ (see Table 5a). As an alternative, it can be oxidized in situ by a variety of techniques (e.g., Botz, 2001). In any case, according to reclamation plans upon mine closure, all tailings materials will be stored in a confined basin, thereby minimizing their interaction with the surrounding environment.

6. Conclusions

The Furtei gold mine lies in a sensitive environment, because of the close proximity to an inhabited area, and specifically to important water reserves and to agricultural activities. The highest potential threat for the environment is mostly represented by mineralized rocks exposed in waste dumps and open pits. Leaching tests, consistent with the water chemistry observed in the area, clearly show that these materials, because of the high sulphide content, have a high capability for acid drainage generation and release of toxic or harmful elements (As, Cd, Co, Cr, Cu, Ni). Mechanical removal (including wind transport) and/or rain leaching of material from waste dumps may contaminate the plain next to the mine, and/or the important water reservoir located within the mining concession. Moreover, the acid, high-metal waters of pit lakes can cause contamination in the local groundwater. Although the ongoing monitoring program has detected so far no changes in the local water chemistry with respect to pre-mining conditions, these threats must be carefully considered in final reclamation plans. Indeed, a partial refill of open pits, and revegetation of exposed rock surfaces is under way. On the other hand, a natural attenuation of acidity and metal load occurs upon interaction between waters and minerals of the propylitic alteration zone. Tailings are also a potentially harmful material, because of the high metal and cyanide contents. However, their confinement to a restricted site should mitigate their environmental impact. Finally, the presence of livestock grazing nearby the mining area suggests a potential contamination of the food chain; however, in the absence of data on the amounts of toxic elements in soils and local vegetation, this kind of risk cannot be quantified.

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References

- Arribas Jr., A., 1995. Characteristics of high sulfidation epithermal deposits and their relation to magmatic fluid. In: Thompson, J.F.H. (Ed.), Magmas, fluids and ore deposits: Mineralogical association of Canada Short course, vol. 23, pp. 419–454.
- Botz, M.M., 2001. Cyanide treatment methods. In: Mudder, T.I. (Ed.), The Cyanide Guide, Mining Environmental Management Journal. Special Edition, vol. 9, pp. 28–30.
- Caboi, R., Cidu, R., Fanfani, L., Lattanzi, P., Zuddas, P., 1999. Environmental mineralogy and geochemistry of the Pb–Zn abandoned Montevecchio-Ingurtosu mining district, Sardinia, Italy. Chronique de la rechérche miniére 534, 21–28.
- Ciccu, R., Imolesi, E., 1996. Assessment of environmental issues of surface mining projects. In: Ciccu, R. (Ed.), Proceedings of 4th International Conference on Environmental Issues and Management of Waste in Energy and Mineral Production, SWEMP 96, DIGITA University of Cagliari, Italy, vol. 1, pp. 173–187.
- Cidu, R., 2000. Impact of small-scale gold mining on water quality. In: Singhal, R.K., Mehrotra, A.K. (Eds.), Proceedings of the 6th International Conference on Environmental Issues and Management of Waste in Energy and Mineral Production, SWEMP 2000, Calgary, Canada. Balkema, A.A., Rotterdam, pp. 607–614.
- Cidu, R., Fanfani, L., 2002. Overview of the environmental geochemistry of mining district in southwestern Sardinia, Italy. Geochemistry: Exploration, Environment, Analysis 2, 243–251.
- Cidu, R., Caboi, R., Fanfani, L., Frau, F., 1997. Acid drainage from sulfides hosting gold mineralization (Furtei, Sardinia). Environmental Geology 30, 231–337.
- Cidu, R., Da Pelo, S., Lattanzi, P., 1999. Environmental mineralogy and geochemistry of the epithermal gold deposit at Furtei, Sardinia. In: Stanley, C.J., et al. (Ed.), Proceedings of the 5th Biennial SGA Meeting, London, England. Balkema, A.A., Rotterdam, pp. 1175–1178.
- Da Pelo, S., 1998. Environmental geochemistry and mineralogy of active and abandoned mine sites. Unpublished PhD Thesis in Earth Sciences, Cagliari-Genova-Torino (in Italian, extended abstract in English in Plinius 21, 1999, 70–74).
- Da Pelo, S., Frau, F., Ardau, C., Rundeddu, L., Lattanzi, P., 2001. Water chemistry at the Montevecchio Levante mine tailings impoundment (Sardinia-Italy). In: Cidu, R. (Ed.), Proceedings of the 10th Water Rock Interaction congress, WRI-10.Villasimius, Italy, vol. 2. Balkema, A.A., Rotterdam, pp. 1201–1204.
- Ficklin, W.H., Plumlee, G.S., Smith, K.S., McHugh, J.B., 1992. Geochemical classification of mine drainage and natural drainages in mineralized areas. In: Kharaka, Y.K., Maest, A.S. (Eds.), Proceedings of the 7th Water Rock Interaction congress, WRI-7, Park City, Utah, USA. Balkema, A.A., Rotterdam, pp. 381–384.
- Frau, F., Ardau, C., 2003. Geochemical controls on arsenic distribution in the Baccu Locci stream catchment (Sardinia, Italy) affected by past mining. Applied Geochemistry 18, 1373–1386.
- Hage, J.L.T., Mudler, E., 2004. Preliminary assessment of three new European leaching tests. Waste Management 24, 165–172.
- Hageman, P.L., Briggs, P.H., 2000. A simple field leach test for rapid screening and qualitative characterization of mine waste dump material on abandoned mine lands. Proceedings Fifth International Conference on Acid Rock Drainage (ICARD), vol. II. Society for Mining, Metallurgy, and Exploration Inc., Littleton, Colorado, pp. 1463–1475. URL: http://crustal. usgs.gov/projects/minewaste/minewaste_pubs.html.
- Jarvis, I., 1992. Sample preparation for ICPMS. In: Jarvis, K.E., et al. (Ed.), Handbook of Inductively Coupled Plasma Mass Spectrometry. Blackie Academic and Professional, Glasgow, UK, pp. 172–224.
- Lattanzi, P., Da Pelo, S., Musu, E., Atzei, D., Elsener, B., Fantauzzi, M., Rossi, A., 2008. Oxidation of enargite: a review. Earth Science Reviews 86, 62–88.
- Lee, P.K., Kang, M.J., Choi, S.H., Touray, J.C., 2005. Sulfide oxidation and the natural attenuation of arsenic and trace metals in the waste rocks of the abandoned Seobo tungsten mine, Korea. Applied Geochemistry 20, 1687–1703.
- Madau, G., Pinna, G., Humphries, B., Orrù, P., 1996. Furtei gold project: environmental baseline study and management plan. In: Ciccu, R. (Ed.), Proceedings of 4th International Conference on Environmental Issues and Management of Waste in Energy and Mineral Production, SWEMP 96, DIGITA University of Cagliari, Italy, vol. 1, pp. 189–196.
- Musu, E., 2007. Dissoluzione ossidativa dell'enargite: evidenze sperimentali e da sistemi naturali (Tesi di dottorato in Scienze della Terra). Università di Cagliari (in Italian).
- Musu, E., Da Pelo, S., Lattanzi, P., Lorrai, M., 2007a. Secondary mineralogy at Furtei, Sardinia Italy: control on toxic element mobility. In: Bullen, T.D., Wang, Y.X. (Eds.), Proceedings of the 12th Water Rock Interaction congress WRI-12, Kunming, China. Taylor and Francis Group, pp. 625–628.
- Musu, E., Da Pelo, S., Lorrai, M., Lattanzi, P., 2007b. Variations and controls on the copper/arsenic ratios in waters at the Furtei gold mine, Sardinia, Italy. In: Cidu, R., Frau, F. (Eds.), Proceedings of the 9th International Mine Water Association Symposium, IMWA 2007, Cagliari, Italy, pp. 441–445. ISBN: 9788890295508330.
- Nicol, S., Orunesu Preiatra, M., Righini, G., Murroni, A., 2002. SGM Furtei gold project: environmental management and monitoring. In: Ciccu, R. (Ed.), Proceedings of 7th International Conference on Environmental Issues and Management of Waste in Energy and Mineral Production, SWEMP 2002, Cagliari, Italy. ISBN: 8890089504, pp. 1237–1242.
- Nordstrom, D.K., 1977. Thermochemical redox equilibria of Zobell's solution. Geochimica et Cosmochimica Acta 41, 1835–1841.

- Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (version 2) A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS Water-Resources Investigations Report 99–4259, Denver, Colorado.
- Plumlee, G.S., Smith, K.S., Gray, J.E., Hoover, D.B., 1995. Epithermal quartz-alunite deposits. In: Du Bray, E.A. (Ed.), Preliminary descriptive geoenvironmental models of mineral deposits. U.S. Geological Survey ,Open File Rept, vol. 95–231, pp. 162–169.
- Plumlee, G.S., 1999. The environmental geology of mineral deposits. In: Plumlee, G.S., Logsdon, M.J. (Eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Society of Economic Geologists, Littleton, CO, pp. 71–116.
- Society of Economic Geologists, Littleton, CO, pp. 71–116. Progemisa, 2003. Caratterizzazione idrogeologica Permesso di Ricerca 'Costa Sa Tiria'. Report Sardinia Gold Mining SpA, vol. 28 (in Italian).
- Ruggieri, G., Lattanzi, P., Luxoro, S.S., Dessì, R., Benvenuti, M., Tanelli, G., 1997. Geology, mineralogy and fluid inclusion data of the Furtei high-sulfidation gold deposit, Sardinia, Italy. Economic Geology 92, 1–19.Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry 17, 517–568.
 Smith, K.S., Ramsey, C.A., Hageman, P.L., 2000. Sampling strategy for the rapid screening.
- Smith, K.S., Ramsey, C.A., Hageman, P.L., 2000. Sampling strategy for the rapid screening of mine-waste dumps on abandoned mine lands. Proceedings Fifth International Conference on Acid Rock Drainage (ICARD), vol. II. Society for Mining, Metallurgy, and Exploration Inc., Littleton, Colorado, pp. 1463–1475. URL: http://crustal.usgs. gov/projects/minewaste/minewaste_pubs.html.