

## Evaluation of the potential release of toxic elements from gold ores and cyanidation tailings in a high sulphidation mining district.

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### ABSTRACT

The Furtei gold mine in Sardinia (Italy) exploits a volcanic-hosted high-sulphidation epithermal deposit. Large amounts of high sulphide materials derived from exploitation are present in open pits, waste rock dumps and cyanidation tailings impoundment. Analyses of waters draining the mining area and laboratory leaching tests showed that waste rock dumps and mineralized rocks have a high potential for acid drainage generation and release of heavy metals. The mineralogical assemblage strongly influences the composition of leachates. Leachates from cyanidation tailings show variable pH (between 6.2 and 9.7, depending on sulphide content of the solid); cyanide concentration varies between 110 µg/l and about 3 mg/l, whereas heavy metals content in leachates is mostly within the limits of Italian regulations for industrial discharges. The overall results provide useful data for the implementation of reclamation programs.

### INTRODUCTION

Metalliferous ore deposits have played an important role in the technologic and economic development of the human society. However, in many cases their exploitation has been accompanied by an adverse impact on the environment, mainly on surface and groundwater systems (e.g., Gray *et al.* 1994). Examples of environmental contamination by mining activity are extensively present in Sardinia (Caboi *et al.* 1996; Caboi *et al.* 1999; Cidu & Fanfani, 2002).

Since the second half of 1980s, the increasing environmental and health consciousness promoted legislation placing the environmental liability for wastes with the operators of the industrial process that generates them. This liability remains beyond closure of the operation (Peterson & Petrie, 1999). Hence, plans for modern mining exploitation, especially in developed countries, must involve the assessment of the environmental impact during exploitation, and specific reclamation plans upon cessation of mining operations (Marcus, 1997). In this context, the potential impact of mining works on the environment is a primary concern in the local communities.

The recently developed gold deposit at Furtei in Sardinia (Italy) is a typical example of volcanic-hosted high-sulphidation epithermal deposit (Ruggieri *et al.* 1997). Exploitation began in 1997 for confirmed reserves adding up to 2,150,000 metric tons at 2.82 gram per tonne Au (Madau *et al.* 1996). It was preceded and is being accompanied by studies of the environmental impact and plans for reclamation after closure (Ciccu & Imolesi 1996, Madau *et al.* 1996, Da Pelo & Lattanzi 1997, Cidu *et al.* 1997, Caboi *et al.* 1999). Open pit mining works are in stand by since December 2002.

The largest environmental effects of open pit mining are the amount of disturbance generated, and the amount of mineralized rock exposed to weathering. The leaching of soluble constituents upon contact with water is regarded as a main mechanism of contaminant release (Twardowska & Szczepanska, 2002). Batch leaching tests provide useful information about the availability of easily leachable constituents in the tested material, although they do not give direct information on the long-term leaching behaviour and on leachate composition at field conditions of waste exposure. However, these tests, together with mineralogical and geochemical data of the waste materials, represent an important contribution to the environmental risk assessment.

The aim of this study was to estimate, both experimentally and in the field, the potential for generation of acid mine drainage and leaching of harmful metals from natural (mineralized and sterile rocks) and mined materials (waste rocks), and processing residues (tailings). This was accomplished through a mineralogical and chemical 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.

### STUDY AREA

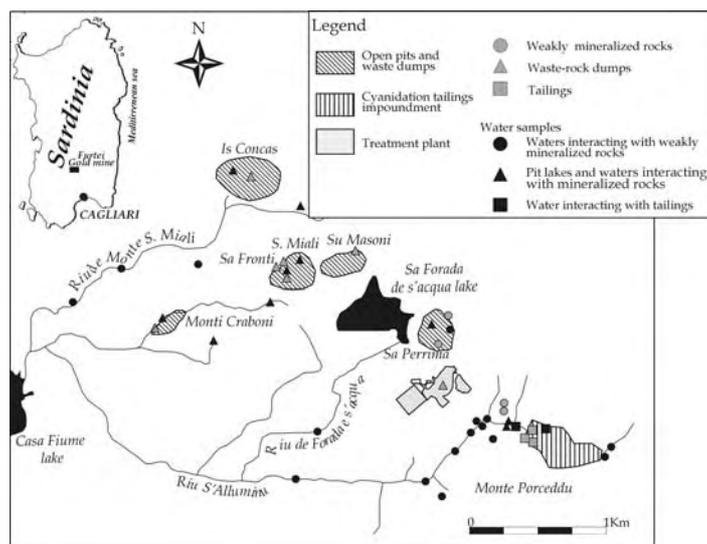
The gold deposit at Furtei is a typical example of a volcanic-hosted high-sulphidation (acid-sulphate) epithermal deposit, linked to calc-alkaline andesitic-basaltic rocks of the Sardinian Oligo-Miocene volcanic cycle (Ruggieri *et al.* 1997). The deposit consists of four main ore bodies, and is associated with extensive alteration of the host rocks, with development of four typical facies of high-sulphidation deposits: vuggy and massive silica, advanced argillic, argillic, and propylitic. In the primary (hypogene) mineralization, the most abundant sulphide is pyrite, followed by copper-arsenic sulphides (mainly enargite, with minor amounts of luzonite and tennantite). In some ore bodies, sphalerite and wurtzite are more abundant. Before exploitation, the primary mineralization was covered by an oxidized (supergene) assemblage, mainly composed of Fe oxyhydroxides, down to depths of 10-50 meters. Other phases commonly present are gypsum and jarosite. Alunite (both hypogene and supergene) is

comparatively rare at Furtei. Several other secondary minerals (mostly Cu-Fe-Al sulphate minerals and arsenates) were also found, but their occurrence is typically restricted to specific environments such as cavities and fissures (Da Pelo, 1998). For five years gold was extracted from the oxidized ore by cyanidation, but with exhaustion of oxidized ore, sulphide ores were also exploited. Tailings from the cyanidation process and from flotation of the sulphide ore are disposed of in an impoundment (Figure 1).

## SAMPLING AND ANALYTICAL METHODS

### Waters

Sampling of waters is routinely performed in the framework of a hydrogeochemical monitoring program. The waters considered in this study were sampled immediately after a heavy rain event in October 2003. They are believed to be representative of natural leaching of exposed material. Sample location is reported in Figure 1.



**Figure 1: Map showing the location of sampling sites in the Furtei area**

Water samples were filtered in situ through a 0.4  $\mu$ m pore-size polycarbonate filter with an all-plastic filtration assembly, and acidified upon filtration for metal analyses. At each sampling site, temperature, pH, alkalinity, redox potential (Eh) 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 (ARL-3520B) and ICP-MS (ELAN 5000). The ionic balance was always in the range of  $\pm 5\%$ ; both precision and accuracy were estimated at  $\pm 10\%$  or better, using randomly duplicate samples and standard reference solution (NIST1643d).

### Solid Samples

Fourteen bulk solid samples were collected respectively from tailings impoundment (Fs1, Fs2, Fs22), waste rock dumps and outcropping mineralized rocks (Fs5, Fs8, Fs9, Fs10, Fs11, Fs12, Fs13), outcrops with low sulphide content (weakly mineralized samples - Fs3, Fs4, Fs6, Fs7) (Figure 1). Tailings samples Fs2 and Fs22 came from sulphide ore treatment, while Fs1 was from oxidized ore. Samples were stored in doubly sealed plastic bags until analyses.

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 and for mineralogical and chemical analyses, all samples were sieved to 2 mm. 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 H<sub>2</sub>O (MilliQ<sup>®</sup> ultrapure water), 3 ml H<sub>2</sub>O<sub>2</sub> (30% Carlo Erba RPE), 14 ml HNO<sub>3</sub> (68% Carlo Erba Suprapur), and 4 ml HF (50% Carlo Erba RPE). The HF was removed by open multiple evaporations to incipient dryness with HNO<sub>3</sub>, and the residue taken up in HNO<sub>3</sub>. Solutions were diluted to 100 ml with 1% HNO<sub>3</sub> in volumetric flasks, and transferred to new HD-polyethylene 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 replicated samples was mostly better than  $\pm 10\%$ . Accuracy was evaluated by replicate analyses of the SRM2710 standard. It was better than  $\pm 10\%$  for Ca, Mg, Na, K, Fe, Al, Ag, As, Ba, Cd, Co, Cu, Ni, Pb, Rb and Zn, and about  $\pm 20\%$  for Mn and Cr. Total carbon and sulphur were determined by a combustion infrared spectrophotometer (LECO CS-444 furnace).

A 24 hours leaching test was performed on portions of 2 mm-sieved sample: 10 g of sample and 200 ml of Milli-





The total concentrations of elements linked to the mineralization are summarized in Figure 3 for major components, and in Table 3 for trace elements.

All solid samples have high amounts of Al due to the high quantity of clay minerals. Waste rock samples show the highest amounts of S and Fe, mostly derived from pyrite. Copper, arsenic and barium are also abundant, due to the presence of enargite and barite.

In the weakly mineralized rocks, iron is mostly linked to crystalline and/or amorphous iron oxyhydroxides, onto which Pb and As are easily adsorbed. Sulphur, when present in high concentration, is principally linked to gypsum (Fs7).

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 presence of carbon is linked principally to calcite.

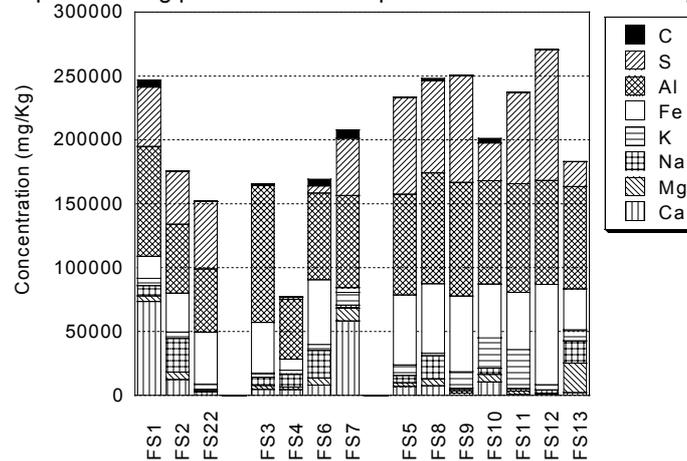


Figure 3: Distribution of major elements in solid samples

	Ag	As	Cd	Co	Cr	Cu	Ba	Mn	Ni	Pb	Rb	Sr	Zn
	mg/Kg												
Waste rock dumps													
FS5	1,8	309	<0,5	23	44	1390	504	194	20	110	40	653	60
FS8	<2,5	99	<10	17	27	1031	232	735	12	70	72	426	93
FS9	0,8	110	0,6	25	31	599	363	86	22	70	57	639	241
FS10	<2,5	83	<0,5	16	14	177	229	1258	7	40	107	209	118
FS11	0,2	141	0,6	16	11	335	325	58	5	40	158	104	129
FS12	1,4	788	<0,5	81	46	3284	569	11	33	88	17	590	27
FS13	0,5	59	<0,5	3	19	57	234	500	8	60	37	137	81
Weakly mineralized rocks													
FS3	0,2	13	0,1	3	40	25	337	89	17	160	17	162	57
FS4	0,5	59	0,1	1	36	56	177	17	5	120	7	182	48
FS6	0,5	39	0,1	5	21	44	329	292	4	60	15	575	47
FS7	<2,5	18	<0,5	12	7	14	78	1475	4	7	45	56	73
Tailings													
FS1	<2,5	210	<0,5	11	37	196	384	277	8	130	28	767	48
FS2	1,6	251	<0,5	9	20	615	448	107	6	80	19	393	36
FS22	1,5	381	<0,5	11	18	690	811	84	34	73	18	360	38

Table 3: Trace element concentrations in solid samples

The batch-leach experiments showed that the release of most elements and the acid generation capacity is mineralogically controlled.

Concentrations of elements in the leached solutions (Table 4) depend not only on their amounts in the solid material, but also on mineral solubility and on pH and Eh conditions. Figure 4 shows metal concentrations in the leachates versus pH. It can be observed that the lowest pH and the highest concentrations of metals occur in leachates from waste rocks. This is in agreement with field evidences. In fact, pit lakes and water draining sulphide mineralized rocks show the lowest pH and the highest metal contents (Table 1, Figure 4).

	pH	Eh mV	TDS g/l	Ca	Mg	Na	K	Alk	Cl	SO <sub>4</sub>	NO <sub>3</sub>	SiO <sub>2</sub>	Fe	Al	Mn
mg/l															
<b>Waste rock dumps</b>															
FS5	2,8	679	1,64	45	34	1	3	<0,1	8	1297	<0,5	0,6	113	132	9,8
FS8	3,7	632	0,96	154	56	1	<3	<0,1	1	725	<0,5	0,7	3,7	4,6	13,2
FS9	2,6	684	2,04	50	17	1	2	<0,1	3	1540	<0,5	0,6	322	97	2,4
FS10	5,0	546	0,92	162	60	1	2	5	1	676	<0,5	0,9	1,4	0,5	12,0
FS11	2,7	676	1,01	6	4	<1	<1	<0,1	2	840	<0,5	0,6	69	86	0,7
FS12	2,6	696	2,60	20	12	11	<1	<0,1	3	1970	<0,5	0,4	482	102	0,06
FS13	3,3	747	0,39	15	39	<1	<0,4	<0,1	1	314	<0,5	2,0	3	14	1,1
<b>Weakly mineralized rocks</b>															
FS3	5,1	509	0,15	2	6	39	2	<0,1	58	40	5,2	1	<0,01	0,1	0,012
FS4	5,7	517	0,02	0	<0,1	4	1	<0,1	4	7	0,9	1	<0,01	<0,01	0,001
FS6	5,9	489	0,12	5	2	22	2	<0,1	31	34	2,4	1,4	1,4	2,4	0,1
FS7	7,6	459	1,74	466	23	34	10	16	3	1186	<0,5	0,9	0,02	0,02	0,002
<b>Tailings</b>															
FS1	9,7	387	1,92	421	<0,2	194	<1	50	176	1061	9	1,2	0,28	2,7	0,002
FS2	6,2	451	0,59	27	8	145	1	10	49	312	38,0	2	0,02	0,02	0,5
FS22	6,7	573	0,28	62	7	5	1	14	2	187	0,9	1,5	<0,01	0,06	0,5

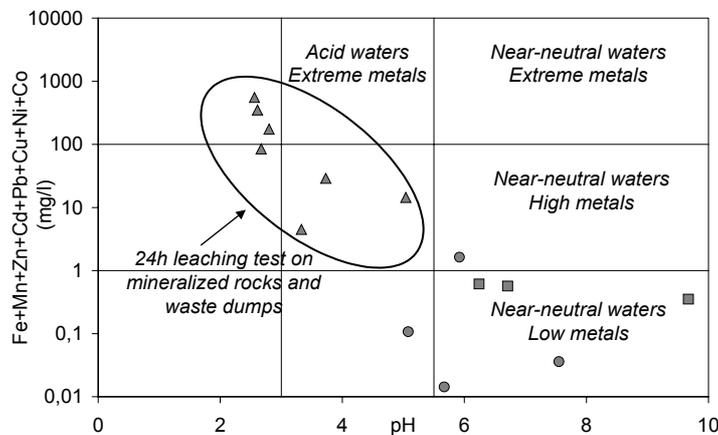
  

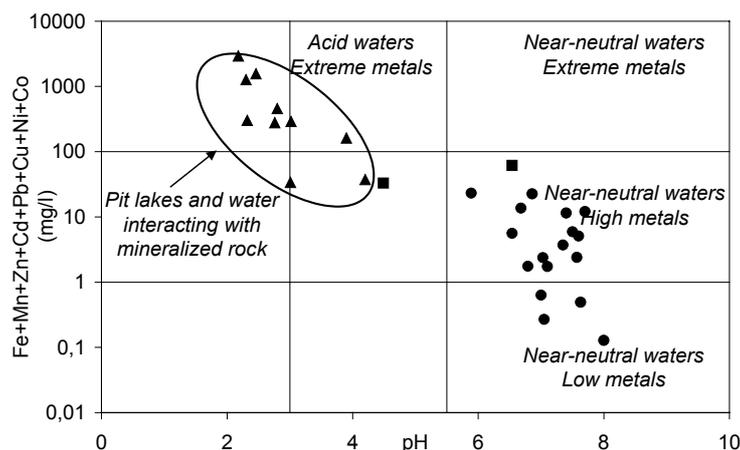
	As	Ba	Cd	Co	Cu	Cr	Ni	Pb	Rb	Sb	Sr	Zn	Hg	CN
µg/l														
<b>Waste rock dumps</b>														
FS5	90	7	12	608	49300	47	330	1	<0,9	<5	11	1270	<0,5	<10
FS8	0,9	1	2	135	11000	1,9	80	<0,9	<0,9	<1	32	840	<0,5	<10
FS9	272	0	8	512	21800	56	505	<0,9	1	<20	19	1800	<0,5	<10
FS10	0,6	2	3	59	122	0,7	24	<0,9	3	<1	102	168	<0,5	<10
FS11	175	1	14	226	13410	24	65	<0,9	2	<10	2	1352	<0,5	<10
FS12	10000	8	2	2600	66940	77	740	1,25	6	<100	63	254	<0,5	<10
FS13	56	1	2	57	724	2,6	26	0,9	<0,9	<1	6	216	<0,5	<10
<b>Weakly mineralized rocks</b>														
FS3	<0,4	22	0,25	4	54	0,4	3	2	2	<1	30	28	<0,5	<10
FS4	<0,4	8	<0,08	0	<7,3	<0,4	<0,07	<0,9	<0,9	<1	70	6	<0,5	<10
FS6	0,8	50	2	2	98	1,3	6	3	3	<1	64	36	<0,5	<10
FS7	<0,4	3	<0,08	0	<7,3	0,5	8	<0,9	2	<1	570	<3	<0,5	<10
<b>Tailings</b>														
FS1	26	18	<0,08	46	19	11,4	7	<0,9	16	3,6	400	<5	<0,5	3300
FS2	1,6	14	0,20	72	30	<0,4	4	<0,9	2	<1	25	16	3	1400
FS22	<0,4	17	0,1	11	9	<0,4	5	<0,9	1	<1	99	7	0,7	110

**Table 4: Concentration of chemical components in the leachates of solid materials (liquid to solid ratio = 20)**

The results are easily explained in terms of sulphide availability in the solid materials. Waste rocks contain significant pyrite and metal sulphides.

Pyrite oxidation results in a low pH environment, where heavy metals are highly mobile. The main Cu-As carrier, enargite, is comparatively sluggish to react (Da Pelo, 1998; Cidu *et al.* 1999). However, the presence of ferric iron from pyrite oxidation speeds up enargite dissolution (Dutrizac & MacDonald 1972), with consequent release of metals to waters. On the other hand, the low sulphide content of weakly mineralized rocks results in non-acid, low metal drainage.





**Figure 4: Ficklin plot (Ficklin *et al.* 1992) of natural waters at Furtei (lower frame), and of leachates of solid materials (upper frame). For natural waters and leachates, the symbols are the same as in Figure 1**

Tailings from the impoundment contain appreciable amounts of metals, and at least in two of them (Fs2, Fs22) the presence of pyrite and enargite can be observed by XRD or SEM. However, this type of material releases low amounts of metals. Specifically, the measured concentrations in the leachates are constantly lower than limits imposed by Italian regulations for industrial effluents, and often within the limits imposed for drinkable water. This is because this material was treated with alkaline cyanide solutions, so that waters interacting with them have near-neutral to alkaline pH. In these conditions, heavy metal mobility is low. There is no guarantee that this condition of low heavy metal mobility can be maintained for long times. However, according to reclamation plans upon mine closure, all this material will be stored in a confined basin, thereby minimizing its interaction with the environment.

## CONCLUSIONS

In the Furtei gold mine, the highest potential threat for the environment is apparently represented by waste rocks and mineralized rocks exposed in open pits. Because of the high sulphide content, this material shows a high capability for acid drainage generation and heavy metal release, and must be carefully considered in final reclamation plans. Tailings are also a potentially harmful material, because of the high metal and cyanide contents. However, their circumneutral to alkaline reaction slows down metal mobility, and their confinement to a restricted site should mitigate their environmental impact.

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