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Hazard Assessment to Workers of Trace Metal Content in Pyrite Cinders

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Pyrite ores (FeS_2), and mixed sulfides (PbS, ZnS, $CuFeS_2$), played a significant role in the mining activities of Colline Metallifere (Southern Tuscany, Italy). At the start of the 20th century a plant located near Scarlino (Grosseto, Italy) began to use these raw materials in the production of sulfuric acid. The manufacturing processes for sulfuric acid included a roasting step where, at a temperature of 900°C, sulfides dissociated into a solid fraction (cinder waste) and into a gaseous fraction (SO_2). Then the SO_2 was heated at 200°C to form SO_3 and subsequently H_2SO_4. Up to 1994, the Scarlino plant had been processed up about 2,500 t/d of mixed sulfides and pyrite, and related iron-enriched wastes had been partially used in the metallurgic industry for the iron pellets production: such past plant's activities (currently, elemental sulfur is utilized for sulfuric acid production) generated a heap of now stocked inside the plant's industrial perimeter.

At present diggers and scrapers are progressively removing cinders to be ground into fine and homogeneous texture and sent, as secondary raw materials, to some brick manufacturing industries located in Italy and other EU countries. Workers involved in removal, grinding and transport, may be exposed to cinder dust containing potentially harmful trace elements. Arsenic, lead and cadmium, appear to be the most dangerous elements present in pyrite cinders.

MATERIALS AND METHODS

The cinder heap has a base of about 50x150 m^2 and a maximum elevation of 25 m from ground level. The heap is divided in four terraces, each 5 m high.

Sixty samples of cinders (50-100 g each) were randomly collected from the four terraces of the quarry front and analysed for their content of As, Pb, Cd.

Analyses were performed by flame and graphite furnace AAS, after pressure decomposition in Teflon vessels with addition of 2 mL HNO_3, according to Stoeppler and Backhaus (1978). Accuracy was measured by means of a standard certified material from U.S. National Institute of Standards and Technology (SRM 2709 and 2710). Precision was about 3% for flame and 7% for graphite furnace, measured as coefficient of variation (C.V.) on 5 homogeneous replicates.

Sub-samples were dried 5h at 105 °C for water content measuring. Because the two main parameters controlling the release of trace elements are the pH, liquid to solid ratio (L/S), and the time of contact with the leaching agent (van der Sloot et

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al., 1996), mobility tests were carried out for 24h in aqueous media at different pH using the same L/S (mL/g) of 20: sub-samples of 12.5 g (dry weight) were shaken in 250 mL of, respectively, CO_2-saturated distilled water and an acid medium (pH 2 by HCl), for 24h.

Electric conductivity was measured in the CO_2-saturated water test, and pH measured for each test. After filtration on 0.45 μm cellulose acetate membranes, the concentrations of selected elements in both the aqueous phases were measured by AAS.

RESULTS AND DISCUSSION

Collected samples contained water at 15-30%, by mass. It was observed that 20% water content (mass/mass) is able to impede dust formation.

Data reported in Table 1 shows concentrations exceeding background levels by 1-2 orders of magnitude for all selected elements.

Table 1. Average concentrations of As, Pb, Cd from 60 cinder samples.

Element	Mean (mg/kg d.w.)	S.D.	Coefficient of Variation (%)	World natural background (mg/kg)[a,b]
As	523	126	24	1-20
Pb	1274	644	51	5-40
Cd	7	5	71	0.1-0.5

[a] data from Friberg et al., 1986.

[b] data from Förstner and Wittman, 1981.

Statistical analysis of data distribution (Figures 1-3) reveals a good, homogeneous distribution of arsenic throughout the heap of pyrite cinders. The variations observed for the other elements are due to the variability in composition of exploited mining bodies at different times. Thus, an increase in the number of samples would not be effective in reducing single data scattering. However, 95% C.L. values (referred to the expected variability of average concentrations) show quite narrow ranges. These, probably, are more representative of actual composition of airborne particles to which workers may be exposed. Data reported in Table 2 shows elevated releases of all elements in the CO_2-saturated medium test (mean pH = 6.3, ranging from pH 5.9 to pH 6.8).

Table 2. Average concentrations of As, Pb, Cd for mobility tests in CO_2 saturated water. Mean pH value: 6.3. Mean electric conductivity: 1,980 μS/cm.

Element	Mean (μg/L)	S.D.	Coefficient of Variation (%)	World natural background (μg/L)[a,b]
As	344	148	43	2-10
Pb	43	47	109	0.5-2.0
Cd	9	6	67	0.01-0.5

[a] data from Friberg et al.,1986.

[b] data from Förstner and Wittman, 1981.

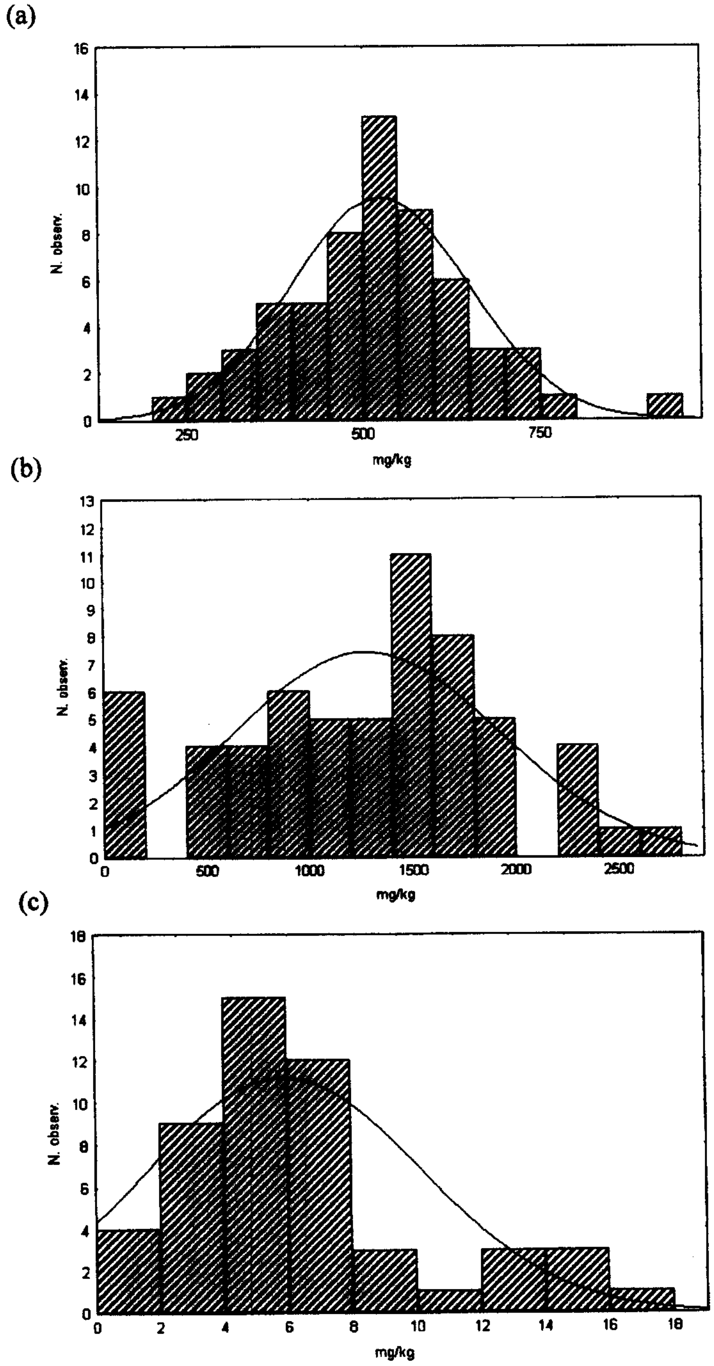

Figure 1. Frequency distribution of arsenic (a), lead (b) and cadmium (c) concentrations in pyrite cinder samples.

By increasing the acidity of the medium (pH 2 by HCl; Table 3), average concentrations of As, Pb and Cd become 1-2 orders of magnitude higher than those at pH 6.3. This increase proves the strong influence of pH on water solubility of metals, since their sorption-desorption processes on different particles and colloids are significantly affected by the presence of H^+ ions in solution (Bourg and Loch, 1995; Bhumbla and Keefer, 1994).

Table 3. Average concentrations of As, Pb, Cd from mobility tests in acid distilled water (pH 2 for HCl).

Element	Mean (µg/L)	S.D.	% Coefficient of Variation
As	3134	1154	37
Pb	5865	501	8.5
Cd	75	28	37

To obtain mobile fraction percentage of each element, the two respective extractable fractions at different pH (mean mobile fraction: total mass of metal in water/mass of sample leached) were calculated and then compared with the total content in solids. Data summarized in Table 4 points out that in contrast to their solubility at pH 6.3, As, Pb and Cd increased their the strong pH-affected mobility respectively about 10, 100, 10 times those obtained at pH 6.3.

Table 4. Mean mobile fraction and mobile fraction percentage of As, Pb, Cd released both in weak-and strong-acid leaching media.

Element	Mean concentration (µg/g d.w.)	Mean mobile mass fraction (g/g d.w.)		Percent mobile fraction	
		pH 6.3	pH 2	pH 6.3	pH 2
As	523	$5.8x10^{-6}$	$52x10^{-6}$	1	10
Pb	1274	$0.7x10^{-6}$	$98x10^{-6}$	0.05	8
Cd	7	$0.15x10^{-6}$	$1.3x10^{-6}$	2	19

These different leaching data found at different pH can be useful in assessing potential occupational exposure to pyrite cinders that may occur during the removal operations of this material.

Apart from accidental ingestions, the main cause of exposure is cinder inhalation from airborne particles: depending on particle size, inhalable dust fractions easily reach both the respiratory system and the gastrointestinal tract (inhalation via mouth), where they are dissolved at different pH by leaching-like mechanisms.

Thus, data reported in Tables 3 and 4 indicates that gastric environment (pH 2 by HCl), rather than the respiratory one, leads to enhanced mobility and absorption. As a matter of fact, dissolution occurring in the acidic gastric environment represents the rate-controlling step in oral adsorption of many metals and arsenic, although their absorption is mediated by intestinal epithelium (Ruby et al., 1999;

Schroder et al., 2003). Then metal ions diffuse through mucosa into the blood stream because of their water solubility (Camner et al., 1986).

Consequently, a maximum daily intake for each element may be identified by a worst-case model: the man standard respiration rate is about 700 L/h (Peters, 1993) and this leads to a 5.6 m^3 of inhaled air for a daily work-shift of 8h. By the maintenance of the airborne dust concentrations below the threshold limit value (TLV) of 10 mg/m^3 proposed by the American Conference of Governmental Industrial Hygienists (ACGIH, 2001), maximum daily intake of cinders will be:

$$10\ \text{mg/m}^3 \times 5.6\ \text{m}^3 = 0.056\ \text{g of pyrite cinders}$$

In order to overestimate the risk (Yang et al., 2002) we can assume that soil-bound metals are 100% available for absorption in the gastrointestinal tract and that it reaches the blood compartment entirely. Considering total concentrations of selected elements in pyrite cinders (Table 1), a maximum daily intake can be calculated as, respectively, 30 µg/d for As, 71 µg/d for Pb and 0.4 µg/d for Cd. These maxima, belonging to background levels (*i.e.*: dietary intake of no exposed populations; Friberg et al., 1986), are not significant for human toxicology.

As potential risks in exposure to pyrite cinders are mainly related to the ingestion of cinder dust, an appropriate safety plan could consist in keeping concentration of airborne particles under current threshold limits (10 mg/m^3). This can be obtained by wetting, when necessary, the heap of cinders to reach a minimum of 20% (by mass) of water in the working area during dry seasons. Current personal protection devices (masks, gloves, overalls) have to be adopted. Workers must be monitored to verify the actual exposure level: the response to inorganic arsenic ingestion is rapid and easily detectable by measuring the levels of metals in urine. A research is in progress to verify the effectiveness of proposed safety measures on a group of potentially exposed workers.

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