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# SOLID-PHASE CHARACTERIZATION OF BLASTED COPPER SLAG IN RELATION TO THE POTENTIAL RELEASE OF TOXIC ELEMENTS

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## Introduction

After being used as an abrasive agent, copper slag is considered a solid waste in Vietnam because appropriate waste treatment techniques and effective management options are not available. Its classification as solid waste is mainly due to the fact that the blasted copper slag (BCS) contains impurities of potentially toxic elements (PTEs), such as As, Cd, Co, Cr, Cu, Mo, Ni, Pb, and Zn that can be released into the environment. A BCS sample that was previously partly characterized using chemical and physical approaches<sup>1</sup> was further studied through a complementary integrated approach with focus on direct PTE associations in solid phases and the influence of pH on the release of PTEs. The aim of this study is to investigate the relationship between the occurrence of PTEs, the sample mineralogy and the potential of mobilization of PTEs. Furthermore, the pH conditions under which the PTEs may be mobilized were also examined to link this with the risk for PTEs release into the environment under effect of external factors (e.g. acid rain, mixing with other waste, liming) at the BCS disposal site.

## Methodology

The slag in the present study has been used as a blasting agent in a shipyard located in South-Central Vietnam. One BCS sample was collected in a dump site nearby the ship factory. Total element concentrations, pH, grain size distribution and mineralogy (X-ray diffraction (XRD) and Field Emission Gun Electron Probe Micro Analysis (FEG-EPMA)) of BCS were investigated as described elsewhere<sup>1</sup>.

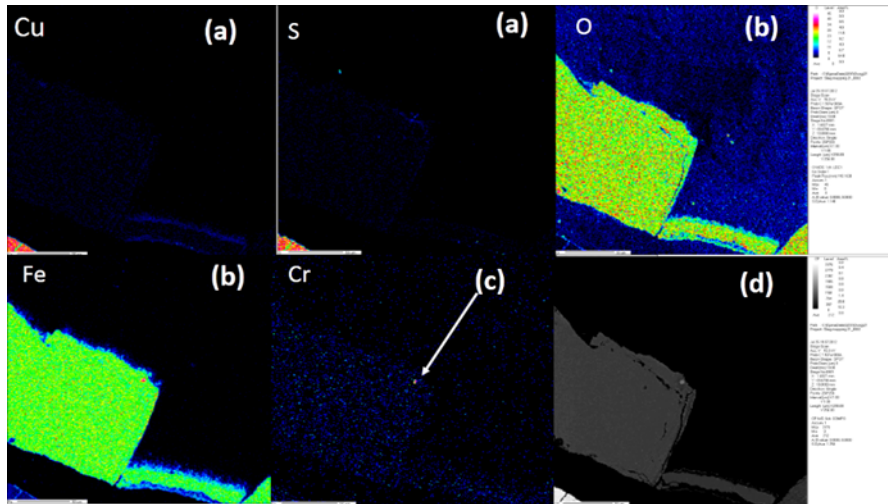
To assess the influence of pH on PTE release, batch extractions with different concentrations of HNO<sub>3</sub> (0.0001, 0.01, 0.1, 0.5, 1 M) were carried out. The suspensions were shaken overnight (24 h) on a reciprocal shaker, then centrifuged (3500 rpm, 10 minutes), decanted and filtered (0.45 µm). Moreover a pH<sub>stat</sub> (pH = 10, 96 h) experiment was also performed to examine the release of PTEs at alkaline pH<sup>2</sup>. Element concentrations (Al, Ca, Fe, K, Mg, P, S, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn) in the leachates were measured by Induced Coupled Plasma Optical Emission Spectrometry (ICP-OES, Varian 720ES).

## Results and discussions

### Solid-phase characteristics

Besides amorphous phases, fayalite, magnetite, maghemite, quartz and elemental copper were the main minerals identified by X-ray diffraction (XRD). Elevated concentrations of Fe, Ca, Al and Si (percentage level) and significant amounts of Cu, Zn, Mo, Pb, As and Cr were found in the BCS<sup>1</sup>.

FEG-EPMA results indicated that three phases could be distinguished among 104 spots of *Energy-Dispersive Spectroscopy* (EDS) analysis. The phase assignment was based on the element having the highest content in that spot except oxygen. Fe-rich phases were the most abundant phases (85 %) followed by Cu-rich phases (12 %) and Si-rich phases (5 %). Fe-rich phases mainly consisted of Fe, O and Si with minor amounts of S whereas Cu-rich phases were composed of Cu, Pb, and S with minor amounts of Si. This suggest that copper in BCS was present not only in metallic phases (as identified by XRD) but also in association with S in the form of sulphides (sulphides of Cu, Cu-Pb, Cu-Pb-Zn). The map of selected areas in thin sections with Wavelength Dispersive X-ray Spectroscopy (WDS) also indicated the co-existence of Cu and S confirming the presence of these sulphide phases which were not detected by XRD (Figure 1). Cr was found in Fe-O rich phases, while Mo was observed in a glass inclusion which was rich in Fe-Si and major amount of Al and Ca.

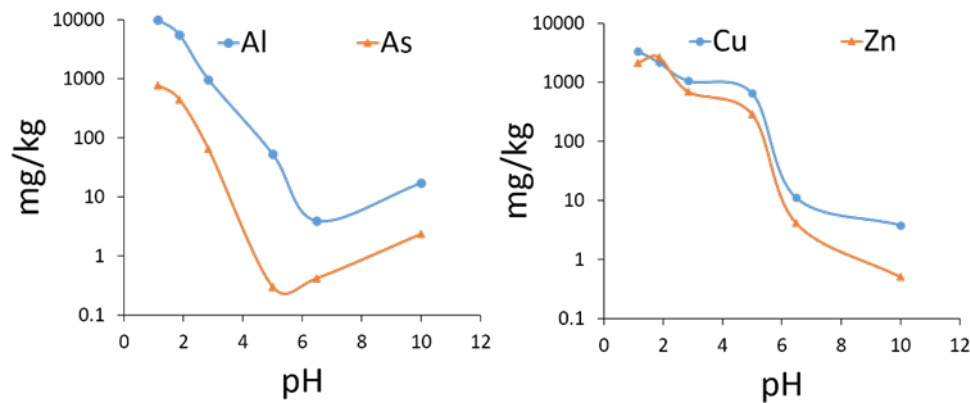


**Figure 1:** Picture from EPMA-WDS analysis, mapping of selected area, (a): the co-existence of Cu-S, (b) Fe-O rich phase, (c): Cr in Fe-O rich phase, (d) backscattered electron image.

### **Leaching behaviour of PTEs under influence of pH and environmental implications**

Based on Vietnamese legislation, the BCS sample is classified as non-hazardous waste<sup>3</sup>. The classification is based on the total concentration of 'hazardous elements' and the leaching of PTEs derived from the Toxicity Procedure Leaching test (TCLP)<sup>4</sup>. However, the TCLP just focuses on a fixed initial pH of a CH<sub>3</sub>COOH solution and considers the leaching at only one pH value. Therefore, pH changes occurring at disposal sites (e.g. as a consequence of acid rain or co-disposal with other acid or alkaline waste) cannot properly be assessed based on this test.

In the present study, the leaching behaviour of PTEs was investigated in a wide pH range (1-10) in order to assess the environmental implications of different management scenarios related to changes in pH. The pH-dependent leaching behaviour of Al, As, Cu and Zn is displayed in Figure 2.



**Figure 2:** pH-dependent leaching behaviour of Al-As and Cu-Zn

Similar release patterns of these elements suggest that they originated from the same host phase or that they display similar sorption behaviour.

In general, the release of all PTE decreases with increasing pH except As and Mo which were observed in higher amounts at alkaline pH (pH 10) compared to neutral pH (pH 7). These elements with tendency to form oxyanions are usually mobilized under alkaline pH. Leaching tests indicated that most of the PTEs showed a low environmental concern in the neutral-alkaline pH range (7-10) due to the low concentrations in the leachate compared to EU leaching limit value for hazardous waste<sup>4</sup>, except As which exceeded this threshold (2 mg/kg, L/S = 10 L/kg) at pH 10. Therefore, special treatment for As should be carried out if liming or co-disposal with other alkaline waste is selected as the management option for this BCS. Moreover, non-controlled dumping of this BCS should be avoided since small particles might be dispersed by wind, particularly because blasting decreases the particle size of the copper slag.

The low release of PTEs under neutral pH can be related to the PTE associations in the solid phase. PTEs in sulphide phases or PTEs occluded in iron oxides or glass phases are poorly mobile under neutral environmental conditions. Most PTEs (As, Cd, Cr, Mo, and Pb) in the BCS showed a high release at acidic pH (pH 1-3) whereas Cu and Zn were also released in significant amounts under mild acid (pH = 5) condition. With respect to absolute concentrations, up to 652 mg Cu/kg and 288 mg Zn/kg were released at pH 5 from BCS (Figure 2). These concentrations exceed the leaching limit values for hazardous waste<sup>5</sup>. However, within the concept of “elemental sustainability”, landfilling of this material or any other application without metal recovery means a loss of valuable metal resources and leads to environmental problems<sup>6</sup>. Thus, recovery of Cu from the slag by acid treatment could be envisaged since an extraction with HNO<sub>3</sub> 1 M during 24 h showed that 39 % of the total Cu

content (or 3369 mg/kg) was released from the BCS in this case. It has been reported that addition of oxidants such as  $H_2O_2$ ,  $NaClO_3$ ,  $K_2Cr_2O_7$  or  $Cl_2$  or increasing the temperature (up to 60-80°C) in the acid leaching process can lead to high recovery rates of metals from the slag (e.g. 80 % Cu, 90 % Co and 90 % Zn)<sup>7</sup>.

## Conclusions

Solid phase characterization of the BCS indicated that PTEs were associated with sulphide phases or occluded in iron oxides or glass phases. PTEs associated to these phases showed a low release under neutral pH conditions, despite of their high concentrations in the BCS. Acidification (e.g. co-disposal with acid waste or acid rain) at disposal sites might cause the release of PTEs from BCS to the environment. On the contrary, liming or co-disposal with alkaline waste seems to immobilize PTEs at desirable level, except for As, which needs special attention. The feasibility of Cu recovery from BCS should be further investigated because of its high content in BCS and the high amount that was released upon acidification.

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