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COMBINATION OF LEACHING TESTS AND MINERALOGICAL CHARACTERISATION TO ASSESS INORGANIC CONTAMINANT MOBILITY IN BLASTED COPPER SLAG

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Abstract

A combination of leaching tests (cascade and pH_{stat} leaching test) and mineralogical and spectroscopic techniques (X-ray Diffraction (XRD) and Electron probe X-ray microanalysis (EPMA)) was applied on blasted copper slag from Vietnam. The slag was enriched in arsenic and heavy metals. Leaching tests showed a low release of most elements because they are occluded in glass phases. Only for Cu, elevated concentrations in the slag and the leachates indicate a potential process for Cu-recovery, as well as an environmental risk for the surroundings of the slag dump site.

Introduction

In recent years, shipping industrial activities developed in Vietnam have used copper slags as abrasive material for preparing the surface of the ships before painting. These blasted copper slags (BCS) are enriched in arsenic and heavy metals (HMs) which can be released in the environment. The slag in the present study has been used as a blasting agent in a shipyard located in South-Central Vietnam. The composition of this BCS and the leachability of inorganic contaminants have never been studied before. Therefore, the composition as well as the potential release of inorganic contaminants from the BCS should be investigated in order to provide essential information for effective management of this slag.

Materials and methods

Three representative samples of BCS were collected in a dump site nearby a ship factory. Part of each BCS sample was crushed in a porcelain mortar and sieved (< 1 mm and < 125 µm fraction) for physico-chemical analysis and leaching tests whereas another part of each sample was also used for leaching tests as bulk sample, without crushing. Total elemental concentration of the BCS samples (Al, Ca, Fe, K, Mg, P, S, As, Cd, Co, Cr, Cu, Mn, Ni and Zn) were determined based on ICP-OES (Varian 720ES, Varian Inc., Walnut Creek, CA, USA) analysis after digestion of the samples by the so-called 4 acid digestion method (concentrated (cc.) HNO_3 + cc.$HClO_4$ + cc.HF + 2.5 M HCl) on a hot plate. Grain size was determined by laser diffraction spectrophotometry (Malvern Mastersizer S long bed, Malvern, Worcestershire, UK). The cascade leaching test (NEN 7349) was performed on the BCS with grain size fractions < 1 mm and < 125 µm to investigate the release of elements from different grain size fractions. The pH_{stat} leaching test (CEN/TS 14429) at pH 4 was also performed on two grain size fractions of BCS, namely the bulk sample (not sieved) and the fraction < 1 mm. A mineralogical characterisation was conducted by X-ray diffraction (Philips PW1830 diffractometer with Bragg/Brentano θ – 2 θ setup, CuK radiation, 45kV and 30mA, graphite monochromator). XRD analysis was performed on the original BCS sample and the residue after pH_{stat} leaching test. Two polished samples of BCS were analysed by electron probe microanalysis (EPMA, Jeol JXA-8530F). In total, 89 point analyses were performed by EPMA.

Results and discussion

General characteristics of BCS

The BCS samples were mainly composed of Fe, Ca, Al and Si (percentage levels). Furthermore, BCS contained significant amounts of Cu, Zn (8419 and 8436 mg/kg respectively), Mo, Pb, As and Cr (2399, 853, 798 and 566 mg/kg respectively). The pH value of BCS (8.13) indicates a weak alkalinity. The < 1mm fraction of BCS in this study showed a higher value (65.1 wt%) compared to Vítková *et al*. (2011)[1] (23.6 wt%,), which might be due to blasting effect on the copper slag analysed in this study.

Leaching test

Although many major elements (Al, Ca, Fe, K, Mg, Mn, P, S, and Si), As, HMs (Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn) and ions (NO_3^- and SO_4^{2-}) were analysed, in the framework of this paper, only As, Cu and Zn release will be discussed because of their environmental concern.

Cascade leaching test

During five consecutive extractions in cascade leaching test ((L/S (liquid/solid) ratios of

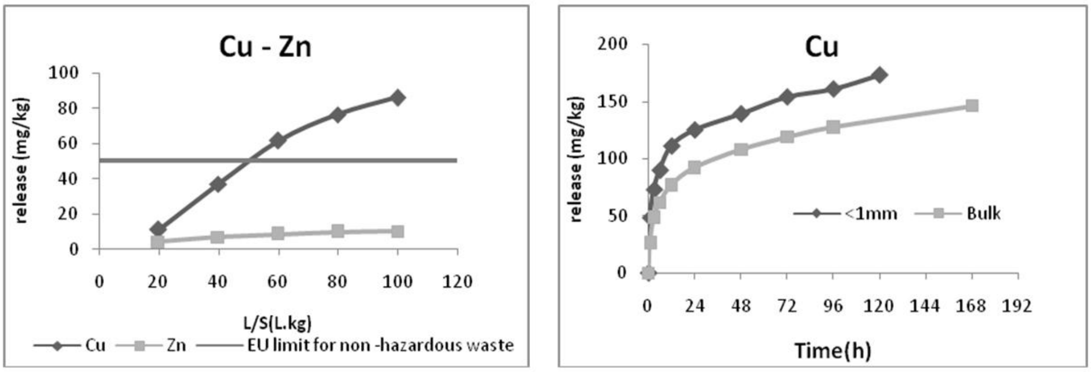

Figure 1: Release of Cu and Zn in the cascade leaching test (left) and Cu in the pH_{stat} leaching test (right)

20, 40, 60, 80 and 100 (l/kg)), Cr and Ni concentrations in the leachates were below detection limit (DL = 0.005 mg/l) while As and some HM (Cd, Cu, Mo, Pb and Zn) concentrations decreased in the leachates of the subsequent fractions.

Comparison of the cumulative mass of As and HMs leached with EU limits for non-hazardous waste (DIN38414-S4 leaching test) showed that the cumulative mass leached was below the EU limit for non-hazardous waste except for Cu. On a relative basis, less that 1% of the total HM content was released during the cascade leaching test, except for Cd and Cu (1%).

pH_{stat} leaching test

In general, the amount of elements released after 120 h were relatively low (< 1% total content) except for some elements such as Cd, Cu, K and Si (1 – 2% of total content).

Generally, elements in the fraction < 1 mm showed a higher release compared to those in the bulk sample (Figure 1). This indicates that grain size is a key factor in determining element release from the BCS. Higher HM concentrations were released during pH_{stat} leaching test compared to the cascade leaching test. This is because leaching of HMs increases as pH decreases[2] and the pH is kept at a constant value of 4 during pH_{stat} leaching, whereas pH was neutral to weakly alkaline during cascade leaching test.

Mineralogical characterisation

In terms of mineralogy, XRD results of original BCS samples revealed the dominance of amorphous phases (> 90 wt%) and the occurrence of fayalite, magnetite, maghemite, quartz and elemental copper. Compact and homogeneous glass phases are typically the major phase in slags because of the rapid cooling process[3]. XRD technique was used to assess changes in mineralogical composition of BCS after pH_{stat} leaching test, but the results did not show any significant compositional changes.

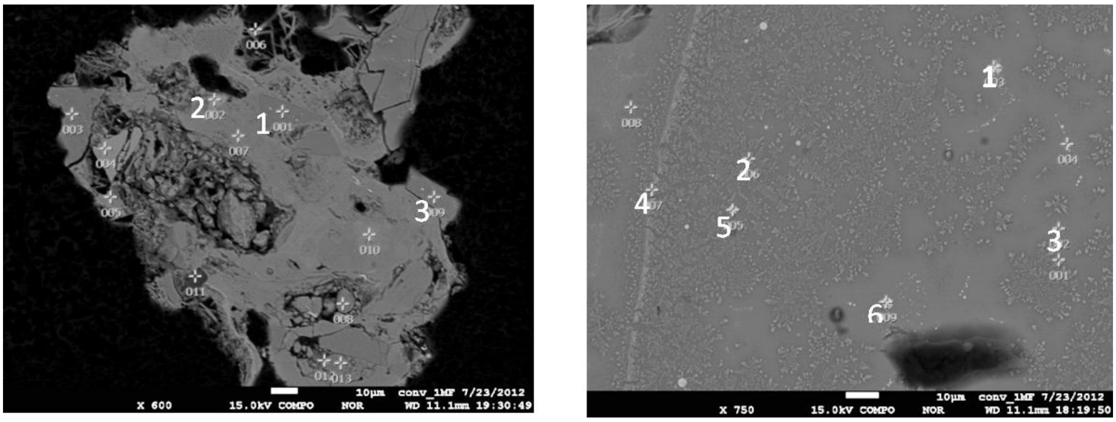

Figure 2: Picture from EPMA analysis. Left: Mo in Fe-Si-Al-Ca phase (1), Fe-Si-Al-Ca-Mg phase (2-3). Right: Cu – Pb – S phase (shapes like droplets 1-6), Fe-Si-Ca-phase (2-3-4-5)

According to EPMA results, Si-Ca-Fe-Al were detected in all examined spots, agreeing well with the occurrence of fayalite, magnetite and maghemite detected by XRD.

In some spots, the EPMA results showed that HMs (Cu, Cr, Pb, Mo and Zn) were detected in the same phase with S and within the matrix of glass phase. This probably explains the low release of elements during leaching tests because the elements are occluded in the glass phase.

Conclusions

Through the investigation of BCS by using a combination of leaching tests and mineralogical characterisation, the potential releases of element under the influence of acidification were assessed. Leaching tests in combination with XRD and EPMA analysis showed a relatively low release of As and HMs from BCS because they might be (partly) immobilised in glass phases. Only for Cu, elevated concentrations in the slag and the leachates indicated a potential process for Cu-recovery, as well as an environmental risk for the surroundings of the slag dump site.

References

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