

# Copper Smelting Flue Dust: A Potential Source Of Germanium

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## INTRODUCTION.

A large number of industrial residues may be regarded as an alternative source of valuable elements (Ge, Ga, Pb, Zn, Ni, among others) to the natural resources owing to the high concentrations of these elements in these wastes. The utilisation of industrial residues for the recovery of valuable elements can provide significant economical and environmental benefits, especially on the reduction of the extractive and environmental cost of mining metal ores or raw materials and the commonly high disposal costs of the residues. Finding disposal sites is becoming increasingly more difficult, due to the limited space and to the restrictive regulations concerning protection of surface and ground water discharge for wastes in disposal sites. This generates significant economic costs for the required water and land management.

Germanium is a valuable element, with a widely disseminate occurrence in the Earth crust (1.0-1.7 ppm, worldwide average, usually placed at 1.4 or 1.5 ppm; Adams, 1992; Butterman and Jorgenson, 2004; Höll et al, 2007) commonly found substituting for zinc in sphalerite and wurtzite structure (Levison, 1980; Höll et al., 2007) and other sulphide species (Höll et al, 2007). It is found as argutite (tetragonal-GeO<sub>2</sub>, insoluble in water), usually substituting for SiO<sub>2</sub> in silicates, but rarely as water soluble hexagonal-GeO<sub>2</sub> (Höll et al., 2007). It is used in the production of novel and high technological industrial applications: manufacture of advanced electronic and optical devices, fiber optics, photovoltaic cells and in the manufacture of thermal solar cells (Moskalyk, 2003; Butterman and Jorgenson, 2004; Guberman, 2011). The zinc ores have large and recoverable quantities of germanium, so nowadays

zinc ore processing is the main germanium source. Previous studies (Font et al., 2005) revealed coal gasification fly ashes as an attractive source of Ge and other valuable elements (Ga, V, Ni). The occurrence of Ge as water soluble species (GeS<sub>2</sub>, GeS and hexagonal-GeO<sub>2</sub>) in the gasification fly ash (Font et al, 2005) allowed devising and patent (Querol et al, 2003; Arroyo et al, 2008) a low cost and environmentally acceptable Ge recovery process from fly ash as an alternative to the common acid leaching Ge extraction process from sphalerite ores. The patented process is based on water leaching of fly ash and subsequent enrichment by using solvent extraction, ending with a high purity (>90%) Ge product.

Flue dust from copper smelting may be regarded as a source of Ge, since this element may occur in relatively high proportions in some Cu deposits, being concentrated in flue dust after smelting procedure. This study focuses on evaluating the potential of copper smelting flue dust as a source of Ge and the possibilities to apply extraction and recovery methods similar to those developed and patented for gasification fly ash. To this aim flue dust samples from a Chilean copper smelting plant were characterised and preliminary extraction tests were performed.

## METHODOLOGY

Two flue dust samples from a Chile copper smelting plant were chemically and mineralogical characterised. The flue dust samples were acid-digested by using a two-step digestion method devised by Querol et al. (1995). The resulting solution was then analysed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for major and selected trace elements, and by Inductively Coupled Plasma-Mass

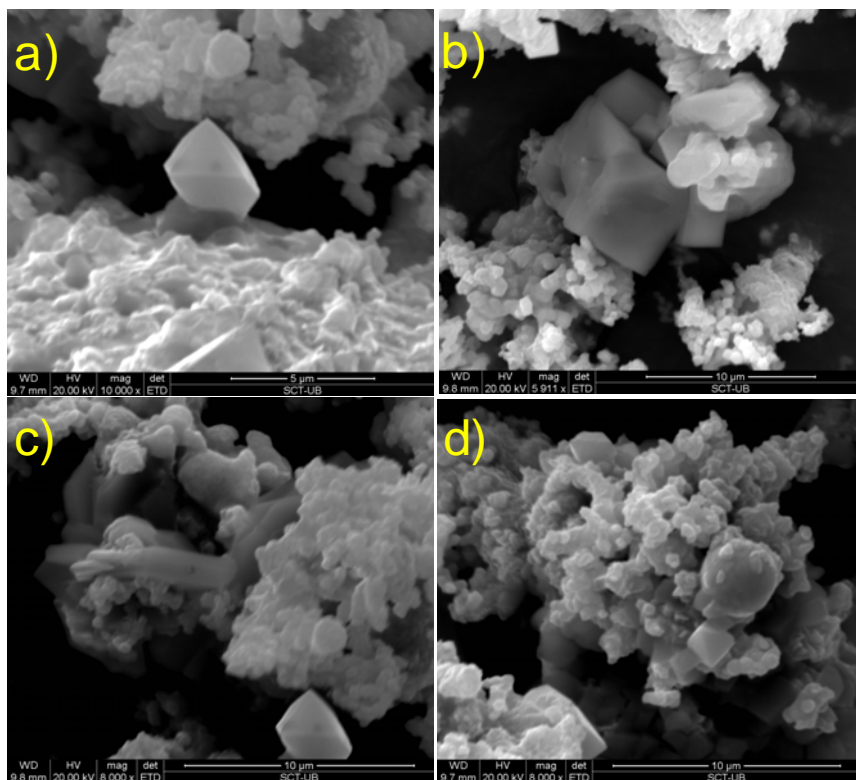
Spectrometry (ICP-MS) for most of trace elements. The fly ash and coal International Reference Material(NBS1633b and SARM19) were also digested to determine the accuracy of the analytical and digestion methods. The mineralogy of solid samples was determined by X-ray powder diffraction (XRD) with a 218 Bruker D5005 diffractometer with monochromatic Cu K $\alpha_{1,2}$  radiation operated at 40KV and 40mA., from 4° at 60° of 2theta range, and a step size of 0.05° and 3s/step. The particle resolved composition and morphology of flue dust were investigated by a Quanta 200 Scanning electron Microscope with energy dispersive X-ray analyser (SEM-EDX). The grain size distribution of the flue dust samples was investigated by means of a laser light scattering-based particle sizer, with a working range from 0.1 to 1000  $\mu$ m. An ethanol media with an ultrasound bath prior to the grain size analysis was used in order to avoid potential dissolution of salts. The European Standard leaching test EN-12457 (according to Council decision 2003/33/EC) was applied to the flue dust to determine the leaching potential of valuable elements as a preliminary extraction test for these elements. The content of major, minor and trace elements of the leachates were determined by ICP-AES and ICP-MS, while pH and conductivity were determined by conventional methods.

## RESULTS AND DISCUSSION

The copper smelting flue dust are characterised by a lognormal and unimodal grain size distribution and very fine grain size (median around 22-28  $\mu$ m). Arsenolite (As<sub>2</sub>O<sub>3</sub>), anglesite (PbSO<sub>4</sub>), sphalerite ZnS and gunningite (ZnSO<sub>4</sub>.H<sub>2</sub>O) are the main crystalline phases detected by XRD. Arsenolite occurs mainly as fine discrete crystals showing the common octahedral

**Palabras clave:** Germanio, Polvo combustión, Fundición cobre, Extracción.

**key words:** Germanium, Flue dust, Copper smelting, Extraction.



**fig 1.** SEM micrographs showing the morphology of the different species and particles present in the Chilean Cu-smelting fly ash: a) arsenolite crystal <5 μm with the common octahedral morphology; b) Zn-Cu-K sulphate/sulphide crystals (center) of around 10μm and fine particles of As, Zn and Cd; c) Particles of Zn-S (center); and d) Rounded particle of Pb, As and Zn surrounded by discrete arsenolite crystals and fine particles of sphalerite.

morphology (Fig. 1a). Very fine particles of As, Zn and Cd and Zn-Cu-K sulphate/sulphide crystals of around 10μm and fine particles are commonly found in this Cu-smelting flue dust (Fig. 1).

Arsenic and Zn attained extremely high concentrations (20-21% and 15-21%, respectively) in flue dust. Other elements such as Pb (6-10%), S (over 7%), Cu (3-5%), Cd (0.5-1.4%), Bi (0.2-2%) and Sb (0.2-0.4%) also occur in high contents. Germanium reached concentrations ranging from 417 to 1375 ppm. The highest Ge concentration in this Cu smelting flue dust is higher, by a factor of 2-3, than those commonly reached in coal gasification fly ash.

The water leaching tests revealed high Ge extraction yields (73-99%) from Cu-smelting flue dust, suggesting a similar speciation for this element than that in coal gasification fly ash. Most probably, Ge occurs as highly soluble hexagonal-GeO<sub>2</sub> and/or GeS<sub>2</sub>. Besides Ge, a large number of other elements (impurities), such as As (48%), Zn (56%), S (81%), Li (87%), B (99%), Cd (53%), K (87%), Na (98%) and Cu (28%) are also extracted

in high proportions.

The high yields attained in this preliminary Ge water extraction tests, allow considering Cu-smelting flue dust as a promising material for the extraction and recovery of this valuable element.

The similar speciation and water extraction yields in this flue dust with respect to that of coal gasification fly ash conduce towards the development of extraction strategies based on the recovery method devised for coal gasification fly ash. Since enrichment methods, previously developed, for Ge in water leachates are highly selective for this element, the large amounts of impurities in Ge leachates from Cu-smelting flue dust are not of high concern to obtain high purity Ge end-products.

Research is currently being focused on the optimisation of extraction conditions (temperature, water/flue dust ratio, extraction time) for Ge, for subsequent enrichment and recovery steps. Furthermore speciation studies of Ge in this flue dust are also carried out to corroborate the mode of occurrence of

this and other valuable elements in Cu-smelting flue dust.

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