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Chemistry and phase evolution during roasting of toxic thallium-bearing pyrite

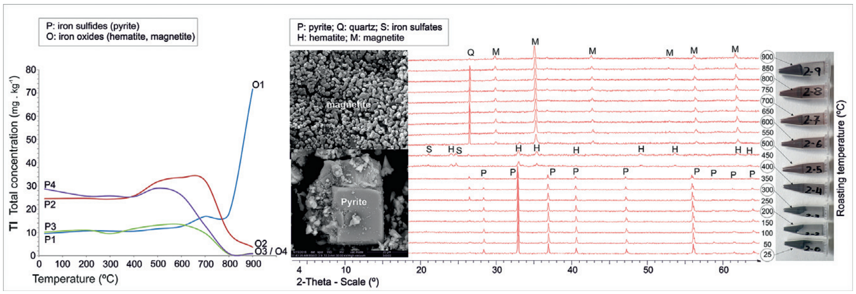
Paula Lopez-Arce*, Javier Garcia-Guinea, Fernando Garrido

Museo Nacional de Ciencias Naturales (CSIC), C/ José Gutierrez Abascal, 2, Madrid 28026, Spain

HIGHLIGHTS

- ICP-MS analyses of roasted pyrites show the concentration or volatility of thallium.
- Initial lower or higher pyrite content develops final hematite or magnetite.
- Tl is concentrated in hematite and volatilized in magnetite wastes.
- Environmental impact on industrial processes involving pyrite roasting or iron wastes.

GRAPHICAL ABSTRACT



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ABSTRACT

In the frame of a research project on microscopic distribution and speciation of geogenic thallium (Tl) from contaminated mine soils, Tl-bearing pyrite ore samples from Riotinto mining district (Huelva, SW Spain) were experimentally fired to simulate a roasting process. Concentration and volatility behavior of Tl and other toxic heavy metals was determined by quantitative ICP-MS, whereas semi-quantitative mineral phase transitions were identified by in situ thermo X-Ray Diffraction (HT-XRD) and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) analyses after each firing temperature.

Sample with initial highest amount of quartz (higher Si content), lowest quantity of pyrite and traces of jarosite (lower S content) developed hematite and concentrated Tl (from 10 up to 72 mg kg^{-1}) after roasting at 900 °C in an oxidizing atmosphere. However, samples with lower or absent quartz content and higher pyrite amount mainly developed magnetite, accumulating Tl between 400 and 500 °C and releasing Tl from 700 up to 900 °C (from 10–29 mg kg^{-1} down to 4–1 mg kg^{-1}). These results show the varied accumulative, or volatile, behaviors of one of the most toxic elements for life and environment, in which oxidation of Tl-bearing Fe sulfides produce Fe oxides wastes with or without Tl. The initial chemistry and mineralogy of pyrite ores should be taken into account in coal-fired power stations, cement or sulfuric acid production industry involving pyrite roasting processes, and steel, brick or paint industries, which use iron ore from roasted pyrite ash, where large amounts of Tl entail significant environmental pollution.

1. Introduction

Research publications on the highly toxic Thallium (Tl) element are increasing in recent years but there are still many unknown

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* Corresponding author.
E-mail addresses: plopez.arce@gmail.com, plopezar@mncn.csic.es (P. Lopez-Arce).

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issues related to its speciation, behavior or interaction with living organism and the environment. Thallium is a heavy metal which generates greater toxicity compared to other toxic elements such as As, Hg, Cd or Pb (Nriagu, 1998). Although Tl concentrations in surface soils commonly range from 0.1 to 2 mg kg^{-1}, with most reported concentrations being <1 mg kg^{-1} (Fergusson, 1990; Tremel et al., 1997), it occurs at high concentrations in metallogenetic epithermal environments (<200 °C) associated with sulfide minerals (Sobott, 1995).

Anthropogenic Tl contamination of soils and water resources mainly results from mining of Tl-rich metal sulfide minerals (Tremel et al., 1997; Nriagu, 1998; Lis et al., 2003; Jakubowska et al., 2007; Xiao et al., 2012; Romero et al., 2015). Industrial roasting processes of Tl-bearing pyrites, such as those that take place in sulfuric acid production plants (Yang et al., 2009; Oliveira et al., 2012), coal combustion processes (Cheam et al., 2000; Gurdal, 2011; Zhuang et al., 2012; Lopez-Anton et al., 2013) or in the cement production industry (Schuhmacher et al., 2009; Huang et al., 2012; Garcia et al., 2014; Kersten et al., 2014) are also a source of Tl pollution. Pyrite ore (FeS_2) or processing of coal pyrite for sulfur extraction has been widely used in modern industry for the production of sulfuric acid. Pyrite ore may contains a wide range of trace elements in variable concentrations, such as Cd, Co, Cr, Mn, Ni, Pb, Tl and Zn (Lopez-Anton et al., 2013), some of which are highly toxic (e.g., Cd, Pb, Tl). In order to extract sulfur dioxide (SO_2) precursor of sulfuric acid, the pyrite concentrate is heated up to 900 °C, leaving a residue of iron oxides. The hematite-rich wastes, known as roasted pyrite ashes, can be used as iron ore in the steel, brick, paint, and cement industries (Perez-Lopez et al., 2009). However, this iron oxide-rich residue might contain significant concentrations of undesirable sulfur and polluting elements. During pyrite ore roasting, a series of physicochemical transformations occurs, resulting in potential dispersion of these trace elements from roasting wastes into the environment (Srinivasachar et al., 1990; Lin and Qvarfort, 1996; Hu et al., 2006; Yang et al., 2009).

The atmospheric emissions from coal-fired power stations are of critical environmental importance. Several studies performed on conventional pulverized coal combustion power plants have found that Tl volatilizes at high temperatures in the boiler oven and it is condensed on the surface of the fly ashes, which are mainly enriched in particles of small size and high surface area, in the cooler parts of the system (Sloss, 2007; Lopez-Anton et al., 2013, 2015). During the melting process of municipal solid waste incineration residues, In, Pd, and Tl are completely evaporated and concentrated in melting furnace fly ash (Jung and Osako, 2007).

In the cement production industry, the use of cement kilns to co-process wastes containing heavy metals is thriving and playing an exceedingly important role in the treatment technology of solid wastes, especially hazardous waste disposal. During co-processing, almost all non-volatile and semi-volatile heavy metals are transferred into cement clinker which significantly increases the heavy metal concentration in the cement production (Huang et al., 2012). Concerns are focused mainly on the emissions of hazardous substances within the flue gas, such as dioxins and volatile heavy metals. In the late 1970's, a cement plant near Lengerich (West Germany) emitted cement kiln dust with high Tl contents, due to co-combustion of Tl-enriched pyrite roasting wastes. Pyrite was added to the crude powdered limestone for the production of special sorts of cement as a final additive containing ferric oxide. Chemical analyses showed that Tl content of this additive was circa 400 mg kg^{-1} (Dolgner et al., 1983). To heat the industrial cement rotary kilns, fuel is partially replaced by mixtures of solids, liquids, and blended wastes with high calorific value. The behavior of each chemical element in a rotary kiln is strongly determined by its volatility. Therefore, the elements can either be incorporated into the crystalline structure of the clinker, concentrated into the powder of the filter or be part of the crusts formed on the inner components of the equipment. Lead and thallium tend to be fixed in the powder due to their high volatilities. As the gases cool, the metals condense on the surface of the particulate material (Lopez-Anton et al., 2015).

According to the International Programme on Chemical Safety (IPCS, 1996), melting point of most Tl compounds is 200–500 °C and boiling point 400–800 °C. During the roasting of Tl-rich pyrite ores in the sulfuric acid industry, Tl sulfides initially in the pyrite ores, vaporized into the flue gas prior to oxidation. However, much of the Tl does not vaporize during the roasting (Yang et al., 2009). Based on thermodynamic predictions, Tl should completely vaporize under oxidizing conditions at temperatures higher than 227 °C (Yan et al., 2001). The Tl (particularly from Tl-sulfide ore) could be incorporated into crystalline Fe oxides during roasting and subsequently migrates downstream associated to fine Fe oxide particles. Chen et al., 2013 showed that in the production of sulfuric acid, Tl was partially vaporized into the flue gas to the various production procedures, partially dissolved into the water after the acid washing, and partially retained in the solid phase of the roasting wastes. Volatile elements are depleted in all solid phases (Yang et al., 2009); the extent of vaporization and subsequent deposition of these trace elements depend on the thermal treatment conditions (e.g., temperature, atmosphere condition, etc.), on the mode of occurrence of the trace elements in raw materials, and on the physical changes and chemical reactions of these elements with S and other compounds during combustion (Bool and Helble, 1995; Querol et al., 1996; Miller et al., 2003; Huang et al., 2004).

There are still many unknown factors and conditions influencing the behavior of Tl during the burning process of Tl-bearing pyrites and its presence into the final wastes, or its volatilization. Historically, the open air slow roasting (named as "teleras") of low grade Cu pyrite ores was performed to remove the S for further precipitation of Cu. These calcinations caused environmental and public health problems until the late 1960s in the worldwide known Riotinto mine district (Lottermoser, 2005). The degradation of the Iberian Pyrite Belt Rivers was parallel to pollution provoked by the fumes of these "teleras" (Ferrero Blanco, 1999), leading to a large volume of toxic clouds of sulfur fumes containing As and causing serious damage to crops and forests by acid rain, as well as diseases that increased mortality of the inhabitants. The study carried out by Hunt et al., 2016 on precious metals in gossanous waste rocks from the Iberian Pyrite Belt, points out the requirement of solid knowledge of environmentally significant elements to assess processability in the move towards sustainable mineral resource development.

The goal of this research is to determine the accumulative or volatility behavior of Tl and other metals and metalloids during roasting of Tl-bearing pyrite ore samples from Riotinto mine district, through its quantitative concentration as a function of the initial and final chemical and mineralogical composition and firing temperature.

2. Material and methods

2.1. Materials and sample preparation

Four natural pyrite ore samples (named as P1, P2, P3 and P4) from Riotinto Mine tailings (Huelva, Spain) were used for the experimental work. The main mining difference is that samples P1 and P2 correspond to powder and brittle pyrite ores whereas samples P3 and P4 are bulk pyrite ores. The samples were grinded in agate mortar to obtain a homogenized grain size between 75 and