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The potential leaching and mobilization of trace elements from FGD-gypsum of a coal-fired power plant under water re-circulation conditions

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ABSTRACT

Experimental and geochemical modelling studies were carried out to identify mineral and solid phases containing major, minor, and trace elements and the mechanism of the retention of these elements in Flue Gas Desulphurisation (FGD)-gypsum samples from a coal-fired power plant under filtered water recirculation to the scrubber and forced oxidation conditions. The role of the pH and related environmental factors on the mobility of Li, Ni, Zn, As, Se, Mo, and U from FGD-gypsums for a comprehensive assessment of element leaching behaviour were also carried out. Results show that the extraction rate of the studied elements generally increases with decreasing the pH value of the FGD-gypsum leachates. The increase of the mobility of elements such as U, Se, and As in the FGD-gypsum entails the modification of their aqueous speciation in the leachates; UO_2SO_4, H_2Se, and $HAsO_2$ are the aqueous complexes with the highest activities under acidic conditions. The speciation of Zn, Li, and Ni is not affected in spite of pH changes; these elements occur as free cations and associated to SO_4^{2} in the FGD-gypsum leachates. The mobility of Cu and Mo decreases by decreasing the pH of the FGD-gypsum leachates, which might be associated to the precipitation of $CuSe_2$ and $MoSe_2$, respectively. Time-of-Flight mass spectrometry of the solid phase combined with geochemical modelling of the aqueous phase has proved useful in understanding the mobility and geochemical behaviour of elements and their partitioning into FGD-gypsum samples.

Introduction

Water streams involved in Flue Gas Desulphurisation (FGD) systems from coal-fired power plants may act as retention sinks for some trace pollutants as a result of partial or total dissolution processes (Córdoba et al., 2011, 2013), the efficiency of which largely depends on chemical properties such as the pH and temperature of the solvent and/or the solubility constant of a specific element, among other parameters. Indeed, in FGD systems under operational conditions of water re-circulation into the scrubber, inorganic trace pollutants initially in sub-saturation in FGD waters may reach equilibrium and a subsequent saturation in the water stream after a number of water re-circulations in the scrubber (Córdoba

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et al., 2011). This process may increase the concentration of trace pollutants in re-circulated waters and give rise to environmental implications such as the emission of elements by entraining particles and droplets of gypsum slurry in the outgoing gaseous stream of the FGD (OUT-FGD) (Córdoba et al., 2011), and/or technical problems, especially if the re-circulation of the water streams is interrupted and/or a water treatment is necessary for hypothetical and eventual discharges to the environment. Other elements retained in high proportions by gypsum sludge and/or FGD-gypsum do not pose this problem because they are extracted from the system by the gypsum by-product.

Although FGD-gypsum reduces the consumption of energy and natural resources, there is a significant concern about the potential release of trace elements in specific applications scenarios. Sanchez et al. (2008) found that B, Cd, Mo, Se, and Tl may be released from FGD-gypsum at levels exceeding either a maximum contaminant level or drinking water equivalent level under some conditions. Other authors (Álvarez-Ayuso et al., 2006; Álvarez-Ayuso and Querol, 2007, 2008; Font et al., 2008; Córdoba et al., 2013) have reported that elements such as F plays a crucial role in the leaching potential of the FGD gypsum end-product as a consequence of the precipitation of F solid species on FGD-gypsum surface.

Investigations on the effect of external factors on the release of elements such as As, Se and Hg from FGD-gypsum have shown that metal release under natural conditions (pH ~ 7) is not an environmental concern (Kairies et al., 2006; Kost et al., 2005). The high alkalinity of the FGD-gypsum and the presence of As and Se in sparingly soluble calcium complexes ($CaSeO_3$ and $Ca_3As_2O_8$) results in low mobilities of the trace metals (Díaz-Somoano and Martinez-Tarazona, 2004; Guo et al., 2004; Jadhav and Fan, 2001; Ghosh-Dastidar et al., 1996). However, metal mobility can be significant at low pH conditions for elements such as Ni, Cu, Li, Mo, Zn, and U. Since metal partitioning and speciation in any solid define their toxicity and mobility, their determination is important in order to understand the environmental consequences of the reuse of FGD-gypsum.

The overall objective of the study is to (1) identify solid phases containing major, minor, and trace elements and the mechanism of the retention of the elements in FGD-gypsum; and to (2) evaluate more fully the role of pH and related environmental factors on the mobility of Li, Ni, Zn, As, Se, Mo, and U from FGD-gypsums, as a basis for comprehensive assessment of element leaching behaviour under a range of environmental conditions. This article presents results obtained from a series of leaching tests of four FGD-gypsum samples from a coal-fired power plant at which the enrichment of inorganic trace pollutants in the re-circulation FGD water has been demonstrated (Córdoba et al., 2012).

1. Materials and methods

1.1. FGD system

The FGD system at this power plant involves a number of water streams categorised as FGD water streams: limestone and gypsum slurries and filtered water. A fraction of processed water is treated before it is used to reduce the high content of salts. The resulting water (treated water) is employed for limestone slurry preparation and is then considered as an FGD water stream. An additional fraction of water (added water) is injected into the scrubber to offset the water loss in the gypsum and in the emitted gas. Filtered water is used for limestone slurry preparation, and the remaining fraction is directly recirculated into the scrubber. The mixture of slurry waters constitutes the main water input into the scrubber. The water output of the FGD systems is constituted by (1) the aqueous phase of gypsum slurry, (2) the loss of crystallization water from gypsum, and (3) the water evaporation due to the contact with the emitted OUT-FGD gas in the scrubber. These inputs and outputs of water offset the water balance through the FGD system at the power plant. Detailed descriptions of the operation of the FGD system at this power plant and the water streams are provided by Córdoba et al. (2012).

The four FGD-gypsum samples called FGD-G1, 2, 3, and 4 were collected from this power plant under the filtered water recirculation to the scrubber and forced oxidation conditions.

1.2. *Identification of mineral and solid phases on FGD-gypsums*

The identification of minor solid phases of trace elements was carried out in addition to X-ray powder diffraction (XRD), by time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis because of their low concentration in the FGD-gypsum. ToF-SIMS is a method of mass spectrometry in which the FGD-gypsum sample is ionised and accelerated by an electric field of a given strength. Since the velocity of the ion depends on the mass-to-charge ratio, the ions acquire the same kinetic energy of other ions with the same charge. The time spent by ions reaching the detector and the experimental parameters allow us to identify the ion mass with great accuracy. Thus, the identification of molecules and ionic clusters such as silicates, sulphates, hydroxides, nitrates, and borates that precipitated on FGD-gypsums may be detected even at low concentrations.

The XRD analysis was carried out by using a HILTONBROOKS diffractometer with monochromatic Cu Kα1,2 radiation operated at 40 kV and 20 mA., from 4-60° 2θ, at a step size of 0.05°, and scan rate of 3 s/step. The ToF-SIMS analyses were performed using a ToF-SIMS IV (ION-ToF, Munster, Germany) operated at a pressure of 5×10^{-9} mbar. Samples were bombarded with a pulsed Bismuth liquid metal ion source (Bi_3^{++}), at energy of 25 keV. The gun was operated with a 20 ns pulse width, 0.3 pA pulsed ion current for a dosage lower than 5×10^{11} ions/cm^2, well below the threshold level of 1×10^{13} ions/cm^2 generally accepted for static SIMS conditions. Secondary ions were detected with a reflector time-of-flight analyzer, a multichannel plate, and a time-to-digital converter. Measurements were performed with a typical acquisition time of 6 s, at a time-to-digital converter time resolution of 200 ps and 100 μs cycle time. Charge neutralization was achieved with a low energy (20 eV) electron flood gun. Secondary ion spectra were acquired from a randomly rastered surface areas of 50 μm × 50 μm within the sample's surface. Secondary ions were extracted with 2 kV voltages and are post-accelerated to 10 keV kinetic energy just before hitting the detector. Mass spectral acquisition was performed within the ION-TOF Ion Spe