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Implications of moisture content determination in the environmental characterisation of FGD gypsum for its disposal in landfills

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Abstract

The leachable contents of elements of environmental concern considered in the Council Decision 2003/33/EC on waste disposal were determined in flue gas desulphurisation (FGD) gypsum. To this end, leaching tests were performed following the standard EN-12457-4 which specifies the determination of the dry mass of the material at 105 °C and the use of a liquid to solid (L/S) ratio of 10 l kg^{-1} dry matter. Additionally, leaching tests were also carried out taking into account the dry mass of the material at 60 °C and using different L/S ratios (2, 5, 8, 10, 15 and 20 l kg^{-1} dry matter). It was found that the dry mass determination at 105 °C turns out to be inappropriate for FGD gypsum since at this temperature gypsum transforms into bassanite, and so, in addition to moisture content, crystalline water is removed. As a consequence the moisture content is overvalued (about 16%), what makes consider a lower L/S ratio than that specified by the standard EN-12457-4. As a result the leachable contents in FGD gypsum are, in general, overestimated, what could lead to more strict environmental requirements for FGD gypsum when considering its disposal in landfills, specially concerning those elements (e.g., F) risking the characterisation of FGD gypsum as a waste acceptable at landfills for non-hazardous wastes.

Keywords: FGD gypsum; Landfilling; EN-12457-4; Leaching; Moisture content

1. Introduction

During the last decades most coal-combustion power plants in order to comply with the legislation regarding the SO_2 emissions to the atmosphere [1–3] have been equipped with flue gas desulphurisation (FGD) installations. Although several FGD processes are available to this end, the wet limestone FGD process is that most widely applied, taking up to about 80% of the market. In this process SO_2 is removed from the flue gas by absorption into limestone slurry, then oxidised to produce sulphate, extracted from the absorber as gypsum slurry, and finally dewatered, producing the so-called FGD gypsum. The process taking place can be summarised in the following reaction:

$$CaCO_3(s) + SO_2(g) + (1/2)O_2(g) + 2H_2O(l) \rightarrow CaSO_4{\cdot}2H_2O(s) + CO_2(g) \quad (1)$$

It is important to note that the limestone slurry used in the desulphurisation process acts as a scavenging system also for volatile elements other than S, such as F, Cl, As, Se and Hg [4–9], present as well in the flue gas emissions, or condensed on the particulate matter (PM) escaping the electrostatic precipitators (ESPs), likewise for other trace elements of environmental concern present in this PM (Cd, Cr, Cu, Ni, Pb, Zn, Ba, Sb and Mo).

FGD gypsum produced from the indicated process can find application in the wallboard manufacture or be used in the cement industry. Nevertheless, it is also employed in a great proportion as a landfill material in mine reclamation or sent to landfills for its disposal. In such cases the leaching of elements of environmental concern must be controlled according to the Council Decision 2003/33/EC [10], presently in force. The Council Decision establishes the criteria and procedures for the acceptance of waste at landfills, their application being compulsory (by 16 July 2005) by European Union (EU) Member States. The procedure to determine the acceptability of waste at landfills consists of the basic characterisation, com-

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pliance testing and on-site verification. Basic characterisation constitutes a full characterisation of the waste (type and origin, composition, consistency, leachability and, where necessary and available, other characteristic properties). A waste is deemed acceptable for a landfill class on the basis of the basic characterisation. Subsequently, the compliance testing and the on-site verification shall be performed with the aim of verifying the classification derived from the basic characterisation. In accordance with the Council Decision 2003/33/EC [10], and as it is specified in the section 3 of its annex, listing the methods to be used for the sampling and testing of waste, the EN standards must be used for the determination of the basic waste properties. Thus, the standards EN-12457/1–4 [11–14] must be employed as leaching tests for granular waste materials and sludges. These standards differ in the liquid to solid (L/S) ratio to employ, the particle size of the waste and the number of stages to perform in the batch leaching test. Among them, the standard EN-12457-4 [14] is generally that followed due to its simplicity (the corresponding leaching test is performed in only one stage), and because it requires lesser material size reduction. Physical modification of wastes should be avoided since as a result their properties could be altered, including their leaching behaviour.

According to the specifications of the standard EN-12457-4, the leaching of waste materials must be performed using: (a) representative samples containing 0.090 ± 0.005 kg of dry mass with a grain size of at least 95% (mass) less than 10 mm, (b) samples without being subjected to drying processes, unless their moisture content does not allow their crushing to reach the required sample grain size (in such cases drying temperature must not exceed 40 °C), (c) deionised water or water of equivalent purity ($5 < pH < 7.5$, conductivity $<0.5\,mS\,m^{-1}$) as leachant, employing a L/S ratio of $10\,l\,kg^{-1}$ dry matter ±2% and (d) an agitation period of 24 ± 0.5 h, using a rotary system at about 5–10 rpm. The standard EN-12457-4 also establishes that, even though the leaching test must be performed using samples without being dried, the leachable contents in the waste material must be calculated on its dry mass, specifying the determination of the dry mass of the material at 105 ± 5 °C according to ISO 11465.

The determination of moisture content at the temperature specified by the standard EN-12457-4 could turn out to be inappropriate for certain materials, namely those risking to lose crystalline water at temperatures about or below 105 °C, as could be the case of FGD gypsum. It has been reported that gypsum transforms into bassanite ($CaSO_4 \cdot 0.5H_2O$) by losing 1.5 molecules of crystalline water per molecule of gypsum when heating at moderate temperature; although there is some controversy, the onset of the dehydration temperature of gypsum to bassanite is generally accepted to be about 100 °C [15].

The main objective of the present work is to assess the implications of moisture content determination as specified by the standard EN-12457-4 in the establishment of FGD gypsum leachable contents, and so in the environmental characterisation of this by-product for its disposal in landfills.

2. Materials and methods

2.1. FGD gypsum

Samples of FGD gypsum were collected from a Spanish coal-combustion power plant equipped with a wet limestone FGD installation. Sample collection was carried out just after the dewatering process of FGD gypsum slurry performed at the power plant before sending it for disposal. Sampling was performed in three consecutive days, obtaining three different samples that were mixed and homogenized to give a single sample.

2.2. Mineralogical characterisation

The mineralogical composition of FGD gypsum samples dried at both 60 °C and 105 °C was determined by X-ray diffraction (XRD) using the reference intensity method (RIM) described by Chung [16,17]. XRD analysis was performed on a Siemens D 501 diffractometer using Cu Kα radiation. Solids were scanned as unoriented powder samples from 4° to 60° 2θ with a 0.04° 2θ step interval and a 1 s per step counting time.

2.3. Moisture content analysis

Moisture content of FGD gypsum samples was determined both at 105 °C (according to ISO 11465, as the standard EN-12457-4 establishes) and at 60 °C. With this aim FGD gypsum samples were dried in an oven at 105 ± 5 °C and at 60 ± 5 °C to constant weight. Moisture content determinations in this way were carried out by triplicate and only mean values are presented.

2.4. Leaching tests

2.4.1. Environmental characterisation of FGD gypsum

Leaching tests were performed following the standard EN-12457-4 as the Council Decision 2003/33/EC establishes. Thus, FGD gypsum samples were subjected to an agitation period of 24 h with deionised water on a vertical rotary shaker (10 rpm), using a L/S ratio of $10\,l\,kg^{-1}$ dry matter. FGD gypsum samples underwent this process without being dried and without being crushed since their particle aggregate size was already below 10 mm, as the mentioned standard requires. Such leaching tests were carried out by triplicate. Leachates were analysed for all those elements considered in the Council Decision 2003/33/EC [10], thus As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo Electron Corporation ICP-MS X Series II apparatus, Cl and sulphate by ion chromatography (IC) using a KONTRON-WATERS unit, Hg using a mercury analyser (model AMA-254) equipped for thermal decomposition, amalgam formation and atomic absorption measurement, and F by fluoride selective electrode using a Thermo Orion ISE-meter (model 710). The leachable content of constituents of environmental concern in FGD gypsum was calculated on the dry mass of the material dried at 105 °C as specified by the standard EN-