Stabilization of leachable trace pollutants from FGD by-products

E. Álvarez-Ayuso and X. Querol

Department of Environmental Geology, Institute of Earth Sciences "Jaume Almera" (CSIC), C/ Lluís Solé i Sabarís, s/n, 08028 Barcelona, Spain.

ABSTRACT

In EU the recent and stringent environmental regulations for waste disposal (Council Decision 2003/33/EC[1] on landfill of wastes) makes flue gas desulphurisation (FGD) gypsum an important environmental issue to be faced by coal combustion-desulphurisation plants, as a proportion of this by-product is used as a landfill material in mine reclamation or just disposed of in landfills. In such cases the leaching behaviour of potential contaminants present in FGD gypsum must be strictly controlled to avoid side-off pollution. Among pollutants present in FGD gypsum, fluoride is one of those of greater environmental concern, and also appears as the critical element for the acceptance of FGD gypsum at landfills for non-hazardous wastes. Therefore, measures to stabilize this by-product for its disposal should be approached in order to minimise the leaching of fluoride, and to avoid the high cost of disposal that would imply the characterization of FGD gypsum as only acceptable at landfills for hazardous wastes. Among the possibilities of waste stabilization, the incorporation of a fluoride retention additive to FGD gypsum before its disposal appears as a suitable option to deal with this environmental problem. In this way the use of amorphous aluminium oxide has been investigated, proving to be a feasible option for this aim, since the fluoride retention process is fast enough to proceed in simulated conditions of disposal, attains a high level of fluoride leaching reduction and assures the classification of this by-product as a waste acceptable at landfills of non-hazardous wastes according to the European legislation on landfill of wastes.

KEYWORDS: FGD gypsum, stabilization, disposal

INTRODUCTION

In order to reduce the emissions of SO_2 to the atmosphere a large number of coal combustion plants have been equipped with wet limestone flue gas desulphurisation (FGD) systems. In this desulphurisation process SO_2 is removed from the flue gas by absorption into limestone slurry to finally produce the so-called FGD gypsum as a by-product of the whole process. Although this by-product can find its way to the market in the wallboard manufacture, a proportion is employed as a landfill material in mine reclamation or disposed of in landfills. In such cases in EU the leaching behaviour of potential contaminants present in FGD gypsum must be controlled according to the Council Decision 2003/33/EC[1] on landfill of wastes recently put in force. It is worth noting that the limestone slurry used in the aforementioned desulphurisation technique acts as an scavenging system not only for sulphur but for a fraction of other toxic elements (F, As, Se, Sb, Hg, Cd, Cr, Cu, Ni, Pb, Zn, Ba, Mo) present either in the gas emissions or in the small particles escaping to the electrostatic precipitators of coal combustion plants before entering in the FGD installation. In a recent study performed by Álvarez-Ayuso et al.[2] on the environmental characteristics of combustion by-products arising from a coal combustion-desulphurisation plant it was found that fluoride was a critical element for the acceptance of FGD gypsum at landfills for non-hazardous wastes, showing fluoride leaching values very close to the fluoride limit (150 mg/kg) established by the Council Decision 2003/33/EC[1] for wastes to be accepted at such landfills. Therefore, measures to control the content of fluoride in FGD gypsum or to stabilize this by-product for its disposal minimising the leaching of fluoride should be approached.

Fluorine is mainly emitted from coal combustion plants as HF, being removed by the limestone slurry employed in the desulphurisation process by means of the precipitation of CaF_2. The solubility product (Ksp) of fluorite is $10^{-10.4}$ at 25 °C and $\mu \approx 0$ [3], and the theoretical solubility of fluorite in such conditions is 17 mg/l. Nevertheless, due to the complexity of the FGD gypsum system, and so the numerous compounds there involved suffering dissolution processes when interacting with water, the theoretical fluorite solubility product value is modified in such a system, mainly due to the higher ionic strength of the medium and to the formation of soluble fluoride complexes. These conditions tend to increase the dissolution of fluorite, and therefore the risk of fluoride leaching.

The objective of this work is to assess the possibility of using amorphous aluminium oxide as a fluoride retention additive to FGD gypsum to minimise its leaching behaviour, evaluating the proposed stabilization system according to the European standard EN 12457-4[4] as established the Council Decision 2003/33/EC[1] on landfill of wastes and according to column leaching studies.

MATERIALS AND METHODS

FGD gypsum. Samples of FGD gypsum were collected from a Spanish coal-combustion power plant equipped with a wet limestone FGD installation. The collected samples correspond to samples once dewatered before being sent for their disposal. Collection was performed three consecutive days, obtaining three different samples that were mixed and homogenized to give a single sample.

Amorphous aluminium oxide. The aluminium oxide used in this study as a fluoride retention additive for the stabilization of FGD gypsum was synthesised using the method described by Sims and Bingham[5]. The precipitated solid was characterized as amorphous aluminium oxide by X-ray diffraction (XRD).

EN 12457-4[4]. Leaching tests were performed on untreated and treated FGD gypsum samples using the European standard EN 12457-4[4] as established the Council Decision 2003/33/EC[1]. FGD gypsum was treated for stabilization by adding increasing amounts of amorphous aluminium oxide to a fresh fixed amount of FGD gypsum, obtaining samples with amorphous aluminium oxide/FGD gypsum ratios in the range 0.1-2 %. Leachates were analysed for all those elements considered in the Council Decision 2003/33/EC[1]. Thus As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, 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 gold amalgam AAS mercury analyser (model AMA-254) and F by fluoride selective electrode using a Thermo Orion ISE-meter (model 710).

Column leaching studies. Polypropylene columns (1.4 x 5 cm) packed with 10 g of either untreated or treated FGD gypsum (amorphous aluminium oxide/FGD gypsum ratios: 0, 0.5, 1 and 2%) were leached with 60 ml of deionised water (~ 400 mm annual rainfall) under a saturated flow regime, collecting successive leach fractions of 4 ml using a fraction collector (Foxy Jr., ISCO). Fluoride concentrations in the leached fractions were determined by fluoride selective electrode.

RESULTS AND DISCUSSION

EN 12457-4[4]. Figure 1 shows the leachable contents in untreated and treated FGD gypsum for all the elements of environmental concern considered in the Council Decision 2003/33/EC[1]. According to this Decision, FGD gypsum could be disposed of in landfills for non-hazardous wastes without being subjected to previous treatment given that all its leachable contents remained below the required limit values for wastes to be accepted at such landfills, though the concentration of fluoride was very close to its corresponding limit value (150 mg/kg). The risk supposed by this high fluoride leaching from FGD gypsum was greatly diminished when treated with amorphous aluminium oxide as a fluoride retention additive. The fluoride leachable content in FGD gypsum decreased progressively with the increasing amounts of amorphous aluminium oxide incorporated to FGD gypsum. The decreases experienced in the fluoride leachable contents were in the range 5-75%, values increasing in the mentioned range with the increasing amorphous aluminium oxide added amounts (0.1-2%). It is important to note that, in spite of the high leachable content of sulphate in FGD gypsum, the effectiveness of amorphous aluminium oxide in the retention of fluoride remained high. Concerning the other elements of environmental concern considered in the Council Decision 2003/33/EC[1], it was found that none of them was significantly affected by the amorphous aluminium oxide treatment at any of the doses subject of study, indicating that no side effects were derived from the studied stabilization system; even more, selenium also displayed a tendency to decrease its leached contents with the increase of amorphous aluminium oxide added amounts. Therefore, the use of amorphous aluminium oxide as a fluoride retention additive appeared as an effective treatment to stabilize FGD gypsum before its disposal. This treatment, in addition to greatly reduce the fluoride leaching from FGD gypsum, implies for coal combustion plants the avoidance of the high cost of disposal that would imply the characterization of this waste as only acceptable at landfills for hazardous wastes.

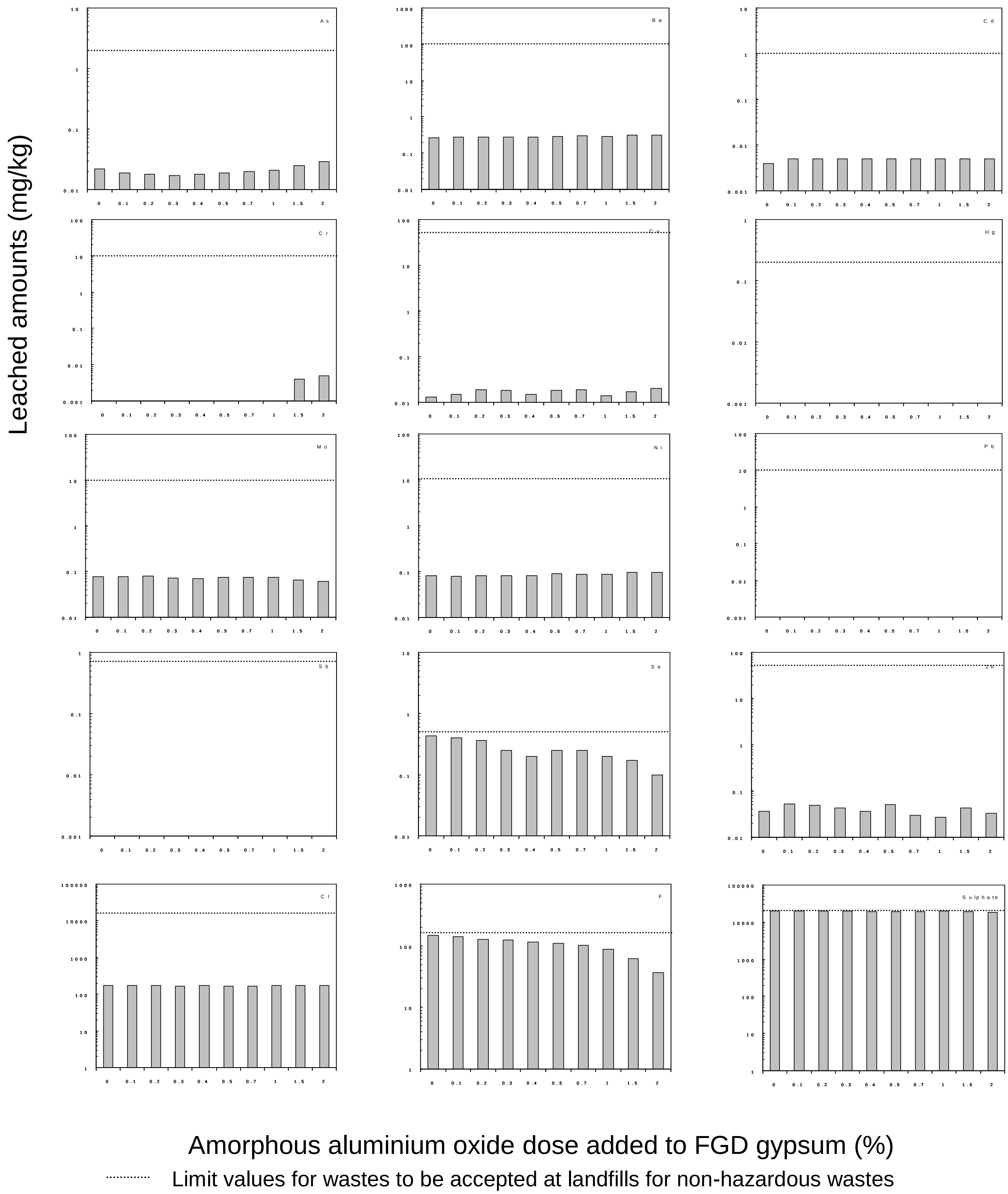

Figure 1. Leachable contents in the untreated and amorphous aluminium oxide-treated FGD gypsum.

Column leaching studies. The cumulative leached amounts of fluoride obtained from the untreated and amorphous aluminium oxide-treated FGD gypsum are shown in Table 1. The total fluoride leached amount from the untreated FGD gypsum column along the percolated water volume was 130 mg/kg. This amount decreased down to 88, 60 and 25 mg/kg when FGD gypsum was treated with 0.5, 1 and 2% amorphous aluminium oxide, respectively, representing correspondingly a reduction of fluoride leached amounts of about 32, 54 and 81%. It is worth noting that high percentages of fluoride leaching reduction were also observed all along the leaching process, even at the earliest stages of leaching. The total fluoride amount leached from untreated FGD gypsum increased progressively in a lineal tendency with total percolated water volume, in accordance with the roughly constant fluoride concentration value found in column eluates. Such behaviour suggests that fluoride leaching is related to the constant solubilization of fluorite as water is percolated.

From the light of these results, it could be derived that amorphous aluminium oxide proves to be an effective additive for the stabilization of FGD gypsum for its disposal in landfills since the fluoride retention process is fast enough to proceed in simulated conditions of disposal and attains high levels of fluoride leaching reduction.

Table 1. Cumulative leached amounts of fluoride from untreated and treated FGD gypsum.

Cumulative volume (ml)	Amorphous aluminium oxide dose (%)			
	0	0.5	1	2
	Cumulative fluoride leached amounts (mg/kg)			
4	7.6	2.1	1.2	0.57
8	16	6.1	2.5	1.2
12	26	11	4.4	2.0
16	35	17	6.9	3.2
20	43	23	9.8	4.6
24	53	30	13	6.1
28	63	37	19	8.1
32	73	44	24	10
36	82	51	29	12
40	92	57	34	14
44	102	64	39	17
48	109	71	45	19
52	117	77	50	21
56	123	83	55	23
60	130	88	60	25

CONCLUSIONS

According to the Council Decision 2003/33/EC[1], FGD gypsum could be disposed of in landfills for non-hazardous wastes, though the concentration of its fluoride leachable content remained very close to the corresponding limit value. The risk supposed by this high fluoride leaching from FGD gypsum was greatly diminished when treated with amorphous aluminium oxide as a fluoride retention additive. Fluoride leachable contents in FGD gypsum decreased in the range 5-75% for amorphous aluminium oxide added amounts of 0.1-2%, assuring the characterization of this by-product as a waste acceptable at landfills of non-hazardous wastes. Furthermore, as was derived from column leaching studies, the proposed stabilization system proved to be highly effective in simulated conditions of disposal, displaying a fluoride leaching reduction value about 81% for an amorphous aluminium oxide added amount of 2%, what means a decrease from 130 to 25 mg/kg in the fluoride leached amount from FGD gypsum during an annual rainfall of 400 mm.

REFERENCES

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