Energy 50 (2013) 438–444

Contents lists available at SciVerse ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

# Influence of an aluminium additive in aqueous and solid speciation of elements in flue gas desulphurisation (FGD) system

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ARTICLE INFO

*Article history:*
Received 2 August 2012
Received in revised form
7 November 2012
Accepted 16 November 2012
Available online 24 December 2012

*Keywords:*
FGD
Gypsum slurry
Modelling tools
Leachates

ABSTRACT

The acidification of the aqueous phase induced by the use of an aluminium additive (sulphate), to increase the $SO_2$ trapping efficiency in flue gas desulphurisation (FGD) systems, results in significant differences in the speciation and partitioning of elements between the aqueous and solid phases of gypsum slurries from two Spanish coal-fired power plants (PP1 and PP2). The Al-additive increases the presence of the aqueous Al–$F_x$ complexes in the gypsum slurry from PP2-2007. In the absence of (PP1) or using lower dosages (PP2-2008) of the Al-additive, the predominance of $MgF_2$ and $CaF_2$ in the FGD-gypsum slurries causes their subsequent precipitation, increasing the leachable potential of gypsum waste. This study evaluates the effect of the Al-additive on the fate of a number of elements during FGD by combining a number of experimental and modelling tools. The results suggest the precipitation of $CaF_2$, $MgF_2$, and $CaUO_4$ in the PP1 FGD-gypsum, and $Al_2O_3$, $AlHO_2$, $KAl_3(OH)_6(SO_4)_2$ and $MgF_2$ in the PP2 2007 and 2008 FGD-gypsum. When Al-additive is added low amounts of heavy metals are found in the leachates of the FGD-gypsums since these remain mostly in solution of gypsum slurry. The reverse behaviour is found for Se.



## 1. Introduction

Enrichment of some inorganic trace pollutants in re-circulated water streams occurs in flue gas desulphurisation (FGD) systems with re-circulation of water [1]. Elements of environmental concern, such as Al, F, Cl, B, As, Se, U, and Hg, form highly soluble salts favouring element enrichment and saturation in the re-circulated water streams of FGD scrubbers [1]. This causes the emission of such elements by entraining particles and droplets of gypsum slurry in the outgoing gaseous stream of the flue gas desulphurisation (OUT-FGD).

Hydrofluoric acid contained in the flue gas may be captured by the sprayed droplets of limestone slurry giving rise to the formation of $CaF_2$. In the presence of aluminium components, HF may also react with limestone to form Al–F compounds, typically represented by $CaAlF_3(OH)_2$-$CaF_2$ [2,3]. These compounds are deposited on the surfaces of limestone particles and consequently may cause a decrease the reactivity of limestone [4–7]. However, these solid F species can also precipitate in the FGD-gypsum end-product. Indeed, some FGD-gypsum exceeds the maximum value of leachable F to be accepted at non-hazardous waste landfills [3]. In order to avoid this, the use of additives has been proposed as measure for preventing the coating of the limestone surface, and for reducing the precipitation of F solid species in the FGD-gypsum, respectively [3]. In the case of FGD-gypsum, other studies have addressed this issue by stabilising the FGD-gypsum before its disposal to mitigate $F^-$ leaching [8,9].

The use of additives for preventing the precipitation of F solid species on FGD-gypsum may also be relevant given that some of novel techniques for sequestering $CO_2$ are based on the formation of $CaCO_3$ via mineral carbonation of FGD-gypsum [10]. According to this study one ton of waste gypsum, which contains approximately 32.5% CaO, can store approximately 0.26 ton of $CO_2$ by the precipitation of stable carbonate compounds.

Although the effect of additives on the leaching of F in FGD-gypsum [11] has been addressed, much less attention has been paid to the influence of additives on the speciation and partitioning of inorganic trace pollutants other than F in the water streams re-circulated to the FGD scrubber. Changes in the speciation of elements and variations of chemical properties e.g. pH and solubility of metal complexes in the aqueous phase of the gypsum slurry could also be expected when Al additives are injected into the scrubber, which could affect the desulphurisation efficiency and/or the abatement capacity for trace pollutants.

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0360-5442/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2012.11.020

The aim of this paper is threefold (i) to investigate the influence of an Al-additive on the pH of the gypsum slurry and the aqueous and solid speciation of elements enriched in the aqueous phase gypsum slurry, especially those of most environmental concern: Al, F, B, Se, Ni, Cu, Mn, As, Hg, and U, and on desulphurisation efficiency; ii) highlight the identification of solid phases and the mechanism of the retention of these elements in FGD-gypsum; and iii) to assess leaching of the FGD-gypsum by-product with respect to the waste acceptance criteria values at landfills. To this end, we selected two coal-fired power plants (PP1 and PP2) at which an enrichment of trace inorganic pollutants in the re-circulation water streams had been demonstrated [1].

## 2. Materials and methods

### 2.1. The FGD system

The FGD system at PP1 and PP2 operates with a forced oxidation system and re-circulation of water from gypsum slurry filtration to the scrubber. These FGD systems include a number of water streams categorised as FGD water streams: limestone and gypsum slurry, and filtered water. At PP1, a fraction of filtered water is used for limestone slurry preparation and the remaining fraction is re-circulated to the scrubber whereas at PP2 the filtered water is directly re-circulated to the scrubber. The main difference between the two FGD systems is the injection of an aluminium-rich additive into the scrubber at PP2 in 2007 (68 kg/h) and 2008 (14 kg/h). At PP2, the Al-additive is added to boost the efficiency of the desulphurisation process as a consequence of the low porosity of limestone. The addition of the Al-additive promotes the interaction between Al and F increasing the capacity of limestone for $SO_2$ (g) retention and preventing the formation of $CaF_2$ particles. A sketch of the FGD system at PP1 and PP2 is shown in Fig. 1. Detailed descriptions of the operation of the FGD system at PP1 and PP2 and the water streams are provided by Córdoba et al. [1,12,13].

### 2.2. Sample collection

The sampling campaigns at PP1 and PP2 were carried out at 100% MCR (maximum capacity) and 100% desulphurisation on two consecutive days in September 2007 at PP1, and in November 2007 and November 2008 at PP2. Limestone and gypsum slurries and filtered water were sampled and analysed at PP1 and at PP2 in 2007 and 2008. FGD-gypsum samples from PP1 and PP2 were also collected and analysed.

### 2.3. Chemical analysis

Water streams were directly analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for major and minor elements and by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) for most trace elements. Chloride contents were measured by High Performance Ion Chromatography (HPIC), and fluorides were determined by an ion selective electrode. The Hg analyses were directly carried out on gypsum and water samples using a LECO AMA 254 gold amalgam atomic absorption spectrometer.

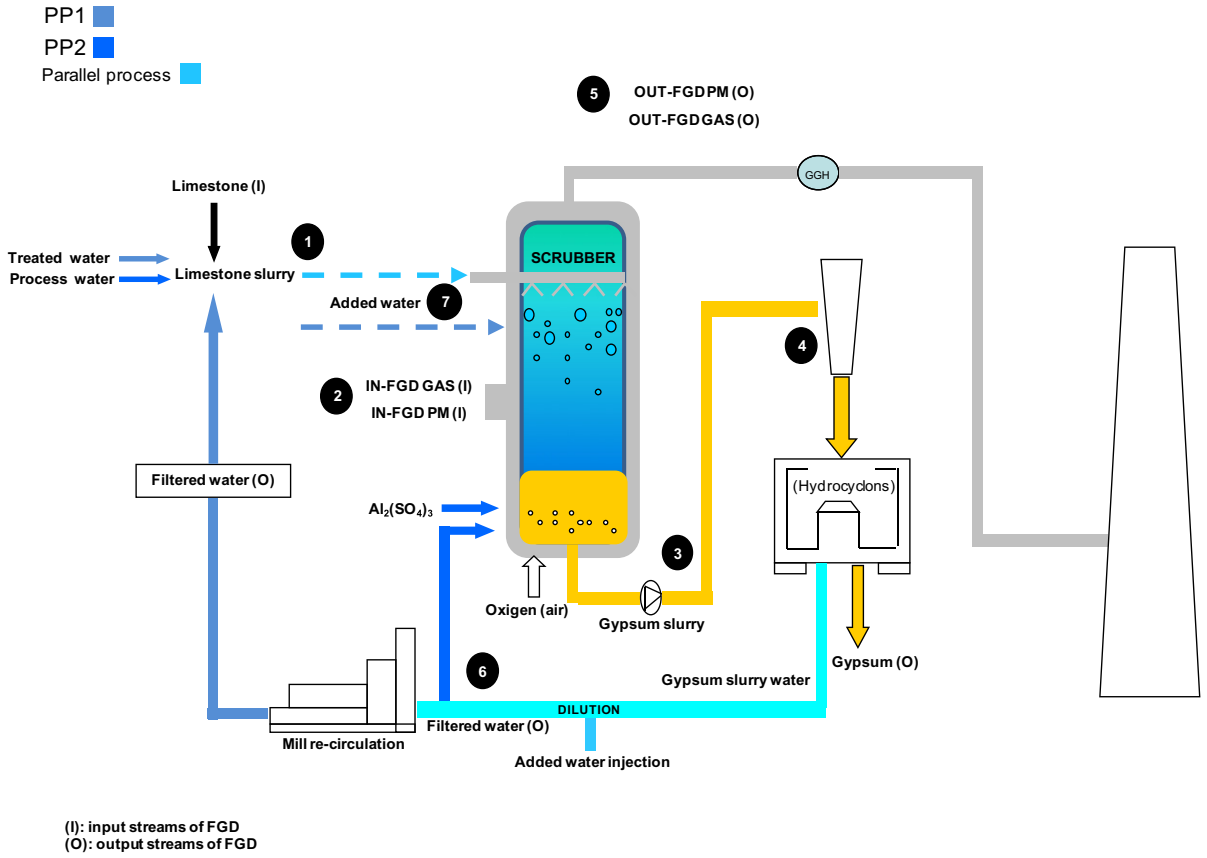


**Fig. 1.** Sketch and process the FGD system at PP1 and PP2. 1. Limestone slurry introduced and sprayed into the scrubber to react with $SO_2$. 2. Gas and PM input flow into the scrubber after combustion process. 3. Formation of gypsum slurry as result of the desulphurisation process. 4. Filtration of gypsum slurry by hydro-cyclones = gypsum slurry water and gypsum production. 5. Cleaned gas and PM flow OUT-FGD. 6. PP1: re-circulation of filtered water for limestone slurry preparation, remaining fraction, if any, is re-circulated to the scrubber, PP2: re-circulation of filter water directly to the scrubber. 7. Water addition to offset the water loss with gypsum and in the OUT-FGD gas.