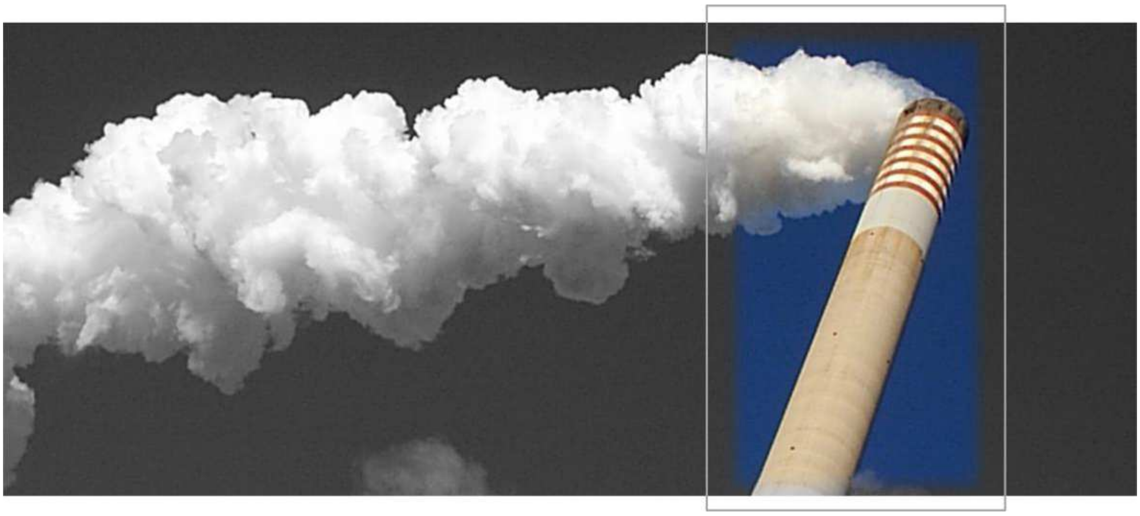
Partitioning and speciation of trace elements at two coal-fired power plants equipped with a wet limestone Flue Gas Desulphurisation (FGD) systems



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INDEX

Abstract

Resumen

Resum

Acronyms

I. Structure of the thesis

1. INTRODUCTION

1.1. COAL

- 1.1.1. Power generation from coal
  - 1.1.1.1. Coal combustion
  - 1.1.1.2. Co-combustion
  - 1.1.1.3. Oxy-combustion
  - 1.1.1.4. Gasification of coal

- 1.1.2. Coal combustion products (CCPs)
  - 1.1.2.1. Behaviour of trace elements during coal combustion

- 1.1.3. Coal-fired emissions and abatement technologies: SO_2, PM, NO_x, and CO_2
  - 1.1.3.1. Abatement for SO_2 emissions
  - 1.1.3.2. Abatement for PM emissions
  - 1.1.3.3. Abatement for NO_X emissions
  - 1.1.3.4. Abatement for CO_2 emissions

- 1.1.4. Emissions of hazardous trace inorganic air pollutants from coal-fired power plants
  - 1.14.1. Mercury emissions from coal-fired power plants

1.2. FLUE GAS DESULPHURISATION (FGD) SYSTEMS

- 1.2.1 Wet FGD systems
  - 1.2.1.1. Wet limestone FGD systems
  - 1.1.2.2. Wet lime and magnesium-lime FGD systems
  - 1.1.2.3. Seawater FGD systems
  - 1.1.2.4. Dual-Alkali FGD systems
  - 1.1.2.5. Ammonia FGD systems

- 1.2.2. Dry and/or semi-dry FGD systems
  - 1.2.2.1. Spray dry FGD systems
  - 1.2.2.2. Furnace sorbent injection
  - 1.2.2.3. Duct sorbent injection
  - 1.2.2.4. Circulating fluid bed (CFB) dry scrubber

1.3. OPERATIONAL CONDITIONS OF WET LIMESTONE FGD SYSTEMS

  - 1.3.1. Reactivity of limestone

- 1.3.2. SO_2
- 1.3.3. pH and temperature
- 1.3.4. Hydrochloric acid
- 1.3.5. Hydrogen fluoride
- 1.3.6. Use of additives
- 1.3.7. Efficiency of the particulate control devices
- 1.3.8. Liquid to gas ratio and residence time in FGD systems
- 1.3.9. Oxidation

1.4. BY-PRODUCTS OF FGD PROCESS

- 1.4.1. Filter water: water treatment or recycling
- 1.4.2. FGD-gypsum

1.5. THE FATE OF TRACE INORGANIC POLLUTANTS IN FGD SYSTEMS

II. Gaps in knowledge and Objectives

2. METHODOLOGY

2.1. DESCRIPTION OF THE POWER PLANTS

2.2. SAMPLE COLLECTION

- 2.2.1. Sampling of solid and water streams
- 2.2.2. Sampling of gaseous stream and particulate matter
  - 2.2.2.1. Sampling of Hg in gaseous phase
  - 2.2.2.2. Sampling of anions and metals in gaseous phase

2.3. CHEMICAL CHARACTERISATION OF SOLID, WATER, AND GASEOUS STREAMS

2.4. LABORATORY EXPERIMENTS

- 2.4.1. Laboratory FGD reactor
  - 2.4.1.1. Mercury sources
  - 2.4.1.2. Synthetic gaseous stream of SO_2 and HCl
  - 2.4.1.3. Reactor vessel
    - 2.4.1.3.1. Limestone and gypsum slurries
    - 2.4.1.3.2. Agitation system
    - 2.4.1.3.3. IN-FGD and OUT-FGD gas
    - 2.4.1.3.4. Temperature and pressure controller

- 2.4.2. Mass flow controller
- 2.4.3. Sir Galahad Mercury Analyser

2.5. THERMODYNAMIC MODELLING TOOLS

2.6. SPECIATION EXPERIMENTS

2.7. LEACHING EXPERIMENTS

2.8. TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY (TOF-SIMS)

2.9. POTENTIOMETRIC TITRATION EXPERIMENTS

3. RESULTS

ARTICLE 1
Partitioning of trace inorganic elements in a coal-fired power plant equipped with a wet Flue Gas Desulphurisation (FGD) system. Fuel 92 (2012), 145-157.

ARTICLE 2
The retention capacity of trace elements by flue gas desulphurisation system under operational conditions of a co-combustion power plant. Fuel 102 (2012) 773-78.

ARTICLE 3
Enrichment of trace inorganic pollutants in re-circulated water streams from a wet limestone flue gas desulphurisation system in two coal power plants. Fuel Processing Technology 92 (2011), 1764-1775.

ARTICLE 4
Unusual speciation and retention Hg at a coal-fired power plant. Environmental Science and Technology 46, (2012), 7890-789.

ARTICLE 5
Influence of an aluminum additive in aqueous and solid speciation of elements in flue gas desulphurisation gypsum slurry. Energy 50, (2013), 438-444.

4. SUMMARY OF RESULTS AND DISCUSSION

4.1. MASS BALANCES, PARTITIONING, AND BEHAVIOUR OF TRACE ELEMENTS

- 4.1.1. Partitioning and behaviour of trace elements in the PCC system (boiler + ESP)
- 4.1.2. Partitioning and behaviour of trace elements in the FGD system
- 4.1.3. Mass balances

4.2. DESULPHURISATION EFFICIENCY AND ABATEMENT CAPACITY OF TRACE INORGANIC POLLUTANTS

4.3. SPECIATION, BEHAVIOUR, AND FATE OF GASEOUS Hg

4.4. ENRICHMENT AND SPECIATION OF INORGANIC TRACE POLLUTANTS IN RE-CIRCULATED WATER STREAMS

- 4.4.1. Enrichment of inorganic trace pollutants in re-circulated water streams
- 4.4.2. Aqueous and solid speciation of inorganic trace pollutants in re-circulated waters
- 4.4.3. Evaluation of the potential leaching of FGD-gypsums

5. CONCLUSIONS

5.1. MASS BALANCES AND RETENTION EFFICIENCIES

5.2. SPECIATION, BEHAVIOUR, AND FATE OF GASEOUS HG

5.3 ENRICHMENT AND SPECIATION OF INORGANIC TRACE POLLUTANTS IN RE-CIRCULATED WATER STREAM

6. FUTURE RESEARCH AND OPEN QUESTIONS

7. REFERENCES

Annex I

Annex II

Abstract

Coal-fired power plants are a major source of emissions for a number of air pollutants including SO_2, NO_x, particulate matter (PM), HCl, HF, and Hg amongst. Hazardous air pollutants such as As, Be, Cd, Cr, Pb, Mn, Ni, Se, and other metals are integral components of fine PM emitted directly from coal-fired power plants. The study of the distribution, fate, and common pathways of trace pollutants at coal-fired power plants is therefore crucial to prevent and/or reduce gaseous and PM emissions.

In this work, intensive sampling campaigns and characterisation programmes were carried out at two power plants in Spain in 2007 and 2008 to study the fate of trace elements. Input and output flows were sampled in the coal combustion unit (boiler and Electrostatic Precipitator (ESP)) as well as in the Flue Gas Desulphurisation (FGD) system at the two power plants under stable operational conditions. Based on the results of the analyses of solid, water, gaseous, and PM samples, mass balance calculations and studies on partitioning for trace elements were conducted for the Pulverised Coal Combustion (PCC), FGD systems, and for the whole installation (PCC+FGD). Assessment of the desulphurisation efficiency and of the emission abatement capacity for inorganic trace pollutants at both power plants was also made on the basis of these results.

Results revealed *(1)* an unusual speciation of Hg in the outgoing gaseous stream of the flue gas desulphurisation (OUT-FGD) system at the two power plants (PP1 and PP2): Hg^0 (71%) was the dominant Hg OUT-FGD species at PP1, whereas Hg^{2+} was the prevalent Hg OUT-FGD species at PP2 in 2007 (66%) and 2008 (87%); *(2)* a different retention of gaseous Hg between the two sampling campaigns at the coal-fired power plant under co-combustion conditions: a higher retention of Hg^{2+} in 2007 (73%) than in 2008 (24%) at PP2; *(3)* a high concentration of trace pollutants and a distinctive behaviour of some elements in the waters of re-circulation to the scrubber at both power plants: Al was enriched in the 2007 aqueous phase of gypsum slurry (by factors of 20 and >60), as was F (by factors of 7.0 and 15), and SO_4^{2-} (by factors of 1.3 and 2.7) with respect to the 2008 gypsum slurry at PP2, and with respect to gypsum slurry at PP1; and *(4)* a characteristic leaching behaviour of some elements from FGD-gypsum: insignificant leaching of heavy metals from FGD-gypsums was found at PP2. The behaviour of Se proved to be the inverse.

In order to corroborate the results obtained at industrial scale and to determine the causes and implications of such results from the scientific and environmental perspectives, laboratory experiments were conducted to reproduce the differences in speciation of gaseous Hg OUT-FGD with respect to that detected at industrial scale.

Thermodynamic modelling tools were employed to study the causes of the different retention and speciation of gaseous Hg OUT-FGD and to determine the causes and effects of the high concentration of elements in the waters of re-circulation at the two power plants. Potentiometric titration experiments for FGD-gypsum samples were conducted to study the leaching behaviour of some elements from FGD-gypsum.

Laboratory experiments confirmed Hg^0 (66-61%) as the dominant species in the OUT-FGD gas at PP1, and Hg^{2+} (56-66%) as the predominant species of Hg at PP2. Experiments indicated that the gaseous speciation of Hg^{2+} OUT-FGD at PP2 in 2007 and in 2008 was caused by the high concentration of HCl and Hg in the IN-FGD gaseous stream. The unusual speciation of Hg^{2+} OUT-FGD at PP2 was probably due to the evaporation of $HgCl_2$ particles from the aqueous phase of the gypsum slurry in the OUT-FGD gas. The Al-additive used at PP2 was responsible for the higher retention of gaseous Hg in 2007 than in 2008.

The capture of a number of elements in the aqueous phase of the gypsum slurry and an enrichment of inorganic trace pollutants in the re-circulated water streams at PP1 and PP2 resulted from the continuous re-circulation of filtered water to the scrubber. The emission of the enriched elements by entraining particles and droplets of gypsum slurry in the outgoing gaseous stream of the FGD was the most significant result of the high enrichment of trace inorganic pollutants in the re-circulated waters.

Thermodynamic modelling tools based on the ion-association aqueous model from the chemical analysis of the aqueous phase of gypsum slurries revealed that the Al-additive i) increased the concentration of F^- in filtered waters at PP2 in 2007, ii) gave rise to the differential behaviour and enrichment of Al^{3+}, F^-, SO_4^{2-}, Mg^{2+}, and $U^{4+, 6+}$ in the aqueous phase of gypsum slurries and filtered waters from PP1 and PP2, iii) led to the formation of SO_4^{2-} complexes with metals increasing their concentrations in the aqueous phase of the gypsum slurry from PP1 to PP2-2008 and 2007, iv) caused the acidification of the aqueous phase of the gypsum slurry from PP2 via aluminium hydrolysis, and v) induced the protonation of the PP2 FGD-gypsum surfaces.

The relatively high leaching values of Se and the absence of significant leaching of heavy metals from the PP2 FGD-gypsums resulted from the protonation of the surface of the FGD-gypsum induced by the addition of $Al_2(SO_4)_3$, and the formation of SO_4-complexes, respectively.

Moreover, results at industrial scale revealed a high retention capacity (92-100%, of the bulk element input to the power plants) for F, Cl, As, and B in the case of the whole installations (PCC+FGD) with the reduction in the emitted gas proportions (0.1-2.1%) below the limits established by the European directive 2001/80/EC for large combustion plants. The PM emission levels fell to 25 mg/Nm^3 (at 6 % O_2), far below the limits established by this directive.

Major, minor, and trace elements were retained via fly ash (FA, 75-80% mean of the input mass of the elements studied) and boiler slag (BS, 8-11%). In decreasing order, FGD-gypsum (4.9-7.9%), filtered water (2.9-7.2%), OUT-FGD PM (0.6-2.0%), OUT- FGD gas (0.6-0.8%), and BS water (0.01-0.03%) were the remaining outgoing streams for major, minor, and trace elements.

Resumen

Las centrales térmicas de carbón pulverizado son una de las principales fuentes antropogénicas de SO_2, NO_x, material particulado (MP), HCl, HF, y Hg a la atmósfera. Otros contaminantes atmosféricos altamente peligrosos como el As, Be, Cd, Cr, Pb, Mn, Ni, Rd, y Se son componentes íntegros del MP y también son emitidos a la atmósfera a través de centrales térmicas de carbón. El estudio de la distribución de contaminantes trazas así como de las rutas más comunes de dichos contaminantes en centrales térmicas de carbón es, por lo tanto, fundamental con el fin de prevenir y/o reducir las emisiones gases y de MP.

En esta tesis, intensivas campañas de muestreo y programas de caracterización se han llevado a cabo en dos centrales térmicas españolas (PP1 y PP2) en 2007 y 2008 con el fin de estudiar la distribución y destino de elementos mayoritarios, minoritarios, y traza. Flujos de entrada y de salida en la unidad de combustión (CCP), así como en el sistema de desulfuración de gases (DGC) fueron muestreados en las dos centrales térmicas en condiciones estables de operación. En base a los resultados analíticos de las muestras sólidas, acuosas, gaseosas, y de MP, cálculos de balance de masa y estudios de partición se llevaron a cabo para el sistema CCP, DGC, y para toda la instalación (CCP + DGC). La evaluación de la eficiencia de desulfuración y de la capacidad de reducción de las emisiones de contaminantes traza inorgánicos también se llevó a cabo en ambas centrales térmicas sobre la base de estos resultados.

Los resultados revelaron *(1)* una especiación diferente de Hg en la corriente de gas de salida de la DGC en las dos centrales térmicas: en PP1, Hg^0 (71%) fue la especie predominante en la corriente de gas de salida de la DGC, mientras que en PP2, Hg^{2+} fue la especie predominante en la corriente de gas de salida en 2007 (66%) y 2008 (87%); *(2)* una retención diferente de Hg gaseoso en PP2 entre 2007 y 2008: en PP2, una mayor retención de Hg^{2+} se obtuvo en 2007 (73%) que en 2008 (24%); *(3)* una alta concentración de contaminantes traza y un comportamiento diferente de algunos elementos en las aguas de re-circulación en ambas centrales térmicas: Al se enriqueció en la fase acuosa de la lechada de yeso de 2007 (por factores de 20 y 60>), como se enriqueció F (por factores de 7,0 y 15), y SO_4^{2-}(por factores de

1,3 y 2,7) con respecto a la lechada de yeso en PP2-2008, y con respecto a la lechada de yeso en PP1, y *(4)* valores de lixiviación de metales pesados relativamente inferiores en comparación a los valores de lixiviación de Se en los yesos de PP2.

Con el fin de verificar los resultados obtenidos a escala industrial, y determinar las causas e implicaciones de estos resultados desde una perspectiva científica y ambiental, experimentos de laboratorio se llevaron a cabo para reproducir las diferencias en la especiación de Hg gaseoso a la salida de la DGC con respecto a la detectada a escala industrial.

Cálculos termodinámicos fueron empleados para estudiar las causas de la diferente retención y especiación de Hg gaseoso fuera de la DGC, así como para la determinación de las causas y efectos de la alta concentración de elementos traza en las aguas de recirculación de ambas centrales térmicas.

Experimentos de valoración potenciométrica se llevaron a cabo en muestras de yeso para estudiar el comportamiento de lixiviación de algunos elementos.

Los resultados de laboratorio confirmaron Hg^0 (66-61%) como la especie dominante en el gas de salida de la DGC en PP1, y Hg^{2+} (56-66%) como la especie predominante en PP2. Los experimentos de laboratorio indicaron que la especiación inusual de Hg^{2+} en el gas de salida de la DGC en PP2 en 2007 y en 2008, se debió a la alta concentración de HCl y Hg en la corriente de gas de entrada a la DGC y fue causada probablemente, por la evaporación de $HgCl_2$ partículas en el gas salida de la DGC procedentes de la fase acuosa de la lechada de yeso. El aditivo de aluminio utilizado en PP2 fue responsable de la mayor retención de Hg gaseoso en 2007 que en 2008.

En las corrientes de agua de recirculación de PP1 y PP2 se determinó un enriquecimiento de contaminantes traza inorgánicos como consecuencia de la continua recirculación del agua filtrada al absorbedor. Como resultado de ello, contaminantes traza inorgánicos saturados en la fase acuosa de la lechada de yeso fueron emitidos por arrastre en la corriente de gas de salida de la DGC.

La modelización termodinámica realizada a partir del análisis químico de la fase acuosa de las lechadas de yeso reveló que el uso del aditivo de aluminio i) aumentó la concentración de F^- en las aguas filtradas de PP2 en 2007; ii) dio lugar al enriquecimiento de Al^{3+}, F^-, $SO_4^{2-,}$ Mg^{2+}, y $U^{4+, 6+}$ en la fase acuosa de las lechadas de yeso y aguas filtradas de PP1 y PP2; iii) indujo la formación de complejos-SO_4^{2-} con metales incrementando sus concentraciones en la fase acuosa de la lechada de yeso de PP1 a PP2-2008 y PP2-2007; iv) produjo la acidificación de la fase acuosa de la lechada de yeso de PP2 a través de la hidrólisis de aluminio; e v) indujo la protonación de la superficie del yeso producido en PP2.

Los valores relativamente altos de lixiviación de Se y la ausencia de valores de lixiviación significativos de metales pesados en los yesos producidos en PP2, fueron consecuencia de la protonación de la superficie yeso por la adición de $Al_2(SO_4)_3$ y la formación de complejos-SO_4, respectivamente.

Además de los resultados anteriormente mencionados, los resultados a escala industrial revelaron una alta capacidad de retención (92-100%, del volumen de entrada del elemento a las centrales térmicas) para F, Cl, As, B y por las instalaciones completas (CCP +DGC) con la consiguiente reducción de gases emitidos (0.1-2.1%) por debajo de los límites establecidos por la directiva Europea 2001/80/CE para grandes instalaciones de combustión. Los niveles de emisión de MP se redujeron a 25 mg/Nm^3 (al 6% O_2), muy por debajo de los límites establecidos por la directiva mencionada.

Elementos mayoritarios, minoritarios y traza se retuvieron en las cenizas volantes (75-80%, promedio de la masa de entrada de los elementos estudiados) y escoria (8-11%). En orden decreciente, yeso (4.9 -7.9%), agua filtrada (2.9 -7.2%), PM (0.6-2.0%), gas (0.6-0.8%), y agua de escoria (0.01-0.03%) fueron los flujos de salida de los elementos mayoritarios, minoritarios y traza.

Resum

Les centrals tèrmiques de carbó pulveritzat són una de les principals fonts antropogèniques de SO_2, NO_x, material particulat (MP), HCl, HF i Hg a l'atmosfera. Altres contaminants atmosfèrics altament perillosos com l'As, Be, Cd, Cr, Pb, Mn, Ni, Rd i Se són components íntegres del MP i també són alliberats a l'atmosfera mitjançant les centrals tèrmiques de carbó. L'estudi de la distribució dels contaminants traça així com de les rutes més comuns d'aquests contaminants en centrals tèrmiques de carbó és, per tant, fonamental amb la finalitat de prevenir i/o reduir les emissions de gasos i de MP.

En aquesta tesi, s'han dut a terme intensives campanyes de mostreig i programes de caracterització en dues centrals tèrmiques espanyoles (PP1 i PP2) durant 2007 i 2008, amb la finalitat d'estudiar la distribució i el destí d'elements majoritaris, minoritaris i traça. En les dues centrals tèrmiques es van mostrejar fluxes d'entrada i de sortida en la unitat de combustió (CCP), així com en el sistema de dessulfuració de gasos (DGC) en condicions estables d'operació. En base als resultats analítics de les mostres sòlides, aquoses, gasoses i de MP, s'han dut a terme càlculs de balanç de masses i estudis de partició pel sistema CCP, DGC, i per a tota la instal·lació (CCP+DGC). També, sobre la base d'aquests resultats, es va realitzar en les dues centrals tèrmiques l'avaluació de l'eficiència de dessulfuració i de la capacitat de reducció de les emissions de contaminants traça inorgànics.

Els resultats van revelar *(1)* una especiació diferent de Hg en el corrent de gas de sortida de la DGC en les dues centrals tèrmiques: a PP1, Hg^0 (71%) va ser l'espècie predominant al corrent de gas de sortida de la DGC, mentre que a PP2, Hg^{2+} fou l'espècie predominant al corrent de gas de sortida al 2007 (66%) i al 2008 (87%); *(2)* una retenció diferent de Hg gasós a PP2 entre 2007 i 2008: a PP2, al 2007, es va obtenir una major retenció de Hg^{2+} (73%) que al 2008 (24%); *(3)* una alta concentració de contaminants traça i un comportament diferent d'alguns elements en les aigües de recirculació en ambdues centrals tèrmiques: Al es va enriquir a la fase aquosa de la lletada de guix de 2007 (per factors de 20 i 60>), com es va enriquir F (per factors de 7.0 i 15), i SO_4^{2-} (per factors d'1.3 i 2.7) respecte a la lletada de guix a PP2-2008, i respecte a la lletada de guix a PP1, i *(4)* valors de lixiviació de metalls pesats relativament

inferiors, en comparació, als valors de lixiviació de Se en els guixos de PP2.

Amb la finalitat de verificar els resultats obtinguts a escala industrial i determinar les causes i implicacions d'aquests resultats des d'una perspectiva científica i ambiental, es van dur a terme experiments de laboratori per a reproduir les diferències en la especiació de Hg gasós a la sortida de la DGC respecte a la detectada a escala industrial.

Per estudiar les causes de la diferent retenció i especiació de Hg gasós fora de la DGC foren emprats càlculs termodinàmics, així com per a la determinació de les causes i efectes de l'alta concentració d'elements traça en les aigües de recirculació d' ambdues centrals tèrmiques.

Es van dur a terme experiments de valoració potenciomètrica en mostres de guix per a estudiar el comportament de lixiviació d'alguns elements.

Els resultats experimentals de laboratori van confirmar Hg^0 (66-61%) com l'espècie dominant en el gas de sortida de la DGC a PP1, i Hg^{2+} (56-66%) com l'espècie predominant a PP2. Els experiments de laboratori van indicar que l'especiació inusual de Hg^{2+} al gas de sortida de la DGC a PP2 al 2007 i 2008, va ser deguda a l'alta concentració de HCl i Hg en el corrent de gas d'entrada a la DGC i fou causada probablement, per l'evaporació de partícules de $HgCl_2$ en el gas sortida de la DGC procedents de la fase aquosa de la lletada de guix. L'additiu d'alumini utilitzat a PP2 fou responsable de la major retenció de Hg gasós en 2007 respecte 2008.

En els corrents d'aigua de recirculació de PP1 i PP2 es va determinar un enriquiment de contaminants traça inorgànics com a conseqüència de la contínua recirculació de l'aigua filtrada a l'absorbidor. Com a resultat de tot això, contaminants traça inorgànics saturats en la fase aquosa de la lletada de guix van ser emessos per arrossegament en el corrent de gas de sortida de la DGC.

La modelització termodinàmica realitzada a partir de l'anàlisi química de la fase aquosa de les lletades de guix va revelar que l'ús de l'additiu d'alumini i) va augmentar la concentració de F^- en les aigües filtrades de PP2 al 2007; ii) va donar lloc a l'enriquiment d'Al^{3+}, F^-, SO_4^{2-}, Mg^{2+}, i $U^{4+,6+}$ en la fase aquosa de les lletades de guix i aigües filtrades de PP1 i PP2; iii) va induir la formació de complexes-SO_4^{2-} amb metalls incrementant les seves concentracions en la fase aquosa de la lletada de guix de PP1 a PP2-2008 i PP2-2007; iv) va induir l'acidificació de la fase aquosa de la lletada de guix de PP2 a través de la hidròlisi d'alumini; i v) va induir la protonació de la superficie del guix produït a PP2.

Els valors relativament alts de lixiviació de Se i l'absència de valors de lixiviació significatius de metalls pesats en els guixos produïts a PP2, foren conseqüència de la protonació de la superficie guix per l'addició de $Al_2(SO_{4)3}$ i la formació de complexes-SO_4, respectivament.

A més dels resultats esmentats anteriorment, els resultats a escala industrial van revelar una alta capacitat de retenció (92-100% del volum d'entrada de l'element a les centrals tèrmiques) per a F, Cl, As, B i per les instal·lacions completes (CCP+DGC) amb la conseqüent reducció de gasos emessos (0.1-2.1%) per sota dels límits establerts per la directiva Europea 2001/80/CE per a grans instal·lacions de combustió, i també per sota del valor llindar d'emissions establert pel Registre Estatal d'Emissions i Fonts contaminants (PRTR). Els nivells d'emissió de MP es van reduir a 25 mg/Nm^3 (al 6% O_2), molt per sota dels límits establerts per la directiva mencionada.

Elements majoritaris, minoritaris i traça van quedar retinguts a les cendres volants (75-80%, promig de la massa d'entrada dels elements estudiats) i a les escòries (8-11%). En ordre decreixent, guix (4.9-7.9%), aigua filtrada (2.9-7.2%); PM (0.6-2.0%), gas (0.6-0.8%), i aigua d'escòria (0.01-0.03%) van ser els fluxes de sortida dels elements majoritaris, minoritaris i traça.

ACRONYMS

AGS	Aqueous phase of Gypsum Slurry
ALS	Aqueous phase of Limestone Slurry
Al-additive	Aluminium additive
ASTM	American Society for Testing and Materials
ASSM	Advances in sustainable Sewage Sludge Management
ASU	Air Separation Unit
BA	Bottom Ash
BAT	Best Available Techniques
BFBC	Bubbling Fluidised Bed Combustion
BPFBC	Bubbling Pressurised Fluidised Bed Combustion
BP	British Petroleum
BREF	Best Available Techniques Reference document
BS	Boiler Slag
B&W	Babcock & Wilcox Power Generation Group
C	Carbon
Ciemat	Centro de Investigaciones Energéticas, Medioambientales y Tec
CFBC	Circulating Fluidised Bed Combustion
COS	Carbonyl Sulphide
CPFBC	Circulating Pressurised Fluidised Bed Combustion
CCPs	Coal Combustion Products
db	dry basis
DeNO$_x$	De-nitrification
EC	European Commission
ECOBA	European Coal Combustion Products Association
EH&E	Environmental Health & Engineering
EIA	Energy Information Administration
ELVs	Emission Limit Values
EPA	Environmental Protection Agency
ESP	Electrostatic Precipitator
EUBIA	European Biomass Industry Association
EU	European Union
EurObserv'ER	Observatoire des énergies renouvelables
FA	Fly Ash
FBC	Fluidised Bed Combustion
FF	Fabric Filter
FGD	Flue Gas Desulphurisation
FW	Filtered water
GA-AAS	Gold Amalgam Atomic Absorbance Spectrometry
GICC	Global Institute of Carbon Capture
GHG	Green House Gas
GS	Gypsum Slurry
H	Hydrogen
HAPs	Hazardous Air Pollutants
HPIC	High Performance Ion Chromatography
Hg^0	Elemental mercury
Hg$_2^{2+}$	Mercurous
Hg^{2+}	Oxidised mercury
Hg$_p$	Mercury particle-bound
HDPE	High Density Polyethylene
ICP-AES	Inductively-Coupled Plasma Atomic-Emission Spectrometry
ICP-MS	Inductively-Coupled Plasma Mass Spectrometry
IN-FGD	Gaseous stream ingoing FGD

IGCC	Integrated Gasification Combined Cycle
IPPC	Integrated Pollution Prevention and Control
IED	Industrial Emissions Directive
ISO	International Organization for Standardization
KEMA	Keuring van Elektrotechnische Materialen
kg	Kilogram
LCP	Large Combustion Plants
L/G	Liquid-to-gas ratio
LLNL	Lawrence Livermore National Laboratory
L/S	Liquid-to-solid ratio
MATS	Mercury and Air Toxics Standards
mg	milligram
MEL	Magnesium Enhanced Lime
MFC	Mass Flow Controller
MPa	Mega Pascal
Mtoe	Million of tones of oil
N	Nitrogen
NETBIOCOF	Network for Biomass Co-firing
Nm^3	Normalise cubic metre
O	Oxygen
OECD	Organization for Economic Co-operation and Development
OUT-FGD	Gaseous stream outgoing FGD
PFBC	Pressurised Fluidised Bed Combustion
PFA	Pulverised Fly Ash
PCC	Pulverised Coal Combustion
PM	Particulate Matter
$PM_{2.5}$	Particulate Matter with diameters lower than 2.5μm
PM_1	Particulate Matter with diameters lower than 1μm
$PM_{0.1}$	Particulate Matter with diameters lower than 0.1μm
PM_{10}	Particulate Matter with diameters lower than 10μm
PMB	Partial Mass Balance
PRTR	Pollutant Release and Transfer Register
PSD	Particle Size Distribution
PW	Process Water
R/P	Reserves-to-production ratio
S	Sulphur
S/Cl	Sulphur-Chlorine ratio
SCR	Selective Catalytic Reduction
SD	Standard Deviation
SDA	Semi Dry Absorption
SI	Saturation Index
SNCR	Selective Non-Catalytic Reduction
Syngas	Synthesis gas
TMB	Total Mass Balance
ToF	Time-Of-Flight
TW	Treated Water
μm	micrometer
μg	microgram
UK	United Kingdom
UNEP	United Nations Environment Programme
wt %	percentage by weight (also %w/w)
XRD	X-ray Powder Diffraction

I. Structure of the thesis

This thesis is structured with an introductory chapter, which also contains a sub-section on gap in knowledge and objectives (Chapter 1), followed by a brief methodology section (Chapter 2) which describes the main characteristics of the power plants under study, together with the main tasks conducted in this thesis. The results are presented in form of five published articles in conjunction with additional unpublished findings (Chapter 3). According to the objectives proposed in this thesis, the following articles are presented:

Objective 1 and 2: *Partitioning of trace inorganic elements in a coal-fired power plant equipped with a wet Flue Gas Desulphurisation system. Fuel 92 (2012), 145-157.*

Patricia Córdoba, Raquel Ochoa-González, Oriol Font, María Izquierdo, Xavier Querol, Carlos Leiva, María Antonia López-Antón, Mercedes Díaz-Somoano, M. Rosa Martínez-Tarazona, Constantino Fernández, Alfredo Tomás.

Objectives 1 and 2: *The retention capacity for trace elements by the flue gas desulphurisation system under operational conditions of a co-combustion power plant. Fuel 102 (2012) 773-78.*

Patricia Córdoba, Oriol Font, María Izquierdo, Xavier Querol, Carlos Leiva, María Antonia López-Antón, Mercedes Díaz-Somoano, Raquel Ochoa-González, M. Rosa Martínez-Tarazona, Pedro Gómez.

Objective 3: *Unusual Speciation and Retention of Hg at a Coal-fired Power plant. Environmental Science and Technology 46, (2012), 7890-7897.*

Patricia Córdoba, M. Maroto-Valer, Carlos Ayora, Ron Perry, Manuela Rallo, Oriol Font, María Izquierdo, Xavier Querol.

Objective 4: *Enrichment of inorganic trace pollutants in re-circulated water streams from a wet limestone flue gas desulphurisation system in two coal power plants. Fuel Processing Technology 92 (2011), 1764-1775.*

Patricia Córdoba, Oriol Font, María Izquierdo, Xavier Querol, Aurelio Tobías, María Antonia López-Antón, Raquel Ochoa-González, Mercedes Díaz-Somoano, M. Rosa Martínez-Tarazona, Carlos Ayora, Carlos Leiva, Constantino Fernández, Antonio Giménez.

Objective 4: *Influence of an aluminium additive in aqueous and solid speciation of elements in flue gas desulphurisation system. Energy 50, (2013), 438-444.*

Patricia Córdoba, Carlos Ayora, Natalia Moreno, Oriol Font, María Izquierdo, Xavier Querol.

A joint discussion of results of the five articles and additional unpublished findings, and a summary of the main conclusions obtained from this work are presented in the two subsequent chapters (Chapter 4 and 5, respectively). Future research and open questions, and references are presented in the final chapters of this thesis (Chapter 6 and 7, respectively). Annexes I and II present a list of participations in scientific meetings and related publications.

Chapter 1

Introduction

1. INTRODUCTION

1.1. COAL

Coal is defined by the American Society for Testing and Materials (ASTM, 1991) as "brown to black combustible sedimentary rock composed principally of consolidated and chemically altered plant". Coal is a heterogeneous and non-uniform material that contains macromolecular organic compounds, inorganic materials, moisture, gases, and oil and tar.

Coal is mainly made of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulphur (S). These elements, with the exception of S, come from the original plant debris accumulated in the peat bog, whereas the origin of S can be marine or continental (leaching of evaporitic rocks or volcanic contribution). Sulphur is found mainly bound to the organic matter and in a lesser extent as sulphide and sulphate species (Stach's et al., 1985).

The formation of coal occurs in three sequential stages *(1)* the formation of peat, mainly by sedimentary deposition of vegetal debris and by biological processes; *(2)* the conversion of peat into coal by geological processes (diagenesis and coalification); and the *(3)* coal ripening by influence of fluids (Stach's et al., 1985).

In 1938, the ASTM established a rank of coal based on their degree of maturation or progressive alteration in natural series from lignite to anthracite according to their fixed carbon content, volatile matter, and calorific value (Table 1.1). In line with the ASTM coal rank, anthracite and bituminous are high-rank coals, whereas sub-bituminous and lignite are low-rank coals.

Table 1.1. Coal classifications (ASTM D388).

Class/Group	Fixed Carbon Dry, Mineral-Matter-Free Basis (%)		Volatile Matter Dry, Mineral-Matter-Free Basis (%)		Gross Calorific Value Limits-Moist^B Mineral-Matter-Free Basis			
					Btu/lb		MJ/Kg^C	
	Equal or		Equal or		Equal or		Equal or	
	Greater Than	Less Than	Greater Than	Less Than	Greater Than	Less Than	Greater Than	Less Than
Anthracitic:								
Meta-anthracite	98	…	…	2	…	…	…	…
Anthracite	92	98	2	8	…	…	…	…
Semi-anthracite	86	92	8	14	…	…	…	…
Bituminous:								
Low volatile	78	86	14	22	…	…	…	…
Medium volatile	69	78	22	31	14,000^B	…	32.6	…
High volatile A	…	69	31	…	13,000^B	14,000	30.2	32.6
High volatile B	…	…	…	…	11,500	13,000	26.7	30.2
High volatile C	…	…	…	…	10,500	11,500	24.4	26.7
Sub-bituminous								
A	…	…	…	…	10,500	11,500	24.4	26.7
B	…	…	…	…	9,500	10,500	22.1	24.4
C	…	…	…	…	8,300	9,500	19.3	22.1
Lignite								
A	…	…	…	…	6,300	8,300	14.7	19.3
B	…	…	…	…	…	6,300	…	14.7

[A] This classification does not apply to certain coals.

[B] Moist refers to coal containing its natural inherent moisture, but not including visible water on the surface of coal.

[C] Mega joules per kilogram.

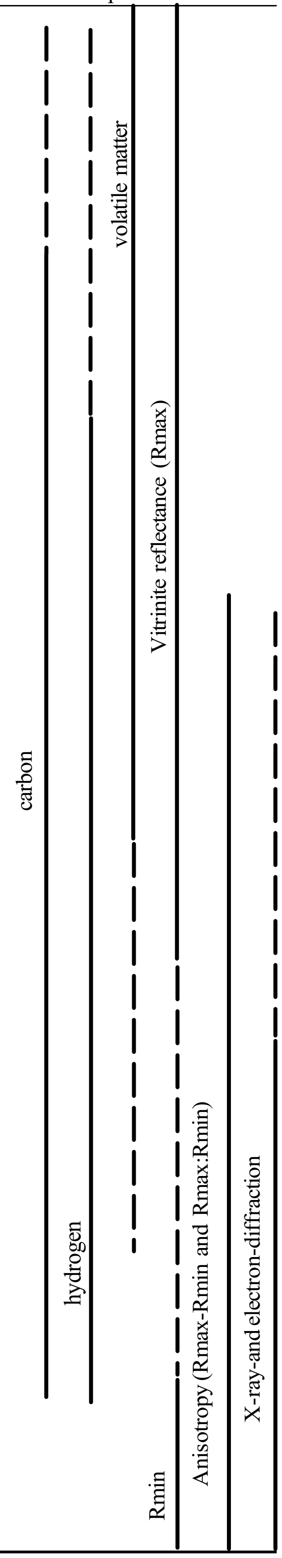
[D] If agglomerating, classify in low volatile group of the bituminous class.

[E] Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of gross calorific value.

Currently, the rank of a coal is determined from the carbon content, volatile mater, fixed carbon, moisture, vitrinite reflectance, and calorific value (Stach's et al., 1985) (Table 1.2). In addition of the above coal rank parameters, other properties such as S content, ash yield, ash melting properties or metal content are determinands for the characterisation of coal quality and utilisation potential.

According to commercial purposes, the most significant parameters of the coal rank are those established by ASTM: fixed carbon content, volatile matter, and calorific value; whereas from a scientific point of view, coal rank properties are defined according to Stach's et al. (1985) classification.

Table 1.2. Classification of high rank coals and anthracites on the basis of different rank parameters (Stach's et al., 1985).

Rank of coal		Reflectance (%)			Ammount in vitrite (daf)			Applicability of various rank parameters
Germany	USA	Rmax	Rm	Rmin	C (%)	H (%)	Volatile matter (%)	
Fettkohle	Medium volatile bituminous Coal	-1.4	-1.3	0.9 -1.4	-87	-5.5	-28	
		-1.6	-1.5				-22	
		-1.8	-1.65		-89		-19	
Esskohle	low volatile bituminous coal	-2.0	-1.85	1.1 – 1.8			-14	
		-2.2	-2.0					
Magerkohle	Semi-anthracite	-2.4	-2.2				-12	
		-2.6	2.35				-10	
					-91	-4	-8	
		-2.8	**-2.5**	1.5 – 2.4				
Anthrazit	Anthracite	-3.0	-2.7	Slow increase of Rmin				
		-3.2	-2.9				-6	
		-3.4	-3.0					
		-3.6	-3.2				-5	
		-3.8	-3.35					
		-4.0	**-3.5**	1.8 – 3.3	- 93.5	-2.5	-4	
		-5.0	-4.35	1.7 – 4.1			-3	
Meta-athrazit		-6.0	-5.1	1.0 – 4.5		-1.5	-2	
	Meta-anthracite			**<2**	- 95.0	-0.8	-1.25	
Semigraphit		-5.10		**0.5**	- 96.5	-0	0	
		->10-18			- 100			
Graphit	Graphite							

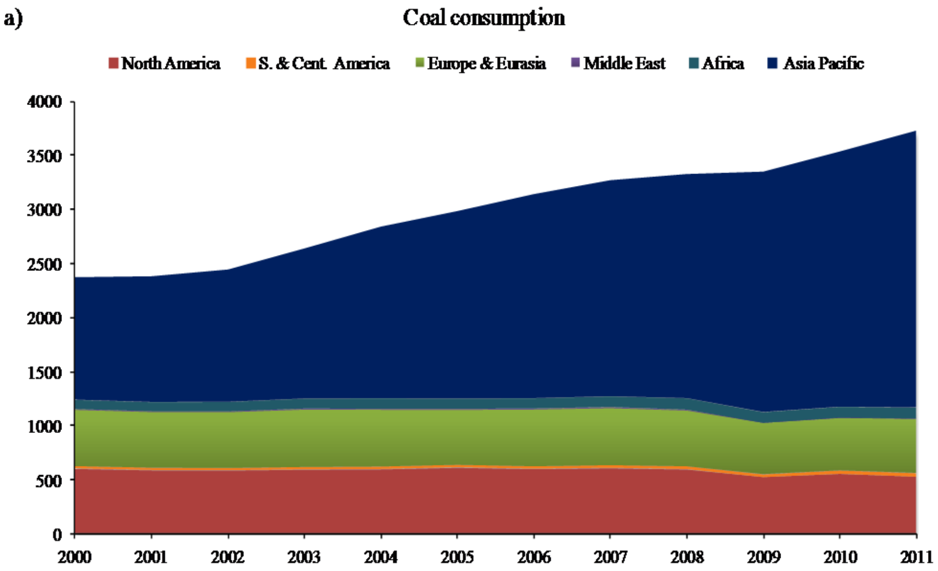
1.1.1. Power generation from coal

Most of the world’s coal production is consumed mainly to generate electricity. In 2011, coal accounted for 30% of global energy consumption, the highest share since 1969 (British Petroleum (BP) Statistical Review of World Energy, 2012).

Coal consumption grew by 5.4% in 2011, the only growth of a fossil fuel above average and the fastest-growing form of energy outside renewable (BP Statistical Review of World Energy, 2012).

Consumption of coal outside the Organization for Economic Co-operation and Development (OECD) countries rose by an above-average 8.4%, led by Chinese consumption growth of 9.7%. OECD consumption declined by 1.1% with losses in the US and Japan offsetting the growth in Europe. The global coal production grew by 6.1% in 2011. Non-OECD countries accounted for virtually all of the growth and China (8.8%) accounting for 69% of global growth (BP Statistical Review of World Energy, 2012, Figure 1.1).

The world proved reserves of coal in 2011 were sufficient to meet 112 years of global production, the largest reserves-to-production (R/P) ratio for any fossil fuel (BP Statistical Review of World Energy, 2012). Europe and Eurasia hold the largest regional reserves and had the highest R/P ratio. The Asia Pacific regions hold the second-largest reserves, while North America had the second-highest R/P ratio (Figure 1.2).



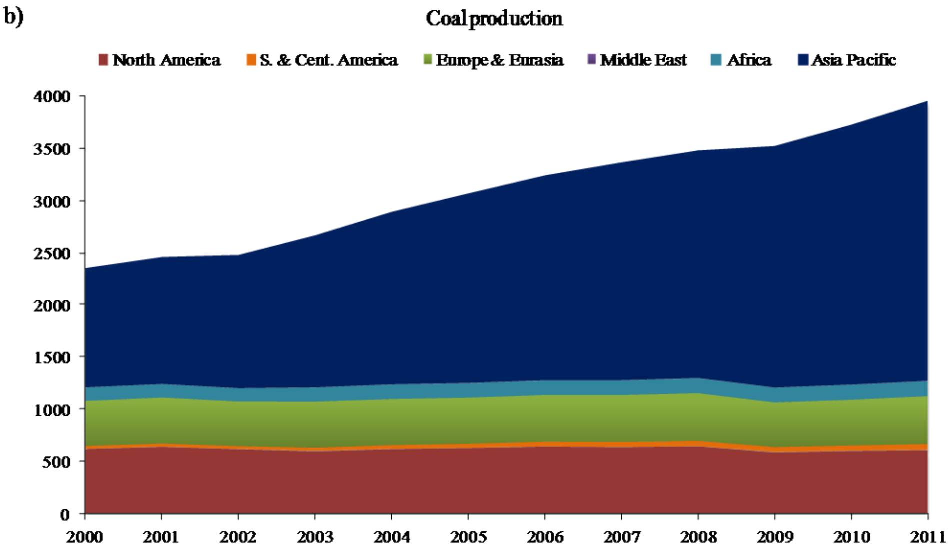


Figure 1.1. Consumptions (a) and production (b) of coal in 2011 (Mtoe), BP Statistical Review World Energy (2012).

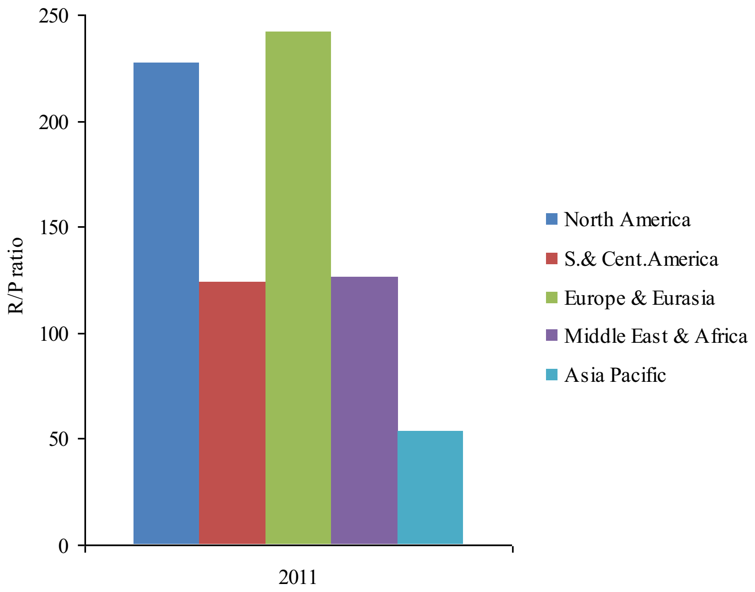


Figure 1.2. World coal reserves-to-production (R/P) ratios in 2011 (coal reserves in million tonnes, BP Statistical Review World Energy, 2012).

1.1.1.1. Coal combustion

Pulverised Coal Combustion (PCC) is the most widely used technology for coal power generation. In this process, coal is milled, pulverized, and injected in the boiler with air to allow combustion *(1)*. Combustion takes place at temperatures from 1300-1700°C, depending largely on coal rank (International Energy Agency (IEA) Clean Coal Centre, 2010). The heat generated is used to produce water vapour to high pressure (25-30 bars) and temperature to power the turbines *(2)* that are connected to a generator which produces the electric energy (Figure 1.3).

Pulverised coal combustion leads to the generation of coal combustion by-products, mostly ashes. The coarser fraction of ashes, bottom ash or slag, is removed from the bottom of the boiler whereas the finest particles, fly ashes are retained from the flue gas stream by the particulate controls *(3)*, usually an Electrostatic Precipitator (ESP) or Fabric Filter (FF). Despite the high efficiency of the ESPs and FFs (>99%, Clarke, 1993; Meij 1994), a small fraction of fly ashes escapes from the controls and reaches the flue gas desulphurisation (FGD) system *(4)* (Figure 1.3). An overview of FGD technologies, as well as a detailed description of by-products of coal combustion, is presented in 1.1.1 and 1.2, respectively.

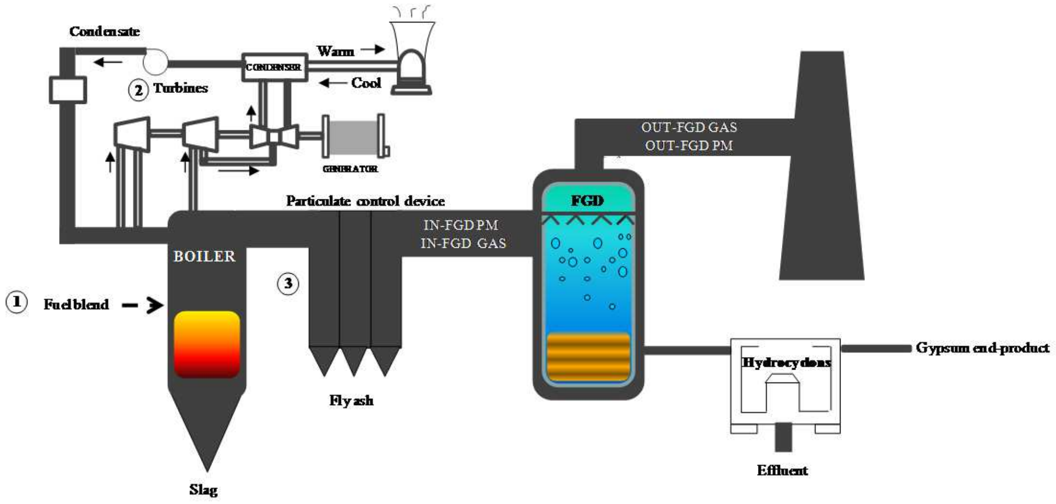


Figure 1.3. Diagram of a coal-fired power plant equipped with a flue gas desulphurisation (FGD) system.

The conventional process of coal combustion can be modified to improve the energetic efficiency of the process and reduce the environmental impacts. The Fluidised Bed Combustion (FBC) allows a better use of the fuel and a better transference of the heat for power generation. The basis for a FBC system and the main difference with respect to the conventional PCC is the formation of a bed of an inert material, such as sand or limestone, through which air is blown from below at sufficient velocity to suspend particles. The melting of the bed is not reached by limiting combustion temperature to 850-950ºC.

Due to the lower temperatures and the longer residence time with respect to PCC, the FBC produces less NO_x emissions and reduces the SO_2 emissions when limestone is added to coal or to the fluidised bed (Clarke, 1993). Currently three different types of FBC are available, the Circulating FBC (CFBC), the Bubbling FBC (BFBC), and Pressurized FBC (PFBC, Reference Document (BREF) on Best Available Techniques for Large Combustion Plants, 2006):

- *Circulating Fluidised Bed Combustion (CFBC)*

This technology is characterised by the use of limestone to react SO_2 produced during combustion. The blend of coal and limestone is a fluidised mass in an air stream whose velocity of the fluidisation falls in the range 3-9 m/s (UNEP-DTIE's Energy Branch, 2007). The CFBC increases the potential reaction time and the level of gas mixing, therefore leading to a more efficient combustion and fixation of SO_2. The retention of SO_2 reaches to 98%, and the emissions of NO_x are lower to 120 mg/Nm^3* (BREFs, 2006). The re-circulation of particles of sorbent favours the fixation of SO_2 contributing in addition, to the temperature control.

- *Bubbling Fluidised bed combustion (BFBC)*

In this process the velocity of the fluidisation of air falls in the range 1-3 m/s (UNEP-DTIE's Energy Branch, 2007). The velocity of air, lower than in CFBC process, is sufficient to produce a suspended bed to altitude <1m. The ashes of combustion are extracted from the bottom of the bed, whereas a minimum proportion is extracted by the clean flue gas cyclones. The emissions of NO_x reach 200-300 mg/Nm^3.

- *Pressurised Fluidised bed combustion(PFBC)*

In the PFBC, air is first pressurised using a gas turbine compressor and routed to the boiler, while hot combustion gases return to the turbine. Combustion takes place at 850-900°C and around 1.6 MPa (Rentz et al., 1999). PFBC systems offer the advantage of smaller plant sizes and a thermal efficiency comparable or slightly higher than that of conventional coal-fired plants. Because of the low combustion temperature, the formation of thermal NO_x is almost avoided, and fuel NO_x can be reduced during combustion by the introduction of NH_3 into the freeboard or before the gas turbine. As for FBC, it is possible to differentiate between Bubbling PFBC (BPFBC) and Circulating PFBC (CPFBC) systems.

* Normal cubic meter set at a particular pressure and temperature which differs between industries.

1.1.1.2. Co-combustion

Co-combustion or co-firing is the simultaneous combustion of two or more fuels in the same power plant in order to produce one or more energy carriers (Hanson et al., 2009). The worldwide electricity demand and the environmental regulations have lead to a market increase of the use of the co-combustion matters such as petroleum coke, sewage sludge, and biomass in coal power generation.

- *Petroleum coke*

Petroleum coke is a termination product from petroleum refining process, and it can be used as electrode or fuel (Gross et al., 2003). The high availability, heating value, and low price of petroleum coke make its combustion for power generation increasingly attractive (Anthony, 1995; Anthony et al., 2001; Jia et al., 2002).

In Europe, a number of PCC power plants implemented the addition up to 40% petroleum coke to the feed coal (Izquierdo et al., 2007). However, the petroleum coke combustion may give rise to an increase in SO_2 emissions, which voids its choice as fuel unless a FGD system is available.

-*Sewage sludge*

Sewage sludge, a type of bio-solid, is a by-product of wastewater treatment. The application as a source of nutrients and organic matter for land remediation and as a fertilizer has been the main use of the sewage sludge in many countries of Europe. Another option has been the disposal of sewage sludge in landfills. However, in countries such as in Poland the sludge dumping at landfills will be after 2013 practically eliminated, and therefore the debate on sludge recycling and disposal has recently been the target of growing interest (Advances in sustainable Sewage Sludge Management (ASSM), 2012).

In the context of new energy policies and legislation, the use of sewage sludge for power generation is promoted, not only by environmental considerations (sewage sludge is burned with zero net CO_2 emissions), but also by economic considerations due to the gain of reducing disposal charges (Cenni et al., 1998). The main drawback of the sewage sludge combustion is mostly related to the high N content, which may lead to high NO_x emissions. The level of some toxic heavy metals and chlorine (Cl) in the raw material may also increase the emissions of hazardous pollutants (metals and dioxins). Furthermore, large mineral matter content could cause additional slagging and fouling problems (Cenni et al., 1998).

In 2007, the co-combustion of municipal sewage sludge with coal was carried out in many European power plants, mainly in Germany, but also in Belgium, Holland, and Austria (Stelmach and Wasielewski, 2007).

- *Biomass*

Biomass can be defined as organic matter (vegetal or animal) and the materials from its nature or artificial transformation (European Biomass Industry Association (EUBIA), 2005). Biomasses include waste from agricultural, ranching, and forestal activities as well as the by-products of the wood transformation.

Although biomass co-firing is one of the most effective means of reducing Green House Gas (GHG) emissions in PCC power plants (European Commission (EC), 2005; Network for Biomass Co-firing (NETBIOCOF), 2006; Leckner, 2007), the chemical properties of biomass have implications for combustion quality and/or impacts on equipment when it is fed as co-matter (EUBIA, 2005).

The co-firing of wood pellets in coal-fired plants is a common practice in Northern Europe and countries such as Denmark, United Kingdom (UK), the Netherlands, and Belgium. The EurObserv'ER (2011) consortium's data indicates that primary energy production from solid biomass increased by almost 8% between 2009 and 2010, which equates an additional contribution of 5.9 Million of tonnes of oil (Mtoe). That is the second biggest increase of the decade behind that of 2003 (9.8%), but with much higher production volumes.

The Netherlands is a country leader in co-firing in Europe. The first co-firing trials were executed in 1993 with 5 to 10 wt % demolition wood, sewage sludge, and petroleum coke in a 1 MW coal-fired power plant at KEMA. Positive results (EUBIA, 2005) from these tests in terms of combustion performance, ash quality, and emissions behaviour led to successful introduction of co-firing in all Dutch coal-fired power plants.

According to Eurobserv´ER (2011), Spain ranked 6th in the production of energy from biomass behind Germany, France, Finland, and Poland. However, in production per capita in the European Union (EU), Spain ranked in 2010 on 18th place, with a rate of primary energy production of biomass (toe)/ in habitant (hab) of 0.103 which is below of the energy production of biomass/in hab rate for the whole EU, which reaches 0.158, and far from the energy production of the Finnish biomass/in hab rate that reaches 1.435.

The increase of the use of co-matters in coal combustion may increase the emissions of some gaseous pollutants, such as SO_2 and NO_x, and consequently there is need to determine whether such variations may affect the retention capacity for trace elements by FGD systems and the volatile behaviour of elements other than S.

Studies on the influence of the co-firing on the leaching of trace pollutants (Izquierdo et al., 2008) revealed that the FA produced from sewage sludge combustion was mainly enriched in P, Zn, Cu, Sb, and Pb, whereas that produced from petroleum coke co-combustion was characterised by high concentrations of V, Ni, and Mo. It would be, therefore, important to carry out studies on the effect of co-combustion, not only in the retention capacity for trace elements by ESPs and FGD systems, but also on the leaching properties of coal-combustion by-products.

1.1.1.3. Oxy-combustion

This technology is based on the coal burn in an O_2-rich atmosphere. Initially, the O_2 is separated from N_2 in a separation unit of air where O_2 of high purity is obtained. The O_2 is transported to the boiler to burn coal or natural gas. The H_2O produced is removed and a proportion of the flue gas (highly enriched in CO_2) is continuously re-circulated into the burner. The remaining proportion of the flue gas is transported to the depuration unit of gases, in which a gaseous stream highly enriched in CO_2 is obtained for its subsequent compression, transport, and geological storage (Global Institute of Carbon Capture (GICC), 2011).

1.1.1.4. Gasification of coal

The gasification of coal is a thermochemical process in which coal is converted into a synthesis gas (syngas) by means of the partial combustion with air or water vapour and low levels of O_2. This process gives rise to a CO-and H_2-rich gaseous stream or syngas that contains the most of the primary energy of coal (EC, 2000).

In addition to CO and H_2, CO_2, CH_4, H_2S, HCl, NH_3, and N_2 are also produced during the gasification of coal. Sulphur present in coal is converted H_2S and in a small fraction to carbonyl sulphide (COS). Due to the reducing atmosphere in the gasifier; the formation of NO_x is avoided during the gasification process. The gasification favours the conversion of N_2 to NH_3 and in a much lower proportion to HCN. In low temperature processes (<650ºC), tar, oil, and phenols are not decomposed, and therefore, they are transported into the gaseous stream. According to the gasifying agent, these components can be used as fuel, in some cases and as a chemical feedstock in other (Prieto, 2006). Different technologies of coal gasification are currently available (Prieto, 2006):

- *Fixed Bed Gasifier*

In this technology a gaseous agent is flowing from the bottom and the fuel is fed the top of the reactor and falls downwards by gravity. Coal moves in counter current to the gas flow, and undergoes the following processes: drying, pyrolyisis, combustion, and gasification (the combustion only in the lower area of the bed where the reactant agents are injected). The gasification of coal takes place under 10-100 bar and at 400-1100ºC.

- *Fluidised Bed Gasifier*

Gaseous agents are blown through a flow of solid particles at sufficient velocity to keep these in a state of suspension. Coal is introduced from the bottom of the gasifier and blended with the bed of particles, reaching the gasification temperature of the bed at 10-25 bar and at 800-1050ºC.

- *Entrained Bed Gasifier.*

Coal and gasifier agents flow in the same direction with velocities higher than the rest of gasifier. The feed of coal is carried out through partial dry (with N_2) or wet (mixture with water) oxidation burner. The temperature of operation is around 1200-1600ºC and 25-40 bar.

- *Integrated Gasification in Combined Cycle (IGCC)*

Integrated Gasification Combined Cycle (IGCC) is characterised by the use of the CO- and H_2-rich gaseous stream resulting from the gasification, usually of coal and/or petroleum coke, in a gaseous turbine and the use of the leftover heat in a vapour turbine (Figure 1.4).

The IGCC entails an initial fractionation of air *(1)* in the Air Separation Unit (ASU). In this unit an O_2 and N_2-rich gaseous stream is generated for the gasification of coal and for increasing the efficiency of the gaseous unit, respectively. In the gasifier, *(2)* coal reacts with the O_2 and H_2O stream to generate a syngas at high temperature (~1500ºC, 25 bar, Prieto, 2006). The syngas stream passes to the FGD system *(3)* in which SO_2 and other gaseous pollutants are removed from the gaseous stream. The cleaned gas, which is commonly composed of approximately 50-60% CO, 20-25% H_2, 5-10% N_2, 5% H_2O, and 5% CO_2 (Triviño, 2003), is then burned in a combined cycle power generation unit *(4)*. In this unit, the gaseous stream is expanded in a gaseous turbine, whereas the leftover heat is expanded in the vapour turbine both connected to generators of electric energy *(5)*. The water vapour condensates as a consequence of the heat exchange with water from the refrigeration tower *(6)*.

The formation of NO_x in the combustion chamber of the gas turbine is suppressed by saturation of the fuel gas with steam prior to combustion and by dilution with N_2 from the air separation unit.

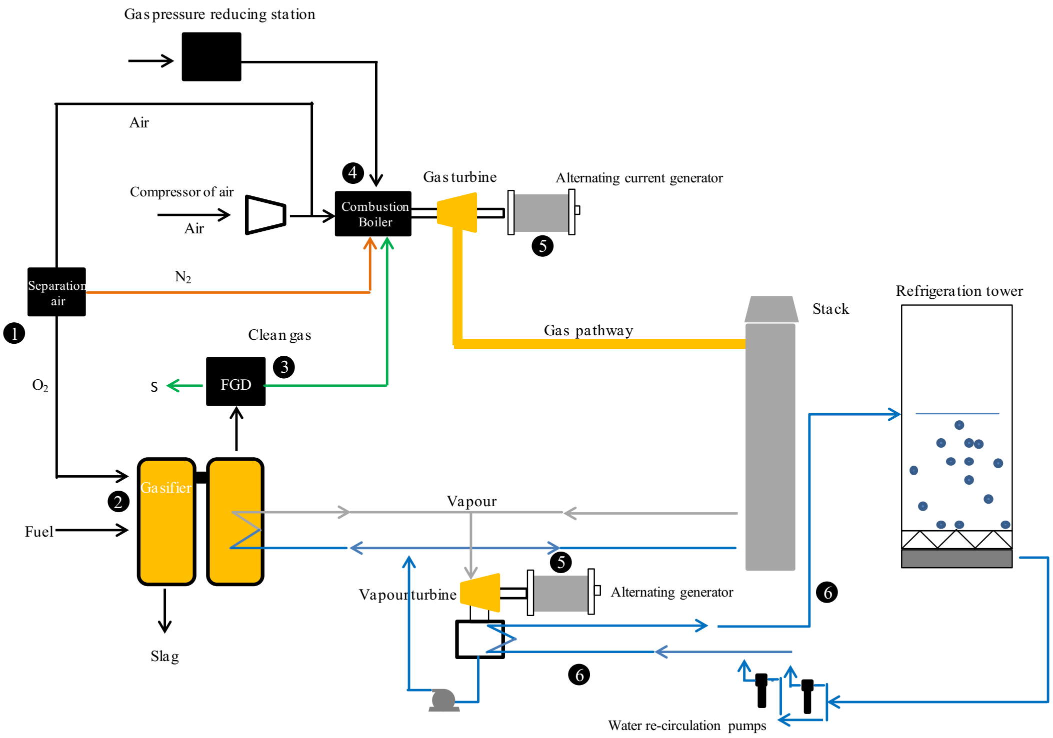


Figure 1.4. Diagram of a coal- fired power plant with Integration Gasification in Combined Cycle (IGCC).

The IGCC power plant of ELCOGAS S.A, located in Puertollano (Ciudad Real), is the only IGCC power plant in Spain, and the second in Europe, and was built as a result of an European Community project under the THERMIE Targeted Project to demonstrate the feasibility of the European IGCC technology (Font et al., 2005). The innovate features designed into the Puertollano IGCC were focused on *(1)* improved the efficiency (45%) under the International Standardization Organization (ISO) conditions (1700ºC, 25 bar) and *(2)* reduced emissions (Font et al., 2005).

1.1.2. Coal combustion products (CCPs)

According to the European Coal Combustion Products Association (ECOBA, 2012), Coal Combustion Products (CCPs) include fly ash (FA), bottom ash (BA), boiler slag (BS) and FBC ash as combustion products, as well as the products from dry or wet FGD, especially Semi Dry Absorption (SDA) product and FGD-gypsum. In this thesis, the products from dry and wet FGD are described subsequent to the FGD systems overview for a better understanding of the FGD-gypsum generation.

Fly ash is a fine powder, which is mainly composed of spherical glassy particles. Fly ash is also known as Pulverised Fly Ash (PFA), a term for FAs in UK derived from firing boilers with pulverised coal and restricted to the fine FAs collected in the ESP (ECOBA, 2012). Fly ashes are made up of spherical high Si-Al-Ca-K-Fe-Ti-Mg vitreous particles with Fe-oxides and Al-Si species, and irregular unburned coal and ash particles. It is generally accepted that vitreous FA particles consist of a relatively pure Al-Si-Ca-K-Fe glass within on which mullite ($3Al_2O_3.2SiO_2$) crystals form a network (Rask, 1985). Coal aluminous-silicate impurities, mainly clays, with much lower proportion of feldspars, melt during combustion and rapidly shape themselves into spherical droplets (Nugteren, 2010). Usually, Fe-oxides are segregated from the melt and give crystalline species such as hematite (Fe_2O_3) and magnetite (Fe_2O_4), within the glass particles. Furthermore, other type of particles such as calcite ($CaCO_3$), lime (CaO), quartz (SiO_2, relict from coal impurities), and gypsum ($CaSO_4.2H_2O$) are formed.

Depending on the type of boiler and coal, siliceous and calcareous FA with pozzolanic and/or latent hydraulic properties can be produced (ECOBA, 2012).

The chemical composition of FAs may differ depending on the technology of combustion but especially on the characteristics of the feed coal. Studies carried out on modelling of gasification flue gas and FA composition (Yang et al., 2001; Díaz-Somoano, 2001; Reed et al., 2001; Argent and Thompson, 2002) and characterisation of industrial scale IGCC by-products (Font et al., 2005), indicate a peculiar mode of occurrence of metals in gasification FA. As aforementioned, while coal combustion FA is constituted by an aluminous-silicate glass, with Ca, Fe, Na, K, Ti, and Mn impurities, and variable amounts of quartz, mullite, lime, hematite, magnetite, gypsum and feldspars, IGCC FA is characterised by a predominant Al-Si glass matrix and variety of fine crystalline reduced species (mostly metal sulphides) as a consequence of the low pO_2 at which fuel is burned (Font et al., 2005).

The coarse fraction of ashes locates in the boiler as BA and/or BS. Bottom ash is a granular material removed from the bottom of dry boilers, which is much coarser than FA. Slag is vitreous grained material deriving from coal combustion followed by wet ash removal of wet bottom furnaces. Bottom ashes are produced at temperatures far below the melting point of the ash, whereas BS is produced at temperatures above the melting point of the ash to ensure liquid ash with sufficient fluidity to flow down the protected walls (BREF, 2006). The melt is quenched in a water filled collector where the contact between water and liquid ash produces the fracturation and crystallisation, and the subsequent formation of BS pellets.

During PCC the rate of production of FA/BS is 80:20 whereas in FBC and IGCC the proportion of productions of FA/BS is 15-35:80-95 and 10-15:85-90, respectively (Font, 2007).

In the EU15 (European Union countries signed a treaty to end internal border checkpoints and controls) approximately 52 million tonnes of by-product of coal combustion were produced in 2009 (ECOBA, 2012). The utilisation for FA in the construction industry accounted for 48% followed by BA with 45% whereas the utilisation rate for BS was 100%. These by-products have been used for many years in the building and construction industry but also they can be used as mineral fillers and as fertilizers. Fly ash is the most important CCP and accounts for nearly 70 wt% of the total produced amount in Europe. According to ECOBA (2012), in 2009 approximately 36 wt% of the total FA produced in Europe was used as addition for the production of concrete (Figure 1.5).

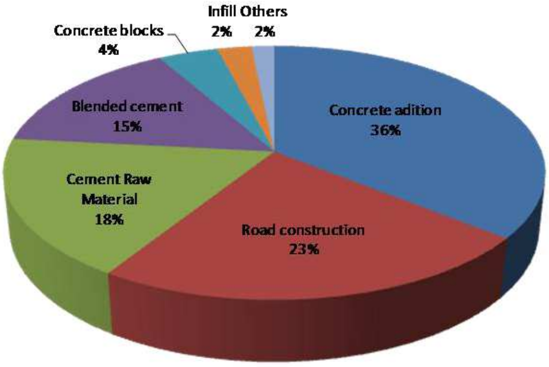


Figure 1.5. Utilization of FA in the construction industry and in underground mining in 2009 (ECOBA, 2012).

1.1.2.1. Behaviour of trace elements during coal combustion

Trace elements are introduced in PCC from coal or co-combustion material. The correlation between the organic content or the different mineral phases in coal with the content of major, minor, and trace elements for different density fractions allows the establishment of trace elements affinities in coal as follows (Querol et al., 1996): *(1)* elements with inorganic affinity: clays and feldspars (Al, K, Mg, Na, P, Ti, Li, Cr, Ni, Cu, Ga, Rb, V, Sr, Y, Sn, Cs, Ba, Ta, Pb, Bi, Th, U, Zr, and REEs); sulphide minerals (S, Fe, Ni, Co, Cu, Zn, As, Se, Mo, Cd, Sb, Hg, W, Pb, and Tl); carbonate minerals (C, Ca, Mn, and Co); sulphate species (S, Ca, Fe, Ba); heavy minerals (B, Ti, Th, and Zr); several mineral phases (Co and W in carbonates and sulphides, and Ni, Cu, and Pb in clays and sulphides); and *(2)* elements with total or partial organic affinity (C, N, S, Be, B, Ge, V, and W).

Studies on the fate of trace elements during combustion have shown that their volatility depends on their affinities and on the physical changes and chemical reactions of these elements with S or other volatile elements during combustion (Dale et al., 1993; Shirpt and Zekel, 1993; Swaine, 1990). The combustion of coal in PCC results in redistribution of elements into approximately 25% BA or BS, and 75% FA and less 0.5% fine particles emitted from the stack (Goodarzi, 2006).

Trace elements have been classified (Smith, 1987; Germani and Zoller, 1988; Meij, 1989; Clarke, 1991) into three broad groups according to their partitioning and behaviour during combustion (Clarke and Sloss, 1992; Meij, 1994).

Group 1 elements are concentrated in the coarse residues (BA or BS), or are partitioned equally between coarse residues and particulates (FA) which are generally trapped by particulate control systems. Elements such as Ba, Ce, Cs, Mg, Mn, and Th are included in this group.

Group 2 correspond to elements that are enriched on the fine-grained particles which may escape particulate control systems. Elements such as As, Cd, Cu, Pb, Sb, Se and Zn are included in this group.

Group 3 is composed by the most volatile elements. Elements such as Hg, B, and halogens are entirely or partly emitted into the air in the vapour phase and are depleted in all solid phases.

Compared to the FA, the BA or BS has low concentration of volatile elements, especially As, Hg, and Se, and halogens (Goodarzi, 2002). In contrast, FA captures most of Group 2 elements (Hower et al., 1993; 1994; 1996; Querol et al., 1999).

Given that the chemical composition and the leaching properties of FA are mainly governed by the PCC and emission control technologies and feed fuel features, the use of secondary fuels entails uncertainty about changes in the behaviour of trace elements during combustion process (Díaz-Somoano, 2006).

1.1.3. Coal-fired emissions and abatement technologies: SO_2, PM, NOx, and CO_2

Coal fired power plants are one of the most significant sources of air pollutants (SO_x, NO_x, Particulate Matter (PM), and trace pollutants). Emissions from large industrial facilities are currently regulated by the EC directives, such as the Integrated Pollution Prevention and Control (IPPC, 1996/61/EC) later replaced by 2008/1/EC, and Large Combustion Plants Directives (LCP, 2001/80/EC), which implement Emission Limit Values (ELVs) for SO_x, $NO_{x,}$ and PM (among other pollutants) from large combustion plants (>50MW). On the other hand, in June 2008, the Directive 2008/50/EC on Ambient Air Quality and Cleaner air for Europe was adopted and published. This directive sets up ambient air concentrations for the above pollutants.

On July 7 in 2010, the European Parliament approved more stringent regulatory standards for NO_x, SO_2 and PM emissions from existing coal-fired power plants with the implementation of Industrial Emissions Directive (IED) (2010/75/EC). The IED that entered into force on 6 January 2011 and has to be transposed into national legislation by Member States by 7 January 2013, is the successor of the IPPC Directive and is based on minimising pollution from various industrial sources throughout the European Union. The IED focuses on several principles, namely *(1)* an integrated approach, *(2)* Best Available Techniques (BAT), *(3)* flexibility, *(4)* inspections, and *(5)* public participation.

The IED´s ELVs must be based on BAT. To assist the licensing authorities and companies to determine BAT, the Commission organised an exchange of information between experts from the EU Member States, industry and environmental organisations. This resulted in the adoption and publication by the Commission of the BAT conclusions and documents (BREFs, 2006).

The concept of BAT as above mentioned, was introduced as a key principle in the IPPC Directive 61/1996/EC (Directive 2008/1/EC codified version). According to IED 2010/75/EC, to obtain a business license, coal-fired power plants must introduce "best practicable technology" to reduce environmental impacts. However, EU Member States may use the “national transition program”. According to this, coal-fired power plants must implement this directive by July 2020; and the old emission controls for acidic pollutants, it must be closed before the end of 2023.

The ELVs of SO_2 (Table 1.3), PM (Table 1.4), and NO_x (Table 1.5), established by the IED according to BAT are defined in accordance of the power generation capacity of the units.

Table 1.3. Emission Limit Values (ELVs) BAT for SO_2 emissions from coal and lignite combustion plants.

Capacity (MW)	SO_2 ELVs (mg/Nm^3)			
	Existing plants		New plants	
	PCC	CFBC/PFBC	PCC	CFBC/PFBC
50-100	200-400 (1)	150-400(3)	200-400 (2)	150-400 (4)
100-300	100-250(5)	100-250(6)	100-200	100-200
>300	20-200(7)	100-200(8)	20-150 (9)	100-200

As shown in Table 1.3, SO_2 ELVs should be as follows: upper level 300 mg/Nm^3 for (1-4); upper level 600 mg/Nm^3 for (5); upper level of 300 mg/Nm^3 for (6); upper level 400 mg/Nm^3 for (7); upper level 200 mg/Nm^3 for (8-9). These variable ELVs were proposed by the industrial sector because it was claimed that for the implementation of the SO_2 ELVs it is necessary to take into account the following issues: *(1)* the fuel characteristics; *(2)* the inlet SO_2

concentration in flue-gas, which affects the BAT achievable levels considering the agreed wet scrubber SO_2 removal efficiencies of 85-98%; and *(3)* the high energy consumption of such a wet scrubber system in relation with the net unit efficiency requirements. One Member State claimed mainly the same upper levels of the ranges except for: (1) which should be 2000 mg/Nm^3 and for (5) which should be 1200 mg/Nm^3. Their rationale was, that for certain existing lignite-fired power plants burning fuel with a high S content the raw flue-gas SO_2 concentrations may reach of 15000-20000 mg/Nm^3 (dry and 6% O_2 conditions), and therefore only sophisticated and large wet FGD systems with SO_2 removal efficiency of 98%, can reach SO_2 emission levels of 300-400 mg/Nm^3 at 6 % O_2. Member States proposed that the upper level ELVs for BAT at >300 MW power plants should be upper level 600 mg/Nm^3.

Despite the aforementioned discussion, SO_2 ELVs for BAT were accepted by the Industry as shown in Table 1.3.

Table 1.4. Emission Limit Values (ELVs) BAT for dust emissions from coal-and lignite-fired power plants.

Capacity (MW)	PM ELVs (mg/Nm^3)					
	Coal and lignite		Biomass-Peat		Liquid fuels for boilers	
	New plants	Existing plants	New plants	Existing plants	New plants	Existing plants
50-100	5-20*	5-30*	5-20	5-30	5-20*	5-30*
100-300	5-20*	5-25*	5-20	5-20	5-20*	5-25*
>300	5-10*	5-20*	5-20	5-20	10-50*	20-50*

* Industry declared alternative value for dust emissions

Table 1.5. Emission Limit Values (ELVs) BAT for NO_x emissions from coal-and lignite-fired power plants.

Capacity (MW)	NO_x ELVs (mg/Nm^3)					
	PCC		Lignite		Coal and lignite	
	New plants	Existing plants	New plants	Existing plants	New plants	Existing plants
50-100	90-300*	90-300*	200-450	200-450*	200-300*	200-300*
100-300	90*-200	90-200*	100-200	100-200*	100-200*	100-200*
>300	90-150	90-200	50-200*	50-200	50-150	50-200

* Industry declared alternative value for NO_X emissions

1.1.3.1. Abatement of SO_2 emissions

Most widespread strategies for controlling SO_x emissions are based on the *(1)* use of low S fuel; *(2)* reduction or removal of S from the feed fuel; *(3)* use of appropriate combustion technologies; and *(4)* emissions control technologies based on FGD technologies (BREFs, 2006).

Although the use of low S fuel is considered as a BAT measure, low S fuel for plants over 100MW may only be considered as a supplementary measure in combination with other measures. The implantation of FGD systems mainly wet scrubber (reduction rate of SO_2 92-98%), and spray dry scrubber desulphurisation (reduction rate 85-92%), are considered as the first option of the BAT measure (BREFs, 2006). An overview of the emission abatement technologies for SO_2 based on FGD systems is discussed in detail in the 1.2 section of this thesis.

1.1.3.2. Abatement of PM emissions

The ESPs and FF are the common technologies to remove PM from the flue gas and are also considered as BAT. Both ESPs and FF are very efficient, achieving levels of >99.8 %wt of the flue gas input. Only for fine particles with diameters lower than 10µm (PM_{10}) and/or smaller ($PM_{2.5}$, PM_1, $PM_{0.1}$) the efficiency of removal decreases to 95-98 % (BREFs, 2006). The ESP is extensively used in large combustion plants and it is capable of operating over a wide range of temperature, pressure, and dust load conditions. ESPs systems can be classified into cold-side (80-220°C) and hot-side (300-450°C) according to the flue gas temperatures. Fabric filters, which generally operate over the temperature range 120-220°C, have become increasingly important over the last decade (BREFs, 2006).

As aforementioned, most of the trace metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Sb, Tl, V, and Zn) may be released during combustion, emitted with a different form of occurrence (e.g. from sulphide in coal to oxides and chlorides in flue gas), and/or condense onto the surface of smaller particles in flue-gas streams. Therefore, most of trace metals are retained in particulate control devices and only specific high volatile metals may escape from ESP and reach FGD systems in a gaseous mode of occurrence.

FGD chemistry (alkaline sorbent) also allows the capture of many pollutants other than S, such as F, As, B, Cl, Se or Hg (Aunela-Tapola et al, 1998; Heebink and Hassett, 2003; Schroeder and Kairies, 2005; Álvarez-Ayuso et al., 2006; Font et al., 2010) both in a gaseous form and/or as PM. Thus importantly, FGD systems can also be considered as a measure for the PM abatement emissions.

1.1.3.3. Abatement of NO_x emissions

Nitrogen oxides emitted during the combustion of fossil fuels include NO, NO_2, and N_2O. The first two constitute the so called mixture of NO_x. In most large combustion installations a large proportion (>90%) of NO_x is made of NO. The abatement of NO_x is based on the De-nitrification ($DeNO_x$) process that aims at reducing NO_x into N_2 and H_2O. The emission control systems that are in use to carry out the $DeNO_x$ process are: Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR). The efficiency of the SCR system ranges (Thambimuthu, 1993) between 80 and 95%, although their use may give rise to unreacted NH_3 emissions and to high $(NH_4)_2SO_4$ FA, whereas SNCR processes are, in general, capable of 30-50% reduction as an average covering different operational conditions (BREFs, 2006).

1.1.3.4. Abatement of CO_2 emissions

One of the most widely proposed strategies for the abatement of CO_2 emissions is based on the CO_2 capture to obtain a CO_2-rich stream for its subsequent compression, transport, and geological storage. Currently, the capture of CO_2 can be carried out in pre-combustion, post-combustion, and during combustion. The capture of CO_2 in pre-combustion systems is based on the production of a H_2 and CO_2-rich gaseous stream from natural gas or syngas. Hydrogen passes through a purification stage and CO_2 (20-40%) is concentrated in the gaseous stream (Burgos, 2009).

CO_2 capture during combustion can be carried out by *(1)* calcinations-carbonation processes; *(2)* oxy-combustion; and/or *(3)* chemical cycles. These processes may yield flue gases of 75 to 95% CO_2. The post-combustion process is based on the capture of CO_2 from the exhaust gas. Post-combustion CO_2 capture can be carried out by *(1)* chemical absorption; *(2)* physical absorption; *(3)* separation with membranes; and *(4)* cryogenic distillation. Current, post-combustion techniques provide low efficiencies (3-15%) of CO_2 capture (Burgos, 2009).

1.1.4. Emissions of hazardous trace inorganic air pollutants from coal-fired power plants

In addition to the large emissions of SO_2, NO_x, PM, and CO_2, coal-fired power generation is responsible for about 50-60% of world-wide Hg emissions, and 77% of acidic gaseous atmospheric emissions (Environmental Health & Engineering (EH&E), 2011).

On December 16, 2011, the U.S Environmental Protection Agency (EPA) approved emission standards to reduce emissions of toxic air pollutants from power plants, especially for Hg and other minor and trace air toxics (Mercury and Air Toxics Standards, MATS). MATS will reduce emissions of heavy metals, including Hg, As, Cr, and Ni; and acidic gases, including HCl and HF. These toxic air pollutants, also known as Hazardous Air Pollutants or air toxics (HAPs), are known or suspected of causing serious health effects (EH&E, 2011).

In Europe, Hg, HCl, HF, As, Ni, Se, Cr emissions from power plants are not currently regulated. However, the Pollutant Release and Transfer Register (PRTR) of industrial emissions into air, water, and land (2006/166/EC) has established threshold emissions for large combustion plants. These threshold emissions values are used only for information purposes without legal binding.

1.1.4.1. Mercury emissions from coal-fired power plants

Mercury is considered to be a serious toxic heavy metal to both humans and the ecosystem because of its high toxicity to the central nervous system and the tendency to bio-accumulate in human body. Currently, about 66% of total worldwide Hg emissions arise from coal-fired power plants, and future predictions point to an increase in this contribution due to the important role of coal combustion in power generation in developing countries (Pacyna et al., 2010).

Bulk Hg content in most coals reaches <0.1 µg/g (Swaine, 1982). Mercury occurs in coals in mineral sulphide impurities, although other forms of occurrence, such as Hg-Se species, have been described (Swaine, 1982). Although Hg levels are usually low, the high feed coal consumption and high combustion temperature account for the relatively high Hg emissions from coal-fired power generation.

Detailed information on reaction pathways for Hg during coal combustion can be found in the literature (Meij, 1989; 1991; 1994; Gullit et al., 1999; Galbreath and Zygarlicke, 2000; Senior et al., 2000; Gibb et al., 2000; Meij and te Winkel, 2003; 2006). During post-combustion with the decreasing temperature, elemental mercury (Hg^0) may remain as a monatomic species or react to form inorganic mercurous (Hg_2^{2+}) and oxidised (Hg^{2+}) compounds. The main oxidised forms of Hg in coal combustion flue gas are assumed to be Hg^{2+} species because of the instability of Hg_2^{2+} compounds at low concentrations (Galbreath and Zygarlicke, 2000).

Chlorine-containing species play a key role for oxidation of Hg^0 in flue gas. Mercury chlorination, the reaction of $Hg^0{}_{(g)}$ with $HCl_{(g)}$ or $Cl_{2\ (g)}$ to form $HgCl_{2\ (g)}$, is generally considered to be the dominant Hg transformation mechanism in PCC flue gas (Galbreath and Zygarlicke, 2000).

Reactive chemical species and oxidation catalysis on FA particles have also been proposed as oxidation mechanism of $Hg^0{}_{(g)}$ to $Hg^{2+}{}_{(g)} + X$. Gulli et al (1999) indicated that calcium compounds can promote the adsorption of Hg_2Cl_2 on FA particles. Indeed, previous works (Meij, 1990) indicated that in the vapour phase Hg levels are low due to the formation and subsequent adsorption of $HgCl_2$.

Abatement of Hg emissions from coal-fired power plants is currently achieved via PM, SO_2 and NO_x emission controls. Gaseous compounds of Hg^{2+} are generally water-soluble and can dissolve in the aqueous phase of the absorbent slurry of wet FGD systems. However, gaseous Hg^0 is insoluble in water and therefore does not dissolve. It is speculated that some of the absorbed Hg ($HgCl_2$) can be converted back to Hg^0 and re-emitted, S (IV) being the main precursor of Hg^0 re-emission (Wo et al., 2009; Stergarsek et al., 2010; Omine et al., 2012).

In view of this, it is evident that HCl, among other flue gases species, plays a significant role in the behaviour, partitioning, and fate of Hg in coal-fired power plants, especially in the FGD systems. Therefore, the improvement of knowledge of Hg chemical transformations in FGD systems, including complex aqueous interactions with HCl and S, is imperative for understanding the transport and fate of Hg in FGD equipped coal-fired power plants.

1.2. FLUE GAS DESULPHURISATION (FGD) SYSTEMS

The term flue gas desulphurisation (FGD) system has traditionally referred to wet scrubbers that remove SO_2 emissions from large electric utility boilers. The FGD systems emerged in the industrial field of the coal-fired power plants and on some industrial processes in the early 1970s in US and Japan, and expanded rapidly in the 1980s (Soud, 2000) in Europe.

In the FGD process, the flue gas interacts with an absorbent medium in either an absorber or a scrubber vessel to produce high solid S slurry.

US EPA (US EPA, 2000) classifies FGD systems as non-regenerable and regenerable processes based on whether the S compounds are separated from the absorbent as a by-product, or discarded along with the absorbent as a waste product; whereas the Clarke and Sloss (1992) classifies the FGD systems as regenerable and non-regenerable, and subdivides the non-regenerable category into wet scrubber and spray dry systems. Other authors (Soud, 2000; Helle et al., 2004) propose the following four categories for the FGD systems: wet scrubbers, spray dry scrubbers, sorbent injection, and regenerable processes; and each major category is divided into several subcategories depending on the specific chemical reactions and flow conditions. Independently of the classification, most of specialised literature (Clarke, 1992; Meij, 1994; Aunela-Tapola et al., 1998; Soud, 2000; Heebink and Hassett, 2003; Schroeder and Kairies, 2005) agrees on the fact that the wet limestone FGD system is the FGD process most widely used because of its high desulphurisation performance and low operating cost.

1.2.1. Wet FGD systems

The wet scrubbers produce a wet product that might be regenerable or non-regenerable. In the regenerable processes (Clark and Sloss, 1992) the sorbent reagent follows a regeneration step which gives rise to SO_2, H_2SO_4, or S^0, and produces a sludge that may be sold to partially offset the cost of operating the FGD system; whereas in the non-regenerable processes S permanently bounds with the sorbent to form a new product that must be disposed of properly or used in specific applications.

Commercial power generation wet FGD system uses limestone ($CaCO_3$), slaked lime ($Ca(OH)_2$), or a mixture of slaked lime and alkaline FA sorbents, which react with SO_2 to form a Ca-S compound (US EPA, 1978).

1.2.1.1. Wet limestone FGD system

The wet limestone FGD process (non-regenerable) is based on complex acid-base reactions that take place under forced or natural oxidation conditions. According to the reactions of the desulphurisation process, two regions can be differentiated in most of the scrubbers: the gas-to-liquid contact zone and the reaction tank. In forced oxidation the following reactions (BREFs, 2006) occur in the gas-to-liquid contact zone with a pH range from 5 to 6:

$SO_{2\,(g)} \leftrightarrow SO_{2\,(aq)}$ (R1) Gaseous SO_2 dissolution

$SO_{2\,(aq)} + H_2O \leftrightarrow H_2SO_{3\,(aq)}$ (R2) Hydrolysis of SO_2

$H_2SO_{3\,(aq)} \leftrightarrow H^+_{(aq)} + HSO_3^- \leftrightarrow H^+_{(aq)} + SO_3^{2-}{}_{(aq)}$ (R3) Sulphurous acid dissociation

$CaCO_{3\,(s)} + H^+_{(aq)} \leftrightarrow Ca^{2+}_{(aq)} + HCO_3^-{}_{(aq)}$ (R4) Limestone dissolution

$HCO_3^-{}_{(aq)} + H^+_{(aq)} \leftrightarrow CO_{2\,(aq)} + H_2O_{(aq)}$ (R5) Acid-base neutralisation

$CO_{2\,(aq)} \leftrightarrow CO_{2\,(g)}$ (R6) Equilibrium: desorption

The following overall reaction in the gas-to-liquid contact zone is obtained by combining the equations expressed above:

$$CaCO_{3\,(s)} + SO_{2\,(g)} + 2H_2O_{(aq)} \rightarrow CaSO_3.2H_2O_{(aq)} + CO_{2\,(g)} \qquad (R7)$$

Reactions initiated in the gas-to-liquid contact zone are completed in the reaction tank. The reaction tank provides an adequate residence time for the complete oxidation of the SO_3^{2-} to SO_4^{2-} according to:

$$CaSO_3.2H_2O_{(aq)} + ½O_{2\,(g)} \rightarrow CaSO_4.2H_2O_{(s)} \qquad (R8)$$

At a lower pH range (4.5 to 5.5, BREFs, 2006) the chemical reaction is different. As shown below, after SO_2 absorption (R1), the primary product of the neutralisation by limestone is $Ca(HSO_3)_2$:

$$CaCO_{3\,(s)} + SO_{2\,(g)} + H_2O \leftrightarrow Ca(HSO_3)_{2\,(aq)} + CO_{2\,(aq)} + H_2O \qquad (R9)$$

$$Ca(HSO_3)_{2\,(aq)} + O_{2\,(g)} + 2H_2O \rightarrow CaSO_4.2H_2O_{(s)} + H_2SO_{4\,(aq)} \qquad (R10)$$

Also in the reaction tank, the partly spent slurry is mixed with fresh limestone slurry to replace the consumed $CaCO_3$. The acidic slurry is neutralised in the reaction tank. As shown below, CO_2 is produced which is later desorbed (BREFs, 2006):

$CaCO_{3\,(s)} + H_2SO_{4\,(aq)} + H_2O \rightarrow CaSO_4.2H_2O_{\,(s)} + CO_{2\,(g)}$ (R11)

Depending on the SO_2 concentrations and the excess air in the flue gas, as well as on the pH of limestone slurry, some systems may be operated in the natural oxidation mode. However, for most applications it is beneficial to control oxidation (US EPA, 2000). In natural oxidation mode, the main product is a mixture 50-60% of $CaSO_3.½\ H_2O$ and $CaSO_4.2H_2O$ in a sludge form which is difficult to dewater, whereas in forced oxidation mode, the final end-product is 90% $CaSO_4.2H_2O$ (BREFs, 2006).

According to the chemistry of the wet limestone desulphurisation process, in wet limestone FGD system with forced oxidation (Figure 1.6), limestone slurry is prepared in a closed ball mill *(1)* and pumped to the scrubber in controlled regime to maintain the pH of the scrubber. In the gas-to-liquid contact zone *(2)*, suspended slurry drops containing sprayed limestone react, depending on pH conditions, with HSO_3^- or SO_3^{2-} resulting from the aqueous dissolution and hydrolysis of SO_2. The slurry drops fall down into the reaction tank after reacting with the flue gas. The oxygen injected *(3)* in the reaction tank by bottom sprinklers reacts with any $Ca(HSO_3)_2$ or $CaSO_3.2H_2O$ yielding a fully oxidised $CaSO_4.2H_2O$ product. The slurry agitators around the reaction tank are used to disperse the solid particles in the gypsum slurry. The generated gypsum slurry may contain 15% wt of suspended solid material. In the filtration process *(4)*, gypsum slurry flows by means of hydro-cyclones to a vacuum filter in which solids are washed with fresh water and concentrate to form the FGD gypsum by-product *(5)*. The FGD-gypsum end-product usually contains 10% of moisture by weight, and is then transported and deposited in landfills (Babcock & Wilcox Power Generation Group (B&W), 1991) or used in different applications. In power plants where water resources are scarce filtered water is re-circulated to the scrubber *(6)*. Power plants with available water resources are usually designed with effluent treatment plants resulting in sludge with a high pollutant load. The PM and gaseous stream outgoing FGD (OUT-FGD) system are emitted through the stack once water droplets are removed from the gaseous stream via mist eliminators.

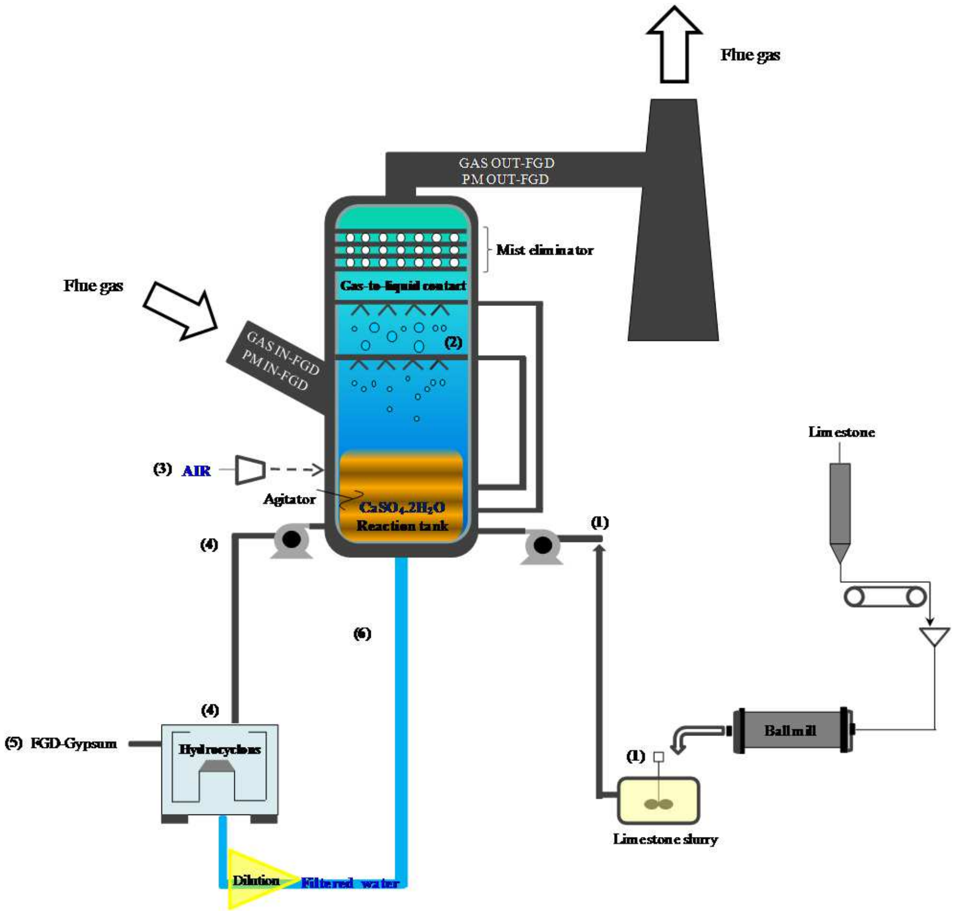


Figure 1.6. Wet limestone FGD systems.

1.1.2.2. Wet lime and magnesium-lime FGD systems

Lime scrubbing uses CaO, usually 90%, to remove SO_2 from the gaseous stream. This slurry is more reactive than limestone slurry, but it is more expensive (Polster et al., 1994). The Magnesium Enhanced Lime (MEL) process (Polster et al., 1994) is a variation of the lime process using a special type of lime, magnesium-enhanced lime (~5-8% magnesium oxide, MgO) or dolomitic lime (~20% MgO).

According to the greater solubility of magnesium salts compared to the calcium sorbents (Polster et al., 1994), the absorber slurry is significantly more alkaline in the first case. Therefore, the MEL based process may achieve high SO_2 removal efficiencies in a significantly smaller scrubber than the limestone scrubbers (Lani and Babu, 1997).

Furthermore, FGD MEL end-products have poorer dewatering characteristics than FGD gypsum from wet limestone FGD (Benson et al., 1997).

The commercial grade of gypsum produced from MEL is brighter than gypsum produced by a conventional wet limestone FGD system with forced oxidation. Brighter gypsum has a potential higher commercial value because it can be used to produce higher value products such as mineral fillers and industrial plasters (Beeglhy et al., 1999).

1.1.2.3. Seawater FGD system

The seawater FGD system utilises the natural alkalinity of seawater to neutralise SO_2. The chemistry of the process is similar to that of wet limestone FGD chemistry with the exception that the limestone is completely dissolved with the seawater and that the chemistry does not involve any dissolution or precipitation of solids (BREFs, 2006).

Due to the presence of HCO_3^- and CO_3^{2-} in seawater, the SO_2 of the flue-gas is absorbed. The acidified absorber effluent is mixed with additional seawater to ensure that the pH is at optimal level for the oxidation process. The introduced air forces the oxidation of HSO_3^- and removes dissolved CO_2. The water is nearly saturated with oxygen and the pH value is restored to neutral before the seawater is discharged back to the sea (BREFs, 2006). In this technique sulphate is completely dissolved in seawater, therefore there is no waste product to dispose of.

1.1.2.4. Dual-Alkali FGD systems

The dual or double-alkali scrubbing is a third non-regenerable FGD process that uses sodium based alkali solution to remove SO_2 from the gaseous stream (US EPA, 1978). In this process SO_2 reacts with the alkaline solution: NaOH, Na_2CO_3, and Na_2SO_3 to primarily form Na_2SO_3 and $NaHSO_3$. The sodium alkali solution absorbs SO_2, and the spent absorbing slurry is regenerated with CaO or $CaCO_3$. It is for this reason that this desulphurisation process is so-called dual or double-alkali scrubbing. Calcium sulphite or sulphate is precipitated and discarded as sludge; whereas the regenerated sodium solution is returned to the absorber. The dual-alkali systems have the advantage of reaching SO_2 retention efficiencies up to 98% (US EPA, 1978).

1.1.2.5. Ammonia FGD system

In the ammonia FGD system, SO_2 is absorbed by aqueous NH_3, resulting in $(NH_4)SO_4$ with a high potential application as a fertilizer by-product (Kamall, 2000). However, the high cost and the marked excess of this fertilizer from other sources in industrialised countries constitute limitations for the use of this process.

1.2.2. Dry and/or semi-dry FGD systems

In this technology SO_2-containing flue gas reacts with an alkaline sorbent typically $Ca(OH)_2$ or CaO (BREFs, 2006). As a result, dry waste is produced, which is generally easier to dispose of than waste produced from wet FGD processes.

1.2.2.1. Spray dry FGD systems

Spray dry absorption is the second most popular FGD system worldwide and mostly used for relatively small to medium capacity boilers using low to medium S (1.5% wt) coal (Zheng et al., 2002). In the dry FGD systems, SO_2 reacts with CaO or $Ca(OH)_2$ sorbent, which is mixed with an excess of water or is slaked to produce lime slurry. Lime slurry is atomized to a cloud of fine droplets in the spray dry absorber where SO_2 is also removed from the flue-gas. Given that water is evaporated by the heat of the flue-gas; waste water treatment is not required in this process. Subsequently, the sorbent is entrained in the flue gas and carried downstream toward a particulate collection device. The resulting by-product is a dry mixture of $CaSO_3.½H_2O$, $CaSO_4.2H_2O$, $CaCl_2$, unreacted lime, and FA depending on the efficiency of the particulate control device.

Although the spray dry scrubber process is sometimes called a semi-dry process because it uses lime slurry, the residue is a dry powder and is collected by ESP or FF. The residue is subsequently recycled and mixed with fresh CaO slurry to enhance CaO utilisation.

The dry spray technique has relatively low costs and energy consumption, approximately 30-50% less than the wet limestone process. However, operational costs are higher due to higher sorbent costs (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, CIEMAT, 2000).

1.2.2.2. Furnace sorbent injection

Furnace sorbent injection involves the direct injection of a dry sorbent into the gaseous stream from the boiler (CIEMAT, 2000). Typical sorbents include $CaCO_3$ and $CaCO_3 \cdot MgCO_3$. In the furnace, the calcination of the sorbent produces reactive CaO particles. The surface of these particles reacts with the SO_2 in the flue gas to form $CaSO_3$ and $CaSO_4$. These reaction products are then captured along with the FA by the particulate control device, typically an ESP or FF. The dry solid residue does not require a further treatment before being discharged to a landfill or being used as a construction material.

1.2.2.3. Duct sorbent injection

Duct sorbent injection is a dry FGD system based on the injection of $Ca(OH)_2$ or $NaHSO_3$ into the flue-gas between the air's pre-heater and ESP or FF. However, water may be injected into the flue gas upstream of the sorbent to enhance the SO_2-sorbent reaction (CIEMAT, 2000). A proportion of the resulting residues, FAs, reaction products, and any unreacted sorbent collected in the particulate control device are re-circulated into the duct to increase sorbent utilization, while the remaining proportion is disposed. Approximately 50-60% SO_2 capture may be expected with the duct sorbent injection using $Ca(OH)_2$, and up to 80% SO_2 capture could be achieved with $NaHSO_3$ sorbent (Babu et al., 1986).

Reported costs of the duct sorbent injection process vary depending on the S content of the fuel and on the plant size (BREFs, 2006).

1.2.2.4. Circulating Fluid Bed (CFB) dry scrubber

The CFB process is a type of dry scrubber in which $Ca(OH)_2$ is injected directly into the CFB reactor. The bed provides a long contact time between the sorbent and flue gas since that sorbent passes through the bed several times. Entrained reaction products are carried by flue gas to a particulate control device (BREFs, 2006).

1.3. OPERATIONAL CONDITIONS OF WET LIMESTONE FGD SYSTEMS

The two most significant factors in wet limestone FGD systems, for economic reasons, are the desulphurisation efficiency (SO_2 retention) and the residual limestone level of the FGD-gypsum (Frandsen et al., 2001). Although the most relevant parameters affecting the design and operation of a FGD scrubber are the liquid-to-gas (L/G) ratio, the reaction tank pH, the absorber gas velocity, the reagent utilisation, and the oxidation fraction (Guitierrez Ortiz, 2010), other chemistry factors of wet limestone FGD systems such as the reactivity of limestone, SO_2 concentration in flue gas, temperature of the scrubber, HCl, HF, and use of additives; and operational conditions of FGD system efficiency, such as the particulate control device efficiencies, residence time in FGD systems, water treatment or recycling, and oxidation process, may also affect the desulphurisation efficiency and the residual limestone level of the FGD-gypsum.

With reference to the above controls, overviews of parameters that may affect on the desulphurisation efficiency and on the residual limestone level of the FGD-gypsum are described within this section.

1.3.1. Reactivity of limestone

Some properties of limestone such as particle size, particle size distribution (PSD), porosity, surface area, and the impurities of limestone may play a significant role in the efficiency of desulphurisation process. These parameters can be considered as key factors of the reactivity of the limestone. The reactivity of limestone is defined as a capacity for providing alkalinity and reacting with the acid resulting from the dissolution of SO_2 into water (Brown et al., 2010).

In the conventional wet limestone-gypsum FGD process, limestone is usually used after being pulverised to an average size of 5-20µm, which consumes a great deal of energy (Kikkawa et al., 2002). When the proportion of limestone is increased to improve the SO_2 removal efficiency, the quality of the FGD-gypsum may decrease to valueless level owing to the residual limestone amounts. Therefore, it is highly recommended that the concentration of limestone in FGD-gypsum to be at a level under a predetermined value (3-4 wt %) to be saleable (Kiil et al., 2002; Gutierrez Ortiz, 2006).

Other factors such as the pH of the scrubber, chloride concentration, efficiency of particulate control devices, and CO_2 stripping may also affect the reactivity of limestone (Walsh, 2006).

1.3.2. SO_2

Depending on the concentration of S in coal and on the operational conditions of the power plant, the content of SO_2 in the gaseous steam that reaches the FGD system may vary greatly (Dou et al., 2009).

In wet FGD processes, SO_2 diffuses through the gaseous phase to the aqueous surface, where it dissolves and is transferred by diffusion or convective mixing into the aqueous phase. The rate at which SO_2 is transferred depends on factors such as the solubility of SO_2 and its displacement from equilibrium (Dou et al., 2009). The SO_2 equilibrium can be expressed as follows (Babcock & Wilcox Power Generation Group, 1991):

$$y^* = \frac{C' \cdot 10^3 \cdot [H^+]}{k_1 \, (k_2 + [H^+])} \qquad \text{(Eq2)}$$

where k_1 (mol/l atm) is the equilibrium constant of $SO_{2\,(g)} \leftrightarrow SO_{2\,(aq)}$; k_2 (mol/l atm) is the equilibrium constant of $CaCO_{3\,(s)} + H^+ \leftrightarrow Ca^{2+}_{(aq)} + HCO^-_{3\,(aq)}$; C´(mmol/l) is the total dissolved concentration of SO_2; $[H^+]$ is the concentration of protons at equilibrium; and y* is the vapour pressure of SO_2 (ppm).

Under acidic conditions (4.0 > pH), the equilibrium pressure of SO_2 increases and as a consequence the absorption into limestone is diminished. However, the pSO_2 can be restored and the absorption rate of SO_2 maximised by the use of buffer additives (Babcock & Wilcox Power Generation Group, 1991).

1.3.3. pH and temperature

The concentration of H^+ has a strong impact on the dissolution rate of limestone and on the SO_2 removal efficiency. FGD systems are designed to operate at optimal pH in the range of 5.0-6.0. At lower pH values, limestone dissolution rate is considerably higher but both SO_2 dissolution into the slurry and its removal efficiency are lower (Walsh, 2006). High pH values result in higher efficiencies of SO_2 removal. There are, however, limitations such as; reaching high pH values requires addition of excess limestone. The excess of limestone as well as raising the pH tend to increase the scrubber scale. Moreover, in the gas-to-liquid contact zone, $CaSO_3$ remains in dissolution only when the concentration of H^+ exceeds its equilibrium value (Babcock & Wilcox Power Generation Group, 1991). The equilibrium pH of $CaSO_3$ is 6.3 with a partial CO_2 pressure of 0.12 atm. Therefore, the dissolution state of $CaSO_3$ is possible for pH values <6.3; pH values >6.3 may give rise to the scrubber scale problems by precipitation of $CaSO_3$ (Babcock & Wilcox Power Generation Group, 1991).

However, it is important to note that with a pH range from 4.5 to 5.5 the primary product of the neutralisation by limestone is $Ca(HSO_3)_2$, which is considerably more soluble than $CaSO_3$ and more easily oxidized to SO_4^{2-} than SO_3^{2-} (Takesita and Soud, 1993). Therefore, in theory, operating with a lower pH range has less risk of scaling and plugging of the scrubber, but the desulphurisation efficiency decreases. This also means that the pH value in the scrubber is dependent of the desulphurisation stage. Therefore, in the gas-to-liquid contact zone the range of pH should be established from 5.0-6.0 to maintain *(1)* an optimal dissolution rate of limestone; *(2)* a proper dissolution rate of SO_2 into limestone slurry; and *(3)* $CaSO_3$ in dissolution thus avoiding incrustation problems in the sprayers.

In view of the evident role of the pH values on the desulphurisation efficiency, the study of the effect of the pH on the partitioning and on the speciation of trace elements, both in the aqueous phase of the gas-to-liquid contact zone and in the reaction tank, as well as on the stability of aqueous complexes and distribution of solid species in the by-products of FGD systems is also significant.

With respect to the effect of the temperature on desulphurisation efficiency (scrubber and flue gas), a lower desulphurisation efficiency is expected due to the lower solubility of SO_2 in limestone slurry at high temperatures (Kiil et al., 1998). Indeed, experimental studies (Zheng et al., 2003) confirm a decrease of the SO_2 desulphurisation efficiency when increasing the temperature of the scrubber. However, the diffusion rates of H^+ towards the limestone particles are enhanced at high temperature. Similarly, CO_2 stripping from the aqueous phase of limestone slurry and the rate of the chemical reactions involved in the desulphurisation process are increased at high temperature (Walsh, 2006).

1.3.4. Hydrochloric acid

Coal combustion gives rise to a gaseous stream enriched not only in SO_2, but also in a number of other gaseous species. Coal chlorine is released primarily as HCl in the high temperature zone of a boiler (Shao et al., 1994). As the combustion gases cool (430-475ºC), a proportion of HCl can be partially oxidised to Cl_2 by the Deacon Process (1875) reaction in the presence of O_2 and H_2O:

$$2HCl_{(g)} + \frac{1}{2}O_{2\,(g)} \leftrightarrow Cl_{2\,(g)} + H_2O_{(g)} \qquad \text{(R13)}$$

However, the presence of SO_2 can inhibit the formation of Cl_2 through the following gas-phase reaction (Griffin, 1986):

$Cl_{2\,(g)} + SO_{2\,(g)} + H_2O_{(g)} \leftrightarrow 2HCl_{(g)} + SO_{3\,(g)}$ (R14)

The predominance of the reactions 13 and 14 will, therefore, it is dependent on the relative ratios of the S and Cl species. If the S/Cl ratio is high, R14 will predominate over reaction R13 in the gaseous phase.

Most studies focussing on the role of HCl in FGD systems deal with the influence of HCl on desulphurisation efficiency. Some authors (Yoo and Kim, 1998; Frandsen et al., 2001) found that Cl^- enhances the SO_2 removal efficiency by an increase of the gas-liquid surface area due to foaming caused by the increase of the limestone slurry level in the reactor when Cl is added. By contrast, Kiil et al (2002) reports that the HCl contributes to *(1)* a pH drop in the absorber, which decreases the SO_2 removal efficiency; and *(2)* increase the residual limestone level in the FGD-gypsum. It is known that the absorption of HCl can also cause problems on the performance of the power plant due to the extreme corrosive behaviour of HCl (Kiil et al, 2002).

According to the above discussion, it is evident that HCl plays a significant role in the desulphurisation process. However, considering (1) the role of HCl in chemical reactions; (2) the presence of Cl-gaseous species in scrubber; and (3) that most of HCl present in flue gas stream IN-FGD is retained in FGD by-products (filtered water and FGD-gypsum); studies on gas-aqueous and aqueous-solid phase interactions between HCl and trace elements are required. The formation of the aqueous Cl-complexes and Cl-solid species in FGD systems is not yet clarified in sufficient detail. The influence of S/Cl ratios in the gaseous stream IN-FGD and in the formation and speciation of aqueous complexes and solid species in FGD systems are also relevant topics to deal with.

1.3.5. Hydrofluoric acid

The concentration of HF in the flue gas IN-FGD is relatively high but lower in comparison with HCl (Davison, 1996; Kiil et al., 2002). The dissolution of HF in the aqueous phase also leads to the decrease of the pH value, reducing thus the SO_2 removal efficiency. Furthermore, HF contained in the flue gas may be dissolved in the aqueous phase of the sprayed droplets of limestone slurry giving rise to the formation of CaF_2. However, in the presence of aluminium compounds, HF may also react with limestone to form Al-F compounds, typically represented by $CaAlF_3(OH)_2$-CaF_2 (Kikawa, 2002; Álvarez-Ayuso et al., 2006). These compounds can coat the surfaces of the limestone particles and consequently cause a decrease the reactivity of limestone (Mori et al, 1981; Maroney et al, 1986; Farmer et al, 1989; Ukawa et al, 1992).

Earlier studies (Font et al., 2008) reported that the speciation of F also 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. In order to avoid this, the use of additives has been proposed as measure for the optimisation of the SO_2 removal efficiency and for reducing the precipitation of F solid species, respectively (Álvarez-Ayuso et al., 2006).

Conversely, it has been speculated that HF and Al may also interact to form highly soluble Al-F_x complexes (Font et al., 2008). *In view of this, it would be necessary to investigate the mechanism and the formation rate of Al-F_x complexes both in the aqueous phase of the liquid-to-gas contact zone and in that of the reaction tank in wet limestone FGD systems.*

1.3.6. Use of additives

As stated above, the use of additives has been proposed as measure for the optimisation of wet FGD efficiencies. Sulphur dioxide removal efficiency of wet FGD systems using limestone can be improved by the addition of various organic acids. A number of studies (Rochelle and King, 1977; Rochelle et al., 1982; Chang and Mobley, 1983; Chi and Lester, 1989) have shown that organic acids with buffering capacity provide an optimal tool for enhancing of the desulphurisation efficiency. When SO_2 dissociates in the liquid between gas and liquid phase, H^+ is produced. Organic acids promote transport of H^+ between gas-aqueous and aqueous-solid phase. The transport of H^+ from the aqueous film to the bulk aqueous phase promotes the dissociation of SO_2, increasing the overall removal rate (Frandsen et al., 2001). However, if the pH value is excessively low, buffer additives may act as scavenging systems for H^+.

Additives such as MgO and Na_2CO_3 can also be used to improve the desulphurisation efficiency. The role of these compounds is based on the capacity of providing alkalinity. The concentration of alkaline compounds dissolved in the aqueous phase of limestone slurry (CO_3^{2-}, HCO_3^-, SO_3^{2-}, and OH^-) is defined as dissolved alkalinity (Babcock & Wilcox Power Generation Group, 1991).

A number of additives may also be used to optimise the SO_2 removal efficiency by reducing the formation of F^- bearing solid species, both on the limestone and on the FGD-gypsum surface. *However, there is a need to investigate if the use of additives may also induce changes on the speciation and partitioning of inorganic trace pollutants, and variations of chemical properties e.g. pH and solubility of metal complexes in the aqueous phase of gypsum slurry. Currently, the implications of the use additives in the leaching of F in FGD-gypsum are the subject of detailed investigation (Álvarez-Ayuso et al.,2006; 2007; 2008), but its influence on the speciation and partitioning of inorganic trace pollutants present in the aqueous phase of gypsum slurry has not been completely clarified.*

1.3.7. Efficiency of the particulate control devices.

Despite the high efficiency of ESPs a small fraction of FA escapes and goes into the FGD system. Given that some metals can condense on the FA surface, these may react with species dissolved in the aqueous phase of gypsum slurry to form aqueous complexes and solid species, and/or act as catalytic of oxidation-reduction reactions of gaseous pollutants. This could modify the behaviour and partitioning of trace elements in streams involved in the FGD process. *It is* *for this reason that studies on the efficiency of particulate control devices may also be relevant in desulphurisation processes.*

1.3.8. Liquid to gas ratio and residence time in FGD systems

The mol ratio of L/G has been found to be one of the most important criterions for reporting the reactor performance from an economic point of view (Hrastel et al, 2007). In FGD systems, L/G values tends to the minimum values (1.1~2.0) to reduce the cost. However, experimental results (Gerbec et al., 1995; Warych and Szymanowski, 2001; Kong, 2001; Zhong et al., 2008; Dou et al., 2009; Gao et al., 2011) found an increase of the SO_2 efficiency with increasing the L/G ratio. An increase of the L/G rate creates a larger mass transfer area, whereas a decrease may create better conditions for gas/liquid mass transfer at the interface because of increased turbulence and better gas distribution, which thereby increase the mass transfer driving force (US EPA, 1978). However, decreasing L/G may decrease the SO_2 removal efficiencies because of the shorter residence time in the scrubber. Indeed, studies have recently shown that the SO_2 removal efficiencies greatly improved by decreasing the gaseous flow rates or increasing the liquid flow rates (Dou et al., 2009).

Providing an adequate residence time of the flue gas into the scrubber to make ensure maximal SO_2 absorption by the alkali slurry is one of the major objective of the FGD optimising tasks (BREFs, 2006).

1.3.9. Oxidation

FGD systems may operate under natural or forced oxidation conditions. In forced oxidation mode, air is injected in the reaction tank by bottom sprinklers to react with any $Ca(HSO_3)_2$ or $CaSO_3$ to ensure fully oxidised gypsum product. In the oxidation process, the pH value also plays a significant role. HSO_3^- is more easily oxidised to SO_4^{2-} than SO_3^{2-} (Takesita and Soud, 1993). Thus, low pH values are also advantageous for the gypsum production. In natural oxidation mode, $CaSO_3$ is partly oxidised by the oxygen contained in the flue-gas. The main product is a mixture 50-60% of $CaSO_3.½ H_2O$ and $CaSO_4.2H_2O$ in a sludge form. Forced oxidation gives rise to 90% $CaSO_4.2H_2O$ (BREFs, 2006).

Forced oxidation systems dewatering is relatively easy because the gypsum crystals are large (0-100µm) in comparison with the crystal size reached by natural oxidation (1-5µm). Additionally, aeration functions can eliminate CO_2 from the water, thereby increasing pH during the neutralisation reaction (BREFs, 2006).

There is a current trend to convert natural oxidation systems to forced oxidation ones because the gypsum end-product is of a better quality (even for landfills) than the sulphite-sulphate sludge from natural oxidation (BREFs, 2006).

1.4. FGD BY-PRODUCTS

The FGD process at coal-fired power plants entails the production of solid and aqueous by-products, FGD-gypsum and filtered water (effluent) from gypsum slurry filtration, respectively. Depending on the characteristics and properties of the by-products and the availability and resources of the power plant, the fate of FGD-gypsum and filtered water can be the disposal in landfills and water treatment or recycling, respectively.

1.4.1. Filtered water: water treatment or recycling

Filtered water is the effluent produced as a result of the gypsum slurry filtration. The fate of this water stream depends on the availability of water near the power plant. As stated before, power plants with available water resources are usually designed with effluent treatment plants producing sludge with a high pollutant load. Where water resources are scarce, the re-circulation of the water to the scrubber from gypsum slurry filtration is preferred owing to the economic and environmental benefits of recycling.

A typical water treatment is based on increasing the pH in order to precipitate metals by formation of metal hydroxides. The use of additives to promote coagulation-flocculation processes are also common measures to deal with the water treatments. As a result of coagulation-flocculation processes, the sludge produced is first sedimented, drained, and disposed of or recycled to the flocculation stage where the sludge particles serve as initial crystallization nuclei promoting more rapid flocculation (BREFs, 2006).

During water re-circulation an enrichment of specific elements trapped in solution by the aqueous phase of the slurry may be expected. However, as regards recycling possibilities of water, there is a lack of investigations focusing on the features of these re-circulating waters. It would be important to determine whether continuous water re-circulations to the scrubber may have effect on desulphurisation process in terms of gaseous emissions and/or on operational conditions of FGD systems.

1.4.2. FGD-gypsum

FGD-gypsum is a synthetic solid by-product obtained by the absorption of SO_2 in the absorbent slurry (Eurogypsum, 2012).

According to ECOBA (2012), in 2009 FGD-gypsum (20.5%) was the second largest by-product generated in the EU15 countries (Figure 1.7). FGD-gypsum finds applications in the wallboard manufacture or be used in the cement industry. Nevertheless, a great proportion of the global production is sent to landfills for its disposal (Álvarez-Ayuso et al., 2006). Other uses such as agricultural lime substitute, amendment for improving soil properties, construction material for roads, and waste stabilisation product have been suggested (Solem-Tishmack et al., 1995; Stehouwer et al., 1995; Payette et al., 1997; Chen et al., 2005; Chou et al., 2005).

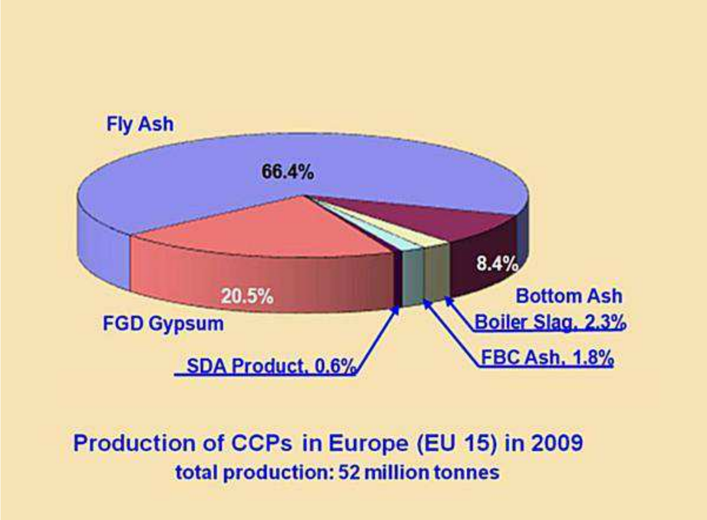


Figure 1.7. Productions of Coal Combustion Products (CCPs) in Europe (EU15) in 2009 (ECOBA, 2012).

The amount of FGD-gypsum produced in Europe (EU15) was approximately 11 million tonnes in 2008. More than 80% of this FGD-gypsum was utilised by the gypsum and cement industry. In total, about 3% of the FGD-gypsum produced was temporarily stockpiled as a raw material base for future utilization, mostly for plasterboard production, and about 7% was disposed of (Eurogypsum, 2012). According to ECOBA (2012), in 2009 the main use of FGD-gypsum was the plaster boards (5.043 kilo tonnes), followed by levelling floor screeds (1363 ktonnes), projection plaster (729 ktonnes), set retarder for cement (660 ktonnes), gypsum blocks (258 ktonnes), and other uses (64 ktonnes).

The properties of FGD-gypsum have to be comparable to that of natural gypsum, since stringent specifications on the properties of the gypsum used for building purposes are required. In order to obtain high-quality FGD-gypsum from flue gas desulphurisation, the FGD process must attain *(1)* a high efficiency of particulate controls; *(2)* causing a low Cl^- and F^- in FGD-gypsum; *(3)* a high efficiency of the forced oxidation process to oxidise the $CaSO_3.2H_2O$ and/or $Ca(HSO_3)_2$ to $CaSO_4.2H_2O$; *(4)* using a high-purity limestone to reduce FGD-gypsum impurities; and *(5)* obtaining a high $CaCO_3$ to $CaSO_4.2H_2O$ conversion efficiency (BREFs, 2006).

The specification and quality standards (Eurogypsum, 2012) for the FGD gypsum product by are shown in Table 1.5.

Table 1.5. Quality standards for FGD-gypsum.

Properties	Requirement
Free moisture	<10 (% by weight)
$CaSO_4.2H_2O$	>95 *(% by weight)
MgO	<0.1(% by weight)
Cl^-	<0.01(% by weight)
Na_2O	<0.06(% by weight)
SO_2	<0.25(% by weight)
pH value	5.0-9.0
Colour	White**
Odour	Neutral
Toxicity	Non-toxic

* The reduction of $CaSO_4.2H_2O$ content by inert constituents is not detrimental to the different areas of applications.
** Different colour values may apply depending on the use of the FGD-gypsum and the final products.

The disposal of FGD by-products in landfills requires the assessment of the long-term environmental impact of the leachates generated. In such cases the leaching of elements of environmental concern are controlled according to the Council Decision 2003/33/EC.

The Council Decision establishes the criteria and procedures for the acceptance of waste at landfills, their application being compulsory (by 16 July 2005) by EU Member States. The procedure to determine the acceptability of waste at landfills consists in a characterisation, compliance testing, and on-site verification. Basic characterisation constitutes a complete characterisation of the waste: type and origin, composition, consistency, leachability, and where necessary and available, other characteristic properties.

In accordance with the Council Decision 2003/33/EC, the EN standards must be used for the determination of the basic waste properties. Thus, the standards EN-12457/1-4 must be employed as leaching tests for granular waste materials and sludge. According to this characterisation, a waste is deemed acceptable for a landfill class.

1.5. THE FATE OF TRACE INORGANIC POLLUTANTS IN FGD SYSTEMS

A number of studies (Querol et al., 1996; Martínez-Tarazona and Spears, 1996; Yan et al., 1999; Vassilev et al., 2001; 2005; Pires and Querol, 2004; Li et al., 2005; among others) have evaluated the partitioning behaviour and fate of trace elements from coal-combustion in power plants under different operational conditions whereas studies on the partitioning, behaviour, and fate of trace elements in coal-fired power plants equipped with FGD system are much more scarce (Meij, 1994; Aunela-Tapola, 1998; Yokoyama et al., 1999; Sandelin and Backman, 2001; Lee et al., 2006). These studies and others (Heebink and Hassett, 2003; Schroeder and Kairies, 2005; Álvarez-Ayuso et al., 2006; Font et al., 2010) have shown that FGD chemistry allows also the capture of many pollutants other than S, such as F, As, B, Cl, Se or Hg both in a gaseous form and/or as PM. One of the most investigated trace elements is Hg.

Coal Hg is converted to gaseous Hg^0 in the combustion flame and is subsequently partially oxidised (35% to 95%) as the combustion gases cool down (Pavlish et al., 2003). Gaseous compounds of Hg^{2+} are generally water-soluble and can absorb in the aqueous phase of the absorbent slurry of wet FGD systems. However, gaseous Hg^0 is insoluble in water and therefore does not absorb. It is speculated that some of Hg^{2+} can be converted back to Hg^0 and re-emitted (Wo et al., 2009; Stergarsek et al., 2010; Omine et al., 2012).

Mercury leaves the power plants mainly in the FA and flue gases; only a minor part is present in the FGD-gypsum, sludge of the waste water treatment plant, and effluent (Meiij, 1994). However, according to other works such as those presented by Álvarez-Ayuso et al (2006) and Cheng et al (2009), the partitioning of Hg OUT-FGD can vary greatly. These authors reported that 60 and 70% of Hg removed by the FGD was found in the FGD-gypsum, respectively, and about 35% and 4%, respectively, was emitted into the atmosphere. This suggests that the partitioning of Hg OUT-FGD could depend on e.g. specific operational conditions of power plants. According to Meij (1991) the temperature of the ESP and the Cl content of the fuel appear to have a profound effect on the speciation of Hg, which in turn greatly affects the emissions. Gullit et al (1999) reported that calcium compounds can promote the adsorption of Hg_2Cl_2 on FA particles, thus increasing the removal in the ESP, and decreasing the incoming proportion of Hg to FGD system.

Regarding the emission abatement capacity for Hg, measurements in US showed that the combination of SCR, ESP, and wet FGD gave rise to Hg removals of 84-89% (Withum et al., 2005). In Japan, 33% Hg removal as reported for ESP and 70% for the combination of ESP and FGD (Yokoyama, 1999). These removals rates for Hg in the US and Japan were similar to the Dutch findings (Meij and te Winkel, 2006), except for the ESP. In this work was also reported that if a high dust SCR for NO_x reduction is present, the total removal of Hg can be up to 90%. As aforementioned in 1.1.4 section, SCR catalysis can act to oxidise a significant proportion of the Hg^0 into Hg^{2+}, thereby enhancing the capture of Hg in downstream wet FGD. Therefore the co-benefit of increased Hg^{2+} through the SCR catalyst is very important to the overall control of Hg emissions from coal-fired power plants (Gretta et al., 2006).

The distribution of moderately and volatile elements such As, Se, F, Cl, and B, has also been studied in FGD systems. Most of specialised literature (Clarke, 1992; Meij, 1994; Aunela-Tapola et al, 1998; Soud, 2000; Heebink and Hassett, 2003; Schroeder and Kairies, 2005) reports that most of trace elements in FGD systems are removed in the aqueous effluent (filtered water) and only a fraction of a few remain in the flue gases (such as B, Hg, and Se). Álvarez-Ayuso (2006) in a study on the abatement capacity of desulphurisation process for trace elements, indicated that Cl (~80%) remained in the effluent arising from the gypsum slurry filtration, whereas S, F, As, and Se were mostly partitioned in the FGD-gypsum with values comprised in the range 90-99%. The abatement for As, Cl, F, S, and Se attained values from 96% to 100%; whereas an abatement capacity about 60% was attained for Hg. This retention efficiency for Hg was consistent with data reported by Meij et al (1992), who found, on average, Hg removal of 54.4±24% when studying the behaviour of Hg in coal-combustion power plants in the Netherlands.

According to these studies, it can be concluded that wet limestone FGD systems reaches high retention efficiencies for trace elements (>90%). However, it is also important to note that the retention efficiency of FGD system for trace elements may be reduced because of the emission of fly dust in evaporate droplets saturated with gypsum (Meij, 1994).

Conversely, it has been reported (Font et al., 2008) that the speciation of 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. In order to avoid this, the use of additives has been proposed as measure for reducing the precipitation of F solid species by stabilising the FGD-gypsum before its disposal to mitigate F leaching (Álvarez-Ayuso et al., 2007; 2008). The proposed stabilisation systems were highly effectives in reducing the precipitation of F.

In view of the above overview on the fate of trace inorganic pollutants in FGD systems, and according to their partitioning and retention efficiencies, it appears that the wet limestone FGD system allows a high retention efficiency of trace elements, especially for moderately and highly volatile elements. However, there is a need to investigate how the retention efficiencies are affected by operational conditions such as pH values, use of additives, water re-circulations to the scrubber, among others.

II. Knowledge gaps and Objectives

Despite the extensive efforts made over the years to evaluate the consequences from coal combustion including the production, utilisation, and disposal of by-products, there are still uncertainties, *many highlighted above in italics*, on factors affecting the desulphurisation efficiency and on the emissions of gaseous trace pollutants and on the behaviour and partitioning of trace elements in PCC and FGD systems. Studies on speciation, partitioning, and fate of major and trace pollutants in the whole PCC-FGD may yield basic data to *(1)* identify environmental problems such as the fate of pollutants during leaching of solid by-products (FA, BS, FGD-gypsum) or the potential enrichment of specific pollutants during water recycling at FGD systems; and *(2)* when possible, modify FGD operational parameters in order to improve, not only the efficiency for SO_2, but also for the emission abatement of hazardous inorganic trace pollutants.

For an optimal operation of the complex PCC-FGD systems, the following issues should be investigated in depth: *(1)* Source of major and trace pollutants (coal, limestone, water, and additives); *(2)* Transformations of major and trace pollutants during PCC and throughout the whole particulate controls and FGD system; *(3)* Partitioning and fate of pollutants during the whole PCC-FGD system; *(4)* Optimal working conditions for attaining the maximal desulphurisation efficiency; *(5)* Key parameters that may be adapted to obtain high S retention and abatement of hazardous trace pollutants by FGD systems; *(6)* Collateral effects of co-combustion on the fate of trace inorganic pollutants in PCC-FGD; and *(7)* Environmental collateral effects arising from the FGD, such as environmental features of generated PCC and FGD by-products or potential enrichment of specific trace pollutants in recycled FGD water streams.

Based on the above key issues, this thesis emerges from the framework of the European Union RFCS-CT-2006-00006: Abatement of Emissions of Trace Pollutants by FGD from co-combustion and environmental characteristics of by-products (ABETRAP), to investigate significant aspects of the knowledge gaps.

The objectives of this thesis are:

1. Evaluation of mass balances and partitioning of a broad array of elements during combustion and around the FGD system for two Spanish power plants.
2. Assessment of the desulphurisation efficiency and the emission abatement capacity for trace inorganic pollutants by the forced-oxidation wet limestone FGD system for the two power plants.
3. Determination of mode of occurrence, behaviour, and fate of Hg and identification of the most significant parameters affecting the fate of Hg at the two coal-fired power plants.
4. Study of the enrichment and chemical speciation of inorganic trace pollutants in re-circulated water streams, and identification of elements of concern as regards leachable potential for subsequent remediation actions at the two power plants.

Chapter 2

Methodology

2. METHODOLOGY

According to the objectives of this thesis, intensive sampling campaigns and characterisation programs were carried out at two Spanish power plants in 2007 and 2008.

Input and output flows were sampled in the coal combustion unit as well as in the FGD system at the two power plants during routine operating conditions. The sampling of solid, water, PM, and gaseous streams was carried out simultaneously with the objective of obtaining accurate and reliable results. For solid and water samples the determination of the content of major, minor, and trace elements, as well as the concentration of Cl^-, F^-, NH_4^+, NO_3^-, SO_4^{2-} and Hg, and the analysis of the mineralogical composition were carried out by different techniques. Leaching tests were also applied for the CCPs.

In upstream (IN-FGD) and downstream (OUT-FGD) gases the concentration of SO_2, B, Se, As, HCl, HF, metals, and the concentration and speciation of gaseous Hg were evaluated simultaneously to the PM measurements in each sampling point.

Based on the results of the analyses of solid, water, gaseous, and PM samples, mass balance calculations and partitioning for trace elements were conducted around PCC, FGD system, and for the whole installation at the two power plants. The assessment of the desulphurisation efficiency and the emission abatement capacity for inorganic trace pollutants at both power plants was also carried out on the basis of these results.

The comparison and evaluation of the results of mass balances allowed quantifying the major and trace elements PCC-FGD partitioning, and the retention efficiency of the FGD systems, as well as the emission abatement capacity for gaseous major and trace pollutants at both power plants. The preliminary results of this thesis yielded unexpected results for the following issues:

1. An unusual and different speciation of Hg in the outgoing gaseous stream FGD between the two power plants.
2. A different retention of gaseous Hg between the two sampling campaigns at the coal-fired power plant under co-combustion conditions.

3. A high concentration of trace pollutants in the re-circulation waters to the scrubber at both power plants.
4. An unusual leaching behaviour of some elements from FGD-gypsum.

With the aim of *(1)* verifying the results obtained in industrial scale; *(2)* ascertain the causes and implications of such results from a scientific and an environmental perspectives; and of *(3)* determining whether the results of the industrial scale sampling campaigns can be reproduced at a laboratory scale, the following laboratory experiments and chemometric tools were proposed:

1. Laboratory experiments were conducted to reproduce the differences on speciation of gaseous Hg OUT-FGD with respect to that detected at industrial scale.
2. Thermodynamic modelling tools were employed to:
   2.1. Study the causes of the different retention and speciation of gaseous Hg OUT-FGD.
   2.2. Study the causes and effects of the high concentration of elements in the waters of re-circulation from both power plants.
3. Speciation experiments for FGD-gypsum samples were conducted to study the Hg speciation and the assignment of different Hg species to specific anions.
4. Potentiometric titration experiments for FGD-gypsum samples were conducted to study the leaching behaviour of some elemental species from FGD-gypsum.

This chapter summarises the most relevant aspects related with the power plants under study, the techniques and experimental methods employed as well as an explanation of the laboratory experiments and chemometric tools proposed. A detail description of the power plants including coal combustion units and FGD systems, as well as the operational and technical conditions during the sampling campaigns is provided in the corresponding published articles of this thesis.

2.1. DESCRIPTION OF THE POWER PLANTS

The study was conducted at two Spanish coal-fired power plants equipped with a wet FGD system with forced oxidation and with water re-circulation to the scrubber. In this thesis the two Spanish power plants are denoted as PP1 and PP2, respectively.

The PP1 power plant has a capacity of 1050MW and is located at Northeast (NE) Spain. In this power plant, the removal of coarse fraction of ashes is based on wet ash removal for wet bottom furnaces whereas the control device for the FA is a cold-side ESP (80-220ºC). This power plant is equipped with 3 power generation units with their corresponding FGD systems. The sampling campaign at PP1 was carried out on 19-20th September 2007. The sampling was performed at 100% MCR (maximum capacity) and 100% desulphurisation in the unit 3. The power plant was fed with 100% coal (60:40 blend of imported bituminous and local high sulphur sub-bituminous coal).

The PP2 power plant has a capacity of 1200MW and is located at Northwest (NW) Spain. In this power plant, the removal of coarse fraction of ashes is based on wet ash removal for wet bottom furnaces whereas the control device for the FA is a cold-side ESP (80-220ºC). This power plant is equipped with 5 power generation units, but only the unit 3 is equipped with FGD system. Two sampling campaigns were carried out at PP2 in two consecutive years in 2007 (14-15th November) and 2008 (26-27th November). The samplings were performed at 100% MCR and 100% desulphurisation of the unit 3. The power plant was fed with 82:18 and 84:16 coal/petroleum coke blends for samplings conducted in 2007 and 2008, respectively. The coal at PP2 is a blend of Spanish anthracitic coals and imported South African bituminous coal. The petroleum coke is a blend of Spanish and imported petroleum-cokes.

Figure 2.1 shows the scheme and sampling points of PP1 and PP2. Detailed descriptions of the FGD system operation from PP1 and PP2, and FGD water streams are reported in chapter 3.

2.2. SAMPLE COLLECTION

The sampling procedure was based on applying the same approach to the two power plants in order to collect samples from all ingoing and outgoing flows to represent the specific burning process at each plant. The sampling points were selected together with the operators and the staff of the power plants to ensure the safety for the sampling personnel and to prevent interruptions in process operations.

Input and output flows were sampled in the coal combustion unit as well as in the FGD systems at both PP1 and PP2 in stable operational conditions with the objective of achieving representative samples during the sampling campaigns. The sampling of solid, water, PM, and gaseous streams was carried out simultaneously in order to obtain accurate and reliable results (Figure 2.1).

2.2.1. Sampling of solid and water streams

Individual Spanish and imported sub-bituminous coals at PP1, and local and imported bituminous coals and petroleum-cokes at PP2, were collected from the feeders. Samples of the feed fuel blends were collected by an automatic sampler in periods of 6 minutes. Fly ashes were sampled from the ESP1 using an automatic sampler. Boiler slag samples were collected from the boiler once discharged into the vessel. Concerning FGD system, samples of limestone and FGD-gypsum were collected in the limestone feeder and in the conveyors after filtering, respectively.

The sampling of water streams in the combustion unit included the process water used for the slag quenching and drainage and the resulting waste water stream, named “slag water”, which were sampled from their respective tanks. Sampled water streams from the FGD system included process water (used for limestone slurry preparation), limestone and gypsum slurries, and filtered water. At PP1 two additional water streams were sampled in the FGD system, namely treated and added water.

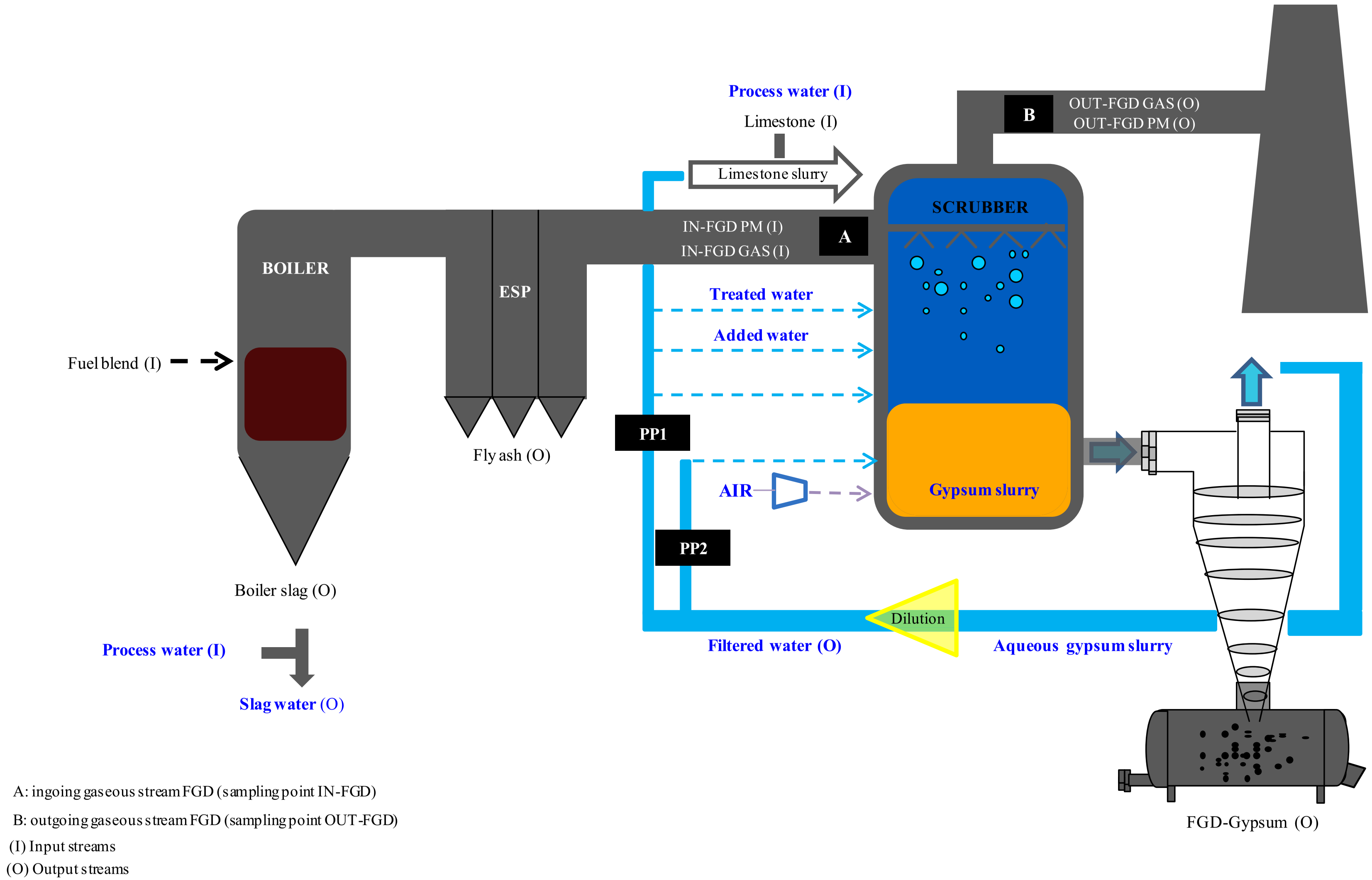


Figure 2.1. Scheme of PP1 and PP2 and sampling points of solid, water, and gaseous streams.

Two samplings per day during two days were performed for solid and water samples, amounting four sample sets at PP1, whereas at PP2, a sampling per day during two days was performed for each sample, collecting two sample sets in 2007 and another two sets in 2008. Table 2.1 and 2.2 summarise the main parameters regarding solid and water stream samplings, respectively. Figure 2.2 and 2.3 show the sampling points of solid and water streams at PP1 and PP2, respectively.

Table 2.1. Main parameters of the sampling of solid streams at PP1 and PP2.

PP1				
	Samplings days	Samplings per day	Amount/sampling	Total amount
SOLID STREAMS				
Raw coals	2	2	20kg	80kg
Feed coal blend	2	2	20 kg	80kg
Boiler slag	2	2	15-20 kg	85-100 kg
Fly ash	2	2	15-20 kg	85-100 kg
Limestone	2	2	15 kg	60 kg
FGD-gypsum	2	2	5kg	20 kg
PP2				
	Samplings days	Samplings per day	Amount/sampling	Total amount
SOLID STREAMS				
Coal	2	1	10 kg	20kg
Petroleum coke	2	1	10 kg	20kg
Feed fuel blend	2	1	10kg	20kg
Boiler slag	2	1	32 kg	64 kg
Fly ash	2	1	5 kg	10 kg
Limestone	2	1	3 kg	6 kg
FGD-gypsum	2	1	3kg	6 kg

Table 2.2. Main parameters of the sampling of water streams at PP1 and PP2.

PP1				
	Samplings days	Samplings per day	Amount/sampling	Total amount
SOLID STREAMS				
Process water	2	2	2L	8L
Slag water	2	2	2L	8L
Treated water	2	2	2L	8L
Added water	2	2	2L	8L
Limestone slurry	2	2	2L	8L
Gypsum slurry	2	2	2L	8L
Filtered water	2	2	2L	8L
PP2				
	Samplings days	Samplings per day	Amount/sampling	Total amount
SOLID STREAMS				
Process water	2	1	3L	6L
Slag water	2	1	3L	6L
Limestone slurry	2	1	3L	6L
Gypsum slurry	2	1	5L	10L
Filtered water	2	1	5L	10L

Figure 2.2. Sampling points of solid and water streams at PP1.

Solid samples once mixed, homogenised, and riffled, were divided into subsamples of 5kg. From each subsample, a solid sample of 1kg was air dried followed by oven drying step at 105ºC, for the analysis of major, minor, and trace elements; whereas a duplicate of each solid sample (1kg) was only air dried for the analysis of Hg. FGD-gypsum samples (1kg) were dried at 45ºC to avoid loss of crystallisation water of gypsum.

Regarding water samples, 500mL of each water stream was *in situ* filtered and kept refrigerated at 4ºC in PVC bottles for the analysis of conductivity, pH, and anions. 100mL sub-samples of each water sample were *in situ* filtered and acidified with 1% HNO_3 ultrapure grade for analysis of major cations and trace elements. Additional 100mL sub-samples of water were refrigerated at 4ºC in a dark glass vessel for the subsequent analysis of Hg. This sample was acidified with 1% HNO_3 ultrapure grade to reach pH <2 and stabilised with $K_2Cr_2O_7$ (80 mg·L^{-1}) according to ISO 5667/3. Samples of water from limestone and gypsum slurries, prior to their storage, were *in situ* decanted and filtered (0.45µm) by means of a vacuum pump for subsequent analyses. The solid fraction from limestone and gypsum slurries followed the same treatment described above for solid samples.

Figure 2.3. Sampling points of solid and water streams at PP2.

2.2.2. Sampling of gaseous stream and particulate matter

Isokinetic samplings of gaseous streams were performed IN-FGD (A) and OUT-FGD (B), simultaneously to the collection of samples from solid and water streams (Figure 2.1). To ensure reliable concentration measurements of gaseous components, a volume ranging from 1.6 to 3.1 m^3 was sampled during around 2.5 h. A total of 73 gaseous and PM samplings were carried out at PP1 during the two consecutive days, whereas at PP2 36 gaseous and PM samplings, during the two consecutive days, were carried out in 2007 and in 2008.

In each set of sampling, the velocity (m/s), temperature (T ºC), humidity (% v), and O_2 (% v dry basis) of the gaseous stream were measured. The isokinetic conditions of gaseous and PM samplings at PP1 and PP2 are shown in Table 2.3 and 2.4., respectively.

Table 2.3. Operational conditions of the Isokinetic measurements in 2007 at PP1.

Point	Sampling day	O_2 (%)	H_2O (%)	Velocity (m/s)	T (ºC)
IN-FGD	19/09/2007	5.8	10.0	17.74	170
	19/09/2007	6.0	10.8	18.75	170
	19/09/2007	5.6	10.0	18.62	180
	19/09/2007	5.6	10.1	18.94	180
	20/09/2007	5.3	10.7	18.78	172
	20/09/2007	5.3	10.0	18.48	170
	20/09/2007	5.5	10.0	18.48	173
	20/09/2007	5.5	10.8	18.81	173
OUT-FGD	19/09/2007	6.7	14.6	22.99	77
	19/09/2007	6.6	14.9	20.66	78
	19/09/2007	6.8	15.3	23.06	78
	19/09/2007	6.8	15.7	20.69	78
	20/09/2007	6.6	14.4	22.98	77
	20/09/2007	6.6	15.4	20.64	77
	20/09/2007	6.6	16.6	23.08	77
	20/09/2007	6.6	15.8	20.66	77

Table 2.4. Operational conditions of the Isokinetic measurements in 2007 and in 2008 at PP2.

Point	Sampling day	O_2 (%)	H_2O (%)	Velocity (m/s)	T (ºC)
IN-FGD	14/11/2007	-	9.8	17.5	110
	14/11/2007	5.9	9.3	15.0	110
	15/11/2007	6.5	10.2	17.5	107
	15/11/2007	6.4	10.5	12.0	107
	26/11/2008	5.9	9.0	15.5	109
	26/11/2008	5.9	9.1	15.3	110
	27/11/2008	6.1	9.5	16.8	110
	27/11/2008	5.9	9.5	17.0	110
OUT-FGD	14/11/2007	6.4	6.0	18.3	49
	14/11/2007	6.2	5.5	18.0	47
	15/11/2007	6.4	5.7	18.6	47
	15/11/2007	6.4	5.5	18.4	48
	26/11/2008	6.4	6.2	18.8	48
	26/11/2008	6.2	6.0	19.0	48
	27/11/2008	6.6	6.0	20.2	48
	27/11/2008	6.4	6.3	20.8	47

At each sampling point, two trains of sampling systems were assembled in parallel for simultaneous sampling with specific trapping solutions, one for the measurement of levels of anions and cations, and the other for the levels and speciation of Hg. The sampling of gaseous streams also included the capture of PM entrained by the gas IN-FGD and OUT-FGD. The sampling procedure of PM is described the subsequent chapter 2.2.2.3.

2.2.2.1. Sampling of Hg in gaseous phase

The measurements of levels and speciation of gaseous Hg was devised according to UNE-EN 13211:2001. This standard system is based on the determination of elemental (Hg^0), oxidised (Hg^{2+}), particle-bound (Hg_p) and total Hg in flue gas generated from coal-fired stationary sources. In such a system, a sample is withdrawn from the flue gas stream isokinetically through probe/filter system, maintained at the flue gas temperature, followed by a series of impingers in an ice bath. The filter within a heated filter chamber collects Hg_p associated with the gas phase while the impingers solutions allow the transfer of Hg gaseous species from the gas to aqueous phase in an ice bath, which promotes the condensation of volatile species.

The Hg sampling system assembled at both power plants consisted in quartz-fibre filter within a heated filter chamber followed by a train of dark glass impingers in an ice bath. A first impinge was filled with 100 mL of HCl to capture Hg^{2+}, the second impinge containing 3 w% H_2O_2 for SO_2 removal (150 mL IN-FGD and 100 mL OUT-FGD), and the two last impingers containing 4 w% $K_2Cr_2O_7$ with 20 w% of HNO_3 for Hg^0 trapping (Figure 2.4).

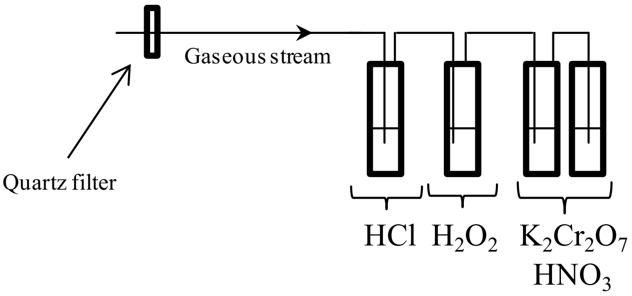


Figure 2.4. Train of sampling for gaseous and particulate Hg.

2.2.2.2. Sampling of phases containing anions and cations of interest

The gas sampling system for measuring levels of anions and cations was devised according to UNE-EN 1911:1998 and UNE-EN 14385:2004. In such a system, two impingers 100mL of de-ionized H_2O (or MilliQ grade water) and two filled with 6 w% HNO_3 and 10 w% H_2O_2 were assembled to determine the concentrations of anions and cations, respectively, in a ice bath (Figure 2.5).

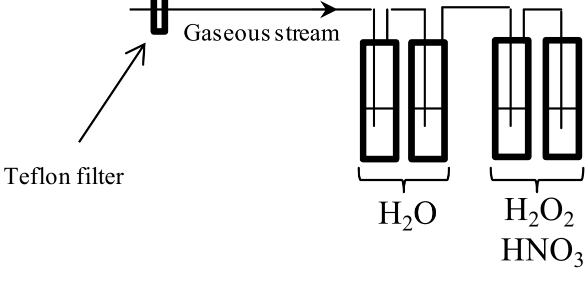


Figure 2.5. Train of sampling for anions and metals.

2.2.2.3. Sampling of PM

The collection of PM was carried out as specified by the Ontario Hydro method, ASTM D6784-02. According to this method, two types of filters were employed for PM collection, performing two sets of sampling in each sampling point. One set of quartz-fibre filters (0.45µm) were performed for further determination of Hg contents and another one for the determination of the rest of pollutants.

Polytetrafluoroethylene (PTFE) filters were used for the PM capture of anions and cations instead of quartz filters, since HF reacts with quartz to form highly volatile $SiF_6^{2-}$with a subsequent loss of fluorine.

2.3. CHEMICAL CHARACTERISATION OF SOLID, WATER, AND GASEOUS STREAMS

Detailed description of the techniques used for the analysis of solid, water, gaseous, and particulate streams is provided in the methodology of the published articles. Tables 2.5, 2.6, and 2.7 summarise the main techniques and instrumentation applied for the characterisation of solid, water, gaseous, and particulate streams, respectively.

Table 2.5. Techniques used for the analysis of solid streams.

	SOLID STREAMS						
	Coal	PC	FFB	Fly ash	Boiler slag	Limestone	FGD-gypsum
MM-Elements	Inductively Coupled-Plasma Atomic Emission Spectrometry (ICP-AES)						
T-Elements	Inductively Coupled-Plasma Mass Spectrometry (ICP-MS)						
Chlorine	ASTM D4208 method (calorimetric bomb) High Performance Ion Chromatography (HPIC)						
Fluorine	Pyro-hydrolitic extraction method ISO 11724 High Performance Ion Chromatography (HPIC)						
Mercury	LECO AMA 254 gold amalgam atomic absorption spectrometer						
Mineralogy	X-ray powder diffraction (XRD), Bruker D5005 diffractometer						

MM-elements: major and minor elements; T-elements: Trace elements; PC: petroleum coke; FFB: feed fuel blend

Table 2.6. Techniques used for the analysis of water streams and trapping solutions from the sampling of gaseous pollutants.

	WATER STREAMS AND TRAPPING SOLUTIONS OF GASES
MM-Elements	Inductively Coupled-Plasma Atomic Emission Spectrometry (ICP-AES)
T-Elements	Inductively Coupled-Plasma Mass Spectrometry (ICP-MS)
Chlorine Nitrate Sulphate	High Performance Ion Chromatography (HPIC)
Ammonium	Ion selective electrode
Fluorine	Ion selective electrode
Mercury	LECO AMA 254 gold amalgam atomic absorption spectrometer

MM-elements: major and minor elements; T-elements: Trace elements
PW: process water; TW: treated water; AW: added water; SW: slag water; LS: limestone slurry; GS: gypsum slurry
FW: filtered water

Table 2.7. Techniques used for the analysis of particulate matter from the gaseous stream samplings.

	PARTICULATE MATTER (PM)
PM	Standard gravimetric methods
MM-Elements	Inductively Coupled-Plasma Atomic Emission Spectrometry (ICP-AES)
T-Elements	Inductively Coupled-Plasma Mass Spectrometry (ICP-MS)
Chlorine Nitrate Sulphate	High Performance Ion Chromatography (HPIC)
Fluorine	Ion selective electrode
Mercury	LECO AMA 254 gold amalgam atomic absorption spectrometer

MM-elements: major and minor elements; T-elements: Trace elements

2.4. LABORATORY EXPERIMENTS

Laboratory experiments were conducted to reproduce at a laboratory scale the differences found on speciation of gaseous Hg OUT-FGD at an industrial scale between PP1 and PP2; and deducing the main causes of such differences. These experiments were developed at the University of Nottingham where a laboratory scale FGD reactor was designed.

2.4.1. Laboratory FGD reactor

The laboratory FGD reactor (Figure 2.6) designed to carry out the experiments consisted of *(1)* Hg sources; *(2)* synthetic IN-FGD gaseous stream; and a *(3)* reactor vessel. A number of devices were employed in conjunction with the FGD reactor to reproduce the realistic FGD system: mass flow controller and Sir Galahad Mercury Analyser instrument for real-time measurements for Hg.

The flue gas components from PP1 and PP2, concerning SO_2 and HCl levels, were reproduced at laboratory scale for the FGD experiments.

Figure 2.6. FGD reactor.

2.4.1.1. Mercury sources

The Hg sources in the laboratory scale FGD experiments consisted of Hg^0 and Hg^{2+} permeation tubes linked in series each in its own temperature-controlled environment to two water baths, which emitted gaseous Hg through permeable wall with a constant rate (Figure 2.7). The permeated Hg was mixed with N_2 (carrier gas) at a controlled flow rate to obtain a known mixture used as reference in gas testing equipment.

Figure 2.7. Hg permeation tube.

2.4.1.2. Synthetic gaseous stream of SO_2 and HCl

Sulphur dioxide was metered into the Hg-laden gas as 100% SO_2 through a rotameter which was sufficiently accurate for the purpose (Figure 2.8).

Figure 2.8. Air, N_2 and SO_2/CO_2 rotameters.

The HCl device calibration consisted in a very small diameter hole (0.5mm) through the cap of a small (~20mL) sample vial (Figure 2.10). Concentrated HCl was placed (10 mL) in the bottom of an empty gas washing bottle. The HCl was evolved from the diffusion device in a gas washing bottle filled with de-ionized water, over a measured time period, with the diffusion device at a known temperature (ambient temperature), and with a known flow of N_2 through it. At the end of a measuring time period (30 min) the dilute HCl solution in the second gas washing bottle was titrated with standard NaOH (0.02M) solution to determine the HCl absorbed.

The experiment permitted a release rate (and therefore delivery rate to our small-scale FGD scrubber) >0.2 mg/min of HCl. In each titration, the temperature and flow condition were checked several times to ensure reproducibility of HCl release. Once the temperature and flow required to yield 0.5 mg/min was established, the experiment was carried out by reproducing concentrations in the actual PP1 and PP2 scrubbers.

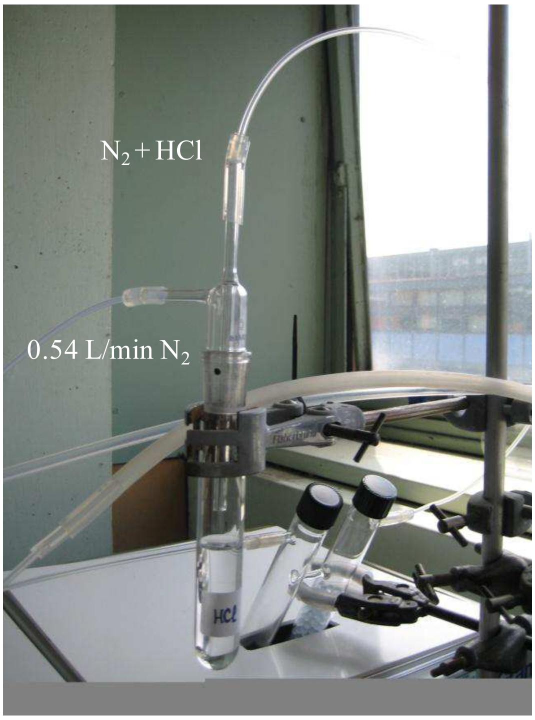


Figure 2.9. HCl device.

2.4.1.3. Reactor vessel

The reactor vessel was designed considering the inputs and outputs involved in the FGD system as well as the most significant parameters identified for these experiments: *(1)* limestone slurry; *(2)* gypsum slurry; *(3)* agitation system (stirrer); *(4)* IN-FGD and OUT-FGD gas; and *(5)* temperature and pressure controller. The connections of the reactor vessel are shown in Figure 2.10.

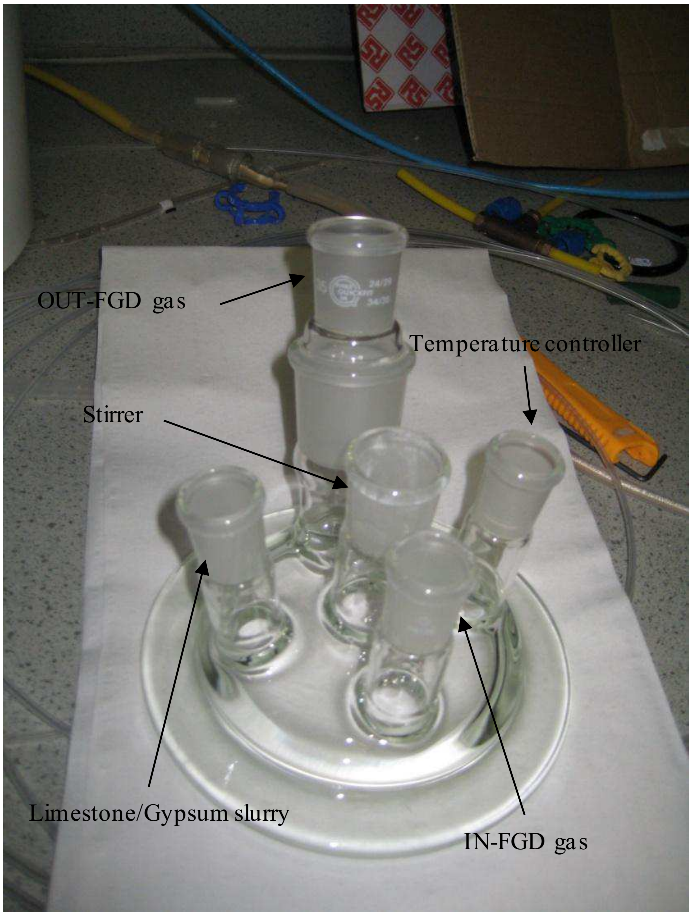


Figure 2.10. Cap of the FGD reactor.

2.4.1.3.1. Limestone and gypsum slurries

Solid and water samples required for these experiments were supplied by both PP1 and PP2 power plants. Limestone slurry was added by means of a glass funnel and gypsum slurry was drawn off by means of the large plastic.

2.4.1.3.2. Agitation system

The limestone slurry inside the vessel was in continuous agitation by an overhead stirrer. The stirrer was introduced into the vessel through the middle cap hole (Figure 2.11).

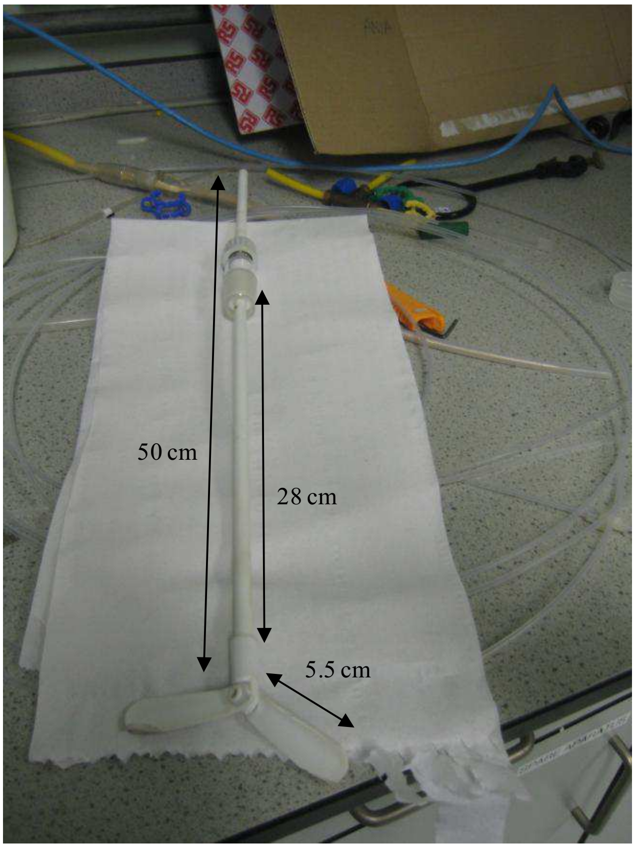


Figure 2.11. Dimensions of the stirrer.

2.4.1.3.3. IN-FGD and OUT-FGD gas

The combined total IN-FGD gas flowed bubbled through a porous sintered glass bubbler into the closed vessel (Figure 2.12). The gas sintered tube device was designed according to the vessel dimensions.

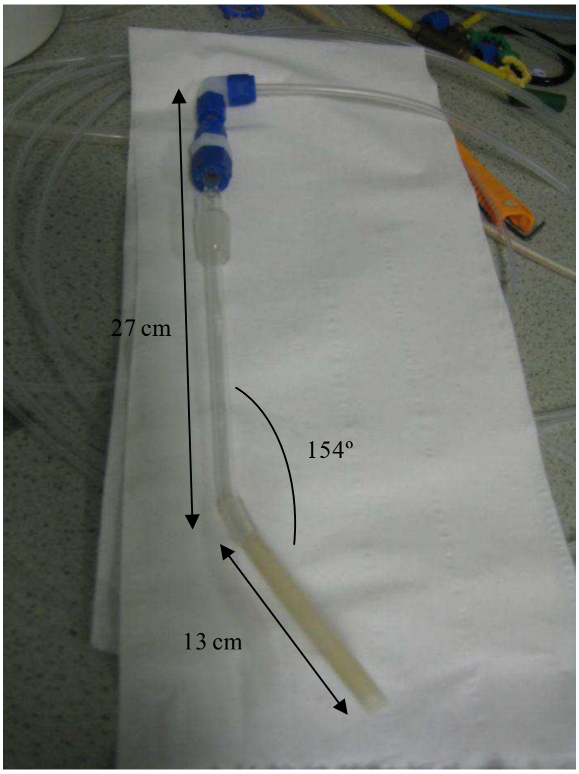


Figure 2.12. Dimensions of the glass sintered tube.

The OUT-FGD real-time measurements for gaseous Hg^0 were conducted by using a Sir Galahad II Mercury Analyser (a detailed description of this device is given in the next section).

Analogous to the real-time measurements of Hg^0 OUT-FGD, a fraction of the OUT-FGD gas flow was piped to the Hg speciation unit based on the Ontario hydro-method. The Hg speciation unit was constructed for Hg^{2+} measurements. In these experiments the Hg speciation unit consisted in three 100 mL 1N KCl solution impingers in series. After 60 minute sampling period all Hg^{2+} IN-FGD and OUT-FGD was trapped in the sampling train. The 300 mL of the KCl solution was combined to one sample for the reduction of Hg^{2+} to Hg^0 by means of a $SnCl_2$ solution. The $SnCl_2$ solution was made as 2% $SnCl_2$ in 10% KOH. In this dissolution all Hg^{2+} is reducing to Hg^0.

At the end of this process the Hg^{2+} converted in Hg^0 was measured by means of the Sir Galahad.

2.4.1.3.4. Temperature and pressure controller

The control of the temperature was realised by means of the external thermometer which gave the correct temperature for the reactor vessel (60ºC).

The control of the pressure was carried out via a manometer connected to the cap of the reactor vessel.

2.4.2. Mass flow controller

The PSA 10.534 series mass flow controller in conjunction with the CavKitCalc software (Figure 2.13) was used to calculate the flow rate and temperature settings required to generate the desired Hg concentration. This unit operated on the principle of dilution a saturated source of Hg at a known temperature. HCl and SO_2 were metered into the mercury-laden gas as 0.1-1.0 v% mixtures through rotameters. In these experiments, the mixture of gases were swept by a constant known flow of N_2~20L/min and air ~2L/min.

Figure 2.13. Mass flow Controller for N_2 carrier gas.

2.4.3. Sir Galahad Mercury Analyser

Real-time measurements for Hg^0 OUT-FGD gas were conducted by using a Sir Galahad II Mercury Analyser model 10.525 (Figure 2.14). This is based on the principle of atomic fluorescence (AF) and consists of a specific gold sand trapping mechanism. The system utilises a low-pressure Hg lamp excitation source with detection by a photomultiplier. Thus, Hg absorbs and fluoresces at the same wavelength, ensuring best selectivity and sensitivity of the detector.

Figure 2.14. Sir Galahad Hg real-time analyser.

2.5. THERMODYNAMIC MODELLING TOOLS

The PHREEQC code (version 2.0, Parkhurst and Appelo, 1999) and the coupled thermodynamic database LLNL was used in this thesis for calculating the aqueous speciation of gypsum slurries and for the saturation index (SI) with respect to selected minerals and solid phases according to the temperature and pH values of scrubbers and concentration of elements in the aqueous phases of the PP1 and PP2 gypsum slurries.

This programme was also used to model kinetic reactions and equations of gaseous Hg with respect to the equilibrium chemistry of the aqueous phases of gypsum slurries from PP1 and PP2 FGD systems.

2.6. SPECIATION EXPERIMENTS

The thermal dissociation rig (PS Analytical Thermogram model 50.042) coupled with the Sir Galahad II Atomic Fluorescence Spectrometer (AFS) Mercury Analyzer model 10.525 was used to determine the mode of occurrence of Hg in PP2 FGD-gypsum from the 2007 and 2008 sampling campaigns. The Hg compounds present in the solid sample were carried through an oven tube in a stream of argon, at a flow rate of 250 ml min^{-1}, and subjected to a programmed rise in temperature of 10ºC min^{-1}. A water trap of silica gel was integrated in the system just before the Sir Galahad detector.

A number of pure Hg compounds ($HgCl_2$, HgS, $HgSO_4$, HgO, Hg_2Cl_2, Hg_2SO_4, and $HgBr_2$) have been tested (Rallo et al., 2010b) at the University of Nottingham to determine their characteristic thermal decomposition profile and temperature. The pure standard Hg compounds were diluted using silica flour (inert material) and $CaSO_4$ (free of Hg) to simulate a similar matrix to the FGD-gypsum sample. Both mercury decomposition profiles and temperature represented a set of ‘‘fingerprints” against which thermal decomposition profiles of FGD-gypsum samples can be compared.

2.7. LEACHING EXPERIMENTS

Leaching tests following the standard EN12457-4 according to the Council decision 2003/33/EC were applied to FGD-gypsums at PP1 and PP2 in order to define the environmental characteristics concerning the leachability of trace pollutants of these by-products in view of their future disposal in landfills.

This consists of a single batch leaching test using Milli-Q (MQ) water as leachant agent at an L/S (liquid to solid) ratio of 10 L/kg and 24h of agitation time in an orbital shaker. Duplicated samples and blanks were all prepared in a similar manner. The leachates were filtered through 0.45µm filters and divided into two aliquots in High Density Polyethylene (HDPE) bottles. One aliquot was used for determination of pH and major anions, whilst the other split was acidified with 1% HNO_3 for further analysis of major and trace metals.

2.8. TIME-of-FLIGHT SECONDARY ION MASS SPECTROMETRY (ToF-SIMS)

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 surface-sensitive analytical method that uses a pulsed ion beam (Cs or microfocused Ga) to remove molecules from the very outermost surface of the sample. The particles are removed from atomic monolayers on the surface (secondary ions). These particles are then accelerated into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector (i.e. time-of-flight). The time spent by ions reaching the detector and the experimental parameters allow us to identify the ion mass with great accuracy.

The ToF-SIMS analyses were performed using a ToF-SIMS IV (ION-ToF, Munster, Germany) operated at a pressure of 5 x 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 5x1011 ions/cm^2, well below the threshold level of 1x1013 ions/cm^2 generally accepted for static SIMS conditions. Secondary ions were detected with a reflector time-of-flight analyzer, a multichannel plate (MCPs), and a time-to-digital converter (TDC). Measurements were performed with a typical acquisition time of 6s, at a TDC time resolution of 200 ps and 100us cycle time. Charge neutralization was achieved with a low energy (20eV) electron flood gun. Secondary ion spectra were acquired from a randomly rastered surface areas of 50µm x50µm 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 Spec software (version 4.1). Each spectrum was normalised to the total intensity.

2.9. POTENTIOMETRIC TITRATION EXPERIMENTS

Potentiometric titration experiments were applied for FGD-gypsum samples to study the leaching behaviour of some elements from PP1 and PP2 FGD-gypsums and identifying the point of zero charge and variation of the 2007 PP2 FGD-gypsum surface charge with pH. The point of zero charge (pzc), in physical chemistry, is a concept relating to the phenomenon of adsorption, and it describes the condition when the electrical charge density on a surface is zero (Rusel et al., 1989; Hunter, 1989; Lyklema, 1995; Kirby, 2010).

The variation of the surface charge of the FGD-gypsum was carried out by potentiometric titration in a N_2-rich atmosphere using 0.02N HCl and 0.02N NaOH. Three samples of 0.3g of FGD gypsum were placed in a vessel containing 100 mL of 1 and 0.01M KCl as background electrolyte. The titrations were carried out by adding 0.2 mL of the titrants by 20 minutes of reaction (Sposito and Holtzclaw, 1977). These experiments were developed at the University of La Frontera (Temuco, Chile).

Chapter 3

Results

The results are presented in form of five published articles in conjunction with additional unpublished findings according to the objectives proposed in this thesis:

- *Partitioning of trace inorganic elements in a coal-fired power plant equipped with a wet Flue Gas Desulphurisation system (objective 1 and 2).*
  Fuel 92 (2012), 145-157.

- *The retention capacity for trace elements by the flue gas desulphurisation system under operational conditions of a co-combustion power plant (objective 1 and 2).*
  Fuel 102 (2012) 773-78.

- *Unusual Speciation and Retention of Hg at a Coal-fired Power plant (objective 3). Environmental Science and Technology 46, (2012), 7890-7897.*

- *Enrichment of inorganic trace pollutants in re-circulated water streams from a wet limestone flue gas desulphurisation system in two coal power plants (objective 4).*
  Fuel Processing Technology 92 (2011), 1764-1775.

- *Influence of an aluminium additive in aqueous and solid speciation of elements in flue gas desulphurisation system (objective 4).*
  Energy 50, (2013), 438-444

ARTICLE 1

Partitioning of trace inorganic elements in a coal-fired power plant equipped with a wet flue gas desulphurisation system

Fuel 92 (2012), 145-157

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ABSTRACT

The abatement capacity of trace elements was studied in a large Pulverized Coal Combustion (PCC) power plant equipped with a wet limestone Flue Gas Desulphurisation (FGD) system. High proportions of most elements were retained as fly ash (FA) as a consequence of the efficiency of the electrostatic precipitator (ESP, 99.6% of FA). The whole plant attains a high retention efficiency (>92%) for most volatile elements. Sulphur and F are retained by the FGD-gypsum, and Cl by the filtered water; whereas the moderately volatile elements, As and B, are retained mainly by FA. Selenium and Hg are still retained by the whole system with relatively high proportions (89 and 71%); however a significant proportion is emitted; Se (11%) and Hg (29%). The gaseous emissions are below the limits with respect to the European directive 2001/80/EC for large combustion plants and the PRTR threshold values. Remediation actions to prevent and/or reduce the gaseous and PM emissions as well as the determination of leachable potential of trace pollutants retained in FGD-gypsum, especially F in view of its disposal, are of significant relevance.

Key words: Trace elements; PCC; FGD; ESP; PRTR threshold.

1. INTRODUCTION

Coal fired power plants are one of the most important sources of air pollutants (SO_x, NO_x, particulate matter (PM), and trace pollutants). Emissions from large industrial facilities are currently regulated by the European Commission (EC) directives, such as the Integrated Pollution Prevention and Control (IPPC, 1996/61/EC) later replaced by 2008/1/EC, and Large Combustion Plants Directives (LCP, 2001/80/EC), which established limits for SO_x, NO_x, and PM emissions (among other pollutants) into the air from large combustion plants (>50MW). In June 2008, the Directive 2008/50/EC on ambient air quality and cleaner air for Europe was adopted and published. This meant a reinforcement of the requirements used in the assessment and the management of air quality, and regulation changes regarding regulated pollutants.

The above new and restrictive environmental regulations, promoted development and implementation of co-combustion techniques by the use of alternative fuels (petroleum coke, sewage sludge, biomass, etc) and De-Nitrification (DNO_x) facilities in coal power plants equipped with Flue Gas Desulphurisation (FGD) systems. The FGD controls acidic gaseous emissions from coal-fired stations (Zhou and Dayal, 1990) and can also be effective in capturing volatile pollutants other than S, such as F, As, B, Cl, Se or Hg (Aunela-Tapola et al., 1998; Meij, 2001; Hasset, 2003; Meij and te Winkel, 2004; Schroeder and Kairies, 2005; Yokoyama and Asakura, 2006; Álvarez-Ayuso et al, 2006) in a gaseous form and/or as PM. Once captured, a certain proportion of the trace pollutants are partitioned into solid by-products (FGD-gypsum) and water streams (aqueous phase of gypsum slurry and filtered water). Low proportions are released in a gaseous and/or PM form.

Recent research indicates (Córdoba et al., 2011) that the enrichment of some inorganic trace pollutants in water streams is the most important consequence of FGD systems with re-circulation of water from gypsum slurry. This enrichment could result in environmental (reduction of the gaseous retention efficiencies and pollution of soil and groundwater) and technical problems (fouling of scrubber and pipes of the FGD). The solid by-products of Pulverized Coal Combustion and FGD (PCC-FGD) plants such as Fly Ash (FA), Boiler Slag (BS), and FGD-gypsum could also produce environmental problems owing to the impurities and the leaching of trace elements such as As, Ba, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn, Cl, and F. Different alternatives are currently under consideration as a means of reducing the amount of FA that must be disposed of, such as incorporation in construction material, ceramic applications, and zeolite synthesis. Nevertheless, given the amount of FA derived and their trace element content, which limits the industrial market, the usual final fate is its discard in lagoons, settling ponds or landfills (Clark et al., 2001; Cheeseman et al., 2003; Reijnders, 2005). The FGD-gypsum can also find its way to the market in wallboard manufacture or be used in the cement industry. However, a great proportion is employed as a landfill material in mine reclamation or just sent to landfills for its disposal (Álvarez-Ayuso et al., 2008).

In this regard, the European Union (EU) by means of the 2003/33/CE Directive established limit values for the aforementioned elements and the criteria and procedures of waste admission in landfills. This standard specifies the limits with which certain substances must comply and which must be analysed in the leachate from a given waste by applying the EN-12457-4 leaching test, and are important for landfill management purposes. However, some technical and environmental matters which hinder compliance have yet to be dealt with.

Compliance with the limit of metals leaching in PCC-FGD solid by-products may be unaffordable not only by the implementation cost, but also by the incomplete knowledge of their partition and speciation in different streams involved in the FGD systems with water re-circulation. The leaching of FA particles reaching FGD system and the continuous re-circulation of filtered water to the scrubber determines the subsequent occurrence and concentration in the FGD-gypsum sludge. Fluorine and metals can be removed and/or immobilised by means of the stabilisation processes (Álvarez-Ayuso et al., 2007; 2008a; 2008b). However, stabilisation processes are corrective measures which in some cases are not enough for the leaching limits compliance and acceptation of PCC-FGD by-products as a non-hazardous waste in landfills.

Prevention measures based on the management of solid (FA, BS, and FGD-gypsum) and water (aqueous phase of gypsum slurry and filtered water) streams before their production and the subsequent disposal in landfills and/or in application scenarios, are preferred owing to the economic and environmental benefits. Processes based on sorption and co-precipitation mechanism, could successfully address the environmental issues of solid by-products. This warrants an in-depth knowledge on the partitioning and speciation of elements in the PCC-FGD system.

With the advent of increasingly restrictive regulations on air, water, and soil quality and the growing concern about health effects of exposure to heavy metals even at trace levels, a comprehensive study (partitioning, speciation, and enrichment) of the abatement capacity of trace inorganic pollutants in the solid, water, and in the gaseous streams in FGD system with water re-circulation is of key relevance.

In order to obtain this knowledge for the future environmental and health regulations as regards the power plants operation, and to gain optimal operational conditions of the FGD system in power plants, the aims of this work are: i) assess the abatement capacity of trace inorganic pollutants by the forced-oxidation wet limestone FGD system in a coal-fired power plant; ii) establish the mass balance and the partitioning of a broad array elements for the whole installation (PCC+FGD); iii) determine the fate of the trace inorganic pollutants based on their retention in the gypsum sludge and/or dissolution into FGD waters, and partitioning among the outgoing FGD streams; and iv) determine the elements of concern as regards emissions and leachable potential for subsequent remediation actions.

2. MATERIALS AND METHODS

2.1. SAMPLE COLLECTION

The sampling campaign at the large power plant was carried out on 19-20th September 2007. The sampling was performed at 100% MCR (maximum capacity) and 100% desulphurisation unit Nº3. The power plant is fed with a blend of local sub-bituminous and imported bituminous coals, and is equipped with a forced-oxidation wet limestone FGD system. The operational conditions over the sampling period are summarised in Table 1.

Table 1. Operational conditions of the power plant during the sampling campaign.

Mean produced electricity (Mw.h) in the sampling hours	337
Load of power plant (capacity, %)	100
Input feed fuel (Coal, t/h)	194
Output FA (fly ash, t/h)	40
Output BS (boiler slag, t/h)	8
BS water (t/h)	3.5
Limestone (t/h)	31
Gypsum ($CaSO_4$. $2H_2O$) (45ºC) (t/h)	46
Gypsum hemi-hydrated ($CaSO_4$. 1/2 H_2O) (105ºC) (t/h)	39
Treated water (t/h)	45
Process water (t/h)	85
Limestone slurry (treated water+ filtered water)(m^3/h)	87
Filtered water (re-circulated to the scrubber, m^3/h)	72
Gaseous stream in FGD (Nm^3/h)	1.392.066
Gaseous stream out FGD (Nm^3/h)	1.621.827
Oxidation Abs	6%

The PCC-FGD system involves a number of water streams that can be separated into 2 groups (Figure 1):

i) Water streams not directly related to FGD: process water and BS water. The process water comes from a nearby ash pond overlying of sulphate and Sr-rich sedimentary rocks and it is used in the BS quenching and drainage, giving rise to BS water which is lead to a water reservoir close to the power plant.

ii) FGD water streams: treated and added water, limestone and gypsum slurries, and filtered water. A fraction of process water is treated to reduce the salt content which gives rise to the treated water stream. Treated water is used for limestone slurry preparation and for maintaining the slurry levels into the scrubber, and is then considered as FGD water stream. The added water is similar in composition to the treated water and is used to offset the water loss because of moisture in the FGD-gypsum and the water evaporation in the scrubber due to the contact with the emitted OUT-FGD gas. Gypsum slurry is the result of the absorption of SO_2 in limestone slurry. In this article, the terms gypsum and limestone slurry are used for the total fraction of the slurries (solid + water) while the terms aqueous phase of gypsum and limestone slurry are employed for the water fraction of the slurries. Gypsum sludge is referred to the solid fraction of the gypsum slurry, and FGD-gypsum is the end-product after filtration process.

Filtered water is the water stream that results after filtration and dilution of the aqueous phase of gypsum slurry. The dilution is carried out by adding of water which leads to lower concentrations of most of elements, especially Cl, in the filtered water than those in the aqueous phase of gypsum slurry.

The most distinctive feature of the FGD system at the power plant is the re-circulation of filtered water to the scrubber. At this power plant, filtered water, after the dilution process, is re-circulated through the limestone mills for limestone slurry preparation and the remaining fraction, if any, is directly re-circulated into the scrubber. This results in a 0.55/0.45 mixture ratio of limestone slurry water and filtered water into the scrubber. This water stream is considered as the overall water input into the FGD system.

The water output of the FGD systems consists of i) the aqueous phase of gypsum slurry; ii) the loss of crystallisation water from FGD-gypsum (18%); and iii) the water evaporation (16%) 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 this power plant.

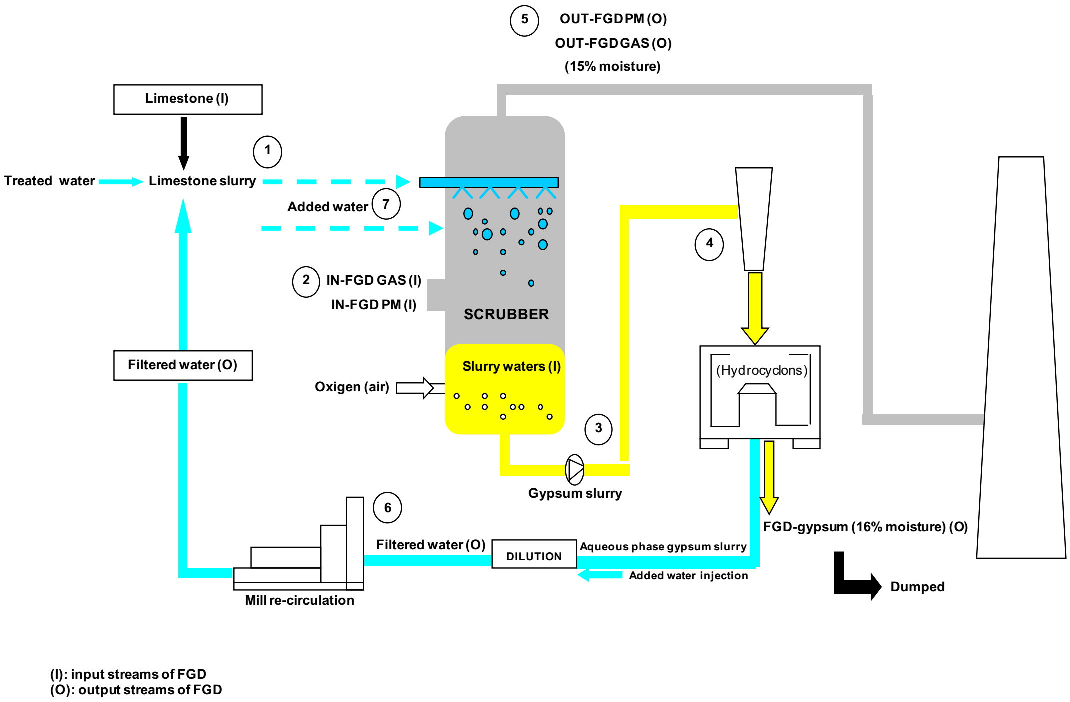


Figure 1. Diagram and process of the FGD system at the power plant. 1: Limestone slurry introduced and sprayed into the scrubber to react with SO_2; 2: Gas and PM input flow into the scrubber after combustion process; 3: Formation of gypsum slurry as result of the desulphurisation process; 4: Filtration of gypsum slurry by hydro-cyclones= aqueous phase of gypsum slurry and FGD-gypsum production; 5: Cleaned gas and PM flow OUT-FGD; 6: Re-circulation of filtered water for limestone slurry preparation after dilution process; and 7: Water addition to offset the water loss with gypsum and in the OUT-FGD gas.

Isokinetic measurements of gaseous streams were performed at two sampling points (Figure 1), IN-FGD and OUT-FGD, simultaneously. Each sampling run lasted about 2.5h. At each sampling point, two trains of sampling systems were assembled with specific trapping solutions, one for the capture of anions and metals, and the other for the capture and speciation of Hg. In the first case, the gas sampling system was devised according to EN 1911 and EN 14385. In such a system, two impingers 100 mL of de-ionized H_2O (or MilliQ grade water) and two filled with 6 w% HNO_3 and 10 w% H_2O_2 were assembled to determine the concentrations of anions and metals, respectively, in an ice bath. The sampling and speciation of gaseous Hg (Hg^0 and Hg^{2+}) was devised according to EN 13211 and Meij and te Winkel (2006). A train of dark glass impingers in an ice bath was used. The Hg sampling system (Meij and te Winkel, 2006) consists of a first impinger filled with 100 mL of HCl to capture Hg^{2+}, the second impinger containing 3 w% H_2O_2 for SO_2 removal (150mL IN-FGD and 100mL OUT-FGD), and the two last impingers containing 4 w% $K_2Cr_2O_7$ with 20 w% of HNO_3 for Hg^0 trapping.

The PM that escapes from the electrostatic precipitator (ESP) and FGD is defined and termed fly ash and fly dust, respectively, by Meij (1994) although the terms IN and OUT-FGD PM are used in this article. A quartz filter was placed before the isokinetic train for PM IN and OUT–FGD collection in the Hg sampling. Polytetrafluoroethylene (PTFE) filters were used for the PM capture of anions and cations instead of quartz filters, since HF reacts with quartz to form highly volatile SiF_6^{2-} with a subsequent loss of fluorine.

A total of 5 raw coals (RC1-RC5) and 13 streams, 6 solid (feed coal blend, BS, FA, PM, limestone, and FGD-gypsum), and 7 water (process water, added water, BS water, filtered water, treated water, and the limestone and gypsum slurries) streams were collected, mixed, and homogenised. Two samplings per day were performed for each material, amounting to four sample sets in the campaign.

2.2. CHEMICAL ANALYSIS

The solid samples were acid-digested in duplicate by using a special two-step digestion method devised by Querol et al (1993). The resulting solution was then analysed by Inductively-Coupled Plasma Atomic-Emission Spectrometry (ICP-AES) for major and minor elements, using the Advantage Radial ER/S device from Thermo Jarrell-Ash. Semi-quantitative analyses were performed to know the range of element concentrations as well as the matrix and the possible spectral interferences. The calibration was performed by means of the international certified standard (1000 and 10.000 ppm). Most of the trace elements were analysed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS), using the X-SERIES II device from Thermo Fisher SCIENTIFIC. The quantitative analyses were performed with an external calibration, using chemical standards of similar matrix of the samples, which covered concentrations range expected forming the calibration lines. The correction for individual sample suppression effects was carried out by means of an internal standard (In 10 ppb). The FA and coal international reference material (NBS1633b and SARM19) were also digested to determine the accuracy of the analytical and digestion methods. Chlorine content of solid samples was determined by following the ASTM D4208 method using a calorimetric bomb to obtain chlorine in solution, which is measured by High Performance Ion Chromatography (HPIC). The determination of F in the solid samples was performed according to the pyro-hydrolitic extraction method described in ISO 11724 standard methods and subsequently measured by HPIC. The Hg analyses were directly carried out on solid and water samples using a LECO AMA 254 Gold Amalgam Atomic Absorption Spectrometer (GA-AAS).

The mineralogy of solid samples was determined by X-ray powder diffraction (XRD) with a Bruker D5005 diffractometer with monochromatic Cu Kα1,2 radiation operated at 40KV and 40mA., from 4 at 60° of 2theta range, and a step size of 0.05° and 3s/step.

Water streams and trapping solutions from flue gas sampling were directly analysed by ICP-AES and ICP-MS for major and trace elements, respectively. Chloride contents were measured by HPIC, and fluorine was determined by ion selective electrode.

The contents of major and trace elements in the filters were determined by digestion using $HF:HNO_3:HClO_4$ with subsequent measurement using ICP-AES and ICP-MS, respectively.

2.3. MASS BALANCE

Mass balance (MB) was calculated by normalising the concentration of each element in a given stream with the corresponding stream flow for the PCC (boiler + ESP), FGD system, and for the whole installation. The MBs were conducted for each sampling day and no significant differences between the mass balances were observed. The very high repeatability provided us with reliable raw data for the MB closure and an overall mass balance, which comprises the mean values of each day, is reported in this study. The flows considered for the overall MB calculations are detailed as follow:

$$MB = [(Flow_{\text{FGD-gypsum}} \times Ci_{\text{FGD-gypsum}}) + (Flow_{\text{OUT-FGD PM}} \times Ci_{\text{OUT-FGD PM}}) + (Flow_{\text{OUT-FGD gas}} \times Ci_{\text{OUT-FGD gas}}) + (Flow_{\text{Filtered water}} \times Ci_{\text{Filtered water}}) + (Flow_{\text{BS}} \times Ci_{\text{BS}}) + (Flow_{\text{FA}} \times Ci_{\text{FA}}) + (Flow_{\text{BS water}} \times Ci_{\text{BS water}}) \;/\; [(Flow_{\text{Limestone}} \times Ci_{\text{Limestone}}) + (Flow_{\text{Mixture water}} \times Ci_{\text{Mixture water}}) + (Flow_{\text{Feed fuel}} \times Ci_{\text{Feed fuel}}) + (Flow_{\text{Treated water}} \times Ci_{\text{Treated water}})] \quad (1)$$

Where the output and input flows ($Flow_x$) are the flows for a given stream ($_x$) IN and OUT of the whole installation and for mass balance calculations; and Ci is the mean concentration of a certain element in the corresponding stream IN and OUT. The Ci of the mixture water is the concentration of a given element in the aqueous phase of limestone slurry and filtered water with respect to the proportion of each water stream in the scrubber (0.55/0.45 mixture ratio of limestone slurry and filtered water, respectively). The flow of mixture water is 80.1 g/h.

3. RESULTS AND DISCUSSION

3.1. MINERALOGICAL AND CHEMICAL CHARACTERISATION

3.1.1. Solid streams

Local coals are characterised by high ash content (26-47%), with quartz, kaolinite, pyrite and traces of feldspars, calcite, and illite being the main crystalline phases. Gypsum and jarosite, which are of secondary origin from the weathering of sulphide minerals, are also detected in samples of these coals. The imported sub-bituminous coal is a low ash coal (14%) characterised by lower contents of quartz, kaolinite, and traces of pyrite, calcite, and feldspars. Local coals show major enrichment in S and As and a minor enrichment in Al, B, Fe, K, Li, Cr, Cu, Ni, Rb, Sb, Se, V and especially in Pb, Zn, and U in comparison with the imported sub-bituminous coal (Table 2).

Table 2. Proximate analysis and concentration of elements in local (RC1-RC4) and imported coal (RC5).

Proximate (% db)	RC1	RC2	RC3	RC4	RC5
Moisture 105°C	7.9	8.2	5.9	7.1	2.8
Ash	47	32	26	33	14
Volatile matter	26	31	34	33	28
Al_2O_3	12	6.6	4.8	7.1	3.6
CaO	1.2	1.5	0.8	2.0	1.2
Fe_2O_3	7.4	7.3	8.8	5.8	0.4
Na_2O	0.1	0.0	0.1	0.1	0.1
SO_3	19	21	25	17	1.5
K_2O	0.9	0.4	0.2	0.5	0.1
MgO	0.4	0.2	0.2	0.3	0.2
mg/kg (db)					
Cl	239	240	21	75	21
F	63	135	176	215	222
Hg	0.09	0.10	0.10	0.09	0.09
Li	183	86	53	84	32
Be	5.0	4.2	4.1	3.0	2.4
B	55	59	36	70	27
Sc	11	7.0	4.3	7.5	6.1
Ti	1793	1250	911	1449	1383
P	356	157	325	280	1185
V	80	50	37	64	30
Cr	56	35	38	37	29
Mn	75	87	40	85	53
Co	10	7.1	11	17	6.6
Ni	29	18	25	36	14
Cu	27	14	13	15	11
Zn	109	142	117	206	35
Ga	21	12	6.8	11	11
Ge	2	1.3	1.4	1.3	2
As	22	26	17	30	2
Se	2.1	2.2	3.0	2.7	1.1
Rb	50	21	8.8	23	4.4
Sr	305	100	151	178	534
Y	15	12	14	15	15
Zr	53	36	27	40	59
Nb	7.8	5.5	4.0	6.0	7.4
Mo	2.7	2.0	5.7	3.8	1.3
Cd	<0.2	<0.2	<0.2	<0.2	<0.2
Sn	3.7	2.1	1.0	2.0	1.5
Sb	2.0	1.2	<0.01	0.9	<0.01
Cs	8.1	3.8	1.7	4.3	1.0
Ba	214	70	55	54	420
La	18	10	11	13	20
Ce	35	22	26	28	40
Pr	4.3	2.7	3.5	3.5	4.0
Nd	19	12	16	16	19
Sm	3.7	2.6	2.8	3.3	3.6
Eu	<0.01	<0.01	<0.01	<0.01	<0.01
Gd	3.4	2.6	3.1	3.4	3.5
Tb	<0.01	<0.01	<0.01	<0.01	<0.01
Dy	2.7	2.1	2.0	2.5	2.7
Ho	<0.01	<0.01	<0.01	<0.01	<0.01
Er	1.3	1.0	0.9	1.1	1.3
Tm	<0.01	<0.01	<0.01	<0.01	<0.01
Yb	1.5	1.1	0.9	1.3	1.5
Lu	<0.01	<0.01	<0.01	<0.01	<0.01
Hf	1.9	1.3	0.9	1.5	2.1
Ta	2.0	0.8	<0.01	1.1	1.5
W	6.2	4.3	2.1	3.3	2.5
Tl	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	23	14	12	16	8.1
Bi	<0.01	<0.01	<0.01	<0.01	<0.01
Th	10	6.5	4.0	7.2	8.4
U	5.8	5.3	6.2	11	3.4

According to the composition of the sub-bituminous local coals and the imported bituminous coal, the feed coal blend is characterised by high ash yield (28-29%, dry basis (db)) and volatile matter (30%, db).

FA consists of an aluminosilicate glassy matrix with minor amounts of quartz, mullite, magnetite, hematite, and traces of anhydrite, calcite, and lime. Similarly, BS is characterised by the predominance of an aluminosilicate glass matrix, with lower contents of quartz, magnetite, hematite, mullite, and traces of anorthite. FA is enriched (FA/BS > 1.3) in S, Sr, B, Zn, Ga, Ge, Se, As, Mo, Sn, Sb, Pb, and especially F and Hg (Table 3).

The limestone used at power plant is 93% $CaCO_3$ purity, with relatively high proportions of SiO_2, Al, Mg, Fe and K, and significant concentrations of carbonate-bearing elements, such as Mn and Sr. Limestone also shows notable concentrations of F, Ti, P , Cl , and U (Table 3).

Gypsum with minor contents of quartz and traces of illite and calcite are the main crystalline phases detected in FGD-gypsum. The notable concentrations of some sulphate-bearing elements, such as Sr and Mn, and significant concentrations of Ba, B, Ti, P, Se, As, Hg, and U should be noted (Table 3).

Table 3. Mean concentration of major, minor, and trace elements in solid streams, and FA/BS ratios.

	Coal blend	FA	BS	FA/BS	Limestone	FGD-gypsum
Al_2O_3	6.7	26	24	1.1	1.0	0.7
CaO	1.5	5.6	5.2	1.1	52	32
Fe_2O_3	5.3	19	23	0.8	0.5	0.3
Na_2O	0.1	0.2	0.2	1.0	0.01	0.02
SO_3	13	0.7	0.1	7.5	0.1	44
K_2O	0.4	1.3	1.1	1.1	0.2	0.1
MgO	0.3	1.2	1.1	1.1	0.8	0.6
mg/kg (db)						
Cl	47	15	20	0.8	24	297
F	197	123	6.9	18	217	931
Hg	0.082	0.043	0.002	22	0.003	0.154
Li	70	298	263	1.1	7.6	4.8
Be	3.0	11	9.4	1.2	<0.01	<0.01
B	43	211	57	3.7	7.9	14
Sc	4.7	23	19	1.2	1.3	0.8
Ti	1420	5468	5198	1.1	293	201
P	566	2014	1380	1.5	178	136
V	57	219	162	1.4	11	6.9
Cr	38	149	153	0.9	7.9	4.8
Mn	82	321	340	0.9	86	56
Co	9.1	33	35	0.9	1.6	0.9
Ni	20	74	74	1.0	8.4	4.2
Cu	17	63	59	1.1	2.7	2.1
Zn	65	309	174	1.8	18	<0.01
Ga	11	47	32	1.5	1.4	0.9
Ge	2.0	7.9	4.7	1.7	<0.01	<0.01
As	21	85	15	5.6	2.2	2.0
Se	1.5	4.7	1.0	4.7	<0.01	2.2
Rb	19	81	71	1.1	8.5	4.6
Sr	258	1001	947	1.1	161	113
Y	13	51	49	1.1	2.3	1.4
Zr	43	197	204	0.9	7.5	5.3
Nb	5.7	17	17	1.0	0.8	0.5
Mo	3.0	14	5.3	2.8	<0.01	<0.01
Cd	<0.2	0.9	<0.1	>9	<0.2	<0.2
Sn	1.9	8.2	3.9	2.1	0.1	0.1
Sb	0.9	3.0	2.0	1.5	<0.01	<0.01
Cs	3.5	15	13	1.2	0.9	<0.01
Ba	166	683	639	1.1	22	16
La	15	57	56	1.0	2.5	1.5
Ce	35	133	131	1.0	5.4	3.1
Pr	3.3	14	13	1.1	<0.01	<0.01
Nd	14	58	56	1.0	2.7	1.7
Sm	2.9	12	11	1.1	<0.01	<0.01
Eu	<0.01	1.9	1.7	1.1	<0.01	<0.01
Gd	2.9	12	12	1.0	<0.01	<0.01
Tb	<0.01	2.0	1.4	1.1	<0.01	<0.01
Dy	2.0	8.5	7.9	1.1	<0.01	<0.01
Ho	<0.01	1.6	1.5	1.1	<0.01	<0.01
Er	1.0	4.3	3.9	1.1	<0.01	<0.01
Tm	<0.01	0.7	0.4	1.0	<0.01	<0.01
Yb	1.1	4.8	4.5	1.1	<0.01	<0.01
Lu	<0.01	0.7	0.4	1.8	<0.01	<0.01
Hf	1.3	6.5	6.4	1.0	<0.01	<0.01
Ta	1.1	2.3	2.5	0.9	<0.01	<0.01
W	2.6	9.4	5.3	1.7	<0.01	<0.01
Tl	<0.01	2	<0.01	>200	<0.01	<0.01
Pb	13	58	30	1.9	1.5	1.4
Bi	<0.01	1.5	<0.01	>150	<0.01	<0.01
Th	6.5	28	25	1.1	0.9	<0.01
U	4.8	22	18	1.2	2.7	2.3

FA: fly ash.

BS: boiler slag.

FA/BS: fly ash/BS concentration ratio.

3.1.2. Water streams

The aqueous phases of limestone and gypsum slurries have very high concentrations of SO_4^{2-}, Mg, Ca, and Cl (Table 4), followed by B, Li, Se, Ba, Mo, and especially Ni, Zn, Co, and U in the aqueous phase of gypsum slurry. This could be related with the relatively high mobility of oxy-anionic species (i.e. As, B, Cr, Mo, Se, and V) and slightly alkaline pH (7.4-7.6) of the aqueous phase of limestone and gypsum slurries. In the case of the limestone slurry, the high contents of the above elements are attributed to the re-circulation of a fraction of filtered water for limestone slurry preparation. Furthermore, U may form stable uranyl complexes with carbonates (Basiric et al., 1991) that may promote presence of U bearing complexes in the aqueous phase of gypsum slurry. The leaching of FA particles reaching FGD system and the continuous re-circulation of filtered water from gypsum slurry filtration may account for the high concentration of aforementioned oxy-anionic species and U complexes in these aqueous phases. As reported in recent studies (Córdoba et al., 2011) the elements enriched in the aqueous phase of gypsum slurry and filtered water at this power plant are Na, Mg, Cl, B, Mn, Se, Cd, Mo, and U because of the filtered water re-circulation.

Filtered water shows a similar composition to the aqueous phase of gypsum slurry, with lower concentrations by a factor around 2 of most of elements owing to the aforementioned water dilution (Table 4).

The levels of As, B, Cr, Mo, S, Se, and V in the treated and added water (Table 4) are far below those of the aqueous phase of gypsum slurry and filtered water. The process and BS water are characterised by high concentrations of Sr, B, Li, Ca, U, Cl, and S; this is probably attributable to aforementioned source of process water and/or a partial leaching of BS components during the quenching and drainage of this by-product.

Table 4. Mean concentration of major, minor, and trace elements in water streams.

	PW	BSW	TW	AW	ALS	AGS	FW
mg/L							
Al	<1	<1	<0.4	<0.2	<5	<10	<10
Ca	433	437	151	102	795	807	763
Fe	<0.1	<0.1	<0.05	<0.025	<0.1	<0.1	<1
K	8.0	8.5	2.8	2.0	61	113	65
Mg	103	99	36	26	1643	3414	1871
Na	42	37	10	5.0	173	300	185
P	<0.5	<0.5	<0.2	<0.1	<2.5	<5	<5
S	434	443	117	71	3048	5725	3419
SO_4^{2-}	1297	1317	351	212	9129	17118	10223
F	0.9	1.1	0.4	0.3	14	40	27
Cl	65	60	55	8.9	797	841	856
Hg	0.002	0.001	0.001	0.002	0.001	0.01	0.002
µg/L							
Li	54	371	19	14	619	1231	705
Be	<0.8	<0.8	<0.8	<0.8	<0.1	1.9	<0.1
B	497	556	128	175	24940	48130	27643
Sc	14	10	5.6	6.9	24	63	31
Ti	5.0	3.5	1.5	1.4	10	31	14
V	8.1	25	4.8	1.5	72	168	94
Cr	2.3	2.4	1.4	1.7	3.4	4.8	3.6
Mn	3.2	11	5.8	2.9	2764	103470	53608
Co	<0.8	1.1	<0.8	<0.8	11	201	85
Ni	5.6	8.2	2.3	<0.8	68	514	236
Cu	56	14	11	1.8	20	53	27
Zn	14	3.7	<0.8	<0.8	<0.1	346	22
Ga	<0.8	0.8	<0.8	<0.8	<0.1	2.6	1.1
Ge	<0.8	1.3	<0.8	<0.8	<0.1	3.2	1.8
As	4.7	14	2.3	0.9	29	52	28
Se	3.2	2.6	1.4	1.8	145	469	262
Rb	4.1	8.0	1.3	1.0	30	72	41
Sr	8111	7669	2717	2008	4822	2582	4395
Y	<0.8	<0.8	<0.8	<0.8	<0.1	2.9	<0.1
Zr	<0.8	<0.8	<0.8	<0.8	<0.1	<1	<0.1
Nb	<0.8	<0.8	<0.8	<0.8	<0.1	<1	<0.1
Mo	3.1	14	0.9	0.9	79	65	51
Cd	<0.8	<0.8	<0.8	<0.8	<0.1	25	8.0
Sn	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Sb	<0.8	1.4	<0.8	<0.8	1.1	1.6	1.0
Cs	<0.8	0.9	<0.8	<0.8	<0.1	1.3	<0.1
Ba	115	158	40	27	59	188	131
La	<0.8	<0.8	<0.8	<0.8	<0.1	1.3	<0.1
Ce	<0.8	<0.8	<0.8	<0.8	<0.1	1.5	<0.1
Pr	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Nd	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Sm	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Eu	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Gd	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Tb	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Dy	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Ho	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Er	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Tm	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Yb	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Lu	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Hf	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Ta	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
W	<0.8	2.4	<0.8	<0.8	1.0	<0.1	<0.1
Tl	<0.8	<0.8	<0.8	<0.8	<0.1	5.0	<0.1
Pb	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Bi	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
Th	<0.8	<0.8	<0.8	<0.8	<0.1	<0.1	<0.1
U	6.7	7.4	2.2	1.7	99	330	219

BSW: boiler slag water; ALS: aqueous phase of limestone slurry; AGS: aqueous phase of gypsum slurry

3.1.3. Gaseous streams

SO_2 is the dominant acidic gaseous pollutant incoming the FGD (IN-FGD), reaching concentrations around 14500 mg/m^{3}N (Table 5). Such high levels dropped after FGD to 800-1100 mg/m^{3}N, which indicate that SO_2 emissions are drastically reduced (94% retention). Fluorine reaches levels up to 25000 µg/m^{3}N in the flue gas incoming FGD, decreasing to <600 µg/m^{3}N after FGD (reduction rate 99%).Chloride levels in the gas IN-FGD exceeded 6000 µg/m^{3}N but are reduced to <300 µg/m^{3}N OUT-FGD (97% retention). Other volatile elements, such as B, Se, and As are also highly retained by FGD (89-96%, Table 5).

The overall retention rates for Hg are around 70% (Table 5), but this value is markedly dependant on Hg speciation. Oxidised Hg is more prone to be retained (89%) while capture rate for elemental Hg were <30%, which is in line with the findings of other authors (Meij and te Winkel, 2006).

Table 5. Mean concentration of gaseous components IN and OUT-FGD and gaseous retention efficiencies.

		mg/m^{3}N	µg/m^{3}N							
		SO_2	Cl^-	F^-	B	Se	As	Hg tot	Hg^{2+}	Hg^0
	IN-FGD	14744	6141	24650	387	96	1.2	7.8	5.9	1.9
Day 1	OUT-FGD	1083	293	603	17	4.0	0.1	2.2	0.8	1.5
	IN-FGD	14445	6282	21387	383	80	1.1	7.8	5.6	2.2
Day 2	OUT-FGD	894	111	136	15	6.5	0.1	2.2	0.6	1.6
Mean of 2 days	% retention	94	97	99	96	94	89	72	89	26

3.1.4. Particulate matter

The accumulated FA particles in gypsum sludge as well as the entrained particles from this material by the OUT-FGD gas, is a limiting factor for an accurate determination of the retention efficiency of PM by wet scrubbers. Given the accumulated fraction of PM cannot be determined, an estimation of the retained proportion of PM was measured by considering the retention efficiency as PM OUT/PM IN ratio. The slightly higher flow of OUT-FGD gas than IN-FGD was also taken into consideration.

PM levels are reduced by half after FGD, and the compositions substantially differ (Table 6).Fly ash particles are the major constituent of the IN-FGD PM (Table 6). The concentrations of most elements decreased in OUT-FGD PM (74% average retention) with the exception of S, Se, and Hg. This could be ascribed to gypsum slurry particles entrained by the outgoing gaseous stream from the FGD, and/or the evaporation of gypsum slurry droplets condensed on filters. However, the low Ca concentrations unbalanced with S, suggest that S may not completely occur in particulate gypsum. It is thought that the high moisture conditions after bubbling in FGD may enhance the oxidation of SO_2, giving rise to intermediate unidentified species between SO_2 and H_2SO_4 that are subsequently emitted and retained by the filter. Sulphur accounts for 70% of PM load OUT-FGD, which decrease the overall abatement of PM from 74% to 34-55%.

Even allowing for the slightly higher gas flow OUT-FGD than IN-FGD (Table 1), the concentration of S and Se in the PM is higher by a factor of 4 and 8, respectively.

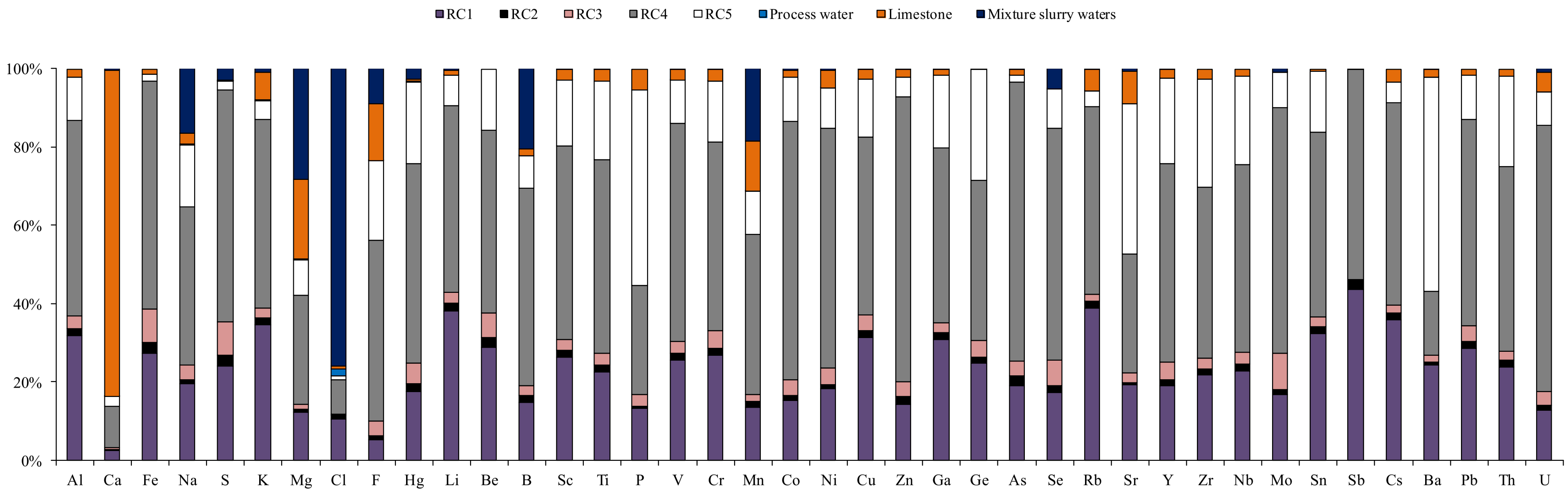
Table 6. Mean concentrations of elements in PM IN and OUT-FGD.

mg/m^{3}N	PM IN-FGD	PM OUT-FGD
Al	5.2	1.2
Ca	2.2	0.5
Fe	4.7	1.0
K	0.3	0.1
Mg	0.2	0.1
Na	0.01	0.01
S	0.9	4.1
µg/m^{3}N		
Li	16	3
Be	0.6	0.1
B	4.3	0.1
Sc	1.3	0.3
Ti	313	57
V	26	4.7
Cr	20	12
Mn	24	6.7
Co	1.9	0.4
Ni	27	8.4
Cu	5.7	4.3
Zn	29	8.3
Ga	3.0	0.6
Ge	0.5	0.2
As	7.9	2.3
Se	3.6	27
Rb	2.2	0.7
Sr	62	12
Y	2.0	0.5
Zr	10	1.9
Nb	1.2	0.3
Mo	3.3	1.6
Cd	0.2	0.3
Sn	1.8	0.3
Sb	0.4	0.1
Cs	0.4	0.1
Ba	31	6.9
La	2.9	0.6
Ce	7.1	1.3
Pr	0.6	0.1
Nd	2.3	0.6
Sm	0.5	0.1
Eu	0.1	0.02
Gd	0.4	0.1
Tb	0.1	0.01
Dy	0.3	0.1
Ho	0.1	0.02
Er	0.2	0.04
Yb	0.2	0.04
Hf	0.2	0.1
Ta	0.3	0.04
W	1.2	0.3
Tl	0.2	0.1
Pb	4.2	0.8
Bi	0.2	0.04
Th	1.3	0.3
U	1.0	0.2
Hg *(ng/m^{3}N)*	1.3	8.8

3.2. ORIGIN OF TRACE ELEMENTS

The blend of local and imported coals, treated water, limestone, and the mixture of the slurry waters are all major sources of trace pollutants at the whole power plant. The contribution of each stream to the input of trace elements was calculated according to their input flows (t/h), and the proportion of each individual coal, in the case of the feed coal blend (19% RC1, 2% RC2, 5% RC3, 52% RC4, and 22% RC5).

The source (relative proportion) of each element to the power plant is depicted in Figure 2. As expected, coal is the main source (>95%) of most elements with the exception of Ca mainly supplied by limestone (84%). Magnesium, Mn, and Sr occurring in marginal carbonates and/or within Ca-carbonate limestone in notable proportions (9-21%). Limestone also yields significant proportions of F (15%), and minor proportions of K, Rb, P, Ni, Cl, and Hg. The mixture of slurry waters is the major source of Cl (76%) and provides relatively high proportions of Mg, B, Na, Mn, and F. The significant proportion of Se (5%), Hg (2.7%), Mo (1%), and U (1%) supplied by this water stream should be pointed out.



RC: raw coal

Figure 2. Source of trace elements (relative proportion) at the whole power plant.

3.3. MASS BALANCE

Mass balances over PPC, FGD, and the whole installation are given in Table 7. The mass balance was carried out for all the analysed elements except for Cd, Tl, Bi, Nb, Eu, Tb, Ho, Tm, and Lu at PCC and at the whole installation and Ge, Pr, and Th in FGD, since the content of these elements were below of the analytical detection limits in the feed coal blend and limestone slurry (solid fraction), respectively.

Mass balance for mean values of the 2 sampling days (Table 7) is closed with excellent OUT/IN ratios at PCC, FGD, and at whole installation with values of 0.94 ± 0.12, 0.90 ± 0.32, and 0.89 ± 0.11, respectively. Very low concentrations of few elements in the FGD streams combined with the high stream flows lead to unreliable results when values are normalised for further mass balance calculations. It is for this reason that the FGD mass balance results are less accurate for some elements than those obtained for PCC system. In spite of this, most elements reached excellent OUT/IN ratios in the FGD ($0.8 \leq OUT/IN \leq 1.2$, Table 7). Regarding the mass balance for the whole installation, the OUT/IN ratios are relatively close to 1 ($0.8 \leq OUT/IN \leq 1.2$). However, the Hg closures for PCC (0.78) and whole installation (0.73) are a notable exception. These relatively low Hg OUT/IN ratios are most probably due to a partial loss of Hg by evaporation in the coal and limestone pulverisation mills. At this power plant, warm air is injected in the pulverisation mill during the coal pulverization process, reaching temperatures around 100-150ºC that may produce a partial evaporation of Hg. Preliminary laboratory tests reveal that around 16% of Hg is lost at the milling conditions used in the power plant. Considering 16% loss of Hg in the mills, the mass balance in the PCC system is closed with an out/in ratio of 1.0, and 0.9 for the whole plant. In order to corroborate this finding, the loss of Hg will be measured in the mills in subsequent samplings at this power plant.

In spite of the above issue, the Hg OUT/IN ratios at this power plant are lower than those reported by Meij and te Winkel (2006), and are similar to those reported in other studies (Aunela-Tapola et al., 1998).

Table 7. Mass balance in the PCC (boiler + ESP), FGD, and whole installation of the power plant.

Mean	PCC			FGD			Whole installation		
kg/h	In	Out	OUT/IN	In	Out	OUT/IN	In	Out	OUT/IN
Al	6860	6500	0.95	164	160	0.98	6968	6655	0.96
Ca	2128	1874	0.88	11806	10580	0.90	13712	12448	0.91
Fe	7201	6396	0.89	105	106	1.01	7281	6498	0.89
Na	92	63	0.69	22	21	1.23	115	85	0.74
S	10404	10278	0.99	10509	9103	0.87	11051	9220	0.83
K	618	481	0.78	64	53	0.84	664	533	0.80
Mg	385	327	0.85	338	297	1.05	734	624	0.85
g/h									
Cl	10362	13694	1.32	78884	62445	0.86	76511	63196	0.83
F	38275	36857	0.97	43057	47199	1.13	49289	52109	1.06
Hg	16	13	0.78	11	11	0.97	17	12	0.73
Li	13571	13768	1.01	325	274	0.90	13811	14026	1.02
Be	586	516	0.88	1	0.4	0.44	586	516	0.88
B	8342	9299	1.11	3618	2634	0.91	11600	11392	0.98
Sc	913	1054	1.15	45	41	0.94	948	1094	1.15
Ti	275468	255746	0.93	9444	9323	0.99	282950	260478	0.94
P	109843	90039	0.82	5573	6224	1.12	115033	96263	0.84
V	10997	9893	0.90	368	331	0.91	11267	10201	0.91
Cr	7384	7051	0.95	267	238	0.89	7567	7270	0.96
Mn	15967	15287	0.96	6574	6430	1.35	25627	21694	0.85
Co	1765	1575	0.89	58	49	0.90	1815	1623	0.89
Ni	3906	3633	0.90	308	224	0.75	4158	3708	0.89
Cu	3354	2959	0.88	92	115	1.27	3435	3069	0.89
Zn	12653	13558	1.07	41	27	0.91	12675	13556	1.07
Ga	2206	2098	0.95	48	41	0.87	2237	2137	0.96
Ge	386	347	0.90	0.7	0.6	0.97	386	347	0.90
As	4031	3475	0.86	82	99	1.23	4097	3564	0.87
Se	291	324	1.10	164	178	1.14	314	372	1.18
Rb	3756	3748	1.00	273	216	0.80	3934	3962	1.01
Sr	50137	46813	0.93	5394	5540	1.01	55358	52267	0.94
Y	2585	2398	0.93	74	65	0.88	2648	2461	0.93
Zr	8365	9331	1.12	244	246	1.01	8562	9568	1.12
Nb	1125	788	0.70	26	25	0.96	1146	813	0.71
Mo	577	580	1.01	9	6	0.71	583	583	1.00
Sn	370	355	0.96	-	-	-	373	361	0.97
Sb	182	148	0.81	-	-	-	182	148	0.81
Cs	682	678	0.99	0.5	0.3	0.79	682	678	0.99
Ba	32181	31871	0.99	736	751	1.02	32746	32592	1.00
La	2817	2695	0.96	80	69	0.86	2878	2761	0.96
Ce	6742	6270	0.93	176	145	0.82	6871	6408	0.93
Pr	638	643	1.01	-	-	-	638	643	1.01
Nd	2734	2740	1.00	87	81	0.93	2805	2819	1.00
Sm	552	567	1.03	0.5	0.2	0.40	552	567	1.03
Gd	560	579	1.03	0.4	0.2	0.50	560	579	1.03
Dy	388	397	1.02	0.3	0.2	0.67	388	397	1.02
Er	192	199	1.03	0.2	0.1	0.50	192	199	1.03
Yb	218	225	1.03	0.2	0.1	0.50	218	225	1.03
Hf	259	305	1.18	0.2	0.1	0.50	259	304	1.17
Pb	2470	2542	1.03	52	65	1.26	2517	2603	1.03
Th	1253	1302	1.04	-	-	-	1277	1301	1.02
U	940	1021	1.09	102	122	1.24	1053	1142	1.08
Mean			0.94			0.90			0.89
std			0.12			0.29			0.11

3.4. PARTITIONING AND BEHAVIOUR OF TRACE INORGANIC POLLUTANTS IN THE BOILER AND ESP

In accordance with the volatility of the elements at the boiler and at the ESP, the elements can be classified as follow:

i. *Low volatility* elements (>80% in FA and <20% in BS): Tl, Mo, Sn, Zn, Pb, Ga, Hf, Cs, V, Th, Li, Al, P, Nb, Ti, Co, Y, Rb, Ce, La, Cu, Zr ,Cr, K, Fe, U, Ni, Sr, Mn, Ge, Ca, Be, Mg, Na, and REE's.

ii. *Moderately volatile elements with high condensation potential in FA and IN-FGD PM*: Selenium, B, and As (62-96%) show a high retention in FA, with a low proportion (0.03-22%) in gas phase (Figure 3).

iii. *Highly volatile elements*: this group includes the most volatile elements, S, Cl, Hg, and F (86-99% in gas phase) (Figure 3).

The volatile behaviour of Hg at ESP may be significantly modified by the operational conditions of power plants. The power plants equipped with $DeNO_x$ facilities and fed with a Cl-rich fuel give rise to high proportions of Hg (50-91%) with FA for disposal (Meij and te Winkel, 2006; Meij, 2006) since these conditions promote the oxidation of Hg^0 to Hg^{2+} (Meij et al., 2002; Meij and te Winkel, 2006). SO_2 concentration in the combustion flue gas is another important operational factor. Researches indicate that high S/Cl ratios promote the occurrence of HCl, depleting Cl_2 concentrations (Lindbauer et al., 1992; Raghunathan and Gullet, 1996). The high S/Cl ratio in the feed coal blend at this power plant promotes the presence of HCl and the subsequent formation of gaseous $HgCl_2$. The Hg gaseous sampling and speciation (Table 5) demonstrate that most of the Hg that escapes from the ESP is oxidised Hg (75%), which indicates a relatively high oxidation of elemental Hg in the coal combustion. The low presence of lime (traces) and unburned carbon (0.7%) in FA accounts for low Hg retention (10%) in FA.

The moderate volatility of Se, As, and B is due to their major sulphide (Se and As) and organic (B) affinity in raw coals (Querol et al., 1995). It is assumed that gaseous Se, B, and As escapes from the ESP as elemental Se and SeO_2 (López-Antón et al., 2007), H_3BO_3 and HBO_2 (Noda and Ito, 2008), and As_2O_3 (Díaz-Somoano et al., 2006), respectively.

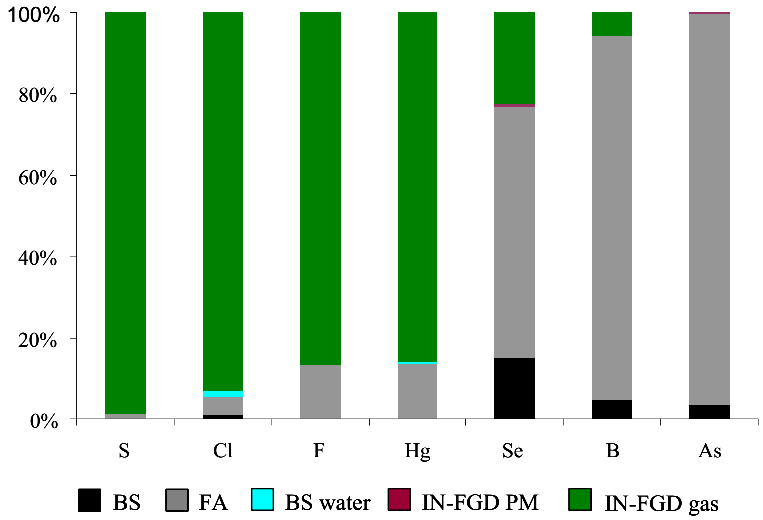


Figure 3. Partitioning of the highly and moderately volatile elements after combustion.

3.5. PARTITIONING AND BEHAVIOUR OF TRACE INORGANIC POLLUTANTS IN THE FGD SYSTEM

Limestone, IN-FGD gas, IN-FGD PM as well as the mixture of slurry waters into the scrubber are the sources of elements in the FGD system.

i. *Limestone is the major input source* (53-100%) of As, Co, Sc, P, Ca, Nd, Ti, Ce, Zr, La, Y, Al, Nb, Fe, Pb, Li, Sr, Ga, Rb, Ba, V, Sn, Cr, Cu, K, U, and Ni.

ii. *IN-FGD gas largely contributes to* S, Hg, Se, and F inputs to FGD (74-97%). The re-circulation of the filtered water also accounts for a relatively significant input of Se (16%) via the mixture water stream.

iii. *IN-FGD PM is most prominent source* for most of the REEs, Hf, Ta, W, Bi, Ge, Zn, Sb, Be, and Tl.

iv. *Mixture of the slurry waters* are the most important input (58-90%) for Mg, Na, Mn, Cd, Tl, Mo, B, and Cl. The high water solubility of species of volatile elements such as B and Cl (Harivandi, 1999) and the re-circulation of the filtered water, account for significant inputs of these elements via the mixture water stream (78-83%). The mixture of the water slurries are also an important source of Zn (30%) because of the filtered water re-circulation.

Based on the proportion in the limestone-based FGD with forced oxidation (Figure 4), elements are grouped as detailed below. The relative proportions of each element in the outgoing streams are calculated with respect to their incoming proportion to FGD.

i) Elements retained in the gypsum sludge

i.1) Moderately and highly volatile elements IN-FGD retained in the gypsum sludge

Most of S (97%) enters FGD as gaseous species, and it is mainly retained as gypsum (90%). A low proportion of S (7.9%) escapes the FGD as gaseous SO_2 (Figure 4). Mercury mainly enters FGD in a gaseous form (95%), and is the element with the highest proportion (33%) that leaves FGD in a gaseous form. A significant proportion of Hg is retained in the gypsum sludge (66%). The relatively high retention of Hg in the gypsum sludge is in agreement with the major occurrence of low solubility Hg-sulphate (Hg^{2+}) in the FGD of this power plant (Rallo et al., 2010). Furthermore, insoluble and highly volatile Hg^0 species can be present in the gypsum sludge since 26% of elemental Hg is retained by FGD (Table 5). These data are in line with earlier works carried out by Yudovich and Ketris (2005), and by Meij et al (1994) and Meij and te Winkel (2006).

Fluorine is mainly supplied by IN-FGD gas (74%, Figure 4). However, a significant fraction (16%) of F enters the scrubber via limestone. A high proportion of F is retained in the gypsum sludge (91%) as fluorite (CaF_2, Meij and te Winkel, 2004), whereas a low proportion of F (1.3%) is emitted as gaseous species.

The IN-FGD gas (82%) is the prevalent source of Se IN-FGD (Figure 4). Relatively high fractions of Se are retained in the gypsum sludge (53%). Gypsum and calcium selenate di-hydrate ($CaSeO_4.2H_2O$) are iso-morphous and their lattice constants are very similar (Pedersen and Semmingsen, 1982; Kruger and Abriel, 1991) showing that selenate can substitute for sulphate in the gypsum structure (Freyer and Voigt, 2003; Fernández-González et al., 2006). Selenium is emitted in relatively high proportions (30%) as PM, whereas a low proportion (5.3%) of Se leaves FGD as a gaseous species. The Se enrichment in OUT-FGD PM can be attributed to: (i) the condensation of volatile Se (IV) species, probably SeO_2 (Meij, 2008), because of the low gas temperatures OUT-FGD (78°C); (ii) the entraining of dissolved droplets of selenium complexes (Akiho et al., 2010) in the aqueous phase of gypsum slurry; and (iii) the entraining of gypsum slurry particles by the OUT-FGD gas owing to the aforementioned substitution of selenate for sulphate in the gypsum structure.

i.2) Elements associated with the highly insoluble Al-Si fraction of limestone and retained as impurities in the gypsum sludge.

Phosphorous, Ca, Nd, Ti, Ce, Zr, La, Y, Al, Nb, Fe, Pb, Li, Sr, Ga, Rb, Ba, V, Sn, Cr, Cu, K, U, Ge, and Ni are incorporated in the gypsum sludge as impurities in a high proportions (75-100%). Nevertheless, notable amounts (23-0.2%) of U, Li, K, Sr, Ni, Sc, V, Cu, and Ba (in decreasing order) are dissolved in the aqueous phase of gypsum slurry (Figure 4). Germanium (98%) and Sn (89%) are mainly retained in the gypsum sludge but enter FGD in a particulate form. In spite of the moderately volatile behaviour of As, most of this element is supplied by limestone (84%) owing to the significant As content in limestone (2 mg/kg) and to the high continuous limestone flow (33t/h). High fractions (90%) of As are retained in the gypsum sludge, most probably as Ca-arsenate (Álvarez-Ayuso et al., 2006). Arsenic emission occurs predominantly as PM (6.6%); whereas a low proportion (0.3%) of As-bearing species is emitted in a gaseous form (Figure 4).

i.3) Elements IN-FGD as PM with a fraction retained in the gypsum sludge.

Beryllium, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Hf, Bi, and Th are the elements that escape from the ESP and enter the FGD as PM. The input and output percentage of these elements in the FGD system is not accurately determined because of the complexity of quantifying the IN and OUT-FGD PM owing to unsatisfactory analytical detection limits. It is worth noting that a very low content of a given element normalised to high flow rates may result in unreliable result which would lead to misleading conclusions. This would explain poor mass balance closure in the FGD system. However, their presence IN-FGD and the subsequent retention in the gypsum sludge are supported by the chemical composition of the filters IN and OUT-FGD and by the retention efficiencies (69-83%) of PM, as discussed in the 1.4 section.

ii) Elements present in the FGD water streams

ii.1) Elements supplied by the mixture of slurry water and those associated with limestone.

The high proportion (41-83%) of Mn, Na, and Mg dissolved in the mixture of slurry waters and their strong carbonate affinities in limestone account for a relatively rapid dissolution in the aqueous phase of limestone slurry (15-43%), which reacts with SO_2 to form the corresponding soluble sulphate complexes in the aqueous phase of gypsum slurry (Figure 4).

ii.2) Elements supplied by the mixture of slurry water and as PM IN-FGD.

The high proportion (30-65%) of Mo, Tl, and Zn dissolved in the mixture of slurry waters and those supplied as fine grain size particles (35-70%) suggests their progressive dissolution and enrichment in the aqueous phase of gypsum slurry and in the filtered water, respectively.

ii.3) Moderately and highly volatile elements dissolved in the aqueous phase of gypsum slurry.

Owing to the continuous water re-circulations to the scrubber, high fractions of B (78%) and Cl (83%) enter and leave (68 and 76%, respectively) FGD via the mixture water stream and in filtered water, respectively, as water soluble species. The high solubility of salts containing these elements promotes their gradual dissolution in the aqueous phase of gypsum slurry and their subsequent enrichment in filtered water after a number of water re-circulations to the scrubber (Córdoba et al ., 2011). Over 20% of these elements are retained in the gypsum sludge and only 0.9% of B and 2.1% of Cl are emitted in a gaseous form (Figure 4).

The FGD partitioning reveals that the retention in the gypsum sludge (55%) and the dissolution of the elements in the aqueous phase of gypsum slurry (28%) can be regarded as the main outputs of the FGD. The remaining outputs (17%) are OUT-FGD PM and gas. These retention percentages were calculated based on the inputs and outputs of the elements in the FGD system. Elements that enter FGD as PM were excluded from consideration owing to the unsatisfactory analytical detection limits in the FGD streams.

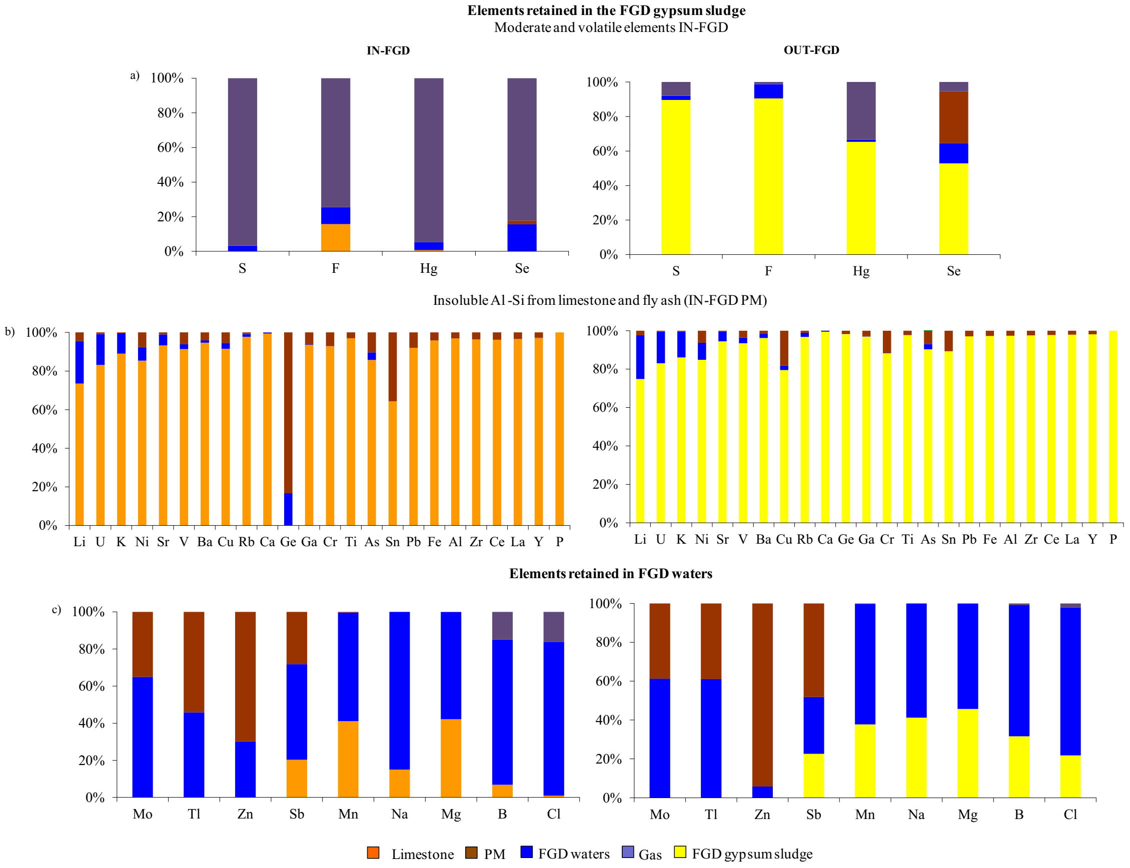


Figure 4. Distribution and partitioning of the elements IN and OUT-FGD streams. (a) IN-FGD (left) and OUT-FGD (right) partitioning of the highly and moderately volatile elements retained in FGD gypsum sludge. (b) IN-FGD (left) and OUT-FGD (right) partitioning of elements associated to the Al–Si of limestone and those as fly ash (PM IN-FGD) retained in the FGD gypsum sludge. (c) IN-FGD (left) and OUT-FGD (right) partitioning of elements retained in FGD waters.

The retention efficiencies obtained by the partitioning studies of FGD displayed a high abatement capacity (92-99%) for most gaseous elements (S, F, Cl, and B) and a relatively high abatement for Se (65%) and Hg (67%). These retention efficiencies are in agreement with those obtained directly by gas measurements IN and OUT-FGD. Thus, S retentions of 92% and 94% are obtained by partitioning studies and gas measurements, respectively. These values attained, 98 and 99% for F, 99 and 96% for B, and 98 and 97% for Cl. The retention efficiencies between partitioning and gas measurements show some discrepancies for Se (65 and 94%, respectively), and slightly differences for Hg (67 and 72%). These differences are attributable to the relatively high emission of Se as OUT-FGD PM and the loss of Hg by evaporation in the coal and limestone pulverization mills, respectively.

It is worth mentioning that the retention and emissions (OUT-FGD PM and gas) percentages obtained in this FGD partitioning are those calculated with respect to the incoming proportion to FGD. Thus, the complete retention and emissions percentages considering the whole installation, with the total input and outputs, may differ.

3.6. ABATEMENT CAPACITY OF WHOLE INSTALLATION FOR TRACE INORGANIC TRACE POLLUTANTS

The partitioning for the whole installation (Figure 5) reveals that the whole output (as mean in %) of major and trace elements is FA (75%), followed by BS (11%), FGD-gypsum (7.9%), filtered water (2.9%), OUT-FGD PM (2.0%), OUT- FGD gas (0.8%), and BS water (0.01%). Thus, high proportions (86%) of most elements are retained by FA and BS.

Moderately volatile and highly volatile elements S, F, Cl, As, and B are retained with a very high efficiency when considering the whole plant (92, 99, 98, 100, and 100%, respectively), which reduces the gas proportions emitted to 7.9, 1.2, 2.1, 0.1, and 0.2%, respectively. The moderately and highly volatile Se and Hg are still retained by the whole system with relatively high proportions (89 and 71%). Arsenic (95%), B (71%), and Se (53%) are mainly retained by FA; S (89%), F (82%) and Hg (56%) by FGD-gypsum; and Cl (75%) by the filtered water.

FA (45-90%) is also the whole output of most non-volatile elements and some water soluble elements (Na, Mg, and Mn), the rest remaining mostly in the BS fraction (9-20%) and filtered water (1-23%). The retention of water soluble elements in the re-circulated filtered water and FGD-gypsum is due to the later contribution of limestone in the FGD system. These elements have limestone as their main origin in the FGD-gypsum.

The main contributions to the PM emissions are the non-retained fly ash by FGD and the particles and droplets from gypsum slurry entrained by the OUT-FGD gas. A notable fraction of Se, As, Zn, Cu, Ni, and Cr (Figure 5) is emitted as PM, Se (11%) being the element with the highest proportion emitted as PM most probably as result of the entraining of gypsum slurry particles by the OUT-FGD gas; whereas the gaseous emission of Hg (29%) is the only produced in a significant amount.

In accordance with our findings, an overall classification for elements for the whole installation based on the volatile behaviour and outgoing streams of PCC-FGD is established (Table 8).

The partitioning results of the trace pollutants at the ESP are similar to those reported by Querol et al (1995) and Alvarez-Ayuso et al (2006) for this power plant, and are consistent with the abatement potential for gaseous pollutants obtained at other wet FGD facilities (Meij, 2008).

Table 8. Classification and distribution of elements for the whole installation based on PCC-FGD outgoing streams.

Non-volatile elements	*Retained in FA and BS*	Tl, Mo, Sn, Zn, Pb, Ga, Hf, Cs, V, Th, Li, Al, P, Nb, Ti, Co, Y, Rb, Ce, La, Cu, Zr ,Cr, K, Fe, U, Ni, Sr, Mn, Ge, Be, Mg, Na, and REE's
	Retained in the FGD	Ca
Moderately volatile elements (High condensation potential in FA and PM)	*Moderately volatile elements retained in FA in the ESP*	B and As
	Mostly retained in the system but a fraction escaping ESP and FGD	Se (PM)
Highly volatile elements	*Retained in the FGD*	S, F, and Cl
	Fraction escaping from the FGD	Hg (Gas)

FA: fly ash; BS: boiler slag; PM: particulate matter

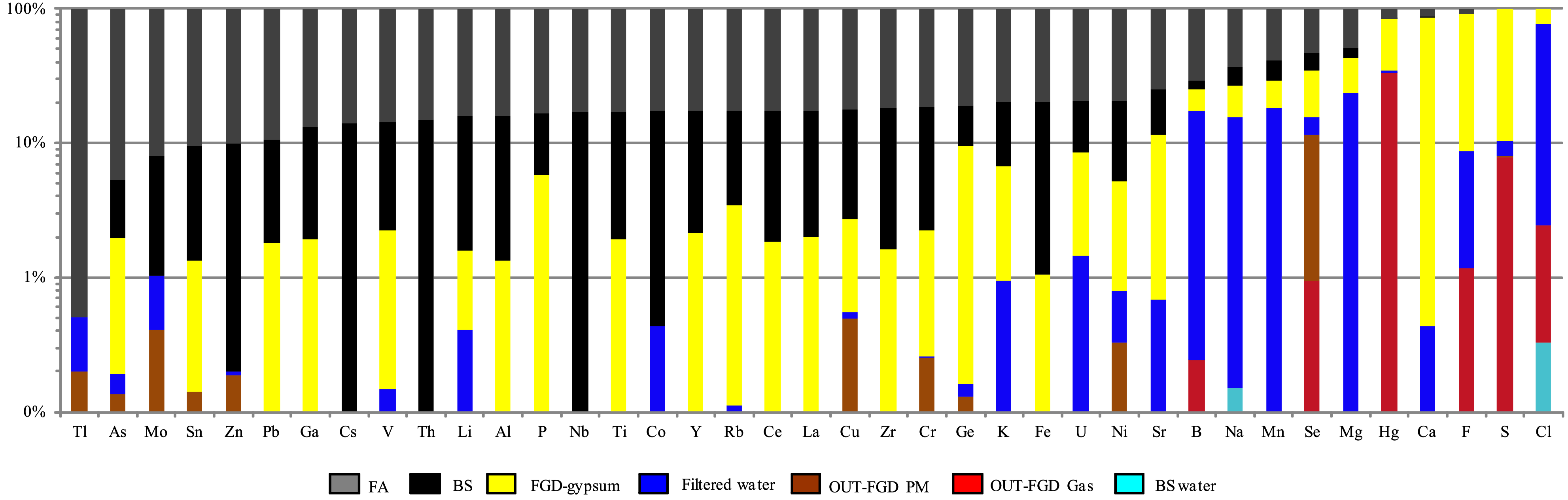


Figure 5. Distribution of the elements over output streams of the whole installation (PCC+FGD).

4. CONCLUSIONS

High proportions of most of the elements are retained as FA (>78%) and BS (<22%) in the ESP and in the boiler, respectively. The ESP retains 99.6%, and therefore a low proportion of ash (0.4%) enters the FGD as PM or gas.

In the wet limestone based-FGD a high retention capacity (92-100%) for S, Cl, F, Se, As, and B is attained with a subsequent reduction in their gaseous emissions below the limits established by the European directive 2001/80/EC for large combustion plants. A relatively high capacity (67 and 71%) for Hg is reached in the wet limestone based-FGD and for the whole installation, respectively. The PM emission levels are reduced down to 25 mg/Nm^3 (at 6 % O_2), far below the limits established by the mentioned directive.

The retention in the gypsum sludge and the dissolution of the elements in the aqueous phase of gypsum slurry and consequently in filtered water can be regarded as the main outputs of the FGD system. Sulphur, F, Hg, Se, and As are mainly retained in the gypsum sludge; whereas Cl and B are retained in the aqueous phase of gypsum slurry.

The main contributions to gaseous and PM emissions are the non-retained fly ash by FGD and the particles and droplets from gypsum slurry entrained by the OUT-FGD gas, especially gaseous Hg and particulate Se, As, Zn, Cu, Ni and Cr. The comparison of the emission rates of elements normalised to kg/year (to compare with the PRTR thresholds) in the period equivalent to operate at 100% capacity in this power plant (6467h), with the Pollutant Release and Transfer Register (PRTR, 2006) threshold values (for information purposes) brings to light that the emission of these elements should be regarded as of concern. The emission rate of gaseous Hg exceeds the PRTR threshold values whereas those of particulate As, Cu, Cr Zn, and Ni are close to these values. In spite of the high retention efficiencies, Cl and F emission rates are below but close to the PRTR threshold values.

Given that most of the aforementioned elements are partially dissolved in the aqueous phase of gypsum slurry, the above issue points out the crucial role of re-circulation of FGD water. Re-circulation promotes enrichment of elements in these waters with the consequent increase of emission by entraining particles and droplets from gypsum slurry by the OUT-FGD gas. Therefore, an increase in the efficiency of the demisters from wet scrubbers and/or other remediation actions are essential to prevent and reduce the gaseous and PM emissions.

Further work will focus on investigating the effect of the different operational conditions of power plants on the behaviour and speciation of major, minor, and trace inorganic pollutants in FGD streams.

Furthermore, the determination of leachable potential of trace inorganic pollutants retained in FGD-gypsum, especially F, should be investigated and remediation actions if required in view of disposal of this by-product.

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Additional findings to Article 1

3.3. MASS BALANCE

The relatively low Hg OUT/IN ratios obtained for the mass balance closure of the PCC and for the whole plant at PP1 were initially related with a partial loss of Hg by evaporation in the coal pulverization mills because of the injection of warm air during the coal pulverisation process. Preliminary laboratory tests revealed that around 16% of Hg is lost at the milling conditions. Considering 16% loss of Hg in the mills, the mass balance in the PCC system closed with an out/in ratio of 1.0, and 0.9 for the whole plant. However, the staff of the power plant confirmed us that warm air injected during the coal pulverisation also goes to the boiler. Therefore, there is no lost of Hg, and consequently the input of Hg to PCC, FGD, and for the whole plant is not altered by the pulverisation process of coal.

Subsequent research at PP1 was focussed on the Hg outputs around the boiler and the whole plant. Owing to the volatile behaviour of Hg a relationship between BS and Hg was discounted. It is for this reason that the research was focussed on FA produced at this coal-fired power plant.

At PP1, FA is captured and collected in 3 consecutive ESPs. According to the particle size distribution of FAs, the concentration of Hg should increase by decreasing the particulate size since most of volatile elements such as Hg tend to condense on the finest particles. Therefore, the highest concentration of Hg in FAs captured in the 3rd hopper could be expected. However, in the 2007 sampling campaign, FA was only collected from the 1st and 2nd ESP hoppers. It was then speculated that FA from the 3rd ESP hopper could also contain a significant concentration of Hg which could contribute to the Hg mass balance closure.

In order to determine whether the Hg concentration correlates with the particle size distribution of FA, we proposed to analyse the concentration of Hg in FAs from the 1st, 2nd, and 3rd ESP hoppers. However, the staff of the power plant could only provide us FA from the 3rd ESP hopper. In spite of this, samples of FAs from the 3rd ESP hopper were collected and analysed in 2012. The result of the Hg analysis showed that FA from the 3rd ESP hopper contained 0.25ppm of Hg a long way above 0.04ppm from the 2007 FA collected from the 1st and 2nd ESP hoppers.

Although we recognize that it is not accurate comparing contents in FAs collected in two different campaigns, we would like to highlight the following issues:

i) Prior studies from our group found a marked increasing trend of concentrations of volatile and moderately volatile trace elements from the 1st and 2nd hoppers to the 3rd hopper, following the sizing trend towards very fine grain size towards 3rd hopper.

ii) There is an order of magnitude of difference between the Hg content in the FAs from the 3rd hopper and 1st and 2nd hoppers, collected in the 2012 and 2007 campaigns, respectively.

Taking into account the above features, we do not discard that the low Hg OUT/IN mass balance ratios for PCC and for the whole plant in 2007 might be due to the fact that FA from the 3rd ESP hopper was not sampled in the 2007 sampling. Although in volume FAs from the 3rd hopper is lower than that from the 1st and 2nd hopper, the high concentration of Hg in the FA from 3rd could contribute to the Hg mass balance closure.

3.6. ABATEMENT CAPACITY OF WHOLE INSTALLATION FOR TRACE INORGANIC TRACE POLLUTANTS.

According to the results of the speciated gaseous measurements of Hg at PP1, Hg^{2+} was more prone to be retained (89%) by the FGD system, while the trapping efficiency for Hg^0 was much lower (26%). In this regard, field data (Chang and Ghorishi, 2003) have shown that, in general, <70% Hg removal efficiency is achieved by wet FGD systems due to two main factors: *(1)* Hg^0 can barely be dissolved in the aqueous phase of the absorbent, leading to low emission abatement efficiencies for this Hg species; and *(2)* some of the absorbed Hg (Hg^{2+}, as e.g., $HgCl_2$) is probably converted back to Hg^0 and re-emitted.

We found it impossible to determine whether the low retention of gaseous Hg^0 at PP1 was due to the low aqueous solubility of this Hg species. However, we were able to test the feasibility of the reemission mechanism of Hg^0 based on the oxidation-reduction reaction of S (IV) species with Hg^{2+} to form Hg^0 and SO_4^{2-} at PP1 under the scrubber conditions in 2007.

Thermodynamic modelling with the input of experimental data is a straightforward way to determine whether a chemical reaction is feasible under specific industrial conditions; thermodynamic calculations carried out to elucidate the behaviour of gaseous Hg at PP1.

Thus, it is postulated that in line with the 2007 scrubbing solution at PP1, $SO_{2\ (aq)}$ once dissolved in the aqueous phase of the scrubbing solution is converted to SO_3^{2-}:

$$SO_{2\ (aq)} + H_2O_{\ (aq)} \rightarrow 2H^+_{\ (aq)} + SO_3^{2-}{}_{(aq)} \quad \text{(R1)}$$

Sulphite would act as a reducing agent for Hg^{2+} according to the follow reaction (at pH 7.6):

$$SO_3^{2-}{}_{(aq)} + \frac{1}{2} O_2 \rightarrow SO_4^{2-}{}_{(aq)} \quad \text{(R2)}$$

$$Hg^{2+}{}_{(aq)} + H_2O \rightarrow Hg^0{}_{(g)} + \frac{1}{2} O_{2\ (g)} + 2H^+{}_{(aq)} \quad \text{(R3)}$$

An overall reaction is obtained by combining R1, R2 and R3 and assuming that most $Hg^0{}_{(aq)}$ would escape to the gaseous phase:

$$SO_{2\ (aq)} + Hg^{2+}{}_{(aq)} + 2H_2O \rightarrow Hg^0{}_{(g)} + SO_4^{2-}{}_{(aq)} + 4H^+{}_{(aq)} \quad \text{(R4)}$$

The thermodynamic reliability of the $Hg^0{}_{(g)}$ re-emission can be demonstrated by comparing the actual Ionic Activity Product (IAP) obtained from the PP1 aqueous experimental data and the equilibrium constant (K) of the Hg^0 re-emission formation derived from the thermodynamic database. The IAP is calculated as:

$$IAP = [aHg^0 \times a\,(H^+)^4 \times aSO_4^{2-}] / [aSO_2 \times aHg^{2+} \times a\,(H_2O)] \quad \text{(R5)}$$

where aSO_4^{2-}, aH^+, and aHg^{2+} are calculated from their solute concentrations and the extended Debye-Huckel model (PHREEQc), and $aSO_{2\ (g)}$ and $aHg^0_{\ (g)}$ are equated with their partial pressure in the PP1 scrubber. The IAP calculated for the scrubber conditions in 2007 is $10^{-23.08}$ a long way below $10^{15.09}$, which is the equilibrium constant of the re-emission of Hg^0 at 60ºC. The IAP<K confirms the thermodynamic feasibility of the postulated process. Therefore, in 2007 at PP1 the relatively lower retention of $Hg^0_{\ (g)}$ in comparison with that of Hg^{2+} might be associated to the re-emission of $Hg^0_{\ (g)}$. However, the low abatement efficiencies for $Hg^0_{\ (g)}$ as a result of the low aqueous solubility of this Hg species into the scrubber cannot be discounted.

ARTICLE 2

The retention capacity for trace elements by the flue gas desulphurisation system under operational conditions of a co-combustion power plant

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ABSTRACT

Water re-circulation to the scrubber and co-combustion of coal with petroleum coke are probably the most significant factors that may affect the retention capacity for trace elements in a coal-fired power plant equipped with a forced-oxidation Flue Gas Desulphurisation (FGD) system. The water re-circulation favours the gradual saturation of most elements in the aqueous phase of gypsum slurry with the subsequent increase in emission by entraining particles and droplets in the outgoing gas of FGD (OUT-FGD). The co-combustion of coal with petroleum coke enhances the formation of gaseous chlorides species, especially of Hg, and the formation of condensed species of Cu, Cr, Ni, Na, Cd, and Zn in OUT-FGD, respectively. High retention capacity (83-100%) for S, Cl, F, As, and B is attained by the whole plant. Selenium and Hg are still retained by the whole plant with relatively high proportions (75-97% and 68-86%). However, significant proportions of Se (23%) in 2007 and Hg (33%) in 2008 are emitted as PM and in a gaseous form, respectively. Remediation actions for gaseous and PM emissions are relevant given the role of the filtered water re-circulation increasing the particles emissions OUT-FGD.

Key words: co-combustion; trace elements; FGD; OUT-FGD gas.

1. INTRODUCTION

Over the past two decades, the worldwide demand for electricity and the environmental regulations have lead to an obliged improvement of the coal combustion techniques by the use of the co-combustion matter (such as petroleum coke, biomass, and sewage sludge) and expanded use of Flue Gas Desulphurisation systems (FGD). Co-combustion is considered a complementary alternative for the economic existence of coal-fired power plants to lower the cost implications. In this regard, the FGD technology has also made considerable progress in terms of efficiency, reliability, and cost (Soud, 2000). In Europe, a number of pulverised coal combustion (PCC) power plants implemented the addition up to 40% petroleum coke to the feed coal (Izquierdo et al., 2007). However, the petroleum coke combustion may give rise to high SO_2 emission, which voids its choice as fuel unless an FGD is available. Co-firing petroleum coke may also modify the chemical environment of Cl because of the resultant high concentrations of HCl in the gaseous stream. For a number of elements, an increase in the HCl concentration favours the formation of gaseous species; whereas increasing concentration of SO_2 in the gas composition enhances the formation of sulphate condensed species (Díaz-Somoano et al., 2006). Indeed, previous research (Font et al., 2007) has shown that, compared to a fuel blend with 4% petroleum coke, a blend with 30%, the increases volatility of Cl, F, Se, S, Tl, Sn, B, and Hg and produces an enrichment in V, Ni, and Mo in fly ashes (FA). However, the partial or total replacement of coal by an alternative fuel in the feed blend may modify not only the emission volume or the content of a number of elements, but also their partitioning and speciation in the solid by-products (Izquierdo et al., 2008).

In power plants located where water resources are scarce, the re-circulation of the water to the scrubber from gypsum slurry filtration is common. Recent studies (Córdoba et al., 2011) on the enrichment of trace inorganic pollutants in the re-circulated waters, revealed that the re-circulation of filtered water gives rise to unusually high concentrations of some elements of major environmental concern such as Al, B, F, Se, Cl, Ni, Zn, and especially Hg and U. This causes the emission of such elements by entraining particles and droplets from gypsum slurry in the OUT-FGD gas, and/or the precipitation of solids in the FGD-gypsum end-product.

Some FGD-gypsum exceeds the maximum value of fluorine in the leachate accepted at non hazardous waste landfills (Álvarez-Ayuso et al., 2006). In order to avoid this, the use of additives has been proposed as measure for stabilising the FGD-gypsum before its disposal to mitigate fluoride leaching (Álvarez-Ayuso et al., 2007, 2008a, 2008b).

The study on a FGD system that operates using an Al-additive and with water re-circulation to the scrubber is, therefore, a crucial subject for an accurate estimation of the emissions of air pollutants, especially of HCl and SO_2, derived from co-firing. Accordingly, the purposes of the present study were i) assess the abatement capacity of the forced-oxidation FGD system with water re-circulation for trace elements at a coal-fired power plant under operational conditions of co-combustion; ii) establish the mass balance of a broad array of elements for the whole installation (PCC+FGD); iii) determine the partitioning and fate of the trace elements based on their retention in the gypsum sludge and/or dissolution into FGD waters; and iv) identify the elements of concern affected by the co-firing of coal with petroleum coke, the addition of Al, and by the water re-circulation.

2. MATERIALS AND METHODS

2. 1. SAMPLE COLLECTION

The sampling campaigns at the large co-combustion power plant (1200MW) were carried out on two consecutive years in 2007 (14-15th November) and 2008 (26-27th November). The samplings were performed at 100% MCR (maximum capacity) and 100% desulphurisation of the unit 3. The power plant was fired with 82:18 and 84:16 coal/petroleum coke blends for samplings conducted in 2007 and 2008, respectively. The coal is a blend of local and low-S imported bituminous coals and a local high-S coal. The petroleum coke is a blend of local and imported petroleum cokes.

The operational conditions of the power plant in the two sampling campaigns are summarised in Table 1. The relatively higher input flow of the feed fuel blend in 2008 (152 t/h) than in 2007 (143 t/h) it should be noted in view of the partitioning results of elements around the PCC (boiler + electrostatic precipitator, ESP) and FGD system.

Table 1. Operational conditions of the power plant in 2007 and 2008.

Operational parameters of the power plant	2007	2008
Mean of produced electricity (Mw.h)	2990811	2895172
Load of power plant (capacity)	100%	100%
Input feed fuel (t/h)	143	152
High S/low S fuel ratio	67/33	67/33
Coal/petroleum coke ratio	82:18	84:16
Output of FA (t/h)	35	37
Temperature of the ESP (^oC)	149	148
Output of boiler slag (BS, t/h)	4.4	5.1
Flow BS water (m^3/h)	54	51
Input flow of limestone (t/h)	8.6	7.9
Output flow of dry (60^oC) gypsum	16	11
Flow process water (t/h)	54	52
Flow limestone slurry water (t/h)	25	20
Flow gypsum slurry water (t/h)	28	28
Flow filtered water (t/h)	28	28
Gaseous stream in FGD (Nm^3/h)	1213935	1400852
Gaseous stream out FGD (Nm^3/h)	1311147	1507790
Oxidation Abs Nm^3/h	6.6	7.7
Al-additive (kg/h)	68	14

The PCC-FGD system involves a number of water streams that can be separated into 2 groups (Figure 1):

i) Water streams not directly related to FGD: process water and Boiler Slag (BS) water. The process water is derived from metamorphic and igneous rocks and is used in BS cooling and drainage giving rise to BS water which is stored in a water reservoir.

ii) FGD water streams: limestone and gypsum slurries, and filtered water. Limestone slurry is prepared with process water and is introduced into the scrubber. Gypsum slurry is the result of the absorption of SO_2 in limestone slurry. In this article, the terms gypsum and limestone slurry are used for the total fraction of the slurries (solid + water) while the terms aqueous phase of gypsum and limestone slurry are employed for the water fraction of the total slurries. Gypsum sludge is referred to the solid fraction of gypsum slurry, and FGD-gypsum is the solid end-product after filtration process.

Filtered water is the water stream that results after filtration and dilution of the aqueous phase of gypsum slurry. The dilution is carried out by adding of water which leads to lower concentrations of most of elements, especially Cl, in the filtered water than those in the aqueous phase of gypsum slurry. Filtered water is directly re-circulated to the scrubber after the dilution process. This result in limestone slurry water/filtered water mixture ratio of 0.47/0.53 (2007) and 0.42/0.58 (2008) into the scrubber. The water mixture ratio of limestone slurry and filtered water constitute the mixture of slurry waters.

The mixture of slurry water constitutes the main water input into the scrubber; whereas the water output of the FGD system is represented by i) the loss of crystallisation water from gypsum (12%); ii) the water evaporation (5.5%) due to the contact with the emitted OUT-FGD gas in the scrubber; and by iii) the aqueous phase of gypsum slurry. These inputs and outputs of water constitute the water balance through the FGD system.

An aluminium additive ($Al_2(SO_4)_3$) is injected into the scrubber to boost the desulphurisation efficiency as a consequence of the low porosity of limestone. Aluminium may form stable $Al\text{-}F_x$ aqueous complexes reducing the precipitation of CaF_2 particles on the limestone surface and, therefore, enhancing the reactivity of Ca with SO_2. The $Al_2(SO_4)_3$ addition varied considerably between the two sampling campaigns. Up to 68 kg/h were added in 2007, whilst the dosage was reduced to 14 kg/h in 2008.

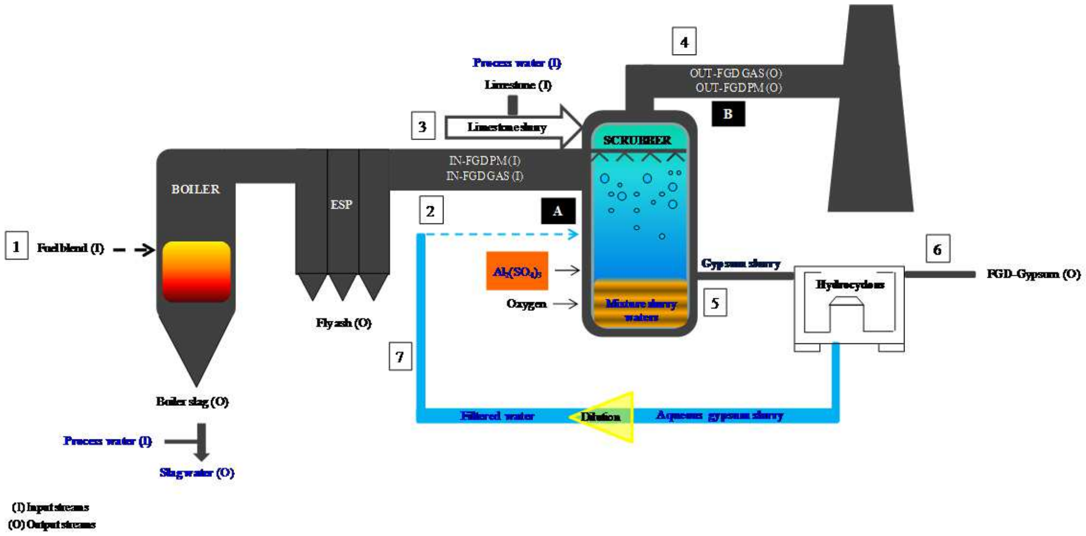

Figure 1. Diagram of the PCC+FGD system at PP2. 1: Injection of the feed fuel blend to the boiler; 2: Gas and PM input flow into the scrubber after combustion process; 3: Limestone slurry introduced and sprayed into the scrubber to react with SO_2; 4: Cleaned gas and PM flow OUT-FGD; 5: Formation of gypsum slurry as result of the desulphurisation process; 6:Filtration of gypsum slurry by hydro-cyclones= aqueous phase of gypsum slurry and FGD-gypsum production; 7: Re-circulation of filtered water to the scrubber after dilution process.

Isokinetic measurements of gaseous streams were performed at two sampling points (Figure 1), IN-FGD (A) and OUT-FGD (B), simultaneously. Each sampling run lasted about 2.5h. At each sampling point, two trains of sampling systems were assembled with specific trapping solutions, one for the capture of anions and metals, and the other for the capture and speciation of Hg. In the first case, the gas sampling system was devised according to EN 1911 (EC, 1998) and EN 14385 (EC, 2004). In such a system, two impingers 100 mL of de-ionized H_2O (or MilliQ grade water) and two filled with 6 w% HNO_3 and 10 w% H_2O_2 were assembled to determine the concentrations of anions and metals, respectively, in a ice bath.

The sampling and speciation of gaseous Hg (Hg^0 and Hg^{2+}) was devised according to EN 13211 (EC, 2011) and Meij and te Winkel (2006). A train of dark glass impingers in an ice bath was used. The Hg sampling system (Meij and te Winkel, 2006) consists of a first impinger filled with 100 mL of HCl to capture Hg^{2+}, the second impinger containing 3 w% H_2O_2 for SO_2 removal (150mL at point A and 100mL at point B), and the two last impingers containing 4 w% $K_2Cr_2O_7$ with 20 w% of HNO_3 for Hg^0 trapping.

The particulate matter (PM) that escapes from the ESP and FGD is defined and termed fly ash and fly dust, respectively, by Meij (1994) although the terms IN and OUT-FGD PM are used in this article. A quartz filter was placed before the isokinetic train for IN and OUT–FGD PM collection in the Hg sampling. Polytetrafluoroethylene (PTFE) filters were used for the PM capture of anions and cations instead of quartz filters, since HF reacts with quartz to form highly volatile SiF_6^{2-} with a subsequent loss of fluorine.

In the 2 sampling campaigns a total of 14 solid streams: 6 local and imported coals, 2 petroleum coke, and other solid streams (feed fuel blend, BS, FA, PM, limestone, and FGD gypsum) were collected, homogenised, and analysed. The water streams process water, BS water, filtered water, and the limestone and gypsum slurries were also collected, homogenised, and analysed. A sampling per day was performed for each material, collecting two sample sets in the corresponding sampling campaigns.

2.2. CHEMICAL ANALYSIS

The solid samples were acid-digested in duplicate by using a special two-step digestion method devised by Querol et al (1993). The resulting solution was then analysed by Inductively-Coupled Plasma Atomic-Emission Spectrometry (ICP-AES) for major and minor elements, using the Advantage Radial ER/S device from Thermo Jarrell-Ash. Semi-quantitative analyses were performed to know the range of element concentrations as well as the matrix and the possible spectral interferences. The calibration was performed by means of the international certified standard (1000 and 10.000 ppm). Most of the trace elements were analysed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS), using the X-SERIES II device from Thermo Fisher SCIENTIFIC. The quantitative analyses were performed with an extern calibration, using an extern standard of similar matrix of the samples, which covered concentrations range expected forming the calibration lines. The intern correction was carried out by means of an intern standard (In 10 ppb). The FA and coal international reference material (NBS1633b and SARM19) were also digested to determine the accuracy of the analytical and digestion methods.

Chlorine content of solid samples was determined by following the ASTM D4208 (2007) method using a calorimetric bomb to obtain chlorine in solution, which is measured by High Performance Ion Chromatography (HPIC). The determination of F in the solid samples was performed according to the pyro-hydrolitic extraction method described in ISO 11724 (2004) standard methods and subsequently measured by HPIC. The Hg analyses were directly carried out on solid and liquid samples using a LECO AMA 254 Gold Amalgam Atomic Absorption Spectrometer (GA-AAS).

The mineralogy of solid samples was determined by X-ray powder diffraction (XRD) with a Bruker D5005 diffractometer with monochromatic Cu Kα1,2 radiation operated at 40KV and 40mA., from 4 at 60° of 2theta range, and a step size of 0.05° and 3s/step.

Water streams and trapping solutions from flue gas sampling were directly analysed by ICP-AES and ICP-MS for major and trace elements, respectively. Chloride contents were measured by HPIC whilst fluorides were determined by ion selective electrode.

The levels of IN and OUT-FGD PM were obtained by standard gravimetric methods. Mercury particulate was determined by GA-AAS directly on filter samples. The contents of major and trace elements in the filters were determined by ICP-AES and ICP-MS, respectively. A prior filter digestion using $HF:HNO_3:HClO_4$ was carried out to obtain the bulk dissolution of the samples for the subsequent analysis.

2. 3. MASS BALANCE

Mass balance (MB) was calculated by normalising the concentration of each element in a given stream with the corresponding stream flow for the PCC (boiler + ESP), FGD system, and for the whole installation in the two sampling campaigns. The MB was conducted for each sampling day and no significant differences between the mass balances were observed. The very high repeatability provided us with reliable raw data for the MB closure and an overall MB, which comprises the mean values of each day, for each sampling campaign is reported in this study. The flows considered for the whole MB calculations are detailed as follow:

$$MB = [(Flow_{\text{FGD-gypsum}} \times Ci_{\text{FGD-gypsum}}) + (Flow_{\text{PM OUT-FGD}} \times Ci_{\text{PM OUT-FGD}}) + (Flow_{\text{GAS OUT-FGD}} \times Ci_{\text{GAS OUT-FGD}}) + (Flow_{\text{Filtered water}} \times Ci_{\text{Filtered water}}) + (Flow_{\text{BS}} \times Ci_{\text{BS}}) + (Flow_{\text{BS water}} \times Ci_{\text{BS water}}) + (Flow_{\text{FA}} \times Ci_{\text{FA}})] / [(Flow_{\text{Limestone}} \times Ci_{\text{Limestone}}) + (Flow_{\text{Mixture water}} \times Ci_{\text{Mixture water}}) + (Flow_{\text{Process water}} \times Ci_{\text{Process water}}) + (Flow_{\text{Fuel blend}} \times Ci_{\text{Fuel blend}})] \quad (1)$$

where the output and input flows ($Flow_x$) are the flows for a given stream ($_x$) IN and OUT of the whole installation; and Ci is the mean concentration of a given element in the corresponding stream IN and OUT of the whole installation.

The Ci of the mixture water is the concentration of a given element in the aqueous phase of limestone slurry and filtered water with respect to the proportion of each water stream in the scrubber (0.53/0.47 and 0.58/0.42 mixture ratio of limestone slurry and filtered water in 2007 and 2008, respectively).

3. RESULTS AND DISCUSSION

3.1. MINERALOGICAL AND CHEMICAL CHARACTERISATION OF SOLID STREAMS

3.1.1. Coal blend, petroleum coke, and feed fuel blend

Quartz, illite, kaolinite, gypsum, and traces of pyrite and calcite/dolomite are the main crystalline phases of the local and the imported bituminous coals. Graphite is the crystalline phase detected in the local and imported petroleum cokes. Quartz, illite, kaolinite, gypsum, and traces of pyrite and calcite are the detectable crystalline phases of the feed fuel blends. Few differences between sampling campaigns are found.

Coal and petroleum coke blends present a similar chemical composition between 2007 and 2008, respectively, with the exception of the higher concentrations of S and Cl in the 2007 petroleum coke than in 2008, and the concentration of S in the 2008 coal blend, higher than in 2007 (Table 2).

The feed fuel blends reveal no significant differences between sampling campaigns. However, it is should be noted the lower concentration of V, Ni, and Ti and the higher levels of F in the 2008 feed fuel blend than in 2007 (Table 2). The former is due to the use in 2008 of an imported petroleum coke with low contents of V, Ni, and Ti; whilst the latter may be attributed to non-homogeneous distribution of F in the feed fuel sample.

Both feed fuels are characterised by a high Cl and Hg content (Table 2) in comparison with the content of Cl in coal from other coal-fired power plants (Córdoba et al., 2012) and the content of Hg in the Yudovich and Ketris (2006) worldwide coal range, respectively. The high concentration of Cl and Hg in the feed fuel blends may be associated to the relatively high concentration of Cl in the petroleum cokes, and the relatively high concentration of Hg in the coal blends.

Table 2. Mean concentration of major, minor, and trace elements in solid streams in 2007 and 2008.

	2007			2008		
	Coal blend	Petroleum coke	Fuel blend	Coal blend	Petroleum coke	Fuel blend
% dry basis (db)						
Al_2O_3	6.7	0.03	6.1	3.2	0.03	6.2
CaO	0.7	0.02	0.7	0.7	0.04	0.7
Fe_2O_3	2.3	0.02	2.1	2.6	0.01	1.9
Na_2O	0.3	0.03	0.2	0.1	0.02	0.2
SO_3	3.0	9.8	4.5	7.5	5.3	4.0
K_2O	1.3	0.02	1.2	0.8	<0.01	1.1
MgO	0.6	<0.01	0.5	0.4	<0.01	0.5
mg/kg (db)						
Cl	172	301	118	160	285	96
F	174	74	186	165	85	229
Hg	0.3	0.1	0.2	0.3	0.1	0.2
Li	63	<0.1	56	68	<0.1	54
Be	1.7	<0.1	1.5	1.7	<0.1	1.4
B	43	8.7	32	55	14	39
Sc	6.7	<0.1	5.3	5.6	<0.1	5.3
Ti	1679	6.8	1535	1849	3.3	1271
P	566	12	411	469	5.8	494
V	152	1727	447	64	1329	285
Cr	39	2.2	46	38	1.1	32
Mn	154	1.2	136	163	0.5	115
Co	11	0.6	8.6	12	1.2	9.2
Ni	43	345	90	23	268	64
Cu	27	0.6	22	31	2.1	25
Zn	78	16	50	69	12	49
Ga	11	1.0	9.7	11	0.9	8.5
Ge	1.0	<0.1	<0.1	0.9	<0.1	<0.1
As	31	1.2	24	30	1.2	23
Se	0.6	0.5	0.7	0.6	0.5	0.3
Rb	49	<0.1	45	52	<0.1	41
Sr	104	1.3	87	78	0.9	82
Y	11	<0.1	9.8	11	<0.1	9.0
Zr	45	<0.1	36	51	<0.1	30
Nb	10	<0.1	8.9	16	<0.1	9.2
Mo	4.7	18	6.6	3.2	16	6.1
Cd	<0.1	<0.1	<0.1	0.2	<0.1	<0.1
Sn	2.0	<0.1	1.5	1.9	<0.1	1.5
Sb	6.1	<0.1	4.2	5.8	<0.1	4.8
Cs	6.8	<0.1	6.0	7.2	<0.1	6.2
Ba	331	5.3	292	300	1.8	246
La	14	0.8	13	18	0.8	11
Ce	34	<0.1	32	37	<0.1	28
Pr	3.4	<0.1	3.2	4.4	<0.1	2.7
Nd	15	<0.1	14	16	<0.1	11.9
Sm	3.1	<0.1	2.9	3.3	<0.1	2.6
Eu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Gd	2.8	<0.1	2.6	3.2	<0.1	2.4
Tb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dy	2.0	<0.1	1.9	2.5	<0.1	1.6
Ho	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Er	1.0	<0.1	0.9	1.2	<0.1	0.4
Tm	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Yb	1.1	<0.1	1.0	1.3	<0.1	0.9
Lu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hf	1.3	<0.1	1.0	1.3	<0.1	0.7
Ta	2.5	<0.1	1.0	1.9	<0.1	1.8
W	3.3	<0.1	1.8	3.2	<0.1	2.4
Tl	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	28	0.4	20	29	0.8	23
Bi	<0.1	<0.1	<0.1	0.5	<0.1	<0.1
Th	7.4	<0.1	6.8	7.7	<0.1	6.0
U	2.1	<0.1	2.0	2.3	<0.1	1.9

3.1.2. Fly ash and boiler slag

Aluminous-silicate glassy matrix with minor amounts of quartz, mullite, and traces of feldspars (albite-anortite) are the main crystalline components of the FA and BS.

The use of petroleum coke, results in high concentrations of S, Cl, V, Ni, and Mo in the 2007 and 2008 FA (Table 3). The major organic affinity of these elements in petroleum coke favors volatilisation and subsequent condensation of these elements as fine species on FA. Indeed, the 2007 and 2008 FA at this power plant is characterised by higher concentrations of V, Ni, and Mo with respect to the FA produced at a power plant feeding with 100% of coal (Córdoba et al., 2012).

Compared to the BS composition, FA is enriched (FA/BS>1.3) in S, Cl, F, B, Zn, Ga, Ge, As, Mo, Cd, Sn, Sb, Pb, and especially in Hg in 2008 (Table 3). The high concentration of most condensing elements on FA suggests the occurrence of condensation episodes during co-combustion. This may contribute to a high load of PM to FGD.

The lower FA/BS concentration ratios for some volatile elements with high condensation potential (S, B, Zn, Sn, Sb, As, Ni and Ga) in 2008 than those in 2007 are probably the result of different slagging conditions by the addition in 2008 of coal gangue. The coal gangue contains carbonate minerals that are likely to act as fluxing agents, reducing the fusion temperature and enhances slagging. These differences could also be caused by variations in the local/imported petroleum coke ratio in the fuel blend.

Table 3. Mean concentration of major, minor, and trace elements in FA, BS, and FA/BS concentration ratios.

	FA 2007	BS 2007	FA/BS	FA 2008	BS 2008	FA/BS
% dry basis(db)						
Al_20_3	24	24	1.0	26	25	1.0
CaO	2.3	2.3	1.0	2.3	2.2	1.0
Fe_2O_3	7.4	8.2	0.9	7.0	7.6	0.9
Na_2O	0.7	0.7	1.0	0.8	0.7	1.0
SO_3	0.5	<0.01	>50	0.4	0.1	3.7
K_2O	3.9	3.9	1.0	3.9	3.9	1.0
MgO	1.7	1.8	1.0	2.0	2.0	1.0
mg/kg (db)						
Cl	133	94	1.4	94	83	1.1
F	135	14	9.6	157	14	11.2
Hg	0.09	0.01	9.0	0.082	0.001	82
Li	197	197	1.0	212	204	1.0
Be	5.6	5.5	1.0	5.3	5.2	1.0
B	70	22	3.2	92	49	1.9
Sc	22	22	1.0	23	23	1.0
Ti	5819	6042	1.0	5526	5498	1.0
P	1644	1011	1.6	1780	1217	1.5
V	1414	1157	1.2	1194	941	1.3
Cr	149	150	1.0	170	157	1.1
Mn	516	558	0.9	566	589	1.0
Co	30	27	1.1	35	31	1.1
Ni	288	227	1.0	229	184	1.2
Cu	81	68	1.2	102	83	1.2
Zn	184	87	2.1	192	104	1.8
Ga	36	22	1.6	38	26	1.5
Ge	3.3	1.2	3.0	3.2	1.2	3.0
As	94	9.2	10	90	9.0	10
Se	1.1	0.1	11	0.9	1.0	1.0
Rb	162	165	1.0	173	171	1.0
Sr	381	368	1.0	293	290	1.0
Y	37	38	1.0	38	37	1.0
Zr	159	177	0.9	158	168	0.9
Nb	32	33	1.0	37	40	0.9
Mo	23	8.1	2.8	22	8.0	2.8
Cd	0.7	<0.1	>7	1.0	<0.1	>10
Sn	6.6	2.0	3.3	7.0	2.8	2.3
Sb	17	6.8	2.5	23	10	2.3
Cs	22	21	1.0	25	24	1.0
Ba	1111	1118	1.0	1125	1086	1.0
La	48	48	1.0	47	46	1.0
Ce	119	125	1.0	117	115	1.0
Pr	12	12	1.0	11	11	1.0
Nd	52	53	1.0	50	49	1.0
Sm	11	11	1.0	11	11	1.0
Eu	1.6	1.6	1.0	1.8	1.7	1.0
Gd	10	10	1.0	10	10	1.0
Tb	1.3	1.3	1.0	1.3	1.2	1.0
Dy	7.2	7.4	1.0	6.9	6.7	1.0
Ho	1.4	1.4	1.0	1.3	1.3	1.0
Er	3.4	3.5	0.8	3.3	3.2	1.0
Yb	3.9	4.1	1.0	3.8	3.7	1.0
Hf	4.6	5.3	0.9	4.6	5.0	1.0
Ta	3.6	4.5	0.8	2.3	4.8	0.4
W	8.4	4.7	1.8	11	6.8	1.6
Tl	1.5	<0.01	>150	1.6	<0.01	>160
Pb	83	34	2.4	102	42	2.4
Bi	1.1	<0.01	>110	1.5	<0.01	>150
Th	27	28	1.0	26	25	1.0
U	7.0	7.0	1.0	8.3	7.6	1.1

3.1.3. Limestone and gypsum

Limestone is of a high purity (>98% calcite) in the two sampling campaigns with only traces of quartz, dolomite, siderite, and rhodochrosite. A comparison of limestone collected in 2007 and 2008 campaigns reveals higher concentrations of B, V, Cr, Ni, Ba and U (by a factor of 1.3-2.2) and lower levels of Y, Mo, La, Ce, and Sm (by a factor of 0.3-0.6) in the 2008 limestone than those in 2007 (Table 4).

The FGD-gypsum contains calcite and traces of cowlesite as main crystalline phases. FGD-gypsum shows relatively higher concentrations (Table 4) of Cl and Mn (by a factor of 1.1-1.3), and lower concentrations of F and B (by a factor of 2.5-4.2, respectively) in 2007 than those measured in the 2008 FGD-gypsum. The concentrations of the remaining trace elements are similar in both samplings.

Table 4. Mean concentration of major, minor, and trace elements in limestone and FGD-gypsum in 2007 and 2008.

	2007		2008	
	Limestone	FGD-gypsum	Limestone	FGD-gypsum
% dry basis (db)				
Al	<0.1	0.1	<0.1	0.1
Ca	39	25	39	25
Fe	0.1	0.1	0.0	0.05
Na	<0.1	<0.1	<0.1	<0.01
S	<0.1	15	<0.1	15
K	<0.1	<0.1	<0.1	<0.01
Mg	0.3	0.2	0.2	0.2
mg/kg (db)				
Cl	807	1519	838	1359
F	14	904	16	2286
Hg	0.0002	0.3	0.002	0.3
Li	<0.01	1.4	<0.01	0.7
Be	<0.01	<0.1	<0.01	<0.01
B	<0.01	7.7	14	31
Sc	<0.01	<0.1	<0.001	<0.01
Ti	8.5	22	11	24
P	<0.01	<0.01	<0.01	<0.01
V	1.2	6.7	2.6	5.6
Cr	0.7	0.8	1.4	2.1
Mn	142	93	121	67
Co	0.8	<0.1	<0.01	<0.01
Ni	4.7	4.7	6.2	4.9
Cu	0.8	1.0	1.0	1.1
Zn	<0.01	0.5	<0.01	4.6
Ga	<0.01	<0.1	<0.01	<0.01
Ge	<0.01	<0.1	<0.01	<0.01
As	<0.01	1.1	0.8	0.9
Se	1.4	1.3	1.7	2.6
Rb	<0.01	<0.1	<0.01	0.7
Sr	186	115	188	120
Y	4.7	3.2	2.8	2.4
Zr	<0.01	<0.1	<0.01	1.1
Nb	<0.01	<0.1	<0.01	<0.01
Mo	1.5	<0.1	<0.01	<0.01
Cd	<0.01	<0.1	<0.01	<0.01
Sn	<0.01	0.6	<0.01	<0.01
Sb	<0.01	<0.1	<0.01	<0.01
Cs	<0.01	<0.1	<0.01	<0.01
Ba	1.6	4.8	3.9	4.6
La	1.6	1.3	<0.001	0.4
Ce	3.1	2.5	1.7	1.8
Pr	<0.01	<0.1	<0.01	<0.01
Nd	1.9	1.5	0.9	1.0
Sm	<0.01	<0.01	<0.01	<0.01
Eu	<0.01	<0.01	<0.01	<0.01
Gd	<0.01	<0.01	<0.01	<0.01
Tb	<0.01	<0.01	<0.01	<0.01
Dy	<0.01	<0.01	<0.01	<0.01
Ho	<0.01	<0.01	<0.01	<0.01
Er	<0.01	<0.01	<0.01	<0.01
Tm	<0.01	<0.01	<0.01	<0.01
Yb	<0.01	<0.01	<0.01	<0.01
Lu	<0.01	<0.01	<0.01	<0.01
Hf	<0.01	<0.01	<0.01	<0.01
Ta	<0.01	<0.01	<0.01	<0.01
W	<0.01	<0.01	<0.01	<0.01
Tl	<0.01	<0.01	<0.01	<0.01
Pb	1.6	1.1	0.4	0.9
Bi	<0.01	<0.01	<0.01	<0.01
Th	<0.01	<0.01	<0.01	<0.01
U	1.0	1.0	1.5	1.1

3.2. CHARACTERISATION OF GASEOUS STREAMS AND PARTICULATE MATTER

3.2.1. Gaseous streams

Sulphur dioxide is the dominant gaseous acidic pollutant IN-FGD reaching levels around 4000–5000 mg/m^{3}N. These levels are reduced down to 500-800 mg/m^{3}N after FGD (Table 5). The levels of gaseous B, Se, and As also decrease after FGD, yielding reduction rates of 67-92% in 2007 and 91-98% in 2008 with the exception of Se reduction rate (37%). The levels of gaseous F and Cl decrease markedly after FGD (retention rate >97%) in both sampling campaigns (Table 5).

Given the relatively high concentration of Hg in the feed fuel blend (Table 2), the concentration of total Hg in the IN-FGD gas is markedly high (Table 5) in the two campaigns, attaining reduction levels of 65% (2007) and 21% (2008). Although Hg primarily occurs as Hg^0 in the OUT-FGD gas in most coal-fired power plants (Córdoba et al., 2012), Hg^{2+} (Table 5) is the dominant species in the OUT-FGD gas at this power plant. The causes that may explain the unusual Hg speciation in the OUT-FGD gas are related with i) the high concentration of Hg and HCl in the gaseous stream, which may promote the formation of gaseous $HgCl_2$ species IN-FGD; ii) the acidic pH and the S/Cl ratio in the scrubber at PP2, which promote the stability of highly soluble $HgCl_2$ complexes in gypsum slurry; iii) the water re-circulation to the scrubber, which contributes to the enrichment of $HgCl_2$ in gypsum slurry (Córdoba et al., 2011); and with iv) the evaporation of particles of $HgCl_2$ from the aqueous phase of the gypsum slurry in the OUT-FGD gas. The potential parameters controlling the Hg speciation and partitioning will be reported in subsequent studies.

Table 5. Mean concentration of gaseous components IN and OUT-FGD and retention efficiencies in 2007-2008.

		mg/m^{3}N	μg/m^{3}N							
		SO_2	Cl^-	F^-	B	Se	As	Hg tot	Hg^{2+}	Hg^0
2007	IN-FGD	4319	7191	14357	187	1.0	0.3	21	18	3.0
	OUT-FGD	779	51	78	15	0.2	0.1	7.4	4.9	2.5
	% retention	82	99	99	92	80	67	65	73	17
2008	IN-FGD	4746	6148	31296	310	1.8	0.8	19	17	2.2
	OUT-FGD	555	93	147	26	1.2	0.01	15	13	2.0
	% retention	88	98	100	91	37	98	21	24	9.1

3.2.2. Particulate matter

The accumulated FA particles in gypsum sludge as well as the entrained particles from this material by the OUT-FGD gas, is a limiting factor for an accurate determination of the retention efficiency of PM by wet scrubbers. Given that the accumulated fraction of PM cannot be determined, an estimation of the retained proportion of PM was measured by considering the retention efficiency as PM OUT/PM IN ratio.

In line with the observations on the FA chemistry, the results of chemical characterisation of PM (Table 6) reveal a high concentration of most condensing elements IN-FGD probably as a result of co-combustion of coal with petroleum coke. The combustion of coal with petroleum coke probably increases the concentration of SO_2 in the gaseous phase, promoting thus, condensation of sulphite and/or sulphate species on FA.

In 2007, the content of Cr is higher in PM (by a factor of 104), in Ni (34), Cu (21), Se (11), U (10), Mo (7), Pb (6), Mn (5), V, As, and Sr (4), Ba and Ti (3), with respect to 2008 IN-FGD PM (Table 6). The contents of most elements tend to decrease in PM OUT-FGD. Only the concentrations in relative absolute value of S (2008 sampling), Se, and especially of Hg (2007 sampling), in PM increases OUT-FGD. The increase of S, Se, and Hg OUT-FGD may be associated to i) the entrainment of particles saturated in the aqueous phase of gypsum slurry in the OUT-FGD gas; ii) the evaporation of gypsum slurry droplets by the outgoing gaseous stream from the FGD; and iii) an increase of SO_2 in the gaseous stream by the combustion of petroleum coke with the high-S coal, which may contributes to the formation of sulphate condensed species OUT-FGD.

PM levels fell considerably after FGD attaining a PM reduction levels of 46-92% and 65-91% in 2007 and 2008 sampling, respectively.

Table 6. Mean concentrations of elements in PM IN and OUT-FGD in 2007 and 2008.

	2007		2008	
mg/m^{3}N	IN-FGD	OUT-FGD	IN-FGD	OUT-FGD
Al	7.6	3.1	2.9	0.7
Ca	2.0	2.1	0.4	0.3
Fe	5.3	1.2	1.1	0.3
K	2.0	0.7	0.6	0.2
Mg	0.9	0.6	0.3	0.2
Na	0.4	0.2	0.1	0.1
P	0.4	0.1	0.1	0.02
S	5.1	3.5	0.5	0.6
µg/m^{3}N				
Li	13	6.3	4.7	1.1
Be	0.4	0.2	0.1	0.04
B	1.9	0.6	<0.001	<0.001
Sc	1.5	0.6	0.6	0.1
Ti	395	150	138	52
V	133	54	37	11
Cr	406	4.9	3.9	1.7
Mn	76	26	16	10
Co	4.2	1.0	0.9	0.3
Ni	220	10.6	6.5	3.1
Cu	57	7.7	2.7	1.2
Zn	55	39	12	5.7
Ga	4.5	1.8	1.3	0.4
Ge	1.0	0.7	0.3	0.1
As	21	12	6.0	3.3
Se	14	17	1.3	0.9
Rb	9.7	3.1	3.4	0.7
Sr	27	21	7.3	2.4
Y	2.9	1.6	1.0	0.3
Zr	13	6.4	4.9	1.9
Nb	2.5	0.8	1.1	0.3
Mo	13	4.3	2.0	<0.001
Cd	0.6	0.3	0.1	0.1
Sn	3.0	0.7	0.4	0.2
Sb	3.4	1.4	1.3	0.4
Cs	1.3	0.5	0.5	0.1
Ba	89	38	29	5.4
La	4.5	2.3	1.4	0.5
Ce	8.9	3.8	2.9	0.7
Pr	1.1	0.6	0.3	0.1
Nd	4.7	2.4	1.5	0.5
Sm	1.0	0.5	0.3	0.1
Eu	0.1	0.1	0.05	0.02
Gd	0.8	0.4	0.3	0.1
Tb	0.1	0.1	0.03	0.01
Dy	0.6	0.3	0.2	0.1
Ho	0.1	0.1	0.04	0.01
Er	0.3	0.1	0.1	0.03
Yb	0.3	0.2	0.1	0.04
Hf	0.5	0.3	0.2	0.1
Ta	0.3	0.04	0.4	0.01
W	2.3	0.6	0.6	0.3
Tl	0.7	0.4	0.1	0.02
Pb	21	5.8	3.8	1.2
Bi	0.7	0.2	0.1	0.1
Th	2.3	1.1	0.8	0.3
U	0.8	0.6	0.2	0.1
Hg (ng/m^{3}N)	7.3	9.4	0.7	1.8

3.3. WATER STREAMS

3.3.1. Process water

Process water shows low concentration of most elements, only B, Sr, and Mn are slightly enriched in this water stream in the two sampling campaigns (Table 7). The main differences are the more acidic pH in the 2007 process water (5.6) than in 2008 (7.7), and the higher concentration of Sc, Ti, Cu, and Zn in the 2007 process water than those in 2008.

3.3.2. Limestone and gypsum slurry waters and filtered water

Aqueous phases of limestone and gypsum slurry have high concentrations of elements associated with soluble salts (Ca, K, Mg, Na, S, Sr, and Cl) and major and minor elements (B, Mn, Cu, Se, Cu Ba, and U, Table 7). The high concentration of these elements in the aqueous phase of limestone and gypsum slurries may be ascribed to the dissolution of limestone components and to the complete re-circulation of the filtered water to the scrubber, respectively. The re-circulation of the filtered water also accounts for the increase in B, Sr, Se, and Ba in the 2008 aqueous phase of gypsum slurry given the similar contribution of these elements by gaseous and PM streams in 2007 and 2008 (Córdoba et al., 2011). The decrease in Ni, Co, Be, Cu, and Th concentrations in the 2008 aqueous phase of gypsum slurry is probably due to the aforementioned lower PM contribution in 2008. Petroleum coke is an important source of V and Ni, but these elements display a different behaviour under the scrubber conditions. The acidic-natured gypsum slurry (pH<5) increases the solubility of Ni with respect to alkaline wastes; whereas V remains highly immobile under slightly acidic conditions of gypsum slurry. Other differences between sampling campaigns are the higher contents of Mg, S, and Al in the 2007 aqueous phase of gypsum slurry than those in 2008 owing to the high dosages of the Al additive (Table 1) and to the addition of MgO during the operational period of 2006-2007.

A high Al-additive dosage to the FGD waters (2007 sampling) enhances the formation of AlF_x complexes (Córdoba et al., 2011) and highly insoluble ralstonite ($NaMgAlF_6.H_2O$). Ralstonite forms an iso-structural solid solution between hydrated Al-fluoride complexes rich in Na and Mg compounds (Pauly, 1965). With lower dosages of Al-additive (2008 sampling), $HF_{(g)}$ reacts with Ca and Mg to form CaF_2 and MgF_2. These solid species may precipitate on gypsum surface increasing the leachable potential of F in the waste product.

Filtered water shows a composition similar to the corresponding aqueous phase of gypsum slurries in the two sampling campaigns (Table 7). The dilution process slightly increases the differences between filtered water and gypsum slurry in terms of element concentration.

Table 7. Mean of major, minor, and trace elements in water streams in 2007 and 2008 samplings.

	2007				2008			
	PW	ALS [a]	AGS [b]	FW[C]	PW	ALS [a]	AGS[b]	FW[C]
pH	5.6	7.0	5.0	5.3	7.7	9.0	4.6	5.1
K (µS/cm)	14915	1807	24932	22484	150	3947	39853	42175
mg/L								
Al	<0.2	<2	642	581	<0.2	0.2	38	27
Ca	18	294	781	728	16	365	950	828
Fe	<0.1	<0.5	14	11	0.1	<0.1	5.9	3.1
K	0.9	4.9	97	87	0.8	7.8	102	73
Mg	8.4	322	10394	9584	7.5	306	5638	4240
Na	3.8	6.9	17	16	3.6	9.3	79	58
Mn	0.03	0.6	510	470	0.1	0.5	416	321
P	<0.1	<1	<10	<10	<0.1	<2.5	<5	<0.1
S	12	667	17551	15947	13	857	12123	9165
F	0.1	12	1273	1055	0.2	6.6	185	169
Cl	2.4	145	3675	3369	4.5	176	3420	3059
B	0.4	3.6	126	116	0.02	7.9	145	117
Sr	0.07	0.4	2.1	2	0.06	0.7	3.9	3.2
NO_3^-	0.5	307	8675	ND	2.4	29	1201	932
SO_4^{2-}	44	1247	45740	47760	40	2570	36370	27495
NH_4	ND	ND	ND	ND	0.2	0.7	15	15
Hg	0.002	0.05	2.0	2.0	0.004	0.02	1.7	1.5
µg/L								
Li	4.1	56	1537	1501	2.4	88	1468	1159
Be	<0.8	<1	12	13	<0.8	<0.1	<0.1	<1
Sc	24	44	166	214	<0.8	1.4	22	18
Ti	5.3	12	86	85	<0.8	1.3	49	29
V	1.1	11	395	356	<0.8	18	158	104
Cr	1.3	4.7	15	14	<0.8	6.6	10	7.7
Co	<0.8	4.2	827	815	<0.8	2.2	505	382
Ni	1.1	52	5214	5303	1.5	29	2779	2099
Cu	5.6	11	319	337	1.4	7.2	196	126
Zn	6.8	46	4776	4777	<0.8	<0.1	4824	3567
Ga	1.1	1.6	18	28	<0.8	<0.1	4.8	2.5
Ge	<0.8	1.1	17	22	<0.8	<0.1	15	14
As	1.3	3.7	67	76	<0.8	2.7	53	38
Se	3.5	38	405	646	<0.8	82	1496	1956
Rb	1.0	5.4	14	15	<0.8	15	71	56
Y	<0.8	<1	77	76	<0.8	<0.1	28	21
Zr	<0.8	<0.1	8.3	7	<0.8	<0.1	18	12
Nb	<0.8	<0.1	1.9	1.3	<0.8	<0.1	<0.1	<1
Mo	<0.8	3.9	56	53	<0.8	4.1	30	21
Cd	<0.8	<1	162	163	<0.8	<0.1	204	159
Sn	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<1
Sb	<0.8	1.2	14	14	<0.8	2.6	29	23
Cs	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1
Ba	8.2	9.1	149	154	7.0	14	295	236
La	<0.8	<0.1	17	17	<0.8	<0.1	6.9	5.4
Ce	<0.8	<0.1	18	18	<0.8	<0.1	8.3	6.7
Pr	<0.8	<0.1	2.3	2.3	<0.8	<0.1	<0.1	<0.1
Nd	<0.8	<0.1	8.9	8.6	<0.8	<0.1	4.6	3.7
Sm	<0.8	<0.1	2.2	2.1	<0.8	<0.1	<0.1	<0.1
Eu	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1
Gd	<0.8	<0.1	4.8	5.5	<0.8	<0.1	2.8	2.6
Tb	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1
Dy	<0.8	<0.1	3.5	3.4	<0.8	<0.1	3.0	2.9
Ho	<0.8	<0.1	1.1	<0.1	<0.8	<0.1	<0.1	<0.1
Er	<0.8	<0.1	2.8	2.7	<0.8	<0.1	3.1	2.3
Tm	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1
Yb	<0.8	<0.1	4.2	4.2	<0.8	<0.1	4.0	3.0
Lu	<0.8	<0.1	1.0	<0.1	<0.8	<0.1	<0.1	<0.1
Hf	<0.8	<0.1	1.1	<0.1	<0.8	<0.1	<0.1	<0.1
Ta	<0.8	<0.1	9.9	5.4	<0.8	<0.1	<0.1	<0.1
W	<0.8	<0.1	2.3	<0.1	<0.8	1.7	2.5	<0.1
Tl	<0.8	<0.1	5.0	4.4	<0.8	<0.1	5.2	4.0
Pb	2.3	<0.1	2.3	2.1	<0.8	<0.1	3.0	2.3
Bi	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1
Th	<0.8	<0.1	6.4	5.4	<0.8	<0.1	<0.1	<0.1
U	<0.8	12	654	568	<0.8	8.0	667	494

PW: process water; ALS: aqueous phase of limestone slurry; AGS: aqueous phase of gypsum slurry; FW: filtered water.

3.4. SOURCE OF TRACE ELEMENTS

The blend of local and imported bituminous coals, petroleum coke, limestone, process water, and the mixture of the slurry waters are the sources of trace elements at the whole power plant. The contribution of each stream to the input of trace elements was calculated according to their input flows (t/h) and is depicted in Figure 2.

In 2007, the blend of coals is the main source (>95%) of most elements with the exception of volatile elements i.e. S, Hg, Cl, B, and F. The mixture of the slurry water (45-72%) constitutes the main source of the aforementioned elements as a consequence of the water re-circulation to the scrubber and the high water solubility of salts containing these elements. In the case of F, the Al-additive promotes the formation of highly soluble AlF_x complexes in the aqueous phase of gypsum slurry (Córdoba et al., 2011). However, in 2008 the blend of coals was the main source of S (49%), B (64%), and F (74%). The low dosage of the Al-additive in 2008 decreased the input of F via mixture of the slurry waters.

Petroleum coke supplies similar proportions of V (80%), Ni (69%), and Mo (50%) in both samplings. The input of S via petroleum coke is slightly higher in 2007 than in 2008 (Figure 2). Limestone provides large amounts of Ca (80-90%) and low proportions of other elements associated with carbonate, Sr, Mg, and Mn and also significant concentration of U, Y, and some REEs in the two sampling campaigns. Owing to the lower limestone flow in 2008, the contribution of this stream for carbonate associated elements (Ca, Mg, Sr, Y, and Mn) and Al-Si fraction is reduced by a factor 1.1-5.4.

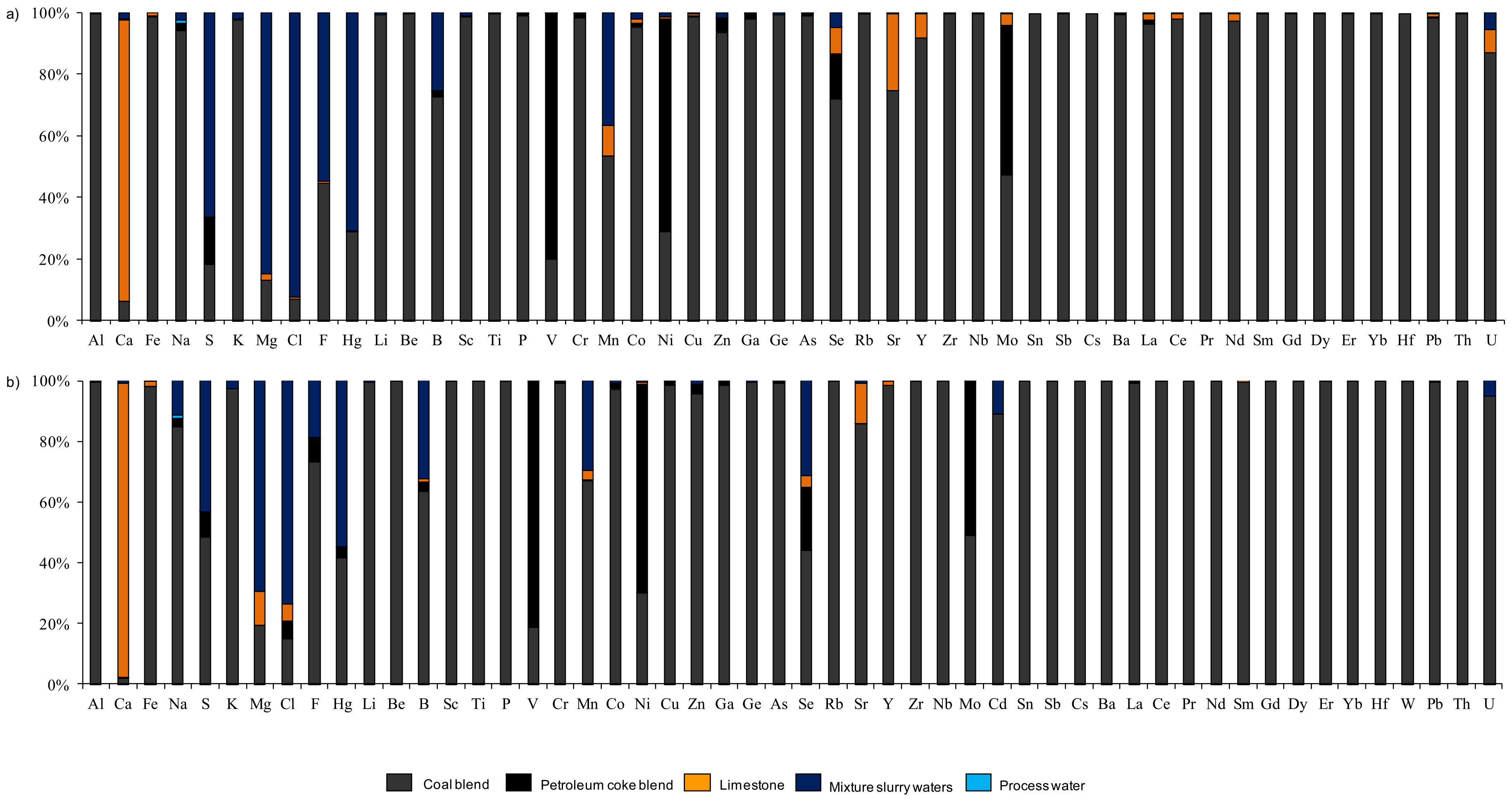

Figure 2. Source of elements in the whole power plant in (a) 2007 and in (b) 2008.

3.5. MASS BALANCES

Mass balances over PCC, FGD, and the whole installation are given in Table 8 and 9. In the two samplings, the mass balances were carried out for all the analysed elements except for Ge, Cd, Eu, Tb, Ho, Tm, Lu, Tl, and Bi at the PCC and at the whole installation. In 2008, Zr, Er, Hf, and Ta were also excluded in the mass balance at the PCC and the whole installation.

The 2007 FGD mass balances were carried out for all the analysed elements except for Cr, Ni, Cu, P, Rb, Nb, Sb, Zr, Mo, Sb, Cs, Hf, Ga, Ta, W, Pb, and REE´s. In 2008, Sn, Be, Ge, Sc, Co, Nb, Sb, Zr, Mo, Sb, Cs, Hf, Ga, Ta, W, Pb, and REE´s were excluded in the FGD mass balance. The concentration of all these elements were below of analytical detection limits in the feed coal blend, limestone slurry (solid fraction), and in the mixture of the slurry waters, respectively.

Mass balance for mean values of the 2 sampling days is closed, with excellent OUT/IN ratios for the PCC and for the whole installation in 2007 and 2008 (Table 8 and 9) with the exception of B both for the PCC and for the whole installation, and Se for the 2007 PCC. The low mass balance closure of these elements might be attributed to i) the complexity of the analytical uncertainties resulting in the loss of B during the acid-digestion procedure; and to ii) the interferences that distort the accuracy of measuring Se concentrations by ICP-MS, despite using collision cell.

The FGD mass balances are less accurate for some elements than those obtained for the PCC system owing to the unreliable results when values are normalised with the corresponding stream flows. Aluminium, in both samplings, K and Na (2007), and S and F (2008) show a low OUT/IN ratio in the FGD probably because of a loss of fine particles during the gypsum slurry filtration, which reduce the output flow of these elements for mass balance calculations (Table 8 and 9).

Table 8. Mass balance of the PCC system (boiler + ESP), FGD, and whole installation in 2007.

Mean	PCC			FGD			Whole installation		
kg/h	In	Out	OUT/IN	In	Out	OUT/IN	In	Out	OUT/IN
Al	4630	4997	1.08	76	37	0.49	4697	5025	1.07
Ca	671	6439	0.96	3421	4068	1.19	4089	4709	1.15
Fe	2067	2052	0.99	13	12	0.93	2086	2058	0.99
Na	243	211	0.87	1.0	0.7	0.72	243	211	0.87
S	2564	2544	0.99	3156	3383	1.07	3248	3455	1.06
K	1427	1271	0.89	5.0	3.3	0.68	1429	1272	0.89
Mg	412	412	1.00	290	301	1.04	700	711	1.02
g/h									
Cl	16892	13902	0.82	109473	118666	1.08	117725	123839	1.05
F	26568	22151	0.83	4687	44078	0.94	56016	48801	0.87
Hg	29	28.5	0.98	77	65	0.85	81	69	0.85
Li	7963	7687	0.97	58	73	1.27	8004	7744	0.97
Be	221	217	0.98	0.8	0.7	0.78	221	217	0.98
B	4522	2727	0.61	3434	3387	0.99	7732	5910	0.76
Sc	762	852	1.12	8.4	6.7	0.80	767	857	1.12
Ti	219253	228632	1.04	551	549	1.00	219451	228702	1.04
P	58747	61363	1.04				58966	61363	1.04
V	63874	54218	0.85	181	187	1.03	63912	54244	0.85
Cr	6592	6324	0.96				6610	5851	0.89
Mn	19468	20427	1.05	14394	14680	1.02	33770	35015	1.04
Co	1228	1175	0.96	35	24	0.70	1258	1194	0.95
Ni	12917	11237	0.87				13105	11207	0.86
Cu	3165	3177	1.00				3181	3143	0.99
Zn	7210	6809	0.94	199	193	0.97	7343	6935	0.94
Ga	1387	1362	0.98				1388	1360	0.98
Ge				1.8	1.5	0.86			
As	3419	3307	0.97	28	36	1.29	3421	3317	0.97
Se	100	57	0.57	50	62	1.25	131	101	0.77
Rb	6437	6363	0.99				6438	6355	0.99
Sr	12457	14850	1.19	1705	1915	1.12	14130	16732	1.18
Y	1397	1460	1.05	46	55	1.19	1439	1512	1.05
Zr	5095	6316	1.24				5095	6309	1.24
Nb	1276	1252	0.98				1276	1250	0.98
Mo	939	854	0.91				977	846	0.87
Cd				5.2	5.0	0.96			
Sn	213	241	1.13	3.7	5.0	1.36	213	248	1.16
Sb	603	628	1.04				603	626	1.04
Cs	852	844	0.99				852	843	0.99
Ba	41718	43524	1.04	127	132	1.04	41736	43548	1.04
La	1864	1888	1.01	20	24	1.17	1879	1906	1.01
Ce	4512	4690	1.04	38	45	1.19	4539	4725	1.04
Pr	461	463	1.01				461	463	1.00
Nd	2008	2020	1.01	23	27	1.20	2025	2042	1.01
Sm	416	421	1.01				416	421	1.01
Gd	366	377	1.03				366	377	1.03
Dy	269	283	1.05				269	283	1.05
Er	128	135	1.05	0.4	0.3	0.67	128	135	1.05
Yb	145	154	1.06	0.5	0.3	0.67	145	154	1.06
Hf	138	185	1.34				138	184	1.33
Pb	2860	3059	1.07				2874	3059	1.06
Th	970	1053	1.09				971	1052	1.08
Ta	149	144	0.97				150	144	0.96
W	263	313	1.19				263	311	1.18
U	270	287	1.06	24	29	1.19	294	315	1.07
Mean			1.00			0.98			1.01
Std			0.12			0.22			0.11

Table 9. Mass balance of the PCC system (boiler + ESP), FGD, and whole installation in 2008.

Mean	PCC			FGD			Whole installation		
kg/h	In	Out	OUT/IN	In	Out	OUT/IN	In	Out	OUT/IN
Al	5014	5843	1.17	18	10	0.60	5028	5850	1.17
Ca	730	702	0.96	3135	2768	0.88	3832	3496	0.91
Fe	20459	2093	1.02	5.0	5.7	1.04	2049	2097	1.02
Na	258	237	0.92	1.9	1.7	0.86	260	239	0.92
S	2439	3381	1.39	3623	2349	0.65	2738	2405	0.88
K	1364	1380	1.01	2.8	2.9	1.03	1366	1383	1.01
Mg	455	515	1.13	126	137	1.09	600	653	1.09
g/h									
Cl	20018	16146	0.81	98507	101014	1.03	116185	108547	0.93
F	34808	49783	1.43	49703	32282	0.65	39826	38223	0.96
Hg	30	36	1.21	70	67	0.97	71	70	0.99
Li	8211	8978	1.09	41	42	1.02	8246	9019	1.09
Be	212	226	1.06				212	226	1.07
B	5857	4276	0.73	4045	3665	0.91	9413	7507	0.80
Sc	805	1195	1.48				806	999	1.24
Ti	192407	234729	1.22	273	351	1.28	192495	234991	1.22
P	75067	72831	0.97				75067	72814	0.97
V	43126	49447	1.15	75	83	1.11	43150	49524	1.15
Cr	4872	7166	1.47	24	26	1.09	4884	7169	1.47
Mn	17363	24155	1.39	10426	9746	0.93	27354	33900	1.24
Co	1391	1474	1.06				1402	1476	1.05
Ni	9754	9488	0.97	135	118	0.88	9863	9602	0.97
Cu	3733	4248	1.14	29	18	0.61	3745	4249	1.13
Zn	7699	7723	1.00	131	134	1.03	7799	7855	1.01
Ga	1289	1541	1.20				1289	1542	1.20
As	3507	3420	0.98	11	17	1.57	3512	3434	0.98
Se	46	43	0.95	68	87	1.28	109	126	1.16
Rb	6183	7343	1.19	6.7	11	1.61	6185	7343	1.19
Sr	12414	12450	1.00	1713	1436	0.84	14019	13885	0.99
Y	1366	1603	1.17	25	28	1.11	1389	1624	1.17
Nb	1441	1582	1.10				1441	1579	1.10
Mo	916	864	0.94				917	864	0.94
Cd				4.5	4.5	1.00			
Sn	251	276	1.10				251	275	1.09
Sb	756	910	1.20				757	910	1.20
Cs	937	1098	1.17				937	1056	1.13
Ba	37249	47585	1.28	74	67	0.90	37287	47650	1.28
La	1679	1980	1.18				1679	1981	1.18
Ce	4181	4970	1.19	20	22	1.08	4195	4991	1.19
Pr	405	484	1.20				405	482	1.19
Nd	1796	2118	1.18	9.9	12	1.23	1804	2130	1.18
Sm	393	460	1.17				393	460	1.17
Gd	369	428	1.16				370	428	1.16
Dy	245	292	1.19				246	293	1.19
Er				0.2	0.1	0.60			
Yb	131	163	1.25	0.2	0.1	0.63	131	163	1.25
Hf									
Pb	3450	4011	1.16	12	12	1.00	3452	4023	1.17
Th	912	1115	1.22				912	1116	1.22
W	400	452	1.13				400	452	1.13
U	293	350	1.20	27	26	0.98	318	376	1.19
Mean			1.15			0.80			0.99
Std			0.27			0.29			0.14

3.6. PARTITIONING AND BEHAVIOUR OF TRACE INORGANIC ELEMENTS IN THE BOILER AND ESP

In accordance with the volatility of the elements at the boiler and at the ESP, the elements can be classified in the two sampling campaigns as follow:

i. *Low volatility* elements (>80% in FA and <20% in BS): Zn, Hf, Pb, U, Zr, Th, Rb, Cs, Mo, Li, Ba, Sn, Mn, Ga, V, Ni, Al, Cr, Sr, Y, Ca, Ti, P, Ge, Be, Mg, Co, Fe, K, Sb, W, Na, Nb, and REEs.

ii. *Moderately volatile* elements with high condensation potential in FA and PM IN-FGD: Boron, Se, and As (73-98%) show a high retention in the FA with a low proportion (0.01-9.2%) in the gaseous phase in both sampling campaigns (Figure 3).

iii. *High volatile* elements: this group includes the most volatile elements, S, Cl, Hg, and F (78-98 % in gas phase, Figure 3).

The 2007 and 2008 partitioning reveals slight differences in the behaviour of elements in the boiler and ESP regardless of the coal/petroleum coke ratio. The main differences are the higher retention of elements, especially of B (18%) and Se (11%) in the 2008 BS than in 2007 because of the addition of coal gangue to the fuel blend that promotes the slagging conditions (Figure 3). Nickel and V, elements that fingerprint the co-firing of petroleum coke, maintain a similar partition in the FA (90%) and BS (10%) in both samplings.

Compared to the 2007 fuel blend with 18% of petroleum coke, in 2008 with 16% of petroleum coke, the gaseous proportion of B, S, and especially of F slightly increases in the post-combustion phase (Figure 3). This may be associated to i) the input flow of the feed fuel blend, which is higher in 2008 than in 2007; and to ii) the significant organic affinity of these elements in the 2008 coal blend. The gaseous proportion of Hg and Cl is constant despite the change in coal/petroleum coke ratio.

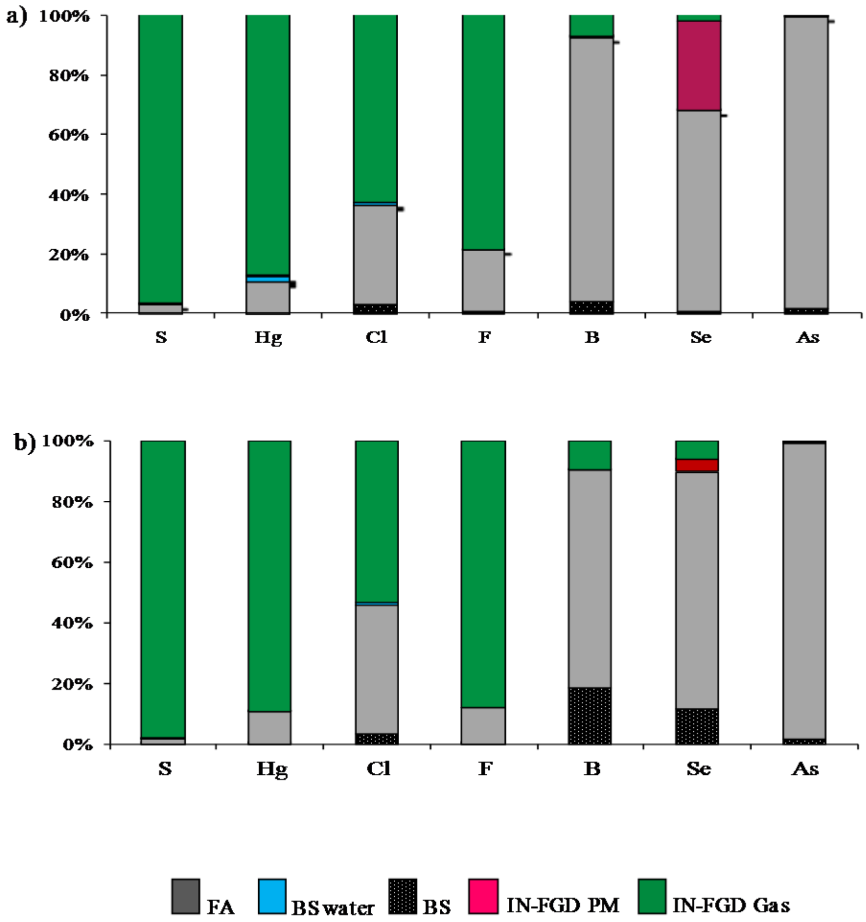

Figure 3. Partitioning of the highly and moderately volatile elements in the PCC in 2007 and 2008. a) Partitioning of the highly and moderately volatile elements in the PCC in 2007; and b) Partitioning of the highly and moderately volatile elements in the PCC in 2008.

3.7. TRACE INORGANIC ELEMENTS IN THE FGD SYSTEM

3.7.1. Partitioning and behaviour of trace inorganic elements in the FGD system

Limestone, IN-FGD gas, PM IN-FGD, mixture of slurry waters, and the Al-additive are the sources of trace inorganic species in the FGD system. The elements excluded for mass balance calculations were also excluded in the partitioning studies of FGD system given that their content were below of the analytical detection limits in limestone slurry (solid fraction), and in the mixture of slurry water.

i. *Limestone is the major input source* (51-100%) of Ca, Sr, Y, and Fe in both campaigns and also of Cu and Cr in 2008.

ii. *IN-FGD Gas* in 2007 largely contributes to S (78%) inputs to FGD. The high water solubility of species of volatile elements such as Hg and F and the re-circulation of the filtered water, account for significant inputs of these elements in the 2007 mixture of slurry waters (63% and 68%). In 2008, S (92%) and F (90%) enter FGD as gaseous species; whereas the proportion (39%) of Hg increases in the 2008 IN-FGD gaseous stream.

iii. *PM IN-FGD* in 2007 is the most prominent source (58-100%) for most of the REEs, Sn, Ge, Be, As, Ti, Ni, Ba, and V. In 2008, with the exception of Ge and Be excluded for the FGD mass balance, and Ni supplied by the mixture of the slurry waters, the remaining elements enter FGD as PM. The contribution of these elements as PM to the FGD is considerably higher in the 2007 sampling than in 2008.

iv. *Mixture of the slurry waters* in 2007 are the most important input (49-94%) for K, Na, Zn, Li, Sc, Co, Cd, Mn, Mg, B, Cl, Hg, F, and U into the scrubber. The high water solubility of B and Cl-bearing species (Harivandi, 1999) in conjunction with the re-circulation of the filtered water, accounts for significant inputs (83-93%) of these elements via the mixture water stream. In 2008, B, Se, Cl, Hg (61-86%) and Li, Zn, Mn, Ni, Mg, U, Cd, K, and Na (50-98%) are also supplied by the mixture of the slurry waters.

v. *Al-additive* is the most important source of Al (74-88%) in 2007 and 2008, and supplies relatively high proportions of S (8%) in 2007.

Based on the element distribution in the FGD system, elements are grouped as detailed below. The relative proportions of each element in the outgoing streams are calculated with respect to their incoming proportion to FGD. The percentages of the partitioning of elements are expressed with respect of total proportion of each element between the in and/or outgoing streams. It is worth noting that elements excluded for mass balances calculations are also excluded for the partitioning studies in the FGD system and for the whole installation.

i. Elements retained in the gypsum sludge

i.1) Volatile elements IN-FGD retained in the gypsum sludge

Most of S (78-92%) enters FGD as gaseous species, and it is mainly retained as gypsum (73%) in both samplings (Figure 4a and 5a). Significant proportions of S escapes the FGD as gaseous SO_2 in 2007 (14%) and in 2008 (18%).

i.2) Elements associated with the highly insoluble Al-Si fraction of limestone and retained as impurities in the gypsum sludge.

Calcium, Fe, Sr, and Y, in both samplings, and Cr and Cu in 2008 are retained as impurities in high proportions (50-100%) in the gypsum sludge (Figure 4band 5b). Aluminium is retained as impurity in the 2007 gypsum sludge (45%). In 2008, their proportion increases to (84%) in the gypsum sludge.

i.3) Elements IN-FGD as PM with a fraction retained in the gypsum sludge.

Titanium, V, As, and Ba, in both samplings, Sn (2007), Pb and Rb (2008) enter FGD as PM and are retained in a high proportion (51-91%) in the gypsum sludge (Figure4b and 5b). The extremely low levels of Be, P, Nb, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Hf, Bi, Th and Cs in the FGD streams introduce a substantial uncertainty when estimating the input and output percentage. This would explain to poor mass balance closure for these elements in the FGD system. However, their presence IN-FGD and the subsequent retention in the gypsum sludge are supported by the chemical composition of the filters IN and OUT-FGD and by the retention efficiencies (69-83%) of PM.

In spite of the typical moderately volatile behaviour of As, most this element entered FGD in 2007 in a particulate form (91%). In 2008, PM (61%) and limestone (24%) are the main sources of As IN-FGD. High fractions (50-60%) of As are retained in the gypsum sludge in both samplings most probably as Ca-arsenate (Álvarez-Ayuso et al., 2006). Significant As emission occurs predominantly as PM (30-43%); whereas low proportions (0.1-0.2%) of As-bearing species are emitted in a gaseous form (Figure 4b and 5b).

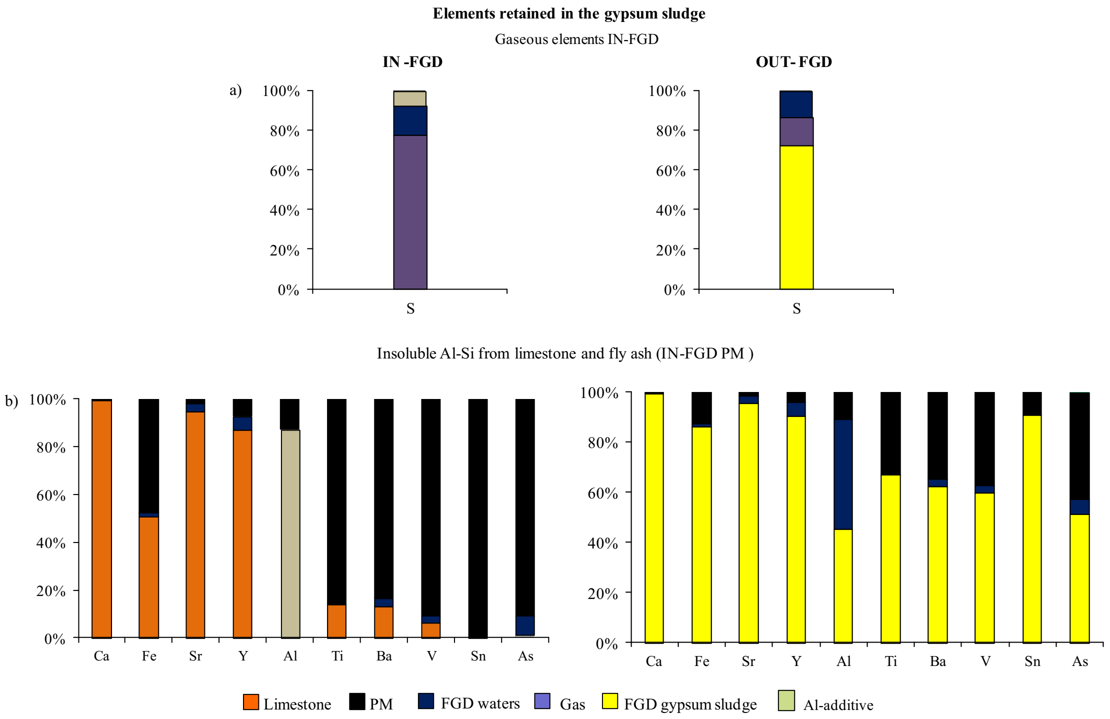

Figure 4. Partitioning of the elements IN and OUT-FGD retained in the gypsum sludge. a) Gaseous components IN (right) and OUT-FGD (left) retained in the gypsum sludge in 2007; b) Elements supplied by limestone and PM IN (right) and OUT-FGD (left) retained in the gypsum sludge in 2007.

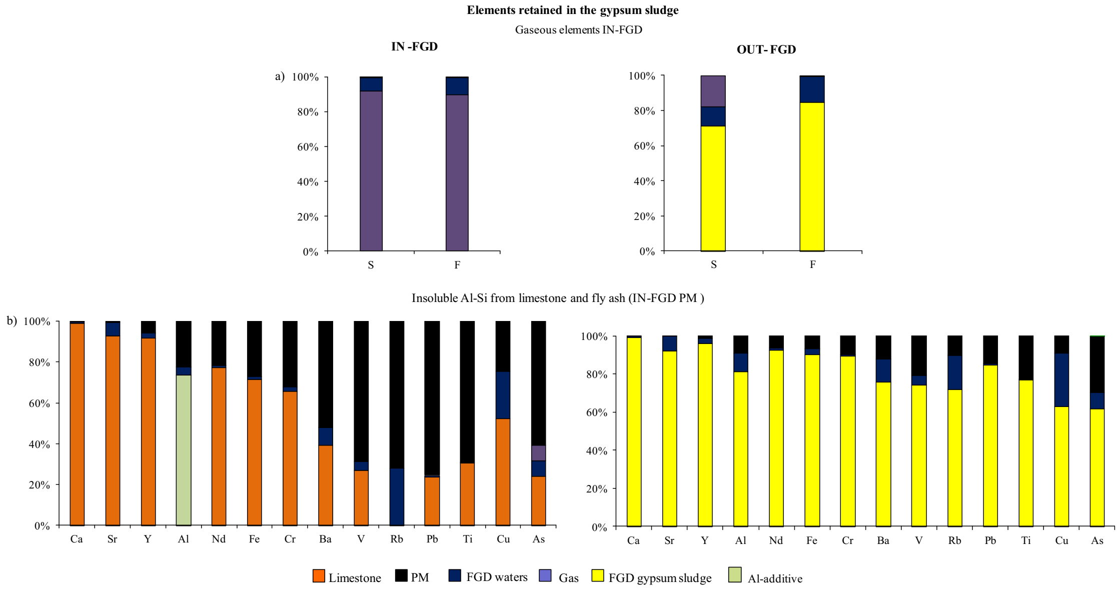

Figure 5. Partitioning of the elements IN and OUT-FGD retained in the FGD gypsum sludge. a) Gaseous components IN (right) and OUT-FGD (left) retained in the gypsum sludge in 2008; b) Elements supplied by limestone and PM IN (right) and OUT-FGD (left) retained in the gypsum sludge in 2008.

Elements present in the FGD water streams

ii.1) Moderately and highly volatile elements dissolved in the aqueous phase of gypsum slurry.

In 2007 and 2008, high fractions of B (90%) and Cl (85%) enter and leave (96 and 83%, respectively) FGD via the mixture water stream and in filtered water, respectively, as water soluble species. The high solubility of salts containing these elements promotes their gradual dissolution in the aqueous phase of gypsum slurry and their subsequent enrichment in filtered water after a number of water re-circulations to the scrubber (Córdoba et al., 2011). Over 5% of B and 18% of Cl are retained in the gypsum sludge and only 0.5-0.9% of B and 0.06-0.1% of Cl are emitted in a gaseous form (Figure 6a and 7a), respectively.

In both campaigns, Hg enters (61-68%) and leaves (64-80%) FGD via the mixture water stream and in filtered water, respectively. High gaseous proportions of Hg escape the FGD in 2007 (14%) and in 2008 (39%).

In 2007, F enters (63%) and leaves (67%) FGD via the mixture of slurry waters and in filtered water, respectively, because of the high dosage of Al-additive used in this campaign (Figure 6a). In 2008, the IN-FGD gas (90%) is the main source of F to FGD (Figure 5a). In 2007, less F (33%) is retained in the gypsum sludge than in 2008 (85%). Low proportions of F is emitted in a gaseous form in 2007 (0.2%) and 2008 (0.4%).

ii.2) Elements supplied by the mixture of slurry water and those associated with limestone.

The high proportion (65-92%) of Mn, Mg, Co, and U dissolved in the mixture of slurry waters and their strong carbonate affinities in limestone account for a readily dissolution in the aqueous phase of limestone slurry, which reacts with SO_2 to form the corresponding soluble sulphate complexes in the aqueous phase of gypsum slurry (55-94%) in both sampling campaigns (Figure 6b and 7b).

ii.3) Elements supplied by the mixture of slurry water and as PM IN-FGD.

In 2007, the high proportion (32-87%) of Na, K, Be, Li, Sc, Cd, Ni, and Zn dissolved in the mixture of slurry waters and those supplied as fine grain size particles (14-59%) suggests their progressive dissolution and enrichment in the aqueous phase of gypsum slurry and filtered water, respectively. In 2008, with the exception of Sc and Be, excluded for FGD mass balance, the concentration of the remaining elements increases via the mixture of slurry waters due to the re-circulation of water to the scrubber. Considerable proportions (26-46%) of Na, K, Be, and Zn dissolved in the aqueous phase of gypsum slurry are subsequently emitted as fine sulphate particles entrained in the OUT-FGD gas (Figure 6b and 7b).

In the 2007 sampling, the mixture of slurry waters (35%) and PM (32%) are the main sources of Se IN-FGD (Figure 6b). In 2008, the Se fraction IN-FGD increases via the mixture of slurry waters (83%) due to the water re-circulation to the scrubber (Figure 7a). Relatively high fractions (35%) of Se are retained in the 2007 and 2008 gypsum sludge, with a significant output in the aqueous phase of gypsum slurry in 2007 (29%) and in 2008 (63%). In 2007, the Se emissions occur predominantly as PM (36%) and in 2008 in a gaseous form (2.3%).

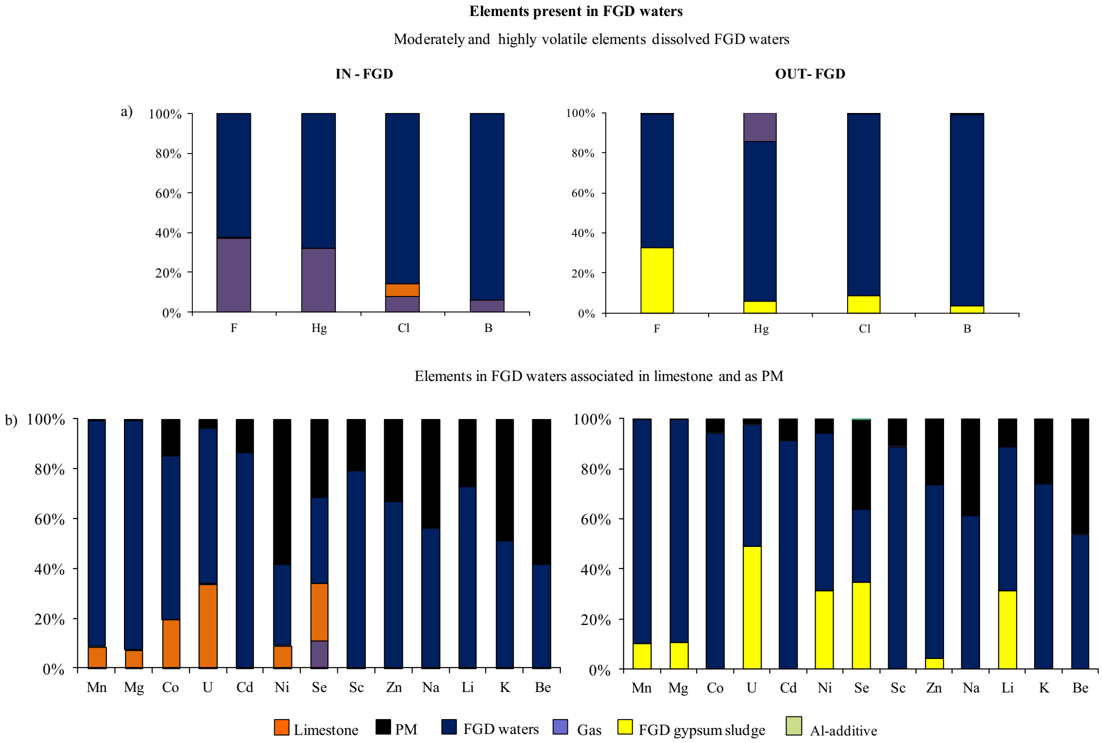

Figure 6. Partitioning of the elements IN and OUT-FGD present in FGD waters. a) Gaseous components dissolved in FGD waters IN (right) and OUT-FGD (left) in 2007; b) Elements in FGD waters and those associated to limestone and PM IN (right) and OUT-FGD (left) in 2007.

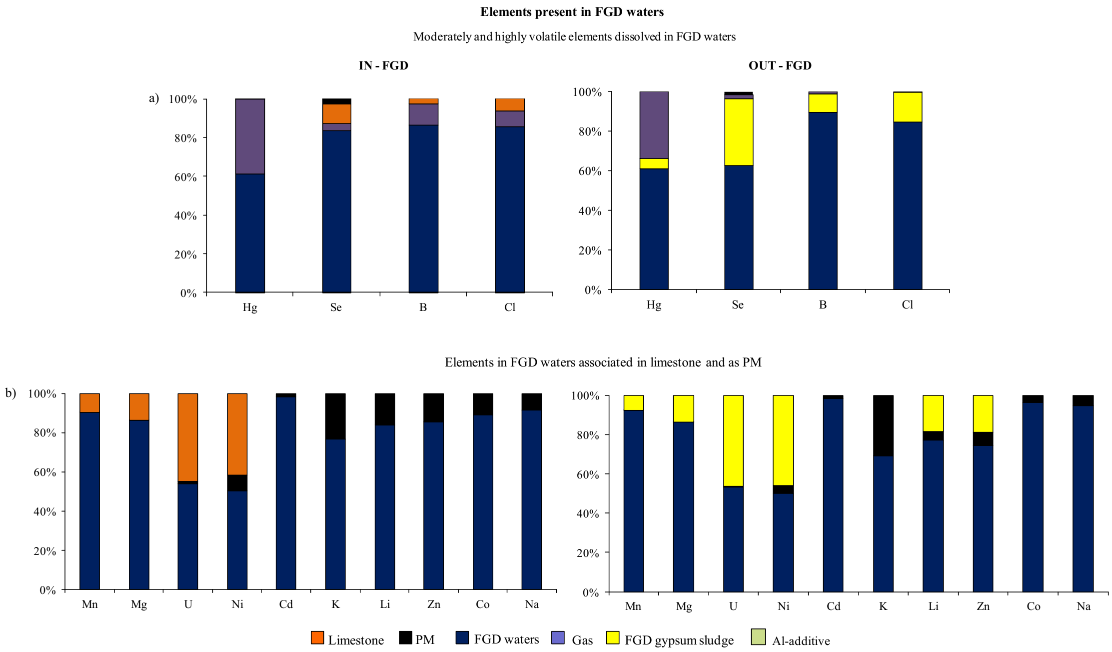

Figure 7. Partitioning of the elements IN and OUT-FGD present in FGD waters. a) Gaseous components dissolved in FGD waters IN (right) and OUT-FGD (left) in 2008; b) Elements in FGD waters and those associated to limestone and PM IN (right) and OUT-FGD (left) in 2008.

The above observations show that the FGD partitioning of elements and more importantly the volatile elements is related to the operational conditions of this power plant. Fluorine and Se show different stream partitioning IN and OUT-FGD between 2007 and 2008 because of the different Al-additive dosage and filtered water re-circulation to the scrubber, respectively. For most elements, especially for Hg, B, and Cl the filtered water re-circulation to the scrubber promotes their gradual saturation from 2007 to 2008 in the aqueous phase of gypsum slurry. The high solubility of Cl, B, and Hg salts promotes their partial dissolution and saturation in the aqueous phase of gypsum slurry after a number of water re-circulations to the scrubber (Córdoba et al., 2011). This causes the emission by entraining particles and droplets from gypsum slurry in the OUT-FGD gas and/or the subsequent precipitation on FGD-gypsum.

3.8. RETENTION EFFICIENCY OF THE FGD SYSTEM

The co-combustion of coal with petroleum coke increases the content of HCl and SO_2 in the gaseous stream at this power plant. The former favours the formation of gaseous chlorides species, especially of Hg, whilst the latter enhances the formation of condensed species of Cu, Cr, Ni, Na, Cd, and Zn entrained in the OUT-FGD gas.

In 2007, the retention efficiencies (fraction of the IN-FGD load for a given element retained in the gypsum sludge and in FGD waters) displays a high abatement capacity (86-100%) for S, F, Cl, B, and Hg, and a relatively high abatement for As (57%) and Se (64%). These retention efficiencies are in agreement with those obtained directly by gas measurements IN and OUT-FGD (Table 5) with the exception of Se (64 and 80%, respectively) and Hg (86 and 65%, respectively). The retention efficiencies also indicate slightly differences for As (57 and 65%, respectively).

In 2008, the volatile and moderately volatile elements are also highly retained (83-100%) by FGD when considering the partitioning studies and the gas measurements, with the exception of Se and (96 and 37%, respectively) and Hg (66 and 21%, respectively) that show higher retention efficiencies by partitioning studies than by gas measurements. By contrast, As shows a higher retention by gas measurements (98%) than by partitioning studies (69%).

The gas retention efficiencies of SO_2 obtained by gas measurements are in agreement with those obtained by partitioning studies, although reveals discrepancies for the SO_2 retention between 2007 and 2008 sampling. Retention of 82% and 88% is obtained for SO_2 by gas measurements in 2007 and 2008, respectively; whereas by FGD partitioning studies the retention of SO_2 is slightly different, 86% and 82% in 2007 and 2008, respectively.

It is worth noting that the retention percentages in Table 5 are exclusively based on gas streams IN and OUT-FGD. It is for this reason that the higher retention efficiencies yielded for As and Se by gas measurements than those by the partitioning studies of FGD can be due to: i) an entrainment dissolved droplets of Se and As complexes in the aqueous phase of gypsum slurry in the outgoing gaseous stream from FGD; and/or ii) PM accumulated in the gypsum sludge subsequently entrained in the outgoing gaseous stream from FGD and retained by the filters.

In 2007, Se (22%) is the element with the highest proportion emitted as PM OUT-FGD most probably as a result of the entraining of gypsum slurry particles in the OUT-FGD gas; whereas the gaseous emissions of total Hg (14%) and S (14%) OUT-FGD are the only significant elements. In 2008, the overall PM emissions are largely reduced including the PM Se emissions (1.2%); whereas the gases emissions of S (17%) and especially of total Hg (32%) increase in OUT-FGD. The low retention of Hg by gas measurements can be associated to the evaporation of particles of $HgCl_2$ from the aqueous phase of the gypsum slurry in the OUT-FGD gas. However, as abovementioned in the 2.3.2 section, the potential parameters controlling the Hg speciation and partitioning will be reported in subsequent studies.

The comparison of the emission rates of elements normalised to kg/year (to compare with the PRTR thresholds) in the period equivalent to operate at 100% capacity in this power plant (5793h), with the Pollutant Release and Transfer Register (PRTR, 2006) threshold values (for information purposes), brings to light that the emission of these elements should be regarded as of concern. In 2007, the emission rates of gaseous Hg and particulate As, Zn, and Ni OUT-FGD exceed the PRTR threshold values; whereas in 2008, the PRTR threshold values are exceeded by particulate As and by gaseous Hg. Nevertheless, the retention capacity for most of gaseous pollutants and the emission levels of Ni as PM are set in the range obtained those in coal combustion plants of similar capacity (Córdoba et al., 2012). This evidences that i) the co-firing coal with 16-18% petroleum coke has little impact on the FGD abatement capacity for the trace elements studied and on the subsequent emissions levels of trace pollutants; and ii) the co-firing of coal with this alternative of fuel does not modify Ni emissions even though the high Ni content in petroleum coke.

3.9. ABATEMENT CAPACITY OF WHOLE INSTALLATION FOR TRACE INORGANIC POLLUTANTS

The 2007 partitioning for the whole installation (Figure 8a) reveals that the whole output (as mean in %) is FA (78%), followed by BS (8.5%), filtered water (7.2%), FGD-gypsum (4.9%), OUT-FGD gas (0.6%), OUT-FGD PM (0.6%), and the BS water (0.03%). In 2008, FA (80%) is still the whole output followed by BS (9.1%). Thus, high proportions of most elements are retained in 2007 (87%) and in 2008 (89%) by FA and BS (Figure 8b).

Moderately volatile and highly volatile elements, F, Cl, As, and B are retained with a very high efficiency when considering the whole plant (99-100%), which reduces their gas proportions emitted in both samplings. In 2007, S (86%) and Hg (87%) are also highly retained. By contrast, in 2008 the retention of gaseous Hg decreases to 68%. The retention of Se increases from 2007 (75%) to 2008 (97%).

Arsenic (98%) is mainly retained by FA; Cl (76-82%) and Hg (58-76%) by filtered water; and S (71%) by FGD-gypsum in both campaigns. In 2007, B (55%) and F (61%) are retained by filtered water; whereas in 2008, FGD gypsum (72%) and FA (48%) are the main output streams for F and B, respectively. In 2007, Se is retained by FA (37%) with a significant proportion retained by FGD gypsum (21%) and filtered water (18%). By contrast, in 2008 filtered water (46%) is the main output stream of this element (Figure 8).

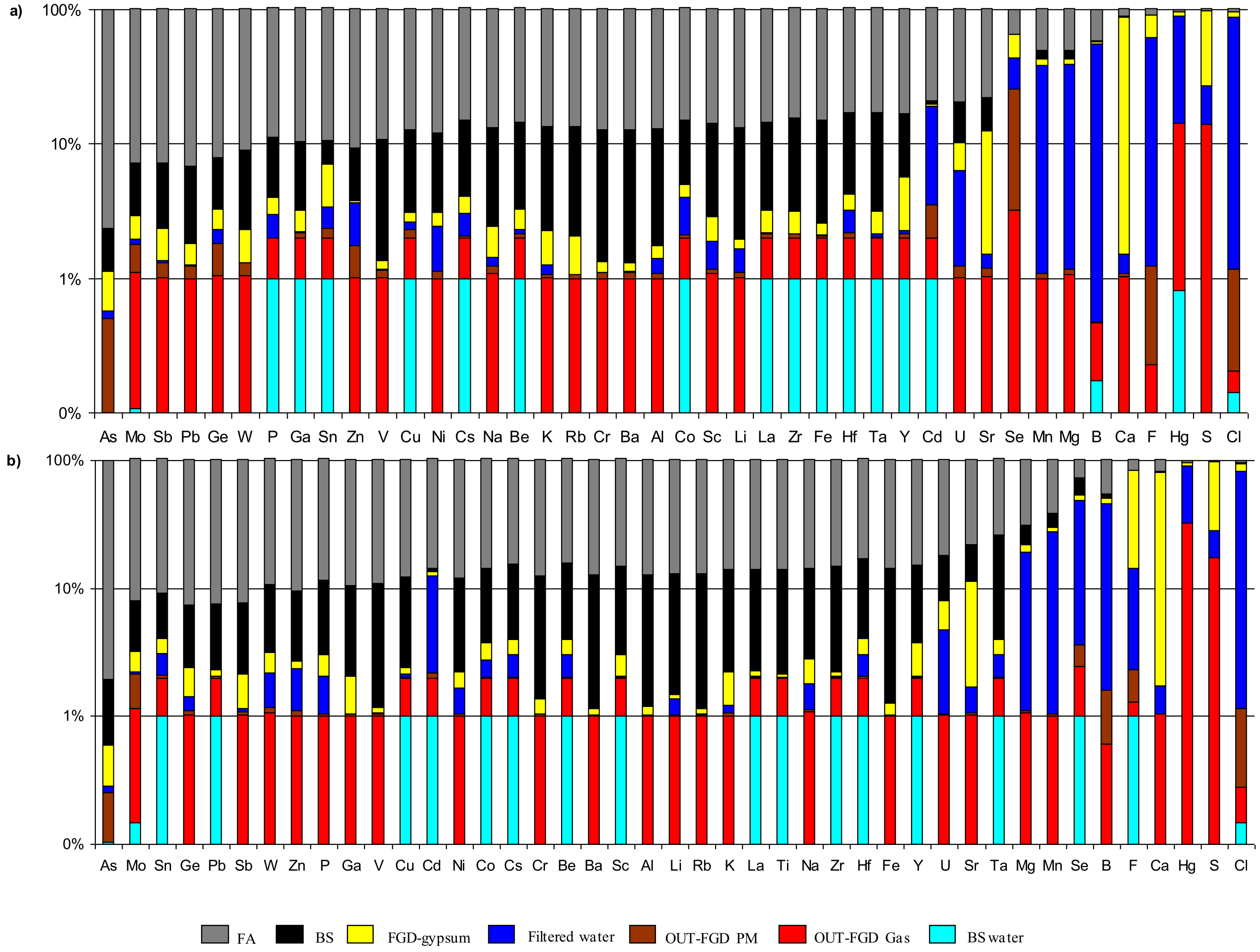

Figure 8. Distribution of the elements over output streams of the whole installation (PCC+FGD) in (a) 2007 and in (b) 2008.

4. CONCLUSIONS

The water re-circulation to the scrubber at this power plant favours the gradual saturation of most elements in the gypsum slurry. This increases the emission by entraining particles and droplets from gypsum slurry in the OUT-FGD gas, and/or the precipitation of solids in FGD-gypsum end-product.

The co-combustion of coal with petroleum coke increases the content of HCl and SO_2 in the gaseous stream giving rise to the formation of gaseous chlorides species, especially of Hg, and the formation of condensed species of Cu, Cr, Ni, Na, Cd, and Zn entrained in the OUT-FGD gas, respectively.

High retention capacity (83-100%) for S, Cl, F, As, and B is attained when considering the whole plant in both sampling campaigns. The retention of Se increases from 2007 (75%) to 2008 (97%). In 2007, the total gaseous Hg is highly retained (86%) by the whole plant; whereas in 2008 the retention of Hg decreases to 68%.

PM emission levels are highly reduced by the FGD facilities (down to 25 mg/Nm^3, at 6% O_2) below the limits (50 mg/Nm^3) fixed by the European directive 2001/80/EC for large combustion plants. The main contributions to gas and PM emissions are the non-retained FA by FGD and the particles and droplets from gypsum slurry entrained in the OUT-FGD gas, especially gaseous Hg and particulate Se, As, Zn, and Ni.

The retention capacity for most of gaseous pollutants at this power plant is within the range obtained in coal combustion plants of similar capacity; evidencing that co-firing coal with 16-18% petroleum coke has little impact on the abatement capacity for the trace elements studied.

Further work will focus on the parameters controlling Hg speciation and partitioning in the FGD. Remediation actions for reducing Se and As emissions among others will be also addressed, given the major contribution of the filtered water re-circulation to the scrubber.

5. ACKNOWLEDGEMENTS

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Additional findings to Article 2

3.8. RETENTION EFFICIENCY OF THE FGD SYSTEM

The desulphurisation efficiencies obtained from the 2007 and 2008 measurements at PP2 revealed a relatively low retention for SO_2 (82-86% and 82-88% for 2007 and 2008) in comparison with those obtained in other FGD systems such as at PP1 (94%).

In wet FGD processes, SO_2 diffuses through the gaseous phase to the aqueous surface, where it dissolves and is transferred by diffusion or convective mixing into the aqueous phase. The rate at which $SO_{2\,(g)}$ is transferred depends on the solubility of SO_2 and its displacement from equilibrium (Dou et al., 2009). Under acidic conditions, the equilibrium pressure of SO_2 increases and as a consequence the gas absorption rate decreases and approximates to zero (B&W, 1991). In fact, at pH values <5.5 in the liquid-to-gas contact zone, the final end-product of desulphurisation is $Ca(HSO_3)_2$ instead of $CaSO_3$ by increasing H^+ in the aqueous phase as follows (Babcock & Wilcox Power Generation Group, 1991):

$$SO_{2\,(aq)} + H_2O \leftrightarrow H_2SO_{3\,(aq)} \qquad \text{(R1)}$$

$$H_2SO_{3\,(aq)} \leftrightarrow H^+_{(aq)} + HSO_3^-{}_{(aq)} \leftrightarrow H^+_{(aq)} + SO_3^{2-}{}_{(aq)} \qquad \text{(R2)}$$

Reactions (1) and (2) illustrate that an increase of H^+ may reduce the absorption of SO_2 from the gaseous to the aqueous phase with the consequent desorption of SO_2.

The acidic pH of the aqueous phase of gypsum slurry in 2007 (5.1) and 2008 (4.6) might, therefore, be regarded, in conjunction with the low porosity of limestone used at this power plant, as major causes of the relatively low efficiencies of desulphurisation at PP2.

ARTICLE 3

Enrichment of inorganic trace pollutants in re-circulated water streams from a wet limestone flue gas desulphurisation system in two coal power plants

Fuel Processing Technology 92 (2011), 1764-1775

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ABSTRACT

The enrichment of inorganic trace pollutants in re-circulated water streams was studied at two power plants equipped with wet limestone Flue Gas Desulphurisation (FGD) system from the first re-circulation cycle of water up to the start of sampling campaigns. To elucidate the enrichment of inorganic trace pollutants as a result of water re-circulation, a partial and total mass balances were undertaken. A Student's t-test was performed to ascertain whether the mean contribution of filtered water affected the balance of elements and their enrichment this water stream. The Student's t-test revealed the mean contribution of filtered water to total mass balance was statistically significant ($p<0.05$) for Na, Mg, Cl, B, Mn, Se, Cd, Mo, and U at first plant, and Na, Cl, K, Mg, Hg, Li, B, F, Ni, Zn, Mn, Co Sc, Ge, Se, at the second one. High levels of inorganic trace pollutants in filtered water could be affected by limestone purity, electrostatic precipitator gas temperature, use of additives, fluoride and/or sulphate complexes, and the S/F and S/Cl ratios in the scrubber, which may reduce the gaseous retention efficiencies in FGD and increase the emission of metals by entraining and/or evaporation of droplets as particulate matter from gypsum slurry.

Keywords: Inorganic trace pollutants; re-circulated waters; FGD; Mass balance; Scrubber.

1. INTRODUCTION

The current power generation policy of the European Union (EU) promotes the implementation of co-combustion techniques and Flue Gas Desulphurisation (FGD) systems at Pulverised Coal Combustion plants (PCC). However, these techniques not only bring environmental and economic benefits but could also have adverse effects on the environment. Hence, the role of the FGD systems in the abatement of trace pollutants at coal power plants has been extensively studied (Aunela-Tapola et al., 1998; Zauter et al., 2000; Meij and Erbrink, 2001; Kikkawa, 2002;Heebink and Hasset, 2003; Helle et al., 2004; Meij and TeWinkel, 2004, 2006, 2007; Schoeder and Kairies, 2005; Álvarez-Ayuso et al., 2006). A number of processes (Zauter et al., 2000) have been used to prevent and remove SO_2. The wet limestone based process is by far the most widely employed because of its high desulphurisation performance, reliability, and efficiency (Kikkawa, 2002). In this process, SO_2 is removed from flue gas combustion by by reaction with the wet limestone in the scrubber giving rise to the formation of gypsum, which is eventually dewatered. The dissolved SO_2 dissociates to HSO_3^-, which is subsequently oxidised to SO_4^{2-} by injected air. Finally, SO_4^{2-} ions combine with Ca^{2+} ions, originating from dissolved limestone, and crystallise as gypsum (Zheng et al., 2003). The overall reaction in a wet limestone FGD system can be written as follow:

$$CaCO_{3\,(s)} + SO_{2\,(g)} + ½O_{2\,(g)} + 2H_2O_{\,(l)} \rightarrow CaSO_4.2H_2O_{\,(s)} + CO_{2\,(g)} \qquad \text{(R1)}$$

FGD chemistry (alkaline sorbent) allows the capture of many pollutants other than sulphur, such as F, As, B, Cl, Se or Hg(Auneala-Tapola et al., 1998; Heebink and Hasset, 2003; Schoeder and Kairies, 2005; Álvarez-Ayuso et al., 2006; Font et al., 2010), in a gaseous form and/or as particulate matter (PM). Once captured, a certain proportion of the trace pollutants is partitioned into solid and water streams. Low proportions are released in a gaseous and/or PM form.

The design of the FGD system depends on the availability of water near the power plant. Power plants with available water resources are usually designed with effluent treatment plants resulting in sludge with a high pollutant load. Where water resources are scarce, the re-circulation of the water to the scrubber from gypsum slurry filtration is preferred owing to the economic and environmental benefits of recycling.

Enrichment of some inorganic trace pollutants in re-circulated water streams is the most important consequence of FGD systems with re-circulation of water from gypsum slurry. High levels of inorganic trace pollutants in re-circulated waters may give rise a high ionic strength which reduces the gaseous solubility and probably, the retention efficiencies in wet FGD. The enrichment may also increase the concentration of trace pollutants in the re-circulated waters up to very high levels compared with that of the natural fresh waters.This could result in environmental (pollution of soil and groundwater) and technical problems (fouling of scrubber and pipes of the FGD), 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. Furthermore, the contribution of other streams (limestone) and the operational conditions of the FGD system, such as use of additives to control the speciation and the partitioning of trace pollutants into FGD streams. Earlier studies (Font et al, 2008) reported changes on the speciation of F when Al additives are injected into the scrubber. These authors showed that the speciation of trace pollutants especially F plays a crucial role in the leaching potential of the FGD gypsum end-product.

Although the solid by-products of PCC-FGD plants such as Fly Ash (FA) and Boiler Slag(BS, Smith, 1987; Solem-Tismak et al., 1995; Querol et al., 1995; Querol et al, 1997a; Querol et al, 1997b; Pires and Querol, 1997; Spears and Martínez-Tarazona, 2004; Reijnders, 2005)and FGD gypsum (Zheng et al.,2003; Font et al, 2010) have been studied and classified, less attention has been paid to the partitioning, speciation, and enrichment of inorganic trace pollutants in FGD water streams with water re-circulation. The study of FGD water streams with water re-circulation is therefore essential for determining and evaluating the partitioning and speciation of inorganic trace pollutants through FGD system.

The objectives of the present work are: i) to study the enrichment and partitioning of inorganic trace pollutants in re-circulated water streams at two large power plants in Spain (PP1 and PP2) equipped with forced-oxidation wet limestone FGD system from the first re-circulation cycle of water up to the start of sampling campaigns; and ii) to assess the contribution of the most important sources (PM incoming scrubber and limestone) to the enrichment of inorganic trace pollutants in re-circulated water streams. Our results will give rise to subsequent modelling studies of inorganic trace pollutant speciation in FGD water streams with water re-circulation and FGD gypsum and to preventive and/or corrective measures for the removal of inorganic trace pollutants in FGD water streams.

2. MATERIALS AND METHODS

2.1. SAMPLING EXECUTION

The sampling campaigns at PP1 (1075 MW) and PP2 (1200 MW) were carried out at 100% MCR (maximum capacity) and 100% desulphurisation on two consecutive daysin September 2007 at PP1 and in November 2007 and November 2008 at PP2. Both power plants were equipped with a wet limestone FGD system with forced-oxidation. PP1 was fed with 100% coal (60:40 blend of imported bituminous and local high sulphur sub-bituminous coal). PP2 was fed with 82:18 and 84:16 coal/petroleum coke blends for samplings conducted in 2007 and 2008, respectively. The coal at PP2 is a blend of Spanish anthracitic coals and imported South African bituminous coal. The petroleum coke is a blend of Spanish and imported petroleum-cokes.

The FGD system involves a number of water streams that can be separated into 2 groups:

i) Water streams not involved directly in FGD: process and BS water. At PP1, the process water comes from a nearby ash pond overlaying of sulphate and Sr-rich sedimentary rocks, whereas at PP2, the process water is located over metamorphic and igneous rocks. In both power plants, the process waters are used in BS quenching and drainage giving rise to BS water.

ii) FGD water streams: treated and added water, limestone and gypsum slurries, and filtered water. At PP1, a fraction of process water is treated before its use to reduce the high content of salts. The resulting water (treated water) is used for limestone slurry preparation, and is then considered as FGD water stream. The added water is similar in composition to the treated water and is used to offset the water loss because of moisture in the FGD-gypsum and in the emitted gas. Gypsum slurry is the result of the absorption of SO_2 in limestone slurry and the term is referred to the total fraction of the slurry (solid + water) while the term aqueous phase of gypsum slurry is employed for the water fraction of the total fraction. Filtered water is the water stream that results after filtration and dilution of the aqueous phase of gypsum slurry. At PP1, a fraction of filtered water is re-circulated to the scrubber after dilution process, which reduces the concentrations of some elements (especially Cl); while the remaining filtered water fraction is used for limestone slurry preparation. This result in a 0.55/0.45 mixture ratio of limestone slurry and filtered water in the scrubber (named mixture water). At PP2, all filtered water is directly re-circulated to the scrubber and the limestone slurry is only prepared with process water which results in limestone slurry water/filtered water ratio of 0.47/0.53 (mixture water). Furthermore, an aluminium additive is injected into the scrubber at PP2 to boost the reaction of F with Al in order to improve SO_2 sorption by Ca.

The mixture of slurry waters constitutes the main water input into the scrubber. The water output of the FGD systems is constituted by i) the aqueous phase of gypsum slurry; ii) the loss of crystallisation water from FGD-gypsum; and iii) 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 both power plants.

It is should be pointed out that the aqueous phase of gypsum slurry is the water stream where the inorganic trace pollutants can be primarily enriched by dissolution. However, given that the filtered water is the water re-circulated to the scrubber, the enrichment of inorganic trace pollutants should be referenced to filtered water.

A total of 13 streams, 6 solid (feed fuel blend, BS, FA, PM, limestone, and FGD-gypsum) and 7 water streams (process water, BS water, treated water, added water, filtered water, and limestone and gypsum slurries) were sampled and analysed at PP1. At PP2, 11 streams, 6 solids (feed fuel blend, BS, FA, PM, limestone, and FGD gypsum) and 5 water streams (process water, BS water, filtered water, and limestone and gypsum slurries) were collected and analysed in the 2007 and 2008 sampling campaigns (Figure 1).

Isokinetic measurements of gaseous streams were performed at two sampling points (Figure 1), IN-FGD (A) and OUT-FGD (B), simultaneously. Each sampling run lasted about 2.5h. At each sampling point, two trains of sampling system were assembled with specific trapping solutions, one for the capture of anions and metals, and other for the capture and speciation of Hg. In the first case, the gas sampling system was devised according to EN 1911 and EN 14385. In such a system, two impingers 100 mL of de-ionized H_2O (or MilliQ grade water) and two filled with 6 w% HNO_3 and 10 w% H_2O_2 were assembled to determine the concentrations of anions and metals, respectively, in a ice bath. The sampling and speciation of gaseous Hg (Hg^0 and Hg^{2+}) was devised according to EN 13211 and Meij and teWinkel (2006). A train of dark glass impingers in an ice bath was used. The Hg sampling system(Meij and teWinkel, 2006) consists of a first impinger filled with 100 mL of HCl to capture Hg^{2+}, the second impinger containing 3 w% H_2O_2 for SO_2 removal (150mL at point A and 100mL at point B), and the two last impingers containing 4 w% $K_2Cr_2O_7$ with 20 w% of HNO_3 for Hg^0 trapping.

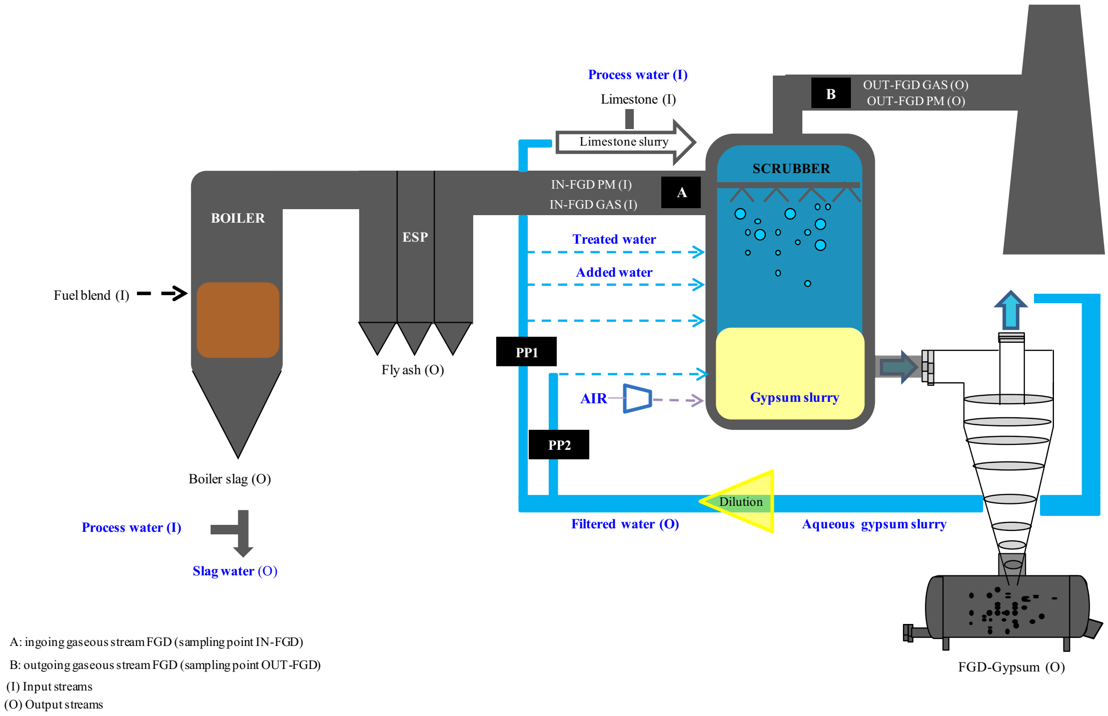

Figure 1.Sampling scheme of PP1 and PP2 and the corresponding samples.

The PM that escapes ESP and FGD is defined and termed fly ash and fly dust (Meij, 1994), respectively, although the terms PM IN and OUT-FGD are used in this article. A quartz filter was placed before the isokinetic train for PM IN and OUT–FGD collection in the Hg sampling. Polytetrafluoroethylene (PTFE) filters were used for the PM capture of anions and metals since HF reacts with quartz to form highly volatile SiF_6^{2-} with a subsequent loss of fluorine.

2.2. CHEMICAL CHARACTERISATION OF SOLID, WATER, AND GASEOUS STREAMS

The solid samples were acid-digested in duplicate by using a two-step digestion method devised by Querol et al (1993). The resulting solution was then analysed by Inductively-Coupled Plasma Atomic-Emission Spectrometry (ICP-AES) for major and minor elements using the Iris Advantage Radial ER/S device from Thermo Jarrell-Ash. Semi-quantitative analyses wereperformed to define the range of element concentrations as well as the matrix and the possible spectral interferences. The calibration was performedusing a series of dilutions from certified traceable standards (1000 and 10000 ppm). Most of the trace elements were analysed by InductivelyCoupled -Plasma Mass Spectrometry (ICP-MS), using the X-SERIES II instrument from Thermo Fisher SCIENTIFIC. The quantitative analyses were performed with an external calibration, using chemical standards of similar matrix of the samples, which covered concentrations range expected forming the calibration lines. The correction for individual sample suppression effects was carried out by means of an internal standard (In 10 ppb). The fly ash and coal international reference material (NBS1633b and SARM19) were also digested to determine the accuracy of the analytical and digestion methods. Chlorine contents in solid samples were determined by ASTM D4208 method using a calorimetric bomb to obtain chlorine in solution, which is measured by High Performance Ion Chromatography (HPIC), and F was determined according to the Pyro-hydrolitic extraction method described in the ISO 11724 standard.

Water streams and trapping solutions from flue gas sampling were directly analysed by ICP-AES and ICP-MS for major and trace elements, respectively. Chloride contents were measured by means of HPIC, whereas fluoride was determined by ion selective electrode. Levels of NH_4^+ in water streams and trapping solutions were analysed using a selective electrode. Mercury analyses were carried out directly on solid, water, and filter samples using a LECO AMA 254 Gold Amalgam Atomic Absorption Spectrometer (GA-AAS).

The levels of PM IN and OUT-FGD were obtained using standard gravimetric methods. The contents of major and trace elements in the filters were determined by ICP-AES and ICP-MS, respectively, after a filter digestion. Particulate Hg was directly determined by GA-AAS on filter samples.

2.3. MASS BALANCES FOR TRACE POLLUTANTS IN FGD WATER STREAMS

The mass balances of FGD water streams operating at PP1 and PP2 during samplings (considering the re-circulation of water streams) were closed with out/in ratios close to 1. Therefore, two mass balances, partial and total mass balances (PMB and TMB) were performed to determine the potential enrichment of inorganic trace pollutants in re-circulated water streams from the first re-circulation cycle of water up to the start of sampling campaigns by normalising the concentration of each element in a given stream with the corresponding sampling flow.

Owing to the impossibility of determining the analytical composition of the FGD waters streams in the first operating cycle of the water re-circulation, an estimation of this cycle was carried out. The first operating cycle estimation was performed by considering the process/treated water as the only water stream for limestone slurry preparation, and by including limestone, gas, PM, and FGD-gypsum as inputs and outputs streams. The first operating cycle estimation was performed considering the following flows:

$$PMB = [(Flow_{FGD\text{-}gypsum} \times C_{iFGD\text{-}gypsum}) + (Flow_{OUT\text{-}FGD\ PM} \times C_{iOUT\text{-}FGD\ PM}) + (Flow_{OUT\text{-}FGDgas} \times C_{iOUT\text{-}FGD\ gas})] / [(Flow_{Limestone} \times C_{i\ Limestone}) + (Flow_{mixture\ water} \times C_{i\ Process/treated\ water}) + (Flow_{IN\text{-}FGDPM} \times C_{i\ IN\text{-}FGD\ PM}) + (Flow_{IN\text{-}FGD\ gas} \times C_{iIN\text{-}FGD\ gas})] \qquad (2)$$

Given the flows considered for this estimation, PMB values ≤ 1 indicate the partial dissolution of a given element in the aqueous phase of gypsum slurry. Two important factors should be borne in mind when considering PMB: a) the solid by-products are produced under re-circulation of water streams. Hence, a number of elements are retained in FGD-gypsum by precipitation if saturation or equilibrium is reached in the aqueous phase; and b) adsorption processes may account for the retention in FGD-gypsum of certain highly soluble elements (such as Cl, B, and Hg).

TMB was performed by considering the process/ treated water as the only water stream for limestone slurry preparation and the filtered water as water output stream. TMB values >1 will therefore suggest elements enriched by re-circulation of filtered water after a number of re-circulations. The flows considered for TMB calculations are detailed as follow:

$$TMB = [(Flow_{FGD\text{-}gypsum} \times C_{iFGD\text{-}gypsum}) + (Flow_{OUT\text{-}FGD\ PM} \times C_{iOUT\text{-}FGD\ PM}) + (Flow_{OUT\text{-}FGDgas} \times C_{i\ OUT\text{-}FGD\ gas}) + (Flow_{Filtered\ water} \times C_{i\ Filtered\ water})] / [(Flow_{Limestone} \times C_{i\ Limestone}) + (Flow_{mixture\ water} \times C_{iProcess/treated\ water}) + (Flow_{IN\text{-}FGD\ PM} \times C_{iIN\text{-}FGD\ PM}) + (Flow_{gas\ IN\text{-}FGD} \times C_{i\ IN\text{-}FGD\ gas})] \qquad (3)$$

where the output and input flows ($Flow_x$) are the flows for a given stream ($_x$) IN and OUT-FGD for mass balance calculations; and C_i is the mean concentration of a certain element in the corresponding stream IN and OUT-FGD. The flows of mixture water are 80.1 and 52.5 g/h for PP1 and PP2, respectively. A number of species were omitted from PMB and TMB (NO_3^- and NH_4^+) given their low concentrations and their partial secondary origin.

Combining information from PMB and TMB will allow us to determine the behaviour and water–solid partitioning of elements in the wet limestone FGD system with re-circulation of filtered water, and their enrichment or depletion in filtered water.

2.4. STATISTICAL ANALYSIS

A Student's t-testwas performed to determine the accuracy of the results and to ascertain statistically whether the differences between PMB and TMB (out/in ratios) were due to an enrichment of inorganic trace pollutants in filtered water. We ascertained whether the mean contribution of filtered water for a given element to TMB was significant ($p<0.05$) and whether the differences between PMB and TMB were attributable to the enrichment of the element in filtered water. The Student's t-testwas applied to mean flow (g/h) from 4 and 6 sub-samples of the filtered water, for each element, at PP1 and PP2, respectively. The Student's t-testwas applied to the elements with differences ≥0.2 for the out/in ratios between PMB and TMB.

3. RESULTS AND DISCUSSION

The solid (limestone), water (process water/treated water and mixture of slurry waters), and gaseous streams IN-FGD (including PM) are the sources of trace pollutants in the FGD system (Table 1). Nevertheless, the characteristics of the feed fuel blend are crucial for the FA composition and also of PM that escapes from the ESP.

Table 1. Source of major, minor, and trace elements to FGD system at PP1 and PP2.

	PP1 2007	PP2 2007	PP2 2008
Limestone	Al, Ca, Fe, Na, K, Mg, Li, Sc, Ti, P, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Sn, Ba, Pb and U (64-100%)	Ca, Fe, Mg, P, Mn, Co, Se, Sr, Y, Mo, Pb, and U (35-100%)	Ca, Fe, Mg, Cr, Mn, Ni, Cu, Se, Sr, Y, and U (61-97%)
IN-FGD PM	Be, Ge, Mo, Cd, Bi, and REEs (99-100%)	Na, K, Li, Be, Sc, Ti, V, Cr, Ni, Cu, Zn, Ga, Ge, As, Rb, Sn, Sb, Ba, Se, and REEs (48-100%)	K, Li, Be, Sc, Ti, P, V, Co, As, Ba, Mo, Zn, Ga, Ge, Pb, and REEs (57-100%)
IN-FGD GAS	S, Cl, F, Hg, B, and Se (68-99%)	S, Cl, F, Hg, and B (90-99%)	S, Cl, F, Hg, and B (80-99%)
Al-additive	-	Al (88%) and S (9%)	Al (77%) and S (0.7%)

IN-FGD PM: fly ash that escapes from the electrostatic precipitator (ESP) and enter into the FGD system.
IN-FGD GAS: gaseous stream that enter into the FGD system.
Al-additive: additive of Aluminium used at PP2.

3.1. CHARACTERISATION OF SOLID STREAMS

3.1.1.Feed fuel blend

The feed fuel blends at PP1 and PP2 are characterised by high ash (28-29%, dry basis (db)). The feed fuel blend at PP1 is characterised by high to moderate contents of S, Fe, and Ca with respect to feed fuel blend at the PP2, and by a number of trace elements such as Sr and U. The feed fuel blend has higher contents of Na, K, Rb, Sb, and Hg at PP2 than at PP1. The petroleum coke co-firing at PP2 gives rise to high contents of V and Ni in the feed fuel blend (Table 2). Both the organic affinity and high contents of V and Ni in the petroleum coke may promote the condensation of these elements in FA and a subsequent higher contribution as PM IN-FGD at PP2 than at PP1.

3.1.2.Fly ash and boiler slag

In line with the observations on the feed fuel blend chemistry, FA at PP1 is enriched in Ca (by a factor of 2), in B (3), Ge (3), and U (3) with respect to FA at PP2. By contrast, the FA at PP2 is enriched in Na (5), K (3), V (6), Ni (4), Rb (2), Sb (7), and Ba (2) (Table 2).

The FA/BS concentration ratio determined for FA at PP2 is similar to that at PP1 despite the use different feed fuel blends. Nevertheless, it should be noted that the FA/BS ratio for elements with a high condensation potential is higher for Ni (1.3), Ge (1.5), As (1.8), Se (1.8), Sn (1.6), Sb (1.3), Zn (1.1), and Pb (1.3) at PP2 than that at PP1 (Table 2). In spite of the volatised proportion of the elements during combustion at PP1 and PP2, the lower ESP gas temperatures at PP2 (149˚C) with respect those at PP1 (170-180˚C) may also account for enhancing condensation during co-combustion and a higher PM contribution to FGD at PP2 than at PP1.

3.1.3. Limestone and FGD-gypsum

The limestone used in the FGD system at PP1 has relatively high contents of Mn and Sr (Table 3). The PP1 limestone also contains significant concentrations of Al, F, Ti, P and minor contents of Cl and U. Conversely, the limestone used at PP2 (Table 3) has a high purity (99% Ca-carbonate), with only Cl, Sr, and Mn being present in significant levels.

FGD-gypsum at PP1 has significant proportions of Ca, S, Mg, Al, and Fe. FGD-gypsum at PP1 also contains high concentrations of F, Cl, Ti, P, Sr, and minor contents of Mn and U. FGD-gypsum at PP2 shows a similar composition with slight differences in some elements (Table 3). FGD-gypsum at PP2 is enriched in Cl, F, Mn, and Hg, and depleted in S, Mg, Al, Fe, and Ti with respect to PP1 FGD-gypsum.

Table2. Mean concentration of major, minor, and trace elements in feed fuel blend, FA, BS, andFA/BS ratios.

	PP1 2007				PP2 2007				PP2 2008			
	Fuel blend	FA	BS	FA/BS	Fuel blend	FA	BS	FA/BS	Fuel blend	FA	BS	FA/BS
% dry basis (db)												
Al	3.5	14	13	1.1	3.2	13	13	1.0	3.3	14	13	1.0
Ca	1.1	4	4	1.0	0.5	2	2	1.0	0.5	2	2	1.0
Fe	3.7	13	16	0.8	1.4	5	6	0.9	1.3	5	5	1.0
Na	0.05	0.1	0.1	1.0	0.2	0.5	0.5	1.0	0.2	0.6	0.5	1.0
S	5.4	0.3	0.04	7.5	1.8	0.2	<0.1	>2	1.6	0.1	0.04	3.7
K	0.3	1	0.9	1.1	1.0	3	3	1.0	0.9	3	3	1.0
Mg	0.2	0.7	0.6	1.1	0.3	1	1	1.0	0.3	1	1	1.0
mg/kg (db)												
Cl	47	15	20	0.8	118	133	94	1.4	96	94	83	1.1
F	197	123	7	18	186	135	14	10.0	229	157	14	11.0
Hg	0.08	0.04	0.002	20	0.2	0.09	0.01	13.0	0.2	0.082	0.001	62.0
Li	70	298	263	1.1	56	197	197	1.0	54	212	204	1.0
Be	3.0	11	9	1.2	1.5	5.6	5.5	1.0	1.4	5.3	5.2	1.0
B	43	211	58	3.7	32	70	22	3.2	39	92	49	1.9
Sc	4.7	23	19	1.2	5.3	22	22	1.0	5.3	23	23	1.0
Ti	1420	5468	5199	1.1	1535	5819	6042	1.0	1271	5526	5498	1.0
P	566	2014	1380	1.5	411	1644	1011	1.6	494	1780	1217	1.5
V	57	219	162	1.4	447	1414	1157	1.2	285	1194	941	1.3
Cr	38	149	153	0.9	46	149	150	1.0	32	170	157	1.1
Mn	82	321	340	0.9	136	516	558	0.9	115	566	589	1.0
Co	9.1	33	35	0.9	8.6	30	27	1.1	9.2	35	31	1.1
Ni	20	74	74	1.0	90	288	227	1.3	64	229	184	1.2
Cu	17	63	59	1.1	22	81	68	1.2	25	102	83	1.2
Zn	65	309	174	1.8	50	184	87	2.1	49	192	104	1.8
Ga	11	47	32	1.5	9.7	36	22	1.7	8.5	38	26	1.5
Ge	2.0	7.9	4.9	1.7	<0.1	3.3	1.2	2.6	<0.1	3.2	1.2	2.6
As	21	85	15	5.5	24	94	9.2	10.0	23	90	9.0	9.8
Se	1.5	4.7	1.0	4.7	0.7	1.1	0.1	11	0.3	0.9	1.0	0.9
Rb	19	81	71	1.1	45.1	162	165	1.0	41	173	171	1.0
Sr	258	1001	947	1.1	87	381	368	1.0	82	293	290	1.0
Y	13	51	49	1.1	9.8	37	38	1.0	9.0	38	37	1.0
Zr	43	197	204	0.9	36	159	177	0.9	30	158	168	0.9
Nb	5.8	17	17	1.0	8.9	32	33	1.0	9.2	37	40	0.9
Mo	3.0	14	5.3	2.6	6.6	23	8.1	2.9	6.1	22	8.0	2.7
Cd	<0.2	0.9	<0.1	>9	<0.1	0.7	<0.1	>7	<0.1	1.0	<0.1	>10
Sn	1.9	8.2	3.9	2.1	1.5	6.6	2.0	3.3	1.5	7.0	2.8	2.5
Sb	0.9	3.4	1.8	1.8	4.2	17	6.8	2.5	4.8	23	10	2.3
Cs	3.5	15	13	1.2	6.0	22	21	1.0	6.2	25	24	1.1
Ba	166	683	639	1.1	292	1111	1118	1.0	246	1125	1086	1.0
La	15	57	56	1.0	13	48	48	1.0	11	47	46	1.0
Ce	35	133	131	1.0	31.6	119	125	1.0	28	117	115	1.0
Pr	3.3	14	13	1.1	3.2	12	12	1.0	2.7	11	11	1.0
Nd	14	56	56	1.0	14	52	53	1.0	11.9	50	49	1.0
Sm	2.8	12	11	1.1	2.9	11	11	1.0	2.6	11	11	1.0
Eu	<0.1	1.9	1.7	1.0	<0.1	1.6	1.6	1.0	<0.1	1.8	1.7	1.0
Gd	2.9	12	12	1.0	2.6	10	10	1.0	2.4	10	10	1.0
Tb	<0.1	1.5	1.4	1.1	<0.1	1.3	1.3	1.0	<0.1	1.3	1.2	1.0
Dy	2.0	8.8	7.9	1.1	1.9	7.2	7.4	1.0	1.6	6.9	6.7	1.0
Ho	<0.1	1.6	1.5	1.1	<0.1	1.4	1.4	1.0	<0.1	1.3	1.3	1.0
Er	1.0	4.3	3.9	1.0	0.9	3.4	3.5	0.9	0.4	3.3	3.2	1.0
Yb	<0.1	4.8	4.5	1.0	1.0	3.9	4.1	1.0	0.9	3.8	3.7	1.0
Hf	1.1	6.5	6.4	1.1	1.0	4.6	5.3	1.0	0.7	4.6	5.0	1.0
Ta	1.1	2.3	2.5	0.9	1.0	3.6	4.5	0.8	1.8	2.3	4.8	0.5
W	2.6	9.3	5.4	1.7	1.8	8.4	4.7	1.8	2.4	11	6.8	1.6
Tl	<0.1	1.6	<0.01	>160	<0.1	1.5	<0.01	>150	<0.1	1.6	<0.01	>160
Pb	13	59	30	1.9	20	83	34	2.4	23	102	42	2.4
Bi	<0.1	1.5	<0.01	>150	<0.1	1.1	<0.01	>110	<0.1	1.5	<0.01	>150
Th	6.5	28	25	1.1	6.8	27	28	1.0	6.0	26	25	1.0
U	4.8	22	18	1.3	2.0	7.0	7.0	1.0	1.9	8.3	7.6	1.0

Table 3.Mean concentration of major, minor, and trace elements in limestone and gypsum at PP1 and PP2.

	PP1 2007		PP2 2007		PP2 2008	
	Limestone	FGD-gypsum	Limestone	FGD-gypsum	Limestone	FGD-gypsum
% dry basis (db)						
Al	0.5	0.3	<0.1	0.1	<0.1	0.1
Ca	37	23	39	25	39	25
Fe	0.3	0.2	0.1	0.1	0.0	0.05
Na	0.01	0.02	<0.1	<0.1	<0.1	<0.01
S	0.03	18	<0.1	15	<0.1	15
K	0.2	0.1	<0.1	<0.1	<0.1	<0.01
Mg	0.5	0.4	0.3	0.2	0.2	0.2
mg/kg (db)						
Cl	24	297	807	1519	838	1359
F	217	931	14	904	16	2286
Hg	0.003	0.154	0.0002	0.3	0.002	0.3
Li	7.6	4.8	<0.01	1.4	<0.01	0.7
Be	<0.1	<0.1	<0.01	<0.1	<0.01	<0.01
B	7.9	14	<0.01	7.7	14	31
Sc	1.3	0.8	<0.01	<0.1	<0.001	<0.01
Ti	293	201	8.5	22	11	24
P	178	136	<0.01	<0.01	<0.01	<0.01
V	11	6.9	1.2	6.7	2.6	5.6
Cr	7.9	4.8	0.7	0.8	1.4	2.1
Mn	86	56	142	93	121	67
Co	1.6	0.9	0.8	<0.1	<0.01	<0.01
Ni	8.4	4.2	4.7	4.7	6.2	4.9
Cu	2.7	2.1	0.8	1.0	1.0	1.1
Zn	18	<0.01	<0.01	0.5	<0.01	4.6
Ga	1.4	0.9	<0.01	<0.1	<0.01	<0.01
Ge	<0.01	<0.01	<0.01	<0.1	<0.01	<0.01
As	2.2	2.0	<0.01	1.1	0.8	0.9
Se	<0.01	2.2	1.4	1.3	1.7	2.6
Rb	8.5	4.6	<0.01	<0.1	<0.01	0.7
Sr	161	113	186	115	188	120
Y	2.3	1.4	4.7	3.2	2.8	2.4
Zr	7.5	5.3	<0.01	<0.1	<0.01	1.1
Nb	0.8	0.5	<0.01	<0.1	<0.01	<0.01
Mo	<0.01	<0.01	1.5	<0.1	<0.01	<0.01
Cd	<0.2	<0.2	<0.01	<0.1	<0.01	<0.01
Sn	0.1	0.1	<0.01	0.6	<0.01	<0.01
Sb	<0.1	<0.01	<0.01	<0.1	<0.01	<0.01
Cs	0.9	<0.01	<0.01	<0.1	<0.01	<0.01
Ba	22	16	1.6	4.8	3.9	4.6
La	2.5	1.5	1.6	1.3	<0.001	0.4
Ce	5.4	3.1	3.1	2.5	1.7	1.8
Pr	<0.1	<0.01	<0.01	<0.1	<0.01	<0.01
Nd	2.7	1.7	1.9	1.5	0.9	1.0
Sm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Eu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Gd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dy	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ho	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Er	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Yb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Lu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Hf	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ta	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
W	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	1.5	1.4	1.6	1.1	0.4	0.9
Bi	<0.1	<0.01	<0.01	<0.01	<0.01	<0.01
Th	0.9	<0.01	<0.01	<0.01	<0.01	<0.01
U	2.7	2.3	1.0	1.0	1.5	1.1

3.2. CHARACTERISATION OF GASEOUS STREAMS AND PARTICULATE MATTER

3.2.1.Gaseous streams

Significant differences in the gaseous streams are observed for S, Hg, F, Cl, B, Se, and As IN-FGD at the two power plants. SO_2 is the dominant specie IN-FGD reaching levels around 14500 mg/m^{3}N at PP1, and 4000-5000 mg/m^{3}N at PP2. These levels are drastically decreased after FGD (Table 4), which indicate that SO_2 emissions are successfully reduced. The levels of B, Se, and As are also higher at PP1 than those in 2007 and in 2008 at PP2. These levels decrease after FGD, yielding reduction rates >89% at PP1, and 67-92% in 2007 and >91% in 2008 with the exception of Se reduction rate (37%) at PP2.

By contrast, the Cl and F levels IN-FGD are higher in 2007-2008 at PP2 than those at PP1 (Table 4). Fluorine and Cl levels decrease markedly after FGD (retention rate>97%) at two power plants. In line with the higher Hg concentration in the feed fuel blend at PP2, the concentration of total Hg IN-FGD is markedly higher in the two campaigns at PP2 than at PP1, attaining reduction levels of 21% and 65% at PP2, and 72% at PP1.The detailed behaviour of gases IN and OUT-FGD and the emissions from PP1 and PP2 are reported elsewhere (Font et al., 2010).

Table 4.Concentration of gaseous components IN and OUT-FGD and gaseous retention efficiencies at PP1 and PP2.

		mg/m^{3}N	µg/m^{3}N							
		SO_2	Cl^-	F^-	B	Se	As	Hg tot	Hg^{2+}	Hg^0
PP1 2007	IN-FGD	14595	6212	23019	385	88	1.2	7.8	5.8	2.0
	OUT-FGD	989	202	370	16	5.2	0.1	2.2	0.7	1.6
	% retention	94	97	99	96	94	89	72	89	26
PP2 2007	IN-FGD	4319	7191	14357	187	1.0	0.3	21	18	3.0
	OUT-FGD	779	51	78	15	0.2	0.1	7.4	4.9	2.5
	% retention	82	99	99	92	80	67	65	73	17
PP2 2008	IN-FGD	4746	6148	31296	310	1.8	0.8	19	17	2.2
	OUT-FGD	555	93	147	26	1.2	0.01	15	13	2.0
	% retention	88	98	100	91	37	98	21	24	9.1

3.2.2.Particulate matter

The higher inputs of most condensing elements in PM at PP2 (Table 5) should be pointed out. At PP2, the content of Cu is higher in 2007 PM (by a factor of 10), in Sb (9), Ni (8), Hg (6), V (5), Pb (5), Se (4), Mo (4), Rb (4), As (3), Ba (3), and Zn (2), with respect to PM IN-FGD at PP1 given the aforementioned higher enrichment of the condensing elements in FA at PP2 than those at PP1. It is also worth mentioning the higher contribution of PM in 2007 than in 2008 at PP2.

The results on chemical characterisation of PM (Table 5) reveals that the contents of most elements tend to decrease in PM OUT-FGD with the exception of S, Se, and Hg. The concentrations of S, Se, and especially Hg (at PP2) in PM increased in OUT-FGD with respect to IN-FGD probably due to the entraining of gypsum slurry particles by the gas OUT-FGD and/or evaporation of gypsum slurry droplets subsequently condensed on filters. PM levels fell considerably (45%) at PP1 and (69-78%) atPP2 after FGD.

Table 5.Mean concentrations of PM IN and OUT-FGD at PP1 and PP2.

	PP1 2007		PP2 2007		PP2 2008	
mg/m^{3}N	IN-FGD	OUT-FGD	IN-FGD	OUT-FGD	IN-FGD	OUT-FGD
Al	5.2	1.2	7.6	3.1	2.9	0.7
Ca	2.2	0.5	2.0	2.1	0.4	0.3
Fe	4.7	1.0	5.3	1.2	1.1	0.3
K	0.3	0.1	2.0	0.7	0.6	0.2
Mg	0.2	0.1	0.9	0.6	0.3	0.2
Na	0.01	0.01	0.4	0.2	0.1	0.1
P	0.2	0.1	0.4	0.1	0.1	0.02
S	0.9	4.1	5.1	3.5	0.5	0.6
µg/m^{3}N						
Li	16	3	13	6.3	4.7	1.1
Be	0.6	0.1	0.4	0.2	0.1	0.04
B	4.3	0.1	1.9	0.6	<0.001	<0.001
Sc	1.3	0.3	1.5	0.6	0.6	0.1
Ti	313	57	395	150	138	52
V	26	4.7	133	54	37	11
Cr	20	12	406	4.9	3.9	1.7
Mn	24	6.7	76	26	16	10
Co	1.9	0.4	4.2	1.0	0.9	0.3
Ni	27	8.4	220	10.6	6.5	3.1
Cu	5.7	4.3	57	7.7	2.7	1.2
Zn	29	8.3	55	39	12	5.7
Ga	3.0	0.6	4.5	1.8	1.3	0.4
Ge	0.5	0.2	1.0	0.7	0.3	0.1
As	7.9	2.3	21	12	6.0	3.3
Se	3.6	27	14	17	1.3	0.9
Rb	2.2	0.7	9.7	3.1	3.4	0.7
Sr	62	12	27	21	7.3	2.4
Y	2.0	0.5	2.9	1.6	1.0	0.3
Zr	10	1.9	13	6.4	4.9	1.9
Nb	1.2	0.3	2.5	0.8	1.1	0.3
Mo	3.3	1.6	13	4.3	2.0	<0.001
Cd	0.2	0.3	0.6	0.3	0.1	0.1
Sn	1.8	0.3	3.0	0.7	0.4	0.2
Sb	0.4	0.1	3.4	1.4	1.3	0.4
Cs	0.4	0.1	1.3	0.5	0.5	0.1
Ba	31	6.9	89	38	29	5.4
La	2.9	0.6	4.5	2.3	1.4	0.5
Ce	7.1	1.3	8.9	3.8	2.9	0.7
Pr	0.6	0.1	1.1	0.6	0.3	0.1
Nd	2.3	0.6	4.7	2.4	1.5	0.5
Sm	0.5	0.1	1.0	0.5	0.3	0.1
Eu	0.1	0.02	0.1	0.1	0.05	0.02
Gd	0.4	0.1	0.8	0.4	0.3	0.1
Tb	0.1	0.01	0.1	0.1	0.03	0.01
Dy	0.3	0.1	0.6	0.3	0.2	0.1
Ho	0.1	0.02	0.1	0.1	0.04	0.01
Er	0.2	0.04	0.3	0.1	0.1	0.03
Yb	0.2	0.04	0.3	0.2	0.1	0.04
Hf	0.2	0.1	0.5	0.3	0.2	0.1
Ta	0.3	0.04	0.3	0.04	0.4	0.01
W	1.2	0.3	2.3	0.6	0.6	0.3
Tl	0.2	0.1	0.7	0.4	0.1	0.02
Pb	4.2	0.8	21	5.8	3.8	1.2
Bi	0.2	0.04	0.7	0.2	0.1	0.1
Th	1.3	0.3	2.3	1.1	0.8	0.3
U	1.0	0.2	0.8	0.6	0.2	0.1
Hg (ng/m^{3}N)	1.3	8.8	7.3	9.4	0.7	1.8

3.3. CHARACTERISATION OF WATER STREAMS

3.3.1.Treated and process water streams

The treated water is characterised by relatively high concentrations of Sr, B, Li, Ca, U, Cl, and S at PP1; probably attributable to aforementioned source of process water. At PP2, the process water shows low concentration of most elements, only B, Sr, and Mn are slightly enriched in this water stream in the two sampling campaigns (Table 6).

3.3.2.Limestone and gypsum slurry and filtered waters

The aqueous phases of limestone and gypsum slurry at PP1 have very high concentrations of S, Mg, Ca, and Cl (Table 6), followed by B, Li, Se, Ba, Mo, and especially Ni, Zn, Co and U in the aqueous phase of gypsum slurry. This could be related with the relatively high mobility of oxy-anionic species (i.e. As, B, Cr, Mo, Se, and V) and the slightly alkaline pH (7.4-7.6) of both aqueous phases. In the case of the limestone slurry, the high contents of the above elements are attributed to the re-circulation of a fraction of filtered water for limestone slurry preparation. Furthermore, U may form stable uranyl complexes with carbonates that may promote presence of U bearing complexes in the aqueous phase of gypsum slurry (Basiric, 1991). The leaching of FA particles reaching FGD system may also account for the high concentration of abovementioned oxy-anionic species and U complexes in the aqueous phase of limestone and gypsum slurries.

At PP2, the aqueous phase of limestone and gypsum slurries have high concentrations of elements associated with soluble salts (Ca, K, Mg, Na, S, Sr, and Cl) and major and minor elements (B, Mn, Cu, Se, Cu Ba, and U), which give rise a high ionic strength in these water streams. The high concentration of these elements in the aqueous phase of limestone and gypsum slurries may be ascribed to the dissolution of limestone components and to the complete re-circulation of the filtered water to the scrubber, respectively. The re-circulation of the filtered water also accounts for the increase in B, Sr, Se, and Ba in the 2008 aqueous phase of gypsum slurry given the similar contribution of these elements by gaseous and PM streams in 2007 and 2008. The decrease in Ni, Co, Be, Cu, and Th in the 2008 aqueous phase of gypsum slurry is due to the aforementioned lower PM contribution in 2008. It is worth mentioning that the high Ni concentrations in the petroleum coke is in line with the acidic-natured gypsum slurry at PP2 ($pH<5$) that increases its solubility with respect to alkaline wastes. Petroleum coke is also an important source of V, but this element reveals a different response and remains highly immobile under slightly acidic conditions. Other differences between sampling campaigns are the higher contents of Mg, S, and Al in the 2007 aqueous phase of gypsum slurry than those in 2008 owing to the high dosages of the Al-additive (68 and 14 kg/h, respectively) and to the addition of MgO during the operational period of 2006-2007 (Table 6).

The differences between PP1 and PP2 in FGD waters are due to the higher concentrations of some elements in the aqueous phase of limestone slurry PP1. This is the result of a fraction of filtered water for limestone slurry preparation, and the different contents of Al (by a factor of 20 to 40) and of F (by a factor of 2 to 20) in the aqueous phase of gypsum slurry at PP2 with respect to those at PP1 (Table 6). The addition of Al to the scrubber at the PP2 modifies the partitioning of these elements, promoting the presence of soluble Al-fluoride complexes and reducing the fraction in FGD-gypsum. In addition, a highly acid insoluble Al-fluoride ralstonite ($NaMgAlF_6.H_2O$) is formed (Font et al., 2008) instead of fluorite (CaF_2), probably because ralstonite forms an iso-structural solid solution between hydrated Al-fluoride complexes rich in Na and Mg compounds (Harivandi, 1999).

Filtered water shows a composition similar to that of the corresponding aqueous phase of gypsum slurries. However, the highly efficient dilution at PP1 increases the differences between filtered water and aqueous phase of gypsum slurry in terms of element concentration. These differences are especially significant for Ni, Zn, and Cd with concentrations over 2 orders of magnitude higher in filtered water at PP2 than at PP1 (Table 6).

Table 6. Mean concentration of major, minor, and trace elements in treated/ process waters, limestone and gypsum slurry waters, and filtered water at PP1 and PP2.

	PP1 2007				PP2 2007				PP2 2008			
	TW	ALS [a]	AGS [b]	FW[C]	PW	ALS [a]	AGS [b]	FW[C]	PW	ALS [a]	AGS [b]	FW[C]
pH	7.3	7.5	7.6	7.4	5.6	7.0	5.0	5.3	7.7	9.0	4.6	5.1
K (µS/cm)	875	10400	17830	11663	14915	1807	24932	22484	150	3947	39853	42175
Flow (t/h)	24	87	71.6	71.6	54	24.5	28	28	52	20.2	28	28
mg/L												
Al	<0.4	<5	<10	<10	<0.2	<2	642	581	<0.2	0.2	38	27
Ca	151	795	807	763	18	294	781	728	16	365	950	828
Fe	<0.05	<0.1	<0.1	<1	<0.1	<0.5	14	11	0.1	<0.1	5.9	3.1
K	3	61	113	65	0.9	4.9	97	87	0.8	7.8	102	73
Mg	36	1643	3414	1871	8.4	322	10394	9584	7.5	306	5638	4240
Na	10	173	300	185	3.8	6.9	17	16	3.6	9.3	79	58
Mn	0.006	3	103	54	0.03	0.6	510	470	0.1	0.5	416	321
P	<0.2	<2.5	<5	<5	<0.1	<1	<10	<10	<0.1	<2.5	<5	<0.1
S	117	3048	5725	3419	12	667	17551	15947	13	857	12123	9165
Si	3.1	11	63	29	1.6	4.1	104	95	0.7	11	77	62
F	0.4	14	87	54	0.1	12	1273	1055	0.2	6.6	185	169
Cl	55	797	841	664	2.4	145	3675	3369	4.5	176	3420	3059
B	0.1	25	48	28	0.4	3.6	126	116	0.02	7.9	145	117
Sr	3.0	4.8	2.5	4.3	0.07	0.4	2.1	2	0.06	0.7	3.9	3.2
NO_3^-	ND	598	1239	594	0.5	307	8675	ND	2.4	29	1201	932
SO_4^{2-}	351	9129	17118	10223	44	1247	45740	47760	40	2570	36370	27495
NH_4	ND	1.0	1.0	0.7	ND	ND	ND	ND	0.2	0.7	15	15
Hg	0.001	0.001	0.01	0.002	0.002	0.05	2.0	2.0	0.004	0.02	1.7	1.5
µg/L												
Li	19	619	1231	705	4.1	56	1537	1501	2.4	88	1468	1159
Be	<0.8	<0.1	1.9	<0.1	<0.8	<0.1	12	13	<0.8	<0.1	<0.1	<0.1
Sc	5.6	25	63	31	24	44	166	214	<0.8	1.4	22	18
Ti	1.5	10	31	14	5.3	12	86	85	<0.8	1.3	49	29
V	4.8	72	168	94	1.1	11	395	356	<0.8	18	158	104
Cr	1.4	3.4	4.8	3.6	1.3	4.7	15	14	<0.8	6.6	10	7.7
Co	5.8	11	201	85	<0.8	4.2	827	815	<0.8	2.2	505	382
Ni	<0.8	69	514	236	1.1	52	5214	5303	1.5	29	2779	2099
Cu	2.8	20	53	27	5.6	11	319	337	1.4	7.2	196	126
Zn	11	<0.1	346	22	6.8	46	4776	4777	<0.8	<0.1	4824	3567
Ga	<0.8	<0.1	2.6	1.1	1.1	1.6	18	28	<0.8	<0.1	4.8	2.5
Ge	<0.8	<0.1	3.2	1.8	<0.8	1.1	17	22	<0.8	<0.1	15	14
As	<0.8	29	52	28	1.3	3.7	67	76	<0.8	2.7	53	38
Se	2.3	145	470	262	3.5	38	405	646	<0.8	82	1496	1956
Rb	1.4	30	72	41	1.0	5.4	14	15	<0.8	15	71	56

Table 6.Continuation.

	PP1 2007				PP2 2007				PP2 2008			
	TW	ALS [a]	AGS [b]	FW[C]	PW	ALS [a]	AGS [b]	FW[C]	PW	ALS [a]	AGS [b]	FW[C]
μg/L												
Y	<0.8	<0.1	2.9	<0.1	<0.8	<0.1	77	76	<0.8	<0.1	28	21
Zr	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	8.3	7	<0.8	<0.1	18	12
Nb	<0.8	<1	<0.1	<0.1	<0.8	<0.1	1.9	1.3	<0.8	<0.1	<0.1	<0.1
Mo	0.9	79	65	51	<0.8	3.9	56	53	<0.8	4.1	30	21
Cd	<0.8	<0.1	25	8.0	<0.8	<0.1	162	163	<0.8	<0.1	204	159
Sn	<0.8	<0.1	<1	<0.1	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<1
Sb	<0.8	1.1	1.6	1.0	<0.8	1.2	14	14	<0.8	2.6	29	23
Cs	<0.8	<0.1	1.3	<0.1	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1
Ba	40	59	188	131	8.2	9.1	149	154	7.0	14	295	236
La	<0.8	<0.1	1.3	<0.1	<0.8	<0.1	17	17	<0.8	<0.1	6.9	5.4
Ce	<0.8	<0.1	1.5	<0.1	<0.8	<0.1	18	18	<0.8	<0.1	8.3	6.7
Pr	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	2.3	2.3	<0.8	<0.1	<0.1	<0.1
Nd	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	8.9	8.6	<0.8	<0.1	4.6	3.7
Sm	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	2.2	2.1	<0.8	<0.1	<0.1	<0.1
Eu	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1
Gd	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	4.8	5.5	<0.8	<0.1	2.8	2.6
Tb	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1
Dy	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	3.5	3.4	<0.8	<0.1	3.0	2.9
Ho	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	1.1	<0.1	<0.8	<0.1	<0.1	<0.1
Er	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	2.8	2.7	<0.8	<0.1	3.1	2.3
Tm	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1
Yb	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	4.2	4.2	<0.8	<0.1	4.0	3.0
Lu	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	1.0	<0.1	<0.8	<0.1	<0.1	<0.1
Hf	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	1.1	<0.1	<0.8	<0.1	<0.1	<0.1
Ta	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	9.9	5.4	<0.8	<0.1	<0.1	<0.1
W	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	2.3	<0.1	<0.8	1.7	2.5	<0.1
Tl	<0.8	<0.1	5.0	<0.1	<0.8	<0.1	5.0	4.4	<0.8	<0.1	5.2	4.0
Pb	<0.8	<0.1	<0.1	<0.1	2.3	<0.1	2.3	2.1	<0.8	<0.1	3.0	2.3
Bi	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	<0.1	<0.1
Th	<0.8	<0.1	<0.1	<0.1	<0.8	<0.1	6.4	5.4	<0.8	<0.1	<0.1	<0.1
U	2.2	99	330	219	<0.8	12	654	568	<0.8	8.0	667	494

PW: process water; TW: treated water; ALS: aqueous phase of limestone slurry; AGS: aqueous phase of gypsum slurry; FW: filtered water

For mass balance calculations it is necessary to normalise the concentration of each element in a given stream with the corresponding stream flow. Low concentrations of a given element together with a high flow rates result in high net inputs into FGD. Nevertheless, a high concentration of a given element and a low flow rate may also take place. Owing to the high S content of the feed fuel at PP1, the limestone and gypsum slurry stream flows (Table 6) considerably exceeds those at PP2.

3.4. FGD MASS BALANCES AND ENRICHMENT OF INORGANIC TRACE POLLUTANTS

PMB and TMB and the Student's t-testof inorganic trace pollutants in FGD at PP1 and PP2 are shown in Tables 7 and 8, respectively. Based on the results of the mass balances, the elements in the FGD waters at PP1 and PP2 may be classified as follows (Table 9):

i. Elements enriched in filtered water (0.7≤PMB≤1.2 and TMB≥1.2)
ii. Elements not enriched in filtered water (PMB≤1.0 and TMB ≤1.2).
iii. Elements with uncertain behaviour (PMB≤0.8 and TMB ≤0.8).

It is important to note that the limit values of PMB and TMB for elements enriched in filtered water were established in accordance with i) PMB values ≤1 indicate the partial dissolution of a given element in the aqueous phase of gypsum slurry; ii) TMB values >1 will suggest elements enriched by re-circulation of filtered water after a number of re-circulations; and with iii) the lowest PMB closure (0.7) reached by an element. The limit values of PMB and TMB for elements not enriched in filtered water and those with uncertain behaviour were established in accordance with the factors considered for elements enriched in filtered water and with the lowest PMB (0.8) and TMB (0.8) closure reached by an element.

Although Student's t-test was only performed in case of differences ≥0.2 in the out/in ratios between PMB and TMB, it was also applied to a few additional elements at each power plant to verify the aforementioned classification based on the mass balances in FGD waters.

3.4.1. Elements enriched in filtered water

The elements enriched in filtered water (0.7≤PMB≤1.2 and TMB≥1.2) are: Na, Mg, Cl, B, Mn, Se, Cd, Mo, and U (PP1), and Na, Cl, K, Mg, F, Hg, Li, B, Mn, Sc, Co, Ni, Cu, Ge, Zn, Se, Cd, and U (PP2).

The enrichment of these elements is attributed to the following factors:

Dissolution of carbonate-bearing elements from limestone and formation of soluble sulphate complexes in the scrubber: Na, Mg, Mn, and U (99%, PP1) and Mg, Mn, and U (89-95%, PP2), and also Cu, Ni, and Co (PP2 in 2008) are supplied by limestone (Table 1). Their probable carbonate affinity in limestone accounts for a relatively rapid dissolution in the aqueous phase of limestone slurry which reacts with SO_2 to form the corresponding soluble sulphate complexes.

Dissolution of elements in gaseous phase in the aqueous phase of gypsum slurry: Cl, B, and Se (68-99%, PP1) and Cl, F, B, and Hg (80-99%, PP2) enter the scrubber in a gaseous form (Table 1). The high solubility of Cl, B (CRC Handbook of Chemistry and Physics 91st, 2010-2011), and Se and Hg salts promotes the partial dissolution in the aqueous phase of gypsum slurry and a high enrichment in the filtered water as a result of continuous water re-circulations.

Dissolution of elements with high condensation potential on fly ash: Mo and Cd (99-100%, PP1) and K, Zn, Ge, and Cd (70-100%, PP2) enter the scrubber as PM (Table 1). The alkaline pH of fly ash and the near-neutral pH of the aqueous phase of limestone slurry promote the dissolution of these elements and other (i.e Se, As, Sb or V) in their oxy-anionic form when flue gas passes through the sprayers.

Contribution of elements by several sources: Na, Sc, and Se (PP2). The process water supplies relatively high contributions of Na (30-50%) and Sc (51%, in 2007 sampling), whereas the remaining fraction enters FGD as PM. Limestone (35-60%), PM (48-16-%), and gaseous (17-23%) streams are the main inputs of Se in the scrubber at PP2 in the two sampling campaigns. These elements are enriched in the filtered water after a number of re-circulations.

The enrichment of Na, Se, and Cd in the filtered water at PP1 should be pointed out. These elements show PMB values that are slightly higher than 1.2, which it is not consistent with the theoretical values of this PMB, which is usually closed to out/in ratios ≤ 1 (Table 7). This may be due to the crucial factors considered in the PMB calculations discussed in the 2.3 section above. However, the enrichment of these elements is clearly patent when comparing the complementary PMB and TMB, which is supported by the statistically significant difference ($p<0.05$). Consequently, the comparison between PMB and TMB suggests the enrichment of these elements in filtered water after a number of re-circulations.

Table 7. PMB and TMB and t-Student of major, minor, and trace elements at PP1.

PP1 2007 (n=4)						
Element	FWAF[a] (g/h)	SD[b]	t	p-value ($p<0.005$)	PMB	TMB
Al	0	0	-	-	1.0	1.0
Fe	0	0	-	-	1.0	1.0
K	4686.8	140.7	-	-	0.8	0.9
Mg	1.3	2436.0	110	<0.001	1.1	2.1
Na	13303.4	403.5	66.95	<0.001	>1.2	6.2
S	2.5	4915.2	-	-	0.9	0.9
F	3898.3	774.2	-	-	1.0	1.2
Cl	47614.9	27656.2	3.44	0.041	1.0	4.2
Hg	0.1	0.01	-	-	1.0	1.0
Li	50.6	0.8	-	-	0.9	1.1
B	1983.6	29.0	136.59	<0.001	0.8	3.4
Sc	2.2	0.2	-	-	0.9	1.0
Ti	1.0	0.1	-	-	1.0	1.0
V	6.8	0.2	-	-	0.9	0.9
Cr	0.3	0.0	-	-	0.9	0.9
Zr	0	0	-	-	1.0	1.0
Mn	3846.9	177.4	43.36	<0.001	1.0	2.4
Ni	16.9	0.7	48.54	<0.001	0.7	0.8
Ga	0.1	0.01	-	-	0.9	0.9
Ge	0.1	0.04	6.96	0.006	0.9	1.1
Se	18.8	3.8	9.83	0.002	>1.2	6.3
Sr	315.4	0.1	-	-	1.0	1.1
Mo	3.7	14.1	24.06	<0.001	0.7	1.9
Cd	0.6	0.1	14.73	0.001	>1.2	15.0
Ba	9.4	0.2	-	-	1.0	1.0
U	15.7	1.7	18.01	<0.001	1.2	1.4

PMB: partial mass balance; TMB: total mass balance; n= degrees of freedom; [a] FWAF: Filtered water mean flows
[b]SD: Standard deviation; - : No significant differences

At PP2, F displays potential enrichment in the 2007 sampling because of the high dosages of Al-additive, which gives rise to high soluble proportions of this element as Al-F aqueous complexes. Sodium, Ni, Zn, Mn, and Co show potential enrichment in the 2008 sampling. The elements that display a particular enrichment pattern with PMB values >1.2 but notably high values of TMB ($2.3<TMB<12.8$) are Mg, Li, and U in the 2007 campaign; and K, Li, Zn, Zr, Se, and Rb in the 2008 campaign. Comparison of PMB and TMB supported by the statistically significant difference ($p<0.05$), suggests the enrichment of these elements after re-circulations of the filtered water (Table 8).

Table 8. PMB and TMB and t-Student of major, minor, and trace elements at PP2 in 2007 and 2008.

PP2 2007 (n=6)							PP2 2008 (n=6)						
Element	FWAF[a] (g/h)	SD[b]	t	p-value	PMB	TMB	Element	FWAF[a] (g/h)	SD[b]	t	p-value	PMB	TMB
Al	16276.9	1881.6	-	-	0.3	0.5	Al	744.6	554	-	-	0.6	0.6
Ca	20384.5	3805.8	-	-	1.0	1.2	Ca	23174.7	3216.7	-	-	0.9	0.9
Fe	311.8	166.9	-	-	0.9	0.9	Fe	86.6	42.6	-	-	1.0	1.0
S	4.5	48252.3	-	-	1.0	1.2	Na	1613.6	360.4	10.97	<0.001	0.8	4.9
K	2438.5	146	40.92	<0.001	0.7	1.3	K	2046.3	385.8	12.99	<0.001	>1.2	4.2
Mg	2.7	13375.2	49.14	<0.001	>1.2	12.8	Mg	119000	26580.8	10.39	<0.001	0.9	6.7
Cl	94341.3	4503.8	51.31	<0.001	1.0	11.0	Cl	85638	1856.7	112.98	<0.001	0.8	10.0
F	29540	3116	23.22	<0.001	0.8	2.5	F	4736.7	880	13.18	<0.001	1.2	1.6
Hg	52.6	11.2	11.55	<0.001	0.7	2.6	Hg	41.4	3.1	32.56	<0.001	1.0	2.5
Li	42	2.6	40.18	<0.001	>1.2	4.6	Li	32.5	5.4	14.75	<0.001	>1.2	6.2
B	3244.7	141.9	56	<0.001	0.9	15.0	B	3277.1	487.7	16.46	<0.001	0.7	6.8
Sc	6	1.5	9.8	<0.001	0.7	2.2	Ti	0.8	0.6	-	-	1.0	1.2
Ti	2.4	0.2	-	-	1.0	1.0	V	2.9	0.5	-	-	1.0	1.1
V	10	6.4	-	-	0.9	1.0	Mn	8982.9	1579.1	13.94	<0.001	0.8	10
Mn	13156.7	599.4	53.76	<0.001	0.8	4.1	Co	10.7	1.9	13.84	<0.001	0.8	8.0
Co	22.8	1.4	40	<0.001	0.1	1.0	Ni	58.8	10	14.44	<0.001	1.0	2.0
Ni	148.5	10.2	-	-	0.3	0.8	Cu	3.5	0.5	18.43	<0.001	1.2	1.5
Cu	9.4	0.4	-	-	0.3	0.5	Zn	99.9	20	12.26	<0.001	>1.2	8.0
Zn	133.8	7.4	43.99	<0.001	0.9	2.9	Se	54.8	13.5	9.95	<0.001	>1.2	7.8
Ga	0.8	0.3	6.39	-	0.4	0.6	Rb	1.6	0.8	5.13	<0.001	>1.2	2.2
Ge	0.6	0.2	8.62	<0.001	0.8	1.3	Sr	91.1	12	-	-	0.9	0.9
Mo	1.5	0.1	-	-	0.2	0.2	Zr	0.3	0.1	9.98	<0.001	>1.2	2.3
Se	18.1	10.2	4.37	<0.001	1.2	1.8	Mo	0.6	0.1	-	-	0.0	0.2
Cd	4.6	0.5	21.63	<0.001	0.8	7.1	Cd	4.4	0.6	16.9	<0.001	0.9	52
Sb	0.4	0.1	-	-	0.4	0.5	Sb	0.6	0.1	-	-	0.4	0.7
Ba	4.3	0.4	-	-	0.9	0.9	Ba	6.6	1.2	-	-	0.8	0.9
Pb	0	0.03	1.58	0.176	0.6	0.6	Tl	0.1	0.02	15.08	<0.001	0.3	1.5
U	15.9	1	40.04	<0.001	>1.2	3.0	U	13.8	13.8	16.84	<0.001	1.0	2.2

PMB: partial mass balance; TMB: total mass balance; n= degrees of freedom; [a] FWAF: Filtered water mean flows; [b] SD: Standard deviation; - : No significant differences

3.4.2. Elements not enriched in filtered water

The elements not enriched in filtered water (PMB≤1.0 and TMB ≤1.2) are: Al, Fe, K, S, F, Hg, Li, Sc, Ti, V, Cr, Ba, Ga, Ge, Sr, and Zr (PP1) and Ca, Ti, S, Fe, V, Sr, and Ba (PP2).

These elements are not enriched in filtered water due to the following factors:

Elements supplied by the highly insoluble Al-Si fraction of limestone: Al, Fe, K, Li, Sc, Ti, V, Cr, Ga, and Zr (PP1); Ti, Fe, and V (PP2).

Elements associated with the carbonate fraction of limestone that reacts with S to form low soluble sulphate species: Ba and Sr (PP1); and Ca, Ba, and Sr (PP2).

Elements in gaseous phase that react with limestone components and are retained in FGD-gypsum as sulphate or fluoride species: S, F, and Hg (PP1); S (PP2 2007).

PM IN-FGD elements not dissolved in gypsum slurry and filtered water: Ge (PP1).

3.4.3. Elements with uncertain behaviour

The elements with uncertain behaviour (PMB≤0.8 and TMB ≤0.8) are: Ni (PP1), and Al, Ga, Mo, and Sb (PP2) and Ni, Cu, and Pb (2007, PP2). These values suggest a rapid dissolution, reaching equilibrium or saturation with subsequent precipitation in the FGD gypsum.

At PP1, Ni supplied by limestone (92%, Table 1) adopts behaviour similar to that of Na, Mg, and Mn. However, the reason for the limited presence of this soluble complex in the filtered water remains unclear and will be investigated in subsequent works.

At PP2, Ga, Sb, Mo, Ni, Cu, and Pb enters the scrubber as PM (54-100%), but limestone is also an important source of Mo (46%) and Pb (35%) in the 2007 sampling (Table 1). Most of the above elements condense as fine sulphate and/or chloride species after combustion. The solubility of these salts (Bigham et al, 1995) under slightly acidic pH (4.6-5.0) in the scrubber would give rise to enrichment of these elements in re-circulated waters. For Al, the use of highly soluble Al-additives explains the high solubility of this metal in the aqueous phase of gypsum slurry. However, the highly acid insoluble ralstonite formation (Font et al., 2008) may also give rise to high fractions (45-81%, depending on Al dosages) of Al trapping, thus avoiding a significant Al enrichment in filtered water. As aforementioned for Ni, the reason for the uncertain behaviour of these species remains unclear and will be investigated in subsequent works.

3.5. COMPARISON OF PP1 AND PP2

Comparison of the results of the PMB and TMB and the enrichment of inorganic trace pollutants at PP1 and PP2 reveal significant differences between PP1 and PP2 resulting from operational conditions. A larger number of elements are enriched in the filtered water at PP2 than at PP1. This is attributed to the following causes:

i. The higher input of soluble PM at PP2 than at PP1 because the lower ESP gas temperatures at PP2 may favour the occurrence of fine condensed species that escape from the ESP and subsequently dissolved in the FGD system. This together with the lower acidic pH of the gypsum slurry (4.6-5.0) at PP2 than pH (7.6) at PP1 may also favour the presence of metal complexes at PP2.

ii. A greater occurrence of fluoride and/or sulphate complexes and the lower S/F (52-140) and S/Cl (28-37) ratios in the scrubber at PP2 than at PP1 (251 and 137 for S/F and S/Cl ratios, respectively) give rise to these enrichment factors for Na, F, Cl, Li, Zn, Ni, Cd, Ge, and Hg in the scrubber at PP2 than at PP1. The rapid dissolution of these elements as soluble sulphate and fluoride complexes promotes their enrichment after water re-circulations.

iii. The differential behaviour and enrichment of Hg between PP1 and PP2. The different Hg enrichment is probably due to the higher Cl content and the lower S/Cl ratio at PP2 than PP1. This promotes the occurrence of highly soluble $HgCl_2$ complexes in filtered water at PP2.

iv. The differential behaviour and enrichment of F and Al is controlled by the use of additives. At both plants, gaseous HF is the major input of F. However, the Al additives at PP2 promote the occurrence of stable Al-F aqueous complexes that increase F concentrations in filtered water. In the absence of additives (PP1), HF reacts with Ca to form insoluble fluorite, which is partially retained in the FGD-gypsum. The use of highly soluble Al-additives at PP2 explains the high solubility of this metal in the aqueous phase of gypsum slurry. However, the highly acid insoluble ralstonite may also give rise to high fractions (45-81%, depending on Al dosages) of Al trapping, thus avoiding a significant Al enrichment in filtered water. In equilibrium with ralstonite, low Mg levels and acidic conditions ($pH<5$) may lead to precipitation of sulphate complexes such as balsaluminite ($Al_4 (SO_4)(OH)_{10}.4H_2O$) (Bigham et al., 1955).

Table 9. Classification of elements based on mass balances at PP1 and PP2.

	Source	PP1 2007	PP2 2007	PP2 2008
Elements enriched in filtered water (0.7≤PMB≤1.2 and TMB≥1.2)	Soluble sulphate complexes	Na, Mg, Mn, and U	Mg, Mn, and U	Mg, Mn, U, Cu, Ni, and Co
	Dissolution of elements in gas phase	Cl, B, and Se	Cl, F, B, and Hg	Cl, F, B, and Hg
	Dissolution of elements as PM IN-FGD	Mo and Cd	K, Zn, Ge, and Cd	K, Zn, Ge, and Cd
	Elements supplied by several sources	-	-	Na, Sc, and Se
Elements not enriched in filtered water (PMB≤1.0 and TMB≤1.2)	Insoluble Al-Si of limestone	Al, Fe, K, Li, Sc, Ti, V, Cr, Ga, Zr	Ti, Fe, and V	Ti, Fe, and V
	Low soluble sulphate species	Ba and Sr	Ca, Ba, and Sr	Ca, Ba, and Sr
	Sulphate/ fluoride species retained in FGD-gypsum	S, F, and Hg	S	-
	IN-FGD PM not dissolved in gypsum slurry	Ge	-	-
Elements with uncertain behaviour (PMB≤ 0.8 and TMB≤0.8)		Ni	Al, Ga, Sb, Mo, Ni, Cu, and Pb	Al, Mo, Ga, and Sb

4. CONCLUSIONS

The results reveal that re-circulation of filtered water at PP1 and PP2 gives rise to unusually high concentrations of some elements of major environmental concern such as, Cd, B, Se, Sc, Ni, Zn, and especially Hg and U.

The elements in FGD waters may be classified as: i) elements enriched in filtered water at PP1 and PP2: Na, Cl, Mn, B, Se, Mg, Cd, and U. Furthermore, Mo is enriched at PP1, and K, Hg, Li, Sc, Ge, F, Ni, Zn, Rb, Zr, and Co at PP2; ii) elements not enriched in filtered water at PP1 and PP2: Ca, Fe, Ti, V, Ti, S, Sr, and Ba. This group of elements also includes Al, K, Li, F, Hg, Cr, Zr, Ga, Ge, and Sc at PP1; and iii) elements displaying an uncertain behaviour at PP1 and PP2: Al, Ga, Cu, Mo, Sb, Pb (PP2), and Ni (PP1).

The enrichment of inorganic trace pollutants in re-circulated waters in wet limestone based FGD systems is heavily dependent on: i) the low purity of limestone may result in high inputs of elements occurring in soluble carbonates promoting the formation of soluble sulphate complexes, which may be crucial at power plants that use fuels with a high S content since increased limestone flows are required for the abatement of SO_2 emissions; ii) the fluoride and sulphate complexes and the S/F and S/Cl ratios of the scrubber. Low S/F and S/Cl ratios in the scrubber promote the presence of soluble metal chloride complexes. A high PM contribution to the FGD system may increase the amount and the presence of metal chloride complexes in re-circulated waters; iii) the ESP gas temperature. Low ESP gas temperature may favour the occurrence of metal condensation on PM, which is subsequently dissolved in the FGD system; and d) the use of additives in the scrubber. Additives may modify the speciation and partitioning of some elements. Thus, high Al dosages enhance the formation of water soluble AlF complexes leading to F-rich FGD waters. In the absence of additives, HF reacts with Ca to form fluorite which is retained in the FGD-gypsum, with the subsequent increase in the leachable potential of this by-product.

Our findings demonstrate that the re-circulation of filtered water from the first operation cycle up to the start of sampling campaigns increases the concentration of some elements of major concern such as U and Hg in FGD waters. High levels of these metals and other pollutants in filtered water give rise a high ionic strength which may reduces the gaseous retention efficiencies and also increase the emission of metals by entraining and/or evaporation of droplets as PM from gypsum slurry. Owing to the strong influence of the operational factors in this enrichment, an in-depth knowledge of such factors is crucial for implementing preventive or remediation measures to reduce the levels of these elements in filtered waters. The application of these measures may be of paramount importance for maintaining a high retention of gaseous pollutants and for reducing the element contents should the re-circulation system be interrupted since the waters would require a decontamination treatment.

Subsequent studies will be focused on the speciation of inorganic trace pollutants in FGD water streams with water re-circulation, the modelling of the FGD solid-liquid processes (sorption, co-precipitation, etc), and on preventive and/or corrective measures.

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ARTICLE 4

Unusual Speciation and Retention of Hg at a Coal-fired Power plant

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ABSTRACT

An unusual and different speciation of Hg in the outgoing gaseous stream of the flue gas desulphurisation (OUT-FGD) system was revealed at two Spanish power plants (PP1 and PP2) equipped with a forced oxidation wet FGD system with water re-circulation to the scrubber. At PP1 and PP2, a high proportion of Hg escapes from the electrostatic precipitator (ESP) in gaseous form, Hg^{2+} being the prevailing Hg (75-86%) mode of occurrence of Hg that reaches the FGD (IN-FGD). At PP1 Hg^0 was the prevalent (71%) speciation of emitted Hg (OUT-FGD) species, whereas at PP2 Hg^{2+} was the prevalent Hg OUT-FGD species in 2007 (66%) and 2008 (87%). The unusual speciation of gaseous Hg OUT-FGD (high proportion of Hg^{2+}) and the different Hg^{2+} retention efficiency between 2007 (73%) and 2008 (24%) at PP2 were attributed to the evaporation of $HgCl_2$ particles from the aqueous phase of gypsum slurry in the OUT-FGD gas and to the Al-additive used at PP2, respectively. The Al-additive induced the retention of Hg as HgS in the 2007 FGD-gypsum thus reducing gaseous emissions of Hg in the OUT-FGD gas.

1. INTRODUCTION

Coal-fired utility boilers release around 50 tons of Hg annually or about one-third of the total anthropogenic emission in the U.S. On December 21, 2011, the US Environmental Protection Agency (EPA) announced the Mercury (Hg) and Air Toxics Standards (MATS) for power plants. The final ruling is designed to prevent 90% of the Hg in coal burned in power plants from being emitted to the air, reduce 88% of acid gas emissions, and cut 41% of SO_2 emissions from power plants. In Europe, Hg emissions from power plants are not currently regulated but the Pollutant Release and Transfer Register (PRTR) of Industrial Emissions into air, water, and land (Regulation (EC) N°166/2006) has established threshold emissions for large combustion plants (10kg/year). These limit emissions are used as the Hg reference rate emission.

Mercury in flue gas combustion usually exists in three forms (Galbreath et al., 2000): oxidised (Hg^{2+}), elemental (Hg^0), and particle-bound (Hg_p). Their relative proportion depends on the coal type and composition, and on combustion and flue gas conditions (Stergarsek et al., 2008). High chlorine contents in coal have been shown to correlate with higher levels of Hg oxidation and retention in the combustion gaseous phase (Hall et al., 1990; 1991; Meij, 1991; Galbreath et al., 1998; Senior et al., 2000; Sliger et al., 2000; Pavlish et al., 2003). A route suggested for the formation of $HgCl_2$ involves the homogeneous reaction of Hg^0 with atomic chlorine (Cl). The kinetics of Cl, chlorine gas (Cl_2) and HCl inter-conversions are therefore an important area of research to better understand Hg oxidation.

Whilst it is widely acknowledged that Hg primarily occurs as Hg^0 in the outgoing gaseous stream of the flue gas desulphurisation (OUT-FGD) systems (Pavlish et al., 2003; Chang et al., 2003; Tanga et al., 2007; Park et al., 2008; Wo et al., 2009; Stergarsek et al., 2010), an unusual and different speciation of Hg in the OUT-FGD gaseous stream was revealed during the sampling campaigns carried out in 2007 and 2008 at two Spanish coal-fired power plants (PP1 and PP2) equipped with a forced FGD system and with water re-circulation (Córdoba et al., 2011). At both power plants, a high proportion of Hg escapes from the electrostatic precipitator (ESP) in a gaseous form, Hg^{2+} being the species that enters the FGD. At PP1, Hg^0 was the prevalent Hg OUT-FGD species (Córdoba et al., 2012a). By contrast, at PP2, Hg^{2+} was found to be the prevalent species in the OUT-FGD gas in 2007 and 2008. The higher gaseous retention of Hg in 2007 than in 2008 at PP2 was another significant result obtained from the sampling campaigns (Córdoba et al., 2012b).

High concentrations of some elements of major environmental concern such as Cd, Cl, Na, Mg, B, F, Se, Mn, Sc, Ni, Zn, and especially Hg and U have recently been found in the aqueous phase of the gypsum slurry and filtered water at these power plants (Córdoba et al., 2011). These elements tend to form highly soluble salts favouring element saturation in the re-circulation waters with a consequent increase in emission by entraining particles from gypsum slurry in the OUT-FGD gas, and/or the precipitation on the FGD-gypsum end-product.

The FGD-gypsum end-product produced at PP2 (Álvarez-Ayuso et al., 2008) exceeds the maximum value of leachable F to be accepted at non hazardous waste landfills (1999/31/EC). To remediate this, an Al-additive is injected into the FGD scrubbers to boost the desulphurisation efficiency by reducing the precipitation of CaF_2 particles on the limestone surface, which limits the reactivity of Ca with SO_2.

In this work, three laboratory experiments were conducted in order to confirm the Hg speciation in the OUT-FGD gas with respect to that detected at PP1 and PP2. An aqueous and solid speciation modelling of elements of environmental concern enriched in the aqueous phase of gypsum slurry was used to better understand the Hg gaseous speciation at PP1 and PP2. The present study also seeks to determine the mode of occurrence of the Hg compound retained in FGD-gypsum samples from PP2 and the causes of the different retention of gaseous Hg OUT-FGD in 2007 and 2008 at PP2.

2. MATERIALS AND METHODS

2.1. FLUE GAS DESULPHURISATION SYSTEM

The FGD system (Figure 1) at PP1 and PP2 involves a number of water streams categorised as FGD water streams: limestone and gypsum slurries, and filtered water. At PP2, limestone slurry is prepared with process water and is piped to the scrubber. Filtered water, which is the product of gypsum slurry filtration, is directly re-circulated to the scrubber after a dilution process to reduce the concentration of Cl. At PP1, a fraction of processed water is treated before using it to reduce the high content of salts. The resulting water (treated water) is employed for limestone slurry preparation, and is then considered as a FGD water stream. An additional fraction of water (added water) is injected into the scrubber at PP1 to offset the water loss in the gypsum and in the emitted gas. Filtered water at PP1 is used for limestone slurry preparation and the remaining fraction is directly re-circulated into the scrubber. This mixture of slurry waters constitutes the main water input into the scrubber. The water output of the FGD systems is constituted by i) the aqueous phase of gypsum slurry; ii) the loss of crystallisation water from gypsum; and by iii) 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 both power plants.

In this article, the terms gypsum and limestone slurry are used for the total fraction of the slurries (solid + water) while the terms aqueous phase of gypsum and limestone slurry are employed for the water fraction of the total fraction.

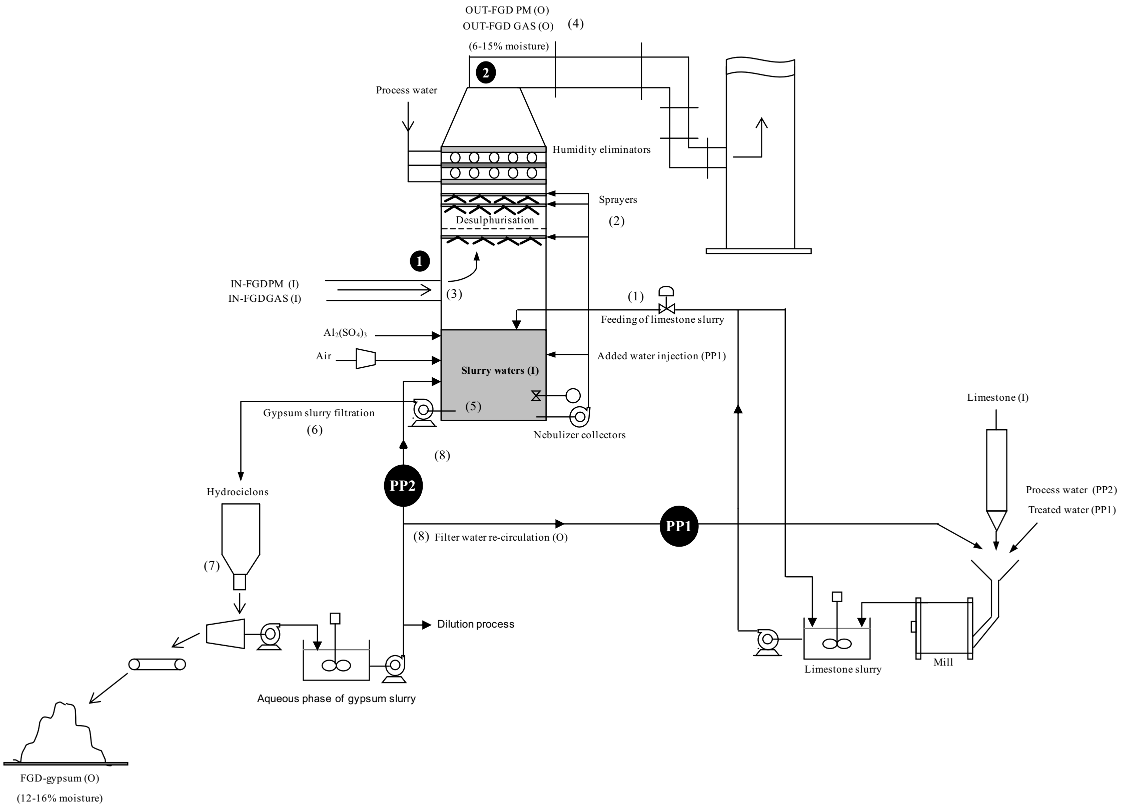
At PP2, $Al_2(SO_4)_3$ was injected into the scrubber to boost the desulphurisation efficiency. The $Al_2(SO_4)_3$ addition varied considerably between the two sampling campaigns. Up to 68 kg/h were added in 2007, whilst the dosage was reduced to 14 kg/h in 2008.

Detailed descriptions of the FGD system operation from PP1 and PP2, and FGD water streams are reported by Córdoba et al. (2011).

2.2. GASEOUS MEASUREMENTS

Isokinetic measurements of gaseous streams were performed at two sampling points (Figure 1), IN-FGD (1) and OUT-FGD (2), simultaneously, during the sampling campaigns. At each sampling point, two trains of sampling system were assembled with specific trapping solutions. The sampling and speciation of gaseous Hg (Hg^0 and Hg^{2+}) was devised according to EN 13211 and Meij and te Winkel (2006).

Mercury analyses were carried out directly on trapping solutions using a LECO AMA 254 Gold Amalgam Atomic Absorption Spectrometer (GA-AAS). The analyses and certified values of Hg (SRM1633b (>0.01) coal fly ash and SARM 20 coal) were also measured to determine the accuracy of the results (Table S1. Supporting information).

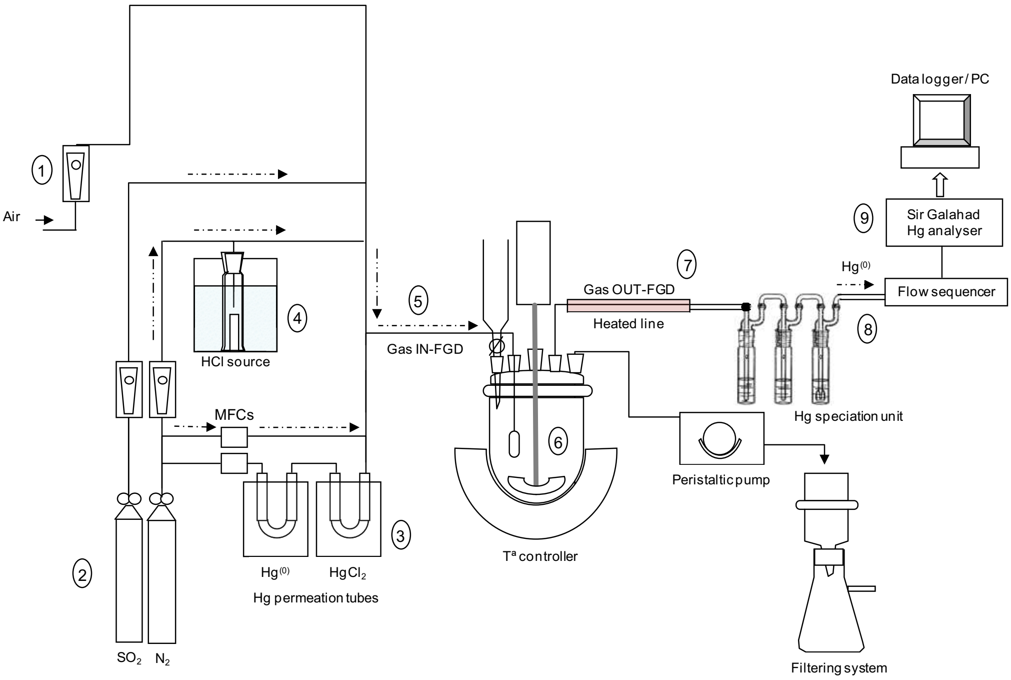


(I): input streams to the FGD; (O): output streams from the FGD

Figure 1. Sketch of the FGD system at PP1 and PP2. (1) Introduction of limestone slurry to the scrubber; (2) Limestone slurry is pumped through the nebulizer collectors and sprayed into the scrubber to react with SO_2; (3) Gas and PM input flow into the scrubber after combustion process; (4) Cleaned gas and PM flow OUT-FGD; (5) Formation of gypsum slurry as result of the desulphurisation process; (6) Extraction of gypsum slurry for the filtration process by hydro-cyclones; (7) Production of gypsum slurry and FGD-gypsum; (8) Re-circulation of filtered water after dilution process: PP1: fraction of filter water is used for limestone slurry preparation; PP2: filter water directly re-circulated to the scrubber.

2.3. EXPERIMENTAL PROCEDURE

The FGD batch (Figure 2) experiments developed at the University of Nottingham were designed to enable the ratio of Hg^0/Hg^{2+} in the gaseous phase (Table S2. Supporting information) to resemble the Hg^0/Hg^{2+} ratio observed during the sampling campaigns at these power plants (Table 1). The Hg sources consisted of Hg^0 and Hg^{2+} permeation tubes linked in series each in its own temperature-controlled environment to two water baths. The PSA 10.534 series, CavKitCalc software, was used to calculate the flow rate and temperature settings required to control the main N_2 carrier gas flow. Two flowmeters were used as suppliers of air $_{(g)}$ and the second carrier gas flow of $N_{2\ (g)}$. A constant mass flow of HCl (coal chlorine is released primarily as HCl) was provided as a source of $Cl_{2\ (g)}$ through a diffusion device at a constant laboratory temperature and with a constant calibrated flow of N_2. Sulphur dioxide was introduced into the mercury-laden gas as 100% SO_2 through a calibrated flowmeter. The flue gas path temperature was maintained at approximately 60ºC by the use of auxiliary heat tapes. The combined total flue gas was introduced into a stirred vessel by a porous sintered glass bubbler to ensure an efficient air transfer from the gaseous to the liquid phase, which constitutes the FGD unit.



MFC: Mass flow controller

Figure 2. Sketch of the batch experiment developed at Nottingham University to mimic the FGD. (1) Suppliers of the air (g); 2: SO_2 (g) and N_2 (g) gas suppliers. The N_2 (g) goes to MFC to calculate the flow rate and temperature settings required to control of the main N_2 carrier gas flow; (3) Hg source: Hg^0 and Hg^{2+} permeation tubes; (4) HCl diffusion device; (5) Combined total IN-FGD flue gas; (6) Desulphurisation process; (7) Combined total OUT-FGD flue gas; (8) Ontario hydro-method Hg speciation unit: Hg^{2+} (g) in the OUT-FGD gas dissolution in the KCl; and (9)Measurement of Hg^0, permanent in the gaseous stream, by Sir Galahad II Mercury Analyzer model 10.525.

Table 1. Concentration of gaseous Hg and proportion of Hg IN and OUT-FGD at PP1 and PP2.

µg/m^3	% Hg^{2+}	%Hg^0	Hg^{2+}	Hg^0	Total Hg
PP1					
IN-FGD	75	25	5.8	2.0	7.8
OUT-FGD	29	71	0.7	1.6	2.2
PP2 2007					
IN-FGD	86	14	18	3.0	21
OUT-FGD	66	34	4.9	2.5	7.4
PP2 2008					
IN-FGD	88	12	17	2.2	19
OUT-FGD	87	13	13	2.0	15

Real-time measurements for Hg^0 were conducted by using a Sir Galahad II Mercury Analyser model 10.525. This is based on the principle of atomic fluorescence (AF) and consists of a specific gold sand trapping mechanism. The system utilises a low-pressure mercury lamp excitation source with detection by a photomultiplier. Thus, Hg absorbs and fluoresces at the same wavelength, ensuring a highly sensitive and selective detector.

Analogous to the real-time measurements of Hg^0 OUT-FGD, a fraction of the OUT-FGD gas flow was piped to the Hg speciation unit based on the Ontario hydro-method. The remaining gas was vented as waste. The Ontario Hg speciation unit consisted of three KCl solution impingers where $Hg^{2+}{}_{(g)}$ in the OUT-FGD gas was dissolved in the KCl solution. The Hg^{2+} trapped in the KCl solution was pumped to an alkaline solution impinger (2% $SnCl_2$ in 10% KOH), where Hg^{2+} was reduced to Hg^0 and then measured by the Sir Galahad device.

Filtered water and process water for limestone slurry preparation were employed to reproduce the FGD system conditions during the sampling campaigns (after a number of filter water re-circulations), and the first stage of addition of filtered re-circulated water to the scrubber, respectively. We sought to determine whether i) the filtered water experiment corroborates the Hg speciation in the OUT-FGD gas at PP1 and PP2; and ii) the predominance of Hg^{2+} in the OUT-FGD gas at PP2 (process water experiment) is caused by the evaporation of $HgCl_2$ particles dissolved in the aqueous phase of the gypsum slurry in the OUT-FGD gas. The solid and water samples required for these experiments were supplied by the power plants.

2.4. GEOCHEMICAL MODELLING

The PHREEQC code (version 2.0) and the coupled thermodynamic database LLNL (1999) was used for calculating the aqueous speciation of gypsum slurries obtained from sampling campaigns, and for the saturation index (SI) with respect to selected minerals and solid phases at temperature (60ºC) of scrubbers and pH values and concentration of trace inorganic elements in the aqueous phases of the PP1 and PP2 gypsum slurries.

2.5. THERMAL DECOMPOSITION OF FGD-GYPSUM

The Thermal Decomposition (TD) method coupled with the Sir Galahad II Atomic Fluorescence Spectrometer (AFS) was used to determine the mode of occurrence of Hg in PP2 FGD-gypsum from the 2007 and 2008 sampling campaigns. This experimental device has been described by some authors in earlier works (López-Antón et al., 2010; Rallo et al., 2010a; 2010b). It consists of a thermal dissociation furnace (PS Analytical Thermogram model 50.042) coupled to an Hg analyser (PS Analytical Sir Galahad Mercury Analyser model 10.525). A number of pure Hg compounds ($HgCl_2$, HgS, $HgSO_4$, HgO, Hg_2Cl_2, Hg_2SO_4, and $HgBr_2$) have been tested (Rallo et al., 2010b) at the University of Nottingham to determine their characteristic thermal decomposition profile (Figure 3) and temperature (Table S3. Supporting information). The pure standard Hg compounds were diluted using silica flour (inert material) and $CaSO_4$ (free of Hg) to simulate a similar matrix to the FGD-gypsum sample. Both mercury decomposition profiles and temperature represented a set of ‘‘fingerprints” against which thermal decomposition profiles of FGD-gypsum samples can be compared.

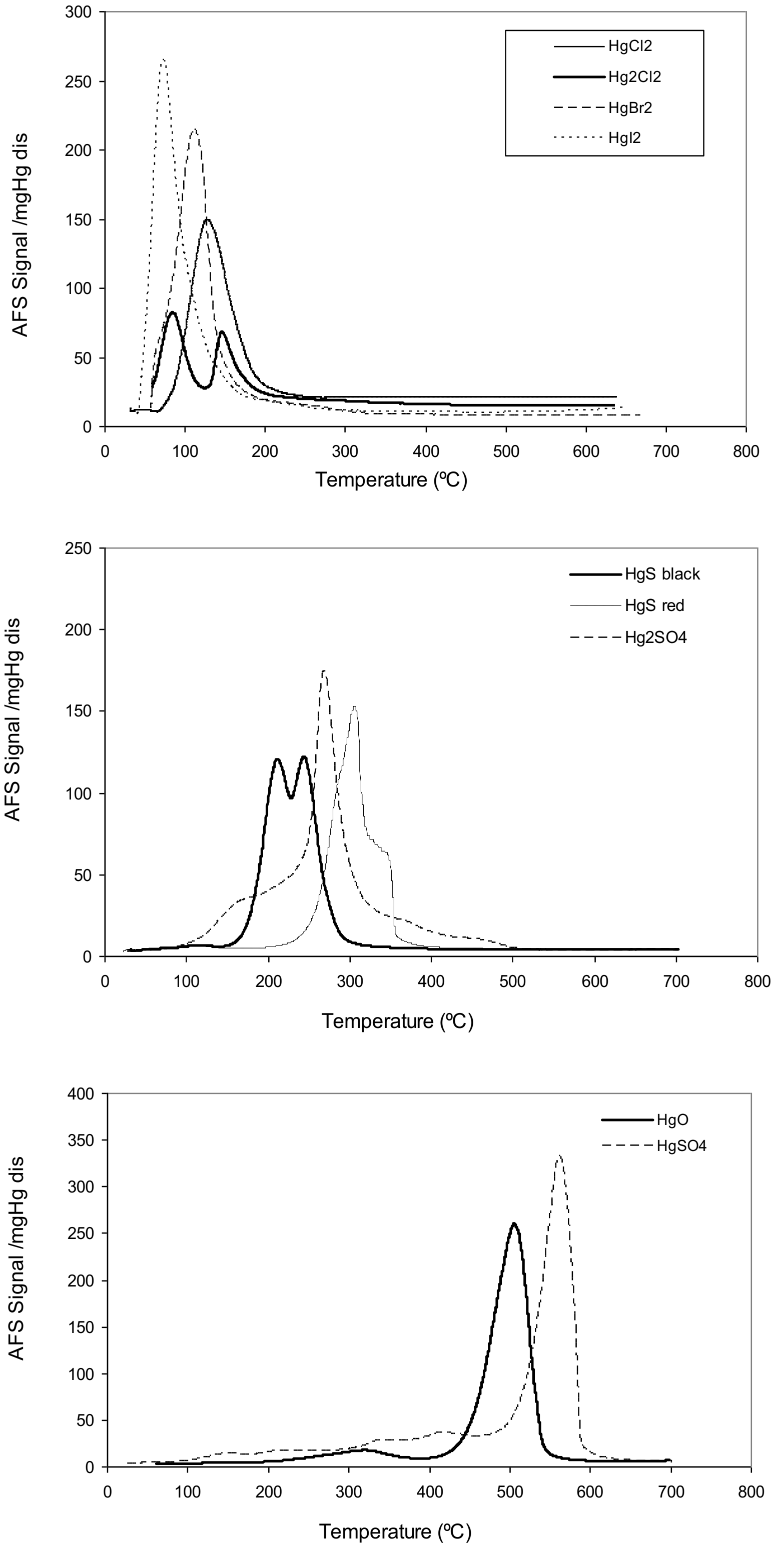


Figure 3. Thermal decomposition profiles of pure mercury compounds.

3. RESULTS AND DISCUSSION

3.1. COMPOSITION OF FLUE GASES

The concentration of total Hg IN-FGD is markedly higher in the two campaigns at PP2 than at PP1 (Table 1). At PP1 and PP2, a high proportion of Hg escapes from the electrostatic precipitator (ESP) in gaseous form, Hg^{2+} (75-86%) being the species that enters the FGD. At PP1 Hg^0 (71%) was the prevalent Hg OUT-FGD species, whereas at PP2 Hg^{2+} was the prevalent Hg OUT-FGD species in 2007 (66%) and 2008 (87%). The gaseous concentration of CO, NO, CO_2, and SO_2 at PP1 and PP2 is depicted in Table 2 and 3, respectively.

Table 2. Gaseous concentration of CO, NO, CO_2, and SO_2 at PP1.

		Moisture (%)	O_2 (%)	CO (ppm)	NO_x (ppm)	SO_2 (ppm)
PP1	IN-FGD	10	5.8	10	696	4718
		11	5.7	6	910	4843
	OUT-FGD	14	6.7	2	614	694
		15	6.6	1	608	592

Table 3. Gaseous concentration of CO, NO, NO_2, CO_2, and SO_2 at PP2.

		Moisture (%)	O_2 (%)	CO (ppm)	NO (ppm)	NO_2 (ppm)	CO_2 (%)	SO_2 (ppm)
2007 PP2	IN-FGD	9.8	6.5	25	381	0	12	1322
		9.3	5.9	25	386	0	12	1390
	OUT-FGD	6.0	6.4	3.0	395	0	13	198
		5.5	6.2	3.1	435	0	13	150
2008 PP2	IN-FGD	9.0	5.9	23	360	0	12	1351
		9.5	5.9	25	388	0	12	1376
	OUT-FGD	6.0	6.4	2.7	333	0	12	145
		6.3	6.6	3.1	379	0	11	140

3.2. GASEOUS Hg SPECIATION IN LABORATORY SCALE EXPERIMENTS

The laboratory experiments carried out with filtered water confirmed Hg^0 (66-61%) as the dominant species in the OUT-FGD gas at PP1, and Hg^{2+} (56-66%) as the predominant species of Hg at PP2 during the overall process of the reaction (Table 4). The highest proportion of Hg^{2+} in the OUT-FGD gas was attained after the 3h experiment.

Mercury speciation in the OUT-FGD gas was found to change over the experiment of the first stage of addition of filtered re-circulated water to the scrubber at PP2. Hg^0 was dominant (62%) after 2h reaction, because of the similar conditions (low concentration of Cl in the aqueous phase of gypsum slurry) of most wet FGD systems (such as PP1). After the 3h reaction, Hg occurred primarily as Hg^{2+} (63%) as a result of increased HCl inputs into the scrubber under acidic conditions of the slurry (pH 4.3). The constant Hg^0 flow (20.2-20.3 ng/min after 2 and 3h reaction, respectively) during the overall desulphurisation process rules out an oxidation process from Hg^0 to Hg^{2+} as a major cause of the unusual speciation of Hg OUT-FGD.

Table 4. Concentration of gaseous Hg and proportion of Hg IN and OUT-FGD in the experimental gaseous stream.

ng/m^3	Hg^{2+}	Hg^0	Total Hg	% Hg^{2+}	% Hg^0
PP1 FW experiment					
IN-FGD	111	40	151	74	26
OUT-FGD (2h reaction)	53	104	157	34	66
OUT-FGD (3h reaction)	37	59	96	39	61
PP2 FW experiment					
IN-FGD	332	42	374	89	11
OUT-FGD (2h reaction)	31	24	55	56	44
OUT-FGD (3h reaction)	37	19	56	66	34
PP2 PW experiment					
IN-FGD	307	68	374	82	18
OUT-FGD (2h reaction)	12	20	32	38	62
OUT-FGD (3h reaction)	34	20	54	63	37

3.3. AQUEOUS AND SOLID SPECIATION OF THE ELEMENTS ENRICHED IN FGD WATERS

The aqueous phase of the gypsum slurries at PP1 (pH 7.6) and PP2 (pH 5.1 in 2007 and 4.6 in 2008) shows high concentrations of elements associated with soluble salts (Ca, K, Mg, Na, S, Sr, and Cl) and major and minor elements such as B, Mn, Cu, Se, Cu Ba, Zn, Ni, and U (Córdoba et al., 2011). The addition of $Al_2 (SO_4)_3$ to the scrubber at PP2 induces the acidification of the gypsum slurry via aluminium hydrolysis (Ochoa-González et al., 2012), and promotes the occurrence of highly soluble AlF_x complexes in the 2007 aqueous phase of the gypsum slurry. As a consequence, Al is enriched in the 2007 gypsum slurry (by factors of 20 and >60), as is F (by factors of 7.0 and 15), and SO_4^{2-} (by factors of 1.3 and 2.7) with respect to the 2008 gypsum slurry at PP2, and with respect to gypsum slurry at PP1(Córdoba et al., 2011), respectively.

These differences are also revealed when comparing the concentration of Cl and Hg. Chlorine is enriched by a factor of 4.00 (2007) and 4.06 (2008), and Hg, by a factor of 200 in the PP2 gypsum slurry aqueous phase with respect to PP1 (Table 5). The lower S/Cl ratios in the scrubber at PP2 than at PP1 (28-37 and 137, respectively) account for the enrichment factors for Cl and Hg in the scrubber at PP2 relative to PP1. This indicates the formation of gaseous chloride species of Hg, primarily $HgCl_2$, in the IN-FGD gas stream, and progressive dissolution of Hg-Cl complexes in the aqueous phase of gypsum slurry at PP2.

The aqueous equilibrium calculations at 60ºC reveal that Hg_2^{2+} and Hg^{2+} present the highest activities of Hg in the aqueous phase of gypsum slurry at PP1 and PP2. The solid phases in the LLNL (1999) geochemical database predict that the aqueous phase of gypsum slurry from PP1 and PP2 is supersaturated (SI>0) in Hg_2Cl_2 (Table S4. Supporting information).

Although the water re-circulation to the scrubber increases the concentration of most trace inorganic elements in the FGD system at PP1 and PP2, the feed fuel blends constitute the main input of Hg and Cl at PP2 (Table 5). A high concentration of Hg and Cl is also present in the PP2 FGD-gypsums (Table 5).

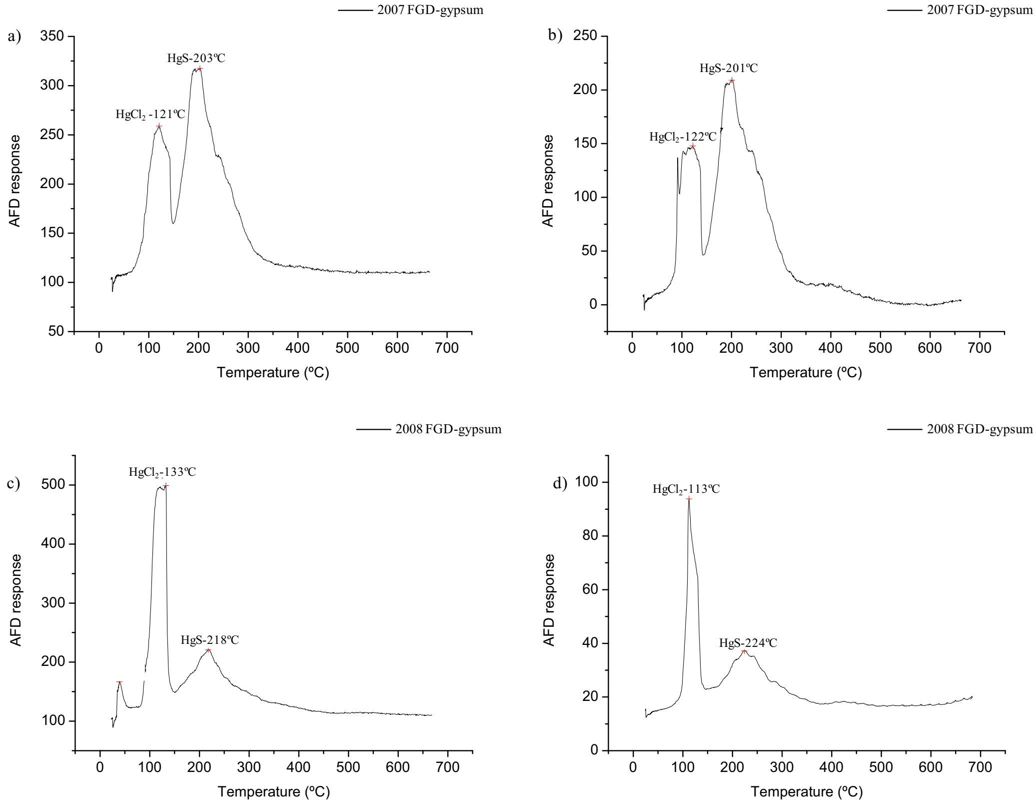
Table 5. Concentration of Hg in solid and water streams at PP1 and PP2.

Hg (ppm)	PP1	2007 PP2	2008 PP2
Feed fuel blend	0.08	0.2	0.2
Aqueous phase gypsum slurry	0.01	2.0	1.7
Water re-circulated	0.002	2.0	1.5
FGD-gypsum	0.1	0.3	0.3
Cl (ppm)			
Feed fuel blend	47	118	96
Aqueous phase gypsum slurry	841	3675	3420
Water re-circulated	856	3369	3059
FGD-gypsum	297	1519	1359

3.4. MODE OF OCCURRENCE OF Hg IN FGD-GYPSUM

Different thermal decomposition profiles are obtained for the FGD-gypsum samples from the PP2 2007 and 2008 sampling campaigns (Figure 4). The high peak of the two 2007 FGD-gypsum samples occurs at approximately 202ºC, which most closely matches the standard curve and temperature of HgS (metacinnabar). The second peak observed at 120ºC suggests the presence of $HgCl_2$ in a lower proportion than HgS in the 2007 FGD-gypsum (Figure 4a and 4b). By contrast, the highest peak of the 2008 FGD-gypsum (Figure 4c and 4d) samples occurs at 112ºC (1st sampling day) and 132ºC (2nd sampling day), which most closely match the standard curve and temperature of Hg_2Cl_2 and $HgCl_2$, respectively. The second peak at approximately 217 and 224ºC suggests the presence of HgS in a low proportion in the 2008 FGD-gypsum. These results reveal a different mode of occurrence of Hg in the FGD-gypsum between 2007 and 2008.

It should be noted that $HgCl_2$ may be present in the FGD-gypsum by i) adsorption on the FGD-gypsum surface; ii) precipitation because of its saturation in the aqueous phase of gypsum slurry; and by iii) dissolution in moisture water of the FGD-gypsum.



AFD signal: atomic fluorescence detector of Hg

Figure 4. Thermal decomposition profiles of FGD-gypsum slurry samples from PP2. a) Thermal decomposition profile of 2007 FGD-gypsum (1st day sampling); b) Thermal decomposition profile of 2007 FGD-gypsum (2nd day sampling); c) Thermal decomposition profile of 2008 FGD-gypsum (1st day sampling); and d) Thermal decomposition profile of 2008 FGD-gypsum (2nd day sampling).

3.5. UNUSUAL SPECIATION OF Hg IN THE OUTGOING FGD GASEOUS STREAM

The experiment of the first stage of addition of filtered re-circulated water to the scrubber at PP2 shows that the gaseous speciation of Hg^{2+} OUT-FGD at PP2 in 2007 and 2008 correlates with the high concentration of HCl and Hg in the IN-FGD gaseous stream, and with the acidic conditions of the scrubber. This indicates that high HCl and Hg inputs in the gaseous phase promote the formation of gaseous chloride species of Hg, primarily $HgCl_2$, in the IN-FGD gas stream. The high water solubility of the gaseous $HgCl_2$ species under acidic conditions of the scrubber would facilitate the progressive dissolution of $HgCl_2$ complexes in the aqueous phase of gypsum slurry at PP2. This is supported by i) the enrichment factors of Cl and Hg, which are higher at PP2 than at PP1; ii) the acidic pH and the S/Cl ratio in the scrubber, which are lower at PP2 than at PP1, promoting the stability of $HgCl_2$ complexes in the aqueous phase; and by iii) the identification of $HgCl_2$ in the FGD-gypsum samples at PP2, which demonstrates the occurrence of $HgCl_2$ complexes in the aqueous phase of the corresponding gypsum slurries.

According to the volatilization behavior of $HgCl_2$ ($HgCl_2$ starts to volatilize at 60-70ºC, Table S3. Supporting information) and the temperature of the wet scrubbers (60ºC), it may be concluded that the unusual speciation of Hg^{2+} OUT-FGD at PP2 is caused by the evaporation of $HgCl_2$ particles from the aqueous phase of the gypsum slurry in the OUT-FGD gas. The thermal decomposition (60ºC) of Hg_2Cl_2 may also contribute to the release of Hg^{2+} to the gaseous phase. However, this process entails kinetics of heterogeneous reactions between the gaseous and aqueous phases currently under research.

3.6. INFLUENCE OF THE AL-ADDITIVE ON HG RETENTION

An interaction between the aqueous and gaseous phase as a function of the different dosage of $Al_2(SO_4)_3$ and the partial pressure relationship of CO_2/CO in the scrubber was initially proposed as cause for the different Hg compounds retained in the FGD-gypsum samples and the different gaseous Hg retention between 2007 and 2008 at PP2.

Thus, it is postulated that in line with the 2007 scrubbing solution, $CO_{(g)}$ IN-FGD would act as a reducing agent for SO_4^{2-} according to the reaction (at pH 5.1):

$$SO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} + 4CO_{(g)} \rightarrow H_2S_{(aq)} + 4CO_{2\,(aq)} \qquad \text{(R1)}$$

The thermodynamic feasibility of this reaction is shown in Figure 5. $CO_{(g)}$ and SO_4^{2-} cannot coexist in equilibrium and react to produce to intermediate compounds $CO_{2\,(aq)}$ and $H_2S_{(aq)}$.

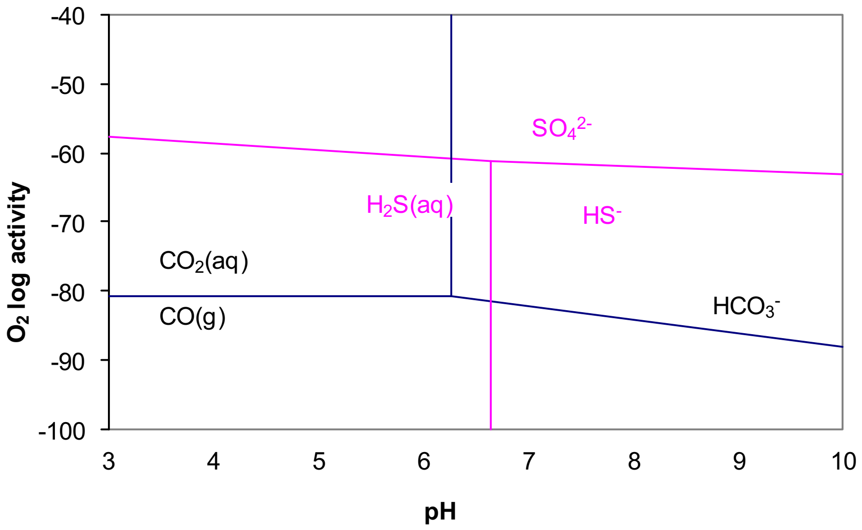


Figure 5. Phases diagram in the 2007 scrubber in equilibrium conditions.

The $H_2S_{(aq)}$ produced in reaction 1 would immediately react with Hg^{2+}, precipitating the highly insoluble HgS metacinnabar:

$$H_2S_{(aq)} + Hg^{2+}_{(aq)} \rightarrow HgS_{(s)} + 2H^+_{(aq)} \qquad \text{(R2)}$$

An overall reaction is obtained by combining equations 1 and 2 and assuming that at acidic pH most CO_2 (aq) would escape to the phase gas:

$$SO_4^{2-}{}_{(aq)} + Hg^{2+}_{(aq)} + 4CO_{(g)} \rightarrow HgS\ (s) + 4CO_{2\ (g)} \qquad \text{(R3)}$$

The thermodynamic reliability of the HgS formation can be demonstrated by comparing the actual Ionic Activity Product (IAP) obtained from the 2007 aqueous experimental data and the equilibrium constant (K) of the HgS formation derived from the thermodynamic database.

The IAP is calculated as:

$$IAP = [aHgS \times a\,(CO_2)^4] / [aSO_4^{2-} \times aHg^{2+} \times a\,(CO)^4] \qquad (Eq1)$$

where aHgS is assumed to be the unity, aSO_4^{2-} and aHg^{2+} are calculated from their solute concentrations (Córdoba et al., 2011) and the extended Debye-Huckel model (PHREEQC), and aCO_2 and aCO are equated with their partial pressures in the scrubber. The IAP calculated for the scrubber conditions in 2007 is $10^{6.23}$ a long way below $10^{78.32}$, which is the equilibrium constant of the formation of HgS at 60ºC. The IAP<K confirms the thermodynamic feasibility of the postulated process. Therefore, in 2007 with high dosages of $Al_2(SO_4)_3$, Hg is partially retained as the HgS metacinnabar in the 2007 FGD-gypsum (Figure 4a and 4b). This process diminishes the evaporation of $HgCl_2$ particles from the aqueous phase of gypsum slurry in the OUT-FGD gas.

By contrast, in 2008 with low $Al_2(SO_4)_3$ dosages, the formation of HgS barely takes place and particles of $HgCl_2$ predominate in the aqueous phase of the gypsum slurry. The partial retention of $HgCl_2$ in the 2008 FGD-gypsum (Figure 4c and 4d) demonstrates the enrichment and saturation of $HgCl_2$ in the aqueous phase of the gypsum slurry. As a consequence, the gaseous emissions of Hg^{2+} OUT-FGD increase in 2008 as a result of the evaporation of particles of $HgCl_2$ in the OUT-FGD gas.

Based on these results, it may be concluded that unusual speciation of Hg^{2+} in the OUT-FGD gas at PP2 is caused by the evaporation of particles of $HgCl_2$ from the aqueous phase of the gypsum slurry in the OUT-FGD gas. The factors that contribute to the unusual speciation of Hg in the OUT-FGD gas at PP2 are i) the formation of gaseous chloride species of Hg, primarily $HgCl_2$, in the IN-FGD gas stream; ii) the acidic pH and the S/Cl ratio in the scrubber at PP2, which promote the stability of highly soluble $HgCl_2$ complexes in gypsum slurry; and iii) the water re-circulation to the scrubber, which contributes to the enrichment of $HgCl_2$ in the aqueous phase of gypsum slurry. The use of $Al_2(SO_4)_3$ can be regarded as directly linked to the amount of gaseous Hg retention in the PP2 FGD system, a consideration that should be taken into account in the management of gaseous Hg emissions from coal-fired power plants.

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Additional findings to Article 4

5. SUPPORTING INFORMATION

Table S1. Experimental and certified values of Hg measurements during samplings campaigns at PP2.

Hg by GA AAS	Experimental value	Certified value			
Reference material		Value	Low	high	
SARM 20	0.21	0.20	-	-	ppm
1633 b	0.13	0.14	0.12	0.16	ppm

Table S2. Data used for the laboratory experiments.

PP1	Plant scale		Lab scale	
SO_2	14594	mg/m^3	280	mg/min
Cl^-	6212	$\mu g/m^3$	0.18	ng/min
$Hg^{(2+)}$	5.8	$\mu g/m^3$	111	ng/min
$Hg^{(0)}$	2.0	$\mu g/m^3$	40	ng/min
Gypsum slurry volume	2800	m^3	0.0028	m^3
Mass	3486000	kg	3.486	kg
Liquid (70%)	2440200	Kg	2.44	kg
Solid (30%)	1045800	Kg	1.05	kg
8% $CaCO_3$ without reaction	83664	Kg	0.08	kg
2% impurities	20916	Kg	0.02	kg
90% $CaSO_4.2H_2O$	941220	Kg	0.78	kg
$CaCO_3$ into the scrubber	941220	Kg	0.78	kg
Ratio $CaCO_3/H_2O$	1/2.5	Kg/L		
PP2	Plant scale		Lab scale	
SO_2	4746	mg/m^3	93	mg/min
Cl^-	6141	$\mu g/m^3$	0.54	ng/min
$Hg^{(2+)}$	16	$\mu g/m^3$	332	ng/min
$Hg^{(0)}$	2.2	$\mu g/m^3$	42	ng/min
Gypsum slurry volume	1.565	m^3	0.002	m^3
Mass	1768450	Kg	1.8	kg
Liquid (86%)	248644	kg	0.25	kg
Solid (14%)	1519099	Kg	1.52	kg
$CaSO_4.2H_2O$ (98.5%)	244914	Kg	0.20	kg
$CaCO_3$ into the scrubber	244914	Kg	0.20	kg
Ratio $CaCO_3/H_2O$	1/3	Kg/L		

Table S3. Thermal dissociation temperatures for Hg compounds.

Mercury compounds	High peak T (ºC)	Start of the peak T-end of the peak T (ºC)
$HgCl_2$	120±10	70-220
Hg_2Cl_2	80±5; 130±10	60-220
$HgBr_2$	110±5	60-220
HgS metacinnabar (black)	205±5; 245±5	170-290
HgS cinnabar (red)	310±10	240-350
$HgSO_4$	540±20	500-600
Hg_2SO_4	280±10	120-480
HgO	505±10	430-560

Table S4. Saturation indexes for Hg solid species in gypsum slurry from PP1 and 992.

	PP1		2007 PP2		2008 PP2	
Hg	Hg_2Cl_2	4.93	Hg_2Cl_2	8.26	Hg_2Cl_2	8.30
	Hg_2SO_4	-3.25	Hg_2SO_4	-0.99	Hg_2SO_4	-0.74

ARTICLE 5

Influence of an aluminium additive in aqueous and solid speciation of elements in flue gas desulphurisation system

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ABSTRACT

Experimental and modelling studies were carried out at two coal-fired power plants (PP1 and PP2) equipped with flue gas desulphurisation (FGD) systems, with the aim of investigating the effect of the dosage of an Al-additive applied to FGD slurries to increase SO_2 emission abatement efficiencies, on the fate of trace inorganic pollutants. The acidification of the aqueous phase induced by the use of the Al-additive (sulphate) results in significant differences in the speciation and partitioning of elements between the aqueous and solid phases of gypsum slurries. The Al-additive favours the occurrence 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 F in gypsum waste. The modelling 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 the Al-additive is added to the limestone slurry lower amounts of heavy metals are found in the leachates of the FGD-gypsums since these remain mostly in the solution of gypsum slurry. The reverse behaviour is found for Se.

Keywords: modelling studies; FGD; gypsum slurry; leachates.

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 (Córdoba et al., 2011). 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 (Córdoba et al., 2011). 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 aluminum components, HF may also react with limestone to form Al-F compounds, typically represented by $CaAlF_3$ $(OH)_2$-CaF_2 (Kikawa et al., 2002; Álvarez-Ayuso et al., 2006). These compounds are deposited on the surfaces of limestone particles and consequently may cause a decrease the reactivity of limestone (Mori et al., 1981; Maroney et al., 1986; Farmer et al., 1989; Ukawa et al., 1992). 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 (Álvarez-Ayuso et al., 2006). 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 (Álvarez-Ayuso et al., 2006). In the case of FGD-gypsum, other studies have addressed this issue by stabilising the FGD-gypsum before its disposal to mitigate F^- leaching (Álvarez-Ayuso et al., 2007; 2008).

The use of additives for preventing the precipitation of F solid species on FGD-gypsum may also be relevant given that some of the novel techniques for sequestering CO_2 are based on the formation of $CaCO_3$ via mineral carbonation of FGD-gypsum (Lee et al., 2012). 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 (Font et al., 2008) 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.

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 (Córdoba et al., 2011).

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 Figure 1. Detailed descriptions of the operation of the FGD system at PP1 and PP2 and the water streams are provided by Córdoba et al. (2011; 2012a; 2012b).

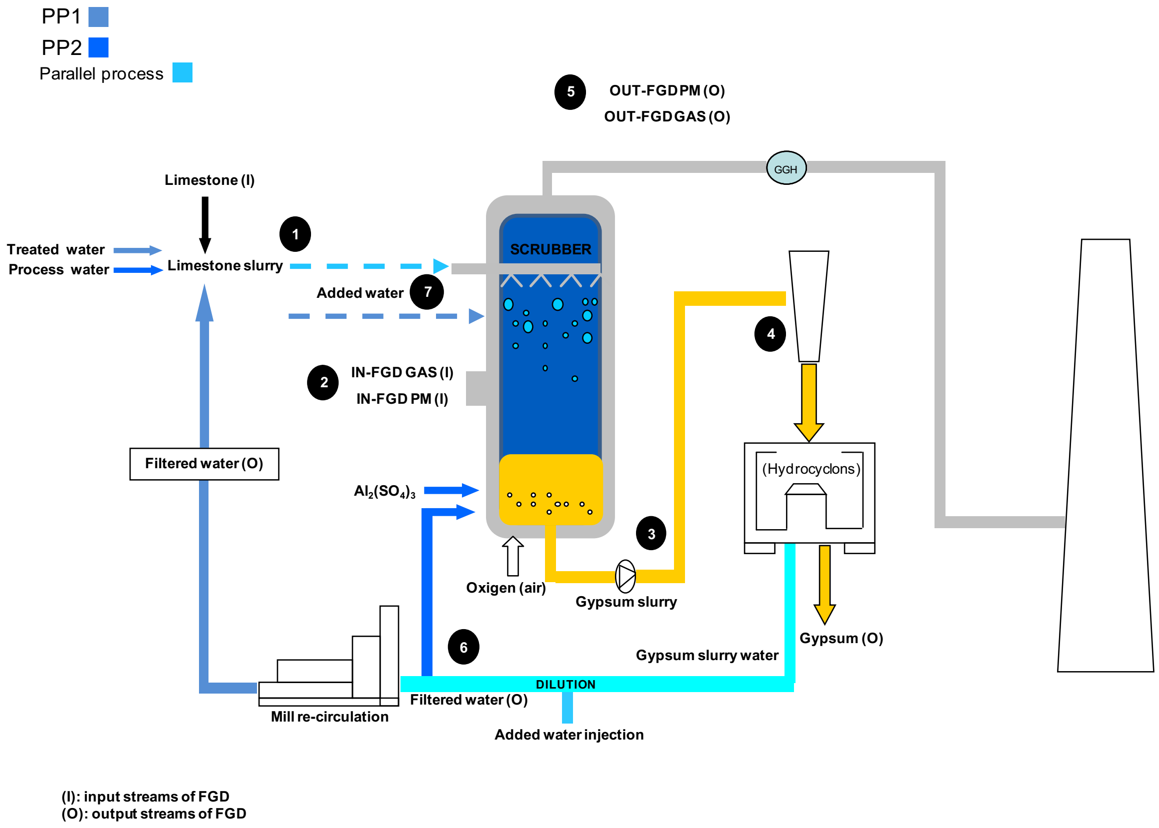

Figure 1. Sketch and process the FGD system at PP1 and PP2. 1. Limestone slurry introduced and sprayed into the scrubber to react with SO_2. 2. Gas and PM input flow into the scrubber after combustion process. 3. Formation of gypsum slurry as result of the desulphurisation process. 4. Filtration of gypsum 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; and 7. Water addition to offset the water loss with gypsum and in the OUT-FGD gas.

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 (GA-AAS).

2.4. GEOCHEMICAL MODELLING

Simulation tools are usable in a wide range of fields of study from energetic systems and chemical processing of crude oil up to pharmaceutical and food processing industry. These tools facilitate simulation, integration, and optimisation of processes (Andrea Tabasová et al., 2012).

The PHREEQC code (version 2.0) and the coupled thermodynamic database Lawrence Livermore National Laboratory (LLNL) (Parkhurst and Appelo, 1999) were used to calculate the speciation of elements enriched in the aqueous phase of gypsum slurry and to obtain the saturation index (SI) of selected minerals and solid phases at temperature (60ºC) and pH values of the aqueous phases at PP1 and PP2. The influence of the addition of $Al_2(SO_4)_3$ on the speciation and stability of some elements, and on pH in gypsum slurry was also modelled. The molality of the aqueous complexes and the initial pH value are those prevalent in gypsum slurry in the absence of additives (PP1).

2.5. IDENTIFICATION OF SOLID PHASES ON FGD GYPSUM

The identification of minor solid phases of trace elements was carried out in addition to X-Ray powder Diffraction (XRD), 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 ToF-SIMS analyses were performed using a ToF-SIMS IV (ION-ToF, Munster, Germany) operated at a pressure of 5 x 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 5x1011 ions/cm^2, well below the threshold level of 1x1013 ions/cm^2 generally accepted for static SIMS conditions. Secondary ions were detected with a reflector time-of-flight analyzer, a multichannel plate (MCPs), and a time-to-digital converter (TDC). Measurements were performed with a typical acquisition time of 6s, at a TDC time resolution of 200 ps and 100us cycle time. Charge neutralization was achieved with a low energy (20eV) electron flood gun. Secondary ion spectra were acquired from a randomly rastered surface areas of 50µm x50µm 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 Spec software (version 4.1). Each spectrum was normalised to the total intensity.

2.6. LEACHING TEST OF FGD-GYPSUM

Leaching tests following the standard EN12457- 4 according to the Council decision 2003/33/EC were applied to FGD-gypsums at PP1 and PP2 in order to define the environmental characteristics concerning the leachability of trace pollutants of these by-products in view of their future disposal in landfills. This consists of a single batch leaching test using Milli-Q (MQ) water as leachant agent at an L/S (liquid to solid) ratio of 10 L/kg and 24h of agitation time in an orbital shaker. Duplicated samples and blanks were all prepared in a similar manner. The leachates were filtered through 0.45μm filters and divided into two aliquots in High Density Polyethylene (HDPE) bottles. One aliquot was used for determination of pH and major anions, whilst the other split was acidified with 1% HNO_3 for further analysis of major and trace metals.

The leaching test of FGD-gypsum samples was conducted following the standard EN12457 to *(1)* obtain the maximum leaching that could be expected from FGD-gypsum in view its disposal in landfills; and *(2)* according to the particle size of the FGD-gypsum. The standard EN 12457-4 establishes this leaching test for granular waste materials and sludge with particle size below 10mm (without or with size reduction).

3. RESULTS AND DISSCUSION

3.1. CHARACTERISATION AND AQUEOUS SPECIATION OF GYPSUM SLURRIES

The aqueous phase of gypsum slurries at PP1 (pH 7.6) and PP2 (pH 5.1 in 2007 and 4.6 in 2008) show high concentrations of major elements associated with soluble salts (Ca, Mn, Cl, and Mg) minor and trace elements such as B, Se, Cu, Zn, Ni, and U. However, in addition to the pH value, significant differences in the aqueous phase of gypsum slurries between PP1 and PP2, and between 2007 and 2008 samplings at PP2, are observed for Al, F, SO_4^{2-}, Mg, and U (Table 1).

At PP2-2007, Al is enriched in the aqueous phase of the gypsum slurry (by a factor of 20 and >60), in F (7 and 15), Mg (2 and 3), and SO_4^{2-} (1.3 and 2.7) with respect to PP2-2008, and PP1, respectively, because of the use of $Al_2(SO_4)_3$ (Table 1). The aqueous equilibrium calculations at 60°C reveal that AlF_3 followed, in decreasing order, by AlF_2^+ and AlF_4^- shows the highest activities of Al and F in the 2007 gypsum slurry aqueous phase; whereas F^- and MgF^+ are the aqueous complexes with the highest activities of F in the PP1 and PP2 in 2008 aqueous phases (Table 2). As can be observed in the modelling diagrams of stability of F complexes vs $Al_2(SO_4)_3$ dosage (Figure 2a), the addition of $Al_2(SO_4)_3$ to the scrubber contributes to the presence of soluble Al-fluoride complexes (AlF_x) in the aqueous phase of the gypsum slurry (PP2-2007) and in consequence, reduces the fraction of CaF_2 and MgF_2 in the solid phase. By contrast, in the absence of (PP1) or using lower dosages of $Al_2(SO_4)_3$ (PP2-2008), F^- and MgF^+ reacts with Ca and Mg to form CaF_2 and MgF_2, which precipitate on the gypsum surface.

Table 1. Mean concentration of major, minor, and trace elements in the aqueous phase of the gypsum slurries.

	PP1 2007	PP2 2007	PP2 2008
	Gypsum slurry	Gypsum slurry	Gypsum slurry
pH	7.6	5.1	4.6
K (µS/cm)	17830	24932	39853
Flow (t/h)	71.6	28	28
mg/L			
Al	<10	642	38
Ca	807	781	950
Fe	<0.1	14	6
Mg	3414	10394	5638
Mn	103	510	416
Cl	841	3675	3420
F	87	1273	185
B	48	126	145
SO_4^{2-}	17118	45740	36370
Hg	0.01	2	2
µg/L			
Ni	514	5214	2779
Cu	53	319	196
Zn	346	4776	4824
As	52	67	53
Se	470	405	1496
Cd	25	162	204
U	330	654	667

The aqueous speciation model reveals that the addition of $Al_2(SO_4)_3$ to the scrubber also induces the formation of SO_4^{2-}-metal complexes in the aqueous phase of gypsum slurry at PP2. Sulphate-metal complexes of Cu, Fe, Mn, Ni, and Zn show the highest activities in the aqueous phase of gypsum slurry at PP2 (Table 2). It is for this reason that their concentrations with the exception of Zn increase significantly in the aqueous phase of the gypsum slurry from PP1 to PP2-2008 and 2007 (Table 1).

Zinc presents the highest activity (Table 2) in the 2007 and 2008 aqueous phase of gypsum slurry as $ZnSO_4$ complex. Conversely to the concentration of Cu, Ni, Mn, and Fe, higher in 2007 than in 2008, the concentration of Zn is slightly higher in the 2008 aqueous phase of gypsum slurry than in 2007 (Table 1). This suggest that the occurrence of Zn in the aqueous phase of gypsum slurry in both campaigns is associated with the presence of SO_4^{2-} in gypsum slurry, therefore, to the addition of the $Al_2(SO_4)_3$ to the scrubber. However, the concentration of Zn is not altered by the different dosage of the $Al_2(SO_4)_3$ in 2007 and 2008. Considering that additional SO_4^{2-} sources into the scrubber were not identified, the relatively higher concentration in the 2008 aqueous phase (4824 µg/L) than in 2007 (4776 µg/L) could be attributed to i) greater number of water re-circulations to the scrubber in the 2008 campaign than in 2007, which may give rise to higher enrichment of elements in the aqueous phase of gypsum slurry; and ii) greater leaching of Zn from FA particles that reach the FGD system.

Despite the fact that the number of water re-circulations to the scrubber cannot be determined, the mean contribution of filtered water to total mass balance with regard to Zn was considerably higher in the 2008 sampling campaign than in 2007 (Córdoba et al., 2011). This factor, and considering that the concentration of Zn in the 2008 FA (192 mg/kg) and 2007 FA (184 mg/kg) is not different enough to explain the slight differences of Zn in the aqueous phases of gypsum slurry, the relatively higher concentration of Zn in the 2008 aqueous phase of gypsum slurry than in 2007 is most probably due to the higher contribution of filtered water re-circulated to the scrubber for Zn in 2008 than in 2007.

The aqueous speciation model reveals that $UO_2(SO_4)_2^{2-}$ aqueous complex shows the highest activity in the 2007 gypsum slurry aqueous phase at PP2 whereas $UO_2(OH)_2$ and UO_2F_2 are the aqueous complexes with the highest activities in the PP1 and PP2-2008 aqueous phases, respectively. The stability diagrams of U complexes vs $Al_2(SO_4)_3$ dosage (Figure 2b), indicates the predominance of UO_2^{2+}-SO_4 complexes by increasing the $Al_2(SO_4)_3$ dosage. This probably account for the higher concentration of U in the 2007 and 2008 gypsum slurries at PP2 than at the PP1 (Table 1).

The aqueous speciation model of elements such as B, As, and Se in the PP1 and PP2 gypsum slurries is not altered despite the use of the $Al_2(SO_4)_3$ additive. Thus, SeO_3^{2-}, $HSeO_3^-$, AsO_3F^{2-}, and $B(OH)_3$ (Table 2), are the predominant aqueous complexes of Se, As, and B, respectively, in the aqueous phase at PP1, and PP2-2007 and 2008.

Table 2. Aqueous speciation model of elements in the aqueous phase of the gypsum slurries at PP1 and at PP2.

	PP1	Activity	PP2	2007 Activity	PP2	2008 Activity
Mg	$MgSO_4$	1.081e-001	$MgSO_4$	3.595e-001	$MgSO_4$	2.062e-001
SO_4^{-2}	SO_4^{2-}	1.361e-002	SO_4^{2-}	1.883e-002	SO_4^{2-}	2.799e-002
Al (III)	_	_	AlF_3	1.653e-002	AlF_3	7.611e-004
	_	_	AlF^{2+}	4.487e-003	AlF_4^-	4.492e-004
F	F^-	2.312e-003	AlF_3	1.427e-002	F-	2.350e-003
	MgF^+	8.309e-004	F^-	1.653e-002	MgF^+	7.497e-004
	CaF^+	5.272e-005	_	_	CaF^+	4.240e-005
As (IV)	AsO_3F^{2-}	7.072e-007	$HAsO_3F^-$	4.281e-007	$HAsO_3F^-$	4.046e-007
B	$B(OH)_3$	4.155e-003	$B(OH)_3$	1.256e-002	$B(OH)_3$	1.408e-002
Se (IV)	SeO_3^{2-}	1.132e-006	$HSeO_3^-$	3.479e-006	$HSeO_3^-$	1.297e-006
U (VI)	$UO_2(OH)_2$	1.201e-003	$UO_2(SO_4)_2^{2-}$	1.927e- 007	UO_2F_2	1.477e-006
Cu	$CuSO_4$	2.435e-008	$CuSO_4$	1.545e-007	$CuSO_4$	1.163e-007
Mn	$MnSO_4$	1.947e-005	$MnSO_4$	5.178e-003	$MnSO_4$	5.472e-003
Fe	_	_	$FeSO_4$	1.032e-004	$FeSO_4$	5.675e-005
Ni	$NiSO_4$	1.641e-007	$NiSO_4$	3.027e-005	$NiSO_4$	2.493e-005
Zn	$ZnSO_4$	2.372e-007	$ZnSO_4$	4.597e-005	$ZnSO_4$	5.385e-005

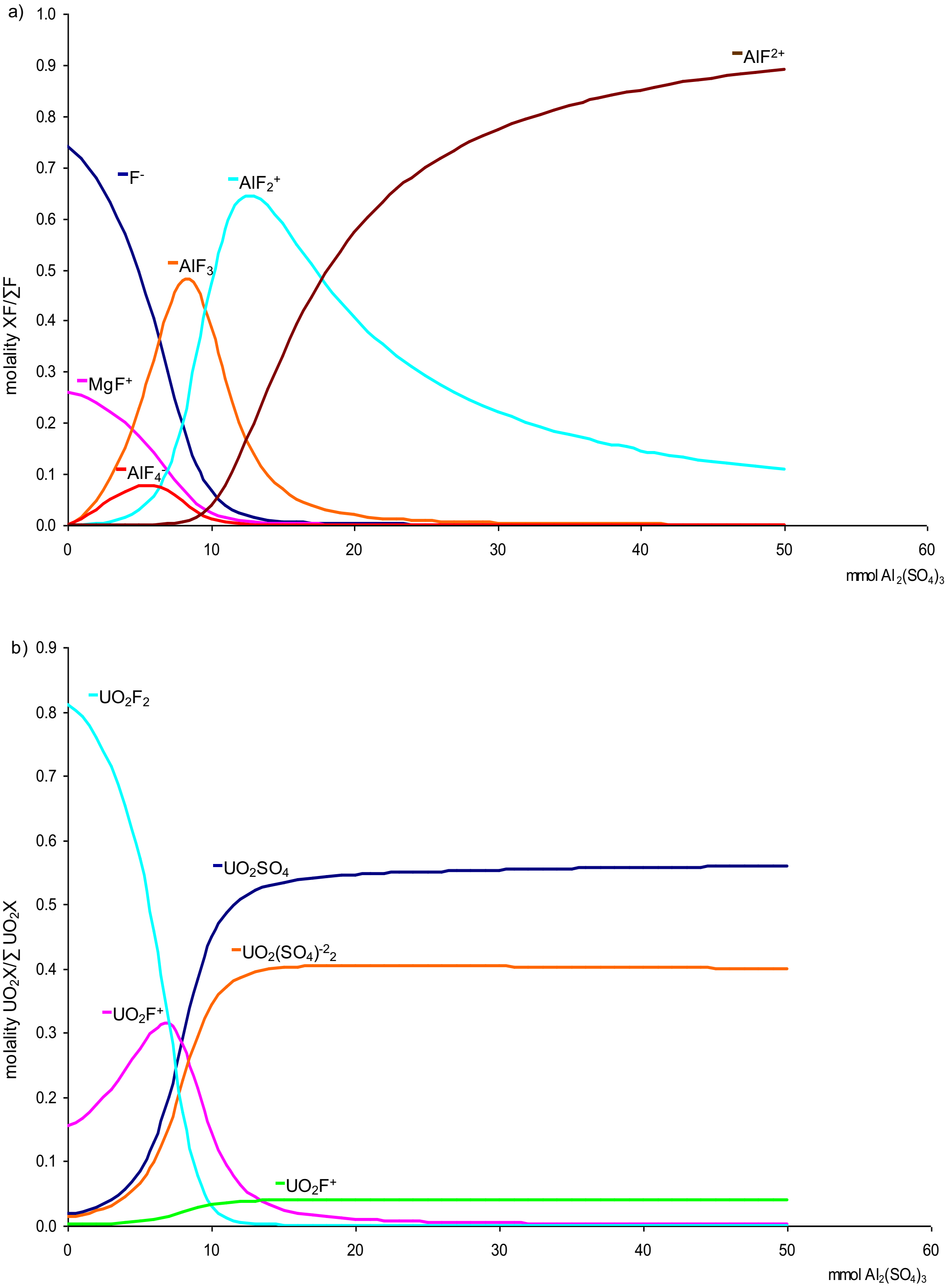

Figure 2. Diagrams of stability of Al-F (a) and U (b) complexes in the aqueous phase of gypsum slurry as function of $Al_2(SO_4)_3$ dosage. The initial solution is the PP1 aqueous phase.

The addition of $Al_2(SO_4)_3$ to the scrubber also causes the acidification of the aqueous phase of gypsum slurry via aluminium hydrolysis (Ochoa-González et al., 2012). As can be observed in Figure 3, the pH of a neutral slurry experiences a rapid drop with increasing $Al_2(SO_4)_3$ even in small dosages. $Al_2(SO_4)_3$ is itself acidic under natural water conditions; with pH values from 4.0 to 5.0, $Al_2(SO_4)_3$ dissolves and subsequently forms $Al(OH)_3$, restoring the H_2SO_4 (Rappold and Lackner, 2010). This result of acidification is observed after the natural buffering capacity of a watershed is depleted and aluminium ion is leached into water bodies (Stigliani and Shaw, 1990).

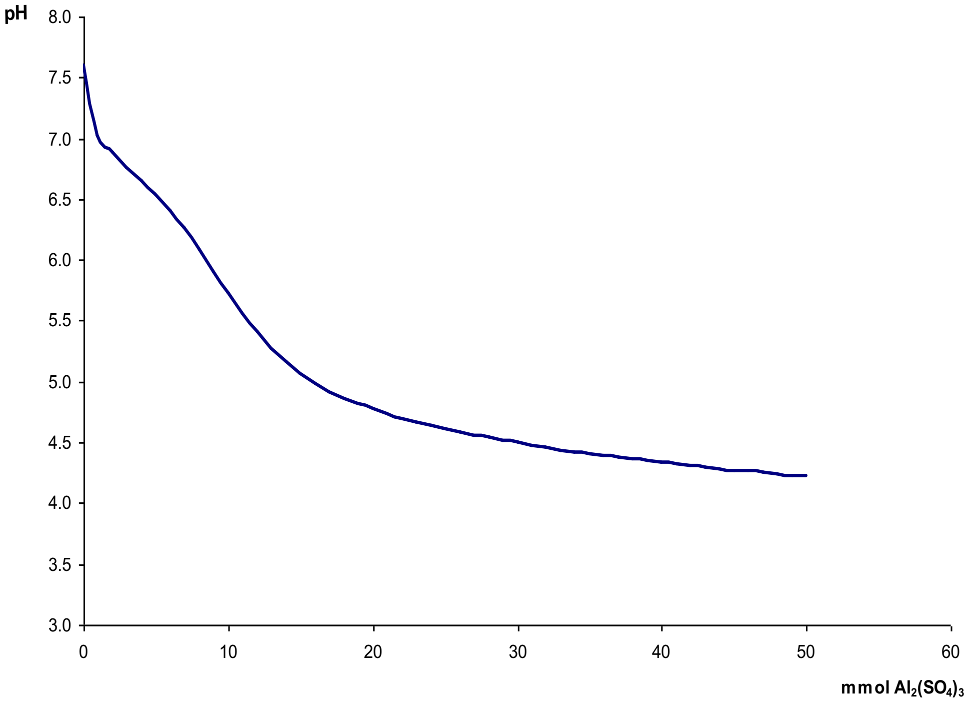

Figure 3. Variation of pH in function of dosages of $Al_2(SO_4)_3$. The initial solution is the PP1 aqueous phase.

Although the addition of $Al_2(SO_4)_3$ at PP2 promotes the interaction between Al and F increasing the capacity of limestone for $SO_{2\ (g)}$ retention, the acidification of the aqueous phase of gypsum slurry induced by the addition of $Al_2(SO_4)_3$ could also affect the desulphurisation efficiency at PP2. The desulphurisation efficiencies obtained from the 2007 and 2008 measurements at PP2 revealed a relatively low retention for SO_2 (82-86% and 82-88% for 2007 and 2008) in comparison with that obtained at PP1 (94%, Córdoba et al., 2012a).

In wet FGD processes, the rate at which $SO_{2\,(g)}$ is transferred depends on the solubility of SO_2 and its displacement from equilibrium (Dou et al., 2009). Under acidic conditions, the equilibrium pressure of SO_2 increases and as a consequence, the diffusion of SO_2 from the gaseous to the aqueous phase decreases:

$$SO_{2\,(aq)} + H_2O \leftrightarrow H_2SO_{3\,(aq)} \qquad \text{(R1)}$$

$$H_2SO_{3\,(aq)} \leftrightarrow H^+_{\,(aq)} + HSO_3^-{}_{(aq)} \leftrightarrow H^+_{\,(aq)} + SO_3^{2-}{}_{(aq)} \qquad \text{(R2)}$$

Reactions 1 and 2 illustrate that an increase of H^+ may reduce the diffusion of SO_2 from the gaseous to the aqueous phase with the consequent desorption of SO_2. According to this, the acidic conditions of gypsum slurry in 2007 (5.1) and 2008 (4.6) could be regarded as cause of the relatively low efficiencies of desulphurisation at PP2.

3.2. IDENTIFICATION OF ELEMENTS AND MOLECULES IN FGD-GYPSUMS

Major solid phases ($CaSO_4.2H_2O$ and $CaCO_3$) were identified in the PP1 and PP2 FGD-gypsums by XRD. Mass spectrometry analysis (Table 3) by TOF-SIMS detected Ca, Mg, Mn, Na, Al, and Fe; molecules of CaOH, Ca_2O_2, and $Ca_2O_2H_2$; ionic groups such as SO_3, SO_4, and HSO_4; monatomic ions of O, and polyatomic such as OH in FGD-gypsums at PP1 and PP2. Molecules of SiO_2 and SO_2; cluster ions of SiO_3, $HSiO_3^-$, and $Si_3H_3O_2$, and Li were also identified in FGD-gypsum at PP1 (Table 3).

Table 3. Intensity of the signal of molecules, clusters, and elements identified on the PP1 and PP2 FGD-gypsum.

	Intensity		
	2007 PP2	2008 PP2	PP1
Molecules	FGD-gypsum	FGD-gypsum	FGD-gypsum
O	4600	6800	110000
OH	5500	5500	800
F	600	2500	3000
Cl	4500	1400	600
SiO_2	-	-	1100
SO_2	220	1400	1150
SiO_3	-	-	950
$SiHO_3$	-	-	800
SO_3	1050	1000	900
SO_4	3000	2900	450
HSO_4	-	-	250
Al	11000	5000	2500
Li	-	-	350
Na	3000	3000	11000
Mg	9800	10000	3000
K	9800	10000	7500
Ca	14000	15000	3000
Fe	3000	3000	500
Mn	2100	1800	1500
CaO	800	100	500
CaOH	14000	14000	2000
Ca_2O_2	3200	3200	400
$Ca_2O_2H_2$	6000	6000	650

Comparison of the intensity signal of F in the 2007 and 2008 FGD-gypsums at PP2 and in the PP1 FGD-gypsum (Figure 4) revealed, that even in large dosages of $Al_2(SO_4)_3$ F continues precipitating as CaF_2 and/or MgF_2 in the 2007 FGD-gypsum at PP2, although in a lower proportion with respect to that in 2008 and with respect to FGD-gypsum at PP1 (Table 3). Therefore, it may be concluded that the $Al_2(SO_4)_3$ dosage employed in the 2007 campaign at PP2 reduces significantly the precipitation of F in the 2007 FGD-gypsum. However, the $Al_2(SO_4)_3$ dosage should be higher in order to prevent the precipitation of F solid phases.

As a result of larger dosages of the $Al_2(SO_4)_3$ in 2007 than in 2008, Al signal is stronger in the 2007 FGD-gypsum (Figure 4). Aluminium, however, is detected in FGD-gypsum at PP1 (Table 2) despite the fact that it was not detected in the aqueous phase (Table 1). This could be due to the presence of higher levels of aluminosilicate phases (mainly clay minerals) at PP1 with respect to PP2 (Table 3). Indeed, an earlier work on the partitioning in the PP1 FGD system (Córdoba et al., 2012a) demonstrated that Al and Si are supplied by the highly insoluble aluminosilicate fraction of limestone (93% Ca carbonate) and are retained as impurities in the

FGD-gypsum sludge. By contrast, the limestone used at PP2 has a high purity (99% Ca carbonate).

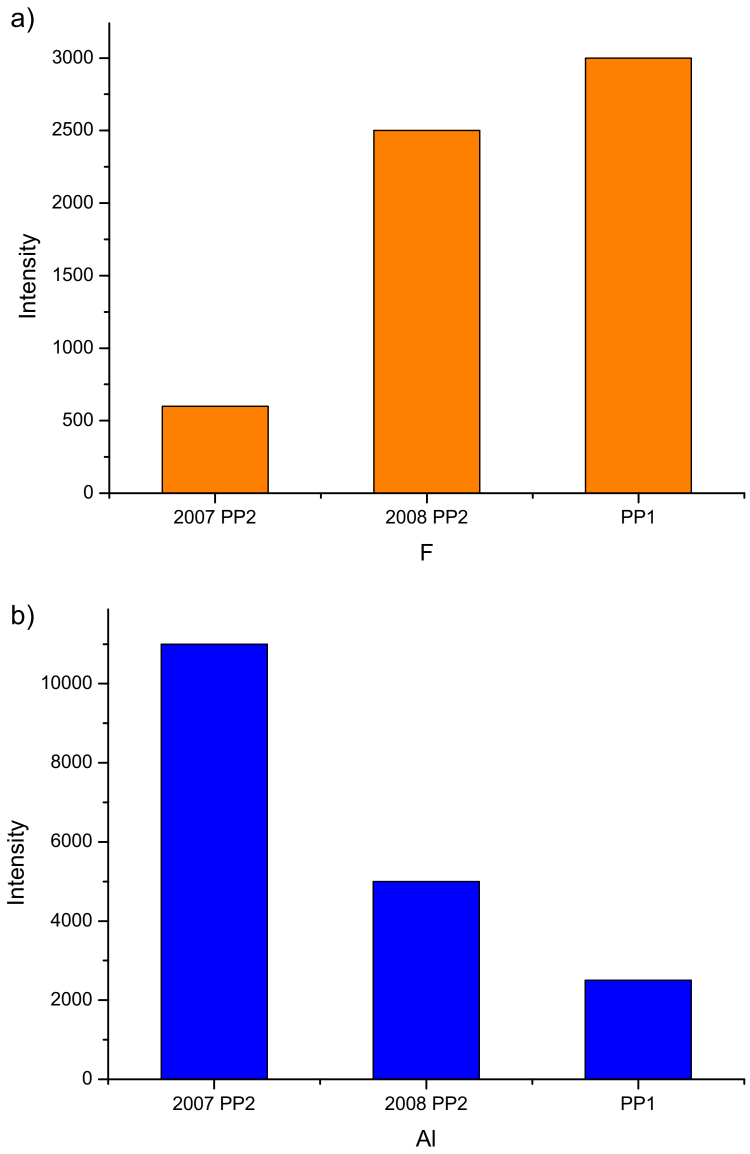

Figure 4. Intensity signal by TOF analysis of F (a) and Al (b) in the PP1 and PP2-2007 and PP2-2008 FGD-gypsums.

The Mg/F intensity ratio is higher in the 2007 FGD-gypsum than in the 2008-PP2 and in the FGD-gypsum at PP1. Given that $Al_2(SO_4)_3$ prevents the formation of MgF_2, the high Mg/F intensity ratio in the 2007 FGD-gypsum suggests that Mg may also precipitate with molecules and/or ionic cluster other than F on the 2007 FGD-gypsum surface. The Ca signal is overlapped by its association with SO_4^{2-} in the structure of gypsum (Table 3).

As regards Cl, a recent study (Córdoba et al., 2012c) on the occurrence of Hg in the FGD-gypsums at PP2 demonstrates that HgS in 2007, and $HgCl_2$ and Hg_2Cl_2 in 2008 are the retained solid phases of Hg. The occurrence of HgS in the 2007 FGD-gypsum is associated with the dosage of $Al_2(SO_4)_3$ in the scrubber, which is higher in 2007 than in 2008. In the 2007 scrubbing solution, $CO_{(g)}$ acts as a reducing agent for SO_4^{2-}, giving rise to $H_2S_{(aq)}$, which immediately reacts with $Hg^{2+}_{(aq)}$, precipitates the highly insoluble HgS metacinnabar. In 2008, using lower dosages of $Al_2(SO_4)_3$, the formation of $H_2S_{(aq)}$ barely takes place with the result that $HgCl_2$ and Hg_2Cl_2 are the predominant species of Hg retained in the FGD-gypsum because of the progressive dissolution of $HgCl_{2\,(g)}$ in the aqueous phase. Consequently, the presence of Cl in the solid phase of the 2007 FGD-gypsum suggests that Cl also precipitates with elements other than Hg.

3.3. OCCURRENCE OF SOLID PHASES: THERMODYNAMIC MODELLING

Of the solid phases included in the LLNL database (Parkhurst and Appelo, 1999), the geochemical modelling predicts saturation of the aqueous phases in CaF_2 and MgF_2 in all the FGD-gypsum samples (Table 4). This is in agreement with the detection of F, Ca, and Mg in the FGD-gypsums by ToF-SIMS analyses. In detail, the lower supersaturation of the PP2 2007 FGD-gypsum is consistent with the lower F signal in TOF-SIMS, and confirms that the $Al_2(SO_4)_3$ dosage is not sufficient to prevent the formation of minor amount of solid CaF_2. The saturation in $CaUO_4$ is predicted in the aqueous phase in the gypsum slurry at PP1. Although U is not detected by ToF-SIMS analysis, this element was detected in considerable concentrations (2 mg/kg) by ICP-MS analysis in the FGD-gypsum samples at PP1 (Córdoba et al., 2012a).

Geochemical modelling reveals that the $Al_2(SO_4)_3$ additive at PP2 also alters the speciation of elements other than F, Ca, and Mg. In PP2-2007 FGD-gypsum, $AlHO_2$ and Al_2O_3 are predicted to be supersaturated whereas in the PP1 and PP2-2008 FGD-gypsums these solid phases are below saturation (Table 3). Although $Al_3Si_2O_5$, $Al_2Si_2O_5(OH)_4$, and $KAlSi_3O_8$ are also predicted to be supersaturated in the PP2-2007 and PP2-2008 FGD-gypsums (Table 4), their precipitation in the FGD-gypsum was not demonstrated because cluster ions of Si are not detected by ToF-SIMS analysis. Therefore, Al could precipitate in the PP2 2007 FGD-gypsum as $AlHO_2$, Al_2O_3, or $Al(OH)_6(SO_4)_2$. The subsaturation (SI<0) of all the Al solid phases prevent us from determining the mode of occurrence of Al in the 2008 FGD-gypsum.

As previously stated, the $Al_2(SO_4)_3$ dosage induces the HgS retention in the 2007 FGD-gypsum. In 2008 as a result of the lower dosages of $Al_2(SO_4)_3$, $HgCl_2$ and Hg_2Cl_2 are the predominant species retained in FGD-gypsum, which is in agreement with the supersaturation of Hg_2Cl_2 in the PP2-2008 aqueous phase. The mode of occurrence of Hg in the FGD-gypsum at PP1 is currently under research.

Table 4. Saturation indices of selected solid phases in the aqueous phase of the gypsum slurries.

	SOLID PHASES	PP1	2007 PP2	2008 PP2
Al	$AlHO_2$	<3.27	1.99	-2.25
	Al_2O_3	<3.39	0.83	-
	$KAl_3(OH)_6(SO_4)_2$	<0.77	4.89	-9.28
Ca	$CaSO_{4}.2H_2O$	0.25	0.15	0.46
	$CaSO_4$	0.01	0.31	0.61
	CaF_2	2.13	0.10	2.04
Mg	MgF_2	2.53	1.11	2.51
U	$CaUO_4$	3.56	-4.35	-6.97
Hg	Hg_2Cl_2	4.93	8.26	8.30

3.4 EVALUATION OF THE POTENTIAL LEACHING OF FGD-GYPSUMS

The comparison of the leaching results and the waste acceptance criteria at landfills (Table 5) reveals that all the FGD-gypsum samples can be accepted at non-hazardous waste landfills. However, it should be stressed that the leaching values of F^- are well above the inert range in the PP1 and PP2 FGD-gypsums and close to non-hazardous waste.

The leaching value of SO_4^{2-} in all the FGD-gypsum samples should be noted. The leaching levels of SO_4^{2-} from the PP1 and PP2 2008 FGD-gypsums fall in the range of inert materials but reaching values close to that of non-hazardous waste, whereas those from the PP2 2007 FGD-gypsum fall in the range of the criteria for non-hazardous materials. The leaching behaviour of SO_4^{2-} is related with the solubility of gypsum therefore preventing measures are not possible.

The leaching values of most of the heavy metals from the FGD-gypsums are far below the non-hazardous limit. Although the comparison of the leaching value of heavy metals between PP1 and PP2 FGD-gypsums doesn´t reveal significant differences, it should be noted that most of heavy metals present higher enrichment in the PP2 aqueous phase of gypsum slurry than in PP1. It is for this reason that higher leaching values of most of the heavy metals in the PP2 FGD-gypsums than in the PP1 should be expected.

The absence of significant leaching of heavy metals at PP2 is related with the protonation of the gypsum surface induced by the addition of $Al_2(SO_4)_3$ and the formation of SO_4-complexes. The point of zero charge (pzc) and variation of the gypsum surface charge with pH is barely known. To our knowledge, only one unpublished work by Shang et al. (2009) describes the variation of surface zeta potential with pH. When the pH is lower than the pzc value, acidic waters donate more H^+ than OH^-, and therefore the adsorbent surface is positively charged (repelling cations). Therefore, it could be considered that the acidic conditions of gypsum slurry in 2007 (pH 5.1) and in 2008 (pH 4.6) caused by the addition of $Al_2(SO_4)_3$ may give rise to the protonation of the surface of the FGD-gypsum. The protonation of the gypsum surface induced by the addition of $Al_2(SO_4)_3$ and the formation of SO_4-complexes probably contribute to the maintenance of metals in solution.

Selenium in the PP1 FGD-gypsum is within the upper inert range and close to non-hazardous waste. This is significant given that Se tends to be enriched in the aqueous and solid phase of the PP1 and PP2 gypsum slurries (Córdoba et al., 2011) which could give rise to future problems in meeting new standards. The presence of Se in solid waste is consistent with its aqueous speciation. Thus, unlike metals, according to modelling Se is present in solution as SeO_3^{2-} and $HSeO_3^-$ regardless of $Al_2(SO_4)_3$ dosage. It is for this reason that Se is attracted by the positively charged gypsum surface.

Nickel and Hg are the only elements that show lower leaching value in the 2007 FGD-gypsum than in 2008, which may be attributable to the different dosage of $Al_2(SO_4)_3$ between samplings. Copper and Zn, and Fe, Mn, and U (not regulated by the directive), maintain similar leaching values in the 2007 and 2008 FGD-gypsums despite of the different dosage of $Al_2(SO_4)_3$.

Table 5. Leachable concentrations of selected elements in PP1 and 2007-2008 PP2 FGD-gypsum and comparison with the criteria for acceptance at landfills according to 2003/33/EC (mg/kg).

	Waste acceptance criteria			PP1	2007 PP2	2008 PP2
	Inert	Non hazardous	Hazardous	Gypsum	Gypsum $Al_2(SO_4)_3$	Gypsum $Al_2(SO_4)_3$
SO_4^{2-}	1000	20000	50000	18694	20758	19382
F^-	10	150	500	122	106	110
Cu	2	50	100	0.02	0.02	0.02
Hg	0.01	0.2	2	<0.01	0.11	0.14
Ni	0.4	10	40	0.04	0.08	0.2
Zn	4	50	200	<0.01	<0.01	<0.01
Fe	-	-	-	<1	19	<1
Mn	-	-	-	12	63	36
U	-	-	-	0.2	0.03	0.03
As	0.5	2	25	<0.01	0.02	0.01
Se	0.1	0.5	7	0.2	0.1	0.06

The absence of significant leaching of heavy metals from the FGD-gypsums is particularly significant in view of the disposal of FGD-gypsum in landfills bearing in mind that the leaching test according to the standard EN12457- 4 is a forced extraction method.

4. CONCLUSIONS

The addition of $Al_2(SO_4)_3$ to the scrubber results in the acidification of the gypsum slurry via aluminium hydrolysis, and enhances the occurrence of the Al-F complexes in the aqueous phase of PP2-2007. By contrast, in the absence of or using lower dosages of $Al_2(SO_4)_3$ (PP1 and at PP2 in 2008), the supersaturation of MgF_2 and CaF_2 in the gypsum slurries leads to their precipitation on FGD-gypsum, increasing the leachable potential of F^- in the waste product.

The acidic conditions of the aqueous phase of gypsum slurry in 2007 (5.1) and 2008 (4.6) could be regarded as cause of the relatively low efficiencies of desulphurisation at PP2 (82-86% and 82-88% for 2007 and 2008) in comparison with that at PP1 (94%).

The thermodynamic and ToF-SIMS results demonstrate that the $Al_2(SO_4)_3$ dosage employed in 2007 reduces significantly the F enrichment in the 2007 FGD-gypsum at PP2 but it is not sufficient to completely avoid its occurrence in FGD-gypsum.

Although minor solid phases of trace elements predicted thermodynamically in saturation were not identified by XRD, the identification of the structural components of such solid phases supports the precipitation processes of CaF_2 and MgF_2, in the PP1 FGD-gypsum, and Al_2O_3, $AlHO_2$, $KAl_3(OH)_6(SO_4)_2$ and MgF_2 in the 2007 and 2008 FGD-gypsums at PP2.

The concentration of heavy metals and uranium in the aqueous phase is significantly increased after the addition of $Al_2(SO_4)_3$ to the scrubber. The lower pH and the protonation of the FGD-gypsum surface induced by the addition of $Al_2(SO_4)_3$ also contribute to the stabilisation of metals in solution. As a result, very low amounts of heavy metals are found in the leachates of the FGD-gypsum. The reverse behaviour is found for Se.

ToF-SIMSS mass spectrometry of the solid phase combined with thermodynamic modelling of the aqueous phase has proved useful in understanding the geochemical behaviour of elements and their partitioning into solid and aqueous phases. Other techniques such as synchrotron light micro X-ray fluorescence, micro-XRD and X-ray absorption spectroscopies may constitute a more accurate approach to the identification of solid phases.

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Additional findings to Article 5

3.5. POTENTIOMETRIC TITRATION OF FGD-GYPSUM

In order to study the leaching behaviour of some elements from PP2 FGD-gypsums, potentiometric titration experiments based on the identification of the point of zero charge and variation of the 2007 PP2 FGD-gypsum surface charge with pH were conducted. These experiments were carried out at Department of Chemical Engineering at the University of the La Frontera, Temuco, Chile.

The variation of the surface charge of the FGD-gypsum was carried out by potentiometric titration in a N_2-rich atmosphere using 0.02N HCl and 0.02N NaOH. Three samples of 0.3g of FGD gypsum were placed in a vessel containing 100 mL of 1 and 0.01M KCl as background electrolyte. The titrations were carried out by adding 0.2 mL of the titrants followed by 20 minutes of reaction (Sposito and Holtzclaw, 1977).

The point of zero charge (pzc) of the 2007 FGD-gypsum is 7.5 (Figure 5.5.). The shape of the potentiometric curves point out that at pH lower than 7.5 the FGD gypsum surface is positively charged (Figure 5.5.). When the pH is lower than the pzc value, acidic water donates more H^+ than OH^-, and therefore the adsorbent surface is positively charged (attracting anions). Conversely, above pzc the surface is negatively charged (attracting cations/repelling anions). Therefore, the acidic conditions of gypsum slurry in 2007 (pH 5.1) and in 2008 (pH 4.6) caused by the addition of $Al_2(SO_4)_3$, probably gave rise to the protonation of the surface of the FGD-gypsum. This, in conjunction with the ion-association aqueous model from the aqueous phase of gypsum slurries, which showed that most of metals occur as metals-SO_4-complexes in the aqueous phase of gypsum slurry, indicates that the occurrence of metals in solution in 2007 and 2008 is dependant of the addition of the $Al_2(SO_4)_3$ into the scrubber. The protonation of the FGD-gypsum surface and the formation of SO_4-complexes induced by addition of $Al_2(SO_4)_3$, may account for the absence of significant leaching of heavy metals from PP2 FGD-gypsum. These two factors probably contributed to maintain metals in solution.

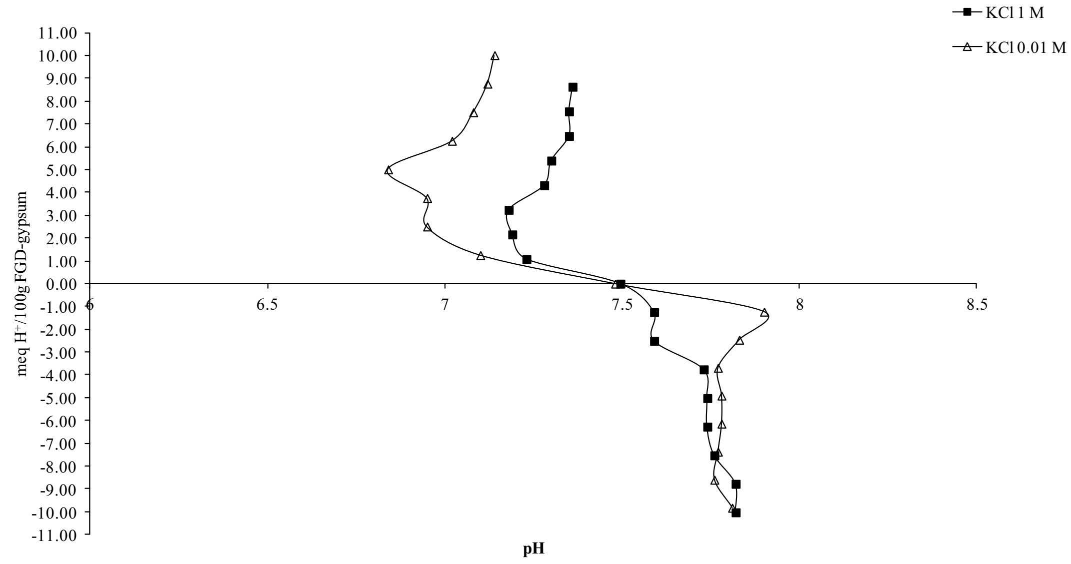

Figure 5. Potentiometric curves and point zero of zero charge (pzc) for FGD-gypsum surface.

Chapter 4

Summary of Results and Discussion

4. SUMMARY OF RESULTS AND DISCUSSION

4.1. MASS BALANCES, PARTITIONING, AND BEHAVIOUR OF TRACE ELEMENTS

Mass balance studies were a useful method to study the transport through and final fate of trace elements from coal-fired power plants. The sampling and analysis of input and output streams in the boiler, ESP, and FGD systems provided an accurate description of the trace element partitioning as evidenced by closure of mass balances and flow rates. The concentration of specific elements in a few cases was below the analytical detection limits for an accurate quantitative analysis. For this reason, the evaluation of mass balances for such elements was limited.

In this work, the partitioning and behaviour of trace elements in the PCC (boiler + ESP) and FGD systems were independently examined as part of the mass balance studies.

4.1.1. Partitioning and behaviour of trace elements in the PCC system (boiler + ESP)

Because coal-combustion processes are well evaluated, general trends in trace element behaviour during combustion have been identified. It is common knowledge that many of the trace elements from coal are partially or totally vaporised during combustion. The degree of vaporisation determines how each element is partitioned between various solid residues and the flue gas (Clarke and Sloss, 1992).

The elements in the PCC system were classified (Articles 1 and 2) in accordance with the volatile behaviour of the elements at the boiler and at the ESP, respectively:

- *Non-volatile elements* (>80% in FA and <20% in slag): Tl, Mo, Sn, Zn, Pb, Ga, Hf, Cs, V, Th, Li, Al, P, Nb, Ti, Co, Y, Rb, Ce, La, Cu, Zr ,Cr, K, Fe, U, Ni, Sr, Mn, Ge, Ca, Be, Mg, Na, and REEs.
- *Moderately volatile elements with a high condensation potential in FA and IN-FGD PM*: Arsenic, Se, and B (62-98% in FA)
- *Highly volatile elements:* S, Cl, Hg, and F (78-99% IN-FGD gas).

This classification of the volatile behaviour of trace elements during combustion is in agreement with most of the literature (Smith, 1987; Germani and Zoller, 1988; Meij, 1989; Clarke, 1991; Clarke and Sloss, 1992), except for some specific elements.

Elements classified as *non-volatile elements* in this study are in line with *Group 1* elements (elements concentrated in the coarse residues or partitioned equally between coarse residues and particulates such as FA or gasifier particulates) from the Clarke and Sloss (1992) classification.

Elements classified as *moderately volatile elements with high condensation potential in FA and IN-FGD PM* in this study are associated with *Group 2* elements (elements enriched in the fine-grained particles which may escape from particulate control systems) from the Clarke and Sloss (1992) classification.

Elements classified as *highly volatile elements* correlate with *Group 3* elements (elements which volatilise readily) from the same classification.

After reviewing various classification systems (Kein et al., 1975; Smith, 1987; Mojtahedi, 1989; Meij, 1989; Clarke, 1991; Yokoyama et al., 1991), it is clear that the elements Ba, Be, Bi, Co, Cr, Cs, Cu, Mo, Ni, Sr, Ta, U, V, and W have in some cases been classified between Group 1 and Group 2. Elements in Group 1 and Group 2, and the relatively volatile elements B and Se have been classified between Group 2 and Group 3.

As in earlier evaluations (Meij, 1994; Álvarez-Ayuso et al., 1996; Sandelin and Backman, 2001; Otero-Rey et al., 2003; Cheng et al., 2009), at PP1 and at PP2, a moderately low partitioning in the gaseous phase was deduced for As (0.03%), B (5.8% and 7.4-9.3%, respectively), and Se (23% and 2.1-5.9%, respectively). Most As and B were retained in FA (97% and 72-90%, respectively) whereas a lower value was obtained for Se (62% and 67-78%, respectively). At PP2 in 2007, a significant proportion as PM was determined for Se (30%).

It should also be noted that for Se (12%) and B (18%) a relatively high partitioning was determined for the 2008 BS because of the addition of coal gangue to the boiler during the 2008 campaign. Coal gangue contains carbonate minerals that act as fluxing and reduce the fusion temperature, enhancing the slagging.

Most of the S, F, and Hg initially present in the feed fuel blends were partitioned in the gas phase with values of 97-99%, 87%, and 86-89%, respectively. A variable proportion in the gas phase was determined for Cl depending on the power plant. In line with the aforementioned literature, 93% of Cl was partitioned in the gas phase at PP1. Only 53-63% of Cl was found in a gaseous form at PP2 because of the relatively high retention of Cl in the FA (33-42%).

4.1.2. Partitioning and behaviour of trace elements in the FGD system

Reliable mass balances demand accurate determinations of trace element contents and flow rates in all inputs and outputs to the facility (Clarke and Sloss, 1992). For this reason, limestone, IN-FGD gas, IN-FGD PM and the mixture of slurry waters in the scrubber were indentified as sources of elements in the FGD system. The mixture of slurry waters was regarded as an input of pollutants to the FGD systems as a result of the re-circulation of filtered water to the scrubber. The deduced contributions of trace elements to the FGD systems are summarised as follows:

- Limestone was the major input source (51-100%) for (As), Co, Sc, P, Ca, Nd, Ti, Ce, Zr, La, Y, (Al) V, Nb, Fe, Pb, Li, Sr, Ga, Rb, Ba, V, Sn, Cr, Cu, K, U, and (Ni).
- IN-FGD gas largely contributed (78-97%) to S, (Hg), (Se), and (F) inputs to FGD.
- IN-FGD PM was the main source (58-100%) of most of the REEs, Hf, Ta, W, Bi, Ge, (Zn), Sb, Be, and Tl.
- The mixture of the slurry waters was the most important input (49-94%) for Mg, Na, Mn, Cd, Tl, Mo, B, and Cl.
- An Al-additive was the most important source (74-82%) of (Al).

These results indicated that trace elements were introduced to the FGD systems mainly from limestone and from the mixture of the slurry waters, and to a lesser extent from the PCC flue gas. Elements in brackets were introduced into the FGD systems from different sources depending on the power plant. The most significant differences are summarised as follows:

- The IN-FGD gas was the main source of Hg (95%), Se (82%), and F (74%) at PP1, whereas the mixture of slurry waters was the main source of Hg (68%), Se (35%), and of F (63%) at PP2 in 2007.
- Fluorine (90%) entered FGD in a gaseous form at PP2 in 2008.
- The main sources of As to FGD were limestone (84%) at PP1, and PM (60-90%) at PP2.
- Limestone (83%) and PM (70%) were the main sources of U and Zn to FGD, respectively, at PP1, whereas the mixture of slurry waters was the main source of U (54-63%) and Zn (66-85%) at PP2.
- Limestone (85%, PP1), IN-FGD PM (58%, 2007-PM), and the mixture of slurry waters (50%, 2008-PP2) were the sources of Ni to the FGD system.
- Because of the use of the Al-additive at PP2, Al was supplied by the Al-additive (73-82%). Limestone (97%) was the main source of Al to FGD at PP1.

The identification of sources of trace elements to the FGD systems is consistent with the findings of Meij and Andeliesten (1989) and Meij (1989 and 1994) at a wet FGD system in The Netherlands, except in the case where elements were supplied by the mixture of slurry waters. To our knowledge, few studies have focused on the characteristics of filtered water re-circulation to FGD systems, which highlights the need to investigate the water re-circulation to the scrubber as a source of trace elements (Article 3).

The partitioning of trace elements in the FGD systems in this study (Articles 1 and 2) was calculated on the basis of the trace element concentration in the input and output streams normalised to the respective flows. In line with these criteria, trace elements in the FGD systems were classified as follows:

- Elements retained in the gypsum sludge

- Moderate and volatile elements IN-FGD retained in gypsum sludge (78-92%): S, (Hg), (F), and (Se).

- Elements associated with the highly insoluble Al-Si fraction of limestone and/or as PM retained as impurities in gypsum sludge (50-100%): P, Ca, Nd, Ti, Ce, Zr, La, Y, Al, Nb, Fe, Pb, Li, Sr, Ga, Rb, Ba, V, Sn, Cr, Cu, K, U, Ge, Be, As, Ni and REEs.

- Elements present in the FGD water streams
- Elements supplied by the mixture of slurry waters and associated with limestone and/or as PM (32-92%): Mn, Na, Mg, Co, K, Be, Li, Sc, Cd, Ni, Mo, Tl, Zn, and U.
- Gaseous components dissolved in the aqueous phase of gypsum slurry (78-90%): B, Cl, (Hg), (F) and (Se).

It is should be pointed out that the aqueous phase of gypsum slurry is the water stream where trace elements can primarily be dissolved. However, given that the filtered water is the water stream that results after filtration and dilution of the aqueous phase of gypsum slurry, therefore, the FGD water output stream, the partitioning of trace elements was referred on filtered water.

The FGD partitioning showed that most of the trace element leaves the FGD system in the filtered water with a few exceptions. Elements in brackets were partitioned between the gypsum sludge and/or filtered water depending on the power plant. As regards the FGD partitioning of moderate and volatile elements, the main differences were:

- Mercury was retained in gypsum sludge (66%) at PP1, whereas Hg was retained in the filtered water (64-80%) at PP2 in 2007 and in 2008.
- Selenium was retained in gypsum sludge (53%) at PP1. Selenium was retained in gypsum sludge (35%) with a prominent proportion emitted as PM (36%) at PP2 in 2007. Selenium was retained in filtered water (63%) in 2008.
- Fluorine was retained in gypsum sludge (91% and 85%) at PP1 and at PP2 in 2008, respectively. Fluorine was retained in filtered water (67%) at PP2 in 2007.

The relatively high retention of Hg measured in gypsum sludge at PP1, the capture of Cl and B from the flue gas by filtered water at the two power plants and the high retention of As, Se, and F in gypsum sludge at PP1 and at PP2 in 2008 are in accord with earlier works carried out by Meij (1994), Aunela-Tapola et al. (1998), Yudovich and Ketris (2005), Álvarez-Ayuso et al. (2006); Meij and te Winkel (2006), Cheng et al. (2009) among others. However, our data on the partitioning of F, Hg, and Se in filtered water at PP2 in 2007 do not tally with those of the aforementioned authors.

These results showed that the FGD partitioning of elements, and especially that of the volatile ones, was governed by the operational conditions at PP1 and PP2. The re-circulation of filtered water to the scrubber proved to be the cause of the partitioning of Hg and Se with a large fraction in the aqueous phase of gypsum slurry and in the filtered water (Article 3). The occurrence of F in filtered water at PP2 in 2007 was also attributed to the Al-additive used at PP2.

4.1.3. Mass balances

Mass balances were determined successfully for PCC, FGD and for the whole installation (PCC+FGD) although the results from the FGD mass balances were less accurate for some elements than for those obtained for the PCC systems. Nevertheless, most elements attained excellent OUT/IN ratios in the FGD (0.8≤OUT/IN≤1.2).

The low mass balance closure for Hg for the PCC (0.73) and for the whole installation (0.78) at PP1 constituted a challenge and considerable efforts were made to determine the causes. Thus, the omission of FA sampling from the ESP 3 at PP1 in 2007 appears to be the most important cause. However, some uncertainties remain (Additional Findings to Article 1). Comparison of the mass balance closure for Hg with the literature shows lower Hg OUT/IN ratios at PP1 than those reported by Meij and te Winkel (2006), but Hg OUT/IN ratios similar to those reported by Aunela-Tapola et al (1998). The latter authors attributed the low mass balance closure for Hg to a complexity of reliable sampling of Hg especially in the flue gas. In this regard, the gaseous sampling procedure of Hg cannot be considered as the main cause of low mass balance closure for Hg given that accurate mass balance closures for Hg have been reported (Meij and te Winkel, 2006).

The low mass balance closure for B and Se at PP2 was another issue to resolve. The mass balances for B for the PCC (0.61-0.73 in the 2007 and 2008 samplings, respectively) and for the whole installation (0.76-0.80) and Se for the 2007 PCC (0.66) were found to be inaccurate. The complexity of the analytical uncertainties resulting in from the possible loss of B during the acid-digestion procedure and the interferences that introduce a positive bias in the accuracy of measuring Se concentrations by ICP-MS, despite using collision cell, were found to be possible causes. Similar results of Se were obtained by Yokoyama et al (1991), who found that the mass balance closure for Se was unreliable at three coal-fired power plants.

4.2. DESULPHURISATION EFFICIENCY AND EMISSION ABATEMENT CAPACITY FOR INORGANIC TRACE POLLUTANTS

The desulphurisation efficiency and the emission abatement capacity for inorganic trace pollutants were evaluated experimentally in accordance with the calculations of the retention efficiencies of the PCC and FGD as independent systems and as the whole installation (PCC+FGD, Articles 1 and 2). The retention capacity of the PCC systems was assessed according to the data obtained from the inputs and outputs in the boiler and in the ESPs, respectively, whereas that for the FGD systems was evaluated according to partitioning studies, considering all input and output streams in the FGD. The retention capacity for the FGD systems was also assessed on gaseous measurements IN and OUT-FGD (excluding PM). The retention capacity for the whole installation was evaluated considering inputs and outputs from the PCC and FGD system as a whole system. These evaluations are reported in the present study (Articles 1 and 2). In this regard, it is worth noting that the most significant evaluation of the desulphurisation efficiency and emission abatement capacity for inorganic trace pollutants is the one that focuses on the whole installation.

According to the foregoing discussion, it is clear that the inherent complexity of the PCC-FGD systems makes it to difficult to account for the retention efficiencies for the PCC and FGD separately, and for the whole installation. The retention and emissions (OUT-FGD PM and gas) obtained in the FGD partitioning studies are those that are calculated with respect to the incoming proportion of elements to FGD. Thus, the retention efficiency and the relative emissions for the whole installation, with the whole input and outputs, may differ.

The determined desulphurisation and retention efficiencies of inorganic trace pollutants as well as the main outgoing streams for the PCC, FGD, and for the whole installation are summarised in Table 4.1 in accordance with the aforementioned criteria for the evaluation of the desulphurisation efficiency and the emission abatement capacity for inorganic trace pollutants.

The retention efficiencies of inorganic trace pollutants for the PCC, FGD, and for the whole installation are described the subsequent chapters 4.2.1., 4.2.2., and 4.2.3., respectively.

Table 4.1. Desulphurisation efficiency and emission abatement capacity for inorganic trace pollutants for the PCC, FGD, and for the whole installation.

	PCC system (boiler + ESP)			FGD system						Whole installation		
	Partitioning studies (Retention efficiency-Output stream)			Partitioning studies (Retention efficiency-Output stream)			Gas measurements (excluding PM)			Partitioning studies (Retention efficiency-Output stream)		
	PP1	PP2 (2007)	PP2 (2008)	PP1	PP2 (2007)	PP2 (2008)	PP1	PP2 (2007)	PP2 (2008)	PP1	PP2 (2007)	PP2 (2008)
SO_2	IN-FGD Gas (99%)	IN-FGD Gas (97%)	IN-FGD Gas (98%)	G (90%)	G (73%)	G (71%)	94%	82%	88%	G (90%)	G (71%) FW (13%)	G (70%) FW (11%)
				OUT-FGD Gas (7.9%)	OUT-FGD Gas (14%)	OUT-FGD Gas (17%)				Gas (8%)	Gas (14%)	Gas (17%)
F^-	IN-FGD Gas (87%)	IN-FGD Gas (79%)	IN-FGD Gas (88%)	G (91%)	FW (67%) G (33%)	G (85%) FW (15%)	99%	99%	100%	G (82%) FA (9%)	FW (61%) G (30%) FA (10%)	G (72%) FA (15%) FW (12%)
	FA (13%)	FA (21%)	FA (12%)									
Cl^-	IN-FGD Gas (93%)	IN-FGD Gas (63%)	IN-FGD Gas (53%)	FW (76%) G (22%)	FW (91%)	FW (85%) G (15%)	97%	99%	98%	FW (75%) G (22%)	FW (76%) G (20%)	FW (82%) G (15%)
		FA (33%)	FA (42%)									
As	FA (96%)	FA (98%)	FA (98%)	G (90%)	G (51%)	G (62%)	89%	67%	98%	FA (95%)	FA (98%)	FA (98%)
				OUT-FGD PM (6.6%)	OUT-FGD PM (43%)	OUT-FGD PM (30%)						
B	FA (90%)	FA (89%)	FA (73%) BS (18%)	FW (68%) G (32%)	FW (96%)	FW (89%) G (9.5%)	96%	92%	91%	FA (72%) FW (17%)	FW (55%) FA (41%)	FA (48%) FW (44%)
		IN-FGD Gas (7.4%)										
Se	FA (62%)	FA (67%)	FA (78%) BS (12%)	G (53%) FW (12%)	G (35%) FW (30%)	FW (63%) G (34%)	94%	80%	37%	FA (53%) BS (13%) G (19%)	FA (37%) G (21%) FW (18%)	FW (46%) FA (28%) BS (19%)
	IN-FGD Gas (23%)	IN-FGD PM (30%)		OUT-FGD PM (30%)	OUT-FGD PM (36%)	OUT-FGD Gas (1.4%)				PM (11%)	PM (22%) Gas (3.0%)	Gas (1.4%)
Total Hg	IN-FGD Gas (86%)	IN-FGD Gas (88%)	IN-FGD Gas (89%)	G (66%)	FW (80%)	FW (61%)	72%	65%	21%	G (56%) FA (14%)	FW (76%) FA (4.2%)	FW (58%) G (5.1%)
				OUT-FGD Gas (33%)	OUT-FGD Gas (14%)	OUT-FGD Gas (34%)				Gas (29%)	Gas (14%)	Gas (32%)
Hg^0	-	-	-	-	-	-	26%	17%	24%	-	-	-
Hg^{2+}	-	-	-	-	-	-	89%	73%	9.1%	-	-	-

FA: fly ash; BS: boiler slag; FW: filtered water; G: FGD-gypsum; IN-FGD PM: ingoing particulate matter stream FGD; OUT-FGD Gas: ingoing gaseous stream FGD
OUT-FGD PM: outgoing particulate matter stream FGD; OUT-FGD Gas: outgoing gaseous stream FGD

4.2.1. The PCC systems

In the PCC system (boiler + ESP) most of the elements were retained as FA (>78%, mean FA retention for the elements studied) and BS (<22%) in the ESP and in the boiler, respectively. The PCC system retained 99.6% of trace elements (as a mean value for the elements studied); with the result that small proportion (0.4%) entered the FGD as PM or in a gaseous form. Retention efficiencies presented in this study are in line with ESPs in the Netherlands (Meij et al, 1985; Meij, 1994).

4.2.2. The FGD systems

As a result of gaseous measurements IN and OUT-FGD (excluding PM), the wet limestone FGD systems attained a high retention capacity (92-100%) for gaseous Cl, F, and B. Significant differences were found concerning the retention efficiencies calculated for gaseous S, Se, and As. The FGD system at PP2 yielded different retention efficiencies for S (82% and 88% in the 2007 and 2008 samplings, respectively), Se (37% and 80%), and As (67% and 98%) with respect to those yielded at PP1 (94% for S and Se, and 89% for As). The non-retained FA by FGD and the particles and droplets from gypsum slurry entrained in the OUT-FGD flue gas were found to be responsible for the relatively lower retention efficiencies for Se and As compared with the other volatile elements (Articles 1 and 2).The causes of the differences in the retention efficiencies measured for S were assessed in the Additional Findings to Article 2, and may be summarised as follows:

- The acidic pH of the aqueous phase of gypsum slurry in 2007 (5.1) and 2008 (4.6) at PP2 could contribute to the reduction of the absorption rate of SO_2 into limestone with the consequent desorption of SO_2.
- The limestone used at PP2 could reduce the desulphurisation efficiency owing to its low porosity, which could limit its capacity to react with SO_2.

4.2.3. The whole installations (PCC+FGD)

The partitioning for the whole installations (PCC+FGD) revealed that most elements were retained by FA and BS (~85-90% as mean values for all elements measured). In decreasing order, FGD-gypsum (4.9-7.9%), filtered water (2.9-7.2%), OUT-FGD emission PM (0.6-2.0%), OUT-FGD emission gas (0.6-0.8%), and BS water (0.01-0.03%) were the remaining outgoing streams.

Calculations showed that 71% of Hg was retained by the whole installation at PP1, and consequently 29% of the Hg input was emitted into the atmosphere. A retention efficiency of 87% was attained for Hg at PP2 in 2007, whereas only 68% of the Hg input was retained by the whole installation in 2008. It should be noted that the retention efficiencies for total Hg at PP2 in 2007 (65%) and in 2008 (21%) based exclusively on gaseous measurements IN and OUT-FGD were even lower than those attained by the whole installation (Table 4.1). This showed that the very low retention efficiency of Hg attained by the FGD system, especially at PP2 in 2008, is the main cause of the low retention efficiencies of Hg calculated for the whole installation. This finding is one of the most significant of this thesis (Article 4). Chapter 4.3 below will describe the causes of this low retention efficiency.

Fluorine, Cl, As, and B were retained with a very high efficiency (92-100%) by the whole installations, and consequently atmospheric emissions fell to 0.1-2.1%. Retention efficiencies of 89% and 92% for Se and S were attained at PP1, respectively, and of 75% and 86% in 2007 and 97% and 83 % in 2008 at PP2, respectively.

Arsenic was mainly retained by FA (95-98%); S mostly by FGD-gypsum (71-89%); and Cl by filtered water (75-82%). Selenium, Hg, B, and F presented a different distribution depending on the power plant:

- Fly ash was the main outgoing stream for Se (53%) and B (71%), and FGD-gypsum for F (82%) and Hg (56%) at PP1.
- Se (37%) was retained by FA, and B (55%), Hg (76%), and F (61%) by filtered water at PP2 in 2007.

- Most Se (46%) and Hg (58%) were retained by filtered water, B by FA (48%), and F (72%) by FGD-gypsum at PP2 in 2008.

The partitioning of As, S, Cl, Se, F, Hg, and B and the retention efficiencies obtained at the whole installation at PP1 are consistent with the results reported by Yokoyama et al (1991), Meij (1994), Sandelin and Backman (2001), Otero-Rey et al (2003), Álvarez-Ayuso et al (2006), and Cheng et al (2009). The partitioning of Se, Hg, B, and F at PP2, especially in 2007, reveals significant differences with respect to the literature. In the aforementioned studies, FA proved to be the commonest outgoing stream for Se and B and FGD-gypsum for Hg and F, whereas in our study FGD filtered water was the major retention sink for these elements at PP2. This finding prompted us to carry out a detailed study of the speciation of these elements in the re-circulated waters (Article 5, chapter 4.4).

4.3. SPECIATION, BEHAVIOUR, AND FATE OF GASEOUS Hg

The relatively low Hg retention efficiencies obtained for the PP2 system and the unexpected differences found in Articles 1 and 2 for Hg speciation on the atmospheric emissions at PP1 and PP2 prompted us to devise laboratory experiments to reproduce the FGD conditions and to test possible hypotheses on the operating parameters accounting for these unexpected findings. The results are published in Article 4.

Mercury speciation in PCC has been reported by Maier et al. (1992), Meij (1997; 1999), Gulli et al (1999), Galbreath and Zygarlicke (1999), Hower et al. (1999), Senior et al (2000), Gibb et al (2000), Tan et al (2004), Meij and te Winkel (2006), and Park et al (2008), among others. All these studies concluded that, regardless of the manner in which Hg is present in coal, $Hg^0{}_{(g)}$ is released during combustion. During post-combustion, and with decreasing temperature, $Hg^0{}_{(g)}$ may remain as a monatomic species or may oxidise to $Hg_2^{2+}$and Hg^{2+} compounds. The reaction of $Hg^0{}_{(g)}$ with $HCl_{(g)}$ or $Cl_{2\,(g)}$ to form $HgCl_{2\,(g)}$ is generally considered to be the dominant Hg transformation mechanism in coal combustion flue gas (Galbreath and Zygarlicke, 2000). On the other hand, it is also generally accepted that Hg^{2+} can be absorbed in the aqueous phase of the absorbent slurry in wet FGD systems and that Hg primarily occurs as Hg^0 OUT-FGD (Pavlish et al., 2003; Chang et al., 2003; Tanga et al., 2007; Park et al., 2008; Wo et al., 2009; Stergarsek et al., 2010). The occurrence of Hg^0 OUT-FGD has been associated with two main factors (Chang and Ghorishi, 2003): *(1)* Hg^0 can barely be dissolved in the aqueous phase of the absorbent, leading to low emission abatement efficiencies for this Hg species; and *(2)* some of the absorbed Hg (Hg^{2+}, as e.g., $HgCl_2$) is probably converted back to Hg^0 and re-emitted.

After comparing our results with the above Hg patterns, an unusual speciation of Hg in the OUT-FGD gaseous stream was revealed at one of the coal-fired power plants evaluated in this thesis. At PP1 and PP2, Hg^{2+} (75-86%) was the dominant Hg species that entered the FGD. At PP1, Hg^0 (71%) was the prevalent Hg OUT-FGD species, whereas at PP2, Hg^{2+} was the prevalent Hg OUT-FGD species in 2007 (66%) and 2008 (87%). The markedly higher retention efficiency of Hg^{2+} in 2007 (73%) than in 2008 (24%) at PP2 was another significant result of this study.

After reviewing the literature on the role of $HCl_{(g)}$ and $Cl_{2\,(g)}$ in Hg oxidation and in the light of the results obtained in the enrichment of Hg in filtered waters at PP2, a number of FGD batch experiments were devised taking into account the operational conditions of the power plants to: *(1)* reproduce at laboratory scale the differences found in Hg speciation in the OUT-FGD gas at PP1 and PP2; and *(2)* determine whether the predominance of Hg^{2+} in the OUT-FGD gas at PP2 was due to the evaporation of $HgCl_2$ particles dissolved in the aqueous phase of the gypsum slurry in the OUT-FGD gas.

Laboratory experiments confirmed Hg^0 (66-61%) as the dominant Hg species in the OUT-FGD gas at PP1, and Hg^{2+} (56-66%) as the predominant species at PP2 (Article 4). The results from the first stage of addition of filtered re-circulated water to the scrubber at PP2 showed that the prevalence of the Hg^{2+} gaseous speciation at OUT-FGD PP2 in 2007 and in 2008 was probably caused by *(1)* the high concentration of HCl and Hg in the IN-FGD gaseous stream, which led to the formation of gaseous $HgCl_2$ in the IN-FGD at PP2, and *(2)* the acidic conditions of the scrubber. Owing to the high water solubility of the gaseous $HgCl_2$ species under acidic conditions of the scrubber, $HgCl_2$ complexes underwent a gradual dissolution in the aqueous phase of gypsum slurry at PP2.

According to the volatile behaviour of $HgCl_2$ and to the temperature of the scrubbers (50-60ºC), it was concluded that the unusual speciation of Hg^{2+} OUT-FGD at PP2 was probably due to the evaporation of $HgCl_2$ particles from the aqueous phase of gypsum slurry in the OUT-FGD flue gas. This was supported by i) the enrichment factors of Cl and Hg, which were higher at PP2 than at PP1; ii) the acidic pH and the S/Cl ratio in the scrubber (promoting the stability of $HgCl_2$ complexes in the aqueous phase), which were lower at PP2 than at PP1; and by iii) the identification of $HgCl_2$ in the FGD-gypsum samples at PP2 by means of a thermal dissociation analysis to determine the mode of occurrence of Hg in FGD-gypsums, which demonstrated the occurrence of $HgCl_2$ complexes in the aqueous phase of the corresponding gypsum slurries.

The different retention efficiencies of Hg measured at PP2 in 2007 and 2008 were initially related to different modes of occurrence of Hg in FGD-gypsums, probably as a result of the different dosage of the Al-additive used at PP2. This prompted us to study the Hg speciation on FGD-gypsum samples in order to support or discount such an assumption. The Thermal Decomposition (TD) method coupled with the Sir Galahad II Atomic Fluorescence Spectrometer (AFS) was used to determine the mode of occurrence of Hg in PP2 FGD-gypsums. The results of the thermal decomposition profiles of FGD-gypsums showed that HgS was the main Hg-bearing species in the two FGD-gypsum samples in 2007 whereas Hg_2Cl_2 and $HgCl_2$ were the main species of Hg present in the FGD-gypsums in 2008 (Article 4). Because thermodynamic modelling with the input of experimental data is a straightforward way to determine whether a chemical reaction is feasible under specific industrial conditions, thermodynamic calculations were made to elucidate the mode of occurrence of Hg in the PP2 FGD-gypsums and the behaviour of Hg at the power plants (Article 4 and Additional Findings to Article 1).

Thermodynamic calculations with experimental data from PP2 in 2007 (Article 4), demonstrated that in 2007 the high dosages of $Al_2(SO_4)_3$ gave rise to the retention of Hg as HgS in the 2007 FGD-gypsum, which led to a decrease in the evaporation of $HgCl_2$ particles from the aqueous phase of gypsum slurry in the OUT-FGD gas. By contrast, in 2008 with the low $Al_2(SO_4)_3$ dosages, the formation of HgS barely took place and particles of $HgCl_2$ predominated in the aqueous phase of the gypsum slurry. The gaseous emissions of Hg^{2+} OUT-FGD probably increased in 2008 as a result of the evaporation of particles of $HgCl_2$ in the OUT-FGD gas.

In the case of PP1, the occurrence of Hg^0 in the OUT-FGD gas and the low FGD retention efficiency for Hg^0 (26%) were probably due to re-emission episodes of Hg^0 and/or to low aqueous solubility of Hg^0 in the scrubber (Additional Findings to Article 1). Thermodynamic calculations based on experimental data from PP1 confirmed the feasibility of the oxidation-reduction reaction of S (IV) species with Hg^{2+} to form $Hg^0_{(g)}$. The mechanism of Hg^0 re-emission has been demonstrated in laboratory experiments by Wo et al (2009), Chengli et al (2010), Stergarsek et al (2010), Omine et al (2012), among others. However, the low abatement efficiencies for Hg^0 as a result of the low aqueous solubility of this Hg species in the scrubber cannot be discounted.

Thus, in line with the results of this study, the low retention efficiency of Hg at the two power plants was markedly dependent on Hg speciation.

The most significant finding of the study of the behaviour of Hg at PP1 and PP2 is that the speciation of gaseous Hg OUT-FGD is governed by the input of SO_2 and especially of Cl in the gaseous stream to the FGD system. The re-emission of Hg^0 OUT-FGD is the common pathway of gaseous Hg in the FGD system, and only a high input of Cl may reduce and/or inhibit the mechanism of Hg^0 re-emission by the formation of Hg-Cl complexes. This is in agreement with the results of Blythe et al (2004), Currie et al (2006), Wo et al (2009), and Omine et al (2012). However, as stated above, most Hg-Cl species are highly volatile and may also be re-emitted as Hg^{2+}. Therefore, it may be concluded that the lower S/Cl ratios and pH values at PP2 with respect to those at PP1 were the determining factors in the different speciation of gaseous Hg OUT-FGD for the two systems.

4.4. ENRICHMENT AND SPECIATION OF INORGANIC TRACE POLLUTANTS IN RE-CIRCULATED WATER STREAMS

Water streams may act as retention sinks for some metals as a result of partial or total dissolution processes, the efficiency of which largely depends on chemical properties such as the pH and temperature of the solvent and/or the solubility constant of the specific element, among other parameters. In the FGD systems, under operational conditions of water re-circulation, 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. The gradual increase in the concentration of inorganic trace pollutants from the sub-saturation to equilibrium and/or saturation because of continuous water re-circulation in the scrubber, accounts for enriched inorganic trace pollutants in the re-circulated water. This process may increase the concentration of trace pollutants in re-circulated waters up to very high levels compared with that of the original input water, which could result in environmental 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 that is used for different applications or for landfilling.

4.4.1. Enrichment of inorganic trace pollutants in re-circulated water streams

The high concentration of major, minor, trace elements in the aqueous phase of the gypsum slurries and filtered waters (Articles 1 and 2), prompted a detailed study of the enrichment of inorganic trace pollutants in re-circulated water streams (Article 3). It should be pointed out that the aqueous phase of gypsum slurry was the water stream where the inorganic trace pollutants were primarily enriched by dissolution. However, given that the filtered water is the water re-circulated to the scrubber, the study of enriched inorganic trace pollutants was focused on filtered water. The enrichment of inorganic trace pollutants in the re-circulated water streams was confirmed by balance studies, and a number of statistical tests.

Mass balances are calculated by measuring flow rates and trace element concentrations in all streams and by taking into account the ratio of the total outgoing and ingoing flows (Clarke and Sloss, 1992). In this regard, the mass balances of FGD water streams operating at PP1 and PP2 during samplings (considering all streams) were closed with out/in ratios close to 1. Therefore, two mass balances, partial and total mass balance (PMB and TMB), were performed to determine the potential enrichment of inorganic trace pollutants in re-circulated water streams from the first re-circulation cycle of water up to the start of sampling campaigns.

Given the impossibility of determining the analytical composition of the FGD waters streams in the first operating cycle of the water re-circulation, an estimation of this cycle (PMB) was made out by considering the process/treated water as the only water stream for limestone slurry preparation and by excluding filtered water as the water output stream. Total mass balances were performed by considering the process/ treated water as the only water stream for limestone slurry preparation and the filtered water as the water output stream. Limestone, IN-FGD gas, IN-FGD PM were included as inputs; and OUT-FGD gas, OUT-FGD PM, and FGD-gypsum were included as output streams.

In line with the criteria for the PMB and TMB, PMB values ≤ 1 indicated the partial dissolution of a given element in the aqueous phase of gypsum slurry and TMB values >1 suggested elements enriched by re-circulation of filtered water after a number of re-circulations. Therefore, the differences between PMB and TMB (out/in ratios) were attributed to an enrichment of inorganic trace pollutants in filtered water because of the contribution of filtered water for a given element to the TMB. This finding led us to assess the accuracy of the results by means of statistical tests.

A Student's t-test was performed to ascertain whether the mean contribution of filtered water for a given element to TMB was significant ($p<0.05$) and whether the differences between PMB and TMB were attributable to the enrichment of the element in filtered water. The

Student's t-test was applied to mean flow (g/h) from 4 and 6 sub-samples of the filtered water, for each element, at PP1 and PP2, respectively. The Student's t-test was applied to the elements with differences ≥0.2 out/in ratios between PMB and TMB.

Based on the results of the mass balances and statistical tests, the elements in the FGD waters were classified as:

- Elements enriched in filtered waters (0.7≤PMB≤1.2 and TMB≥1.2): Na, Cl, Mn, B, Se, Mg, Cd, and U. Molybdenum was also enriched at PP1, and K, Hg, Li, Sc, Ge, F, Ni, Zn, Rb, Zr, and Co at PP2.
- Elements not enriched in filtered waters (PMB≤1.0 and TMB ≤1.2): Ca, Fe, Ti, V, Ti, S, Sr, and Ba. This group of elements also included Al, K, Li, F, Hg, Cr, Zr, Ga, Ge, and Sc at PP1.
- Elements with an uncertain behaviour (PMB≤0.8 and TMB ≤0.8): Al, Ga, Cu, Mo, Sb, Pb (PP2), and Ni (PP1).

The enrichment of these elements was attributed to (Article 3): i) dissolution of carbonate-bearing elements from limestone and formation of soluble sulphate complexes in the scrubber; ii) dissolution of elements in a gaseous form in the aqueous phase of gypsum slurry; iii) dissolution of elements with high condensation potential on FA; and to iv) the contribution of elements from other sources.

In accordance with the results of the mass balances and the statistical tests, a higher enrichment of inorganic trace pollutants in re-circulated waters at PP2 than at PP1 was demonstrated. In addition to the elements enriched at both power plants, K, Hg, Li, Sc, Ge, F, Ni, Zn, Rb, Zr, and Co were also enriched in the re-circulated waters at PP2. This was attributed to: i) the different temperature of the ESPs, ii) the different pH value of the aqueous phases of the gypsum slurry, iii) the different occurrence of aqueous complexes and diverse S/Cl and S/F ratios in the scrubbers, iv) the differential behaviour and enrichment of Hg in the scrubbers, and v) the use of an Al-additive at PP2.

As regards this last factor (v), this study revealed that the use of an Al-additive to improve the desulphurisation efficiency at PP2 was responsible together with the filtered water re-circulation to the scrubber for the high enrichment of trace pollutants in filtered waters at PP2 (Articles 3 and 5): i) the Al-additive promoted the occurrence of stable Al-F aqueous complexes, which increased the F concentrations in filtered waters; ii) the different dosage of the Al-additive gave rise to the differential behaviour and enrichment of Al, F, SO_4^{2-}, Mg, and U; and iii) the lower dosages of the Al-additive in 2008 led to the formation of $CaF_{2,}$ increasing the potential leaching of F^- from FGD-gypsum. In this regard, earlier studies (Font et al, 2008) have demonstrated that the speciation of trace pollutants, especially F, plays a crucial role in the leaching potential of the FGD gypsum end-product.

The emission of particles and droplets from gypsum slurry in the outgoing gaseous stream of the FGD was identified as the most important result of the high enrichment of inorganic trace pollutants in the re-circulated waters. Such a result contrasted with the evaluation desulphurisation efficiency and abatement capacity of inorganic trace pollutants. The main contributions to PM emissions were the non-retained FA by FGD and the particles and droplets from gypsum slurry entrained by the OUT-FGD flue gas, especially particulate Se, As, Zn, Cu, Ni and Cr. At PP2, the emission rates of particulate As and Ni exceeded the PRTR threshold values, whereas the emission rate of Zn at PP1 was close to these values. These findings are significant given the absence of prior studies on the effects, causes, and consequences of filtered water re-circulation in FGD systems.

4.4.2. Aqueous and solid speciation of inorganic trace pollutants in re-circulated water streams

The study of the enrichment of inorganic trace pollutants in the re-circulated water streams yielded valuable insights into the role of Al-additive in the aqueous and solid speciation of elements (Article 3). As a result, subsequent studies focused on the speciation of inorganic trace pollutants in FGD water streams with special emphasis on the influence of the Al-additive on the speciation and partitioning of inorganic trace pollutants in the re-circulated water streams (Article 5). The study of the aqueous and solid speciation of trace inorganic pollutants was carried out with an ion-association aqueous model, PHREEQC code (version 2.0), and with a coupled thermodynamic database LLNL (Parkhurst and Appelo, 1999), using the chemical analysis of the aqueous phase of gypsum slurries as input data. The results were as follows:

- As a result of the higher dosages of $Al_2(SO_4)_3$ in 2007, AlF_x complexes showed the highest activities of Al and F in the 2007 gypsum slurry aqueous phase; and F^- and MgF^+ were the aqueous complexes with the highest activities of F at the PP1 and PP2 in 2008 aqueous phases.
- The supersaturation of MgF_2 and CaF_2 in the gypsum slurries led to their precipitation on FGD-gypsum at PP1 and at PP2 in 2008.
- The addition of $Al_2(SO_4)_3$ to the scrubber induced the formation of SO_4^{2-} complexes with metals increasing significantly their concentrations in the aqueous phase of the gypsum slurry from PP1 to PP2-2008 and 2007.
- U-SO_4^{2-} aqueous complexes showed the highest concentration in the 2007 gypsum slurry aqueous phase at PP2 whereas U-$(OH)_2$ and U-F_2 were the aqueous complexes with the highest activities in the PP1 and PP2-2008 aqueous phases, respectively. This accounted for the higher concentration of U in the 2007 and 2008 gypsum slurries at PP2 with respect to PP1.
- The addition of $Al_2(SO_4)_3$ to the scrubber at PP2 induced the acidification of the aqueous phase of the gypsum slurry via aluminium hydrolysis. The acidification of the gypsum slurry induced by the addition of $Al_2(SO_4)_3$ is consistent with earlier works carried out by Ochoa-González et al (2012).

The results of the speciation of solids led to the use of an alternative tool to confirm the occurrence of minor solid species predicted in saturation in the FGD-gypsums. TOF mass spectrometry combined with thermodynamic model of the aqueous phase of gypsum slurries helped us to gain a better understanding of the geochemical behaviour of elements and their partitioning into solid and aqueous phases (Article 5). The identification by TOF of structural components of solid phases predicted thermodynamically in saturation supported the precipitation processes of the following species: i) CaF_2 and MgF_2 in the PP1 FGD-gypsum; and ii) Al_2O_3, $AlHO_2$, $KAl_3(OH)_6(SO_4)_2$ and MgF_2 in the 2007 and 2008 FGD-gypsums at PP2. This demonstrated that although the $Al_2(SO_4)_3$ dosage in 2007 significantly reduced the F enrichment in the 2007 FGD-gypsum at PP2, it was not sufficient to totally avoid its occurrence in the FGD-gypsum.

4.4.3. Evaluation of the potential leaching of FGD-gypsums

According to earlier studies (Álvarez-Ayuso et al., 2006; 2007; 2008) the FGD-gypsum may exceed the maximum value of leachable F^- to be accepted at non hazardous waste landfills. The identification of F solid species, especially, in FGD-gypsums allowed us to assess the causes of potential leaching problems of FGD-gypsums (Article 5).

Comparison of the leaching results of this thesis with the waste acceptance criteria at landfills revealed that the leaching values of F^- were well above the inert range in the PP1 and PP2 FGD-gypsums and close to the limit for non-hazardous waste. The leaching levels of SO_4^{2-} from the PP1 and PP2 2008 FGD-gypsums fell within the range of inert materials but reached values close to that of non-hazardous waste, whereas those from the PP2 2007 FGD-gypsum fell within the range of the criteria for non-hazardous materials. The leaching behaviour of SO_4^{2-} was related to the solubility of gypsum the main by-product of FGD with the result that preventive measures could not be implemented.

The absence of significant leaching of heavy metals at PP2 was probably the result of the protonation of the surface of the FGD-gypsum induced by the addition of $Al_2(SO_4)_3$ and the formation of SO_4-complexes. These two factors helped to maintain the metals in solution. The behaviour of Se proved to be the inverse due to its anionic form.

Comparison of the leaching values for trace elements for 2007 and 2008 PP2 FGD-gypsums showed that Ni and Hg were the only elements with a lower leaching potential in the

2007 FGD-gypsum when compared with that from FGD-gypsum in 2008. This was attributed to the different dosage of $Al_2(SO_4)_3$.

Chapter 5

Conclusions

5. CONCLUSIONS

5.1. MASS BALANCES AND RETENTION EFFICIENCIES

Geochemical mass balance studies proved to be a useful method for studying the fate of trace elements at coal-fired power plants. Mass balances were determined very successfully at PCC, FGD, and at the whole installation (PCC+FGD). The FGD mass balances were less accurate for specific elements than those obtained for PCC systems and for the whole installations.

In the PCC system (boiler + ESP) most of the elements were retained as FA (>78%, mean FA retention for the elements studied) and BS (<22%) in the ESP and in the boiler, respectively. The PCC system retained 99.6% as the mean of the trace elements studied with the result that a low proportion of them (0.4%) escaped from ESP and entered the FGD as PM or in a gaseous form.

The whole installations (PCC+FGD) attained a high retention capacity (92-100%, of the input of bulk trace elements to the power plants) for F, Cl, As, and B with a subsequent reduction of their emitted gas proportions (0.1-2.1%), far below the emission limits established by the European directive 2001/80/EC for large combustion plants. The PM emission levels fell to 25 mg/Nm^3 (at 6 % O_2), far below the limits established by this directive.

Different retention efficiencies were determined for Se and S for the whole plants. The whole installation at PP1 attained a retention efficiency of 89% and 92% for Se and S, respectively, whereas the whole installation at PP2 attained retention efficiencies from 75-97% and 83-86% for Se and S, respectively.

The whole system (PCC+FGD) at PP1 retained 71% of the Hg input, which accounted for 29% of the Hg input emission into the atmosphere, mostly in a gaseous form. The whole system at PP2 in 2007 attained a retention efficiency of 86% of Hg, whereas the retention efficiency fell to 68% in 2008. The low retention efficiencies calculated for Hg in the FGD system at PP2 (65% in 2007 and 21% in 2008) contributed significantly to the lower retention efficiencies of Hg for the whole installation.

The partitioning for the whole installations revealed that major, minor, and trace elements were retained via FA (75-80% as the mean of the input mass of the elements studied) and BS (8-11%). In decreasing order, FGD-gypsum (4.9-7.9%), filtered water (2.9-7.2%), OUT-FGD PM (0.6-2.0%), OUT- FGD gas (0.6-0.8%), and BS water (0.01-0.03%) were the remaining outgoing streams for major, minor, and trace elements. An overall classification for elements based on the volatile behaviour and outgoing streams of PCC-FGD was established in accordance with our results and is summarised in Table 5.1.

Inaccurate mass balance closures were obtained for Hg, B, and Se at PP1 and PP2. In the case of Hg, the absence of sampling of FA from the ESP 3 in the FA sampling probably accounts for the low Hg OUT/IN ratios obtained for the PCC system and for the whole installation at PP1. Nevertheless, some uncertainties remain. In the case of B and Se, the complexity of the analytical uncertainties resulting in the loss of B during the acid-digestion procedure and the interferences that resulted in inaccurate measurements of Se concentrations when determined by ICP-MS, despite using collision cell, probably accounted for the possible causes of the low B and Se OUT/IN ratios at PP2.

Table 5.1. Overall classification of elements based on the volatile behaviour and outgoing streams of PCC-FGD.

	Non-volatile elements		Moderately volatile elements (high condensation potential in FA and PM)		Highly volatile elements	
	Retained in FA and slag (85-89%)	*Retained in the FGD (80-86%)*	*Mostly retained in FA in the ESP (95-98% for As) (48-71% for B)*	*Mostly retained in the system but a fraction escaping from ESP and FGD (11-22%)*	*Retained in the FGD (80-96%)*	*Fraction escaping from the FGD (13-32%)*
PP1	Tl, Mo, Sn, Zn, Pb, Ga, Hf, Cs, V, Th, Li, Al, P, Nb, Ti, Co, Y, Rb, Ce, La, Cu, Zr ,Cr, K, Fe, U, Ni, Sr, Mn, Ge, Be, Mg, Na, and REE's	Ca	As and B	Se (PM)	S, F, and Cl	Hg (Gas)
2007 PP2	Tl, Mo, Sn, Zn, Pb, Ga, Hf, Cs, V, Th, Li, Al, P, Nb, Ti, Co, Y, Rb, Ce, La, Cu, Zr ,Cr, K, Fe, U, Ni, Sr, Mn, Ge, Be, Mg, Na, and REE's	Ca	As	Se (PM)	S, F, B, and Cl	Hg (Gas)
2008 PP2	Tl, Mo, Sn, Zn, Pb, Ga, Hf, Cs, V, Th, Li, Al, P, Nb, Ti, Co, Y, Rb, Ce, La, Cu, Zr ,Cr, K, Fe, U, Ni, Sr, Mn, Ge, Be, Mg, Na, and REE's	Ca	As and B	-	S, F, B, Se, and Cl	Hg (Gas)

5.2. SPECIATION, BEHAVIOUR, AND FATE OF GASEOUS Hg

FGD batch experiments confirmed the unusual and different speciation of Hg in the OUT-FGD gaseous stream at the two coal-fired power plants under study. Thermodynamic tools proved useful in reproducing the behaviour of gaseous Hg at the two coal-fired power plants. The occurrence and the low retention of gaseous Hg^0 in the OUT-FGD gas at PP1 were probably due to re-emission episodes of Hg^0 and/or the low aqueous solubility of Hg^0 in the scrubber. The unusual speciation of gaseous Hg^{2+}OUT-FGD at PP2 was probably caused by the evaporation of $HgCl_2$ particles from the aqueous phase of the gypsum slurry in the OUT-FGD gas.

The different retention efficiencies of Hg measured at PP2 in 2007 and 2008 were attributed to different modes of occurrence of Hg in the FGD-gypsums as a result of the different dosage of the Al-additive PP2. The thermal decomposition profiles of FGD-gypsums analysed with the PS Analytical Thermogram and the Sir Galahad II Mercury Analyzer revealed that HgS was the main Hg-bearing species in the two 2007 FGD-gypsum samples, whereas Hg_2Cl_2 and $HgCl_2$ were the main species of Hg present in the FGD-gypsums in 2008.

Thermodynamic modelling showed that the high dosages of $Al_2(SO_4)_3$ led to the retention of Hg as HgS in the 2007 FGD-gypsum, which resulted in a decrease in the evaporation of $HgCl_2$ particles from the aqueous phase of gypsum slurry in the OUT-FGD gas. By contrast, in 2008 with low $Al_2(SO_4)_3$ dosages, the formation of HgS barely took place and particles of $HgCl_2$ predominated in the aqueous phase of the gypsum slurry. The gaseous emissions of Hg^{2+} OUT-FGD probably increased in 2008 as a result of the evaporation of particles of $HgCl_2$ in the OUT-FGD gas.

The behaviour and speciation of gaseous Hg at PP1 and PP2 were governed by the input of Cl and SO_2 IN-FGD to the FGD system. The re-emission of Hg^0 OUT-FGD is the common pathway of gaseous Hg in the FGD system and only a high input of Cl may reduce and/or inhibit the mechanism of Hg^0 re-emission by the formation of Hg-Cl complexes. The S/Cl ratios and pH values that were lower at PP2 than at PP1 were the determining factors in the different speciation of gaseous Hg OUT-FGD between PP1 and PP2.

5.3. ENRICHMENT AND SPECIATION OF INORGANIC TRACE POLLUTANTS IN RE-CIRCULATED WATER STREAMS

The gradual increase in the concentration of inorganic trace pollutants from the sub-saturation to the equilibrium and/or subsequent saturation because of continuous water re-circulations to the scrubber led to an enrichment of such pollutants in re-circulated water streams. Elements retained by gypsum sludge and/or FGD-gypsum did not pose this problem because they were extracted from the system with dewatered gypsum.

The partial and total mass balances (PMB and TMB) and the statistical tests were useful methods for determining the enrichment of inorganic trace pollutants in filtered waters. Partial mass balance was carried out by considering the process/treated water as the only water stream for limestone slurry preparation and by excluding filtered water as the water output stream. Total mass balances were performed by considering the process/ treated water as the only water stream for limestone slurry preparation and the filtered water as the water output stream.

PMB values ≤1 indicated the partial dissolution of a given element in the aqueous phase of gypsum slurry, and TMB values >1 suggested elements enriched by re-circulation of filtered water after a number of re-circulations. Therefore, the differences between PMB and TMB (out/in ratios) were attributed to an enrichment of inorganic trace pollutants in filtered water because of the contribution of filtered water for a given element to the TMB. Comparison of PMB and TMB supported by the statistically significant difference ($p<0.05$) suggested the enrichment of a given element after re-circulations of the filtered water. In the light of our findings, an overall classification based on the behaviour of major, minor, and trace elements in FGD waters was established and supported by the results from thermodynamic modelling (Table 5.2).

Table 5.2 Classification of elements in FGD waters.

	Source	PP1 2007	PP2 2007	PP2 2008
Elements enriched in filtered water (0.7≤PMB≤1.2 and TMB≥1.2)	Soluble sulphate complexes	Na, Mg, Mn, U	Mg, Mn, U	Mg, Mn, U, Cu, Ni, Co
	Dissolution of gaseous elements	Cl, B, Se	Cl, F, B, Hg	Cl, F, B, Hg
	Dissolution of PM elements	Mo, Cd	K, Zn, Ge, Cd	K, Zn, Ge, Cd
	Several sources	-	-	Na, Sc, Se
Elements not enriched in filtered water (PMB≤1.0 and TMB ≤1.2)	Insoluble Al-Si of limestone	Al, Fe, K, Li, Sc, Ti, V, Cr, Ga Zr	Ti, Fe, V	Ti, Fe, V
	Low solubility sulphate species	Ba, Sr	Ca, Ba, Sr	Ca, Ba, Sr
	Sulphate and fluoride species retained in FGD-gypsum	S, F, Hg	S	-
	IN-FGD PM not dissolved in gypsum slurry	Ge	-	-
Elements with uncertain behaviour (PMB≤0.8 and TMB ≤0.8)		Ni	Al, Ga, Sb, Mo, Ni, Cu, Pb	Al, Mo, Ga, Sb

The enrichment and saturation of Al, F, Cl, B, As, Ni, Se, U, and Hg in the re-circulated water streams led to the emission of such elements by entraining particles and droplets of gypsum slurry in the OUT-FGD flue gas (atmospheric emissions). The emission rates of gaseous Hg and particulate As, Zn, and Ni OUT-FGD exceeded the PRTR threshold values (for information purposes) at PP2 in 2007. By contrast, the PRTR threshold values were exceeded by particulate As and gaseous Hg in 2008. The emission rates of particulate Zn from PP1 were close to these values.

Using the results from the chemical analysis of the aqueous phase of gypsum slurries as input data, the ion-association aqueous modelling revealed that the addition of $Al_2(SO_4)_3$ to improve the desulphurisation efficiency at PP2 was responsible for the differential partitioning and behaviour of trace elements and for the variation of the chemical properties in the aqueous phase of the gypsum slurries at PP1, and PP2-2007 and PP2-2008.

The $Al_2(SO_4)_3$ i) increased the concentration of F^- in filtered waters at PP2 in 2007, ii) gave rise to the differential behaviour and enrichment of Al^{3+}, F^-, SO_4^{2-}, Mg^{2+}, and $U^{4+,\ 6+}$ in the aqueous phase of gypsum slurries and filtered waters from PP1 and PP2, iii) induced the formation of SO_4^{2-} complexes with metals increasing their concentrations in the aqueous phase of gypsum slurry from PP1 to PP2-2008 and 2007, iv) caused the acidification of the aqueous phase of gypsum slurry from PP2 via aluminium hydrolysis, and v) produced the protonation of the PP2 FGD-gypsum surfaces.

The identification of F solid species, which is supported by thermodynamic modelling and by TOF analysis in the FGD-gypsums, demonstrated that although the $Al_2(SO_4)_3$ dosage employed in 2007 significantly reduced the F enrichment in the FGD-gypsum at PP2, it was not sufficient to totally avoid its occurrence in FGD-gypsum.

As regards the evaluation of the potential leaching of FGD-gypsums, the leaching values of F^- were well above the inert range in the PP1 and PP2 FGD-gypsums and close to non-hazardous waste. The leaching levels of SO_4^{2-} from the PP1 and PP2 2008 FGD-gypsums fell within the range of inert materials but reached values close to those of non-hazardous waste, whereas those from the PP2 2007 FGD-gypsum fell within the range of the criteria for non-hazardous materials.

The relatively high leaching values of Se and the absence of significant leaching of heavy metals from the PP2 FGD-gypsums were probably the result of the protonation of the surface of the FGD-gypsum induced by the addition of $Al_2(SO_4)_3$ and the formation of SO_4-complexes.

Chapter 6

Future Research and Open questions

6. FUTURE RESEARCH AND OPEN QUESTIONS

Gaseous and particulate retention efficiencies for trace inorganic pollutants have been shown to depend largely on operational conditions from coal-fired power plants. Re-circulation of water to FGD system promotes enrichment of specific trace inorganic pollutants in filtered waters that are trapped in the flue gas and retained in the aqueous phase, with the consequent increase of emission by entraining particles and droplets from gypsum slurry by the OUT-FGD gas. In this sense, evaluation of the retention capacities for trace inorganic pollutants by demisters from wet FGD scrubbers are needed in order to prevent and/or reduce PM emissions.

Investigation is needed in order to elucidate the low mass balance closure for Se for the PCC system; and for Hg for the PCC system and for the whole installation found in this thesis.

Results showed that gaseous Hg emissions from large coal-fired power plants are an issue to deal with. In Europe, Hg, HCl, HF, As, Ni, Se, and Cr emissions from power plants are not currently regulated. The Pollutant Release and Transfer Register (PRTR) of Industrial Emissions into air, water, and land (2006/166/EC) has established threshold emissions for large combustion plants, only for information purposes without currently being legal binding. Therefore, more restrictive environmental regulations in term of emissions of trace inorganic pollutants from large industrial facilities are needed to address this, as it is now possible to modify the processes and achieve best practice.

The environmental regulations have lead to an obliged reduction of NO_x emissions by implementation of SCR and SNCR techniques at coal-fired power plants. SCR catalysis can act to oxidise a significant proportion of the Hg^0 into Hg^{2+}, thereby enhancing the capture of Hg in wet FGD systems. Further work should focus on the influence of SCR and SNCR on the retention capacities for trace inorganic pollutants other than Hg in coal-fired power plants equipped with FGD systems.

Modelling tools with experimental data have shown that the use of additives can modify not only the behaviour and speciation of the target elements, but also the retention efficiencies for trace inorganic pollutants. A further step could now be the implementation of a standard model for the estimation of retention efficiencies.

Chapter 7

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7. REFERENCES

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Annex 1

The results of this thesis have been presented in national and international scientific conferences and scientific meetings:

P. Córdoba, O. Font, M. Izquierdo, X. Querol. The enrichment of trace pollutants in FGD water streams from two Spanish power plants. Power Plant Air Pollutant Control "MEGA" Symposium. Volume I, 121-122. D.L: 278917/08. Baltimore (U.S.A) , 30-3/08-09/2010. Oral communication.

O. Font, **P. Córdoba**, M. Izquierdo, X. Querol. Partitioning, abatement, and emission of NO_x and NH_4^+ species in a large Spanish power plant. Power Plant Air Pollutant Control "MEGA" Symposium. Power Plant Air Pollutant Control "MEGA" Symposium. Volume I, 121-122. D.L: 278917/08. Baltimore (U.S.A) , 30-3/08-09/2010. Oral communication.

P. Córdoba, O. Font, M. Izquierdo, X. Querol, C. Ayora, A. Giménez. Enrichment and speciation of elements in re-circulated waters from desulphurisation at two Spanish power plants. World of Coal Ash Conference, Denver (U.S.A), May 9-12, 2011. Oral communication.

P. Córdoba, M. Maroto-Valer, C. Ayora, R. Perry, M. Rallo, O. Font, M. Izquierdo, X. Querol. The fate of Hg at two coal power plants equipped with FGD. International conference on coal science & technology (ICCS&T). Oviedo (Spain), 9-13 October, 2011. Oral communication.

P. Córdoba, C. Ayora, N. Moreno, O. Font, M. Izquierdo, X. Querol. Influence of an aluminium additive in the aqueous and solid speciation of elements in the flue gas desulphurisation system. Sino-European Symposium on Environment and Health (SESEH), 2012. Oral communication.

Annex 2

Patricia Córdoba, María Eugenia González, Aixa González, Natalia Moreno, Carlos Ayora, Noelia Sepúlveda, Rodrigo Navia, Xavier Querol. Remove of Selenium from FGD waters by a non-conventional adsorbent by-product (In preparation).

Raquel Ochoa-González, Aida Fuente Cuesta, **Patricia Córdoba**, Mercedes Díaz-Somoano, Oriol Font, M. Antonia López-Antón, Xavier Querol, M. Rosa Martínez-Tarazona, Antonio Giménez. Study of boron behaviour in two Spanish coal combustion power plants. Journal of Environmental Management 2011; 92 (10):2586-2589.

R. Ochoa-González, **P. Córdoba**, M. Díaz-Somoano, O. Font, M.A. López-Antón, C. Leiva, M.R. Martínez-Tarazona, X. Querol, C. Fernández Pereira, A. Tomas, P. Gómez, P. Mesado. Differential partitioning and speciation of Hg in wet FGD facilities of two Spanish PCC power plants. Chemosphere 2011; 85:565-570.

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