PARTITIONING AND SPECIATION OF SELENIUM IN WET LIMESTONE FLUE GAS
DESULPHURISATION SYSTEMS: A REVIEW

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ABSTRACT

This paper presents a general review of the selenium chemistry and fate in wet limestone flue gas desulphurisation (FGD) systems and major factors associated to the operation of wet limestone FGDs affecting Se oxidation. Selenium chemistry in FGD waters is more than the interconversion between selenite and selenate; selenium can form a complex array of chemical aqueous complexes some of them analogous to those of sulphur as well as interact with polyoxosulfur anions. However, most of Se- aqueous complexes that may encounter in FGD waters are still unidentified. FGD water re-circulation, fly ashes (FAs) accumulated in the FGD scrubber, oxi-reduction potential (ORP), water flow quantity, flow variability, and pressure are operating FGD conditions that may influence the implementation of effective strategies in management and control of Se in FGD waters. These operating FGD conditions may have a strong influence in the reaction kinetics and the mass transfer of water and constituents through the water treatment processes for Se. Other factors that can also affect selenium removal in FGDs are oxidizing and reducing agents complexing or chelating agents and/or competing oxyanions. Development of effective strategies in management and control of Se is also complicated by difficulties in measuring and analyzing selenium speciation in FGD wastewaters. The effect of sample handling and preservation methods on selenium speciation is not well understood yet and analytical methods may not achieve accurate total selenium concentrations in complex FGD wastewater matrices.

KEYWORDS: flue gas desulphurisation (FGD); polyoxosulfur anions; FGD water re-circulation; fly ashes (FAs); oxi-reduction potential (ORP).

1. INTRODUCTION

Coal-fired power plants are a major source of emissions for a number of air pollutants including SO₂, NO_x, particulate matter (PM), HCl, HF, and Hg. 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 [1].

During coal combustion, Se is volatilized as elemental Se⁰ and SeO₂. In the boiler, gaseous SeO₂ can be chemisorbed on the fly ash (FA) surface and/or remain in the gas phase [2-4]. The particulate bound Se is removed in the particulate collection device, while the remaining Se enters the wet Flue Gas Desulphurisation (FGD) scrubber as gas-phase or particulate Se [5]. In the FGD system, particulate Se dissolves in the aqueous phase of the absorbent slurry, while gaseous Se diffuses first through the gas to the aqueous phase where it dissolves and undergoes a series of chemical reactions. However, since the presence and form of various components in an actual FGD water depends on the operating conditions, the behavior of selenium in an actual FGD is not well understood.

In a wet limestone FGD with forced oxidation, selenium primarily exists as selenite (SeO₃²⁻) and selenate (SeO₄²⁻), but it can form a complex array of chemical aqueous complexes whose formation depends on the oxidation air rate contribution to the oxidation-reduction potential (ORP) conditions as well as the presence and concentration of redox-active species in FGD scrubbers. High ORP conditions, often desired to maintain SO₂ removal performance of FGD scrubbers, promotes the formation of dithionate (S₂O₆²⁻) and/or peroxydisulfate (S₂O₈²⁻), which tend to interfere with most selenium removal technologies [6]. Coal-fired power plants have reported inconsistent treatment success with respect to reducing total Se concentrations because Se removal varies over time and with FGD system design and operating factors. A potential additional reason for this observation is the presence of unknown Se species in FGD wastewaters. Recently, Petrov et al [7] identified selenocynate (SeCN⁻) and selenosulfate (SeSO₃²⁻) for the first time and 9 unknown Se species in FGD waters from six power plants in the United States (US) that do not correspond to any commercially available standard material.

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4 84 In power plants located where water resources are scarce the re-circulation of the water to the scrubber
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6 85 from gypsum slurry filtration is common. Studies [8] on the enrichment of inorganic trace pollutants in the
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8 86 re-circulated waters, revealed that the recirculation of filtered water gives rise to unusually high
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10 87 concentrations of Se among others. This causes the emission of Se by entraining particles and droplets
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12 88 from gypsum slurry in the OUT-FGD gas, and/or the precipitation of solids in the FGD-gypsum end-
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18 91 Additionally, there are analytical challenges with respect to understanding Se behaviour in FGD. Sample
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20 92 handling and preservation methods for FGD waters are not well established yet. On the other hand,
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22 93 analytical methods may not achieve accurate total selenium concentrations in complex FGD wastewater
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24 94 matrices and selenium speciation procedures tend to fail to account for the presence of any other
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26 95 selenium species besides selenite and selenate. These studies have shown that the Se chemistry in wet
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28 96 FGD systems is highly complex and not completely understood, thus extrapolation and scale-up of these
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30 97 results may be uncertain.
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34 99 The objective of this paper is to present a general review of the Se chemistry and fate in wet limestone
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36 100 FGDs (most common) and to expose the major factors associated to the operation of wet limestone FGDs
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38 101 affecting Se oxidation, with particular reference to (1) the oxi-reduction potential and oxidizing agents; (2)
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40 102 Se interaction with polyoxosulfur anions; (3) efficiency of the particulate control devices and filter water re-
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42 103 circulation to the scrubber; and (4) sample handling and preservation methods for FGD waters; and (5)
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44 104 Se analysis technology. The paper highlights the need to study in depth a number of issues in view of the
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46 105 existing and forthcoming worldwide regulations of Se in FGD wastewaters.
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48 106 49 50 51 107 2. Wet FGD

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53 108 The wet scrubbers produce a wet product that might be regenerable or non-regenerable. In the
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55 109 regenerable processes [9] the sorbent reagent follows a regeneration step which gives rise to SO₂,
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57 110 sulfuric acid (H₂SO₄), or elemental sulphur (S⁰), and produces a sludge that may be sold to partially offset
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59 111 the cost of operating the FGD system; whereas in the non-regenerable processes [10-12] S permanently
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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 Ca(OH)_2 and alkaline FA sorbents, which react with SO_2 to form a Ca-S compound [13].

2.1. Wet limestone FGD

The wet limestone FGD process (non-regenerable) is based on complex acid-base reactions that take place under forced or natural oxidation conditions [10-12]. 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 [10] occur in the gas-to-liquid contact zone with a pH range from 5 to 6:

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

The reactions described above which are 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-} as follows:

At a lower pH range (4.5 to 5.5), [14] the chemical reaction is different. As shown below, after SO_2 absorption (R1), the primary product of the neutralization by limestone is $\text{Ca}(\text{HSO}_3)_2$:

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 [14]:

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 [14]. In natural oxidation mode, the main product is a mixture of $\text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (50-60%) in a sludge form which is difficult to dewater, whereas in forced oxidation mode, the final end-product is around 90% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [14].

2.1.1. Forced oxidation and Oxidation-Reduction Potential (ORP) in wet limestone FGD

As previously stated, 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 $\text{Ca}(\text{HSO}_3)_2$ or CaSO_3 to ensure fully oxidised gypsum product. Additionally, aeration functions can eliminate CO_2 from the water, thereby increasing pH during the neutralisation reaction [14].

Because sulfite (SO_3^{2-}) is the predominant sulfur species in FGD waters, variables affecting its oxidation such as the presence of strong oxidizers have a direct impact on the ORP at which the FGD system operates [15]. The ORP or redox is the activity or strength of oxidizers and reducers in relation to their concentration. While a solution with a positive voltage will oxidize other sources, a solution with negative voltage will reduce them. The nominal ORP values of wet FGDs may range from a moderate ORP values of approximately 100 mV to 300 mV. However, there are others FGD units that operate at higher ORP values, often above 500 mV [15].

Copper (Cu), manganese (Mn), and iron (Fe), in decreasing order, are the top liquid-phase metal catalyst with respect to their activity in SO_3^{2-} oxidation [16]. The Electric Power Research Institute (EPRI) [17] conducted a serial of bench-scale wet FGD experiments to investigate the impacts of these metals on ORP in SO_3^{2-} oxidation early reported by Ulrich [16]. Since the strength activity of Cu, Mn, and Fe is opposed to their concentration in FGDs, in these experiments, Cu (1 mg/L) was added at the lowest concentration to the bench-scale FGD slurry liquor, Mn (45 mg/L) at an intermediate concentration, and Fe (512 mg/L) at the highest concentration. Tests were conducted at a bench-scale scrubber under typical baseline conditions (~200mV), reagent-grade calcium carbonate and 10 mg/L of Mn (as MnSO_4) to provide some SO_3^{2-} oxidation catalyst.

Results showed that a small dose of cupric ion (Cu^{2+}) to the FGD slurry caused significant increase in ORP from ~170 mV to nearly 400 mV, which indicated its significant impact on both the SO_3^{2-} oxidation and ORP. In the Mn experiments, while the addition of total Mn (45 mg/L) increased the ORP over a period of an hour to approximately 400 mV, an additional Mn dose of 260 mg/L showed no further effect on ORP. Both the SO_3^{2-} and peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$) concentrations remained low during this test. In the Fe experiments, the addition of Fe (512 mg/L) caused a decrease in reaction tank ORP from 125 mV to below 100 mV. A further spike was added to bring the total Fe concentration to nearly 900 mg/L, but no further impact on ORP was observed. The liquor-phase SO_3^{2-} concentrations remained low during this test (<3 mg/L), but the $\text{S}_2\text{O}_8^{2-}$ concentrations were not reported.

These test results indicate that the ORP is an important operating factor of wet FGD absorbers. Monitoring the dominant oxidation states and phases of metals present in the slurry, and the phase partitioning of slurry constituents might allow to determine how aqueous complexes will probably react to other aqueous complexes and solid species also present in the slurry [15].

3. Partitioning and speciation of selenium in wet limestone FGD

During coal combustion, Se is volatilized as elemental Se^0 and SeO_2 . In the boiler, gaseous SeO_2 can be chemisorbed on the FA surface and/or remain in the gas phase (Figure 1). The chemisorption of SeO_2 on FAs depends on the temperature and gas composition as well as on the FA chemistry [5]. It has been observed that Se might react with Ca and form stable compound such as calcium selenite (CaSeO_3) during post combustion environment as shown below [18-19]:

FAs are generally captured in particulate control devices with a very high efficiency. However, a small fraction may escape from the control and reach the FGD system [1; 20-21]. Once in the FGD, FA components can be dissolved in the aqueous phase of the slurry or retained in the gypsum sludge (Figure 1). Selenium chemisorbed in FAs (e.g. as SeO_3^{2-}) may then be dissolved in the aqueous phase of the slurry to form an array of Se-aqueous complexes and/or solid species.

If SeO_2 remains in the gas phase, which will depend on the flue gas temperature, a proportion of gaseous SeO_2 can either react with moisture in flue gas to form H_2SeO_3 and subsequently condense in the scrubber as the flue gas undergoes a rapid quench to a temperature between 50-60°C [22], or diffuse through the gas to the aqueous phase as SeO_2 where it will dissolve to form selenous acid (H_2SeO_3):

The pH slurry will determine if H_2SeO_3 will dissociate to HSeO_3^- and/or SeO_3^{2-} . The rate of oxidation-reduction reactions will depend on the ORP and oxidizing agents among other factors.

However, the occurrence of harmful acidic gases during pulverized coal combustion (PCC) other than SO_2 , such as HCl may play a significant role in the partitioning, speciation, and fate of Se. During combustion, coal chlorine (Cl) is released primarily as HCl in the high temperature zone of a boiler [23]. As the combustion gases cool ($430\text{-}475^\circ\text{C}$), a proportion of HCl can be partially oxidised to Cl_2 by the Deacon Process [24] reaction in the presence of O_2 and H_2O :

However, the presence of SO_2 can inhibit the formation of Cl_2 through the following gas-phase reaction [25]:

Although SeO_2 is released in a lower concentration compared to that of SO_2 during coal combustion, SeO_2 can also inhibit the formation of Cl_2 through the following gas-phase reaction:

Gaseous SeO_3 may either be chemisorbed on FA following R12, or diffuse through the gas to the aqueous phase where it will dissolve to form H_2SeO_3 following R13. Either way, a proportion of Se will either be dissolved in the aqueous phase of the gypsum slurry forming Se-aqueous complexes, or concentrated in the gypsum sludge as Se-solid species. Depending on the abatement capacity of the FGD system, a given proportion of Se will be emitted into the atmosphere. However, if the FGD system operates with water re-circulation to the scrubber, Se dissolved in filtered water from gypsum slurry

filtration will be reintroduced into the FGD scrubber while the remaining proportion, dissolved in the FGD wastewater, will follow a co-precipitation and/or adsorption treatment process for the removal of Se.

Additionally, halide injection, using calcium bromide (CaBr_2), a reliable and cost effective method in the United States (US) for enhancing mercury (Hg) emissions reduction, has shown to have an impact on Se speciation. CaBr_2 injection increases the oxidized mercury (Hg^{2+}) fraction in the flue gas, being more easily captured by a FGD or activated carbon. However, though the exact mechanism is not known, bromide injection results in increased gas-phase Se entering the flue gas desulphurisation equipment [26]. It has been postulated that the liberated bromide can react with gas-phase Se forming compounds that do not condense on ash unlike SeO_2 , or reacts with Se adsorbed on FA releasing it back in gas phase, thereby causing an increase in the gas-phase Se emissions.

A possible mechanism for the increase of gas-phase Se entering the flue gas desulphurisation process when adding CaBr_2 would be the reaction with SeO_2 (g) to produce SeO_3 (g):

Gaseous SeO_3 , as stated above, may follow either R12 or R13. In both cases, Se can reach the FGD system either with FAs not captured in the particulate control device or as gaseous H_2SeO_3 diffusing through the gas to the aqueous phase. These are no conclusive results and therefore, more research is needed to understand the effects of halide injection on Se speciation and to understand the exact mechanism under which a Se conversion may occur.

3.1. What is the selenium chemistry in wet limestone FGDs?

It has been widely reported and discussed [6-7;15;17;27] that in wet limestone FGDs, with ORP values ≥ 300 mV, Se will predominantly exist in the selenite (SeO_3^{2-}) form can be treated easily by co-precipitation and/or adsorption treatment. In contrast, with ORP values ≤ 300 mV, Se can be oxidised to selenate (SeO_4^{2-}), being hard to precipitate and treated effectively in the process. In 2011, Petrov et al [7]

found 13 different Se species in FGD waters and conclusively identified only two of them selenocynate (SeCN⁻) and selenosulfate (SeSO₃⁻). This fact indicates that Se chemistry in FGD waters is more than the interconversion between SeO₃²⁻ and SeO₄²⁻. A possible explanation for this observation is that Se chemistry may vary over time and with FGD system design and operating factors associated to each full-scale power plant.

3.1.1. Wet limestone FGD operating factors: ORP and oxidizing agents

Besides SeO₃²⁻ and SeO₄²⁻, as stated above, Se can form a complex array of chemical aqueous complexes whose formation also depends on the oxidation air rate contribution to the ORP conditions as well as the presence and concentration of redox-active species in FGD scrubbers. High ORP conditions, often favoured to maintain SO₂ removal performance of FGD scrubbers, promotes the formation of dithionate (S₂O₆²⁻), peroxydisulfate (S₂O₈²⁻), peroxymonosulfate (HSO₅⁻), and/or hypochlorite (OCl⁻) which tend to interfere with most Se removal technologies [6]. These species are considered potential oxidising agents involved in most mechanisms of SeO₃²⁻ oxidation in FGDs.

Akiho et al [27] in a study on the effect of oxidising agents (H₂O₂, S₂O₈²⁻, ClO⁻) on SeO₄²⁻ formation in a wet FGD indicated that S₂O₈²⁻ ion is the predominant oxidising agent that oxidizes SeO₃²⁻ to SeO₄²⁻. However, with Mn²⁺ addition, S₂O₈²⁻ oxidises Mn²⁺ to MnO₂, which captures some dissolved SeO₃²⁻. Authors indicated that the oxidation of SeO₃²⁻ to SeO₄²⁻ was promoted by the sulphate ion radical (SO₄⁻) which resulted from decomposition of S₂O₈²⁻, without acid catalyst, according to [28-29]:

where the first step of the reaction is either R18:

or R19:

In both reactions, $\text{SO}_4^{\cdot-}$ radicals are formed. The authors proposed that SeO_3^{2-} oxidation by $\text{SO}_4^{\cdot-}$ could be in line with an earlier work [30] on the oxidation mechanism of Ti^{2+} to Ti^{3+} by $\text{SO}_4^{\cdot-}$ using acrylonitrile. It was determined that acrylonitrile scavenges $\text{SO}_4^{\cdot-}$ by producing a sediment of polyacrylonitrile, therefore, a possible oxidation by $\text{SO}_4^{\cdot-}$ would be completely inhibited [30]. Akiho et al [27] prepared solutions containing SeO_3^{2-} , $\text{S}_2\text{O}_8^{2-}$, with and without acrylonitrile to reproduce the same conditions. Results showed that the oxidation of SeO_3^{2-} occurred in the solution lacking acrylonitrile, but did not occur in the presence of acrylonitrile. It was postulated then that the oxidation of SeO_3^{2-} in the solution containing $\text{S}_2\text{O}_8^{2-}$ is a radical reaction with $\text{SO}_4^{\cdot-}$ [27]:

which could be parallel to the oxidation of Mn^{2+} in a solution containing $\text{S}_2\text{O}_8^{2-}$ by a radical reaction with $\text{SO}_4^{\cdot-}$ [27]:

Where SeO_3^{2-} and Mn^{2+} are oxidised by reaction with two $\text{SO}_4^{\cdot-}$. The highly reactive $\text{SO}_4^{\cdot-}$ is converted to SO_4^{2-} immediately, resulting in SeO_4^{2-} and MnO_2 as oxidation end-species. Additionally, authors tested the oxidation rates of both SeO_3^{2-} and Mn^{2+} species. Results revealed that Mn^{2+} is oxidised faster to MnO_2 than SeO_3^{2-} to SeO_4^{2-} because of the difference in the reaction rate between SeO_3^{2-} and Mn^{2+} , and $\text{SO}_4^{\cdot-}$. These results could suggest that the addition of Mn^{2+} is a potential measure to prevent SeO_3^{2-} oxidation in actual FGD plants. However, it is well known that Mn^{2+} may also cause corrosion problems in FGDs.

In an earlier study [31], authors also evaluated the effect of metallic ion on Se oxidation using solutions containing SeO_3^{2-} , SeO_4^{2-} , $\text{S}_2\text{O}_8^{2-}$ and additives. It was found that with no additives, the concentration of

S₂O₈²⁻ decreased progressively (20 h), and SeO₃²⁻ was oxidised to SeO₄²⁻ completely. Additionally, they found that the concentration of SO₄²⁻ increased with the decrease of S₂O₈²⁻ probably as a result of S₂O₈²⁻ decomposition irrespective of the Se oxidation reaction. With addition of Fe³⁺, Ni²⁺, and Ti⁴⁺, no changes in the Se and S₂O₈²⁻ concentration were found.

An extensive study by the Electric Power Research Institute (EPRI) [32] on the Se speciation and management in wet FGD systems indicated that solid-phase manganese [Mn(IV)] catalytically oxidises SeO₃²⁻ to SeO₄²⁻ under moderate to high ORP conditions. Bench-scale experiments showed that under specific experimental conditions (35 mg/kg Mn and ORP from 0 to 600 mV), SeO₃²⁻ oxidation increases progressively in time, reaching its highest oxidation (80%) at 400 mV after six hours. These results are in agreement with those reported by Searcy et al [33]. These authors indicated that conditions that produce solid phase Mn also promote SeO₃²⁻ oxidation to SeO₄²⁻, but conditions that favour dissolved Mn (excluding Mn species in high oxidation states) do not favour SeO₄²⁻ formation. EPRI also conducted experiments combining Mn, ORP, and additives in solutions to test the degree of SeO₃²⁻ oxidation. The use of additives and their effects on Se speciation will be discussed in subsequent sections.

3.1.2. Role of ORP-oxidizing agents- additives on selenium oxidation

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 [34-36] have shown that organic acids with buffering capacity provide an optimal tool for enhancing of the desulphurisation efficiency. When SO₂ 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 SO₂, increasing the overall removal rate [37]. However, if the pH is excessively low, buffer additives may act as scavenging systems for H⁺. Although the use of organic acids has been demonstrated as an optimal measured to boost the SO₂ efficiencies, the effect of organic additives on the retention efficiency of pollutants other than SO₂ has been questioned. A study by Heidel et al [38] based on the chemical reduction and re-emission of Hg compounds from slurries of a lab-scale

wet FGD system, revealed a negative impact on Hg retention by the addition of formic and adipic acids most probably associated to the strong reducing properties of formic acid.

Adipic acid, dibasic acid (DBA), and acetic acid have also been studied as a strategy to manage Se in FGD waters, however, no conclusive results have been determined. In 2011, EPRI published an extensive study [32] based on a serial of bench and pilot-scale experiments to determine how different additives and operating factors could affect SeO_3^{2-} oxidation in FGD scrubbers. The effect of DBA (mixture of adipic, succinic, and acetic acid) on SeO_3^{2-} oxidation was tested in a “clear-liquor” (sodium hydroxide as absorbent without solids) containing 35 mg/kg Mn at variable ORP (~400 mV) at bench-scale. Day-test results showed no variation in SeO_3^{2-} oxidation in the presence of Mn with and without DBA. However, results after 48h of storage showed that in only Mn-non DBA samples, SeO_3^{2-} was completely oxidised and in Mn-DBA samples SeO_3^{2-} oxidation inhibited. Authors [32] concluded that SeO_4^{2-} may be converted back to SeO_3^{2-} during sample storage, which prevented them from concluding the effect that DBA could have on SeO_3^{2-} oxidation with time after blow down from the absorber in full-scale FGDs. As it will be discussed later, preservation methods and sample storage to determine Se concentration may have a significant impact on Se speciation.

EPRI’s clear-liquor tests [32] with 5 mg/kg Mn and adipic acid at 200 mV ORP showed little or no SeO_3^{2-} oxidation in samples analysed by ICP-MS after 48h of sampling. Samples with only Mn showed 27% to 47% SeO_3^{2-} oxidation. Similar results were obtained in “clear liquor” tests using acetic acid and Mn. In samples containing only Mn, SeO_3^{2-} oxidation ranged from 18% to 38%, while those containing acetic acid, SeO_3^{2-} oxidation was $\geq 13\%$ [32]. These results showed that both DBA and acetic acids could be potential measures to control Se oxidation in FGD scrubbers. However, these tests were carried out using a “clear liquor” solution that does not represent actual FGD operating conditions at full-scale power plants. FGD slurries are generally characterised by complex slurry matrices containing a high concentration of inorganic trace pollutants and solids as a consequence of the continuous filtered water re-circulations to the scrubber as revealed by Córdoba et al [8] in a study describing the enrichment of inorganic trace pollutants in complex FGD waters from two full-scale power plants. Therefore, FGD

slurries with complex matrices may overlap and/or diminish the benefits of using organic acids to prevent SeO_3^{2-} oxidation. It is for this reason that the extrapolation and scale-up of the use of additives at full-scale FGDs may be uncertain.

EPRI's bench-scale tests [32] carried out to determine if DBA and acetic acid could inhibit SeO_3^{2-} oxidation in the presence of solids reacted from a natural limestone under high ORP conditions (150-300 mV), revealed that the oxidation rates of SeO_3^{2-} in the natural limestone were higher than those carried out with the clear liquor and reagent solids. These results questioned about the benefits of using DBA to control Se oxidation in FGDs. Acetic acid did not inhibit SeO_3^{2-} oxidation, instead, Se dissolved in the aqueous phase of the natural limestone was oxidised to SeO_4^{2-} . EPRI's bench-scale tests [30] using FGD slurry and limestone slurry from a pilot host facility revealed that low ORP (200 mV) decreased the oxidation rate of SeO_3^{2-} . However, the comparison between the low ORP and the low ORP and DBA tests showed that there was no benefit of DBA on SeO_3^{2-} oxidation. As expected, ferric chloride prevented Se from oxidation probably as a result of its adsorption or precipitation.

Pilot-scale scrubber tests were also conducted by EPRI [30] to observe full-scale trends in Se behaviour and to test the effectiveness of two control strategies: 1) reduce ORP by decreasing oxidation air rate and 2) add ferric chloride to the scrubber. Results were divided into liquid-phase Se and solid-phase selenium results according to the baseline, natural oxidation, and iron tests, respectively. Although the interpretation of the results was complex due to the amount factors tested, it was found that the Se enrichment in the fine particulates was modest or negligible, which was ascribed to its co-precipitation with the gypsum during the baseline and natural oxidation tests. In contrast, under low ORP conditions, SeO_3^{2-} was formed and remained in the slurry liquid phase. Authors concluded that by decreasing the oxidation air, Se phase partitioning shifted to the solid phase of the scrubber slurry, suggesting this strategy as an option for managing Se behaviour in FGD scrubbers.

These studies show the high complexity of selenium chemistry in FGD scrubbers. There are no conclusive recommendations for the management and control of Se in FGDs. Selenium chemistry varies

from a FGD to another as well as its operating conditions, studies showed that the identification of factors involved in Se chemistry, partitioning and fate are crucial to rule-making and the need of novel solutions for dealing with Se discharges in water bodies and in stack emissions. If the partitioning and fate of Se in an actual FGD have to be managed, it is highly recommended to evaluate the operating factors under which a specific FGD operates. Otherwise, recommendations about Se management can hardly be implemented.

3.1.3. Selenium and sulphur donors

Because sulfur and selenium have similar chemistries and sulfur forms a wide variety of species in FGD waters, it can be plausible that Se could form a number of analogous compounds to those of sulphur [39] as well as interact with polyoxosulfur anions to form Se-S aqueous complexes. Selenosulfate has recently been identified for the first time in FGD waters. Further research to study the interaction between Se and polyoxosulfur anions and possible formation of Se-S aqueous complexes in FGD waters should be addressed.

Sulfite (SO_3^{2-}), trithionate ($(\text{SO}_3)_2^{2-}$) and thiosulfate ($(\text{S}_2\text{O}_3)_2^{2-}$) tend to form Se complex ions such as selenosulfate (SeSO_3), selenotrithionate ($(\text{SeSO}_3)_2^{2-}$) and selenopentathionate ($(\text{SeS}_2\text{O}_3)_2^{2-}$) increasing the concentration of dissolved Se in untreated FGD waters. While the formation of selenosulfate can be considered the result of the dissolution and reaction of elemental selenium with sulphite [40] in the aqueous phase of the FGD slurry, the substitution of sulfur by Se in selenotrithionate and selenopentathionate anions may give rise to array of Se-S stable compounds and/or isomers whose identification can be a challenge because of their complex structures.

H_2SeO_3 formed in FGD either by the reaction of SeO_2 with moisture in flue gas, or diffusion gaseous SeO_2 through the gas to the FGD aqueous phase, may react with bisulfite (HSO_3^-) to form selenotrithionate ($(\text{SeSO}_3)_2^{2-}$) as follows:

As a result, two isomers of the selenotritrithionate can be formed. $\text{OSe}(\text{OSO}_2)_2^{2-}$ with O-bonded Se and the other with S-bonded Se, $\text{Se}(\text{SO}_3)_2^{2-}$. The O-bonded isomer is formed first and this converts slowly to the S-bonded isomer. The stoichiometry of this reaction was confirmed by Ball and Mine [40] in lab-scale experiments when evaluating the reaction of SeO_3^{2-} and SO_3^{2-} . In the reaction, hydrogen sulphite reacts with selenous acid quantitatively at a ratio of 3:1 $\text{SO}_3^{2-}/\text{H}_2\text{SeO}_3$ stoichiometry to give selenotritrithionate. The mechanism of R22 could also be parallel to that established for the reaction of thiolates and selenous acid according to the reaction below [40]:

Alternatively, selenopentathionate ion ($(\text{SeS}_2\text{O}_3)_2^{2-}$) can be produced by the reduction of H_2SeO_3 with thiosulfate in acid solution. This reaction was used as the basis of an iodimetric method of analysis for selenites [41]:

The feasibility of R27 depends, therefore, on the pH conditions in FGD scrubbers among other factors.

In the presence of sulphite and thiosulfate ions, equilibrium is established between selenotritrithionate and selenopentathionate in solution as follows [41]:

Where addition of SO_3^{2-} ion acceptor, displaces the equilibrium to the right, and the SO_3^{2-} group in the selenotritionate is replaced by thiosulfate; thus the selenotri- and pentathionates can be regarded as sulphito- and thiosulphato- complexes, respectively.

Selenopentathionate may also undergo slow decomposition to produce Se^0 and the trithionate ion. It is well known that the addition of excess sulphur donor to -SSeS- species causes decomposition to Se^0 and the corresponding -SS- species. Therefore, the decomposition of selenopentathionate may occur as follows [41]:

This reaction could be the result of an electrophilic attack by SO_3^{2-} taking place at the sulphur attached to Se [41], which can occur in non-forced-oxidized FGD scrubber purge waters when these waters are retained in surface impoundments at ambient temperature for several weeks or more [42].

3.1.4. Selenium aqueous complexes

Selenocyanate (SeCN^-) has been recently identified in FGD waters for the first time. The formation of selenocyanate (SeCN^-) could be the result of the reaction between Se^0 and free cyanide (CN^-), as is observed in other types of industrial process waters, e.g., in gold mining operations [43], but there are no conclusive results though.

Hydrogen cyanide (HCN) can be formed as an intermediate product in coal combustion, but it generally does not persist in the flue gas [44]. Analytical results reported by Petrov et al [7] indicated that a fraction of the initially produced HCN reacts with Se species (possibly Se^0), either in the flue gas or in the scrubber, to form selenocyanate by currently unknown mechanisms.

Based on the above conclusion, two mechanisms are proposed that may explain the formation of SeCN^- aqueous complexes by a gas- and aqueous-phase reactions. In the first mechanism, the HCN formed as an intermediate product in coal combustion would react with SeO_2 (g) to give $(\text{SeCN})_2$ in FGDs:

In the FGD, $(\text{SeCN})_2$ may then oxidize tiosulphite ion ($\text{S}_2\text{O}_3^{2-}$) to tetrathionate ion ($\text{S}_4\text{O}_6^{2-}$) in the FGD scrubber giving 2SeCN^- :

A second mechanism for SeCN^- formation in the FGD scrubber could occur as a consequence of the reaction between H_2SeO_3 and thiocyanic acid (HSCN) to give selenium dithiocyanate ($\text{Se}(\text{SCN})_2$) as follows:

The oxidation of thiocyanic acid by H_2SeO_3 has been shown to take place in an analogous way as that found for H_2SeO_3 oxidation of most thiols and thiolates generating the corresponding selenotrisulfide and disulfide products [45]. Solid selenium dithiocyanate contains isolated $\text{Se}(\text{SCN})_2$ molecules with S-bonding to Se and a cis arrangement of the CN groups. $\text{Se}(\text{SCN})_2$ may then decompose to give SeCN^- :

Although there is no experimental data confirming the reactions described above, R30-33 may be considered as potential mechanisms in which SeCN^- aqueous complexes may occur in FGDs. More research is needed to understand the exact mechanism for the generation of SeCN^- .

3.1.5 Organic-selenium compounds

The use of additives may also influence the speciation of Se within the wastewater matrix, contributing to the formation of organo-selenium compounds.

Bench-scale continuous flow biological activated sludge treatability studies with FGD wastewater demonstrated that the addition of scrubber additives to improve SO₂ removal had a significant impact on the biological treatment of FGD wastewaters [46]. Specifically, the use of DBA, containing manufacturing by-products, impacted the speciation of Se within the wastewater matrix, contributed to the formation of unidentified organo-selenium compounds that were recalcitrant to microbial removal. The addition of formic acid, however, was found to enhance the downstream biological treatment process and to provide efficient SO₂ removal. Additionally, analysis of the scrubber wastewater by IC-ICP-MS revealed that the soluble oxyanions of Se, SeO₃²⁻ and SeO₄²⁻, represented a significantly greater fraction of the total Se present in the sample matrix, with significant reductions in the levels of complexed Se.

Organoselenium compounds undergo photo-oxidation in water, and their mineralization eventually yields inorganic Se species. Volatile species of selenium H₂Se, CH₃SeH, (CH₃)₂Se, and (CH₃)₂Se are also known to be formed in Se-containing water bodies. However, their identification in FGD waters has not been demonstrated yet. These reduced Se complexes do not elute from standard IC columns; therefore, different analytical methods are required.

Selenium aqueous complexes and polyoxosulfur reactions described above are just few examples of possible mechanisms that Se and sulphur may form in FGD waters. Selenium chemistry in wet FGD systems is highly complex and not completely understood. Therefore, research challenges with respect to the management of Se in FGDs rely on elucidating factors affecting SeO₃²⁻ oxidation and how these factors interfere in the management and control strategies for Se in FGD wastewaters.

3.1.6. ORP effect on the capture of inorganic trace pollutants other than selenium

High ORP (≥ 500 mV) can also cause negative effects on the SO_2 performance and capture of inorganic trace pollutants other than Se. Persulfate which is formed under high-ORP conditions has the ability to convert some chloride to their respective elemental state, chlorine [13]:

The concentration of chlorine in absorber slurry is present as three species in equilibrium within the aqueous phase: dissolved gas (Cl_2), hypochlorous acid ($\text{HOCl}^\cdot$), and ionic hypochlorite (OCl^-):

Under the typical wet FGD operating range, equilibrium conditions promote $\text{HOCl}^\cdot_{(\text{aq})}$. The resulted acidic conditions will cause an increase of the equilibrium pressure of SO_2 , thereby decreasing the gas absorption rate of $\text{SO}_{2(\text{g})}$ to zero. The rate at which $\text{SO}_{2(\text{g})}$ is transferred depends on the solubility of SO_2 and its displacement from equilibrium [13].

Mn normally soluble as ionic Mn^{2+} will also oxidise and precipitate out as MnO_2 with ORP values higher than 500 mV. When MnO_2 contacts metal as part of a deposit, it serves as a galvanic cathode to exacerbate the fluoride and chloride driven under-deposit corrosion mechanism [13]. Corrosion accelerated by Mn precipitation can be rapid and severe.

By contrast, Hg re-emission events have been reported to increase when FGDs operate with low ORP values due to the elemental state being thermodynamically favored in wet FGD slurry under these conditions [12]. Possible chemical pathways for Hg reemission to occur are shown in R36 and 37:

4. Operating PCC-FGD factors affecting selenium emissions

4.1. Efficiency of the particulate control devices and filter water re-circulation to the scrubber

Despite the high efficiency of particulate control devices, e.g. electrostatic precipitators (>90%) [47-50], a small fraction of FA escapes and goes into the FGD system. Once in the FGD, FA components may be dissolved in the aqueous phase of the absorbent slurry or retained in the solid fraction.

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 [1]. In this latter case, water streams may act as retention sinks for some metals as a result of partial or total dissolution processes, its efficiency 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 [8]. As a consequence, 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 [8]. This process may increase the concentration of trace pollutants such as Se in re-circulated waters to very high levels compared to that of the original input water. The increase of the Se concentration may 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 eventual discharges to the environment [8]. In this regard, the EPA, under authority of the Clean Water Act, has recently promulgated new effluent guidelines [55] for water discharges from steam electric power plants that specify effluent limits for arsenic, mercury, selenium, and nitrogen in wastewater discharged from wet scrubbers. With this new regulation, power plants under operational conditions of water re-circulation to the FGD scrubber may need to implement more restricting measures to prevent enrichment of selenium and other trace pollutants in FGD wastewaters for eventual discharges to the environment and/or wastewater treatments.

Other elements retained in high concentrations 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.

FAs not dissolved in the aqueous phase of the absorbent slurry may be retained in the solid fraction (gypsum sludge) and subsequently extracted from the system by the FGD-gypsum, and/or may be retained in the solid fraction and subsequently entrained with the outgoing flue gas FGD (OUT-FGD) as PM. The accumulated FA particles in gypsum sludge as well as the entrained particles from this material and those of gypsum and limestone slurry by the gas OUT-FGD are limiting factors for an increase of PM emissions and for an accurate determination of the retention efficiency of PM by wet scrubbers. Since the accumulated fraction of PM into the scrubber cannot be determined, an estimation of the retained proportion of PM is usually measured by considering the retention efficiency as PM OUT/PM IN ratio [51].

In Europe, after 1990, experience with wet FGDs have indicated collection efficiencies of PM by wet FGDs ~90% [51-52]. However, an intensive sampling (7 sampling campaigns) and characterization program [54] executed at two Spanish, three Greek, and one Dutch power plants, fed with different fuels and with different designs of wet FGD systems, reported PM collection efficiencies in the range of 47-79% as a consequence of the entrainment of droplets containing Se (among others) from gypsum slurry and/or from corrosion of the steel (mainly Fe, Cr, Ni, Zn or Pb) by the OUT-FGD gas [54]. It can therefore be stated that the actual removal efficiencies of fly ashes by wet limestone FGDs are usually underestimated because of the entrainment of unreacted limestone and gypsum slurry particle episodes.

These experiences at full-scale power plants show how FGD operating conditions can also contribute to PM Se emissions as non-retained fly ash by FGD and particles and how droplets from gypsum slurry can be swept out by the gas OUT-FGD.

5. Analysis of selenium: state-of-the-science

Development of effective strategies in management and control of Se is complicated by difficulties in measuring and analysing Se speciation in FGD wastewaters. Current analytical challenges in understanding Se behaviour in FGD are the sample handling and preservation methods not well established yet, and the analytical methods that yield inaccurate total Se concentrations in complex FGD wastewater matrices. Selenium speciation fail to account for the presence of any other Se species besides SeO_3^{2-} and SeO_4^{2-} [32].

5.1. Sample handling and preservation

The sampling of a FGD water stream should entail the collection of a small water volume for case of transportation and at the same time be satisfactory for analytical purposes. This implies that the FGD water should be handled in such a way that no significant changes in composition occur before the tests are made. Sample preservation refers to how a sample is handled and stored between the time when the sample is collected from the FGD system and the time when the samples is analysed.

Pre-treatment of samples constitutes an important step prior to analysis and may be required depending on the Se fraction to be measured. For Se and other metals, it is most appropriate to collect both a filtered and an unfiltered sample to differentiate between total and dissolved metals present in the matrix as some metals may partially sorb to filters. If total Se is to be determined, what includes all Se forms, inorganically and organically bound, and both dissolved and particulate, a pre-digestion procedure of the unfiltered sample should be performed. If only total inorganic dissolved Se is to be analysed, then the sample should be filtered through a preconditioned or prewashed membrane filter (0.45 μm) of polycarbonate or cellulose esters [56-60]. In general, metals in suspended particles can be assessed either by digestion of the particles retained in the filter followed by the digest analysis, or expressed as the difference between the total and dissolved contents.

Similarly, the acidification of the sample is also an important factor to consider. It is necessary to use an ultrapure acid preservative to prevent contamination as well as to make the dilution negligible or sufficiently reproducible for a dilution correction factor. The acidification of the sample will also depend on

the technique used to determine Se concentration and speciation and the requirements of sample matrix. Non-preserved samples, in addition to acting as a blank or baseline, can also give information about changes produced by the dilution caused by acidifying the sample.

In most of the studies where the partitioning and speciation of Se in FGDs have been studied, FGD waters were collected either directly from the flue gas absorber or from the solids separator overflow but no detail information about collection and preservation procedures were reported. In different studies at full-scale power plants [20-21; 52; 55], collected and refrigerated FGD water samples were filtered to $<0.45\mu\text{m}$ with a syringe filter, acidified at 1% HNO_3 and analysed during the next 24 or 48h by ICP-MS. However, no comparative collection and preservation methods were carried out.

Recently, significant efforts have been made by researchers to develop different sampling procedures in order to address the gap in current knowledge about how these factors may affect Se chemistry, partitioning and fate in FGDs.

In a study [7] in which FGD waters were obtained from six power plants in the United States, samples were collected in plastic containers filled completely to minimize headspace and exclude ambient air to avoid sample oxidation during transport and storage. Chemical preservation was excluded to avoid potential Se speciation changes. Samples were then shipped overnight on ice and were placed in an inert atmosphere glovebox after receipt. In the glovebox environment kept at 95% nitrogen and 5% hydrogen, a portion of each sample was syringe-filtered to $(0.45\mu\text{m})$ and stored in the glovebox for the duration of the project. Qualitatively results revealed that Se speciation in the samples remained intact for the duration of the project (up to 1 year), but minor quantitative changes were seen in some samples over time, indicating the need of further studies on the stability and preservation of Se species in this type of matrices.

EPRI [32] also studied three different approaches for FGD water preservation and storage. These three approaches consisted of filtering the samples through a $0.45\mu\text{m}$ pore size filter followed either by 1)

acidification of the sample at 1% HCl; 2) cryo-freeze in a bath of liquid nitrogen; and/or 3) no preservation. Samples left un-preserved and those acidified to 1%HCl were shipped on water-based ice while those cryo-frozen in a bath of liquid nitrogen were shipped on dry ice overnight and stored in refrigerators or nitrogen-filled gloves. These three approaches were applied to bench- and field-scale FGD samples, respectively, and were analysed within two days after collection. Results from bench-scale FGD showed that the cryo-freezing technique best preserved the Se speciation in the bench-scale FGD samples, while results from field sample preservation studies showed that filtered and unpreserved samples provided the best results.

5.2. Analysis and matrix interferences

In the selection of an analytical techniques to determine total Se or Se speciation it is necessary to consider the analytic concentration range, the physical and chemical properties of the matrix mentioned above and the possible interferences.

Se analysis has two common problems when it comes to determining its speciation a) the low concentration of the species, which are quite often below the limits of quantification and b) the matrix interferences [59]. Speciation of an element is generally achieved using hyphenated methods combining an efficient separation with a sensitive and selective detection. Speciation into different inorganic and organic species is needed for some biological samples and can be a complex task [61].

Colorimetric/spectrophotometric analyses [56; 62-64] are classical approaches to access Se and its speciation. Spectrophotometric methods are based on more or less specific reactions of colour metal complexes which can be assessed on the basis of the absorption of a certain wavelength of radiation passing through a studied solution. However, they have become obsolete as they are time-consuming and do not ensure a sufficiently low detection limit.

The most common spectrophotometric method to determine Se is the catalytic reduction of methylene blue to seleno-sulphides by sulphides [65]. Initially, methylene blue (MB) is reduced by sulphide as follows:

Subsequently, selenite (IV) is reduced to elementary selenium:

Selenosulphides are then stabilized by polysulphides:

Finally, a catalysed reduction of MB by selenosulphides takes place according to:

The sensitivity of the method can be enhanced to below 50 ng/mL, by applying a cationic surfactant such as cetyltrimethylammonium bromide (CTAB).

Another reagent for spectrophotometric determination of selenium is 6-amino-1-naphtho-sulphonic acid

The method is free from interference and allows achieving a detection limit of 80 ng/mL [64]. Also, selenium reacts with 2, 3-diaminenaphthalene in the presence of a catalyst such as bromide forming a complex which can be extracted by cyclohexane in an acid environment. The detection limit of the method is 12 ng/mL [65].

Instrumental methods, on the other hand, ensure shorter analysis time and higher detection capabilities. For applications where Se is present at mg/L (as in several wastewater samples), nitrous oxide/acetylene flame Atomic Absorbance Spectrometry can be employed. Electrothermal Atomic Absorption Spectrometry (ETAAS), also known as graphite furnace, is able to quantify selenium, using appropriate matrix modifiers (commonly Pd/Mg or Ni), with detection limits of 1-2 µg/L [56-68]. Plasmic spectrometric methods have also been extensively reported for elemental Se analysis [69-72].

Hydride generation (HG) used in combination with atomization of the hydride in AAS [73] and Atomic Fluorescence Spectrometry (AFS) [74] is a well-known separation technique. However, it is a chemical reaction that provides selenium separation as gas from the original matrix; therefore, variations in the sample matrices could result in changes in the reaction efficiency and does not quantify directly selenite and organo-selenide species.

High Performance Liquid Chromatography (HPLC) in combination with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) have similar performance to HG in terms of detection limits in complex matrices. HPLC-ICP-MS quantifies directly selenite and selenate and detects selenomethionine, methylseleninic acid, and selenocynate in the same run as inorganic species, and potentially offer more detailed information on individual organoselenide species. Difficulties in Se determination by ICP-MS are associated to its high ionization potential (9.75 eV) compared to argon (15.75 eV) and, as a consequence, its low ionization in an Ar plasma [75]. Additionally, Ar polyatomic interferences, especially $^{40}\text{Ar Ar}^+$ and $^{40}\text{Ar }^{38}\text{Ar}$ dimers, prevent selenium determination from its most abundant isotopes ^{80}Se and ^{78}Se . Hence, the less interfered and less abundant ^{82}Se isotope is generally monitored [76]. The problem of argon-based polyatomic interferences can be solved with the use of ICP-MS systems equipped with a collision/reaction cell (CRC). A dynamic CRC introduces helium, hydrogen, or other gases to the gaseous stream skimmed from the argon plasma to break down interfering molecules. By reducing matrix interferences, the risk of false positive is diminished and complex matrices need not to be diluted, resulting in lower detection limits. However, a constraint that has not been addressed as a limiting factor for Se quantification in FGD wastewaters with complex matrices is the possible interferences of the CRC.

Hydrogen or impurities contained in gases, can cause hydride formation from elements such as bromine. Therefore, in samples containing bromine as in the case of FGD wastewaters there would be an interference on ^{80}Se and ^{82}Se from bromine hydride. As a result, the ^{78}Se signal needs to be monitored to avoid misinterpretation of the results and alleviate the need for correction equations.

The determination of selenium by CSV entails the mixture of the sample with a copper solution to form a selenium copper compound, which is adsorbed to the surface of an electrode via a cathodic voltage. During the stripping process, selenium changes oxidation state by gaining electrons, which creates a current that is directly proportional to the selenium concentration in the sample. However, the determination of selenium by ASV entails, however, the selective oxidation of selenium during an anodic potential sweep.

Successful treatment with respect to reducing total Se concentrations in FGD wastewaters relies not only on establishing sample handling and preservation methods, but also on solving HPLC-ICP-MS dynamic CRC uncertainties that FGD wastewaters may cause by highly complex matrices containing bromine and other analytical techniques.

6. Operating FGD factors affecting removal technologies for selenium

Selenium removal from FGD wastewaters is definitely more challenging than most contaminants because of its complex chemistry. Selenium in FGD wastewaters may form an array of highly soluble aqueous complexes and particulate forms which make it difficult to treat. While prevention and reduction strategies for selenium cannot always be implemented, selenium management and control rely on treatment technologies. Technologies can be divided into physical, chemical and biological treatment technologies; their success in reducing selenium concentration in FGD wastewaters will depend on water matrix influences, system design and cost [77].

FGD wastewaters, as mentioned above, 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 [8]. These parameters along with water flow quantity, flow variability, and pressure will affect each technology by influencing the reaction kinetics, the mass transfer of the water and the constituents through the water treatment process [77]. Therefore, FAs not dissolved in the aqueous phase of the absorbent slurry, accumulated in the FGD scrubber, can also affect the physical, chemical and biological treatments of selenium. As mentioned in above sections, other matrix components on the water matrix that will affect selenium removal may be the oxidizing and reducing agents, complexing or chelating agents and/or competing oxyanions. Additionally, as it has been mentioned along this manuscript, selenium chemistry in FGD scrubbers varies overtime and with operating conditions. Therefore, the application prevention strategies and/or treatment options for selenium in FGD wastewaters may differ from full-scale power plants.

Although treatment technologies for Se in FGD wastewaters are not addressed in this manuscript, it should be pointed out that there is extensive literature documenting studies on Se removal technologies that can be consulted. Santos et al [61] reported an excellent overview of treatment options and recent advances in Se sorption methods. Chemical reduction, coagulation based processes, biological methods, membrane separation, and ion exchange and adsorption are among the treatment processes explained and described in detail in the abovementioned review. CH2MHILL [77] also reported an extensive review of available technologies for the removal of Se from water. In this review authors evaluated different technologies for the removal of Se from water derived from different industry sectors.

7. Conclusions

Selenium chemistry in FGD waters is more than the interconversion between selenite and selenate.

Selenium is capable of forming a complex array of chemical aqueous complexes some of them

analogous to those of sulphur as well as interact with polyoxosulfur anions to form Se-S aqueous

complexes. Both selenocynate (SeCN^-) and selenosulfate (SeSO_3^-) aqueous complexes have recently

been identified in FGD waters. However, most of Se-aqueous complexes encountered in FGD waters are

still unidentified. Two reasons may account for this observation: analytical methods may not achieve

accurate total selenium concentrations in complex FGD wastewater matrices and selenium speciation procedures that fail to account for the presence of any other selenium species besides selenite and selenate.

Research challenges with respect to the management of Se in FGDs rely on elucidating factors affecting selenite oxidation and how these factors interfere in the management and control strategies for Se in FGD wastewaters. High ORP conditions, often attained to maintain SO₂ removal performance of FGD scrubbers, promotes the formation of dithionate (S₂O₆²⁻), peroxydisulfate (S₂O₈²⁻), peroxymonosulfate (HSO₅⁻), and/or hypochlorite (OCl⁻), which are potential oxidizing agents involved in most mechanisms of selenite oxidation in FGDs.

FGD water re-circulation, accumulated in the FGD scrubber, water flow quantity, flow variability, and pressure are FGD operating conditions that may affect the implementation of effective strategies in management and control of Se. Their effect in FGD waters might influence the reaction kinetics and the mass transfer of the water and constituents through the water treatment processes. Other matrix components on the water matrix that will affect selenium removal might be the oxidizing and reducing agents complexing or chelating agents and/or competing oxyanions.

Development of effective strategies in management and control of Se is also complicated by difficulties in understanding the effect of sample handling and preservation methods on selenium speciation and determining analytical methods capable to yield accurate total selenium concentrations in complex FGD wastewater matrices.

Identification of factors involved in selenium chemistry, partitioning and fate are crucial to rule-make and lead to novel solutions for dealing with selenium discharges in water bodies and in stack emissions. If the partitioning and fate of selenium in an actual FGD have to be managed, it is highly recommended to evaluate the operating factors under which a specific FGD operates. Otherwise, recommendations on selenium management can hardly be implemented.

8. Acknowledgements

The corresponding author gratefully acknowledges the Oak Ridge Institute for Science and Education (ORISE), U.S Department of Energy, Office of Science, for awarding a ORISE postdoctoral fellowship to Dr. Patricia Córdoba.

9. References

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FIGURES

FIGURE 1. Partitioning and fate of selenium during PCC-FGD.

FIGURE 1.