The stability of arsenic and selenium compounds that were retained in limestone in a coal gasification atmosphere

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ABSTRACT

The aim of this work was to evaluate the stability of arsenic and selenium species retained in a lime/limestone mixture obtained by using limestone as a sorbent for gas cleaning in a coal gasification atmosphere. It was found that the stability of arsenic and selenium species produced by the gas–solid reactions with lime/limestone may be affected by their exposure to air and by their contact with water. The results confirm the conclusions of a previous work in which $Ca(AsO_2)_2$ and CaSe was postulated as the products of the reaction between the arsenic and selenium species present in a coal gasification atmosphere with lime/limestone. Moreover it was proved that the compounds ($Ca(AsO_2)_2$ and CaSe) may undergo transformations when the sorbents post-retention are stored or disposed of in air. From the results obtained by XAFS it was possible to identify the $Ca_3(AsO_4)_2$ produced by the oxidation of the $Ca(AsO_2)_2$ on the sorbent surface. The XAFS results for selenium showed that the CaSe formed on the sorbent was transformed to form several species, but mainly elemental Se. These changes in the speciation of arsenic and selenium may explain the behavior of the sorbent post-retention during the water solubility test. Although the selenium compounds and the products that may originate from their decomposition in water are not toxic, in the case of arsenic, species like $Ca(AsO_2)_2$ and $Ca_3(AsO_4)_2$ may lixiviate, and generate toxic arsenic compounds in solution that could pose a risk when the sorbent is finally disposed of.

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1. Introduction

Limestone and lime are widely employed as sorbents for sulfur capture in coal power generation processes. They have also been proved to have good retention characteristics for other elements such as arsenic and selenium [1–4]. It is well known that arsenic is a toxic element and that selenium may also represent a risk at high concentrations. Different species of both these elements may be present in flue gases from coal power generation plants [5–7]. In order to avoid the problems that these elements may originate in the coal gasification process, a study was carried out on arsenic and selenium capture by limestone/lime at different temperatures [4]. In this study theoretical calculations using thermodynamic data at equilibrium suggested that $Ca(AsO_2)_2$ and CaSe would be the main products of possible reactions with lime/limestone. After the sorption experiments, CaSe was identified by XRD. Arsenic was also identified in the form of $Ca(AsO_4)_2$ the formation of which was not predicted in a gasification atmosphere and was ascribed to the oxidation of $Ca(AsO_2)_2$ on the post-retention sorbent [4]. Because the

sub-products produced in gas cleaning processes in energy generation from coal combustion, are recovered or disposed of as a waste, the transformations that the toxic arsenic and selenium compounds undergo in these sub-products, need to be controlled.

The toxicity of an arsenic-containing compound depends on its valence state (zero-valent, trivalent, or pentavalent), its form (inorganic or organic), and the physical conditions that govern its absorption and elimination. In general, inorganic arsenic is more toxic than organic arsenic while trivalent arsenic is more toxic than pentavalent or elemental arsenic. Although calcium arsenite and calcium arsenate are species of low water solubility, they may dissolve depending on the oxygen content, pH and redox potential of the solvent [8]. Selenium is a toxic element at high concentrations but it is also a nutritionally essential element. Hydrogen selenide is the most toxic selenium compound over a short term and selenium sulfide is the only selenium compound that has been shown to be carcinogenic in animals. Although the U.S. EPA [9] has established that elemental selenium is not classifiable from the point of view of human carcinogenicity, CaSe identified as the main product of selenium capture in limestone in a gasification atmosphere [4], is known to decompose in water and may undergo transformation via different reactions.

The capture of toxic trace elements in non-regenerable solid sorbents requires a good knowledge of the composition of the species

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captured and of the transformations that occur on the sorbent surface. This knowledge is not only necessary in order to understand the retention mechanism of the toxic species, but also to be able to predict its future behavior in the sorbent waste and to prevent the possibility of lixiviation when the waste is finally disposed of. Thus, inferring the modes of occurrence of arsenic and selenium in the post-retention sorbent and their possible transformation is a matter of considerable importance.

The objective of the present work was to evaluate the transformations of arsenic and selenium compounds retained in lime/limestone during coal gasification when these sorbents are stored or disposed of in air or exposed to an aqueous environment.

2. Materials and methods

2.1. Samples

Some of the samples used in this work (As1, As2, As3, Se1 and Se2), were sorbents post-retention obtained from a previous work [4]. In addition samples Se3 and Se4 were prepared specifically for the present study. The retention experiments were carried out using laboratory-scale equipment already described in the previous work [4], in a gas atmosphere typical of a coal gasification process (57.6%, v/v CO; 3.30%, v/v CO_2; 18.8%, v/v H_2; 4.00%, v/v H_2O balanced with N_2) but in the absence of sulfur species in order to avoid competitive reactions. Samples As1, As2 and As3 were obtained after the retention of arsenic species in the gas atmosphere at 350, 550 and 750 °C, respectively. Se1 and Se2 were obtained after the retention of selenium species in the gas atmosphere under the same conditions at 550 and 750 °C, respectively. The raw material used as sorbent was limestone subjected to thermal treatment at 900 °C in a coal gasification atmosphere. After treatment the mineral phases identified were a mixture of lime and limestone, lime representing the greater proportion. The lime/limestone sorbent was found to have a greater porosity than the original limestone, the surface area values being $4.9 \, mg \, g^{-1}$ for the raw material and $9.7 \, mg \, g^{-1}$ after the thermal treatment. Samples As1, As2, As3, Se1 and Se2 were stored in air during 48 months and Se3 during 6 months. The sample Se4 was kept for the same period of time (6 months) in argon.

X-ray diffraction (XRD) and X-ray absorption fine structure spectroscopy (XAFS) were employed to identify the arsenic and selenium species in the sorbents post-retention [10–11]. The sorbents post-retention were analyzed after being stored in air for more than 1 year. In addition, fresh post-retention sorbents containing selenium were prepared and divided into two sub-samples that were stored in air and argon atmospheres for several weeks before being analyzed.

A least-square fitting method [10,11] was used to estimate the relative fractions of As^{3+} and As^{5+} in the sorbent samples by means of X-ray absorption near-edge structure (XANES). The spectra were fitted to pseudo-Voight functions for individual As^{3+} and As^{5+} absorption peaks and an arctangent function for the arsenic absorption edge using the WINXAS program [12]. Estimates of selenium speciation were derived from FEFF6 modeling of extended X-ray absorption fine structure spectroscopy (EXAFS). FEFF6 model functions for elemental Se, CaSe, and sodium selenate were calculated using the TKAtoms program [13] and the experimental data were fitted to the FEFF6 functions using the SIXPack software [14].

2.2. Theoretical calculations using thermodynamic data at equilibrium

Thermodynamic equilibrium calculations were performed on HSC-Chemistry 5.1 software to predict the solubility of the compounds formed or transformed on the sorbent surface in an aqueous solution. The thermodynamic stability of each species was inferred from Eh–pH diagrams. Stable areas were evaluated as a function of pH and electrochemical potential scales.

2.3. Water solubility test

A water solubility test was carried out by stirring the sorbent post-retention in water at 40 °C for 2 h. The proportion of sorbent to water was 0.1 g of sorbent per 25 ml of water. After extraction, the solid was filtered and the arsenic and selenium contents in the solutions were determined by ICP-MS. The redox potential and pH were monitored during extraction by means of a pH-meter.

3. Results and discussion

$Ca_3(AsO_4)_2$ and CaSe had been identified by XRD in the post-retention sorbent [4]. The formation of CaSe in the experimental conditions employed had been theoretically justified by thermodynamic calculations. However, the formation of $Ca_3(AsO_4)_2$ under gasification conditions could not be predicted [4]. The presence of $Ca_3(AsO_4)_2$ in the sorbent is probably due to the oxidation of $Ca(AsO_2)_2$ which occurs during the manipulation of the sorbent between the retention experiments and the XRD analysis. To confirm this supposition and to see whether CaSe may undergo a similar oxidation process, the samples were stored in air and later characterized not only by XRD but also by XAFS spectroscopy.

Arsenic and selenium XAFS spectra of the first set of sorbents post-retention which had been exposed to air for 48 months (As1, As2, As3, Se1 and Se2), are presented in Figs. 1 and 2, respectively. Fig. 1 shows that the proportion of oxidized arsenic differs considerably in the three samples. The arrows in the As XANES plot indicate the position of the peaks for each individual arsenite and arsenate species. The spectra clearly show that the three samples contain both As^{3+} and As^{5+} in different proportions. On the basis of previously obtained data for mixtures of arsenite and arsenate species, approximate compositions were estimated (Table 1). From the data it can be inferred that the arsenic retained as $Ca(AsO_2)_2$ underwent oxidation, giving rise to $Ca_3(AsO_4)_2$. Maximum retention capacities (MRCs) for arsenic decrease as the temperature rises but the proportion of compound oxidized cannot be attributed to the conditions of the retention experiment (Table 1). In the case of the As EXAFS/RSF spectra (Fig. 1), the difference in peak position between the arsenite and arsenate species cannot be reliably resolved and cannot be quantified.

The study on selenium capture in lime/limestone was carried out at two temperatures, 550 and 750 °C [4] and the samples obtained after the retention process, Se1 and Se2 were also analyzed by XAFS spectroscopy (Fig. 2) after being exposed to air. The selenium in these samples also exhibits different oxidation states. In sample Se1, the dominant oxidation state is as elemental Se, minor amounts of oxidized species being identified. The predominant state of oxidation of sample Se2 is also elemental Se, although in this case the quantity of oxidized selenium species is significantly higher (Fig. 2). Unlike the fresh post-retention samples [4] in which CaSe was identified as the main species of selenium, after exposure to air, oxidized Se (SeO_3^{2-} and/or SeO_4^{2-}) and elemental Se were the predominant species. This demonstrates that after a long period in air, CaSe undergoes hydrolyzation and oxidation. The amounts of elemental Se and oxidized Se species in these samples were estimated from FEFF modeling of the contributions of elemental (Se–Se) and oxidized (Se–O) Se coordination shells to the EXAFS regions (Fig. 2). Based on this fitting, the percentages of each form of Se are given in Table 2. To confirm these findings, a fresh
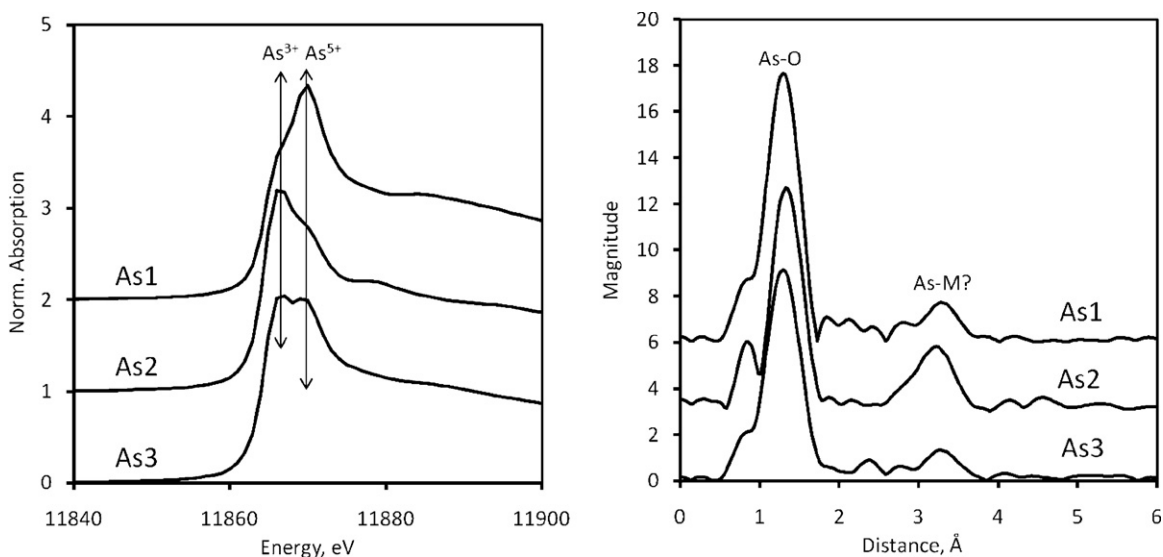
Fig. 1. Arsenic XANES spectra (left) and radial structure functions (RSFs) obtained from the arsenic EXAFS region (right) of post-retention limestone/lime samples stored for 48 months.
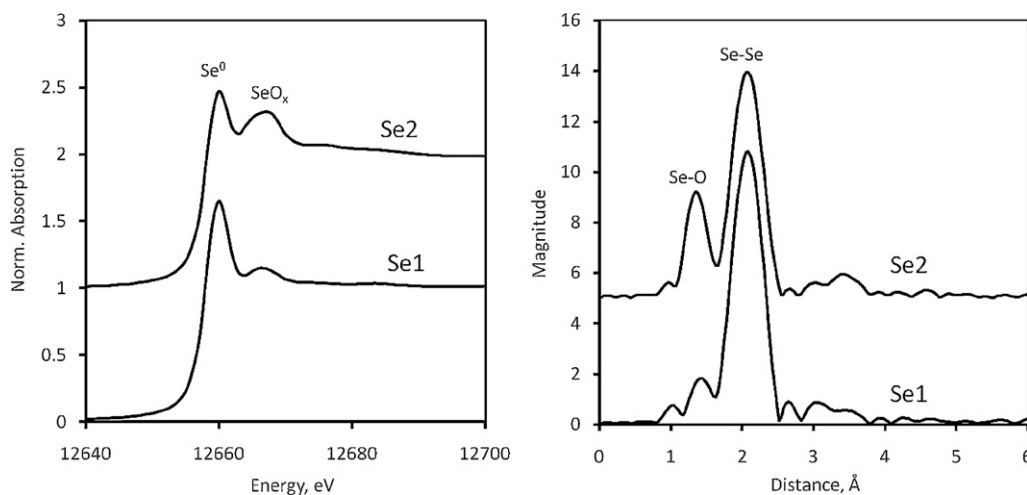

Fig. 2. Selenium XANES spectra (left) and radial structure functions (RSFs) obtained from the selenium EXAFS region (right) of post-retention limestone/lime samples stored for a long period.

Table 1
Quantity of arsenic retained at different temperatures, water solubility and percentage of As in different oxidation states estimated from XAFS data.

Sample	Results of retention experiments		Results of water solubility experiments at 26 °C			Results of XANES	
	T (°C)	MRC (mg g^{-1})	pH	Redox potential (mV)	% As dissolved	% As as As^{3+}	% As as As^{5+}
As1	350	17.8 ± 1.40	10	−159	33	60–65	35–40
As2	550	15.2 ± 1.29	11	−224	24	90–95	5–10
As3	750	8.92 ± 0.63	10	−172	34	80–85	15–20

sample of sorbent post-retention was prepared at 550 °C and then divided into two sub-samples. One sub-sample (Se3) was stored in air and the other (Se4) in argon. Both samples were analyzed by XAFS and XRD after 6 months. The characterization of these samples

(Figs. 3 and 4) indicates that CaSe is the principal product formed when selenium is captured in limestone/lime in a coal gasification atmosphere. CaSe was identified by XRD (Fig. 3) and XANES (Fig. 4), in the sample stored in argon (Se4), whereas in the sample stored in

Table 2
Quantity of selenium retained at different temperatures, water solubility and percentage of Se in different oxidation states estimated from XAFS data.

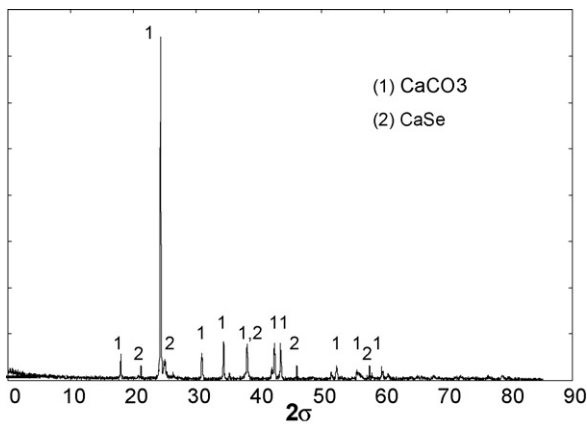| Sample	Results of retention experiments		Results of water solubility experiments at 26 °C			Results of XANES	
	T (°C)	MRC (mg g^{-1})	pH	Redox potential (mV)	% Se dissolved	% Se as Se^0	% Se as SeO$_x^{2-}$
Se1	550	51.8 ± 5.96	11	−209	15	90–100	0–10
Se2	750	65.9 ± 4.88	11	−234	12	75–85	15–25

Fig. 3. X-ray diffractogram of post-selenium retention limestone/lime samples stored under argon atmosphere.

air (Se3) elemental selenium was the main species present, corroborating the transformation of CaSe when the post-retention sorbent is disposed of in air. Using FEFF6 analysis and least-square fitting of the EXAFS region, it was calculated that 80–90% of the total selenium was CaSe in the sample stored under argon, whereas only

40–50% was identified as CaSe in the sample exposed to air, the remainder occurring in the form of elemental Se.

The results of the water solubility test are presented in Tables 1 and 2. No relationship was found between the percentage of As dissolved and the total quantity of arsenic in the sample (MRC value), i.e. arsenic is dissolved in the minimum proportion in the sample that was used as sorbent at 550 °C, in which the arsenic concentration was intermediate. This would imply random conduct if the proportion of As^{5+} in the sample were not taken into consideration. However, bearing in mind that analysis by XANES provides an approximate estimation of the proportion of arsenite and arsenate species in the sorbent samples, a clear relationship between the quantity of arsenic dissolved in the water and the proportion of the different oxidation states can be observed (Table 1).

The solubility of $Ca(AsO_2)_2$, $Ca(AsO_4)_2$ and CaSe in wastes under the alkaline conditions originated by the dissolution of the sorbent can be theoretically estimated using a thermodynamic equilibrium approach. The Eh–pH diagrams for the arsenic and selenium species obtained in similar conditions to the solubility tests are shown in Fig. 5. It can be observed that arsenate ions are formed in the water solution at pH > 9.0. In the case of selenium selenide, the ions are stable even in an acid solution (pH < 5.0). The upper and lower stability limits for water are represented in the diagram by dotted lines.
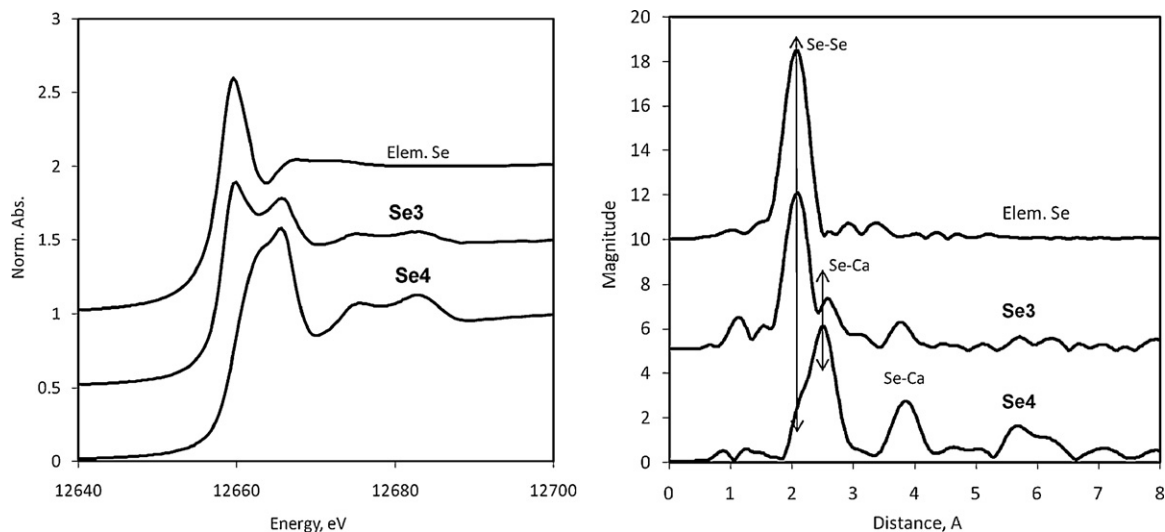

Fig. 4. Selenium XANES spectra (left) and radial structure functions (RSFs) obtained from the selenium EXAFS region (right) of elemental Se and two post-retention subsamples: one stored under argon and the other exposed to air.
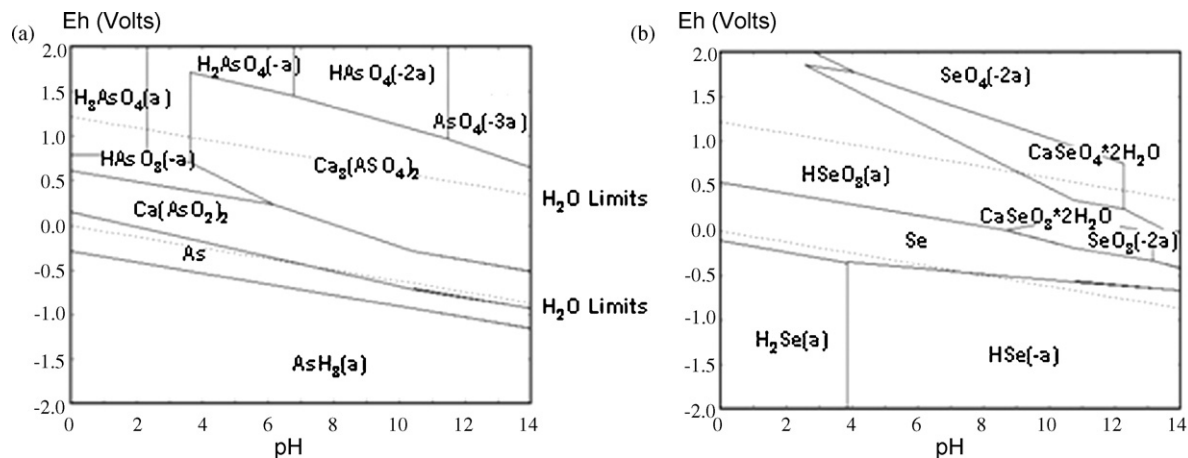

Fig. 5. Eh–pH diagrams predicted by thermodynamic equilibrium calculations for (a) arsenic and (b) selenium in experimental conditions.

The Eh and pH values for the water solubility tests carried out at 26 °C are presented in Tables 1 and 2. If these values are taken into account it may be concluded that the experimental results agree with the theoretical predictions. Although in pure water arsenic and selenium will prevail in solution as a neutral species, in the solutions obtained from the limestone/lime sorbent, the pH value ranged from 10 to 11. In these conditions arsenate ions are stable. In fact, the maximum dissolution of arsenic takes place in the post-retention sorbents which as can be seen from XANES results, showed the highest proportion of As[5+] (Table 1). The redox potential increases as the concentration of aqueous ions increases. In the case of selenium an increase in selenium solubility is accompanied by an increase in the proportion of Se[−2] in the sorbent. This can be expected, given that CaSe is an ionic compound which decomposes in water.

4. Conclusions

The results of this work confirm that CaSe is the main product formed when selenium species are retained in lime/limestone in a coal gasification atmosphere and that this compound undergoes oxidation when it is exposed to air. The results also demonstrate that, although $Ca(AsO_2)_2$ is the main species to be formed when arsenic is retained in a gasification atmosphere, this species oxidizes in air and is transformed into $Ca_3(AsO_4)_2$. Although the products resulting from CaSe decomposition are not toxic, dissolved arsenate may pose a risk for the environment and human health especially when these wastes are stored or disposed of in air.

Acknowledgments

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