TRACE ELEMENT REMOVAL FROM HOT GASIFICATION FLUE GASES USING SOLID SORBENTS

M. DÍAZ-SOMOANO
M. A. LÓPEZ-ANTÓN
M. R. MARTÍNEZ-TARAZONA*

Instituto Nacional del Carbón (CSIC)
Francisco Pintado Fe 26, 33011 Oviedo, Spain

*to whom all correspondence should be addressed:
Tel: +34 985118988; Fax: +34 985 297662
e-mail: rmtarazona@incar.csic.es

ABSTRACT

Coals contain elements which, although usually found in concentrations lower than 1% (trace elements), can give rise to environmental or technological problems. After gasification most of these elements may occur in gas phase in different proportions. In order to avoid the problems that the presence of trace elements in gas phase can originate during coal gasification processes, a suitable technology needs to be developed. The systems currently being studied and developed for gas cleaning in coal gasification, focus on the removal of sulphur, particulate matter, nitrogen, alkali metals and halogens but not on corrosive or toxic trace elements. Nevertheless, the reduction of trace elements using solid sorbents in gas phase at high temperatures appears to be a promising method for combustion systems.

The main objectives of this work were to determine the capacity of different solid sorbents for retaining arsenic, selenium, cadmium and zinc species in gases from coal gasification systems at 550 and 750 ºC and to find out how the sorbent characteristics and operational variables (temperature and gas composition) influence retention. To attain these objectives *the sorption capacity* (mg of element per g of sorbent) and the *efficiency* (percentage of element retention) were determined. The study was carried out in a laboratory scale reactor, in which the sorbent was employed as a fixed bed, using synthetic gas mixtures. At the end of each experiment, the sorbent bed (mixture of sorbent + sand) was finely ground and dissolved in a microwave oven with HF, HNO_3 and H_3BO_3, and the element in solution was determined by ICP-MS.

The results are discussed in the light of the data for combustion conditions reported in the literature, and possible retention mechanisms are proposed. Different amounts of arsenic, selenium, cadmium, and zinc can be retained in solid sorbents at high temperatures. It was observed that, in a coal gasification atmosphere, limestone, fly ashes and metallic oxide mixtures containing spinels, were the best sorbents, though in each case the retention capacity depended on temperature and atmosphere. Retention capacities between 16-24 mg g^{-1} were obtained using limestone and fly ashes for arsenic retention. For selenium, the maximum retention capacities ranging between 50-56 mg g^{-1} were attained using limestone. Alumina in a gasification atmosphere containing HCl was the best sorbent for zinc removal (52 mg g^{-1}). The lowest retention capacities were obtained for cadmium, these being <1 mg g^{-1} for the different sorbents tested. Retention probably proceeds through different mechanisms, but in most cases a chemical reaction is involved.

KEYWORDS: Trace element, solid sorbent, retention, gasification, high temperature

1. INTRODUCTION

Most of the elements are present in coal in different proportions, and although some are in concentrations lower than 0.1% (trace elements) these may give rise to various environmental or technological problems during energy production. Although information about the presence of trace elements in flue gases from gasification systems is scarce, it can be assumed that

after coal gasification some of these elements are present as compounds in gas phase in different proportions. In fact, elements such as As, Cd, Se and Zn, among others, have been identified in raw gases from coal gasification [1], [2]. To avoid the problems these elements may originate during coal gasification processes (e.g.corrosion, or environmental pollution), a suitable technology needs to be developed to reduce their presence in flue gases. One possible option is to capture these trace elements inside the gasification plant by means of sorbents. However, to develop the necessary technology, research must be carried out into their possible retention by materials that might serve as sorbents. Until now, gas cleaning for coal gasification has been mainly focused on the removal of sulphur compounds [3], [4], and to a lesser extent of corrosive halogens and alkali metal species in gas phase at high temperatures by adsorption on different sorbents [5], [6]. Relatively little research has been carried out on the removal of trace elements [7], [8], [9], [10], [11]. Much work remains to be done in order to develop the appropriate sorbents and conditions for capturing harmful trace elements and understanding the mechanisms that govern their retention capacity.

In spite of the different conditions of combustion and gasification environments, a study of the retention of trace metal elements during coal combustion and wastes incineration [12], [13], [14], [15], [16], [17], [18], [19], [20], [21], [22], [23], [24] may provide a useful basis for developing a similar methodology in coal gasification atmospheres. In previous works, studies of lead and cadmium retention in bench-scale thermo-gravimetric reactors with fixed beds, using silica, alumina, kaolinite, emathite and lime, at 700ºC and 800ºC, in gas atmospheres of CO_2, O_2, N_2 and H_2O [13], [14], [15], have demonstrated that bauxite and, to a lesser degree, kaolinite, are effective sorbents for the removal of cadmium in combustors and incinerators. Although bauxite and kaolinite captured approximately the same amount of lead from flue gas, kaolinite has a larger capacity for lead removal, the overall sorption process being a combination of adsorption, condensation, diffusion and chemical reaction. Experiments carried out in a simulated waste heat boiler using sand, limestone, alumina, bauxite and zeolite [16] confirmed that bauxite, zeolite and limestone are effective sorbents for both lead and cadmium capture.

The efficiency of direct sorbent injection for the control of trace metal emission using hydrated lime, limestone, kaolinite and bauxite was also tested in a previous research study [17]. Reductions in submicrometer concentrations of Sb, As, Hg and Se were observed when hydrated lime and limestone were injected. In contrast the total amount of As, Cd and Pb captured increased when hydrated lime, limestone and kaolinite were used. The capacity of silica, diatomaceous earth, kaolinite, bauxite, alumina and attapulgite clay, to capture arsenic, cadmium, chromium, lead and nickel was evaluated comparatively, kaolinite, and attapulgite clay showing the greatest promise as potential sorbents [18]. Some of these sorbents were also tested for their capacity to retain arsenic and selenium compounds at high temperatures in combustion atmospheres, and in this case calcium hydroxide was found to be the most effective. It was observed that the capture mechanism in these cases does not involve simple physical adsorption but proceeds by means of chemical reactions that give rise to solid products [20], [21]. Arsenic retention in combustion atmospheres was also evaluated using mixtures of metal oxides, or metal oxide and zeolite, with an efficiency level of up to 70% [22].

From the published work cited above it can be inferred that most of the knowledge obtained until now on trace element retention in solid sorbents has been acquired from studies at laboratory scale, carried out in combustion and waste incineration conditions. Consequently, the sorption mechanisms are still not fully understood. The present work is based on a series of studies [7], [8], [9], [10], [11], performed in order to ascertain the capacity of different solid sorbents, commonly used in combustion systems, for retaining trace element species in hot gases from gasification systems.

2. EXPERIMENTAL SECTION

A number of solid materials were tested as sorbents. These solids have already been studied for trace element retention in combustion systems and can be classified into two groups: i) natural products and industrial wastes (kaolinite, limestone and fly ashes) and ii) commercial products (alumina and metal oxide mixtures). Kaolinite and limestone were taken from deposits located in Asturias (Spain), while the fly ashes were collected from a fluidized bed

power plant (La Pereda-Asturias) in which limestone is used in the bed. The sorbents were characterised by means of several techniques. X-ray Fluorescence (XRF) and Inductively Coupled Plasma-Mass (ICP-MS) were employed to determine the elemental composition. The crystalline species were identified by X-ray Diffraction (XRD). The particle size was determined in a Coulter Counter apparatus, while the surface area was measured by volumetric adsorption of nitrogen at 77K.

Sorption experiments were carried out using a lab-scale device (Figure 1) which consisted of a quartz reactor equipped with two tubes, one inside the other and heated by two furnaces. The trace element in gas phase was obtained from the evaporation of a solid compound. The sorbent and element source were placed inside the inner tube but heated separately in the two furnaces. Three synthetic gas mixtures, typical of coal gasification, containing 58% CO, 3% CO_2, 19% H_2 and 4% H_2O, balanced with N_2 were employed. Mixture I only contained gases. Mixture II also had 0.05% of HCl, while Mixture III contained 0.9% of H_2S. These gas mixtures carried a known concentration of the element compound out through the sorbent bed in vapour phase at a flow rate of 0.5 l min^{-1}. The element not retained by the sorbent was captured in impingers containing HNO_3 0.5N. The sorbent bed, 2.5 cm in diameter and 1.1 cm in height, was prepared by mixing 1 g of sorbent with 3 g of sand. The retention experiments for arsenic and selenium were performed at 550 and 750 ºC and for cadmium and zinc at 750 ºC. The conditions of the experiments evaluated for each element (temperature and gas composition), were fixed according to a theoretical study based on thermodynamic equilibrium data [2]. In order to avoid sorbent transformations during the experiments, the sorbent was subjected to thermal treatment before being used, in the same gas composition at 900ºC, except for the metal oxide mixtures for which the maximum operation temperature was 600 ºC. The amount of element retained in the sorbent was analysed by ICP-MS after dissolution in a microwave oven. The sorption capacity (mg of element per g of sorbent) and efficiency (percentage of element retention) were then evaluated. To determine maximum retention capacity (MRC), a series of experiments were conducted, in which the quantity of the element was gradually increased until the sorbent was saturated.

The amount of sulphur retained when it was present in the gasification atmosphere (mixture III), was determined in an automatic analyser. Water solubility tests and thermal stability studies of sorbent post-retention were also carried out. The water-soluble fraction was obtained by stirring a portion of the sorbent bed mixed with Milli-Q water in an ultrasonic bath at 40ºC for two hours [8], [17]. Desorption was evaluated in an element-free gasification atmosphere at the same temperature as the retention experiment.
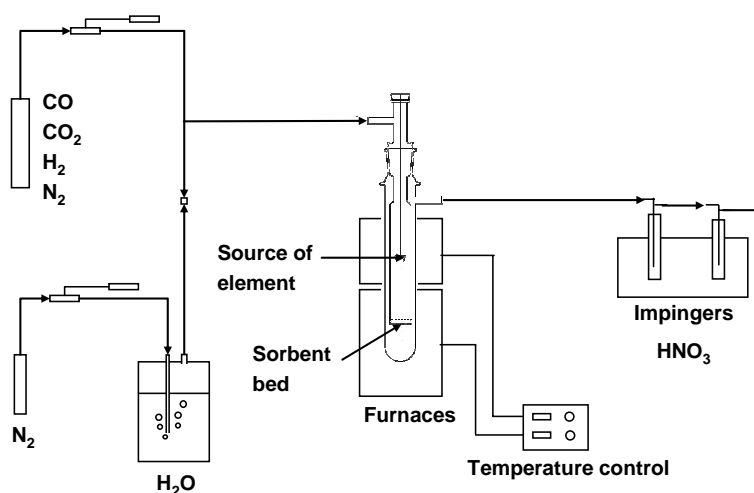

Figure 1. Schematic diagram of the experimental device

3. RESULTS

The sorbents used in this study were non-porous solids of a low surface area with the exception of alumina. The original alumina had a surface area of 118 m^2 g^{-1} which decreased to 82.5 m^2 g^{-1} after thermal treatment at 900ºC before the solids were used as sorbents. The particle sizes of the sorbents ranged from 14.6 to 26.0 µm (Table 1). It was found that their characteristics changed after the conditioning treatment at 900ºC in the gasification atmosphere. Their final composition is given in Table 2.

Table 1. Average Particle Size (A.P.S.) and surface area (S. Area) of the sorbents

	Kaolinite	Limestone	Fly ash	Alumina	ZT	ZFT
A. P. S	15.7	14.6	25.7	26.0	19.3	19.3
S. Area	11.5	4.91	11.9	118	6.54	0.30

The capacity and efficiency of these sorbents for retaining As, Se, Cd and Zn compounds in gas phase at different temperatures and atmospheres are discussed in the following sections. In a general overview of the results presented in Tables 3-7, significant differences can be observed between the sorbents and elements depending on the experimental conditions. The maximum retention capacities range between a maximum of 56 mg g^{-1}, obtained for the retention of selenium using metal oxide mixtures, and a minimum; 0.001 mg g^{-1}, for cadmium using limestone. It should be noted that the retention of Cd was lower than 1 mg g^{-1}, except in the case of fly ashes where a 10% retention efficiency was achieved. Although capture may vary at 550 and 750ºC, no relationship between the influence of temperature and the retention of elements was found. In some cases an increase in temperature entailed increasing retention, as in the case of arsenic in fly ashes in the gas atmosphere referred to as mixture I. However, the amount of arsenic captured in the limestone in mixture I decreased. The influence of the gas atmosphere also varies for different elements and sorbents, but in general this influence is not as strong as when the gas atmosphere contains sulphur or chlorine compounds. The most remarkable exception was the retention of Zn in alumina which increased significantly in the presence of chlorine.

The results show that there is no universally optimum sorbent, temperature or atmosphere for trace element capture. Nevertheless some of the sorbents may be considered more generally applicable than others. The conditions that determine their applicability are discussed below.

3.1. Kaolinite

Kaolinite was employed as a sorbent for retaining Pb, Cd, Cu, Cr and alkali in combustion and waste incineration atmospheres, efficiencies being in the order of 30-50 % for Pb, 10-% for Cd and Cr, 20 % for Cu and close to 100% for alkalis, depending on the temperature and experimental conditions [12], [15], [16], [19]. However, as far as we know, there are no published works on the retention of As, Se and Zn by this sorbent nor on combustion or gasification atmospheres. In our work, the maximum retention capacity for kaolinite was 6 mg g^{-1}, whereas efficiencies ranged between 35 and 19 %, for arsenic and selenium in the gasification atmosphere free of H_2S, these efficiencies decreasing considerably in the presence of H_2S (Table 3). The different behaviour in the presence of H_2S may be due to the different gaseous species theoretically predicted for both atmospheres [2] or to the condensation of sulphur on the surface of the solid [23]. The amount of sulphur retained by the kaolinite sorbent during the thermal treatment was 0.4 mg g^{-1}, the proportion of the S/element retained during the experiments being 1.6 mg g^{-1} S/0.66 mg g^{-1}. Because kaolinite is a non-porous solid with a low specific surface area physical adsorption can be expected to be low. Moreover, the high experimental temperatures and efficiencies point to a more complex mechanism than merely physical adsorption, involving various gas-solid interactions. Desorption occurred for As, Se and Cd in proportions varying from 40 to 80 %, which clearly suggests the involvement of physical adsorption mechanisms. Water solubility was found to be low for the different elements (2-16%), the highest value being that of arsenic.

The low retention obtained for cadmium and zinc was not influenced by the gas composition (Table 3). As already mentioned kaolinite is a good sorbent for Cd in combustion

atmospheres, where retention takes place via chemical reaction, the new species being identified by means of XRD [14], [15], [16]. However, as these species require an oxidant atmosphere, these reactions do not occur in a gasification atmosphere.

Table 2. Crystalline species identified in the thermally treated sorbent

Sorbent	Original	Mixture I	Mixture II	Mixture III	Mixture IV
Kaolinite	Kaolinite, 1Md $(Al_2Si_2O_5(OH)_4)$ Pyro-illite, 2M1 $(Al_2Si_4O_{10}(OH)_2)$ Cuarzo (SiO_2)	Aluminium Silicate $(Al_2Si_4O_{10})$ Quartz (SiO_2)			
Limestone	Calcite $(CaCO_3)$	Lime (CaO) Calcite $(CaCO_3)$ Portlandite $(Ca(OH)_2)$	Calcite $(CaCO_3)$ Portlandite $(Ca(OH)_2)$ Hydrophillite $(CaCl_2)$	Oldahmite (CaS) Lime (CaO) Portlandite $(Ca(OH)_2)$	
Fly ash	Quartz (SiO_2) Anhidrite $(CaSO_4)$ Hematite (Fe_2O_3) Illite $(KAl_2Si_3AlO_{10}(OH)_2)$	Quartz (SiO_2) Anhidrite $(CaSO_4)$ Oldahmite (CaS) Hematite (Fe_2O_3) Illite $(KAl_2Si_3AlO_{10}(OH)_2)$			
Alumina	γ-Aluminium oxide (Al_2O_3)	Aluminium oxide (Al_2O_3) γ-Aluminium oxide (Al_2O_3)			
ZT	Zn, Ti Oxide (Zn_2TiO_4) Rutile (TiO_2) Cincite (ZnO)	Zn, Ti Oxide (Zn_2TiO_4) Rutile (TiO_2) Wurtzite (ZnS)		—	
ZFT	Franklinite $(ZnFe_2O_4)$ Cincite (ZnO) Rutile (TiO_2)	Franklinite $(ZnFe_2O_4)$ Wurtzite (ZnS) Rutile (TiO_2)		—	

Table 3. Maximum retention capacities (MRC, mg g^{-1}) and efficiencies (E, %) in kaolinite

Element	T (ºC)	Mixture I		Mixture II		Mixture III	
		MRC	E	MRC	E	MRC	E
As	550	6	35	—	—	1	10
	750	6	24	—	—	0	0
Se	550	6	13	—	—	2	5
	750	6	19	—	—	3	12
Cd	750	0.008	<1	0.008	<1	—	—
Zn	750	1.5	19	1	18	—	—

3.2. Limestone

Limestone/hydrated lime is a sorbent that is frequently used to capture sulphur compounds in energy production from coal in both types of process, combustion and gasification. As demonstrated in previous works arsenic and selenium can be retained in limestone in a combustion environment in which case retention capacities range between 2-7 mg g^{-1} and 2-13 mg g^{-1}depending on temperature, respectively [20], [21]. This work also shows that limestone acts as a good sorbent for arsenic in a gasification atmosphere. In fact, high retention capacities were obtained for both arsenic and selenium (Table 4). For arsenic the retention capacity decreased with temperature and in the presence of H_2S. However for selenium, it remained nearly the same in all conditions. This different behaviour is possible due to the retention of sulphur. Amounts ranging between 80 and 200 mg g^{-1}, were found in the sorbent post-retention, these quantities increasing with temperature. This suggests that sulphur and selenium are captured simultaneously, while in the case of arsenic the presence of sulphur in the gas mixture produces a decrease in retention capacity. The reason for this may be the formation of a different species of arsenic, AsS(g), in the gas atmosphere containing sulphur, as predicted by the theoretical data at equilibrium [2]. The desorption test indicated that the arsenic and selenium compounds retained are stable. Moreover, whereas the arsenic retained presents a high solubility in water, selenium water solubility is low. XRD examination of the post-retention sorbent indicates that $Ca(AsO_2)_2$ and CaSe are the products of the chemical interaction [8]. A similar mechanism was proposed in the literature for the retention of these elements by limestone in combustion, where $Ca_3As_2O_8$ and $CaSeO_3$ were the compounds identified [20], [21].

Few previous cases have been reported of cadmium and zinc retention by limestone in combustion or gasification atmospheres. In incineration gas conditions calcium oxide has been found to be an effective sorbent for cadmium retention [15]. In this work low retention capacities were obtained for these elements. The differences observed for cadmium retention in gasification atmospheres compared to the results in the literature for combustion can be attributed to the properties of the different species of cadmium present in both atmospheres [2].

Table 4. Maximum retention capacities (MRC,mg g^{-1}) and efficiencies (E,%) in limestone

Element	T (ºC)	Mixture I		Mixture II		Mixture III	
		MRC	E	MRC	E	MRC	E
As	550	16	95	—	—	<1	6
	750	9	22	—	—	<1	2
Se	550	50	55	—	—	53	70
	750	65	92	—	—	56	76
Cd	750	<0.001*	<0.1	0.001	<0.1	—	—
Zn	750	0.5	2	0.2	3	—	—

3.3. Fly ashes

The capture of trace elements in fly ashes in combustion power stations has been extensively studied in the evaluation of the evaporation/condensation process in flue gases. These studies show that volatile elements such as As, Cd, Zn, etc. condense on the smaller size fly ash particles in flue gases [7]. Moreover, some works have explored the possibility of recycling the fly ashes to improve trace element capture [23]. The capacity of fly ashes to act as sorbents has also been evaluated. The work in this area has mainly concentrated on mercury capture, and especially on the capacity of the unburned coal particles present in fly ashes to retain this element [24]. As in the case of the other sorbents, fly ashes were tested in the present work as a fixed bed sorbent. In the conditions of this work efficiencies close to 100 % were achieved for arsenic, maximum retention occurring at high temperature (750ºC). Although efficiencies were found to be lower for selenium and zinc, the retention capacities for these elements were as high as 25 and 16 mg g^{-1} respectively (Table 5). A decrease in

retention capacities and efficiencies was observed when H_2S was present, depending on temperature, unlike the case of arsenic and selenium. However, sulphur retention by fly ashes, of between 8-15 mg g^{-1}, was lower than the retention of sulphur by limestone. It should also be noted, that when fly ashes were used as sorbent the highest retention of cadmium was achieved. The arsenic and selenium retained in the fly ashes were partially lost in the post-retention desorption test, selenium loss amounting to 60%. Both elements show low solubility in water, 5-10%. Although the mechanisms governing retention in fly ashes are still not fully understood, possible reactions between calcium or iron oxides, and arsenic and selenium compounds, may partially explain these retentions [7].

Table 5. Maximum retention capacities (MRC, mg g^{-1}) and efficiencies (E,%) in fly ashes

Element	T (ºC)	Mixture I		Mixture II		Mixture III	
		MRC	E	MRC	E	MRC	E
As	550	16	100	—	—	17	73
	750	24	99	—	—	2	0
Se	550	26	50	—	—	16	33
	750	25	83	—	—	25	67
Cd	750	0.8	10	0.3	4	—	—
Zn	750	16	21	3	11	—	—

3.4. Alumina

In previous published works carried out in the oxidising conditions of a combustion atmosphere low retention capacities for Pb and Cd were obtained using aluminium oxide as sorbent [19]. Similar results were also achieved in our work for gasification. Although alumina is the sorbent with the largest surface area, it was not the most efficient in retaining As, Se, and Cd, or even S in the gasification atmosphere containing H_2S. Low quantities of sulphur in the alumina post-retention were found (0.4-1.2 mg g^{-1}), which continued to decrease with temperature. However the capture of Zn was significantly higher than for all the other sorbents (Table 6). In the gas atmosphere containing HCl, alumina retained about 50 mg of zinc per g of sorbent at 750ºC, with an efficiency close to 70%. Arsenic, selenium and cadmium were eliminated during post-retention heating while the zinc retained was thermally stable. Moreover, only Zn, did not dissolve during the water solubility tests. In general, physical adsorption mechanisms are proposed to explain the retention of trace elements by alumina. However, the different retention capacities in the case of zinc suggest a more complex or stronger interaction involving a gas-solid interaction. This interaction is probably activated by the presence of HCl via a mechanism of sorbent activation [10].

Table 6. Maximum retention capacities (MRC, mg g^{-1}) and efficiencies (E,%) in alumina

Element	T (ºC)	Mixture I		Mixture II		Mixture III	
		MRC	E	MRC	E	MRC	E
As	550	4	23	—	—	3	23
	750	1	19	—	—	2	0
Se	550	1	4	—	—	0.9	3
	750	1	2	—	—	0.4	1
Cd	750	0.004	<0.1	0.003	<0.1	—	—
Zn	750	14	77	52	78	—	—

3.5. Metal oxide mixtures

Metal oxides or metal oxide mixtures are materials that are extensively used as sorbents in a variety of applications, although in coal power generation, the most important is the use of metal oxide mixtures as sorbents for H_2S in gasification processes [4]. This makes these sorbents very attractive for the parallel or simultaneous retention of other species in the same process. The metal oxide mixtures studied in this work were only used at 550 ºC because at temperatures of 750 ºC in the gasification atmospheres they decomposed. They are currently being evaluated and used to remove $H_2S(g)$ in hot gas cleaning systems, and have shown a remarkable capacity for retaining significant amounts of sulphur during our experiments. High retention capacities were achieved with these solids for arsenic and selenium depending on the gas atmosphere and sorbent, values of 50 mg g^{-1} being attained in case the of selenium (Table 7). The element retained is not thermally stable and so the sorbent may be regenerated. The species retained is not soluble in water.

The retention mechanism consisted mainly of chemical reactions, as was saw from the Fe-As associations observed by EDX in the ZFT post-retention sorbents and from the formation of new compounds (e.g. ZnSe and FeSe) observed by means of XRD [9].

Table 7. Maximum retention capacities (MRC, mg g^{-1}) and efficiencies (E,%) in the metal oxide mixtures and in the gas atmosphere of mixture III

Element	T (ºC)	ZT		ZFT	
		MRC	E	MRC	E
As	550	<1	2	21	66
Se	550	56	83	55	77

4.   CONCLUSIONS

Although the behaviour of the sorbents depends on the type of element, gas composition and temperature, in general, limestone, fly ash and metal oxide mixtures may be considered as good sorbents for the capture of arsenic and selenium, their retention capacity depending on temperature and gas composition. Fly ashes may also behave as an efficient sorbent for cadmium, and may be considered as the second most efficient for retaining zinc. Nevertheless, the best sorbent for zinc was alumina in a gas atmosphere containing HCl. The results of this work suggest that it may possible to use these solids as multi-pollutant sorbents considering that limestone and metal oxide mixtures are currently employed to remove sulphur from hot gas removal in gasification systems. Furthermore, fly ashes are wastes from the coal conversion process, so that using fly ashes as solid sorbent would be advantageous from the point of view of cost and availability.

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