

Review

# Behavior of Pb During Coal Combustion: An Overview

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**Abstract:** Despite the progress in understanding heavy metals behavior during coal combustion, mitigation of heavy metals emissions is still a tough challenge due to a complex character of this phenomenon. Several lists of potentially toxic elements have been presented; in most cases, Pb belongs to the elements with the greatest environmental and human-health concern. The review paper is focused upon the behavior of Pb during coal combustion, with particular attention paid to decreasing its emissions. It summarizes the dominant parameters affecting its redistribution among coal combustion streams. As gaseous emissions can quite easily pass through the particulate control device, attention was paid primarily to Pb distribution between condensed and volatilized phases. A crucial factor enhancing Pb volatility is the presence of organic or inorganic chlorides, which is discussed in detail, including their chlorination mechanisms and interactions with other fuel/flue gas species. Components decreasing Pb volatility and promoting the formation of condensed phases are also discussed (higher levels of moisture, Na, O<sub>2</sub> etc.). Factors enhancing Pb volatility, as well as factors facilitating Pb retention, are discussed with the view of fluidized-bed combustion, pulverized-fuel combustion, or co-combustion of coal with wastes.

**Keywords:** lead; coal combustion; volatility; emissions; chlorine; retention

## 1. Introduction

According to the World Coal Association [1], coal will continue to play an essential role in meeting global energy needs—more than one third of the electricity production will be covered by coal in the coming decades [1]. Since coal is a significant source of major, minor and trace elements, coal combustion in power stations still remains significant with respect to environmental and human-health concerns. Despite the fact that some of these elements are studied primarily with the view of their further industrial utilization (yttrium [2], rare earth elements [3,4], Ge and Ga [5], etc.), most minor and trace elements attract the researchers' attention due to their toxicity and as a human health hazard [6].

Significant progress was achieved during the last decades in meeting the challenges associated with air emissions during coal combustion. Technologies are available for coal cleaning prior to combustion [7], for the retention of ash particles (electrostatic precipitators, fabric filters etc.) [8], for an abatement of nitrogen oxides (NO<sub>x</sub>) emissions (low NO<sub>x</sub> burners, selective catalytic/non-catalytic reduction), etc. Sulfur emissions are mitigated through dry/wet desulphurization technologies [9,10], which provide promising achievements also for some other elements, such as Hg, As, Se, Cl and Br [11]. Due to its toxicity and volatility, world-wide attention is paid to Hg retention from flue gas, revealing good results for activated carbon [12], unburned carbon [13–16], manganese-based adsorbents [17], etc.

Environmental concern relates also to other heavy metals (HMs) being potentially released from power stations and exhibiting harmful effects on human health. Despite the progress in understanding the HMs' behavior, mitigation of HM emissions is still a tough challenge due to a complex character

of this phenomenon. Several lists of potentially toxic elements have been presented [18–21]; in most cases, Pb belongs to the elements of greatest environmental and human-health concern.

The review paper is focused upon the behavior of Pb during coal combustion, with particular attention paid on decreasing its emissions. It summarizes and discusses the dominant parameters affecting its redistribution among coal combustion streams, and namely between condensed and volatilized phases.

## 2. Pb in Coal

*Low-rank coals.* According to Ketris and Yudovich [22], Clarke values for Pb in low rank coals and the corresponding ashes are 6.6 and 38 ppm. The typical mode of occurrence of Pb in these coals (according to Finkelman et al. [23]) is their monosulfides (galena) association of ca. 50% followed by 25% in silicates and 10% in pyrite. In low rank coals, some Pb can be organically associated, and in the Appalachian Basin coals, Pb occurs also as PbSe (lead selenide, or also clausthalite) [23].

*High-rank coals.* Average levels of Pb in high rank coals and related coal ashes [22] are higher than those in low rank coals/ashes—9.0 and 55 ppm. Dominant association of Pb in high rank coals is similar to low rank coals (55% in monosulfides). Its occurrence in pyrite is more abundant (35%), whereas its affinity to (alumino)silicates is generally low (5%) [23]. Minor carbonate-associated Pb has also been reported in literature [24,25].

With no regard to coal rank, generally ca. 5–25% of Pb is firmly bound in (alumino)silicate minerals, whereas other forms as sulfides, selenides, pyrite, carbonates and organic association prevail, which is in line with quite high Pb volatility, making Pb available for the interactions with other coal/flue gas/ash components [26].

## 3. Melting and Boiling Points of Pb and Its Target Compounds

Melting/boiling points of Pb and its compounds are important in terms of combustion temperature and volatility [27]. However, as Pb and similarly also other HMs are not usually present as pure metals, and typically interact with other fuel/flue gas components, creating e.g., oxides, chlorides, sulfates etc., then the melting/boiling points of these species might be even more important and might illustrate Pb combustion behavior more accurately.

Melting and boiling points of Pb and its target compounds are summarized in Table 1.

**Table 1.** Melting points (m.p.) and boiling points (b.p.) of lead (Pb) and its target compounds.

Metal	m.p.	Pb	327 °C [28,29]
	b.p.	Pb	1744 °C [28,29]
Oxides	m.p.	PbO	886 °C [28,29]
		PbO <sub>2</sub>	290 °C decomp.* [29]
		PbO <sub>3</sub>	370 °C decomp.* [29]
		PbO <sub>4</sub>	930 °C decomp.* [29]
	b.p.	PbO	1516 °C [28], 1470 °C [29]
Chloride	m.p.	PbCl <sub>2</sub>	501 °C [26,29]
	b.p.	PbCl <sub>2</sub>	950 °C [28], 954 °C [29]
Sulphate	m.p.	PbSO <sub>4</sub>	1170 °C [28]
Sulphide	m.p.	PbS	1113 °C [30]
Selenide	m.p.	PbSe	1065 °C [30]

\* decomposition.

Data summarized in Table 1 clearly document that the melting and boiling points of PbO are much higher than those of chloride. Regarding the temperature in the combustion chamber and during flue gas quenching, this phenomenon is a dominant reason why interaction of Pb with chlorine, oxygen, moisture, etc. strongly affects its volatility and further post-combustion behavior. For example, shifting the equilibrium from the oxide to chloride typically results in higher Pb volatility (if no other factors

are not taken into account, e.g., the availability of calcareous minerals). Therefore, Table 1 provides useful information for the discussions in the sections below.

#### 4. Dominant Parameters Affecting Pb Behavior

Behavior of Pb is governed by both fuel characteristics and operating conditions. As it is a complex phenomenon, even a moderate change in fuel composition or experimental conditions (or both) might lead to substantially different results (which is likely a dominant reason why literature conclusions are not always fully consistent). The most important parameters are summarized below:

##### 4.1. Fuel Characteristics

- Pb concentration in fuel (not only in coal, but also in combustion additives, municipal solid waste, refuse-derived fuel, sewage sludge, agricultural/forest residues and other wastes co-combusted with coal). It strongly affects the levels in solid combustion products and emissions.
- Mode of occurrence of Pb in fuel, which controls namely its volatility in the combustion chamber.
- Fuel granulometry (particle-size)
- Concentrations of interacting components, such as:
  - Chlorine
  - Moisture
  - Alkaline metals
  - Sulfur
  - Phosphorus, etc.

##### 4.2. Operating Conditions

- Combustion temperature. It is undoubtedly one of the most important parameters affecting the volatility (of not only Pb, but also of all interacting species), melting/sintering (fritting) processes and particle agglomeration.
- Combustion additives/adsorbents. Adding suitable combustion additives can efficiently reduce the negative impact of Pb present in the fuel (by affecting Pb redistribution among coal combustion products). Different approaches can be used or combined:
  - Prior-to-combustion adsorbent treatment
  - Co-combustion of additive and fuel in combustion chamber
  - Adsorbent injection into post-combustion zone
  - Combination of the aforementioned approaches
- Major flue gas composition. Oxygen level is a crucial characteristic in this context. Moreover, the behavior of Pb might be different in traditional  $N_2/O_2$  and oxy-fuel  $CO_2/O_2$  atmospheres.
- Pressure in the combustion chamber. Change in the pressure can also affect Pb species formed in the combustion process
- Kinetic aspect. It should be mentioned in the overall evaluation as well, because kinetic constraints may prevent the establishment of equilibrium distributions (e.g., gas velocity, dwell-time in the combustion chamber etc.).

Resultant Pb behavior is given by a combination of the aforementioned effects that can be of both synergistic or inhibitory character, which will be discussed in detail in the sections below.

#### 5. Effect of Chlorine on Pb Behavior and Related Interactions

Chlorides formed by the interaction of Pb (and other HMs) with Cl-species typically exhibit lower melting points than their corresponding oxides (and mostly lower than the combustion

temperature [31]). This is the very reason why interactions with Cl and its compounds still attracts the researchers' attention [32].

In coal, Cl is predominantly present in pore moisture as chlorides, such as NaCl or KCl [33]. Even if a minor organic association of Cl (0.5–25%) in coal has also been reported [34], the effect of inorganically-bound Cl is dominant during coal combustion without additives. Despite being of minor significance in most coals, organically-associated Cl could enhance Pb volatility as well. A higher fraction of organically-bound Cl is typically more likely in the case of low rank coals for two reasons: (i) Low rank coals were not submerged in considerable depths where basinal brines (increasing inorganic Cl levels) were abundant, and (ii) a low extent of coalification keeps functional groups more abundant in coal organic matter (providing active sites for Cl retention) [34]. From this point of view, the enhancing effect on Pb volatility by organic Cl is more probable in the case of coals with Cl of syngenetic origin (i.e., those arising from a common 'ancestor').

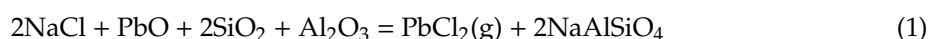
Regarding the increasing amount of industrial, agricultural and forest residues or municipal solid waste (MSW) (with respect to the theory that we might reach 2.2 billion tons of MSW/year by 2025 [35]), there is a trend toward a co-combustion of coal and various types of waste. Then, the presence of plastics can introduce organically-bound Cl into the combustion systems (e.g., in the form of polyvinylchloride (PVC)) [36–38]. If sewage sludge is co-combusted with coal, higher levels of ferric (iron(III)) chloride (FeCl<sub>3</sub>) can be expected, and in the case of traditional MSW incineration the effect of NaCl originating from food residues should be taken into account as well [36]. Some occurrence of calcium chloride (CaCl<sub>2</sub>) and aluminum (tri)chloride (AlCl<sub>3</sub>) can also be expected in all the aforementioned cases.

All these organic and inorganic chlorides can enhance the volatility of Pb; but the mechanism and the volatilization efficiency can be substantially different.

### 5.1. PVC vs. NaCl

*Effect of PVC.* It has long been known that polyvinylchloride (PVC) can efficiently enhance the volatility of Pb [39]. Rio et al. [40] concluded ca. 10–15% volatility increase for Pb at 850 °C; increased volatilization of Pb at 950 °C by PVC addition (from 11% to 30%) was reported by Li et al. [41]. Chiang et al. [42] documented the volatilization increase of Pb from 3% to 53% due to PVC chlorination—the detected chlorination products in fly using PVC at 850 °C were namely oxychlorides PbOCl<sub>2</sub> and PbO<sub>2</sub>Cl. Wang et al. [31] observed the decrease in volatilization temperature of Pb from 600–700 °C to ca. 500 °C in the presence of PVC, which was attributed to indirect low-temperature chlorination. According to Wang et al. [31], PVC releases HCl at ca. 240 °C that reacts with PbO, thereby enhancing Pb volatility. At higher temperatures (700–900 °C), PVC increases the volatilization fraction of Pb as well.

*Effect of NaCl.* In contrast, NaCl did not decrease the volatilization temperature of Pb, but its direct high-temperature chlorination enhances Pb volatility at 700–900 °C. The optimal effect of NaCl on increasing Pb volatility was observed in the temperature range of 800–900 °C, which is lower than the temperature needed for the release of HCl from NaCl [31]. Therefore, direct chlorination is more likely in this case (than an indirect chlorination mechanism via HCl). However, direct chlorination of PbO by NaCl requires also some other necessary components (such as H<sub>2</sub>O, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> etc.) [31,43]. For example, in the presence of silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>), the reaction equation of Pb chlorination by NaCl is (Equation (1)) [43]:



The volatilization percentage of Pb (in air) at 973 K was ca. 30% and about 75% at 1223 K (data plotted in graph for 30 min dwell time). In the case of longer dwell time (90 min), 98% of Pb was volatilized in the form of lead(II) chloride (PbCl<sub>2</sub>). Thus, not only the thermodynamic aspect, but also the kinetic limitations could play an important role [43].

## 5.2. Comparison of Inorganic Chlorides

The effect of individual inorganic chlorides is different as well [44,45], and relates to a direct/indirect chlorination mechanism. The direct chlorination mechanism is typical for NaCl [44,45]; nevertheless, it results in the lowest volatilization of Pb by NaCl of all tested inorganic chlorides. Unlike NaCl, other chlorides like MgCl<sub>2</sub>, CaCl<sub>2</sub> or FeCl<sub>3</sub> first release chlorine (in the form of HCl and/or Cl<sub>2</sub> by reaction with H<sub>2</sub>O or O<sub>2</sub>), followed by an interaction with Pb [45,46], according to Equations (2)–(4):



Yu et al. [45] observed the most significant increase of Pb volatility (at 950 °C) in the presence of FeCl<sub>3</sub>·6H<sub>2</sub>O, followed by CaCl<sub>2</sub> and NaCl, which is consistent with the conclusion of Nowak et al. [44] reporting efficient Pb volatilization enhanced by MgCl<sub>2</sub> and CaCl<sub>2</sub> (unlike the effect of NaCl, being quite low).

Aforementioned results suggest that PVC (present e.g., in wastes) is more problematic in the case of a formation of hazardous gaseous Pb emissions than NaCl (which is the case of pure coal combustion). Therefore, if coal is co-combusted with plastics-containing wastes (e.g., refuse-derived fuel), the increasing Pb volatility requires special attention. If coal is co-combusted with sewage sludge, higher levels of FeCl<sub>3</sub> (and corresponding enhanced Pb volatility) can be expected as well.

For this reason, not only gaseous emissions of Cl species (Cl<sub>2</sub>, HCl etc.), but also the enhanced volatility of Pb (and some other HMs) [47] should be taken into account if waste materials are added to coal during combustion.

## 5.3. Other Relating Interactions

As Pb chlorination is not a discrete phenomenon, there is still an effect of other interacting species or adsorbents used. The presence of PVC or inorganic chlorides not only enhance Pb volatility, but also exhibit the ability to modify the retention efficiency on the adsorbents.

*Kaolinite, bauxite, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> adsorbents.* Chen et al. [48] observed the different influence of PVC and NaCl on Pb retention on kaolinite, bauxite and Al<sub>2</sub>O<sub>3</sub> (during laboratory fluidized-bed combustion experiments). At 700–900 °C, bauxite was the best adsorbent for Pb if PVC was present (in comparison to Al<sub>2</sub>O<sub>3</sub> and kaolinite); but if NaCl was used, its retention efficiency was the worst. If Pb was not converted to chlorides (low or negligible amount of NaCl/PVC), a high retention efficiency can be obtained by kaolinite [49], for which a high temperature is recommended ( $t > 1000$  °C) [24,50,51]. If SiO<sub>2</sub> is to be used as a Pb adsorbent, the conversion of PbO to PbCl<sub>2</sub> (e.g., by organic Cl below 350 °C) can hinder Pb retention on SiO<sub>2</sub> because PbO retention on SiO<sub>2</sub> is more efficient than that of PbCl<sub>2</sub> [52]. Optimal temperature for the retention was 1000 °C and the retention product was PbO·SiO<sub>2</sub> [24].

*Effect of CaO.* Namely in fluidized-bed combustion, calcareous minerals (e.g., CaO) are typically present at high levels and can substantially affect Pb behavior. Wang et al. [31] observed adsorption of HCl (originated from PVC) by CaO, thereby inhibiting Pb volatilization at temperatures below 700 °C. However, at higher temperatures, the retained chlorine was released back (and was available for the interaction with Pb again). In the case of NaCl, the effect of CaO on Pb volatilization was not observed (probably due to the direct chlorination mechanism).

If coal is combusted without an addition of wastes, the effect of CaO depends upon the Cl association in coal. As Cl in most coals is present predominantly in the form of NaCl or KCl, the significant effect of CaO cannot be expected. Nevertheless, it can be important in the case of coals with Cl of dominant syngenetic origin, where a higher fraction of organically-bound Cl can be presumed [34]. However, to our best knowledge, there are no studies elucidating the interaction between organic Cl in coal and CaO and their effect on Pb (or other HMs) volatilization.

Tang et al. [53] reported that adding 10% CaO or CaCO<sub>3</sub> to synthetic MSW (flour, paper, wood sawdust, high-density polyethylene (HDPE), textiles, rubber and leather) did not show any increase in the Pb residual rate at 700 °C (i.e., no effect on Pb retention in ash); at 800–1000 °C the residual rate even slightly decreased, even if chlorine was present in these wastes. The results are still consistent with the conclusions of Wang et al. [31], stating that the efficient retention temperature of CaO was below 700 °C (at higher temperatures, CaCl<sub>2</sub> can release chlorine back for Pb chlorination).

*Effect of Na.* Another element that can participate in these interactions is Na. Durlak et al. [54] observed the effect of decreasing Na levels in MSW (in the waste feed) on an increasing percentage of Pb in fly ash related to bottom ash (from 36% up to 60%). It was attributed to the competition of Pb and Na for free Cl, hindering the formation of Pb–Cl species. Moreover, the affinity to Cl is in the order Na > Pb > most HMs [36,55]. For example, Pb forms chloride more easily than Cd [56–59]. Therefore, metal chlorides can be formed only if the Cl level is high enough (otherwise only NaCl is formed). Hence, Na present in higher concentrations can indirectly decrease Pb volatility as well.

Kuo et al. [60] document a significant increase of Pb retention if sodium nitrate (Chile saltpeter, NaNO<sub>3</sub>) (1.2% Na) was added to artificial solid waste (sawdust, metal nitrates solution, polyethylene (PE))—Pb retention increased from ca. 10% (at 700, 800 and 900 °C) to 15% (700 °C), 20% (800 °C) and >40% (900 °C). Improved Pb retention was attributed to an agglomeration-promotion effect that is enhanced with increasing temperature. Na was added in the form of NaNO<sub>3</sub>, (i.e., no Cl was added), which is in line with the observation of Peng et al. [61]. Hence, Na can improve Pb retention by two different mechanisms—by an interaction with Cl (thereby decreasing its concentration available for interaction with Pb)—and by agglomeration-promotion effect.

However, this agglomeration effect (advantageous for the retention of Pb) is thought to be inevitable in relation to the overall combustion process (e.g., due to fouling and slagging).

## 6. Effect of Moisture

There is a consensus in literature that a higher moisture level in the combustion chamber and flue gas can shift the equilibrium towards the formation of Pb (and other HMs) oxides, thereby suppressing the formation of chloride counterparts [28,41,54,62], which results in suppressed Pb (and other HMs) volatility. Due to the presence of H<sub>2</sub>O vapor in the oxy-fuel atmosphere [62], this effect can be significant during oxy-fuel combustion. It should be taken into account also if coal is co-combusted with wastes, where some of them can contain higher percentages of H<sub>2</sub>O (sewage sludge, agricultural residues etc.) [63,64], or if coal-water slurry is combusted [65,66].

*Presence of Cl.* As expected, not only higher moisture levels, but also higher Cl content is needed to observe this phenomenon. Li et al. [41] reported the negligible effect of H<sub>2</sub>O (0–39.4%) on the Pb retention rate in bottom ash at both 700 °C and 950 °C if no Cl was added to synthetic MSW—the effect of moisture level was only within ca. 2% range. Increased Pb retention in bottom ash with increasing H<sub>2</sub>O levels (from 0 to 39.4%) was more significant if 1–5% Cl was added to MSW [41] (and combusted at 950 °C). Then, Pb retention in bottom ash (due to higher moisture content) increased by ca. 10–15% (which was still of minor significance in comparison with higher volatility caused by increasing Cl levels—from ca. 90% retention at 0% Cl via ca. 60% retention for 1% Cl up to ca. 10% retention for 5% Cl). These results of Li et al. [41] are consistent with those of Meng et al. [67] concluding quite good retention (ca. 90–100%) of Pb from synthetic MSW in bottom ash at both 700 °C and 900 °C if no Cl was added. However, this quite good retention efficiency (in the absence of Cl) slightly decreased at both temperatures with increasing moisture levels from 5 to 62% [67]. Hence, as the suppression of Pb volatility by H<sub>2</sub>O (at ca. 950 °C) is due to an intensification of the transfer from PbCl<sub>2</sub> to PbO [41,67,68], it is observed only if the concentration of Cl is high enough to form PbCl<sub>2</sub>.

*Effect of temperature.* In addition to this, Meng et al. [67] observed the decrease in Pb volatility due to moisture (in the presence of Cl) only at 950 °C. At 700 °C (in the presence of 1% PVC and 0.5% NaCl), higher moisture content even promoted Pb volatilization and its release from bottom ash. At 700 °C, Pb retention in bottom ash decreased from ca. 60% to ca. 30% when the H<sub>2</sub>O level increased from 5%

to 62%. At 950 °C (in the presence of 1% PVC and 0.5% NaCl), adding more H<sub>2</sub>O moderately increased Pb retention in bottom ash, but it was still quite low (ca. below 18%).

Equilibrium calculations of Durlak et al. [54] also documented the conversion of PbCl<sub>2</sub>(g) to PbO due to increasing moisture content (up to 35%). As the related temperature was 950 °C, these conclusions are consistent with those of Meng et al. [67] suggesting that the temperature of 950 °C promotes this effect. It is in line with the depressed volatilization of Pb by H<sub>2</sub>O within the temperature range of 950–1000 °C in a simulated laboratory incinerator observed also by Youcai et al. [28].

Nevertheless, it should be mentioned in this context that the results of Morf et al. [69] did not confirm the decrease of Pb volatility due to moisture in flue gas in an MSW incinerator plant with a grate furnace (with 1000–1015 °C combustion temperature and 1.04–1.48% Cl in wet input waste).

*Physical aspect of higher moisture content.* In addition to aforementioned chemical influence, there are also some physical consequences of higher moisture levels in fuel—this effect is typically observed if no extra Cl was added to the fuel [28,54,67]. Results of laboratory-scale incinerator tests document that higher moisture content can even slightly enhance Pb volatility due to prolongation of the devolatilization process and due to longer time needed for reaching the desired temperature (or at the limited time available during laboratory combustion tests) [28]. According to Durlak et al. [54], if the incineration temperature is not controlled properly, increasing H<sub>2</sub>O levels can lead to a decrease in temperature (shifting equilibrium PbO–PbCl<sub>2</sub> towards PbCl<sub>2</sub>(g), thereby increasing Pb volatility).

Therefore, the effect of H<sub>2</sub>O is not straightforward, and the overall influence depends (at least) on Cl content and the temperature (or dwell time at laboratory experiments). Meanwhile, the effect of Cl increasing Pb volatility is much stronger than that of moisture that only slightly hinders this (prevailing) inevitable effect [41].

In any case, as most of these interesting results were obtained either from equilibrium calculations or laboratory-scale horizontal tube incinerators, pilot-scale or full-scale experimental data are needed to observe the complex effect of aforementioned parameters under real full-scale conditions.

## 7. Effect of Atmosphere

It is generally accepted that increasing O<sub>2</sub> concentration shifts the equilibrium from PbCl<sub>2</sub> toward PbO, which typically results in decreased volatility [70]. For efficient CO<sub>2</sub> retention, oxy-fuel combustion is widely used. So there is a need to elucidate the behavior of Pb (and other HMs) under the CO<sub>2</sub>/O<sub>2</sub> atmosphere as well, because there are only a few studies focused upon the comparison of traditional N<sub>2</sub>/O<sub>2</sub> and oxy-fuel CO<sub>2</sub>/O<sub>2</sub> atmospheres (in this context).

Li et al. [71] observed that the volatility of Pb in our 21%O<sub>2</sub>/79%CO<sub>2</sub> atmosphere was moderately restrained, while Jerzak [72] observed an increase in the mole fractions of Pb species in the gaseous phase if air was changed to a 30% O<sub>2</sub>/70% CO<sub>2</sub> atmosphere. Zheng and Furimsky [73] predicted the behavior of Pb in an oxy-fuel and air combustion, concluding no noticeable differences. Oboirien et al. [74] compared relative enrichment in ash (vs. coal mineral matter) at 900 and 1000 °C for two coals under air and oxy-fuel atmospheres—the different effect of N<sub>2</sub>/O<sub>2</sub> and CO<sub>2</sub>/O<sub>2</sub> was observed. In air, in the case of both studied coals, Pb exhibited lower volatility at 900 °C and a higher volatility at 1000 °C (evaluated as enrichment in ash vs. coal mineral matter). In CO<sub>2</sub>/O<sub>2</sub> atmospheres, one coal exhibited high volatility at both temperatures, whereas Pb in the other was not volatile even at 1000 °C. The latter coal (with non-volatile Pb) contained higher CaO, Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O and Pb concentrations and more inertinite (Cl content was not reported). So it can be suspected that some of these species might retain Pb in a CO<sub>2</sub>/O<sub>2</sub> atmosphere. Meanwhile, according to Wang and Tomita [75], during both combustion and pyrolysis atmospheres, Pb volatility depends also on heating rate.

## 8. Effect of Sulfur and Phosphorus

*Effect of S.* Yao and Naruse [55] reported the occurrence of lead(II) sulfate (PbSO<sub>4</sub>) within the optimal temperature range of 500–1100 K (if the temperature further increased, the fraction of PbSO<sub>4</sub> decreased rapidly). According to Zhao et al. [76,77], Cenni et al. [78] or Lundholm et al. [79], PbSO<sub>4</sub>

was a dominant form at temperatures below 730 °C (the melting point of  $\text{PbSO}_4$  is higher than 886 °C). At lower temperatures, Pb can create also  $4\text{PbO}\cdot\text{PbSO}_4$ , which is stable up to ca. 800–850 °C.

The formation of these (condensed) species can be propitious for decreasing Pb emissions at lower temperatures (e.g., in fluidized-bed combustion). At pulverized-fuel combustion, the combustion temperature exceeds the optimal thermal-stability range of these species.

Luan et al. [80] compared the binding energies of Pb-sulfide, -chloride, -sulfate and -phosphate, concluding that lead's chloride and sulfide could be easily formed, while its sulfate and phosphate exhibited quite high binding energy values. However, in addition to the propitious effect of S on Pb volatilization (via sulfide formation), there is still an effect of oxygen. Excess oxygen can interact with S, forming  $\text{SO}_2$ , and it can also oxidize sulfides to sulfates, thereby decreasing their volatility [81]. Moreover, namely during fluidized-bed combustion, an excess of Ca-bearing desulfurization additives (whose amount is much higher than that of Pb) can compete with Pb during the interaction with S.

*Effect of P.* Not only S- but also P-species can possibly stabilize the emission of Pb (and some other HMs) through the formation of phosphates [40,76]. Rio et al. [40] document a decrease of Pb emissions via waste modification by phosphoric acid ( $\text{H}_3\text{PO}_4$ ) prior to combustion which decreased Pb volatility at 600 °C from 25% to ca. 18–19%, and at 850 °C from 50% to 20%. If P was included in equilibrium calculations,  $\text{Pb}_3(\text{PO}_4)_2$  was predicted in the temperature range of 400–1100 °C [82]. Due to high binding energy [80] for the reaction between Pb and phosphate and typically low P levels in most coals [22], prior-to combustion treatment (with extra added P) should be a better alternative to provide noticeable retention results.

## 9. Conclusions

The review paper is focused to the behavior of Pb during coal combustion with particular attention paid on decreasing its emissions. It summarizes and discusses the effect of dominant parameters affecting its redistribution among coal combustion streams. As gaseous emissions can pass through the precipitator quite easily, special attention was paid to Pb distribution between condensed and volatilized phases.

In coal, prevailing sulfidic Pb association facilitates its volatilization during the combustion [83], even at lower combustion temperatures (e.g., during fluidized-bed combustion). Moreover, some waste materials co-combusted with coal might contain Pb concentrations comparable or even higher than those in coal, such as tires (20 ppm) [84], pickling sludge (33 ppm) [85], or waste-activated sludge from municipal wastewater treatment (138 ppm) [86]. Then, the creation of condensed species would be propitious for its retention in bottom ash or fly ash (preventing passing through the particulate control device in gaseous form). However, formation of the condensed species can be hindered namely by the presence of organic and inorganic chlorides. NaCl (or KCl) are typically present in most coals; higher levels of  $\text{FeCl}_3$  can be expected namely in sewage sludge [87,88]. In addition to the Cl present in the organic matter of coal, organic Cl present in PVC is contained, e.g., in refuse-derived fuel that can be co-combusted with coal or (along with NaCl from food residues) in municipal solid waste.

PVC releases HCl first at lower temperatures and chlorinates Pb indirectly, thereby decreasing its volatilization temperature and increasing its volatility. In contrast, NaCl chlorination mechanism is direct (requiring some other components— $\text{H}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , etc. [31]). Other inorganic chlorides (like  $\text{MgCl}_2$ ,  $\text{CaCl}_2$  or  $\text{FeCl}_3$ ) increase the Pb volatility through indirect volatilization, releasing HCl or  $\text{Cl}_2$ , and exhibiting a more significant increase of Pb volatility in comparison with NaCl [44–46]. Therefore, in the case of pure coal combustion, where Cl is present predominantly in the form of NaCl (or KCl), increase or Pb volatility is expected to be lower than in the case of co-combustion with (Cl-containing) wastes, namely plastics (PVC) or sewage sludge ( $\text{FeCl}_3$ ), where indirect chlorination can increase Pb volatility more efficiently.

Optimal retention of Pb differs in dependence on individual conditions, e.g., on concentration of Cl available for the interaction, temperature, presence of interacting species, etc.



Coal is co-combusted with wastes typically in fluidized-bed power stations where Ca-bearing desulfurization additives are added to the combustion chamber for the desulfurization of flue gas.

As CaO has the ability to retain HCl originated from the low-temperature decomposition of PVC, it can mitigate the increase of Pb volatility by PVC. However, this effect was observed only below ca. 700 °C; at higher temperatures it does not work, and CaCl<sub>2</sub> can even release chlorine back, enhancing Pb volatility. The effect of (a real) organically-bound Cl is suspected to be similar. Since the combustion temperature in the fluidized-bed chamber is higher than 700 °C (ca. 850 °C), from this perspective, injection of CaO into the flue gas stream could be more beneficial. The effect of CaO on NaCl-chlorinated Pb was not observed. Chlorination of Pb can be moderately mitigated by the presence of moisture, but temperatures higher than the fluidized-bed combustion temperature (850 °C) are recommended in this case (ca. 950 °C). Creation of PbSO<sub>4</sub> is also possible, but due to the huge amount of calcareous desulfurization additives, this effect is suspected to be quite low.

Good retention results were observed if kaolinite was used as a Pb adsorbent. However, optimal capture efficiency can be achieved at higher temperatures ( $t > 1000$  °C, optimally ca. 1200 °C) and if Pb is dominantly present in its PbO form (i.e., if there is a low/negligible Cl effect). Therefore, this is more feasible at pulverized-fuel combustion, because the fluidized-bed combustion temperature is below this range (ca. 850 °C), and due to an addition of wastes, the Cl content could be quite high in the fluidized-bed power station.

Release of Pb in emissions is not the only challenge attracting researchers' attention in the field of coal combustion. There are also other heavy metals whose emissions are to be mitigated. The influence of the factors discussed in this paper could be expected as well (even if their significance might be quite variable, for individual metals, such as: Cd, Cr, Cu, Ni, Zn, etc.).

Herein, Pb behavior and volatility was discussed, with particular attention paid on decreasing its (gaseous) emissions. Despite the fact that it was not the objective of this paper, it should be mentioned that the distribution of Pb changed by the aforementioned factors might result in changed concentrations and occurrence modes in solid coal combustion products, which consecutively affects their future fate (landfilling, industrial utilization, environmental toxicity, etc.)

Particular attention is currently being paid (e.g.,) to an abatement of CO<sub>2</sub> emissions (e.g., oxy-fuel combustion [71]), to decreasing fouling/slagging by staged coal combustion [89], or mitigating NO emissions using low-NO burners [90]. As these modern combustion technologies provide promising results for wider industrial utilization, detailed elucidation of heavy metals behavior also under these conditions would be beneficial.

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