

Review

# Behavior of Cd during Coal Combustion: An Overview

Lucie Bartoňová \* , Helena Raclavská , Bohumír Čech and Marek Kucbel 

ENET Centre, VSB-Technical University of Ostrava, 708 00 Ostrava-Poruba, Czech Republic; helena.raclavska@vsb.cz (H.R.); bohumir.cech@vsb.cz (B.Č.); marek.kucbel@vsb.cz (M.K.)

\* Correspondence: lucie.bartonova@vsb.cz

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**Abstract:** Due to the unfavorable combination of its toxicity and high volatility, Cd is contained in most lists of potentially hazardous air pollutants with the greatest environmental and human-health concerns. The review paper evaluates the behavior of Cd during combustion (incineration) processes and its redistribution among condensed fractions (bottom ash/slag, fly ash) and volatilized fractions (that passes through most particulate control devices). The paper addresses all important effects of Cd interactions, such as presence of organic or inorganic chlorides, moisture levels, S, P and Na concentrations, flue gas composition etc. Possibilities of using various adsorbents (either within in-furnace regime or applied in post-combustion zone) are evaluated as well. Special attention is paid to mitigating its emissions factors; decreasing Cd volatility and facilitating Cd retention are discussed with the view of various combustion (incineration) conditions and the feed fuel composition.

**Keywords:** cadmium; coal combustion; volatility; emissions; chlorine; retention; wastes

## 1. Introduction

Coal contains almost all the elements from the periodic chart. These elements differ by their concentrations, modes of occurrence, toxicity and behavior during coal combustion at power stations [1]. These factors influence not only the perspectives of their potential extractions from coal/ashes (such as rare earth elements (REE) [2,3], Y [4], Ge-Ga [5] etc.) but also their negative impact on the environment.

Environmental hazards are created by the coal characteristics (including the levels and associations of interacting species) and additionally by the operational conditions, such as the combustion technology, temperature, atmosphere, air-pollution control devices and proper use of desulfurization additives [6–8] or adsorbents [9–11].

Despite the progress achieved during the last decades, the decreasing of emissions of toxic elements is still a tough challenge. The overall environmental and human-health hazards of individual elements are given by their partitioning among bottom ash (slag), fly ash and emissions, as well as by their toxicity.

Wagner and Hlatshwayo [12] summarized and evaluated six lists of potentially hazardous air pollutants. All these lists contain Hg and As, two toxic elements exhibiting high volatility, which is in line with wide attention in the literature that is paid to Hg [13–15] and As [8,16,17]. Another two elements are present in all these lists—Pb and Cd. The behavior of and possibilities of decreasing Pb emissions were discussed in our previous paper [18]; therefore, this review paper is focused on Cd, due to the unfavorable combination of its high toxicity and volatile character hindering its quantitative retention.

Owing to the increasing amount of industrial, agricultural, forest and domestic wastes, there is a trend toward co-combustion of coal with these waste materials. For example, the amount of municipal solid waste (MSW) of the cities (in world-wide scale) may reach 2.2 billion tonnes per year

by 2025 [19,20]. Moreover, if an effective and efficient solid waste management is not applied, it can result in health hazards or negative impact on the environment [21]. Therefore, possible interactions of various wastes with coal during co-combustion is discussed herein as well.

The objective of this review paper is to address all important aspects relating to Cd behavior and interactions during combustion (incineration) processes with particular attention paid on decreasing its emissions.

## 2. Cd (and Cl) in Coal

### 2.1. Concentrations of Cd

Clarke values for Cd concentrations in low-rank and high-rank coals are 0.24 and 0.20 ppm, which is ca. one- or two-orders of magnitude lower than those of Pb and Cr [22]. Since Cd concentrations in coal are rather variable, Biswas and Wu [23] provided typical Cd concentrations range in coal (entering combustors) being 0.033–0.64 ppm. For the comparison, Table 1 provides also Cd levels in other related materials, such as in municipal solid waste (ash) [24] or some coal combustion additives (limestone or urea) [25]. It can be deduced from these data that if some of these materials are co-combusted with coal (e.g., in fluidized-bed power stations) the amount of Cd introduced into the combustion chamber with a waste might be significantly higher than its input mass in coal. In contrast, if limestone (ca. 0.01 ppm Cd) or urea (ca. 0.03 ppm Cd) [25] are put into the furnace due to flue gas cleaning, their low Cd concentrations might result in a diluting effect.

**Table 1.** Cadmium levels in target materials.

Material	Cd Concentration (Range)	References
Coal	0.033–0.64 ppm	[23]
Low rank coal (ash)	0.24 (1.1) ppm	[22]
High rank coal (ash)	0.20 (1.2) ppm	[22]
Municipal solid waste	0–90 ppm	[23]
Municipal solid waste incineration fly ash	50–450 ppm	[24]
Municipal wastewater sludge	100 ppm	[23]
Sewage sludge ash	2.3–94 ppm	[24]
Limestone	0.01 ppm	[25]
Urea	0.03 ppm	[25]

### 2.2. Associations of Cd

The sulfidic (chalcophylic) associations of Cd [26,27] is even more dominant than that of Pb (ca. 80% Cd in low-rank coals and 65% Cd in high-rank coals [28]), which relates primarily to Cd occurrence in sphalerite. There is also some affinity to pyrite (mainly in high rank coals—25%) and ca. 10% silicate-associated Cd in both high-rank and low-rank coals [28]. Organic affinity of Cd has been observed in Waterberg Coalfield coal [29], Huaibei Coalfield coal [26] or in coal form Upper Silesian Coal basin [30].

During coal combustion, Cd behaves as one of the most volatile elements, which corresponds well with its dominant sulfidic affinity accompanied by minor occurrence in organic matter or carbonates; according to Finkelman [28], only ca. 10% of Cd (in average) is firmly bound in (alumino) silicates.

### 2.3. Cl in Coal (and Wastes)

Due to the abundant and widely-discussed interactions of Cd with Cl during combustion, Cl levels in coal are important as well. Clarke values of estimated Cl concentrations in brown coals and hard coals (and their ashes) are 120 and 340 ppm (and 770 and 2100 ppm in corresponding ashes) [31,32]. Therefore, even if Cd concentrations in low-rank and high-rank coals are similar, higher Cl content in high-rank coals might favor Cd volatilization (release) from these coals.

Even though organically-bound (covalent bond) Cl may also be present in coals, its occurrence in inorganic chlorides (NaCl, KCl etc.) is undoubtedly the most abundant; some “semi-organic” Cl (i.e., anion  $\text{Cl}^-$  sorbed on organic matter from pore water) was observed as well [31,32].

Fluidized-bed combustion technology is spreading quickly around the world [33] which enables to use also low-grade fuels (biomass, wastes, etc.) whose composition and Cl levels are of fluctuating quality. For example, refuse-derived fuel typically contains PVC (polyvinyl chloride), sewage sludge often contains higher levels of  $\text{FeCl}_3$ , NaCl is present in food residues and biomass may contain higher Cl (and moisture) concentrations [34–36]. All these different Cl forms exhibit different effects on Cd volatilities (which will be discussed in Section 5).

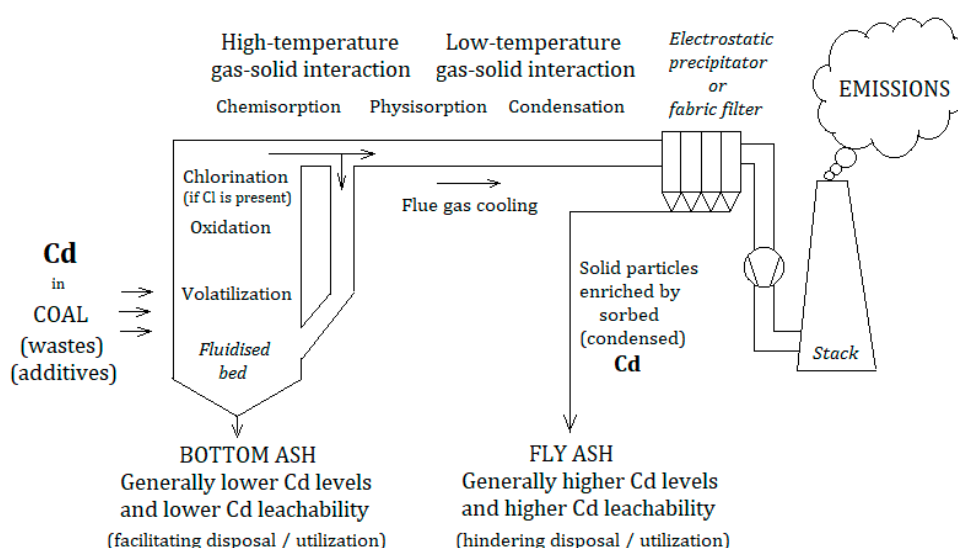
### 3. Melting/Boiling Points of Cd Compounds

Based on thermodynamic equilibrium calculations in oxidizing atmosphere (not considering Cd-Si and Cd-Al interactions) [37], the most abundant Cd-compounds during coal combustion are CdO,  $\text{CdCl}_2$ ,  $\text{CdSO}_4$  and Cd. Melting/boiling points of these compounds are crucial for detailed evaluation of Cd transformations during coal combustion and are listed in Table 2.

**Table 2.** Melting points (m.p.) and boiling points (b.p.) of Cd and its target compounds.

Compound	m.p./b.p.	Temperature	References
Metal	Cd m.p.	321 °C	[38,39]
	Cd b.p.	767 °C	[38,39]
Oxide	CdO m.p.	1540 °C (sublimation)	[39]
	CdO b.p.	Sublimation at 900 °C	[38]
Chloride	$\text{CdCl}_2$ m.p.	564 °C	[38–40]
	$\text{CdCl}_2$ b.p.	960 °C	[38–41]
Sulfate	$\text{CdSO}_4$ m.p.	1000 °C	[38,40]

It is noteworthy to mention also the melting points of some the most abundant interacting species that typically occur during coal combustion, e.g., NaCl (801 °C) [42], KCl (770 °C) [42],  $\text{CaCl}_2$  (ca. 800 °C) [43],  $\text{CaSO}_4$  (1400 °C) [43].



**Figure 1.** Partitioning of Cd during coal combustion at fluidised-bed power station.

As melting/boiling points of  $\text{CdCl}_2$  are lower than those of CdO or  $\text{CdSO}_4$ , formation of  $\text{CdCl}_2$  leads to increased volatility of Cd, which is quite hindering to its quantitative capture (which will be discussed in detail in Section 5). The fraction of Cd that does not condense during flue gas cooling or is

not retained by additives or ash particles might remain in gaseous form that can easily pass through particulate control device (electrostatic precipitator or fabric filter) as depicted in Figure 1.

#### 4. Combustion/Retention Experiments without Extra Cl Added

##### 4.1. In-Furnace Adsorbents

Various adsorbents were tested for Cd retention in combustion/incineration processes (bauxite, kaolinite,  $\text{Al}_2\text{O}_3$ , silica sand, apatite, zeolite, mullite, scallop etc.) Nevertheless, as efficient Cd retention is a complex phenomenon (depending at least on the temperature, dwell time, atmosphere and concentrations of interacting species) [44], results observed in individual combustion/retention experiments are quite variable, which is shown in Table 3. For example, bauxite is a promising adsorbent of Cd. Nevertheless, in different studies [45–49] the retained fraction of Cd is rather fluctuating—from 7–14% [46,48,49] up to 68–74% [45,47] despite the combustion temperature was similar (700–800 °C), which can be attributed to different composition of the feed and different experimental conditions (including time factor). Similar results are documented also for kaolin(ite) that is widely used for Cd retention as well [45,46,48–51]—herein, the retention efficiency ranges from 4% [46] up to 44% [48,49].

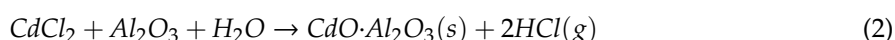
**Table 3.** Effect of adsorbents on Cd retention.

Experiment	Evaluated	Adsorbent	Results	References
CdCl <sub>2</sub> , thermogravimetric reactor, 800 °C	Metal adsorbed	Bauxite	74% *	[45]
		Alumina	55% *	
		Limestone	23% *	
		Emathlite	12% *	
		Kaolinite	11% *	
		Silica	4% *	
Synthetic solid waste (with Cd-nitrate), fluidized bed incinerator, 700 °C (900 °C)	Cd adsorption efficiency	$\text{Al}_2\text{O}_3$	9% (4%) *	[46]
		Bauxite	14% (9%) *	
		Kaolinite	5% (5%) *	
Wood + Cd-acetate, fluidized-bed incinerator, 750 °C	Percent capture	Bauxite	68% *	[47]
		Zeolite	50% *	
		Lime	40% *	
		Sorbent mixture	75% *	
Dried sewage sludge + 5% adsorbent, drop-tube furnace, 800 °C	Captured fraction	Kaolin	44% *	[48,49]
		Zeolite	27% *	
		Limestone	22% *	
		Scallop	19% *	
		Mullite	15% *	
		Apatite	14% *	
		Bauxite	7% *	
		Silica	4% *	
Alumina	2% *			
Coal + kaolinite, electrically heated combustor	Relative enrichment factor	1100 °C	0.4 *	[50]
		1200 °C	2.1 *	
		1300 °C	0.75 *	
Coal + kaolinite, electrically heated combustor, 1100 °C	Concentration	Kaolinite	0.38 ppm *	[50]
		Bauxite	0.40 ppm *	
		CaO	0.39 ppm *	
Sewage sludge + additive (5:1), thermogravimetric analyzer, 1200 °C	Fixed ratio of Cd	No additive	25% *	[51]
		CaO	20% *	
		Kaolin	22% *	
Coal + CaCO <sub>3</sub> modified by 3 different additives, muffle furnace, 900 °C	Cd-capturing rate	Na <sub>2</sub> CO <sub>3</sub>	22.83%	[52]
		K <sub>2</sub> CO <sub>3</sub>	57.37%	
		Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	47.55%	
Fluidized-bed incinerator, artificial solid waste (with Cd-nitrate), 900 °C	% retention (on silica sand)	no Na added	5% *	[53]
		1.2% Na added	46% *	

\* Rough estimation (data from diagram).

#### 4.1.1. Bauxite

An effective retention of Cd can be achieved by bauxite [45–47], mostly at lower temperatures (700–800 °C) [45,47]. However, at higher temperatures (1100 °C) the ability of bauxite to retain Cd was observed as well [50]—in this experiment, adsorbent pre-mixed with coal was combusted in a vertical tube reactor at 1100 °C and bauxite provided better retention results than kaolinite and CaO (based on evaluation of particles with medium size). At lower temperatures (700 or 900 °C), during synthetic MSW incineration bauxite was better adsorbent of Cd than kaolinite and Al<sub>2</sub>O<sub>3</sub> [46], which might indicate that the admixture of other minerals/components in bauxite might favor Cd retention in comparison with pure Al<sub>2</sub>O<sub>3</sub>. Moreover, (at 700 °C) bauxite was the best adsorbent not only for Cd but also for Cr, Pb and Cu. Interaction of CdO and CdCl<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub> can be described by Reactions (1) [47] and (2) [45,47].



#### 4.1.2. Kaolinite

Yao and Naruse [48,49] tested 9 adsorbents for in-furnace retention of Cd during dried sewage sludge combustion in drop-tube furnace at 800 °C. The most efficient Cd capture was observed in the case of kaolinite (31.55 m<sup>2</sup>/g), followed by zeolite (21.40 m<sup>2</sup>/g), limestone (1.87 m<sup>2</sup>/g), scallop (0.85 m<sup>2</sup>/g), apatite (35.14 m<sup>2</sup>/g) ~mullite (8.60 m<sup>2</sup>/g), bauxite (0.92 m<sup>2</sup>/g), silica (1.29 m<sup>2</sup>/g) and alumina (1.23 m<sup>2</sup>/g)—captured fractions of Cd are given in Table 3. The results indicate that specific surface area is not the only affecting factor. Efficient retention by kaolinite can be described by Reaction (3) [48,49] and is in line with the conclusion that the retained Cd in residual ash may be in the form of binary oxides CdO·Al<sub>2</sub>O<sub>3</sub> or CdO·SiO<sub>2</sub> [25].



Kaolinite was also tested during high-temperature combustion. Chen et al. [51] presented better retention of Cd on kaolin than on CaO if added to sludge prior to combustion at 1200 °C (in TGA); however, it is interesting that absolutely the best retention results were observed if no adsorbent was added to the sludge (as shown in Table 3).

Wendt and Lee [54] document efficient retention of Cd (and Pb) using blended adsorbent containing kaolinite and calcite (with admixture of lime) injected into flame in vertical combustor at 1160 and 1280 °C; the former temperature was better for the retention of Pb, the latter was advantageous for the capture of Cd (if there was no Pb). If both Cd and Pb were present, the lower temperature (1160 °C) was good also for the retention of Cd, which was interpreted by surface melt formed on the adsorbent particles due to the enhancing effect of Pb.

#### 4.1.3. Silica Sand

Silica sand can also adsorb heavy metals (HMs) including Cd [55,56]. However, in both studies, the retention of Cd was somewhat worse than that of Pb and can be described by Reaction (4) [47]



The effect of Na (if NaNO<sub>3</sub> was added to silica sand) on the retention of Cd and Pb was studied by Kuo et al. [53]. The presence of Na increased the retention ability of silica sand at 700–900 °C; at 900 °C the increase was the most significant—from ca. 5% retained Cd (no Na) up to ca. 46% (for 1.2% Na). If Na was added at 800 and 900 °C, the retention of Cd was even better than that of Pb (ca. 41% Pb vs. 46% Cd at 900 °C). The observation was attributed to the formation of low-melting-point eutectics on the adsorbent particle surfaces; the effect of physical co-condensation was presumed as being also possible.

#### 4.1.4. Calcareous Adsorbents

Calcareous adsorbents were tested for the retention of Cd as well. In general, if no extra Cl (or S) was added to the feed, then bauxite, kaolinite or zeolite typically provide more efficient retention (than calcareous adsorbents). However, in the case of higher Cl (or S) levels in the feed, calcareous adsorbents (CaCO<sub>3</sub> or CaO) provided usually better results, which will be discussed in detail in Section 5.2.1.

#### 4.2. Other Approaches

Instead of adding kaolin directly into the furnace, suspension of water with kaolinite can be used also in semi-dry spray tower at 150–170 °C [57]. Synthetic solid waste was combusted at 800 °C and in semi-dry spray tower limestone, kaolinite, Al<sub>2</sub>O<sub>3</sub> or no sorbent (i.e., only water) were applied. For the retention of Cd, the best results were achieved by spraying with water without any adsorbent, while in the case of other HMs, added adsorbents provided better results than water.

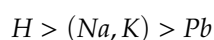
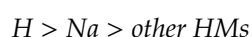
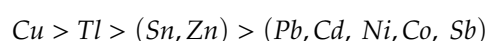
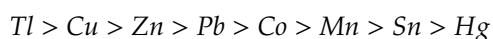
Peng et al. [55] reported promising Cd-retention results by means of low-temperature two-stage fluidized bed incinerator where artificial MSW was combusted. The temperature at the first stage was 550, 650 and 750 °C, at the second (filtration) stage it was always 800 °C. The best Cd retention was obtained at 550 °C (at the first stage). Efficient Cd capture in this low-temperature two-stage system was attributed to Cd vaporization, chemical adsorption and filtration in the second stage, which is in line with conclusions of other studies [58,59]. It is worth mentioning that Cd retention at 650 °C (the 1st stage) was lower than that at 550 °C but almost all this decrease was retained later during the filtration at the 2nd stage. Then, the overall retention of Cd at 650 °C was only slightly lower than that at 550 °C (due to efficient filtration at the second stage).

### 5. Effect of Cl

In general, the effect of Cl on behavior of Cd (and other HMs) is studied namely due to shifting CdO-CdCl<sub>2</sub> equilibrium toward the formation of chloride [60]. As chlorides of most metals (including Cd) exhibit higher volatility than oxides, there are two dominant reasons why attention is paid to this phenomenon:

- (i) Due to enhanced emissions of Cd (and other HMs) during combustion/incineration processes (high volatility of CdCl<sub>2</sub> favors Cd occurrence in gaseous form that might easily pass through the air-pollution control device).
- (ii) Due to removal of HMs from combustion (incineration) ashes which facilitates their further technological utilization. High volatility of CdCl<sub>2</sub> facilitates Cd release from bottom ash leading to lower Cd concentrations and better ash utilization perspectives. In contrast, due to volatilization/condensation mechanism, certain fraction of Cd might condense/adsorb on fly ash particles increasing Cd levels there (Figure 1). Moreover, these fractions often exhibit increased leachability.

Affinity of individual elements to Cl is different—approximate sequences of these affinities can be found in the literature [61–64]:



There is a consensus in the literature that Cd exhibits lower affinity to Cl than Pb [65].

The idea of close partitioning of Cd and Cl during coal combustion is supported (i.a.) by strong positive linear relationship between relative enrichment factors of Cd and Cl in filter ash and cyclone ash [66].

Papers documenting the (typically enhancing) effect of Cl on Cd volatility are abundant in the literature—Table 4 provides at least some typical illustrative examples of this effect. As shown in Table 4, various Cl-bearing compounds are able to influence Cd partitioning, such as NaCl, PVC, NH<sub>4</sub>Cl, FeCl<sub>3</sub>, CaCl<sub>2</sub> or MgCl<sub>2</sub>. Despite some similar features, the effect of individual chlorination agents is different.

There is a consensus in the literature that there are two general chlorination mechanisms—direct and indirect one. Direct chlorination is thought to be a prevalent mechanism in the case of NaCl where (high-temperature) direct reaction between NaCl and Cd (or other HMs) oxides occur [67]. Indirect chlorination is more common and was observed (e.g.,) in the case of PVC, CaCl<sub>2</sub> or MgCl<sub>2</sub> and is based on (low-temperature) release of chlorination agent (HCl, Cl<sub>2</sub>) that is followed by its reaction with CdO (or other HMs oxides) [68].

**Table 4.** Effect of Cl compounds on Cd volatility.

Experiment	Parameter Evaluated	Chlorine Added	Results	References
Bitum. coal + SRF *, ca. 1200 °C	Relative enrichment factor in filter ash vs. cyclone ash (related to Al)	- 1 and 2% NaCl 2 and 4% PVC	5–7 8 and 10 6 and 23	[66]
Bitum. coal + SRF *, ca. 1200 °C	TEM-EDS analysis of filter ash aerosols from vaporization mode	- 1% NaCl 2% PVC	<0.5%Cd/<0.5%Cl 1.5%Cd/6%Cl 1%Cd/1.5%Cl	[66]
Solid waste, 900 °C	Volatilized fraction of Cd	- 1 and 3% Cl (NaCl) 1 and 3% Cl (PVC)	47% 85 and 90% 90 and 95%	[68]
Wastewater sludge, 850 °C	Volatilization rate	No NH <sub>4</sub> Cl (0.1% Cl) With NH <sub>4</sub> Cl (0.5% Cl)	40% 85%	[69]
Simulated MSW, 800 °C	Percentage in fly ash and flue gas **	No FeCl <sub>3</sub> With FeCl <sub>3</sub>	20% in fly ash ***, 80% in flue gas ***, 80% in fly ash ***, 20% in flue gas ***	[70]
MSW fly ash, 800 °C	Removal percentage of Cd from fly ash	- 100 g/kg Cl (NaCl) 100 g/kg Cl (MgCl <sub>2</sub> ) 100 g/kg Cl (CaCl <sub>2</sub> )	50% ***, 48% ***, 90% ***, 76% ***	[71]

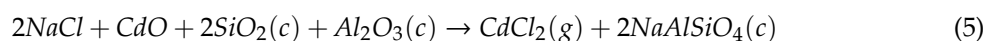
\* Solid recovered fuel; \*\* Percentage in bottom ash was within a few % (neglected); \*\*\* Rough estimation (from diagram).

### 5.1. Direct Chlorination (Effect of NaCl)

Direct chlorination mechanism of Cd (and other HMs) is typically discussed in the case of NaCl [71], which is present in coals, MSW (food residues), sludges, calcareous additives etc.

During simulated MSW incineration in horizontal tube furnace (900 °C, 60 min), NaCl did not lowered volatilization temperature of Cd (it remains within the range 600 °C–700 °C) but NaCl enhanced the volatilization rates at 700 °C–900 °C [68]. Enhanced Cd volatilization initiated at 700 °C–800 °C, which is lower than the temperature of HCl release from NaCl (t > 900 °C); therefore, the indirect chlorination mechanism is less probable in this case [68].

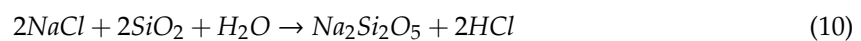
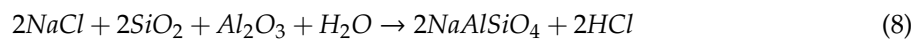
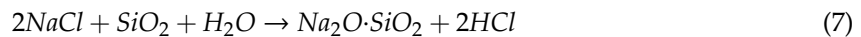
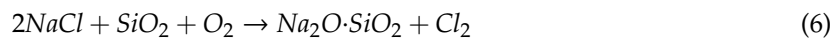
Based on thermodynamic calculations, it was concluded that both SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are needed for direct chlorination via NaCl (Reaction (5)) [68]:



According to Nowak et al. [71] and Chan et al. [41], reaction of NaCl with H<sub>2</sub>O and O<sub>2</sub> (releasing HCl and Cl<sub>2</sub>) is less probable than evaporation of NaCl without reacting. However, in the case of direct

chlorination, NaCl evaporation or melting is favorable because the mixture of Cl and Cd (or other HM) is not typically homogeneous.

This is consistent with the conclusion of Yu et al. [42]: when temperature reaches melting point of NaCl (801 °C) or KCl (770 °C), NaCl or KCl become liquid phase; then, the reaction rates between liquid NaCl/KCl and SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> can be accelerated. At higher temperatures, NaCl or KCl was further vaporized into gas phase and the formation of HCl or Cl<sub>2</sub> through gas-solid reaction can occur (as described in Reactions (2)–(6)) [42,67]:



In contrast, CaCl<sub>2</sub> or MgCl<sub>2</sub> directly react with H<sub>2</sub>O and/or O<sub>2</sub> releasing HCl and/or Cl<sub>2</sub> (i.e., Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> are not needed for this release) and are thought to be more efficient chlorination agents.

However, it should be mentioned in this context that when MSW incineration fly ash was roasted in the rotary reactor at 1000 °C (60 min), added NaCl even slightly lowered the Cd removal [71]. The authors hypothesized that NaCl could probably form azeotropes (vapor pressure minima) with HM chlorides.

The results are opposite to those of Wang et al. [68] (where NaCl enhanced Cd volatilization at 700 °C–900 °C); probably due to higher temperature (1000 °C) used in the study of Nowak et al. [71] where NaCl might favor surface melt on the particles which supports Cd retention and thereby hinders Cd evaporation.

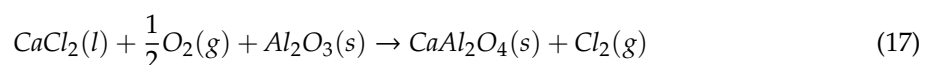
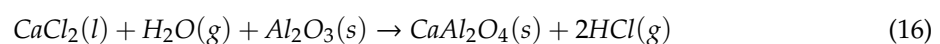
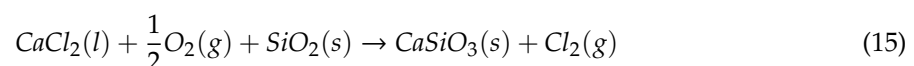
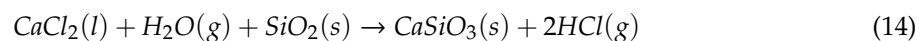
## 5.2. Indirect Chlorination

Indirect chlorination is more common than direct mechanism and is based on release of HCl or Cl<sub>2</sub> from Cl-donor followed by interaction of Cl-containing species (HCl, Cl<sub>2</sub>) with CdO (or other HM oxides) typically increasing its volatility.

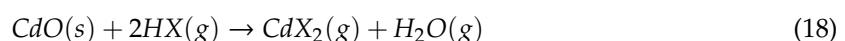
Step 1 is the formation of HCl/Cl<sub>2</sub> by interaction with O<sub>2</sub>/H<sub>2</sub>O [24,32,42] (Reactions (7)–(9)):



Interactions with (alumino)silicates are given [24] by Reactions (10)–(13):



Step 2 is chlorination of CdO (in oxidizing atmosphere) [72] (Reaction (14)):

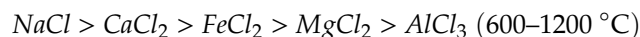




where X = Cl, Br, F, I.

Since Cl levels are typically higher than those of Br, F and I, interactions of CdO and HCl are expected to be more abundant than those with HBr, HF and HI.

Individual chlorination agents exhibit different tendency to release Cl, which can be quantified by equilibrium partial pressures over these chlorination agents; equilibrium partial pressures increase in the sequence [41]:



Cd removal during muffle-furnace incineration tests with MSW incineration ashes was evaluated after addition of NaCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> in the temperature range of 800 °C–1200 °C [71]. Due to the naturally high volatility of Cd, the experiments at 900–1200 °C were quite inconclusive for all chlorination agents as all removal efficiencies (volatilities) were nearly 100%. Nevertheless, at 800 °C, only increasing amount of MgCl<sub>2</sub> and CaCl<sub>2</sub> enhanced original Cd volatility (50%) up to ca. 90% in the case of MgCl<sub>2</sub> (100–150 g Cl/kg) or up to ca. 85% in the case of CaCl<sub>2</sub> (150–200 g Cl/kg). As these experiments were conducted with the aim to remove Cd (and other HMs) from the ash, roasting time was set as 20 h. Therefore, application of these results for the estimation of the volatility of Cd during e.g., fluidized-bed combustion (FBC) at 850 °C can be quite misleading as dwell time in high-temperature zone in fluidized bed is significantly shorter.

These results are consistent with very high volatility of Cd at 1000 °C (60 min) when addition of NaCl, AlCl<sub>3</sub>, MgCl<sub>2</sub>, FeCl<sub>3</sub> and CaCl<sub>2</sub> were tested. Without these agents, the Cd removal exceeded 80% and if 0.3 g Cl was added (by aforementioned agents) the removal reached ca. 95% and was comparable for all these chlorination agents [41]. Nevertheless, also in this case, 60 min roasting time is still too long to be used also for the evaluation of Cd volatility at power station (these experiments were conducted with the aim to remove HMs from the ash).

Indirect chlorination mechanism was considered as the most probable underlying mechanism of MgCl<sub>2</sub> [71]; in the case of CaCl<sub>2</sub> it prevails as well (even if direct chlorination might also occur [71]).

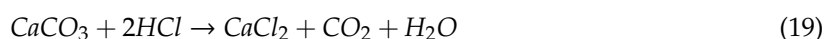
### 5.2.1. Indirect Chlorination by PVC and Interactions with Calcareous Minerals

A typical example of an indirect chlorination agent is PVC releasing HCl at ca. 240 °C (in oxidizing atmosphere) [68,73,74], which corresponds with low-temperature volatilization.

During incineration experiments with simulated MSW [68], PVC lowered initial volatilization temperature from 600–700 °C to ca. 500 °C (which is initial volatilization temperature of CdCl<sub>2</sub>). At higher temperatures ( $t > 600\text{ }^\circ\text{C}$ ) it enhanced the vaporization rates (in contrast to NaCl that did not lower volatilization temperature). In the presence of PVC in the feed waste, Cd reached a maximum volatilization rate at 600–700 °C, which is lower than in the case of Pb (800 °C–900 °C).

HCl released from PVC (or other indirect chlorination agents) enhances the volatility of Cd and other HMs, unless it is retained by ash components, e.g., by calcareous additives used during FBC [75–77].

There is a consensus in the literature that CaO can adsorb HCl (g) forming CaCl<sub>2</sub> with optimal temperature range of ca. 500 °C–650 °C. However, at higher temperatures (than ca. 700 °C) the retained Cl is released back which is then available for the chlorination of Cd and other HMs again [68,76,77]. Interaction with CaCO<sub>3</sub> has also been described in the literature [43] with optimal temperature range of 600–850 °C (Reaction (15)):



This is consistent with observations of Tang et al. [78] adding CaO or CaCO<sub>3</sub> to MSW and evaluating Cd retention in bottom ash. At 700 °C–800 °C, some (moderate) capture of Cd in bottom ash was observed, whereas at 900 °C the release of Cd from bottom ash was even enhanced, due to experimental temperature exceeding the optimal temperature range of 500 °C–650 °C (releasing retained Cl back).

The effect of temperature evaluated by Liu et al. [43] led to a similar conclusion. Sewage sludge conditioned with  $\text{FeCl}_3/\text{CaO}$  (due to dewatering) was incinerated at 600 °C–700 °C released slightly less Cd than without conditioner. However, at 800 °C–900 °C, sludge with  $\text{FeCl}_3/\text{CaO}$  released more Cd [43]—the latter case corresponds with the temperature exceeding the optimal retention range.

According to Li et al. [52], the retention ability of  $\text{CaCO}_3$  can be improved by  $\text{K}_2\text{CO}_3$  or  $\text{Al}_2(\text{SO}_4)_3$  modification—the defects created during limestone modification enhanced the retention ability.

Results from recent studies indicate that the presence of PVC during the combustion/incineration of coal/waste with Cd increases its volatility and potential fractions released in emissions. Calcareous additives could suppress this unfavorable effect; but if added directly into the furnace, the temperature is usually too high for efficient retention of chlorination agents [43,52,68,78,79]. However, if limestone is applied within a semi-dry spray tower, good Cd retention results were achieved, which was documented by Chen et al. [57]. Synthetic solid waste (sawdust, PP and Cd-nitrate) was incinerated at 700 °C–800 °C and semi-dry spray tower operate at the temperature of 150 °C–170 °C. If no PVC was added in the feed waste, the best (10%) Cd retention results were received by water injection (i.e., no adsorbent). When PVC was added to synthetic waste, absolutely the best overall Cd retention was observed if limestone was used in semi-dry spray tower (nearly 40% Cd retention), followed by water (21%), kaolinite (13%) and  $\text{Al}_2\text{O}_3$  (10%). If NaCl was added to the feed waste, limestone injection exhibited somewhat lower Cd retention (28% Cd retention), which was the best result of all adsorbents injected in the experiment with NaCl.

Another promising adsorbent for Cd retention (if combusted/incinerated with PVC) is  $\text{NaHCO}_3$  [80]. During rotary kiln incineration (850 °C) of limestone (200 kg) doped with 2 kg PVC (with 0.5%  $\text{Cd}^{2+}$ ), overall Cd retention achieved by post-incineration injection of  $\text{NaHCO}_3$  was 96.3%.

In summary, emissions of Cd (or potentially of other HMs) could be reduced by controlling Cl content in coal but namely in co-combusted wastes. Other promising approach is to apply adsorbent capturing chlorination gases, e.g., calcareous additives ( $\text{CaO}$ ,  $\text{CaCO}_3$  etc.). In FBC, such additives are already widely applied. However, they are typically added directly to high-temperature zone where the combustion temperature is ca. 850 °C which is too high to retain HCl. Therefore, from the perspective of the efficient retention of Cd (or possibly also other HMs), low-temperature application is expected to provide better retention results.

## 6. Effect of Moisture

In addition to different moisture levels in individual coals, even more significant effect can be expected if coal is co-combusted with wastes, from which some typically contain higher moisture levels, such as sewage sludge, agricultural or forest residues, etc. [81,82].

The moisture effect should be also taken into account in the case of oxy-fuel combustion [83] or if coal-water slurry is combusted [84,85]. Different drying methods applied to MSW could also have some effect [86].

### 6.1. Effect of Moisture (No Extra Cl Added)

No noticeable effect of moisture levels on Cd distribution was concluded by Durlak et al. [87] or Morf et al. [88]. Other studies document increasing Cd emissions with increasing moisture levels [89–91].

During pyrolysis of real MSW, release of Cd gradually increased with increasing moisture levels from 0% via 30% up to 65% [90]. The overall enhancement of Cd release corresponding to increase of moisture level up to 65% was ca. 10% (from 60% to 70%) and it was attributed to prolonged pyrolysis time thereby enhancing the volatility of Cd (and some other HMs) [90].

During incineration (at 950 °C) of MSW (paper, flour, cotton, sawdust, polystyrene,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and Cd-acetate) [89,91], original Cd retention rate in bottom ash (ca. 18%) moderately decreased with increasing moisture levels (in the former study [89] moisture level increased up to 62%  $\text{H}_2\text{O}$  and in

the latter [91] up to 39.4% H<sub>2</sub>O). Prevailing physical aspect of the moisture effect on Cd volatility was concluded in these two studies as well [89,91] and prolonged evaporation and longer combustion time were evaluated as dominant reasons of increased Cd volatility. In these two studies [89,91], the incineration time was set as 6 min; therefore, any prolongation might result in increased Cd volatility. In contrast, if MSW was incinerated by Morf et al. [88], the incineration time of 2 h was probably long enough to suppress the effect of some further little prolongation due to moisture evaporation. Equilibrium calculations by Durlak et al. [87] evaluated thermodynamic effect of chemical reactions; kinetic effects are not usually included in such studies [92].

### 6.2. Effect of Moisture in the Presence of Cl

Cd is one of the most volatile elements, which results in typically low remaining fractions in bottom ash after combustion. If extra Cl is added, Cd volatility further increases leaving behind only a few % of Cd in bottom ash (which somewhat hinders evaluation of the moisture effect).

During synthetic MSW incineration at 950 °C without extra Cl added [91], bottom ash retained ca. 18% of Cd while if 1% of Cl was added, there was practically no retention (<ca. 1–2%)—these data are for 0% moisture. If % H<sub>2</sub>O increased up to 39.4%, the retention of Cd in bottom ash slightly increased but still remained quite low (ca. < 5%). This effect is in line with thermodynamic equilibrium calculations [91] showing two dominant competitive species: CdCl<sub>2</sub> (g) and CdO (s). As the fraction of Cd (g) is within only a few %, the distribution of Cd between CdCl<sub>2</sub> (g) and CdO (s) governs overall Cd volatility and its release from bottom ash. Specifically, at 950 °C [91], increase of moisture from 10 to 35% lead to decrease of CdCl<sub>2</sub> (g) fraction by ca. 20% (and this Cd fraction is almost totally converted to CdO(s) because increase of Cd (g) makes only a few %). And the conversion of gaseous CdCl<sub>2</sub> to condensed CdO decreases Cd volatility. Overall, if Cl is present in sufficient amount in the feed fuel, the volatility enhanced by Cl prevails on the retention effect brought about by moisture (there are two opposite effects of Cl and moisture).

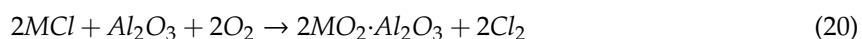
## 7. Effect of Atmosphere

### 7.1. Effect of O<sub>2</sub> Level

The air/coal ratio is an important factor controlling Cd volatility and emissions [68,92]. According to thermodynamic equilibrium calculations simulating pulverized coal combustion, all Cd remained in the solid phase at 900 K if air/coal ratio was at least 1.1; decrease of the air/coal ratio to 1.0 resulted in all Cd to be in the vapor phase (even at 600 K). In the case of FBC, an increase of the air/coal ratio from 1.0 to 1.1 changed Cd distribution significantly toward its enhanced fractions in the solid phase. Nevertheless, these calculations are based on reaching the chemical equilibrium.

As for the experimental results, it is noteworthy that (at least) 3 different conclusions about effect of % O<sub>2</sub> on Cd volatility can be found in the literature [93–95]:

(i) Decrease of Cd volatility by increased % O<sub>2</sub> (which is consistent with thermodynamic calculations [92]) was concluded for incineration of Al<sub>2</sub>O<sub>3</sub> impregnated with CdCl<sub>2</sub> at FBC reactor at 850 °C for 1 h [93]. The observation was explained via the Reaction (16) [93]:



(where increasing % O<sub>2</sub> shifts the equilibrium to the right in favor of the formation of non-volatile 2MO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>) [93].

As the dwell time in the high-temperature zone was long enough (1 h), the kinetic limitations were thereby diminished and the experimental reasons are in line with thermodynamic equilibrium calculations.

Thermodynamic equilibrium calculations conducted by Yan et al. [62] concluded different effect of oxidizing/reducing conditions for low-ash coal and high-ash coal. In the case of high-ash coal, volatilization of Cd in different atmospheres occurs in similar temperature regions (oxidizing

atmosphere at 550–800 K; reducing at 600–800 K) while in the case of low-ash coal, volatilization in oxidizing atmosphere occurs at higher temperatures (800–1000 K) than in the case of reducing conditions (600–700 K). In this case, reducing conditions facilitate Cd volatilization.

(ii) Increasing Cd volatility with increasing % O<sub>2</sub> in the inlet atmosphere was observed during co-combustion of lignite and waste activated sludge for 30 min at 1000 °C in horizontal tube furnace [94]. Vaporization percentage of Cd increased from ca. 35% (10% O<sub>2</sub>) up to ca. 50% (30% O<sub>2</sub>) and it was explained through enhanced intensity of combustion by higher % O<sub>2</sub> (increasing local temperature to some extent).

(iii) No noticeable effect of % O<sub>2</sub> on Cd volatilization was concluded during the combustion of two coals at 21% O<sub>2</sub> (in N<sub>2</sub>) and 6.35% O<sub>2</sub> (in N<sub>2</sub>) atmospheres at 800 and 900 °C [95]. The crucible containing the coal was lifted up and down inside the vertical furnace and no matter which temperature was used, % O<sub>2</sub> did not affect Cd volatility in these two studied coals. It should be mentioned that the weight loss of Cd (from the coal) was quite low: ca. 35% was volatilized at both temperatures and O<sub>2</sub> levels from the first coal; in the case of the second coal, at 800 °C ca. 25% (for both O<sub>2</sub> levels) and at 900 °C ca. 50% of Cd was released. As Cd is a typical high-volatility element, the aforementioned volatilized fractions are surprisingly low, which might correspond with the very character of these combustion experiments, as they were conducted with the aim to simulate the initial stage of flame quenching (i.e., during the time needed only for the release of volatile matter, its ignition and burnout). Therefore, some Cd still remained in the rest of the sample and it could be hypothesized that O<sub>2</sub> level is more important for the interaction with the rest of the sample (than for the volatiles burnout).

## 7.2. Effect of “the Rest” of the Atmosphere

Not only % O<sub>2</sub>, but also the composition of “the rest” of the combustion/incineration atmosphere can play an important role [78,96], which is studied namely due to oxy-fuel combustion technology where CO<sub>2</sub> can be captured due to recycling of the flue gas and oxygen is used instead of air (thereby increasing CO<sub>2</sub> content up to 95%) [96]. Thus, instead of N<sub>2</sub>/O<sub>2</sub> atmosphere, CO<sub>2</sub>/O<sub>2</sub> is used in oxy-fuel combustion.

Thermodynamic equilibrium calculations [97] concluded that distribution of Cd (and other HMs) in oxy-fuel combustion was nearly the same as in the case of air combustion. However, real incineration experiments with synthetic MSW [78] (flour, paper, sawdust, HDPE, texture, rubber, leather and Cd-acetate) in tubular furnace revealed certain differences in Cd volatility in CO<sub>2</sub>/O<sub>2</sub> and N<sub>2</sub>/O<sub>2</sub> atmospheres. In both atmospheres, the Cd residual rates at 1000 °C were almost zero; at 900 °C they were nearly the same—ca. 27–28%. However, at 700 °C and 800 °C, Cd residual rates were higher in CO<sub>2</sub>/O<sub>2</sub> (oxy-fuel atmosphere) than in N<sub>2</sub>/O<sub>2</sub> (air): ca. 68% for CO<sub>2</sub>/O<sub>2</sub> and 52% for N<sub>2</sub>/O<sub>2</sub> at 700 °C and 25% (CO<sub>2</sub>/O<sub>2</sub>) and 22% (N<sub>2</sub>/O<sub>2</sub>) for 800 °C. The suppressed Cd volatility in CO<sub>2</sub>/O<sub>2</sub> was more pronounced at lower temperatures, which was explained through higher specific heat capacity of CO<sub>2</sub> than N<sub>2</sub> resulting in delaying the ignition of the MSW and lowering the combustion temperature (in the case of CO<sub>2</sub>/O<sub>2</sub> atmosphere) thereby decreasing the emissions of Cd. As the incineration time was the same for both atmospheres, these results are not contradictory to thermodynamic equilibrium calculations [97] where kinetic limitations are not usually taken into account. Lower volatilization rate of HMs as a result of a lower particle combustion temperature in oxy-fuel combustion (hence affecting the elemental enrichment in ash) was concluded also by Roy and Bhattacharya [98], Font et al. [99], Oboirien et al. [100] or Suriyawong et al. [101].

## 8. Effect of S

Thermodynamic equilibrium calculations (under oxidizing conditions) concluded the occurrence of CdSO<sub>4</sub> up to ca. 730 °C [102]–750 °C [103,104]. Some authors evaluated the maximum temperature of the predominant CdSO<sub>4</sub> occurrence to be ca. 600 [37] or 630 °C [48] (these minor differences probably originate from different interacting components, atmosphere composition and concentrations of Cd and SO<sub>4</sub><sup>2-</sup>). In any case, even during FBC in power stations (where the combustion temperature is quite

low—ca. 850 °C), CdSO<sub>4</sub> (s) is not stable. If the temperature exceeds 600–700 °C (up to ca. 1000 °C), there is a coexistence of multiple phases whose composition is dependent on levels of interacting components. If the presence of chlorides, silica and alumina (along with S) is taken into account, there are namely CdCl<sub>2</sub> (s), CdAl<sub>2</sub>O<sub>4</sub> (s), CdSiO<sub>3</sub> (s) and CdO (s). Then, the highest temperature ( $t > ca. 1000\text{--}1100\text{ }^{\circ}\text{C}$ ) is characterized by prevalent occurrence of Cd (g) as the aforementioned species are not stable in this high-temperature region [102,105,106].

At lower temperatures ( $t < ca. 600\text{--}700\text{ }^{\circ}\text{C}$ ), Cd is not the only element that binds sulfates—there are also Na<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub> (as Na and Ca are common elements in coal, wastes or desulfurization additives) or Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, HgSO<sub>4</sub>, PbSO<sub>4</sub> etc. [48]. Individual metals bind S according to their affinities; according to Yao and Naruse [48], if concentration of S is low, alkali metals are preferred to form condensed phases with it and with increasing S concentration, Cd followed by Pb, Hg and Cr create their sulfates as well.

Binding energies calculated for interaction between Cd and S<sup>2-</sup>, Cl<sup>-</sup>, sulfate and phosphate document quite high values for sulfates and phosphates (in comparison with sulfides and chlorides); it means that in case of co-existence of all these species, the formation of sulfides or chlorides is preferred [69]. This is consistent with moderate increase of % Cd in bottom ash during laboratory combustion (at 850 °C) of synthetic MSW with Cd-acetate and S or Na<sub>2</sub>S added [107].

In any case, theoretic equilibrium calculations indicate that oxidizing conditions and higher temperatures are not favorable for efficient retention of Cd by S, which is consistent (e.g.,) with experimental results presented by Luan et al. [69] where S added to wastewater sludge combusted at 850 °C did not change noticeably the volatilization rate of Cd (which was ca. 40–41% no matter if S was added).

Decrease of Cd retention by SO<sub>2</sub> injection during co-combustion of coal, biomass and waste secondary fuels (in FBC reactor) was reported in the literature as well [37,57,107]. Thermal instability of CdSO<sub>4</sub> in combination with the combustion temperature of 850 °C (in laboratory combustor used for synthetic MSW) might be the probable reason why the addition of Na<sub>2</sub>SO<sub>4</sub> increased % Cd in flue gas [101].

Nevertheless, there are also studies documenting that adding Na<sub>2</sub>SO<sub>4</sub> might favour the retention of Cd [46,57]. Chen et al. [46] combusted synthetic solid waste (plastics, sawdust and Cd-nitrate) at 700 °C in reactor simulating FBC along with 3 different sorbents—kaolinite, bauxite and Al<sub>2</sub>O<sub>3</sub> (added into the combustion chamber). Retention rate of Cd on kaolinite, bauxite and Al<sub>2</sub>O<sub>3</sub> was ca. 8%, 13% and 8%, respectively. If Na<sub>2</sub>SO<sub>4</sub> was added into the combustion chamber (under the same conditions), Cd retention efficiency increased up to 25%, 21% and 34%. It means that the most efficient capture of Cd was achieved by adding Na<sub>2</sub>SO<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> to synthetic solid waste (directly at combustion chamber with 700 °C). Without Na<sub>2</sub>SO<sub>4</sub>, the best retention was achieved by bauxite (ca. 13%), which is still quite low in comparison with combined effect of Na<sub>2</sub>SO<sub>4</sub>–Al<sub>2</sub>O<sub>3</sub>.

Chen et al. [57] published later the results of other similar experiment. Synthetic solid waste (plastics, sawdust and Cd-nitrate) was combusted at 700 °C in the reactor simulating fluidized-bed incineration. In this case, a semi-dry spray tower (150–170 °C) was installed for injection of water with 4% of kaolinite, Al<sub>2</sub>O<sub>3</sub>, limestone or without any adsorbent. The best overall retention of Cd was observed if no adsorbent (i.e., only H<sub>2</sub>O injection in semi-dry spray tower) was used—ca. 10%. When Na<sub>2</sub>SO<sub>4</sub> was added to the feed waste, overall Cd retention increased up to 50% if combined with limestone injection. If no adsorbent was used, Na<sub>2</sub>SO<sub>4</sub> itself increased the Cd retention from ca. 10% to ca. 13%. If limestone adsorbent was used without addition of Na<sub>2</sub>SO<sub>4</sub> to the feed waste, the retention was even worse (<5%). Therefore, there is a synergic effect of Na<sub>2</sub>SO<sub>4</sub> and limestone that efficiently increase Cd retention.

Yu et al. [93] observed significant increase of Cd vaporization when SO<sub>2</sub> was added into N<sub>2</sub> atmosphere in FBC reactor (at 850 °C) during combustion of CdCl<sub>2</sub>-impregnated porous Al<sub>2</sub>O<sub>3</sub> matrix. After 30-min incineration time ca. 30% Cd was vaporized in pure N<sub>2</sub>; if 2000 ppm SO<sub>2</sub> and 5000 ppm SO<sub>2</sub> was present, vaporization percentage of Cd increased up to 90% and 95%. It is interesting that

the effect on Pb was much lower (vaporization did not exceed 20%) and Zn and Cu did not show any significant evaporation.

It is known that sulfate phase may be formed at low temperature in the presence of S; at higher temperatures it does not play a significant role as  $\text{CdSO}_4$  is decomposed at  $t > 850\text{ }^\circ\text{C}$  [93,108].

## 9. Effect of P

Binding energy for interaction between Cd and phosphate is the highest from the energies related to  $\text{Cl}^-$ ,  $\text{S}^{2-}$  and sulfate. Natural levels of P in most coals are low (200–250 ppm) [22]. Nevertheless, the major advantage of phosphates is their high thermal stability (unlike e.g., sulfates).

If P content in wastewater sludge was increased from 3.2% to 7% P (in the form of  $\text{P}_2\text{O}_5$ ), Cd volatilization at  $850\text{ }^\circ\text{C}$  decreased from 40% to ca. 17% [69]. Promising results were presented also for sediment combustion (at  $600\text{ }^\circ\text{C}$  and  $850\text{ }^\circ\text{C}$ ) previously treated with phosphoric acid ( $4.50\text{ PO}_4^{3-}$ ). Cd vaporization % almost does not change with temperature increase from 600 to  $850\text{ }^\circ\text{C}$  (15 and 17% vaporized) [80].

## 10. Conclusions

Concentrations of Cd in coal are quite low (0.033–0.64 ppm) [23]; however, (e.g.,) in MSW or municipal wastewater sludge it can be significantly higher: 0–90 and ca. 100 ppm, respectively [23]. In contrast, desulfurization additives as limestone (ca. 0.01 ppm Cd) or urea (ca. 0.03 ppm Cd) might exhibit diluting effect on Cd concentrations [25]. In coal, Cd is associated with mono/disulfides with some minor occurrence in organic matter or (alumino)silicates. Due to high Cd volatility (with exception of typically minor (alumino)silicate-bound fraction), most Cd is easily volatilized and exhibit potential risk of being emitted to surrounding atmosphere either in gaseous form or in sub-micron particles. Therefore, particular attention is paid to mitigating these emissions.

Different approaches for decreasing emissions could be used: pre-combustion treatment, mid-combustion or post-combustion control [52].

Within the pre-combustion treatment, increase of Cd retention was achieved by  $\text{H}_3\text{PO}_4$  treatment [69].

For their use in high-temperature (i.e., in-furnace) regime, kaolinite [54] and bauxite [50] exhibited promising results at  $1100\text{--}1200\text{ }^\circ\text{C}$ . Moreover, Cd retained within high-temperature capture (typically by melted or at least agglomerated particles) should be more resistant to leaching than Cd physically sorbed/condensed during low-temperature regime. For the commonly used desulfurization adsorbents (CaO, limestone etc.) exhibiting efficient retention of S and other elements (e.g., As) [8], even FBC temperature might be too high to provide efficient retention of chlorination agents that otherwise enhance Cd (and some other HMs) volatility. Optimal temperature range in this case is  $500\text{--}700\text{ }^\circ\text{C}$  [43,68,75,76]. Lower temperatures typically also favor Cd retention by S [37,48,102].

Post-combustion treatment of flue gas (using adsorbents in low-temperature regime) has also been tested. Promising results has been achieved using semi-dry spray tower working at  $150\text{--}170\text{ }^\circ\text{C}$  [57] spraying suspension of 5% adsorbent (in water). The adsorbents were efficient for most HMs but in the case of Cd the best results have been observed if water without adsorbents was used.

Detailed information related to thermodynamic distribution of individual Cd (or other HMs) species in dependence on temperature, atmosphere, interacting-species concentrations etc. can be found in the literature. These calculations are often in line with laboratory experiments, namely if combustion/incineration/adsorption dwell time is long enough. Nevertheless, as typical coal combustion in power stations provides (at maximum) a few minutes in high-temperature zone, future trend (in mitigating HMs emissions) could be directed toward the evaluation of time factor, i.e., the kinetic aspect of the HMs volatilization/retention.

In any case, using pre-combustion treatment or in-furnace additives/adsorbents changes the composition and other characteristics of combustion (incineration) ashes, which may significantly affect their further technological utilization or environmental impact (e.g., leaching). Similarly, using

low-temperature adsorbents may either affect the fly ash quality or even create new wastes. All these alternatives should be taken into account as studies evaluating these aspects are currently quite scarce. The effect on fouling/slagging could be evaluated as well. Mitigating emissions of HMs is not the only challenge related to the coal combustion; new technologies are developed to decrease emissions of CO<sub>2</sub>, NO<sub>x</sub> and other pollutants and distribution of HMs under these conditions should be evaluated as well.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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