

Gaseous CdCl_2 and PbCl_2 adsorption by limestone at high temperature: mechanistic study through experiments and theoretical calculation

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Abstract: There is a risk of heavy metal emission during solid waste incineration, and the capture of gaseous semi-volatile metal by mineral sorbents is an effective method for its pollution control. As a cheap and common additive for combustion industry, limestone is an effective sorbent for controlling various gaseous pollutants, but its high-temperature sorption mechanism for gaseous metal chlorides has not been systematically studied yet. In this study, an experimental study in a fixed bed furnace and density functional theoretical study were conducted to investigate the adsorption mechanism of gaseous CdCl_2 and PbCl_2 by limestone at high temperature. The capture performance was greater at a higher temperature due to the formation of an enhanced pore structure through limestone decomposition, while the efficiency decreased at temperatures higher than 700 °C because of the negative movement of the reaction equilibrium. Additionally, the higher equilibrium constant of CdCl_2 caused more effective adsorption than PbCl_2 . According to theoretical calculations, both limestone and lime can adsorb molecular metal chlorides while lime has higher adsorption energies due to its more active surface. For a commercial application, it is recommended to inject limestone into the furnace at a high temperature to capture heavy metal more effectively.

Key Words: Limestone; Heavy metal chloride; High temperature; Adsorption; Density functional theory.

1. Introduction

Incineration has become popular for solid waste treatment, because of its high efficiency of volume reduction and energy recovery. However, the secondary pollutants of heavy metals within wastes can raise wide concern, as they can be released to the atmosphere and seriously harm people's health. The incineration temperature in a furnace is usually over 800 °C, which is higher than the melting points of some metals or their compounds. Those elements including K, Na, Pb, Cd and Zn named semi-volatile metals, migrate following the mechanism of vaporization-condensation, which means they are vaporized during combustion and then condense into a solid phase at a lower temperature [1,2]. This feature causes those metals to tend to enrich in fine particles through heterogeneous and homogeneous nucleation, and are more likely to escape from the particulate control system. Capturing heavy metals by means of a sorbent within a furnace is an effective method to reduce their emission to the atmosphere. Since many developing countries have not established complete classification/separation methods of solid waste, food waste and plastic waste, it is somewhat inevitable that waste containing high concentrations of chlorine are fed into the incineration furnace as a fuel. When high chlorine content waste presents at a high

temperature, typically heavy metals such as lead and cadmium tend to form chlorides other than oxides during combustion, and chlorides like PbCl_2 and CdCl_2 are more volatile which means heavy metals are more likely carried out of the furnace by ultrafine particles through the vaporisation-condensation mechanism [3]. Thus, the high probability of forming chlorides and their inherently highly volatile nature leads to concern over their behaviours and the effective control of heavy metal chlorides at high temperature [4].

Limestone (CaCO_3) or lime (CaO), which is widely used as a desulphurisation agent, also has a favourable sorption ability on acid gases like HCl , arsenic oxides and selenium dioxide [5]. For semi-volatile metals, silicates like kaolin have been demonstrated as effective sorbents for their capture [6-8]. Due to the diversity of gaseous pollutants in an incineration furnace, the cost of pollutant removal could be significantly decreased if limestone could solve both heavy metal and acid gases pollution problems [9-11]. The general reaction formula between lime and a two-valence metal oxide is $n\text{CaO} + \text{MO} = n\text{CaO} \cdot \text{MO}$, where M is a symbol of heavy metal. As for metal chloride, the general formula is $n\text{CaO} + \text{MCl}_2(\text{g}) = (n-1)\text{CaO} \cdot \text{CaCl}_2 \cdot \text{MO}$ [12]. Here, the stoichiometric number of CaO is set as n , because the heavy metal is regarded as a trace element of which the quantity is much lower than calcium.

Density functional theoretical (DFT) calculation based on the first principle theory has been widely used to reveal the reaction mechanism, which has been reported to study the adsorption mechanisms of arsenic and selenium oxides by lime [13,14]. In our previous work, the method also has been used to study the adsorption of heavy metal chlorides by kaolin [14]. However, all studies on high-temperature metal adsorption by lime/limestone were conducted by experimental methods, while the theoretical research at an atomic scale is still incomplete. Therefore, this study will investigate the adsorption mechanism of heavy metals by lime and limestone through both theoretical and experimental methods to compensate that gap.

In this work, high-temperature adsorption of two typical chlorides of heavy metal, PbCl_2 and CdCl_2 in gaseous phase by limestone was investigated using a two-stage fix bed reactor for the gas-solid reaction. Limestone was selected as the sorbent instead of lime because limestone is a natural mineral while the production of lime from limestone costs extra energy and the storage of lime is also a problem during its storage where lime can absorb moisture and CO_2 to return limestone. Thermal equilibriums of the reaction between heavy metal chloride and calcium oxide or calcium carbonate were calculated to display the reaction tendency. Since both calcium oxide and calcium carbonate may exist at the operating temperature in the experiments, DFT calculations were conducted to compare the adsorption activities of different sorbent surfaces between limestone and lime at an atomic scale.

2. Materials and Experimental methods

2.1 Materials

Adsorption of PbCl_2 and CdCl_2 by limestone (CaCO_3) were investigated in this study. Each chemical had a purity of 99.9% and was tested by thermo-gravimetric analysis (TGA) to determine the decomposition/vaporisation temperature and heating procedures for the adsorption experiment. The TGA results are shown in Figure 1, where the heating rate was 10°C per minute. PbCl_2 and CdCl_2 began to lose weight at 480°C and 500°C respectively and were fully vaporised below 760°C , while limestone decomposed between 620 - 860°C , and retained a mass fraction of 56% corresponding CaO .

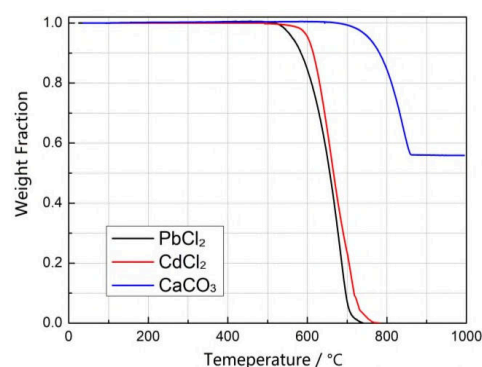


Figure 1. Thermo-gravimetric analysis of lead and cadmium chlorides and limestone

2.2 Adsorption test

Figure 2 shows a schematic of the two-stage fixed bed reactor that was utilised to experimentally study the adsorption of gaseous heavy metals. The reactor vessel is constructed from quartz and had a height of 750 mm and an inner diameter of 40 mm. Temperatures of the two electrical heating zones were controlled with respective thermocouples. Heavy metals were evaporated at the upper zone and the adsorbed by the sorbent at the lower zone. A ZrO crucible was hung in the upper zone and was loaded with 0.05 g PbCl₂ and 0.05 g CdCl₂, the vaporised gaseous heavy metal was carried by N₂ (130 mL/min). The gas stream passed over the sorbent layer and finally the gas was scrubbed by a HNO₃ solution in absorption wash bottles to prevent potential pollution.

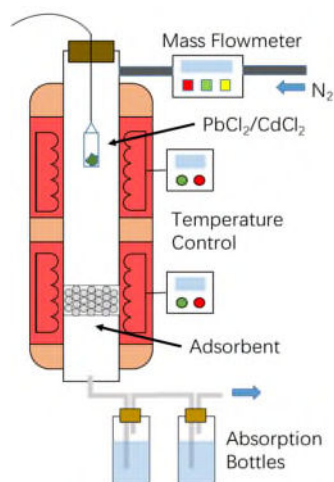


Figure 2. Schematic diagram of the fixed bed reactor

According to the thermal behaviours from TGA, the temperature of the upper zone was set to 800 °C to ensure the heavy metals were vaporised thoroughly. The sorbent was preheated to the operating temperature before the heavy metals were heated and vaporised to ensure the adsorption reactions occurred at the desired temperatures. Therefore, the temperature control procedures were as follows: (1) The sorbent was heated to a set point (600, 700, 800 and 900 °C) in 30 minutes and then held at that temperature; (2) The heavy metals were then heated to 800 °C in 30 minutes; (3) The temperatures in both zones was maintained for 30 minutes; (4) The whole furnace was cooled down to the ambient temperature. Tests were performed in triplicate and the average results of the three tests were utilised in further analysis.

2.3 Analysis methods

The adsorption product was digested thoroughly by HNO_3 to obtain the total amount of adsorbed heavy metals. Then the concentrations of heavy metals in the solution were measured by atomic absorption spectrometry (AAS), and the distributions of heavy metals were calculated as the following equation:

$$X_a = M_a / M_0 \quad (1)$$

Where, X_a is the adsorption efficiency of heavy metal, while M_0 and M_a are masses of heavy metal used for vaporization and in the digestion solution, respectively. Three parallel tests were conducted for each condition. The crystal phases, surface areas and the morphologies of the sorption product were analysed by X-ray diffraction (XRD), Brunauer–Emmett–Teller method (BET) and scanning electron microscopy (SEM) respectively.

2.4 Computational methodology

DFT calculation was performed with Cambridge Serial Total Energy Package (CASTEP), where the generalized gradient approximation (GGA) within Perdew-Burke-Ernzerhof (PBE) form was used to model the exchange and correlation interactions. The interactions between the ions and the electrons were described by the ultrasoft pseudopotential. The cutoff energy was 500 eV for plane-wave basis and the convergence parameters were set as 0.01 eV/Å for maximum stress, 5×10^{-6} eV/atom for energy and 5×10^{-4} Å for maximum displacement.

The surface energy E_{surface} was defined as:

$$E_{\text{surface}} = (E_{\text{sorbent}} - n \cdot E_{\text{bulk}}) / 2S \quad (2)$$

In Equation (2), E_{sorbent} and E_{bulk} is the energy of the sorbent slab and the total energy of one primary bulk cell of the sorbent respectively, n is the multiple of the sorbent slab by a bulk cell, S is the surface area of the slab and the factor $1/2$ relates to the termination surface of both top and bottom layers.

For the surface with polarity, the surface energy $E_{\text{surface},p}$ was defined as:

$$E_{\text{surface}} = (E_{\text{sorbent}} + n_{\text{atom}} \cdot (E_{\text{binding}} - E_{\text{atom}}) - n \cdot E_{\text{bulk}}) / 2S \quad (3)$$

Where, the subscript *atom* refers to the added atoms for neutralisation, of which the number was n_{atom} and the energy was E_{atom} ; E_{binding} is the binding energy of the added atom with the surface.

The adsorption energy $E_{\text{adsorption}}$ was calculated according to Equation (4):

$$E_{\text{adsorption}} = E_{\text{product}} - E_{\text{sorbent}} + E_{\text{sorbate}} \quad (4)$$

Where, E_{product} and E_{sorbate} refer to the total energy of the reaction product and ideal energy of the sorbate respectively. A negative value of adsorption energy means a stable combined product is formed between the sorbate and the sorbent. Electron distribution difference was also calculated based on the change between the electron density before and after the reaction. Moreover, Mulliken charge distribution was calculated to further reveal the bonding mechanism.

2.5 Computational structure

The atomic structures and its scale of CdCl_2 and PbCl_2 were drawn in Figure 3(a) and 3(b). Moreover, the cell parameters of crystal structures for CaO and CaCO_3 were determined by geometry optimisations, where they were (i) $a = b = c = 4.811$ Å, $\alpha = \beta = \gamma = 90^\circ$ and (ii) $a = b = 5.057$ Å, $c = 17.282$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, respectively.

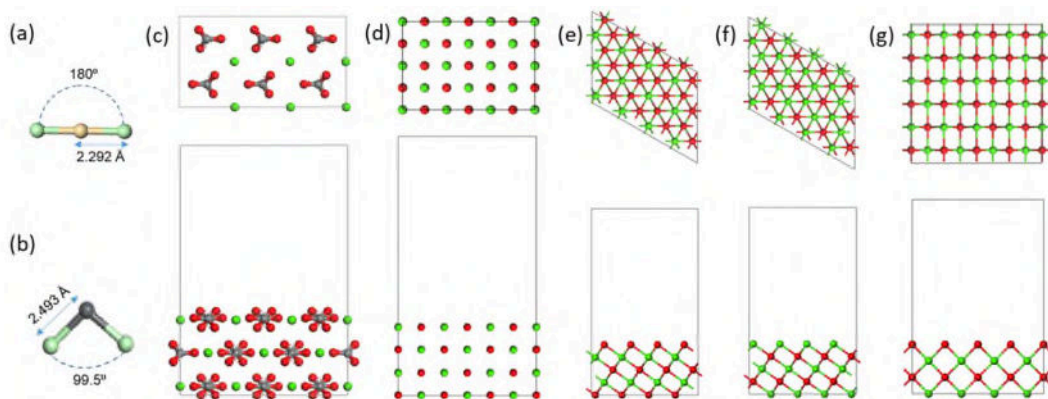


Figure 3. Structural models of metal chlorides and sorbent surface. (a) CdCl_2 ; (b) PbCl_2 ; (c) CaCO_3 (104); (d) CaO (001); (e) CaO (111)n; (f) CaO (111)p; (g) CaO (220). Colours of Elements: Light green, Cl; Light yellow, Cd; Dark grey, Pb; Green, Ca; Red, O; Grey, C.

The crystal phase curves of the adsorption product were drawn in Figure 4. Calcite was the only crystal phase at 600 °C, and lime appeared at 700 °C while the peaks of calcite were weaker for the decomposition of calcite. At 800 °C and 900 °C, the peaks of calcite disappeared indicating its thorough decomposition, and the peaks of lime remained. No peak was related to the heavy metals because the mass of heavy metal used in the experiment was too little to reach the detection limit of the XRD instrument. There was only one peak of (104) surface for calcite, while for lime, three strong peaks were displayed in the XRD curves where the peak of (001) was strongest and the other two presented (111) and (220) surfaces. It has been reported that (001) surface for CaO and (104) surface for CaCO_3 are the most stable and typical surfaces for each crystal [13,15,16], while the other two surfaces of lime also might have considerable proportions of surface area and they could potentially adsorb gaseous molecules. Therefore, those surfaces detected in the sorbent materials would be all studied by DFT method for its chlorides adsorption.

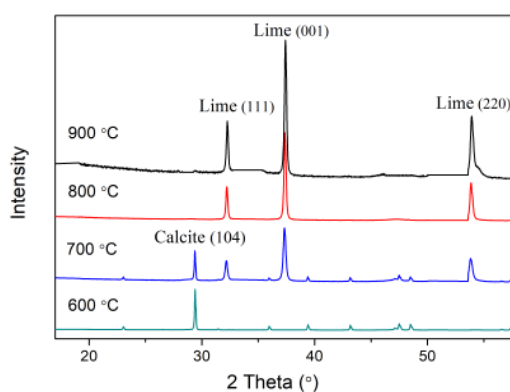


Figure 4. The XRD curves of the adsorption product.

As shown in Figure 3(c)-(g), sorbent surfaces for CaO and CaCO_3 were built with a vacuum slab in the thicknesses of 15 Å, and their bottom layers were all constrained. The k-point grid was set as $2 \times 2 \times 1$ for all cases. For the surface reaction calculations, we used $(1 \times 3 \times 3)$ supercell for CaCO_3 (104) surface, $(2 \times 3 \times 2)$ supercell for CaO (001) surface, $(4 \times 3 \times 2)$ supercell for CaO (111) surfaces and $(4 \times 3 \times 2)$ supercell for CaO (220) surface to avoid periodic interaction between the adjacent sorbates. Particularly, there were two kinds of surfaces of CaO crystal at (111) direction, where were the surface exposed with Ca atoms and O atoms respectively, and named as (111)p and (111)n

accordingly. Thus, in consideration of the polarity of the surfaces, to avoid the potential electrostatic interaction between the adjacent periodic cells along Z axis, an extra layer of Ca atoms or O atoms were added at the bottom of that bulk.

Since there might be various potential adsorption sites for the sorbate, different initial positions for the sorbate were tested. Among with all possible adsorption sites for each reaction system, only the results with the lowest final energy were discussed in the main text while other results were given in the Supplementary Materials.

3. Results and discussions

3.1 The adsorption product and efficiency

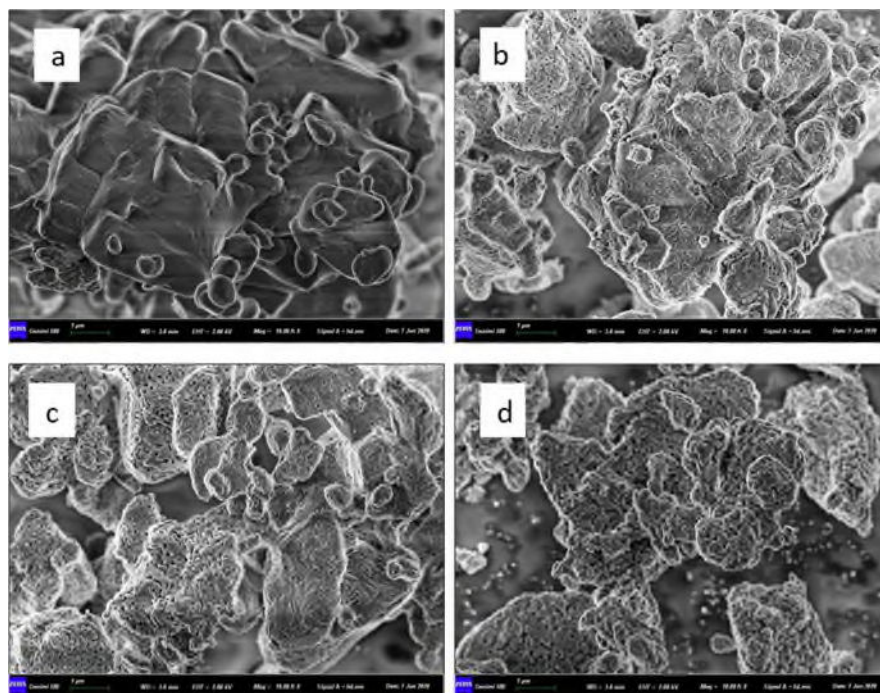


Figure 5. The SEM images of the adsorption product. (a) 600 °C; (b) 700 °C; (c) 800 °C; (d) 900 °C.

The electron microscope images of the adsorption product were shown in Figure 5 at 10,000x magnification. The sample at 600 °C that was almost calcite shows smooth surface, while many pores appeared on the surface of the sample at 700 °C resulted from the release of CO₂. The morphologies for 800 °C and 900 °C samples were similar, where there were more pores with a larger size on their surface as all calcite was converted to lime.

Table 1 BET analysis for the sorbents heated at different temperatures

Heating temperature (°C)	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
Not heated	0.4	0.001	10.7
600	1.5	0.003	6.9
700	17.1	0.061	14.2
800	21.6	0.107	19.8
900	12.5	0.088	28.1

BET analysis also proved the morphology observations (Table 1). The raw limestone had low surface area and small pore volume, while they increased slightly after heated

at 600 °C because its decomposition started (see TGA analysis in Figure 1). At 700 °C, the specific surface area and pore volume were dramatically expanded and then they reached their peak values at 800 °C. The pore size was also enlarged with the heated temperature rising. However, the surface area and pore volume decreased at 900 °C which might be resulted from sintering.

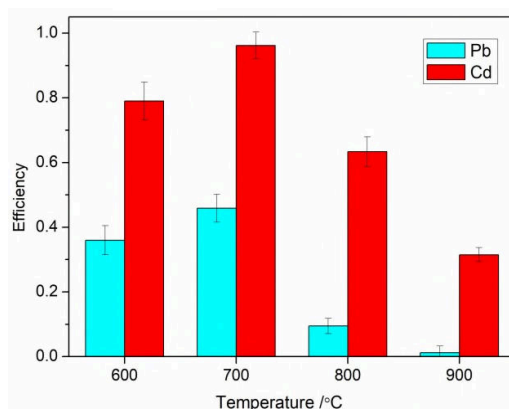


Figure 6. Adsorption efficiencies of lead and cadmium by limestone at different temperatures

The adsorption efficiencies of heavy metals are shown in Figure 6. The adsorption ability of cadmium was much higher than lead at each reaction temperature, and for either element, the efficiency increased at 700 °C and decreased after that temperature. According to the morphology and BET analysis, the promotion could be attributed to the considerable pore structure generated from limestone decomposition, which enlarged the surface area of the sorbent. For the reaction products at 800 and 900 °C, the pores on the sorbent surface were even more developed, but their efficiencies declined.

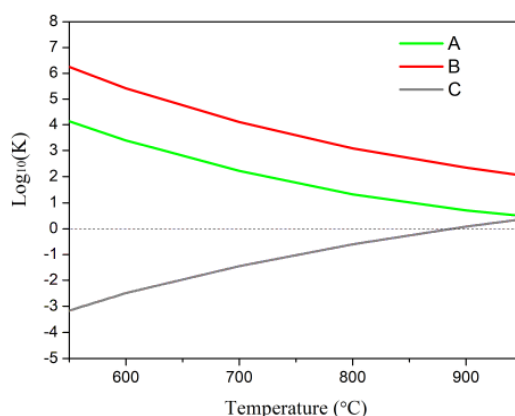


Figure 7. Equilibrium constant (K) for possible reactions. A: $\text{PbCl}_2(\text{g}) + \text{CaO} \leftrightarrow \text{CaCl}_2 + \text{PbO}$; B: $\text{CdCl}_2(\text{g}) + \text{CaO} \leftrightarrow \text{CaCl}_2 + \text{CdO}$; C: $\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2(\text{g})$

With the assumption that gaseous metal chloride reacted with lime or limestone and then formed CaCl_2 and metal oxide in the solid phase, their equilibrium constants (K) for the related reactions were calculated and their results were drawn in Figure 7, where the curve of limestone decomposition was also displayed. The curves for cadmium are higher than that for lead, which indicates higher reactivity of reaction between cadmium chloride and Ca-based minerals, and the higher capture efficiency of cadmium than lead in the experimental results can be attributed to that thermal equilibrium calculation. The K value declines at a higher temperature for the reaction between lime and metal

chloride (reaction A or B), which means the reaction balance moves negatively and the less conversion of gaseous metal chloride. Here, we assumed that the reactions between limestone and metal chloride could be a two-step process: CaCO_3 was decomposed firstly and then CaO reacted with metal chlorides, which means CaCO_3 did not directly react with chlorides. Based on that assumption, from the point of thermal equilibrium, there might be a proper temperature point for the reactions which were affected by both of the limestone decomposition and the reactivity decline of lime.

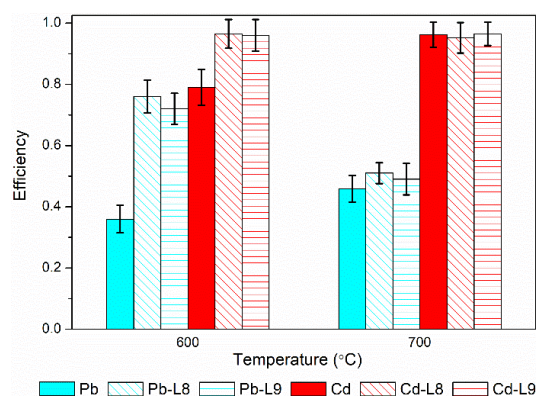


Figure 8. Comparison of adsorption efficiencies between limestone (calcite) and lime. Abbreviation: L8, lime produced at 800 °C; L9, lime produced at 900 °C

To prove the different effect of the lime at a lower temperature, limestone was heated at 800 °C and 900 °C for calcination and then its adsorption performance was tested at 600 or 700 °C, of which the results are shown in Figure 8. The efficiencies of lime for capturing two metals at 600 °C were much higher than those of limestone, although they presented less difference at 700 °C because a part of limestone had already converted to lime in the former test. The capture performance enhanced by calcination could be caused by the higher surface area, while the efficiency differences between L8 and L9 were not remarkable though L8 had a preferable porous structure. However, it is still uncertain whether the chemical property of the sorbent had also promoted and affected the adsorption.

3.2 DFT calculation

3.2.1 Comparisons of adsorption energies

In the thermal equilibrium calculations, it was assumed that the reaction between limestone and metal chloride was divided into two steps, and that the limestone should be converted to lime before it reacted with the metal chloride. However, it is still unknown whether the surface of limestone can directly adsorb metal chloride molecules and form chemical bonds. Therefore, DFT calculations were conducted to examine if there is chemical adsorption by limestone and to reveal the adsorption mechanism at an atomic scale for the two sorbents and two sorbates respectively.

Table 2. Surface energies of sorbents	
Surface	Surface energy (eV/nm ²)
CaCO_3 (104)	2.7
CaO (001)	4.0
CaO (220)	9.70
CaO (111)p	17.1
CaO (111)n	12.9

Listed in Table 2, the surface energies of CaCO_3 (104) surface was 0.48 eV/nm^2 , lower than the three CaO surfaces, indicating that the surfaces of lime were more active than that of calcite. CaO (001) surface was proved to be the most stable surface among the four surfaces of CaO , and the comparison of surface energies was also relative with XRD analysis (see Figure 4) where (001) surface occupies the strongest peak, because a more stable surface is easier to be constructed during the crystallisation. (220) and (111) surfaces belong to the peaks of the second and third intensities respectively, and their surface energies were much higher.

Table 3. Adsorption energies of the two metal chlorides (absolute value)

Sorbate	Surface	Adsorption energy (eV)
CdCl_2	CaCO_3 (104)	1.04
	CaO (001)	1.42
	CaO (220)	4.28
	CaO (111)p	5.37
	CaO (111)n	6.26
PbCl_2	CaCO_3 (104)	1.33
	CaO (001)	1.70
	CaO (220)	5.53
	CaO (111)p	5.46
	CaO (111)n	8.06

As shown in Table 3, the adsorption energies on CaCO_3 (104) surface for both metal chlorides were lower than those on all surfaces of CaO surfaces. Furthermore, the values were even over 5 eV, much higher on the more active surfaces of CaO (220) and (111). So besides the expansion of surface area, the surface of lime is more active than limestone for CdCl_2 and PbCl_2 adsorption, leading to a greater capture capability of lime.

On the other hand, PbCl_2 had higher adsorption energies on each surface than CdCl_2 based on the DFT calculation, but its adsorption efficiency was lower in the experiment. In fact, the limit of a reaction depends on their thermal equilibrium, while adsorption energy affects how easy the reaction runs, which is related to the reaction kinetic. In this study, it seems that the factor of reaction equilibrium was more significant when comparing the capture efficiencies between the two elements.

3.2.2 The adsorption products on CaO (001) and CaCO_3 (104) surfaces

Since CaO (001) and CaCO_3 (104) surfaces are the typical surfaces for each crystal, where the adsorption reactions could more probably occur than other minor surfaces, we compared adsorption products on these two surfaces in this section.

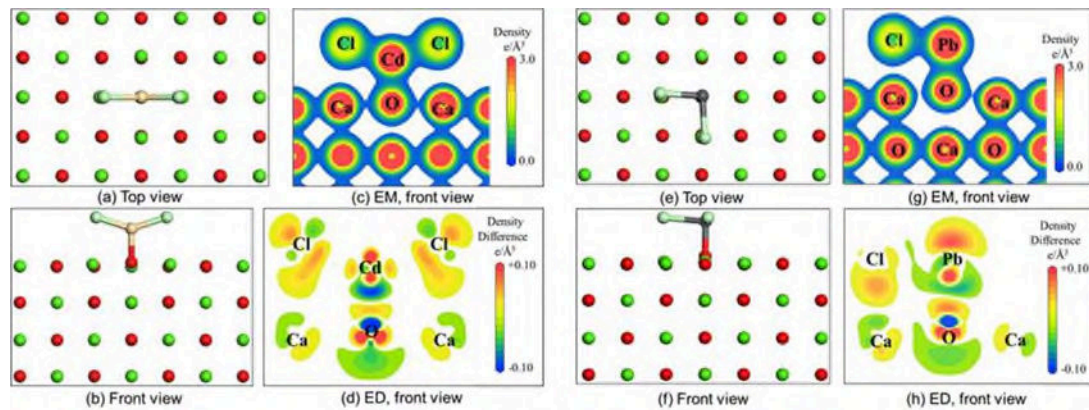


Figure 9. Adsorption product of CdCl₂ (9a-9d) and PbCl₂ (9e-9h) on CaO (001) surface within their electron density mapping (EM) and electron density difference (ED).

The atomic structures and electron density distributions of the adsorption product on CaO (001) surface are drawn in Figure 9. For both metal chlorides, the heavy metal atom was shown to be near an oxygen atom on the CaO surface, and either of the two chlorine atoms were near a calcium atom. Also, there was a symmetry axis passing the lead or cadmium atom, but from the top view, the adsorbed CdCl₂ molecule laid in a line while the PbCl₂ molecule laid in an “L” due to their initial molecule shapes.

The electron density distributions of both adsorption products indicate that covalent bonds were formed between the heavy metal atom and an oxygen atom (Figure 9c and 9g) as they had the overlap of electron clouds, and that the covalent bonds remained between chlorine atoms and the heavy metal atom. However, chlorine atoms did not connect with any calcium atom on the top layer, and the oxygen atom connected with a lead or cadmium atom decreased bonding with other calcium atoms. The mapping of electron density differences also shows that the charge of oxygen tended to move towards the mid-point of Pb-O or Cd-O segment line. Moreover, an ionic bond seemed to be built between either chlorine atom and the nearest calcium atom (Figure 9d and 9h).

As listed in Table 4, the distances between chlorine atoms and lead or cadmium atoms after reaction were longer than that of the raw sorbate so that the bindings between chlorine atoms and the heavy metal atom were weaker, but the chlorine atoms gained more charge from calcium atoms on the top layer. Moreover, the heavy metal atom also gained charge from chlorine and oxygen atoms due to the weakened Cl-M bonds and the covalent M-O bond.

Table 4. Distances between atoms of the sorbate and the nearest atoms on the sorbent surface; Mulliken charges of the sorbates before and after reactions. Note: Symbol M refers to Pb or Cd; the calcium atoms and the oxygen atom were the nearest ones to the chlorine atoms and heavy metal atom respectively.

Sorbate or adsorption product	CdCl ₂	CaO-CdCl ₂	CaCO ₃ -CdCl ₂	PbCl ₂	CaO-PbCl ₂	CaCO ₃ -PbCl ₂
Distance of Cl ¹ -M /Å	2.292	2.404	2.379	2.493	2.632	2.604
Distance of Cl ² -M /Å	2.292	2.404	2.358	2.493	2.637	2.604
Distance of O-M /Å	-	2.196	2.276	-	2.282	2.337
Distance of Cl ¹ -Ca ¹ /Å	-	3.065	2.938	-	2.855	2.908
Distance of Cl ¹ -Ca ² /Å	-	3.065	2.971	-	2.852	2.859
Charge of Cl ¹	-0.49	-0.53	-0.52	-0.45	-0.52	-0.52
Charge of Cl ²	-0.49	-0.53	-0.51	-0.45	-0.52	-0.52
Charge of M	0.98	0.74	0.99	0.91	0.74	0.95
Charge difference of MCl ₂	0	-0.32	-0.04	0	-0.30	-0.09

Figure 10 shows the adsorption products of metal chlorides on the CaCO₃ (104) surface. Similar to the adsorption on the CaO (001) surface, cadmium or lead atom formed a bond with an oxygen atom of a carbonate group with an overlap of electron clouds (Figure 10c and 10i), while chlorine atoms connected with their nearest calcium atom without that (Figure 10f, 10i, 10m) to form ionic bonds. However, when comparing the atom distances and atomic charges between the adsorption products on the two surfaces, there was a notable difference between the charge of the two heavy metal atoms, while other parameters were very close. The distances of Cl-M were longer, which means the attraction of electron by chlorine atoms was weaker and the heavy metal atom regained

the electron from the chlorine. Meanwhile, some of their electrons were moved to the oxygen atoms on the top layer of the sorbent, so the charges of heavy metals increased from 0.98 to 0.99 for Cd, and from 0.91 to 0.95 for Pb (see Table 4). Also, displayed in the mapping of electron density difference (Figure 10d, 10g and 10j), both M-O bonds show less charge movement than the reaction with CaO. As a result, the bonding strength of M-O for CaCO_3 reaction was weaker than that for CaO reaction, and there was also less adsorption energy.

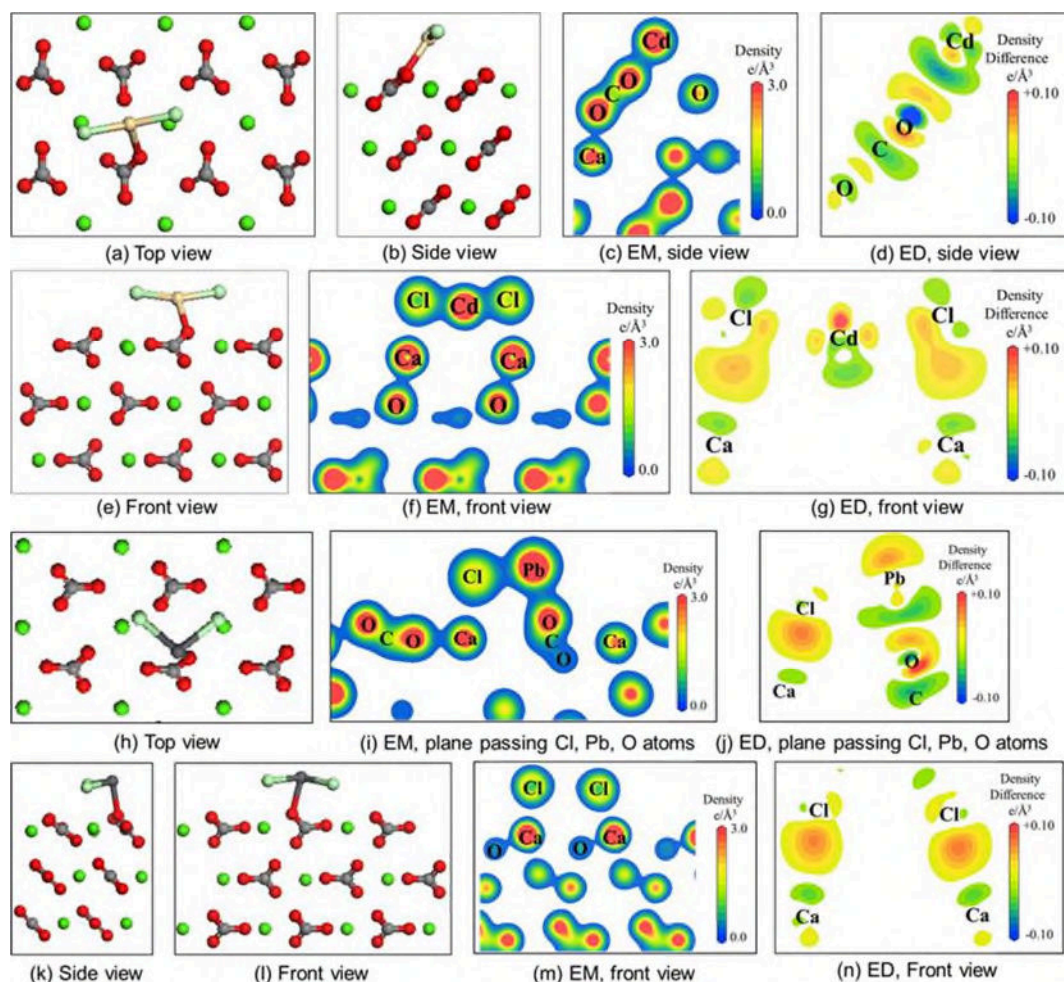


Figure 10. Adsorption of CdCl_2 (10a-10g) and PbCl_2 (10h-10n) on CaCO_3 (104) surface within their electron density mapping (EM) and electron density difference (ED).

3.2.3 Adsorption on CaO (220) and (111) surfaces

The atomic structure images of the adsorption products of CdCl_2 and PbCl_2 on CaO (220), (111)p and (111)n surfaces are shown in Figure 11. These surfaces with high surface energies have much higher adsorption energies than the major surfaces discussed above, indicating their greater sorption activity, though they are the minority of the total CaO surface.

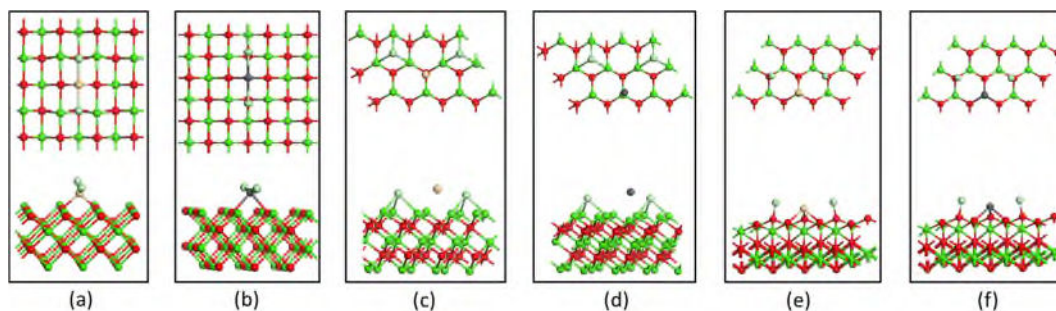


Figure 11. Adsorption products on CaO (220), (111)p and (111)n surfaces. (a) CdCl₂-CaO (220); (b) PbCl₂-CaO (220); (c) CdCl₂-CaO (111)p; (d) PbCl₂-CaO (111)p; (e) CdCl₂-CaO (111)n; (f) PbCl₂-CaO (111)n.

For the adsorption products of CaO (220) surface, both CdCl₂ and PbCl₂ molecules lay along the “gap”, where symmetrically the heavy metal atom connected with two O atoms, and either Cl atom connected with two Ca atoms. Such double-connection formed more bonds, also the bond lengths were shorter (CdCl₂: Cd-O 2.207 Å, Cl-Ca 2.876 Å; PbCl₂: Pb-O 2.284 Å, Cl-Ca 2.762 Å), causing higher adsorption energies than those of CaO (001)-MCl₂.

On CaO (111)p surface, the Cl atoms were moved to the centre of the Ca-triangle and each of them bonded with the three Ca atoms respectively. Meanwhile, either Cd or Pb seems to lose its connection with Cl (distance between Cd-Cl: 4.133 Å; Pb-Cl: 5.001 Å) but was located upon a calcium atom (distance between Cd-Ca: 3.059 Å; Pb-Ca: 2.982 Å). Listed in Table 5, heavy metal atoms gained electrons from the calcium atoms to form bonds, so Cd or Pb was still captured on the sorbent surface in this case.

Table 5. Atomic populations (Mulliken) of the adsorbed sorbates on CaO (111)p surface

	Species	s	p	d	f	Total	Charge (e)
CdCl ₂	Cd	1.76	0.94	9.98	0	12.7	-0.70
	Cl ¹	1.95	5.56	0	0	7.51	-0.51
	Cl ²	1.95	5.56	0	0	7.51	-0.51
PbCl ₂	Pb	2.02	2.64	10	0	14.66	-0.66
	Cl ¹	1.95	5.56	0	0	7.51	-0.51
	Cl ²	1.95	5.56	0	0	7.51	-0.51

Adsorption energies were highest on CaO (111)n surface. Each Cl atom was connected with an O atom respectively, and the heavy metal atom was bonded with other three O atoms on the top layer, while the distance between Cd or Pb and Cl was too long to form a bond.

3.3 Discussion

Based on the experimental studies, the adsorption ability by lime was greater than that by limestone, because lime obtained a rich pore structure after limestone decomposition. When it comes to industrial application, though the capture efficiency is lower at a higher temperature, limestone can still be injected into the furnace where is hotter than 700°C, so that it will be converted into lime which will subsequently give it a higher efficiency to capture gaseous metal chlorides in the flue gas between 600-700 °C.

On the other hand, according to the DFT calculations, both heavy metal chlorides can form chemical bonds on the surfaces of both sorbents with considerable adsorption energies, but the surfaces of lime performed more active for the process and its adsorption product was more stable. Therefore, besides the expansion of the porous

structure, the conversion to lime also increases its surface activity to enhance its sorption ability.

Moreover, since the flue gas contains various components for solid waste combustion, many components may affect the adsorption performance. For example, SO_2 may play a competitive role on lime adsorption reactions, and HCl can also react with lime and may occupy the reaction sites [17,18]. Therefore, the effect of the atmosphere should be investigated in future work.

4. Conclusion

In this work, the adsorption mechanisms of gaseous CdCl_2 and PbCl_2 by limestone at high temperature were investigated by experimental and theoretical methods. In the experimental study, initially the adsorption efficiency increased at a higher temperature due to the formation of pore structure caused by limestone decomposition, but then dramatically decreased because of the negative movement of the reaction equilibrium. Adsorption products CaO (001) and CaCO_3 (104) surfaces were compared by DFT method, as they are the most stable and typical surfaces for each crystal. At an atomic scale, both metal chlorides could be adsorbed on surfaces of both calcite surface and lime by chemical bonds, where the heavy metal atoms connected with an oxygen atom through a covalent bond and either chlorine atoms bonded with a calcium atom on the top layer respectively. However, the more stable surface of calcite and the weaker covalent bond between heavy metal and oxygen atoms caused lower adsorption energies on the calcite surface than those on the lime surfaces. Additionally, CaO (220) and (111) surfaces as minor surfaces that observed on lime were also studied, and they performed much higher adsorption activities for both metal chlorides. Therefore, lime has more active surface than limestone for adsorption of the two metal chlorides.

Overall, limestone is suggested to be sent into the furnace at a higher temperature to form lime for more effective adsorption in commercial applications. Furthermore, because the equilibrium constant for the lead reaction was less than the cadmium reaction with the calcium sorbents, limestone is more suitable to capture CdCl_2 than PbCl_2 in a furnace.

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