

Control of heavy metals during incineration using activated carbon fibers

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Abstract

Activated carbon fibers (ACFs) were applied to control heavy metals in incineration flue gas. Three heavy metal species (Cr, Cd and Pb), three ACFs, various adsorption temperatures (150, 250 and 300 °C) and weights of ACFs were experimentally determined. The results indicated that the effects of the type of ACF and the weight of the ACFs on the solid-state Cr removal were insignificant. The extent of solid-state Cd and Pb removal was related to the knitting structure of ACFs and the physical characteristic of the metals. The removal efficiencies of the solid-state and gaseous metals at various reaction temperature followed the order 250 > 150 > 300 °C and 300 > 250 > 150 °C, respectively.

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1. Introduction

Incineration is one of the most effective techniques for disposing of municipal solid waste. However, poor design or operation can result in pollutants to be emitted. The pollutants contain heavy metals, organic compounds and acidic gases. When emitted to the atmosphere, they cause environmental hazards and diseases in humans [1].

During incineration, heavy metals cannot be destroyed but can be partially or completely vaporized at high temperature. Metal vapors nucleate to form new particles under supercritical conditions, or condense onto fly ash due to supersaturation as the temperature in the air pollution control devices (APCDs) decreases [2,3]. Earlier works examined the control of heavy metals from flue gas [4–8]. The conventional method of controlling heavy metals emitted from flue gas is to use powdered adsorbents to capture metals. Related results demonstrate that most silica aluminum species (such as kaolinite, bauxite, and aluminum oxide) can be used to adsorb heavy metals and each adsorbent has its own optimal operating conditions. However, fly ash that contains heavy metals cannot be removed using these powdered adsorbents.

In Taiwan, a spray dryer integrated with a fabric filter is conventional used as the air pollution control devices (APCDs) for

incinerators. Our previous study showed that the removal efficiency of fly ash by APCDs exceeded 95%. The results also indicated that APCDs effectively removed the heavy metals and acidic gases. However, the removal efficiency of polycyclic aromatic hydrocarbons (PAHs) using APCDs was only 40% [9]. Moreover, the conventional APCDs suffer from numbers shortcomings, including the need to add large amounts of alkaline chemicals to the spray dryer and the jamming of the spray nozzle by the alkaline chemicals during operation. Therefore, our recent study explores the removal of PAHs using an ACF adsorber to reduce the disadvantages of conventional APCDs [10]. The results revealed that the removal efficiencies of PAHs exceeded 90%. Previous studies have also shown that ACFs effectively remove SO₂ [11,12]. This work is the first to investigate experimentally the removal of heavy metals by ACFs to evaluate the potential of an ACF adsorber to replace conventional APCDs in incinerators and estimate the removal efficiencies of heavy metals, PAHs and SO₂ using ACFs as adsorbents during incineration.

Activated carbon fibers (ACFs) provide many advantages, including faster adsorption and desorption kinetics, much higher surface areas, a uniform micropore structure and a lower drop in pressure [13–18]. ACFs are widely utilized to remove low-concentration organic compounds from flue gas [13,17,18]. The use of ACFs to remove toxic heavy metals from wastewater has also been investigated [19,20]. However, the removal of heavy metals from flue gas by ACFs has rarely been studied.

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Heavy metals produced by incineration can be condensed and adsorbed on fly ash or nucleate to form new particles. ACFs efficiently remove fly ash. Hence, heavy metals can be removed through adsorption and condensation by ACFs and by the interception of fly ash by ACFs. This work investigates the removal efficiencies of both gaseous metals and solid-state metals by ACFs. Gaseous metals and solid-state metals were defined according to the concentrations of the metals condensed or adsorbed on the ACFs and on the fly ash, intercepted by ACFs, respectively. Flue gases that contained organic compounds and heavy metals were generated using a fluidized bed incinerator to burn feedstocks. Three heavy metal species (Cr, Cd and Pb), three activated carbon fibers, three adsorption temperatures (150, 250 and 300 °C) and various weights of activated carbon fibers were used.

2. Experimental

2.1. Preparation of artificial feedstock

The artificial incinerator feedstock consisted of sawdust, polypropylene (PP) and a heavy metal solution to simulate real flue gas. These feed materials were enclosed in a polyethylene (PE) bag. Three metals (Cd, Cr and Pb) were dissolved in distilled water that contained 0.5 wt.% nitrate. Table 1 presents the feedstock compositions and operating parameters of the adsorption bed.

2.2. Adsorbents and apparatus

Three commercial ACFs obtained from Taiwan Carbon Technology Co. Ltd. in Taiwan were used in this experiment. All ACFs samples were used directly in this study with the original properties of the three commercial ACFs. The weight of the ACFs used for each test was 0.51–0.54 g (equal to 1–2 mm bed

Table 1

Feedstock compositions and experimental operation parameters

Test	ACF type	Adsorption temperature (°C)	ACFs weight (g)	ACFs thickness (mm)
Run 1	ACF-A	150	0.53	1
Run 2	ACF-B	150	0.54	1
Run 3	ACF-C	150	0.54	2
Run 4	ACF-A	250	0.54	1
Run 5	ACF-A	300	0.51	1
Run 6	ACF-A	150	1.12	45
Run 7	ACF-A	150	1.64	45
Run 8	ACF-A	150	2.28	45

Composition of artificial feedstocks (g/bag): sawdust=0.7, polypropylene=0.33, PE bag=0.22, Cd=0.044, Cr=0.123, Pb=0.026.

height). Table 1 lists the operating parameters of the adsorption bed.

Fig. 1 displays the incineration system, which comprised a laboratory-scale fluidized-bed incinerator equipped with the ACFs adsorber. The height and inner diameter of the ACFs adsorber were 150 and 80 mm, respectively. The fluidized-bed material of 200 g silica sand was plunged into the combustion chamber. Three thermocouples were used to determine the temperature profile in the major incinerator, the inlet of the ACFs adsorber and the outlet of the ACFs adsorber. The combustion gases were treated in the ACFs adsorber, and then released into the atmosphere.

2.3. Experimental procedure

An excess air factor of 50% was applied to estimate the required amount of air and the 60 L/min of air was then introduced into the incinerator at room temperature (25 °C). The operating temperature of the combustion chamber was controlled at 800 °C. Initially, the combustion chamber was preheated to the desired temperature using electrical heaters. When the temper-

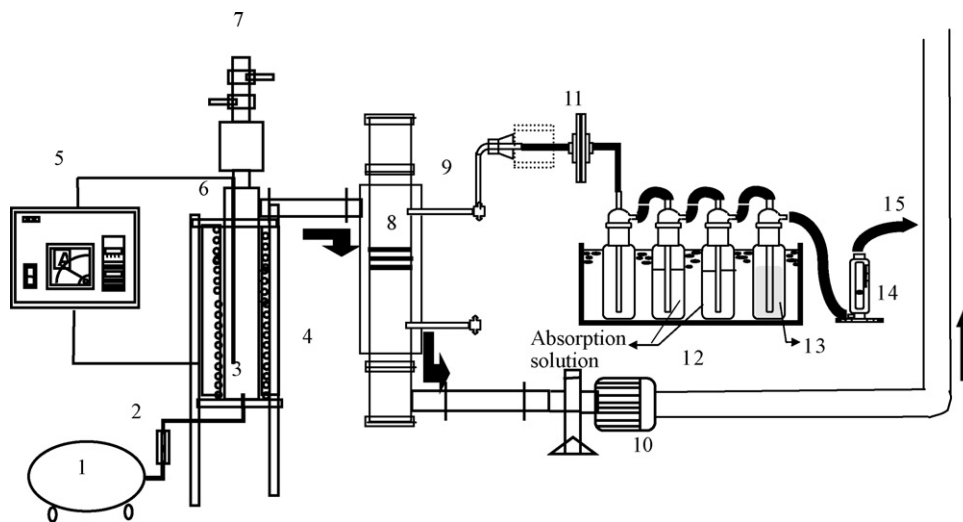


Fig. 1. Experimental system of fluidized-bed incinerator, ACFs adsorber and sampling train for heavy metal: (1) air compressor, (2) flowmeter, (3) combustion chamber, (4) electrical heater, (5) thermal feedback controller, (6) thermocouple, (7) feeder, (8) ACFs adsorber, (9) sampling probe, (10) induced fan, (11) filter holder, (12) impingers (50 mL HNO₃ + 50 mL H₂O₂), (13) silica gel, (14) flow meter, and (15) connect of vacuum pump.

Table 2
Specific surface area and porosity of ACFs by N₂ isotherms

Sample	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	V_{T}^{b} (cm ³ /g)	V_{micro} (<2 nm) (nm, %)	V_{meso} (2–50 nm) (nm, %)	Average pore diameter (by BET, nm)
ACF-A	1229	0.601	0.402 (67)	0.199 (33)	1.956
ACF-B	971	0.470	0.344 (73)	0.126 (27)	1.936
ACF-C	412	0.198	0.170 (86)	0.028 (14)	1.918
Run 1	3	0.004	0	0.004 (100)	4.849
Run 2	2	0.005	0	0.005 (100)	8.353

^a BET surface area.

^b Total pore volume at $P/P_0 = 0.98$.

ature reached a steady state, the artificial feedstock was fed into the incinerator at the rate of one bag per 15 s. The concentration and temperature of the flue gas were stable as the incinerator temperature reached a steady state. Then, the ACFs adsorber was actuated and the sampling was conducted. The sampling flow rate and time were 10 L/min and 4 min, respectively. The experiment was continuously conducted until the sampling was completed.

2.4. Sampling and analytical methods

The flue gas was sampled prior to and after the ACFs adsorber to estimate the removal efficiency of the solid-state metals. The U.S. Environmental Protection Agency Method (M5) was used to sample the metals (Fig. 1). The flue gas, containing heavy metals and fly ash, was isokinetically sampled using a stainless probe and then passed through a filter holder that was packed with a glassy filter to collect particles. Finally, the flue gas was passed through impingers that contained a mixed solution of 200 mL 5% HNO₃ and 10% H₂O₂ to absorb the remaining gaseous metals. The glassy filters were pretreated by microwave digestion (CEM MARS-5), and then the concentration of solid-state metals was analyzed by ICP-MS (Inductively Coupled Plasma Mass, PE-SCIEX ELAN 6100 DRC). The standard addition method was adopted, and a recovery efficiency of $100 \pm 15\%$ was obtained in each analysis. When the experiments were finished, the ACFs were also pretreated by microwave digestion and the digestion liquid was analyzed by ICP-MS to estimate the concentrations of gaseous metals.

2.5. Characterization of ACFs

N₂ adsorption–desorption isotherms were obtained by using an ASAP 2010 vacuum volumetric sorption instrument at 77 K to determine the Brunauer–Emmett–Teller (BET) surface area and the Barrett–Joyner–Halenda (BJH) pore volume of various ACFs. Before N₂ sorption analysis, the samples were preheated at 493 K for degassing and cooled to room temperature in vacua. The photomicrographs of the ACFs were acquired from a Zeiss Axioplan 2 microscope equipped with an AxioCam HR color CCD (charge couple device) camera. An X-ray powder diffractometer (Siemens D5000) was used to identify the heavy metal species in the fly ash collected on the ACFs. The textural characteristics (pore volume, surface area and pore size) of the ACFs reported in this work were also discussed elsewhere [10].

3. Results and discussion

3.1. Characterization of ACFs

Table 2 shows the specific surface area and porous structure of the ACFs. The results indicate that the specific surface areas of ACFs follow the order ACF-A > ACF-B > ACF-C. The order of the mesopore proportions in the ACFs is ACF-A > ACF-B > ACF-C. The micropore volumes of ACFs follow the order ACF-A > ACF-B > ACF-C. The BET surface areas are proportional to the total pore volumes [10].

3.2. Effects of three ACFs on removal of mixed metals

Fig. 2 illustrates the effects of three ACFs on the removal efficiency of fly ash and solid-state metals (Cr, Cd and Pb). The results indicate that the removal efficiency of fly ash exceeded 90% and the best adsorbent of fly ash removal was ACF-C. Fig. 3 presents the knitted structure of the ACFs. The knitted structure of a piece of ACF-C was tighter than those of ACF-A and ACF-B. Moreover, the fly ash was removed immediately by the ACF-C at the beginning of the experiment. However, the fly ash wriggled through a gap in the ACF-A and ACF-B at the beginning of the experiment. Sampling was conducted immediately after the ACFs were placed in the fixed-bed reactor. Therefore, ACF-C removed more fly ash than did either ACF-A or ACF-B.

Fig. 2 also shows that ACF-C was the best adsorbent of solid-state Cd and Pb at 150 °C. Additionally, the removal of solid-state Cd by ACF-C exceeded that of Pb. The removal of solid-state metals was related to the physical properties of the

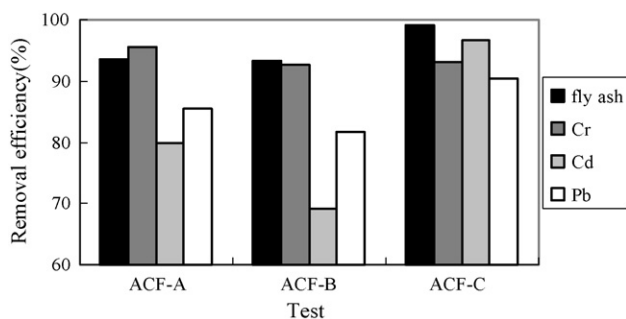


Fig. 2. The effects of three ACFs on the removal efficiency of fly ash and solid-state metals (Cr, Cd and Pb): Run 1 (ACF-A), Run 2 (ACF-B), and Run 3 (ACF-C).

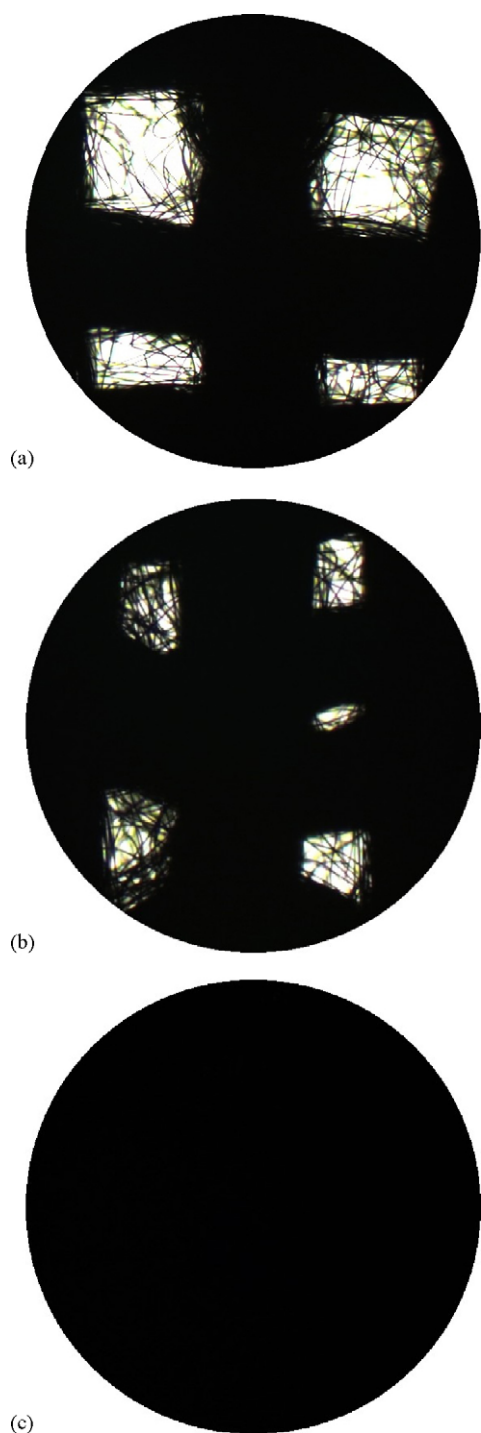


Fig. 3. The knitted structure of a piece of ACF: (a) ACF-A, (b) ACF-B, and (c) ACF-C (25 \times).

metals and the knitted structure of the ACFs. The high volatility of Cd and Pb resulted in the high concentrations of Cd and Pb distributed in the fly ash and gas phase. Our earlier study indicated that the proportions of metals in fly ash followed the order Cd > Zn > Pb > Cr > Cu [3]. Furthermore, the knitted structure of a piece of ACF-C is tighter than that of ACF-A or ACF-B (as shown in Fig. 3). The removal efficiency of fly ash by ACF-C exceeded that by the other two ACFs. Therefore, the removal efficiency of solid-state Cd and Pb by ACF-C

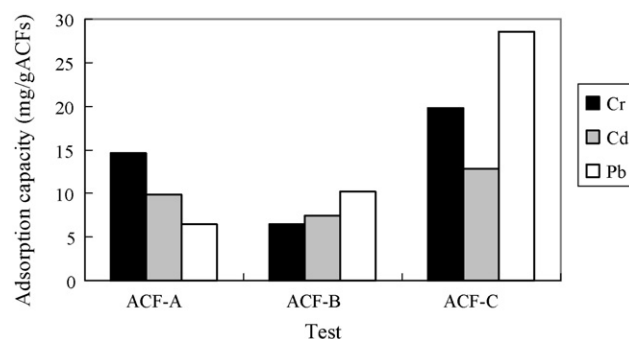


Fig. 4. The effects of three ACFs on the adsorption capacity of gaseous metals (Cr, Cd and Pb): Run 1 (ACF-A), Run 2 (ACF-B), and Run 3 (ACF-C).

exceeded by ACF-A or ACF-B and that of solid-state Cd by ACF-C exceeded that of Pb.

The effect of the type of ACF on the Cr removal was insignificant. Table 3 lists the boiling points and volatilities of various metals. The boiling points of various metal compounds of Cr (such as Cr and Cr₂O₃) may exceed the incineration temperature of 800 °C (Table 3) and the concentrations of Cr distributed in the fly ash and the gas phase may have been lower than that in the bottom ash. Therefore, the change in the surface structure of ACFs does not apparently affect the removal of Cr.

Fig. 4 plots the effects of three ACFs on the adsorption capacity of gaseous metals. The results reveal that the best adsorbent of the gaseous metals was ACF-C. The removal mechanisms of the gaseous metals by ACFs include condensation, physical adsorption and chemical adsorption. Since the ACFs controlled the metals at 150 °C by condensation, the metals condensed on the surfaces of the ACFs blocked the pores in the ACFs. Moreover, the removal efficiency of fly ash by ACF-C was the highest. The fly ash provided greater specific surface area and increased the opportunities for the condensation of metals onto the fly ash. Therefore, the removal efficiency of the mixed metals by ACF-C exceeded that by ACF-A or ACF-B.

Table 2 also shows the specific surface area and porous structure of various ACFs after the experiments. Since the BET surface areas and the pore volumes of micropores of ACFs decrease significantly during the experiments, the heavy metals in the flue gas not only adsorb or condense on the surface of ACFs but also enter the pores by diffusion to occupy the adsorption sites. Almost all of the surface areas of the ACFs are utilized.

3.3. Effects of adsorption temperature on removal of mixed metals

Fig. 5 shows the effect of adsorption temperature on fly ash and solid-state metals (Cr, Cd and Pb) removal. The effect of temperature on fly ash removal was insignificant, because ACFs removed the fly ash by the filtration mechanism. The removal efficiency of fly ash was related to the knitting structure of various ACFs.

Fig. 5 indicates that the removal efficiencies of solid-state metals at various adsorption temperatures follow the order 250 > 150 > 300 °C. The mixed metals that are adsorbed

Table 3
Melting, boiling points and vapor pressures of various metal compounds [3,21–23]

	Cd	Pb	Cr
Element			
Melting point (°C)	320.9	327.5	1890
Boiling point (°C)	765	1744	2482
Vapor pressure (mmHg)	1 at 394 °C, 10 at 484 °C, 100 at 611 °C	1 at 973 °C, 10 at 1162 °C	1 at 1616 °C, 10 at 1845 °C
Oxide			
Melting point (°C)	900 (CdO)	888 (PbO)	2435 (Cr ₂ O ₃)
Boiling point (°C)	1559	–	4000
Vapor pressure (mmHg)	1 at 1000 °C, 10 at 1149 °C	1 at 943 °C, 10 at 1085 °C	–

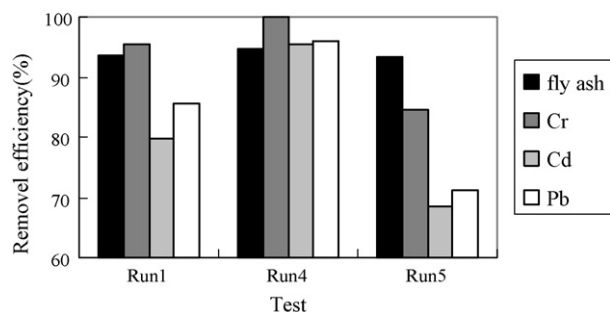


Fig. 5. The influences of adsorption temperature on fly ash and solid-state metals (Cr, Cd and Pb) removal: Run 1 (150 °C), Run 4 (250 °C), and Run 5 (300 °C).

physically or condensed on the fly ash may evaporate and desorb at 300 °C. Furthermore, the metals condensed on the ACFs surface at 150 °C blocked most of the pores on the surfaces of ACFs, reducing the opportunities for metals to enter the pores and reducing the concentration of metals physically adsorbed onto the ACFs. Consequently, the removal of mixed metals was highest at 250 °C.

Fig. 6 displays the effects of the adsorption temperature on the adsorption capacity of gaseous metals. The results indicate that the removal efficiency of the gaseous metals (Cr, Cd and Pb) increased with the adsorption temperature. Chemical adsorption may have occurred between the gaseous metals and the ACFs. The mixed metals adsorbed physically or condensed on the ACFs evaporated and desorbed at 300 °C, increasing the specific

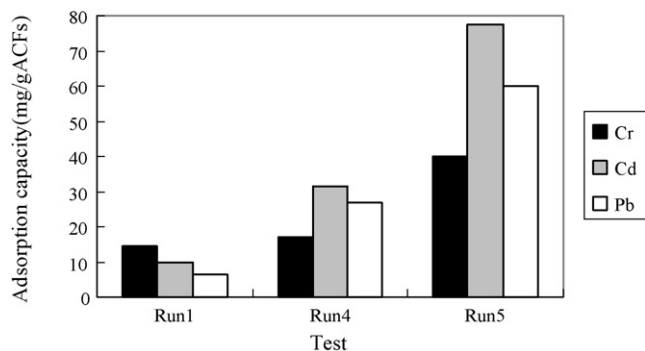


Fig. 6. The influences of adsorption temperature on the adsorption capacity of gaseous metals (Cr, Cd and Pb): Run 1 (150 °C), Run 4 (250 °C), and Run 5 (300 °C).

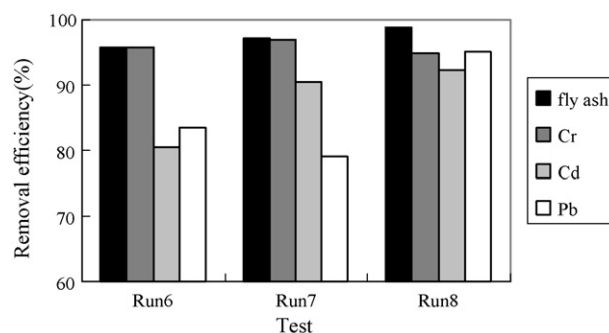


Fig. 7. The effects of the weight of ACFs on the removal efficiency of fly ash and solid-state metals (Cr, Cd and Pb): Run 6 (1.12 g), Run 7 (1.64 g), and Run 8 (2.28 g).

surface area for chemical adsorption. Therefore, the order of the removal efficiencies of gaseous metals at various adsorption temperature was 300 > 250 > 150 °C.

3.4. Effects of the weight of ACFs on removal of mixed metals

Fig. 7 presents the effects of the weight of ACFs on the removal efficiency of fly ash and solid-state metals (Cr, Cd and Pb). The results indicate that the removal efficiency of Cd increased greatly with the weight of ACFs, whereas the removal of fly ash increased negligibly. However, the Pb removal increased greatly until the weight of ACFs was 2.28 g. The order of boiling points of the heavy metals is Cr > Pb > Cd (Table 3) and the proportion of Cd partitioned in fly ash greatly exceeded that of Pb [3]. Moreover, the increase in the weight of ACFs increases the filtration opportunity of the fly ash, especially for micro-particles. Therefore, a significant amount of Cd was removed by removing the fly ash and an increased adsorption capacity was required to control Pb in the flue gas.

The results revealed that the effects of the weight of ACFs on the Cr removal were insignificant. The boiling points of various metal compounds of Cr greatly exceeded 800 °C (the temperature of the incineration). Most metal compounds of Cr are distributed in the bottom ash and the concentration of the gaseous Cr is low [3]. Therefore, the adsorption capacity of a single ACF sufficed to adsorb Cr in flue gas.

Table 4
Identification of heavy metal species distributed in fly ash collected on ACFs

Sample	Heavy metal species
Run 1	CrO, CdO, PbO, Cr ₂ O ₃
Run 2	CrO, CdO, PbO, Cr ₂ O ₃
Run 3	CrO, CdO, PbO, Cr ₂ O ₃
Run 4	CdO, PbO, Cr ₂ O ₃
Run 5	CdO, PbO, Cr ₂ O ₃
Run 6	CdO, PbO, Cr ₂ O ₃
Run 7	CdO, PbO, Cr ₂ O ₃
Run 8	CdO, PbO, Cr ₂ O ₃

3.5. Identification of heavy metal species in fly ash by X-ray diffraction (XRD)

Table 4 lists the heavy metal species in fly ash collected by the ACFs. It demonstrates that such oxide compounds as CrO, CdO, PbO and Cr₂O₃ were present in fly ash, indicating that heavy metals really can condense and adsorb onto fly ash and then be removed by ACFs.

4. Conclusion

This study investigated the removal of three heavy metals from the incineration flue gas using the ACFs. The results demonstrated that the best adsorbent of gaseous metals at 150 °C was ACF-C. The effects of the type of ACF and the weight of ACFs on Cr removal were insignificant. The removal efficiency of Cd increased with the weight of ACFs and that of Pb increased to an ACF mass of 2.28 g. The results also indicated that the removal efficiencies of the solid-state metals and the gaseous metals at various reaction temperature follow the order 250 > 150 > 300 °C and 300 > 250 > 150 °C respectively. The results demonstrated the feasibility of using a ACFs adsorbent to remove the heavy metals from incineration flue gas.

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