Leaching Behavior of Circulating Fluidised Bed MSWI Air Pollution Control Residue in Washing Process

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Abstract: In this study, air pollution control (APC) residue is conducted with water washing process to reduce its chloride content. A novel electrical conductivily (EC) measurement method is proposed to monitor the dynamic change of chloride concentrations in leachate as well as the chloride content of the residue. The method equally applies to various washing processes with different washing time, liquid/solid ratio and washing frequency. The results show that washing effectively extracts chloride salts from APC residues, including those from circulating fluidized bed (CFB) municipal solid waste incineration (MSWI). The most appropriate liquid/solid ratio and washing time in the first washing are found to be around 4 L water per kg of APC residue and 30 min, respectively, and washing twice is required to obtain maximum dissolution. The pH value is the major controlling factor of the heavy metals speciation in leachate, while chloride concentration also affects the speciation of Cd. Water washing causes no perceptible transfer of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) from the APC residue to leachate. The chloride concentration is strongly related with electrical conductivity (EC), as well as with the concentrations of calcium, sodium and potassium of washing water. Their regression analyses specify that soluble chloride salts and EC could act as an indirect indicator to monitor the change of chloride concentration and remaining chloride content, thus, contributing to the selection of the optimal washing conditions.

Keywords: circulating fluidized bed (CFB); municipal solid waste incineration (MSWI); air pollution control (APC) residue; washing; chloride; electrical conductivity (EC)

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1. Introduction

Incineration has been increasingly prevalent in municipal solid waste (MSW) disposal in China. By the end of 2012, 142 large-scale municipal solid waste incineration (MSWI) power plants (77 stoker grate incinerators, 59 fluidized bed incinerators and six pyrolysis furnaces and rotary kiln furnaces) were in operation, and the total MSW incineration capacity reached 154,000 tons per day [1]. However, air pollution control (APC) residue derived from the incineration is classified as a hazardous waste, due to the significant amounts of easily leachable toxic heavy metals and of trace quantities of extremely toxic organic compounds (polychlorinated dibenzo-p-dioxins and dibenzofurans, in brief, dioxins) therein [2,3]. Therefore, these hazardous wastes pose terrible threats to the environment and human health if careful and adapted disposal methods are lacking.

According to Chinese environmental policies, direct disposal in landfills should be avoided as much as possible [1]. A relatively promising treatment is to transform the APC residue into a secondary raw material used for making cement and concrete aggregates [4–6]. However, APC

residue is generally comprised of high concentrations of salts, especially chloride. The specification limits subsequent application in cement production, as chlorides reduce the quality of cement and accelerating the corrosion of embedded steel [7]. Another aspect is high-temperature chloride cycling (sublimation + condensation), detrimental to the operating performance of the cement kiln [8]. Furthermore, chlorides provide convenient conditions to generate organic pollutants, such as dioxins, in the low temperature regions of cement kilns [9]. Thus, removing chloride salts is required as pre-treatment to improve the utilization potential of APC residues.

In previous studies, the removal of salts by washing with water has been suggested as a method to increase the stability of APC residues [10–12], but few reports focus on monitoring the dynamic evolution of these compounds in the wastewater derived from washing, and how to estimate the remaining chloride salt in the residue, particularly for circulating fluidized bed (CFB) MSWI APC residue. Because a certain amount (<20%, *w/w*) of brown coal can be added to the waste as auxiliary fuel for maintaining the fluidized bed temperature, the average concentration of pollutants and salts may be lower than in stoker incineration APC residue, making the former more suitable for recycling. In this paper, different washing processes, featuring different contact time, liquid/solid ratio and frequencies, have been investigated and tested, to establish a convenient and effective method to solve the above-mentioned problems.

2. Materials and Methods

2.1. Materials

The APC residue samples were taken from the baghouse filter of a circulating fluidized bed incinerator located in Zhejiang Province, China. The incinerator has a capacity of 800 tons per day, and operates at approximately 850–950 °C. The flue gas treatment involves spray neutralization with a hydrated lime suspension and activated carbon injection.

2.2. Methods

The samples were preliminary dried in an oven at 105 °C. During the washing experiments, the deionized water employed as washing solvent was mingled with APC residue in polytetrafluorethylene (PTFE) 100 mL screw-top containers. Then, the solution was horizontally vibrated on a water bath oscillator with the bath temperature sustaining at 25 °C. After separation by vacuum filtration, the washed residue was dried for 24 h at 105 °C and then was analyzed for its chemical composition using X-ray fluorescence equipment (XRF, Thermoscientific ARL ADVANT'X IntelliPowerTM 4200, Wilmington, DE, USA). The main crystalline phases of untreated and washed APC residues were identified by X-ray diffraction analysis (XRD, X'Pert PRO PANalytical B.V., Almelo, The Netherlands). The specific surface area and pore size distribution were determined by an Autosorb-1-Csurface area analyser (Quantachrome Instruments, Boynton Beach, FL, USA). The metal concentrations in leachate were measured by inductively coupled plasma combined with atomic emission spectrometry (ICP-AES, iCAP6300, Shanghai, China). Ionic liquid Chromatogram (792-BASIC, Herisau, Switzerland) has been used for the determination of chlorides and sulphates in the leachate. The speciation of heavy metals in leachate was simulated by the Visual MINTEQ3.0 software (Kungliga Tekniska Hogskolan, Stockholm, Sweden). The concentration of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in APC residue was analyzed by a high resolution gas chromatograph (HRGC)/high resolution mass spectrometer (HRMS) (JMS-800D, JEOL Co., Tokyo, Japan), and the procedure for clean up was conducted according to USEPA method 1613B. The EC and pH of the leachate were measured using a pH meter (S470 SevenExcellence™, Mettler Toledo, Shanghai, China) and a conductivity meter (S700 SevenExcellence™, Mettler Toledo). The cumulative weight loss of the APC residue after washing was calculated from:

$$\frac{M_{origin} - M_{residue}}{M_{origin}} \tag{1}$$

where M_{origin} and $M_{residue}$ represent the mass of untreated APC residue and the dry mass of washed ash, respectively. The chlorine mass reduction was calculated from:

$$\frac{M_{origin}f_{origin} - M_{residue}f_{residue}}{M_{origin}f_{origin}} \quad (2)$$

where f_{origin} and $f_{residue}$ are the chlorine content of untreated APC residue and of washed ash, respectively.

The first washing process, consisting of two successive stages, was carried out to determine the optimal washing conditions for the first washing step. In the first stage, a group of experiments was conducted at a liquid(milliliter)/solid(gram) (abbreviated as L/S) ratio of 10/1 and mixing times varying from 5 min to 24 h, to determine the optimal contact time. The second stage involved experiments with different L/S ratios batch runs including 1/1, 2/1, 4/1, 6/1, 8/1, 10/1, 12/1, 16/1 and 20/1 to determine the optimal water intensity and the washing time was selected on basis of the first-stage results. During the process, 10 g of APC residue was used in each single experiment, the vibration speed was controlled at a constant of 200 r/min.

Double and triple washing processes were conducted to investigate the effect on dissolution of washing frequency and to obtain the maximum dissolution level of APC residue chlorides in the water. Their experimental conditions were arranged based on the first washing results and 10 g of APC residue was used in each experiment.

3. Results and Discussion

3.1. The Characteristics of Unwashed APC Residue and Washing Time

The main elements of APC residue were analyzed by XRF and the results are shown in Table 1 (APC residue 1).

Table 1. The comparison of main elements in different fly ashes.

No.	1	2	3	4
Fly ash type	APC residue	APC residue [13]	ESP fly ash [14]	Coal fly ash [15]
Furnace type	CFB	Stoker	Stoker	N
CaO	22.05	25.16	19.50	11.77
SiO_2	21.28	4.73	7.30	50.09
Al_2O_3	13.00	1.77	3.20	24.91
Cl	7.81	31.72	21.98	N
MgO	6.15	1.25	2.61	0.40
Fe_2O_3	5.73	0.95	1.39	7.60
Na_2O	5.43	10.92	13.07	0.14
SO_3	3.05	7.98	9.76	N
P_2O_5	2.81	1.20	1.72	N
K_2O	2.01	10.57	11.21	1.19
TiO_2	1.03	1.17	2.77	1.17
ZnO	0.904	0.85	3.02	N
CuO	0.381	0.2	N	N
BaO	0.215	N	N	N
Mn_2O_3	0.146	N	N	0.10
PbO	0.133	0.49	N	N
Cr_2O_3	0.0941	0.2	N	N

Unit: % (w/w). BF-Baghouse Filter; CFB- Circulating Fluidised Bed; ESP-Electrostatic Precipitator; N-No mention.

In addition, the table was extended to report major elements from coal fly ash, APC residue and ESP fly ash from a stoker MSWI, cited for comparison. Compared to APC residue 1, the APC residue 2 and ESP fly ash 3 from the stoker MSWI had a much higher content of Cl, Na, and K, which

were detrimental to the recycle of APC residue in construction by reducing the quality of cement and accelerating the corrosion of embedded steel [7]. In addition, the content of Si and Al in APC residue 1 were much higher than that in APC residue 2 and ESP fly ash 3, making its elemental composition the closest with coal fly ash among these three MSWI fly ashes. It is known that coal fly ash has been reused in many aspects, such as in construction, as a low-cost adsorbent, a lightweight aggregate raw material, as a road sub-base, and in zeolite synthesis [16]. In conclusion, APC residue 1 shows better quality for recycle than the other two.

The concentration of the main cations, anions and heavy metals in the leachate from different washing times are shown in Table 2 (single washing, L/S: 10/1). The major elements in the leachate were Cl^-, Ca, Na and K, of which the concentration increased from 3200 mg/L, 1187 mg/L, 768 mg/L and 611 mg/L at 5 min to 6178 mg/L, 1772 mg/L, 1171 mg/L and 993 mg/L at 30 min, respectively. After 30 min, these four elemental concentrations remained relative stable. Other compounds, such as sulphate, Al, Mg and Fe exhibited values of 209 mg/L, 1.44 mg/L, 0.12 mg/L and 0.004 mg/L, respectively. Among the heavy metals, the concentration of Ba, Pb, Zn, Cr, Cu were 1.11 mg/L, 0.34 mg/L, 0.25 mg/L, 0.53 mg/L, 0.08 mg/L, respectively, and other element, such as Ni, As, Cd, Ag, Mn, and Se were lower than 0.01 mg/L. These phenomena could be explained by different leaching mechanism controls on solution concentration for various elements. For example, Cl, K and Na are largely associated with soluble salts, and controlled by their availability in the solid phase, while Ca and S are controlled by their solid phase availability and anhydrite solubility [17].

As a result of the release of significant amounts of calcium hydroxide formed by hydrolysis of calcium silicates and aluminosilicates [18], the pH of the dissolution promptly reached 11.12 during the 5 min and then reached 11.12–11.8, remarkably exceeding the Chinese integrated wastewater discharge standard values (6–9)(GB8978-1996) [19]. However, EC and cumulative weight loss increased from 28.5 mS/cm, 5.60% to 53.32 mS/cm, 9.64%, respectively, during 30 min. After 30 min, EC and cumulative weight loss showed no obvious change. Therefore, the EC has almost no correlation with washing time after 30 min and a short time is enough to ensure sufficient dissolution of the more soluble components.

Table 2. Ionic species concentration in leachate from different washing time.

| Ionic Species Concentration (mg/L)	Leachate from Different Washing Time								
	5 min	10 min	20 min	30 min	1 h	4 h	6 h	18 h	24 h
Cl^-	3200	4745	5963	6178	6129	6229	6324	6186	6324
SO_4^{2-}	211	172	220	209	198	144	149	151	103
Ca	1187	1370	1796	1772	1706	1670	1653	1720	1694
Na	768	1098	1132	1171	1143	1124	1242	1101	1127
K	611	731	965	993	968	912	870	913	939
Al	0.69	0.89	1.41	1.44	2.18	12.94	10.11	16.11	5.47
Mg	0.09	0.09	0.10	0.12	0.18	0.24	0.26	0.21	0.11
Fe	0.033	0.003	0.003	0.004	0.004	0.004	0.004	0.020	0.002
As	ND	0.004	ND	ND	0.002	0.001	ND	ND	ND
Cd	0.001	ND	0.003	ND	<0.001	0.001	<0.001	ND	ND
Cr	0.61	0.48	0.71	0.53	0.45	0.17	0.18	0.02	0.02
Cu	0.06	0.07	0.27	0.08	0.08	0.04	0.04	0.02	0.02
Ni	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pb	0.66	0.52	1.37	0.25	0.11	0.01	<0.01	<0.01	0.01
Se	0.014	0.020	0.027	0.013	0.018	0.019	0.004	0.010	ND
Zn	0.80	0.58	0.96	0.34	0.20	0.05	0.04	0.01	0.01
Ba	1.05	0.93	2.64	1.11	1.34	1.66	1.65	1.36	1.85
pH	11.12	11.62	11.84	11.85	11.88	11.63	11.42	11.76	11.60
EC (mS/cm)	28.20	39.55	51.45	53.32	52.53	53.50	53.77	52.93	54.15
Cumulative weight loss (%)	5.60	7.61	9.42	9.64	9.48	9.42	9.56	9.41	9.51

ND: The concentration was lower than the detection limit of the ICP (<0.001 mg/L).

3.2. Different L/S Ratios

Thereafter, an appropriate washing time of 30 min was adopted to ensure sufficient dissolution of the soluble salts from APC residue. Figure 1 indicates that Cl^-, Ca, Na and K were the major components in the leachate accounting for over 97% (*w/w*) of the total materials dissolved into the water, yet dependent of L/S ratios. The distribution trend of the four elements remained relatively stable. But the higher L/S ratio could cause more cumulative weight loss and less residue remaining chloride before the L/S ratio attained 6 (Figure 2). The chlorine mass reduction maintained the highest value at an L/S ratio of around 4–12, but slightly declined at an L/S ratio of 16 and 20.
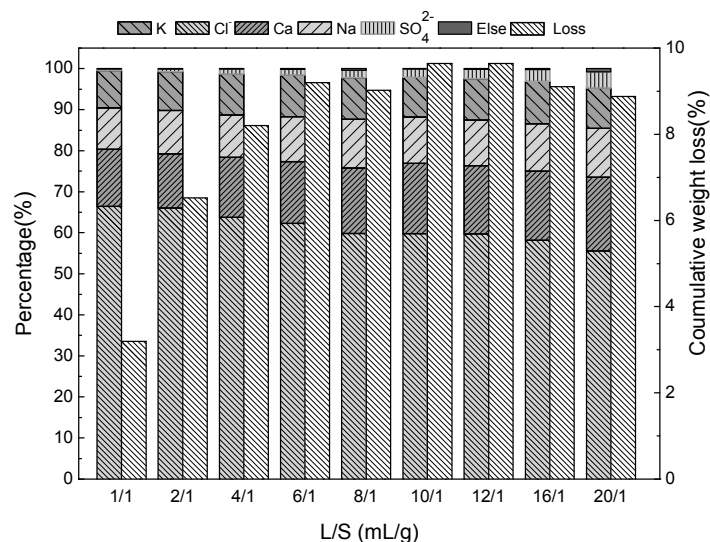
Figure 1. The distribution of components in the leachate and cumulative weight loss of air pollution control (APC) residue.
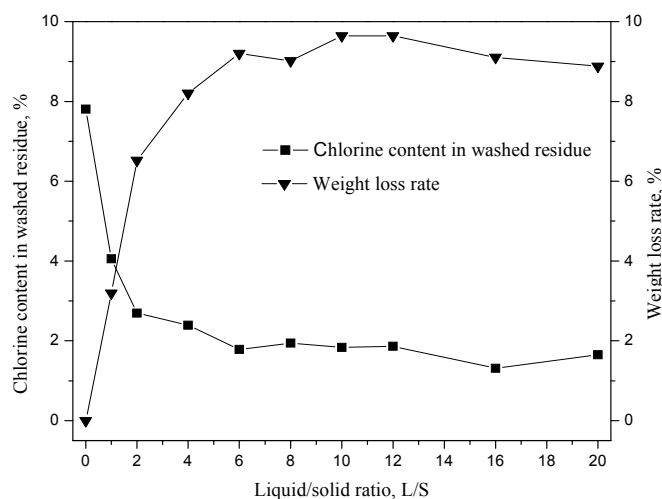
Figure 2. The evolution of chlorine content in washed residue and weight loss vs. L/S.

Therefore, to obtain the maximum chloride reduction and conservation of water, an L/S ratio of 4 is the optimal option in the first washing process. Yang et al. [20] suggested that the optimal L/S-ratio for washing APC residue from stoker MSWI is an L/S of 20–25/1, which was much higher than the results in the present work. That is mainly because the chlorine content in stoker MSWI APC residue is much higher than that in CFB MSWI APC residue, which is agreement with the conclusion in Section 3.1.

The leaching content of heavy metals shows a different evolution at increasing of L/S-values (Figure 3). A rising L/S caused more transfer of Cr and Ba from the APC residue particles into the leachate. The leaching content of Cu, Se and Zn were relatively stable. Particularly, the leaching amount of Pb decreased after the L/S was greater than 6, which might had something to do with its chemical property. Pb is an amphoteric metal, so the strong alkalinity of leachate is supposed to help its dissolution. However, the alkalinity of leachate was weakened by rising L/S, inducing the lessening of Pb in leachate.
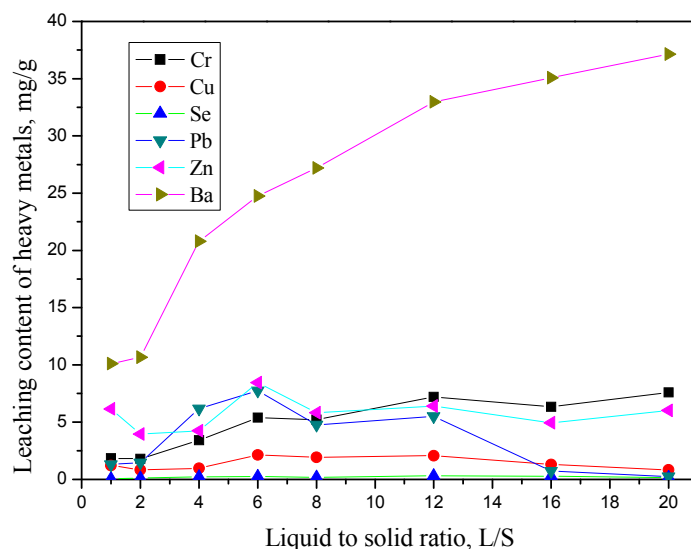
Figure 3. The evolution of the leaching content of heavy metals vs. L/S.

The concentrations of heavy metals gradually decreased with an increasing L/S ratio due to the higher dilution (Table 3). The exhibited concentration of heavy metals, such as Cr, Cu, Pb, Se, Zn, and Ba, at an L/S ratio of 4 significantly declined at the L/S ratio of 8, which may meet the Chinese integrated wastewater discharge standard values (1.5 mg/L for Cr, 0.5 mg/L for Cu, 0.1 mg/L for Se, 1.0 mg/L for Pb, 2.0 mg/L for Zn). Others heavy metals, such as Ni, As, Cd, Ag and Mn, were below 0.05 mg/L after the L/S ratio of 2.

Table 3. The evolution of the concentration of heavy metals vs. L/S.

| Heavy Metals	L/S	Cr	Cu	Se	Pb	Zn	Ba
	1	4.10	2.71	0.11	2.87	13.68	22.47
	2	1.24	0.58	0.073	1.00	2.73	7.36
	4	0.99	0.28	0.062	1.79	1.23	6.03
	6	0.99	0.39	0.047	1.42	1.55	4.54
Concentration	8	0.70	0.26	0.025	0.64	0.78	3.65
	10	0.53	0.084	0.013	0.25	0.34	1.10
	12	0.63	0.180	0.028	0.48	0.56	2.88
	16	0.41	0.085	0.018	0.046	0.32	2.27
	20	0.39	0.043	0.008	0.013	0.31	1.91
Waste water limits	–	1.50	0.50	0.10	1.00	2.00	UL

Unit: mg/L; UL: Unlimited.

3.3. Double and Triple Washing

Based on an appropriate operating condition (200 r/min, L/S ratio: 4/1, 30 min), as derived from the first washing experiments, the following group conditions were chosen for testing the double washing, including three L/S ratios (4/1, 6/1, 10/1), two speeds (250 r/min, 200 r/min) and

two washing times (30 min, 60 min) (Figure 4). The results show that the chloride mass dissolved into the water ranged from 9.76 mg/g to 10.01 mg/g, and that the cumulative weight loss was about 2.88%–3.00%. Obviously, most of the easily soluble components were washed out during the first washing and it is difficult to dissolve these remaining components during the second washing. Factors, such as L/S ratio, speed and time, have no apparent effect on improving the dissolution of these less soluble components.
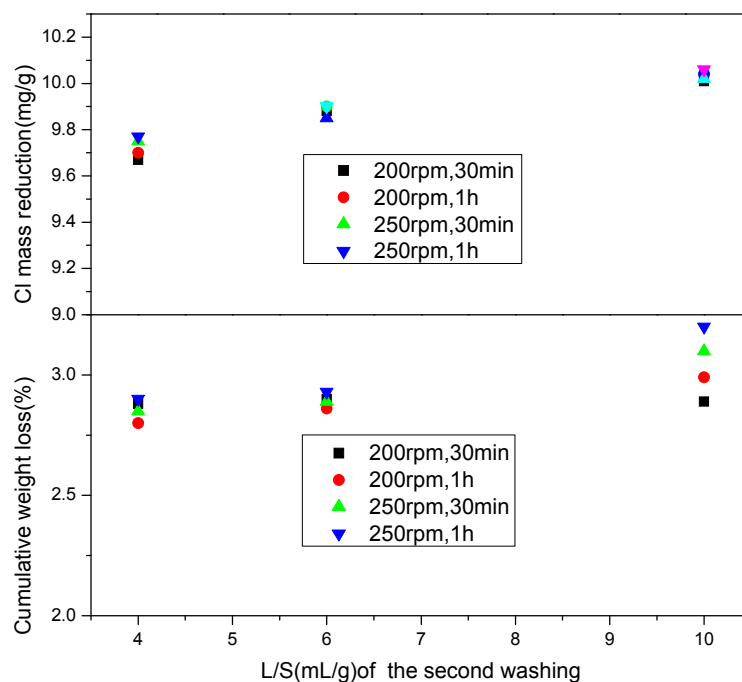

Figure 4. Chlorine mass reduction and cumulative weight loss of APC residue.

Zhu et al. [21] used X-ray absorption near edge structure(XANES) and XRD to analyze the chloride chemical form and found that insoluble chloride may be present in the form of Friedel's salt (such as $[Ca_2Al(OH)_6]Cl \cdot 2H_2O$) and other insoluble forms related to $CaCl_2$. After the first and second washing, the readily water soluble species (especially chlorides) were greatly leached out (83% for Cl, 26% for Na, 60% for K, 11% for Ca, 8% for S). Sulfur was difficult to extract since its main forms are gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$), which are insoluble in water. Other forms of Na and K could be insoluble aluminosilicates, such as $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ and $Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$. Since washing twice could leach out 11% of the total soluble chloride in the raw APC residue, it is necessary, in the washing process, to remove as much chloride as possible.

Following the suitable twice-washing conditions (200 r/min, L/S ratio: 4/1, 30 min), also one set of triple washing experiments was conducted. The speed, L/S ratio and time were 250 r/min, 4/1 and 30 min, respectively. Yet, this triple washing had little effect on the dissolution of soluble components. During the triple washing, the chlorine mass reduction was only 0.5 mg/g and the cumulative mass reduction was less than 1%. Thus, the major soluble components are almost completely leached out in the first and second washing, and higher washing frequencies are superfluous due to a weak leaching effect and extravagant water consumption.

A comparison of the XRD diffraction pattern of the APC residue before and after washing indicated that washing did not substantially modify the nature of the crystalline phases of APC residue (Figure 5). Obviously, the intensities of the XRD peaks corresponding to easily water-soluble components, such as potassium chloride (KCl) and sodium chloride (NaCl), were all significantly reduced in the XRD spectra of washed ashes.
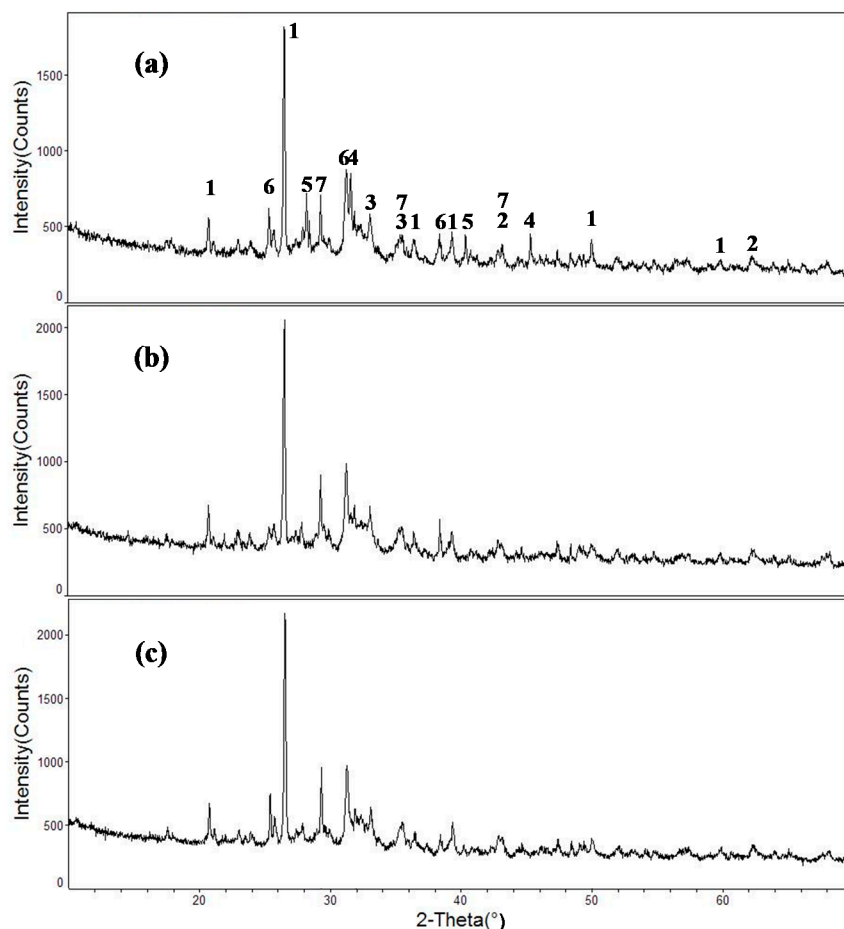
Figure 5. X patterns of APC residue before and after washing: (**a**) untreated APC residue; (**b**) first washed APC residue; (**c**) twice washed APC residue. 1: SiO_2; 2: MgO; 3: Fe_2O_3; 4: NaCl; 5: KCl; 6: $CaSO_4$; 7: $CaCO_3$.

Chen et al. [22] indicated that the water-soluble chlorides, such as KCl, NaCl and calcium chloride hydrate ($CaCl_2·2H_2O$) are easily washed away from APC residue, but calcium chloride hydroxide (Ca(OH)Cl) might not be easy to leach out at room temperature. In Figure 5, no crystalline peaks of $CaCl_2·2H_2O$ and Ca(OH)Cl were found, implying that they may still be present as amorphous and/or complex crystalline phases. Due to the fact that calcium chloride ($CaCl_2$) is hydroscopic and easily forms $CaCl_2·2H_2O$ during the washing process [21], the main phase of Ca, which could be greatly leached out, was $CaCl_2·2H_2O$ rather than $CaCl_2$ and Ca(OH)Cl. The XRD spectra of the residue after the first and twice washing were nearly unchanged, indicating that the most easily soluble components were already dissolved during the first wash.

The pore size became larger (Figure 6) and the specific surface area (BET) increased from 3.17 to 4.2, 4.61 and 4.65 m^2/g, respectively, after the first, second and third washing. The results were as expected: as NaCl, KCl and $CaCl_2$ dissolve into the water, new pores will appear and the diameter of old pores will become larger. The BET of APC residue after triple washing only had a minor increase, indicating that triple washing has little effect on the removal of soluble salts, as proposed before.
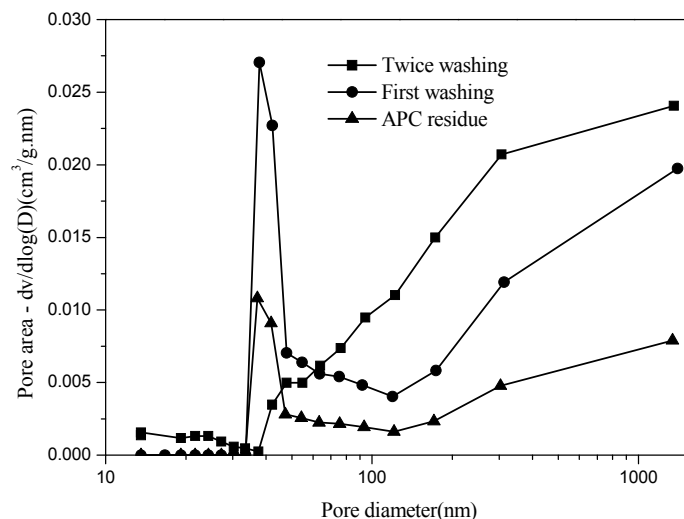
Figure 6. The pore distribution after the first and second washing.

3.4. Speciation of Heavy Metals and the Concentration of Dioxins

An appropriate condition (washing time 30 min, L/S 4) for single washing could be attained in Sections 3.1 and 3.2. At this condition, the pH value and the concentration of main cations, anions and heavy metals in the leachate (pH, Cl^-, SO_4^{2-}, PO_4^{3-}, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, $Cr(OH)^{2+}$, Cd^{2+}) were imported into the software Visual MINTEQ3.0 to simulate the speciation of heavy metals (Zn, Cu, Cd, Pb), and the results are shown in Table 4.

Table 4. The form distribution of heavy metals in the leachate.

Elements	Existing Form	Form Distribution (%, *w/w*)
		(pH = 10.85)
Zn	$ZnOH^+$	0.1
	$Zn(OH)_2$ (aq)	**77.9**
	$Zn(OH)_3^-$	**21.5**
	$Zn(OH)_4^{2-}$	0.5
Cu	$CuOH^+$	0.3
	$Cu(OH)_4^{2-}$	0.9
	$Cu(OH)_3^-$	**76.2**
	$Cu(OH)_2$ (aq)	**22.6**
Cd	Cd^{2+}	5.9
	$CdOH^+$	**12.7**
	$Cd(OH)_2$ (aq)	**36.7**
	$Cd(OH)_3^-$	0.3
	$CdCl^+$	**30.7**
	$CdCl_2$ (aq)	**11.9**
	$CdSO_4$ (aq)	0.2
	$CdCO_3$ (aq)	1.6
	$Cd(CO_3)_2^{2-}$	0.1
Pb	$PbOH^+$	3.5
	$Pb(OH)_2$ (aq)	**51.4**
	$Pb(OH)_3^-$	**44.8**
	$Pb_3(OH)_4^{2+}$	0
	$Pb(CO_3)_2^{2-}$	0.1
	$PbCO_3$ (aq)	0.2

aq: aqueous.

The main speciation of Zn were $Zn(OH)_2$ (aq) and $Zn(OH)_3^-$, those of Cu were $Cu(OH)_2$ (aq) and $Cu(OH)_3^-$, and Pb was mainly present as $Pb(OH)_2$ (aq) and $Pb(OH)_3^-$, while Cd mainly appeared as $CdCl_2$ (aq), $CdCl^+$, $Cd(OH)_2$ (aq) and $CdOH^+$. The three heavy metals, Cu, Pb and Zn showed similar speciation, which were hydroxide and hydroxide combined with OH^-, the leachate was strongly alkaline so that Cu, Pb, and Zn could easily combine with OH^-. For Cd, besides the pH value of the solution, the chloride concentration was another important factor to determine speciation. The proportion of $CdCl_2$ (aq) rises as the chloride concentration increases. Therefore, the pH value is the major factor for controlling the form of heavy metals in leachate, while the chloride concentration also had an important effect.

The 2,3,7,8-substituted PCDD/Fs congener patterns were very similar in raw APC residue and the residue after washing twice (L/S 4, washing time 30 min, vibration speed 200 r/min). The I-TEQ concentration of PCDD/Fs increased from 2.59 I-TEQ ng/g to 2.81 I-TEQ ng/g, mainly because of the weight loss of APC residue (see Figure 7). Since PCDD/Fs are non-water soluble organic pollutants, the water washing process could not cause any real transfer of PCDD/Fs from solid to liquid, except if particles were leached out during washing.
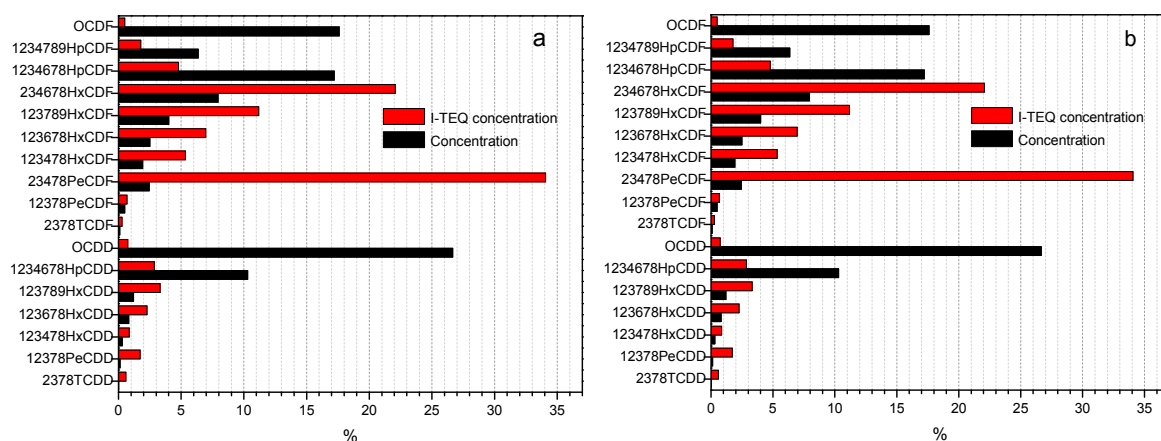
Figure 7. Ploychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) toxic congener pattern in APC residues (**a**) raw APC residue; (**b**) residue after washing twice.

For comparison, the I-TEQ concentration of PCDD/Fs analyzed in different types of fly ash and arising in different incinerators is shown in Table 5. Clearly, the MSWI APC residue contained much more PCDD/Fs than fly ash from coal firing. Moreover, both Chen et al. [23] and Lu et al. [24] reported that CFB incineration was superior to stoker incineration in controlling dioxins, because, in their research, the PCDD/Fs concentration of APC residue from CFB was lower than the corresponding concentration in stoker APC residue, as shown in Table 5. Conversely, Yun et al. [25] reported that the CFB furnace produced more toxic APC residue than the stoker plant. In the present work also, a rather high value of 2.594 I-TEQ ng/g was found for the CFB APC residue. A dioxins toxicity comparison between CFB APC residue and stoker APC residue seems unfavorable for this particular case, but the CFB APC residue seems to contain less dioxins, in general, from the data shown in Table 5. It may have something to do with the addition of coal, since the combustion of coal cannot really contribute any dioxins in APC residue. In addition, Dias-Ferreira et al. [26] found that the concentration of PCDD/Fs in ESP fly ash was much higher than that in APC residue, because the electrostatic precipitators might lead to the formation of dioxins [27].

Table 5. The concentration of PCDD/Fs in different fly ashes from different incinerators.

	No.	Location	Incinerator	Furnace Type	Fly Ash Type	PCDD/Fs (ng/g)	I-TEQ (ng/g)
Present work	1	China	MSWI	CFB	APC residue	156.5	2.594
Chen et al. [23]	2	China	MSWI	Stoker	APC residue	19.2	0.456
	3		MSWI	Stoker	APC residue	236	2.680
	4		MSWI	CFB	APC residue	25.1	0.897
	5		MSWI	CFB	APC residue	21.7	0.138
	6		EPPI	N	Coal fly ash	0.059	0.001
	7		EPPI	N	Coal fly ash	0.536	0.002
	8		EPPI	N	Coal fly ash	0.142	0.003
Lu et al. [24]	9	China	MSWI	Stoker	APC residue	60.11	0.47
	10		MSWI	Stoker	APC residue	167.56	5.16
	11		MSWI	CFB	APC residue	9.37	0.18
	12		MSWI	CFB	APC residue	9.32	0.24
	13		MSWI	Stoker	APC residue	58.83	0.79
	14	France	MSWI	Stoker	APC residue	192.03	6.83
Celia et al. [26]	15	Denmark	MSWI	Stoker	ESP fly ash	197	2.01
	16	–	MSWI	Stoker	APC residue	4.85	0.18
Yun et al. [25]	17	–	MSWI	CFB	APC residue	132	1.8
	18	–	MSWI	CFB	APC residue	190	2.5
	19	China	MSWI	Stoker	APC residue	63	0.71
	20	–	MSWI	Stoker	APC residue	42	0.55

EPPI–electrical power plant incinerator; N–No mention.

3.5. Regression Analysis

The results in Table 2 and Figures 1 and 5 indicate that chloride salts were the main electrolytes in leachate. The pH value of the resulting leachate had no correlation with chloride concentration, while the EC value of leachate showed strong positive association with chloride concentration, as shown in Table 1. At a constant temperature, the EC value was an important index reflecting the concentration of electrolytes in solution. Therefore, the EC value could be an effective parameter for online monitoring and operation optimization during water washing.

Based on the above results from the three different washing processes, regression analyses of the chloride concentrations and the sum concentrations of Ca, K and Na, as well as EC for the leachates, are shown in Figure 8.
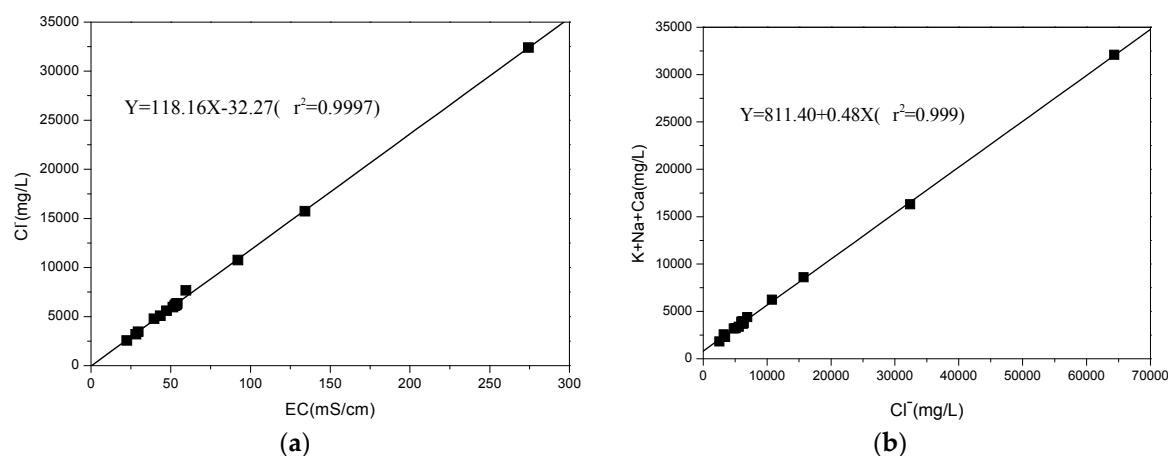
Figure 8. Regression analysis of chloride concentrations against EC values (**a**) and the sum of the concentration of Ca, K and Na against chlorides (**b**) for the leachates.

The results showed that the coefficient of determination (r^2) values were all above 0.99. The strength of these relationships confirmed that the main components leached out of APC residue during

the washing processes were water-soluble chloride salts. Therefore, by the means of continuously monitoring the EC of the leachate and combining the corresponding regression equation, the chloride concentrations could be obtained indirectly and dynamically. The significant advantages of this are less time consumption and the results are more convenient to understand with respect to the dynamic change of the leachate during washing process. When washing APC residue, the EC value of the leachate could be regarded as a reference indicator for choosing the appropriate conditions, such as time, L/S ratio and frequency.

The chlorine content of the dried residue could be estimated on basis of the EC value and the above-mentioned regression equations. According to the equilibrium of chloride before and after washing, the Equation (3) was used.

$$M_{origin}f_{origin} = M_{\text{residue}}f_{\text{residue}} + C_{Cl}V_r10^{-3} \tag{3}$$

C_{Cl} (mg/L) and V_r(L) represent the chloride concentration of the leachate and the volume of the leachate, respectively. Then, Equations (4)–(6) could be obtained by transformation.

$$f_{origin} = \frac{M_{\text{residue}}}{M_{origin}}f_{\text{residue}} + \frac{C_{Cl}V_r}{M_{origin}}10^{-3} \tag{4}$$

$$f_{origin} = (1 - \varphi_{loss})f_{\text{residue}} + C_{Cl}(L_s - \frac{W_\alpha}{\rho_{\text{water}}})10^{-3} \tag{5}$$

$$f_{origin} = (1 - \varphi_{loss})f_{\text{residue}} + C_{Cl}(L_s - W_\alpha)10^{-3} \tag{6}$$

where φ_{loss} is the cumulative weight loss (%) after washing, L_s is the liquid to solid ratio during washing (L/kg), ρ_{water} is the density of water at room temperature, and W_α is the coefficient of water absorption of APC residue (kg/kg), W_α can be calculated using Equation (7).

$$W_\alpha = (m_1 - m_0)/m_0 \times 100\% \tag{7}$$

where m_0 is the weight of dry APC residue (kg), m_1 is the weight of water-saturated APC residue (kg). Cl^-, Ca, Na and K accounted for over 97% of the total materials dissolved into the water as in Figure 1, φ_{loss} could be calculated from:

$$\varphi_{loss} = \frac{V_r\sum\limits_{1}^{n} C_i}{M_{origin}}10^{-3} \approx \frac{V_r(C_{Cl} + C_{Ca} + C_K + C_{Na})}{M_{origin}}10^{-3} \tag{8}$$

where C_{Ca}, C_{Na}, C_K are concentrations of Ca, Na, K in the leachate, respectively, mg/L. According to regression analyses:

$$C_{Ca} + C_K + C_{Na} = aC_{Cl} + b \tag{9}$$

$$\varphi_{loss} \approx (L_s - W_\alpha)[(1 + a)C_{Cl} + b]10^{-3} \tag{10}$$

Finally, f_{origin} can be calculated from:

$$f_{origin} \approx \left\{1 - (L_s - W_\alpha)[(1 + a)C_{Cl} + b]10^{-3}\right\} f_{\text{residue}} + C_{Cl}(L_s - W_\alpha)10^{-3} \tag{11}$$

C_{Cl} can be indirectly obtained through the EC value. Thereby, the chloride content of the washed ash f_{residue} can be calculated approximately if the EC is known.

Soluble chloride salts in MSWI APC residue can largely increase the risk of application in cement production, and chloride cycling is detrimental to the operating performance of the cement kiln. Water washing pretreatment is an efficient way to remove the chloride salts from CFB MSWI APC residue; moreover, the chloride concentration of leachate and the remaining chloride content of the

residue can be monitored by measuring EC values of the leachate. Since coal combustion can hardly contribute any chloride salts in APC residue, and the addition of an amount of coal is usually less than 20%, the EC measurement is supposed to be applied for other APC residues from other CFB incinerators. Yang et al. [20] also found that, for stoker MSWI APC residue, chloride concentration in the leachate could be determined by online monitoring the EC values of the leachate. In conclusion, water washing pretreatment is essential for cement solidification of APC residue or co-combustion of APC residue in cement producing kiln, and EC measurement is a practical method in their water washing pretreatment.

4. Conclusions

Washing is effective to extract all water soluble chloride salts from CFB MSWI APC residue. These are significantly leached out (83% for Cl, 26% for Na, 60% for K, 11% for Ca), but compounds incorporating Al, Mg, Fe and heavy metals exhibit an extremely low release. The appropriate water intensity and washing time in the first washing are found to be around 4 L water per kg of APC residue and 30 min, respectively, and washing twice allows to obtain the maximum dissolution. The pH value is the major factor for controlling the form of heavy metals in leachate, while the chloride concentration has an important effect on the speciation of some (e.g., Cd) of the heavy metals. The water washing process can barely cause any transfer of PCDD/Fs from APC residue to leachate, unless the washing liquor would contain entrained particles. EC can be regarded as an indirect parameter to monitor the dynamical change of chloride concentrations in the leachate and content in the residue from different washing processes. Water washing pretreatment is essential for cement solidification of APC residue or co-combustion of APC residue in a cement-producing kiln, and EC measurement is a practical method in the water washing pretreatment.

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