Chlorides behavior in Raw Fly Ash Washing Experiments

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Abstract:

Chloride in fly ash from municipal solid waste incinerators (MSWIs) is one of obstructive substances in recycling fly ash as building materials. As a result, we have to understand the behavior of chlorides in recycling process, such as washing. In this study, we used X-ray absorption near edge structure (XANES) and X-ray diffraction (XRD) to study the chloride behavior in washed residue of raw fly ash (RFA). We found that a combination of XRD and XANES, which is to use XRD to identify the situation of some compounds first and then process XANES data, was an effective way to explain the chlorides behavior in washing process. Approximately 15% of the chlorine in RFA was in the form of NaCl, 10% was in the form of KCl, 51% was $CaCl_2$, and the remainder was in the form of Friedel's salt. In washing experiments not only the mole percentage but also the amount of soluble chlorides including NaCl, KCl and $CaCl_2$ decreases quickly with the increase of liquid to solid (L/S) ratio or washing frequency.

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However, those of insoluble chlorides decrease slower. Moreover, Friedel's salt and its related compound ($11CaO \cdot 7Al_2O_3 \cdot CaCl_2$) were reliable standards for the insoluble chlorides in RFA, which are strongly related to $CaCl_2$. Washing of RFA promoted the release of insoluble chlorides, most of which were in the form of $CaCl_2$.

Keywords: fly ash; washing; chloride behavior; X-ray absorption near edge structure (XANES)

1 Introduction

We have proposed a new recycling system for fly ash generated from municipal solid waste incinerator —— WCCB system —— Washing, Calcinating and Changing/ Converting the treated fly ash into the raw material in cement industry [1], because the operation of rotary kiln is good enough to treat organic pollutants such as dioxins [2]-[4] and heavy metal can be stabilized in the cement product, while some component in fly ash, such as SiO_2, CaO and so on, can be raw material for cement [5]. One important purpose of this system is to reduce the chlorides from fly ash as much as reasonable, because there is strict limitation of chlorine concentration in cement industry, since chlorides will erode the steel embedded in cement [6] and high concentration of chlorides in the raw material of cement will possibly lead to rotary kiln shutdown [4]. As to erosion, the effect of different chlorides is different [7]-[8]. WCCB system decreases the chlorides in fly ash by utilizing two characteristics of chlorides. One is to get rid of the soluble chlorides, and the other is to let the heat-unstable chlorides away.

Raw fly ash (RFA) from the boilers of municipal solid waste incinerators (MSWIs) is a kind of fly ash, and the fly ash collected from the bag filter are strongly connected with RFA. In our previous research, we have explained the chlorides distribution in RFA by combining X-ray absorption near edge structure (XANES) with X-ray diffraction

(XRD) [9]. However, we did not explain the chlorides distribution in the washed residue of RFA, that is we did not know the change of each kind of chlorides during the washing process so that it is difficult for us to determine the washing condition we chose is suitable or not. Some researchers have identified NaCl, KCl and $CaCl_2$ in the fly ash by XRD, or deduced the percentage of soluble chlorides by washing experiment [10]-[13], however, they did not specify the molar contribution of each chloride to all the chlorides, and there are few researches about the chlorides distribution in the washed fly ash residue [10]-[13].

In this paper in order to discuss the chlorides behavior in RFA washing process, we conducted washing experiments under relatively acceptable conditions to obtain the residual samples [1]. We used X-ray near edge structure (XANES) and XRD to analyze chloride speciation in residue from RFA washing experiments. Consistent with previous studies, we verified the existence of some chlorides by XRD. XANES and linear combination fitting (LCF) methods were also used to identify other chlorides and to perform corresponding chloride speciation analysis.

2 Experimental Material and Methods

2.1 Experimental Material

RFA from the boiler and gas quenching tower of a continuous stoker-type MSWI was used. The composition of the RFA was examined by X-ray fluorescence (XRF-1700, Shimadzu Corp., Kyoto, Japan), inductively coupled plasma-atomic emission spectrometry (ICP-AES; IRIS Intrepid; Optronics Co., Ltd., Tokyo, Japan) and ion chromatography (DX-AQ AI-450; Nippon Dionex KK, Tokyo, Japan), which is for checking chlorine concentration in the samples and JIS A 1154 (JCI SC4) was used as the pre-treatment method for those samples. Aluminum, sodium, potassium, copper,

lead, and chromium were analyzed by ICP-AES. The corresponding data of each RFA is shown in Table 1.

2.1.1 Samples from washing experiments

Single- and double-washing experiments were performed [1]. Samples from washing experiments are listed in Table 2. In the primary single-washing experiments, we found that the liquid (ml)/solid (g) (L/S) ratio is more important to reduce chlorine content in the residue than mixing time and speed.   Therefore, we fixed the mixing time and speed and set the L/S ratio from 2 to 10 in single-washing experiments [1]. We found that when the L/S ratio is greater than 3, the chlorine content in the residue decreases slower; hence we chose the residue from the RFA-W-3# experiment for analysis. Residues from the RFA-W-6# and RFA-W-8# experiments were chosen for chloride analysis from samples with L/S > 3. To determine how washing frequency affects the washing process, we selected one residue from the double-washing experiment in which the washing solution was ion exchange water.   The samples were dried by heating to 105°C for 24 h. The washing solution from both steps of the double-washing process was dried to attain solid samples RFAT1 and RFAT2. RFAT1 was the dried solid of the washing solution from the first step and was similar to the washing solution of the RFA-W-3# experiment. RFAT2 was the dried solid of the washing solution from the second step. This detailed process is available as supplementary data (Fig. SI-1).

2.2 Methods and Apparatus

2.2.1 XRD.

XRD (RINT-Ultima+/PCQ2; Rigaku Corp., Tokyo, Japan) was used to confirm the existence of crystal chlorides in the RFA washed residues.   Information from the XRD

studies was then used for XANES data analysis.

2.2.2 XANES.

The XANES experiments were performed at a synchrotron radiation facility in Tsukuba, Japan (beam lines BL-9A and BL-11B at the Photon Factory) [14]-[16]. The energy range of chlorine checked is 2815~2855 eV. The spectral data were collected in Fluorescence Yield (FY) and Total Electron Yield (TEY) in BL11B and in Conversion Electron Yield (CEY) in BL-9A.

2.2.3 Linear Combination Fitting (LCF).

We used the commercial software REX 2000 ver. 2.3 (Rigaku Corp.) for LCF analysis [9]. The residual value (R) was calculated by Eq. (1) and used to evaluate the raw data from LCF analysis:

$$R = \frac{\sum \left(XANES_{Measured} - XANES_{Calculated} \right)^2}{\sum \left(XANES_{Measured} \right)^2} \tag{1}$$

2.2.4 Analysis procedure

We chose reference chlorides based upon elemental concentration, our previous studies, and information found in other reports [9], [13], [17], [18]. Based on the XRD spectra of samples and the relationships among the samples, we confirmed the existence of some chlorides in the residues ("A" group chlorides); the chlorides that were left formed the "B" group chlorides. We then fixed the "A" group chlorides and added one to three more chlorides from the "B" group for LCF analysis. The combination with the minimum R value was chosen. In previous studies, we successfully deduced the chloride chemical forms in RFA by combining data from XANES with XRD data [9],

which offered basic information for us to do this analysis and according to new condition we refined the chlorides for each group. This analysis procedure is just for the samples from washing experiments.

2.2.5 XANES spectra of the reference chlorides

In previous studies, we found that approximately 15% of the chlorine in RFA was in the form of NaCl, 10% was in the form of KCl, 51% was $CaCl_2$, and the remainder was in the form of Friedel's salt [9]. Hence, the following reference chlorides were included in this study: NaCl, KCl, $CaCl_2 \cdot 2H_2O$, $[Ca_2Al(OH)_6]Cl \cdot 2H_2O$, and $11CaO \cdot 7Al_2O_3 \cdot CaCl_2$. We used $CaCl_2 \cdot 2H_2O$ instead of $CaCl_2$ because $CaCl_2$ is hydroscopic and can easily form $CaCl_2 \cdot 2H_2O$ during the washing process. Although we heated the residue at 105°C for 24 h, in some sample calcium chloride hydrate could still be found [9]; here we use $CaCl_2 \cdot 2H_2O$ to represent the calcium chloride hydrates formed in the residues from washing experiments. $[Ca_2Al(OH)_6]Cl \cdot 2H_2O$ is also known as Friedel's salt, and $11CaO \cdot 7Al_2O_3 \cdot CaCl_2$ is one of the products formed when Friedel's salt is heated between 290 and 670°C [17]. Moreover, $11CaO \cdot 7Al_2O_3 \cdot CaCl_2$ can change into Friedel's salt when it is placed in water. For convenience, we use "F670" to represent $11CaO \cdot 7Al_2O_3 \cdot CaCl_2$ in this report. When Friedel's salt was heated at 105°C for 24 h, the structure of Friedel's salt changed because a strong peak could be observed around 2Θ=11.3°as detected by XRD, which is indicative of Friedel's salt; however, the compound could not be absolutely identified as Friedel's salt with a Figure of Merit (FOM) value of less than 10. Hence, F670 was also included in this study to represent that structure in some degree. In our previous research [9], we have included CaClOH in the analysis of RFA, however, the final result shows that concentration of CaClOH in RFA is too little to check out in XRD and CaClOH is easy to resolve into water, so in

this research, we did not include CaClOH. Figure 1 shows the Cl K-edge XANES spectra of the reference chlorides.

Friedel's salt and calcium chloroaluminate (F670) were made and analyzed by XRD [9], [17]; other reference chlorides were purchased from Nacalai Tesque (Kyoto, Japan), Soegawa Rikagaku (Tokyo, Japan), or Nichika Corporation (Kyoto, Japan).

3 Results and Discussions

3.1 Elemental concentration and residue mass percent in residues from RFA washing experiments.

The concentration of Cl, Ca, Na, K, Al, S, and Si and their corresponding mass percentages are shown in Table 3. The residue mass percent represents the ratio of the amount of remaining dried washed residue to the amount of RFA that was used in the washing experiments. Data shown in Table 3 suggest that double-washing does significantly change the chlorine content or the residue mass percent. The L/S ratio had less of an influence than washing frequency on the chlorine content and mass residue when the L/S ratio was larger than 6, because in the RFA-W-6# experiment, we used the same amount of water as in the double-washing process, and in the RFA-W-8# experiment, we used more water during double-washing. The chlorine concentrations in RFAT1 and RFAT2 were 1.66% and 0.511%, respectively.

3.2 XRD results

RFA-W-3#, RFA-W-6#, RFA-W-8#, RFA-W-II#, RFAT1, and RFAT2 were examined by XRD (Fig. 2), and RFA-W-3# was confirmed to contain NaCl and KCl. Because RFA-W-6# and RFA-W-8# comprise residues from single-washing, the presence of NaCl and KCl in RFAT1 suggests that NaCl and KCl must also exist in RFA-W-6# and

RFA-W-8#. Because RFAT2 is the dried solid of the washing solution from the second step of the double-washing experiment, NaCl and KCl should also be found in RFA-II#; however, the concentration of chlorine in RFA-W-II# is 0.961% so that chlorides can not be detected by XRD clearly. NaCl and KCl, therefore, were designated as "A" group chlorides for RFA-W-3#, RFA-W-6#, RFA-W-8#, and RFA-W-II#. The remaining chlorides were $CaCl_2 \cdot 2H_2O$, Friedel's salt, and F670.

3.3 Chlorine K-edge XANES spectra of samples

Figure 3 shows the chlorine K-edge XANES spectra of RFA-0# (RFA, labeled as RFA-0#), RFA-W-3#, RFA-W-6#, RFA-W-8#, RFA-W-II#, RFAT1, and RFAT2. The shapes of the spectra from the residues are similar, with a vale appearing after the first peak. The absorption threshold was ~2820 eV, and the photon energy of the atomic absorption jump was ~2826 eV. The spectrum of RFA-0# has more fine structures compared to RFA-W-3#, RFA-W-6#, RFA-W-8#, and RFA-W-II#, for example, in the big valley of RFA-0# spectrum, there is a small valley on the left, and after the big valley, there followed a small peak and a small valley and then a small peak, however, as to RFA-W-3#, RFA-W-6#, RFA-W-8# and RFA-W-II#, it is difficult to distinguish small valley in the first big valley and after the big valley there seems only a long peak. The continuous small short waves in the spectra especially in the spectrum of RFA-W-3# are noises. The differences between these individual samples are related to the overall curve characteristics. The spectrum of RFAT1 has many characteristics that are similar to the spectrum of $CaCl_2 \cdot 2H_2O$, which suggests that $CaCl_2 \cdot 2H_2O$ might also exist in residues from single-washing experiments. Although the spectrum of RFAT2 has some NaCl characteristics (e.g., a peak ~2837 eV), the shape of the spectrum of RFAT2 is most like that of $CaCl_2 \cdot 2H_2O$, suggesting that a portion of chlorine in RFAT2

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was in the $CaCl_2 \cdot 2H_2O$ form.

We next analyzed the chlorine K-edge XANES spectrum of RFA-W-3# and concluded that the "A" group chlorides in RFA-W-3# are NaCl and KCl and that the "B" group chlorides are $CaCl_2 \cdot 2H_2O$, Friedel's salt, and F670. Hence, we fixed NaCl and KCl and combined one more compound from the "B" group for LCF analysis. The results are shown in Table 4. Among mixtures (1) to (4), mixture (4) had the minimum R value, which suggested that F670 was possibly in RFA-W-3# among the "B" group chlorides. Next, we fixed NaCl, KCl, and F670 and added one more chloride to get combination (5). We then tried the combination of "NaCl + KCl + $CaCl_2 \cdot 2H_2O$ + Friedel's salt + F670" and the result was combination (6) (Table 4). Mixture (6) had the lowest R value of all the mixtures. The portion of chlorine in the insoluble chloride form in combination (4), combination (5), and combination (6) were 72%, 79%, and 44%, respectively. The remaining chlorine in RFA-W-8# was ~61% of the chlorine in RFA-W-3#, which suggests that the portion of chlorine in an insoluble chloride form in RFA-W-3# should be less than 61%. Therefore, combination (6) is the most reliable. Using similar analyses, the distributions of chloride in RFA-W-6#, RFA-W-8#, and RFA-W-II# were also obtained (Table 5). We included the distribution of chlorides in RFA-0#. It is clear that RFA-0# has higher mole percentage of soluble chlorides (NaCl, KCl, $CaCl_2$) and less mole percentage of Friedel's salt and F670 than the washed residue. And in fact, except NaCl, KCl and $CaCl_2$/ $CaCl_2 \cdot 2H_2O$, Friedel's salt and F670, the insoluble chlorides in this research, stand for all the other chlorides, which include not only chlorides that is difficult to dissolve into water under certain condition but also some very minor soluble chlorides in very low concentration that can not be detected by XRD or XANES.

Friedel's salt and F670 are regarded as insoluble chlorides. The proportion of insoluble

chlorides gradually increase with increasing L/S ratio or washing frequency, and the proportion of soluble chlorides such as NaCl, KCl, and $CaCl_2 \cdot 2H_2O$ decreases. The increasing value of R from RFA-0# to RFA-W-II# suggest that the insoluble chlorides may have changed during the washing process.

3.4 Chloride behavior in RFA washing experiments

Using results from LCF analysis of the residues shown in Table 5 and the chlorine content and residue mass percent from Table 3, the amount of chlorine in different chemical forms can be calculated. For example, Formula (2) can be used to calculate the amount of chlorine in the NaCl form (Cl_{NaCl}) that was left in the residues after 100 g of FA was washed under each condition:

$$Cl_{NaCl} = 100\,gram \times residue\% \times Cl\% \times m_{Cl,NaCl} \quad , \tag{2}$$

where *residue*% is the percentage of residue left after the RFA was washed and $m_{Cl,NaCl}$ is the molar percentage of chlorine in the NaCl form among all chlorides in the residue. Figure 4 shows the amount of chlorine in different chemical forms in the residues. Both the soluble and insoluble portions decreased, especially in residues from RFA-W-6#, RFA-W-8#, and RFA-W-II#. We included Friedel's salt and F670 together as "insoluble chloride"; Friedel's salt belongs to the AFm phases in the cement field [6]. These phases include Kuzel's salt ($3CaO \cdot Al_2O_3 \cdot 0.5CaCl_2 \cdot 0.5CaSO_4 \cdot 10H_2O$), sulfate AFm ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot nH_2O$), hydroxy AFm ($3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot nH_2O$), hemicarboaluminate ($3CaO \cdot Al_2O_3 \cdot 0.5Ca(OH)_2 \cdot 0.5CaCO_3 \cdot 10.5H_2O$), monocarboaluminate ($3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10H_2O$), stratlingite ($2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$), and U-phase ($4CaO \cdot 0.9Al_2O_3 \cdot 1.1SiO_2 \cdot 0.5Na_2O \cdot 16H_2O$) [6]. According to Glassers, Friedel's salt can easily change to Kuzel's salt or U-phase in the presence of Ca^{2+} and SO_4^{2-} or OH^- [6]. In other studies, at least 80% of insoluble chlorine (which was confirmed to be Friedel's salt by XRD) in bottom ash could be removed by

continuous washing [19] at pH 9 and in the presence of Ca^{2+} and SO_4^{2-}. The pH values of all washing solutions in our experiments were less than 10. We also examined the concentration of Ca^{2+} and SO_4^{2-} in RFAT1 and RFAT2. RFAT1 contained 3470 mg/l Ca^{2+} and 2260 mg/l SO_4^{2-}, and RFAT2 contained 1783 mg/l Ca^{2+} and 2500 mg/l SO_4^{2-}. Hence, Friedel's salt could have gradually changed into Kuzel's salt or U-phase. Double-washing was generally more effective in removing soluble chlorides than single-washing (Fig. 4). In the RFA-W-6# experiment, the same amount of water as in the RFA-W-II# experiment was used, but less soluble and insoluble chlorides remained in RFA-W-II# than in RFA-W-6#. Hence, some insoluble chlorides were washed out. Moreover, some chlorides in RFAT1 and RFAT2 must have come from the insoluble chlorides in RFA. This may be particularly true for chlorides in RFAT2 because reductions in the amount of chlorine from insoluble chlorides were largest from RFA-W-3# to RFA-W-II#. Nevertheless, the information above does not reveal the kinds of chlorides released by the insoluble chlorides in RFA or their proportional amounts. Therefore, we calculated the chloride distribution in RFAT1 and RFAT2 from the data given in Fig. 4; the chloride distributions are shown in Table 6. By comparing data in Table 6 with data in Table 5, we deduced that the chlorine released from insoluble chlorides should be NaCl or $CaCl_2 \cdot 2H_2O$, because the molar percentage of chlorine in KCl form in Table 5 is comparable to that data in Table 6.

Next, the concentration of Na^+, K^+ and Ca^{2+} in RFAT1 and RFAT2 was assessed. The molar amount of each element was calculated based on the concentration of each element per liter. The molar ratios of Na^+, K^+, and Ca^{2+} were calculated and are shown in Table 7. The Ca^{2+} increased in the second step of double-washing, and Na^+ and K^+ decreased in this step. In this research with limited condition, we speculate that most of the chlorides from insoluble chlorides were in the form of $CaCl_2$, which is in accordance

with our analyses. Taken together, we conclude that the washing process removes mostly $CaCl_2$ and in the second step of double-washing, the most of the released chlorides from insoluble chlorides might be $CaCl_2$.

3.5 Insoluble chlorides in RFA during washing experiments

Collectively, our results suggest that the insoluble chlorides might have changed during the washing process. Therefore, we used the chlorine K-edge XANES spectra of RFA-W-3# and RFAT1 to simulate RFA-0# and the chlorine K-edge XANES spectra of RFA-W-II# and RFAT2 to simulate RFA-W-3# (Fig. 5). That is to use RFA-W-3# and RFAT1 as the reference chlorides instead of NaCl, KCl, $CaCl_2$ or Friedel's salt to process the LCF analysis of chlorine K-edge XANES spectrum of RFA-0#. So does the simulation of chlorine K-edge XANES spectrum of RFA-W-3#. From the data shown in Fig. 4, we calculated the amount of chlorine move to RFAT1 and RFAT2 to determine the chlorine distribution between RFAT1 and RFA-W-3# and RFAT2 and RFA-W-II#. Relative to RFA-0#, 34% of the chlorine went to RFA-W-3# and 66% of the chlorine was derived from RFAT1. Relative to RFA-W-3#, 35% of the chlorine remained in RFA-II# and 65% of the chlorine went to RFAT2. In comparison with data shown in Fig. 5, the simulation of RFA-0# did not demonstrate a linear relationship among RFA-0#, RFA-W-3#, and RFAT1, while that of RFA-W-3# exhibited a linear relationship with RFA-W-3#, RFA-W-II#, and RFAT2. However, the R value of the simulation of RFA-W-3# with RFA-W-II# and RFAT2 was 0.072, and the R value of the LCF analysis of RFA-II# was 0.078 (Table 5), both of which are considered high. These results suggest that the insoluble chlorides changed in both the first and second steps of the double-washing procedure and that most of the released chlorides were $CaCl_2$, as we explained in the session of "Chloride behavior in RFA washing experiments". The chlorine content in RFAT1 and RFAT2 and the data from Table 6 were then used to

calculate the amount of chlorine released from insoluble chlorides: 0.216% in RFAT1 and 0.158% in RFAT2. In all, these analyses are consistent with the former measurements that indicate a decreased amount of chlorine in insoluble chlorides with increasing L/S ratios or washing frequencies.

4 Conclusions

The analysis of XANES spectra by LCF combined with XRD is effective for the determination of chloride behavior in RFA washing process. Our washing experiments further suggest that suitable combinations of chloride compounds in the washing residues of RFA. Furthermore, we found that it was reasonable to use Friedel's salt and its related compound as standards for the insoluble chlorides in RFA and its residues. The insoluble chlorides in RFA are complex and are strongly related to $CaCl_2$ or similar chloride compounds. They appear to change during the washing process, and this released chloride was mostly found in the $CaCl_2$ form. Double-washing was more effective than single-washing to reduce chlorides from RFA.

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Figure captions

Fig. 1 Chlorine K-edge XANES spectra of reference chlorides

Fig. 2 XRD results of samples from RFA washing experiments: a) XRD spectra of residues; b) XRD spectra of RFAT1 and RFAT2

Fig. 3 Chlorine K-edge XANES spectra of RFA washing samples: a) XANES spectra of residues; b) XANES spectra of RFAT1 and RFAT2

Fig. 4 Behavior of chlorine in different chemical form in washing residues of RFA

Fig. 5 Simulation result of RFA-0# and RFA-W-3#: a) Simulation result of RFA-0#; b) Simulation result of RFA-W-3#

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3   Fig. 1

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8   a)

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10   b)

11   Fig. 2

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14   a)   b)

15   Fig. 3

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17

18   Fig. 4
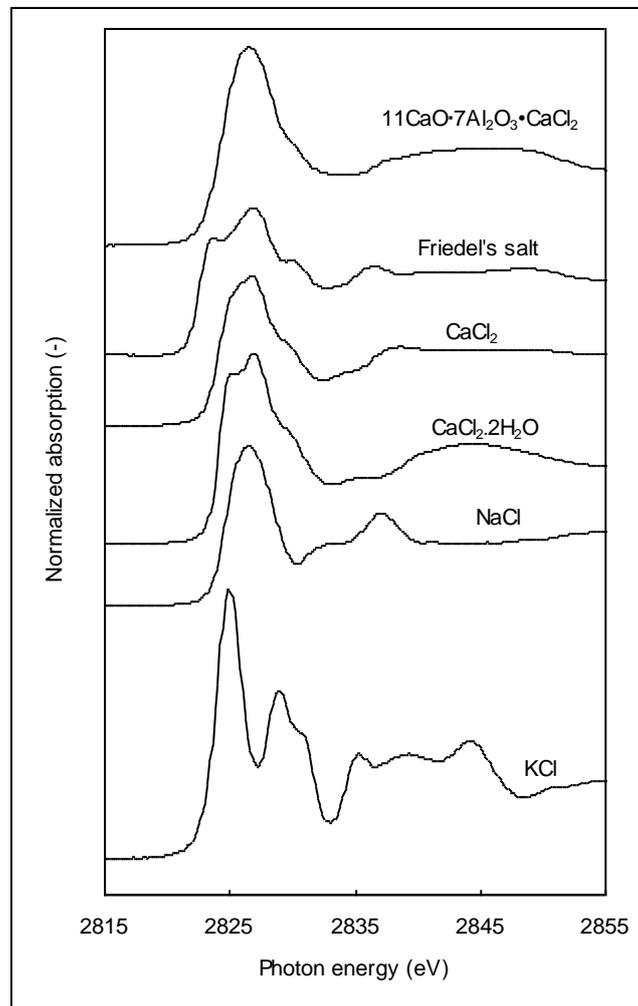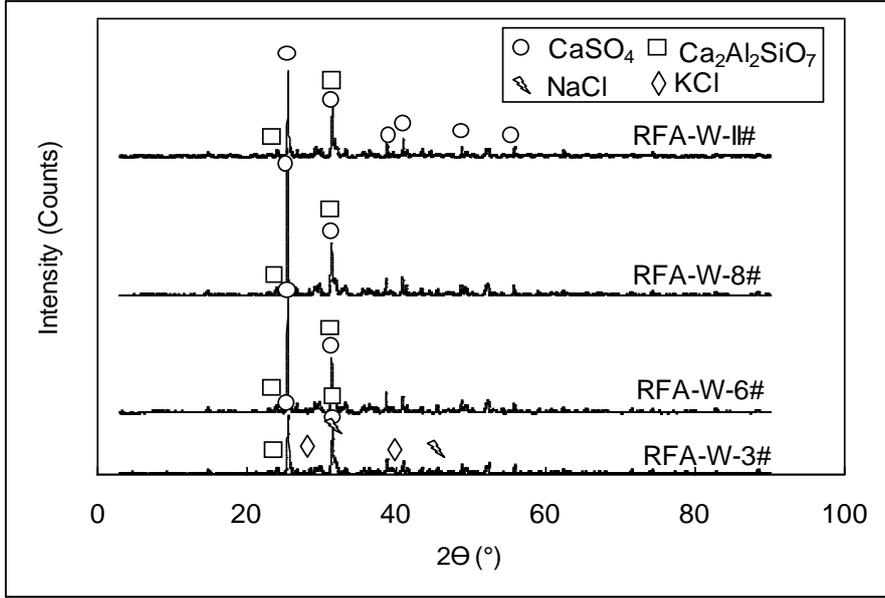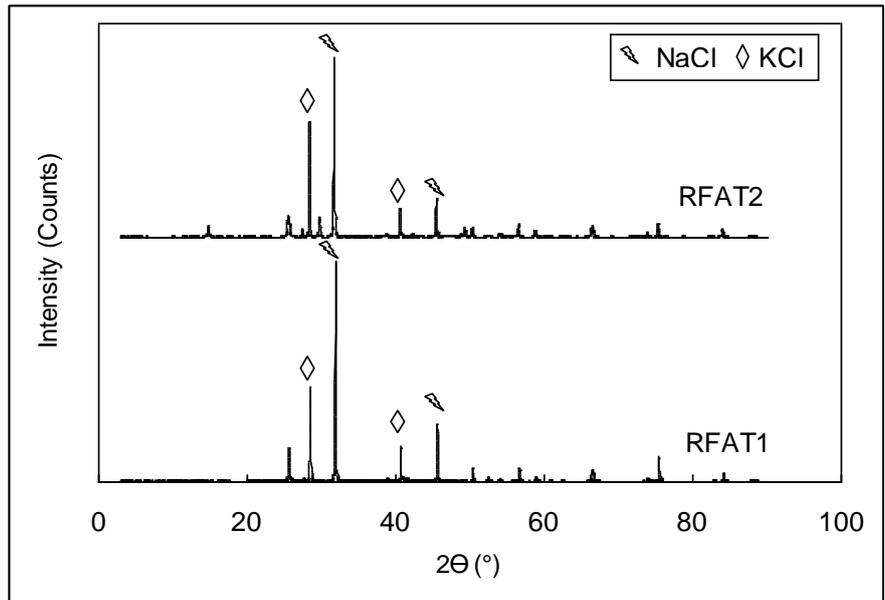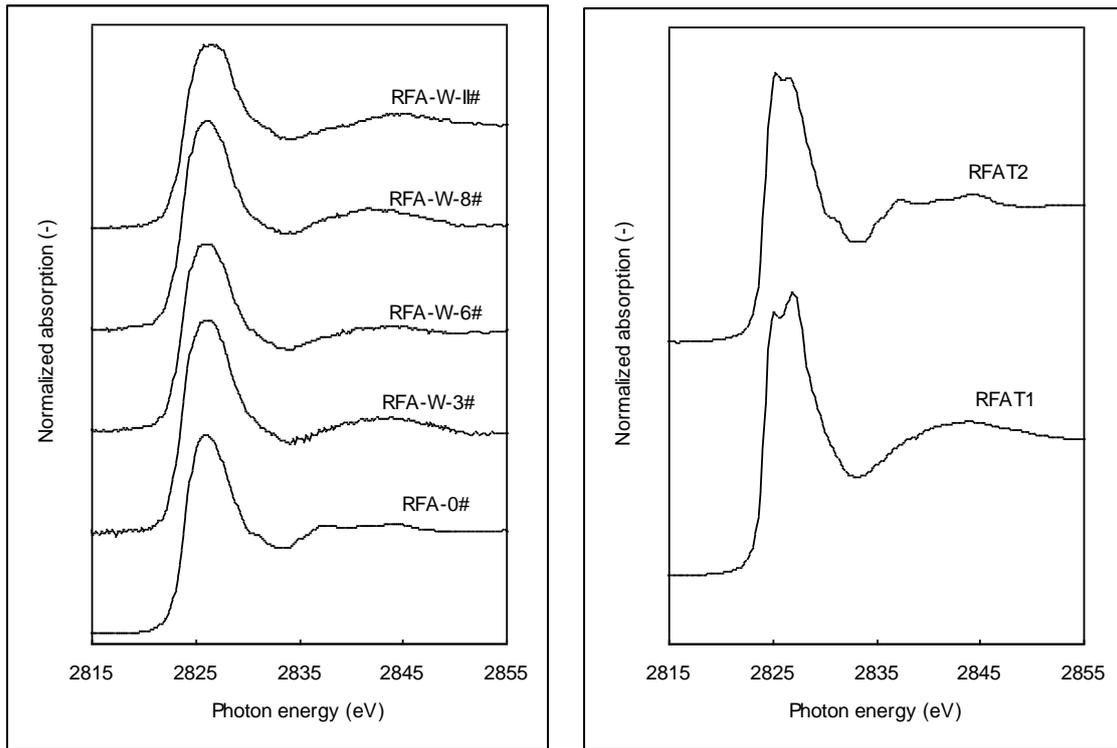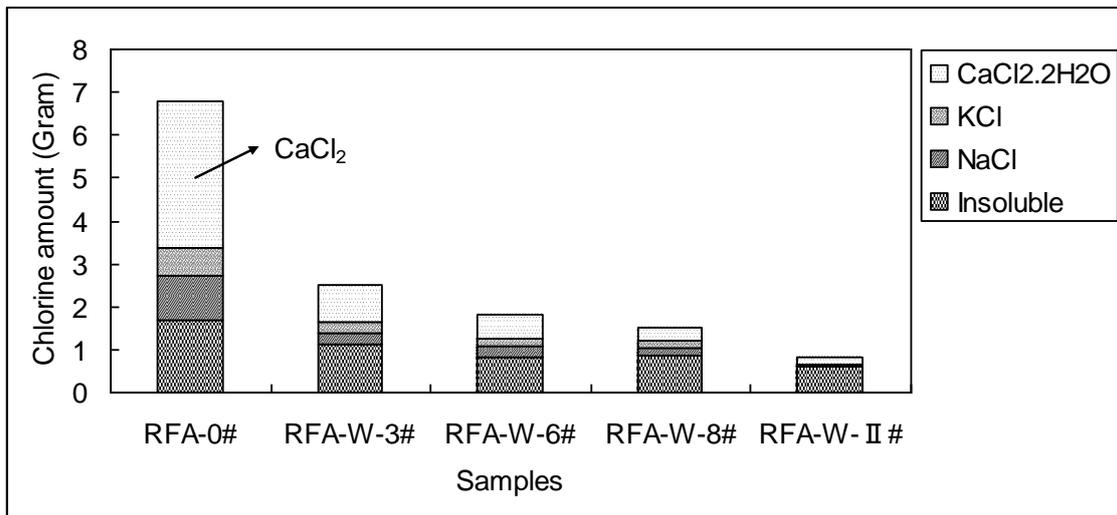
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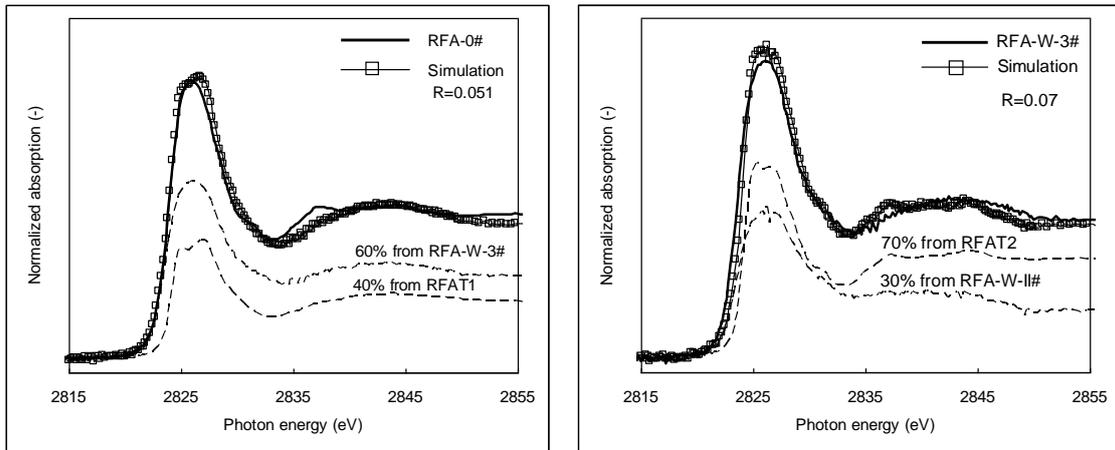
a)   b)

Fig. 5

Table 1 Element content of raw fly ash (%)

Element	RFA	Element	RFA	Element	RFA	Element	RFA
O	37.3	S	3.31	Na	2.13	Pb	0.387
Si	4.97	Br	0.111	Mg	1.12	Cu	0.238
C	3.24	P	0.666	Al	3.11	Zn	0.223
Cl	6.81	K	2.25	Ca	24.7	Fe	2.32

Table 2 samples from washing experiments [1]

code	Washing experiment		L/S ratio	Mixing time	Mixing speed
W-3#			3	5 min	150 rpm
W-6#	Single-washing		6	5 min	150 rpm
W-8#			10	5 min	150 rpm
W-II#	Double-washing	1 step	3	5 min	150 rpm
		2 step	3	10 min	150 rpm

28   Table 3 Concentration of some elements in the RFA washing residues and residue mass percent

29   (weight %)

samples	Cl	Ca	Na	K	Al	S	Si	Residue mass percent
RFA-W-3#	2.81	25.1	0.844	1.28	3.36	3.76	5.31	89.2
RFA-W-6#	2.11	24.5	0.831	1.29	3.39	3.88	5.22	87.0
RFA-W-8#	1.76	24.2	0.807	1.23	3.49	3.94	5.38	86.1
RFA-W-II#	0.961	24.5	0.682	1.02	3.71	3.86	5.62	84.8

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31   Table 4 LCF analysis results of RFA-W-3# (molar %)

	NaCl	KCl	$CaCl_2 \cdot 2H_2O$	Friedel	F670	R
(1)	58	42				0.143
(2)	23	21	56			0.091
(3)	29	19		52		0.083
(4)	5	23			72	0.076
(5)	6	15		33	46	0.049
(6)	12	11	33	38	6	0.043

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33   Table 5 LCF analysis results of RFA-0#, RFA-W-3#, RFA-W-6#, RFA-W-8#, RFA-W-II#,

34   RFAT1 and RFAT2 (molar %)

Samples	NaCl	KCl	$CaCl_2$	$CaCl_2 \cdot 2H_2O$	Friedel	F670	R
RFA-0#	15	10	51		25		0.046
RFA-W-3#	12	11		33	38	6	0.043
RFA-W-6#	13	9		32	45	1	0.052
RFA-W-8#	11	11		20	42	16	0.052

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RFA-W-II#	6	3		19	40	33	0.078
RFAT1	25	6		69			0.057
RFAT2	30	10		60			0.069

Table 6 Chlorides distribution in RFAT1 and RFAT2 deduced from the Figure 4 (molar %)

Samples	NaCl	KCl	$CaCl_2 \cdot 2H_2O$	Chlorine from insoluble chlorides
RFAT1	17	9	61	13
RFAT2	14	15	40	31

Table 7 Concentration and molar ratio of Na^+, K^+ and Ca^{2+} in RFAT1 and RFAT2

Samples		Na^+	K^+	Ca^{2+}
RFAT1	Concentration (mg/l)	4140	3750	3470
	Molar ratio (%)	49.6	26.5	23.9
RFAT2	Concentration (mg/l)	1550	1370	1780
	Molar ratio (%)	45.8	23.9	30.3

Supporting information
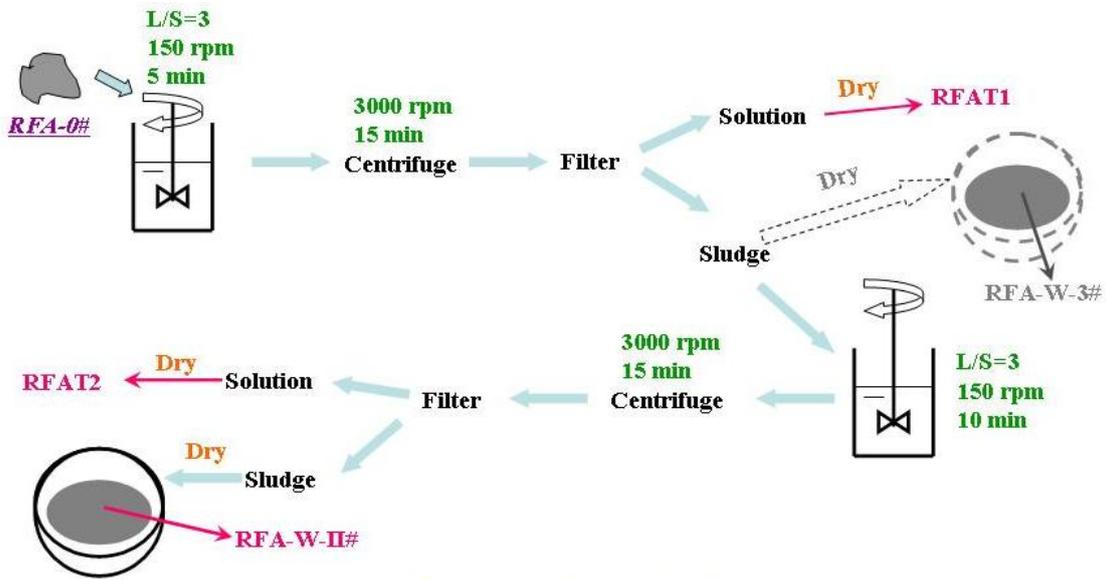
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51   Fig. SI-1 Washing process of double-washing experiment

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