Abstract: The high chloride content of municipal solid waste incineration (MSWI) fly ash and hazardous waste incineration (HWI) fly ash has considerably affected their disposal. This study focused on investigating the three-stage counter-current (TSC) water-washing process to reduce the chlorine content efficiently under the premise of low water consumption. The liquid–solid ratio (LSR) and washing time were investigated, a chloride migration model was established, and the characteristics of the water-washing solution (WWS) and washed fly ash were investigated. The results showed that the dechlorination effect of TSC washing could reach more than 99% in a low liquid–solid ratio (LSR) of 2–4 kg/L. The most appropriate LSR and washing time were found to be around 3:1 L/kg and 15 min per stage, respectively. The concentration of Cl⁻ in WWS reached over 90 g/L, which is very high among industrial saline wastewater. Some heavy metals were also contained in the WWS, and lead was the main heavy metal, followed by zinc, copper, and arsenic. The concentration of WWS of different stages was calculated by a model, and the transfer characteristic of chloride was strongly related to the mass balance between the liquid contained in the solid–liquid separation residue (SR) and the separated liquid. After washing, due to the dissolution of soluble salt, the specific surface area of fly ash increased, and thus the absorption ability of the washed fly ash was greater than the raw one. This study provides a washing condition reference for highly chlorinated fly ash, the basic data of WWS, and the chloride migration model that is a preliminary calculation method to improve the water-washing process.

Keywords: municipal solid waste incineration fly ash; hazardous waste incineration fly ash; water washing; chlorine salt; dechlorination; desalination; heavy metal

1. Introduction

In China, incineration disposal of municipal solid waste (MSW) and hazardous waste (HW) develops rapidly due to the advantages of volume reduction and energy recovery [1,2], and an increasing amount of fly ash is produced by MSWI and HWI, accounting for approximately 3%–10% of the total incineration waste [3]. According to estimates, in China, the amount of MSWI fly ash generated in 2019 was approximately 7.91 million tons out of a total of 121.74 million tons of MSWI, and the amount of HWI fly ash generated in China was 0.42 million tons out of 6.49 million tons of HWI [4,5]. Most fly ash contains chlorine salts, heavy metals, dioxins, and other pollutants, and is difficult to dispose of [6,7]. Landfill is the main disposal method of fly ash, which is simple but has serious shortcomings, such as covering large areas, high environmental risks, and wasting the resource contained in the fly ash, and is being gradually eliminated [8,9]. Meanwhile,
resource utilization measures such as asphalt solidification and cement solidification are developing rapidly in recent years [3].

There are two main kinds of MSW incinerators in China: fluidized bed (FB) incinerators and grate-furnace (GF) incinerators. The chlorine content in the fly ash of the GF incinerator is much higher than that of the FB incinerator, reaching 19%–32% [10,11]. The chlorine content of HWI fly ash depends on the fuel characteristics, and the chlorine content of some fly ash reaches more than 30% [12]. Due to the high chlorine content in fly ash, many treatment methods are difficult to directly implement. For example, landfill volume is limited due to the soluble chlorine salt, the solidification effect of chelating agent geopolymers or calcium carbonate oligomers are negatively affected, and the proportion of the fly ash as a cement additive is limited because chlorine salt in fly ash complicates the resource-based production process, aggravates the corrosion of equipment, and reduces the product quality, providing convenient conditions for the production of dioxin [6,10,13–16]. Therefore, it is imperative to adopt a dechlorination process.

Fly ash can be dechlorinated through acid treatment, alkali treatment, thermal treatment, and water-washing, etc. [17,18]. Acid can dissolve 90% of the substances in fly ash, including the majority of heavy metals, and heavy metals can be recycled from waste liquid through electrochemical methods [19–21]. Alkali washing can solidify heavy metals in fly ash and retain nearly 100% of the calcium [22,23]. However, acid and alkali treatments consume a lot of reagents and increase the cost of waste liquid disposal. As a result, these methods are not suitable for large-scale industrial applications without a combined process such as the recovery of heavy metals. Thermal treatment is an effective method to detoxicate MSWI fly ash, but the development of this method is limited by its high energy cost [24]. Recently, a new thermal dechlorination method using molten salts such as NaCl-CaCl₂ was proposed [25,26]. In this process, not only were organic pollutants decomposed, but the heavy metals were also stabilized. However, a great amount of waste salt was generated, which has a greater impact on the environment than WWS. Compared with other methods, water washing is an effective, simple, low-cost, and relatively mature process; in addition, sodium chloride, potassium chloride, and other resources can be extracted from the WWS. Therefore, an increasing number of water-washing production lines are being built and put into operation in China.

The research of T. Mangialardi, et al. [27] was one of the earliest that proved water washing is an effective method to remove chloride and improve the resource utilization characteristics of MSWI fly ash. Recent studies have further proved its feasibility and effectiveness, but the disposal of WWS has not received sufficient attention [20,28,29]. In the past few years, direct evaporation of WWS has produced a large amount of waste salt, which has caused environmental risks. Today, the resource utilization technology for WWS is developing, but costs a large amount of energy, especially when adopting a high liquid–solid ratio (LSR), producing a large volume of WWS [30]. To achieve a better dechlorination effect under a low LSR, a multistage counter-current water-washing process has been proposed, and chlorine salts, including sodium chloride and potassium chloride, can be distracted from WWS by evaporation [31]. TSC water washing is developing in China, but most research has not focused on reducing the LSR, and thus most experimental data cannot be directly applied to practical engineering [32–34]. Moreover, research on the physical and chemical properties of the WWS produced under TSC water washing is insufficient, the complex components contained in the WWS are not clear, and the study of the relationship between washing conditions and the composition of the WWS is inadequate. Therefore, the existing water-washing research cannot guide practical engineering. Furthermore, there exists no chloride migration model describing the chloride-transfer mechanism, and when changing the washing condition, it is not possible to estimate the change of main components in WWS. Therefore, to optimize the washing condition, establishing a chloride transfer model is helpful to reduce the experimental workload.
Existing research often focuses on the effect of dechlorination or heavy metal removal, and the disposal of WWS has not been studied sufficiently. The more WWS is produced, the more complex its composition is, and the higher the disposal cost will be. TSC water washing can guarantee an acceptable dechlorination effect under a lower LSR, and is developing quickly in China. The main purpose of this research was to explore the best washing condition for high-chlorine fly ash under TSC water washing, the detailed physical and chemical properties of WWS, and the chloride migration model. The dechlorination effects of single-stage, two-stage, and TSC washing were compared, and the best conditions were obtained. The physical and chemical characteristics of the WWS were given, and the model of chloride transfer in TSC water washing was established. The relationship between the concentration of WWS of all stages and the total mass loss of fly ash under the common LSR was preliminarily explored. The characteristics of fly ash before and after water washing were studied, which provides a reference for the subsequent disposal of fly ash.

2. Materials and Methods

2.1. Materials

Fly ash α (FA α) was taken from the baghouse filter of a rotary hazard waste kiln incinerator in Quzhou, Zhejiang province; fly ash β (FA β) was taken from the baghouse filter of a GF MSW incinerator in Ningbo, Zhejiang province. The X-ray fluorescence equipment (XRF) results of the fly ash are listed in Table 1, and the X-ray diffraction analysis (XRD) pattern of FA α is shown in Figure 1. The fly ash samples were dried in an oven at 105 °C for 24 h before the experiment, and the water content of FA α and FA β was 2.1% and 1.6%, respectively. All the chemicals employed deionized water (DW) and were of analytical grade (Sinopharm Chemical Reagent, China).

Table 1. XRF results of raw fly ash.

<table>
<thead>
<tr>
<th>No.</th>
<th>Element</th>
<th>Raw FA α</th>
<th>Raw FA β</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ca</td>
<td>32.06</td>
<td>22.83</td>
</tr>
<tr>
<td>2</td>
<td>Cl</td>
<td>30.26</td>
<td>28.58</td>
</tr>
<tr>
<td>3</td>
<td>Na</td>
<td>8.02</td>
<td>5.87</td>
</tr>
<tr>
<td>4</td>
<td>K</td>
<td>5.33</td>
<td>4.18</td>
</tr>
<tr>
<td>5</td>
<td>S</td>
<td>2.34</td>
<td>1.83</td>
</tr>
<tr>
<td>6</td>
<td>Si</td>
<td>1.27</td>
<td>1.27</td>
</tr>
<tr>
<td>7</td>
<td>Mg</td>
<td>0.76</td>
<td>0.77</td>
</tr>
<tr>
<td>8</td>
<td>Al</td>
<td>0.59</td>
<td>0.34</td>
</tr>
<tr>
<td>9</td>
<td>Zn</td>
<td>0.85</td>
<td>0.56</td>
</tr>
<tr>
<td>10</td>
<td>Fe</td>
<td>0.56</td>
<td>0.35</td>
</tr>
<tr>
<td>11</td>
<td>Ti</td>
<td>0.104</td>
<td>0.101</td>
</tr>
<tr>
<td>12</td>
<td>Pb</td>
<td>0.130</td>
<td>0.046</td>
</tr>
</tbody>
</table>
The chlorine in MSWI fly ash mainly comes from polyvinyl chloride (PVC) plastic and kitchen waste, and the organic chlorine in the PVC material decomposes to form hydrogen chloride gas under 300 °C and is absorbed by alkaline substances injected into the air pollution control (APC) system [35]. The chlorine in kitchen waste mainly exists in the form of chlorine salt [36]. During the combustion process, the chlorine salt forms fine particles, which are discharged from the furnace with the flue gas and captured by the APC system. The source of chlorine in HWI fly ash depends on the incinerated hazard waste. The chlorine contained in this sample mainly comes from Chlor-alkali plants, medical waste, and other industrial waste. Table 1 shows that the chlorine content of FA $\alpha$ and FA $\beta$ was 30.26% and 28.58%, respectively, and the composition of other elements was also similar.

2.2. Experimental Procedures

The circulating procedure of TSC water washing and its experimental procedure are shown in Figure 2. In the circulating procedure, the third-stage fly ash was washed with water, the second-stage fly ash was washed with the second-stage WWS, and the raw ash was washed with the first-stage WWS, that is, the high-chlorine ash was washed in the solution with a high concentration and the low-chlorine ash was washed in the solution with a low concentration. Five-step washing was employed to simulate the circulating procedure. As shown in Figure 2, in the simulating process, fly ash was washed with DW in Step 1, and the liquid used to wash was gradually changed to the solution obtained by solid–liquid separation in the corresponding stage of the formal step. Twenty g of fly ash was taken in each step, and the DW or the liquid obtained by solid–liquid separation in previous step was taken as the feed solution. All the washing solution was heated in the water bath to 25 °C before use, and temperature of the mixture was maintained at 25 °C during the washing process. Figure 3 shows the experimental devices. The mixing process was realized through a magnetic stirrer, and the solid–liquid separation device is a vacuum suction filter. After vacuum suction filtration, the obtained washing residue was dried at 105 °C to obtain dry washed fly ash. The soluble chloride content of washed fly ash was calculated through Cl$^-\,$ concentration of the leaching solution. The leaching process was taken by a horizontal oscillator to vibrate for 8 h and stand for 16 h under the condition of 110 ± 10 times/min and 40 mm amplitude, the ambient temperature is 25 ± 3 °C, and the liquid–solid ratio of DW and fly ash was 100:1 mL/g. To confirm the reliability of the experimental design, the concentration of Cl$^-\,$ of WWS obtained in different steps is
shown in Figure 4. It can be seen that after step 3, the concentration of Cl\(^-\) became stable and the concentration of WWS in step 4 was almost the same as that in step 5. Therefore, the WWS obtained in step 5 could be considered similar to the WWS obtained in circulating conditions.

Figure 2. Circulating procedure and experimental procedure: (a) circulating procedure; (b) experimental procedure.

Figure 3. Experimental devices.
A washing condition experiment was conducted to study the dechlorination effect and the characteristics of WWS. According to previous studies, the influence degree of LSR, temperature, stirring speed, and washing time on the dechlorane effect is as follows: LSR > washing time > temperature > stirring speed [37]. Additionally, in previous studies, LSR was usually greater than five, and washing time was usually longer than that taken in engineering [38–40]. To be closer to the practical washing condition, in the washing condition experiment, the LSR and washing time was similar to the value adopted in engineering practice, and the orthogonal experiment with an LSR of 2–4 and washing time of 5–30 min was adopted. To study the influence of washing time, a washing time experiment was carried out to study the dechlorination effect with a washing time ranging from 5 min to 5 h, and the LSR was 3 L/kg. FA β was washed as a supplementary experiment mainly to research the characteristic of raw and washed fly ash coupled with the properties of the WWS. The washing experiment conditions of the experiments are listed in Table 2. All the experiments in this paper were repeated three times, and the average of the three measured values was taken as the experimental result.

Table 2. Washing experiment condition.

<table>
<thead>
<tr>
<th>Fly Ash</th>
<th>Experiment</th>
<th>Stirring Rate r/min</th>
<th>Temperature °C</th>
<th>LSR g/mL</th>
<th>Washing Time min</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA α</td>
<td>Washing Condition</td>
<td>500</td>
<td>25</td>
<td>2, 2.5, 3, 4</td>
<td>5, 10, 20, 30</td>
</tr>
<tr>
<td>FA α</td>
<td>Washing Time</td>
<td>500</td>
<td>25</td>
<td>3</td>
<td>5–300</td>
</tr>
<tr>
<td>FA β</td>
<td>Supplementary Experiment</td>
<td>500</td>
<td>25</td>
<td>3</td>
<td>20</td>
</tr>
</tbody>
</table>
2.3. Analytical Methods

The specific surface area and pore size distribution were determined by an Autosorb-1-Surface area analyzer (TriStar II 3020 V1.01, Micromeritics, Atlanta, GA, USA). Grain size was measured using a laser diffraction particle size analyzer (Beckman Coulter LS13320, Los Angeles, CA, USA). The chemical composition of raw and washed fly ash was analyzed using XRF (Thermoscientific ARL ADVANT’X IntelliPowerTM 4200, Wilmington, DE, USA). The main crystalline phases of raw and washed fly ash were identified by XRD (X’Pert PRO PANalytical B.V., Almelo, Netherlands). The metal concentrations in WWS were measured by inductively coupled plasma combined with atomic emission spectrometry (ICP-AES, iCAP6300, Shanghai, China). Ionic liquid Chromatogram (IC) (792-BASIC, Herisau, Switzerland) was used for the determination of chlorides and sulfates in the leachate.

3. Results and Discussion

3.1. Main Components in WWS and the Influence of Different Washing Conditions

The mass fraction of soluble chlorine in washed fly ash should be less than 2%, and it is recommended to be less than 1% according to the Technical Specification for Pollution Control of Fly-ash from Municipal Solid Waste Incineration when the washed fly ash enters the cement kiln for collaborative disposal [41]. It also provides a reference for other ways to dispose washed fly ash. As is depicted in Figure 5, after washing, the content of soluble chlorine, potassium, and sodium in fly ash was greatly reduced, and the mass fraction of soluble chlorine was reduced to less than 2%, or less than 1% in some conditions. Increasing the LSR can reduce the soluble chlorine content and residual amount of fly ash, but considering the cost of disposing WWS, for fly ash with a chlorine content of about 30%, the suggested water-washing effect can be achieved when the LSR is 3 kg/L and the washing time is 15 min per stage.

![Figure 5. The mass fraction of soluble chlorine in washed fly ash.](image-url)
Y. Mao et al. [34] compared single, double, and triple water-washing processes and found that when LSR = 3 L/kg, the chlorine content was reduced from 9.4% to around 2.4%, 0.9%, and 0.6% in the three processes, respectively. As estimated based on the mass loss of 20%, the dechlorination effect was around 80%, 93%, and 95%, respectively. Compared with TSC washing, washing twice or three times did not show obvious advantages, but produced two- or three-times the volume of WWS. Y. Wang [42] studied the dechlorination effect of two-stage and TSC water-washing processes, and when LSR = 3 L/kg, the mass percentage of chlorine in fly ash was reduced to 20% and 8.1% in the two processes, respectively, and the dechlorination effect was around 87% and 95%, respectively. This reveals that two-stage counter-current water washing did not show a great dechlorination effect when LSR = 3 L/kg, and TSC water washing is the suggested dechlorination method for high chlorine waste incineration fly ash.

It is worth noting that within 5–30 min, the chlorine content of washed fly ash decreased at first and then increased with the extension of washing time. This phenomenon is also shown in Figure 6. Prolonging the washing time when LSR = 3 L/kg, it could be found that the best washing time was 10–15 min, and with the further increase of washing time, the dechlorination effect decreased, which is consistent with the results of another study [43]. After the washing time reached about 2 h, the concentration of Cl$^-$ became stable and close to the best dechlorination effect again. The changing trend of concentrations of K$^+$ and Na$^+$ is the same as that of Cl$^-$. This phenomenon might be caused by calcium sulfate precipitation.

In the experiment, we found that calcium sulfate precipitation continuously formed in WWS. Equation (1) reflects the generation process of precipitation, and Figure 7 is the XRD diagram of precipitation. We noticed that some sodium chloride was detected in the precipitation. Accordingly, the changing trend of Cl$^-$ in WWS could be explained by the fact that, at the same time as soluble salt dissolution during the washing process, calcium sulfate precipitation continued to form. On the one hand, some chlorine salts were adsorbed on the surface of precipitation; on the other hand, the quality of the filter residue
increased, which increased the liquid volume contented in the filter residue. It might be inferred that with time, calcium sulfate crystals would continue to grow, the specific surface area would decrease, and the absorption ability would decrease, making the adsorbed chloride re-dissolve into WWS. With the further extension of washing time, the adsorption process would reach equilibrium, the ion concentration would stop changing, and the Cl\(^-\) concentration would be close to the best dechlorination effect. Therefore, washing time should be controlled within 45–60 min, in total, of the whole process [42].

\[ \text{SO}_4^{2-} + \text{Ca}^{2+} \rightarrow \text{CaSO}_4 \]  

(1)

Figure 7. XRD diagram of precipitation.

The concentration of alkali metals, chlorine, and heavy metals under different washing conditions is shown in Table 3. The main components of the WWS were K\(^+\), Ca\(^{2+}\), Na\(^+\), and Cl\(^-\), and their concentrations decreased with the increase of LSR. There was a maximum value of the concentration for K\(^+\), Na\(^+\), and Cl\(^-\) when the washing time was between 5 min and 30 min. If the washing time exceeded the optimal value, the concentration decreased instead. It is noted that the fluctuation of the concentration of Ca\(^{2+}\) in WWS was less than that of K\(^+\), Na\(^+\), and Cl\(^-\). The wastewater that needs to be effectively disposed comes from various industries, such as residential and industrial wastewater containing 1.6–3.2 g/L sodium chloride, oilfield sewage containing 3.5 g/L sodium chloride, pharmaceutical wastewater containing 23 g/L sodium chloride, and potassium chloride, etc. [44–47]. The salt content of these wastewaters is mostly lower than 50 g/L. Therefore, the salt content of the WWS is at the top level in high-salinity wastewater, which is conducive to the recovery of chlorine salt by evaporation crystallization.

Table 3. The concentration of alkali metals, chlorine, and heavy metals under different washing conditions.

<table>
<thead>
<tr>
<th>LSR L/kg</th>
<th>Washing Time (min)</th>
<th>Main Ions g/L</th>
<th>Main Heavy Metals mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K(^+)</td>
<td>Ca(^{2+})</td>
</tr>
<tr>
<td>2:1</td>
<td>5</td>
<td>35.5</td>
<td>30.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>48.6</td>
<td>34.8</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>53.0</td>
<td>35.3</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>49.8</td>
<td>33.5</td>
</tr>
<tr>
<td>2.5:1</td>
<td>5</td>
<td>23.1</td>
<td>20.8</td>
</tr>
</tbody>
</table>
In general, the changing trend of heavy metal concentration in WWS was similar to that of main ions. Among the heavy metal elements, lead had the highest concentration, which poses a major difficulty for its subsequent disposal. Lead exists as a variety of hydroxyl complex ions under an alkaline aqueous solution, and there is a complex chemical equilibrium between various forms [48]. \( \text{PbOH}^+, \text{Pb(OH)}_2, \text{Pb(OH)}_3^-, \text{Pb}_2\text{OH}_3^+, \text{Pb}_4(\text{OH})_4^{4+}, \text{and Pb}_6(\text{OH})_8^{4+} \) are the main forms of \( \text{Pb} \) (II) in wastewater under alkaline conditions. When the pH value is 10.1–11.0, the minimum solubility of lead is 4.959 mg/L [49]. Beyond this value, the solubility of lead will increase. In past research, it has been estimated that the concentration of heavy metals decreases greatly when the pH of WWS decreases to below 8 [27]. The concentration of lead in this research was less than 0.6 mg/L. However, for WWS where the concentration of lead is much higher than that of other heavy metals, reducing the pH to below 8 would not be adequate, and heavy metals should be removed by adding a chelating agent, precipitant, or by other methods.

Among other heavy metals, barium is often ignored because barium ions and sulfate ions cannot coexist. However, in the newly prepared WWS, the concentration of barium was higher than that of zinc. With the extension of the storage time, the concentration of barium in the WWS prepared under the condition that \( \text{LSR} = 3 \text{ L/kg} \) and washing time was 20 min, the concentration of barium was 7 and 3 mg/L in the first two days after preparation and gradually dropped to less than 0.1 mg/L by the fifth day. Therefore, pre-standing for several days is an effective measure to remove barium. In addition to barium and lead, the WWS also contained a small number of heavy metal elements such as zinc, copper, and arsenic (a kind of metalloid but considered as a kind of heavy metal in broad sense). In addition to the five abovementioned elements, when \( \text{LSR} = 3 \text{ L/kg} \), the concentration of selenium was 0.015–0.03 mg/L, nickel was 0.008–0.02 mg/L, chromium was 0.008–0.012 mg/L, cadmium was 0–0.01 mg/L, and beryllium was 0–0.001 mg/L.

These heavy metal elements are often removed by precipitation with a chelating agent and carbonate precipitant, and the precipitation then re-enters the washed fly ash for collaborative solidification in subsequent steps. For the strongly alkaline WWS, introducing flue gas containing \( \text{CO}_2 \) into the WWS is also a feasible method, and its removal effect is limited by the content of alkaline substances contained in WWS. If \( \text{CO}_2 \)-containing flue gas is introduced during the washing processes, the concentration of calcium and heavy metals in the WWS would be greatly reduced. By controlling the \( \text{CO}_2 \) inlet rate, stirring rate, inlet time, and temperature, calcium sulfate and calcium carbonate can form coprecipitation to reduce carbon dioxide emission, the amount of precipitant, the calcium content in WWS, and pH [50,51]. Fly ash also contains insoluble chloride, and it is also harmful in fly ash disposal. Zhu et al. [52] analyzed the chemical form of chloride by X-ray absorption near-edge structure (XANES) and XRD, finding that insoluble chloride may exist in Friedel’s salt and other insoluble forms related to \( \text{CaCl}_2 \). Insoluble chlorine can be removed by acid pickling, but the cost is high and the waste solution produced...
contains a large number of heavy metals. Therefore, the key to the development of the insoluble chlorine removal method is to find a kind of low-cost and effective acid to dissolve the substances in fly ash and reduce the energy consumption when disposing the waste solution.

3.2. Chloride Transfer Model

To clearly understand the transfer mechanism of soluble salt in the TSC washing process, a chloride transfer model needs to be established. In establishing the model, the content of the solid–liquid separation residue (SR), moisture content of the SR, mass loss rate under different LSRs, and the respective proportions of K\(^+\), Ca\(^{2+}\), Na\(^+\), and Cl\(^-\) should be given. Limited by experimental conditions, the average moisture content of the SR after suction filtration was 53.7%, higher than a practical number. When R = 2:1, 2.5:1, 3:1, and 4:1, the average washing mass loss rate was 42.0%, 42.7%, 44.5%, and 45.7% respectively. The respective proportions of K\(^+\), Na\(^+\), and Cl\(^-\) were calculated in the concentration of each ion in the WWS obtained when the washing time was 20 min, and the proportion of Ca\(^{2+}\) was estimated as half of the concentration.

Table 4 shows the concentrations of K\(^+\), Ca\(^{2+}\), Na\(^+\), and Cl\(^-\) of TSC WWS when the washing time was 20 min. The first-stage dechlorination effect was calculated by the soluble chlorine residue of the SR, and the second and third-stage dechlorination effects were converted according to the chlorine concentration of the washing liquid.

\[
\text{DE}_n = \text{DE}_1 \cdot \frac{c_n}{c_1}
\]

where DE\(_n\) and DE\(_1\) represent the dechlorination effect of the \(n\)th stage and the first stage, respectively, and \(c_n\) and \(c_1\) are the concentrations of the \((n+1)\)th stage and the first stage.

When the LSR was 21, 2.5, and 3 L/kg, the concentration of the second-stage WWS and the third-stage WWS reached around 30% and 8% of the concentration of first-stage WWS, respectively; however, when LSR = 4 L/kg, it was only 18% and 4%, respectively, which proves that when the LSR was higher than 4, increasing the washing stage could not greatly improve washing effect. Therefore, TSC water washing is more suitable for those the conditions in which LSR < 4 L/kg.

Table 4. The main component in WWS obtained from different stages.

<table>
<thead>
<tr>
<th>Liquid Solid Ratio</th>
<th>Washing Stage</th>
<th>K(^+) g/L</th>
<th>Ca(^{2+}) g/L</th>
<th>Na(^+) g/L</th>
<th>Cl(^-) g/L</th>
<th>Dechlorination Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>1</td>
<td>53</td>
<td>35.3</td>
<td>55.6</td>
<td>160.4</td>
<td>97.5%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13.7</td>
<td>17.7</td>
<td>15.5</td>
<td>56.2</td>
<td>34.2%</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.3</td>
<td>7.0</td>
<td>4.1</td>
<td>16.4</td>
<td>10.0%</td>
</tr>
<tr>
<td>2.5:1</td>
<td>1</td>
<td>31.9</td>
<td>23.2</td>
<td>39.2</td>
<td>125.5</td>
<td>98.3%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9.5</td>
<td>13.3</td>
<td>10.8</td>
<td>39.5</td>
<td>30.9%</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.9</td>
<td>4.5</td>
<td>2.5</td>
<td>9.8</td>
<td>7.7%</td>
</tr>
<tr>
<td>3:1</td>
<td>1</td>
<td>26.2</td>
<td>22.0</td>
<td>32.0</td>
<td>94.7</td>
<td>99.0%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.8</td>
<td>11.3</td>
<td>7.7</td>
<td>30.5</td>
<td>28.9%</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.1</td>
<td>4.3</td>
<td>1.4</td>
<td>7.5</td>
<td>7.8%</td>
</tr>
<tr>
<td>4:1</td>
<td>1</td>
<td>19</td>
<td>17</td>
<td>22.3</td>
<td>69.8</td>
<td>99.3%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.6</td>
<td>4.0</td>
<td>3.3</td>
<td>12.7</td>
<td>18.1%</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.4</td>
<td>1.6</td>
<td>0.5</td>
<td>2.6</td>
<td>3.7%</td>
</tr>
</tbody>
</table>

The concentrations of KCl and NaCl in WWS were far from reaching their solubility in the first stage, but even after sufficient mixing, the second- and third-stage SR still contained certain potassium and sodium ions. The reason why the soluble salt could not be fully removed by single-stage washing is that the SR still contained a certain amount of
liquid that contains chlorine salt. In addition, the SR might have a certain adsorption effect on chlorine salt. The particle size analysis of the fly ash showed that the average particle size of the raw and the washed FA α was 42.82 μm and 16.85 μm, respectively. The destruction of the original structure after the dissolution of soluble salt caused a decrease in pore size and an increase in pore area [53]. The BET results showed that the specific surface area of the raw and the washed FA α was 4.30 m²/g and 13.67 m²/g, respectively, and the average pore diameter was 127.29 nm and 239.51 nm, respectively. The increase in specific surface area and pore size reflects that the adsorption ability of the fly ash increased after the dissolution of soluble salt. Therefore, the liquid concentration contained in the SR is higher than that of the washing solution produced by separation. According to the above-performed analysis, when the dissolving process was sufficiently carried out, the difference between the mass of the SR of the previous stage and the mass of the SR of the current stage was equal to the difference between the mass of the dissolved substances of the WWS after the separation of the previous stage and the WWS after the separation of the current stage. Therefore,

\[ m_0 - m_2 = c_1v_1 - c_2v_2 \]  \hspace{1cm} \text{(3)}

\[ m_2 - m_3 = c_2v_2 - c_3v_3 \]  \hspace{1cm} \text{(4)}

\[ m_3 - m_4 = c_3v_3 \]  \hspace{1cm} \text{(5)}

where \( m_0, m_1, m_2, \) and \( m_3 \) are the masses of the dry SR after the first stage of water washing and the masses of the dry SR before each stage of water-washing, respectively. \( c_0 \) and \( c_2 \) are the concentrations of the first-stage and the third-stage WWS, respectively, and \( V_0, V_1, \) and \( V_2 \) are the volumes of the first-, second-, and third-stage WWS respectively. After the first stage of washing, part of the liquid entered the SR, and the volume of the obtained WWS was

\[ v_1 = R \cdot m_1 - j \cdot m_2 \]  \hspace{1cm} \text{(6)}

where \( j \) is the moisture content of the filter cake. The SR was not dried in the second- and third-stage washing, so the liquid content of the wet SR was approximately unchanged before and after washing, and the volume of WWS was

\[ v_2 = v_3 = v_4 = R \cdot m_3 \]  \hspace{1cm} \text{(7)}

The salt content of the later stage WWS was equal to that in the SR, and the SR absorbed some salt,

\[ k \cdot m_2 \cdot j \cdot c_1 = c_2 \cdot R \cdot m_1 \]  \hspace{1cm} \text{(8)}

\[ k \cdot m_3 \cdot j \cdot c_2 = c_3 \cdot R \cdot m_2 \]  \hspace{1cm} \text{(9)}

where \( k \) is the salt content coefficient of the SR, which is related to the composition and quality of the SR, liquid phase concentration, and other factors. The results in Table 5 were obtained according to the experimental and calculated data. The actual concentration of the solution was calculated by the sum of the concentrations of K⁺, Ca²⁺, Na⁺, Cl⁻ and slightly soluble substances. The slightly soluble substances are represented by calcium sulfate and calcium hydroxide, and the concentration was about 4 g/L.

\[ c_a = c_K + c_{Ca} + c_{Na} + c_{Cl} + c_{SS} \]  \hspace{1cm} \text{(10)}

where \( c_a \) is the actual concentration of the solution, and \( c_K, c_{Ca}, c_{Na}, c_{Cl}, \) and \( c_{SS} \) are the concentrations of K⁺, Ca²⁺, Na⁺, Cl⁻, and slightly soluble substances, respectively. Simultaneous Equations (3)–(9) and the concentration of WWS at all levels when \( k = 1 \) and \( k = 2.5 \) can be calculated. The results are listed in Table 5.
Table 5 shows that when LSR was 2.5, 3, and 4 L/kg, the calculated data were consistent with the actual value when $k = 2.5$. The concentration of WWS at all stages can be calculated through the abovementioned equations, and the concentration of various main ions in WWS at all levels can be estimated according to the proportion of ions in WWS, which provides a reference for the follow-up study of washing characteristics at all stages and the improvement of the washing process.

In production line, the liquid used to wash the fly ash is mainly produced by evaporation process of WWS, and some clean water is added to the supply. To improve the process, industrial saline containing chloride can replace the clean water. On the one hand, industrial saline could be disposed; on the other hand, more salt could be produced. Then, Equation (5) should be changed as Equation (11), where $c_4$ and $v_4$ are the concentration and volume of the industrial saline, respectively. If the dechlorination effect was not ideal, clean water could be used as the washing liquid in stage 3 and the industrial saline could be additionally added in stage 1 and 2. Then, the Equations (3) and (4) should be replaced by Equations (12) and (13), where $c_{a2}$ and $c_{a3}$ are the concentrations of the industrial saline added in stage 1 and 2, respectively, and $v_{a2}$ and $v_{a3}$ are the volumes of these salines. Therefore, using the migration model, the workload in improving the washing process could be reduced.

$$\begin{align*}
m_3 - m_4 &= c_4v_3 - c_4v_4 \\
m_1 - m_2 &= c_1v_1 - c_2v_2 - c_{a2}v_{a2} \\
m_2 - m_3 &= c_2v_2 - c_3v_3 - c_{a3}v_{a3}
\end{align*}$$

Although this model successfully predicted the relationship between the concentrations of WWS at all stages and the desalting effect of such fly ash under the condition of TSC water washing, it is still limited in processing similar kinds of fly ash. For the convenience of calculation, the content of CaCl$_2$ was estimated based on the hypothesis that the calcium contained in CaCl$_2$ accounts for half of the total calcium, which is applicable to the situation that the lime injection amount in the APC system is moderate. The amount of slightly soluble substances was estimated according to the solubility, but, in fact, due to the complexity of fly ash and WWS components, this amount may fluctuate slightly. Therefore, when the composition of fly ash is quite different, the calculation process needs to be modified. The modification of the abovementioned calculation process and the calculation method of $k$ are the directions for further improvement of this model.
3.3. Elemental Composition of Fly Ash before and after Water-Washing

The main elements of the washed fly ashes were analyzed by XRF and the results are shown in Table 6. Calcium in raw fly ash accounts for more than 20% of the mass, which is related to the amount of quicklime or hydrated lime injected into a dry or semi-dry deacidification system [6,54]. The mass fraction of sodium is 5%–10% followed by potassium. Potassium is the most valuable element in fly ash which can be recycled as potassium chloride, and its mass fraction is about 5%. Sodium and potassium in fly ash mainly come from kitchen waste and biomass, and its content varies greatly with the composition of waste collected from different areas [36]. As the WSS is alkaline, it is not conducive to the dissolution of most heavy metals. Therefore, heavy metals still exist mainly in the washed fly ash. As high-temperature disposal methods such as cement rotary kiln co-processing and sintering can effectively reduce the environmental mobility of heavy metals, the leaching of heavy metals can be avoided by disposing washed fly ash through such methods, which have been developing rapidly in recent years.

Table 6. The XRF results of the main elements in different fly ashes.

<table>
<thead>
<tr>
<th>No.</th>
<th>1-1</th>
<th>1-2</th>
<th>1-3</th>
<th>1-4</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Washed FA α (LSR = 3:1 L/kg)</td>
<td>Washed FA β (LSR = 3:1 L/kg, t = 20 min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Washing Time (min)</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Ca</td>
<td>46.17</td>
<td>41.97</td>
<td>43.40</td>
<td>45.83</td>
<td>30.11</td>
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<tr>
<td>Cl</td>
<td>3.80</td>
<td>1.54</td>
<td>2.82</td>
<td>3.03</td>
<td>1.15</td>
</tr>
<tr>
<td>Na</td>
<td>0.89</td>
<td>0.49</td>
<td>0.69</td>
<td>0.91</td>
<td>0.50</td>
</tr>
<tr>
<td>K</td>
<td>0.58</td>
<td>0.32</td>
<td>0.42</td>
<td>0.68</td>
<td>0.24</td>
</tr>
<tr>
<td>S</td>
<td>4.21</td>
<td>3.54</td>
<td>4.24</td>
<td>4.40</td>
<td>2.56</td>
</tr>
<tr>
<td>Si</td>
<td>3.46</td>
<td>3.34</td>
<td>3.55</td>
<td>3.20</td>
<td>2.54</td>
</tr>
<tr>
<td>Mg</td>
<td>2.22</td>
<td>2.16</td>
<td>2.34</td>
<td>2.16</td>
<td>1.58</td>
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<tr>
<td>Al</td>
<td>1.09</td>
<td>1.08</td>
<td>1.18</td>
<td>1.06</td>
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<tr>
<td>Zn</td>
<td>1.53</td>
<td>1.56</td>
<td>1.57</td>
<td>1.54</td>
<td>0.93</td>
</tr>
<tr>
<td>Fe</td>
<td>1.08</td>
<td>1.16</td>
<td>1.15</td>
<td>0.98</td>
<td>0.64</td>
</tr>
<tr>
<td>Ti</td>
<td>0.328</td>
<td>0.323</td>
<td>0.341</td>
<td>0.285</td>
<td>0.185</td>
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<tr>
<td>Pb</td>
<td>0.252</td>
<td>0.283</td>
<td>0.262</td>
<td>0.284</td>
<td>0.096</td>
</tr>
</tbody>
</table>

4. Conclusions

In this paper, the TSC water-washing process was adopted to dispose of high-chloride-waste incineration fly ash, and the influence of different washing conditions, chloride transfer mechanisms, and dechlorination mechanisms were studied.

1. TSC water washing could achieve a dechlorination effect better than 99% for high-chlorine fly ash with a chlorine content of 30% in a low LSR and reduce the soluble chlorine to less than 1% in washed fly ash. Its dechlorination effect was 76% better than that of single-stage water washing and 21% better than that of two-stage counter-current water washing. The best washing effect could be achieved when LSR = 3:1 and t = 15 min.

2. The salt content of the WWS was at the top level in high-salinity wastewater. When LSR = 3 kg/L, the concentration of Cl\(^-\) in WWS reached 94 g/L, and the concentration of K\(^+\), Ca\(^2+\), and Na\(^+\) also reached 22–33 g/L. The concentration of lead in the WWS was the highest among heavy metals, followed by zinc, copper, and arsenic.

3. The chloride-transfer characteristic in the TSC water-washing process is strongly related to the liquid contained in the SR. By introducing the salt content coefficient of the SR, the concentration of WWS at all stages could be calculated through a model.
The model revealed that reducing the moisture content of the SR after suction filtration could improve the dechlorination effect. This model can guide the design of the fly ash washing process, but still needs further optimization.

4. The mass fraction of chlorine in the fly ash reached around 30%. The calcium content in fly ash mainly depends on the calcium oxide or calcium hydroxide injected in air pollution control process, reaching more than 20%. Potassium and sodium in fly ash mainly come from industrial waste, kitchen waste, or biomass, and the potassium content determines the value of the crystalline salt of the fly ash washing solution. After washing, the pore size and specific surface area of fly ashes increased and the adsorption capacity was promoted.

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

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