Molten hydroxide for detoxification of chlorine-containing waste: Unraveling chlorine retention efficiency and chlorine salt enrichment

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ABSTRACT
Hazardous waste dechlorination reduces the potential of creating dioxins during the incineration process. To investigate the salt effect on waste dechlorination, molten hydroxides with a low melting temperature were utilized for the pre-dechlorination and decomposition of chlorine-containing organic wastes (COWs) including trichlorobenzene (TCB), perchloroethylene, hexachlorobenzene and chlordane. The results showed that a eutectic mixture of caustic sodium and potassium hydroxides (41 wt.% NaOH and 59 wt.% KOH) led to a low melting point below 300°C and a relatively high chlorine retention efficiency (CRE) with TCB as a representative COWs. The amounts of hydroxides, reaction time, and temperature all had notable influence on CRE. When the mass ratio of hydroxides to TCB reached 30:1, approximately 98.1% of the TCB was destroyed within 2.5 hr at 300°C with CRE of 71.6%. According to the residue analysis, the shapes of reaction residues were irregular with particles becoming swollen and porous. The benzene ring and C–Cl bonds disappeared, while carboxyl groups formed in the residues. The stripped chlorine was retained and condensed to form chloride salts, and the relative abundance of the chloride ions associated with the mass of TCB in residues increased from 0 to 75.0% within the 2.5 hr reaction time. The observed concentration of dioxins in residues was 5.6 ngTEQ/kg. A reaction pathway and possible additional reactions that occur in this dechlorination system were proposed. Oxidizing agents may attack TCB and facilitate hydrogenation/dechlorination reactions, making this process a promising and environmentally friendly approach for chlorine-containing organic waste treatment.

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Introduction
Chlorine-containing organic wastes (COWs) such as pesticides are increasingly being used to control diseases and pests worldwide, with an estimated three-billion kilograms used in the world annually (Pimentel and Burgess, 2014). The illegal use and discharge of these pesticides has become a major concern in many countries, specifically with respect to their toxicity, persistence and bioaccumulation (Couto et al., 2013; Pecorini et al., 2016). Although many forms of these wastes (e.g., dichlorodiphenyltrichloroethane (DDT)) were already banned in the 1980s, they still persist in many countries and require appropriate treatment (Xu et al., 2013).
Incineration and cement rotary kiln co-processing are alternative techniques for treatment and disposal of COWs (Vermeulen et al., 2012; Zhao, 2017). Nevertheless, the high chlorine content in these organic wastes creates a substantial risk of generating dioxins, furan and toxic metal gases, which are invariably difficult and expensive to remove (Zhao, 2017). Moreover, organic waste rich in chlorine decreases the quality of cement produced in co-processing cement rotary kilns, creating a barrier to the widespread use of cement rotary kiln co-processing for contaminant stabilization (Malkow, 2004; Marias, 2003; Wang and Ni, 2014).

Many emerging non-incineration technologies have also been developed for the dechlorination and treatment of persistent pesticides. Heterogeneous catalytic processes designed to treat organic chlorinated compounds in the aqueous phase with a catalyst consisting of zero-valent iron (Orth and Gillham, 1996; Xiao et al., 2011), bimetal (Kim et al., 2008; Liu et al., 2017; Schrick et al., 2016), or noble metal (Crock et al., 2017; Nutt et al., 2005) are well known. However, the catalysts used for the dechlorination process can be inhibited by chloride ions generated during the reaction, leading to decreased process efficiency and an increase in regeneration obstacles (Xiao and Jiang, 2014). Mechanochemical (MC) destruction, a relatively new non-combustion technology based on high-energy ball milling, is another treatment method that effectively destroys various persistent organic pollutants (POPs)-containing waste and other halogenated organic compounds (Li et al., 2017; Sui et al., 2017). Unfortunately, this technology consumes large amounts of additives such as Calcium Oxide (CaO) and remains in the research stage (Nomura et al., 2005).

Molten salt (MS) comprises a single salt or mixture of multiple salts with a relatively low melting point, which has a variety of applications in many sectors and plays a crucial role in the areas of energy storage, environmental contaminant treatment and resource sustainability (Frangini and Masi, 2016). It has demonstrated multiple advantages in the destruction of organic waste: (1) acting as a stable medium for heat exchange and permitting fluctuation of the process parameters (Zhao et al., 2010); (2) being capable of dissolving substances like halogens, oxides, glass, and plastic; (3) retaining hazardous acidic gases (HCl, H2S, SO2, NO2, CO2) and preventing their discharge with process exhaust; (4) providing certain catalysts that optimize the underlying treatment reaction (Gat et al., 1993).

Molten carbonates (e.g., Na2CO3 and K2CO3), have been applied in dechlorination and contaminant destruction as a flameless thermal process (Yao et al., 2014). Many kinds of COWs containing toxic heavy metals and chlorine (including ion-exchange resins, chlorinated solvents, waste electrical components and plastics) have been successfully treated by molten carbonates (Adamson, 1998; Lin et al., 2018; Yao et al., 2011). Eutectic melting of Na2CO3 and K2CO3 at 650–750°C can dechlorinate and detoxify chlorine-containing pesticides and scrub out the acid gases (SO2, HCl) contained in the gas bubbles (Kovarik et al., 2015). The viscosity of this molten medium is higher than water, inhibiting the emission of gases and leading to a more complete reaction.

Oxygen is indispensable to provide the oxide species to degrade the organic compounds in this process. Upadhye (Upadhye and Wilder, 1994) found that waste rubbers can be disposed by MS process with the 20% excess air coefficient. Pandeti (Pandeti and Buckley, 2004) studied the incomplete combustion products (PICs) and kinetic model for the destruction of chlorobenzene (CBs) in different amounts of oxygen. CBs came into contact with molten Na2CO3 directly, and chloride was removed. However, the existence of PICs and CO is detrimental for this system, and no dioxin-like matters (PCDD/Fs) were found in the gases by Hsu et al. (1998).

High-temperature (usually 550–750°C) carbonate mixtures are energy intensive and costly (Flandinet et al., 2012; Yao et al., 2011). Thus, researchers have focused on lowering the eutectic point of molten salts (Raade and Padowitz, 2011). Mixed salts have a much lower melt temperature, for example NaOH–Na2CO3 and KOH–Na2CO3, with eutectic temperature of 300–500°C, which has been applied for the decomposition of polychlorobiphenyl (Takeda et al., 2008, 2012). Still, research on molten hydroxides has been limited, particularly regarding the treatment of chlorine-containing pesticides and analysis of residues after reactions.

In our previous study, hydroxide solution and molten hydroxide were used for dissolution of spherelite, lead, and zinc waste for the recovery of the useful components (Zhao and Stanforth, 2001; Zhang and Zhao, 2009; Zhao and Stanforth, 2000) and preparation of porous carbon materials (Dai et al., 2019). Herein, the aim of our work focused on the dechlorination efficiency of COWs with different mixing ratios of molten hydroxide. Influencing factors like reaction time and temperature were studied to optimize the dechlorination efficiency. The reaction residue characteristics were tested to obtain fundamental data for the underlying treatment process. Additionally, the dechlorination pathways and mechanisms of trichlorobenzene (TCB) in molten hydroxides were evaluated in greater detail.

1. Materials and methods

1.1. Chemicals and materials

All chemicals including TCB, Perchloroethylene, NaOH, and KOH were provided by Aladdin Industrial Corporation (China) in analytical grade and used without purification. Hexachlorobenzene and chlordane were purchased from Beijing Solarbio Science & Technology Co., Ltd., China. A uniform mixture of 41 wt.% NaOH and 59 wt.% KOH was prepared by fusion at 300°C and then crushing to obtain fine particles with a size less than 0.15 μm. The melting point of the hydroxide mixture was studied using differential scanning calorimetry (DSC) and thermogravimetry (TG) in N2 atmosphere (SDT Q600, TA Co., USA).

1.2. Dechlorination with molten hydroxide

The molten hydroxide dechlorination process was executed in a lab-scale furnace heated by electricity and controlled by a proportional–integral–derivative controller (PID) (Fig. 1). It mainly consists of a feeding hopper with air injection, a reaction vessel (inner diameter 4.0 cm, height 10 cm) made of Inconel 600 high temperature alloy, and an off-gas filter. The molten salt reaction is performed in the vessel and a
thermocouple is placed in the bottom of vessel to monitor the temperature of the molten salt. An alkaline solution and organic solvent were utilized for the adsorption of possible acid gases and incomplete combustion products.

The typical operation included the following steps: (1) the vessel was heated to the desired temperature through the temperature control system. At this time NaOH and KOH mixture were melted; (2) 2.0 g of TCB and air with a purity of 99.999% were introduced in the bottom of the vessel; (3) Molten hydroxide reacted with TCB; (4) Emitted gases were absorbed by the alkaline solution and n-hexane; (5) When the reaction was completed, the system was cooled to 50°C before opening the vessel; (6) Salt residues were replaced with new salts after reaction.

1.3. Sampling and analysis

Upon completion of the reaction, the mass loss was recorded according to the change in the total mass, and the mass loss ratio (MLR) was calculated via Eq. (1). Solid residue was then removed from the vessel and immediately well mixed. To determine the chlorine content, 4 g of the salt residues were removed and dissolved in 40 mL of deionized water, then further diluted to 100 mL before analyzing by ion chromatography (Dionex ICS-1100, Thermo Fisher Scientific Inc., USA). The Chlorine retention efficiency (CRE) was calculated using Eq. (2) based on the amount of chloride ion remaining in the residue.

\[
\text{MLR} = \frac{m_0 - m_t}{m_0} \times 100\%
\]

\[
\text{CRE} = \frac{m_t (\text{Cl})}{m_0 (\text{TCB}) \times \eta} \times 100\%
\]

where \(m_0\) (g) is the initial weight of TCB plus hydroxide mixture, \(m_t\) (g) is the weight of the residue after the reaction. \(m_0\) (TCB) is the weight of TCB, \(\eta\) is the weight percentage of chlorine in TCB with the value of 58.69%, \(m_t\) (Cl) is the chlorine content in the residues.

Four gram of the residues was selected and extracted for 60 min by n-hexane facilitated by ultrasonication. The TCB content and intermediate components were qualitatively and quantitatively analyzed by gas chromatography mass spectrometry (Shimadzu Q2010P, Japan). The dioxins (PCDD/Fs) in the residues were tested according to the US Environmental Protection Agency method 1613 (US Environmental Protection Agency, 1994). The concentrated samples were analyzed by means of high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS; Agilent 6890 N/EOL JMS-800D, USA) with a DB-5MS (60-m length × 0.25-mm ID × 0.25-μm film) column, using helium as the carrier gas (Zhan et al., 2016). The toxic equivalents (TEQ) were calculated using World Health Organization 2005 factors (Bhavsar et al., 2008).

1.4. Characterization of the residues

The morphologies and microstructures of the salt residues were characterized by a scanning electron microscopy/energy dispersive X-ray spectroscopy and mapping system (SEM, Inspect F, FEI Co., USA). The crystallinity was measured using X-ray diffraction (XRD, D8 Advance Sol-X, Bruker Co., USA). Chemical compositions were tested with X-ray photoelectron spectroscopy (XPS, Thermo Electron ESCALAB 250, USA).

2. Results and discussion

2.1. Hydroxide composition for treatment of TCB

The melting temperature is an important consideration for selection of molten salts. A lower melting temperature is generally preferred, so long as the mixture is capable of maintaining thermal stability and reducing the power consumption (Yao et al., 2011). In this process, a NaOH and KOH mixture was selected as the medium for the dechlorination and destruction process due to its low eutectic point and high viscosity (Table 1). The melting point of NaOH is (318 ± 5)°C and the eutectic point decreases with the addition of KOH. With a mole ratio of 0.5, the NaOH and KOH mixture has a relatively low eutectic point of (182 ± 8)°C. Meanwhile its viscosity is similar to that of crude oil, prolonging the dwell time of the TCB and enabling cracking of the long hydrocarbon chains (Stuhlfpfarrer et al., 2016).

A CRE comparison is presented in Fig. 2 with different ratios of NaOH and KOH at 300°C. It is important to note that NaOH or KOH alone have relatively high melting points. Thus, at 300°C, there was little to no melting, resulting in a low CRE. Solid particles could not participate in the dechlorination reaction and most of the TCB escaped. Only a small amount of TCB was decomposed as result of pyrolysis. With mole ratios of 0, 0.1 and 1.0, the TCB can be hardly dechlorinated by the hydroxide, with CRE of 10.18%, 20.37% and 5.34% respectively because of the partial melting condition. The melting of the hydroxide mixture is of primary importance in the dechlorination process, possibly due to the base-catalyzed decomposition, which was consistent with a former work (Xiao and Jiang, 2014). The mole ratio of 1:1 NaOH and KOH demonstrated the highest CRE of 68.96%, mostly attributed to the low eutectic point. Hydroxide alkalinity played an important role...
in dechlorination with its large amount of hydrogen donors. However, different from the base-catalyzed reaction, the dechlorination reaction occurred without excess organic hydrogen donors in this process (Hu et al., 2011). This may be attributed to the intermediate products acting as the hydrogen donors. Research indicates that long chain alkanes such as octadecane and polyhydric alcohols can act as hydrogen donors in a catalytic dechlorination reaction (Kawahara and Michalakos, 1997). During the reaction, the hydroxide melt effectively destroyed the benzene ring and intermediate products that formed during the reaction, which then facilitated the dechlorination reaction (Li et al., 2014).

### 2.2. Dechlorination with different amounts of hydroxide mixtures

A further evaluation of hydroxide amount was applied to the dechlorination process (Fig. 3). The TCB absorbed in hexane represents the portion that escaped from the system by volatilization during the heating process. It was seen that when the amount of hydroxide melt increased, the TCB detected in the washing water decreased, which indicated that the molten hydroxide medium effectively retained the TCB, and the CRE increased. The reaction resulted in an increase in CRE from 9.64% to 71.56%. When the mass ratio of hydroxides to TCB reached 30:1, there was virtually no TCB loss, and a high CRE of 71.56% was achieved. The molten salt reaction was performed in a cylindrical vessel, and the amount of molten hydroxide was proportionate to the contact time between the material and the molten salt, which determined the treatment efficiency (Griffiths et al., 2010). The viscosity of molten salt, which is higher than water, inhibits the emission of gases and leads to further destruction (Stuhlpfarrer et al., 2016).

### 2.3. Effect of reaction time and temperature

The influence of reaction and temperature was investigated in 0.75 mol ratio hydroxide mixtures. As shown in Fig. 4, the CRE increased with both temperature and reaction time. The rate of reaction was relatively high, as the CRE rose to 59.03% in the first 30 min. With prolonged reaction time, CRE slowly increased to 75.06% and the MLR increased at the same time. This indicated that the stepwise dechlorination reaction occurred in the melt medium in 2.5 hr. TCB was first dechlorinated by the alkaline molten salts. Intermediate products were then generated, and acted as hydrogen donors to improve the dechlorination (Yang et al., 2008). The limited amount of hydrogen donors inhibited further reaction, resulting in a maximum CRE of 75.06%. The generation of intermediate products and CO2 resulted in a mass loss, which was reported previously (Lin et al., 2016). In this process, the CRE change was found to be synchronous with the MLR change, implying that intermediates play an important role in treatment effectiveness.

Fig. 4a–c present the dechlorination reaction at different temperatures. At 150°C, the CRE was low because the hydroxides had not yet melted, and only small amounts of TCB were decomposed at this temperature. This was verified by the high amount of mass loss. The mass loss greatly decreased at 200°C, and the dechlorination efficiency was enhanced at higher temperature. It attained 97% of the MLR at

### Table 1 - Eutectic point and viscosity of the hydroxide mixture melts.

<table>
<thead>
<tr>
<th>NaOH/ (KOH + NaOH) (mol ratio)</th>
<th>Eutectic point (°C)</th>
<th>Viscosity ($x 10^{-3}$ Pa·sec)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>318 ± 5</td>
<td>4.000</td>
<td>Janz (1967)</td>
</tr>
<tr>
<td>0.1</td>
<td>308 ± 12</td>
<td>2.300–4.000</td>
<td>This study</td>
</tr>
<tr>
<td>0.3</td>
<td>256 ± 18</td>
<td></td>
<td>This study</td>
</tr>
<tr>
<td>0.5</td>
<td>182 ± 8</td>
<td></td>
<td>This study</td>
</tr>
<tr>
<td>0.7</td>
<td>240 ± 11</td>
<td></td>
<td>This study</td>
</tr>
<tr>
<td>0.9</td>
<td>300 ± 9</td>
<td></td>
<td>This study</td>
</tr>
<tr>
<td>1.0</td>
<td>380 ± 10</td>
<td>2.300</td>
<td>Janz (1967)</td>
</tr>
<tr>
<td>Air</td>
<td>–</td>
<td>0.018</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>–</td>
<td>0.102</td>
<td></td>
</tr>
<tr>
<td>Crude oil</td>
<td>–</td>
<td>8.000</td>
<td></td>
</tr>
</tbody>
</table>

*: not available.

Fig. 2 – Different mole ratios of NaOH in hydroxide mixtures for the dechlorination reaction at 300°C for 120 min; the molar content of the mixture was set at 0.75 mol. CRE: chlorine retention rate.

Fig. 3 – Different amounts of selected hydroxide mixtures for the dechlorination reaction at 300°C for 120 min. CRE: chlorine retention rate.
400°C. Details are presented in Fig. 4c. Though CRE was improved with the increase of temperature, it could not accelerate the dechlorination rates in this process, which implies that the reaction was partially controlled by physical characteristics and interaction. The viscosity of the melt decreased with increasing temperature according to the equation below (Lovering, 1982).

\[
\mu = 164.771 - 6148.33T + 78034T^2 - 3.3 \times 10^7T^3
\]

where, \(\mu\) is the viscosity of the melt and \(T\) (°C) is the temperature. A low viscosity promotes the dissolution of HCl and more Cl ions are retained.

2.4. Mass balance of chlorine atoms

To exclude possible errors in the experiment, the chlorine mass balance was calculated during the dechlorination reaction (Table 2). The relative abundance of chlorine associated with TCB in treatment residues and washing water decreased from 100% to 24.5% within the 2.5 hr. treating time, while the chloride ion increased from 0% to 75.0%. The total chlorine atom recovery rate was as high as 94.1%–99.5%. In this process, almost all chlorine atoms in the TCB were removed and retained in the molten hydroxide medium. Destruction of TCB was obtained and almost no other chlorine-containing intermediate products were generated.

2.5. Evidence for salt enrichment with chlorine

To further investigate the structural changes and chlorine distribution, the original samples and residue demonstrating the best CRE were analyzed. The residue is generally hard and yellow with a small portion of black substance, as shown in Fig. 5a–b. SEM maps showed the presence of highly porous material in the residues (arrows in Fig. 5c–d) caused by the release of volatile gas during the destruction. A significant amount of the hydroxides participated in the reaction and turned into chloride salt. Only a small portion remained unreacted. The residue shape was irregular and became more swollen and porous with increased reaction time.

For the determination of the spatial distribution of Cl, EDS mapping (Fig. 6) was employed. The C and Cl elements can be clearly observed, indicating the existence of chlorine-containing organic substances. The spatial maps of Na, K and O related to the NaOH–KOH showed that they were almost homogeneously spread across the sample surface. This means that the hydroxide composition remains unchanged in the residues after reaction, which is important for reutilization of the hydroxide for further reaction.

The XRD patterns of residues are presented in Fig. 7. The major crystalline phases of the residues after reaction were NaOH (JPCDS card no. 73-0380), KOH (JPCDS card no. 77-1221) and NaCl (JPCDS card no. 73-0380). The NaOH and KOH were associated with the remaining unreacted hydroxides. NaCl (or

### Table 2 - Chlorine mass distribution during the dechlorination reaction.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>TCB distribution</th>
<th>Chlorine atoms distribution</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount in residues and washing water (mg)</td>
<td>Percentage (%)</td>
<td>Amount in residues and washing water (mg)</td>
</tr>
<tr>
<td>0</td>
<td>1173.88</td>
<td>-</td>
<td>692.94</td>
</tr>
<tr>
<td>0.5</td>
<td>418.61</td>
<td>35.66</td>
<td>770.76</td>
</tr>
<tr>
<td>1.0</td>
<td>345.00</td>
<td>29.39</td>
<td>819.25</td>
</tr>
<tr>
<td>1.5</td>
<td>288.77</td>
<td>24.60</td>
<td>854.58</td>
</tr>
<tr>
<td>2.0</td>
<td>287.13</td>
<td>24.50</td>
<td>880.64</td>
</tr>
<tr>
<td>2.5</td>
<td>287.60</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- : not detected.
KCl) was formed by the reaction of molten hydroxide and the degradation products of TCB. Moreover, compared with 30 min reaction, the residues observed after 120 min had higher concentrations of NaCl, which indicates that a longer reaction time results in the production of a larger amount of NaCl.

The EDX analysis shown in Table 3 confirmed the enrichment of chlorine in the residues. The atomic

Fig. 5 – Photos and SEM of the residues. (a, b) photograph of the residue after reaction. (c, d) SEM maps. The arrow points to the mesoporous sections of in the residue.

197

Fig. 6 – Elemental mapping image (surface scanning pattern) of molten residues.
percentage of Cl increased from 0.17% to 2.12% in the chloride salt surface. Meanwhile, the decrease of C element demonstrated that about 36% of carbon was transformed to CO2 in this process.

To determine the change in the organic carbon, Fourier transform infrared (FT-IR) spectra of the residues with different reaction times were measured and presented in Fig. 6b. The original TCB particles displayed strong absorption bands at roughly 600–700 cm\(^{-1}\) (C–Cl stretching vibration), 1300 cm\(^{-1}\) (CH bending vibration from CH–Cl), 1429 cm\(^{-1}\) (CH bending from CH\(_2\)), and 3000 cm\(^{-1}\) (CH stretching from CH–Cl). Compared to TCB, the residue spectra changed significantly. The primary differences occurred in the 500–1500 cm\(^{-1}\) range. As the reaction progressed, the absorption bands at 3018 cm\(^{-1}\) assigned to CH stretching from –CH=CH– disappeared, suggesting that the molten hydroxide eventually destroyed the C=C bonds. The two bands at 2456 cm\(^{-1}\) were attributed to the possible generation of –C=O– and –C≡C– bonds. On the other hand, the absorption band at 1580 and 1600 cm\(^{-1}\) assigned to CH bending from CH–Cl were replaced by strong absorption bands at 1428 cm\(^{-1}\), clearly indicating the removal of chlorine and generation of carboxyl groups. A set of bands at 881 and 697 cm\(^{-1}\) considered to be characteristic peaks of aromatic structures emerged in the residues, indicating the existence of cyclization/aromatization reactions. The peaks at around 600 cm\(^{-1}\) corresponding to C–Cl decreased to some extent, implying that part of the chlorine was removed by the molten hydroxide (Zhao et al., 2018).

The surface elemental composition of the residues was analyzed by X-ray photoelectron spectroscopy (XPS) (Fig. 8). C1s and Cl 2p\(_{3/2}\) peaks were present in the XPS spectra (Fig. 8a). C=O (289.0 eV), C–O (286.7 eV) and O–C=O (288.6 eV) groups (Yang et al., 2016) were discovered in the residues, while the content of C–C/C=C (284.0 eV) corresponding to the benzene ring decreased (Fig. 8b–e). This was further verified by the XPS carbon data obtained from the 30 and 120 min residue (spectra not shown), as shown in Table 4. The C–C groups decreased from 57.45% to 43.25%, and changed into C=O groups with 35%–40% of the carbon content, which was consistent with the FT-IR analysis above. In the molten hydroxide medium, TCB was dechlorinated and the benzene ring was destroyed, resulting in the formation of C–O and O–C=O groups. Moreover, the binding energy assigned to inorganic Cl (201.86 eV) was observed over the spectral regions of Cl 2p\(_{3/2}\), further verifying that dechlorination had occurred during the reaction. The main components of the residue were hydroxide and chloride salt, which can be recovered after the reaction.

\[ C_6H_3Cl_3 + MOH + O_2 \rightarrow MCl + CO_2 + H_2O + \text{intermediate products} \]  

Even though the CRE was sufficiently high and most chlorine was captured, as shown by the above results, dioxins may also be present due to the thermal process that takes place when treating the hazardous waste. In this molten process, TCB was selected as a model compound and we reacted it with molten NaOH-KOH in the temperature range of 200–400°C. Thus, dioxins could be generated by the pathways of “de novo synthesis” and “precursor synthesis”. In particular, TCB and macromolecular carbon (also called residual carbon) most likely produce PCDD/Fs with some catalytic compositions (Cu, Fe) by “de-novo synthesis” (Zhao, 2017). Dioxins in the residues were tested and the results are shown in Table 5. The toxic equivalents (TEQ) were calculated using World Health Organization 2005 factors and results. The observed concentration of dioxins in terms of TEQ values was 5.6 ng TEQ/kg.

Different levels and profiles of PCDD/Fs in fly ash samples from multiple industrial sources were compared based on

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**Table 3 – The atomic percentage of each element in the residues after reaction, obtained from the EDX measurement.**

<table>
<thead>
<tr>
<th></th>
<th>Cl (at.%)</th>
<th>C (at.%)</th>
<th>O (at.%)</th>
<th>Na (at.%)</th>
<th>K (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residues after 30 min</td>
<td>0.17</td>
<td>11.11</td>
<td>58.32</td>
<td>15.12</td>
<td>15.30</td>
</tr>
<tr>
<td>Residues after 120 min reaction</td>
<td>2.12</td>
<td>7.08</td>
<td>59.34</td>
<td>14.62</td>
<td>16.75</td>
</tr>
</tbody>
</table>

---

**Fig. 7 – XRD spectra (a) and FT-IR analysis (b) of the residues.**
Fig. 8 - XPS spectra of the TCB (a–d) and residues (e–h) over the spectral regions of C 1s, O 1s, Cl 2p and Na 1s.
previous research. The PCDD/F TEQs in fly ash samples from seven industrial sources (secondary copper, zinc, aluminum smelting and hazardous waste incineration, iron ore sintering, thermal wire reclamation, and municipal solid waste incineration) were higher than 100 ng TEQ/kg, and the PCDD/F TEQs of fly ash samples from most other industrial sources were lower than 100 ng TEQ/kg (Liu et al., 2015a, 2015b). Generally, municipal solid waste incineration generated fly ash containing 0.66–68.9 μg TEQ/kg dioxins (Zhao, 2017). Therefore, the dioxin concentration of residues in the current process is much lower than that from municipal solid waste incineration processes. Low PCDD/Fs emissions have also been reported by Hsu et al. (1998) during the MSO treatment of PCB-contaminated waste. Results revealed that PCDD/Fs formation through the “de-novo” route may be suppressed during the molten hydroxide process, as chlorine is retained in the salt bath. Therefore, hazardous waste dechlorination in this process reduces the potential for creating dioxins, with the process itself producing relatively low amounts of dioxins in the residues. However, attention should also be paid to the dioxin formation in the residues in future work.

### 2.6. Other wastes and mechanism interpretation

The above results indicated that molten NaOH–KOH was effective for dechlorinating TCB, and the CRE of TCB reached 75.06%. In addition, the system was also effective for the removal of other organochlorine compounds, including perchloroethylene, hexachlorobenzene and chlordane. Results showed that the removal and dechlorination efficiencies were 98.42%, 96.35% and 93.26% respectively (Table 6). The CREs of three wastes were 93.36%, 75.39% and 78.35% respectively. Results showed that PICs were present in the residues for hexachlorobenzene and chlordane, which are complicated chlorine-containing wastes. To further characterize the system, the dechlorination mechanism was examined with TCB as a representative compound.

Few articles have described the mechanism of the molten hydroxide reaction. In the early studies, researchers did not fully understand the mechanism of the molten hydroxide reaction. In the early studies, researchers did not fully understand the mechanism of the molten hydroxide reaction. In the early studies, researchers did not fully understand the mechanism of the molten hydroxide reaction. In the early studies, researchers did not fully understand the mechanism of the molten hydroxide reaction.

![Fig. 9 – Proposed pathway for chlorine removal in the molten hydroxide medium.](image)
appreciate the molten salt chemistry involved and assumed that the molten salts were acting as a catalyst (Yao et al., 2014). However, Griffiths and Volkovich (2008) explained that oxygen dissolves chemically in molten salt and forms oxidizing species. In this process, a reaction pathway was proposed according to the results (Fig. 9). Based on previous research, molten salts provide a stable medium for free ions to participate in a reaction. First, oxygen is chemically dissolved in molten salt and forms oxidizing species, hydroxyl radicals and O$_2$ (Yao et al., 2014). These species are easily generated at high temperatures with sodium-based catalysts (Takanabe et al., 2017). These strong oxidizing agents attack TCB and facilitate a hydrogenation/dechlorination reaction. When C$_6$H$_6$, C$_4$H$_4$, and other intermediate products are generated from the decomposition of TCB, they act as hydrogen donors and participate in the dechlorination reaction. As the reaction proceeds, chloride ions are stabilized in the form of a chloride salt.

3. Conclusions

Removal of TCB could be realized by reaction with molten salt. A molten salt mixture (41 wt.% NaOH and 59 wt.% KOH) displayed the best CRE of 68.96% compared with other hydroxide compositions. Three factors were examined including the amount of hydroxide used in the reaction, the reaction temperature, and the reaction time. When the mass ratio of hydroxide and TCB reached 30:1 at a temperature of 300°C and reaction time of 150 min, high CRE (71.56%) was achieved. Higher temperature enhanced the CRE but did not accelerate dechlorination rates in this treatment process. Residue analysis indicated that C-Cl bonds were eliminated and the benzene ring was destroyed, resulting in decreases in the corresponding bands in the FT-IR spectra. The results of this investigation further indicated that oxidizing species may be present in the salt medium, enabling rapid cracking of long hydrocarbon chains. According to residue analysis, chlorine was retained and enriched to form chloride salts in the residues, and the relative abundance of chloride ions associated with TCB increased from 0 to 75.02% within 2.5 hr. reaction time. Attention should be paid to the dioxin concentrations in the residues when applying this process.

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