Review

Review on fate of chlorine during thermal processing of solid wastes

Peng Lu¹, Qunxing Huang¹⁎, A.C. (Thanos) Bourtsalas², Nickolas J. Themelis², Yong Chi¹, Jianhua Yan¹

1. State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China
2. Earth Engineering Center, Columbia University, New York, NY 10027, USA

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ABSTRACT

Chlorine (Cl) is extensively present in solid wastes, causing significant problems during the thermal conversion of waste to energy or fuels, by combustion, gasification or pyrolysis. This paper introduces the analytical methods for determining the Cl content in solid materials and presents the concentrations of Cl in various types of wastes, as reported in literature. Then, it provides a comprehensive analysis on the Cl emission behavior and Cl species formed during the thermal processing of the inorganic and organic Cl sources. The challenges resulted from the reactions between the formed Cl species and the ferrous metals, the heavy metals and the organic matters are summarized and discussed, e.g., high temperature corrosion, heavy metal evaporation and dioxin formation. The quality degradation of products (oil, char and syngas) by Cl is analyzed. Finally, the available controlling methods of Cl emission, including pre-treatment (water washing, sorting, microwave irradiation and stepwise pyrolysis) and in-furnace (absorbents, co-treatment and catalysts) methods are assessed.

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⁎ Corresponding author.
E-mail addresses: 11427070@zju.edu.cn, (P. Lu), hqx@zju.edu.cn, (Q. Huang).

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Introduction

Chlorine (Cl) widely exists in environment, such as in seawater (NaCl) and in plants and animals as an essential micronutrient (Johnson et al., 1957). Since the successful extraction of Cl by Scheele in 1774, modern industry has a deliberate demand for the synthesis of a vast array of chlorinated compounds (Stringer and Johnston, 2001). Today, Cl is mainly produced from salts by electrolytic process. European Cl production in 2016 was 9461 kton, which has been applied in many fields, as presented in Fig. 1 (Euro Chlor, 2017). The principal application of Cl is the production of polyvinyl chloride (PVC) plastics (32.5%). Cl can also be used in water treatment, in agrochemicals as herbicides and pesticides, in pharmaceutical drugs and in bleaching (pulp and paper), etc. (Cincinelli et al., 2012) Cl-containing persistent organic pollutants (POPs) have the potential to migrate widely throughout the ecosystem, ultimately accumulating in fatty tissues of organisms (Suntio et al., 1988). The unrecyclable plant residues, animal bodies and used chlorinated products are finally discarded as solid wastes.

The rapid growth of waste materials generated by humanity and the scarcity of landfilling space near cities have resulted in a major environmental problem. This has led to the development of many thermal processing technologies, whose objective is materials and energy recovery. Global production of the post-recycled municipal solid waste (MSW) was about 1.3 billion tons in 2012 and is likely to reach 2.2 billion tons by 2025 (Hoornweg and Bhada-Tata, 2012). As we transit to a circular economy, some of this waste could supply up to 10% of the total global industrial energy. However, the various waste materials that range from mixed municipal solid waste (MSW), municipal plastic waste (MPW), food waste (FW), forestry and agricultural residue (FAR), and hazardous waste (HW), contain Cl, that associates to challenges in the operation of the thermal processing techniques, e.g., high temperature corrosion (HTC), heavy metal evaporation and dioxin formation by reacting with ferrous metals, heavy metals and organic matters in furnace.

The released Cl species react with ferrous metals leading to the HTC in the superheaters and boilers section of combustion facilities, which is considered one of the biggest challenges of the industry. The waste-to-energy (WTE) plants have to operate to lower steam parameters, <450°C, as compared to other power plants, to avoid HTC, and this results in a significant reduction of the efficiency and the subsequent revenues of the WTE plants (Nielsen et al., 2000). Typically, potassium chloride (KCl) and sodium chloride (NaCl) are the main cause of HTC, due to the facts that potassium (K), sodium (Na) and Cl are relatively volatile elements and the melting points of these chlorides are relatively low. Also, Cl will promote the evaporation rate (ER) of heavy metals originally existed in the solid wastes by the formation of chlorides (Wang et al., 1999). The evaporated heavy metal chlorides deposit on the surface of fly ash, act as catalysts for the formation of some poisonous pollutants (e.g., dioxins), and make the fly ash a hazardous material (Lu et al., 2007).

The reactions between Cl and organic matters promote the formation of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and other organic chlorinated compounds (Lu et al., 2007). Solid waste combustion is one of the major sources of PCDD/Fs (or dioxins), which are produced through high-temperature (500-800°C) homogeneous reactions and low-temperature (200-400°C) heterogeneous reactions (McKay, 2002).

The presence of chlorinated compounds degrades the quality of char, oil and syngas produced from the pyrolysis/gasification of solid wastes. For example, a high Cl content in oil causes problems when used in petrochemical plants which have a limitation of 10 ppm Cl in oil (Kaminsky, 1995). Also,
the corrosion, heavy metal and dioxin problems will seriously restrict the usage of these products as fuels when Cl exists.

There are numerous studies related to the distribution and speciation of Cl during thermal processing of solid wastes and the associated challenges. The fate of Cl depends on the source, concentration, operating conditions (e.g., temperature, pressure and reaction atmosphere) and the use of catalysts/absorbents (Ma et al., 2002; Ma and Rotter, 2008; López et al., 2011, 2012; Du et al., 2014).

This review introduces the available analytical methods for the determination of Cl content in solid materials, the Cl sources and concentrations, the Cl distribution and speciation during thermal processing (combustion, gasification and pyrolysis), the reactions involved Cl species in furnace and related challenges (HTC, heavy metal evaporation and dioxin formation), and the degradation of product quality by Cl. Also, the controlling methods to hinder the emission of Cl species are presented and discussed. This review provides comprehensive information for a better understanding of the fate of Cl during the thermal processing of solid wastes.

1. Quantification and sources of chlorine in solid wastes

1.1. Chlorine quantification methods

There are numerous Cl sources in solid materials, e.g., plants, animals, food, plastic products and other chlorinated products in daily life. It is essential to accurately quantify the Cl concentrations in different sources for any efforts of addressing its detrimental effects. The Cl in solid materials is classified into volatile (released into gas phase after combustion) and non-volatile Cl (remained in ash after combustion) or organic (or water-insoluble Cl) and inorganic Cl (or water-soluble Cl) (Ma et al., 2010).

Several methods are available for determining Cl content in solid materials, which can be classified into four categories, i.e., combustion, hydrolysis, extraction (Wang et al., 2010; Rahim et al., 2013b) and spectroscopy (Pereira et al., 2014) methods, as presented in Table 1. The combustion methods are the most commonly used methods, e.g., bomb combustion (BC), flash combustion (FC), muffle/tube furnace combustion (MFC) and microwave-induced combustion (MIC). Combustion methods are capable to quantify the total Cl content (TCC) due to the high operating temperatures (>1000°C). Although Cl may still exist in the residues after combustion, the amount is negligible comparatively to the corresponding TCC (Silva et al., 2014). However, the non-volatile Cl in ash is not negligible by MFC at relatively lower temperatures (<1000°C), which can be further quantified by water washing (Ma et al., 2010) or spectroscopy analyses. Water washing methods are specially used for the determination of water-soluble Cl. The remained water-insoluble Cl in dried solid matters can be quantified by combustion methods. Digestion (acid and microwave) methods have the problem of analyte loss due to the formation of volatile Cl-compounds (Pereira et al., 2014). Spectroscopy methods can achieve non-destructive analyses on solid materials (Nécémer et al., 2003), e.g., X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA). The minimum detection limit of INAA is in the sub-ppm range with an accuracy in the region of 5% (Pollard and Heron, 2008). However, non-destructive methods have very strict requirement on the homogeneity of solid sample. The choice of specific Cl quantification method depends on the species, content and distribution of Cl in solid materials.

A number of Cl detection techniques are available, e.g., ion chromatography (IC), ion selective electrode (ISE), titration, coulometry, inductively coupled plasma-optical emission spectrometry (ICP-OES) or -mass spectrometry (ICP-MS), XRF and INAA (Wang et al., 2010; Rahim et al., 2013b; Pereira et al., 2014). IC is the most widely applied technique with a detection limit of 0.02 µg/mL. The combination of bomb combustion and ion chromatography (BCIC) for the quantification of TCC in solid recovered fuels (SRF) has been standardized by European committee (EN 15048:2011). Fig. 2 shows the flow chart of the

### Table 1 - Quantification methods of Cl content in solid materials (Wang et al., 2010; Rahim et al., 2013b; Pereira et al., 2014).

<table>
<thead>
<tr>
<th>Methods</th>
<th>Instrument</th>
<th>Relevant standard</th>
<th>Cl species</th>
<th>Cl detection techniques</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion</td>
<td>Bomb</td>
<td>EN 15048:2011</td>
<td>Total Cl content (TCC)</td>
<td>Ion chromatography (IC); ICP; ISE</td>
<td>Oxygen bomb combustion</td>
</tr>
<tr>
<td></td>
<td>Flame</td>
<td>EN 14582–2007</td>
<td>TCC</td>
<td>IC, titration, coulometer</td>
<td>Schoeniger flask combustion</td>
</tr>
<tr>
<td></td>
<td>Muffle/tube furnace</td>
<td></td>
<td>Volatile Cl or TCC</td>
<td>IC</td>
<td>Elemental analyzer; Eschka method</td>
</tr>
<tr>
<td></td>
<td>Microwave system</td>
<td>ASTM D6721-01</td>
<td>TCC</td>
<td>IC</td>
<td>Microwave-induced combustion</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>Hydrolysis furnace</td>
<td></td>
<td>TCC</td>
<td>Micro coulometer</td>
<td>Oxidative hydrolysis</td>
</tr>
<tr>
<td>Extraction</td>
<td>Elution devices</td>
<td>EN ISO 16995-2015</td>
<td>Water-soluble Cl (inorganic Cl)</td>
<td>ICP</td>
<td>Deprotized water washing</td>
</tr>
<tr>
<td></td>
<td>Digestion devices</td>
<td></td>
<td>TCC</td>
<td>Spectroscopy analyses</td>
<td>Acid digestion; Microwave digestion</td>
</tr>
<tr>
<td>Spectroscopy</td>
<td>Spectral devices</td>
<td></td>
<td>TCC</td>
<td></td>
<td>X-ray fluorescence; Instrumental neutron activation analysis</td>
</tr>
</tbody>
</table>
most recommended method (combustion coupled with IC) for the determination of TCC in solid materials. The basic principle is to release all of the Cl contained in the solid sample ($m_0$, mg) as ions that are captured in absorbent solution, dilute the solution to a certain volume ($V_0$, L), and analyze it by IC to obtain the Cl concentration ($C_0$, mg/L); the latter is used to calculate the Cl content in the solid samples ($\alpha_0$). Alkaline solution is usually used to capture the Cl species released from the combustion. A typical alkaline solution is 2.52 g Na$_2$CO$_3$, 2.54 g NaHCO$_3$, and 25 mL of 30% H$_2$O$_2$ in one liter of de-ionized water (Ma et al., 2010). Coulometer is also used to determine the Cl content, e.g., in elemental analyzer, which quantifies the TCC by determining Cl in gas through coulometer detector and Cl in ash through water washing separately. Elemental analyzer belongs to the MFC methods and allows for the measurement of samples with a wide range of Cl content (30–1000 μg) due to the sample gas splitting option (Ma et al., 2010). A limit of TCC quantification by MIC and further ICP-OES determination is 6 μg per gram of sample (Müller et al., 2011).

1.2. Chlorine sources and contents in solid wastes

The plant residues (e.g., crop residues, deciduous trees and shrubs), scraps from manufacture of woody products, the leftovers, and the unrecoverable woody and artificial chlorinated products are finally discarded as solid wastes to be Cl sources. The Cl concentrations in different types of solid wastes are shown in Table 2 and can be divided into inorganic and organic Cl sources.

The principal inorganic Cl sources in solid wastes are the forest and agricultural residues (FAR), the FAR derived products like paper and cardboard and the food waste (FW). Alkali chlorides (salt, e.g. KCl) are the main forms of inorganic Cl (Rahim et al., 2013a). The Cl in FAR is easily evaporated and transferred into the gas phase as acid or alkali chlorides during thermal processing (Du et al., 2014). There is also a small amount of organic Cl (<5% of total Cl) in FAR that forms compounds with the carbons present. The Cl in FAR is a micronutrient with a content of 0.01–0.7 wt.% (Björkman and Strömberg, 1997), which plays a catalytic role in the photosynthetic and enzymatic processes and is closely related to the plant grown process (Tillman et al., 2009). The amount depends on the closeness of the feedstock to the sea, the use and the quality of the fertilizers, the leaching from the soil by the rain, the technique used to harvest, and the treatment and storage methods. Compared with forestry residue (FR), agricultural residue (AR) has a relatively higher Cl content (Coda et al., 2001; Tillman et al., 2009; Du et al., 2014). The Cl content in FR or FR derived products like paper is typically lower than 0.1 wt.% (Tillman et al., 2009; Ma et al., 2010). Whereas the Cl content in AR is typically higher than 0.2 wt.% (Tillman et al., 2009; Gai and Dong, 2012).

FW is another important inorganic Cl source due to the presence of salt (NaCl and KCl), which significantly contributes to the total Cl in MSW. A contribution of 45% to total Cl in MSW from FW was identified by Ma et al. (2010). However, FW is not suitable to be thermally treated due to the high moisture content and the low heating value. Instead, FAR is an ideal feedstock for thermal processing due to the relatively homogeneous composition and the high heating value.

The principal organic Cl sources in solid wastes are chlorinated plastics (e.g., polyvinyl chloride (PVC), chlorinated polyethylene (CPE), polyvinyl dichloride (PVDC)) (Coda et al., 2001; Liu et al., 2017), electronic waste, textiles, leathers, rubbers (Rotter et al., 2004), pesticides and herbicides (Zhu et al., 2008). Organic chlorinated compounds are the main forms of Cl in organic Cl sources, which are generally anthropogenic. Chlorinated plastics are the dominant sources of organic Cl in MSW and refuse derived fuel (RDF), while other sources contribute negligible amounts. It is estimated that chlorinated plastics contribute to total Cl in MSW between 38% and 72% (Aracil et al., 2005; Ma and Rotter, 2008). Ma et al. (2010) found that the Cl content and Cl speciation of different plastic products varied, as presented in Table 3. The Cl content in non-packaging plastics (6.28 wt.%) was significantly higher than that of packaging plastics (1.38 and 0.56 wt.%). The latter had significant contents of inorganic Cl (13.0% and 40.0%) by the contamination of retained food waste (Rotter et al., 2004). PVC is the most important chlorinated plastic, which contains about 56 wt.% Cl and is widely used in a variety of products, including wire and cable insulation, window frames, boots, food foil, medical devices, automotive interiors,
packaging, credit cards and synthetic leathers (Anuar Sharuddin et al., 2016).

MSW and RDF or solid recovered fuel (SRF) are heterogeneous materials with complex components (e.g., plastic, paper and FW). Both inorganic Cl in food and yard waste and organic Cl in chlorinated products (e.g., plastics) exist, resulting in a total Cl content of 0.5–1.0 wt.% in MSW (Themelis, 2010; Zhou et al., 2014). In Finland, a classification for recovered fuels (RDF or SRF) based on Cl content is suggested as Class I–III with less than 0.15 wt.%, less than 0.5 wt.% and less than 1.5 wt.%, respectively (Zevenhoven et al., 2002). The Cl content in RDF is significantly influenced by the processing technologies used in the materials recovery facilities (MRF), e.g., sorting and recovery methods.

### 2. Chlorine emission behavior from solid wastes

#### 2.1. Inorganic chlorine from salt

As discussed in Section 1.2, FAR and FW are the most important inorganic Cl sources in solid wastes. FW is not an efficient feedstock for thermal processing and therefore, FAR is selected as a representative source to study the emission behavior of inorganic Cl. The release of Cl in FAR can be divided into two stages (Björkman and Strömberg, 1997; Knudsen et al., 2004; Du et al., 2014). Cl is released in the form of HCl in the first stage at temperatures lower than 600°C (Eq. (1)) (Dayton et al., 1999) through a possible mechanism expressed by Eq. (2) (Björkman and Strömberg, 1997).

**Stage 1**: FAR → Intermediate product + Volatiles + HCl  
\[ 2\text{KCl} + n\text{SiO}_2 + \text{H}_2\text{O} → \text{K}_2\text{OSiO}_2 + 2\text{HCl} \]  

The low-temperature HCl releasing is governed by a reaction of KCl with proton-donating sites in the char matrix, e.g., carboxylic, phenolic groups or a H₂O molecule (Zintl et al., 1998).

Cl is mainly released in the form of KCl(g) in the second stage at temperatures higher than 600°C (Eq. (3)) (Dayton et al., 1995) by direct evaporation (Mojtahedi and Backman, 1989). The evaporation rate (ER) of NaCl and other alkali chlorides is not comparable with that of KCl (Björkman and Strömberg, 1995). The evaporation rate (ER) of NaCl and other alkali chlorides is not comparable with that of KCl (Björkman and Strömberg, 1995).

**Stage 2**: Intermediate product → Char or Ash + KCl_g  
\[ \text{K}_2\text{OSiO}_2 + 2\text{HCl} → 2\text{KCl} + n\text{SiO}_2 + \text{H}_2\text{O} \]  

Fig. 3 shows the Cl distribution in gas, char and oil during the pyrolysis of biomass materials (wheat straw, rice husk and sawdust) (Du et al., 2014). At 200°C, about 25% Cl evaporated to the gas phase and 60% was left in char. Increasing the temperature from 200 to 600°C resulted in a reduction of Cl in char to 15%, whereas Cl in gas was increased to 55%–70%. This finding suggests that most Cl species are released through the devolatilization process (<600°C). At temperatures >600°C, the influence of temperature on Cl transformation became very limited. At 1000°C, 7%–10% Cl remained in the char. This value was different to the findings of Knudsen et al. (2004), where they examined the behavior of Cl from biomass samples, i.e., rice, barley, wheat, carinata and rape, in

### Table 2 – Cl content in different types of solid wastes.

<table>
<thead>
<tr>
<th>Type</th>
<th>Sources</th>
<th>Examples</th>
<th>Chlorine content (wt.%, dry basis)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic Cl sources</td>
<td>Forestry residue (FR)</td>
<td>Willow wood, hybrid poplar, sawdust, woody products (e.g., paper and cardboard)</td>
<td>0.01–0.10</td>
<td>Wang et al., 2001; Moilanen, 2006; Tillman et al., 2009; Ma et al., 2010; Themelis, 2010</td>
</tr>
<tr>
<td></td>
<td>Agriculture residue (AR)</td>
<td>Rice straw, wheat straw, corn stover</td>
<td>0.10–0.72</td>
<td>Tillman et al., 2009</td>
</tr>
<tr>
<td></td>
<td>Food waste (FW)</td>
<td></td>
<td>0.03–1.38</td>
<td>Ma and Rotter, 2008; Ma et al., 2010</td>
</tr>
<tr>
<td>Organic Cl sources</td>
<td>Plastics</td>
<td>Polyvinyl chloride (PVC)</td>
<td>46.00–56.70</td>
<td>Aracil et al., 2005; Yuan et al., 2014</td>
</tr>
<tr>
<td></td>
<td>Other products</td>
<td>Daily plastic products (packaging, non-packaging)</td>
<td>0.25–6.28</td>
<td>Ma et al., 2010; Rotter et al., 2004</td>
</tr>
<tr>
<td>Mixed Cl sources</td>
<td>Municipal solid waste (MSW)</td>
<td>A mixture of plastics, FW, textiles, papers...</td>
<td>0.50–1.00</td>
<td>Themelis, 2010; Zhou et al., 2014</td>
</tr>
<tr>
<td></td>
<td>Refuse derived fuel (RDF)</td>
<td></td>
<td>0.15–1.58</td>
<td>Zevenhoven et al., 2002; Moilanen, 2006; Liu et al., 2017</td>
</tr>
<tr>
<td></td>
<td>Sewage sludge</td>
<td></td>
<td>0.03–0.27</td>
<td>Werle and Wilk, 2010</td>
</tr>
</tbody>
</table>

### Table 3 – Cl content and Cl speciation in different plastics (Ma et al., 2010).

<table>
<thead>
<tr>
<th>Plastics</th>
<th>Cl content (wt.%, dry basis)</th>
<th>Organic Cl</th>
<th>Inorganic Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-packaging</td>
<td>6.28</td>
<td>99.3%</td>
<td>0.7%</td>
</tr>
<tr>
<td>Packaging bottles</td>
<td>1.38</td>
<td>87.0%</td>
<td>13.0%</td>
</tr>
<tr>
<td>Packaging films</td>
<td>0.56</td>
<td>60.0%</td>
<td>40.0%</td>
</tr>
<tr>
<td>and bags</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
a combustion environment. They observed a nearly complete release of Cl to the gas phase at temperatures above 800°C. This may be explained by the fact that the evaporation of KCl from the char is slower than that from the ash due to a greater diffusional resistance in char. However, both studies agreed that the functional groups of char may affect the release of Cl-bearing species. The amount of Cl in liquid oil was relatively low, accounting for about 15–20%, without any changes at different temperatures. The Cl in liquid product was mainly attributed to the solubility of chlorides in water-rich bio-oil rather than the condensation of organic Cl species.

2.2. Organic chlorine from plastics

As explained in the previous section, PVC is the most representative source of organic Cl, and that is why PVC is selected as a representative to study the emission behavior of organic Cl. A two-stage mechanism has been widely recognized for PVC degradation (McNeill et al., 1995; Miranda et al., 1999b, 2001; Starnes Jr, 2002). The first stage is the dehydrochlorination (DHC) process and subsequent formation of conjugated double bonds in polyene chains at 200–360°C (Eq. (4)).

Stage 1: PVC → Intermediate product + HCl

\[ \text{DHC} \text{ is a free radicals chain reaction initiated by allylic Cl and tertiary labile structure defects formed by polymerization (Starnes Jr, 2002). The products during this stage are HCl, and a small amount of benzene, alkyl aromatic and condensed ring aromatic hydrocarbons (McNeill et al., 1995).} \]

The second stage is the cracking/decomposition of the de-HCl PVC and the formation of char at 360–520°C (Eq. (5)).

Stage 2: Intermediate product → Char + Volatiles

Alkyl aromatic, condensed ring aromatic hydrocarbons, and a small amount of HCl, chlorinated compounds and benzene are the products in this stage (McNeill et al., 1995; Miranda et al., 2001). A detailed review about the structural and mechanistic aspects of the thermal degradation of PVC can be found in the literature (Starnes Jr, 2002).

The releasing behavior of HCl is influenced by experimental conditions, catalysts/absorbents and interactions between volatiles and residues (McNeill et al., 1995; Miranda et al., 1999b; Ma et al., 2002; Wikström et al., 2003a; López et al., 2011, 2012; Zhou et al., 2016). Table 4 shows the Cl distribution in the products produced from the pyrolysis of PVC (Ma et al., 2002). More than 90% of total Cl in PVC is released as HCl in the first stage (200–360°C). A lower operating pressure like vacuum and a longer retention time at operating temperatures may enhance the release of HCl (Miranda et al., 1999b; Ma et al., 2002). The presence of oxygen (O2) in the atmosphere will lead to the formation of Cl2 from HCl through the Deacon reactions (Wikström et al., 2003a, 2003b). The addition of catalysts/absorbents (e.g., Fe2O3 and CaO) can significantly fix the HCl and change the distribution of Cl in products, as it is discussed in detail in the following part of this review.

Zhou et al. (2016) used a wire-mesh reactor (atmospheric pressure) to study the Cl content in the residue char produced from PVC pyrolysis at 200–500°C. Their results clearly proved that the DHC reaction occurred at a temperature as low as ~200°C. However, significant DHC reaction was only found at ~300°C. The Cl content in the residue was 84% of the original Cl in PVC at 300°C, then dramatically decreased to ~18% at 360°C, and finally decreased to ~0.7% at 450°C. The Cl content in char at 450°C (~0.7%) was significantly lower than the result of McNeill et al. (1995) (10% of initial Cl remained in char at 500°C) probably due to the minimized interaction between volatiles and pyrolysing particles resulted from their special designed wire-mesh reactor. The trapping effect of residue char may hinder a part of HCl emission through some chemical/physical ways by the carbon matrix or additives in PVC. Thus, the Cl in solid residue may exist in two forms: (1) organic forms binding with carbons and (2) inorganic forms like trapped HCl.

Cl exists in the liquid products in the forms of organic chlorinated compounds (e.g., benzyl chloride and chlorobenzene) and absorbed HCl. A higher temperature and a lower heating rate may promote the formation of chlorinated compounds in oil (Ma et al., 2002; Gui et al., 2013). However, the formation mechanisms of chlorinated compounds are still unclear. McNeill et al. (1995) concluded that the 1.75 wt.% chlorinated compounds in PVC pyrolysis oil were generated from the aromatization and cyclization reactions. Gui et al. (2013) suggested that the chlorinated compounds were released from char, whereas Miranda et al. (1999a) believed that the presence of secondary reactions of PVC pyrolysis products was a significant factor. The released polar HCl molecular may attack the generated double bonds, forming organic chlorinated compounds (Lingaiah et al., 2001).

The co-treatment of PVC and FAR has also been extensively studied and commercially applied (e.g., MSW/RDF incineration.}
The main interactions during co-treatment of PVC and FAR can be summarized as follows (Sørum et al., 2001; Duangchan and Samart, 2008; Kuramochi et al., 2008; Çepelioğullar and Pütün, 2014; Zhou et al., 2015a; Tang et al., 2018): (1) The DHC of PVC accelerates the FAR pyrolysis at low temperatures (<350°C) probably due to the HCl that acts as an acid catalyst; (2) A higher char yield is obtained from the co-pyrolysis of PVC and FAR. However, the reactivity and Brunauer–Emmett–Teller (BET) surface area of char produced from the mixtures are lower than theoretical results; (3) A lower oil yield is obtained from the co-pyrolysis of PVC and FAR materials; (4) FAR acts as an absorbent or as a co-treatment agent to reduce the HCl emission.

Fig. 4 summaries the Cl emission behavior during thermal processing of solid wastes. In pyrolysis/gasification, most Cl released in the forms of HCl and KCl into the syngas, whereas some organic chlorinated compounds will be formed in oil/tar and char. In combustion, more than 95% Cl is released into the flue gas and fly ash, only less than 5% Cl is retained in the bottom ash mainly in the form of inorganic chlorides. Organic chlorinated compounds in the solid wastes are almost completely destroyed, except for the formation of some trace species, e.g., dioxins.

2.3. Chlorine related reactions and challenges

The released Cl species during thermal processing participate in various reactions in the furnace, leading to several significant challenges, e.g., HTC, heavy metal evaporation and dioxin formation. This part introduces the effects of different Cl species on these reactions and challenges.

2.4. Reactions with ferrous metals

Cl species react with ferrous metals in heat exchangers causing serious corrosion problems. The sequence of reactions related with Cl that may cause HTC is presented in Fig. 5. The main factors affecting HTC are the flue gas temperature, the composition of the feedstock (contents of alkali metals, Cl and S), the velocity of the flue gas, the tube temperature and the deposit composition. In addition, a high partial pressure of O2 and the presence of SO2 may further enhance HTC.

The deposits on the heat exchangers of incinerators mainly contain K, Na, Ca, Mg, Si, S and Cl. Cl plays a key role that facilitates the transport of alkali from the inside of fuel to the surface (Baxter et al., 1998), especially K, and enhances the alkali metals emission from ash above 500°C (Olsson et al., 1997).

The gaseous Cl species (HCl and Cl2) lead to the formation of volatile metal chlorides by Eqs. (6)-(7) (Nielsen et al., 2000).

\[
\begin{align*}
M + Cl_2 &\rightarrow MCl_2 \\
M + 2HCl &\rightarrow MCl_2 + H_2 
\end{align*}
\]

where, M can be Fe, Cr and Ni, which are the main elements of heat exchangers.

The volatile metal chlorides formed diffuse to the surface of heat exchangers. A loose metal oxide layer will be formed by oxidation reactions and provides no protection against further attack (Eqs. (8)-(9)).

\[
\begin{align*}
2MCl_2 + 3/2O_2 &\rightarrow M_2O_3 + 2Cl_2 \\
2MCl_2 + 1/2O_2 + 2H_2O &\rightarrow M_2O_3 + 4HCl 
\end{align*}
\]

Eqs. (6)-(9) indicate that even a small amount of gaseous Cl (HCl and Cl2) can continuously transport the metals from the metal surface to the O2-rich outer surface resulting in serious HTC problem. However, Cl2 and HCl are regarded less corrosive than alkali chlorides in deposits due to relatively low partial pressures in the flue gas (Ma and Rotter, 2008).
The presence of alkali chlorides (KCl and NaCl) in the deposits are widely regarded as the main cause of HTC. The sulfation of deposited alkali chlorides is an important corrosion mechanism (Nielsen, 1998; Amand et al., 2006). Alkali chlorides react with gaseous SO₂ or SO₃ forming condensed alkali sulfates and HCl or Cl₂. The generated HCl and Cl₂ diffuse toward the metal surface of heat exchangers to cause corrosion (Eqs. (6)–(9)). The SO₃ pathway is believed to be faster than the SO₂ pathway. Only a small amount of SO₃ is present in the flue gas. However, SO₃ can be catalytically formed, for example by Fe₂O₃ (Nielsen et al., 2000). The sulfation reactions are expressed by Eqs. (10)–(11).

$$2\text{MCl} + \text{SO}_2 + \text{O}_2 \rightarrow \text{Cl}_2 + \text{M}_2\text{SO}_4$$  \hspace{1cm}  (10)

$$2\text{MCl} + \text{SO}_2 + 0.5\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{M}_2\text{SO}_4$$  \hspace{1cm}  (11)

where, M can be K and Na; SO₂ can be replaced by SO₃.

The presence of alkali chlorides in deposits may cause corrosion well below the melting points of the chlorides by the formation of eutectics. The melting points of pure KCl and NaCl are 772 and 801°C. But some low-temperature eutectics form the presence of other substances can be formed, such as KCl-CrCl₂ (370–374°C), KCl-CrCl₂ (462–475°C) and NaCl-CrCl₂ (437°C) (Nielsen et al., 2000). MSW and RDF/SRF, are challenging feedstock due to the presence of heavy metals, such as Zn and Pb. Deposits containing PbCl₂ or ZnCl₂ can melt at temperatures as low as 300°C (Lindberg et al., 2016). Molten phases on the surface of heat exchangers further increase the corrosion rate (Nielsen et al., 2000).

### 2.5. Reactions with heavy metals

Previous research (Table 5) reveals that the increase of Cl content from either organic chlorides (e.g., PVC) or inorganic chlorides (e.g., NaCl, KCl, CaCl₂ and FeCl₃) will increase the amount of most of heavy metals (e.g., Cd, Zn, Cr, Cu) partitioned in the fly ash by the formation of easily evaporated chlorides. These heavy metal chlorides, which can be formed through direct chlorination and indirect chlorination mechanisms, have higher vapor pressures than corresponding oxides. For indirect chlorination, chlorides firstly form HCl and/or Cl₂ by reacting with H₂O and/or O₂ (Eqs. (8)–(9)). The generated HCl or Cl₂ then react with heavy metals or heavy metal oxides to form chlorides (Eqs. (6)–(7)). The direct chlorination converts the heavy metal oxides (MO) into chlorides (MClₓ) by Eq. (12) (Jakob et al., 1996).

$$\text{xMO} + x\text{RCl}_2 + y\text{SiO}_2 \rightarrow x\text{MCl}_x + x\text{RO} \cdot y\text{SiO}_2$$  \hspace{1cm}  (12)

where, R can be K, Na, Ca, Mg and Fe. SiO₂ can be replaced by alumina (Al₂O₃), aluminum silicates, or sodium aluminum silicates.

The evaporation rate of heavy metals depends on the Cl releasing ability of chlorides and the competitive Cl affinity of heavy metals (Chan et al., 1996; Luan et al., 2013). CaCl₂, MgCl₂ and FeCl₃/FeCl₂ are generally agreed to be more effective for the evaporation of most of heavy metals than NaCl and KCl due to a relatively stronger ability to release Cl, which is favorable for the indirect chlorination. MgCl₂ is especially effective for the evaporation of Zn (Mattenberger et al., 2008; Nowak et al., 2012). NaCl and KCl have relatively higher vapor pressures than other metal chlorides, leading to the direct evaporation at high temperatures without releasing enough Cl. However, NaCl and KCl are found to be effective for the evaporation of metals with a refractory volatility, such as Cr and Cu (Mattenberger et al., 2008; Wang et al., 1999) by direct chlorination (Nowak et al., 2012). The promoting effect on evaporation by chlorides is likely to be in accordance with the evaporation ability of heavy metals themselves (Wang et al., 1999, 2001; Tang et al., 2008; Luan et al., 2013). The evaporation of Cd and Pb are more strongly promoted by chlorides than that of Ni, Cu, Zn and Cr probably due to a greater affinity to Cl.

As introduced in Section 2.2, the thermal processing of organic chlorides (mainly PVC) releases most Cl as HCl at low temperatures (200–360°C). The availability of H and Cl in organic chlorides may enhance the formation of HTC and heavy metal chlorides. As a consequence, the formation of heavy metal chlorides from organic chlorides may occur through indirect chlorination. Tang et al. (2008) observed that the evaporation of heavy metals was significantly promoted by PVC and the promoting effect of PVC on the evaporation of heavy metals was larger than that of inorganic chlorides (NaCl, CaCl₂, FeCl₃). On the contrary, other studies found that most of the inorganic chlorides (NaCl, KCl, MgCl₂, FeCl₃) were more effective than organic chlorides (PVC, C₂Cl₄, etc.) (Wang et al., 1999; Li et al., 2015). Obviously, there are some contradictions, which need to be further clarified in
future research. Future work on this area should focus on the effect of different chlorides (organic and inorganic) on heavy metal volatilization under various reaction atmospheres (reducing/oxidizing, high moisture content).

2.6. Reactions with organic matters

The released Cl species also react with the organic matters forming organic chlorinated compounds, especially PCDD/Fs, which are generated from precursors or macromolecular carbons that are catalytically chlorinated and oxidized (Yang et al., 2015). De novo process is the key mechanism in the PCDD/Fs formation during combustion (Takaoka et al., 2005). One of the essential substance of PCDD/Fs is Cl, which comes from gas phase (Cl\(_2\), HCl and Cl radical) or solid phase in fly ash (inorganic and organic chlorides). Cl\(_2\) promotes PCDD/Fs formation more than HCl during the de novo process due to a much stronger oxidizing and chlorinating ability. Although HCl is the dominant gas phase Cl species in the combustion zone, it is regarded as a weak carbon chlorinating agent. However, HCl will exhibit equal efficiency to Cl\(_2\) with the existence of O\(_2\) through the Deacon Reaction catalyzed by metal chlorides (Eq. (13)) (Wikström et al., 2003a, 2003b).

\[
4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O} \quad (13)
\]

Cl radical derived from HCl and Cl\(_2\) is also believed to be active. HCl can react with oxidizing radicals (e.g., OH) to form Cl radical (Gullett et al., 2000; Zhou et al., 2015b), as expressed by Eq. (14).

\[
\text{HCl} + \text{HO} \rightarrow \text{Cl} + \text{H}_2\text{O} \quad (14)
\]

Except for Cl species in gas phase, Cl will be accumulated in the fly ash after incineration even if the Cl content in the solid wastes is low. Relatively small concentrations of Cl in biomass (~0.5 wt.% Cl) can produce high concentrations (>10 wt.% of Cl in fly ash. The Cl concentration in MSW incinerator fly ash is typically from 1.8 to 9.1 wt.% (Zhou et al., 2015b). Previous studies (Addink et al. 1998, Wikström et al. 2003b) show that the dominant inorganic chlorides in the fly ash are more important than the gas phase Cl species in the de novo process due to being Cl donors (chlorinating agents) and acting as heterogeneous catalysts. The promoting effect of metal chlorides on dioxins formation is more dominant than that of metal oxides. Among different inorganic chlorides, CuCl\(_2\) is found to be very effective for de novo reactions. Typical reactivity orders are KCl < CaCl\(_2\) < FeCl\(_2\) << CuCl\(_2\) (Kuzuhara et al. 2003), FeCl\(_2\) < ZnCl\(_2\) << CuCl\(_2\) (Chin et al. 2012) and NaCl < MgCl\(_2\) < KCl < AlCl\(_3\) (Lu et al. 2007). Addink and Altwickier (2001) used \(^{37}\text{Cl}\) isotope to study the effect of inorganic chlorides (NaCl and CuCl\(_2\)) and organic chlorides naturally existing in the ash on the de novo formation of dioxins. They found that the most important Cl sources in the ash for de novo formation of dioxins were metal chlorides (e.g., CuCl\(_2\)) and the preexisting C-Cl bonds in the organic Cl. The alkali metal chlorides (e.g., NaCl) are observed to be insignificant sources due to the fact that the transfer of Cl between Cu and carbon is much faster than that of Na and carbon. Weber et al. (2001) subsequently gave the Cl transfer equation (Eq. (15)) from metal chlorides (e.g., CuCl\(_2\)) to the macromolecular carbon structure in the ash, which occurred very fast.

\[
2\text{CuCl}_2 + \text{C}_x \cdot \text{H} \rightarrow 2\text{CuCl} + \text{C}_x \cdot \text{Cl} + \text{HCl} \quad (15)
\]

CuCl\(_2\) chlorinates carbon to form organic chlorides like PCDD/Fs. The formed CuCl can also react with carbon to form PCDD/Fs and elemental Cu, which then reacts with Cl\(_2\) or HCl to form original CuCl\(_2\). A significant amount of CuCl is oxidized by O\(_2\) into intermediate copper oxochloride, which then reacts with Cl\(_2\) or HCl to form original CuCl\(_2\) (Takaoka et al., 2005). CuCl\(_2\) is not only a strong catalyst for Deacon Reaction (Eq. (13)), but also a Cl source for PCDD/Fs formation, since it has the ability to provide more Cl than other substances (Zhou et al., 2015b).

---

Table 5 – Literature summary about the effects of chlorides on the evaporation of heavy metals.

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Chlorides</th>
<th>Experimental conditions</th>
<th>Main conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd, Cu, Zn</td>
<td>NaCl, KCl, FeCl(_3), PVC, C(_2)Cl(_4)</td>
<td>Combustion of simulated MSW at 900°C (Wang et al., 1999).</td>
<td>1. Evaporation rate (ER) was promoted by organic and inorganic Cl, relating to availability of Cl from chlorides and affinity of a metal to Cl; 2. Effect on the volatility of medium or refractory volatility heavy metals: KCl &gt; NaCl &gt; PVC &gt; C(_2)Cl(_4); 3. ER increasing tendency by Cl: Zn &gt; Cu &gt; Cr.</td>
</tr>
<tr>
<td>Pb, Cu, Zn</td>
<td>NaCl, CaCl(_2), FeCl(_3), PVC</td>
<td>Combustion of tannery sludge at 500-900°C (Tang et al., 2008).</td>
<td>1. Effect on the volatility of heavy metals: PVC &gt; FeCl(_3) &gt; CaCl(_2) &gt; NaCl, relating to the releasing ability of Cl;</td>
</tr>
<tr>
<td>Cr</td>
<td>NH(_4)Cl</td>
<td>Combustion of sewage sludge at 850°C (Luan et al., 2013).</td>
<td>2. ER increasing tendency by Cl: Pb &gt; Cu &gt; Zn &gt; Cr.</td>
</tr>
<tr>
<td>Cd, Pb, Ni, Cu, Zn</td>
<td>MgCl(_2)</td>
<td>Combustion of sewage sludge at 1100°C (Li et al., 2015).</td>
<td>1. ER increasing tendency by addition of Cl: Cd (44.9%) &gt; Pb (6.8%) &gt; Ni (4.6%) &gt; Cr (1.7%) &gt; Cu (1.3%) &gt; Zn (1.2%).</td>
</tr>
<tr>
<td>Cr, Ni, As</td>
<td>NaCl, CaCl(_2), MgCl(_2), PVC</td>
<td>Combustion of MSW fly ash at 800, 1000 and 1200°C (Nowak et al., 2012).</td>
<td>1. MgCl(_2) was more effective than PVC for ER of most of heavy metals; 2. Chlorides especially promoted ER of mid-volatile metals Cu and Zn.</td>
</tr>
<tr>
<td>Cr</td>
<td>MgCl(_2), CaCl(_2), FeCl(_3), AlCl(_3)</td>
<td>Combustion of MSW ash at 500-1050°C (Chan et al., 1996).</td>
<td>1. Effect on Zn evaporation: MgCl(_2) = FeCl(_3) = CaCl(_2) &gt; NaCl = AlCl(_3); 2. NaCl had a high vapor pressure leading to direct evaporation without supply enough Cl; 3. AlCl(_3) was easily to release Cl at low temperatures at which the rate of chlorination of Zn was not significant.</td>
</tr>
</tbody>
</table>
3. Product quality degradation by chlorine

The released Cl species into the syngas and oil, and the retained Cl species in char lead to significant quality degradation. Impurities like Cl seriously restrict the use of MPW pyrolysis oil. The Cl content in MPW oil is typically 50–1000 ppm (Kaminsky, 1995; Bhaskar et al., 2002; Cho et al., 2010). However, Cl content in oil should not exceed 10 ppm if it is used in existing petrochemical plants (Kaminsky, 1995). If the MPW-derived oil is used in catalytic cracking to produce gasoline or to be used directly as fuel oil, the chloroorganic compounds create problems (Lingaiah et al., 2001). To overcome this, a dechlorination process is required to reduce the Cl content in liquid oil, which increases the complexity of the system and the cost.

The presence of Cl in char causes the same problems discussed in Sections 3.1–3.3 when it is used as a fuel. The forms of Cl in char are: (1) the slightly changed organic materials and char components, (2) the inorganic chlorides, and (3) the absorbed Cl species (Vassilev et al., 1999). Hwang et al. (2006) identified the contents of easily water-soluble Cl (12.82 mg/g), hardly water-soluble Cl (0.71–0.83 mg/g) and water-insoluble Cl (1.68 mg/g) in dry MSW char by water washing method. It is necessary for char to satisfy the Cl criterion of lower than 0.5 or 0.1 wt.% to be used as fuels for a shaft blast furnace or a cement kiln, respectively (Hwang et al., 2007).

HCl is the major Cl species in syngas, although Cl₂ and other trace organic Cl species like dioxins may exist. The typical concentration of HCl in the syngas is 40–700 ppmV (Ohtsuka et al., 2009). The beneficial use of syngas is extremely sensitive to HCl, which has been shown to decrease the activity of various metal catalysts during chemical synthesis like methanol synthesis and Fischer Tropsch (FT) synthesis. For example, the formation of low-melting-point chlorides or modification of electronic structure of active metal sites (Shin and Keane, 1998). Tremblay et al. (2007) tested the performance of solid oxide fuel cells (SOFCs) with 20 and 160 ppmV HCl. The impact of HCl on the SOFC performance was immediate and a 13.3%–51.5% loss in performance was observed. Substantial hot corrosion of gas turbine blades occurs with concentrations of Cl as low as 0.024 parts-per-billion (ppbV) (Woolcock and Brown, 2013). Thus, the purification of HCl in syngas is required to the level of ppm for integrated gasification combined cycle (IGCC) applications and to the level of ppb for fuel cells or chemicals synthesis applications (Baek et al., 2015).

4. Controlling methods of chlorine emission

Since the emission of Cl species causes above mentioned problems, it is essential to effectively control it. Table 6 presents a summary of the controlling methods of Cl emission during the thermal processing of solid wastes. These include pre-treatment and in-furnace methods.

4.1. Pre-treatment methods

Pre-treatment methods, such as water washing, sorting, microwave irradiation and stepwise pyrolysis, are effective for Cl emission control before the thermal processing. Water washing can remove most water-soluble Cl in solid wastes, which is especially effective for the biomass materials due to the fact that most Cl in biomass is water-soluble. Heating, bubbling, stirring and a smaller particle size can accelerate the release of water-soluble Cl (Hwang et al., 2006). Deng et al. (2013) achieved more than 80% removal efficiency of fuel Cl for wheat straw, rice straw, cotton stalk and rice hull by water washing at 30–90°C.

Sorting is the way to remove components with high Cl contents from mixed wastes, for example, PVC in MPW. However, PVC is not currently recycled and therefore mixed in the non-recyclable plastics (NRP), which account for 50–85 wt.% of MPW (Kikuchi et al., 2008; Tsiamis and Themelis, 2013). The high Cl content prohibits the usage of NRP in WTE facilities. If NRP is not well treated and finally mixed in MSW, the produced RDF may contain a high level of Cl content. Kikuchi et al. (2008) proposed a two-step sorting method to use MPW in a more efficient way: (1) PET bottles, high density PE (HDPE) bins and films were manually sorted and then distributed to the secondary market; (2) the remaining fraction (Cl = 2.2 wt.%) was separated into two groups, Cl-poor plastics (≤ 0.5 wt.%) for processing in a combustion facility and Cl-rich plastics for landfilling. They observed that the sink-float process based on the density of different plastics was efficient. The density of PVC is larger than most of other plastics, e.g., polypropylene (PP), PE, polystyrene (PS) and polyurethane (PU), resulting in the accumulation of PVC in the underflow during sink-float process. Fig. 6 presents the optimum integrated process which significantly increased the amount of Cl-poor plastics (overflow) for combustion (from 13% to 47.5%) and decreased the amount of Cl-rich plastics (underflow) for landfilling (from 52% to 16.9%).

Microwave irradiation is used to reduce Cl content of MPW by inducing the DHC of PVC plastics at relatively low temperatures (200–360°C). Microwave absorbents receive the energy to heat materials to temperatures of ~300°C, resulting in the release of most Cl as HCl. But the cost of this method is significant high and needs further investigation.

The mechanism of the stepwise pyrolysis is similar to the microwave irradiation, which is usually divided into two steps: (1) low temperature pre-pyrolysis at 200–360°C to release most Cl as HCl by DHC, and (2) normal thermal processing (pyrolysis, gasification or combustion) of the de-Cl materials at higher temperatures.

4.2. In-furnace methods

In-furnace methods focus on the reduction of Cl species into the flue gas or onto the fly ash. The addition of absorbents is the main strategy since the evolved HCl is trapped by means of physical and/or chemical adsorption and retained in the solid fraction. Metal absorbents (e.g., CaO, CaCO₃, Ca(OH)₂, Na₂CO₃) (López et al., 2011), natural minerals (e.g., dolomite) (Karayildirim et al., 2006), biomass (especially woody biomass) (Kuramochi et al., 2008) and petrochemical residues (Ali and Siddiqui, 2005) have been used as effective absorbents. The absorption/fixation efficiency depends on the Cl content in raw materials, the absorbents (type and amount) and the operating conditions.
Horikawa et al. (1999) compared the effects of nine metal oxides on the fixation of HCl evolved from the degradation of PVC at 300°C. CuO, MgO and CaO exhibited excellent fixation ability of HCl with a fixation ratio of 26.5%–68.2%.

Calcium-based absorbents are the most popular choices due to abundant sources, relatively cheap price and high efficiency by reactions presented in Eqs. (16)–(18).

\[
\text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} \quad (16)
\]

\[
\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \quad (17)
\]

\[
\text{Ca(OH)}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} \quad (18)
\]

Table 6 – Literature summary about the controlling methods of Cl emission during thermal processing of solid wastes.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Experimental conditions</th>
<th>Main conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-treatment Water washing</td>
<td>Deionized water; Wheat straw, rice straw, corn stalk, cotton stalk, candlenut wood and rice hull at 30–90°C (Deng et al., 2013).</td>
<td>1. Washing removed more than 80% of fuel Cl for wheat straw, rice straw, cotton stalk and rice hull; 2. For corn stalk and candlenut wood, removal efficiency of Cl were 28%–56% and 49%–55%, respectively.</td>
</tr>
<tr>
<td>Sorting</td>
<td>Classifying pre-sorted mix plastics into two groups: Cl-poor and Cl-rich plastics (Kikuchi et al., 2008).</td>
<td>1. By sorting mixed plastics into two groups to get more Cl-poor plastics (Cl &lt;0.5 wt.%) for waste-to-energy (WTE) application and less Cl-rich plastics (Cl ~4.6 wt.%) for landfilling.</td>
</tr>
<tr>
<td>Microwave irradiation</td>
<td>Organochloride waste mixture before they were mixed to form SRF at 220–300°C (Liu et al., 2017).</td>
<td>1. 280°C is the optimal temperature; 2. A highest dehydrochlorination (DHC) ratio of 87% was achieved; 3. Cl content of SRF decreased from 1.58% to 0.328%.</td>
</tr>
<tr>
<td>Stepwise pyrolysis</td>
<td>Mixed plastics (PVC, polystyrene (PS), polyethylene (PE), polyethylene terephthalate (PET)) at 275–300°C for 30–120 min (López et al., 2011).</td>
<td>1. After stepwise pyrolysis at 300°C for 60 min, Cl content in oil decreased to 0.2 wt.% (60% reduction). Cl content in solid is the lowest of 0.1 wt.% (66.7% reduction).</td>
</tr>
<tr>
<td>In-furnace Absorbents: CaCO₃, CaO, Ca(OH)₂, Na₂CO₃, NaHCO₃, dolomite, etc.</td>
<td>CaCO₃; Mixed plastics (PVC, PS, PE, PET) at 500°C for 30 min with a stoichiometric relation CaCl of 3:1 (López et al., 2011).</td>
<td>1. CaCO₃ decreased Cl in gas by 59%, whereas increased Cl in oil and solid by 20% and 2.1 times, respectively; 2. Combination of stepwise pyrolysis and absorbent is not worthwhile due to no reduction of Cl in oil and small reduction (23%) of Cl in gas.</td>
</tr>
<tr>
<td>Co-treatment: Cl-rich materials (e.g., plastics, FW and AR) with Cl-poor materials (e.g., FR, oil shales and coal)</td>
<td>Co-pyrolysis of demolition wood and PVC film with Cl contents of 0.5 -6 wt.% at 600°C (Kuramochi et al., 2008).</td>
<td>1. HCl emission was reduced by the presence of wood; 2. Hemicellulose significantly reduced HCl emission by fixing most Cl molecules into residue.</td>
</tr>
<tr>
<td>Catalysts: ZSM-5 zeolite, red mud (Fe₂O₃, Al₂O₃, etc.), Zn-Al catalysts, Si-Al (SAI) catalysts, Mg-Zn catalysts, iron oxides, etc.</td>
<td>ZSM-5 zeolite; Mixed plastics (PVC, PS, PE, PET) at 440°C for 30 min (López et al., 2012).</td>
<td>1. Catalyst decreased Cl in gas by 81%, whereas increased Cl in oil and solid by 500% and more than 300%; 2. Combination of stepwise pyrolysis and catalyst reduced Cl in oil by 75% compared with catalytic pyrolysis, but still increased Cl in oil by 50% compared with conventional thermal pyrolysis; 3. Combination of first a low temperature step without catalyst, and second the catalytic pyrolysis step can avoid the poison effect of HCl on catalyst.</td>
</tr>
<tr>
<td>Al-Zn composite catalyst; PE/PVC at 420°C; Polypropylene (PP)/PVC at 380°C and PS/PVC at 360°C (Tang et al., 2003).</td>
<td>1. Al-Zn composite catalyst accelerated degragation; 2. Catalyst showed good ability for fixation of HCl; 3. Catalyst decreased Cl content in oil.</td>
<td></td>
</tr>
</tbody>
</table>
boiler. Aho and Ferrer (2005) carried out the co-combustion of meat and bone meal (MBM, Cl-rich materials) with three types of coal (Cl-poor materials) in a pilot scale circulating fluidized bed (CFB) reactor. They indicated that coal ash contains elements (Al, Si and S) that were able to trap alkali chlorides. The Cl concentration in the deposits can be reduced through the increasing concentration of SO2 in the gas by sulphation reactions (Eqs. (10)–(11)). Aluminum silicates in coal ash can also help to trap alkalis chlorides through Eqs. (19)–(20) (Aho and Ferrer, 2005). Other elements, such as Ca, Fe and P in the ash of sludge, coal and biomass are also important for alkali chlorides capture during co-combustion with Cl-rich materials (Kassman et al., 2013).

\[
\text{Al}_2\text{Si}_3\text{O}_6\text{OH}_4 \rightarrow \text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O} \quad (19)
\]

\[
\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{MCl} + \text{H}_2\text{O} \rightarrow \text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{HCl} \quad (20)
\]

where M can be K and Na.

Metal oxides in the Cl-poor materials may play an important role as absorbents when they are co-treated with Cl-rich materials. Tiikma et al. (2006) attributed the fixation of Cl evolved from co-pyrolysis of PVC waste and Estonian oil shales (Dictyonema shale, Kukersite, its semicoke, ash and oil coke) at 520°C to the existence of CaCO3, free CaO and shales (Dictyonema shale, Kukersite, its semicoke, ash and Cl-rich materials. Tiikma et al. (2006) attributed the fixation of Cl to the Cl-poor materials of PVC. Blázso and Jakab (1999) identified that metals (aluminum, zinc, iron) and oxides of large enough metal ion radius (ferric oxide and titanium dioxide) reduced the onset temperature of DHC, by attracting Cl and by weakening the C–Cl bonds in PVC. Depressed HCl formation was also found in those cases due to the chlorides formed (iron, zinc, Ca/Zn carboxylate, cupric oxide and titanium dioxide), which however lowered the activity of catalysts. López et al. (2012) observed a negative influence from the stepwise pyrolysis of MPW on the ZSM-5 zeolite catalyst activity due to the evolved HCl. The optimum process in terms of higher quality and lower Cl content of the products was the combination of a low temperature stepwise pyrolysis without catalyst, which was followed by the catalytic pyrolysis step.

The effect of absorbents/catalysts on the Cl content of the oil produced is contradictory in the literature. López et al. (2011, 2012) found that the Cl content of oil produced from the pyrolysis of MPW increased dramatically when using CaCO3 or ZSM-5 zeolite as absorbent/catalyst. Similar observations were made by Yanik et al. (2001) who used red mud, SiO2–Al2O3 catalyst and γ-Fe2O3 as absorbents/catalysts. This phenomenon was explained by the retention of HCl by the absorbents/catalysts that enabled the polymer cracked products to react with HCl, thereby generating chlorinated compounds. However, Uddin et al. (1999), Tang et al. (2003), Zhou et al. (2004) and Shah et al. (1999) got decreasing Cl contents in the oil when Si-Al catalyst, FeOOH, Fe2O3, Al-Zn catalyst, Mg-Zn catalyst and Na2CO3 were used. Therefore, the effect of different absorbents/catalysts on the formation of chlorinated compounds in liquid products (oil or tar) requires further research and clarification.

5. Concluding remarks

This paper reviewed the comprehensive Cl fate during the thermal processing of solid wastes, from sources, emission behavior, reactions and related challenges, to controlling methods. The main conclusions of this study are:

1. Combustion coupled with ion chromatography is the most recommended method for the determination of total chlorine content in solid wastes. Forestry and agricultural residues and food waste are the major inorganic Cl sources. PVC is the major organic Cl source.

2. In pyrolysis/gasification, most Cl in solid wastes is released into the syngas in the forms of HCl and KCl, whereas some organic chlorinated compounds are formed in oil/tar and char. In combustion, more than 95% Cl is released into the flue gas (including fly ash), only less than 5% Cl is retained in the bottom ash in the form of inorganic chlorides.

3. Direct corrosion by HCl and Cl2, sulfation reactions of deposited alkali chlorides and molten deposits are the three main causes for high temperature corrosion. Alkali chlorides play the most important role. Cl is
effective for the promoting of most of heavy metals evaporation by formation of heavy metal chlorides through direct or indirect chlorination. Both gas phase and solid phase Cl promote dioxin formation. Chlorides in fly ash particles are more important than gas phase Cl due to dual functions of Cl donors and catalysts.

(4) The presence of Cl degrades the quality of the pyrolysis and gasification products (oil, char and syngas).

(5) Pre-treatment and in-furnace methods are effective for Cl emission control. The former is costly and the latter creates some negative effects, e.g., the disposal of used absorbents/catalysts and the increase of Cl content in oil.

Although there are numerous studies on the Cl fate during thermal processing of solid wastes, there are still several contradictory or unclear aspects, which require further research.

(1) The formation mechanism of organic chlorinated compounds in the oil produced from pyrolysis and the effects of absorbents/catalysts.

(2) The effects of different chlorides (organic and inorganic) on the evaporation of heavy metals.

(3) The dataset concerning the effects of reaction atmospheres on the Cl fate during the thermal processing of solid wastes is incomplete. For example, the Cl emission behavior of PVC in oxidizing atmosphere and the evaporation of heavy metals when chlorides are present in reducing atmosphere are not well researched.

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