



Chlorine characterization and thermal behavior in MSW and RDF

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ARTICLE INFO

Article history:

Received 12 July 2009

Received in revised form 17 January 2010

Accepted 21 January 2010

Available online 28 January 2010

Keywords:

Chlorine

Municipal solid waste (MSW)

Waste incineration

Analytical methods

Volatilization

Corrosion

ABSTRACT

Chlorine, as a key element causing high temperature corrosion and low efficiency in waste-to-energy plants, and its thermal behavior has widely drawn attention. In this study, the chlorine content in eight fractions of municipal solid waste (MSW) was quantified and characterized using five analytical methods. The influence of the operating temperature, and fuel additives like sulfur and silica on the volatilization of chlorine in combustion process was also investigated. The results showed: these fractions cover a wide range of chlorine content from 0.1 wt.% in wood to >6 wt.% in non-packaging plastics (dry basis). Polyvinylchloride (PVC) from packaging, electrical wire insulation etc. in plastics and chloride salts (mainly NaCl) in kitchen waste are the main sources of organic and inorganic chlorine. The increase of the operating temperature from 700 °C to 1000 °C has more influence on the HCl formation for kitchen waste than that for PVC. Sulfur addition leads to 20–40% higher HCl formation rate in most fractions. Silica supports the chlorine release at relatively low temperatures between 700 °C and 850 °C. These findings enhance to understand the thermal behavior of chlorine in MSW and RDF (refuse derived fuel) in waste-to-energy plants and lead to the suggestions for a fuel management for waste derived fuels in order to avoid chlorine induced corrosion.

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1. Introduction

Growing quantities of municipal solid waste (MSW), rapidly declining availability of sanitary landfill sites, increasing costs for treatment and disposal, and more strict environmental regulations have restricted the development of landfills in many countries. Incineration, with the advantage of energy recovery and volume reduction (~90%) [1], is an alternative technology in future waste management. To improve the combustion behavior of waste, non-combustibles are removed and combustibles are processed to refuse derived fuel (RDF) as a fuel product, which has more uniform particle size distribution and higher heating value than untreated MSW [2–4]. Solid recovered fuel (SRF) is referred to as a RDF with described properties meeting defined quality criteria (CEN/TS 15359:2006 Solid recovered fuels—Specifications and classes). Nowadays, around 130 million tonnes of MSW and RDF are incinerated annually all over the world in over 600 waste-to-energy (WTE) plants producing heat and power [1]. However, WTE plants have the weakness of a low energy efficiency of 15–25% (at 420 °C and 40 bar steam parameters) [5], due to the low steam temper-

ature to prevent severe boiler corrosion, fouling, and slagging [6]. New WTE plants have a maximal reachable electrical efficiency of 30% (at 580 °C and 289 bar steam pressure) as shown at the Amsterdam MSW incinerator [7]. Compared to that, hard coal-fired power plants in Germany have an average efficiency of 37% [8] that can be improved up to 47% [9]. The high chlorine content in MSW & RDF plays an important role in the corrosion mechanism. A high concentration of chlorine during combustion stimulates the formation of eutectics in fly ashes with a relatively low melting point. These fine fly ash particles condense on the superheaters and low melting chlorides are enriched in the deposits with the consequence that, above 450 °C, hot superheater tubes are sensitive to chlorine induced corrosion [10] leading to unscheduled shutdowns of the entire operation. To minimise the costly chlorine-associated problems, it is important to study the chlorine concentration in waste, chlorine species and thermal behavior of chlorine.

MSW and RDF are quite heterogeneous and their complex matrix leads to the great challenge for quality assured analytical methods in determining chlorine concentration. First standards to determine total chlorine content (TCC) were developed based on coal, afterwards modified by CEN (European Committee for Standardization) for MSW (CEN/TC 292), for biofuel (CEN/TC 335) and for SRF (CEN/TC 393). For SRF, the combustion in a calorimetric bomb is a standardized method to determine TCC (CEN/TS 15408:2006). For biofuel, CEN/TC 335 developed a “quick test” for water-soluble compounds (CEN/TS 15105:2005). In practical

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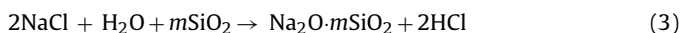
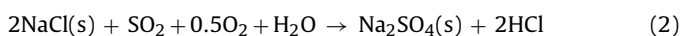
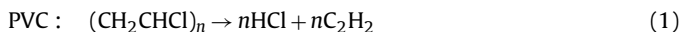
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Table 1
Formation constants (K_p) of HCl from different inorganic chlorides at different temperatures [21].

Formation constants (K_p)	700 °C	800 °C	900 °C	1000 °C
NaCl	6×10^2	5×10	7	1
KCl	1×10^3	1×10^2	2×10	5

research, MSW was often sorted into several fractions, which were further determined TCC by various analytical methods, such as the oxygen bomb [11,12], improved quartz furnace methods with a differentiation of combustible and incombustible chlorine [13,14], water extraction to distinguish water-soluble and water-insoluble chlorine [15], Schoeniger flask method, elemental analyzer (EA) and X-ray fluorescence [16]. However, only the TCC is not sufficient to predict the thermal behavior of chlorine in the combustion process, and detailed data characterizing the TCC are lacking. It is useful to provide information of the chlorine species in waste, such as organic and inorganic chlorine and combustible and incombustible chlorine in this study.

In waste, chlorine has two main sources: plastics, mainly polyvinyl chloride (PVC), as the source of organic chlorine and kitchen waste as the source of inorganic chlorine, which both have a distinctly different thermal behavior. Organic chlorine compounds have a low binding energy (PVC 397 kJ/mol), compared to inorganic chloride salts (NaCl 787 kJ/mol, KCl 717 kJ/mol) [2]. In combustion process, the PVC starts to release HCl between 200 °C and 360 °C [17] and near completely decomposes at 550 °C [18], due to a thermal decomposition combined with a de-polymerization. This thermal transformation of chlorinated hydrocarbons is shown in Eq. (1) [19]. NaCl and KCl in waste volatilize at 800 °C [20] and partly transform into HCl. Table 1 shows the equilibrium constant (K_p) of HCl from NaCl and KCl depending on the temperature. Chloride is transforming to HCl easier as the equilibrium constant is increasing. On the other hand, less HCl was formed as the equilibrium constant become smaller at higher temperature [21]. Kanter et al. [22] investigated how NaCl transforms into HCl, and found that after 1.5 h at 780 °C 55% of the NaCl intake was emitted as HCl, while 40% remained in the sand. Wang et al. [23] found that the conversion of NaCl into HCl is much lower than that of PVC and that temperature plays a key role in the chlorine volatilization both for PVC and NaCl. The low recovery of chlorine (refers to $[\text{HCl in the flue gas}]/[\text{total Cl input}] \times 100$) from inorganic chloride was associated with most chlorine remaining in the sand bed, supposedly due to sintering effects [18]. SO_x has an effect to improve the conversion rate of NaCl to HCl and prevents chlorine from being bound in the boiler deposits (Eq. (2)) [24]. Moreover, some inorganic materials such as SiO_2 and Al_2O_3 play a role in the formation of HCl from NaCl (Eq. (3)) [23].



(Na could also be replaced by K).

MSW and RDF are characterized by undefined chlorine contents, undefined chlorine species, and a varying fuel matrix in terms of its elemental composition. Few studies [13,16] did consider the influence of the fuel matrix on chlorine volatilizations. Thus, there is still a need for analytical measurements, as well as for studies on chlorine thermal behavior during combustion process in real waste samples. This study bridges the “classical” approach of chlorine characterization as the total content and the investigation of the thermal chlorine behavior in different waste matrices. The three objectives of the investigations are: to seek a rapid, accurate, quantitative method for the determination of chlorine in MSW and

RDF; to characterize, in typical waste fractions, the chlorine species which have further influence on thermal behavior of chlorine during combustion process; to study the chlorine thermal behavior, especially the volatilization process. To perform this work, eight waste fractions relevant to chlorine content, were chosen for further analytical investigation. Five analytical methods (calorimetric bomb, Schoeniger flask method, elemental analyzer, elution test and muffle furnace) were compared. Afterwards, the effects of operating parameters such as temperature, sulfur and silicon addition, on chlorine volatilization were studied in order to give recommendations for the reduction of the corrosion risk by an adapted fuel and combustion management.

2. Material and methods

2.1. Material

For this study single waste fractions after sorting out from mixed residual household waste were chosen in order to achieve a better understanding of the various chlorine sources in waste. In two sorting campaigns in Berlin and Dresden, respectively, 1 tonne of residual household waste was hand-sorted into approximately 50 fractions for waste characterization. Kitchen and garden wastes were chosen as the source of inorganic chloride salts (NaCl, KCl) and 3 types of plastic as the source of organic bound chlorine. Since all samples were sorted out of mixed residual waste from private households, the samples still contained the impurities resulting from wet adhesions. Paper, textiles and wood fractions were also investigated, as all of them are relevant to the TCC.

- Household kitchen waste—Org1.
- Household garden waste—Org2.
- Packaging plastic bottles and containers—PI1.
- Packaging plastic films and bags—PI2.
- Non-packaging plastic products—PI3.
- Paper, cardboard—Paper.
- Textile including clothes, carpets, old shoes and others—Textiles.
- Wood—Wood.

These fractions cover a wide range of chlorine concentration varying from 0.1 wt.% (dry basis)¹ to 10 wt.% [2,16], which represent large variations in fuel composition in WTE plants. Moreover, some of these are the target fractions to process household waste to RDF/SRF as well.

2.2. Sample preparation

Since samples must be representative and homogeneous for test portions of less than 100 mg, shredding and grinding are important procedures in sample preparation. As a first step, 20–100 kg of raw samples were size reduced down to less than 25 mm using a shredder (UniCut, MeWa). After pre-shredding, the original sample was, following the quartering principle, manually divided into increments. Representative mass reduction was repeated until reaching three sub-samples of 0.5–2.0 kg, which were independently further dried till reaching a constant weight at 70 °C, and ground to the maximum particle size of 1 mm by a cutting mill (SM2000, Retsch). In a next step all three sub-samples were further ground to a particle size <250 μm by an ultra centrifugal mill (ZM1000, Retsch) to improve the homogeneity of the sample. Fig. 1 summarizes the sample preparation procedure as indicated in the previous publication [16].

¹ If without extra explanation, the sample for analysis is in dry basis.

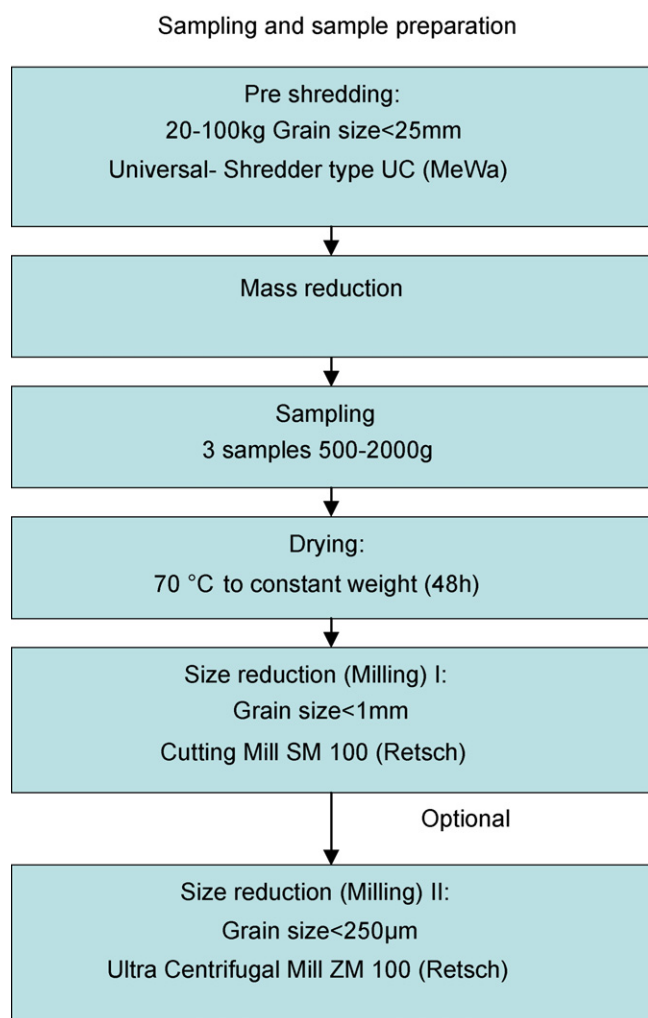


Fig. 1. Sample preparation.

For the elution test, the pre-shredded and dried matter (particle size < 25 mm) was used. After the subsequent elution and decantation, the remaining sample was dried again and ground < 1 mm for further analysis of the eluted solid matter.

2.3. Analytical methods

Factors such as availability of the equipment, speed, simplicity, accuracy, precision and detection limits all influence the choice of analytical techniques. In this study, bomb combustion (BC) and Schoeniger flask combustion (SFC) as the standardized methods are chosen to detect the TCC. The elemental analyzer method (EA) was improved to not only determine chlorine concentration, but also to determine the chlorine bond in the ash. The muffle furnace method was primarily used in this study for chlorine determination to detect chlorine bond in ash. An elution test provides the possibility to distinguish organic and inorganic chlorine.

2.3.1. Bomb combustion (BC)

The combination of bomb combustion and ion chromatography (IC) for the determination of chlorine in SRF has been standardized by European committee for standardization (CEN/TS 15408: 2006). The principle of BC is the complete destruction of the organic matter of waste through incineration. The high combustion temperature of 1000–1500 °C and oxygen partial pressure of 30 bars ensure the

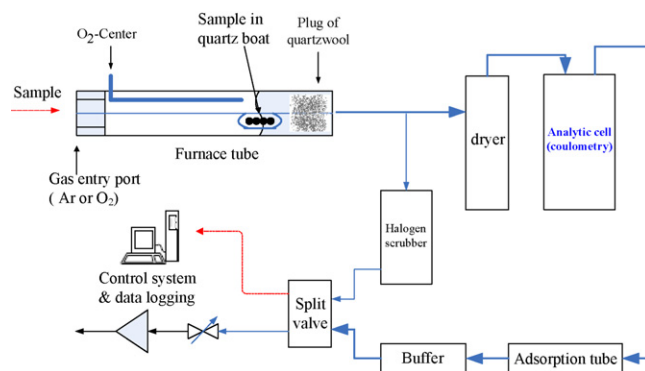


Fig. 2. Flow diagram for analyzing chlorine by elemental analyzer.

transfer of organic halogen into the corresponding halogenides and their absorption in the solution.

An oxygen bomb (IKAC 7000) with stainless steel reactor (210 ml volume) is used, with 10 ml of an absorbent solution (2.52 g/l Na₂CO₃, 2.54 g/l NaHCO₃, 25 ml 30% H₂O₂ in 1 l de-ionized water). After combustion of 100–500 mg test sample, the bomb should be slightly shaken to improve the absorption efficiency. After repeated rinsing, the solution with the absorbed Cl⁻ is transferred into an aliquote volume. After filtration the chlorine concentration is determined by IC (Metrohm® IC 732), which consists of an anion-exchange column (Metrosep-Anion-Dual2, 75 mm × 4.6 mm i.d.), a suppressor, a conductivity detector with thermostat and an injection valve with a 20 µl sample loop.

2.3.2. Schoeniger flask combustion (SFC)

Oxygen flask combustion apparatus according to Schoeniger for the fast and economical combustion decomposition of organic substances can be used for subsequent analysis of hetero elements such as F, Cl, Br, I, S, P. The SFC method is a well proven technique for the combustion and subsequent analysis of chlorine [25]. This method was standardized by the ASTM (American Society for Testing and Materials) E 442 and withdrawn 1997 [26]. Specifically for the characterization of solid waste, a European Standard (EN 14582: 2007) exists. The combustion of the sample involves placing 20 ml of absorbent solution (2.52 g Na₂CO₃, 2.54 g NaHCO₃, 25 ml 30% H₂O₂ in 1 l de-ionized water) in a flask. 50–100 mg of test sample is placed in a cotton wool plug (30–40 mg) which is placed in a platinum wire attached to the stopper of the flask. The flask is flushed with oxygen and the stopper is afterwards placed in the flask. After combustion, one should wait about 20 min and shake the flask carefully. Afterwards, the absorbent solution is transferred to a 100 ml volumetric flask and the Schoeniger flask rinsed with de-ionized water. The chlorine concentration in the absorption solution is analyzed by IC.

2.3.3. Elemental analyzer (EA)

An automated instrumental analyzer—the elemental analyzer (Analytik Jena multi® EA 2000) is used, as shown in Fig. 2. The sample is burnt in an oxygen rich atmosphere in a quartz tube covered by fine quartz sand to improve the heat transfer and to avoid uncontrolled combustion when suddenly meeting oxygen. The temperatures are chosen with 700 °C, 850 °C and 1000 °C. The estimated chlorine amount per sample is kept almost constant by varying the weight of the samples. For the efficient combustion a test sample weight between 30 and 150 mg is recommended. After combustion, the emission gas flow is split and, after drying, its HCl content is determined by a coulometric detector. The sample gas splitting option allows for the measurement of samples with a wide range of chlorine content from 30 to 1000 µg.

After combustion, ash residues remain in the sample/combustion vessel. To detect not volatilized chlorine, following additional procedure is developed to distinguish chlorine in the gas and chlorine in the residues, named combustible chlorine and incombustible chlorine, respectively. The residues are carefully rinsed with de-ionized water and diluted to 50/100 ml, since the residual ash is suspected to contain water-soluble chlorine. The solution is shaken manually for 2 h to dissolve the residual chlorine sufficiently. After filtration, the chloride concentration in the solution is measured by IC. Chlorine condensing on the tube surface is not considered in this work neither as combustible nor as incombustible content.

To determine the influence of sulfur components in the waste and SO_x influence on chlorine volatilization, additional $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ as a source of sulfur was put on the surface of samples. The operating condition were kept constant as in the previous test the same with previous tests.

2.3.4. Muffle furnace

The muffle furnace, with a 30 times larger amount of sample than EA with 100 mg sample, has a good temperature control. It is adopted to analyze non-volatile content of chlorine. The experiments are carried out keeping constant air flow, at various temperatures (700, 850, and 1000 °C) for 2 h. Five independent tests for each fraction are conducted. After combustion, until the

temperature in the chamber decreases to room temperature, the crucibles are taken out. The ashes are transferred and leached with 100 ml de-ionized water. After continuous shaking for 2 h and filtering the solid particles, the Cl content in the solution is finally detected by IC. Assuming the easily solubility of chlorides in ashes, the results can also be considered as incombustible chlorine. The combustible chlorine can be calculated as the difference between total chlorine content and incombustible chlorine in the original sample.

2.3.5. Elution procedure

For the elution procedure 100 g of dried sample with a particle size of <25 μm and 1 l de-ionized water are continuously shaken in a 2 l PE-Bottle for 24 h. The water is then decanted as carefully as possible with a sieve <200 μm . The bottle with the wet sample is weighed, considering the adhering water has already dissolved chlorine. For the second elution, fresh water is now added to make up the volume to 1 l (taking into account the adhering water). This procedure repeats twice. After filtration at 20 μm the chloride concentration in all liquid elution samples is measured by IC. After the last elution, the dewatered sample is dried and ground down to a particle size <1 mm. The insoluble chlorides in dried solid matter are quantified by SFC. The procedure is shown in Fig. 3 [27]. Water-soluble chlorine released by elution procedure is referred to as inorganic chlorine and non-water-soluble

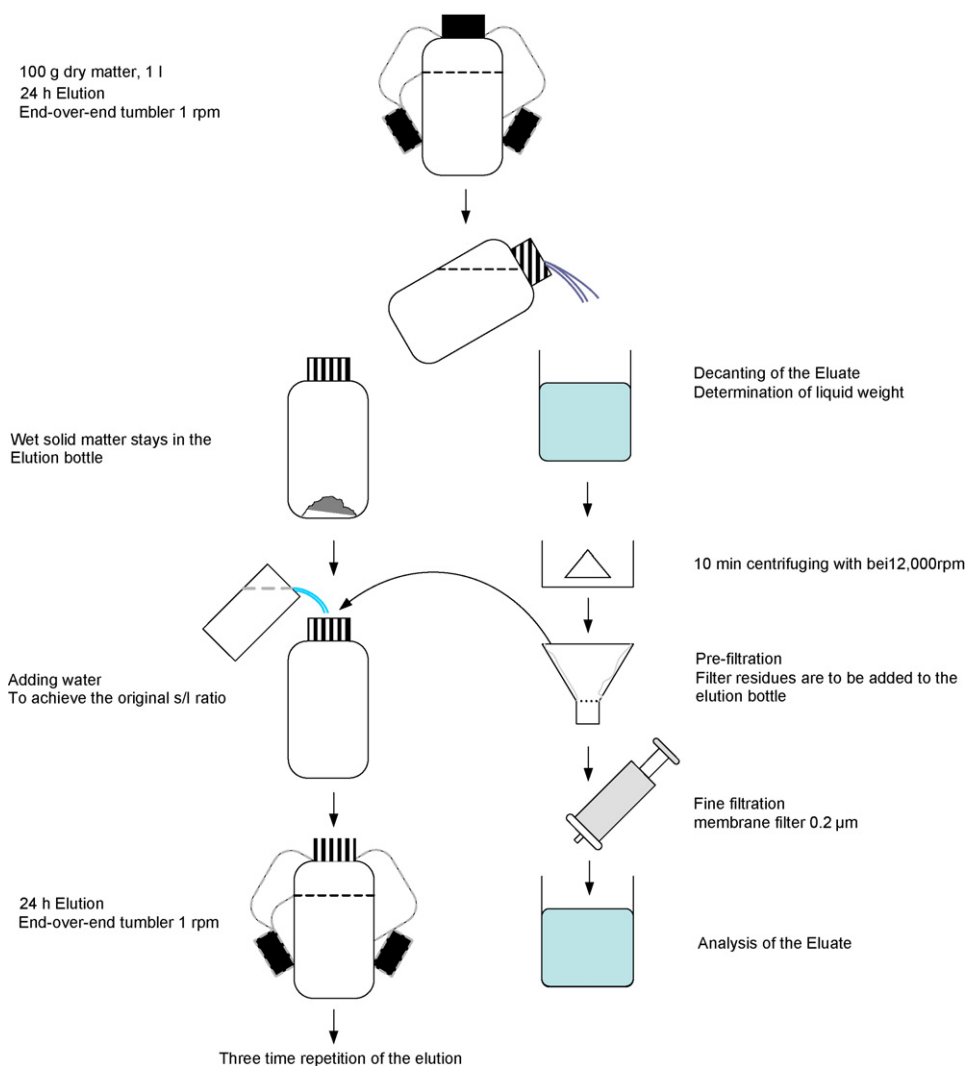


Fig. 3. Elution procedure [27].

chlorine in solid matter is referred to as organic chlorine in this work.

2.3.6. Overview of the experimental set-up

Table 2 compares the set up and the conditions of each analytical method.

3. Results

3.1. Chlorine content

3.1.1. Comparison of the detection of TCC by analytical methods

The detected TCC in relevant MSW fractions by four analytical methods is shown in Fig. 4. There are significant differences among the chlorine content in the regarded fractions, varying from 0.1 wt.% in wood to >6.0 wt.% in non-packaging plastics (PI3). 1.3 wt.% chlorine content in textiles is rather high compared to other fractions, because old shoes contain PVC as well. Generally, the plastics have a larger standard deviation than other fractions due to their heterogeneous characteristics.

The systematic differences among analytical methods are low for fractions with a low chlorine content (<0.3 wt.%), such as Org2, Paper and Wood, and increase with the increasing chlorine content. In most cases, SFC detects more chlorine in fractions with a high chlorine content, especially non-packaging plastics. The elution test detects clearly more chlorine in organic kitchen or garden waste (Org1 and Org2), which proves the assumption that a large amount of inorganic chloride salts exist in organic waste and can be water soluble.

3.1.2. TCC and chlorine load in waste

Since eight chlorine relevant fractions were chosen among 50 fractions of residual household waste, only the minimum chlorine load in the mixed household waste can be assessed and the specific contribution of each fraction can be determined. Table 3 shows the weight percentage of each fraction in raw waste, as determined with a sorting analysis in Germany, their water content and the mean of TCC in dry basis by three analytical methods (SFC and BC, and EA), and the calculated TCC in mixed household waste. The minimum TCC is 2.8 mg/g raw waste by SFC and BC, 2.4 mg/g raw waste by EA on the basis of the given waste composition.

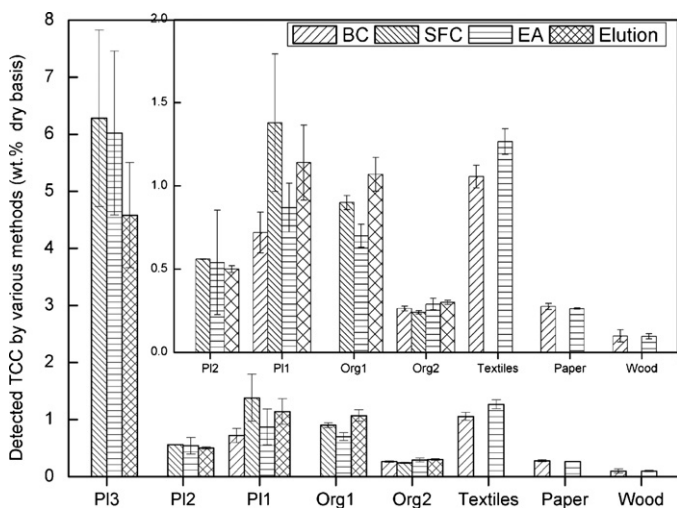


Fig. 4. Detected TCC in relevant waste fractions by four analytical methods (no. of tests = 3–6 per fraction, temperature for EA = 850 °C, the error bars represent standard deviation). Note: the smaller picture shows the samples PI2, PI1, Org1, Org2 textiles, paper and wood with a different y-axis scale.

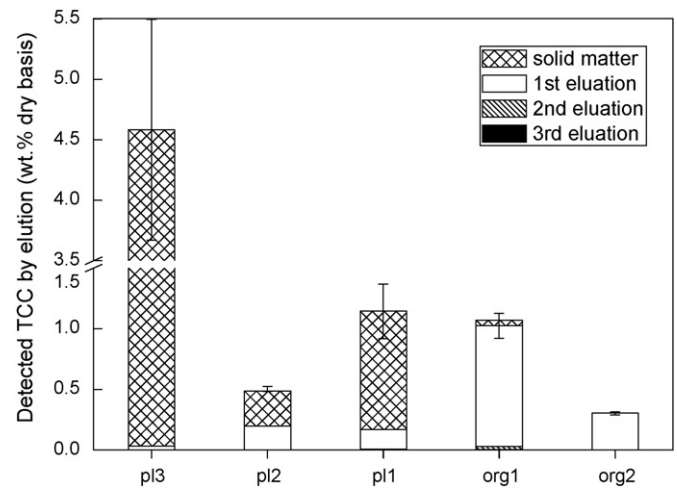


Fig. 5. Chlorine content and differentiation of the species in relevant waste fraction determined by a three-step elution test and determination the insoluble chlorine content in the solid matter by SFC (no. of tests = 3 per fraction, the error bars represent standard deviation of the TCC).

Table 3 also shows chlorine specific contribution of each fraction to the chlorine load (measured by EA). Kitchen waste has the largest contribution of nearly 45% because of the biggest weight percentage. Plastics (PI1, PI2, PI3 in total) contribute one third to the TCC, largely through PI3 with approximately 20%. Moreover, textiles account for more than 15% of the chlorine load in the waste streams, since textiles also contain the old shoes that are potentially made of PVC. On the other hand, textiles may absorb the adherence from kitchen residues when collected in mixed waste. Garden waste (Org2), paper and wood in total contribute only less than 10% to the TCC in waste. The TCC in MSW depends mainly on the varying composition of waste and its weight percentage of chlorine relevant fractions.

3.2. Chlorine species: organic chlorine and inorganic chlorine

To predict the thermal behavior of chlorine in MSW and RDF in incineration process, knowledge of TCC in each fraction is insufficient. A differentiation of organic bound chlorine and inorganic chloride salts allows for an estimation of the corrosion potential of fuel.

Chlorine is characterized and quantified in terms of its water solubility, which is grouped in inorganic chlorine (soluble after 3 steps of elution) and organic chlorine (non-soluble solid residues), respectively. As presented in Fig. 5, the organic chlorine and inorganic chlorine for PI3, PI2, PI1, Org1, Org2 is 4.5 wt.% and 0.03 wt.%, 0.3 wt.% and 0.2 wt.%, 1 wt.% and 0.15 wt.%, 0.05 wt.% and 1 wt.%, <0.01 wt.% and 0.3 wt.%, respectively. In the first elution step, approximately 95% of the leachable chlorine is released. Even after three elution steps non-leachable, supposedly organic bound chlorine, is still fixed in the solid matter. This phenomenon is clear in all plastic fractions and less in the samples Org1 and Org2.

Non-packaging plastics (PI3) have a significant organic chlorine content which is not soluble after repetitive washing. Kitchen and garden waste (Org1, Org2) consist of over 95% inorganic chloride salts. PI1, PI2 have two sources of chlorine: a certain content of organic bound chlorine and inorganic chlorine (mainly NaCl) from food adhesions. The soluble chlorine load in PI1 and PI2 deriving from contamination by kitchen waste (Org1) accounts for about 15 to 40% of the TCC in both fractions. Films (PI2) have lower organic bound chlorine content but more adhesions of inorganic chlorides than bottles and containers (PI1) due to the bigger material surface of films.

Table 2
Comparisons of chlorine analytical methods.

Methods	Bomb combustion	Schoeniger flask combustion	Elemental analyzer (quartz tube furnace)	Muffle furnace	Elution test
Standardized	CEN/TS 15408:2005	ASTM E 442, BS EN 14582	–	–	CEN/TS 15105: 2005 (solid biofuel)
Device type	IKA C 7000	Elementar, Mikro K	EA 2000	Naber N 60 H, 10 kW, T_{max} : 1340 °C	–
Sample weight (g)	0.1–0.5	0.050–0.1	Up to 3	~3	100
Temperature (°C)	1000–1500	Depend on sample matrix	Up to 1000	Up to 1200	–
Air pressure (ATM)	30	1	1	1	–
Absorbent solution	2.52 g/l Na ₂ CO ₃ , 2.54 g/l NaHCO ₃ , 25 ml 30% H ₂ O ₂ in 1 l de-ionized water	De-ionized water			
Absorption volume (ml)	10	20	50	100	1000
Time for preparation (min)	15	15	0	0	24 h
Time for analysis (min)	20	20	10	180	30
Detection item	Absorption + gas	Absorption	Gas + residue	Residue	Liquid elution + solid matter
Chlorine detection	Ion chromatography	Ion chromatography	Coulometer + ion chromatography	Ion chromatography	Ion chromatography + Schoeniger flask combustion
Chlorine species	Total chlorine content	Total chlorine content	Combustible chlorine + incombustible chlorine	Incombustible chlorine	Organic chlorine + inorganic chlorine

Table 3
Contribution of a single waste fraction to chlorine content and chlorine load in residual household waste.

Fraction	Weight percentage: W_t (wt.%)	Water content: M (%)	Chlorine content in dry basis fraction: Cl (mg Cl/g fraction)		Chlorine content in raw waste ^a = $W_t \times Cl \times (1 - M)$ (mg Cl/g raw waste)		Specific contribution to Cl load (%)
			SFC and BC	EA	SFC and BC	EA	EA
PI1	1.7	19	13.8 (SFC)	8.7	0.19	0.12	5.0
PI2	5.1	22	5.6 (SFC)	5.4	0.22	0.21	8.9
PI3	0.8	2	62.8 (SFC)	60.2	0.49	0.47	19.5
Org1	34.8	56	9.0 (SFC)	7.0	1.38	1.07	44.3
Org2	3.9	48	2.4 (SFC)	2.9	0.05	0.06	2.4
Textiles	3.9	23	10.6 (BC)	12.7	0.32	0.38	15.7
Wood	3.7	17	2.8 (BC)	2.6	0.08	0.08	3.3
Paper	3.4	38	1.0 (BC)	1.0	0.02	0.02	0.9
TCC in mixed household waste (mg Cl/g raw waste)					2.8	2.4	100

^a The chlorine content in raw waste is calculated by specific chlorine content (dry basis) of every MSW fraction multiplying its weight percentage in raw MSW exclusive water content.

3.3. Thermal behavior of chlorine

3.3.1. Combustible chlorine and incombustible chlorine

The thermal behavior of chlorine species is investigated by EA with an adapted procedure. After incineration, chlorine in the waste partly releases into gas phase as HCl (combustible chlorine) and rest stays in the ash (incombustible chlorine) [14]. Fig. 6 presents detected combustible and incombustible chlorine in each fraction after incineration in the EA at 850 °C. The detected incombustible chlorine is low in all samples with less than 0.01 wt.%. In most fractions, the ratio between combustible chlorine and incombustible chlorine is 95:5.

Additionally, the incombustible chlorine is further investigated in the muffle furnace with a ~30 times larger amount of test sample (~3 g). Fig. 7 shows the detected TCC in waste fractions by SFC and the incombustible chlorine by muffle furnace and EA. The detected incombustible chlorine by muffle furnace for PI3 and Org1 is 1.9 wt.% and 0.9 wt.% at 700 °C, 0.2 wt.% and 0.1 wt.% at 850 °C, 0.15 wt.% and 0.01 wt.% at 1000 °C, respectively. Whereas, detected TCC of Org1 by SFC is 0.9 wt.% which is quite close to the incombustible chlorine at 700 °C by muffle furnace. Moreover, the muffle furnace generally determines a higher amount of incombustible chlorine than EA, especially between 700 °C and 850 °C. After 850 °C, incombustible chlorine tends to reach a plateau value for both tests in the EA and in the muffle furnace.

3.3.2. Temperature influence

In this study, the influence of temperature on chlorine volatilization, determined by EA, is shown in Fig. 8. The detected combustible

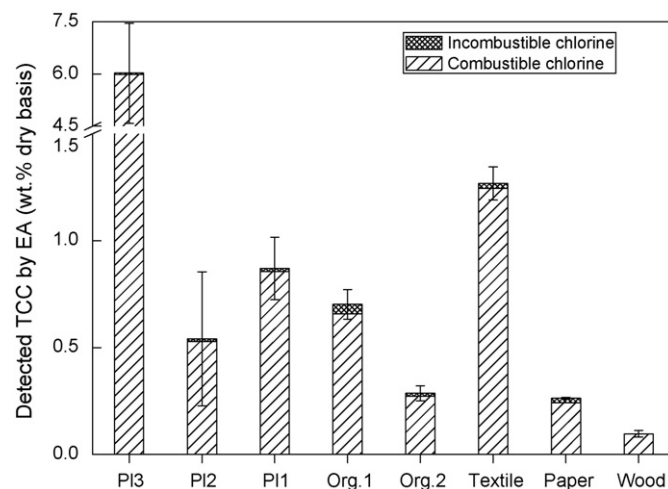


Fig. 6. Detected combustible and incombustible chlorine content in relevant waste fraction determined at 850 °C by EA (no. of tests=5 per fraction, the error bars represent standard deviation).

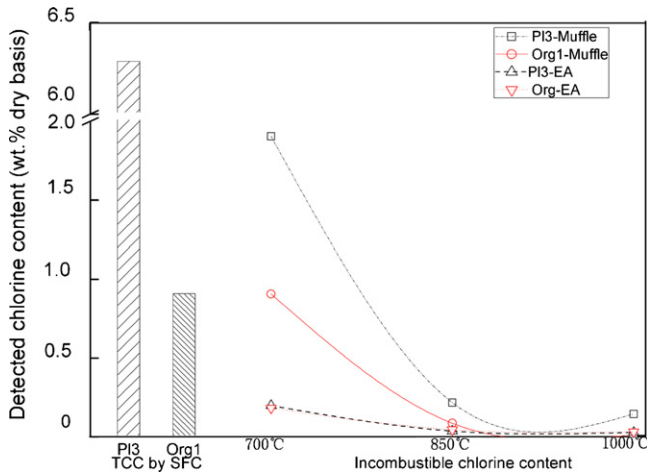


Fig. 7. TCC of non-packaging plastics (PI3) and kitchen waste (Org1) and its detected incombustible chlorine content in EA and muffle furnace (no. of tests = 5 per fraction, the error bars represent standard deviation).

chlorine in Org1 and P11 tends to increase with the temperature increasing while the effect for PVC containing plastic seems to be less visible. From 700 °C to 1000 °C, the conversion rate of chlorine volatilized into gas phase increases by 1.8% in PI3 and 15.1% in Org1, as the typical representatives of inorganic and organic waste. For fractions with a low chlorine content (<0.3 wt.%) like wood and Org2, the temperature has little impact on chlorine conversion. However, this phenomenon is not statistically confirmed and interfered by the high variability of detected chlorine content due to the heterogeneous nature of the waste fractions and the low sample size used for this test.

3.3.3. Influence of sulfur and silica

The influence of adding magnesium sulphate (MgSO₄·7H₂O) on the chlorine volatilization is illustrated in Fig. 9. The sulfur addition resulted in a concentration of 5 ± 2 wt.% sulfur in each test. That equals a mol ratio of S:Cl is (10 ± 5):1 for fractions with a low chlorine content (Org2, Paper, Wood) and (5 ± 3):1 for fractions with a medium chlorine content (PI2, PI1, Org1, Textile). As expected, there is an increase of the detected chlorine after sulfur addition,

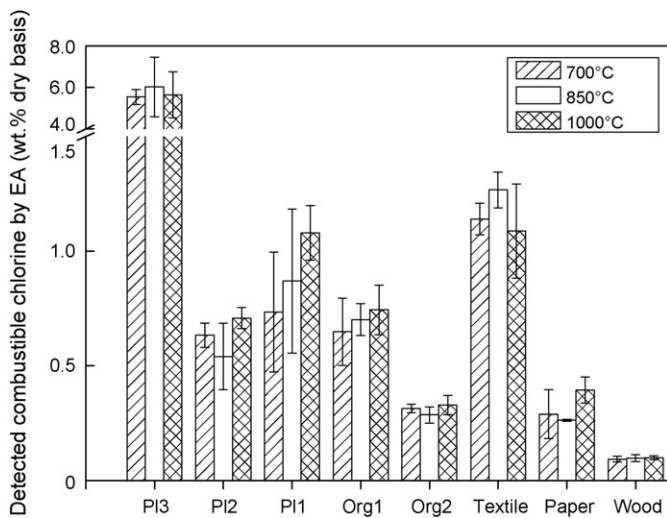


Fig. 8. Temperature influence on chlorine volatilization measured as the detected combustible chlorine content by EA (no. of tests = 5 per fraction, the error bars represent standard deviation).

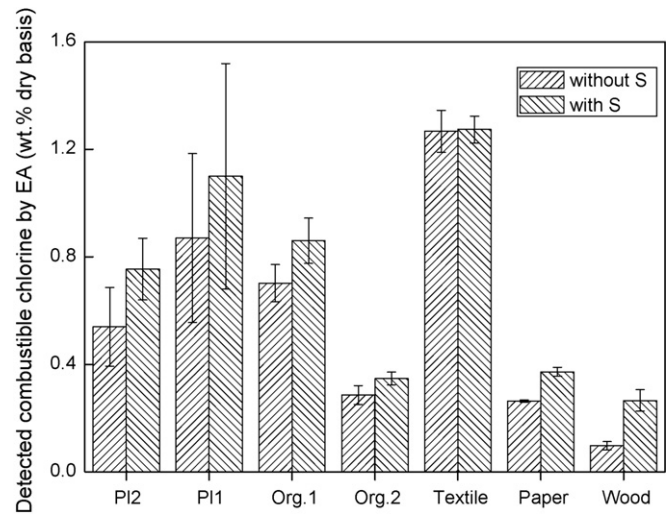


Fig. 9. Influence of magnesium sulphate addition on chlorine volatilization at 850 °C measured as detected combustible chlorine by EA (no. of tests = 5 per fraction, the error bars represent standard deviation).

apart from textiles. The increase rate is most pronounced for wood with 170%, followed by the other fractions between 20% and 40%.

Fig. 7 also shows the difference between the EA and the muffle furnace test results, especially between 700 °C and 850 °C. A major difference in the experimental set up between both tests is the addition of quartz sand to the test sample.

4. Discussion

4.1. Chlorine relevance in MSW/RDF

The calculated minimum TCC of MSW based on the waste composition in Berlin is found to be 2.4 g/kg raw waste which is rather low and indicates that possibly other sources of chlorine are relevant besides the investigated fractions. For the Amsterdam MSW incineration plant TCC of 4.1 g/kg raw waste is reported (3.1 g/kg raw waste in stack emission, 0.4 g/kg in slag, 0.5 g/kg in fly ash, and 0.1 g/kg in fly dust) [22]. Based on the data presented here, plastics (PI1, PI2, PI3 in total) contribute to one third of the TCC, and organic waste (Org1, Org2) contains approximately 50% of TCC. Kanters et al. [22] reported that ca. 50% of the chlorine load of regular MSW is due to inorganic chloride and ca. 45% due to PVC. Our results also show that both plastics and organic kitchen waste, are equally important as the chlorine sources in MSW.

4.1.1. PVC

In this study, non-packaging plastics PI3 (mainly PVC) contain the highest chlorine content with >6 wt.% and contribute to 20% of the minimum TCC of 2.4 g/kg raw waste. Even though the production of chlorinated plastics has decreased in the last decade, many PVC products have a life time of 5–30 years. Thus, the reduction of chlorine in MSW will not be visible within the next decades. According to the report by Schirmer et al. [28], the TCC in RDF is around 0.7–0.8 wt.% depending on the RDF processing procedure. Even if all PVC could be completely separated from RDF by automatic sorting, TCC of below 0.5 wt.% cannot be assured due to the contribution of other waste fractions. This means that WTE plants still have to implement an elimination stage for HCl-gas.

4.1.2. Kitchen waste

Kitchen waste contains the majority of chlorine in household waste (45% of chlorine load according to the waste composition determined in this study), with a specific chlorine content of 1 wt.%.

Mainly consisting of water-soluble alkali chloride salts, kitchen waste contributes significantly to high temperature corrosion. To avoid harm to the superheater, an option can be separating the kitchen waste through mechanical processing. Regarding household waste derived fuel, also the fuel yield will drastically go down due to the large weight percentage of kitchen waste. The results also show significant contamination of other waste components such as plastic films (PI2) with inorganic chlorine which can be assumed as originating from kitchen waste adhesions. Mechanical separation would lower the fuel yield even further.

Alternatively the water soluble inorganic chlorine can be removed selectively by a water washing pretreatment prior to combustion. This is an expensive solution. Some remedies like straw washing have already been undertaken in the field of biomass combustion and co-combustion to minimize the corrosion and slagging, since biomass also contain high inorganic chlorides (eg. potassium chloride) [29].

4.2. Assessment of analytical methods for TCC

Generally, the detected TCC determine by BC is 15–25% lower than those by other methods. The reason may be the difficulty of a complete combustion in the bomb, which was particularly observed for plastics. As reported, the analytical results also suffer from incomplete combustion in the bomb method [30]. The SFC test detects the highest chlorine content in particular for plastics with a TCC > 5 wt.%. On the other hand, the fact that more chlorine is detected by elution in Org1 and Org2 means the thermal analytical methods (BC, SFC, EA) underestimate the TCC of organic samples. Due to the good solubility of chlorine, the elution test seems to be appropriate to determine completely the inorganic chlorine because over 95% of inorganic chlorine is leached out after first elution. Another advantage of the elution test is its non-destructive detection and enabling the distinction of organic and inorganic chlorine, which has significant meanings for the prediction the thermal behavior of chlorine. The EA and the muffle furnace provide the opportunity to analyze the combustible and incombustible chlorine. However, the EA test shows a weakness in the detection of incombustible chlorine and in dealing with the heterogeneity of waste derived samples due to the small sample size.

In EA tests, low recovery of incombustible chlorine shows that most of chlorine converts into the gas phase. However, for most fractions, it detects a lower TCC than other methods what suggest that chlorine, once volatilized, condenses in the device before being detected in the coulometric cell. For the good combustion in the device the addition of silica is necessary, but also responsible for the increased volatilization rate. Concerning the detection of incombustible chlorine, muffle furnace is an improved method, which offers the possibility to analyze larger samples. This has clear advantages for the representativeness of the extraction of sub-samples.

Hwang et al. [15] showed that 85% of easily water-soluble chlorine in char derived from MSW was leached out in the first washing procedure. According to this study, the TCC consists of 85% of easily water-soluble chlorine, 5% of hardly water-soluble chlorine and 10% of non-water-soluble chlorine. His findings and our results are similar and essential not only to understand the solubility of chlorine compounds in water but also to identify the predominant speciation of chlorine which influences its thermal behaviors.

4.3. Chlorine species and their thermal behavior

In this research, the TCC has been grouped into organic and inorganic chlorine, combustible and incombustible chlorine.

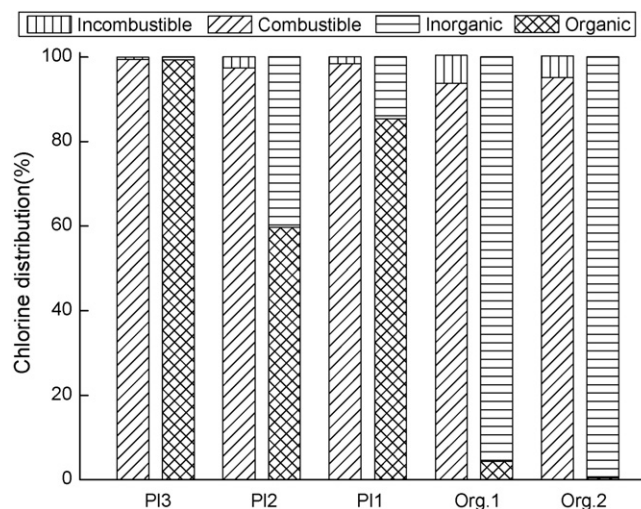


Fig. 10. Distribution of chlorine species differentiate between “organic” and “inorganic” chlorine by elution test and “combustible” and “incombustible” chlorine by EA test ($T = 850^{\circ}\text{C}$).

Combining Figs. 4 and 5 and indicating the relative distribution of organic/inorganic and combustible/incombustible chlorine, it is interesting to find correlations among the fractions.

As shown in Fig. 10, plastics have significant different chlorine species from organic waste fractions. In PI3, the ratio between organic chlorine and inorganic chlorine is similar to the ratio between combustible chlorine and incombustible chlorine. It was found that the inorganic chlorine is negligible in PI3, resulting in a complete conversion of organic bound chlorine to HCl, according to Eq. (1).

In difference, the amount of incombustible chlorine in organic waste is more than that in plastics. The reason is inorganic chloride salts, such as NaCl and KCl, in kitchen and garden waste have higher binding energy than plastics, and these salts are partly transferred into the gaseous phase as HCl, with a large amount of non-volatile chlorine remaining in the residual ash. Since inorganic chloride species can not offer free hydrogen, the emission rates of HCl from organic waste fractions are much lower than that from plastic [18].

Kanters et al. [22] pointed out that the organic and inorganic chlorides are equally abundant in MSW, and the HCl emission versus chloride remaining in ash is 80/20. Watanabe et al. [14] found 2.7 g combustible chlorine and 1.0 g incombustible chlorine per kg raw waste, which is equal to a ratio of 63:37.

These results, in addition to the fact that the combustible chlorine content depends on a large number parameters like sample matrix (silica content), additives, oxygen supply and temperature suggest that a simple “standard test” able to assess of thermal chlorine behaviour is not possible to develop.

4.4. Assessment of operational parameters on chlorine volatilization

4.4.1. Influence of temperature

4.4.1.1. On PVC. In Fig. 7, the tendency of volatilized chlorine into gas phase (as HCl formation) from PI3 (mainly PVC) at different combustion temperatures is shown. Apart from the peak value of chlorine concentration at $T = 850^{\circ}\text{C}$, the chlorine concentrations at 700°C and 1000°C are similar. Wang et al. [23] reported that the HCl conversion rate from PVC in a pyrolyzer increased slightly with temperature from 660°C to 800°C .

4.4.1.2. On kitchen waste. Our finding of kitchen waste in Fig. 7 agrees well with other studies [23] that temperature plays a visible

role in the HCl formation from kitchen waste. Wang et al. [23] also pointed out that the HCl conversion rate of total chloride input from NaCl in flue gas also increased with temperatures.

An average boiler-temperature of 820–880 °C is considered as a typical operating temperature in MSW incinerators [9]. The presented data in Fig. 10 show that 90% chlorine in PVC and kitchen waste volatilize into gas phase at 850 °C, which confirms the full scale findings [31] with 10% of chlorine remaining in the bottom ash. However, sodium and potassium chlorides in waste are reported to vapor-condense on tube surfaces in a wide temperature range from flue gas at 650–950 °C on the tube surface at 350–650 °C [32]. The alkali chlorides deposition may further lead to high temperature corrosion.

4.4.2. Influence of sulfur

Fig. 8 indicates an influence of sulfur on HCl formation. Duo and Leclerc [33] pointed out 150 ppm SO₂ in the flue gas leads to higher HCl than 0.1 ppm SO₂ by thermodynamic equilibrium calculations. Co-firing of MSW with sulfur-containing coals to improve the calorific value in China is in common practice [1].

Sulfation in the combustion chamber leads to more HCl and less vaporized salts. Subsequently those do not condense on the superheater, resulting in less corrosion but higher demand for reagents for HCl and additional SO₂ removal in the scrubber resulting in increase of operational cost.

The chloride salts would be converted quantitatively by sulfur, if present, to HCl over entire range of flue gas temperatures [33] according to Eq. (2). The ratio of S addition/Cl in this study is over 5, providing sufficient sulfur for reaction. Sulfur content is usually very low in wood fraction (0.76 mg/g MSW [14]), so Eq. (2) become dominant and increase of HCl is significant by 170%. Comparably, barely HCl increase from textile after sulfur addition may attribute to itself already contains high sulfur content (7.3 mg/g MSW [14]). Sulfur content for rest fractions varying in the range of 2.0–3.2 mg/g MSW [14], correspondingly the HCl get an increase by 20–40%. In summary, the increase of HCl formation during the combustion depends not only on the sulfur addition, but also on sulfur in waste itself. Mixing sulfur rich with chloride rich waste fractions can have a similar effect of maximizing HCl and minimizing vaporized chlorides which can potentially condense at the superheater.

A similar reaction principle is used in the “ChlorOut” process where ammonium sulfate is sprayed into the hot turbulent zone prior to the superheater aiming at sulfation of corrosive gaseous alkali chlorides in the flue gas [34,35]. This approach of avoiding corrosive deposits on the superheater requires an additional sulfur source, which will increase the cost for sulfur removal in the flue gas.

4.4.3. Influence of silica

Fig. 7 shows a higher transfer rate of chlorine into gas phase in the EA than the muffle furnace. The reason might be that alkali chloride salts react with silicates in the presence of water vapor forming HCl, as indicated in Eq. (3). Silica accelerates the transfer rate of inorganic chloride salts into HCl, leading to high HCl conversion even at a relatively low temperature (700 °C), resulting in less chlorine detected in ash. According to Wey et al. [21] silicon sinters easily with alkaline and alkaline-earth metals and has a negative influence on decreasing the fluidization quality of fluidized bed incinerators. The influence of silica requires further qualitative investigations since MWS usually is characterized by high ash and silica content which might have an influence of the chlorine behavior in the combustion chamber.

5. Conclusions

Based on the work thus far, following conclusions can be drawn:

- (1) The chlorine content in representative MSW samples covers a wide range from 0.1 wt.% in wood to 6.3 wt.% (dry basis) in PVC. The minimum chlorine content in the investigated household waste is 2.4 mg/g raw waste. Non-packaging plastics due to a widely use of PVC contain highest concentration of chlorine, contributing 20% to the total chlorine load. Kitchen waste as the largest chlorine fraction occupies 45% of total chlorine load. Influencing the waste properties by separating fractions from the waste could be an option for PVC, not for kitchen waste.
- (2) The Schoeniger flask combustion method detects highest chlorine content in plastic samples compared to other methods, while the elution test recovers more chlorine in organic waste fractions, which probably distinguishes organic and inorganic chlorine. The bomb combustion method despite being a standardized method shows 20% less chlorine in most samples. Elemental analyzer and muffle furnace provide the opportunity to analyze the combustible and incombustible chlorine. However, EA test shows the weakness in detection of incombustible chlorine in very small waste derived samples.
- (3) Regarding the chlorine binding form, inorganic chloride salts in the kitchen waste fraction are dominating with more than 95% of its TCC. Non-packaging plastic consists of nearly 100% organic chlorine. Different chlorine species also lead to the different thermal behavior of chlorine.
- (4) The distinction between inorganic and organic chlorine content does not correlate with the differentiation between combustible and incombustible chlorine. Due to the various influence factors on chlorine volatilization, standard tests to determine the incombustible chlorine content do not seem sufficient meaningful.
- (5) A significant part of the organic and inorganic chlorine is transferred at the typical combustion temperature >850 °C into the gas phase either as vaporized chlorides or HCl. Hence the temperature is not a proper parameter to influence chlorine volatilization rate in waste incineration processes.
- (6) Sulfur addition to the fuel leads to 20–40% higher HCl formation rate in most fractions, apart from 170% in wood and 0% in textiles. Silica plays a positive role in chlorine releasing at a relatively low temperature between 700 °C and 850 °C. With systematically investigating these effects recommendation for a fuel management for the incineration of waste and waste derived fuels can be made.

Acknowledgements

The financial support from the Fok Ying-Tong Education Foundation (Project No. 101056), National Natural Science Foundation of China (Project No. 90610020) and National Program on Key Basic Research Project (973 Program Project No. 2004CB719704) are gratefully acknowledged. Authors are also thankful to European Commission for their financial support through Asia-Link Program (Project No. CN/ ASIA-LINK /025 (110-744)).

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