TNO Industrial Technology

Laan van Westenenk 501
P.O. Box 541
7300 AM Apeldoorn
The Netherlands

www.tno.nl

T +31 55 549 36 34
F +31 55 549 32 72

TNO report

I02/01333/RAD **CEF-12**

Review on corrosion in waste incinerators, and possible effect of bromine.

Date	1 October 2002
Author(s)	ir. P. Rademakers (TNO IND) ing. W. Hesseling (TNO-MEP) ir. J. van de Wetering (Akzo Nobel AMC)

Copy no	
No. of copies	5
Number of pages	51
Number of appendices	
Sponsor	CEFIC-EBFRIP Brussel Ing. L.A. Tange, Mr. R. Montaigne
Project name	
Project number	007.61037/01.01

Contents

1 Summary

Experts from TNO and Akzo Nobel have carried out a review on the effect of bromine containing compounds on the corrosion of the boiler parts of waste to energy plants. The bromine containing compounds may result from waste (plastics) from electrical and electronic equipment (WEEE) after removal of electronic parts.

This review describes that all existing waste-to-energy plants (WTE) suffer more or less corrosion. The corrosion of boiler parts as waterwalls and superheater has to be ascribed to a combination of relatively high chlorine levels, high temperatures in the flue gas, en deposit formation on heat transfer surfaces. Design and operation aspects play an important role. In practice heating values and impurity levels of waste can show considerable variations. The corrosion mechanisms include deposit build up, evaporation of metalchlorides, and melting of salt deposits. For Fe base alloys the formation of volatile ironchlorides, instead of protective oxide, is the main driving force, Ni base alloys being more resistant. Sulphurdioxide can be beneficial, it helps to convert metalchlorides in less harmful hydrogenchloride.

Information about a possible additional corrosion effect of bromine (or fluorine) is lacking. To estimate possible effects of co-firing WEEE, the presence of bromine compounds and the relative amounts were considered. Possible bromine compounds, vapour pressures and eutectic melting temperatures were compared with chlorine compounds. With regard to the mechanisms, thermodynamic data were gathered both for bromine and chlorine compounds and phase stability calculations were made. This study revealed that both Fe-chlorides and Fe-bromides have considerable vapour pressures at relatively low temperature, and do not differ very much. Phase stability calculations have shown that the formation of Fe-chlorides and Ni-chlorides is expected to be favoured before Fe-bromides and Ni-bromides. With respect to molten salts melting points of bromine salts are in the same range as chlorides or even higher.

With regard to the possible effect of co-firing bromine containing compounds from WEEE the following conclusion can be drawn:
As long as the amounts of WEEE, that can be mixed and co-fired with Municipal Solid Waste, are limited to e.g. 3 %, from this study and the data obtained it can be expected, that corrosion mechanisms are dictated primarily by chlorine, and corrosion rates of boiler parts will not change noticeable when WEEE is added to MSW. In practice verification of this expectation is recommended, and two types of tests co-firing WEEE are proposed. A short test to get information on bromine distribution and deposits composition, and a long term test in a WTE-plant, to study possible effects on combustion residues, deposits formation and corrosion rates.

Keywords: waste incineration, waste-to-energy, corrosion, chlorine, chloride, bromine, bromide, impurities, waterwalls, superheaters, boiler steels, resistant alloys.

2 Introduction and objectives

Important innovations in the electrical and electronic (E&E) industry are enhanced by the applicability of plastics. Rapid technology changes increase the amounts of waste electrical and electronic equipment (WEEE). For reasons of safety in many applications flame retardants are used in plastics. As increasing amounts are expected and in Europe activities are going on for energy recovery, the Association of Plastics Manufacturers (APME) and the European Brominated Flame Retardants Industry Panel (EBFRIP), have demonstrated that energy recovery in modern Waste-to-Energy (WTE) plants is an efficient waste management option. Promising trials were done in the 'Tamara' facility in Karlruhe, Germany (10-12, 15, 96). Bromine is mostly used as brominated flame retardant (BFR) in plastics. As in general halogens e.g. chlorine, bromine, fluorine can enhance corrosion, operators of waste to energy plants (or incinerators) are reluctant to burn big amounts of bromine containing waste.

In the present situation enhanced corrosion in waste incinerators amongst other factors is caused by chlorine and sulphur containing compounds. However the possible effects of additional bromine containing waste are not clear. Therefore a brief review of existing knowledge is carried out. The scope is limited to the boiler parts of waste-to-energy plants (WTE) which use both domestic and industrial waste. Modern incinerators are equipped with energy recovery facilities, to produce steam and/or electricity, and with a flue gas clean-up system. Extensive thermodynamic calculations and experimental work is not yet included.

Objectives

- To get information on possible effects of bromine from tests or experience in practice a limited inventory of existing literature will be made and international networks will be contacted.
- To make an estimate of compounds that could be formed, based on data obtained from thermodynamic calculations and process conditions (e.g. phase stability data, melting points, and if possible vapour pressures).
- To study the possibility of condensing bromine compounds, which might influence present corrosion rates, regarding the process conditions, types of waste and the relative amount of bromine.
- Produce a final report describing the existing knowledge on possible effects of bromine on corrosion of boiler parts of WTE plants.

3 Approach

The project is carried out by experts each with their specific experience.

TNO Industry:	corrosion of materials in waste-to-energy plant.
TNO MEP:	process conditions in waste incinerators.
Akzo Nobel:	processes, equipment and corrosion related to chlorine/chlorides.

Regular contact with the EBFRIP representative is included.
Tasks are shared between the partners mentioned above.

The approach described in this report comprises:

1. An inventory of existing knowledge about the role of halogens with respect to their behaviour in the process, the governing corrosion mechanisms, and the effect in particular of chlorine on corrosion. The approach consists of an assessment of process conditions and critical boiler parts, identification of major corrosion mechanisms, and behaviour of different types of alloys.
2. An assessment of the possible effect of bromine, based on knowledge of chlorine corrosion on the one hand, and the process conditions and thermodynamic data of possible bromine compounds on the other hand. Data for chlorine and bromine containing compounds are compared such as phase stability (free energy of formation), vapour pressures, melting points and low melting eutectics.

The stability diagrams have been computed by TNO-INDUSTRIE, with the aid of ThermoCalc software. The literature search has been performed using databanks such as CAPLUS. METADEX. In addition TNO-MEP used PICARTA, an innovative search engine with links to a broad field of scientific areas.
Used keywords a/o. are:

CORROSION,
INCINNERATOR or MUNICIPAL or MSW, INCINERATOR,
BR or BROMIN?, or HBR or HYDROGEN BROMIDE,
(FIRE OR FLAME) (W)RETARD?
HIGH TEMPERATURE CORROSION
HIGH(W)TEMPERATURE(S)CORROSION
HCl
HALOGEN not (CL OR CHLORI?)
WTE

Recent international conferences and reports have been studied such as “Thermische Abfallverwertung 2000”, November 2000, Essen (Germany). In addition international networks have been contacted such as IEA and COST 522 partners.
In the Netherlands several operators of WTE plants were asked, if there was experience with corrosion related to bromine content of the waste.

4 Waste to energy plants

4.1 Burning technology and types of plants.

In Waste-to-Energy plants (WTE plant) waste is burned under controlled conditions and heat is recovered to provide steam or hot water for industrial or domestic users, or for electricity generation. Combined heat and power (CHP) in WTE's provides both heat and electricity. As an average for every 100,000 tonnes of WTE capacity about 8 MW of electricity could be produced to the grid, enough to meet the needs of about 12,000 homes. There are many WTE plant manufacturers around the world. Although each system has some unique features, combustion systems can be divided into two broad categories based on the fuel characteristics:

- Mass burn – the as-received Municipal Solid Waste (MSW), with the exception of oversized material (appliances and furniture etc.), is fed directly into the furnace and burned on a moving grate or hearth without pre-treatment such as size reduction, shredding or material separation prior to burning. Design values for the Lower Heating Values (LHV) are typical 9 to 10 MJ/Kg. Due to variation in input and season effects LHV values of 12 MJ/Kg and higher have been reported.

- Refuse Derived Fuel – the as-received MSW is usually shredded to reduce the size and sorted, to recover and remove metals, glass and other products, to produce refuse derived fuel (RDF). This concentrates the combustible components of MSW, as organic materials and paper, resulting in a fuel with a higher heating value. The sorted material has a more uniform size and improved handling characteristics, and is burned in a suspension (Fluid bed Boiler) or grate fired furnace. Design values for LHV are typical 12 MJ/Kg. Due to variation in input the LHV can reach higher values e.g. of 14 MJ/Kg. Plants burning RDF are not described separately in this report.

Mass burning technologies were developed in Europe at the turn of the century and have undergone substantial advancement over the past 20 years. By installing advanced combustion control systems, altering the configuration of the furnace and the location of the air injection ports, the combustion performance of these systems has been greatly improved. These improvements have lowered emissions of trace organics and raised the thermal efficiency of the furnaces. In addition, some facilities now process waste (e.g. by mixing) before feeding it to a mass burn plant and consider the extra cost to be warranted because the system runs more smoothly.

The main sections of a conventional plant for incineration of municipal waste are:
- entrance zone with weighing facility and refuse receiving area
- shed to tipping and storing waste to be incinerated
- incineration furnace and with auxiliary equipment
- with furnace integrated thermal equipment for heat recovery.
  (boiler with water steam system and steam turbine)
- flue gas treatment system
- residue treatment equipment
- electrical installations and control system
- auxiliary equipment and buildings.

Nowadays world wide hundreds of WTE-plants are in operation. Most of them are equipped with grates, boilers and flue-gas treatment. The most widely used WTE process is mass burn with either wet, dry or semi-dry gas cleaning systems.

The main moving grate systems are:
- Roller grates
- Co-current reciprocating grate
- Counter current reciprocating grate

The grate system and boiler are large and robust in order to cope with most articles in the waste stream. The burned out residue falls from the end of the grate into a water quench bath, where it is removed mechanically. The ash (bottom ash) is de-watered. After magnetic separation of ferrous metals, to be sold as scrap, the ashes are disposed or utilised. In the Netherlands the bottom ash is altered, according a specific certified method and re-used in road constructions.

After the heat from the hot combustion gases has been recovered in the boiler, the gases are cleaned to remove fine particulates (fly ash), acid gases and organic compounds. There is a variety of air pollution control (APC) equipment installed in WTE's. Some facilities remove fine fly ash particles from the hot gases using electrostatic precipitators, prior to wet scrubbing by alkaline solvents to remove the acid gas components and flue gas condensation/reaction products. Units that utilise dry or semi-dry scrubbing systems (involving injection of an alkaline powder as a slurry) generally utilise fabric bag filters downstream of the scrubber systems to remove fly ash and other residue fractions (scrubber residues, condensation/reaction products). Additional APC measures, e.g. use of high active surface area carbon-based sorbents are used more and more for mercury control and reduction of organic emissions. The scrubber residues and bag filter dust are known as the APC residues and are often combined with the fly ash. Both the fly ash and APC residues (scrubber residues, bag filter dust and other sorbent residues) contain potentially harmful material, such as heavy metals or traces of micro-pollutants and are often combined prior to storage in airtight systems. Fly ash and APC residues are usually conditioned by adding water prior to transport for landfilling.

In Table 1 a typical mass balance of a WTE-plant is presented. The composition of the products and residues are influenced by the composition of the input waste.

Table 1. Mass balance of a typical WTE-plant

Input mass (kg)		Output mass (kg)	
Waste	1	Flue gases to Atmosphere	8.6
Air	8	Bottom ash	0.34
		Fly-ash	0.05
		Residues of flue gas treatment	0.03

In practice different plant designs are used. A schematic view of some typical boilers is given in Figure 1. Each system has its own characteristics with respect to temperature profiles, gas mixing, ash separation, and heat transfer surfaces.

The main heat transfer surfaces are:
- the boiler walls made as membrane waterwall tubes operation as evaporator,
- superheater tube bundles,
- evaporator tube bundles and economiser tubes.

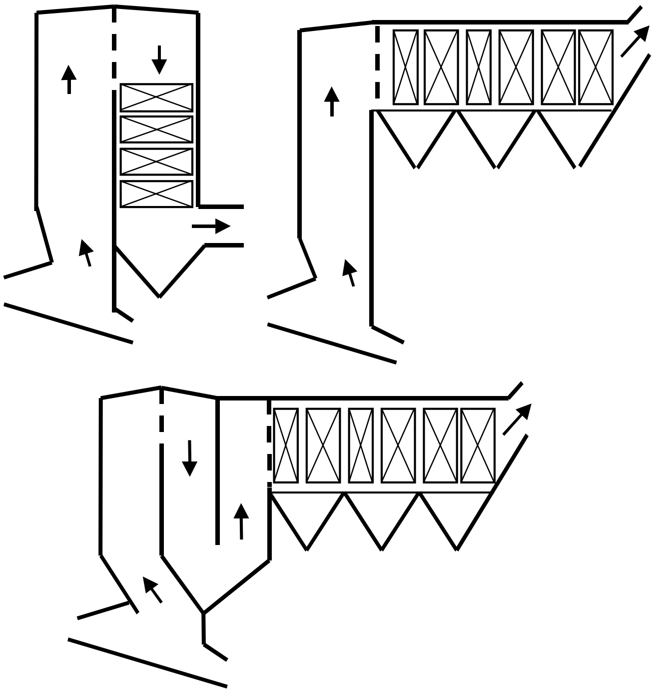

Figure 1. Schematic view of three different WTE boilers.

Important design factors are:

- design heating value of the waste,
- vertical vs. horizontal set-up; this is often a question of space and experience.
- passes and turnovers; are expected to enhance mixing and particle separation,
- secondary air injection nozzles; enhance mixing and combustion (excess air),
- vertical vs. horizontal tubes, has effect on deposit build up and cleaning,
- temperature profile in the flue gas path.

The design heating value of the waste determines plant limitations, because of the thermal capacity of the boiler, and the mechanical waste load capacity of the system. In many countries there is a tendency to separate waste e.g. in green waste, glass and residual waste. Both separation and wintertime drying can result in an increase of the heating value. In this way systems designed for a heating value of 9 MJ/Kg sometimes has to accommodate waste with heating values up to 12 MJ/Kg. Because of economics operators tend to keep the waste input at a high level, with high thermal loads of the entire system as a consequence.

Waterwalls and superheaters are sensitive to corrosion. As corrosion is enhanced by high temperatures it is important keep temperature differences between gas and metal low. Temperature peaks can be reduced by evaporator screen tubes and evaporator bundles before the superheater.

4.2 Waste composition and amounts

The composition of the waste varies per country depending of cultural traditions and economical situation. The majority of waste that is treated by combustion is Municipal Solid Waste (MSW) with little or no pre-processing. MSW is a heterogeneous resource originating from domestic and institutional sources. In various countries MSW also includes industrial and general trade waste. In most European countries commercial waste is collected separately. In Table 2 and Figure 2 a typical composition of the Dutch waste to burn in a WTE plant is presented.

Table 2. Typical composition of Dutch waste input of WTE (~1995).

Component	Composition wt. %
Organic	34.7
Paper	29.4
Plastics	10.4
Glass	4.0
Metals	4.7
Textile	4.4
Wood	2.7
Miscellaneous, burnable	5.0
Miscellaneous, not burnable	4.7
Total	100

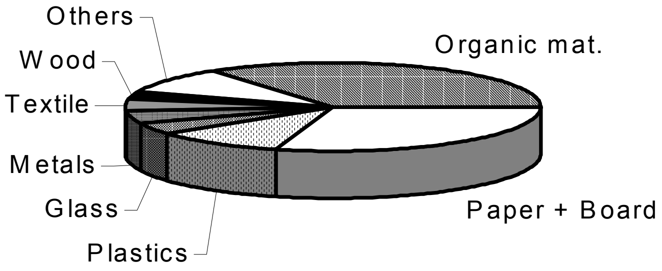

Figure 2. Characteristics of MSW.

Estimates for waste generation quantities in Europe and America are provided in Table 3.

Table 3. Summary of Municipal Solid Waste Data.

	North America		Europe				
Country	Can	USA	D	F	NL	S	GB
Year	1994	1994	1992	1990	1993	1994	1994
Waste 10^6 Tons/year							
Paper & paperboard	8.49	79.6	8.65+	10.2	3.74	1.2	6.64
Glass	0.97	13.5	5	4.08	0.41	0.18	1.86
Metals	3.94	15.5	1.69	1.7	0.12	0.11	1.46
Plastics	1.76	19.6	2.65	2.04	0.5	0.22	2.24
Wood		13.7				0.03	
Putrescibles**	7.7		11.75	8.5	3.6		4.04
Food		13.9				1.31	
Yardwaste		31.7					
Textiles			0.65			0.06	0.42
Other	2.05	18.7	13.14	7.48	2.54	0.16	3.34
Total amount	22.3	208	43.5	34	11	7.2	41.1
Per Capita (kg/day)	2.02	2.04	1.45	1.6	1.93	2.2	1.95
Composition (%)							
Paper & paperboard		38.1	19.9	30	31.2	37.4	33.2
Glass		4.2	11.5	12	3.4	5.5	9.3
Metals		6.3	3.9	5	1	3.4	7.3
Plastics		9.3	6.1	6	4.2	6.9	11.2
Wood		6.3				1	
Putrescibles* *			27	25	30	40.9	20.2
Food		5.8					
Yardwaste		12.4					
Textiles			1.5			1.9	2.1
Others		9.5	30	22	21.1	5	16.7

** organic material

The US EPA has indicated that that over 200 million tonnes of municipal solid waste are generated in the USA in 1994. This equates to about 2 kilograms per person per day. Comparable levels of waste generation per capita were reported for Canada, the Netherlands, Sweden and the UK. Estimates for Germany were low (1.45 kg/day) as the German waste paper generation data provided was post-diversion for recycling, whereas the data for the other countries refers to pre-diversion.

4.3 Process conditions and impurity levels

Process conditions.

Above the grate combustion temperatures are mostly between 850 °C and 950 °C , but incidentally as high as 1100°C. Although excess air is used local variations in waste and process conditions can result in products of incomplete combustion (PIC) as dioxin, furans and other compounds and high CO concentrations. The European authorities have introduced guidelines for solid waste combustion. In these guidelines the process conditions in the furnaces are regulated. According to these guidelines the temperatures at the 2 second residence time (considered from the 1 meter level above the last air injection point (secondary air or tertiary air) should be above 850°C. In the first pass of the boiler heat is transferred from hot flue gases to the walls, which consist of membrane type evaporator tubes. In most plant designs the lower parts of these walls are covered with refractory or tiles. Waterwalls and evaporator screen tubes can reduce the gas temperature to values of about 700°C, which is generally seen as an acceptable inlet temperature for the superheater tube bundles. The superheater material temperatures can incidentally rise to even higher temperatures, depending on either the construction of the heat exchanger (co-current or counter-current) and process conditions. Subsequently heat is transferred from the hot gas to the tubes of the superheaters, evaporators and economisers and/or air heaters.

Impurity levels in waste, flue gas and ashes.

In chapter 4.1 the origin of the waste was presented based on sorting analyses. In this chapter the elemental composition of the waste is discussed and compared to that of WEEE (Waste of Electrical and Electronic Equipment).

In Table 4 the typical composition of Dutch waste is presented in macro elements.

Table 4. Typical composition of Dutch waste (1994)

Compound/Properties	Value
C	27.44 wt%
H	3.83 wt%
O	16.51 wt%
N	0.91 wt%
S	0.19 wt%
P	0.1 wt%
F	0.011 wt%
Cl	0.59 wt%
Br	0.015 wt%
ash	19.61 wt%
water	30.8 wt%
LHV	9.5 MJ/kg

In Table 5 the assumed concentrations of heavy metals in the waste are presented.

Table 5. Calculated heavy metal composition of Dutch waste input, based on 1994 data in g/kg waste.

	Concentration in g/kg	
Compound	Min	Max
Cd	0.01	0.01
Cu	1.26	1.63
Hg	0.0004	0.0006
Mo	0.01	0.01
Pb	0.22	0.56
Sb	0.02	0.04
Zn	0.63	1.04
Cl	3.96	6.89
Br	0.11	0.19
S	1.48	2.96
As	0.01	0.01
Cr	0.16	0.28
Se	0.00	0.00
F	0.10	0.20

It has to be emphasised that more recent data were not available. After 1994 in the Netherlands electrical and electronic equipment is collected separately for recovery of several materials. Accordingly it is expected that present data for specific elements can be much lower (see 4.4).

In comparison to bromine for chlorine there is much more known about the original sources. In Table 6 the chlorine input in Dutch WTE’s is presented.

Table 6. Chlorine input in Dutch MSWI’s.

	Cl (g/kg)	% of total stream	ton/yr.
Organic	2 – 4	10 – 30	2000 – 4000
Paper	1 – 3	5 – 20	800 – 2500
Plastics	20 – 30	35 – 36	5700 – 8600
Rest not burnable	0.2 – 1	0 – 5	100 – 400
Rest burnable	10 – 15	10 - 25	2100 – 3100
Total			10700 – 18600

4.4 Expectations on relative amounts and possible effects.

After 1994 already for several years now in the Netherlands electrical and electronic equipment is collected separately for recovery of several materials. This will be required in 2006.

Accordingly for specific elements present data can be much lower. Some estimates obtained from EBFRIP are:

Br	0.0040 – 0.0070	wt %
Sb	0.0010 – 0.002	wt % (typical Sb/Br ratio = 1:3 to 1:4)
F	< 0.1	wt %
Cl	0.4 – 0.8	wt % (typical Br/Cl ratio 1:120 to 1:150)

In WEEE brominated flame retardants are used. Estimations on future amounts of flame retardants and bromine input in Dutch MSWI's are subject to uncertainties. According to EBFRIP the following figures can be used as an indication for relative amounts to be expected in the near future waste streams in the Netherlands:

Plastics in WEEE	18,000	ton/yr.
Brominated WEEE	6,000 to 7,000	ton/yr.
Bromine	120 to 140	ton/yr. (based on 2 wt% Br)

In general an increase of the bromine input into MSWI's will be expected. Compositions of WEEE used in combustion experiments are presented in Table 7.

Table 7. Composition of WEEE used for experiments in TAMARA (10-12,15,96).

		Mix 1	Mix 2	TV 1	TV 2	TV 2	TV 2	PWB
LHV	MJ/kg	31	25.4	38	35.7			16
As	%	10.6	18.9	1.2	1.2			48
C	%	67.4	56.6	82	81.5			54
H	%	6.8	6	7.2	7.1			5.6
N	%	2.9	2.8	1	0.7			1.9
S	%	0.11	0.1	0.03	0.02			0.2
O	%	8.2	8.2	1.1	3.2			8.4
Cl	g/kg	31.3	56.4	19	6.9	1.5	3.5	23
K	g/kg	0.8	0.07	<0.02	0.5	0.6	0.8	0.7
Ca	g/kg	10	1.3	<0.01	0.5	0.9	1	18
Cr	g/kg	0.07	0.006	<0.001	<0.02	0.03	0.2	0.2
Mn	g/kg	0.06	0.004	<0.001	0.007	<0.02	<0.12	0.2
Fe	g/kg	1.6	0.08	<0.002	0.15	0.64	0.2	3.1
Ni	g/kg	0.1	0.008	<0.001	0.016	0.03	0.03	0.5
Cu	g/kg	2.7	0.08	<0.001	0.02	0.06	0.14	66
Zn	g/kg	0.9	0.04	<0.001	0.2	0.3	0.22	1.3
As	g/kg	0.02	0.02	0.06	0.03	0.03	0.02	0
Br	g/kg	13.1	17.4	34.9	26.6	26	25	19
Rb	g/kg	<0.01	-	<0.001	<0.02	0.05	<0.02	<0.02
Sr	g/kg	0.07	0.004	<0.001	<0.007	<0.02	<0.01	0.2
Mo	g/kg	0.006	0.1	0.006	0.005	0.005	0.005	0
Cd	g/kg	0.07	0.1	0.07	0.02	0.02	0.01	0
Sb	g/kg	7	7.2	24	14.5	13	10.9	5.7
Sn	g/kg	0.6	0.9	0.17	0.07	0.08	0.3	5.5
Ba	g/kg	0.4	<0.03	<0.02	0.12	0.3	0.1	0.8
Pb	g/kg	3.5	1	0.22	0.15	0.2	0.2	4.9

In practice separate collection of WEEE en further recovery of PWB is expected by EBFRIP to result in a combustible fraction, with a composition comparable with Mix 2 from Table 7. This would result in a WEEE with a LHV of about 25 GJ/ton and chlorine and bromine levels of 5.6 wt% and 1.7 wt% respectively.

The effect of mixing

Comparing the composition of WEEE with the normal waste composition that is buned in MSWI (Municipal Solid Waste Incinerators) leads to the conclusion, that WEEE both has a higher LHV and higher bromine and chlorine levels. This would result in an increase of these components in the flue gas, and probably also in the bottom ash, if WEEE is mixed with the waste.

To estimate the effects of mixing of WEEE with MSW indicative calculations are made. For the calculations assumptions are made concerning the composition, an average type of MSW is chosen to be mixed with a WEEE composition similar to Mix 2 of the burning experiments (Tamara).
Results are given in Table 8 and Figure 3.

Table 8. Indicative calculations of effects of mixing of MSW with WEEE.

	MSW	WEEE Mix2	1% WEEE	2% WEEE	3% WEEE
LHV MJ/Kg	9,50	25,40	9,66	9,82	9,98
Br wt%	0,005	1,74	0,022	0,040	0,057
Cl wt%	0,70	5,64	0,75	0,80	0,85
S wt%	0,30	0,10	0,30	0,30	0,29

As can be seen the effects are limited. The heating value (LHV) increases a little. The increase can be considered as between the usual fluctuations of the waste composition. According to expectations the increase of the bromine content is most pronounced, although the bromine levels after mixing are still low.

The possibility to mix WEEE with MSW will depend on logistics and the facilities at the WTE plant.

The flue gases produced by the combustion of waste contain gaseous acidic substances such as HCl, SO_2 and HBr. Flue gases contain also particulates, which at higher temperatures forms ash deposits on boiler tubes. These ashes contain alkali (Na, K) and heavy metals (Pb, Zn) chlorides, oxides and sulphates.
In the next section it will be explained that corrosion in WTE plants depends on many factors in particular the presence of chlorine containing compounds and deposit formation. It is generally accepted that corrosion increases with the concentration of Cl in input, flue gas and ashes, up to some concentration level, above which no further corrosion enhancement does occur (saturation regime). WTE plants, because of the high chlorine levels and deposit build up, are expected to operate in the last regime.

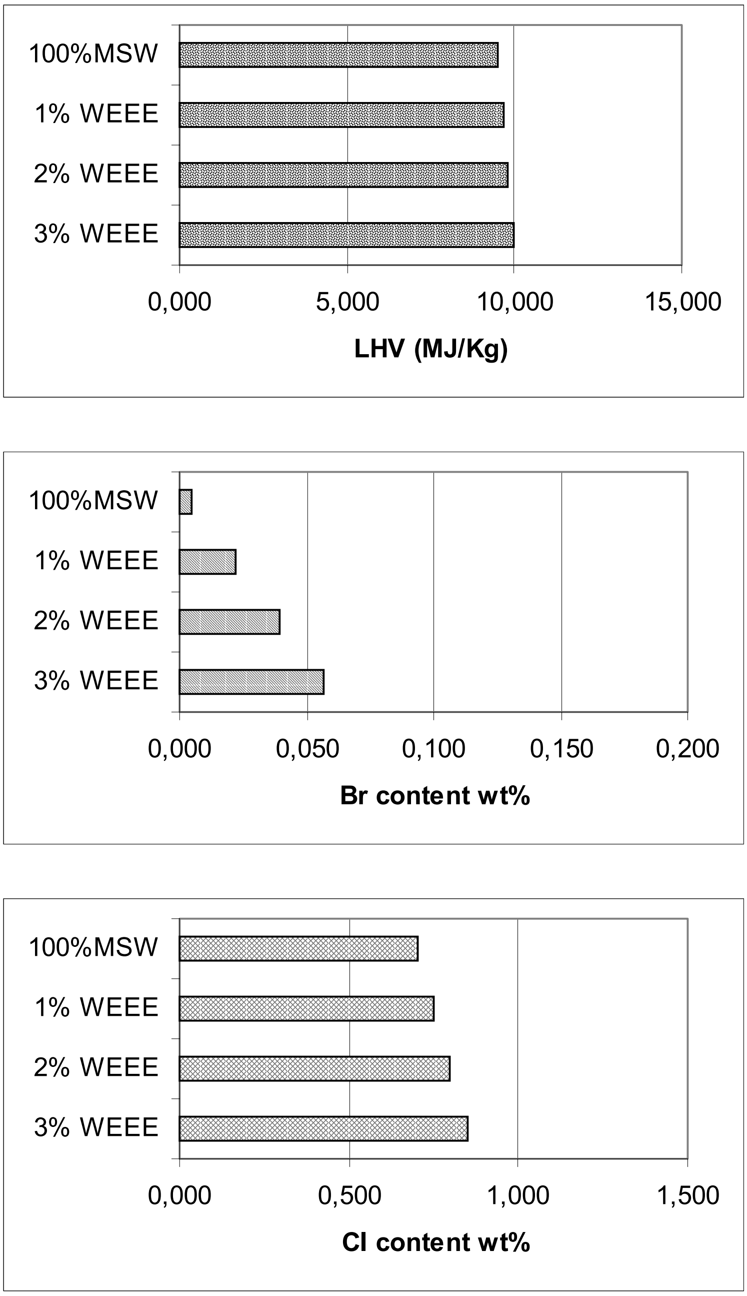

Figure 3. Indicative effects of mixing WEEE with MSW.

Partitioning of impurities

As the MSW is combusted, halogen compounds are distributed over bottom ash, fly ash, boiler ash and the gas phase. The details of this distribution are determined by the conditions on the grate. The occurrence of hot and cold spots determines whether halogenated compounds will evaporate or remain in the bottom ash. Fly ash and boiler ash are generated by the condensation of halogenated compounds on soot and partially combusted light particles that are blown away from the grate. Halogenated compounds in the bottom ash can not contribute to corrosion and are therefore “harmless” from the perspective of the boiler operator. Boiler ash, fly ash and halogen in the gas phase can contribute to corrosion. Thus one needs to know, not only whether the total amount of bromine and chlorine will change, but also whether the distribution of these compounds over the ashes and the gas phase will be affected.

The partitioning of halogenated compounds between the various ash types and the gas phase is determined among others by:

- The heating value of the MSW
- The type of halogenated compounds in the MSW
- Details of combustion on the grate (local temperatures and gas velocities).

Generally speaking, an increase in LHV will cause an increase in the fraction of halogen that is released to the gas phase. As can be seen in Figure 3, the increase of LHV due to an increasing amount of WEEE in the waste is marginal and does certainly not exceed the fluctuations of LHV one can normally expect. Therefore the effect of an increasing LHV on the partitioning of halogenated compounds can safely be neglected.

Little is known of the effect of the type of halogenated compounds on the distribution of bromine and chlorine between the phases. In existing WTE plants about 95% of chlorine and bromine is passed to the boiler area, and about 5% is captured in the bottom ash. Tests performed in the TAMARA facility indicated that the fraction of both chlorine and bromine from WEEE in the bottom ash can vary between 5% and 20 %, depending on the type of WEEE plastic. By adding WEEE to MSW it can be expected that in between 80% and 95% of the total chlorine and bromine increase, will be released to the boiler area. This is shown on figure 4. The input values of figure 3 should be multiplied by e.g. 0.85 to give a realistic estimate of the increase in bromine and chlorine that will become available in the boiler area.

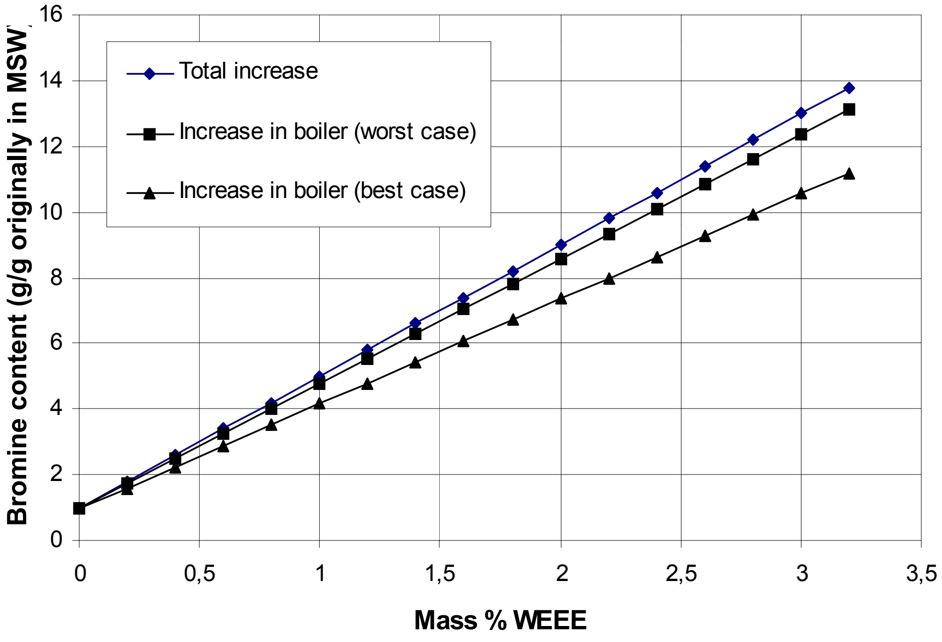

Figure 4. Relative effects of mixing WEEE with MSW and release to boiler.

The most plausible explanation for the large variation in partitioning of chlorine and bromine is the effect of mixing. When chlorinated and brominated compounds occur simultaneously, they mutually affect the vapour pressures of these compounds. Usually the vapour pressure of a compound is lowered in the presence of another compound if both compounds mix well. A lower vapour pressure will result in a lower release of chlorine and bromine from those compounds to the gas phase., and an increased fraction of that compound in the bottom ash.

Addition of bromine containing compounds could also lower the vapour pressures of compounds already present in MSW. In that case, addition of WEEE would result in a decrease of chlorine in the gas phase. This is very unlikely to occur however. Such a change in thermodynamic equilibrium can only occur if mixing on molecular level is accomplished. However in practice possibilities for mixing WEEE with MSW are limited. The safest assumption is that the presence of WEEE does not affect the release of chlorine and bromine from the rest of the MSW.

With the addition of up to 3% of WEEE to MSW the chlorine input will increase with 0.15 wt%, and the bromine input will increase with 0.05 wt%. Between 80% and 95% of this increase will eventually become available to change corrosion of boiler parts. These amounts are very limited, as compared both to the total chlorine and bromine amounts already released from regular MSW, and expected variations in the composition of present MSW. The chlorine and bromine from regular MSW that already was available for corrosion, will most likely not be affected by a limited addition of WEEE.

5 Corrosion of boiler parts

5.1 Corrosion sensitive areas.

In WTE plants the flue gas environment is very aggressive due to gas components such as CO, Cl_2 , HCl, S, alkali metals, and heavy metals such as Zn and Sn, which are able to form chlorides with high vapour pressures. By cooling down, gases form deposits on tube walls by condensation or sublimation. In addition soft and sticky particles can adhere to the heat transfer surfaces. These deposits contain salts like chlorides and sulphates, oxides, silicates and unburned particles, resulting in low oxygen partial pressures near the metal surface. In addition melting and fluxing of low melting point compounds can accelerate corrosion.

The for corrosion most sensitive areas are the heat transfer surfaces like waterwalls in the first pass of the boiler, screen tubes between the passes, and the superheater tube bundles. The areas are shown in Figure 5. This study is focussed on the most sensitive parts. Most modern waste-to-energy plant are operated with steam pressures of 40 bar and steam temperature of 400 °C. Some modern designs for reasons of efficiency make use of higher steam parameters. In these designs one method to avoid excessive corrosion is to place a part of the superheater separate in relatively clean flue gas from combustion of clean fuels.

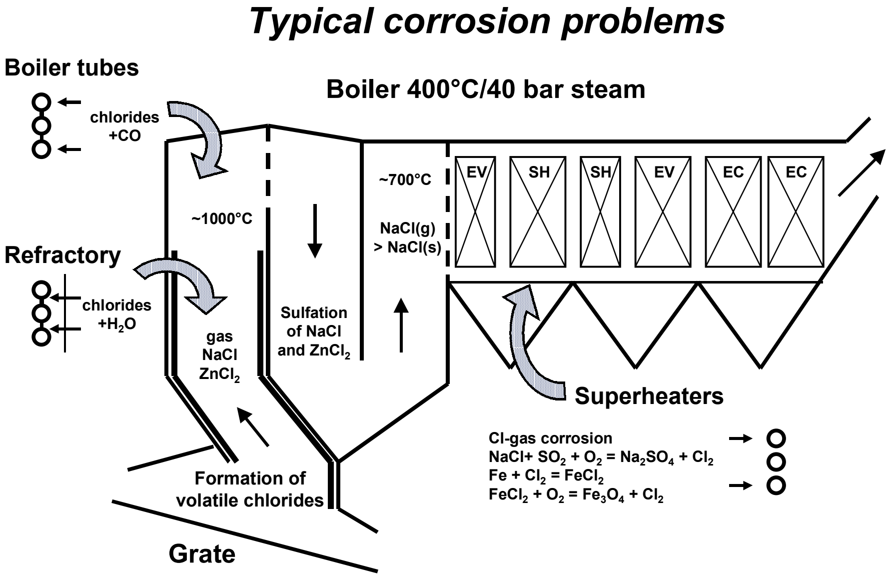

Figure 5. Typical corrosion problems in waste-to-energy plant.

The process conditions relevant to these parts are briefly described in Table 9.

Table 9. Boiler parts and temperature levels.

Boiler part	Steam system	T metal °C	T gas °C
Waterwall	Evaporator 265 °C	~ 300°C	~ 1000-800 °C
Screen tubes	Evaporator 265 °C	~ 300 °C	~ 800-700 °C
Superheater	Steam 400 °C	~ 450 °C	~ 700-600 °C

5.2 Impurities and corrosion mechanisms

The current understanding of the mechanisms of high temperature corrosion in waste combustion plant is reviewed in several papers.

In the first pass above the grate in-furnace corrosion by high CO levels and reducing atmospheres is well known. In practice a pragmatic solution is a refractory lining. which is applied on the waterwalls in the first pass of most incinerators.
In addition to CO reducing conditions in these areas can also result from deposit formation enhanced by the temperature gradient and condensing substances. In fact alkalimetal chlorides have been found in deposits near the metal surface.

It is generally accepted that the high level of chlorides in the waste is the core of the problem. High temperature corrosion in waste incinerators is caused by chlorine either in the form of HCl, Cl_2 , or combined with Na, K, Zn, Pb, Sn and other elements. In particular both gaseous HCl with and without a reducing atmosphere and molten chlorides within the deposit are considered major factors.
Sulphur compounds, which under certain circumstances are corrosive compounds itself, can enhance or reduce the corrosion by chlorine.
The most important factors in high temperature corrosion are the metal temperature and the temperature difference between gas and metal, de flue gas composition, deposits formation and reducing conditions, and the SO_2 / HCl ratio.

The following mechanisms can be distinguished.

- Corrosion by HCl/Cl_2 or SO_2/SO_3 containing gas under oxidising or oxidising/reducing conditions.
- Corrosion by solid or molten deposits of metal chlorides and sulphates.

These mechanisms are well described by several authors, and one of the pictures explaining the various steps is given in Figure 6.

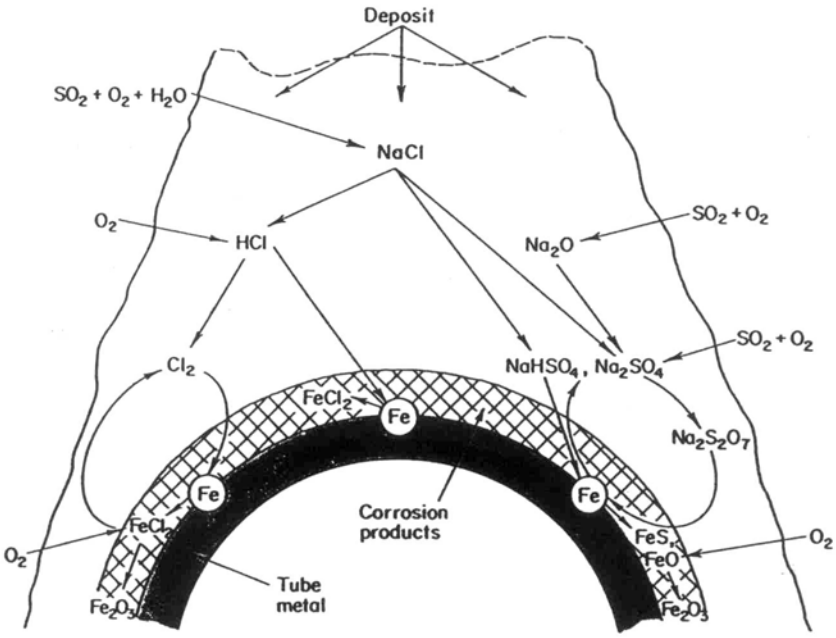

Figure 6. Sequence of chemical reactions explaining corrosion of incinerator boiler tubes (Ref. 60, Krause, 1986, 1993).

Corrosion by chlorine containing gas

This mechanism is generally accepted for metal temperatures above about 450°C and is mentioned ‘active oxidation’.
Alkali chlorides in particular NaCl, $CaCl_2$ and KCl can be present already, or can be formed by the combustion and subsequent reaction of alkali oxides:

$$Na_2O + 2HCl = 2NaCl + H_2O \qquad [1]$$

Under ideal conditions (good mixing, sufficient residence time) alkali chlorides can, provided there is enough SO_2 and O_2, be sulphated according to the reaction:

$$2NaCl + SO_2 + \frac{1}{2} O_2 + H_2O = Na_2SO_4 + 2HCl \qquad [2]$$

This would result in formation of sulphates and volatile HCl. At the relatively low tube wall temperatures of most waste incinerators the sulphates are not very harmful and the HCl formed will be transported to the flue gas clean up system.
However if the gas reaches the cooler tube walls before the reaction is completed the alkali metals will tend to condense on the cooler metal. In this case on the metal further sulphate formation can occur under the release of HCl which causes high chlorine partial pressures and enhanced corrosion.

Without SO_2 at 500 °C NaCl and iron oxides can form Cl_2 according:

$$2NaCl + Fe_2O_3 + \frac{1}{2} O_2 = Na_2Fe_2O_4 + Cl_2 \qquad [3]$$

$$6NaCl + 2Fe_3O_4 + 2\ O_2 = 3Na_2Fe_2O_4 + 3Cl_2 \qquad [4]$$

Calculations of the dissociation constant of HCl as a function of temperature indicate that under oxidising conditions up to gas temperatures of 600°C chlorine is present as Cl_2 , whereas above 600°C in the presence of water vapour formation of HCl is enhanced according to the reaction:

$$H_2O + Cl_2 = 2HCl + ½\ O_2 \qquad [5]$$

At about 500°C Cl_2 can penetrate pores or cracks in an oxide layer. At the low oxygen partial pressures as exist near the metal-oxide scale boundary the metalchlorides are the more stable phase. The reactions (3-4) can result in a Cl_2 partial pressure sufficiently high to react directly with the steel to form $FeCl_2$.

$$Fe + Cl_2 = FeCl_2 \ \text{(solid)} \qquad [6]$$

The vapour pressures of metalchlorides will depend primarily on the temperature and the HCl content of the gas. In addition the type of oxide (and alloy) can influence the vapour pressure considerable.
Some values are given in Table 10. The vapour pressure of $FeCl_2$ already at low temperatures is relatively high. As a result formation of $FeCl_2$ can decrease the adherence of the oxide scale or can cause spallation of the oxide layer.

Table 10. Vapour pressures of metalchlorides at 450°C in equilibrium with mixed oxides.

		Vapour pressure in bar	
Mixed oxide	Metal chloride	At 1000 ppm HCl	At 2200 ppm HCl
Fe_3O_4	$FeCl_2$	6.2×10^{-3}	2.9×10^{-2}
$FeCr_2O_4$	$FeCl_2$	2.2×10^{-6}	1.0×10^{-5}
$FeCr_2O_4$	$CrCl_2$	1.0×10^{-13}	1.0×10^{-13}
$FeAl_3O_4$	$AlCl_3$	1.3×10^{-15}	1.4×10^{-14}

Iron chlorides form, and due to their volatility, migrate out from the corrosion product. At higher oxygen partial pressures near the oxide-gas interface, these chlorides are converted to oxides and liberate chlorine. These new oxides are not formed as a perfect layer and do not offer protection. Part of the liberated chlorine migrates back through the oxide/deposit to react with the metal at the oxide-metal interface, and form metal chlorides again.

$$FeCl_2 \ \text{(solid)} = FeCl_2 \ \text{(gas)} \qquad [7]$$

$$4FeCl_2 + 3O_2 = Fe_2O_3 + 2Cl_2 \qquad [8]$$

$$3FeCl_2 + 2O_2 = Fe_3O_4 + 3Cl_2 \qquad [9]$$

In this process the chlorine has a catalytic effect on the oxidation of the metal resulting in enhanced corrosion. The kinetics of active oxidation is mainly determined by the evaporation and outward diffusion of $FeCl_2$. Similar chlorine corrosion and regeneration cycles may proceed via $FeCl_3$ and it is possible for the ferrous iron to be oxidised to the ferric state which, when oxidised liberates chlorine as well.

$$4FeCl_2 + 4HCl + O_2 = 4FeCl_3 + 2H_2O \qquad [10]$$

$$4FeCl_3 + 3O_2 = 2Fe_2O_3 + 4Cl_2 \qquad [11]$$

With regard to volatility different compounds can be compared based on the temperature T_4 at which the vapour pressure reaches 10^{-4} bar. For some compounds vapour pressure values are given in Table 11.

Table 11. T_4 temperatures of metalchlorides of main alloying elements.

Metal chloride	T_4 (°C)
$FeCl_2$	536
$FeCl_3$	167
$CrCl_2$	741
$CrCl_3$	611
$NiCl_2$	607

From all these figures it can be explained that low alloy steels and iron base alloys have a limited resistance against active oxidation. High alloyed materials and in particular nickel base alloys have a much better resistance, which can be explained by the fact that chlorides are more difficult to form and, once formed, their relatively low volatility.
Except for the $FeCl_3$ most T_4 temperatures are well above 500°C indicating that this mechanism is most relevant to superheaters and less to evaporators.

Effect of sulphur content

In the previous section it is mentioned that in the flue gas, under good mixing conditions and sufficient residence time, chlorides can be sulphated with SO_2 and O_2 according to reaction (2), under formation of Na_2SO_4 and volatile HCl. At the relatively low tube wall temperatures of typical waste incinerators the sulphates are not very harmful and the HCl formed will be transported to the flue gas clean up system. So to some extent SO_2 can be beneficial (13, 42, 43, 49). From tests sulphur to chlorine ratio's of 3 to 4 are mentioned (60). Laboratory tests revealed the effect with 500 to 1000 ppm SO_2 in the gas atmosphere. The values suggest that relatively high sulphur levels are needed to be effective.

Corrosion by deposits of metal chlorides and sulphates

In waste incinerators deposit formation is one of the main reasons for corrosion at relatively low metal temperatures (evaporators. membrane waterwalls). The deposition of sulphates and chlorides occurs both by condensation from the gas phase and from attachment of small more or less sticky particles.
Analyses of deposits have shown that outer scales contain mainly sulphates like $CaSO_4$, Na_2SO_4 , K_2SO_4 , $ZnSO_4$ and $PbSO_4$. The inner scales near the metal surface show considerable amounts of chlorides like $CaCl_2$, KCl , $ZnCl_2$, and $PbCl_2$.

These salts are believed to be formed from HCl and metals or metal oxides during waste burning. In the presence of HCl at least at higher temperatures and low oxygen partial pressures the chlorides can be more stable than the oxides. Insufficient sulphating of the chlorides in the flue gas, due to relatively low SO_2/SO_3 contents, will result in deposition of chlorides.
The effects of cyclic reactions resulting in 'active oxidation' are described above.
In addition chloride and sulphate mixtures can have relatively low melting points. which can reach the metal temperature of evaporator tubes as is shown in Table 12.

It is generally accepted that formation of salt mixtures is the main reason for metal corrosion in the temperature range of 250 to 400°C. The reason is that salts are able to convert the protective oxide layers in complex metal oxi-chlorides.

Table 12. Melting temperatures Tm of chlorides and sulphates.

Composition in weight %	Melting point Tm (°C)
$48ZnCl_2 + 52\ KCl$	250
$82ZnCl_2 + 18KCl$	262
$84ZnCl_2 + 16KCl$	262
$73ZnCl_2 + 27PbCl_2$	300
$31NaCl + 69PbCl_2$	410
$21KCl + 79PbCl_2$	411
$17NaCl + 83\ PbCl_2$	415
$39ZnCl_2 + 50KCl + 11PbCl_2$	275
$35ZnCl_2 + 48NaCl + 17PbCl_2$	350
$16NaCl + 40KCl + 44PbCl_2$	400
$K_2SO_4 + Na_2SO_4 + ZnSO_4$	384
$KCl + ZnCl_2 + K_2SO_4 + ZnSO_4$	292

High alloyed materials in particular nickel base alloys such as Alloy 625 have a much better resistance than iron base alloys.

Corrosion by sulphates

At high metal temperatures other corrosion reactions can be induced by sulphur compounds. Apart from Na_2O and K_2O in oxidising flue gas SO_2 and SO_3 can be formed. If the deposits contain compounds like iron oxides that can catalyse the reaction from SO_2 in SO_3 , the partial pressure for SO_3 may be high enough to produce pyrosulphate at temperatures between 320 and 480°C according:

$$Na_2SO_4 + SO_3 = Na_2S_2O_7 \qquad [12]$$

$$Na_2S_2O_7 + 3Fe = Fe_2O_3 + FeS + Na_2SO_4 \qquad [13]$$

At about 500°C sulphates and pyrosulphates can become unstable and react with the (protective) oxide. At temperatures of 550°C and higher the tri-sulphates can attack the metal according:

$$Na_2S_2O_7 + Fe_2O_3 = 2Na_3Fe(SO_4)_3 \qquad [14]$$

$$19Fe + 2Na_3Fe(SO_4)_3 = 6Fe_3O_4 + 3FeS + 3Na_2S \quad [15]$$

subsequently:

$$Na_2S + 2O_2 = Na_2SO_4 \quad [16]$$

$$3FeS + 5O_2 = Fe_3O_4 + 3SO_2 \quad [17]$$

$$2SO_2 + O_2 = 2SO_3 \quad [18]$$

The SO_3 liberated is available again to react with Na_2SO_4 resulting in cyclic corrosion reactions, which are enhanced in the presence of chlorides. The sulphate corrosion mechanisms can occur in big boilers of power stations, operated with substantial impurity levels in the fuel and at high steam temperatures. In waste incinerator superheaters metal temperatures up to now are limited to about 450°C and sulphate corrosion is not expected.

5.3 Boiler materials and lifetimes.

During the last 10 years in Europe a lot of information has been obtained from WTE plants concerning boiler materials, corrosion rates and life times.
In the Netherlands various materials were exposed in a WTE superheater (18).
Exposure times reached about one year. As corrosion is a thermal enhanced process, results were used to calculate the activation energies, to make extrapolations for different temperatures and times. Results are given in Figure 7. The 15Mo3 steel is a low alloy steel with 0.3% Mo, the alloy 625 is a Ni-base material with Cr, Mo and Nb (Cb in American literature).

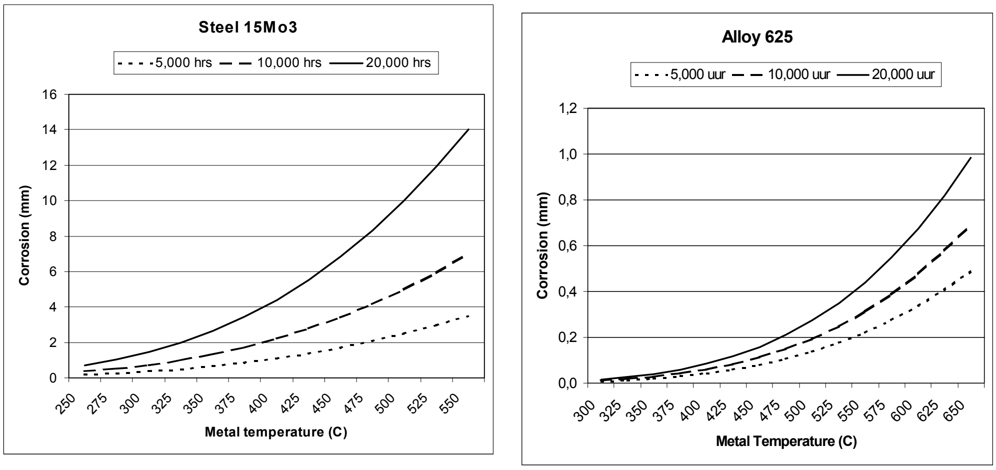

Figure 7. Extrapolated corrosion data for boiler steel 15Mo3 and Alloy 625.(18)

The experience is growing, and more recent data from Dutch WTE plants confirm the previous results. Some data both on waterwall corrosion and superheater corrosion are given in Table 13.

Table 13. Experience on corrosion rates for boiler parts of Dutch WTE plants.

Boiler part	**Evaporator tubes**	**Superheater tubes**
Tube wall temperature	~ 250-300 °C	~ 400-530 °C
Tube arrangement	Membrane wall	Bundles
Material	C-steel (St.35.8)	Low alloy steel (15Mo3)
Typical corrosion rates	0.15-0.30 mm/yr.	0.20-0.40 mm/yr.
High corrosion rates	0.30-2.0 mm/yr.	0.40-4.0 mm/yr.

In fact most WTE plants show corrosion of low alloy boiler steels. Differences in corrosion rates primarily have to be explained by the process conditions in particular high gas temperatures and relatively high heating values, and by deposit formation. In addition many design aspects as mentioned before play an important role.

In other countries similar data are obtained, and sometimes even higher corrosion rates are mentioned as can be seen in Table 14.

Table 14. Experience on corrosion rates for boiler parts (62).

Boiler part	**Evaporator tubes**	**Superheater tubes**
Tube wall temperature	~ 200-300 °C	~ 400-530 °C
Tube arrangement	Membrane wall	Bundles
Standard material	C-steel. low alloy steel (St.35.8/15Mo3)	Low alloy steel (15Mo3/21/4Cr1Mo)
Corrosion rates	0.08-0.24 mm/yr.	0.08-0.40 mm/1000h
High corrosion rates	0.8-2.4 mm/1000h	0.8-4.0 mm/1000h

5.4 Corrosion protection.

To reach economic life times for components corrosion rates should not exceed the typical values, because wall thickness' of water/steam tubing is limited to e.g. 5 to 6 mm. The high rates in Table 13 are regarded as unacceptable, and may result in major superheater repairs after 1 to 2 years and membrane wall repairs after 2 to 5 years.

There are several methods to reduce corrosion and developments continue:
- improvement of the combustion process, to get milder conditions,
- improved process control, in particular temperature control of the flue gas,
- modification of the design in particular a) flow dynamics and mixing b) the arrangement of the steam system,
- application of more resistant materials.

The first three methods influence the conditions in the boiler near the tube walls. Temperature stability and deposits play an important role. The last method has to do with the boiler tubes itself.
With respect to more resistant materials for boiler tubes up to now most promising are Ni-base alloys e.g. Alloy 625.

From the mechanisms described before it can be understood that Ni is more resistant than Fe. With respect to the materials there are several options and the experience is growing:

- Application of composite tubing consisting of two layers, with the inner layer from a boiler steel and the outer layer made from an highly resistant material (e.g. Ni-base alloy). This technique is a/o. applied for superheaters.
- Application of surface welding (cladding); both waterwalls and superheaters are being clad with a resistant material like Alloy 625.
- Application of resistant coatings from resistant materials, e.g. by high velocity oxygen flame (HVOF), a technique able to produce high quality coatings.
- Application of refractory lining or ceramic tiles in particular on the walls in the first pass.

Information on corrosion data in WTE environments with specified amounts of bromine containing compounds is lacking. Some tests were carried out (16) in gas containing high HBr and HCl contents, in temperature range of 400 to 800ºC. Corrosion data for alloy 625 in HBr are comparable with HCl.

6 Possible effect of bromine

6.1 Effect of bromine containing compounds

6.1.1 Corrosion in gaseous bromine environments

Many metals or alloys react readily with halogen gases at elevated temperatures to form volatile metal halides. Many metal halides also exhibit low melting points. Sublimation of the metalhalides often takes place at a considerable rate at relatively low temperatures. For these reasons alloys containing elements that form highly volatile or low melting can suffer (severe) halogen induced high temperature corrosion. The resistance of various metals (or alloys) to halogenation is related to physical and thermodynamic properties of metal halide reaction products. Depending on these properties metals may be passivated against halogen attack by deposition of solid reduction products on the metal surfaces. On the other hand such product compounds could accelerate corrosion rates. For example if liquid or volatile metalhalides are formed under the circumstances (temperature, partial pressures) involved, passivation may be prevented and high corrosion rates are observed.

The basic features of corrosion in bromine environments are in literature mostly described in combination with other halogens and hydrogen halides (8), since much properties are fairly comparable. Literature only dealing with the corrosivity of bromine and its derivatives is very scarce.

- free energy of formation

The thermodynamic stability of any condensed phase relative to a tentative chemical reaction can be determined by calculation from a knowledge of the standard free energies of formation for each reactant and products compound, plus consideration of any deviation from standard conditions for the phase involved.

Tabular data and parametric functions for the Gibbs energies of formation for halide compounds have been compiled. In Figures 8 and 9 standard free energies of formation are respectively presented of condensed transition metal bromides and transition metal chlorides. As can be deduced from these figures the free energy of a metal bromide tend to be higher than the corresponding metal chloride. Differences are however small.

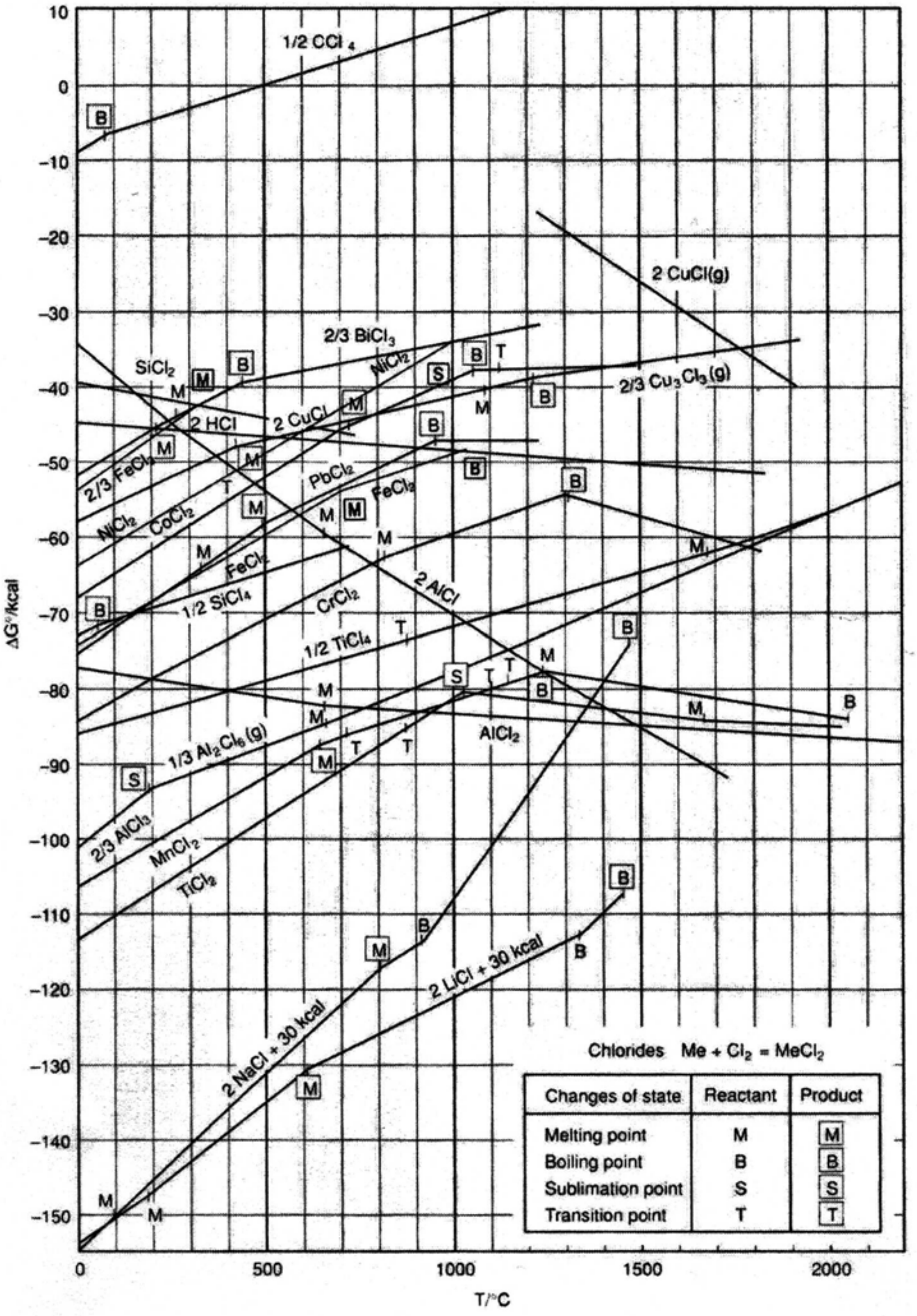

Figure 8. Standard free energies of formation for metal chlorides (88) (lower values indicate higher stability, 'formed more easily')

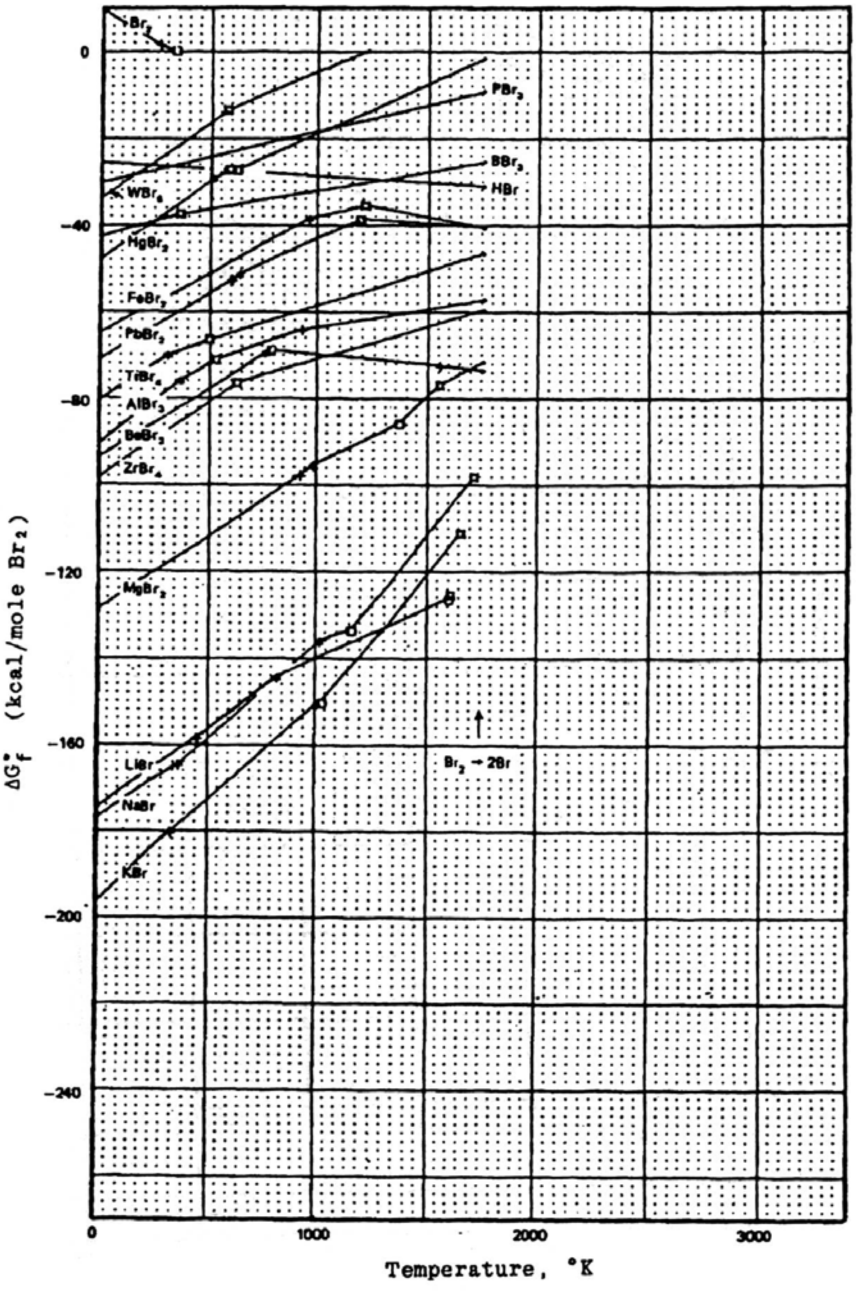

Figure 9. Standard free energies of formation for metal bromides (8)

The melting temperatures metal halides and the temperatures at which a vapour pressure of 10^{-4} atm. is reached are compiled for metal chlorides and bromides in respectively tables 15 and 16 (8, 89). It is well established that chlorides and bromides have the lowest temperatures at which vapour pressures of 10^{-4} atm. are reached. In general the data for comparable bromides and chlorides differ not very much. For evaluating the role of halogen and hydrogen halide corrosion in MSWI especially the values for iron, chromium and nickel, major constituents of commonly used alloys in this service are of importance.

Table 15. Melting points, temperatures at which chloride vapour pressure reaches 10^{-4} atm, and boiling points of various chlorides (8,89)

Chlorides	Melting point °C	Temperature at 10^{-4} atm, °C	Melting point °C
$FeCl_2$	676	536	1026
$FeCl_3$	303	167	319
$NiCl_2$	1030	607	987
$CoCl_2$	740	587	1025
$CrCl_2$	820	741	1300
$CrCl_3$	1150	611	945
CrO_2Cl_2	-95	-	117
CuCl	430	387	1690
$MoCl_5$	194	58	268
WCl_5	240	72	-
WCl_6	280	11	337
$TiCl_2$	1025	921	-
$TiCl_3$	730	454	750
$TiCl_4$	-23	-38	137
$AlCl_3$	193	76	-
$SiCl_4$	-70	-87	58
$MnCl_2$	652	607	1190
$ZrCl_4$	483	146	-
$NbCl_5$	205	-	250
$NbCl_4$	-	239	455
$TaCl_5$	216	80	240
$HfCl_4$	434	132	-
CCl_4	-24	-80	77
NaCl	801	742	1465
KCl	772	706	1407
LiCl	610	665	1382
$MgCl_2$	714	663	1418
$CaCl_2$	772	1039	2000
$BaCl_2$	962	-	1830
$ZnCl_2$	318	349	732
$PbCl_2$	498	484	954

Table 16. Melting points, temperatures at which chloride vapour pressure reaches 10^{-4} atm, and boiling points of various bromides (8, 89).

Bromides	Melting point °C	Temperature at 10^{-4} atm, °C	Melting point °C
$FeBr_2$	689	509	974
$FeBr_3$	-	156	-
$NiBr_2$	965	580	919
$CoBr_2$	678	-	-
$CrBr_2$	842	716	-
$CrBr_3$	>800	615	-
$CrBr_4$	-	516	-
CuBr	488	435	1318
WBr_5	276	-	-
WBr_6	309	-	-
$AlBr_3$	97	53	255
$SiBr_4$	5	-	153
$MnBr_2$	695	-	-
$ZrBr_4$	450	169	-
$NbBr_5$	267	-	361
$HfBr_4$	424	137	-
$TiBr_4$	-	-	232
$TaBr_5$	267	145	347
NaBr	750	690	1393
KBr	740	671	1383
LiBr	550	630	1310
$MgBr_2$	710	626	1230
$CaBr_2$	742	-	1800
$BaBr_2$	854	-	-
$ZnBr_2$	398	320	650
$PbBr_2$	373	432	914

Combustion tests in the Tamara pilot waste incineration plant have pointed out that volatilisation of heavy metals is strongly promoted by both the chlorine and bromine content of the waste. Especially for copper, zinc, antimony, tin and lead a significant increase of the transfer into the fly ashes could be observed. In figure 10 the correlation can be seen between the amount of some metals transferred out of the fuel bed and the molar sum of these halogens in the inventory in the fuel (97). These combustion tests were performed with bromine concentrations between 0.5 and 1.0 wt%, levels more than 100 to 150 times higher than the typical concentration in MSWI's.

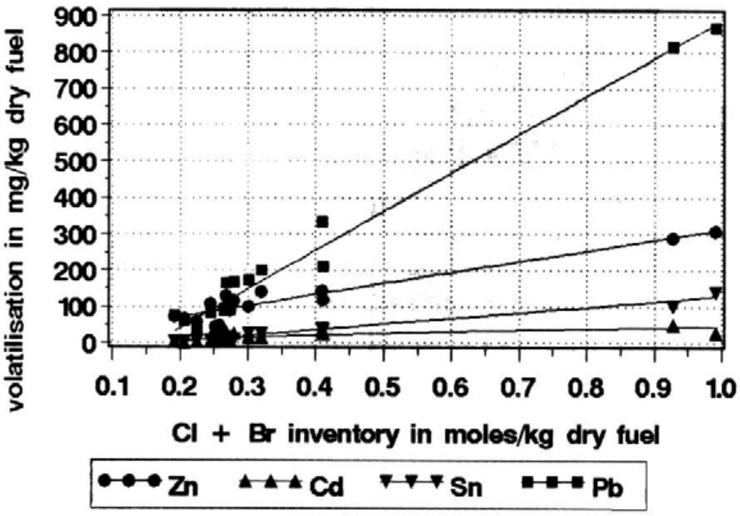

Figure 10. Volatilisation of Zn, Cd, Sn and Pb as a function of the accumulated molar Cl and Br inventory in the fuel (96).

Iron

Iron forms two binary bromides $FeBr_2$ and $FeBr_3$. $FeBr_2$ melts at 698°C and has a vapour pressure of 10^{-4} atm at about 510 ºC and is stable to above 900 °C under a 1 atm bromine pressure. $FeBr_3$ has a vapour pressure of 10^{-4} atm about 155°C, but according to (8) this salt decomposes at 140 °C under a 1 atm atmosphere bromine pressure. So iron may be expected to form a solid bromide scale with a significant evaporation rate at relative low temperatures. $FeCl_3$ and $FeBr_3$ both show very low temperatures of respectively 167°C and 155°C at which a vapour pressure of 10^{-4} atm is reached. Corresponding temperatures for nickel and chromium bromides are much higher.

Bromine reacts with nickel to form a scale of $NiBr_2$. This salt melts at about 965 °C. At 700 °C the vapour pressure of $NiBr_2$ is 5.65×10^{-3} atm. At lower temperatures a $NiBr_2$ scale may protect nickel from rapid reaction with bromine. Because of its high vapour pressure $NiBr_2$ scale will begin to evaporate well below its melting point.

The vapour pressure of $NiBr_2$ as function of temperature can be described by (90):

$$\text{Log } P_{NiBr2\,(atm)} = +\,16.681 - (13.112/T) - (0.3497 \times 10^{-3}).T - 1.711 \log T \quad [19]$$

At each temperature the vapour pressure is roughly double that for $NiCl_2$. The evaporation rates for $NiBr_2$ are postulated to be comparable to those of $NiCl_2$ in absence of experimental data on $NiBr_2$ evaporation (8). In the nickel chlorine reaction, $NiCl_2$ evaporation measurably influences the reaction kinetics above about 450°C and dominates the kinetics above 550°C.

Alloys

Relatively little data have been reported on the performance of metals and alloys in bromine environments compared to chlorine. In Table 17 (20) corrosion rates of several alloys in bromine at 300°C and 500°C are given. Nickel exhibited good corrosion resistance in bromine at 300°C and 500°C. Copper corroded very rapidly at 300°C. This is explained by the relatively low temperature of 435°C at which a vapour pressure of 1×10^{-4} atm is reached for CuBr.

Table 17. Corrosion rates of several alloys in bromine at 300 and 500°C (20).

Alloy	Temperature °C	Time days	Weight loss mg/cm^2	Corrosion rate Mm/yr.
Ni-201	300	11	0.28	<0.03
			0.16	<0.03
			0.14	<0.03
Duranickel 301	300	10	0.17	<0.03
			0.07	<0.03
400	300	2	7.07	1.5
			6.65	1.5
Copper	300 (a)	<1	Rapid attack	-
Ni-201	500	10	3.83	0.15
			1.40	0.06
Duranickel 301	500	10	2.14	0.09
			3.64	0.15

(a) tests were terminated before 300 °C was reached because rapid corrosion attack.

6.1.2 Corrosion by molten salt mixtures including bromine salts.

Formation of low-melting-point salts may be responsible for fireside corrosion of furnace tubes and superheater tubes (20). Deposits can be regarded as being composed of two types of material: carry-over and condensation deposits. Carry-over deposits consist of particles of fuel, which may be completely, or partially combusted. Condensation deposits are formed when components are selectively vaporised at higher temperatures from the fuel or ash in the combustion chamber, and deposited in the cooler heat transfer surfaces in the upper furnace. The composition of the condensation deposit is usually quite different from those of the carry-over deposit. Compounds, which do not exist as such in the fuel, can be formed by the evaporation-condensation mechanism.

Attack by molten ash-salt mixtures in MSW combustors is essentially a form of hot corrosion, wherein chlorine compounds rather than sulphur compounds are regarded as the primary aggressive species (91). The corrosiveness of chlorides stems to a large degree from their low melting points, especially eutectic mixtures of alkali and heavy metal chlorides in MSWI deposits. Constituents, which are frequently detected in significant amounts in deposits, include chloride, sulphur, potassium, sodium, cadmium, zinc, lead, tin, and mercury. All these elements may contribute to the formation of low melting point salts. Melting points and compositional data for liquid phases possibly present in MSWI condensation deposits are shown in Table 18.

Table 18. Melting point and compositional data for liquid phases possibly present in MSWI condensation deposits (55)

System	Melting point (°C)	Composition
$KCl-ZnCl_2$	232	40% KCl
$NaCl-ZnCl_2-PbCl_2$	238	30% NaCl, 14 % $PbCl_2$
$KCl-ZnCl_2-PbCl_2$	238	43% KCl, 6 % $PbCl_2$
$KCl-ZnCl_2-PbCl_2$	239	19% KCl, 13 % $PbCl_2$
$KCl-ZnCl_2-PbCl_2$	250	49% KCl, 8 % $PbCl_2$
$KCl-ZnCl_2$	250	52% KCl
$Na_2Cl_2-ZnCl_2$	262	29% Na_2Cl_2
$CaCl_2-ZnCl_2$	270	99% $ZnCl_2$
$KCl-ZnCl_2$	274	35% KCl
$KCl-ZnCl_2-PbCl_2$	275	50% KCl, 11 % $PbCl_2$
$ZnCl_2$	283	100% $ZnCl_2$
$ZnCl_2-ZnSO_4$	300	11% $ZnSO_4$
$Na_2Cl_2-ZnSO_4$	305	61% $ZnSO_4$
$KCl-ZnCl_2-PbCl_2$	325	54% KCl, 19 % $PbCl_2$
$NaCl-ZnCl_2-PbCl_2$	350	48% NaCl, 17 % $PbCl_2$
$KCl-ZnCl_2-PbCl_2$	375	59% KCl, 24 % $PbCl_2$
$K_2SO_4-Na_2SO_4-ZnSO_4$	384	27% K_2SO_4, 33% Na_2SO_4
$K_2SO_4-Na_2SO_4-ZnSO_4$	385	17% K_2SO_4, 29% Na_2SO_4
$K_2SO_4-Na_2SO_4-ZnSO_4$	388	22% K_2SO_4, 37% Na_2SO_4
$CaCl_2-NaCl-PbCl_2$	391	17% $CaCl_2$, 36% NaCl
$K_2SO_4-Na_2SO_4-ZnSO_4$	392	35% K_2SO_4, 22% Na_2SO_4
$K_2SO_4-Na_2SO_4-ZnSO_4$	392	21% K_2SO_4, 37% Na_2SO_4
$K_2SO_4-Na_2SO_4-ZnSO_4$	398	33% K_2SO_4, 20% Na_2SO_4
$KCl-NaCl-PbCl_2$	400	40% KCl, 16 % NaCl
$K_2Cl_2-PbSO_4$	403	1:3 K_2 : Pb // 1:11 Cl_2 : SO_4
$NaCl-PbCl_2$	410	31% NaCl
$KCl-PbCl_2$	429	23% KCl
$KCl-ZnCl_2$	430	69% KCl

Especially lead salts are presumed to be the major corrosive compound for corrosion of superheater tubes (temperatures of about 566°C). Mixtures of NaCl, KCl and $FeCl_2$ are reported to be highly corrosive for furnace-wall tubes at about 260°C for both carbon steel and stainless steel AISI 304 (95).

Bromine salts are not mentioned in the available literature on high temperature corrosion in MSWI's, so no statement can be made regarding their corrosivity. However from (96) and the data reflected in Table 16 bromine salts may very well be expected to be a constituent of the scales and deposits on the tube walls in MSWI's. From the original source from which Table 18 is deduced a similar table is compiled for molten mixtures of bromine salts and mixtures of bromine salts with other halide salts, Table 19 (55, 80). Data concerning melting points for salt mixtures including bromide salts are less available than chloride salt mixtures.

Table 19. Melting points of (eutectic) salt mixtures involving bromine salts

Possible molten bromide salts and mixtures with chloride salts in MSWI deposits (weight %)	
Salt Mixture (wt.%)	Melting point (°C)
24 KBr -76 $CaBr_2$	546
44 NaBr -56 $CaBr_2$	517
43 KBr-57 KCl	728
100 $PbBr_2$ - 0 $PBCl_2$	371
85 NaBr - 15 $PbBr_2$	323
49 NaBr - 51 KBr	626
91 KBr - 9 $PbBr_2$	349
25 NaBr - 75 NaCl	738
40 $PbCl_2$ - 60 KBr	369
58 KCl - 42 NaBr	610

6.2 Effects of bromine containing compounds relative to other halides.

In chapter 5 of this study the currently most widely accepted models on the corrosion mechanism in MSWI's are reflected. These models describe that corrosion in chloride-contaminated environments is governed by competing oxidation-chlorination reactions, which in turn are closely dependent on the type of metal (or alloy) and adjacent micro-environments. The specific factors influencing these competing reactions are thermodynamic factors free energies of formation, relative stability of products, vapour pressures, etc as well as kinetics which in turn relate to physical-chemical properties of the product (density, volume, diffusivity, expansion coefficients, etc). In literature on corrosion in MSWI hardly any comments are made regarding the role of halides other than chlorides. For evaluating corrosion in oxidation-chlorination environments it is said to be of crucial importance to know which attack mode predominates because unlike oxides, chlorides are ineffective corrosion barriers (19).

In the study of corrosion mechanisms in MSWI environments thermodynamic analysis, mainly used to set-up thermochemical stability diagrams, plays a predominant role. These diagrams are very useful in these studies, however one should be aware of its limitations. Such diagrams often fail to accurately predict corrosion products that actually form in complex multi-component environments because these depend on the specific reaction kinetics and alloy composition. Another shortcoming mentioned is the fact that vapour pressures of volatile species that may be in equilibrium with condensed phases, are not taken into account. The way thermochemical studies can be performed is extensively discussed in (92).

Thermochemical studies on corrosion mechanisms often focus on the comparison of the stability domain of (transition) metal oxides and chlorides versus partial oxygen and chlorine pressures. Metal oxides and sulphides tend to be in general more stable than the halides and as can be deduced from figures 8 and 9 the chlorides are in general more stable than the bromides. However in practice the relative concentrations will naturally dictate what phases are produced, so it is very well possible to form metal halide compounds wherever the partial pressure of the halogen is sufficiently high compared with the oxygen partial pressure. In figure 11 a thermochemical stability diagram for the metal-oxygen-chlorine system at 400 °C is shown (19).

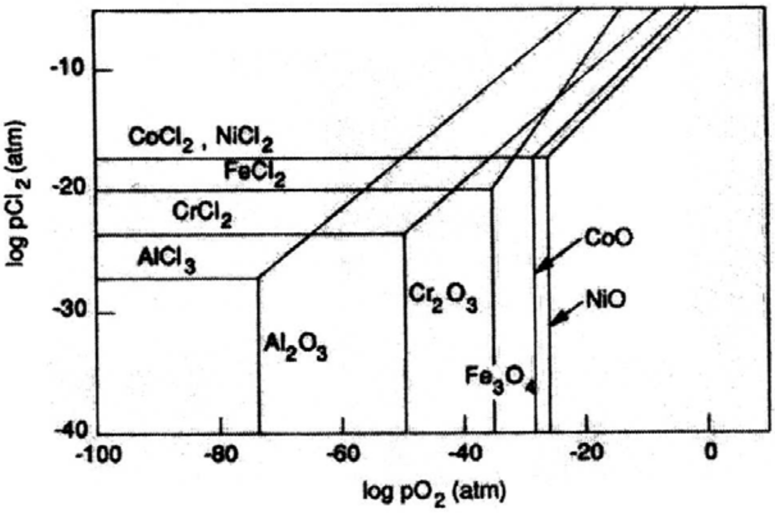

Figure 11. Thermochemical stability diagram for several metal oxygen-chlorine systems at 400 °C (19)

From this diagram it can be predicted that attack by chlorine is more likely to occur in reducing or oxygen-deficient conditions. It is commonly accepted that the partial pressures of oxygen can vary strongly over the thickness of the oxide layer. At the metal interface oxygen pressure can be sufficiently low for halides to be the more stable compounds. More outwards where oxygen partial pressures increase, halides are transformed into oxides. In this way oxidation is promoted by intermediary halogen species. The released chlorine in this transformation process in turn reacts with the metal tube metal to form more $FeCl_2$ or other metal chlorides and as a result a cyclic reaction takes place beneath the oxide scale.

This prediction from thermochemical analyses that metalchlorides can be formed at the metal-oxide interface is in general confirmed by analyses on the composition of scale layers formed in MSWI's in practice.

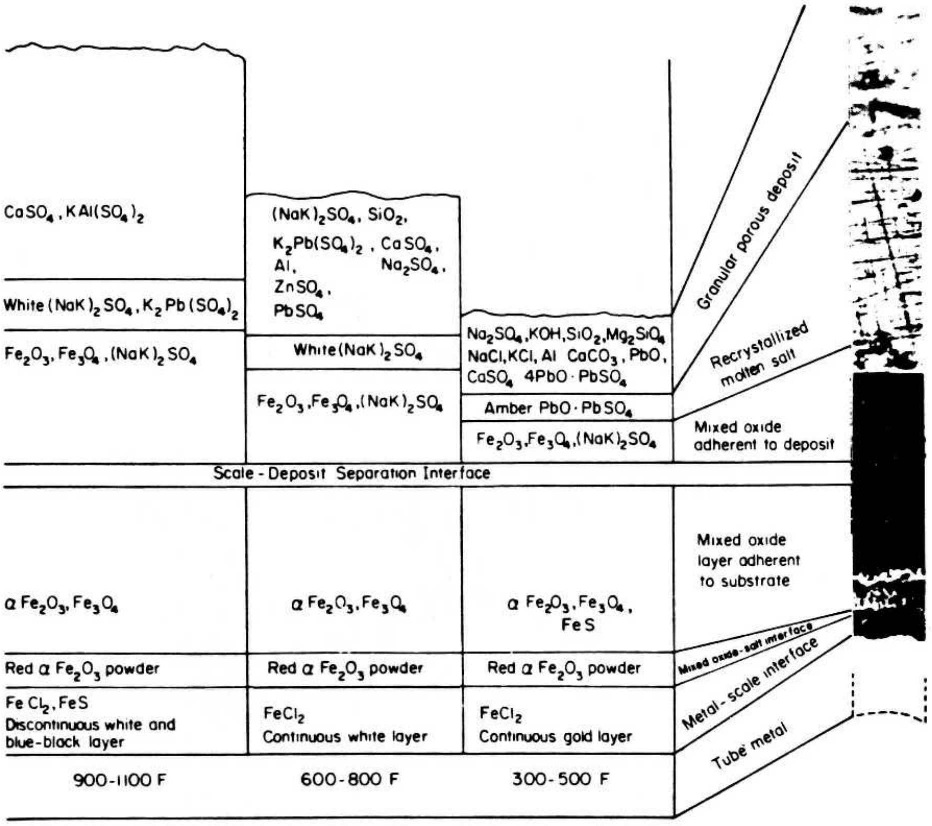

Figure 12. Compounds Identified by X-Ray diffraction of deposit and scale layers on corrosion probe specimens exposed to bulk refuse Incineration (60)

Figure 12 shows the multiple layer structure formed on corrosion probes. The layer directly adjacent to the metal is observed to be mainly a ferrous chloride layer. More outward situated layers consist of metal oxides and sulphides due to the higher sulphur and oxygen partial pressures as compared to the chlorine partial pressure. The most external layers are a result of carry-over and condensation deposits. In other studies on the composition of fire side deposits in MSWI's more differentiated observations were made, chlorides turned to be a constituent of both top and bottom layers however invariably the highest chloride levels were detected in the bottom layers (93).

Besides thermochemical analyses, reaction kinetics are of high importance in mechanistic studies on halide corrosion, since these determine the rate of transport of gaseous halides species by diffusion through pores and cracks in otherwise protective oxide scales. One of the major effects reported for chloride influencing kinetics is that it changes the morphology of the oxide layer to create porosity, leading to more rapid attack, although the amount of chlorides is relative low. Such voids at the metal/oxide interface promote scale spallation as well as internal attack by subsurface penetration of chlorides (19).

- Mechanism for bromine corrosion in presence of oxidants

As stated before information on the corrosion of metals in bromine environments is very limited. In a study on the high temperature corrosion behaviour at 1000 K of Fe-Cr and Ni-Cr alloys in Ar-H_2O-HBr gas mixtures it was observed that a bromide rich corrosion product layer was formed directly adjacent to the alloy with more outward layers consisting out of oxides. It is stated that the role of HBr gas in promoting the metal (in this case nickel) oxide in the scale was similar to the well-known intermediate role of halogen species in accelerating metal oxidation. It was also concluded that HBr promoted scale spallation and evaporation of nickel from the alloy substrate and nickel oxide in the scale (94). Although a temperature of 1000 K is well above the wall temperatures encountered in MSWI's it is remarkable that the proposed mechanism for bromine corrosion resembles very much the currently widely accepted models for chloride corrosion in MSWI's.

- Thermochemical study Me-O-Cl-Br

When the limited available literature on bromine in high temperature corrosion is compared with the chlorine it parallels can be observed. Free energies of formation of these halide salts, melting points, vapour pressures of their salts and even the proposed mechanism of bromine and chlorine corrosion are quit similar. In the models on the roll of chlorine and hydrogen chloride in MSWI corrosion a mechanism relying on a cyclic oxidation-chlorination process is assumed. Normally chlorine compounds are much more abundant in MSWI fuel than bromine compounds, concentration of bromine compounds is reported to be 100 to 150 times lower than chlorine (96). One of the major topics to be dealt with is to evaluate whether bromine can interfere in this mechanism or not.

Thermodynamical approach

A thermochemical approach could be helpful to start the evaluation. As an extension to this literature study it was therefore decided to perform an explanatory thermochemical study on the systems Fe-O-Cl-Br and Ni-O-Cl-Br at 400 °C an temperature typical for wall temperatures in MSWI's. For the Fe-system, iron (metallic), Fe_3O_4, $FeCl_2$ and $FeBr_2$ are taken into account. For nickel the compounds are metallic nickel, NiO, $NiBr_2$ and $NiBr_2$.

For the Ni-O-Cl-Br system the results are shown in Figures 13 to 16.

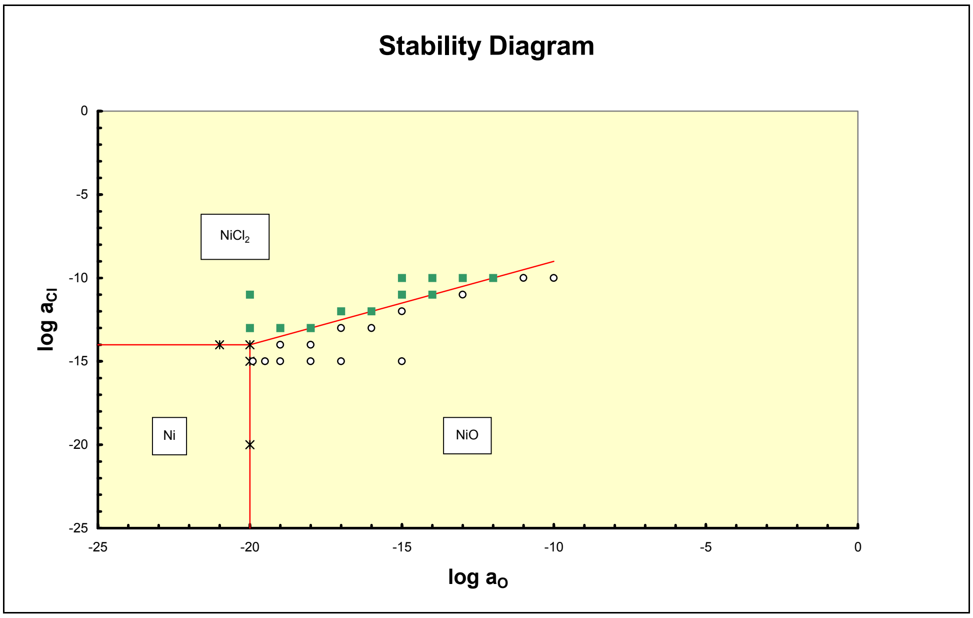

Figure 13. Thermochemical stability diagram for Ni-O-Cl at 400°C.
No bromine activity.

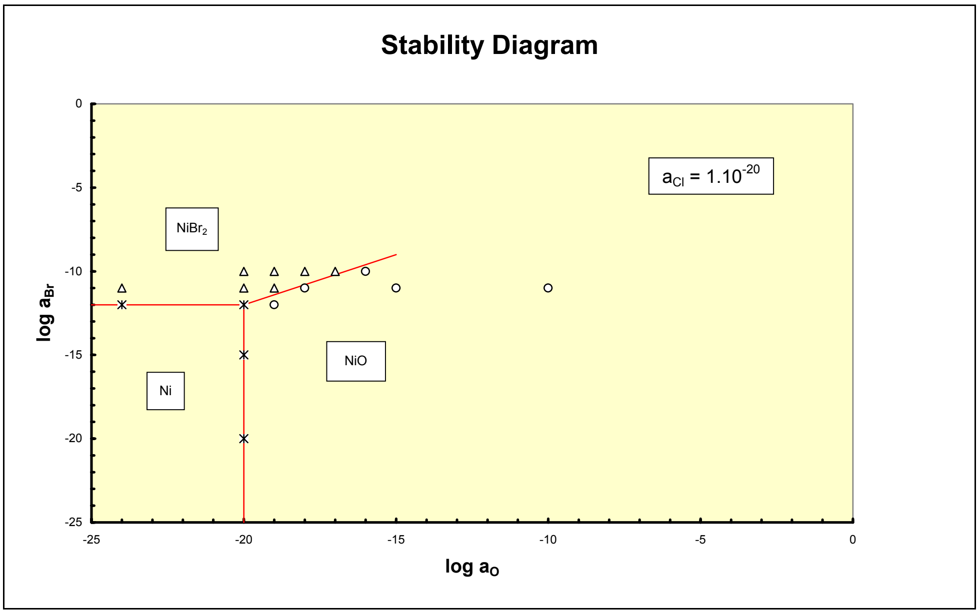

Figure 14. Thermochemical stability diagram for Ni-O-Cl-Br at 400°C
with a chlorine activity of 1 x 10^{-20} *mol/l.*

Comparing figures 13 and 14 it can be seen that that $NiCl_2$ is the more stable at lower activities than $NiBr_2$. If at the metal surface chlorine and bromine activities are equal it can be expected that $NiCl_2$ will be the most stable phase, only when the bromine activity is about 100 times higher than chlorine $NiBr_2$ will be more stable.

A similar calculation with much higher chlorine activities is shown in figure 15. Now the $NiCl_2$ is more stable than metallic Ni, and the stability area of $NiBr_2$ is further limited.

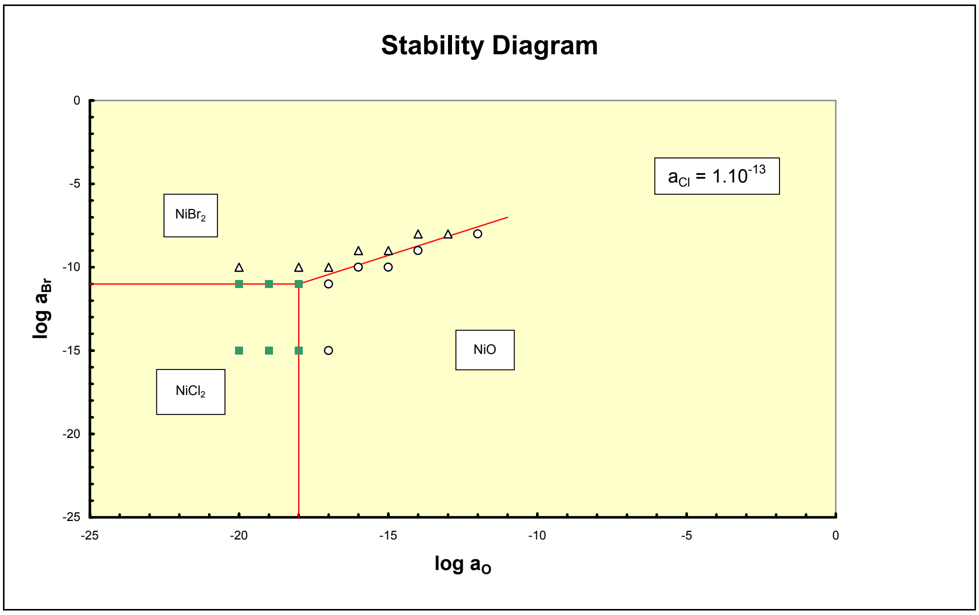

Figure 15. Thermochemical stability diagram for Ni-O-Cl-Br at 400°C with a chlorine activity of 1 x 10^{-13} *mol/l.*

Comparable results have been obtained for iron. From figures 16 and 17 it can be seen that $FeCl_2$ is more stable than $FeBr_2$ at the same activity.

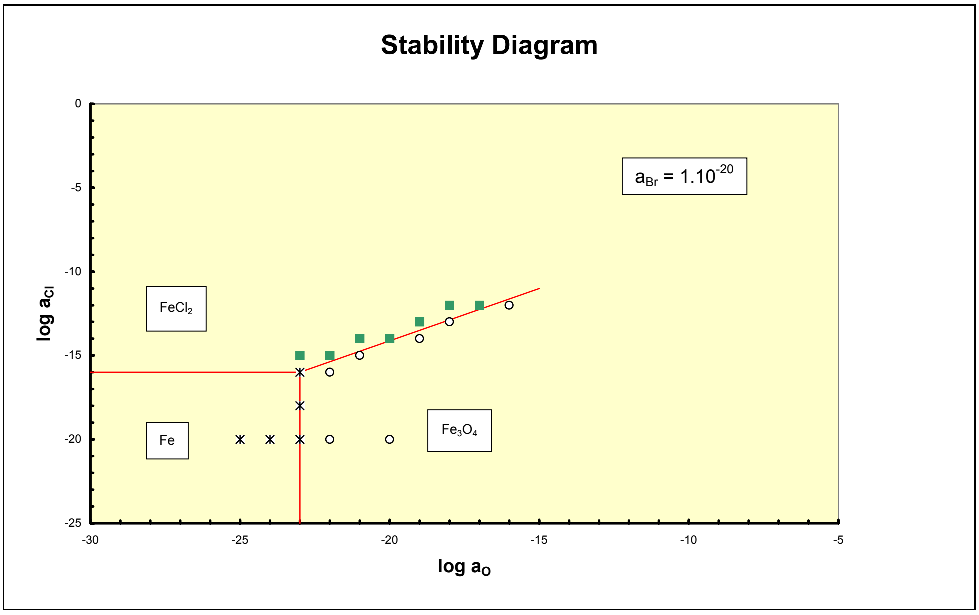

Figure 16. Thermochemical stability diagram for Fe-O-Cl-Br at 400°C with a chlorine activity of 1 x 10^{-20}

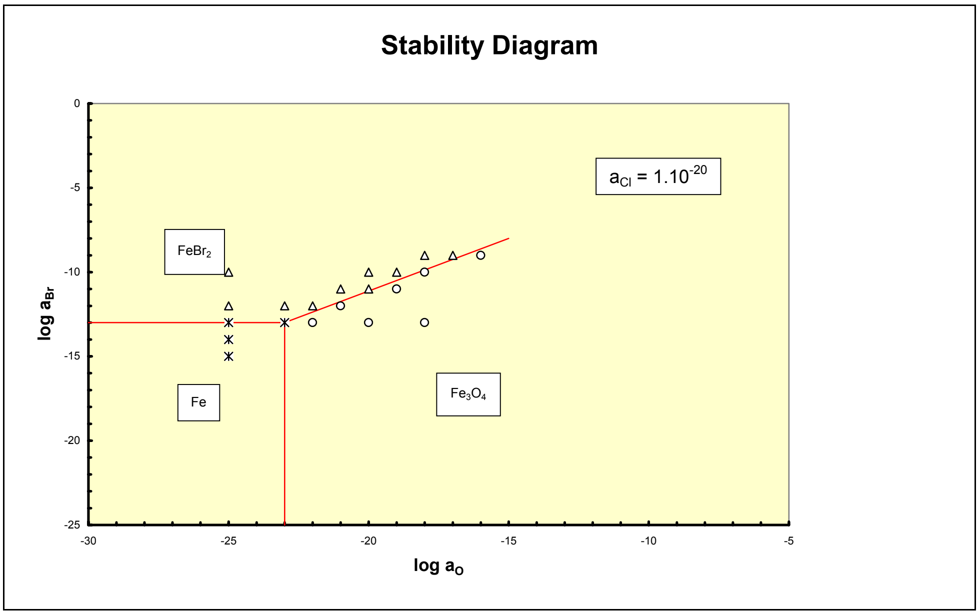

Figure 17. Thermochemical stability diagram for Fe-O-Cl-Br at 400°C with a bromine activity of 1 x 10^{-20} mol/l.

The thermochemical analysis is the first approach to identify possible reactions and to compare qualitatively the corrosion potential of bromine versus chlorine.
It is obvious that from this analysis no decisive conclusions regarding the role of bromine in MSWI corrosion can be drawn. The reason is that such analysis does not include kinetics of possible corrosion reactions, and little is known about the influence of bromine on kinetics. However since the concentration of bromine in the fuel of MSWI is normally far less than chlorine it can be assumed that only when bromine has a major impact on corrosion kinetics (much higher than chlorine has at the same concentrations) an effect of bromine may be expected.

Partitioning of bromine in the gasphase.

As free Br_2 is relatively stable, it can pass a gas cleanup system and cause corrosion in downstream equipment its formation has to be suppressed.
The Tamara study, carried out with relatively high WEEE contents, revealed that Br was primarily present as HBr (10, 11, 15, 96). However as soon as the Br concentration in the gasphase exceeded 300 mg/m^3 the appearance of elementary Br_2 was observed. The presence of Br_2 was accompanied by the disappearance of SO_2, and the finding that all S in the gas is present as SO_3. From these observation it is speculated that Br_2 formation is suppressed as long as enough SO_2 is available.

In addition other authors (13) mention reactions which can help to form volatile substances. SO_2 might be beneficial to form volatile HBr, comparable with the sulphation reaction of chlorine containing substances, due to the possible reaction:

$$SO_2 + 2H_2O + Br_2 = 2HBr + H_2SO_4 \qquad [20]$$

At high temperatures and high molecular oxygen levels hydrogenbromide HBr can oxidise. In literature it is mentioned that high temperature oxidation of HBr between

490°C and 635°C is almost entirely a homogenous reaction resulting in H_2O and Br_2 (63). The mechanism suggested is:

$$HBr + O_2 = HO.OBr \qquad [21]$$
$$HBr + HO.OBr = 2HO.Br \qquad [22]$$
$$HBr + HO.Br = H_2O + Br_2 \qquad [23]$$

Obviously only at relatively high HBr concentrations these reactions can proceed. Added inert gases decrease the rate, probably by accelerating the decomposition of the intermediate complex HO.OBr. With regard to the low HBr concentrations in MSWI flue gas it is not expected that these reactions will contribute to free Br_2.

7 Conclusions

With regard to the possible corrosion effect of bromine in the waste of a WTE plant the following conclusion can be drawn from this study:

- As long as the amounts of WEEE, that can be mixed and co-fired with Municipal Solid Waste, are limited to e.g. 3 %, from this study and the data obtained it can be expected that corrosion mechanisms are dictated primarily by chlorine, and corrosion rates of boiler parts will not change noticeable when WEEE is added to MSW. In practice verification of this expectation is recommended.
- In the present waste-to-energy plants the input waste shows considerable variations in heating value and chlorine content. Up to now variations in the composition of the waste and the heating value are not very well identified and measured.
- Corrosion in the present WTE is primarily caused by relatively high chlorine levels in the waste, high temperatures in the flue gas, en deposit formation on the relatively cool boiler heat transfer surfaces. The most sensitive areas are the boiler parts with high temperature differences between gas and metal (e.g. membrane waterwalls) or with high metal temperatures (e.g. superheaters)
- All WTE suffer corrosion albeit that corrosion rates vary and depend very much on factors related to design on the one hand, and waste composition and process conditions in particular temperatures profiles in the boiler on the other hand.
- The literature, and contacts with plant operators revealed, that little is known about a possible additional effect of e.g. WEEE on the corrosion. Calculations have shown that the addition of up to 3% of WEEE to MSW can increase the chlorine input with 0.15 wt%, and the bromine input with 0.05 wt%. As part of this will be captured in the bottom ash, 80% to 95% of this increase will eventually become available to affect present corrosion of boiler parts These amounts are very limited, as compared to present impurity levels and variations in the present composition.
- Both chlorine and bromine compounds have considerable vapour pressures at relatively low temperature, and data of comparable chlorine and bromine compounds do not differ very much. The same holds for melting points.
- Corrosion mechanism include formation and evaporation of Fe-chlorides. With respect to volatility both Fe-chlorides and Fe-bromides are comparable and have relatively low temperatures at which a pressure of 10^{-4} can be reached. In this respect nickel and chromium show much higher temperatures (lower volatility's). This can explain the better corrosion resistance of nickel base alloys.
- Corrosion by molten salts In WTE plants is primarily caused by chlorides. Much data on melting points of bromine containing mixtures are not available. As far as data can be compared melting points are in the same range or lower for chlorides.
- Based on phase stability calculations the formation of Fe-chlorides and Ni-chlorides is expected to be favoured before Fe-bromides and Ni-bromides.
- With limited amounts of WEEE in MSW the concentrations of bromine containing compounds will be very low, and the raw gas bromine content can be kept well below 300 mg/m^3 in such a way that formation of free Br_2 can be avoided.

8 Recommendations

The following activities could further contribute to a better understanding of the effect of burning or co-firing bromine containing flame retardant residue:

- Short term tests with co-firing WEEE in a hazardous waste incinerator e.g. in a rotary furnace for chemical waste, to collect steel samples with in practice grown deposits. The input levels of bromine, chlorine and sulphur have to be determined. In these tests cooled probes (to simulate a superheater or evaporator tube) have to be used to study build up of deposits, and analyse deposits for bromine and chlorine, depending on location in the system and the temperature level. If possible these trials should last sufficiently long (e.g. 3 month).
- Long term field tests in a modern WTE plant including analyses of gas and deposits from different areas in the plant. At least two field tests are necessary. One reference test with the usual integral waste, and one or more tests with co-firing WEEE during an equal period in the same boiler, or in the same time at another equal boiler. To get information on deposits and effects on corrosion rates these tests should last long enough, e.g. 6 month, and be as steady as possible. To get corrosion data, metallography has to be carried on boiler parts like superheater tubing.

Ir. P. Rademakers	Ing. W. Hesseling	Ir. J. van de Wetering
TNO IND	TNO MEP	Akzo Nobel AMC

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10 Abbreviations

APC = Air Pollution Control
APME = Association of Plastics Manufacturers in Europe
BFR = Brominated Flame Retardant
CEFIC = European Chemical Industry Council
CHP = Combined Heat and Power
COST = European Co-operation in the field of Scientific and Technical Research
EBFRIP = European Brominated Flame Retardant Industry Panel
ECN = Energy Research Centre of the Netherlands
E&E = Electrical and Electronic Industry
EPA = Environment Protection Agency
IEA = International Energy Agency
LHV = Lower Heating Value (net caloric fuel value)
MSW = Municipal Solid Waste
MSWI = Municipal Solid Waste Incinerator
PIC = Products of Incomplete Combustion
RDF = Refuse Derived Fuel
TNO = Netherlands Organisation for Applied Scientific Research
WEEE = Waste from Electrical and Electronic Equipment
WTE = Waste to Energy