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Emission Measurements During Incineration of Waste Containing Bromine

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Content

Preface

Background

The most common use for BFRs is in building materials, textiles and electronic supplies, e.g. TVs, PCs and photocopiers. In incineration plants with good combustion BFRs will decompose and form other brominated compounds, mainly hydrogen bromide (HBr).

In addition, other brominated compounds will also be formed, in particular brominated organic compounds, such as dioxins where chlorine is fully or partly substituted by bromine (brominated and brominated/chlorinated dioxins).

There have been few Studies regarding incineration of plastics containing BFRs at full-scale incineration plants with a modern flue gas cleaning system.

The Norwegian Ministry of the Environment presented in the autumn of 2002 a working plan for reducing the emissions and discharges of BFRs. One action is to investigate the emissions from incineration of waste containing BFRs.

The project has been organised as follows:

Management group:

- Håkon Jentoft, Norwegian Solid Waste Assosiation (NRF)
- Bernt Ringvold, Norwegian Pollution Control Authority (SFT)
- Ole Viggo Svendsen, Elektronikkretur AS
- Tor Christian Svendsen, Hvitevareretur AS
- Hallgeir Betele, Renas
- Fredrik Eide Aas, Stena Miljø AS
- Gerhard Dürbeck, Oslo kommune renovasjonsetaten
- Nordic working group for Thermal Treatment

Reference group:

- NRF’s working group for Thermal Treatment
- NRF has been the secretary for the project.

The work has been done by Kjelforeningen Norsk Energi. Authors are Dag Borgnes and Bente Rikheim.

Abstract

Project objective

The objective of the project is to investigate the emissions of dioxin-compounds that may occur from incineration of plastic waste containing brominated flame retardants (BFRs) together with waste from households and the commercial sector. The decomposition of BFRs will also be investigated.

The project results will serve as a basis for both the authorities and the owners of incineration plants, to make decisions about whether, and under what conditions, this type of waste may be incinerated.

Literature search and initial studies

The objective of the literature search and initial studies is to establish a detailed program for measurements. It should also be the basis for comparison and evaluation of the results from the measurements.

Studies in small-scale pilot plants

Incineration tests with waste containing BFRs have been carried out in small-scale pilot plants in Sweden (University of Umeå) and in Germany (TAMARA Plant).

The results from Sweden, where the content of bromine was increased up to 1-2 % by weight, showed that the concentration of halogenated dioxins in untreated flue gas was significantly higher with BFRs than without.

At the TAMARA-Plant, the content of bromine varied from 0 to approximately 0,2 % by weight. Increasing the content of bromine showed no increase in the concentration of chlorinated dioxins, or in brominated or brominated/chlorinated dioxins in untreated flue gas.

Measurements on full-scale plants

Studies of emissions of brominated dioxins to air were earlier carried out on incineration plants in Denmark, Sweden and Norway. Measurements performed in Denmark also included brominated/chlorinated dioxins. All plants were equipped with advanced flue gas treatment systems. Measurements were performed during incineration of waste from households and the commercial sector (waste with low BFR content), and results showed very low levels for all analysed dioxins.

There is little relevant data of emissions of BFRs from waste incineration plants. We have found results from emission measurements carried out at a Japanese incineration plant burning plastic waste containing

BFRs, mixed with waste from households and the commercial sector. Total input of BFRs was less than 500 g/hr, and the emission to air of PBDE (polybrominated diphenyl ethers) and TBBPA (tetrabrombisphenol) was respectively 3,5 and 8 ng/Nm^3.

Incineration tests at three Norwegian plants

The main goal of the incineration tests was to establish the flue gas concentration of brominated, chlorinated and brominated/chlorinated dioxins before and after flue gas cleaning, and with different proportions of plastic waste containing BFRs. To verify the input, the contents of bromine and chlorine in all output flows (bottom ash, fly ash, scrubber water and flue gas) were analysed. The decomposition of BFRs was investigated by analysing BFRs in output flows.

Execution of tests

The incineration test included sampling and analysis at two larger plants for mixed municipal waste, and one smaller plant for ground/shredded industrial waste. The brominated waste added was waste from a plant for demolition of electric and electronic devices. It was estimated to contain approximately 1 % by weightbromine. Approximately 80% of this contained PBDE.

The most extensive measurements were performed at the largest municipal waste incineration plant in Oslo (Klemetsrud Plant). The plant has two incinerator lines, each with the capacity of incinerating 10 tons of waste per hour. Each line is equipped with a flue gas cleaning system, consisting of a bag house filter with active coal injection, and a wet scrubber.

At this plant sampling and analysis were carried out in three different situations:

- No addition of brominated waste
- Mix with 5 % by weight brominated waste; i.e. approximately 0,05 % by weight bromine in total waste.
- Mix with 10 % by -weight brominated waste; i.e. approximately 0,1 % by weight bromine in total waste.

At the second plant (FREVAR Plant, Fredrikstad) measurements were carried out with no addition of BFRs.

At the third and smaller plant (Energos Plant, Ranheim) measurements were performed incinerating a mix with 0 and 20 % by weight bromine containing waste (i.e. 0,2 % by weight bromine in the total mix).

Results and conclusions

The incinerating conditions during sampling and measurements at Klemetsrud Plant (Oslo) were normal for the plant, with average CO-levels at approximately 20-30 mg/Nm^3. During sampling at the FREVAR Plant average CO-levels were approximately 50 mg/Nm^3. At FREVAR Plant they also experienced some problems with the fabric filters during the measurements.

At the Energos Plant (Ranheim) CO was not detectable, which indicates that incineration was good.

Bromine in output flows

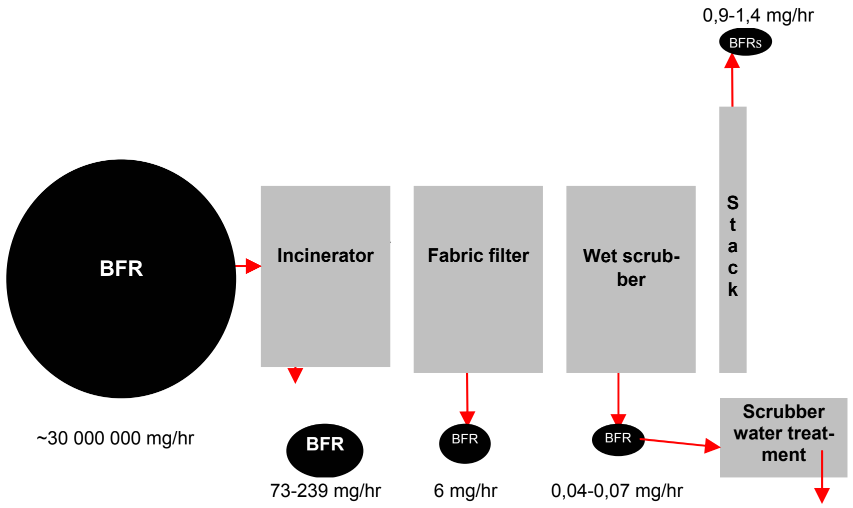
Measured results for gaseous bromine in untreated flue gas during incineration of normal waste mix indicates a bromine content equal to or lower than what is common for waste from households and the commercial sector.

Measured results of bromine in output flows at Klemetsrud Plant (Oslo) and at the Energos Plant (Ranheim) indicate that the content of bromine in the plastic mixture was correctly estimated.

Brominated flame retardants (BFRs)

The amount of BFRs in the waste mixture used in the tests at Klemetsrud Plant (Oslo) was not analysed, but calculated/estimated to be approximately 30 kg/hr. The measured results confirm that BFRs decompose in the incineration process. The amount of BFRs in output flows is less than 0,001 % by weight of the total amount of BFRs in the waste mix (see figure below).

Observed input and output flows of brominated flame retardants at Klemetsrud Plant (Oslo) with 10 % by weight addition of brominated waste.



The concentration of BFRs in flue gas from Klemetsrud Plant (Oslo) was 14-22 ng/Nm^3. This equals 0,9-1,4 mg/hour and approximately 0,01 kg/year, assuming 8000 running hours/year at the same emission level. A Danish study (Miljøstyrelsen, 1999) estimates the total national Danish emissions of BFRs from incineration to be < 0,04 tons. A report from the Norwegian National State Pollution Control Authority (SFT), estimates the national emissions from combustion in Norway to be < 0,01 tons (1998), i.e. < 10 kg/year.

At the Energos Plant (Ranheim) the reported concentration of BFRs in the flue gas was <5 ng/Nm^3.

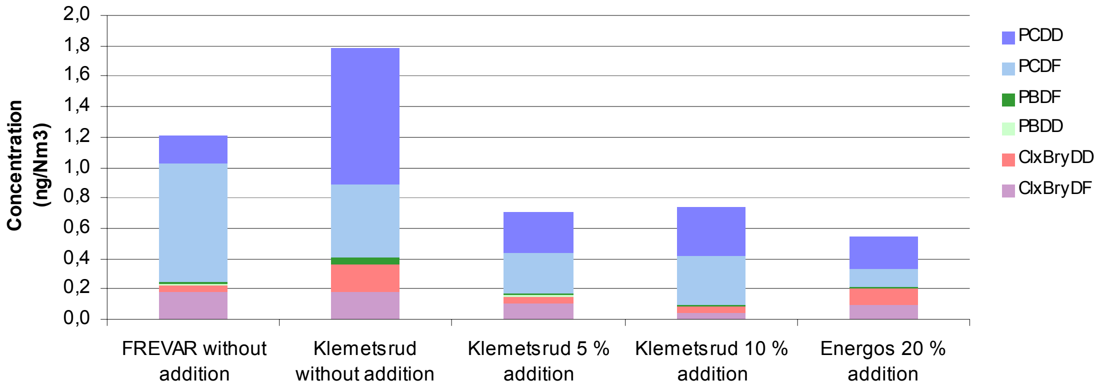
The concentration of BFRs in bottom ash from the tests at Klemetsrud Plant (Oslo) shows levels far below the threshold value stated in the Hazardous Waste Directive.

DekaBEDE and TBBPA (Tetrabrombisphenol A) are the dominating compounds of BFRs in the bottom ash at Klemetsrud Plant (Oslo). In the flue gas dekaBEDE has the highest concentration level.

Concentration of dioxins in emissions to air (after cleaning)

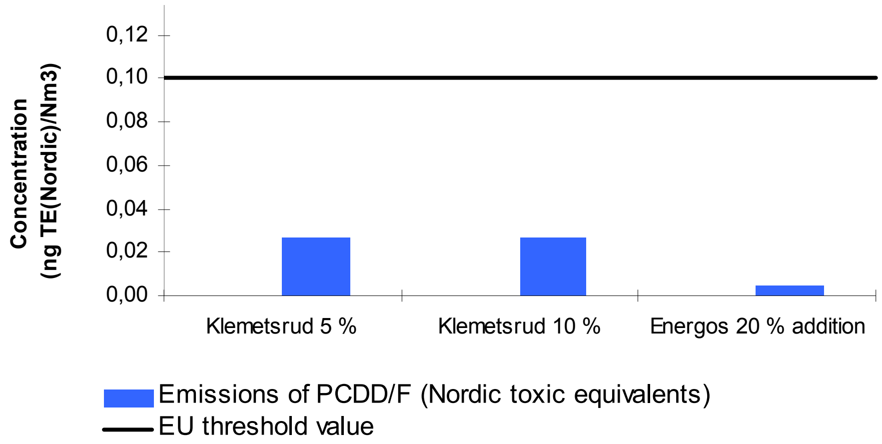
The figure below shows emissions of chlorinated, brominated and chlorinated/brominated dioxins without any addition of brominated waste, and with the addition of 5 % by weight, 10 % by weight and 20 % by weight bromine containing waste.

Emissions of chlorinated, brominated and chlorinated/brominated dioxins. The results are reported as actual emission, not toxic equivalents.



Emissions of chlorinated dioxins (PCDDs/Fs), in terms of Nordic toxic equivalents, resulting from the addition of brominated waste, are presented in the figure below.

Emissions of chlorinated dioxins (PCDDs/Fs), in terms of Nordic toxic equivalents, resulting from addition of brominated waste.



Uncertainty in sampling and analysis, variations in operating conditions and waste mixture, differences between laboratories with respect to methods of analysis (especially dioxins), makes comparison of results difficult. We may although draw the following main conclusions:

- Increasing the content of BFRs in the waste gave no significant increase in the emissions of chlorinated dioxins, or either brominated and chlorinated/brominated dioxins
- The emission level is highest for chlorinated dioxins, lower for chlorinated/brominated dioxins and lowest for brominated dioxins

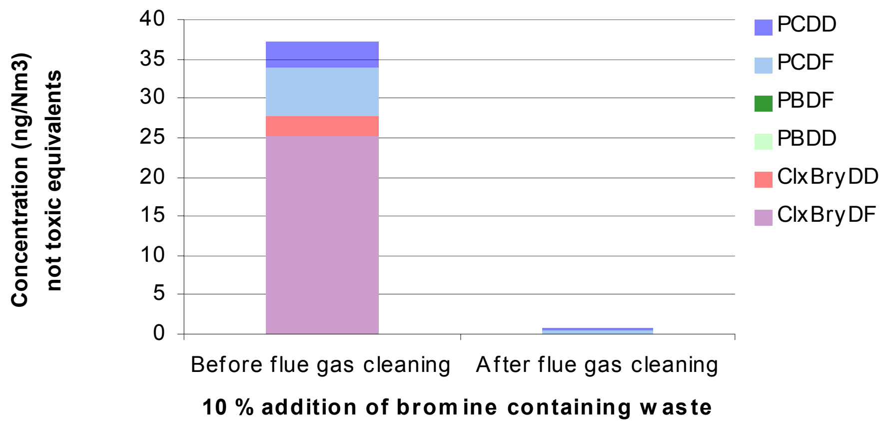
- The emission levels for chlorinated dioxins, reported as Nordic toxic equivalents, are low compared to emission threshold value in the EU-directive for incineration of waste. The reported emission levels were 0,03 ng/Nm^3 and 0,006 ng/Nm^3 respectively for the Klemetsrud Plant (Oslo) and Energos Plant (Ranheim), and the EU threshold value is 0,1 ng/Nm^3.
- The emission measurement results indicate that the incineration efficiency and the operating conditions of the flue gas treatment systems are of greater importance to the resulting emission levels for dioxins, rather than the bromine content level.

Concentration of dioxins in emissions before and after cleaning

Measurements of dioxins in the flue gas before and after flue gas cleaning were carried out with addition of 10 % by weight bromine containing waste at the Klemetsrud Plant (Oslo)

The concentration of chlorinated/brominated dioxins before cleaning was approximately 28 ng/Nm^3, which was three times the concentration of chlorinated dioxins. After cleaning the concentration was approximately 0,1 ng/Nm^3. This gives a removal efficiency for chlorinated/brominated dioxins of >99% and for chlorinated dioxins approximately 93%. The removed dioxins end up in the fly ash from the fabric filter, which is treated as hazardous waste.

Concentration of chlorinated, brominated and chlorinated/brominated dioxins in flue gas before and after flue gas cleaning, Klemetsrud Plant (Oslo). The levels are given as actual measured levels, not corrected for toxicity.



1. Background and Objective

The most common use of BFRs is in building materials, textiles and electronic supplies, e.g. TVs, PCs and photocopiers. In incineration plants with good combustion BFRs will decompose and form other brominated compounds (Söderström, G. et al, 2000), mainly hydrogen bromide (HBr) (Vehlow, J. et al, 1998). Additionally, other brominated compounds will also be formed, in particular brominated organic compounds, such as dioxins where chlorine is fully or partly substituted by bromine (brominated and brominated/chlorinated dioxins).

The formation of brominated/chlorinated dioxins during incineration of waste with BFRs has been proven earlier, in the project "Co-incineration of brominated flame-retardants and MSW in small-scale reactor" in 2000 (financed by the Nordic PA-group and documented in TEMA-Nord Report No 2001:512). The tests were carried out at Umeå University, in at laboratory pilot plant with no flue gas treatment.

There have been few studies regarding incineration of plastics containing BFRs at full-scale incineration plants with a modern flue gas cleaning system.

The Norwegian Ministry of the Environment presented in the autumn of 2002 a working plan for reducing the emissions and discharges of BFRs. One action is to investigate the emissions from incineration of waste containing BFRs.

The objective of the project is to investigate the emissions of dioxin-compounds that may occur from incineration of plastic waste containing brominated flame-retardants (BFRs) together with waste from households and the commercial sector. The decomposition of BFRs will also be investigated.

The project results will serve as a basis for both the authorities and the owners of incineration plants, to make decisions about whether, and under what conditions, this type of waste may be incinerated.

This report is based on separate reports from incineration tests at Klemetsrudanlegget (Oslo) (Kjelforeningen-Norsk Energi, 2004), and at FREVAR (Kjelforeningen-Norsk Energi, 2004b), which also include detailed description of measurement methods and analysis results.

The incineration tests at Energos Ranheim are reported in a report from TÜV Nord Umweltschutz (2003).

2. Terms and Abbreviations

Brominated flame-retardants (BFRs)

Name specific compound	IUPAC-no*.	Abbreviation	Abbreviation groupname	Groupname
TBA		TBA	TBA	Tribromanisol
4,4'-DiBB	15	DiBB		
2,2',4,5'-TetBB	49	TetBB	PBB	Polybrominated Biphenyls
2,2',5,5'-TetBB	52			
2,2',4,4',5,5'-HexBB	153	HeksaBB		
2,4,4'-TriBDE	28	TriBDE		
2,2',4,4'-TetBDE	47			
2,3',4',6-TetBDE	71	TetBDE		
3,3',4,4'-TetBDE	77			
2,2',4,4',5-PenBDE	99			
2,2',4,4',6-PenBDE	100	PeBDE	PBDE	Polybrominated diphenyl ethers
2,3',4,4',6-PenBDE	119			
2,2',3,4,4',5'-HexBDE	138			
2,2',4,4',5,5'-HexBDE	153	HexBDE		
2,2',4,4',5,6'-HexBDE	154			
2,2',3,4,4',5',6-HepBDE	183	HepBDE		
DecaBDE	209	DecaBDE		
TBBPA		TBBPA	TBBPA	Tetrabrombisphenol A
alpha-HBCD				
beta-HBCD		HBCD	HBCD	Hexabrom-cyklododecane
gamma-HBCD				

* Indexes according to International Union of Pure and Applied Chemistry (IUPAC).

Chlorinated dioxins (PCDD+PCDF)
PCDD = polychlorinated dibenzo-p-dioxins
PCDF = polychlorinated dibenzofurans

Brominated dioxines (PBDD+PBDF)
PBDD = polybrominated dibenzo-p-dioxins
PBDF = polybrominated dibenzofurans

Brominated/chlorinated dioxins (ClxBryDD+ClxBryDF)
ClxBryDD, PXDD = polychlorinated/brominated dibenzo-p-dioxins
ClxBryDF, PXDF = polychlorinated/brominated dibenzofurans

3. Incineration of Plastics Containing Brominated Flame-Retardants

3.1 Plastics from EE-waste

Brominated flame-retardants are being found in i.e. electric and electronic (EE) products. In Norway and Sweden there is established extensive collection systems for discarded EE products. As a consequence of new EU regulations, similar systems will have to be established in all EU/EEA countries within the end of 2005.

Table 1 shows the amounts of plastics from EE-waste, based on the information from collection companies in Norway (Svendsen, T. C., 2003).

Table 1 Amounts of plastics from EE-waste, based on the information from collection companies (tons/år)

Collection company	Separated plastics (tons/år)	Plastics in shredderfluff (tons/år)
Elektronikkretur AS	1800	180
Hvitevareretur AS	150	4000
RENAS AS	45	239
Total	1995	4419

As will be seen from Table 1, approximately 2000 tons separated plastics is generated yearly from EE-waste. This is bigger plastic items with and without BFRs, which relatively easy may be sorted out manually, for example the cover of a data monitor, back-cover of a TV and soap container in a dishwasher. These plastic components will mainly be incinerated in advanced waste incinerators with adequate flue gas cleaning.

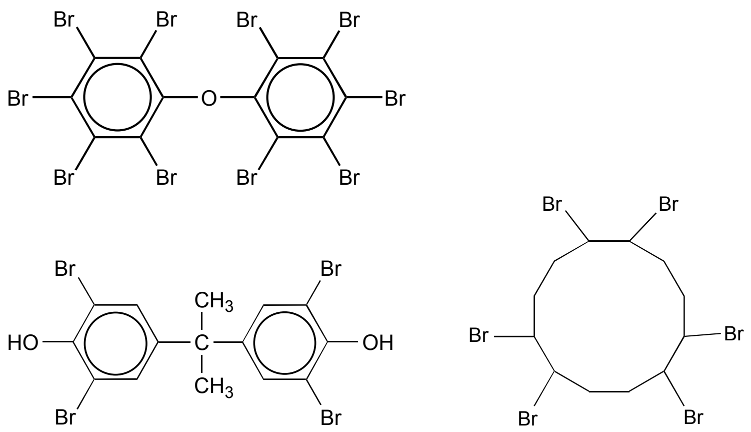
The largest amount of plastics will however be found in the so-called shredderfluff, with an amount of approximately 4400 tons/year. Shredderfluff is the waste fraction from wrecked car/scrap metal fragmenting plants, and it contains (among other things) a mix of plastics, rubber, wood, concrete, and small amounts of metals. In Norway, shredderfluff is normally deposited in landfills.

3.2 Emissions of brominated flame-retardants

The most applied brominated flame-retardants are the group polybrominated diphenylethers (PBDE) and the compunds tetrabromobisphenol A (TBBPA) og hexabromocyclododecane (HBCD).

Figure 1 shows and example of polybrominated diphenylethers (DeBDE), TBBPA and HBCD.

Figure 1 Polybrominated diphenylether (DeBDE), TBBPA og HBCD.



Decabromodiphenyl ether (DeBDE) *Tetrabromobisphenol A (TBBPA)*
Hexabromocyclododecane (HBCD)

In incinerators with good combustion, the BFRs will decompose and form other brominated compounds (Söderström, G. et al, 2000), mainly hydrogenbromide (HBr) (Vehlow, J. et al, 1998).

3.3 Formation and emissions of chlorinated, brominated and brominated/chlorinated dioxins

Chlorinated dioxins is a collective term for organic compounds consisting of dibenzo-p-dioxins and dibenzofurans with 1-8 chlorine substituents in different positions. This gives a total 210 different plychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Chlorinated dioxins and furans are often referred to as ”dioxins”.

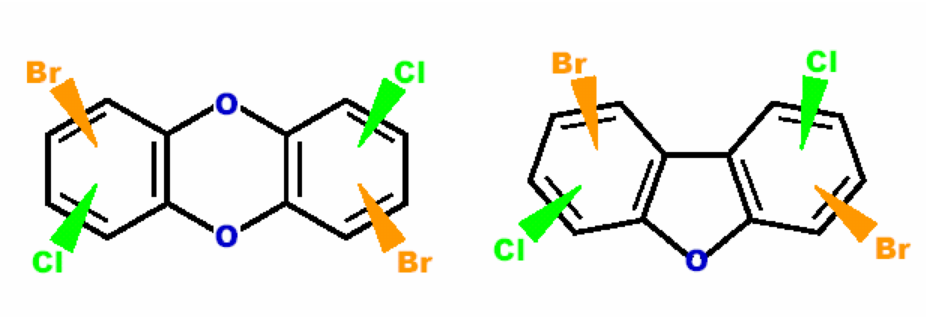
Brominated dioxines is a collective term for the corresponding 210 organic compounds substituted with bromine instead of chlorine. These are normally also reffered to as PBDD og PBDF (polybrominated dibenzo-p-dioxins og polybrominated dibenzofurans).

Brominated/chlorinated dioxins includes dibenzo-p-dioxins and dibenzofurans with both bromine and clorine substituents, in total 4600 different compounds. See figure 2.

Air emissions of chlorinated dioxins are regulated through the standard regulations for incineration, and the emissions are checked every 6 or 12 months. The emission limit value is given in terms of toxic equivalents, which is generated by weighted calculation, giving each compound a relative weight value between 0 and 1, depending on the toxicity. 2,3,7,8-tetrachlorine dibenzo-p-dioxin is known as the most toxic compound, and therefore has the relative weight value 1.

Toxic equivalents terms is however not established for compounds of brominated and brominated/chlorinated dioxins.

Figure 2 Brominated/chlorinated dibenzo-p-dioxins and dibenzofurans



Formation of dioxins

The formation of dioxins during incineration has been studied extensively for nearly 30 years.

Different formation mechanisms has been found:

- De Novo synthesis
- Precursor reactions
- Secondary halogenations in flue gas

In the de Novo synthesis, the formation takes place by chlorination of compounds in flue gas containing carbon. The chlorination step is assumed to occur as HCl combine to form Cl_2 (the Deacon-reaction), with subsequently chlorination of aromatics. The Deacon-reaction is catalysed by (among others) compounds of copper, and is favoured by oxygen excess.

Chlorinated dioxins may also be formed from precursors, for example chlor-phenols, which can condensate on particle surfaces, and also by halogenation of non-chlorinated dioxins and furans in flue gas. Studies have shown that the highest formation of dioxins takes place at temperatures between 200-600° C.

Emissions of dioxins may also occur if the incinerated waste or the added combustion air contains dioxins. To minimize the formation of chlorinated dioxins, one has found the following to be important:

- Short residence time at temperatures favouring dioxin formation
- Efficient combustion
- Minimize chlorine content in waste
- Minimize particle content in flue gas
- Increased sulphur/chlorine content ratio
- Minimize oxygen excess
- Minimize content of metals which can act as catalysers (especially copper)

Several studies have shown that there is no clear relation between the rate of dioxin formation and the chlorine content (SFT, 1994) (Wikström, E., 1999). However, some waste incineration tests indicate that dioxin formation increases with increasing chlorine content, when the chlorine content exceeds a certain value.

Several studies of waste incineration have shown that combustion efficiency is of greater importance for the dioxin formation, rather than the chlorine content.

Formation mechanisms for brominated and brominated/chlorinated dioxins are less investigated. It is however reasonable to assume that mechanism has similarities with the formation mechanism of chlorinated dioxins.

Incineration plants which comply with the regulations of the EU-directive for waste incineration, are all equipped with flue gas cleaning systems which reduce the concentration of chlorinated dioxins in the flue gas substantially. The similarities between chlorinated, brominated and brominated/chlorinated dioxins indicates strongly that the cleaning efficiency is also high for brominated and brominated/chlorinated dioxins.

4. Former Incineration Tests

Swedish, Danish and Finnish environmental authorities has been contacted to get data from incineration tests including measurements of brominated and brominated/chlorinated dioxins.

Information has also been gathered from universities and research communities in Sweden, Denmark and Germany, and also through search on the Internet. Articles from the last three Dioxin conferences (2001, 2002, 2003) are also examined.

The objective of this work has been to establish a detailed measurement program. The possibility to estimate input amounts of bromine from measurements/calculations of output bromine containing flows (bromine in bottom ash, fly ash, flue gas and scrubber water) is also investigated. The work should also form basis for comparison and evaluation of measurement results from the incineration test.

4.1 Brominated and brominated/chlorinated dioxins

4.1.1 Incineration tests in pilot plants

Emissions and formation of brominated dioxins is investigated in a pilot plant in Germany. The TAMARA Plant has a capacity of 250 kgs of waste per hour, and is equipped with textile filter, quenching and a wet scrubber. At this plant incineration tests of polystyrene- and polyurethane foam containing BFRs has been carried out, together with waste from households and smaller industries/businesses (Vehlow, J. et al, 1996).

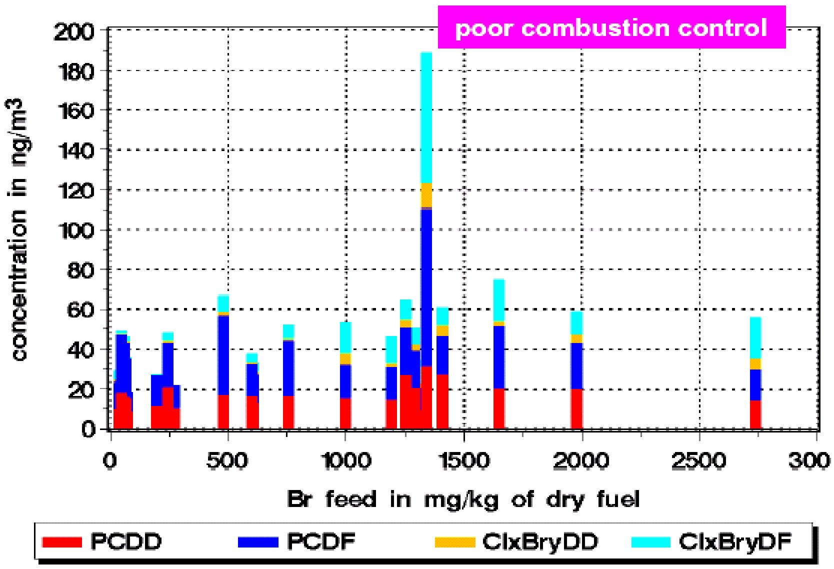
The incineration temperature was ranging from 850 to 950 ºC. The additional inputs of bromine during the tests were ranging up to 6 times the original bromine content in the household waste.

Measurement results showed low concentrations of brominated dioxins, and the study concluded that incineration of limited amounts of specific foams in efficient plants with “state of the art” flue gas cleaning, is environmentally acceptable.

Tests with incineration of plastics from EE-waste, together with waste from households and smaller industries/businesses, have also been carried out in the TAMARA Plant (Vehlow, J. et al, 1997). The tests included four different types of plastics, with different contents of bromine.

Measurements of brominated, chlorinated, and brominated/chlorinated dioxins in flue gas, both prior to and after cleaning, were carried out. The tests also included analysis of bromine content in the plastics, bromine-, chlorine- and antimony-content in bottom ash, fly ash and flue gas before cleaning. Antimony is often added to enhance the effect of BFRs. It was concluded that EE-waste containing bromine and bromine and chlorine did not increase the total formation of dioxins. Figure 3 shows concentration levels of PCDDs/Fs and Cl_xBr_yDDs/Fs in flue gas before cleaning as a function of the bromine content in the waste.

Figuer 3 Concentration levels of PCDDs/Fs and Cl_xBr_yDDs/Fs in flue gas before cleaning as a function of the bromine content in the waste, recorded from incineration tests with EE-waste at TAMARA Plant, Germany (Vehlow, J. et al, 1997).



The formation of brominated dioxins from co-incineration of household waste and brominated flame-retardants is investigated in a 5kW incineration reactor (fluidised bed) in pilot scale at the university of Umeå (Söderström, G. et al, 2000). Different types of flame-retardants were added in amounts corresponding to a ”worst case scenario” for batch wise incineration of flame retarded products med BFRs. The incineration temperature was slightly above 800 ºC.

The results from the studies in Umeå showed that the formation of halogenated dioxins were much higher when adding BFRs, than with only chlorine present. Additionally, the study showed that bromine caused significant higher formation of halogenated dioxins than the equal amount of chlorine, which is assumed to relate to the ratio between Br_2 and HBr, which again is substantially different from the ratio between Cl_2 and HCl. The conclusion from the study is that batch incineration of wastes containing BFRs should be avoided.

4.1.2 Measurements at full scale plants

In 2002 measurements of emissions of brominated dioxins were carried out at Energos Hurum Plant, Norway (Energos Hurum Energigjenvinning) with normal waste composition (wastes from households and small industries/businesses).

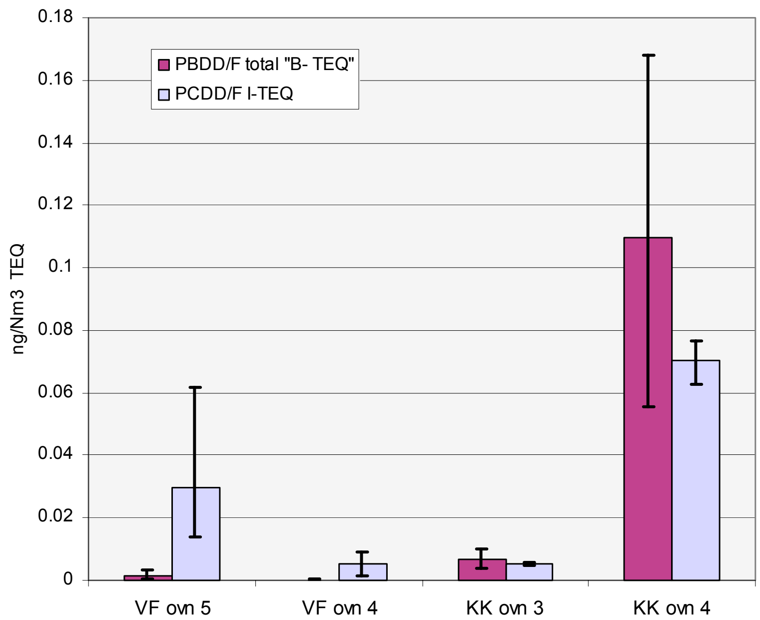
It was found 0,003 ng/Nm^3 tetrabrominated dibenzo-p-dioxins. Concentrations of other single compounds were lower than the detection limit, i.e. than 0,0001-0,02 ng/Nm^3. Note that the concentrations is given as actual measured values, not as toxic equivalents (Energos ASA, 2002).

In 1999 measurements of brominated dioxins were carried out at Uppsala Energi, Sweden and at Renova, Gothenburg, during incineration of ordinary municipal waste. Both plants are equipped with advanced flue gas cleaning systems, with low emissions of chlorinated dioxins (substantially lower than 0,1 ng/Nm^3 in 1999). The emissions of brominated dioxins were lower than the detection limit for the measurements, i.e. < 0,05 ng/Nm^3 for all measured dioxins (Westas, H., 2000).

Autumn 2002, Danmarks Miljøundersøgelser carried out a study regarding the content of brominated, chlorinated and brominated/chlorinated dioxins in flue gas and in remains from flue gas cleaning at Vestforbrænding (VF) (wastes from households and small industries/businesses) and Kommunekemi (KK) (hazardous waste) (Vikelsøe, J., 2000). Both plants were equipped with advanced flue gas cleaning systems.

Figure 4 shows comparison of PBDDs/Fs and PCDDs/Fs in flue gas from the plants after cleaning

Figur 4 Comparison of PBDDs/Fs and PCDDs/Fs in flue gas from Vestforbrænding and Kommunekemi (after cleaning). PBDDs/Fs total ”B-TEQ” og PCDD/F I-TEQ, ng/Nm^3. (Vikelsøe, J., 2000).



4.1.3 Comparison of test programs from earlier tests

Table 2 shows the added amount of bromine/brominecontaining plastics in earlier testprograms in small-scale pilot plants.

Table 2 Former test programs/measurements

Plant/test description	Share BFR-plastics [% by weight]	Bromine content in BFR-plastics [% by weight]	Bromine content in waste [% by weight]
TAMARA Polystyrene- and polyurethanefoam + waste from housholds and small industry/ businesses	1-3	2,2-4,2	0,02-0,08
TAMARA Plastics from EE-waste + waste from housholds and small industry/ businesses	3-12	0,4-1,5	0,01-0,18
Umeå University Waste from housholds and small in-dustry/businesses added different BFRs	-	-	0,9-1,7

Table 3 shows the measurements included in incineration tests with brominated dioxins and/or chlorinated/brominated dioxins.

Table 3 Measurements included in incineration tests with brominated dioxins and/or chlorinated/brominated dioxins

	Analyzed parameters in waste	Analyzed parameters Raw flue gas	Analyzed parameters Clean flue gas	Additional analyzed parameters
TAMARA PS- og PU- foam + waste from housholds and small industry/ businesses	Bromine, chlorine	PXDDs/Fs		Bromine in fly ash
TAMARA Plastics from EE-waste + waste from housholds and small industry/ businesses	Bromine, chlorine, antimony (Sb), PXDDs/Fs[0] and flame-retardants[1]	Bromine (HBr, Br_2) , chlorine, antimony (Sb), PXDDs/Fs	PCDDs/Fs Non-brominated dioxins	Bromine, chlorine, antimony (Sb) in bottom- and flyash
Umeå Universitet Waste from housholds and small businesses added different BFRs	Bromine, chlorine and flame-retardants [2]	Cl_2, HCl, Br_2, HBr, PXDDs/Fs[3]		
Uppsala Energi,Renova Waste from housholds and small industry/businesses			PXDDs/Fs	
Vestforbrænding Waste from housholds and small industry/businesses			PXDDs/Fs	PXDDs/Fs in residue from flue gas cleaning
KommunekemiHazardous waste			PXDDs/Fs	PXDDs/Fs in residue from flue gas cleaning

0) PXDDs/Fs: Dioxins containing bromine and/or chlorine
PBB, PBDE, TBBA
DeBDE, TBBP-A, HBCD
PCDD, PCDF, TeBCDD, TeBCDF, TeBDF, TeBDD

Relatively extensive incineration tests, with different input of bromine, have been carried out at pilot plants both in Sweden and Germany. In both tests analysis were carried out with respect to brominated and brominated/chlorinated dioxins on raw flue gas only (before cleaning).

Analysis of brominated dioxins in flue gas after cleaning is carried out on some Swedish and Danish waste incineration plants, with normal waste composition.

Our literature search and preliminary studies indicated clearly a need for more incineration tests and studies of brominated and brominated/chlorinated dioxins, especially in full scale plants. The scope of former studies indicates that the main goal with such tests should be to decide the concentrations in flue gas of brominated, chlorinated and brominated/chlorinated dioxins before and after cleaning, and at different levels of bromine content in the waste. To verify the input of bromine and chlorine, all output flows (bottom ash, fly ash, water from scrubbers and flue gas) should also be analyzed for bromine and chlorine.

4.2 Brominated flame-retardants

An article presented by Chen, Y. et al (Dioxin 2003) reports from sampling and analysis of emissions of BFRs and brominated dioxins carried out at an incineration plant burning wastes from households and small industry/businesses. The plant is not described in the article, nor the waste or the operating conditions of the plant. The method used to determine BFRs and dioxins is not the same as the methods used in the tests at Klemetsrud Plant, Oslo and Energos Plant, Ranheim. It is carried out five series of measurements of air emissions from a waste incinerator and 3 series from an electric smelter. Average results are quoted in Table 4. Seven congeners of PBDE (BDE-28, -47, -100, -99, -154, -153, -183) was detected in all the samples. The three most dominating congeners is BDE -47, -99 og -28 and both the tests shows equal distribution between the congeners.

Table 4 Emissions of BFRs and brominated dioxins from waste incinerator and electric smelter. (Chen, Y. et al, 2003).

	BFRs (ng/m^3)	Brominated dioxins (ng/m^3)
Waste incinerator	99±31	0,275-4,01
Electric smelter	68±25	0,079-0,485

An article presented by Tamade, Y. et al, Japan (Dioxin 2003) reports from measurements during incineration of plastic waste with BFRs. The measurements include analysis of brominated dioxins and furans, PBDE and TBBPA on the input waste, such as back covers from TVs, dust from

TVs, and also in mass flows from a recovery plant for plastics, and finally in mass flow from an incineration plant.

The incineration plant was equipped with an electric precipitator and a fabric filter. The incinerated waste was a mixture of residues from the plastic waste recovery plant (with BFRs) and waste from households and small industry/businesses. The waste was analysed with respect to content of PBDE, TBBPA and brominated dioxins. Total input amount of PBDE and TBBPA were 18-360 g/hr and 6,2-96 g/hr respectively. Analysis of brominated dioxins and furans in air emissions showed a total concentration of 0,014 ng/Nm^3. Air emission of PBDE and TBBPA was 3,5 and 8 ng/Nm^3 respectively. Bottom ash and filter dust showed a content of PBDE of 300 and 470 ng/g respectively. The content of TBBPA in bottom ash and filter dust was 20 and 1,3 ng/g respectively.

Due to few studies and lack of emission limit values for BFRs from waste incineration, we have also looked at reported concentration levels in other types of samples.

A study of indoor dust in common households in Germany includes analysis of 40 samples (taken from vacuum cleaners) with respect to 10 different PBDE congeners (BDE-28, -47, - 49, -85, -99, -100, -153, -154, -183, -209) (Knoth, W. et al, 2003). The results show huge variations in concentrations between the different congeners, and also between the samples. BDE-209 was the dominating congenere in 35 of the 40 samples, as BDE-99 dominated in 4 of the samples. The source for PBDE in the samples was reported unknown, with exception for some samples of dust from mattresses which showed high levels of dekaBDE. Average total concentration of the 10 PBDEs in the 40 samples was determined to 1404 ng/g.

The Norwegian Institute for Air Research (NILU) has taken samples of sediments for analysis of BFRs in the Drammen river, Norway (Fjeld et al, 2004).

Samples of sediment were taken at seven different spots in the river, four samples from the inner Drammensfjord and one sample in the marine environment of the fjord. The sum of PBDEs analysed showed a concentration level of 4-80 ng/g. The BDE-209 congenere dominated in all samples.

NILU have also made studies of BFRs in leachate from landfills (Schlabach. M. et al, 2002).

Samples were taken from sediments in leachate from 6 larger landfills. PBBs were not detected in any of the samples. PBDE-209 was detected in all samples, with a concentration level in the range of 0,49-91 ng/g wet weight. The three HBCD-isomeres was detected in almost all samples, and the concentrations was in the range <0,1-84 ng/g wet weight for HBCD. TBBPA was detected in all sediment samples from the landfills, with a concentration level in the range of 01,9-44 ng/g wet weight.

PBDE-209 and HBCD are also detected in samples of moss, which implies that the compounds may be transported by air. NILU has estimated that maximum discharge from a larger landfill might rate up to 1-10 g/year per single compound of PBDE, HBCD and TBBPA. The concentrations found in the inestigations are at the same levels as concentrations found in sewage sludge in Sweden.

Table 5 Results from different studies of BFRs

Type of study	BFR-compound	µg/g	ng/m³
Air emissions from waste incineration	PBDE		99
Air emissions from electric smelter	PBDE		68
Dust from households	PBDE	1,4	
River sediments	PBDE	0,004-0,08	
Sediments from landfill leachate	PBDE HBCD TBBPA	0,0005-0,09 <0,0001-0,08 0,001-0,044	
Bottom ash from incinerator, Japan	PBDE TBBPA	0,3 0,02	
Fly ash from incinerator, Japan	PBDE TBBPA	0,47 0,0013	
Air emissions from incinerator, Japan	PBDE TBBPA		3,5 8

Our preliminary studies and literature search indicated clearly a need for more incineration tests and studies of emissions and decomposition of BFRs in connection with waste incineration.

4.3 Studies of other bromine compounds at Klemetsrud Plant, Norway

In 2002 measurements of brominated and brominated/chlorinated organic compounds were carried out at the Klemetsrud Plant in Norway. The measurements were performed by Kjelforeningen-Norsk Energi (Kjelforeningen-Norsk Energi, 2002).

In 1998 incineration tests with EE-waste were carried out at the same plant, and online measurements of a variety of brominated components in flue gas were performed (not dioxins). A portable GC was used for the measurements (Det Norske Veritas, 1998). In parallel measurements of emissions of chlorinated dioxins after flue gas cleaning was performed. The results indicated an increased level of dioxins during incineration of EE-waste. It should be noted that this was before active coal injection and fabric filtration were introduced at the plant.

5. Incineration Tests at Three Norwegian Waste Incineration Plants

Measurements of emissions of brominated and brominated/chlorinated dioxins, and brominated flame-retardants (BFRs) are carried out during incineration of waste with both normal and increased content of BFRs in the waste. For verification of input, analysis of bromine and chlorine in output flows were made. Decomposition of BFRs during incineration was also investigated by analysis of BFRs in output flows.

Tests and measurements were carried out at the following Norwegian plants:

- Klemetsrud Plant, Oslo : municipal waste incinerator, capacity 2 x 10 tons/hr
- Energos Plant, Ranheim : municipal waste incinerator*, capacity 1,5 tons/hr
- FREVAR Plant, Fredrikstad : municipal waste incinerator, capacity 2 x 5 tons/hr

* source separated and shredded waste

5.1 Measurement program

The program for measurements during tests at three Norwegian waste incineration plants are shown in Table 6 below.

Table 6 Program for measurements during tests at three Norwegian waste incineration plants

	Type of waste	Analysed parameters in flue gas *before* cleaning	Analysed parameters in flue gas *after* cleaning	Other analysed parameters
Klemetsrud-Plant	Waste from households and small industry/businesses	HCl, Cl_2, HBr, Br_2	Chlorinated, brominated and chlorinated / brominated dioxins	-
	Waste from households and small industry/businesses + 5 % by weight brominated waste	HCl, Cl_2, HBr, Br_2	Chlorinated, brominated and chlorinated / brominated dioxins	-
	Waste from households and small industry/businesses + 10 % by weight brominated waste	Chlorinated, brominated and chlorinated / brominated dioxins HCl, Cl_2, HBr, Br_2	Chlorinated, brominated and chlorinated / brominated dioxins BFRs	Bromine, Chlorine and BFRs in bottom ash, fly ash, flue gas, scrubberwater
FREVAR Plant	Waste from households and small industry/businesses Hospital waste	HCl, Cl_2, HBr, Br_2	Chlorinated, brominated and chlorinated / brominated dioxins	-
Energos Plant	Industrial waste	HCl, Cl_2, HBr, Br_2	Chlorinated and brominated dioxins	-
	Industrial waste + 20 % by weight brominated waste	HCl, Cl_2, HBr, Br_2	Chlorinated, brominated and chlorinated / brominated dioxins HCl, Cl_2, HBr, Br_2 BFRs	Bromine, Chlorine and BFRs in bottom ash

Sampling and analysis of dioxins during tests with no addition of brominated waste at Klemetsrud Plant, and all sampling and analysis at Energos Plant, were performed by the German consultancy TÜV. Kjelforeningen-Norsk Energi did all other sampling at Klemetsrud Plant, and at FREVAR Plant. NILU laboratory made the analysis of dioxins and BFRs, Eurofins laboratory (Oslo) analysed the flue gas samples, and Analytica laboratory made the bottom ash, filter dust and scrubber water analysis.

5.2 Characterization of the brominated waste

Data from literature regarding bromine content in municipal waste from households and small businesses, indicates typical bromine content of 0,003-0,006 % by weight of bromine. One source (Söderström, G. et al, 2000) reports typical content of 0,004 % by weight from a study in 1992, but that the level has increased the last decade. In comparison is normal chlorine level in municipal waste approximately 0,75 % by weight (Söderström, G. et al, 2000).

The brominated waste added to the municipal waste was generated in a demolition plant for electric and electronic waste (Stena Miljø AS, Oslo). In total approximately 70 tons brominated waste were generated for the incineration tests.

Stena Miljø AS has calculated the level of bromine in the actual mixture (brominecontaining plastics) which were used in the tests at Klemetsrud and Energos Plants. The calculations gave the following levels : 27 % by weight brominated plastics, 16 % by weight wooden material, 57 % by weight plastics without bromine (Aass, F.E., 2003a). The bromine level in plastics is reported to be 3-4,5 % by weight, and the bromine level in the total mixture approximately 1 % by weight (Sjølin, S., 2003).

Approximately 80 % by weight of the brominated plastics is reported to contain PBDE (polybrominated diphenylethers).

Exact level of BFRs in the plastics is not known, but is earlier reported to be approximately 12 % by weight (SFT, 2003) (Aass, F.E., 2003b). This is determined mainly from PCs and monitors, and the level relatively uncertain.

A Danish report from 1999 reports the content of TBBPA and other BFRs separately in different electronic products (Miljøstyrelsen i Danmark, 1999). Reported levels are:

- Colour TVs :
  - a) TBBPA 12 % by weight
  - b) BFRs 12 % by weight

- PCs
  - a) TBBPA 12-14 % by weight
  - b) BFRs 12-14 % by weight

Levels in printers, photocopiers and fax-machines are reported to be lower.

As the brominated plastics used in the tests mainly origins from TV- and monitor-cabinets, it is assumed a BFR-level in the plastics of 12 % by weight.

Stena Miljø AS has also reported that the waste mix may contain approx. 1 % by weight PVC (Aass, F.E., 2004), from which on may derive that the chlorine level in the waste is significantly lower than in municipal waste from households and businesses.

The Norwegian State Pollution Control Authority (SFT) has done a preliminary analysis of BFRs in 60-100 kgs of plastic waste from the Stena Miljø AS demolition plant.

The total concentration level of BFRs was determined to be approximately 20 000 mg/kg, i.e. 2 % by weight.

The level of BFRs in the these plastics is therefore lower than the assumed levels for the plastics used in the tests. Still, the samples analysed by SFT may not necessarily be representative for the brominated waste used in the tests. Further, SFT showed that octaBDE and decaBDE was the dominating BFR-compounds, with a level of 8 000 - 9 000 mg/kg for each of the compounds.

Figure 5 shows brominated waste used in the incineration tests (before shredding).

Figur 5 Brominated waste used in the incineration tests (before shredding).

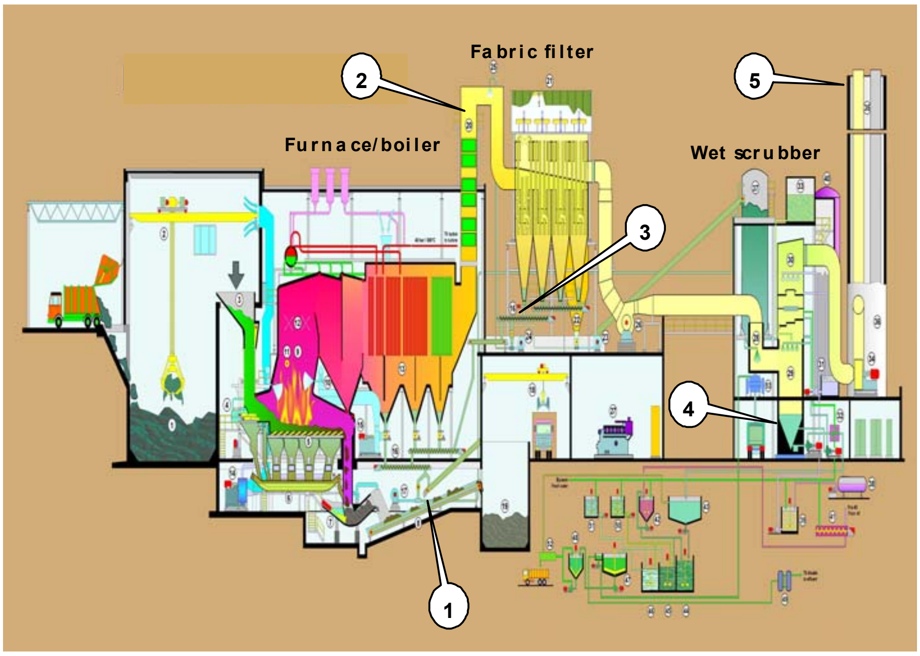
5.3 Description of plants and sampling points

5.3.1 Klemetsrud Plant

Measurements are carried out at Oslo Municipality's incineration plant at Klemetsrud in Oslo. The plant incinerates untreated municipal waste from households and businesses in 2 lines, each with a capacity of approx. 10 tons/hr. Each line is equipped with a flue gas cleaning system, consisting of active coal injection, a fabric filter and a wet scrubber.

A sketch of the plant, with marking of the sampling points, is shown in figure 6.

Figure 6 Sketch of Klemetsrud Plant, with marking of the sampling points.



1 Bottom ash Total bromine, total chlorine. Brominated flame-retardants.
2 Raw flue gas Gaseous bromine and chlorine. Brominated, chlorinated, brominated/chlorinated dioxins
3 Filter dust Total bromine, total chlorine. Brominated flame-retardants.
4 Scrubber water Total bromine, total chlorine. Brominated flame-retardants.
5 Cleaned flue gas Brominated, chlorinated, brominated/chlorinated dioxins. Brominated flame-retardants.

Measurements without addition of bromine containing waste

Measurements of brominated, chlorinated, brominated/chlorinated dioxins were done on line 1 by TÜV in parallel to the annual emission control measurements October 16th -17th 2003. Measurements of total bromine and chlorine in raw flue gas were done on line 2 December 18th 2003 by Kjelforeningen-Norsk Energi.

Measurements with addition of bromine containing waste

The measurements with addition of bromine containing waste were done October 28th and 30th 2003 by Kjelforeningen Norsk Energi.

Measurements were done with two different mixtures:

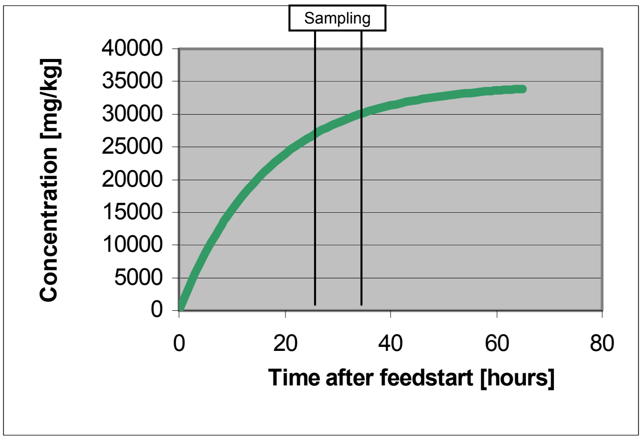
- Low addition: 5 % by weight addition of bromine containing waste. This mixture gives a feed rate for bromine containing waste of approx. 0,5 tons/hr, i.e. slightly above 5 % by weight. The resulting bromine feed rate was approx. 5 kg bromine/hr.
- High addition: 10 % by weight addition of bromine containing waste. It is possible to feed up to 2 tons/hr of bromine containing waste at line 2 at the Klemetsrud Plant. This is however an unrealistic high share, because it may significantly affect the incineration conditions. A realistic maximum addition is approx. 1 ton/hr (10 % by weight

bromine containing waste). This mixture gives a feed rate of approx. 10 kg bromine/hr.

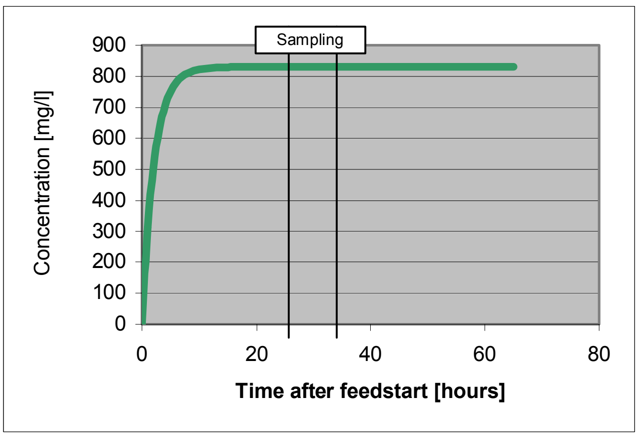
In order to maintain stable concentrations in output flows from the process, feeding of bromine containing waste to the incinerator has to start in due time before sampling.

Figure 7 shows the calculated theoretical change in concentration of bromine in filter dust, and in circulating fluids in scrubber (HCl-step). One can see from the figure that the concentration level in filter dust during sampling period is approx. 80-90 % by weight of maximum concentration level, and that the actual time of feed start, 24 hours before sampling, was sufficient to maintain a stable concentration level in circulating fluids in scrubber.

Figure 7 Calculated change in concentrations of bromine in filter dust and circulating fluids in scrubber (HCl-step).



Concentration change in filter dust



Concentration change in circulating fluids in scrubber

5.3.2 Energos Plant

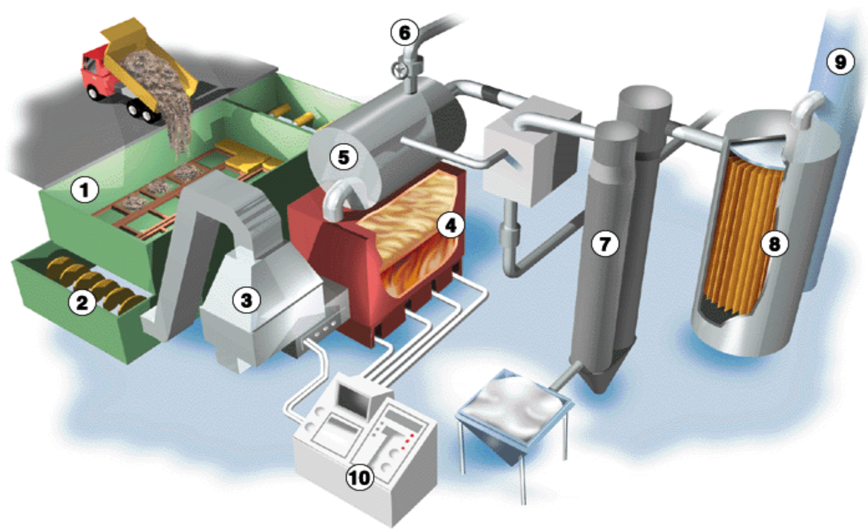
The Energos Plant at Ranheim incinerates annually approx. 10 000 tons of waste. The plant has approx. 4 MW thermal output, and a steamproduction of approx. 25 GWh/year, supplied to a neighbouring industrial plant, Peterson Linerboard Ranheim (PLR). The waste is a mixture of waste from PLR and other industries.

The flue gas is treated in a fabric filter after injection of coal and lime. Output flows are bottom ash/slag, fly ash and emissions to air from stack.

A flow sheet for the plant is shown in Figure 8. The waste is fed from the storage silo (1) with the conveyor (2) into the 2nd storage (3). From this storage the waste is fed in portions onto the fire grate in the primary chamber of the furnace (4). On the fire grate the waste is dried, gasified and burned-out at sub-stoichiometric conditions. A conveyor brings the waste through the primary chamber, and to the output shaft, where the burned waste falls down as slag. The flue gases are led through the boiler (convection unit) (5) and are cleaned in the fabric filter (8) after addition of activated carbon and lime.

Measurements with and without addition of 20 % by weight of bromine containing waste were carried out November 11th-13th 2003 by TÜV. The sampling points are positioned right into the inlet to the filter (8), and in the vertical outlet of the filter/inlet to stack (9).

Figure 8 Flow sheet for the Energos Plant at Ranheim



1. Storage silo	2. Conveyor
3. 2nd storage	4. Furnace
5. Boiler	6. Steam system
7. Reactor	8. Filter system
9. Chimney	10. Control- / monitoring system

5.3.3 FREVAR Plant

FREVAR Incineration Plant is owned by Fredrikstad municipality. The plant incinerates approximately

78 000 tons waste annually, using two incineration furnaces. The plant produces 185 GWh steam per year, and has 99 % utilization of the produced energy (FREVAR, 2004).

The waste is fed into the feedershaft with a crane. From the shaft, the waste is fed in portions onto the fire grate. On the grate, the waste is dried, combusted and burned out. The movable grate takes the waste through the furnace to the outgoing shaft, into which the burned waste drops down as slag.

The flue gases are burned in a secondary combustion zone over the grate. The flue gas is cleaned in an electric precipitator, wet scrubber and a fabric filter. Active coal is added prior to the wet scrubber, and activated carbon and lime prior to the fabric filter.

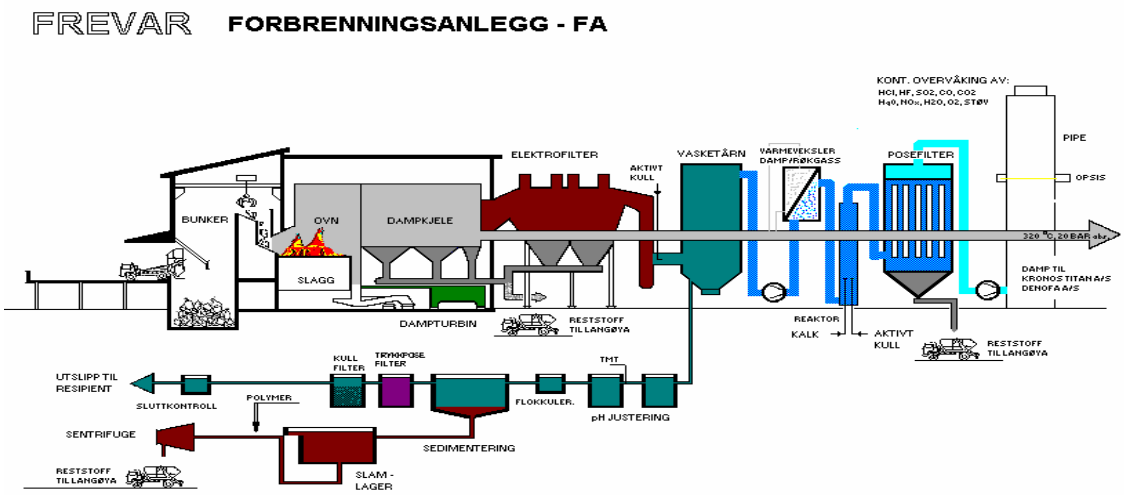
The flue gases from the two furnaces are led in to the same duct before the scrubber, and let out trough a joint stack.

FREVAR also has a incinerator for hospital waste. The flue gas from this furnace is quenched and treated through a separate wet scrubber, before it is led in to one of the other furnaces for further combustion and cleaning. Annual control measurements at FREVAR are normally done with the hospital waste incinerator running.

Measurements of gaseous bromine and chlorine, and brominated, chlorinated and brominated/chlorinated dioxins were carried out parallel to the annual control measurements on November 5th 2003, by Kjelforeningen Norsk Energi.

A flow sheet of the plant is shown in Figure 9.

Figure 9 Sketch of the FREVAR incineration plant for household waste (FREVAR, 2004*)*, with sampling points.



6.Results

6.1 Operating conditions

The combustion conditions were normal during sampling and measurement at the Klemetsrud plant, with CO-levels of approximately 20-30 mg/Nm^3. CO-levels during sampling at FREVAR Plant were approx. 50 mg/Nm^3. At the Energos Plant, CO was not detected during measurements, which indicates a very effective combustion.

Some problems were experienced with the fabric filter at FREVAR Plant during the sampling period.

6.2 Measurements of gaseous bromine in flue gas before cleaning

Results of measurements of gaseous bromine in flue gas before cleaning are shown in Table 7.

Table 7 Results from measurements in uncleaned flue gas with different addition of bromine containing waste

Plant	Addition of bromine containing waste	Gaseous bromine			
		HBr		Br_2	
		mg/Nm^3	kg/hour	mg/Nm^3	kg/hour
Klemetsrud Plant	No addition	3,6	0,2	0,1	0,007
	5 % by weight addition	6	0,4	0,3	0,02
	10 % by weight addition	40	2,5	2,3	0,1
FREVAR Plant	No addition	1,2	0,08	<0,5	<0,03
Energos Plant	No addition	< 2,15	< 0,014	< 2,15	< 0,014
	20 % by weight addition	97-200[1)]	0,95-1,97	< 2,15	< 0,014

1) During the approx. 12 hour sampling period, the HBr-concentration in raw flue gas varied from approx. 97 to 200 mg/Nm^3, with the highest level during the last sample.

The measurement results for gaseous bromine in uncleaned flue gas, with a normal waste composition, indicates a bromine level equal to, or slightly lower than what is normal for waste from households and small businesses (0,003-0,006 % bromine by weight).

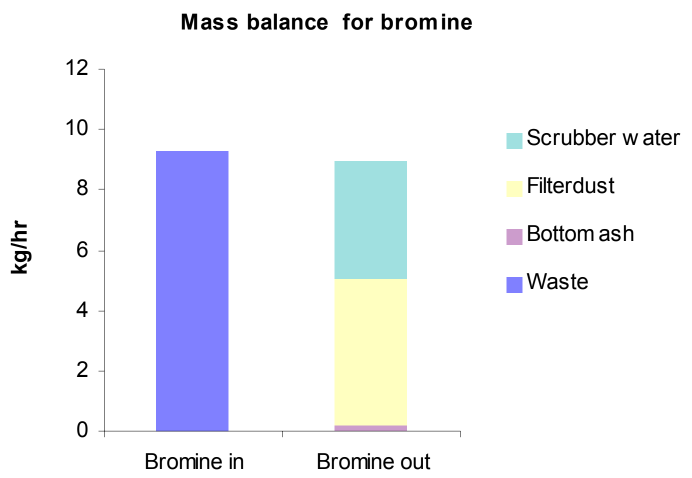
Results from measurements during addition of bromine containing waste, shows a clear increase in the HBr-concentration in uncleaned flue gas, compared to results from measurements with no brominated waste.

At the Energos Plant, gaseous bromine was also measured after the filter. The concentration was < 2,2 mg/Nm^3, which leads to a removal efficiency of >97 % for the filter.

6.3 Mass balance for bromine

Figure 10 shows a mass balance for bromine after addition of 10 % by weight bromine containing waste at Klemetsrud Plant.

Figure 10 Mass balance for bromine after addition of 10 % by weight bromine containing waste at Klemetsrud Plant.



From Figure 10, we can see that the mass balance of bromine from Klemetsrud Plant shows good correspondence between input and output flows in the plant.

At the Energos Plant, 20 % by weight of bromine containing waste was fed into the furnace.

Table 8 shows resulting bromine levels in input and output mass flows.

Table 8 Bromine in input and output mass flows, Energos Plant

Mass flow	Amount (kg/hour)
Bromine in input waste (total input)	2,1
Bottom ash	0,045
Flue gas before filter	0,95-1,97
Flue gas after filter	0,014
Total output (excl. bromine in filterdust)	1,0-2,0

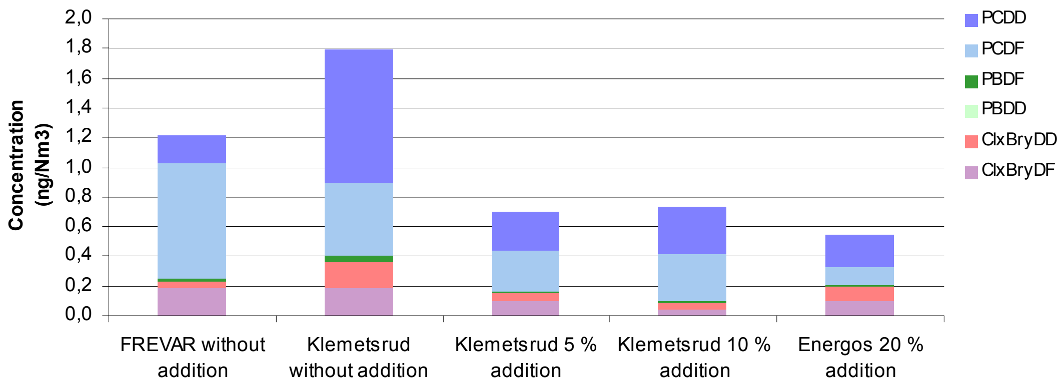
During the approximately 12 hours of sampling and measurement, the bromine content in flue gas before filter varied between approximately 1-2 kgs/hr, with the highest level during the last measurement. According to Energos, it is very likely that the adsorption-/desorption-processes in the boiler system leads to a slow increase of HBr-level in flue gas. Bromine in filterdust is not measured.

6.4 Brominated, chlorinated and brominated/chlorinated dioxins

Concentrations in emissions to air (flue gas after cleaning)

Figure 11 shows resulting emissions of brominated, chlorinated and brominated/chlorinated dioxins with no addition of brominated waste, and with the addition of 5 % , 10 % and 20 % by weight of brominated waste respectively. The results are reported as the actual concentration levels, not as toxic equivalents.

Figure 11 Total emissions of the brominated, chlorinated and brominated/chlorinated dioxins analysed.



From Figure 11 one can see that the emissions of *chlorinated dioxins* (PCDDs+PCDFs, as actual concentrations, not toxic equivalents) from Klemetsrud Plant were approx. 1,5 ng/Nm^3 with no addition of brominated waste, and approx. 0,5 ng/Nm^3 with 5 % and 10 % by weight of bromine containing waste. At the FREVAR Plant, the emissions of chlorinated dioxins were approx. 1 ng/Nm^3 (with no addition of bromine containing waste). The Energos Plant had an emission concentration of approx. 0,3 ng/Nm^3 with the addition of 20 % bromine containing waste.

Further, one can see that the emission of *brominated dioxins* (PBDDs+PBDFs) was very low, both with and with no addition of bromine containing waste.

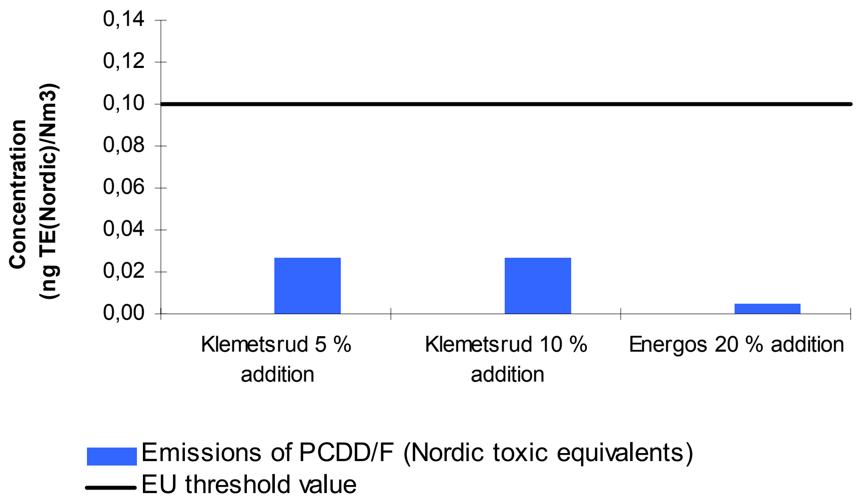
The emissions of *brominated/chlorinated dioxins* (ClxBryDDs+Clx BryDFs) with no addition of brominated waste (Klemetsrud and FRE-

VAR plants) were apparently higher than with addition of brominated waste (Klemetsrud and Energos plants).

Resulting concentrations of brominated/chlorinated dioxins (ClxBryDDs+ClxBryDFs) during measurements with addition of brominated waste, were less than half of the concentrations of chlorinated dioxins (PCDDs+PCDFs).

The emissions of *chlorinated dioxins (PCDDs/Fs), presented as nordic toxic equivalents***,** resulting from addition of brominated waste, is shown in Figure 12.

Figure 12 Emissions of chlorinated dioxins (PCDDs/Fs), presented as Nordic Toxic Equivalents, resulting from addition of brominated waste



From Figure 12, one can see that the emissions of chlorinated dioxins, presented as Nordic Toxic Equivalents, were approx. 0,03 ng/Nm^3 from the Klemetsrud Plant, both with addition of 5 % and 10 % by weight of bromine containing waste. From the Energos Plant, the concentration level was 0,006 ng/Nm^3 with addition of 20 % by weight of bromine containing waste.

The corresponding emission limit value in the EU-directive for waste incineration is 0,1 ng/Nm^3.

Uncertainty in sampling and analysis, variations in operating conditions and waste mixture, differences between laboratories with respect to methods of analysis (especially dioxins), makes comparison of results difficult. We may however draw the following main conclusions:

- Increasing the content of BFRs in the waste gave no significant increase in the emissions of chlorinated dioxins, or either brominated and chlorinated/brominated dioxins
- The emission level is highest for chlorinated dioxins, lower for chlorinated/brominated dioxins and lowest for brominated dioxins
- The emission levels for chlorinated dioxins, reported as Nordic toxic equivalents, are low compared to the emission threshold value in the

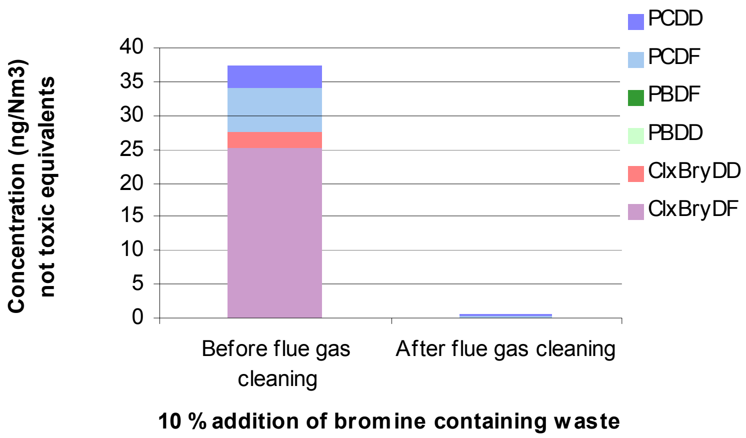
EU-directive for incineration of waste. The reported emission levels were 0,03 ng/Nm^3 and 0,006 ng/Nm^3 respectively for the Klemetsrud Plant (Oslo) and Energos Plant (Ranheim), and the EU threshold value is 0,1 ng/Nm^3.

The emission measurement results indicate that the incineration efficiency and the operating conditions of the flue gas treatment systems are of greater importance to the resulting emission levels for dioxins, rather than the bromine content level.

Flue gas concentrations before and after cleaning

Measurements of dioxins in flue gas before and after cleaning were carried out with addition of a high proportion (10 % by weight) bromine containing waste, see Figure 13.

Figure 13 Concentrations of brominated, chlorinated and brominated/chlorinated dioxins analysed in raw flue gas/emission outlet from Klemetsrud Plant, resulting form addition of 10 % by weight of bromine containing waste.



Concentration of brominated/chlorinated dioxins before cleaning is significantly higher than the corresponding concentration of chlorinated dioxins. After cleaning, the brominated/chlorinated dioxins amounts to only 10-20 % of the total emissions of dioxin compounds. Dioxins removed from flue gas are found in the filter dust. The filter dust from incineration plants is treated as hazardous waste.

6.5 Brominated flame-retardants (BFRs)

Table 9 shows concentrations of BFRs in bottom ash, filter dust, water from the scrubber and in emissions to air from tests with addition of bromine containing plastics at Klemetsrud and Energos Plants.

Table 9 Concentrations of BFRs from incineration tests with addition of bromine containing plastics at Klemetsrud and Energos Plants.

		Level of BFRs	
	Unit	Klemetsrud Plant	Energos Plant
Bottom ash	mg/kg	0,034-0,1	<0,016
Filter dust	mg/kg	0,04	-
Scrubber water (untreated)	ng/l	0,01	-
Emissions to air (after cleaning)	ng/Nm^3	14-22	< 5

From table 9, one can see that the concentration of BFRs in flue gas from Klemetsrud Plant was 14-22 ng/Nm^3. This equals 0,9-1,4 mg/hour and approximately 0,01 kg/year, assuming 8000 running hours/year at the same emission level. A Danish study (Miljøstyrelsen, 1999) estimates the total annual Danish emissions of BFRs from incineration to be < 0,04 tons. A report from the Norwegian National State Pollution Control Authority (SFT), estimates the national emissions from combustion in Norway to be < 0,01 tons/year (1998), i.e. < 10 kg/year.

At the Energos Plant (Ranheim) the reported concentration of BFRs in the flue gas was <5 ng/Nm^3.

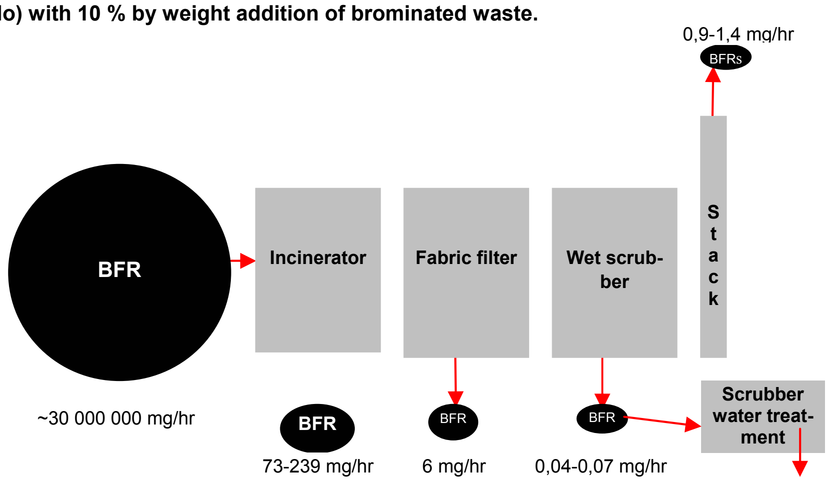
The concentration of BFRs in bottom ash from the tests at Klemetsrud Plant (Oslo) shows levels far below the emission limit value of 0,25 % by weight stated in the Hazardous Waste Directive.

DekaBDE and TBBPA (Tetrabrombisphenol A) are the dominating compounds of BFRs in the bottom ash from Klemetsrud Plant. In water from the scrubber and in the flue gas, dekaBEDE has the highest concentration level.

The amount of BFRs in the waste mixture used in the tests at Klemetsrud Plant was not analysed, but calculated/estimated to be approximately 30 kg/hr, based on a share of bromine containing plastics of 27 % by weight, and an assumed content of BFRs in the plastics of 12 % by weight.

Figure 14 shows input and output flows of brominated flame-retardants at Klemetsrud Plant (Oslo) with 10 % by weight addition of brominated waste.

Figure 14 Input and output flows of brominated flame-retardants at Klemetsrud Plant (Oslo) with 10 % by weight addition of brominated waste.



The results indicates that the BFR-level in output flows amounts to less than 0,001 % by weight of the total BFRs in the waste mixture

Sammendrag

Målsetting

Målet med prosjektet er å kartlegge utslipp av ulike dioksinforbindelser ved forbrenning av plast med bromerte flammehemmere (BFH) sammen med restavfall fra husholdning og næring**.** Nedbrytningen av BFH ved forbrenning av avfallet skal også undersøkes.

Prosjektet skal bidra til å gi miljømyndighetene grunnlag for å vurdere om, og under hvilke betingelser, denne avfallstypen kan forbrennes i fullskala avfallsforbrenningsanlegg. For eiere av forbrenningsanlegg vil prosjektet danne grunnlag for vurdering av brenning av denne typen avfallsfraksjoner.

Bakgrunn

De vanligste anvendelsesområdene for BFH er bygningsmaterialer, tekstiler og elektriske artikler som for eksempel TV-er, PC-er og kopimaskiner. I avfallsforbrenningsanlegg med god forbrenning vil BFH brytes ned og danne andre bromerte forbindelser, hovedsakelig hydrogenbromid (HBr). Det vil imidlertid også dannes andre bromerte forbindelser, bl.a. en rekke ulike bromerte organiske forbindelser, deriblant dioksiner der kloratomene er helt eller delvis erstattet av bromatomer (bromerte og bromerte/klorerte dioksiner).

Det er foretatt få undersøkelser av forbrenning av plast med BFH i fullskala avfallsforbrenningsanlegg med moderne renseutrustning.

Miljøverndepartementet utarbeidet høsten 2002 en handlingsplan for reduksjon av utslipp av BFH. Ett av tiltakene er å kartlegge utslipp ved forbrenning av avfall som inneholder BFH.

Litteraturstudier og forberedende undersøkelser

Formålet med litteraturstudiet og de forberedende undersøkelser var bl.a. å kunne fastlegge et detaljert måleprogram. Arbeidet skulle også danne sammenliknings- og vurderingsgrunnlag for måleresultater som framkom i forbrenningsundersøkelsen.

Undersøkelser ved småskala forsøksanlegg

Det er utført forbrenningsundersøkelser med BFH-holdig avfall på småskala forsøksanlegg i Sverige (Umeå Universitet) og Tyskland (TAMARA-anlegget). Undersøkelsene i Sverige, der brominnholdet ble økt opp til ca 1-2 vektprosent, viste at konsentrasjonen av halogenerte dioksiner i urenset røykgass var vesentlig høyere med BFH enn uten.

Ved TAMARA-anlegget ble brominnholdet variert fra 0 til ca 0,2 vektprosent. Økende innhold av BFH i brenselet ga ingen økning i konsentrasjonene av klorerte dioksiner, og heller ikke av bromerte eller klorerte/bromerte dioksiner i urenset røykgass.

Målinger på fullskalaanlegg

Utslipp til luft av bromerte dioksiner er tidligere undersøkt ved avfallsforbrenningsanlegg i Danmark, Sverige og Norge. Målingene i Danmark omfattet også bromerte/klorerte dioksiner. Alle anleggene var utstyrt med avansert renseutrustning. Målingene ble utført ved forbrenning av restavfall fra husholdning og næring, og ga svært lave utslippsnivåer for alle analyserte dioksiner.

Det foreligger få relevante data for utslipp av BFH fra avfallsforbrenningsanlegg. Ved et japansk avfallsforbrenningsanlegg er det utført målinger med forbrenning av plastavfall med BFH sammen med restavfall fra husholdning og næring. Totalmengde BFH inn på anlegget var under 500 g/time, og utslipp til luft av PBDE (polybromerte difenyletere) og TBBPA (tetrabrombisfenol A) var henholdsvis 3,5 og 8 ng/Nm^3.

Forbrenningsundersøkelser ved tre norske avfallsforbrenningsanlegg

Hovedmålet med forbrenningsforsøkene var å fastlegge røykgasskonsentrasjoner av bromerte, klorerte og bromerte/klorerte dioksiner før og etter rensing ved varierende innhold av plast med bromerte flammehemmere i avfallet. For kontroll av inngående brom- og klormengde ble også brom- og klorinnhold i utgående strømmer (bunnaske, flyveaske, vann fra våtvasker og røykgass) bestemt. Nedbrytning av BFH ved forbrenning av avfallet ble undersøkt ved å foreta analyser av BFH i utgående strømmer fra anleggene.

Gjennomføring

Forbrenningsundersøkelsen omfattet prøvetaking og analyser ved to større anlegg for ubehandlet restavfall fra husholdning og næring og et mindre anlegg for kvernet industriavfall. Det bromholdige avfallet som ble tilsatt ordinært avfall kom fra Stena Miljø AS sitt anlegg for demontering av elektrisk og elektronisk avfall. Stena Miljø AS estimerte dette avfallet til å inneholde ca 1 vektprosent brom. Ca 80 vektprosent av den bromerte plasten ble angitt å inneholde PBDE (polybromerte difenyletere).

De mest omfattende målingene ble gjennomført ved Klemetsrudanlegget i Oslo. Ved anlegget forbrennes avfall på 2 linjer, hver med kapasitet på ca 10 tonn avfall pr time. Hver linje er utstyrt med røykgassrensing bestående av posefilter med injeksjon av koks og våtvasker.

Ved Klemetsrudanlegget ble det foretatt prøvetaking og analyser ved tre ulike betingelser:

- Uten innblanding av bromholdig avfall
- Med innblanding av 5 vektprosent bromholdig avfall, dvs. ca 0,05 vektprosent brom i totalblandingen
- Med innblanding av 10 vektprosent bromholdig avfall, dvs. ca 0,1 vektprosent brom i totalblandingen

Ved FREVAR-anlegget ble det foretatt målinger uten innblanding av plast med bromerte flammehemmere.

Målingene ved Energos Ranheim ble foretatt med 0 og 20 vektprosent bromholdig avfall (dvs. opptil 0,2 vektprosent brom i totalblandingen).

Resultater og konklusjoner

Forbrenningsforholdene under prøvetaking og måling ved Klemetsrud-anlegget var normale, med gjennomsnittlige CO-nivåer på. ca 20-30 mg/Nm^3. Ved prøvetaking på FREVAR-anlegget var gjennomsnittlig CO-nivå ca 50 mg/Nm^3. Ved Energosanlegget ble det ikke registrert CO i røykgassen i måleperiodene, noe som tilsier svært gode forbrenningsforhold. Det var driftsproblemer med renseanlegget (posefilteret) ved FREVAR i måleperioden.

Brom i utgående massestrømmer

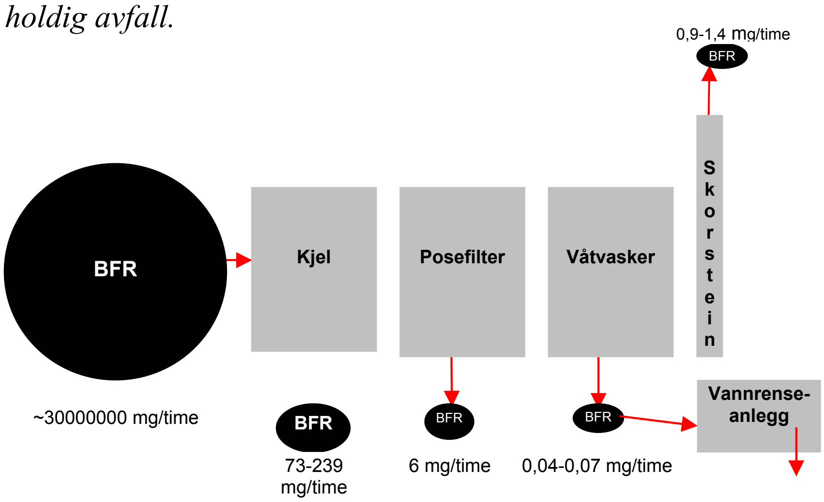
Måleresultatene for gassformig brom i urenset røykgass ved normal avfallssammensetning tilsier brominnhold på nivå med eller noe lavere enn det som er vanlig i restavfall fra næring og husholdning.

Målingene av brom i utgående strømmer både ved Klemetsrudanlegget og ved Energos Ranheim tyder på at brominnholdet i plastblandingen var riktig estimert.

Bromerte flammehemmere (BFH)

Mengden BFH i brenselblandingen benyttet ved Klemetsrudanlegget er ikke målt, men beregnet og anslått til ca 30 kg/time (30 000 000 mg/time). Måleresultatene tilsier at BFH i avfallet brytes ned i forbrenningsprosessen. Mengden BFH i utgående strømmer utgjorde under 0,001 vektprosent av BFH-mengden i brenselblandingen, se figuren nedenfor.

Oversikt over inn- og utgående mengde bromerte flammehemmere på Klemetsrudanlegget med 10 vektprosent innblanding av bromholdig avfall.



Konsentrasjonen av BFH i utslipp til luft ved Klemetsrudanlegget var 14-22 ng/Nm^3. Dette tilsvarer 0,9-1,4 mg/time og ca 0,01 kg/år forutsatt 8000 driftstimer med samme utslippsnivå. I en dansk undersøkelse (Miljøstyrelsen i Danmark, 1999) anslås det totale nasjonale utslippet til luft av BFH fra forbrenning til <0,04 tonn. I en rapport fra SFT (SFT, 1999) er utslipp av BFH fra forbrenning i Norge estimert til < 0,01 tonn (1998), dvs <10 kg/år.

Ved Energos Ranheim var konsentrasjonen av bromerte flammehemmere i utslipp til luft < 5 ng/Nm^3.

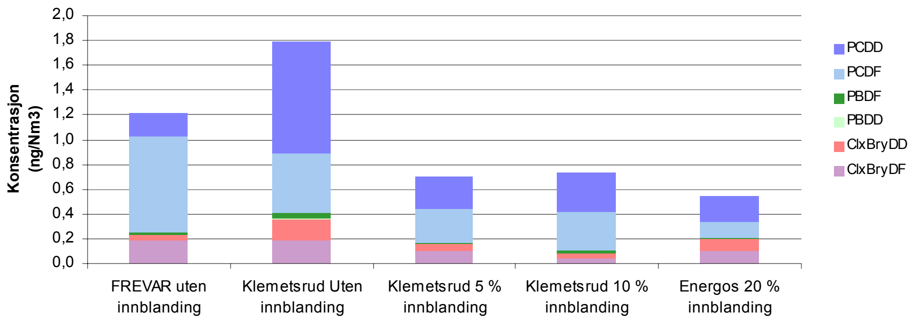
Konsentrasjonen av bromerte flammehemmere i bunnasken fra forbrenningsforsøket på Klemetsrudanlegget og Energos Ranheim ligger langt under grenseverdien på 0,25 vektprosent i forskrift om farlig avfall.

DekaBDE og TBBPA (Tetrabrombisfenol A) er de dominerende forbindelsene i bunnasken ved Klemetsrudanlegget. I utslipp til luft er det bestemt høyest konsentrasjon av dekaBDE.

Dioksinkonsentrasjoner i utslipp til luft (etter rensing)

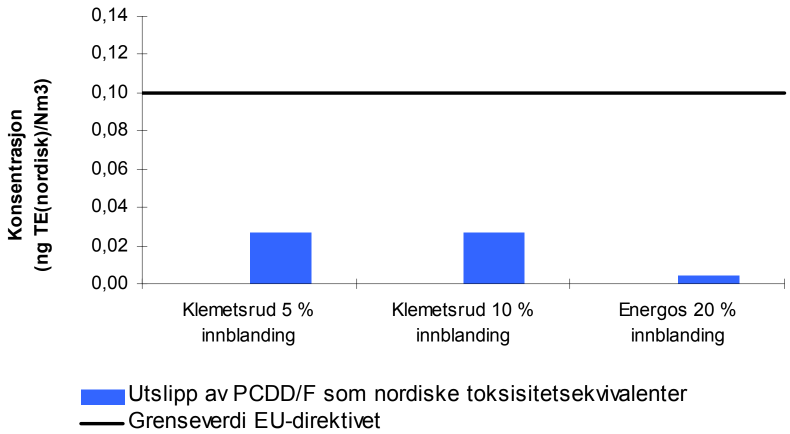
Figuren under viser utslipp av klorerte, bromerte og klorerte/bromerte dioksiner uten innblanding av bromholdig avfall og med innblanding av 5 vektprosent, 10 vektprosent og 20 vektprosent bromholdig avfall. Utslippene er gitt som reelle måleverdier og ikke som toksisitetsekvivalenter.

Utslipp av klorerte, bromerte og klorerte/bromerte dioksiner. Utslippene er gitt som reelle måleverdier og ikke som toksisitetsekvivalenter.



Utslippet av klorerte dioksiner (PCDD/F) som nordiske toksisitetsekvia-lenter med innblanding av bromholdig avfall, er vist i figuren under.

Utslippet av klorerte dioksiner (PCDD/F) som nordiske toksisitetsekvialenter med innblanding av bromholdig avfall



Usikkerhet i prøvetaking og analyser, variasjoner i driftsforhold og bren-selsammensetning og ulik metodikk knyttet til analyser av særlig diok-siner gjør at sammenlikningen av måleresultater er vanskelig. Likevel kan følgende hovedkonklusjoner trekkes:

- økende innhold av bromerte flammehemmere i avfallet ga ingen signifikant økning i utslipp av klorerte dioksiner, og heller ikke av bromerte eller klorerte/bromerte dioksiner
- utslippsnivået er høyest for klorerte dioksiner, lavere for klorerte/bromerte dioksiner og lavest for bromerte dioksiner
- utslippet av klorerte dioksiner regnet som nordiske toksisitetsekvivalenter var lavt ved målingene med innblanding av bromholdig avfall, hhv. 0,03 og 0,006 ng/Nm^3 ved Klemetsrud- og Energos-anleggene. Grenseverdien i EU-direktivet om forbrenning av avfall er 0,1 ng/Nm^3

- måleresultatene tyder på at forbrenningseffektiviteten og driftsforhold ved renseanlegg for utslipp til luft er av større betydning for dioksinutslippet enn brominnholdet

Dioksinkonsentrasjoner før og etter rensing

Målinger av dioksiner i røykgassen før og etter rensing ble foretatt med innblanding av 10 vektprosent bromholdig avfall på Klemetsrudanlegget. Konsentrasjonen av klorerte/bromerte dioksiner (som reelle måleverdier og ikke som toksisitetsekvivalenter) før rensing var ca 28 ng/Nm^3, dvs. omtrent tre ganger konsentrasjonen av klorerte dioksiner. I utslippet (etter rensing) var konsentrasjonen av klorerte/bromerte dioksiner ca 0,1 ng/Nm^3. Dette gir en rensegrad på over 99 % for klorerte/bromerte dioksiner. Rensegrad for klorerte dioksiner var på ca 93 %. Dioksinene som renses ut finnes i filterstøvet. Filterstøv fra avfallsforbrenningsanlegg behandles som farlig avfall.

Konsentrasjon av klorerte, bromerte og bromerte/klorerte dioksiner i røykgassen før og etter rensing, Klemetsrudanlegget. Konsentrasjonene er gitt som reelle måleverdier og ikke som toksisitetsekvivalenter.