



The presence of zinc in Swedish waste fuels



Frida Jones^{a,b,*}, Mattias Bisailon^c, Daniel Lindberg^a, Mikko Hupa^a

^a Åbo Akademi University, Biskopsgatan 8, FI-20500 Åbo, Finland

^b SP Technical Research Institute of Sweden, Box 857, SE-501 15 Borås, Sweden

^c Profu AB, Götaforsliden 13, 431 34 Mölndal, Sweden

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ABSTRACT

Zinc (Zn) is a chemical element that has gained more attention lately owing to its possibility to form corrosive deposits in large boilers, such as Waste-to-Energy plants. Zn enters the boilers in many different forms and particularly in waste, the amount of Zn is hard to determine due to both the heterogeneity of waste in general but also due to the fact that little is yet published specifically about the Zn levels in waste. This study aimed to determine the Zn in Swedish waste fuels by taking regular samples from seven different and geographically separate waste combustion plants over a 12-month period. The analysis shows that there is a relation between the municipal solid waste (MSW) content and the Zn-content; high MSW-content gives lower Zn-content. This means that waste combustion plants with a higher share of industrial and commercial waste and/or building and demolition waste would have a higher share of Zn in the fuel. The study also shows that in Sweden, the geographic location of the plant does not have any effect on the Zn-content. Furthermore, it is concluded that different seasons appear not to affect the Zn concentrations significantly. In some plants there was a clear correlation between the Zn-content and the content of other trace metals.

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1. Introduction

Zinc (Zn) enters Waste-to-Energy (WtE) plants with the different waste fuels. It is hard to determine a general form of Zn since waste mixtures are very heterogeneous. The Zn-content depends on numerous factors, such as household consumption patterns, industrial/commercial activity, season, economic climate, and possibly geographical location. In the database *AvfallsAtlas*,¹ information from different waste fraction characterization studies have been collected and summarized, giving the possibility to show the waste fractions with the highest contribution to the share of Zn in waste. In *Table 1* different waste fractions are listed with the minimum and maximum reported Zn-content in the database. The merging of different types of materials within each fraction, such as a summary of all plastic materials, also means that the origins of the waste fractions are merged. Therefore, all of the fractions presented in *Table 1* include waste collected as Municipal Solid Waste (MSW), Industrial and Commercial Waste (ICW), and Building and Demolition Waste (BDW). From here on the three-letter abbreviations will be used.

The internal variation of Zn within each fraction also indicates how difficult a general determination of Zn-content in a waste mixture would be, for example, in the Textile/leather/rubber-fraction where the Zn-content varies from around 30 to 18,000 mg/kg waste. Furthermore, although the difference between the materials in the textile/leather/rubber-fraction is obvious there is also a major difference within the glass fraction with reported measurements varying between close to 0 and 10,000 mg/kg. A study of the details behind *Table 1* reveals that the materials contributing the most to the Zn-content in waste are rubber tires, glass, plastics treated with flame retardants, and PVC plastics.

Zinc oxide (ZnO) is a frequently used chemical as an additive in numerous products (Klingshirn et al., 2010; Moezzi et al., 2012). The most dominant application of ZnO is within the rubber industry where it is used in many types of rubber, and has been for over a century (Depew, 1933a, 1933b, 1933c). Predominantly ZnO is used in the car industry, activating the sulfur crosslinking and also for improving the absorption of frictional heat in tires, as well as being used in belts, windshield wipers, hoses, oil seals, trim and mountings International Zinc Association-Zinc Oxide Information Centre (2012). In addition, ZnO is also used in heat resistant glass, cooking wear glass, and specialty glass, such as photochromic lenses. ZnO is also a main ingredient for the production of a flame retardant zinc borate (XZnO·YB₂O₃) which exists in various forms, differing by the Zn/B-ratio and number of attached hydrates. Zinc borate is added to a number of materials and products, such as plastics, textiles, and rubber (Shen et al., 2008).

* Corresponding author. Address: SP Technical Research Institute of Sweden, Energy Technology, Box 857, SE-501 15 Borås, Sweden. Tel.: +46 (0) 10 516 57 67.

E-mail address: frida.jones@sp.se (F. Jones).

¹ *AvfallsAtlas* (WasteAtlas) is a closed database developed by Profu AB, www.profu.se/indexaa.htm. Contact person Mattias Bisailon (mattias.bisailon@profu.se) or Johan Sundberg (johan.sundberg@profu.se).

Table 1
Waste fractions and their Zn-content, summarized information from the database *AvfallsAtlas*.

Waste fraction	Minimum (mg/kg)	Maximum (mg/kg)
Cardboard/paper/corrugated cardboard	13	160
Plastics	15	10,000
Kitchen and garden waste	14	125
Textile/leather/rubber	32	17,640
Glass	<1	10,000
Wood/RWW ^a /CCA ^b /sleepers	27	539
Scrap/electronic waste	101	210
Sanitary products/diapers	14	29
Other combustibles	150	322
Other non-combustibles	12	150

^a RWW = Recovered waste wood.

^b CCA = pressure-treated wood with copper, chromium and arsenic.

Traditionally, ZnO has been used in the production of photocopy paper and linoleum; however, nowadays these materials are produced differently, and paint which was once a dominating area of use for ZnO, only represents a small part of the present usage [International Zinc Association-Zinc Oxide Information Centre \(2012\)](#). However, even if the production of many products might have changed, and the usage of ZnO has shifted to other areas, the ZnO once added in different materials will most likely still appear in the waste streams today when the materials are discarded.

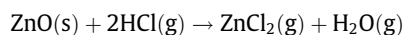
Another Zn-compound (zinc stearate, $Zn(C_{18}H_{35}O_2)_2$) is used as a heat stabilizer in common materials, such as PVC. Often it is used in combination with other chemical compounds like those of Ca, Ba or K ([MacKenzie and Willis, 1983](#); [Minagawa, 1989](#)). Owing to the flexibility, mechanical properties, and electrical properties in materials stabilized with the Ca/Zn-combination it is used in a variety of PVC based plastics, such as potable water pipes, healthcare products, water bottles, cable covering, and toys [PVC Europe \(2012\)](#). All these components are possible fractions in all three waste fractions (MSW, ICW, and BDW). In combination with Ba the most common materials include flexible foils, flooring, wall covering, fabric coating, and footwear. Moreover, the K/Zn-combination is used as a stabilizer for foam layers in cushion flooring, foamed wallpaper and foamed fabric coating [PVC Europe \(2012\)](#). All these are common products that can be found in MSW, ICW, and BDW.

Material recovery is conducted, some at the source on household level and some at treatment facilities, but with methods vary due to differences between municipalities in Sweden. However, after pretreatment Zn-content are still present in various concentrations in all of the three waste streams.

During combustion Zn from the fuel is released and is available to form gaseous products in the flue gas. Previous studies indicate that Zn readily forms $ZnCl_2$, which melts at low temperatures creating sticky melts and increased deposit formation on boiler heat exchanger surfaces ([Sarofirm and Helble, 1993](#); [Verhulst et al., 1996](#); [Ljungdahl and Zintl, 2001](#); [Backman et al., 2005](#); [Niemi et al., 2006](#); [Åmand et al., 2006](#); [Enestam et al., 2011](#); [Enestam, 2011](#); [Sjöblom, 2011](#); [Bankiewicz et al., 2012](#)). [Elled et al., 2008](#), suggests that the formation of $ZnCl_2$ is thermodynamically favoured between 450 and 850 °C at reducing conditions while at oxidizing conditions, the formation is initiated at 400 °C and gradually increases with temperature. However, the calculations also show that reducing conditions increase the release of gaseous Zn-content to the flue gas but in the case of oxidizing conditions, the retention of Zn in the solid ash is strong.

The most common form of Zn, ZnO, is thermally stable with a melting temperature of 1975 °C. ZnO is insoluble in both water

and alcohol ([Verhulst et al., 1996](#)). This hinders volatilization at combustion temperatures under the melting temperature. However, at elevated temperatures it readily reacts with hydrochloric acid (HCl) to form gaseous $ZnCl_2$:



[Verhulst et al. \(1996\)](#) have shown with thermodynamic equilibrium calculations that the amount of chlorine highly affects the volatility of Zn. In addition, they suggest that the presence of water decreases the volatilization of Zn by shifting the equilibrium to the left in reaction. This means that in the presence of HCl in the flue gas also could contribute to the formation of $ZnCl_2$.

In a study of Zn in fly ash aerosols and ash deposits in a full scale boiler, [Enestam et al. \(2011\)](#) doped wood chips with ZnO to increase the Zn-content. They showed that Zn can be released from its oxide form during the combustion process.

2. Methods

To obtain a good overview of the Zn-content in Swedish waste fuel, seven waste combusting plants spread over Sweden with 1000 km between the southernmost and the northernmost were investigated in this project. There were two Bubbling Fluidised Bed (BFB) boilers and five grate fired boilers. This ratio is in accordance with what the distribution of Sweden's waste combustion plants were at the time for the study approximately 25% were FB-boilers and plants with grate fired boilers.

At each of the seven plants studied, six solid waste samples were collected over a twelve month period. The samples are mixtures of MSW, ICW, and BDW, either shredded and mixed (plant A and B) or in its original form directly from the bunker (plant C–G). In [Table 2](#), the plants are described with the type of combustion technique and the mean average of MSW during the sampling campaign, the table also illustrates which months the samples were taken. The time for sampling was based on plant availability, which leads to irregularity in time for some of the plants.

2.1. Plants A and B

Fuel that is combusted at BFB-boilers needs to undergo pre-treatment before combustion, to ensure a particle size suitable for the combustion technique. The incoming fuel is often a mixture of MSW, ICW, and to some extent BDW, but all fractions are shredded and mixed at a preparation site, before being placed in the bunker and subsequently fed into the boiler via an overhead crane.

The sampling procedure was highly facilitated by the pre-treatment of the waste which makes the fuel mixture more homogeneous even if this fuel is much more heterogeneous than, for example, pure biomass fuels. In addition to this, in Sweden some sorting has normally already been done at source by the households to exclude material like glass, metals, paper, cardboard and food waste. The extent to which sorting is done is different in the various regions in Sweden when it comes to which and how much of the material that is separated before the waste is collected to go to combustion.

When the fuel entered the boiler system, it is possible to collect a fuel sample via a hatch that is placed close to where the fuel drops down towards the combustion bed. The samples at plant A and B were collected by repeatedly inserting a shovel directly into the falling waste stream in a specific pattern until a sample of 30 kg was gathered. Samples were taken according to the information in [Table 2](#).

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