

Ash Deposits Characterization in a Large-Scale Municipal Waste-To-Energy Incineration Plant

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Chemical and mineralogical compositions of deposits from a municipal solid waste incineration plant in Oslo, Norway, have been characterized. Ash deposits are analysed via a combination of scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDX), X-ray powder diffraction (XRD) and X-ray fluorescence (XRF). The results show that the deposits formed have a clear layered structure along the thickness, in terms of density and morphology. The combination of different analytical techniques is also capable of characterizing chemical and mineralogical compositions of the collected deposits along the thickness of the deposits. The key ash transformation and chemical reactions involved in deposits formation in this plant are investigated and summarized. The primary deposits, mainly melted sulphates and chlorides, initially build on heat transfer tube surfaces and act as a sticking surface to particles and aerosols passing by. The secondary deposits are dominated by calcium sulphates, silicates, and calcium and silicon oxides formed in the combustion chamber. Within the deposits, interactions of different mineralogical phases take place, leading to formation of new chemicals and further sintering of deposits.

1. Introduction

Incineration plays an important role in disposing of and managing Municipal Solid Waste (MSW) worldwide. Through incineration, the amount and volume of MSW can be significantly reduced and therefore preserve landfill space and reduce negative effects of the waste on environment and water. Incineration of MSW allows recovery of energy and minerals from the solid waste stream. In addition, during the MSW incineration process, a number of contaminants in the MSW can be destroyed (Becidan et al. 2015). Combined with material recycling and biological treatment, incineration of MSW can give great contributions to an efficient and sustainable MSW management system.

MSW is a mixture of inhomogeneous materials with large proportions of ash that contains high concentrations of sulphur, chlorine, alkali and alkali earth metals, and minor amounts of heavy metals like lead and zinc (Eichelet et al. 2013). During incineration, these ash forming elements in the MSW will volatilize and transform through complex chemical and physical processes, and will be transported together with particles from the fuel bed in the flue gas (Becidan M et al. 2015). These volatiles and fine ash/fuel particles result in formation of deposits on heat transfer surfaces in the convective section of the boiler. Due to further accumulation and sintering of the deposits, the heat transfer from the flue gas to the heat transfer tubes can be significantly reduced, causing reduced energy efficiency of the plant. Additionally, excessive formation of corrosive deposits will also lead to corrosion of heat transfer tubes and will increase maintenance costs (reduce components' lifetime) and unplanned shutdowns. Therefore, detailed characterization and studies on deposits from MSW incineration plants are critical to understand and predict ash transformation and the related deposits formation process.

2. Experimental methods and materials

Two deposit samples were collected from the Klemetsrud Waste-to-Energy (WtE) plant during the planned annual shutdown in summer 2015. Klemetsrud WtE plant is currently the largest WtE plant in Norway and is

the main facility converting household and commercial&industry (C&I) wastes from Oslo city and neighbouring communities (as well as foreign customers) into energy. The total waste throughput capacity of the plant is 310 000 tons per year and it produces up to 160 GWh electricity and 630 GWh district heat per year. The first sample (about 1 kg) studied is from line #1 and was collected from a tube in the first overheater section. The second sample (about 1 kg, too) is from line #2 and was collected in the first pass (near the access hatch). The gas temperature in these zones is about 750°C. The two deposit samples were photographed and labelled after collection. For investigating deposits formation mechanisms, the samples were taken from the inner to the outer section of a given deposit sample as shown in Figure 1 (a). For the deposit sample collected from line #1, there is a thin layer in the inner most part of the deposit, which has a dense and compact structure. This deposit layer was separated from the main deposit body and named the thin inner layer. The chemical and mineralogical compositions of representative parts of the deposits were examined by X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis. Different parts of the deposit were firstly separated and ground into powders. An X-ray fluorescence (XRF) analyzer (Bruker, S8 Tiger) was used for quantifying concentrations of main elements in the samples, and are presented as oxides. Mineralogical compositions of the samples were identified by an X-ray diffractometer (Bruker D8 Advance) equipped with a Cu k-alpha radiation and LynxEye detector. Semi-quantitative analyses were performed for collected data by using the evaluation program TOPAS plus with the ICDD-PDF2 database. The morphology and microchemistry of the samples were examined by scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX). The SEM was operated to take backscattered electron images for illustrating elemental distribution in a scanned area.

3. Results and discussion

3.1 General appearance and structure of the deposit

Figure 1 (a) and (b) show general views of the structure and appearance of bulk deposits and the thin inner layer. It can be seen that the deposit has a compact structure. The cone shape of the deposit also implies that the deposit formed in a gas flow. The outer layer part of the deposit has a rather loose structure and dust-like morphology. It indicates accumulation of fly ash particles on the surface of the deposit. On the other hand, the inner most part of the deposit has a curved and dense structure, which forms as a result of accumulation of ash on the heat transfer tube surface. The thin inner layer has a more solid structure and dark red and brown spots and areas can be found.

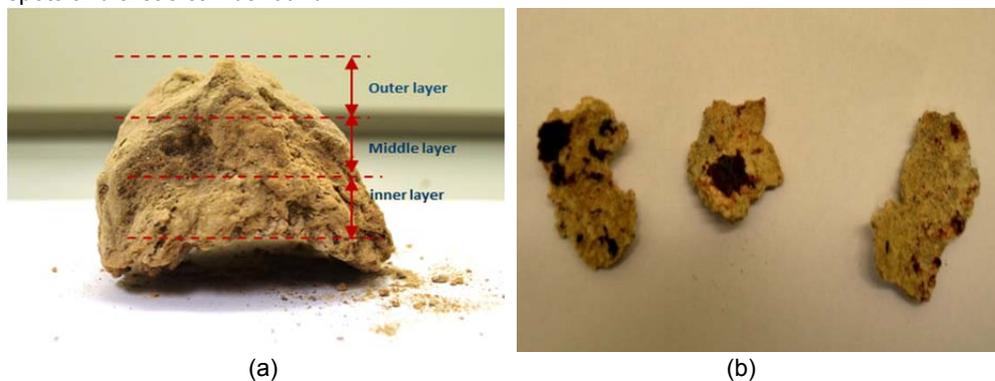


Figure 1: Photos of (a) bulk deposit sample and (b) thin inner layer.

3.2 Chemical and mineralogical analysis

Figure 2 and 3 shows the chemical compositions of different parts of the deposit samples collected from line #1 and line #2. It can clearly be seen that Ca and S are two dominant elements in the deposit samples. The volatile elements, including Cl, Na and K, are also enriched in the deposit samples. These elements are released from the fuel bed, transformed in subsequent chemical/physical processes and transported by the flue gas, and can condense on fly ash particles or/and heat transfer tube surfaces in cooler regions of the WTE plant. As shown in Figure 2, the chemical compositions of different parts of the deposits along the thickness are considerably different. Evidently high concentrations of S, K, Na, Zn and Pb are detected in the thin inner layer that is directly in contact with the heat transfer tube surfaces and considered as primary deposits. It indicates presence of different sulphates in the thin inner layer. This finding agrees well with a previous study by Reichelt et al. (2013) reporting that the primary deposit in the MSW plant consists mainly of different sulphates, rich in K, Na, Pb and Zn. These elements rapidly release during combustion of MSW and react with other elements, leading to formation of KNaSO_4 , Na_2SO_4 , PbSO_4 , $\text{K}_2\text{Pb}(\text{SO}_4)_2$, $\text{K}_2\text{Zn}(\text{SO}_4)_2$, $\text{K}_3\text{Na}(\text{SO}_4)_2$,

$\text{Ca}(\text{Na},\text{K})_2(\text{SO}_4)_2$ and $\text{Na}_2\text{Ca}(\text{SO}_4)_2$. These compounds normally have low melting temperatures and will exist as vapours, aerosols and droplets and will condense on the cooler heat transfer tube surfaces. They will there act as glue to bind and capture fly ash particles passing by, initiating formation of an ash deposit (Reichelt et al. 2013). About 2 wt% of Cl is also determined in the thin inner layer part of the deposit. Considering high contents of alkali metals, Zn and Pb and alkali chlorides, ZnCl_2 and PbCl_2 should also be present in the thin inner layer sample. These chlorides have low melting points and will also contribute to formation of primary deposit. On the other hand, a low amount of chlorides in the primary deposit (thin inner layer part of the deposit) can also be attributed to sulphation of these chlorides, with release of HCl as a gaseous product (Becidan et al. 2009). As shown in Figure 2(a), the concentrations of Ca along the thickness of the deposit increase significantly, with decrease of S, K, Na, P and Zn at the same time. It suggests that the main body of the deposit contains mainly calcium sulphates. In the deposit sample collected from line #1, a certain amount of Si, Al and Fe are also detected. These elements are non- and less volatile elements that are normally contained in solid residues (i.e., bottom ash) in the bottom section of the boiler. The solid residues might be transported by the gas flow from the fuel bed, leading to entrainment of particles in flue gas and subsequent deposits as well (Phonegphiphat et al. 2011).

Figure 4 displays major mineralogical phases identified in different parts of the deposit sample collected from line #1. Figure 4(a) shows that KNaSO_4 , CaSO_4 , Na_2SO_4 and $\text{K}_2\text{Ca}(\text{SO}_4)_3$ are main mineral phases in the thin inner layer part of the deposit sample. It is in a good agreement with XRF analysis results showing that S, K, Na and Ca are the most abundant elements there. In addition, a big lump in the XRD spectrum indicates presence of considerable amounts of amorphous phases in the thin inner layer sample. Semi-quantitative XRD analysis confirms this assumption as around 26 wt% of amorphous phases were identified in this sample. These amorphous phases are normally contained in melted or fused materials that have poor crystallinity and cannot be identified by XRD directly. As shown in Figure 4(b), along the thickness of the deposits, CaSO_4 , NaCl and KCl are the three major mineral phases observed in different parts of the deposit sample. In addition, small amounts of SiO_2 and $\text{Ca}_3\text{Al}_2\text{O}_6$ are also detected in the different parts along the thickness of the deposit sample. Moreover, the amount of amorphous phases is about 14 wt%, which is considerably lower than that of the thin inner layer. Figure 5 shows XRD spectrums of the different parts of the deposit sample collected from line #2. Similar to the deposit sample from line #1, more mineral phases are detected from the inner part of the deposit sample. For the outer part of the deposit sample, CaSO_4 is identified as the only major mineral phase.

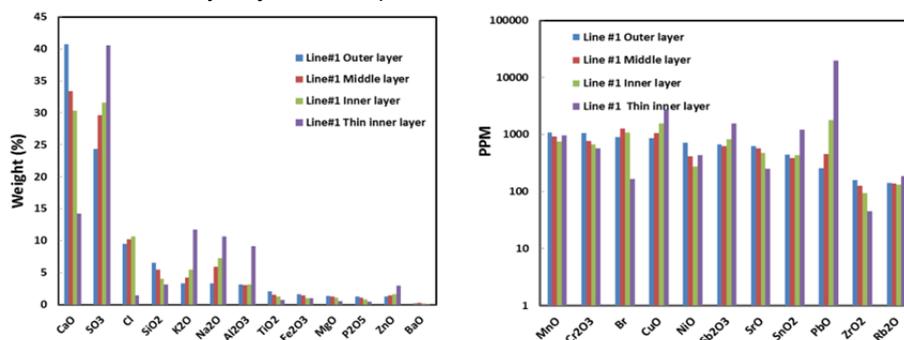


Figure 2: Chemical compositions of different parts of deposit collected from line #1.

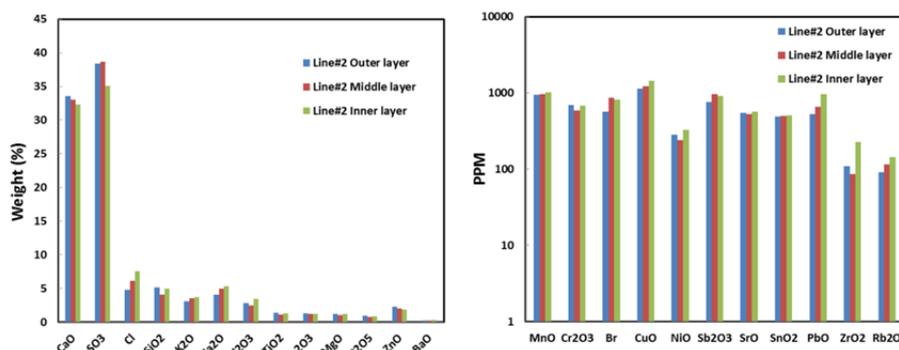


Figure 3: Chemical compositions of different parts of deposit collected from line #2.

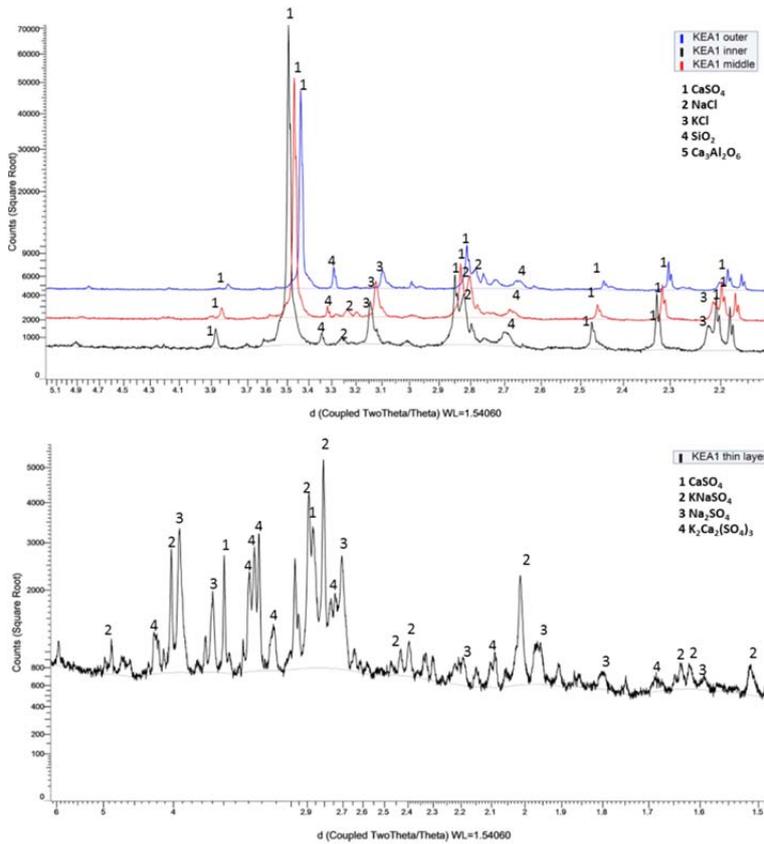


Figure 4: Mineralogical composition of different parts of deposit sample collected from line #1.

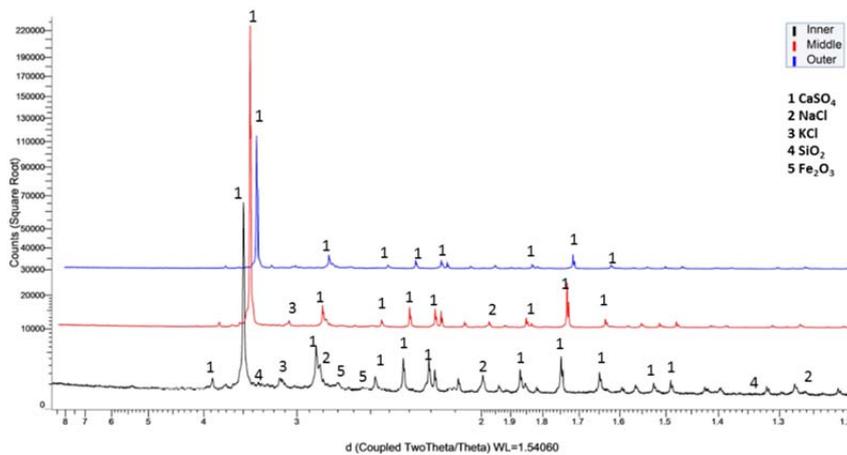


Figure 5: Mineralogical composition of different parts of deposit sample collected from line #2.

3.3 SEM-EDX analysis

Compared to the deposit sample collected from line #1, XRF analysis results reveal clear differences of chemical compositions in the sample from line #2 along the thickness of it. Therefore, more detailed SEM-EDX analyses are carried out for the deposit sample collected from line #2. Figure 6 and 7 show SEM images of respectively the inner and outer layer part of the deposit sample collected from line #1. Figure 6(a) displays that the inner layer deposit is characterized by compact frameworks and dense structure. The dense structure of the inner layer deposits (Figure 6(b)) is built up mainly by a large number of conglomerated particles with presence of molten films. EDX analysis reveals that Ca and S are two dominant elements in the molten parts, indicating formation and melting of CaSO₄. In the centre of Figure 6(b), many white spots and patches can be

easily seen. According to EDX analysis, K and Cl are the main elements detected in these spots and patches that are crystallized KCl stick on the deposit surface.

Figure 7(a) shows a general view of the outer layer deposit. Compared to the inner layer deposit, the outer layer deposit is made up by alternations of compacted sintered materials and loose agglomerated particles. Figure 7(b) displays a closer view of the surface area indicated by a rectangle in Figure 7(a). It vividly shows formation of a large amount of melted material that has smooth and intact surface. There are many white cubic particles embedded in the molten material, which are KCl crystals according to EDX element analysis. Several spherical particles are also sticking on the molten materials. Some of these spherical particles might be smooth spheres of molten matter. On the other hand, some of them may be spherical quartz grains covered by either molten or crystalized materials, which appear as smooth or coarse surfaces (Phonegphiphat et al. 2011). There is a cluster of particles in the upper right corner of Figure 7(b). These particles are rich in calcium and sulphur, which might be partially sulphated CaO particles. In general the EDX analysis agrees well with the XRD analysis and reveals that the deposit sample contains mainly S and Ca, with presence of small amounts of K and Na.

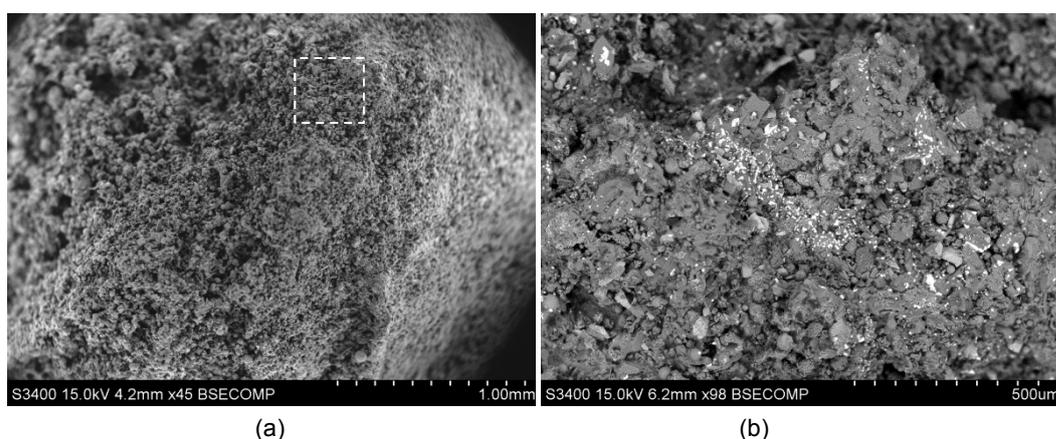


Figure 6: (a) SEM image of inner layer of the collected deposit sample, (b) the surface of the deposit sample.

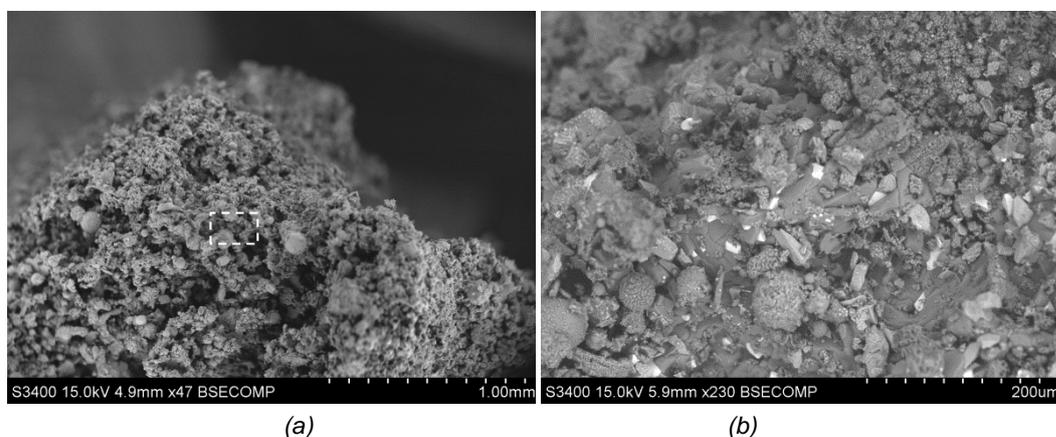


Figure 7: (a) SEM image of outer layer of the collected deposit sample, (b) the surface of the deposit sample.

4. Conclusions

Ash deposits from the Klemetsrud Waste-to-Energy (WtE) plant were collected and characterized in terms of chemical and mineralogical compositions. In addition, morphology and micro-structure of the ash deposits were examined by SEM-EDX. The results show that both chemical and mineralogical compositions along the thickness of the deposit are considerably different. The inner layer deposit contains mainly S, Ca and alkali metals. Together with SEM-EDX analysis results, the XRD analysis indicates that primary deposits contain melted sulphates and small amounts of chlorides. These molten phases will condense on heat transfer tube surfaces. Along the thickness of the deposits, both chemical and mineralogical compositions change significantly. The outer layer deposit contains mainly Ca, S, Cl and alkali metals. The major mineral phases are CaSO_4 and alkali chlorides that melt and act as the glue for building up the deposits. The molten phases

incorporate silicates and oxides contained in particles entrained from the combustion process, leading to formation and sintering of ash deposits. Such advanced analysis and characterisation studies are seldom carried out on industrial samples and bring valuable information on the mechanisms at work and the parameters of importance.

Acknowledgments

This publication has been funded by CenBio – Bioenergy Innovation Centre. CenBio is co-funded by the Research Council of Norway (193817/E20) under the FME scheme and the research and industry partners.

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