

Gas generation in incinerator ash

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ABSTRACT

In recent years, explosions have occurred in certain phases of ash management in Sweden. Investigations have revealed that hydrogen may have been present in all cases. It is supposed that the hydrogen is generated by chemical reactions of aluminium and other metals within the ash in the presence of water.

The purpose of this study was to increase the knowledge of hydrogen generation in incinerator ash. Thereby, guides for appropriate ash management can be introduced and the risk for further explosions prevented.

The study has comprised analyses of the ash properties, such as chemical and physical composition, of ash from 14 incineration plants. Different fractions of ash materials representing different parts of the process in each plant have been analysed. Furthermore, the fuel and the technical differences between the plants have been analysed. A tool for measuring the gas generation in the laboratory has been developed and the gas generation in the different ash materials at natural and increased pH was measured.

Based on the results the following recommendations can be given. The content of elemental aluminium or the hydrogen generation potential should be analysed regularly for ash materials from municipal waste incineration plants. Metal separation – including non-magnetic metals – of the fuel for waste incineration plants is necessary. Good ventilation of the ash after wetting, together with storage in oxygen rich environment is desirable.

Key words: ash, hydrogen, aluminium, explosion, incineration

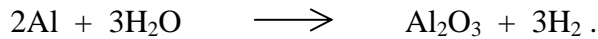
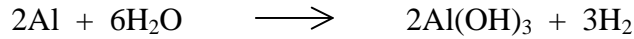
1 INTRODUCTION

In recent years, explosions have occurred in certain phases of ash management in Sweden. The explosions have occurred during storage of municipal and industrial waste incinerator filter ash in rock shelters, during transport of quenched municipal and industrial waste incinerator bottom ash on a conveyor and during storage of wetted cyclone ash in a container. Investigations revealed that hydrogen may have been present in all cases. This has drawn the attention to the problem with gas generation in incinerator ash.

According to a minor literature study (Suèr et al, 2004) gas generation in ash has been reported and some studies has been performed on ash from incinerated municipal waste because of problems due to the gas generation. It has for example caused explosions in landfill (Musselman et al, 2000; Magel, 2003) and in flue dust separation system (Mizutani et al, 2000). When using ash in road construction gas generation in the ash layer has destroyed overlaying asphalt (Alkemade et al, 1994). Furthermore, cracks in concrete and stabilised layers due to gas generation in ash have been reported (Husain & Krasznai, 1994; Oberste-Padtberg & Schweden, 1990; Péra et al, 2000).

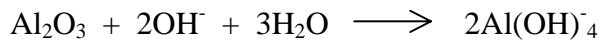
On the other hand the gas generation is utilised when fly ash is used for cement production in the manufacturing of lightweight concrete (Oberste-Padtberg & Schweden, 1990).

Suèr et al (2004) and Håkansson et al (2004) concluded that it is mainly hydrogen that is generated in ash by chemical reactions of aluminium and other metals within the ash in the presence of water at alkaline conditions. The reaction between elemental aluminium and water can be written

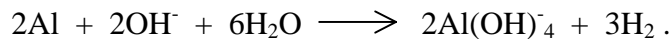


The content of elemental aluminium decides how much hydrogen can be generated, but pH is also an important factor. On exposure to oxygen and/or water, particles of elemental aluminium obtain protective coatings of for example aluminium oxide. The coatings prevent reactions between water and the aluminium, but at high pH the protective coatings are dissolved. This can be described with the following reactions:

Reaction between aluminium oxide and hydroxide ions



and the following reaction between elemental aluminium and hydroxide ions



Other metals that may occur in ash can also generate hydrogen (Suèr et al, 2004; Magel, 2003). Metals that have been mentioned are zinc, iron, copper and chromium.

If ash is exposed to unlimited volumes of water at high pH, the maximum amount of hydrogen that can be generated in the ash – the hydrogen generation potential – can be measured.

The purpose of this study was to increase the knowledge of hydrogen generation in incinerator ash. Thereby, guides for appropriate ash management can be introduced and the risk for further explosions prevented. The study was performed during 2004 and 2005 on commission of the Swedish Thermal Engineer Research Institute and comprised the following activities (Arm et al, 2006):

- Develop a tool for measuring the hydrogen generation potential.
- Analyse what gas are generated apart from hydrogen.
- Analyse if there are other reactive metals in addition to aluminium.
- Investigate the connection between hydrogen generation and type of fuel, incinerator type and ash fraction.
- Investigate the connection between hydrogen generation and other chemical properties of the ash.
- Analyse why elemental aluminium remains in the ash.

Only the main parts of the study are described in this paper.

2 MATERIALS AND METHODS

The study comprised 33 ash materials from 14 incineration plants. The plants were chosen to include both fluidised bed boilers and grate fired boilers. The fuels used varied from pure biofuel to municipal solid waste.

Sampling and preparation of ash materials

Sampling comprised bottom ash and filter or cyclone ash from all the plants. In addition idle pass ash was sampled from a few plants. When possible, the ash samples were collected directly from the process and therefore dry. However the bottom ashes from the grate fired boilers, which are quenched in water, were damp. The sampling containers were totally filled in order to minimise air contact and oxidation of the ash. The containers were made of plastic and had a tight fitting lid.

Total content analysis was performed on one subsample from each ash. Damp ashes were dried in 40°C and coarse materials were crushed to pass the 4-mm sieve. Non crushable material (e.g. metals) was cut in small pieces.

Measurements of hydrogen generation

The hydrogen measurements were based on a method developed by Mizutani et al (2000) and on previous studies on SGI. Each ash sample was put in a 120 ml gas-tight bottle together with a magnet. The bottle was sealed with a rubber cork and 5 M NaOH solution or de-ionised water was injected with a syringe to a L/S-ratio of at least 2. Ash and liquid were mixed with a magnetic stirrer and the gas volume produced was measured with a 100 ml glass syringe. The length of the optimal reaction time was determined to 72 hours.

The hydrogen generation potential i.e. the generation of hydrogen when ash is mixed with 5 M NaOH solution was measured for all 33 ash samples. Duplicates were measured, but for bottom ash samples (that are less homogenous than fly ash samples) three replicates or more were measured.

For those ash samples that showed high hydrogen generation potential also a more realistic level of gas generation was measured. This was done by means of reaction in de-ionised water. Determination of pH values in a mixture of ash and water was also performed for these samples.

For one plant, a municipal solid waste incinerator with a fluidised bed, the effect of ash storage was evaluated by comparing the hydrogen generation in totally fresh ash with that of ash which had been in contact with air for 42 and 60 days. One filter ash and one idle pass ash were stored on trays and stirred at regular intervals before measuring the hydrogen generation.

Hydrogen generation from other metals than aluminium

Copper, iron and lead were chosen for this test on the basis of their electrode potentials. Pieces of metal were pulverized with hack saw and the hydrogen generation potentials were measured as above.

SEM/EDS and XRD

Analyses with scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDS) and x-ray diffraction were performed to get insight into the chemical composition of different ashes, especially the occurrence of different aluminium forms. Three ash materials from fluidised bed boilers were chosen – two idle pass ash and one filter ash.

The morphology and elemental composition of the predominant particles, especially aluminium particles, was determined with SEM/EDS. The EDS analysis can determine if different forms of aluminium are to be found on different depths in an aluminium particle. The XRD was used to determine the predominant (more than 5%) crystalline compounds.

3 RESULTS

Hydrogen generation in ash studied

The hydrogen generation potential of the ash studied varied between 0 and 75 litres of gas per kilogram ash (Table 1).

For most samples considerably less hydrogen was generated in de-ionised water, i.e. at the natural pH of the ash, compared to in NaOH solution. For some ashes the difference was small and for one sample even more hydrogen was generated in water than in NaOH solution. pH values in a mixture of ash and water (L/S ratio=2) for samples measured at natural pH are listed in Table 1. Total content of aluminium for all 33 samples are also listed.

Table 1. Hydrogen generation and total content of aluminium in ash materials. pH values apply to a mixture of ash and water. BA = bottom ash, FiA = Filter ash. VA = idle pass ash, CA = cyclone ash

Plant	Fuel	Ash fraction	Hydrogen generation, mean value (l gas/kg ash)		pH in ash	Total content of Al (% of dry matter)
			At elevated pH	At natural pH		
BRA	DIP/Bio/RT	BA	0			7,2
		FiA	0			5,9
ESK	Bio	BA	0,1			3,9
		FiA	0			2,5
HAN 13	Bio	BA	0,1			3,5
		FiA	2,1			2,0
HAN 14	Municipal/ industrial waste	BA	0			5,2
		VA	9,0	1,4	11,9	5,5
		FiA	42,8	2,3	11,6	7,8
HOG	Industrial waste	BA	0			6,8
		VA	11,1	12,2	12,3	5,9
		FiA	24,9	7,0	12,0	6,4
KIR	Municipal waste	BA	28,8	0	10,5	7,4
		FiA	1,3			5,5
LID	Municipal/ industrial waste	BA	0			5,0
		VA	43,7	25,5	11,3	7,8
		CA	72,0	37,0	10,6	11,7
		FiA	0			2,8
LIN	RT/plastic/bio	BA	3,0			9,3
		CA	40,3	31,3	11,7	8,4
MUN	Bio	BA	0,2			6,0
		FiA	3,3			4,8
NYN	RT	BA	0,2			7,2
		VA	8,3	6,8	12,4	6,4
		FiA	2,1			4,3
SUN	Municipal/ industrial/(bio)	BA	0			4,0
		FiA	23,3	13,5	11,8	5,6
SOD	Industrial waste	BA	20,2	1,6	10,7	8,4
		FiA	0			4,3
UME	Municipal/ industrial	BA	18,7	2,0	11,7	7,1
		FiA	4,9			4,4
VAS	Bio/(RT)	BA	0			4,0
		FiA	2,1			5,4

Effect of oxidation

The effect of oxidation differed between the two ashes studied (filter ash and idle pass ash). In the filter ash the hydrogen generation potential was reduced significantly after

42 and 60 days of exposure to air. The hydrogen generation potential of the idle pass ash was low and influenced by oxidation to a lesser extent. (Figure 1)

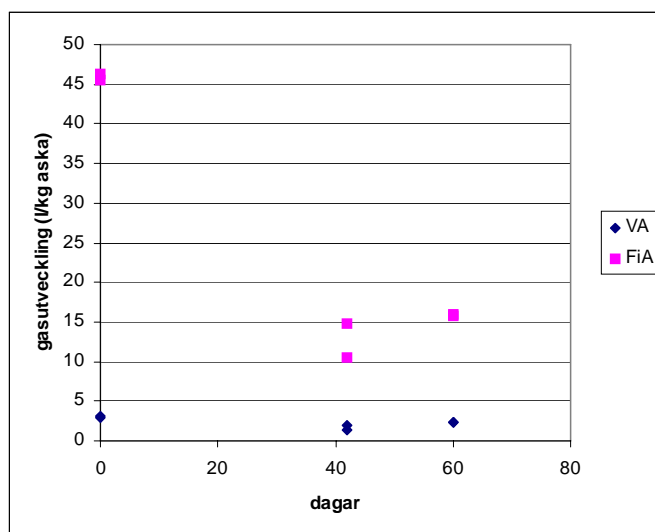


Figure 1. Hydrogen generation potential of fresh and aged ash (l gas/kg ash). Filter ash (FiA) and idle pass ash (VA).

Hydrogen generation from other metals than aluminium

Among the metals tested, only iron generated hydrogen in contact with NaOH solution. However, the amounts were very small, 9.3 litre gas per kilogram metal. Hydrogen generation from aluminium powder was measured for comparison and generated 1174.5 litre gas per kilogram metal (the theoretical maximum generation is 1354 l litre gas per kilogram metal). It was also observed that aluminium generated hydrogen even in pure, de-ionised water.

SEM/EDS and XRD

According to the SEM/EDS analysis used bed sand i.e. quartz and different types of felspar occurred in one of the idle pass ashes (LID in Table 1). Pure aluminium particles were also relatively frequent (yet approximately less than every 20:th grain). The analysed particles were approximately 200 µm broad and did not seem to have been melted to any major extent during their transport through the incineration plant. EDS point analyses of the particles did not show any major difference in composition between the surface and the inner parts. This means that no significant oxidation of the aluminium particle has occurred. The XRD analyses showed presence of quartz, felspars, anhydrite, calcite and elemental aluminium in the sample.

The other idle pass ash (HAN 14 in Table 1) also contained used bed sand and pure aluminium particles but the latter to a lesser extent. The analysed particles were approximately 50 µm broad and did not seem to have been melted either. EDS point analyses of the particles showed a somewhat higher oxygen concentration on the surface compared to that of inner parts i.e. the aluminium particles have oxidised partly during their transport through the incineration plant. According to the XRD analyses quartz, felspars, anhydrite and possibly some elemental aluminium were present in the sample.

The SEM/EDS analyses of the filter ash (MUN in Table 1) showed typical filter ash particles containing potassium, sulfur, chlorine and calcium apart from used bed sand. No other aluminium compounds apart from the felspars in the bed sand could be detected. According to the XRD analyses quartz, anhydrite, calcite, portlandite, sylvite

felspars and some further silicate were present, but no elemental aluminium could be detected.

4 DISCUSSION

Effect of oxidation

Filter ash that had been stored in oxygen rich environment generated significant less hydrogen than fresh filter ash of the same origin. This could be explained by oxidation that consumes elemental aluminium and in the same time gives a protective oxide coat. An explanation of the different behaviour of the idle pass ash could possibly be that all available elemental aluminium was oxidised already in the furnace.

Hydrogen generation from other metals than aluminium

Besides aluminium, only iron generated hydrogen. However, the generation in NaOH was so small that it is not likely with any considerable hydrogen generation in de-ionised water. Thus elemental iron in the ash can have an impact on the hydrogen generation, at least at high pH. Magel (2003) reported hydrogen generation from iron and copper at pH 13.5, but not at pH 9.3–11.4.

Some other metals that were not tested (for example zinc) could possibly contribute to the hydrogen generation. Large pieces of metal are common in bottom ash, but there is limited knowledge of the total content of different metals in ash. The reason is that large metal pieces are separated before total content analysis of the ash. In this study, large pieces of metal were included in the hydrogen generation measurements. However, considering the incomparably high potential of hydrogen generation that was measured for aluminium, the contribution from other metals is probably of minor importance. Furthermore Péra et al (2000) mixed bottom ash with aluminium, lead, magnesium and zinc respectively in a NaOH solution and only observed hydrogen generation from the ash–aluminium mixture.

Impact of aluminium content on hydrogen generation

In a total content analysis of aluminium both elemental and non-elemental aluminium contribute. This means that some ash containing little elemental aluminium can have rather high aluminium content. Thus, the total aluminium content does not give a complete picture of the hydrogen generation potential of the ash.

Furthermore, for fluid beds a great deal of the bottom ash consists of sand that has an aluminium content of around 5%. The aluminium in sand occurs in form of different aluminium silicates i.e. non-elemental aluminium. The bottom ash from a fluidised bed could therefore have high total aluminium content and at the same time low hydrogen generation potential, which makes it difficult to distinguish any connections between total aluminium content and hydrogen generation potential.

Aluminium survives the incineration

An interesting observation was that aluminium particles could pass through the incineration without melting and without any substantial oxidation of the particle surface. The melting point of aluminium is 660°C, but the furnace temperature is usually higher in both fluidised bed boilers and grate fired boilers. Solid aluminium oxide (Al_2O_3) is the stable form of aluminium in a boiler. However, unmelted aluminium particles were found in the ash. This was clearly shown in the SEM analyses.

Most of the aluminium particles in one of the idle pass ash had a diameter of around 200 μm according to the SEM analysis. Mizutani et al (2000) who separated particles in

fly ash by means of sieving on the 125 µm-sieve before gas generation measurements found that in most cases the coarse fraction had at least twice as high gas generation potential as the fine fraction.

Impact of fuel

The largest hydrogen generation potential, 75 litres gas per kilogram ash, was obtained by one of the idle pass ash from industrial and municipal waste incineration. This is not surprising since hydrogen generation most likely is caused by elemental aluminium. Sources of elemental aluminium in municipal waste are for example soft drink-cans, aluminium foil and barriers in juice packages. All bio fuel incinerator plants produced ash with small hydrogen generation (Figure 2).

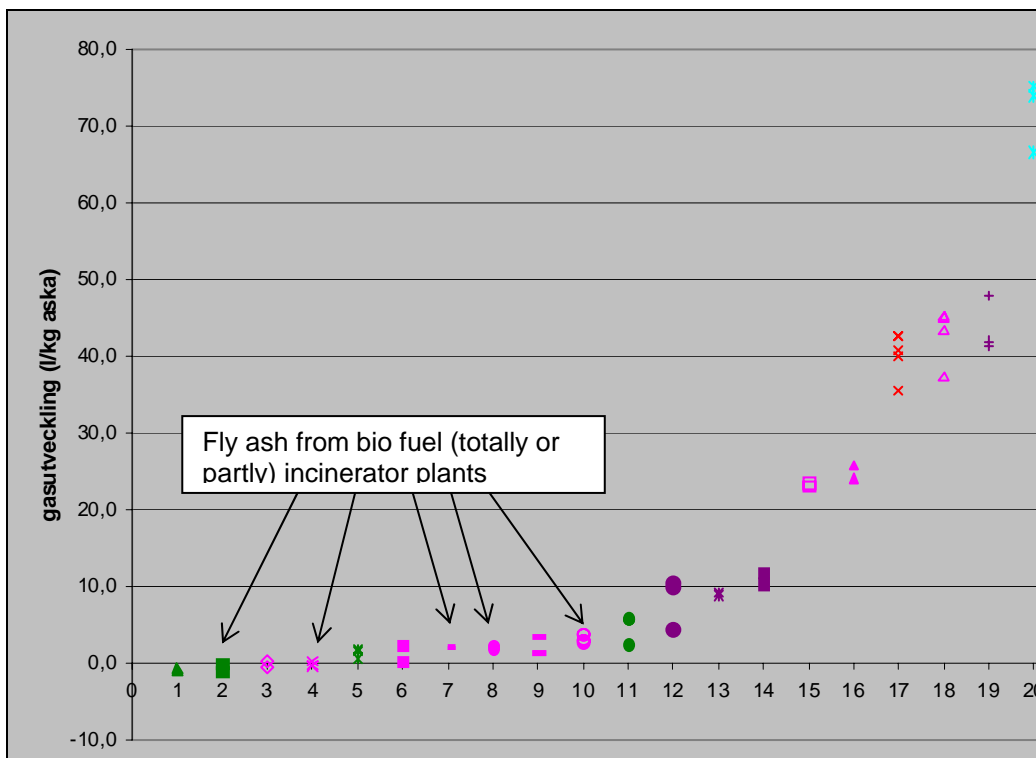


Figure 2. **Impact of fuel:** Potential of gas generation for 20 fly ash materials. The ash samples are arranged in order of generated gas. Not highlighted ash samples originate from waste incinerator plants (at least 67% waste).

Difference between fluidised bed boilers and grate fired boilers

For bottom ash it was found that grate fired boilers had higher hydrogen generation potential than bed sand from fluidised bed boilers. The reverse result applied for filter ash – most filter ash from fluidised bed boilers had considerably larger hydrogen generation potential than the corresponding ash materials from grate fired boilers. A higher gas velocity and a more fine-grained fuel in the fluidised bed boiler could possibly explain this. Furthermore, the ratio between surface area and weight of the fuel is larger in a fluidised bed, which means that the fuel is easily transported by the flue gas. Thin aluminium foil could for example pass the furnace quickly without any appreciable oxidation. The fuel in grate fired boilers can not be transported equally easy and aluminium is then melted to large particles that accompanies the bottom ash and contribute to a high hydrogen generation potential.

Potential of gas generation – actual gas generation

Prediction of the hydrogen generation in an ash material requires knowledge of the maximum amount of hydrogen that can be generated – the hydrogen generation potential – and the future conditions that could be expected.

The amount of hydrogen that can be generated depends on the content of *elemental* aluminium. It is therefore not sufficient to measure the total aluminium content alone. Laboratory tests, where the ash can react with unlimited volumes of water at high pH, can give a measure of the ash's hydrogen generation potential. However, at real conditions during conveying from the quench tank and during rain at landfills, pH is mostly lower and hydrogen generation is smaller and occurs more slowly.

5 CONCLUSIONS

- Prediction of the hydrogen generation in an ash material requires knowledge of the maximum amount of hydrogen that can be generated – the hydrogen generation potential – and the future conditions that could be expected.
- The amount of hydrogen that can be generated depends on the content of elemental aluminium. It is therefore not sufficient to measure the total aluminium content alone.
- Aluminium is the dominating reactive metal within the ash.
- Aluminium particles can survive incineration without melting and without substantial oxidation of the particle surface.
- The fuel has an impact on the amount of hydrogen generated in that way that bio fuel incinerator plants produce ash with low hydrogen generation potential.
- The incinerator type and the ash fraction have the following impact: Bottom ash from grate fired boilers have higher hydrogen generation potential than bed sand from fluidised bed boilers. The reverse result applies for filter ash – most filter ash from fluidised bed boilers has considerably larger hydrogen generation potential than the corresponding ash materials from grate fired boilers.

Based on the results the following recommendations can be given. The content of elemental aluminium or the hydrogen generation potential should be analysed regularly for ash materials from municipal waste incineration plants. Metal separation – including non-magnetic metals – of the fuel for waste incineration plants is necessary. Good ventilation of the ash after wetting, together with storage in oxygen rich environment is desirable.

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REFERENCES

- Alkemade A.M.C., Eymael M.M.T., Mulder E. and de Wijs W. *How to prevent expansion of MSWI bottom ash in road construction?* In: Environmental aspects of construction with waste materials (WASCON 1994)
- Arm M., Lindeberg J., Rodin Å., Öhrström A., Backman R., Öhman M. and Boström D. *Gas generation in ash*. Report 957, Swedish Thermal Engineering Research Institute, Stockholm 2006 (in Swedish with an English summary)
- Husain A. and Krasznai J. *Compaction of radioactive incinerator ash: Gas generation effects*. Waste Management 14, pp 521–530, 1994
- Håkansson K., Suèr P. and Lindeberg J. *Gas generation in ash from Högdalen, Uppsala and Söderenergi, Final report*, Swedish Geotechnical Institute, Linköping 2004 (in Swedish)
- Magel G. *Mineralogische und chemische Untersuchungen zur abiotischen Wasserstoffentwicklung in Müllverbrennungsrückständen*, PhD Thesis, Ludwig-Maximilians Universität, 2003
- Mizutani S., Sakai S. and Takatsuki H. *Investigations of hydrogen generation from municipal solid waste incineration fly ash*. Journal of Material Cycles and Waste Management 2, 16–23, 2000
- Musselman C., Straub W., Bidwell J., Carpenter J. and Presher J. *Gas generation at a municipal waste combustor ash monofill-Franklin, New Hampshire*. In Sustainable construction: Use of incinerator ash, R.K. Dhir, T.D. Dyer and K.A. Paine, editors, Thomas Telford, Dundee 2000
- Oberste-Padtberg R. and Schweden K. *Zur Freisetzung von Wasserstoff aus Mörteln mit MVA-Reststoffen*. Wasser, Luft und Boden 6, 61–62, 1990
- Péra J., Coutaz L., Ambroise J. and Chabannet M. *Problems encountered with the use of municipal solid waste incinerator bottom ash in concrete*. In proceedings of the 22nd international conference on cement microscopy, Montreal 2000
- Suèr P., Håkansson K. and Rogbeck J. *Gas generation in ash – literature study*”, Swedish Geotechnical Institute, Linköping 2004 (in Swedish)

Standards and test methods

- ASTM D3683. "Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption"
- ASTM D3682. Standard Test Method for Major and Minor Elements in Combustion Residues from Coal Utilization Processes
- SGI-metod "Determination of pH of ash", Swedish Geotechnical Institute, Linköping
- SP metod 0510 "Main element: –Al, Si, Fe, Mn, Ti, Ca, Mg, Ba, Na, K, P", Statens provnings och forskningsinstitut, Borås
- SP metod 2573 "Methods for the determination of metallic aluminium", Statens provnings- och forskningsinstitut, Borås
- SS-ISO 10390 "Soil investigations – Determination of pH".

