



# Treating landfill gas hydrogen sulphide with mineral wool waste (MWW) and rod mill waste (RMW)



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## ABSTRACT

Hydrogen sulphide ( $H_2S$ ) gas is a major odorant at municipal landfills. The gas can be generated from different waste fractions, for example demolition waste containing gypsum based plaster board. The removal of  $H_2S$  from landfill gas was investigated by filtering it through mineral wool waste products. The flow of gas varied from 0.3 l/min to 3.0 l/min. The gas was typical for landfill gas with a mean  $H_2S$  concentration of ca. 4500 ppm. The results show that the sulphide gas can effectively be removed by mineral wool waste products. The ratios of the estimated potential for sulphide precipitation were 19:1 for rod mill waste (RMW) and mineral wool waste (MWW). A filter consisting of a mixture of MWW and RMW, with a vertical perforated gas tube through the center of filter material and with a downward gas flow, removed 98% of the sulfide gas over a period of 80 days. A downward gas flow was more efficient in contacting the filter materials. Mineral wool waste products are effective in removing hydrogen sulphide from landfill gas given an adequate contact time and water content in the filter material. Based on the estimated sulphide removal potential of mineral wool and rod mill waste of 14 g/kg and 261 g/kg, and assuming an average sulphide gas concentration of 4500 ppm, the removal capacity in the filter materials has been estimated to last between 11 and 308 days. At the studied location the experimental gas flow was 100 times less than the actual gas flow. We believe that the system described here can be upscaled in order to treat this gas flow.

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## 1. Introduction

Demolition waste with plaster board can produce landfill gas with extreme concentrations of sulphide, up to 63 000 ppm (parts per million) in laboratory studies (American Public Health Association, 1971). Hydrogen sulphide, further called sulphide or  $H_2S$ , with an odor threshold of 0.1–0.5 ppb (parts per billion), is an important odorant in landfills (Termonia and Termonia, 1999; Gostelow et al., 2001; Devai and Delaune, 2002) even after a number of waste management regulations have been introduced over the last decade, including a ban of organic waste and an increased recycling of many waste fractions including plaster board and other sulphur containing demolition wastes (Cuhls et al., 2002). Recent field measurements of landfill gas show that concentrations above 5000 ppm  $H_2S$  is not uncommon according to our experience from Norwegian municipal solid waste (MSW) landfills, with extreme levels reaching 30 000 ppm. Previous studies have shown that iron oxide and a mixture of bottom ash and iron oxide reduced top cover emissions, mainly by their content of prevalent metals such as Fe, Mn and Zn, while organic materials including sewage sludge

compost, spruce bark and wood chip were less efficient in  $H_2S$  removal (Bergersen and Haarstad, 2008). Also MSW incineration bottom ash has been shown to be useful in removing both  $H_2S$  and  $CO_2$  from landfill gas (Mostbauer and Lechner, 2008). Organic filters showed a theoretical potential sulphide removal capacity varying between 4 mg/kg and 244 mg/kg, while metal rich filters showed a sulphide removal capacity in the order of 6000–8000 mg/kg (Bergersen and Haarstad, 2008). This study also showed the importance of the water content in the sulphide removal. Incinerator ash also shows moderate removal of  $H_2S$ , up to 3–4 g/kg dry weight (Ducom et al., 2009; Parker et al., 2009). Mineral wool waste (MWW) and rod mill waste (RMW) are residues from the production of mineral wool. These products have properties that promote sulphide removal, such as a high gas conductivity and high content of metals, see Tables 1 and 2. The total estimated waste production of MWW and RMW from the plant that supplied materials for this study is approximately 1000 tons per year, and 8000 tons slag per year (Rockwool, personal communication). The major part of the waste is landfilled since there are few recycling opportunities. The removal of sulphide gas can be obtained both in the landfilled waste body, and from the extracted or emitted landfill gas. This study focuses on the latter option.

The objective of this study is to investigate the efficiency of metal rich mineral wool waste in removing hydrogen sulphide

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**Table 1**

Metal content (mg/kg dry matter) in the materials based on a leaching test of mineral wool waste (MWW) and rod mill waste (RMW) used in the experiment.

	MWW	RMW	TV <sup>a</sup>
pH	5.2	5.6	
EC	0.14	0.19	
Sb	<0.002	<0.01	
As	<0.0003	0.024	8
Ba	0.01	0.041	
Pb	<0.0003	<0.01	60
Cd	<0.00004	<0.0005	1.5
Cr	<0.0004	0.73	50
Cu	<0.0004	0.11	100
Hg	<0.0005	<0.0005	1
Mo	<0.001	0.017	
Ni	0.0069	0.11	60
Se	0.0063	<0.01	
Zn	0.018	0.18	200
SO <sub>4</sub>	<5	45	

<sup>a</sup> Threshold value, natural levels (Klif, 2009).

**Table 2**

Metal content (mg/kg dry matter) measured with XRF, and relative standard deviation (RSD in %,  $n = 6$ ), and the estimated sulphide adsorption potential (g/kg) in mineral wool waste (MWW) and rod mill waste (RMW).

Metal	MWW	RSD	RMW	RSD	Adsorption <sup>a</sup>	
					MWW	RMW
Fe	22 593	1.9	455 724	0.2	13	260
Mn	955	12	1653	12	0.6	0.9
Cu	163	16	277	17	0.08	0.14
Ni	354	16	409	21	0.2	0.2
Cr	222	16	289	13		
Zn	78	20	131	20	0.0	0.06
Pb	17	40	24	43	0.013	0
Hg	18	41	24	59	0.003	0.004
As	9	54	13	61	0.019	0
Cd	13	73	n.d.		0.013	
Total	24 422		458 544		14	261

<sup>a</sup> See Bergersen and Haarstad (2008).

from landfill gas. The work was divided into two phases. In the first the main question is: Can the emissions of sulphide with landfill gas be reduced by filtering it through waste from the mineral wool industry? Is there a difference depending on the filter materials being either mixed or packed in separate layers? During the second phase we investigated whether MWW mixed with RMW could also be used as a filter material for H<sub>2</sub>S treatment of landfill gas. The efficiency of the mixes of filter materials is analyzed in both phases of this study. The removal of sulphur from the landfill gas will be compared to estimates of the filter materials sulphide removal potentials calculated from their metal content (Table 1). pH, Electrical conductivity (mS cm<sup>-1</sup>), metal content (mg/kg dry matter) in the materials based on standard leaching tests of mineral wool waste (MWW) and rod mill waste (RMW) used in the experiment.

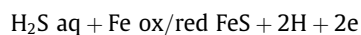
## 2. Materials and methods

### 2.1. Location

The experiment was carried out at the Solgård Landfill in Moss, about 50 km south of Oslo at approx. 59°50' North. The landfill is still operational and has received in the order of 1 500 000 tonnes of municipal solid waste over 32 years, according to the operator, or nearly 50 000 tonnes annually. The annual gas production at the site, calculated as the average from 2007 until 2011, is approximately 3.7 million N m<sup>3</sup>, or ca. 400 N m<sup>3</sup>/h, with an average concentration of ca. 4500 ppm H<sub>2</sub>S.

### 2.2. Processes and material properties

The two most likely processes occurring between sulphide and metals in water; corrosion and precipitation, are described below. We use the precipitation to calculate the removal potential of the metals. Corrosion is an oxidative process releasing positive metal ions and electrons. The corrosion of a metal with H<sub>2</sub>S gas follows a type III process (Camp and Meserve, 1974). The metals in the waste products from the mineral wool processing are in the form of oxides, which are practically insoluble in water:



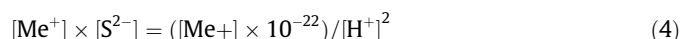
The major products from sulphide precipitation are most likely metal sulphides, see also Bergersen and Haarstad (2008). Sulphide occurs as H<sub>2</sub>S at pH 6 or lower protonating according to:



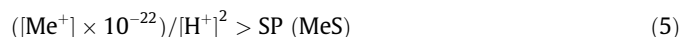
Ionisation of H<sub>2</sub>S depends on pH; at pH 9 there is nearly no H<sub>2</sub>S, at pH 7, approximately 48% and at pH 6, about 90% of the sulphide is H<sub>2</sub>S gas. The water solubility of H<sub>2</sub>S is high; 7100 mg/l at 0 °C, and 3925 mg/l at 20 °C. As a consequence leachate in landfills constitutes an important H<sub>2</sub>S reservoir. The water solubility of non-reactive gases is proportional to the gas partial pressure according to Henry's law. A saturated solution will have a concentration of [H<sub>2</sub>S] at 0.1 M:



By introducing a metal the solubility product of the metal and sulphide becomes:



If the solubility product (SP) of the given metal sulphide is less than the concentration given by Eq. 4 metal sulphide (MeS) will precipitate from the solution;



At low pH the filtration effect of metal sulphides will be lower. The solubility products of the metals in the filter materials used in this experiment varied from 10<sup>-36</sup> (CuS) to 10<sup>-14</sup> (MnS). The potential sulphide removal is estimated based on the content on a dry weight basis of metals that are having known solubility products as metal sulphides, see below. Iron is by far the most important metal in the mineral wool waste.

The sulphide removal processes are water based so the removal efficiency will increase with the water saturation. The contact area between the metals in the filter media and the water is also important for sulphide removal.

The mineral wool waste products, rod mill waste and mineral wool waste all come from the wool production. The rod mill waste is from the oven, and the mineral wool waste is wool discarded from different parts of the production. The density of the mineral wool waste (MWW) and rod mill waste (RMW) used in the experiment was 0.10 kg/l and 0.57 kg/l. The specific weight of the mixture of MWW and RMW was 0.67 kg/l. The filter materials are relatively stable as demonstrated in the leaching tests showing low metal concentrations (Table 1). The water content was about 8% both in the MWW and RMW. The water retention decreases with increasing particle size. The materials do not contain toxic levels of metals.

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