# Long Term Reactivity of Land Filled Slag from Lead Production

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A slag landfill site for slags from lead production was operated by the BSB Recycling GmbH in Braubach, Germany, until 1990. Due to the closure in 1990 it is necessary to provide the landfill with a surface cover according to the German legislation “TA Abfall”. To build such a surface cover a profiling of the landfill is required up to a depth of 11 m. Previous investigations of the dump however revealed temperatures up to 400 °C inside of the pile. Therefore an investigation was started to identify possible risks during profiling under this conditions and to predict the remaining reaction period. Three holes were drilled through the landfill, showing that the reaction inside is proceeding from bottom to top and that this reaction is/can be independent of water and/or air admission. Identified hazards were especially a high arsenic concentration in the appearing steams even during the drilling process. By analysing the chemical reactions inside the landfill the reaction progress was assessed. Together with the assumed constraints the remaining reaction period was evaluated to be approximately 66 years.

Keywords:

Lead production – Lead slag – Slag landfill – Reacting landfill – GDMB lead award

### Langzeitreaktivität deponierter Schlacken aus der Bleiproduktion

Eine Schlackedeponie für Bleischlacken wurde bis 1990 in Braubach von der BSB Recycling GmbH betrieben. Auf Grund der Schließung 1990 wurde es nötig, die Halde im Rahmen der TA Abfall mit einer Oberflächenabdeckung zu versehen. Um diese Abdeckung auflegen zu können muss die Halde bis zu einer Tiefe von 11 m profiliert werden. Vorhergehende Untersuchungen der Halde zeigten allerdings, dass innerhalb des Haldenkörpers Temperaturen bis 400 °C herrschen. Daher wurde eine geothermisch-metallurgische Untersuchung durchgeführt, um mögliche Gefahren während der Profilierung unter diesen Bedingungen zu identifizieren und nach Möglichkeit die verbleibende Reaktionszeit vorherzusagen. Dazu wurden drei Bohrungen in die Halde abgeteuft, die zeigten, dass die Reaktionen innerhalb der Deponie von unten nach oben verlaufen und unabhängig von Wasser und/oder Luftzutritt sind/sein können. Gefährlich sind hohe Arsenkonzentrationen in den entstehenden Dämpfen, die auch bereits während der Bohrungen auftraten. Durch die Analyse der chemischen Reaktionen innerhalb der Halde wurde der Reaktionsfortschritt bestimmt und zusammen mit den angenommenen Rahmenbedingungen wurde die verbleibende Reaktionszeit zu etwa 66 Jahren bestimmt.

Schlüsselwörter:

Blei-Produktion – Bleischlacke – Schlackendeponie – Reagierende Deponie – Bleipreis

### Réactivité à long terme de scories déposées de la production de plomb

### Reactividad a largo plazo de escoria descargada originando de la producción de plomo

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## 1 Introduction

A landfill site for slags from lead production was operated by the BSB Recycling GmbH in Braubach, Germany, until 1990. Different types of lead slag were landfilled together with layers of rubble and soil. Today the dump is overgrown with grass, bushes and trees according to the natural vegetation. The landfill site consists of approx. 250,000 m$^3$ slag (mainly soda and low amounts of shaft furnace slags), rubble and spoil deposited on an area of around 15,000 m$^3$. Due to the closure in 1990 it is necessary to provide the landfill with a surface cover according to the German legislation “TA Abfall”. To build such a surface cover a profiling of the landfill is required up to a depth of 11 m. Previous investigations of the dump however revealed temperatures up to 400 °C inside of the pile, so the building of a surface cover was found to be impossible. Therefore an investigation was started to identify the proceeding processes inside the landfill, possible hazards and to predict the remaining reaction period. To do this it was decided to drill three holes at different spots of the landfill down to natural ground analysing the drilling cores chemically and also partly mineralogical. DTA/TG (differential thermoanalysis/thermogravimetry) supported the explanation of the found results.

## 2 Drilling procedure/Experimental part

Before drilling the positions of the holes were determined by measuring the surface temperature of the landfill. According to the temperature distribution the positions for the three bores were set to:

- Hole 1 (B1) should have been drilled at the hottest point, through the hot core into the natural ground. This was technically not possible, so the hole was drilled as close to this point as possible. The drilling depth was 26.30 m down to natural ground.
- Hole 2 (B2) was sunk 16.20 m before it had to be stopped due to an impenetrable layer of pyrite The expected depth until natural ground was 30 to 40 m.
- Hole 3 (B3) was sunk 10 m before it also had to be stopped due to an impenetrable layer of pyrite. The expected depth to natural ground was 10 to 15 m.

During the drilling (Figure 1) a layer index was made (slag layers were identified, later by chemical analysis) and the temperature of the drilling core was measured directly after pulling. From each drilling part (see Figure 1) at least one sample every meter was taken and directly stored in airtight metal buckets. During the drilling also gas samples were taken sporadically and analyzed for their arsenic content. Before sealing the drilled holes a fibre-optical temperature measurement system was installed for future temperature monitoring.

Fig. 1: Drilling equipment (left) and received drilling cores (right)

## 3 Experimental analysis

The following analysis was done by ICP and also partly by mineralogical and DTA/TG investigations of samples from different drilling depth. With the obtained results stable products of possible reactions were calculated with FactSage® (Program for the execution of thermodynamically calculations) in the found temperature range. The calculated results were then compared with the compounds found in the slag landfill.

### 3.1 Chemical analysis

Each of the 50 samples taken during the drilling was analysed for its Pb, Fe, Na, Si, S, C and As content. With the result the samples were classified as slag or interlayer. A detailed balance of the results for B1 shows that the core consists to 67 % of slag and to 33 % of covering material which is in accordance to the expected relation of slag : covering material of 2 : 1.

Correlating the carbon content of the core with the temperature profile (shown for B1 in Figure 2) it becomes obvious that the carbon content is a lot lower in the deeper slag layers than in the upper. The main border of this effect is the depth of the main reaction zone at 16.5 m. A second, smaller decrease in the carbon content can be seen below the second reaction zone. From this effect it is possible to infer that carbon is consumed during the reaction within the landfill and leaves the pile as gaseous compound or as readily soluble product after leaching. So in this case the

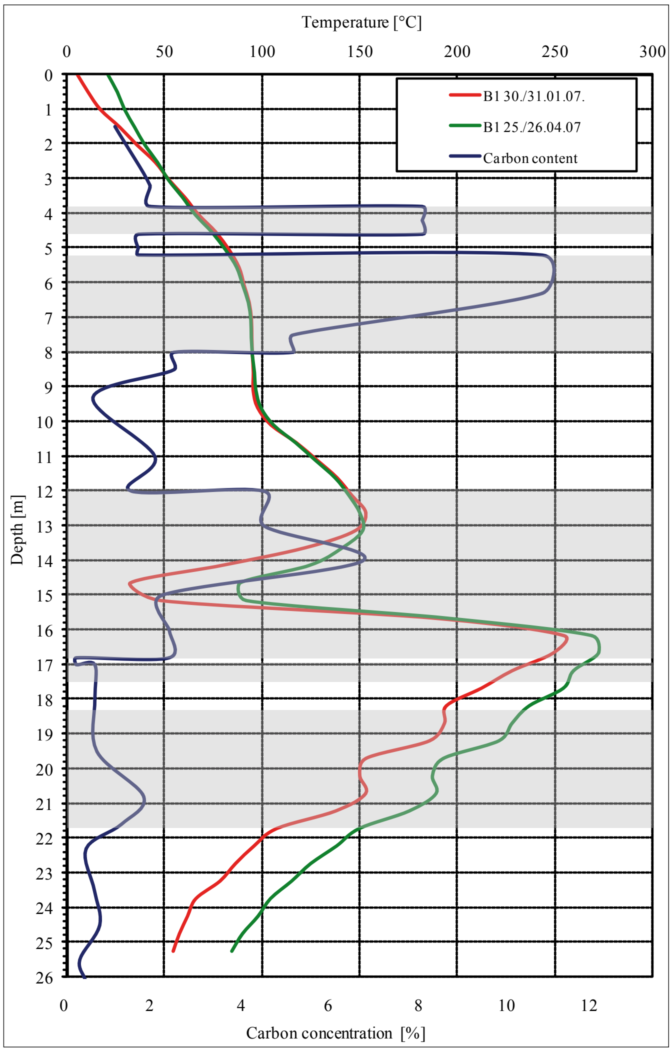

Fig. 2: Correlation of the temperature distribution and the carbon content of B1 (gray bars indicate slag layers)

reaction inside the landfill is proceeding from bottom to top. The described correlation is also valid for B2, where the carbon concentration also decreases for slag layers below 10 m. For B3 this correlation can not be seen, probably due to the low temperature within the drilling hole which was always below 100 °C.

Analysing from which temperature on a decrease in the carbon concentration can be seen leads to the result that this temperature is at around 150 °C as well for B1 as also for B2. For B1 this implies that a 4.6 m wide slag layer is below the reaction zone and a height of 8.4 m is not reacted above the reaction zone. Assuming that B1 is representative for the hole landfill 65 % of the slag within the landfill is not/not fully reacted.

During the drilling samples of the gases leaving the borehole were taken and analysed for As. All samples showed As concentrations between 5.5 µg/m³ and 107 µg/m³. This could be also confirmed by the chemical analysis even if the detection limit there was with 0.1 % pretty high. Profiling of the landfill is therefore extremely dangerous and should be avoided.

### 3.2 Mineralogical analysis

Five samples from different depths of B1 were XRD analysed, which were classified as slag in four cases. The detectable compounds can be classified as follows:

| | |
|---|---|
| 6 m: | PbS, PbO, $PbSO_4$, Pb, $FeS_x$, $Fe_3O_4$ |
| 9 m (interlayer): | PbS, $FeS_2$, $SiO_2$, $Na_2SO_4$ |
| 14 m: | PbS, PbO, $PbSO_4$, Pb, $FeS_x$, $Fe_3O_4$ |
| 19 m: | PbS, $PbSO_4$, $FeS_{0,95}$, $Fe_3O_4$, $Fe_2O_3$, $SiO_2$, $Na_2SO_4$ |
| 21 m: | PbS, PbO, $PbSO_4$, $FeS_x$, $Fe_3O_4$, $Fe_2O_3$ |

Calculation of the stable products on the basis of the detected iron and lead compounds with FactSage® in a temperature range of 100 °C to 300 °C results into the following compounds:

- with addition of carbon:
  - 100 °C: PbS, $Fe_2O_3$, $PbCO_3$
  - 200 °C - 300 °C: $CO_2$, PbS, $Fe_2O_3$
- with addition of water / oxygen and carbon:
  - 100 °C: $CO_2$, $PbO{\cdot}PbSO_4$, $Fe_2O_3$, $H_2SO_4$
  - 200 °C - 300 °C: $CO_2$, $PbSO_4$, $Fe_2O_3$

Correlation of this results with the temperature profile shows that the compound $Fe_2O_3$ is only found in the layers below the reaction zone/highest temperature. Since this compound is one of the stable products of a couple of possible reactions, this again is an indication for the theory that the landfill is reacting from bottom to top. On the other hand it is only possible to find metallic lead in the upper slag layers; in the bottom layers it is already consumed by the chemical reaction.

### 3.3 Thermo-gravimetrical analysis

The mineralogical analysed samples were subsequently analysed thermo-gravimetrical, showing a clearly decreasing weight loss (removal of volatile substances) in the temperature range up to 300 °C from the top of the bore down. This decrease can again be correlated to the temperature profile analogue to the $Fe_2O_3$ detection. In total the evaporation of volatile substances is more than doubled for slag samples from a depth above the maximum temperature.

Apart from that the difference between the diverse slag DTA graphs is mainly in the height of the peaks and the occurrence of reactions within the different slags. All samples showed two exothermal reaction peaks at approx. 120 °C and 150 °C, whereas this peaks are a lot smaller for the two samples from bigger depth (19 m, 21 m). The two not reacted slags from 14 m and 6 m also show a small exothermic peak at approx. 80 °C and some additional peaks between 150 and 300 °C, which could not be exactly identified. Therefore it can be assumed that the slags slowly start with the chemical reaction above 80 °C, but the proper conversion of the compounds begins at around 120 °C and the main reactions start at temperatures above 150 °C.

It is also worth mentioning that all slags show again an additional evaporation at temperatures above 490 °C.

## 4 Forecast of the remaining reaction time

To forecast the reaction time it is necessary to know the starting time of the chemical reaction. Due to the fact that we do not securely know what was starting the reaction this is the main uncertainty. Maybe the necessary energy to start the reaction was reached by one of the fires appearing in former years or maybe the pressure within the pile in combination with some chemical reactions and the thermal isolation caused the temperature necessary to start the ongoing reactions. Another and probably the most likely explanation is that the slag was not cooled down to a sufficient degree before landfilling, since high temperatures can be maintained for a long time within huge slag lumps. Supposing that the last possibility was the case and that the reaction was started directly after the first landfilling (1970) it was proceeding for 37 years at the time of the drilling. The earlier described chemical analysis in correlation with the drilling depth showed that 35 % of the landfill already reacted.

Based on this and assuming curve linearity the main reaction zone will reach the top of the landfill in 2075. If the reaction was started by a fire or another different event the reaction would be finished much earlier. Therefore it is advisable to monitor the temperature distribution within the drilling holes for the next couple of years to possible reduce the forecasted reaction period.

## 5 Assessment

The presented investigation showed that the slag landfill in Braubach, Germany is reacting from bottom to top and that this reaction is/can be independent of water and/or air admission. Merely the stable products vary partly depending if the reaction is proceeding with water and/or air or without. A minimum temperature of approximately 150 °C is necessary to start the chemical reaction of the slag components and if the temperature inside the landfill exceeds 490 °C, the formation of gaseous compounds will increase. At a further increase of the temperature the danger of an uncontrolled self-ignition of the landfill exists, the self-ignition temperature for $FeS_2$ for example is 565 °C. Therefore no actions should be taken to provide the landfill with a surface cover before all chemical reactions are finished. A profiling of the landfill or a moving of parts of it is also inadvisable due to the high arsenic concentrations already measured in the occurring gases during the drilling process.

Possible reactions were analysed and stable products were calculated. However this investigation of the thermochemical equilibria, as well as a previous study of the mass flows within the Braubacher landfill can not give a secure final statement about the residual reaction time, due to a huge uncertainty ascertaining the necessary constraints. The main uncertainty in this case is the determination of the starting time of the chemical reaction. Assuming that the reaction was started directly after the first landfilling (1970), the main reaction zone will reach the top of the landfill in 2075 (assuming that the reaction progress is linear). If the reaction was started by a fire or another different event the reaction would be finished much earlier. Therefore it is advisable to monitor the temperature distribution within the drilling holes for the next couple of years to possible reduce the forecasted reaction period.

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