Life prediction of dump reactivity caused by slags from lead production

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Abstract

A slag landfill site for slags from secondary 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 German legislation. To build such a surface cover profiling of the landfill is necessary 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 wells 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 appearing in the water vapours even during the drilling process. By analysing the chemical reactions inside the landfill the reaction progress was assessed. The thermochemical analysis between 150 °C and 450 °C offered the possible chemical reactions inside of the pile. Together with the assumed constraints the remaining reaction period was evaluated to be approximately 66 years.

1 Introduction

A landfill site for slags from secondary lead production [1] was operated by the BSB Recycling GmbH, Germany until 1990. The landfill is located directly in Braubach, close to the river Rhine in a natural vale. Three water feeds are blocked by sheet pile walls. Unknown water amounts/distributions enter only by rain and through the adjoining rock face. The waste water of the landfill is guided to the factory-owned waste water plant and is internally recycled within the landfill. Different types of lead slag were landfilled together with layers of rubble and soil to prevent/extinguish sporadically appearing fires, started probably by self-ignition of the slag. 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 soil deposited on an area of around 15,000 m^3. Over the years also arsenic containing materials were processed periodically leading to partially higher arsenic concentrations within the dump. The problem of arsenic containing lead regarding the contamination of vegetation and soil was already analysed by Temple et al. in the 1970’s [2]. Due to the closure in 1990 it is necessary to provide the landfill with a surface cover according to the German legislation “Deponieverordnung” [3]. To build such a surface cover a profiling of the landfill is required up to a depth of 11 m. Previous investigations (about 10 years ago) 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 and profiling was considered too hazardous without knowing the processes taking place inside. Today high temperatures are still present within the pile as can be seen at various spots where hot fumes are leaving the landfill (see *Fig. 1*).

A simple model of the dump covering the filled ground and the gas as well as the water flow within the landfill was published in 2003 [4] (see *Fig. 2*), but there was no attempt to determine the processes running inside the dump. Therefore an investigation was started to identify the continuing processes inside the landfill, possible hazards and to predict the remaining reaction period. To do this it was decided to drill three wells at different locations in the landfill down to natural ground analysing the drilling cores chemically and also partly mineralogical. DTA/TG measurements (differential thermo-analysis/thermogravimetry) supported the explanation of the found results. During


Figure 1: Hot fume leaving the landfill

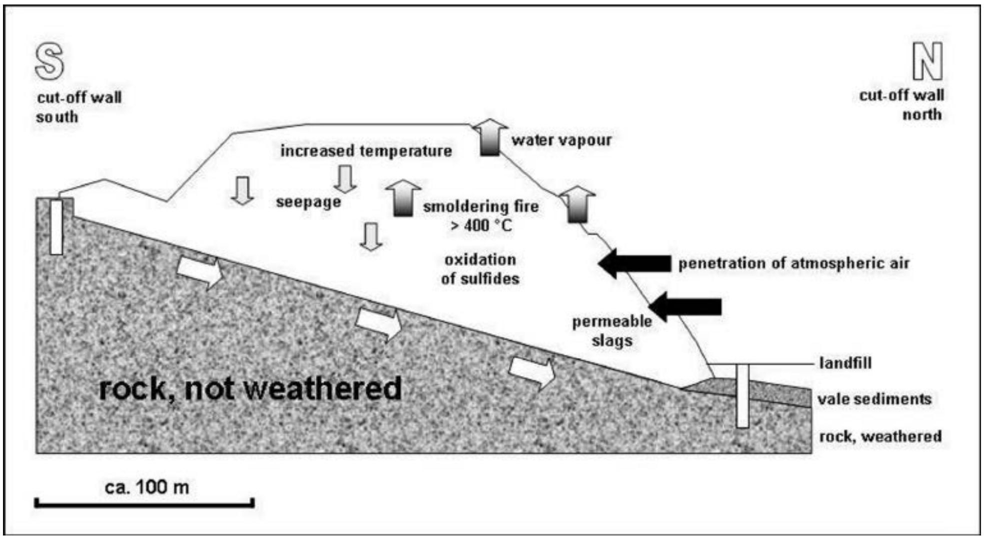

Figure 2: Model of the Braubacher landfill [4]

drilling the temperature was recorded against the depth and before sealing the drilling holes a fibre-optical temperature measurement system was installed for future temperature monitoring.

Literature screening showed that there was a similar case in Spain, also for a landfill from a battery recycler, already investigated [5]. The authors proposed that the landfill needs water and/or oxygen to proceed with the reaction, assuming that the components within the landfill are mainly Fe_2O_3/FeS (48.8 %), $Na_2O{\cdot}SiO_2$ (29.5 %), Na_2CO_3 (4.1 %), C (3.6 %) and Pb (4.5 %). This composition was also ascertained in the present case via analysis of the slags by BSB Recycling before landfilling. Possible reactions in this case are the exothermic dissolution of soda in water (initiation of consecutive reactions), oxidation of iron and reactions with elemental carbon or sulphur. If this is found to be correct, the whole process might be speeded up, by watering the pile.

2 Drilling procedure/Experimental part

The drilling positions were selected by measuring the surface temperature of the landfill. Therefore temperature sensors were mounted linear into the dump, 50 cm below the surface and the temperature was measured for a couple of months showing the temperature distribution shown in *Figure 3*.

According to the temperature distribution the positions for the three bores were set (see Fig. 3):

- 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 well was drilled as close to this point as possible. The drilling depth was 26.30 m down to natural ground.

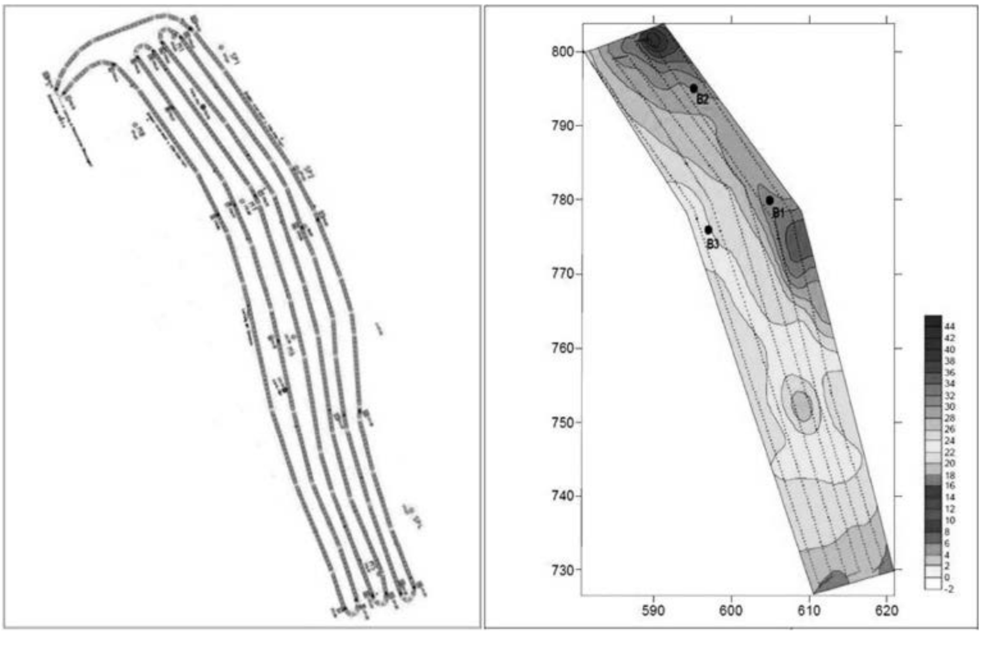

Figure 3: Course of the fibre-optical temperature cable (left) and horizontal temperature distribution showing the positions of the bores (measured by GESO GmbH Jena, Germany)

Figure 4: Picture of the drilling equipment (left) and the received drilling cores (right)

- 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 amounted 30–40 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 10–15 m.

The drilling (see *Fig. 4*) was performed in November 2006 by the Wiedtal-Schützeichel KG, Germany. During the drilling (see Fig. 4) a layer index was made (slag layers were identified, later by chemical analysis) and the temperature of the drilling core was measured directly after unearthing it. From each drilling core (see Fig. 4) 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.

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). It contains different modules for the calculation of equilibriums, chemical reactions and to ascertain thermochemical data based on different databases) in the found temperature range. The calculated results were then compared with the compounds found in the slag landfill.

3.1 Temperature distribution

The temperature measured during drilling is in average slightly lower and more homogenous than the temperature measured with the fibre-optical cable. Due to the long drilling time (more than 24 h) the temperature measured directly is not reflecting the temperature distribution inside the landfill. Therefore the temperature measured via the fibre-optical cables was taken into account, with an integration time of 70 seconds continuously over a 23 h period and with a spatial resolution of 0.5 m. The temperature distribution is displayed in *Figure 5* for all drilling holes at two different measurement cycles having a time lag of 3 months. Slag layers are indicated by a grey bar.

The temperatures measured in April are in average slightly higher than in January, as expected. It can be seen, that the temperature in B3 is rising linearly without any temperature peaks. The same can be said for B1 and B2 down to approx. 6 m indicating that in these zones no chemical reactions are taking place. Below 6 m B1 and B2 both show plateaus of around 90 °C, indicating that some endothermic chemical reaction is taking place. For B1 this plateau is going down to 9.80 m and for B2 to 7.60 m. After that the temperature again rises linearly interrupted only by a soil interlayer (B1: 11.9 m, B2: 10 m). Below both temperature distributions exhibit a different shape, B2 is still rising whereas the temperature curve of B1 is showing two temperature maxima, one of 150 °C at 12.5 m–13.0 m and another one at 16.5 m at 250–280 °C.

3.2 Chemical analysis

During drilling samples of the liberated gases were taken. All samples showed the presence of As at concentrations between 5.5 $\mu g{\cdot}m^{-3}$ and 107 $\mu g{\cdot}m^{-3}$ probably

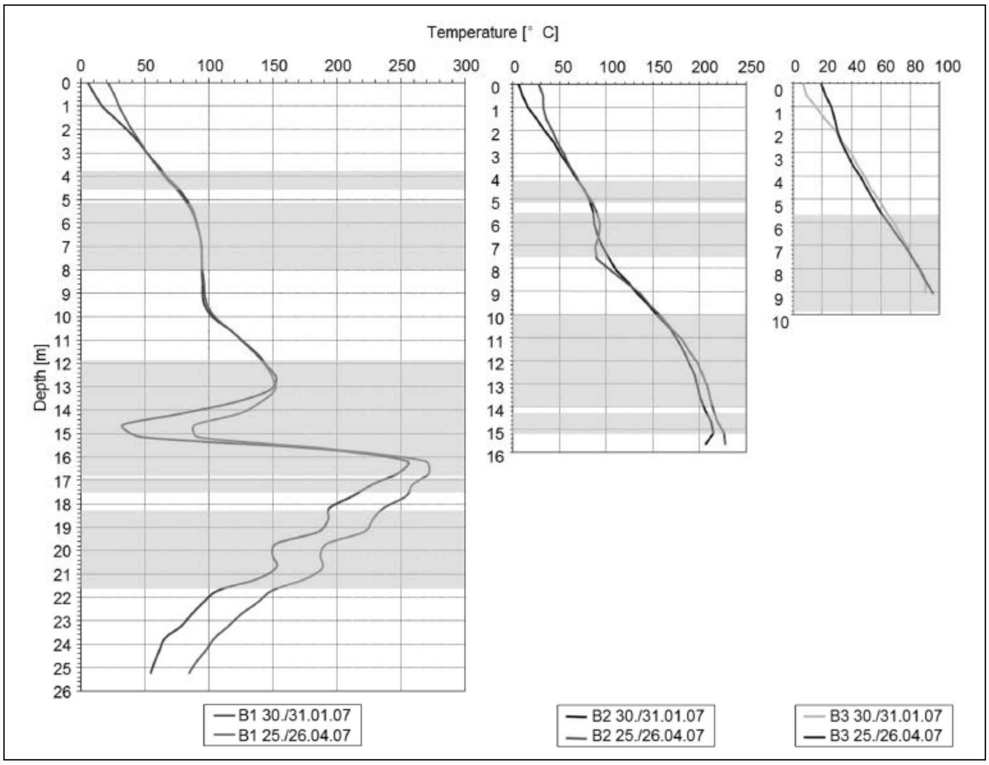

Figure 5: Temperature distribution within the three different drilling holes measured two times with an interval of three months (slag layers are indicated by grey bars)

in form of AsH_3. This could be also confirmed by the chemical analysis of the slag samples despite the fact that the detection limit there was pretty high (with 0.1 %, see Table 1). Profiling of the landfill is therefore extremely dangerous and should be avoided. All those samples taken during the drilling (50) were analysed also for their Pb, Fe, Na, Si, S and C content and could be classified as slag or interlayer (see Fig. 5). As an example *Table 1* shows the average chemical analysis of the slag layers in B1. 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. Correlation of the chemical analysis with the drilling depth and the temperature allows for a clear statement using the carbon and to a certain extent also the lead content. Correlating the carbon content of the core with the temperature profile (shown for B1 in Figure 6) it becomes obvious that the carbon content is much 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 reaction inside the landfill is proceeding from bottom to top. The described correlation is also valid for B2, where the carbon concentration also

Depth [m]	Pb (%)	Fe (%)	Na (%)	Si (%)	S (%)	C (%)	As (%)
21,70 - 20,70	9,8	24,5	6,9	5,4	12,6	1,34	0,2
18,30 - 20,70	8,4	18,0	7,6	11,0	10,3	0,61	b. d.
18,00 - 17,50	6,4	22,0	11,0	6,8	14,7	0,57	b. d.
17,50 - 16,90	6,1	36,0	1,4	2,1	19,4	0,19	b. d.
16,80 - 14,20	10,1	27,5	1,7	4,6	18,5	2,0	b. d.
14,20 - 13,20	13,0	26,0	5,2	5,4	10,8	6,1	b. d.
13,20 - 11,90	6,8	21,5	5,8	9,9	9,0	2,7	b. d.
8,00 - 5,20	14,0	31,0	1,2	5,8	11,6	8,9	b. d.
4,60 - 3,80	11,5	31,0	1,1	3,3	14,8	7,3	b. d.

b. d.: below the detection limit of 0.1 %

Table 1: Chemical composition of the layers within the drilling core of B1

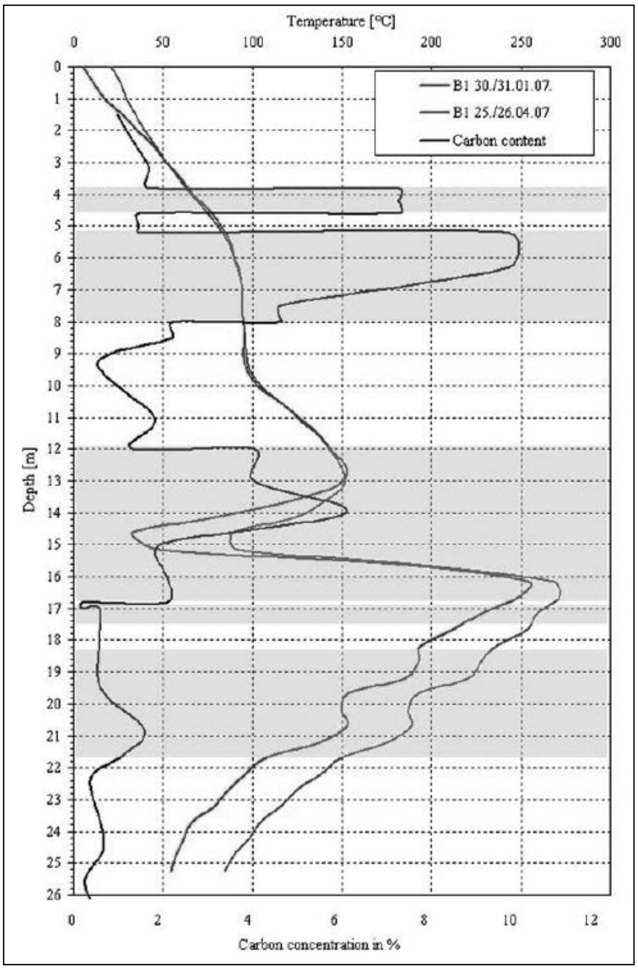

Figure 6: Correlation of the temperature distribution and the carbon content of B1 (slag layers are indicated by grey bars)

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.

Regarding the lead content it was especially noticed that the intermediate layers from a greater depth contain much more lead than the upper intermediate layers (1.4 % in contrast to 0.03 %), raising the suspicion that a slightly soluble compound is forming during the reaction (e.g. $PbSO_4$). This would also explain why the lead content is increasing again in the slag layers below 18 m.

Analysing the temperature from which a decrease in the carbon concentration can be observed 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 seam with a height of 8.4 m is not reacted above the reaction zone. Assuming that B1 is representative for the whole landfill 65 % of the slag within the landfill is not/not fully reacted.

3.3 Mineralogical Analysis

The mineralogical analysis was done by IML, a partner institute of IME at RWTH Aachen University. Five samples from different depths of B1 were analysed using XRD, classified as lead slag in four cases. The detectable compounds can be attributed 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, *$NaAlSi_3O_8$, $KAl_2Si_3AlO_{10}(OH)_2$, $(Mg,Fe)_6Si_4O_{10}(OH)_8$*
14 m:	PbS, PbO, $PbSO_4$, Pb, FeS_x, Fe_3O_4, *$(Na,Ca)Al(Si,Al)_3O_8$*
19 m:	PbS, $PbSO_4$, $FeS_{0,95}$, Fe_3O_4, Fe_2O_3, SiO_2, Na_2SO_4, *$NaMn_4Si_5O_{14}(OH)$, $Na_2Pb_3(SO_4)_3Cl$*
21 m:	PbS, PbO, $PbSO_4$, FeS_x, Fe_3O_4, Fe_2O_3, *$Na_2Pb_3(SO_4)_3Cl$, $Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$*

Italic: low detection reliability

The detected components vary from the ones assumed in the introduction before [4], resulting in the rejection of the reaction theory published there. As a consequence own thermochemical calculations of the stable products on the basis of the detected iron and lead compounds with FactSage® took place in a temperature range of 100 °C to 300 °C, resulting into the following diagram when C, O_2 and H_2O is added:

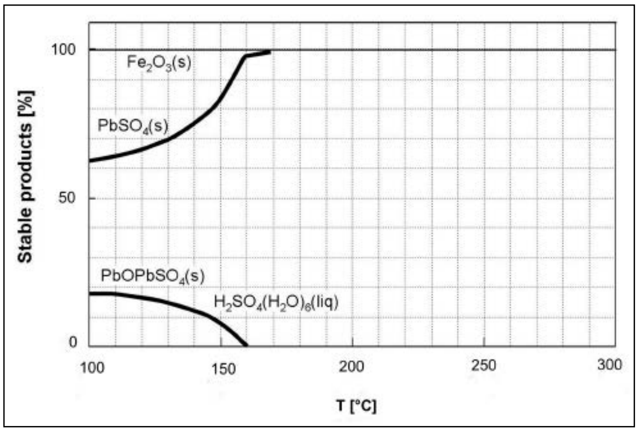

Figure 7: Calculation of stable products with addition of C, O_2 and H_2O

If only C is added the stable products are only PbS and Fe_2O_3, accordingly Fe_2O_3, $FeCO_3$, PbS and $PbSO_4$ if carbon is added substoichiometric.

Correlation of these 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.

Table 2: Proposed chemical reactions inside of the pile using software FactSage®

ΔG in kJ at different temperatures in °C	150	300	450
$Pb + O_2 (g) = PbO$	-353.6	-324.4	-294.1
$PbO + CO (g) = Pb + CO_2 (g)$	-69.6	-70.1	-72.9
$PbS + 2 O_2 (g) = PbSO_4$	-672.3	-619.3	-566.6
$PbS + Fe = Pb + FeS$	-353.9	-335.2	-318.2
$2 As_2S_3 + 9 O_2 (g) = 2 As_2O_3 + 6 SO_2(g)$	**-2564.4**	**-2494.1**	**-2419.8**
$PbCl_2 + Na_2O + CO(g) = 2NaCl + Pb + CO_2 (g)$	-333.6	-334.5	-336.6
$PbCl_2 + 2 NaOH + CO(g) = 2NaCl + Pb + CO_2 (g) + H_2O (g)$	-198.3	-218.1	-230.6
$Fe_2O_3 + As_2O_5 = 2 FeAsO_4$	-38.7	-59.0	-80.3
$2 FeAsS + 5 O_2 = Fe_2O_3 + As_2O_3 + 2 SO_2$	-1750.1	-1665.5	-1589.9

3.4 Thermoanalysis

DTA/TG investigations were done using the STA 409 CD-Simultaneous TG-DSC by Netzsch, designed for simultaneous TG-DSC or TG-DTA measurements (crucible material Al_2O_3, Argon atmosphere). The temperature ranged from room temperature up to 600 °C. An example for the obtained graphs can be seen in *Figure 8*.

The previously mineralogical analysed samples show at the DTA/TG analysis a decreasing weight loss (removal of volatile substances) in the temperature range up to 300 °C from the top of the bore down. This decrease is independent of the water content of the sample, but can however be correlated to the temperature profile analogue to the detected Fe_2O_3 level. In total the evaporation of volatile substances is more than doubled for samples from a depth above the maximum temperature (< 16.5 m for B1).

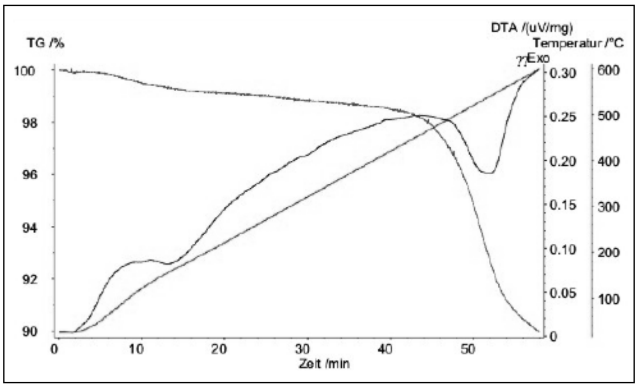

Figure 8: DTA/TG analysis for a slag sample from 21 m depth in an argon atmosphere

Apart from that the difference between the diverse 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 these peaks are much smaller for the two samples from greater depths (19 m, 21 m). The two not reacted slags from 14 m and 6 m also show a small exothermal 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. A possible reaction at 80 °C is the formation of $PbCO_3$ and at 120 °C (according to FactSage® at 130 °C) the conversion to PbS and CO_2. It is also worth mentioning that all slags show evaporation effects at temperatures above 490 °C. Furthermore the interlayer from 9 m depth also shows a couple of reactions which are mainly endothermic. A detailed analysis of possible chemical reactions between 150 °C and 45 °C was shown in the *Table 2*.

The formation of As_2O_3 by oxidation of different sulfides between 150 °C and 450 °C might be at most present in this system.

4 Forecast of the remaining reaction time

To forecast the remaining reaction time for the heap it is necessary to know the starting time of the chemical reaction. Due to the fact that we do not confidently 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. From the high sulphur content found in the cores and the appearance of pyrite, bioleaching was also considered as a possibility to reach the starting temperature of above 80 °C. Literature [6][7][8] however shows that thermophilic microorganisms are found to increase the temperature within a heap only up to 80 °C and that the oxygen content is an essential parameter for their performance. Therefore this reason for the increased temperature within the landfill was considered unlikely, first because the oxygen content inside the landfill is extremely low and also the temperatures reaches much higher values than 80 °C, making it impossible for these organisms to survive. 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 had been 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 had already reacted. Finding a correct mathematical model to predict the reaction time of the landfill based on the found data is impossible, not only because the already explained necessary constraints are missing but also because it is not possible to design a three dimensional temperature model of the landfill, due to lacking data. So as a first assessment of the remaining reaction time a linear mathematical model is chosen. Based on the facts and assumptions as well as assuming curve linearity the following simple equation (see Eq. 1) is obtained:

$$y = 0{,}95\cdot(x-1970) \qquad (1)$$

y: Percentage of the landfill reacted; x: year

According to this equation the main reaction zone will reach the top of the landfill in 2075. To adjust the mathematical model to get a more precise and reliable result as well as to asses if the estimated constraints are correct, it is advisable to monitor the temperature distribution within the drilling holes for the next couple of years/decades to more accurately define the forecasted reaction period.

5 Assessment

The mineralogical analysis showed that the components within the landfill were different to those assumed earlier in this investigation, resulting in a rejection of the previously published reaction theory stating the need of water/oxygen for the reaction to proceed. The present experimental analysis however 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. This result is especially important due to the fact that up to now it was assumed that the landfill needs at least one of these components for the reaction and that the reaction is proceeding from top to bottom.

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 is for example 565 °C [9]. Therefore no actions should be taken to provide the landfill with a surface cover before all chemical reactions have ended. 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 thermo chemical 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 possibly reduce the forecasted reaction period.

6 Acknowledgement

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