Original Paper

Laboratory trials to incorporate sulphur in the vitrification of filter ashes from incineration plants and hydrolytic investigation of the melt products[1)]

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Incineration of refuse in incineration plants produces toxic dusts in the waste gas filters which have to be disposed of. Vitrification is one possibility of immobilization of such dusts which are contaminated by heavy metals, sulphates and chlorides. Under oxidizing melting conditions, alkaline sulphates and chlorides would volatilize and would have to be precipitated again. Therefore, in this work reducing melts were used. Thus, it was possible to reduce the sulphate to sulphide and to incorporate the latter in the glass matrix to an efficiency of up to 100%. This is experimentally proved by melting batch compositions of a filter ash from a refuse incineration plant with glass forming additives as well as model glasses. The reduction of $CaSO_4$ and formation of sulphides is induced by means of suitable additions of the elements carbon, iron, zinc, titanium, manganese, silicon, and aluminium, separately and in combination. The sulphides CaS, FeS, ZnS, MnS and Al_2S_3 are present in the melt product mainly in glassy form and only for a small part in a crystalline phase. The melts with additions of manganese and silicon show the best properties with respect to vitrification, incorporation of the sulphur and hydrolytic resistance of the product. By means of leaching tests using the Soxhlet equipment, products of great hydrolitic resistance are proved falling under the hydrolytic class III at least.

Laborversuche zur Einbindung des Schwefels bei der Verglasung von Filterasche aus Müllverbrennungsanlagen und hydrolytische Untersuchung der Schmelzprodukte

Bei der Verbrennung von Müll in Müllverbrennungsanlagen (MVA) fallen in den Abgasfilteranlagen toxische Stäube an, die entsorg werden müssen. Eine Möglichkeit zur Inertisierung solcher mit Schwermetallen, Sulfaten und Chloriden verunreinigter Stäube is die Verglasung. Bei oxidierendem Schmelzen würden sich Alkalisulfate und -chloride verflüchtigen und müßten wieder abgeschieder werden. Daher wurde in dieser Arbeit reduzierend geschmolzen. Dadurch war es möglich, den sulfatischen Schwefel in sulfidischen zu überführen und diesen mit Wirkungsgraden bis zu 100% in die Glasmatrix einzubinden. Dies wird experimentell durch Schmelzen von Gemengeversätzen einer MVA-Filterasche mit glasbildenden Zusätzen und Modellgläsern nachgewiesen. Die Reduktion von $CaSO_4$ und die Bildung von Sulfiden erfolgen mittels geeigneter Zusätze der Elemente Kohlenstoff, Eisen, Zink, Titan, Mangan, Silicium und Aluminium, einzeln und kombiniert. Die Sulfide CaS, FeS, ZnS, MnS and Al_2S_3 liegen im Schmelzprodukt überwiegend glasig und nur zu einem geringen Teil kristallin vor. Die Schmelzen mit Mangan- und Siliciumzusatz zeigen die besten Eigenschaften hinsichtlich Verglasung, Einbindung des Schwefels und hydrolytischer Beständigkeit des Produktes. Durch Auslaugetests mit Hilfe der Soxhlet-Apparatur wird der Nachweis von hydrolytisch sehr beständigen Produkten erbracht, die zumindest der hydrolytischen Klasse III angehören.

1. Introduction and objectives

Since the end of the 70s, great emphasis has been put on the development of the immobilization of radioactive waste and various possibilities have been investigated [1 and 2]. Vitrification was preferentially carried out by employing borosilicate glasses whose properties can be optimized by various additives. It was reasonable also to develop modified processes of silicate glass formation for the immobilization of nonradioactive, but toxic waste. Refuse incineration produces residues such as fly ashes containing a number of potentially hazardous elements such as e.g. chromium, lead, cadmium, mercury, arsenium, with filter dust or filter ash being the solid residue arising at dedusting of the raw gases [3]. It is the aim of the numerous immobilization methods to convert nonrecyclable residual materials into a state allowing a nonharzardous disposal above ground on low grade dumps [4 and 5]. Reports from industry and research on possibilities and solutions put the emphasis on vitrification [6 and 7] since the produced glassy mineral materials can be easily disposed of. Until 1990, amounts of about 9 000 000 t/a of refuse and about 400 000 t/a of residues from waste gas purification (filter ash, residues from dry and wet sorting) were estimated for refuse incineration plants. According to [8], the incineration of 1 t of refuse produces about 26 kg of filter ash.

In the literature on the immobilization of residues (vitrification, solidifying, compacting, etc.) mainly aspects of process engineering are dealt with. Several au-

Table 1. Chemical composition (results of XRF analysis in wt%) of filter ash FA-RH with a sulphur content of 3.4 wt%

oxide or element	analysis	oxide or element	analysis
SiO_2	24.70	PbO	0.95
Al_2O_3	13.20	BaO	0.25
CaO	19.40	CdO	0.046
MgO	1.86	SrO	0.059
Na_2O	4.70	PdO	0.014
K_2O	5.60	Rb_2O	0.020
TiO_2	1.60	ZrO_2	0.030
P_2O_5	0.89	SnO_2	0.30
Fe_2O_3	4.32	Sb_2O_3	0.109
Cr_2O_3	0.11	MoO_3	0.010
ZnO	3.82	F	0.32
MnO	0.14	Cl	7.20
NiO	0.024	Br	0.073
CuO	0.14	SO_3	10.10

hors, however, also in detail describe investigations of he physical and chemical properties of the residues [9 nd 10]. Comparing the chemical analysis of a vitrified roduct with that of the filter ash it is found that some lements are not bonded in the glass product or only to very small portion. These are mainly sulphur compounds and chlorides (filter ashes contain up to 5 wt% ulphur and 7.5 wt% chloride), which leave the melting nd as SO_2 and HCl and have to be recovered by means f a downstream waste purification plant. The legal gulations concerning this task are clearly described in 1]. The relatively time-consuming and costly vitrification of filter ashes due to additional waste gas purification and waste management was the starting point for ie dissertation on which this paper is based [12]. It was tended to look for theoretical and practical possibilies to incorporate especially the sulphur compounds olatilizing during the vitrification into a glass matrix.

. Fundamentals

he melt products of fly ashes from refuse incineration ants consist of amorphous and crystalline phases [13]. heir properties and thus also their environmental comatibility are mainly determined by the kind and composition of phases. Three of the main components of the ondensed system are in the system $SiO_2 - Al_2O_3 - CaO$. he composition range is mainly in the stability field of northite, a calcium aluminosilicate; at sufficiently high aO content also gehlenite is formed [14]. As shown by e chemical analysis of the filter ash from a Lower nine refuse incineration plant (FA-RH) (table 1), which as used in this work, the filter dusts are a mixture of licates, chlorides, sulphates as well as metal and heavy etal oxides. The "standard free energy diagram for oxles" by Richardson [15] provides information on the xygen affinity of the relevant elements as a function of mperature and oxygen partial pressure. The thermodynamic stability of the oxides decreases in the order: aO, MgO, Al_2O_3, SiO_2, Cr_2O_3, Na_2O, ZnO, K_2O, FeO,

CdO, NiO, PbO, Fe_2O_3, Cu_2O, CuO, HgO. The reactivity towards carbon increases in reverse order, i.e., HgO is very reactive towards carbon, but CaO is not. It is of great significance here that at all temperatures >1250 °C, all the heavy metals can by reduced by carbon, with the main components of the filter ashes, CaO, MgO, Al_2O_3, SiO_2 being not yet converted. Under reducing conditions for the melting of filter dusts at temperatures from 1250 to 1500 °C, the oxides of zinc, cadmium and mercury are converted into the metallic state and evaporate from the melt due to their high vapour pressure. On the other hand, the heavy metals such as iron, nickel, chromium and copper arising with reducing conditions remain in the silicate melt due to their low vapour pressure and precipitate from the latter because of their limited solubility and high density.

Filter ash contains sulphates, mainly in form of $CaSO_4$ (about 15 wt%) which reacts in the temperature range necessary for the production of glass. The solubility of sulphates in alkali silicate glass is relatively low [16 to 18]. A high sulphide solubility, however, in liquid $CaSiO_3$ (containing up to 4.5 wt% sulphur) is stated in [19 and 20] for silicate and aluminate slags (blast furnace slags). Therefore, it should be attempted to dissolve the sulphur present in the filter ash in the melt by reducing the sulphate components to sulphide ones. The following two criteria are of special significance for the formation of the metal sulphides:

a) only such sulphides should be formed which have a very low water solubility;

b) at a melting temperature of 1300 to 1400 °C, the metal sulphides should be present still in the solid or the liquid phase or should not thermally decompose after their formation.

Figure 1 illustrates the sulphur affinity of some metals as a function of temperature according to data from [25]. It shows that especially the formation of FeS, ZnS and MnS should be aimed at. These sulphides also have a high hydrolytic resistance and can be embedded into the glass matrix. A detailed description of the properties of sulphides is given by Jellinek [21]. The formation of CaS which is of low hydrolytic resistance cannot be prevented as can be seen from thermodynamic calculations [12]. Owing to the high solubility of CaS in reducing calcium silicate melts this negative influence should be minimized because of the protective glass matrix. Although the sulphides of the heavy elements of groups IB and IIB of the Periodic Table belong to the least soluble compounds known, according to [22], a possible complexation of the metal sulphide in wet medium should be taken into consideration. In table 2 some physical properties of the most important sulphides are given [23].

The filter ash used contains up to 15 wt% $CaSO_4$ due to the addition of calcium oxide with waste gas purification for the incorporation of sulphur. The calculations of the thermodynamic stability carried out in [12] show that a complete decomposition of pure $CaSO_4$ occurs
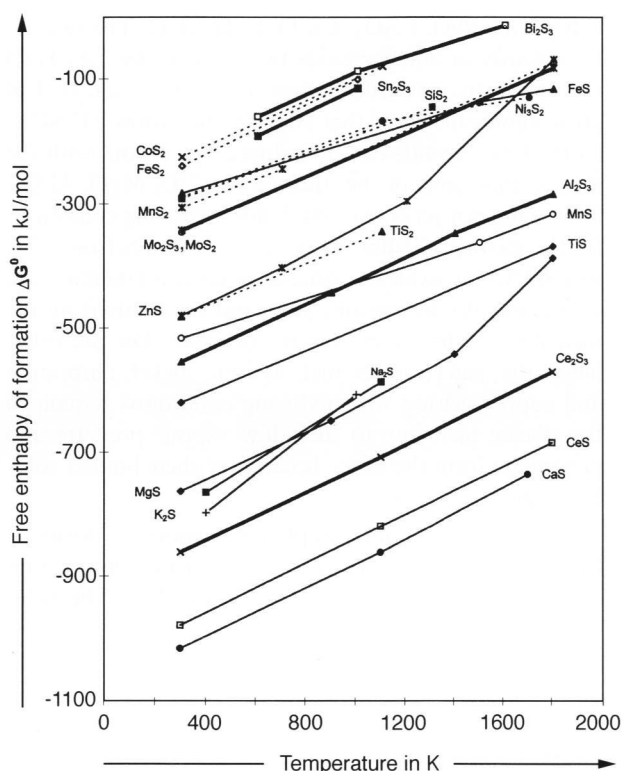
Figure 1. Free enthalpy of formation of various sulphides from the elements in dependence on temperature (based on 1 mol S_2) [25].

only above 2000 °C. In the silicate melt, however, the decomposition reaction starts already at 1200 °C. Therefore, additional measures are necessary to prevent the sulphur from volatilizing during the vitrification of filter ash at 1400 °C. This can be achieved by reducing the sulphur present as sulphate in the filter ash into a suitable sulphide before the actual melting. Table 3 shows the result of some calculations on the formation of sulphides from $CaSO_4$ which served as a basis for carrying out a number of melting experiments. Melting tests were made with filter ash with glass forming additives as well as with model glasses. The latter are not dealt with in this paper.

3. Experimental

Pre-trials showed that the used filter ash has a flow temperature of about 1230 °C, so that in general a melting temperature of 1400 °C was chosen for the melting experiments to achieve a melt which was as homogeneous as possible. The employed raw materials were chemicals of analytical grade (Merck, Darmstadt, or Heraeus, Hanau (Germany)) if not stated otherwise in [12]. The formulas were based on 100 g of filter ash for comparison. In each run, 40 g of the batch were weighed in an Al_2O_3 crucible (Degussa, Frankfurt/M. (Germany)), provided with a lid and heated up to 1400 °C at 10 K/min in an electric furnace (Nabertherm, Bremen (Germany)). Then the samples were taken from the furnace without residence time and placed on a metal plate for rapid cooling. The additions to the filter ash were meant to achieve an optimum vitrification and to test different melting conditions (oxidizing/reducing) in order to reach a high leaching resistance of the product. Besides glass forming additives such as SiO_2, carbon, iron, zinc, titanium, manganese, silicon and aluminium were added to the batches separately and in combination. The batch compositions are listed in tables ! and 5.

4. Analyses

X-ray fluorescence analysis (RFA, PW 1410, Philip Kassel (Germany)) was used to determine the chemica composition of the oxidic materials. Besides X-ray fluor escence analysis, various combustion methods were use for the determination of sulphur and carbon [12]; for th significant melts (beginning with melt no. 49), a metho developed by LECO Corporation (USA) was employe [24], the accuracy was about ± 8 %. X-ray diffractio method (PW 1729, Philips, Kassel) was used to identif crystalline components in the melt products.

The leaching trials on the glasses were carried out t means of a Soxhlet test where the sample is continuous exposed to distilled water of 99 °C over a definite peric of time (28 or 30 d). There are different ways of pro cedure. The equipment used in this work was based c the model of the Kernforschungszentrum, Karlsruh (Germany). This consists of the evaporator filled wit 100 ml (or 200 ml) H_2O, the Soxhlet receptacel (of 5 n capacity) for holding the sample and the condensat The water vapour condensates in the condenser a ranged above and the water drips into the Soxhlet recep tacle that functions like a siphon or is emptied automat cally after filling. The measuring error is about ± 5 %.

Table 2. Physical properties of the most important sulphides (from [23])

sulphide	density in g/cm^3	melting point in °C	boiling point in °C	solubility in cold H_2O in g/100 r
Na_2S	1.856	1180	decomposed	15.4
CaS (oldhamite)	2.59	decomposed	decomposed	0.0021 (decomposed)
MnS (alabandite)	3.99	decomposed	decomposed	0.00047
FeS (troilite)	4.74	1193 to 1199	decomposed	0.00062
ZnS (wurtzite)	3.98	1700	1185	0.00069
TiS	4.12	–	–	insoluble

Table 3. Formation of sulphides: thermodynamic study using the equitherm programme; temperature: 1400 °C

no.	sample no.	reactants (in mol)	products (in mol)			reaction enthalpy ΔG in kJ/mol
			solid	liquid	gaseous	
1		$1CaSO_4 + 4C$	CaS	–	4CO	−638.9
2		$1CaSO_4 + 1Fe + 3C$	$0.36CaO + 0.64CaS$	$0.36FeS + 0.64FeO$	3CO	−595.5
4		$1CaSO_4 + 1Zn + 3C$	$0.28CaO + 0.72CaS + 0.04ZnO + 0.28ZnS$	–	$0.68Zn + 0.68CO_2 + 2.32CO$	−619.8
5		$1CaSO_4 + 1Mn + 3C$	$1CaO + 1MnS$	–	3CO	−698.0
9	50	$1CaSO_4 + 3Ti + 0.5Fe + 0.5C$	$0.02CaO + 0.98CaS + 0.02TiS + 1.04TiO + 1.47TiO_2 + 0.47TiC + 0.03C + 0.5Fe$	–	–	−1292.1
2		$1CaSO_4 + 1Fe + 1.5Si + 0.2C$	$0.22CaS + 0.71CaSiO_3 + 0.03Ca_2SiO_4 + 0.76SiO_2 + 0.01C + 0.19Fe$	$0.03Fe + 0.78FeS$	0.19CO	−959.2
6		$1CaSO_4 + 1Zn + 1.5Si + 0.2C$	$0.21CaS + 0.72CaSiO_3 + 0.03Ca_2SiO_4 + 0.74SiO_2 + 0.79ZnS$	–	$0.2CO + 0.2Zn$	−1014.7
8	56	$1CaSO_4 + 1Mn + 1.5Si$	$0.01CaO + 0.13CaS + 0.43Ca_2SiO_4 + 1.07SiO_2 + 0.13MnO + 0.87MnS$	–	–	−1046.9
1	55	$1CaSO_4 + 1Fe + 2Al$	$0.05CaO + 0.34CaS + 0.61CaAl_2O_4 + 0.39Al_2O_3$	$0.34Fe + 0.66FeS$	–	−1176.7

Table 4. Batch compositions used for the melts of filter ashes no. 33 to 50

raw material		batch compositions of the melts in g											
name	chemical formula	no. 33	no. 35	no. 36	no. 42	no. 43	no. 44	no. 45	no. 46	no. 47	no. 48	no. 49	no. 50
filter ash	analysis see table 1	100	100	100	100	100	100	100	100	100	100	100	100
ground quartz	SiO_2	50	50	50	50	50	50	50	50	50	50	50	50
sodium carbonate decahydrate	$Na_2CO_3 \cdot 10H_2O$	18.46	18.46	18.46	18.46	18.46	18.46	18.46	18.46	18.46	18,46	18.46	18,46
titanium dioxide	TiO_2	3	3	3	3	3	3	3	3	3	3	3	3
alumina	Al_2O_3	4	4	4	4	4	4	4	4	4	4	4	4
aluminium (powder)	Al	–	–	–	–	–	–	–	9.47	9.47	9.47	9.47	–
carbon (active carbon)	C	4.68	4.68	4.68	5.46	4.68	4.68	4.68	–	5.07	5.07	–	5.07
zinc (powder)	Zn	2.81	–	15.44	–	–	15.79	7.34	–	–	–	–	–
iron (powder)	Fe	3.16	12.63	–	7.54	13.33	–	6.32	–	–	7.02	3.51	3.51
titanium (wire pieces)	Ti	–	–	–	–	–	–	–	–	–	–	–	11.58

Investigations of the hydrolytic resistance were also carried out on several samples according to DIN 12111 [6] and ISO 719 [27], respectively. The results show that the glasses fall under the hydrolytic classes II or III.

Moreover, an autoclave test was employed on a trial basis. With this test, the leaching depends on the temperature and the number of leaching periods. Details, especially about the correlation to the Soxhlet test, are reported in [12]. In table 6 some data of this autoclave test are compared with those of the Soxhlet test.

Results and discussion

The objective of all the melts was first of all to dissolve as much sulphur as possible. Dependent on the compo-sition, there is a maximum possible sulphur content of 2.35 to 2.75 wt% in the product. On condition that the sulphur is completely dissolved by the product, a maximum sulphur incorporation of 2.55 ± 0.2 wt% is yielded with respect to the molten basis composition (filter ash and glass forming additives).

The melts no. 35, 42 and 43 are based on batch compositions where iron or iron and carbon were added. In the cooled glass matrix there were spherical and metallic gleaming inclusions which were determined as FeS. The measured sulphur content corresponded to a sulphur incorporation of about 75%. Melts no. 36, 44, 45, 53 and 63 are based on batch compositions where zinc and carbon, zinc and iron as well as with melt no. 63 zinc and

Table 5. Batch compositions used for the melts of filter ashes no. 53 to 63

| raw material | | batch compositions of the melts in g | | | | | | | | | |
name	chemical formula	no. 53	no. 54	no. 55	no. 56	no. 57	no. 58	no. 59	no. 61	no. 62	no. 63
filter ash	analysis see table 1	100	100	100	100	100	100	100	100	100	100
ground quartz	SiO_2	50	50	50	40	30	30	30	40	30	30
calcined soda	Na_2CO_3	–	–	–	10.27	10.27	6.16	10.27	14	10.3	10.3
sodium carbonate dekahydrate	$Na_2CO_3 \cdot 10H_2O$	18.46	18.46	18.46	–	–	–	–	–	–	–
barium carbonate	$BaCO_3$	–	–	–	–	–	21.24	–	–	–	–
titanium dioxide	TiO_2	3	3	3	–	–	–	–	–	–	–
alumina	Al_2O_3	4	4	4	–	–	–	–	–	–	–
aluminium (powder)	Al	–	–	10	–	–	–	–	1	–	–
carbon (active carbon)	C	4.68	2.34	–	–	3.87	4.3	–	–	–	–
zinc (powder)	Zn	7.34	9.12	–	–	–	–	–	–	–	7
iron (powder)	Fe	6.32	–	5.97	–	–	–	–	2	1.5	–
manganese (powder)	Mn	–	–	–	6	6	–	–	6	6	–
silicon (flakes)	Si	–	–	–	4.6	–	–	4.6	4.6	4.6	4.6

Table 6. Leaching trials on hydrolytic resistance. Samples: monoliths, about 0.5 g. Soxhlet: 30 d (28 d from sample no. 56). Leachin in distilled water at 99 °C. Autoclave: leaching, 24 h at 133 °C and 2 bar

sample no.	SO_3 content in wt%	density in g/cm³	Soxhlet (leaching)	autoclave (leaching in mg/cm²)
43	4.9	2.5	0.97	–
46	4.9	2.5	5.0	–
49	6.3	2.5	3.2	–
50	6.8	2.5	5.6	–
54	4.6	2.5	0.53	–
56	6.7	2.5	0.75	5.4
58	5.1	2.5	1.5	1.6
59	7.3	2.5	8.7	3.0
61	6.6	2.5	0.21	5.2

silicon were added. In none of these melts metallic inclusions were found. The sulphur incorporation with melt no. 63, however, only amounted to about 53 as about 87 % of the added zinc had evaporated. Thus, zinc is not very suitable for the sulphur incorporation unless the flux content of the batch is chosen so high that a melting temperature of below 1300 °C is possible, which, however, would mean a loss of the hydrolytic resistance. The filter ash melts no. 33 and 50 are based on batch compositions where titanium particles, iron and carbon powders were added. The formation of TiS/TiS₂ was intended. By means of X-ray diffraction TiS and CaS were proved. The sulphur content of sample no. 50 as determined by the LECO method amounted to 2.7 %, corresponding to a sulphur incorporation of 100 %. However, only TiO_2 (rutile) but no TiS and TiS₂, respectively, could be proved. Melts no. 46 to 49 and 55 are based on batch compositions with additions of aluminium, iron and carbon. The ignition loss of melt no. 55 amounted to only 14.5 % (in contrast to 18 to 22 % with the other melts) which can be put down to a new formation of $CaAl_2O_4$ and Al_2O_3 according to the thermodynamic study (table 3, no. 21). This is

confirmed by thermogravimetric measurements [12]. I means of X-ray diffraction corundum, quartz, cristob lite, anorthite, FeS, CaS, Al_2S_3 and ZnS could be prove It can be concluded from the incorporation of sulphur about 95 % that the melting temperature of 1400 °C w chosen too high as the evaporation of small amounts aluminium and AlS cannot be excluded. Melts no. 56, 5 59 and 61 were carried out with additions of manganes silicon and carbon, with manganese, silicon, aluminiu and iron being added to melt no. 61. There was a sulph incorporation of about 100 % for the above melts, exce for melt no. 57 where only 88 % of the sulphur was inco porated. The proof of graphite in the melts containing si con is remarkable; it is missing in all the melts without t addition of silicon. The melt products were very britt The results of the Soxhlet leaching tests on the significa melt products show that, except for sample no. 59, the r sistance of the products of the present work is partly larg compared to the values found in literature on the vitri cation of fly ashes [9]. Whereas 2.8 g/(m² d) is stated minimum value in [9], here also values <1 g/(m² d) a achieved.

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6. Conclusion

A qualitatively new approach shows the possibility of incorporating sulphur contained as CaSO$_4$ in filter ashes from refuse incineration plants in form of sulphide into a glass matrix. Additions of aluminium, silicon and ti-tanium result in melts with the highest sulphur disso-lution, whereas the addition of manganese facilitates the glass formation. The hydrolytic resistance of the prod-ucts is sufficiently good. Put into practice, these results could lead to a simplification of the waste gas purifi-cation which has up to now been necessary with the melting procedures of filter ashes.

Apart from the vitrification of filter ashes, the pos-sible development of novel glass types or materials is shown by the use of metal powders for incorporating sulphur in a glass matrix.

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