Original Paper

Experience in operation of a pilot plant melting residual substances[1])

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A pilot plant to melt residual substances was operated over a period of more than four months. To examine any extreme situations, residues from incineration plants were used. The results obtained from these trials are very positive and encouraging for use in industrial applications. It has been achieved that the glass represents a satisfactory and long-term stable sink for major heavy metals, and another sink has been provided for other heavy metals through arrestment in a filter systems. Furthermore, any organic contaminants contained in the substances have been successfully destroyed. Contrary to conventional sheet glass melts, good performance and specific values have been confirmed. Using a special treatment technique, a major drawback involved with industrial residues, i.e., heterogeneity of basic material, has been reduced such that the future production of glass products with defined properties is considered to be possible. Preference is given to large-scale recovery in complex residues melting systems from a technological, economic and environmental point of view.

Betriebserfahrungen mit einer Pilotanlage zum Einschmelzen von Reststoffen

Über einen Zeitraum von mehr als vier Monaten wurde eine Pilotanlage zum Schmelzen von Rückständen betrieben. Zum Studium der Extremsituationen wurden dazu Rückstände aus Müllverbrennungsanlagen verwendet. Die mit diesen Rückständen erzielten Ergebnisse sind insgesamt sehr positiv und aussichtsreich für eine industrielle Anwendung. So konnte erreicht werden, daß für wichtige Schwermetalle das Glas eine gute und langfristig stabile Senke darstellt. Für weitere Schwermetalle ist über den Weg der Abscheidung in einer Filteranlage eine weitere gesamtverfahrenstechnische Senke eingerichtet worden. Die vollständige Zerstörung der organischen Schadstoffe in den Substanzen wurde erreicht. Im Vergleich zu einer konventionellen Tafelglasschmelze sind gute Leistungen und spezifische Kenngrößen nachgewiesen worden. Mit Hilfe einer speziellen Aufbereitungstechnik ist der größte Nachteil industrieller Rückstände – die Heterogenität des Ausgangsmaterials – so vermindert worden, daß die Herstellung von Glaserzeugnissen mit definierten Eigenschaften für die Zukunft positiv beurteilt werden kann. Der großtechnischen Verwertung im Rahmen komplexer Rückstandsschmelzanlagen wird in technologischem, wirtschaftlichem und ökologischem Sinne der Vorzug eingeräumt.

1. Introduction

Increasing problems that are currently being encountered in processing and dumping of environmentally relevant residues and those residues containing harmful substances from industry, trade and private households, together with the objective to implement a recirculation management system, will require new considerations to be made with respect to the recovery and utilization of these residues or of valuable substances contained therein.

Such considerations resulted in both FLACHGLAS AG, Gelsenkirchen (Germany), and Deutsche Babcock Anlagen GmbH, Oberhausen (Germany), developing a concept for treatment of residues, with the objective to immobilize any toxic substances and to destroy any harmful organic substances. At the same time, both companies have examined possibilities to produce new products or replace existing products.

When developing such a concept, comprehensive experience was gathered with the operation of a pilot plant, which was running continuously for a period of four months, with a melting rate of 2.5 to 5.0 t/d. The trials were performed using residues produced by the incineration of household waste. The residual substances employed were grate ashes (= mixtures of grate slag and boiler ash) and filter dust. The studies carried out were based on the "worst case" in terms of pollutant amounts and meltability.

Preliminary considerations made resulted in the development of the aforementioned pilot plant, taking the following (generally applicable) principles with respect to glass technology into account:

a) precise knowledge of the origin of the raw materials as well their technological properties;

b) compliance with a specific product-oriented range of chemical composition;

Received September 29, revised manuscript October 29, 1994.
Eine deutsche Fassung dieser Arbeit liegt in der Bibliothek der Deutschen Glastechnischen Gesellschaft, Mendelssohnstraße 75–77, D-60325 Frankfurt/M., vor.

[1]) Presented in German at: 68th Annual Meeting of the German Society of Glass Technology (DGG) on June 1, 1994 in Bad Salzdetfurth (Germany).

c) compliance with a specific particle range;

d) availability of sufficient quantities.

The pilot plant was comprised of the processing stages: "slag treatment", "batch production", "glass melting plant", "processing", "waste gas treatment" and "analytics of educts and products". The plant was installed and operated at the location of a waste incineration plant.

2. Grate ash treatment

The objective of grate ash treatment is to "translate" the melting process requirements in terms of range of particle size, metal content and moisture. Furthermore, any possibilities of homogenizing the chemical composition were investigated. Figure 1 shows the chosen treatment process in the form of a basic flow diagram. It should be noted that the input into the processing plant consisted of pretreated grate ashes, which were subjected to an initial processing stage (coarse screening, magnetic separation) by a company specialized in grate ash treatment. The plant (figure 1) processed an overall amount of about 110 t of grate ashes, which had been processed previously. The results can be summarized as follows:

- Depletion of ferrous and non-ferrous metals using weak and strong field magnets and eddy-current separators has been successfully completed. Table 1 shows a distinct depletion of the major metals, i.e. iron, zinc and copper.
- Depletion of the metal content results in a relative enrichment especially for silicium and sulphur. Table 1 shows this with respect to the most important elements. Figure 2 directly compares the mean values of treated and untreated grate ashes.
- However, the most significant result of the processing trials was the homogenization of chemical composition, which is illustrated in table 1 and figure 3. As can be seen from the figure, the variation range of chemical composition was reduced by a power of ten on the average, the chosen processing technique offering an efficient instrument to qualify heterogenous substances as an acceptable glass raw material for residue glass, and fulfilling the prerequisites to consider production of higher-quality glass products.

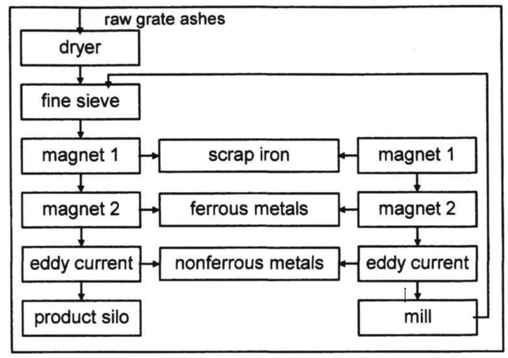


Figure 1. Basic flow diagram of the treatment of grate ashes.

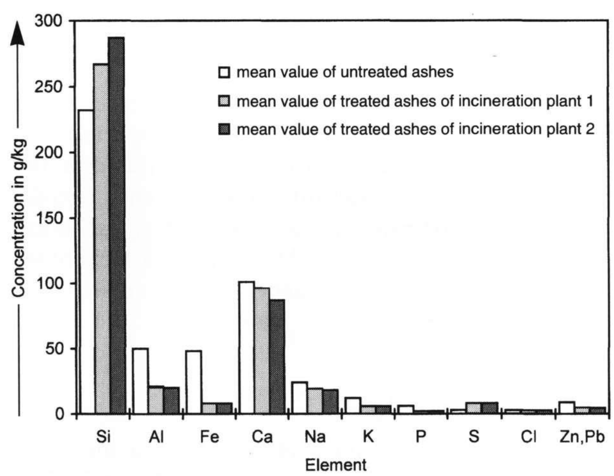


Figure 2. Comparison of mean values of various elements in untreated and treated grate ashes.

Table 1. Variations and mean values of untreated and treated grate ashes

element	variation of untreated ashes (in g/kg) according to [1]		variation of treated ashes (in g/kg) of incineration plant 1		variation of treated ashes (in g/kg) of incineration plant 2		mean value of		
	min	max	min	max	min	max	untreated ashes (in g/kg) according to [1]	treated ashes (in g/kg) of incineration plant 1	treated ashes (in g/kg) of incineration plant 2
silicium	140	320	270	281	281	296	232	267	287
aluminium	5	95	19	23	18	22	50	21	20
iron	20	110	6.8	9.5	6.8	9.5	48	8	8
calcium	30	140	92	102	81	92	101	96	87
sodium	5	35	16	21	11.9	23	24	19	18.1
potassium	3	21	5.5	6.1	5.3	5.9	12	5.8	5.6
phosphorus	3	34	1.6	2.3	1.6	2.3	6.1	2	2
sulphur	2	4	6	12.2	6	12.2	2.9	8.1	8.1
chlorine	0.3	6.3	2	3.7	2	3.7	2.7	2.8	2.8
zinc	0.5	21	1.7	2.2	1.5	2.7	4.8	1.9	1.9
lead	0.6	5.2	1.4	3.6	1.4	2.1	1.6	1.8	1.6
copper	0.2	7	0.7	1.1	0.7	1.1	2.2	0.86	0.85

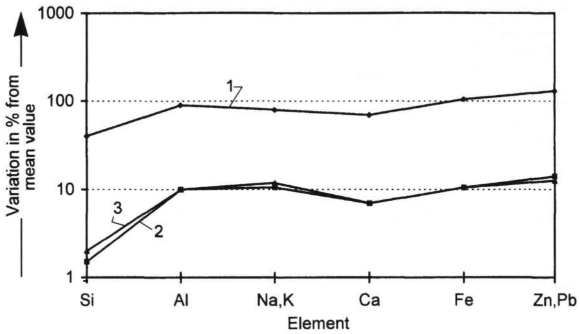


Figure 3. Variation range of selected elements contained in grate ashes. Curve 1: untreated ashes; curve 2: treated ashes of incineration plant 1; curve 3: treated ashes of incineration plant 2.

These results were achieved using a material which – in terms of homogeneity, particle range and moisture – gave extremely bad melting conditions. Based on this statement, one may expect other residues having similar unfavourable properties also may be used as a glass raw material by means of a suitable processing technology. Processing of residual substances will be an indispensable part of residues melting plants.

3. Batch production

The pilot trials were aimed at producing a melt consisting of the pure substances (grate ashes and filter dusts), as well as a melt consisting of mixtures of the aforementioned residues and other aggregates.

A tower system was applied in view of reduced requirements for accuracy. Dosing devices were used to feed a sum weighing unit with relevant substances from the residues silos, the recipes weighed were dry mixed in a compulsory mixer and subsequently moistened, remixed and specific amounts thereof fed to the tank silo. This simple batch plant essentially complied with the requirements and assured a continuous melt to be produced as well as mass balances of the overall system to be performed.

4. Glass melter

The glass melter was used to examine and analyze a number of processes. This especially applied to materials and energy balances, the melting technology, heating and feeding techniques, production and treatment of metallic melts in the furnace, furnace lining and, finally, issues in connection with the processability of the glass. These issues were preliminarily handled and defined by performing comprehensive laboratory testing, resulting in the development of a special type of furnace which was lined with a large number of different, preselected refractories.

The chosen heating system was based on oxygen and oil, taking into account that vitrification plants were to be integrated in the existing waste incineration system and existing waste gas cleaning technology was to be used. This target requires the waste gas volumes to be drastically reduced. Findings from thermoanalytical examinations included a very high salt content in the waste gases, which was in conflict with regenerative or recuperative air preheating (sublimation).

The furnace had to be lined in such a way that no pollutant emissions were allowed to escape to the ambient air. This required special action to be taken in the feeding area, the glass drainage and waste gas flue. Processing of the glass on the pilot plant was of minor importance; dry granulates were used which, however, due to their special construction, allowed the forming behaviour to be examined. Apart from the melting furnace, waste gas treatment was required.

This process essentially included the following components: evaporation cooler, cloth filter, induced draught as well as the required pipelines, adjusting devices and measuring equipment. The waste gas was further treated in the waste gas cleaning unit of the incineration plant. The trials were performed by using comprehensive measuring and analytical equipment in order to capture all the technical/technological parameters. Educt and product analytics was performed through process control.

Prior to producing the residues melt, the pilot plant was "calibrated" using float glass, i.e., an initial melting step with float glass batch was carried out and the key parameters based on the known float glass composition were defined. Thus, all the pilot furnace variables could be compared with those of a float glass melt and evaluated.

5. Results of pilot trials

The designed pilot plant melting capacity was 2.5 t/d; this rate was achieved with float glass and grate ashes, whilst the rate could be increased to up to 5 t/d using mixtures and especially filter dust melt.

The overall operating time was 2880 h, of which 400 h refer to float glass ($\approx$ 41 t), 650 h to slag melt ($\approx$70 t), 450 h to remelts and mixtures ($\approx$ 47 t) and 450 h to filter dust ($\approx$ 55 t). The remaining time was required for toughening, down-times, constructional modifications, repairs and cooling down.

The results obtained from the trial operation are shown in the following figures, including operating cycles with pure grate ashes (100 %) and pure filter dust (100 %).

5.1. Mass balances and distribution of elements

Figure 4 shows the mass balances for grate ashes and filter dust with respect to sump, glass, volatiles and dust. In particular, clear differences become apparent regarding glass, volatiles and dust. As far as grate ashes are concerned, 95 % of the input, in comparison to only

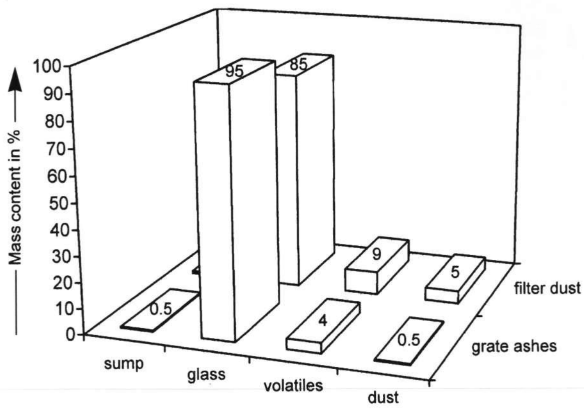


Figure 4. Mass distribution of grate ashes and filter dust in glass, volatiles, dust and sump after melting.

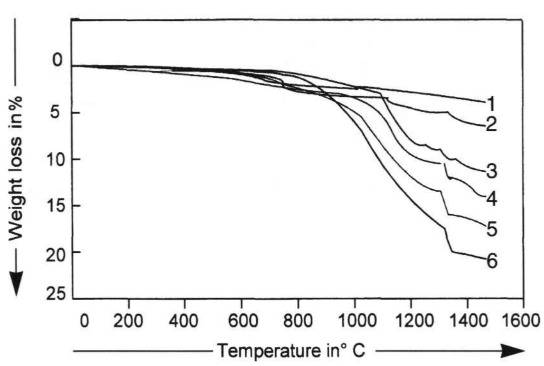
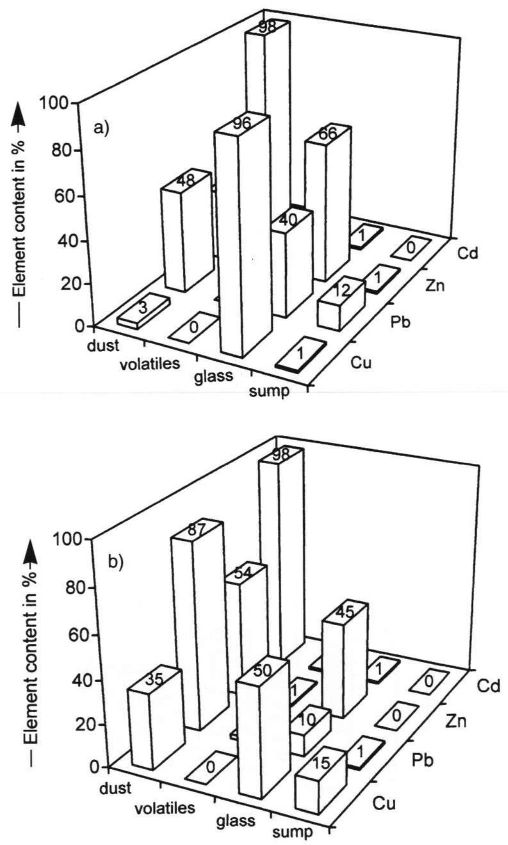


Figure 5. Results of thermogravimetric analyses (after [3]) of grate ashes, filter dust and different mixtures of these residues. Explanations to curves 1 to 6:

curve no.:		1	2	3	4	5	6
content (in %)	grate ash	100	80	60	40	20	0
	filter dust	0	20	40	60	80	100

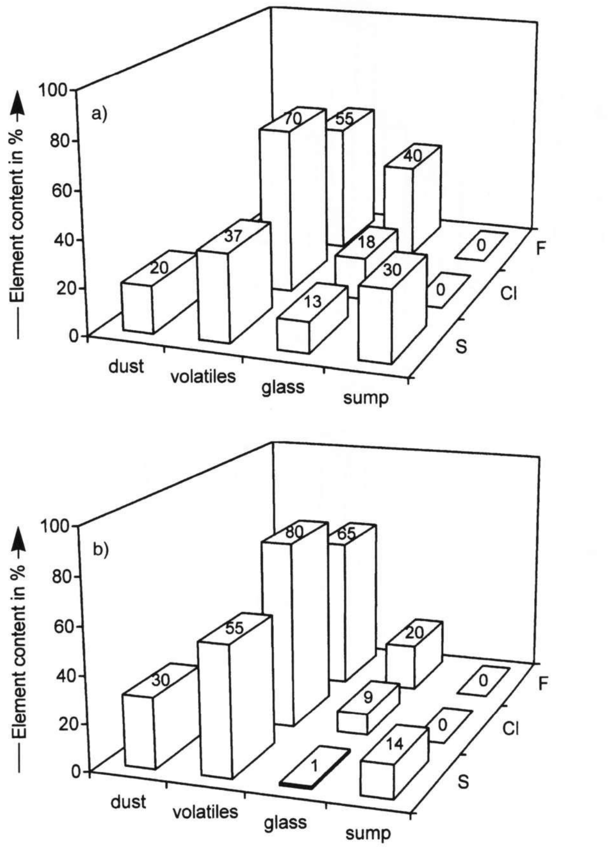


Figures 6a and b. Distribution of elements Cu, Pb, Zn and Cd in a) grate ashes, b) filter dust.

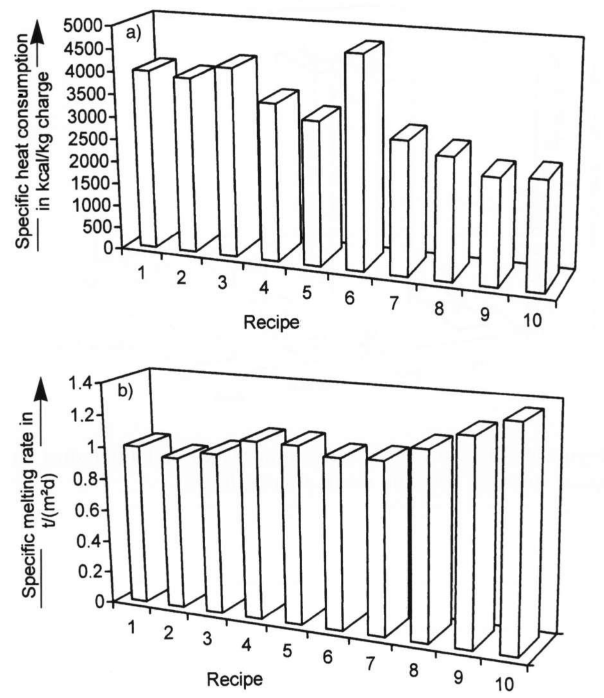
85 % of filter dust, were produced to glass. This is mainly due to two reasons. On the one hand, the amount of volatile substances in filter dust is much higher (chlorides, fluorides, sulphates – total: 10 %), compared to volatiles contained in grate ashes (about 4 %). The impact of thermal pretreatment is also illustrated in figure 5, which shows results of thermogravimetric analyses for different mixtures of substances, the effect of filter dust mixtures (in %) on the loss of weight during heating-up, due to halogenide evaporation, becoming apparent. On the other hand, dusting of the filter dust (due to the process techniques applied) in the feeding area was by far more important than with grate ashes. Dusting can be influenced by taking appropriate technological measures. The larger amounts of sump with filter dust result from the more reducing melt and thus from metal compounds reduced to sulphides and reguline metals, whereas the content is higher due to filter dust treatment not being performed.

If the distribution of heavy metals in the various substance flows is considered, the following situation is seen: Figure 6a shows the distribution of heavy metals for 100 % grate ashes. It becomes obvious that the glass is a clear sink for copper, zinc and lead. The fewer amount of lead primarily results from the extremely high percentage of carbon input and thus the reduced amount of lead. This may also be explained by the lead content in the sump. The reduced batch reduction potential will also result in controllability of retention levels. As expected, the glass is no sink for cadmium and mercury. Only 1 % of cadmium was found in glass, 98 % in dust, and 1 % in volatile substances. However, the amount of 98 % in the dust also shows possibilities of almost completely separating cadmium in the cloth filter. Therefore, an overall technological sink was found for cadmium. The dust, which also contained zinc and copper amounts not present in the glass, is a heavy metal concentrate which should be checked for possible recovery in a metallurgical process.

At first sight already, the distribution of heavy metals in filter dust melts as shown in figure 6b, is different. Particularly, retention rates for copper, lead and zinc are by far lower compared to grate ash melts. As with grate ash melts, the evaporated heavy metals are principally found in the dust. The stronger transport function is essentially due to the high amount of halogenides. As



Figures 7a and b. Distribution of elements S, Cl and F in a) grate ashes, b) filter dust.



Figures 8a and b. Comparison of specific heat consumptions (figure a) and specific melting rates (figure b) of the 10 following recipes:

recipe no.:		1	2	3	4	5	6	7	8	9	10
content (in %)	green float glass	100	0	0	0	0	0	0	0	0	0
	clear float glass	0	100	70	50	25	0	0	0	0	0
	grate ash	0	0	30	50	75	100	80	50	20	0
	filter dust	0	0	0	0	0	0	20	50	80	100

mentioned previously in connection with mass balances, the issue of primary dusting in the feeding area is of major importance and contributes to the balances being unfavourable. As expected for filter dust, the glass was no sink for cadmium and mercury. In this case, the same reasons applied as for grate ashes; from a thermal point of view, the compounds are too instable as to be integrated in the glass forming process. The balances of the anionic elements sulphur, chlorine and fluorine are illustrated in figures 7a and b. As anticipated, the retention rate of fluorine in the glass for grate ash melt was relatively high, as well as the relatively high evaporation of anions, part of these remaining in the dust with the evaporated heavy metals, the majority, however, was found in volatile substances and had to be separated in the washing stages of the waste incineration plant. A remarkable amount of sulphur was discovered in the sump, which confirms sulphides being formed as a result of the high amount of carbons, these heavy metal sulphides accumulating on the tank bottom. Of course, sulphide formation also offers the chance of increasing the retention rates of heavy metals; these microcrystalline sulphides may be incorporated in the glass network instead of going into the sump.

For filter dust, the situation with regard to the anions discovered in the glass and the dust was found to be less favourable; the amount of anions in volatile substances is clearly higher.

Generally, the results obtained confirm that very different reactions may and will take place in view of the different input conditions.

5.2. Technological results

As mentioned in section 4., a comprehensive basic data collection with respect to the float glass melt was performed, in view of comparability and evaluation. A number of process parameters will be hereafter compared with the results of residues melting.

Figure 8a shows a comparison of specific heat consumption for 10 different recipes; energy requirements are reduced with the amount of filter dust increasing. Figure 8b compares the achieved specific melting rates with each other; this clearly shows that residues melts can be produced more easily compared to float glass, and that residues melts contain apparent differences to the benefit of filter dust.

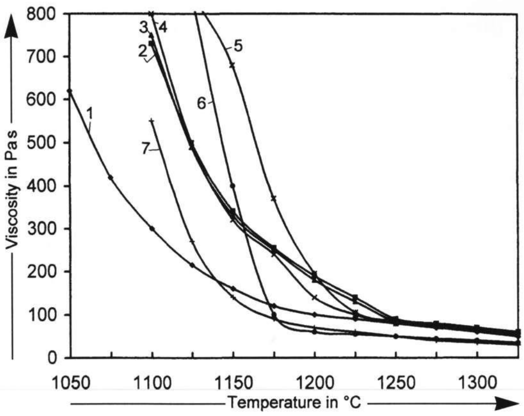


Figure 9. Viscosity as a function of temperature of clear float glass and glasses from grate ashes, filter dust as well as from mixtures of these residues.

Explanations to glass types no. 1 to 7:

glass no.:		1	2	3	4	5	6	7
content (in %)	clear float glass	100	50	0	0	0	0	0
	grate ash	0	50	100	80	50	20	0
	filter dust	0	0	0	20	50	80	100

Figure 9 shows the viscosity curves, which confirm significant differences between typical glass products, especially with respect to processing, and the various residues glasses. All of the mixtures as well as the pure grate ash and filter dust melts are extremely "short" glasses, which, due to their properties, are not suitable for mechanical processing. The only exception could be the production of mineral wool type fibres; the melts for this forming process show a similar viscosity curve. Considerable development work will be required in connection with the qualification of residues glasses for the production of glass that can be mechanically processed.

5.3. Furnace lining

Considering preliminary tests performed as well as the raw material composition, the melts could be classified in the anorthite class. Based on alkali and iron contents and the alkaline earths/silicic acid ratio, filter dusts can be expected to have a high basicity, whilst low basicity is expected for slags. This requires the use of basic materials. Furthermore, such a lining (preferably chromium oxide or chrome/corundum-containing materials), involves the risk of spinel formation due to the high iron content.

5.4. Product quality

The main objective of the pilot trials was to achieve an acceptable leach resistance so as to continue the project on this basis. Preliminary trials had shown that the legally required test ("DEV S4") was too superficial as to supply a clear statement, and too inaccurate because of firm bonding of metal ions in the glass matrix. Therefore, the Swiss Eluate Test SET was used which is not based on distilled water, but on acid environment. In addition, the specimen had to be comminuted (about 10 µm), thereby providing a very large active surface for acid attacks. These modifications allowed for considerable differences between the glass types to be discovered. In order to compare this with float glass, the float glass mixtures were eluated using grate ashes and dusts, to obtain information about (generally accepted) sheet glass.

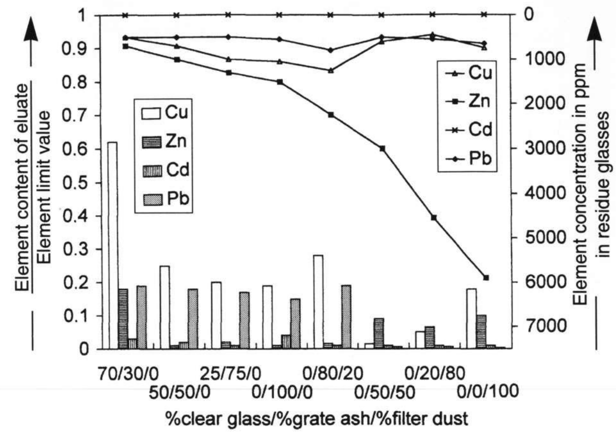


Figure 10. Comparison of elution results (according to the Swiss elution test) with limit values (after [2]) and concentrations in residue glasses for Cu, Zn, Cd and Pb.

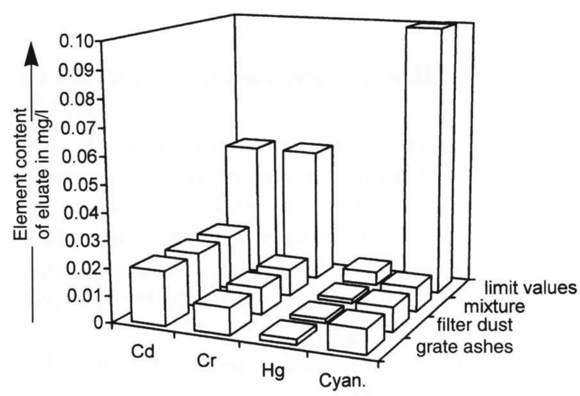


Figure 11. Comparison of elution results for Cd, Cr, Hg, cyanide according to [2]; limit values for dumping class 1.

Figure 10 illustrates this comparison in the form of superimposed elution and concentration gradients. As expected, the mixture comprising 70 wt% float glass and 30% grate ashes gave the worst elution results, i.e., the doped sheet glass had the highest leaching rates. On the other hand, residues glasses achieved excellent elution results which were distinctly below the limit values imposed by the Drinking Water Regulations (TVO). The relationship to the absolute limit values according to [2] is shown in figures 11 and 12 with respect to residue glass. These figures clearly confirm that residue glasses are extremely leach-proof, which is the main condition to successfully exploit this technology.

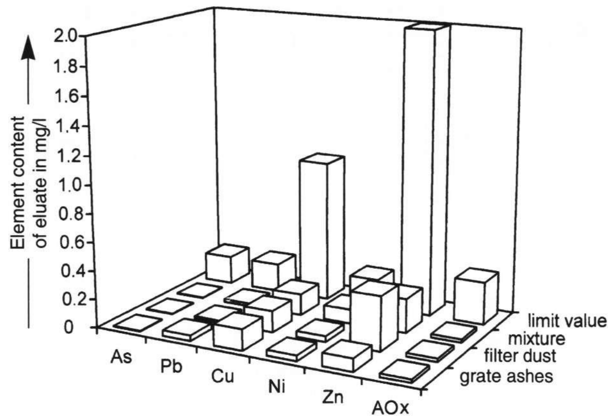


Figure 12. Comparison of elution results for As, Pb, Cu, Ni, Zn, AOx (definition of AOx see [2]) according to [2]; limit values for dumping class 1.

6. Summary

Principally, the following statements result from the trials performed:

a) The results achieved from eluate examinations with pilot melt products confirm a very good leach resistance of grate ash as well as filter dust melts, eliminating any concerns regarding the mobility of the heavy metals (and also for long-term behaviour). The products comply with "TA Siedlungsabfall" requirements for dumping class 1 [2].

b) Under conditions of sufficient immobility, the glass is a good sink for essential heavy metals.

c) The cloth filter, together with forced sublimation, represents a further sink for the remaining heavy metals, except for mercury which is separated in subsequent washing stages.

d) The dioxin analysis shows a destruction rate of $>99.8\,\%$, and, therefore, the melting process is an additional sink for harmful organic substances.

e) The residues melt can be efficiently controlled, and results can be transferred to big-scale production. In part, better energetic and melting results are achieved than with sheet glass melt under comparable conditions.

Summarizing the findings and results obtained from the described pilot trials, one comes to the conviction that pursuance of the project up to the development and operation of industrial plants will be possible and, above all, useful. These trials on melts of waste incineration residues being undoubtedly the most difficult to control, have resulted in a melting process which is an efficient treatment technique not only for such residues, since a large number of other industrial residues and waste can be recovered by using this technology.

Based on the results achieved from the trials, the authors concluded that only further development of the technique up to the production of saleable products is the right way to go to positively effect ecological balances. Vitrification of residues, for its own sake, i.e., for dumping purposes, is not beneficial from an energetical and economical point of view. Therefore, work will be continued in this field.

7. References

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