

# Phase chemistry study of products from the vitrification processes AshArc and Deglor

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AshArc and Deglor are two new complementary vitrification processes for residues from incineration of municipal solid waste. The hazardous fly ash and bottom ash are converted into a glassy product (main product), a heavy metal salt fraction, a metal fraction (AshArc only) and an off-gas. AshArc is a reductive melting process based on DC arc furnace technology, whereas the Deglor process is based on a glass tank furnace with a more oxidizing gas atmosphere.

Samples from pilot and technical scale operations of both processes were analyzed in detail using methods from petrography and chemical analysis by electron microprobe and X-ray fluorescence. Both processes produce homogeneous glassy melts with variable amounts of metal-rich minute inclusions. For the reductive AshArc process with a relatively short retention time in the furnace the melt contains a minor fraction of metal and metal sulfide inclusions enriched in iron, copper and lead, as well as traces of chromium spinel. Deglor samples are either free of inclusions or contain traces of metal sulfide enriched in copper, iron, nickel and lead.

The residues contain heavy metal concentrations below those stipulated for inert waste materials according to Swiss legislation except for zinc in some samples.

## Phasenchemische Studie an Produkten aus den Verglasungsverfahren AshArc und Deglor

AshArc und Deglor sind zwei neue, sich ergänzende Verglasungsprozesse für die Reststoffe aus Müllverbrennungsanlagen. Die schadstoffbeladenen Filterstäube und Rostaschen werden in ein glasartiges Hauptprodukt, in eine Schwermetallsalzfraktion, in eine metallische Fraktion (nur bei AshArc) sowie ein Abgas umgewandelt. AshArc ist ein reduktiver Prozess basierend auf der Gleichstromlichtbogentechnik. Das Deglor-Verfahren verwendet einen speziellen Glaswannenofen mit einer oxidativen Gasatmosphäre.

Schmelzprodukte aus Pilot- und technischen Anlagen beider Verfahren wurden mit petrografischen Methoden untersucht und mittels Elektronenmikrosonde und Röntgenfluoreszenz chemisch analysiert. Beide Verfahren erzeugen homogene Glasschmelzen mit oder ohne diverse metallreiche Kleinsteinschlüsse. Beim reduktiven AshArc-Verfahren mit einer relativ kurzen Verweilzeit im Ofen enthält die Glasphase einen kleinen Anteil an metallischen und metallsulfidischen Einschlüssen angereichert an Eisen, Kupfer und Blei, sowie Spuren von Chromspinel. Deglor-Gläser sind entweder einschlußfrei oder enthalten kleinste Mengen Metallsulfide angereichert an Kupfer, Eisen, Nickel und Blei.

Die Rückstände beider Prozesse enthalten Schwermetallkonzentrationen unterhalb der Grenzwerte für Inertstoffe gemäß der Schweizerischen Technischen Verordnung über Abfälle, mit Ausnahme von Zink in einigen Proben.

## 1. Introduction

Municipal solid waste incineration (MSWI) is a viable strategy for treating the residual waste fraction that cannot be recycled. The volume of the input is decreased by 90% and energy can be recovered in form of electricity and/or district heat. The toxic emissions to air are minimal using state-of-the-art flue gas cleaning systems. However, the incineration process produces a residue of bottom ash (25 wt% of the waste), fly ash (2.5%) and further flue gas cleaning residues. Fly ash from MSWI plants is hazardous waste because it contains dioxins, furans and soluble heavy metal compounds. Therefore, fly ash requires further treatment or safe (underground)

storage. Bottom ash is less polluted but the acceptance of the material for reuse is still low. Today, the normal bottom ash treatment consists of storage (several weeks), magnetic iron separation, crushing and sieving. In Germany 50% of the bottom ash from MSWI (1.5 mill t of ash) is treated for use in road construction or as generic construction material on landfill sites (mineral ash fraction 0 to 32/50 mm) and for metal recycling (scrap iron) [1].

Smelting of the ash fractions results in glass-like products that can be used for different purposes [2]. An overview on smelting processes for residues from MSWI is published elsewhere [2 and 3]. Because of the high energy demand of these processes it is necessary to minimize the amount of ash to be smelted. The bottom ash is the largest residue fraction. It contains elemental metals (scrap iron, brass, aluminium) as well as inert materials

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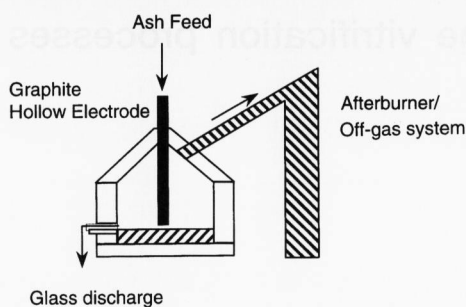


Figure 1. Sketch of the AshArc furnace.

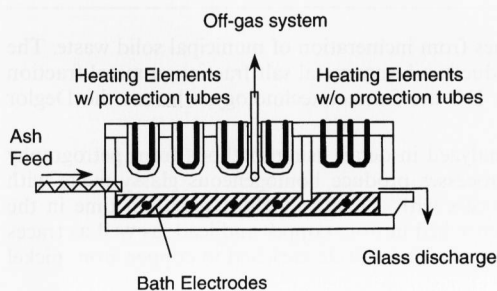


Figure 2. Sketch of the Deglor furnace.

like ceramics, stones and broken glass. It is not necessary to bring these fractions to a smelting process. The InRec process recovers the materials that can be recycled without further treatment, and separates a mineralic fraction from the bottom ash that holds most of the pollutants (residual carbon, salts, heavy metal compounds) by mechanical processes like sieving or windsifting [4]. This fraction amounts to only 1/3 of the total bottom ash (100 kg per ton of waste). This part of the bottom ash has commonly a grain size between 0 and 2 mm and is supplied for smelting in the AshArc process with or without addition of fly ash.

The AshArc process (figure 1) uses a DC arc furnace with a hollow graphite electrode through which the ash is continuously fed into the furnace. The ash is smelted by the heat of the arc plasma. The temperature in the bath is approximately 1500°C. The hollow graphite electrode is consumed during operation and is continuously pushed forward. This results in a reductive atmosphere in the furnace by which metals and heavy metal compounds can be reduced to the elements and sink down to form a layer of metallic alloy, or are evaporated through the off-gas system. CO leaves the furnace and is oxidized in the afterburner of the off-gas system. This type of furnace is widely used in the metallurgical industry. Details for this application are given elsewhere [5].

An experiment in a technical DC arc furnace with a throughput of 2 t/h was performed with MSWI bottom ash and fly ash and mixtures of both. A total of 50 t of ash had been smelted. The retention time in the furnace was typically 1 h. Samples from this experiment are in-

vestigated in the present study. Technical aspects of the tests are published elsewhere [6].

The Deglor process is a second option for ash smelting (figure 2). The furnace is designed for the treatment of fly ash only due to the limited throughput (today's maximum = 500 kg/h). The ash is fed via a screw conveyor into a specially designed glass tank that is heated by protected heating elements in the roof of the furnace and molybdenum bath electrodes within the electrically conducting melt. Most of the heavy metal compounds are evaporated due to the high temperatures (about 1350°C) via the off-gas system. Heavy metal oxides that are not evaporated are incorporated in the silicate glass. The melt leaves the furnace via a siphon and an overflow brick to the adjacent outlet furnace. The retention time of the melt in the Deglor furnace is about 20 h. The Deglor process is described in detail elsewhere [7].

The Deglor process is tested at the laboratory, pilot and commercial scales. The first commercially operated Deglor plant is located in Japan where fly ash containing salts from the flue gas system is treated. The process was adapted to handle these ash-salt mixtures with high chloride concentrations ( $\text{CaCl}_2$ ). For this material the addition of cullet (approximately 25%) to the ash is necessary to produce a glassy product. The content of chloride in fly ash varies in wide ranges also without flue gas cleaning products [8]. For the present study samples from the commercial Deglor plant as well as from a pilot plant (throughput of 20 kg/h) have been examined. Previous studies focusing on the bulk chemical and physical characterization of Deglor products are published elsewhere [9 and 10].

## 2. Sample material, analytical methods and sample preparation

Three samples of each the Deglor process and the AshArc process were examined as part of this study (table 1).

Doubly polished circular thin sections of a thickness of 20  $\mu\text{m}$  and a diameter of 2.5 cm were prepared from each sample according to standard methods of petrographic rock preparation. The thin sections were examined with a petrographic microscope under reflected and transmitted light. Samples were carbon-coated in order to create a conducting surface for examination with the scanning electron microscope (SEM) and for quantitative chemical analysis with the electron microprobe (EMP).

Another part of the sample was pulverized and used for the quantitative determination of cadmium and lead by atomic absorption spectroscopy (AAS) [11], for investigation by X-ray diffraction (XRD) and for the manufacturing of powder pellets (trace elements) and fused pellets (major elements) for quantitative wavelength-dispersive X-ray fluorescence analysis (WD-XRF).

Table 1. Overview of glassy products from the AshArc furnace (AA) and the Deglor process (DEG)

sample	process material	macroscopic description
AA1	{ mixture of bottom ash (0 to 5 mm) and fly ash (75:25)	black, homogeneous, opaque glass; powder: grey
AA2	fly ash only	very dark glass (black), barely visible flow bands; powder: black
AA3	{ fly ash only, long residence time in furnace	very dark glass (black), barely visible flow bands; powder: black
DEG1	pilot plant, fly ash without salts	black-green glass with flow bands; powder: light grey
DEG2	{ pilot plant, mixture of fly ash cont. salts and cullet	green-black homogeneous glass, transparent at edges, 'pillow'-like surface; powder: whitish green
DEG3	{ commercial plant, mixture of fly ash cont. salt and cullet	dark green glass; powder: light grey

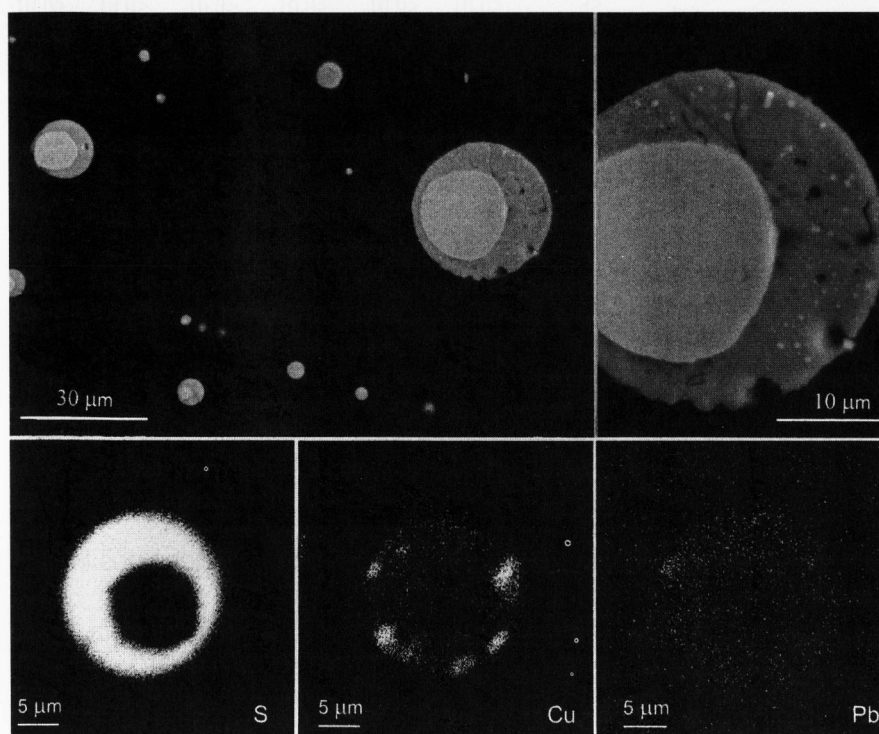


Figure 3. Sample AA1: BSE images (top row) of two-phase inclusions with a bright core of iron and a rim of an iron-sulphur phase with minor copper and lead concentration. Detail on right shows minute bright particles rich in copper and lead within the iron-sulphur phase (medium grey). The glass matrix appears black. Element distribution images for a two-phase inclusion (bottom row) are shown for sulphur, copper and lead.

### 3. AshArc samples

#### 3.1 Macroscopic and microscopic features

Three residues from the AshArc furnace, AA1, AA2 and AA3, were examined (table 1), and were shown to be X-ray amorphous:

a) Sample AA1: A large number of mainly two-phase, spherical inclusions of up to 30 µm in diameter were observed (figure 3). The core consists of virtually pure iron and is bound by an iron-sulphur phase that may also contain significant quantities of copper as well as very small inclusions of a lead-sulphur phase (figure 3, right). The ratio of the area of the metallic region to the dominant sulfide region is similar for most of the

inclusions and is about 1:2. Evaluation of 20 back-scattered electron images has shown that, on average, the metal sulphide inclusions cover 0.8% of the total area ( $\sigma = 0.2$ , range: 0.5 to 1.3). The glassy matrix is homogeneous except for areas with feathery crystallites with a diameter of up to 0.5 mm. Annealing of the pulverized sample at 1050°C caused a weight increase of 1.1% and a colour change to olive-brown with macroscopically discernible black spheres.

b) Sample AA2: A single large inclusion with a diameter of 0.6 mm consists of a core of iron with traces of copper and phosphorus as well as small segregations (5 µm) of an iron-sulphur phase containing traces of





Figure 4. Sample AA2: BSE image of hexagonal inclusions of chromium spinel and minute spherical inclusions of an iron-sulphur phase.

copper and chromium. The chemical composition of the rim is very inhomogeneous: it consists of an iron-sulphur phase with varying amounts of chromium, copper, nickel, tin, and silver. Element distribution images show that copper and iron participate in mutual substitution. Some areas are also zinc-enriched. The lead concentration appears to be slightly higher in this sulphur-rich rim than in the core phase or in the glass matrix.

Examination at a greater magnification revealed the presence of a large number of spherical inclusions (mostly smaller than 1 μm) in the glass matrix (figure 4) that cannot be chemically analyzed without matrix interference but consist of an iron-sulphur phase. Next to the round inclusions, occasional angular crystals of about 3 μm in size can be seen, some with hexagonal cross-sections (figure 4). They consist of a chromium-rich phase with an increased zinc concentration and are inferred to be chromian spinel.

c) Sample AA3: Only chromium-rich angular crystals (spinel) and spherical micrometer sized inclusions of an iron-sulphur phase similar to those in AA2 were detected in this sample. The total volume of the metal-rich inclusions is too small to be determined reliably from back-scattered electron images, but appears to be smaller than in AA2.

### 3.2 Composition of the glass matrix

Over 75 wt% of the glass matrix of the AshArc samples consist of the oxides of aluminium, calcium and silicon (table 2). The CaO/SiO<sub>2</sub> ratio of sample AA1 is, however, different to that of AA2 and AA3. AA1 is the result of smelting a mixture of bottom ash and fly ash (see table 1), whereas samples AA2 and AA3 are derived from fly ash only. It is known that fly ash contains more CaO and less SiO<sub>2</sub> [3]. Also the higher chlorine content can be explained by the difference in input materials.

The microprobe analyses show chemical homogeneity at the scale of a thin section. In addition to elements

Table 2. Average composition (in wt%) of the glass matrix from microprobe analyses; values preceded by < indicate the limit of detection

	sample					
	AA1	AA2	AA3	DEG1	DEG2	DEG3
Al <sub>2</sub> O <sub>3</sub>	18.00	17.06	17.19	15.91	12.70	11.99
BaO	0.23	0.20	0.18	0.25	<0.08	<0.08
CaO	19.46	29.22	29.36	30.89	31.24	34.93
Cl	0.14	0.33	0.21	0.60	1.50	2.74
Cr <sub>2</sub> O <sub>3</sub>	0.16	0.56	0.47	0.40	0.42	0.38
CuO	<0.04	0.05	0.06	0.07	<0.04	<0.04
FeO	4.51	4.45	4.53	3.17	1.39	0.51
K <sub>2</sub> O	2.00	1.55	1.51	1.03	0.81	0.34
MgO	3.19	4.23	4.27	3.33	2.08	1.51
MnO	0.32	0.36	0.36	0.14	0.12	0.06
Na <sub>2</sub> O	3.23	4.16	3.99	2.14	3.08	2.73
Ni	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
P <sub>2</sub> O <sub>5</sub>	0.86	2.92	2.72	1.45	0.51	0.58
PbO	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
SO <sub>3</sub>	0.12	1.60	1.33	1.07	0.03	0.54
Sb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SiO <sub>2</sub>	45.52	29.79	29.83	35.82	45.40	43.38
Sn	<0.01	<0.01	<0.01	0.01	<0.01	<0.01
TiO <sub>2</sub>	2.24	2.95	2.96	1.96	0.66	0.59
ZnO	0.08	0.30	0.46	1.66	0.25	0.31
total	100.05	99.72	99.43	99.90	100.21	100.58

with concentrations slightly above detection limit, the averages of FeO and SO<sub>3</sub> also show large standard deviations most likely due to interference with sub-μm-size inclusions rich in iron-sulphur phase.

Samples AA2 and AA3 that originated from the same experiment had almost identical compositions, including trace elements. However, the chlorine, chromium and zinc concentrations differ by up to 50 %.

### 3.3 Analysis of the metal sulfide inclusions in samples AA1 and AA2

The inclusions in sample AA1 can be subdivided into an almost sulphur-free core and a sulphur-rich rim (table 3). The core (no. 5) consists of up to 98 wt% iron and has higher concentrations of arsenic, copper, antimony, tin and tungsten than the rim. The rim is segregated in iron-rich (no. 38) and copper-rich (no. 6) regions. The mole ratio of Fe/S is close to 1 in the iron-rich region. The sulphide rim incorporates greater quantities of manganese and chromium than the core. The copper-rich regions also appear to have elevated phosphorus and lead concentrations. The core of the inclusion in sample AA2 contains over 95 wt% iron with increased concentrations of antimony, tin, nickel and phosphorus compared to the glass matrix (table 3, no. 30). The rim consists of an iron-sulphur phase with an Fe/S ratio of approximately 1, and a chromium content exceeding 3.5 wt% (no. 39), as well as bluish regions seen under incident light that consist of a copper-iron-sulphur phase with areas of increased silver and zinc contents (no. 40).

Table 3. Average composition (in wt%) of metal and sulphide inclusions of samples AA1 and AA2; values preceded by < indicate the limit of detection

	AA1			AA2		
	no. 5	no. 6	no. 38	no. 30	no. 39	no. 40
As	0.06	<0.02	<0.02	—	—	—
Co	0.06	<0.01	<0.01	—	—	—
W	0.58	<0.03	<0.03	—	—	—
Ag	—	—	—	0.03	<0.02	0.12
Cr	0.01	0.08	0.12	0.06	3.56	0.07
Cu	0.16	29.32	0.67	0.99	1.68	48.84
Fe	98.72	39.58	63.85	96.66	58.01	18.47
Ni	—	—	—	0.43	0.03	<0.02
Mn	<0.01	0.08	0.09	—	—	—
P	<0.01	0.10	<0.01	0.83	<0.01	0.26
Pb	<0.06	0.40	<0.06	<0.10	<0.10	<0.10
S	0.06	30.58	34.77	0.04	36.93	28.70
Sb	0.22	0.03	0.04	0.25	<0.02	0.03
Sn	0.24	0.02	0.03	0.20	<0.04	<0.04
Ti	0.06	0.05	0.08	—	—	—
Zn	<0.02	<0.02	<0.02	0.06	0.04	0.13
total	100.16	100.23	99.64	99.56	100.25	96.62

### 3.4 Bulk chemistry

The bulk composition determined by XRF confirms the results of the glass analyses obtained by EMP (table 2). Larger differences can be expected for those elements found in increased concentrations in the inclusions (table 3). This is true for FeO in sample AA1 in which the bulk content and glass composition differ by about 2 wt%. Table 4 displays the concentrations of the trace elements measured on powder pellets by XRF.

The bulk copper concentration is significantly higher in sample AA1 (473 ppm) than in the glass (below detection limit of 310 ppm), indicating that a significant portion of copper is bound to metal sulphide inclusions. Measurements of zinc in the glass matrix and in the bulk material suggest that most of it is fixed in the glass matrix. All heavy metal concentrations in the glass are below the limits defined for inert materials by Swiss legislation [12] except for zinc in sample AA3 (limit: 1000 ppm).

Sample AA1 contains a relatively large proportion of metallic iron. A strongly reducing environment can be assumed due to the presence of the sulphide metal in-

clusions in the sample. Correspondingly, all iron in the glass matrix likely exists as divalent iron (i.e., 70 % of total iron), the remaining 30 % is part of the metal sulphide inclusions. In sample AA2 and AA3, 90 % of the iron is present in a divalent state.

### 3.5 Discussion of AshArc residues

The results demonstrate that in terms of the major elements the residues from the AshArc furnace are homogeneous at the scale of a sample. In each of the three samples, inclusions made up less than 1 vol.%. Increased concentrations of iron, copper and sulphur were found in the inclusions. For most of the minor and trace elements homogeneity can only be qualitatively supported (i.e., element distribution maps) because of the relatively high detection limit of the microprobe for many metals. For example, the total cadmium content is about a factor of 1000 below the detection limit of the EMP. Local increases in the lead concentration were detected both qualitatively (SEM study) and quantitatively. This was also true for silver, chromium, nickel, antimony, tin and tungsten.

Most zinc is bound in the glass matrix, although an increased concentration was observed and measured in the sulphide rim. The proportion of the more easily soluble components chlorine, K<sub>2</sub>O, Na<sub>2</sub>O and SO<sub>3</sub> varies between 5.5 (AA1) and 7.6 wt% (AA2). The role of sulphur in glass melting is discussed elsewhere [13 and 14]. Apart from sample AA3 with a zinc content of 3300 ppm, the samples show low concentrations of heavy metals and most of those are bound in the glass matrix. Since the small number of metal sulphide inclusions often contain relatively high concentrations of chromium, copper, nickel, lead, antimony, tungsten and occasionally zinc, the release of these elements would depend on the amount of inclusions and their accessibility. A simple method for determining the amount of inclusions appears to be annealing at 1050 °C and examining the change in weight: samples with abundant inclusions will increase in mass due to oxidation primarily of metallic iron contained in the inclusions.

## 4. Deglor samples

### 4.1 Macroscopic and microscopic features

There were three glassy residues from the Deglor process examined. Samples DEG1, DEG2 and DEG3 (table 1).

Table 4. X-ray fluorescence bulk analysis of trace elements (in ppm) in the AshArc and Deglor samples. Cadmium and lead measured by AAS

sample	Ba	Cr	Cu	Nb	Ni	Pb	Rb	Sr	V	Zn	Zr	Cd	Pb*
AA1	1826	929	473	24	8	55	44	357	67	614	220	0.015	49
AA3	1536	2114	397	24	31	149	20	373	62	3279	201	0.108	136
DEG1	2120	1974	397	14	93	106	20	390	77	13050	2612	1.088	79
DEG2	441	1456	32	76	31	95	19	602	31	2548	607	0.250	92
DEG3	360	1810	72	10	21	87	14	279	21	2183	429	0.326	109

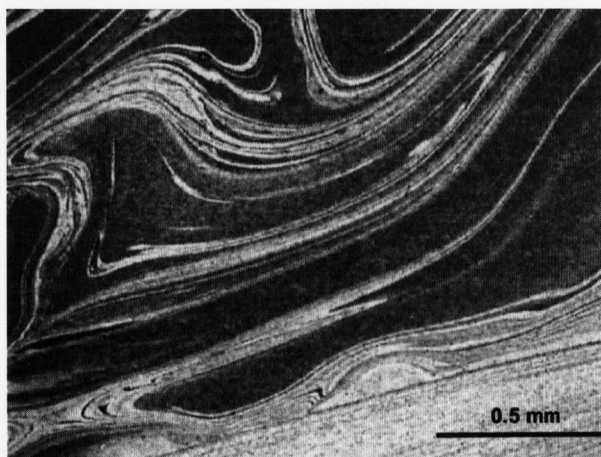


Figure 5. Sample DEG1: Thin section viewed in transmitted light with flow bands in Deglor glass.

Sample DEG3 was from a commercial plant in Japan. All three samples were shown to be X-ray amorphous.

a) Sample DEG1: Macroscopically and microscopically visible flow bands (figure 5) are due to refraction on small spherical inclusions (0.5 to 1.5  $\mu\text{m}$ ). These inclusions were too small to be analyzed independent of the glass matrix. However, it was possible to demonstrate that the inclusions consist of an iron–zinc–sulphur phase with minor copper and nickel contents. In some of the inclusions it was possible to identify much smaller particles (0.1  $\mu\text{m}$ ) in which lead could be preferentially detected. Evaluation of 32 back-scattered electron images showed the average proportional area of the iron–zinc–sulphur inclusions to be 0.15 % ( $\sigma = 0.09$ , range: 0 to 0.3). Annealing of the pulverized sample material resulted in a weight increase of 0.1 %, sintering and a change in colour to olive brown.

b) Sample DEG2: No metallic inclusions were identified. Annealing the pulverized sample at 1050 °C caused a weight increase of about 0.08 % and strong sintering.

c) Sample DEG3: This sample is composed of very homogeneous glass. The observed inclusions were smaller than 1  $\mu\text{m}$  and the EDS spectrum indicated apart from the elements of the interfering matrix a relative large amount of chlorine reflecting the high chlorine content in the feed, and also an increased chromium content. The number and size of the inclusions were too small to allow their area to be determined by image processing.

### 4.2 Composition of the glass matrix

Over 80 wt% of the Deglor glass matrix consists of the oxides of aluminium, calcium and silicon (table 2) with similar  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  but variable  $\text{SiO}_2$  contents. The contents of other elements vary over a wide range of concentrations: e.g., 0.6 to 2.7 wt% for chlorine, and 0.5 to 3.2 wt% for  $\text{FeO}$ . Samples DEG2 and DEG3 have a higher chlorine content because the ash contained also

salts from the flue gas cleaning system. This had a positive effect on the heavy metal content of the glass products, e.g., zinc was effectively evaporated as chloride due to the higher chlorine input in the feed [10]. The  $\text{SiO}_2$  concentration in these samples is higher because cullet was used as additive.

Analogous to the AshArc samples, the iron–zinc–sulphur inclusions in sample DEG1, which are less than 1  $\mu\text{m}$  in size, are responsible for the large standard deviations for  $\text{FeO}$  and  $\text{SO}_3$ . The chlorine content of sample DEG2 also varies but cannot be explained.

### 4.3 Bulk chemistry of the Deglor samples

The analysis of major elements by XRF confirms the microprobe analyses of the glass matrix. Of the trace elements (table 4), distinctly lower chromium values were measured by XRF analysis compared to microprobe analysis of the glass matrix for reasons presently not understood.

The Deglor samples contain significantly more cadmium than the AshArc samples (table 4). Sample DEG1, with more than 1 ppm cadmium, 13050 ppm zinc and 380 ppm copper, has the highest concentration of heavy metals. Sample DEG1 also has the highest phosphorus concentration of all the Deglor samples – a simultaneous occurrence of phosphorus, zinc and cadmium is common.

Comparing the  $\text{FeO}$  content of the glass matrix (formal total  $\text{FeO}$ ) with the effectively measured ferrous  $\text{FeO}$  (by acid digestion and complexation) shows that at least between 75 (DEG2) and 95 % (DEG3) of the total iron content exists in divalent form.

### 4.4 Discussion of Deglor residues

Deglor residues comprise homogeneous glass with almost no inclusions. Only a limited comparison can be made between samples due to the differences in composition of the input material. The Deglor samples contain significantly more cadmium than the AshArc samples. However, the concentration is still well below the limit of 10 ppm for inert materials according Swiss legislation [12]. The proportion of the more easily soluble components, chlorine,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{SO}_3$ , lies between 4.8 and 6.4 wt%.

The addition of cullet to the feed is a viable method to smelt ashes containing a lot of  $\text{CaCl}_2$  that cannot be easily evaporated because the vapour pressure is too low. The alkali oxides in the cullet transform  $\text{CaCl}_2$  to  $\text{CaO}$  while  $\text{NaCl}$  preferentially partitions into the vapour phase. Although rather high heavy metal concentrations have been measured for the glass products (e.g., zinc is well above the 1000 ppm limit for Swiss inert materials [12]), the results from leaching tests are excellent. The glass satisfies the most stringent leaching requirements in accord with the German, Japanese and Swiss legislation [7].



## 5. Discussion and conclusions

The investigations show that the AshArc and Deglor smelting processes produce homogenous glassy products from MSWI residues with variable amounts of several types of metal-rich minute inclusions, such as metal alloys, sulphidic alloys, and traces of oxide and silicate. The AshArc process generates a product with lower heavy metal concentrations due to the reducing atmosphere in the furnace compared to the Deglor process.

Some heavy metals such as lead and copper are significantly enriched in metal-rich inclusions. Even if the volumetric proportion of inclusions is distinctly smaller than 1 %, enrichment factors of 1000 to 10 000 (as estimated for lead) between melt and sulphidic inclusions lead to a significant portion of total lead bound to metal-rich inclusions. The leaching behaviour of a residue with respect to lead becomes then a function of both, the rate of deterioration of the glass matrix as well as the accessibility and decomposition rate of the metal sulphides. Also, the partitioning behaviour of metals between melt and additional refractory phases may influence the effectiveness of heavy metal depletion by evaporation during the thermal process. An indirect indication that a large part of cadmium and lead is concentrated in the inclusions in AshArc residues was provided by the fact that the standard deviations from the AAS measurements were much higher for the AshArc samples with abundant inclusions than for the Deglor samples (below) with only few inclusions.

The heavy metal zinc is very soluble in silicate melt and does not partition preferentially into metallic alloys or sulphides as do copper, nickel and lead. The latter heavy metals are not observed to enter silicate mineral structures which is in contrast to zinc that can occur as a major component in several calcium aluminosilicates (e.g., melilite) where it is present in fourfold coordination. This is indicative of potentially tighter bonding of ZnO in silicate melt compared to other heavy metals. Structural studies of the local order in oxide glasses show indeed that the Zn–O coordination is fourfold [15]. This may explain the ineffectiveness of loss of zinc by evaporation despite its relatively high vapour pressure measured in pure metal vapour or chloride vapour systems [16]. Zinc concentrations in some glassy residues remain a problem compared to the current limits for total concentration (1000 ppm) set by Swiss legislation for inert materials [12], even though the leaching behaviour by any accepted standard is well within limiting aqueous concentrations. It is known that ZnO in the glass matrix improves the leaching resistance in alkali and acidic solutions [17].

Glassy residues have a potential to substitute raw materials for building materials such as concrete and ceramics, or may be designed for other value-added purposes. In theory, such use offers a more economical and more sensible return for the investment of process energy compared to disposal in a landfill. Present legislation in Switzerland [12] does provide, however, little incentive to

pursue such avenues due to the granted permission for (limited) export of fly ash and flue gas cleaning residues for cheap underground disposal in Germany.

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