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5.4 Characteristics, Behavior and Durability of High Temperature Materials

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Foreword

For the purposes of long-term environmental protection and sustainable development, the Swiss authorities have decreed an obligation to incinerate the entirety of non-recyclable municipal solid wastes (MSW), effective as of January 2000 [3]. Today, the conditions to achieve this requirement, *i.e.* the total incineration capacity of the country, are technically fulfilled for the next 25-30 years via a network of 28 incineration plants, which can absorb *ca.* 3×10^6 t MSW/yr. The mass of MSW collected and incinerated every year throughout the country leads to the production of secondary residues from incineration, namely bottom ash (BA; *ca.* 750×10^3 t/yr), fly ash (FA; *ca.* 46.5×10^3 t/yr) and filter cake (FC; *ca.* 11.625×10^3 t/yr). Because of their high content in toxic metals and their high leachability, these secondary residues cannot be recycled for civil engineering applications, and must therefore be deposited in landfills as stabilized or inert material, depending on the properties of the residues [4, 24, 25].

It is therefore pertinent to address the potentialities of the advanced thermal treatment technologies which are said to produce inert secondary residues, hereafter referred to as high temperature materials, which might be reused as a secondary raw material resource. This has been the aim of an in-depth study [167] initiated by the Swiss Agency for Environment, Forests and Landscape (SAEFL/BUWAL), which is in charge of the technical, economical and social aspects of waste policy for the country. This section surveys the main scientific issues resulting from the determination of the characteristics (physical, chemical and microscopic features) and behavior (leachability during corrosion) of 23 secondary materials produced by various high temperature treatment processes. On the basis of these issues, but without consideration of the energetic compatibility and social sustainability of such processes, possible answers are provided for a better future in waste management.

5.4.1 Frame of the Study

The Swiss Technical Ordinance on Waste [3] requires a revision which is informed by consideration of long-term sustainability and environmental impacts of wastes and secondary residues. Within this frame, the SAEFL has addressed basic questions on the long-term durability of the materials originating from alternative high temperature treatment technologies (hereafter referred to as HT materials and HT processes). These questions are summarized as follows:

- Taken as a generic class of residues, do the intrinsic characteristics and long-term behavior of the so-called HT materials exhibit substantial improvements over conventional BA, FA and FC residues?
- If so, is it possible to distinguish between the different types of HP processes and their input material in order to design general rules for process optimization toward HT materials in compliance with the concept of sustainability?
- Which guidelines can be derived from the results to revise the TOW in the direction of a more sustainable management of waste in Switzerland?

HT Materials and Standards

To answer these questions, a series of 23 by-products originating from 16 various HT treatment processes developed by 10 different companies in Switzerland, Germany, France and Italy, were extensively studied. HT materials were produced under realistic conditions (*e.g.* from wastes representative of average MSW) and were sampled so as to avoid interpretation biases.

The classification of HT samples is based on the input material from which they were produced; this makes no assumption of the various technologies used to produce HT materials. Two main families of processes, schematically depicted in Figure 5.55, can be distinguished on the basis of their dominant input material:

- In-line processes: These include technologies which operate at higher than normal temperature during incineration.
- Post-processes: These include technologies which treat the residues obtained by conventional thermal treatment of MSW. Two additional sub-categories are given, depending on the dominant type of residues:
  - Post-processes for BA: treat mostly the BA fraction of residues.
  - Post-processes for FA: treat mostly the FA fraction of residues.

This study does not present the exhaustive physico-chemical status of HT treatment processes of wastes and their residues, but, to the best of our knowledge, it is the first of its kind to embrace such a broad range of technologies and input materials (MSW, BA, FA, or mixtures thereof with additives).

For comparative and normalization purposes, the study was also performed on 3 HT standards, SON68, R2bis and R3. SON68 is the non-radioactive surrogate of the nuclear high-level waste (HLW) glass R7T7 designed in France to inertize fission products of nuclear power plants. This borosilicate glass is one of the most studied HLW glasses [18, 52, 77, 162] and is thus an ideal analytical standard and control for our bulk chemical analyses and corrosion tests. R2bis and R3 are HT materials produced in France by the HT treatment of FA under different conditions [57, 58].

HT samples and standards were identified by physical, chemical and microscopic analyses (static picture), their behavior was assessed under corrosive conditions (dynamic behavior), and their long-term durability was estimated with a thermodynamic model (thermodynamic stability).

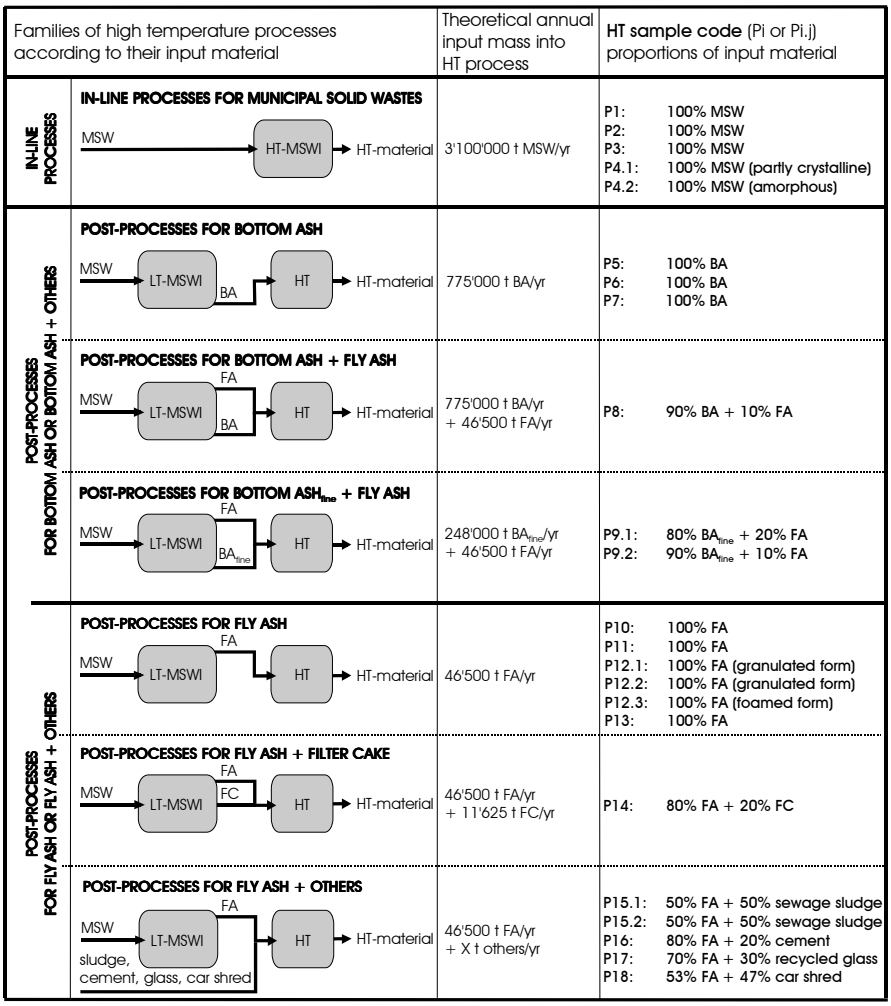

Fig. 5.55. Classification of HT samples on the basis of the input material from which they were produced. In-line processes directly transform MSW into HT material. Post-processes transform residues of MSW incineration (BA, FA, FC, or mixtures of them with possible additives). The codes Pi or Pi.j given to the HT samples denote (i) the process type for a given input material, and when applicable (j) the variations in the operating conditions of this process (*e.g.* different treatment temperatures, or quenching rates, or proportions of input materials). The theoretical annual input mass into HT process is the theoretical mass of input material that should be handled by the given process to treat the total amount of MSW or residues, on the basis of the Swiss waste picture in 2000.

5.4.2 Characteristics of HT Materials: The Static Picture

With respect to the status of knowledge acquired over decades on the characteristics and stability of nuclear high level waste glasses [33, 71, 234, 235, 247], many physical (morphology, crystallinity), microscopic (surface and inner structure) and chemical features (proportions in major and trace elements) of an HT material may play an important role in its long-term behavior. These features are presented and discussed in the next sections.

Morphology

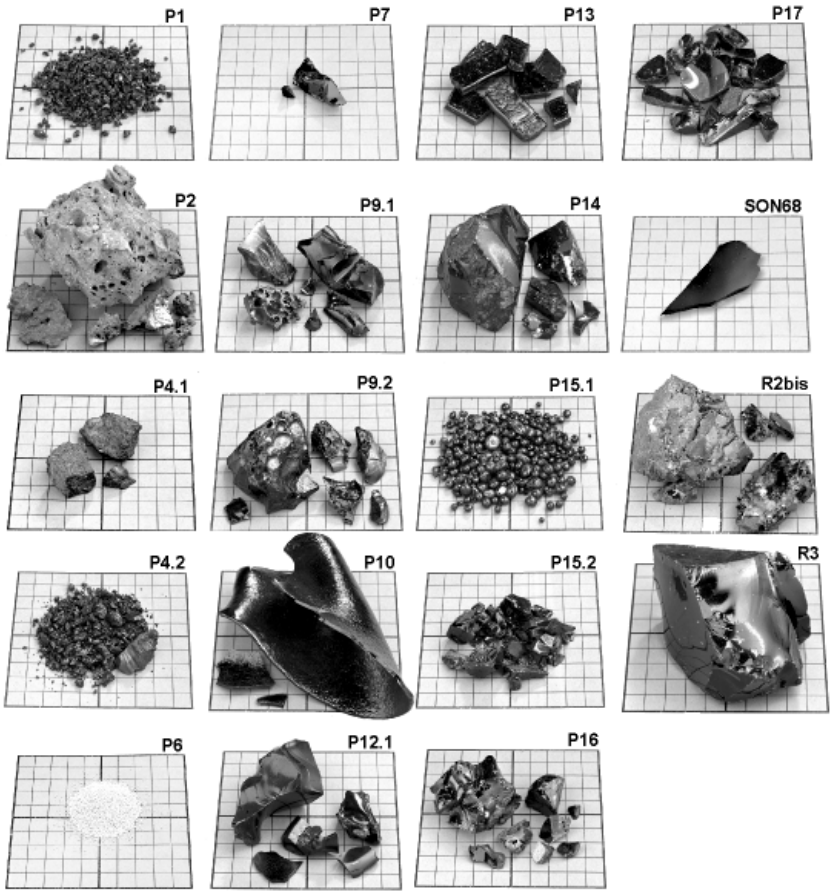

Fig. 5.56. Examples of the various morphologies of the studied HT materials in their original state. The samples are on a 10 cm^2 scaling grid with 1 cm^2 subdivisions. Note the visual dissimilarities between samples prepared from the same HT processes but under slightly different conditions (*e.g.* P4.1 and P4.2; P9.1 and P9.2; P15.1 and P15.2)

Figure 5.56 shows that HT materials exhibit a broad range of morphologies. They range from millimeter-sized grains or granules to thin or thick plates and regularly shaped beads, and to medium or large irregular blocks; their visual appearance extends from homogeneous (glassy aspect) to highly heterogeneous (non glassy or vitrocrystalline). The final morphology of HT materials is affected by the quenching techniques which are used in the different HT treatment processes, but it is not influenced by the input material (MSW, BA, FA, FC, additives). Nevertheless, it is expected that the larger the size of the HT materials the more stable they should be when subjected to corrosion.

Crystallinity

HT materials have been produced at high temperatures (> 1000 °C, except for P6 and P11, obtained at 900 °C) favoring the build up of a silicate melt which may partly crystallize upon slow quenching, or contain relicts of mineral phases inherited from the input material. The degree of crystallinity of the HT material or the proportion of crystalline inclusions in the silicate matrix is a key parameter for classification purposes; it can be determined by semi-quantitative X-ray diffraction.

HT materials containing less than 2 % crystalline components are considered to be vitreous (*i.e.* they have a glassy matrix); HT materials are considered to be vitrocrystalline when they contain negligible amounts of crystalline components, and as crystalline when their crystalline components become significant. Although difficult to quantify unambiguously, HT samples never exhibited purely crystalline characteristics; thus, HT materials belong exclusively to the families of vitreous and vitrocrystalline materials (vitrocrystalline samples are assigned an asterisk, *e.g.* P2*, to distinguish them from vitreous samples). Figure 5.57 shows typical diffraction patterns of HT samples. It can be seen that vitrocrystalline samples still exhibit a background pattern indicative of silicate glass.

Among the phases identified in vitrocrystalline HT samples, quartz is ubiquitous; albeit ($NaAlSi_3O_8$) and melilite (gehlenite) are also frequently identified, but to a lesser extent. Other exotic phases are present from time to time: diopside ($CaMg(SiO_3)_2$), pyroxenes, forsterite (Mg_2SiO_4), portlandite, Fe-Mg-spinels, Fe-Ti-oxides.

It is difficult to draw unambiguous conclusions on the presence of crystalline components in HT materials; crystalline inclusions may be depleted or enriched in heavy metals, and their individual leachability will be either beneficial or detrimental to the overall stability of the HT material [17, 205, 226]. Nevertheless, the silicates and metal oxides identified in HT materials tend to be more resistant to corrosion than silicate glass is. In addition, the metal-embedding characteristics of our HT materials are expected to be stronger than the conventional residues of incineration (BA, FA, FC).

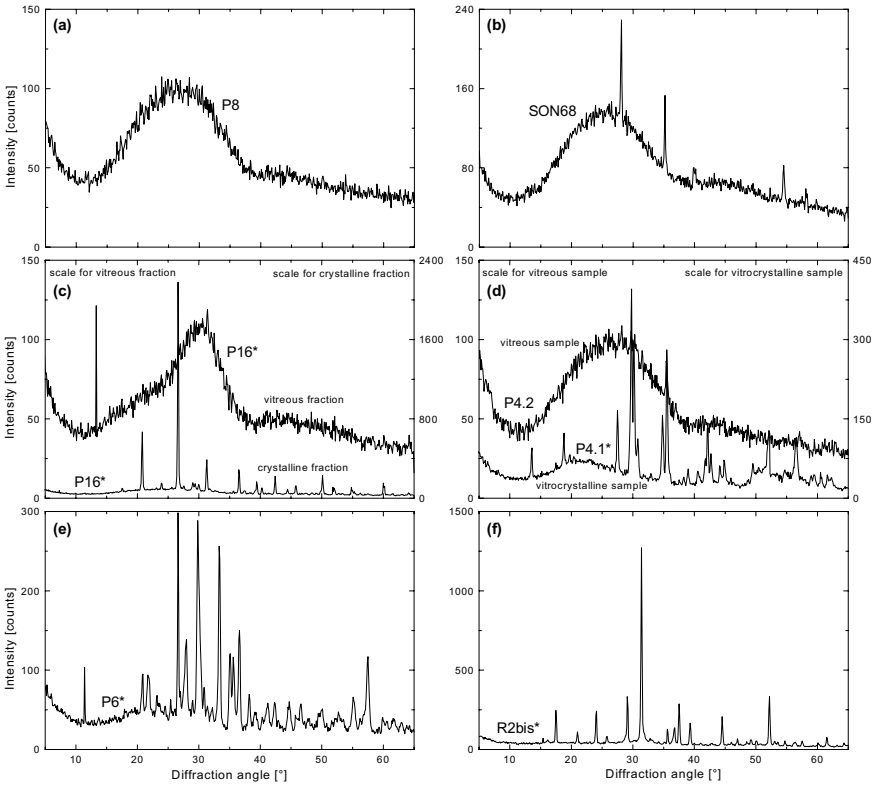

Fig. 5.57. Typical X-ray diffractograms of 100-125 µm ground HT materials, showing either purely vitreous characters (a, b), contrasted vitreous/vitrocrystalline characters (c, d), or purely vitrocrystalline characters (e, f). In Figure 5.57c, the sample P16* (partly vitreous, partly vitrocrystalline) shows large scale heterogeneities. In Figure 5.57d, samples P4.1* (vitrocrystalline) and P4.2 (vitreous) originate from the same HT process, but were obtained from variations in the quenching step

Surface and Inner Structure

The specific surface area S_{spec} of HT materials is a key parameter that directly influences their chemical reactivity at the solid-solution interface, and, in turn, their long-term durability. S_{spec} is partly controlled by the proportion of crystalline inclusions in the glassy matrix of HT materials and partly by the HT process itself, in particular the quenching step.

S_{spec} was determined for 100-125 µm ground HT materials. Taking the standard HLW glass SON68 as the reference for durability with respect to S_{spec} (S_{spec}(SON68) = 383 cm^2/g ; by comparison, S_{spec} = 230 cm^2/g for 100 µm glass spheres) one can discriminate three families of HT materials: Samples with S_{spec}

similar to SON68 (*i.e.* S_{spec} < 600 cm^2/g ; S_{spec}:S_{spec}(SON68) < 1.5), samples with S_{spec} larger than SON68 (*i.e.* S_{spec} = 600-1000 cm^2/g), and samples with S_{spec} much larger than SON68 (*i.e.* S_{spec} > 1000 cm^2/g). With the exception of P1 (S_{spec} = 607 cm^2/g), vitreous HT materials exhibit a low specific surface area, close to that of SON68. Alternatively, HT materials P12.1*, P16* and R2bis* also display a low S_{spec} though they are vitrocrystalline. Vitrocrystalline HT materials P2*, P6* and P11* are characterized by very high values of S_{spec} (3600, 8200, respectively 7000 cm^2/g); they are expected, *a priori*, to exhibit a higher reactivity during the initial stages of corrosion. Nevertheless, these values of S_{spec} reflect ground samples, not the initial status of HT materials.

The surface structure and bulk inclusions of 100-125 μm ground HT materials were characterized through scanning electron microscopy. A close examination of micrographs (Fig. 5.58) indicates that there is fairly good agreement between S_{spec} and the apparent roughness of HT materials, regarding their extent in surface and bulk mineral inclusions (an indication of the inhomogeneity of the samples).

With respect to surface roughness, HT materials were classified as smoother than, similar to, or rougher than the standard SON68. Surprisingly, HT samples exhibit fewer mineral inclusions than the standard SON68, or at most the same proportions of inclusions, whatever their vitreous or vitrocrystalline state. Nevertheless, the combination of the roughness and inclusion features confirms that vitrocrystalline HT materials are less favorable than SON68, with the exception of sample P16* (roughness similar to SON68 and fewer inclusions than SON68). As previously observed, there is no relationship between the surface and inner structure of HT materials (S_{spec}, roughness, inclusions) and the family of processes by which they were produced.

Semi-quantitative and detailed petrographic analyses of surface and bulk mineral inclusions indicate the presence of a very large palette of phases, the most abundant ones being spinels, alloys, plagioclase, quartz, gehlenite, melilites, pyroxene, silicates and metallic inclusions. Many of them exhibit metal enrichment (in particular Cr, Cu, and Zn, which are the dominant trace elements in most HT samples).

Major Elements

The composition of HT materials (Fig. 5.59) plays a dominant role in their durabiliy [93, 205]. Although subtle changes in the proportion of certain elements may affect their characteristics, it has been shown that silicon, the dominant network-forming element, is the most critical parameter for the durability of glasses. Aluminum may also influence durability, acting either as a network-forming element in tetrahedral sites or as a network-modifying element in octahedral sites. By contrast, calcium (and to a lesser extent magnesium) is a network-modifying element which detrimentally affects glass durability.

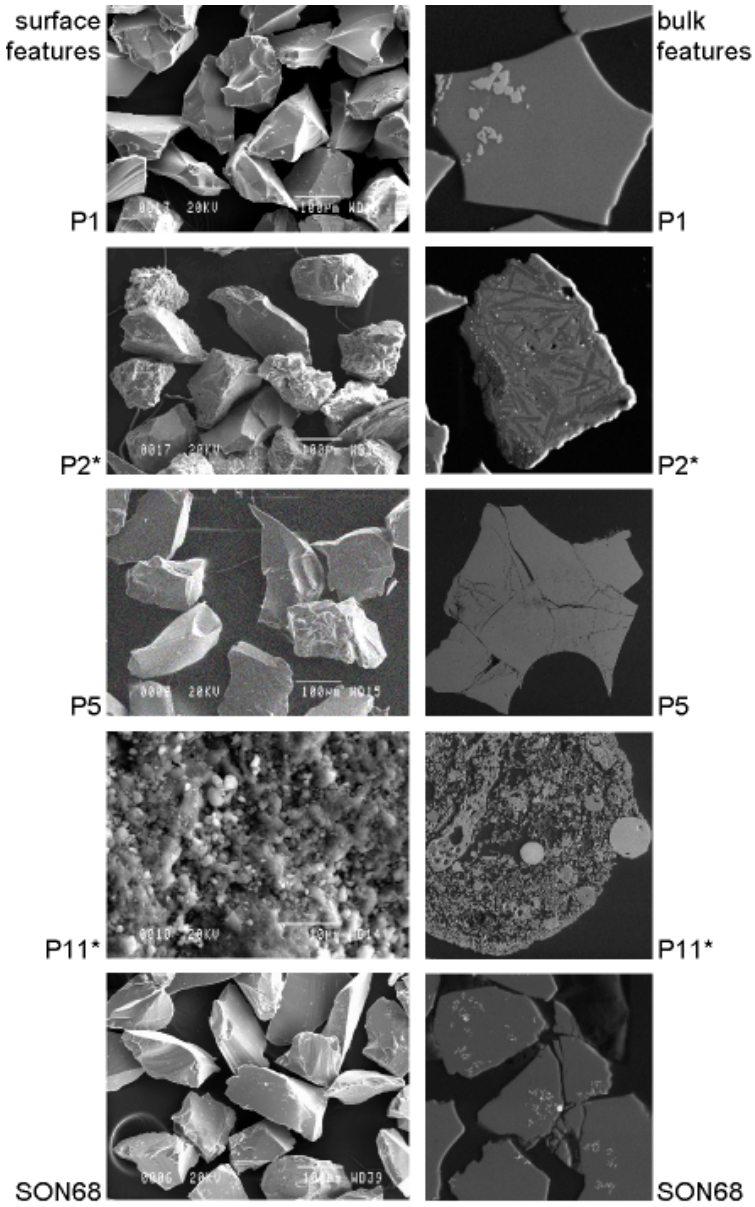

Fig. 5.58. Scanning electron micrographs of 100-125 µm ground HT materials. Left: Surface features (apparent roughness; SEM in secondary electrons mode). Right: Bulk features (density of mineral inclusions; SEM in backscattered electrons mode on resin-embedded and polished samples)

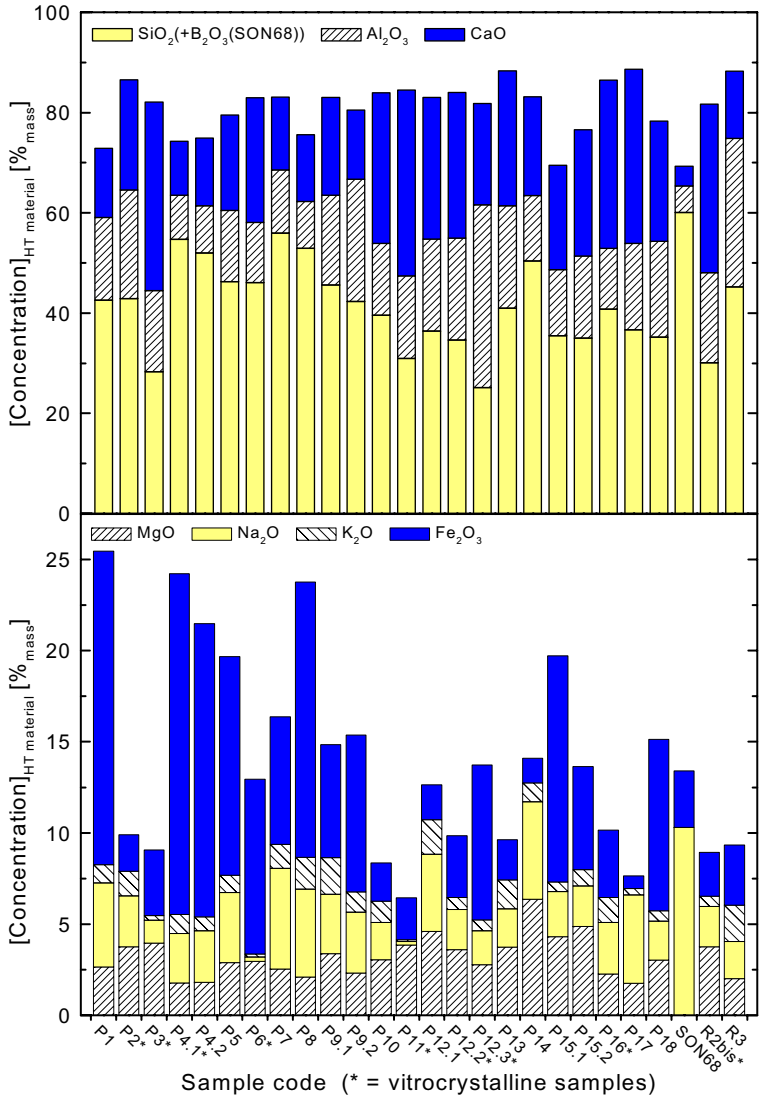

Fig. 5.59. Proportions of the major constituents in HT materials. Top: SiO_2 (network-forming), Al_2O_3 (network-forming or modifying) and CaO (network-modifying); for the HT standard SON68 (borosilicate glass), SiO_2 and B_2O_3 (added during vitrification for better control on the plasticity of the melt) have been summed up. Bottom: MgO, Na_2O, K_2O and Fe_2O_3

Our HT materials have physical and microscopic characteristics similar to glasses, and we expect them to exhibit contrasting features connected with their Si, Al and Ca content; in particular, SiO_2-rich HT materials should have a longer lifetime when subjected to corrosion.

For all samples and standards, $[SiO_2 + Al_2O_3]$ = 45-75 %; this is an indication that HT materials should exhibit a high durability, at least the vitreous ones. There is no relationship between proportions of major constituents and crystallinity, though CaO and SiO_2 are inversely related. This is true in particular for HT materials produced by post-processes for fly ash, where the ratio $[SiO_2]$:[CaO] tends to be much lower (1.4 for P10-P18) than for in-line processes (2.94 for P1-P4.2) or post-processes for bottom ash (2.92 for P5-P9.2).

MgO, Na_2O, K_2O and Fe_2O_3 exhibit large variations from one material to another: their sums range between 6 % and 25 %, with no influence from process family or crystallinity. It is known that alkali-poor glasses are more durable than alkali-rich ones, because the latter build up phase-separated glasses with reduced resistance to corrosion [205, 224]; however, these constituents should not drastically influence the durability of HT materials, as the sum of their concentrations never exceeds 7 %, except for the standard HT material SON68 ($[Na_2O + K_2O]$ = 10 %).

Trace Elements

The concentrations of heavy metals in HT materials with regard to environmental impacts and possible recycling are of utmost importance. Of course, a high amount of metal in an HT material does not necessarily translate into a large release of the metal under corroding constraints.

Overall, the concentrations of metals in a HT material are a good indication of the efficiency of the HT process in solubilising them and embedding them in the matrix of the material during melting. In addition, $[metal]_{HT\ material}$ is a useful comparative parameter with respect to the existing trigger values of the TOW, even if these apply exclusively to residues of conventional incineration (BA, FA, FC).

Figure 5.60 shows the concentrations of nine environmentally relevant metals in HT samples and standards. There is indeed no correlation between the families of HT processes and the metal contents $[metal]_{HT\ material}$, although several HT processes for fly ash accumulate larger amounts of the most volatile elements Cd, Zn, Pb and Sb.

For comparative purposes, Table 5.17 highlights the limited number of HT materials that would be admitted for disposal in landfills for inert materials on the exclusive basis of the Swiss legislation. Most HT materials contain between 1 and 5 metals that exceed the TOW limits. Indeed, it would be misleading to assess the critical sustainability of HT materials on the exclusive basis of their metal content without determining their release rate during corrosion.

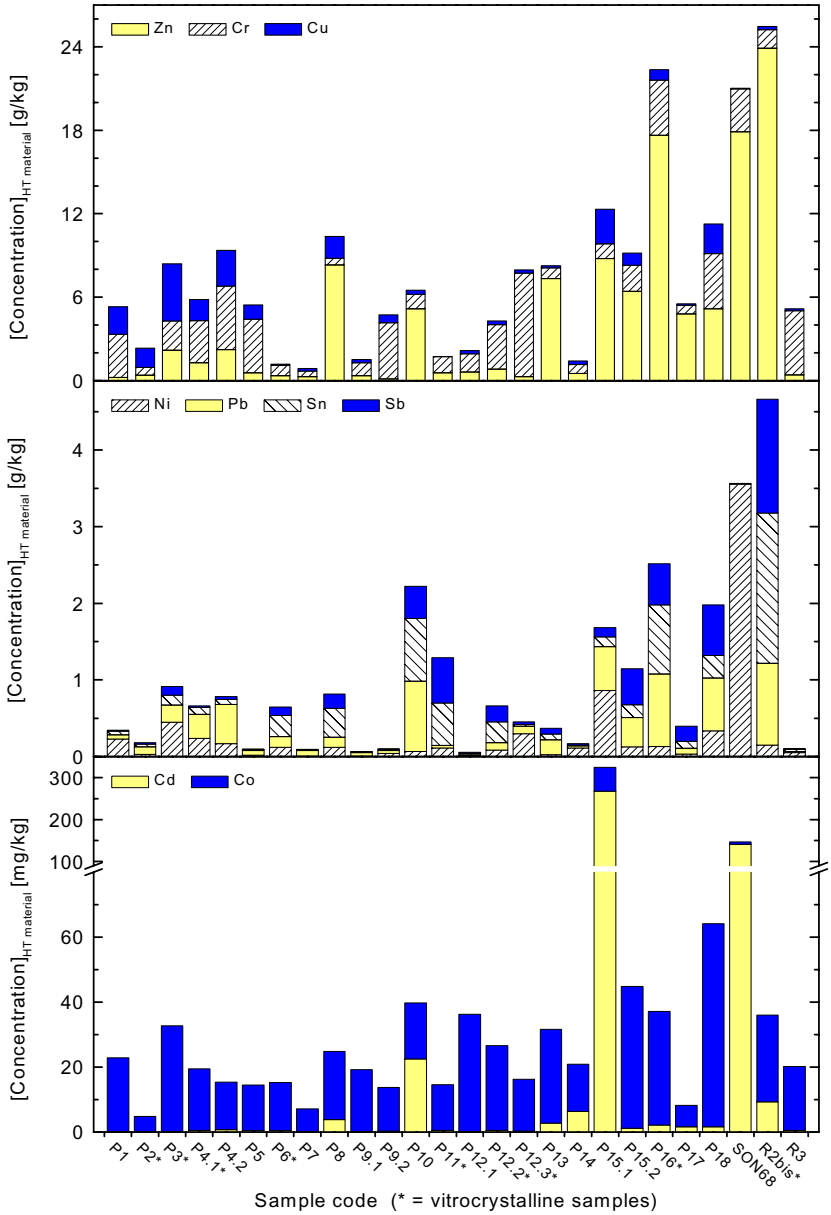

Fig. 5.60. Concentrations of nine environmentally relevant metals in HT materials

Table 5.17. Matrix of admissibility for disposal of HT materials in landfills for inert materials, according to the maximum allowed concentrations of heavy metals (TOW trigger value ; in parentheses). For HT materials that would not be admitted, the numbers indicated are the ratio $[Element]_{HT\ material}$:$[Element]_{TOW\ limit}$. Cr, Sn, Sb, Co, which are not listed in the TOW, are not mentioned here

HT material	Admissible in landfills for inert material	Elements above the maximum concentration allowed by TOW				
		Zn (1 g/kg)	Cu (0.5 g/kg)	Ni (0.5 g/kg)	Pb (0.5 g/kg)	Cd (0.01 g/kg)
P1	no		4 ×			
P2*	no		2.8 ×			
P3*	no	2.2 ×	8.2 ×			
P4.1*	no	1.3 ×	3 ×			
P4.2	no	2.2 ×	5.1 ×		1.02 ×	
P5	no		2.1 ×			
P6*	yes					
P7	yes					
P8	no	8.3 ×	3.1 ×			
P9.1	yes					
P9.2	no		1.1 ×			
P10	no	5.2 ×			1.8 ×	2.3 ×
P11*	yes					
P12.1	yes					
P12.2*	yes					
P12.3*	yes					
P13	no	7.4 ×				
P14	yes					
P15.1	no	8.8 ×	5 ×	1.7 ×	1.2 ×	26.7 ×
P15.2	no	6.4 ×	1.8 ×			
P16*	no	17.6 ×	1.5 ×		1.9 ×	
P17	no	4.8 ×				
P18	no	5.2 ×	4.3 ×		1.4 ×	
SON68	no	17.9 ×		7.1 ×		14.1 ×
R2bis*	no		23.9 ×		2.1 ×	
R3	yes					

The Global Static Picture of HT Materials

Taken as a whole, HT materials do not show obvious trends with respect to their physical, microscopic or chemical characteristics. It is thus difficult to draw general conclusions pertaining to the quality of these materials, because of the wide diversity of their parent processes (in-line or post-processes) and input materials. Nevertheless, the following differentiations can be summarized:

- HT materials are either homogeneous and vitreous, or heterogeneous and vitrocrystalline. The former should be less reactive under corroding conditions, while the mineral phases of the latter could account for contrasting reactivities. Purely crystalline materials were not identified.
- HT materials either exhibit a smooth surface with a small specific surface area and few mineral inclusions, or a rough surface with a large S_{spec} and a high density of inclusions. With some exceptions, these characteristics fit well together with the other physical characteristics (*i.e.* a vitreous material is homogeneous, with a small S_{spec}, a smooth surface and only few mineral inclusions, if any).
- With respect to the TOW limiting values for admissibility in landfills for inert materials, HT products either contain acceptably low proportions of toxic metals or too high proportions of these elements. It is not possible to differentiate between HT materials on the basis of their major constituents, in particular SiO_2, CaO and Al_2O_3, which account for *ca.* 70-90 % of the total mass of samples, as there is no reference material that could be used as a boundary for classification purposes. However, HT materials with a high ratio ($[SiO_2] + [Al_2O_3]$):[CaO] should theoretically exhibit a moderate reactivity.

Although a clear relationship between all physical, microscopic and chemical characteristics is difficult to establish, a combination of the measured parameters into a single descriptive figure would help to find plausible explanations for the expected behavior and durability of HT materials under corroding conditions. This is the purpose of the ternary diagram depicted in Figure 5.61.

The diagram combines all parameters discussed previously, *i.e.* vitreous or vitrocrystalline state, low or high specific surface area, surface smoothness or roughness, presence of few or many mineral inclusions, and a content in toxic metals below or above the TOW limiting values. Several minerals and rocks or anthropogenic materials are also indicated for comparison. Remarkably, HT materials belong to the domain of compositions that are able to form a silicate structure (area above the larnite - gehlenite - mullite boundary).

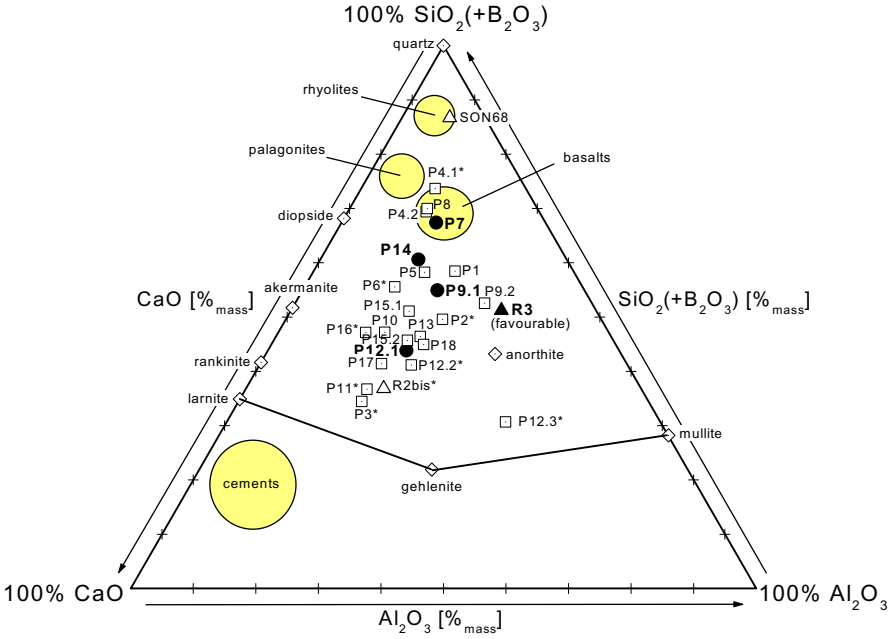

Fig. 5.61. Ternary SiO_2 - Al_2O_3 - CaO diagram of HT materials (solid circles and dotted squares), HT standards (solid and open triangles), rocks (rhyolites, palagonites, basalts ; areas), minerals (dotted diamonds) and cements (area). The line joining the minerals larnite, gehlenite and mullite is the boundary between silicate networks and crystalline structures (ortho-silicate). For HT materials, it is considered that [SiO_2] + [Al_2O_3] + [CaO] (+ [B_2O_3] for SON68) = 100 %. HT materials exhibiting an exclusively favorable static picture are depicted with a solid circle ; HT materials with at least one less favorable characteristic are depicted with a dotted square

A detailed analysis of data indicates that vitrocrystalline HT materials are distributed across the lower part of the diagram (with the exception of P4.1*). This is also roughly the case for HT materials which either present a high S_{spec}, a rough surface, or many mineral inclusions. On the other hand, HT materials containing toxic metals above the TOW limits are spread throughout the diagram, without relationship to their physical or microscopic characteristics.

In the ternary diagram of Figure 5.61, HT materials have globally favorable characteristics (dotted circles) when all their physical, microscopic and chemical characteristics are propitious to a lower reactivity and a higher durability (*i.e.* vitreous and low S_{spec} and smooth and only few inclusions and no toxic metal above the TOW limits). On the other hand, and under worst-case conditions, HT materials with at least one of their characteristics classified as detrimental are considered less favorable.

Only a limited number of HT materials (P7, P9.1, P12.1, P14 and the HT standard R3) exhibit consistently favorable static properties. It must however be kept in mind that this restrictive classification is not exact, as it is based on qualitative operator-dependent parameters (smoothness, density of inclusions), quantitative parameters (crystallinity, S_{spec}), and TOW trigger values which were not originally designed for HT materials.

In conclusion, HT materials cannot be clearly distinguished according to their origin. The large variability in input materials, thermal processes and quenching modes makes it difficult to extract obvious parameters controlling the final static picture of these products. The static picture of HT materials is therefore not sufficient to establish pertinent guidelines for their recycling or disposal into landfills. Nevertheless, the determination of the physical, microscopic and chemical characteristics of HT materials forms a sound basis for comparison and interpretation of their behavior under conditions of corrosion, as discussed in the next section.

5.4.3 Behavior of HT Materials: The Dynamic Picture

As already stated, there is no *a priori* relationship between the toxic metal content of HT materials and their long-term behavior, and it is thus not possible to forecast the evolution of a given type of HT material disposed of in a landfill or reused in civil engineering applications on the sole basis of its concentrations of metals.

For instance, a CaO-rich HT material will develop high pH values during corrosion, which may accelerate dissolution of the glassy matrix on a short-term basis; under these conditions, however, the apparent release of metals may diminish as a consequence of metal hydroxide precipitation. In addition, a high pH may favor the long-term formation of secondary zeolites, acting as a physico-chemical barrier against further corrosion. Likewise, an HT material with a high density of mineral inclusions shall have a higher reactivity under corroding constraints, but some of these mineral phases may be efficient metal scavengers. Consequently, one relies on the direct determination or estimation of the long-term behavior of HT materials under typical situational conditions to assess their compliance with respect to environmental impacts.

With nuclear HLW glasses, several corrosion experiments have been performed over a span of decades under real conditions of leaching (e.g. [33, 56, 71]). For a given HLW glass formulation, these long-term experiments highlight the consequences of specific constraints on the release of radionuclides and other species in the environment. However, for obvious practical reasons, one cannot consider testing a given HT material over a period of decades prior to making a decision about its final destination. As a consequence, one relies on the estimation of the long-term behavior of HT materials by means of accelerated corrosion tests, as is also the case for nuclear HLW glasses [18, 27, 33, 162].

Accelerated corrosion tests usually offer accurate insight into the mechanisms of matrix corrosion and kinetics of species release. However, these tests can only give rough estimates of the long-term behavior of the tested materials, because

they are always performed under conditions far from realistic corrosion (*e.g.* high temperature, high concentrations of leachants, high reactive surfaces, *etc.*). One must thus keep in mind that accelerated corrosion tests, whatever their set-up, offer responses for situations of worst-case conditions.

Conditions of Accelerated Corrosion

In order to obtain the most accurate picture of the behavior of HT materials, the experimental set-up of the accelerated corrosion was performed under carefully controlled and reproducible conditions. For experimental reasons and because of the diversity of the HT materials (small granules, fragments, large blocks) a specific corrosion test, hereafter referred to as the Strasbourg test, was developed for this study; its main features are:

- Type of test: Static (no flow-rate, no stirring, closed vessel);
- Leachant: Ultrapure water (pH evolves freely during corrosion);
- Sample preparation: 100-125 µm ground HT materials;
- Ratio sample:leachant: *ca.* 50 mg:100 mL;
- Temperature: 90 °C;
- Duration: 1 day, 3 days, 10 days;
- Post-corrosion measurements: Analysis of the leachates for their pH and content in major, minor and trace elements; determination of the microscopic surface features of the corroded samples.

The chemical analyses of leachates are expressed either in absolute concentration $[C_i]_{leachate}$ (*i.e.* concentration of element i in leachate, in [g/L]), or in apparent normalized loss NL_i (NL_i [g/m^2] = $\{[C_i]_{leachate} \times V_{leachant}\} / \{[C_i]_{HT\ material} \times S_{HT\ material}\}$, with $V_{leachant}$ = volume of leachant [L], $[C_i]_{HT\ material}$ = concentration of element i in the HT material [g element/g sample], and $S_{HT\ material}$ = surface of HT material exposed to leachant [m^2]).

Absolute concentrations are useful in the comparison of the release of one given element from different HT materials, while apparent normalized losses are helpful in the comparison of the releases of different elements from one given HT material; in this context, NL_i values provide access to the mechanisms of corrosion (*e.g.* differentiation between congruent and selective releases from one HT material). To a certain extent, apparent normalized losses also help in comparing the mechanistic behaviors of different samples for one given element.

Surface Features after Corrosion

The micrographs in Figure 5.62 are a pertinent starting point in the discussion of the physico-chemical consequences of the corrosion of HT materials. These micrographs exhibit the surface structure of HT materials prior to corrosion and after 10 days corrosion. A qualitative estimate of the modifications undergone by samples during corrosion was also performed by a comparison of the apparent

roughness, the density of mineral inclusions and the analysis of the mineral phases present at their surface, prior to and after corrosion.

Corroded HT materials exhibit almost systematically an amorphous gel layer and crystalline secondary phases. In some instances, pits and holes with preferential corrosion pathways are visible. Although experiments were performed without stirring, several samples show traces of spallation of the gel layer, suggesting that corrosion may be a discontinuous process. It is expected that the growing gel layer acts as a diffusion barrier and reduces further hydrolysis of the silicate network. Additionally, the gel layer is supposed to be chemically more durable than the silicate network, thus reducing the overall rate of corrosion. However, exfoliation of the gel layer leaves a fresh and reactive surface, which may momentarily accelerate corrosion, at least locally; this phenomenon suggests that mechanical constraints could partly govern the premature disaggregation of HT materials.

The petrographic analysis of secondary mineral phases identified at the surface of corroded HT materials yields a large, yet not exhaustive, variety of species, and a high sample-to-sample variability, suggesting that the surface reactivity of HT materials is influenced by the composition of their silicate network. The most abundant minerals identified are aluminosilicates, calcium phosphates, iron-rich phases, minerals enriched with magnesium, and even zeolites. The distinction between primary and secondary minerals is indeed difficult for HT materials showing a high heterogeneity (*e.g.* P2*, P6*, P11*). Nevertheless, no assumption can be made as to the role of these mineral phases, which may either act as scavengers of trace metals or enhance their release in solution. It is, however, expected that secondary mineral phases increase the surface heterogeneity of HT materials, and hence their specific surface area.

Release of Major Elements

The apparent matrix dissolution of HT materials, expressed as the absolute concentrations of the major elements Si (network-forming), Al (network-forming or modifying) and Ca (network-modifying) released in the leachates after 1 day, 3 days and 10 days of corrosion, is shown in Figure 5.63. Information on the true release of elements, *i.e.* their extraction from the silicate network, is not readily accessible because significant proportions of many elements released are usually immobilized into secondary minerals at the surface of corroded HT materials, or precipitated at the surface or in solution during corrosion, and also because most glasses have been observed to develop a gel layer which partly scavenges the extracted elements [61, 62, 89, 148, 172].

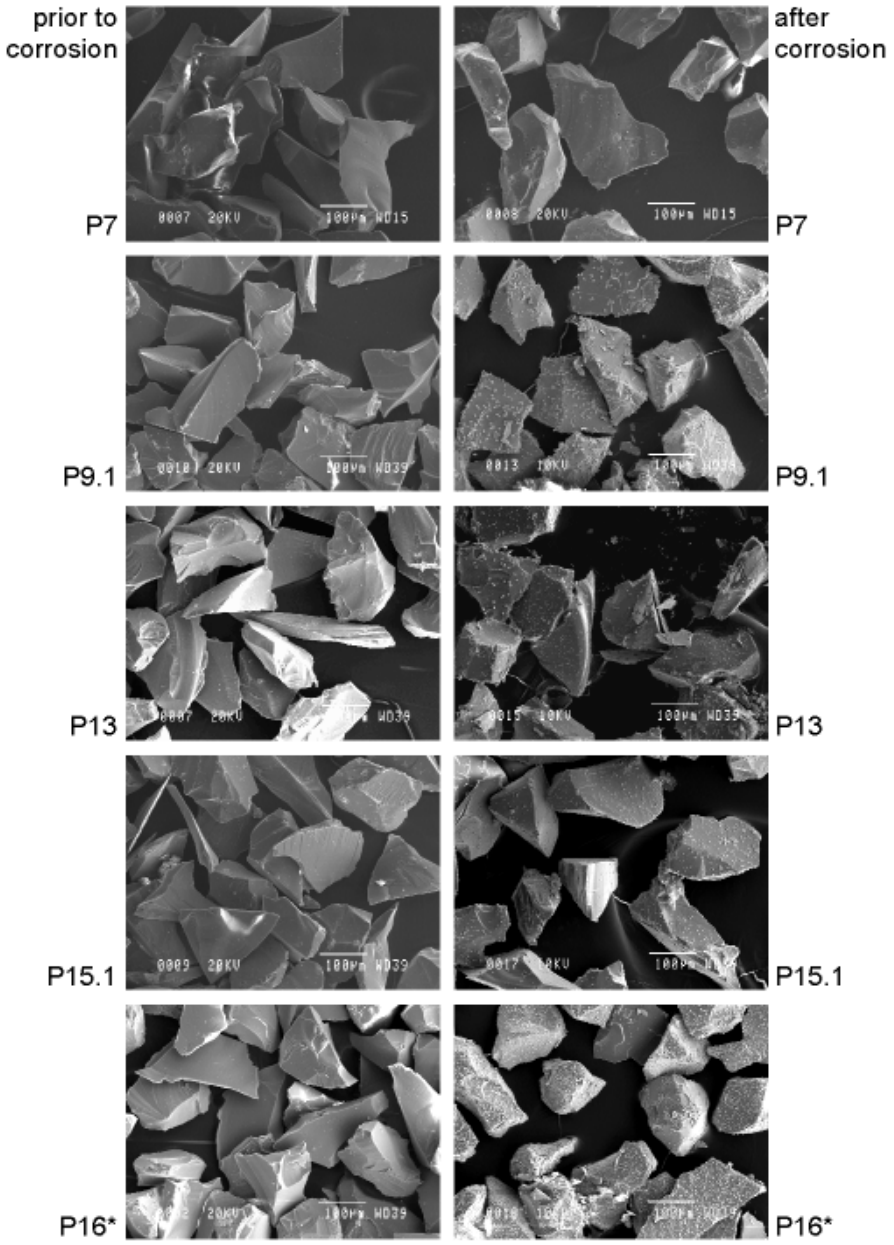

Fig. 5.62. Scanning electron micrographs (SEM in secondary electrons mode) of the surface features of 100-125 µm ground HT materials. Left: Prior to corrosion. Right : After 10 days corrosion in H_2O at 90 °C

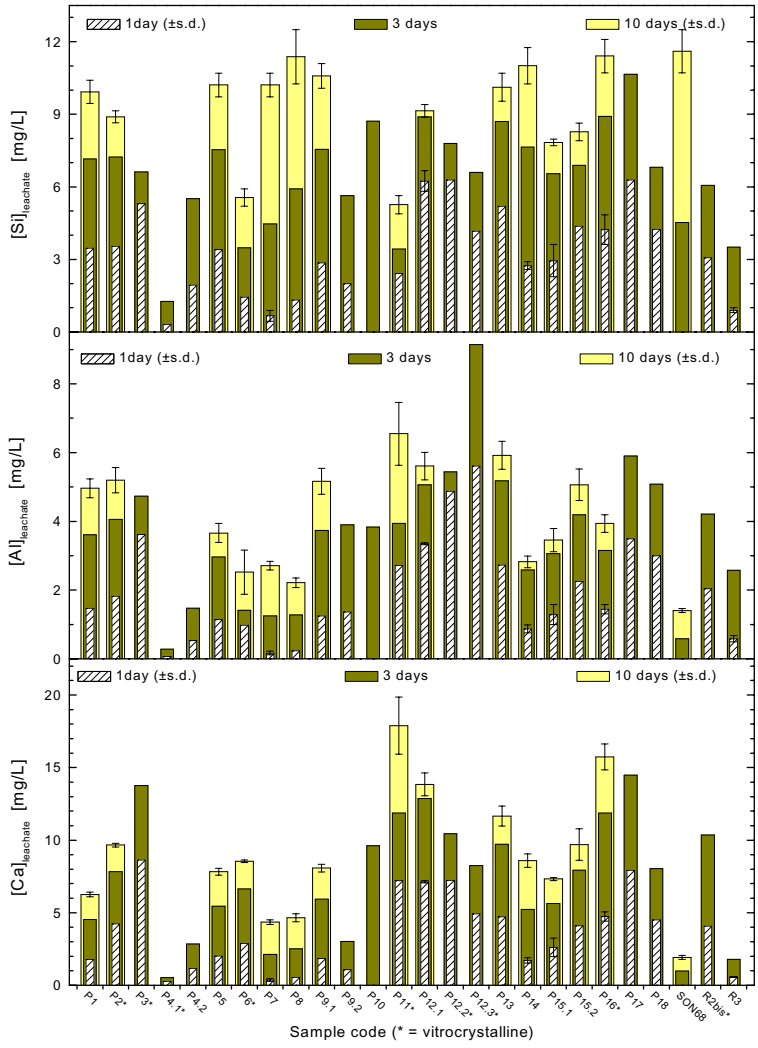

Fig. 5.63. Concentrations of Si, Al and Ca measured in the 0.2 µm filtered leachates of the Strasbourg test after 1 day, 3 days and 10 days corrosion of *ca.* 50 mg ground HT materials in 100 mL H_2O at 90 °C. For duplicate analyses, the minimum and the maximum concentrations are also displayed as error bars

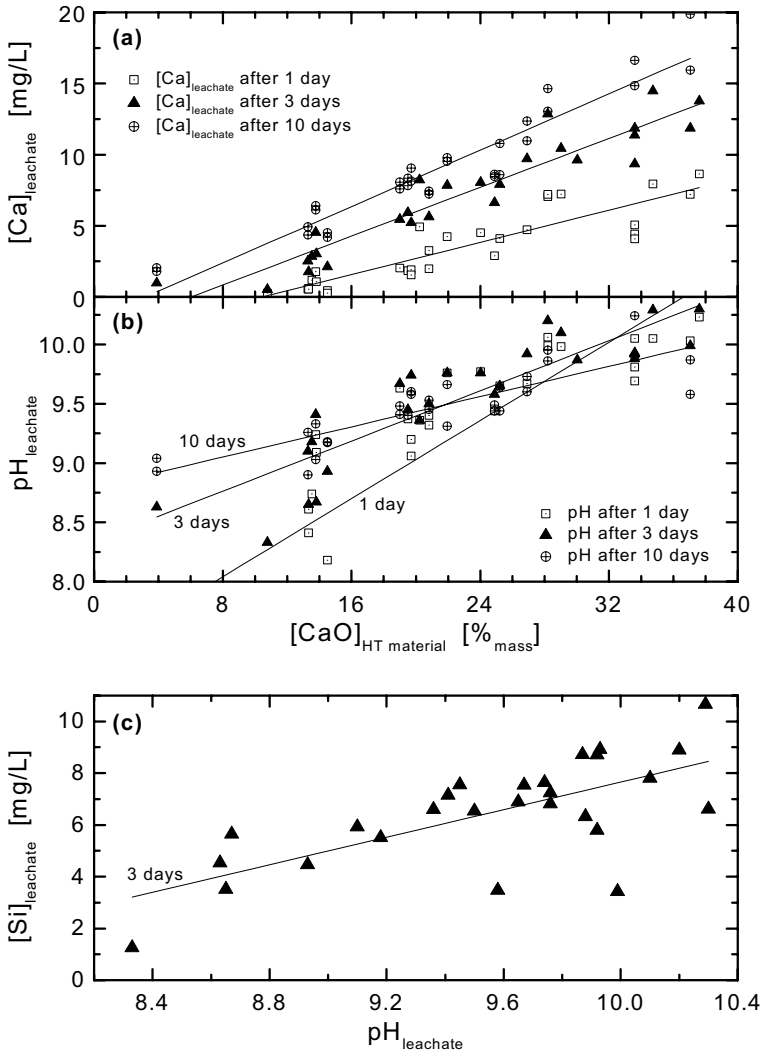

Fig. 5.64. Relationships between strongly correlated parameters measured in the leachates. (a) $[Ca]_{leachate}$ *vs.* $[Ca]_{HT\ material}$ shows the direct influence of the amount of calcium in the matrix of HT materials on the release of this element after 1 day, 3 days and 10 days corrosion. (b) $pH_{leachate}$ *vs.* $[Ca]_{HT\ material}$ shows that the pH of the leachate is mostly, but not exclusively, controlled by the the amount of Ca in the matrix of HT materials. (c) $[Si]_{leachate}$ *vs.* $pH_{leachate}$ (after 3 days corrosion) shows that the dissolution of the matrix is pH-dependent

The concentrations of major elements released in solution increase with corrosion time. The trend is, however, different from sample to sample, and from element to element. After 1 day of corrosion, the release of silicon ranges from 0.4 mg/L (P7) to 6.7 mg/L (P12.1), but the difference is less pronounced after 3 days (1.3 mg/L (P4.1*) to 10.7 mg/L (P17)), and even less after 10 days (4.9 mg/L (P11*) to 12.5 mg/L (P8, SON68)); this indicates that the release of Si stabilizes over time. Similar observations can be made for the release of aluminum and calcium, but the global sample-to-sample fingerprints of Si, Al and Ca do not superimpose; this suggests that matrix dissolution follows specific pathways (*e.g.* different solution chemistries and/or secondary phases formed). These differences cannot be explained in terms of process families (in-line processes, post-processes) or crystallinity of the HT materials.

Figure 5.64 shows the strong relationships which exist between $[Ca]_{HT\ material}$, $[Ca]_{leachate}$, $pH_{leachate}$ and $[Si]_{leachate}$. In fact, calcium, a network-modifying element, is easily extracted from the silicate network of HT materials (Figure 5.64a), and the released amounts of Ca are directly related to the proportion of Ca in the HT materials. This alkaline-earth is present in fairly large amounts in samples (11 % (P4.1*) to 38 % (P3*), except for SON68 (4 %)), and its release primarily governs the pH of the leachates (Figure 5.64b) as given by the following reactions:

$$\{CaO\}_{HT\ material} + 2H_2O \rightarrow Ca^{2+} + 2OH^-$$

$$\{CaSiO_3\}_{HT\ material} + 2H_2O \rightarrow Ca^{2+} + H_4SiO_4 + 2OH^-$$

$pH_{leachate}$ increases with time, but the effect is more pronounced between 1 and 3 days than between 3 and 10 days, indicating that pH stabilizes rapidly during matrix dissolution, as is observed for Ca, Al and Si.

Silicon, in turn, dissolves under the influence of alkaline conditions (Figure 5.64c), as expected from the mechanisms of glass corrosion described in [56, 205], which shows that the higher the pH, the less stable the silicate network :

$\{\equiv Si\text{-}O\text{-}Si(OH)_3\}_{HT\ material} + OH^- \rightarrow \{\equiv Si\text{-}O^-\}_{HT\ material} + H_4SiO_4$ (hydrolysis of the external silicate network)

$\{\equiv Si\text{-}O\text{-}Si\equiv\}_{HT\ material} + OH^- \rightarrow \{\equiv Si\text{-}O^-\}_{HT\ material} + \{HO\text{-}Si\equiv\}_{HT\ material}$ (hydrolysis of the internal network)

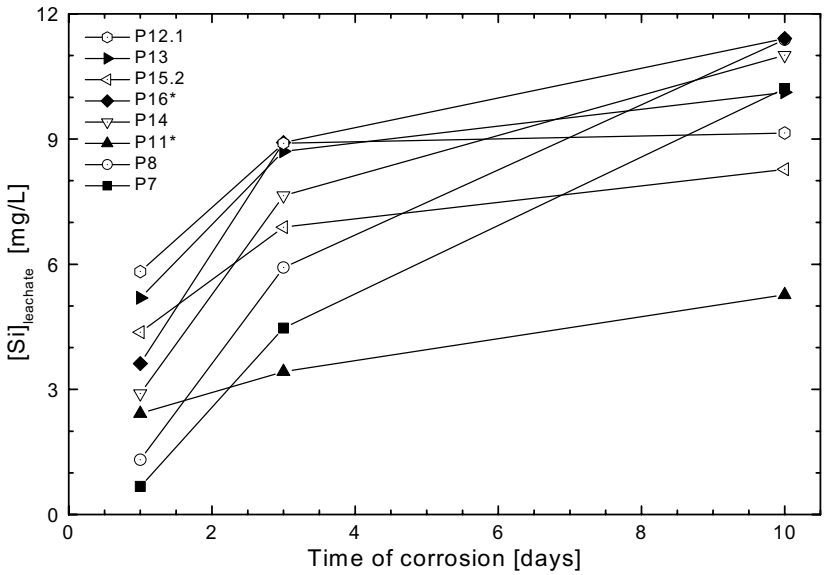

Fig. 5.65. Evolution of the concentration of Si in the leachates of several HT materials corroded during 1 day, 3 days, and 10 days. The temporal fingerprint is different from sample to sample

Mechanistically, corrosion of HT materials by pure water leads to the release of Ca, which in turn increases the pH of the leachate, with a concomitant enhancement of matrix dissolution and Si release; the apparent rate of these mechanisms decreases with time but is sample-dependent, as exemplified in Figure 5.65. These observations suggest that Ca-poor HT materials (*i.e.* Si-rich HT materials) are less prone to corrosion, and thus more durable, than Ca-rich HT materials, without a strong influence of other physico-chemical parameters. However, the variable short-term behavior of HT materials, at least with respect to the dominant component SiO_2, makes it difficult to accurately predict their long-term stability with regard to corrosion, or even to make a classification of HT materials on the basis of their dynamic picture.

Although the evolution of the major elements Al, Ca, Na and K in the leachates does not superimpose onto the evolution of Si, their trend is globally similar to that of Figure 5.65: Concentrations in the leachates stabilize over time. On the other hand, Mg exhibits a different behavior: After an increase between 1 and 3 days of corrosion, $[Mg]_{leachate}$ drastically decreases, indicating the formation of Mg-rich secondary phases, either in solution or at the surface of the corroded HT materials. This is in agreement with the identification of abundant Mg-rich secondary mineral phases at the surface of samples after corrosion.

Release of Trace Elements

The time profiles of the major elements indicate that the strong element-to-element and sample-to-sample differences follow no specific trend with respect to the physical, microscopic and chemical characteristics previously discussed. This is also clearly observed for the trace elements Cr, Co, Ni, Cu, Zn, Cd, Sn, Sb and Pb, which show highly contrasting fingerprints in leachates, both in terms of element-to-element and sample-to-sample dissimilarities. Table 5.18 summarizes the average and maximum concentrations of these trace elements measured in the leachates, along with the maximum amount of concentrations permitted according to the TOW leaching test used for the disposal of wastes and residues of incineration in landfills for inert materials.

Indeed, the Strasbourg test developed for this study and the TOW leaching test cannot be directly compared: The former is performed in ultra-pure water at 90 °C during a period of 10 days, with a ratio mass:volume = 50 mg:100 mL, *i.e.* under more aggressive conditions than the latter, which is performed in CO_2-saturated water at room temperature [2]. Nevertheless, the measured concentrations of trace elements released during corrosion are remarkably low (Co, Cd, Sn, Pb : below 1-5 µg/L ; Cr, Ni, Cu, Zn, Sb : below 10-100 µg/L) and systematically beneath the maximum concentrations allowed by Swiss regulations. By comparison, untreated bottom ash or fly ash usually leads to much higher metal concentrations in leachates when corroded under the conditions of the TOW leaching test.

Table 5.18. Average and maximum concentrations of metals measured in the leachates after 1 day, 3 days, 10 days corrosion of HT materials under the conditions of the Strasbourg test (50 mg ground HT material in 100 mL H_2O at 90°C, without stirring). HT standards (SON68, R2bis, R3) are omitted. For comparison, the maximum concentrations of metals allowed by the TOW test for disposal of residues in landfills for inert materials are given

	1 day corrosion		3 days corrosion		10 days corrosion		TOW limit
Elements	$[M^{n+}]_{mean}$ [µg/L]	$[M^{n+}]_{max}$ [µg/L]	$[M^{n+}]_{mean}$ [µg/L]	$[M^{n+}]_{max}$ [µg/L]	$[M^{n+}]_{mean}$ [µg/L]	$[M^{n+}]_{max}$ [µg/L]	$[M^{n+}]_{max}$ [µg/L]
Cr	b.d.l.	b.d.l.	b.d.l.	b.d.l.	30	40	50
Co	0.18	0.40	0.05	0.14	0.04	0.09	50
Ni	b.d.l.	b.d.l.	b.d.l.	b.d.l.	14	22	200
Cu	b.d.l.	b.d.l.	b.d.l.	b.d.l.	14	19	200
Zn	19	25	37	113	27	47	1000
Cd	0.06	0.10	0.04	0.10	1.1	2.7	10
Sn	0.20	0.64	0.20	0.65	0.13	0.69	200
Sb	2.9	10	6	26	7	38	no limit
Pb	0.27	0.74	0.37	2.2	0.29	2.5	100

b.d.l. below detection limit

Although a detailed mechanistic interpretation of the results is not possible, trace metals extracted from the silicate network can be scavenged by the amorphous gel layer or by secondary minerals which form at the surface of the HT materials, thus explaining the very low concentrations in the leachates. This is of course a favorable behavior of HT materials with regard to the initiation of toxic metals into vitreous and vitrocrystalline silicate networks.

Without making any distinction between elements, processes, or duration of the leaching experiments, the release of major, minor and trace elements in leachates is not congruent: Apparent normalized release rates r_{norm} ($r(i)_{norm} = dNL_i/dt$) range between *ca.* 10^{-4} g/m^2·d and *ca.* 30 g/m^2·d. Alkali elements (Na and K, but not Rb) are released at higher rates ($r(i)_{norm}$ around 0.5-1.8 g/m^2·d) than network-forming and network-modifying elements (Si, Al, Ca, Mg, Sr, Ba ; $r(i)_{norm}$ around 0.2-0.6 g/m^2·d); indeed, the former are mostly released in solution without side reactions, while the latter are partly re-incorporated into secondary minerals, thus highlighting the complex solution and secondary phase chemistries involved and the non-congruency of the mechanisms of release [18, 88]. Fe and Mn ($r(i)_{norm}$ around $2 \cdot 10^{-2}$ g/m^2·d) are almost exclusively precipitated into secondary minerals during matrix dissolution, leaving no Fe or Mn in the leachates. Trace elements exhibit highly contrasting behaviors, and are either retained in crystalline phases (*e.g.* Cr-, Ni- and Co-spinels, Zn-melilite) or dissolved in the leachate. Apparently, process families influence the normalized release rates of major elements (in-line processes > post-processes for FA > post-processes for BA).

What is probably the most important feature observed during corrosion is the possibility to discriminate HT materials with respect to the initial stages of network hydrolysis: As shown in Figure 5.66, short-term release rates are highly differentiated from one sample to another, but they rapidly decrease to small, similar values ($r(i)_{norm}$ around 0.2 g/m^2·d). This suggests that the physico-chemical characteristics of HT materials influence their initial reactivity, but that the dissolution rates also converge to low limiting values, whatever the nature of the HT materials.

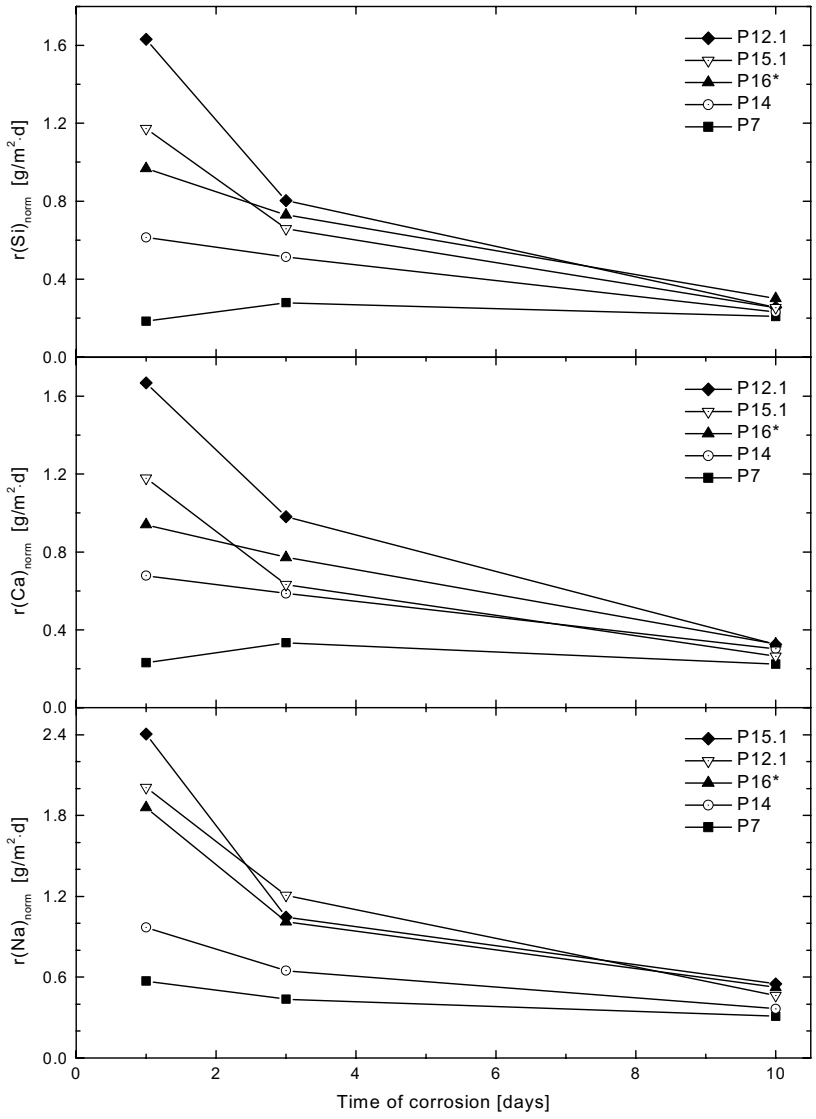

Fig. 5.66. Temporal evolution of the apparent normalized release rates of some major elements in HT materials. Although the initial rates (*i.e.* after 1 day) are different from sample to sample, the rates measured after 10 days tend to a limiting value, whatever the HT material

The Global Dynamic Picture of HT Materials

Figure 5.67 compares HT materials with respect to their corrosion behavior. Materials with a normalized release rate $r(Si)_{norm} \leq$ SON68, such as P1, P2*, P4.1*, P6*, P7, P11* and R3, are considered to have a consistently favorable dynamic picture.

Although the classification is based on relative terms (comparison of $r(Si)_{norm}$), the following considerations can be taken into account for a clearer characterization of HT materials with respect to their behavior during corrosion: Microscopically, several materials develop a gel layer and secondary mineral phases, but their effect is not known in detail. Short-term corrosion (*i.e.* initial release rate) shows large differences from sample to sample and from element to element; this allows for differentiation between fast-reacting and slow-reacting HT materials during the first steps of matrix hydrolysis. Overall, release rates rapidly decrease towards low values (r_{norm} around 0.2 g/m^2·d for Si, Al, Ca after 10 days of corrosion). Finally, the release rates of trace elements are highly scattered, but their concentrations in leachates are systematically and remarkably very low; even under the drastic conditions of the Strasbourg test, $[metal]_{leachate}$ are below the TOW limits for admissibility into landfills for inert materials.

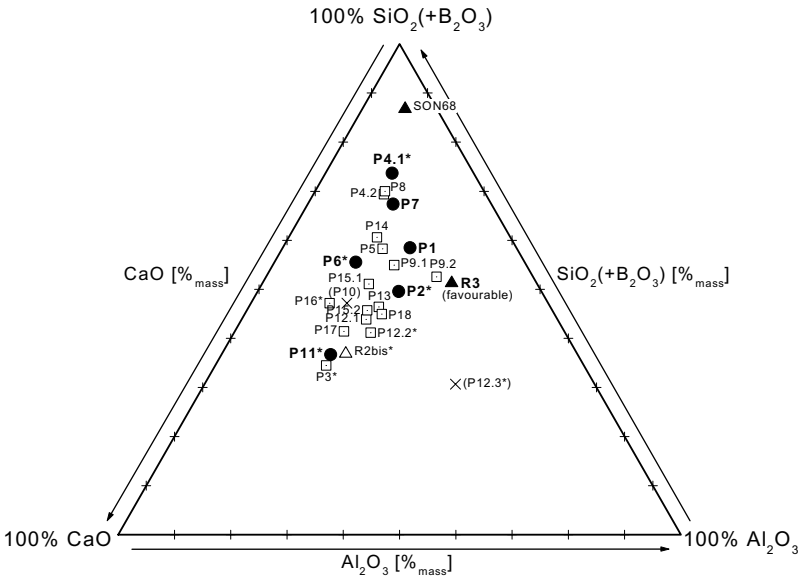

Fig. 5.67. Ternary SiO_2 - Al_2O_3 - CaO diagram of HT materials (solid circles, dotted squares and crosses) and HT standards (solid and open triangles). HT materials exhibiting a favorable dynamic picture (*i.e.* with $r(Si)_{norm} \leq$ SON68) are depicted with a solid circle. HT materials P10 and P12.3* are depicted with crosses, because their normalized release rate could not be calculated (S_{spec} missing). The classification is based on the 3 days corrosion experiment, which was performed on the whole set of samples

The results of the corrosion tests show that the behavior of HT materials during corrosion is in agreement with observations on nuclear glasses and analog materials. Under the conditions of the Strasbourg test, the concentrations of major, minor and trace elements measured in solution are very low (< 20 mg/L for major elements and < 100 µg/L for trace metals after 10 days corrosion at 90 °C). HT materials comply with the conditions of the TOW leaching test for admissibility into landfills for inert materials, even when their content in toxic metals is above the TOW limits (see 5.4.2).

The chemistry of the leachates at the beginning of corrosion is governed by the composition of HT materials, but it evolves rapidly towards similar patterns of behavior. Corrosion is controlled by the pH of the leachate, which is in turn in direct correlation to the amount of CaO present in HT materials. It follows that SiO_2-rich/CaO-poor HT materials are less prone to corrosion, even during the initial stages of alteration.

As already stated, the legitimacy of the actual TOW regulation for the assessment of wastes and residues (*i.e.* the TOW limits on the content of toxic metals and their release during leaching tests) may be addressed. For instance, HT materials like P1, P2* and P4.1* release only minute amounts of toxic metals in the leachates of the Strasbourg test, but could not be admitted into a landfill for inert materials because they contain excessively high proportions of several metals.

5.4.4 Durability of HT Materials: The Thermodynamic Picture

Undoubtedly, the assessment of the long-term stability of HT materials requires realistic conditions of corrosion (*e.g.* burial, landfill disposal, reuse in road construction or other civil engineering applications) during an appreciable amount of time (months to years) in order to allow for kinetically slow mechanisms to take place. This approach is, however, technically difficult to perform, and the alternative of accelerated corrosion experiments is a convenient way to overcome the limitations of real-time alteration experiments. Nevertheless, accelerated corrosion, with its cohort of operational parameters (high temperature, high reactive surface, *etc.*) forcing the solid-solution far from equilibrium, may either overestimate or underestimate in an uncontrolled manner the dissolution rates when extrapolated to realistic conditions.

Another way to estimate the relative durability of HT materials is to make use of thermodynamic models, amongst which the strongly documented thermodynamic assessment of glass hydration is certainly the most appropriate and convenient. The approach requires only a limited number of parameters (composition of HT material; thermodynamic hydration constants of the constituents) for the calculation of the relative stability of an HT material, and its application to a large palette of glasses and analog materials makes it practical for comparative purposes.

In this context, the seminal work of Paul and Newton [159, 160, 165, 166] on the thermodynamics of hydration of glasses and vitreous materials opens strong

opportunities for the estimation of the durability of HT materials on the basis of their composition. According to the concept of Paul and Newton, a glass is a homogeneous assembly of silicate polyhedra of the different constituents present. When subjected to water corrosion, the glass hydrates in proportion to its overall thermodynamic characteristics. The approach is based on simplifying assumptions, *i.e.* the release of species from the glass matrix is a congruent process and no secondary products form at the surface of the glass. The overall free energy of hydration ΔG_{hydr} represents the thermodynamic ability of the glass to hydrate spontaneously in water, and it can be estimated as the molar-weighted sum of the free energies of hydration $\Delta G_{hydr}(i)$ of the individual constituents of the glass.

This concept was later refined and successfully used to predict the long-term stability of nuclear HLW glasses that must be stored in deep geological repositories [33, 71, 111-113, 174, 175, 221]. In addition, it has been observed empirically that there is a fairly good relationship between calculated ΔG_{hydr} of several glass types (HLW, natural, ancient and commercial glasses) and the apparent normalized release rate of major elements during accelerated corrosion experiments. However, the approach had never been used before to predict the relative stability of materials originating from the high temperature incineration of municipal solid wastes or their residues [167, 168].

Application of the Concept of Glass Hydration to HT Materials

A correct definition of glass or vitreous material is required to apply the concept of glass hydration to HT materials. During the high temperature incineration of municipal solid wastes or their residues, the elements present in the melt combine in a liquid phase. Provided that the quenching (cooling down of the melt) is rapid, the liquid phase transforms into a more or less homogeneous solid. This solid is characterized by a 3-dimensional network of tetrahedrons MO_4^{4-} (M = Si, Al, B ; network-forming elements), with network-modifying elements (Ca, Mg, Na, K, Fe) and trace elements being dissolved or intercalated into the matrix. This network is analogous to the homogeneous assembly of silicates in a glass, rather than simply the sum of its oxides.

Therefore, provided that the raw composition of a vitreous HT material is known (and expressed as the oxides of the constituents; *e.g.* SiO_2, Al_2O_3, CaO, Na_2O, K_2O, Fe_2O_3, *etc.*), an assembly of silicates and residual oxides can be built (*e.g.* $CaSiO_3$, $MgSiO_3$, Na_2SiO_3, K_2SiO_3, *etc.*), each having its own free energy of hydration $\Delta G_{hydr}(i)$. In the frame of the present study, the concept of the free energy of hydration of glasses was applied to the vitreous HT materials and extended to the vitrocrystalline HT materials, considering that the structural inhomogeneities (mineral inclusions) of the latter induce only insignificant distortions of the assembly of silicates.

Provided that the hydration of the individual silicates and residual oxides governs the overall dissolution of the HT material, one expresses the free energy of hydration as $\Delta G_{hydr} = \Sigma(X_i \times \Delta G_{hydr}(i))$, where X_i is the molar fraction of the

constituent (i) in the HT material, and the individual values of $\Delta G_{hydr}(i)$ being available in the literature for most silicates and oxides, or calculated as $\Delta G_{hydr}(i) = -RT \times \ln(K_{hydr}(i))$. The more negative values of ΔG_{hydr} correspond to materials that hydrate more spontaneously, *i.e.* that dissolve easily in water. The thermodynamic approach thus consists of estimating the durability of HT materials on the basis of their thermodynamic propensity to corrode, and to relate this durability to the release rate determined experimentally.

Thermodynamic Stability of HT Materials

After conversion of HT materials (expressed as oxides) into the silicates $CaSiO_3$, $MgSiO_3$, Na_2SiO_3, K_2SiO_3, $BaSiO_3$, $ZnSiO_3$, $ZrSiO_4$ and residual oxides SiO_2, Al_2O_3, CaO, Fe_2O_3, MnO_2, TiO_2 (+ B_2O_3, Li_2SiO_3, Cs_2O_3, Nd_2O_3, $SrSiO_3$, NiO, MoO_3, La_2O_3, Ce_2O_3 for the HT standard material SON68), their $K_{hydr}(i)$ are extrapolated for T = 90 °C [18], and their free energy of hydration is calculated as $\Delta G_{hydr}(i) = -RT \times \ln(K_{hydr}(i))$ (for details on the approach, see Perret *et al.*, 2002). The overall free energy of hydration is then calculated as explained above. $K_{hydr}(i)$ values for trace elements are either unknown or subject to large variabilities. These trace elements were therefore not included in the calculation of ΔG_{hydr}, except for Ba, Zn, Zr (known $K_{hydr}(i)$; non-negligible concentrations in several samples). It is estimated that the error in ΔG_{hydr} caused by the missing contribution of trace elements is negligible, except for Cr (up to 7500 mg/kg) and Cu (up to 2500 mg/kg) in some samples.

Figure 5.68 shows the dependency of the calculated ΔG_{hydr} of HT materials on the pH of the leachate, over a much wider range of pH values (1 to12) than the ones measured during the 1-10 days corrosion experiments. The results obtained for vitrocrystalline HT materials are shown for comparative purposes, assuming that their crystallinity is not large enough to impair the overall free energy of hydration. Taken collectively, the thermodynamic stability reaches a maximum at around pH = 5-7.5. As expected from theoretical considerations and experimental observations [166], the hydration becomes more spontaneous under alkaline conditions than under acidic conditions.

Although the observed sample-to-sample variability in ΔG_{hydr} is large ($\Delta G_{hydr,max}$ = +0.1 kcal/mol for P4.1*, the most stable sample; $\Delta G_{hydr,min}$ = -12.6 kcal/mol for P10, the least stable sample), the average stability of HT materials is comparable to that of the durable HLW glass SON68; this is a positive indication of the long-term stability of HT materials. Overall, HT materials produced by post-processes for FA are less stable (ΔG_{hydr} = -9.6 kcal/mol ± 2.0) than the ones produced by in-line processes (-4.7 kcal/mol ± 3.1) or post-processes for BA (-5.0 kcal/mol ± 1.5). This can be accounted for by the higher amount of CaO in HT materials produced from FA.

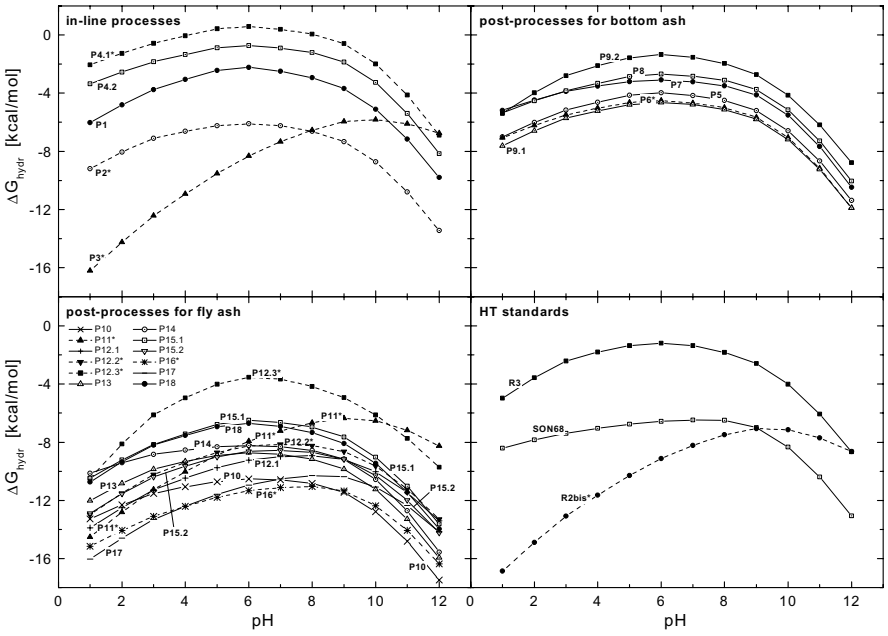

Fig. 5.68. Calculated free energy of hydration ΔG_{hydr} of the HT materials in function of the pH. Solid curves apply to purely vitreous HT materials, for which the model of Paul and Newton was originally designed. Dotted curves apply to vitrocrystalline HT materials. The pH values of the leachates after 1 day, 3 days and 10 days range between 6.7 and 10.3

The overall free energy of hydration of a given HT material is primarily governed by the constituents present in abundant proportions and exhibiting large $\Delta G_{hydr}(i)$ values. $CaSiO_3$ (17-63 %mol ; $\Delta G_{hydr}(i)$ = -16 kcal/mol), and to a lesser extent Na_2SiO_3 and $MgSiO_3$, are the species which contribute mostly to the reduction in thermodynamic stability of HT materials. By comparison, the stabilizing contribution of the oxides SiO_2, Al_2O_3, CaO, Fe_2O_3 and MnO_2 is weaker than the destabilizing contribution of most silicate polyhedra. Nevertheless, calculations clearly show that HT materials containing the largest possible proportions of network-forming elements and the lowest possible proportions of network-modifying elements exhibit the highest thermodynamic stabilities.

Combining Rates of Corrosion and Thermodynamic Stabilities

As previously stated, there exists a clear relationship between the overall free energy of hydration of glasses from different origins and their release rate during corrosion experiments. This empirical relationship was obtained by means of an accelerated corrosion test, the MCC-1 test [33, 66]. This test was designed to assess the leachability of nuclear HLW glasses; it is a static test performed on glass cubes in water, at 90 °C over a period of 28 days.

Due to the intrinsic nature of several of the HT materials, it was not possible to prepare polished monoliths for all samples, and thus the MCC-1 test could not be used. Nevertheless, the MCC-1 and Strasbourg tests can be compared in terms of leaching efficiency ($S_{HT\ material}/V_{leachant})\times t$ ($S_{HT\ material}$ = surface exposed to leachant; $V_{leachant}$ = volume of leachant; t = duration of the corrosion experiment). For the MCC-1 test, $(S/V)\times t$ = 2.8 d/cm. For the Strasbourg test, $(S/V)\times t$ = 0.2-2 d/cm (1-10 days corrosion, S_{spec} = 400 cm^2/g). Thus, both tests can be compared, as their leaching efficiency is in the same order of magnitude.

The validation of the ΔG_{hydr} approach for HT materials is given in Figure 5.69. Apparent normalized release rates of Si, measured after 1, 3, and 10 days of corrosion are plotted in function of the calculated values of ΔG_{hydr}. The results of the MCC-1 test obtained on a series of 115 glasses of different origins [174] are superimposed for comparison.

Whatever the duration of the Strasbourg test, Figure 5.69 exhibits a strong relationship between $r(Si)_{norm}$ and ΔG_{hydr}. The HT standard SON68 (Strasbourg test) yields results very close to the ones obtained for nuclear HLW glasses (MCC-1 test), confirming that both tests are comparable for similar samples and short-term corrosion. A rough difference of 10 kcal/mole between two HT materials translates into an approximate one order of magnitude difference between their dissolution rates. This demonstrates that the thermodynamic approach of the free energy of hydration, though limited by simplifying assumptions, can be applied for the discrimination of HT materials during the initial stage of matrix hydrolysis. After 3 days and 10 days corrosion, the influence of the differences in ΔG_{hydr} on the release rates vanishes. This suggests that the behavior of HT materials depends on the conditions of corrosion, and evolves toward limited and uniform matrix dissolution (*ca.* 0.25 $g/m^2 \cdot d$, calculated from the release of Si after 3 and 10 days).

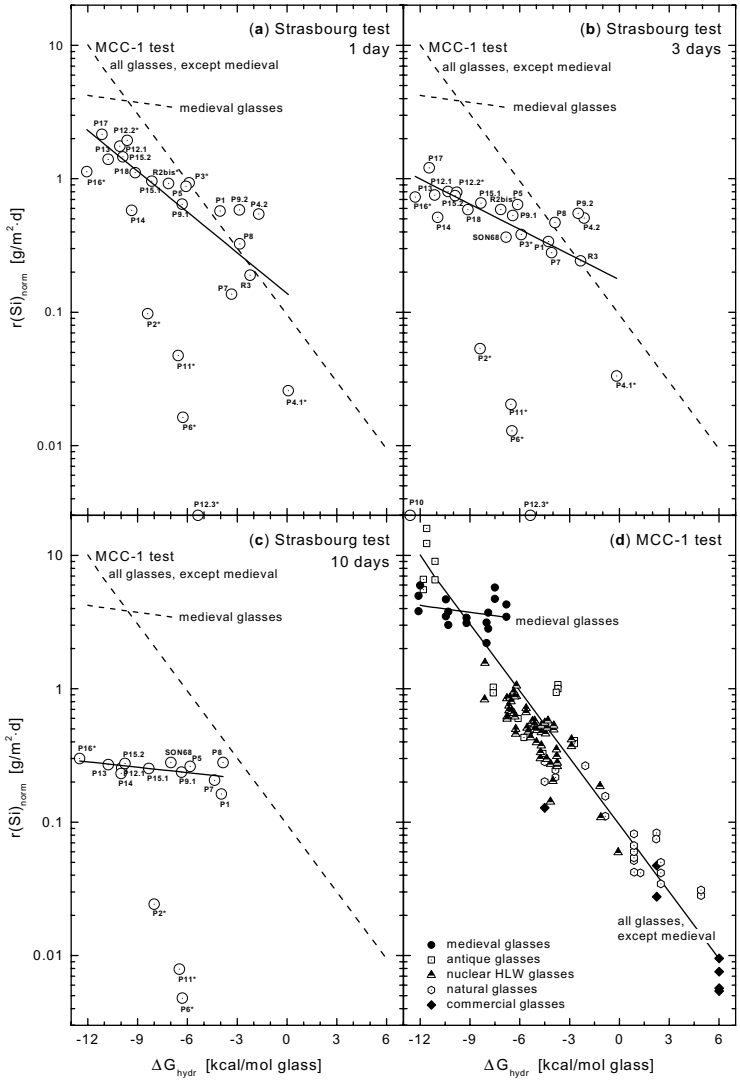

Fig. 5.69. Relationship between the normalized apparent release rate of Si in HT materials, $r(Si)_{norm}$, measured after (a) 1 day, (b) 3 days, respectively (c) 10 days of corrosion under the conditions of the Strasbourg test, and the free energy of hydration of HT materials, ΔG_{hydr}, calculated for the pH values measured after 1, 3, 10 days corrosion. The linear fits exclude P2*, P6* and P11* (S_{spec} too large), respectively P10 and P12.3 (S_{spec} missing). (d) Literature-extracted results [174] of $r(Si)_{norm}$ *vs.* ΔG_{hydr} obtained for 115 glasses of different origins corroded under the conditions of the MCC-1 test (reproduced as dashed lines in plots (a-c))

Figure 5.69 also indicates that the technical discrepancy between the MCC-1 test (blocks) and the Strasbourg test (powder) complicates a comparative interpretation. Blocks corroded under the conditions of the MCC-1 test react under a regime of initial corrosion, while the Strasbourg test facilitates the formation of Si-rich secondary phases, leading to a regime of quasi-equilibrium. This explains the differences in slopes between both tests. However, HT materials (Strasbourg test ; 10 days corrosion) and medieval glasses (MCC-1 test) exhibit similar flat slopes, probably because of the high proportions of Mg in both types of materials; indeed, Mg favors the formation of protective secondary phases on the surface of corroded glasses [61]. Overall, ΔG_{hydr} of HT materials lies within the range of the thermodynamic stabilities of nuclear HLW glasses.

The Global Thermodynamic Picture of HT Materials

It is difficult to extract simple information from the results of the thermodynamic approach, mostly due to the wide diversity of HT materials. Nevertheless, HT materials can be categorized with respect to their free energy of hydration, in comparison to the one of the durable HT standard SON68. In this respect, Figure 5.70 highlights the most and least durable HT materials; it must however be remembered that the results for vitrocrystalline samples are semi-quantitative.

The long-term durability of HT materials is estimated to range between 10^3 years and 10^4 years. This estimation is based on the observed durability of medieval and antique glasses ($\geq 10^3$ years; [226, 261-263], and on the extrapolated durability of nuclear HLW glasses ($\geq 10^4$ years; [263]). Figure 5.69 indicates that medieval, antique and nuclear HLW glasses can be considered (thermodynamically) pertinent analogs of HT materials. The results also show that there is no thermodynamic discrimination of HT materials in relation to their parent process.

Although Si and Ca govern the thermodynamic picture of HT materials, the calculation of ΔG_{hydr} involves the contribution of many other silicates or oxides with different hydration behaviors. The thermodynamic approach provides valuable information for HT process developers on one hand, and for waste management and environmental policy on the other: Subtle changes to the final composition of waste materials (*e.g.* more Si, Al, and in particular Mn; much less Ca) drastically increase their overall thermodynamic stability without impairing their ability to trap toxic metals. For example, 1 $\%_{mol}$ MnO_2 in the HT materials would contribute to +1.3 kcal/mol of their overall free energy of hydration, counteracting the destabilizing influence of, *e.g.*, 8 $\%_{mol}$ $MgSiO_3$.

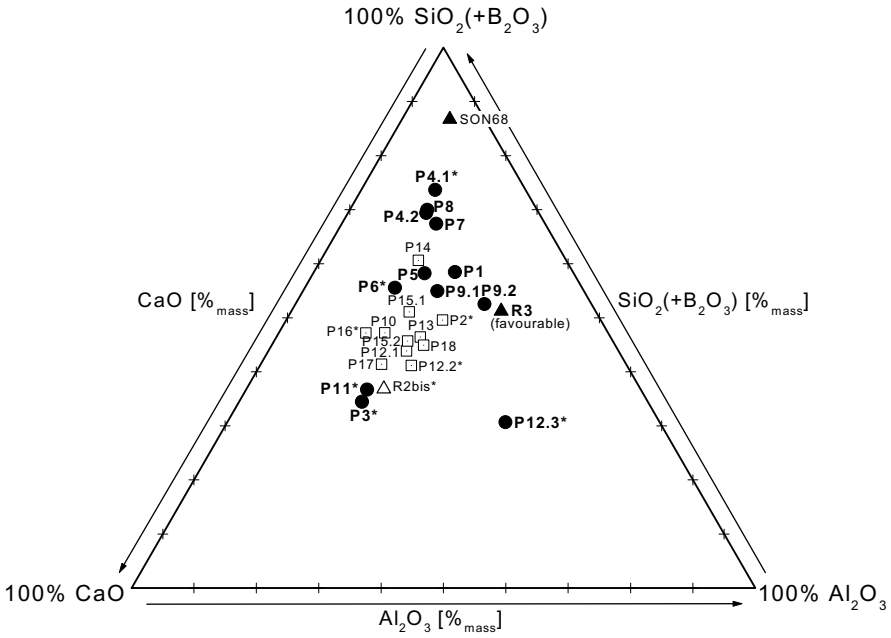

Fig. 5.70. Ternary SiO_2 - Al_2O_3 - CaO diagram of HT materials (solid circles and dotted squares) and HT standards (solid and open triangles). HT materials exhibiting a favorable thermodynamic picture (*i.e.* with $\Delta G_{hydr} \geq$ SON68) are depicted with a solid circle. For each HT material, ΔG_{hydr} was calculated for the pH value measured at the end of the 3 days corrosion experiment

5.4.5 From Facts to Policy

The global survey of the physico-chemical characteristics (static picture), the behavior under aggressive conditions of accelerated corrosion (dynamic picture), and the estimated long-term durability (thermodynamic picture) of HT materials produced from different sources (MSW, BA, FA, FC, or combinations of them) offers the following results and information.

Static Picture

- HT materials cannot be distinguished on the basis of their parent process or on the basis of the input material (MSW, BA, FA or combinations of them). Globally, the process types (in-line or post-processes) do not noticeably influence the final physico-chemical characteristics of the products, provided

that they are operated at higher temperatures than conventional MSW incinerators.
- The size and aspect of HT material is mostly dictated by the quenching technique.
- HT materials are either vitreous or vitrocrystalline; none of them are crystalline. This characteristic is governed by the quenching technique.
- Most HT materials exhibit a favorably low specific surface area (< 600 cm^2/g for the 100-125 μm ground fraction) and are expected to have a poor reactivity towards leachants. Specific surface area and vitreous/vitrocrystalline state are not directly linked.
- With some exceptions, HT materials are microscopically smooth; mineral inclusions, either inherited from the starting wastes and residues, or produced during quenching, are relatively rare.
- Network-forming (Si), intermediate (Al, Fe) and network-modifying (Ca, Mg, Na, K) elements govern the status of HT materials. The sum of SiO_2 (25-56 %), Al_2O_3 (9-37 %) and Fe_2O_3 (1-19 %) ranges between 48 % and 82 %, while network-modifying elements are present in moderate amounts (CaO = 11-38 %; MgO = 2-6.5 %; Na_2O = 0.2-5.5 %; K_2O = 0.1-2 %; sum = 16-43 %).
- HT materials contain significant amounts of toxic metals, which is an indication of the favorable ability of HT processes to embed these metals in the vitreous or vitrocrystalline matrix. However, the high levels of metals in several HT materials would make them inappropriate for disposal into landfills for inert materials with respect to actual Swiss regulations.

Dynamic Picture

- During corrosion of HT materials in water (Strasbourg accelerated test), the pH of leachates increases but stabilizes rapidly. pH is mostly governed by the release of Ca in solution, which in turn directly correlates to the amount of Ca in HT materials.
- High pH values (pH > 9.5) enhance the hydrolysis of the silicate network. SiO_2-rich/CaO-poor ([SiO_2]:[CaO] > 2) samples develop lower pH during corrosion and exhibit a higher stability than CaO-rich samples.
- The leaching of major, minor and trace elements is not congruent, and the behavior of HT materials is highly differentiated during the initial stage of corrosion under the conditions of the Strasbourg test (1 day), but element releases systematically decrease toward small, undifferentiated values.
- Alkali (Na, K) are released at higher rates ($r(i)_{norm}$ = 0.5-1.75 $g/m^2 \cdot d$) than alkaline earths (Ca, Mg, Sr, Ba), network-forming (Si) and intermediate (Al) elements ($r(i)_{norm}$ = 0.2-0.6 $g/m^2 \cdot d$). This reflects the differentiated incorporation of these elements into secondary minerals formed during corrosion.
- The maximum releases of toxic trace metals during the batch corrosion experiments are systematically below the maximum limits allowed by Swiss regulations. In most instances, $[metal]_{leachate}$ is < 100 μg/L (Cr, Ni, Cu, Zn, Sb),

and even below 5 µg/L (Co, Cd, Sn, Pb); on this basis, all HT materials would be admissible into landfills for inert materials.
- Microscopically, the majority of HT materials develop a protective amorphous gel layer during corrosion, sometimes partly exfoliated, with visible pits and holes; the formation of secondary mineral phases completes the apparent surface modifications caused by corrosion.

Thermodynamic Picture

- The theoretically maximum thermodynamic stability of HT materials is calculated to be around pH = 5-7 (*i.e.* HT materials would have the highest stability if $pH_{leachate}$ could be confined around 5-7); experimentally, most HT materials are slightly less stable ($pH_{leachate}$ = 6.7-10.3 during the Strasbourg test).
- Taken collectively, the thermodynamic stability of HT materials compares with the one of the standard nuclear HLW glass SON68 (ΔG_{hydr} = -0.16 kcal/mol for the most stable, -12.6 kcal/mol for the least stable, -6.8 kcal/mol for SON68), which is a favorable indication of their long-term durability.
- SiO_2-Al_2O_3-rich and CaO-MgO-poor HT materials exhibit the highest thermodynamic stabilities. In this respect, post-processes operating fly ash as their main input material produce on average HT materials with lower stabilities than post-processes for bottom ash and in-line processes for municipal solid wastes.
- For medium-term corrosion (Strasbourg test, 10 days corrosion) the combined dynamic and thermodynamic behavior of HT materials resembles that of medieval glasses. On shorter terms (1 day corrosion), HT materials can be compared to nuclear HLW glasses. From these results, the estimated durability of HT materials spans between 10^3 years and 10^4 years.

Assessment of HT Materials: A New Paradigm

As can easily be concluded from the information herein, HT materials, despite differences in their static, dynamic and thermodynamic pictures, behave collectively favorably in comparison to bottom ashes or fly ashes produced by conventional low temperature MSW incinerators. Whatever their status and reactivity, HT materials release very low amounts of toxic metals, at least in batch mode under the aggressive conditions of the Strasbourg test. Thus, the information acquired from the characterization of our HT materials allows one to derive general guidelines for the quality of a globally favorable HT product originating from the high-temperature treatment of municipal solid wastes or their residues:

- No process family yields high-temperature materials with a consistently superior quality;
- A tendency towards superior properties is expected for HT materials with a high macroscopic homogeneity, a low specific surface area, and a high Si:Ca ratio or a high Si content;

- The production of HT materials should be performed at a high temperature (T > 900 °C) to guarantee a vitreous or vitrocrystalline state;
- HT processes should have an energy consumption efficient enough to meet the requirements of sustainable development; according to the principles of risk prevention, HT processes should lead to HT materials from which metals have been extracted.

With regard to the establishment of environmental guidelines for the possible disposal or reuse of HT materials, we are faced with the following dichotomy: On the one hand, HT materials have a high propensity to embed toxic metals in their matrix, and most of them would thus not fulfill the requirements of the existing TOW with respect to their metal content. On the other hand, HT materials are very stable during corrosion, and their low metal releases, which are much lower than the TOW limits, allow them to comply with the requirements of the existing TOW with respect to their leachability in toxic metals.

Hence, the existing Swiss regulation on waste management, originally designed for bottom and fly ashes and their impact on the environment, is no longer appropriate for the proper redirection of HT materials. Provided that high temperature incineration technologies would be gradually introduced in Switzerland, the assessment of the ultimate fate of their products should thus be based on updated regulations, taking into account the high efficiency of HT materials in inertizing toxic metals over long-term periods.

Our results show that these materials have favorable static, dynamic and thermodynamic characteristics; these results should be considered as a sound environmentally oriented database to be used within the framework of the revision of the Swiss regulations on the sustainable management of wastes and their residues.

Undoubtedly, other considerations should also be taken into account in order to assess the complete picture of such materials. For example, energy fluxes required to operate HT processes and the economical and environmental impacts of elevated energy consumption must be estimated. The possibility of optimizing HT processes toward the fine tuning of the final characteristics of HT materials (*e.g.* use of stabilizing additives) must be explored. Redirection of HT materials to civil engineering purposes (*e.g.* foundation layers for road construction; additives for the production of cement or concrete, see section 3.5) must also be assessed in terms of ecological, technical and economical feasibility (*e.g.* liberation of metals under various conditions of use, mechanical stability, cost-effective use of surrogate materials). Finally, the environmental definition of reusable *vs.* non-reusable HT materials needs to be translated on a local and regional scale and for short- to long-term periods of time, in terms of predicted fluxes of toxic substances released to the ecosystems by these materials, in comparison to other natural and anthropogenic fluxes.

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