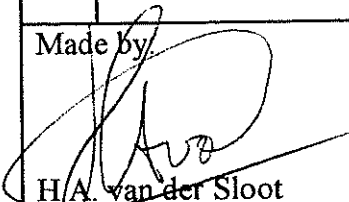
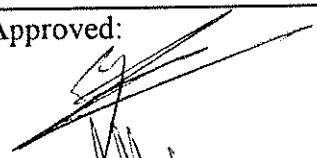
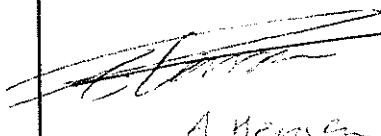
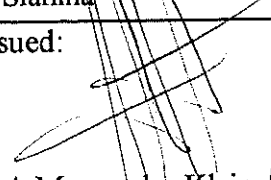


# LEACHING CHARACTERISTICS OF LEAD-ZINC PRIMARY SMELTERS SLAGS

Final report BRE2-CT-94-0585

H.A. VAN DER SLOOT  
D. HOEDE

Revisions		
A		
B		
Made by:  H.A. van der Sloot	Approved:  J. Slanina	ECN-Fuels Conversion & Environment
Checked by:  A. Heuser	Issued:  C.A.M. van der Klein (9/12/97)	

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# 1. INTRODUCTION

Lead and zinc primary smelters in Europe produce and dispose every year about 1 Mt of slag. The objectives of the ECN contribution to the Brite Euram project on valorization of primary lead and zinc slags are to facilitate the beneficial uses for Pb and Zn slags by determining their leaching characteristics under a number of different exposure conditions and thus to define the boundary conditions for environmentally sound application of slags. This type of characterization can be used at the same time to model release and to identify means to improve leaching properties of slag. While in recent years, significant improvements in both "conventional" (lead blast furnace or ISF) or "new" (Kivcet - QSL) processes have been achieved, the solid slags generated by these processes are still largely dumped. The five smelters operate the processes mentioned here under :

SMELTER	COUNTRY	FURNACE TYPE
BRITANNIA ZINC	United Kingdom	ISF
METALEUROP	France	ISF
MIM Hüttenwerke	Germany	ISF
ENIRISORSE (Temav)	Italy	ISF
BERZELIUS Stölberg	Germany	QSL
METALEUROP	France	LBF
ENIRISORSE (Temav)	Italy	Kivcet

The main goal of the work is to reach a common approach and understanding of the leaching properties of "metallurgical slag". This implies a better understanding of the phenomena involved in the leaching process in order to be able to adapt, if necessary, the metallurgical process to produce a slag which chemical composition, particle size and morphology, will result in reduced leachability. Slags from other industrial processes such as blast furnace slag, steel slag and phosphate slag are used in coastal protection and in roadbase applications [1,2]. The environmental consequences of these applications have been shown to meet strict utilisation criteria. For Pb and Zn slag, a similar situation is pursued.



## 2. EXPERIMENTAL

### 2.1 Material

To reach the objectives, slags from the seven plants under consideration were sampled in such a way as to obtain three samples representing different operating conditions for each furnace. The sampling of the slag was carried out over one month to obtain homogeneous lots both for studying the leaching behaviour and for studying the material treated for beneficial application. All 21 samples were subjected to full chemical characterisation, determination of relevant physical properties, determination of fine mineralogical composition and leaching according to the most commonly applied leaching procedures in Europe. The leaching tests applied are: the French X31-210 [3], the DEV S4 [4], an acetic acid extraction similar to the EP tox [5], a modified version of the Swiss TVA [6] and the British repetitive shaker test [7]. Most of this work was carried out by other partners in the project. Data obtained by these partners will be addressed in this report (section 3.1.2). A selection of 5 samples was made to carry out a more detailed characterization of leaching behaviour in Task 1.3. These samples were: LBF MER lot2, KIVCET 1, ISF MER Lot c, ISF BZ 2, ISF MIM Gran3.

Samples were size reduced to  $< 125 \mu\text{m}$  for chemical analysis and to assess the availability for leaching. A Retch jaw crusher with tungsten carbide plates was used to crush the slags. For size reduction to  $125 \mu\text{m}$  a rotary disk mill was applied. For the column leaching test and other batch extraction procedures, material could be used without prior sample treatment as material was obtained in the proper size range (95 %  $< 4 \text{ mm}$ ).

### 2.2 Characterisation and leaching behaviour

To gain information on the factors controlling release from Pb/Zn slag tests addressing specific aspects of leaching have been applied such as a test to assess the pH dependence of leaching [8] and experiments to evaluate the redox properties of the slags [9]. Specific aspects of leaching addressed are: the particle size distribution, the mode of stirring, method of filtration, the sensitivity to the liquid/solid ratio as obtained from a column test, test performance in closed bottles and exposed to the atmosphere and finally special exposure conditions such as sea water and acid rain water. A number of leaching tests are applied for this purpose, which described shortly below.

Leaching in a column reflects the behaviour of a material under percolation conditions. For this purpose the column test according to NEN 7343 [10] has been carried out covering the liquid to solid (LS, l/kg) range 0.1 - 10. This tests gives an indication of leaching behaviour on the long term. Presently, a test of this nature is being standardized in the framework of CEN TC 292.

The availability for leaching according tot NEN 7341 [11] is carried out to assess the distribution between potentially assessable chemical phases and mineral incorporation of elements.

To assess the behaviour of slags as a function of pH, pH static tests are carried out using a liquid to solid ratio of  $LS = 10$  and pH control in the pH range from  $\text{pH} = 4 - 12$ . A pH controller is steered by computer dosing  $\text{HNO}_3$  or  $\text{NaOH}$  depending on whether acid or base is required. Presently, a test covering this aspect of leaching is being standardized in the framework of CEN TC 292.

In CEN TC 292 a compliance test for granular materials has been developed [12]. It consists of three extraction options. Here the two step option  $LS = 2$  and  $LS = 2 - 10$  has been applied to be able to relate the test results to the column test data. In addition, two pH

controlled experiments were carried out as described in the proposed concise test for granular materials [13,14]. The pH conditions applied are pH 4 and pH 12 (LS=10).

Reducing behaviour of slags was tested with an draft standard NVN 7348 [9].

Seawater leaching experiments have been carried out at LS=10 with seawater for 1 and 7 days leaching time. The experimental conditions are the same as described in the CEN TC 292 compliance tests option B: LS=10.

To study the consequences of ageing of slags for the leaching behaviour, an experiment was set up in which a container was filled with slag to a height of 0.7 m. The material was left outside is exposed then influences of wet/drying by rain, freeze/thawing over the winter period and exposed to carbonation uptake of  $\text{CO}_2$  from the air. In addition, three containers have been set up in which at three levels porous cups were installed to be able to analyze porewater pH and  $E_H$  with time. One container ( $h = 0.7\text{m}$ ,  $\text{Ø} = 0.4\text{ m}$ ) was filled with slag and kept fully saturated, the second was intermittently wet and dry and the third was kept wet under a fine sand cover. All ageing experiments were started on April 20th 1995. At regular intervals porewater was extracted to measure pH,  $E_H$  and conductivity. The experimental setup is given in figure 1.

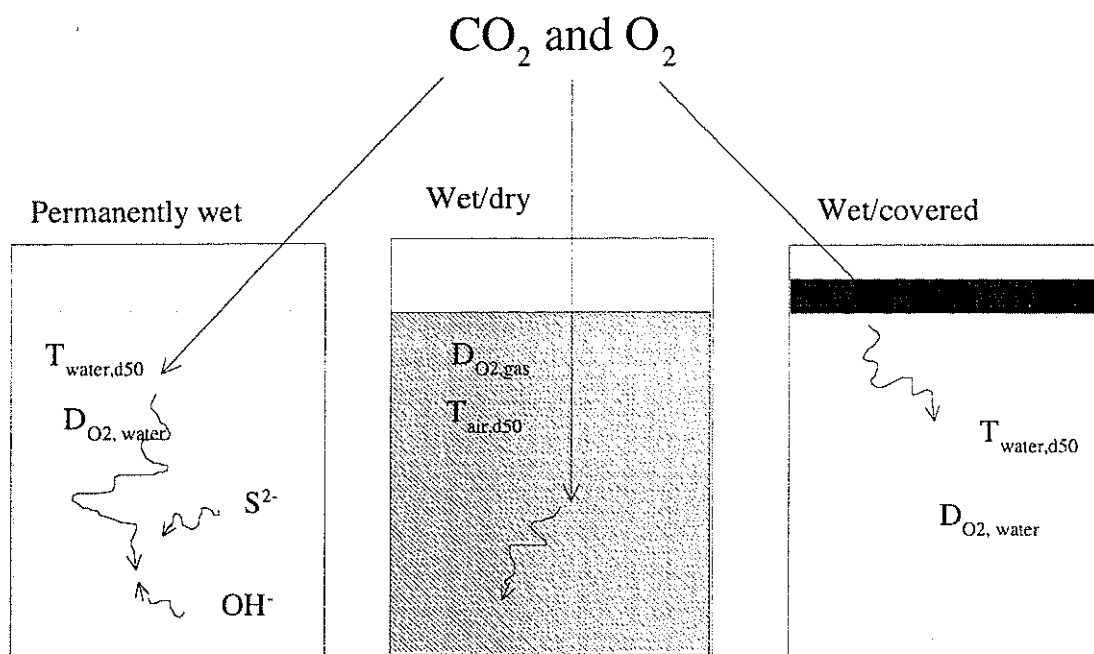


Figure 1. Experimental setup for testing ageing of slag.

## 2.3 Analytical methods

The leachates obtained from the various leaching tests were analyzed by Induced Coupled Plasma Emission for metals, by hydride generation technique in combination with Atomic Absorption Spectrometry for As, Sb and Se and by Ion chromatography for sulphate, Cl and F.



## 2.4 Geochemical speciation

The role of the chemical speciation of elements in the slag matrix and its influence on the leaching properties of slag is addressed in two ways: by analysing the leaching behaviour of pure phases assumed to be present in the slag matrix and by geochemical modelling [15] using the data from the pH static leaching test as input. The ageing of slags covers changes due to carbonation, oxidation and slow changes in mineral phases. These aspects are covered by laboratory testing and field exposure measurements.

## 2.5 Release modeling

Using the laboratory data reported earlier [16], the release under specific application conditions can be predicted by taking into account the site/ scenario specific parameters, such as application height, density after compaction, infiltration rate, time frame of interest and changes in leaching controlling conditions, such as pH and redox.

Leaching in a column reflects the behaviour of a material under percolation conditions. For this purpose the column test according to NEN 7343 [10] was carried out covering the liquid to solid (LS, l/kg) range 0.1 - 10. For granular material, the main aspect is to relate the liquid to solid ratio as obtained from a column experiment to a time scale. This can be achieved by the following relation:

$$LS_{\text{practice}} = j * N / (d_s * h)$$

with

$LS_{\text{practice}}$	liquid/solid ratio reached in practice (l/kg)
$j$	period of field exposure (y)
$N$	net infiltration rate (mm/y)
$d_s$	bulk density of the slag in $\text{kg/m}^3$
$h$	height in m

From the column data a retention value ( $K$ ) is derived that reflects to what extent the element of interest is retained in the slag matrix relative to the potentially leachable fraction for that element, which is regarded as an upper limit for release under environmental conditions. The release curves as observed in the column test may show non-ideal behaviour due to changes in pH during the experiment, whereas the  $K$  value is specific for a narrow pH regime. In those situations, the release at the higher LS ratios is taken as most representative.

For the calculation of the release ( $E_p$ ) in case of a percolating system the following formula is used to calculate the release at the relevant LS reached in the field [17,18]:

$$E_p = d_s * h * \text{Avail.} * [ 1 - e^{-LS_{\text{practice}}/K} ] \text{ in mg/m}^2$$

with

$d_s$	density of the secondary raw material in $\text{kg/m}^3$
$h$	height of the applied secondary construction material (m)
Avail.	the availability or potential leachability of the element of interest (mg/kg)
$K$	constant related to the degree of interaction of the constituent of concern with the matrix (l/kg)
LS	liquid/solid ratio (l/kg)

This formula is very similar to the one used in the Regulation for Construction Materials [18], which does not account for variations in  $K$  due to chemical conditions.

If information on the change of pH with time in the field is known a more accurate prediction of the release can be made by modifying the retention value for each LS interval for which the pH can be considered reasonably constant. In this context it is important to realize that mildly alkaline material exposed to atmospheric CO<sub>2</sub> will neutralize in time. This process is accelerated under moist unsaturated conditions.

Two hypothetical applications are considered to illustrate the calculation of long term release. These are an application of slag in a road construction and the utilization of slag in an embankment. For an application of slag under an impermeable asphalt cover, percolation data are less appropriate as the main mechanism of release under those conditions is diffusion. Data obtained with the newly developed compacted granular leach test [19] are more relevant for such situations, as the granular material behaves in that case as a monolith. In that type of application care should be taken to prevent infiltration through the slags at the side of the road, where the stabilization layer extends from under the asphalt cover.

## 2.6 Comparison with regulatory criteria

The leaching behaviour of slags is compared with existing regulatory criteria [18,20,21] and placed in perspective to other related materials to determine to what extent and under which conditions Pb/Zn slag can be utilized.

## 2.7 Quality control aspects

As soon as beneficial application of slag is considered, technical specifications and more stringent environmental requirements must be met. This implies the development of a QA/QC system of slag quality control to ensure constant product quality for an end user.

## 3. RESULTS

### 3.1 Slag characterisation and leaching behaviour of slag

Slag characteristics and the leaching behaviour of slag under a range of test conditions are discussed in subsequent sections below.

#### 3.1.1 Physical and mineralogical properties of slag

Through proper collection of 21 lead and zinc primary smelter slag samples from smelting installations in 4 European countries, it has been possible to cover a broad spectrum of slag qualities from both a chemical and mineralogical point of view. Zn assays ranging from 5 to almost 12 % and Pb assays ranging from 0.7 to 5 % have been measured with one extreme sample of 14% Zn and 13% Pb. All slags exhibit a same general size distribution trend, covering the 0.2 - 4 mm size range, with very few materials finer than 100  $\mu\text{m}$ . This renders them similar to natural washed sands obtained in quarry operations. Mineralogical investigations have shown that granulated slag consist all largely of a Fe-Ca bearing aluminosilicate glass, as reflected by the presence of moderate amounts of  $\text{SiO}_2$ , FeO and CaO, together with minor amounts of  $\text{Al}_2\text{O}_3$ . Both in lead and zinc slags, metallic lead droplets are embedded in this aluminosilicate glass phase and are largely inaccessible. Accounting for less than 1 % of the slag material, their diameter varies from one slag to the other, probably depending on the viscosity of the slag and on the performance of the forehearth.

#### 3.1.2 Comparison of national leaching tests for lead and zinc slags

The national leaching test procedures for all slag from the different facilities have been placed in perspective by plotting them in relation to the pH dependent leaching data as obtained from the pH static leach test. In the case of non-controlled pH conditions, the pH of solution is dictated by the slag itself and evolves in the neutral to alkaline range (pH 7 to 10). The higher values reflect the behaviour of slags with an elevated lime content. In this pH domain the leachability of Pb and Zn is generally moderate to low 1 - 10 mg/kg. In the case of acidic pH, either under  $\text{CO}_2$  flushing or under acetic acid leaching, all analysed elements exhibit higher releases. In figure 2 all test data are given in relation to the final pH in the leachate. The measurement of pH in leachates is rather critical due to the low buffer capacity of Pb and Zn slag. Exposure to  $\text{CO}_2$  in the atmosphere may result in pH shifts that could lead to erroneous conclusions and less consistent behaviour than actually occurring. More stringent recommendations for leach test protocols would be required to obtain more reliable results. Placing leach test data in perspective by plotting the data in a graph of leaching as a function of pH proves to be very useful as it leads to a consistent picture of material behaviour. Test conditions may vary in terms of pH, but the generic leaching pattern is largely respected.

#### 3.1.3 Leaching behaviour of Pb/Zn slag

##### *- Acid Neutralisation Capacity.*

The availability for leaching according tot NEN 7341 [11] is carried out to assess the distribution between potentially leachable chemical phases and mineral incorporation of elements. For Pb and Zn, in particular, the difference between total composition and availability illustrates the degree to which these elements are incorporated in the matrix. An additional property derived from this test is the Acid or Base Neutralisation Capacity (ANC/BNC) that can be derived from the acid or base consumption to reach the preset pH value of 7. For Pb/Zn slags this in the order of 0.0015 - 0.007 Mol/kg. The relatively low

Acid Neutralisation Capacity compared to other types of industrial slags imply that Pb/Zn slags do not significantly affect their surroundings in terms of pH control. On the contrary, the pH of the surrounding medium is important in assessing slag utilisation/disposal scenarios. Application in acidic environments should therefore be avoided.

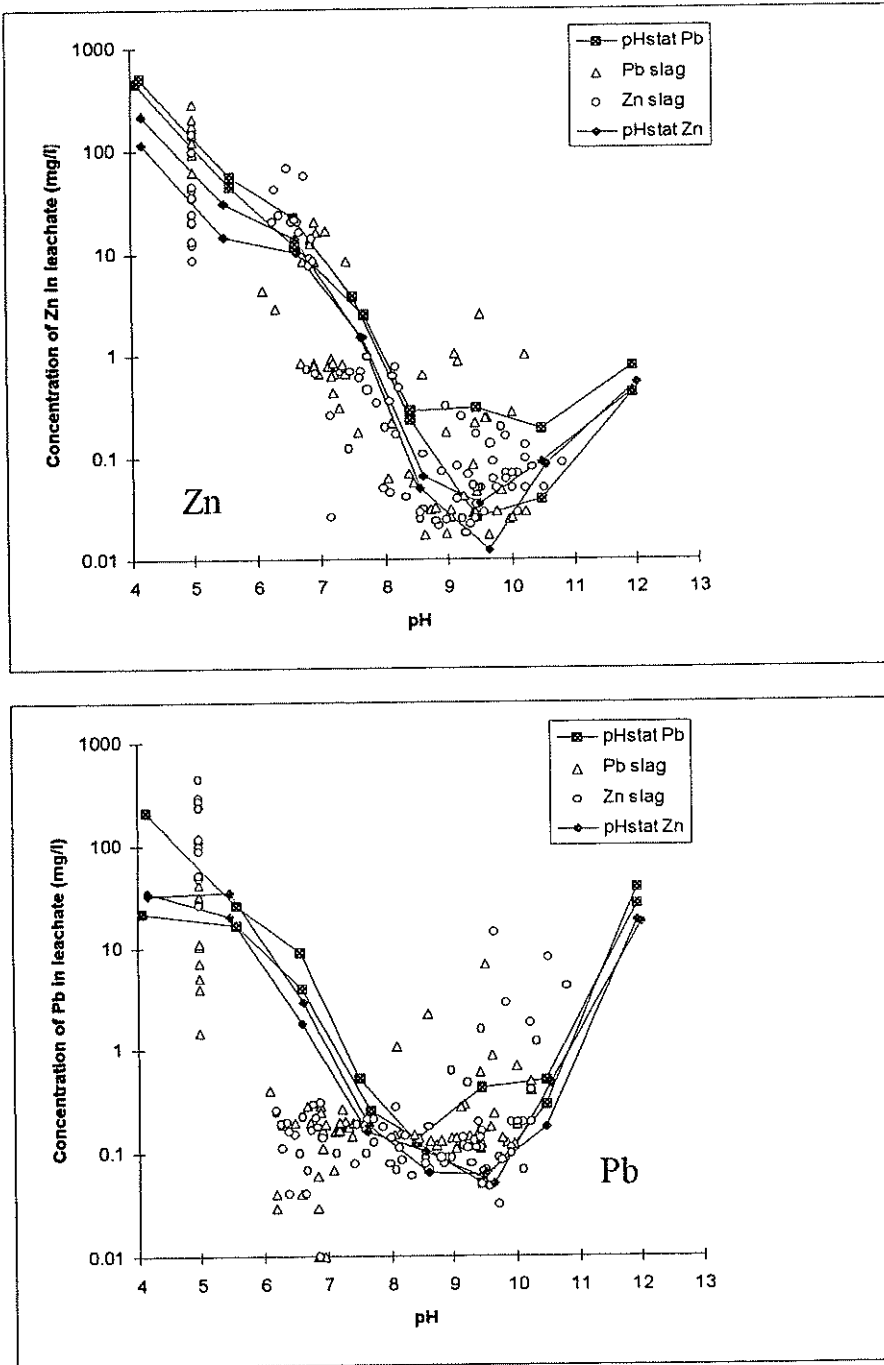


Figure 2. Results of pH dependent leaching behaviour for Pb and Zn from Pb and Zn slags in comparison with regulatory test data (X31-210, DEV S4, EP tox and TVA)

- Reducing properties of Pb/Zn slag.

Using a recently modified procedure [9] the reducing properties of Pb and Zn slags has been assessed. At low pH (pH < 5) the slag material exhibits clearly reducing properties,

as the redox potential is more than 50 mV below the pH -  $E_H$  curve for normal oxidized water. At pH 7 - 11, however, the reducing properties are not apparent. This is in strong contrast with types of reducing slags such as steel blast-furnace slag. This type of slag has been shown to exhibit reducing properties over the entire pH range, which was attributed to the leaching of reduced S - species as main carriers of reducing capacity (S partly presents as the relatively soluble CaS). In the case of Pb and Zn slag the leachability of sulphur species is very limited. S is apparently tied up in insoluble mineral phases (e.g. ZnS, PbS, FeS). In the case of Pb and Zn slag, the reducing properties are governed by reduced Fe and Mn species. Since these constituents show a very strong pH dependence in their leaching behaviour [15], this is reflected in the measured reducing properties of the slag as a function of pH. Mildly reducing conditions develop only at pH < 6 (see figure 3).

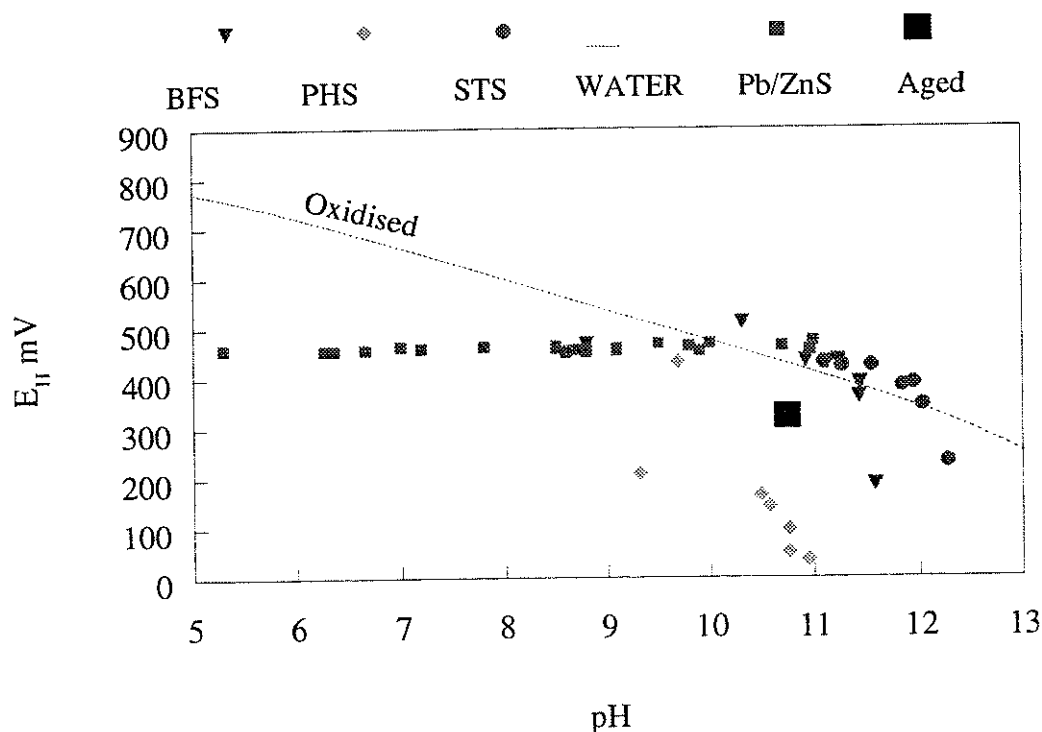


Figure 3. *Reducing properties of Pb/Zn slag in comparison with other types of slag (BFS- blast furnace slag, PHS- phosphate slag, STS - steelslag, Pb/ZnS - Pb/Zn slag, Aged- aged sample of Pb/Zn slag)*

*- pH dependence of leaching.*

To assess the behaviour of slags as a function of pH, pH static tests are carried out using a liquid to solid ratio of LS = 10 and pH control in the pH range from pH = 4 - 12. A pH controller is steered by computer dosing HNO<sub>3</sub> or NaOH depending on whether acid or base is required. The amount of acid or base is kept small to avoid significant change in the initial liquid to solid ratio. In figure 4 the pH dependent leaching behaviour is given for a selection of elements Al, Cu, Cr, Mn, Pb and Zn. In Appendix I additional data for Ca, Al, Si, Mg, Fe, Mn, B, Cl, Li, K, Na, Ba, Mo, As, Sb, Cd, Cu, Cr, Co, F, Ni, P, Pb, Ti, S, Se, Sn, Sr, V, Zn are available. The general trend in the leaching behaviour has been found to be very similar for a given element almost irrespective of its origin. It reflects the degree of solubility control by mineral phases at the surface of the slag. The difference in leaching levels between slags is in part due to the alkalinity of slags. This consistent behaviour can be exploited further to optimize slag properties for use or disposal. The leaching by

mineral acids as carried out by other partners has been placed in perspective against the pH static leach tests data. The general observation is that the leaching behaviour is not significantly different from that established by pH-stat leaching using nitric acid. Other acids may show somewhat deviating leaching behaviour for particular elements, which can be explained by known chemical interactions. Such reactions form in most cases a drawback rather than an advantage. Example: lower Pb leachability after an extraction with sulphuric acid in the pH range 4 - 8, which is not representative for any field condition.

*- Leaching as a function of liquid to solid ratio (L/S).*

Leaching in a column reflects the behaviour of a material under percolation conditions. For this purpose the column test according to NEN 7343 [10] has been carried out covering the liquid to solid (LS, l/kg) range 0.1 - 10. This tests gives an indication of leaching behaviour on the long term. In figure 5 the column test results for Pb are graphically presented as a function of LS. The solubility control of the metals implies that the release rate will be constant over time. In column tests, Pb shows a continuous increase of the cumulative release with time, which is consistent with the identified release mechanism (solubility controlled release). For comparison the availability for leaching as obtained by NEN 7341 is indicated for each of the slags. The leaching behaviour differs significantly for the slags studied. The pH of the slags with the highest leachability for Pb is either rather low (pH 5) or high (pH10). The parameters derived from the leaching curve as a function of LS can be used for long term release prediction purposes (see section 3.2). The total composition, which well above the concentrations reflected by the availability are clearly not relevant from an environmental point of view.

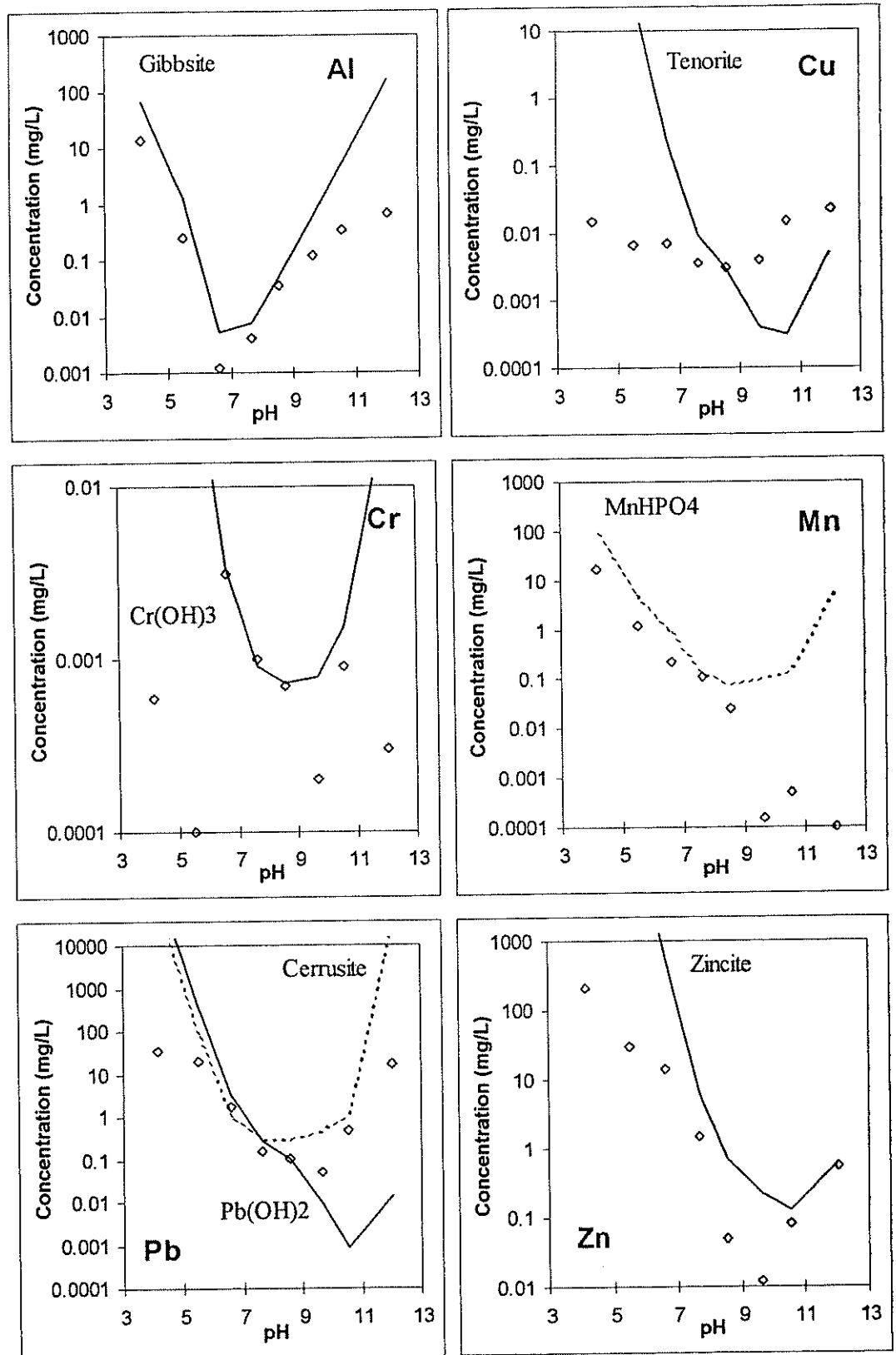


Figure 4. *pH dependence of leaching and geochemical modelling of leaching behaviour from Pb/Zn slag (using MINTEQA2)*

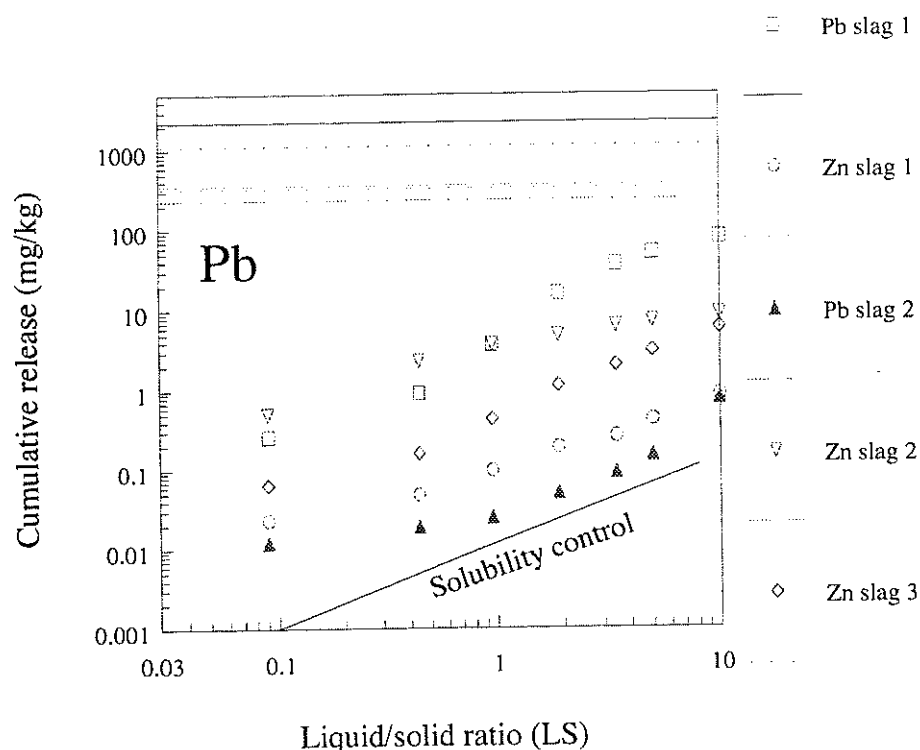


Figure 5. Column test data of Pb for four Pb and Zn slags showing cumulative release expressed in mg/kg covering the liquid to solid ratio 0.1 to 10. The availability test data are included as horizontal lines

*- Leaching in seawater.*

Leaching experiments have been carried out at LS=10 with seawater for 1 and 7 days leaching time. The experimental conditions are the same as described in the CEN TC 292 compliance tests option LS=10. The results of the measurements are presented in figure 6 and placed in relation to the pH dependent leach data generated with the pH-stat test. As can be seen the leaching of a few relevant elements is increased significantly relative to a fresh water system (i.e. more than a factor 10 in many cases). For some elements this relates to complexation with Cl<sup>-</sup> (e.g. Cd) and subsequent mobilization. For several other elements the change in ionic strength appears to be the most crucial factor. In general, the conclusion can be drawn that utilization of the untreated slag in the marine environment is not a favourable option.



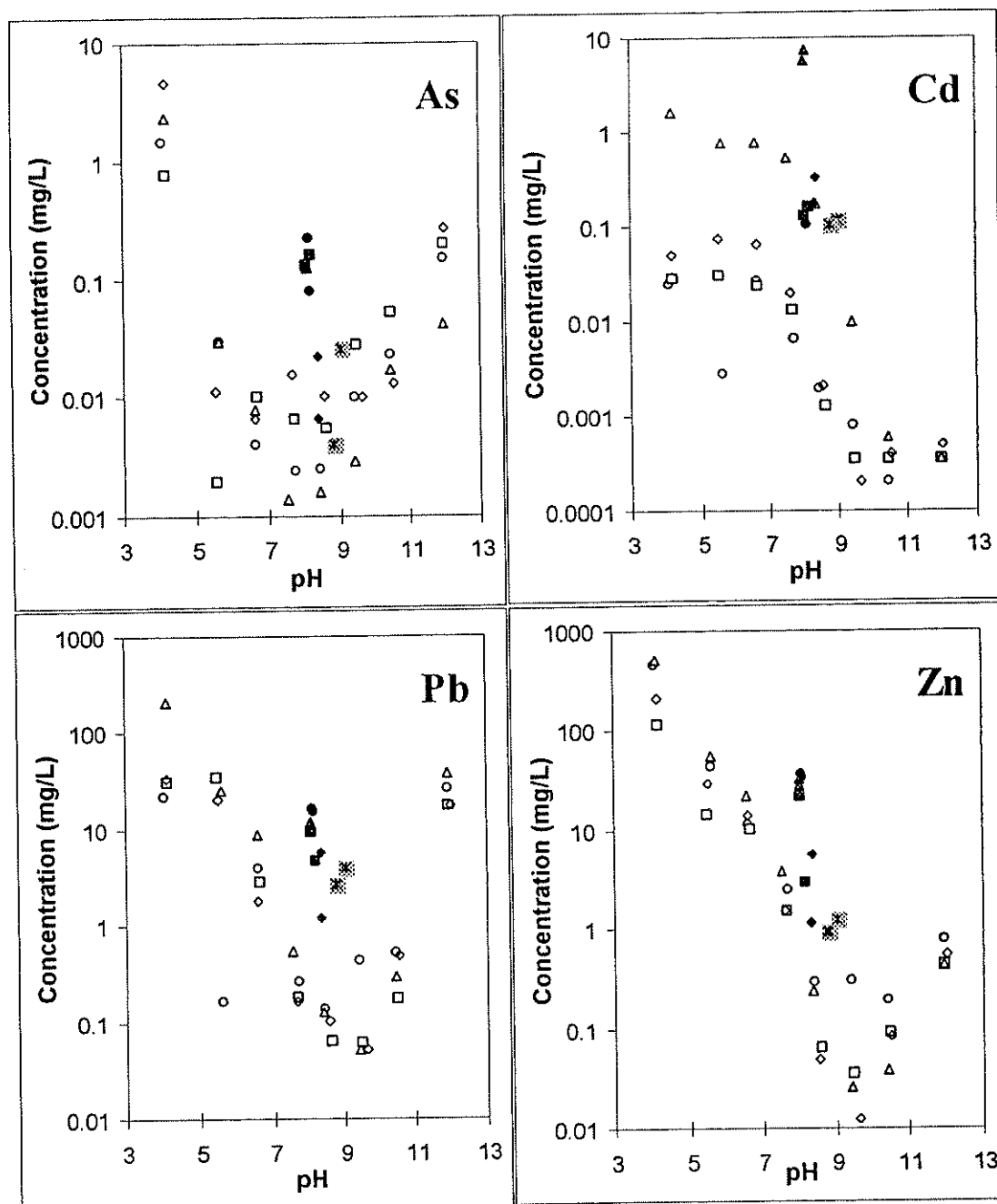


Figure 6. *Leaching of Pb/Zn slag in seawater (solid symbols) relative to fresh water (open symbols) leaching at different pH values.*  
 ○ LBF MER lot2; □ ISF MER lotC; △ KIVCET 1; ◇ ISF BZ 2;  
 \* ISF MM Gran 3

*- Role of ageing in leaching from slag.*

To study the consequences of ageing of slags on the leaching behaviour through exposure to the atmosphere and moisture, three containers have been set up in the laboratory in which at three levels porous cups have been installed to be able to analyze porewater pH and  $E_H$  with time. One container ( $h = 0.7\text{m}$ ,  $\varnothing = 0.4\text{m}$ ) was filled with slag and kept fully saturated, the second was intermittently wet and dry and the third was kept wet under a fine sand cover. After one year the porewater in the bottom of the container was analyzed

for a range of major and trace constituents to be compared with the pH-stat leaching information. In figure 7 the pH and  $E_H$  profiles as observed with contact time at different levels in the containers is given. In the permanently wet container the uptake of  $O_2$  and  $CO_2$  is slow and consequently the oxidation/carbonation proceeds relatively slow compared to the other configurations. In the intermittently wet/dry cycling container, the changes are most pronounced as the interaction with  $O_2$  and  $CO_2$  are largest (gas phase diffusion  $10^4$  times faster than in water). In the container with a fine sand cover the change in pH and redox is least affected as the uptake of  $CO_2$  and  $O_2$  is further restricted. In figure 8 the pH- $E_H$  graph is given with the data of the ageing experiments. For the most part, the conditions are oxidized. Mildly reducing conditions can develop in systems that are relatively closed from the atmosphere. The pH may remain around pH = 10 for a long time depending on the degree of exposure to the atmosphere. The site specific conditions determine which condition of the one tested here will prevail. In general, the element featuring solubility controlled release will show concentrations in the leachate after ageing that correspond with the pH dependent leaching curve. For soluble constituents, the LS-factor between lab- tests (usually  $LS=10$ ) and field condition (often  $LS < 1$ ) leads to an order of magnitude higher concentrations in porewater measurements ( e.g. B, Na, K, Mo, Li). It is important to consider the solubility and availability control of the different elements to isolate true deviations from apparent deviations due to differences in LS between field and lab.

### 3.2 Modelling of geochemical speciation

For an assessment of the long term behaviour of slag modelling is crucial. This implies both modelling of the chemical speciation of slag leaching as well as the release as a function of time. The chemical speciation modelling is linked with bulk mineralogical analysis.

#### 3.2.1 Leaching behaviour of pure phases

The concentrations dictated by solubility pure Pb phases has been modelled. In figure 9 the modelling data are presented.

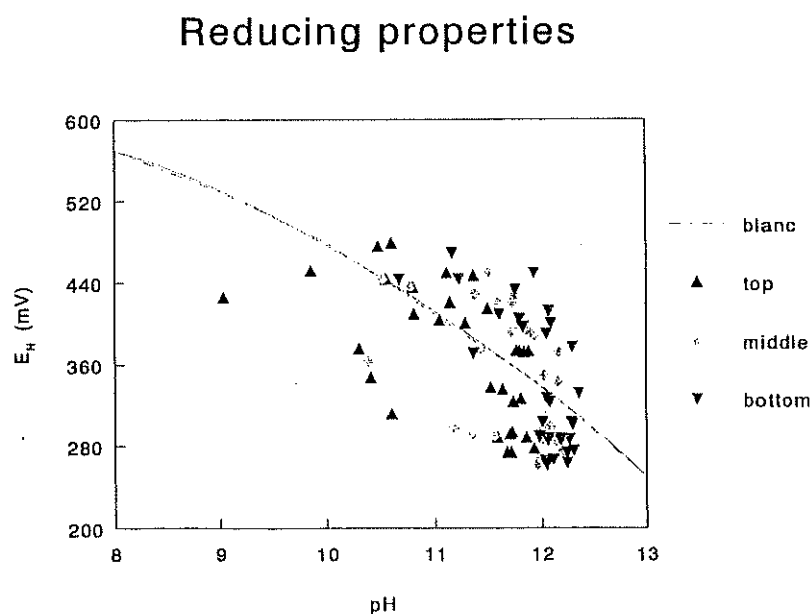


Figure 8. *Reducing properties*

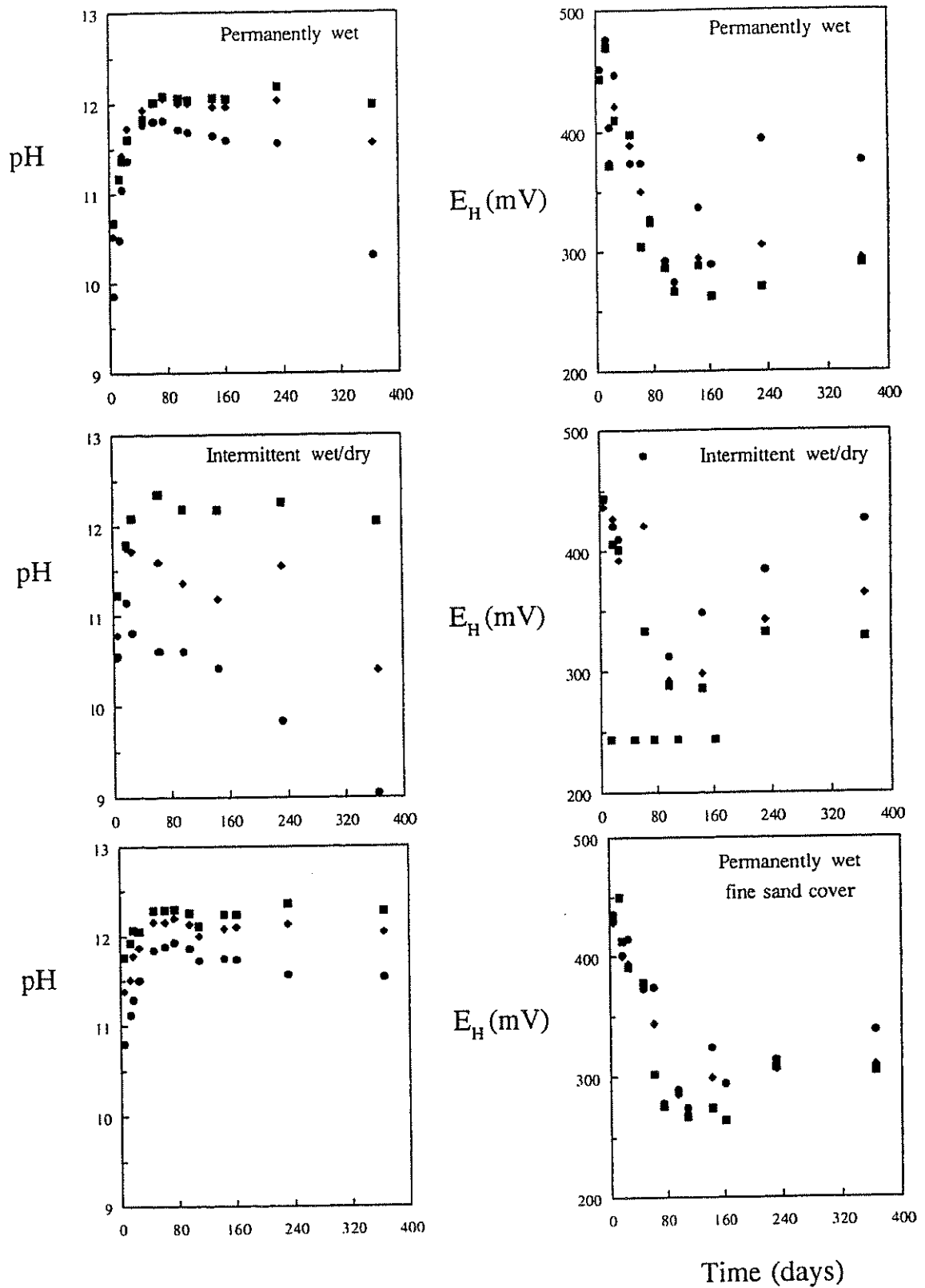


Figure 7. Aging experiments Pb/Zn slag. ● top; ◆ middle; ■ bottom of tank

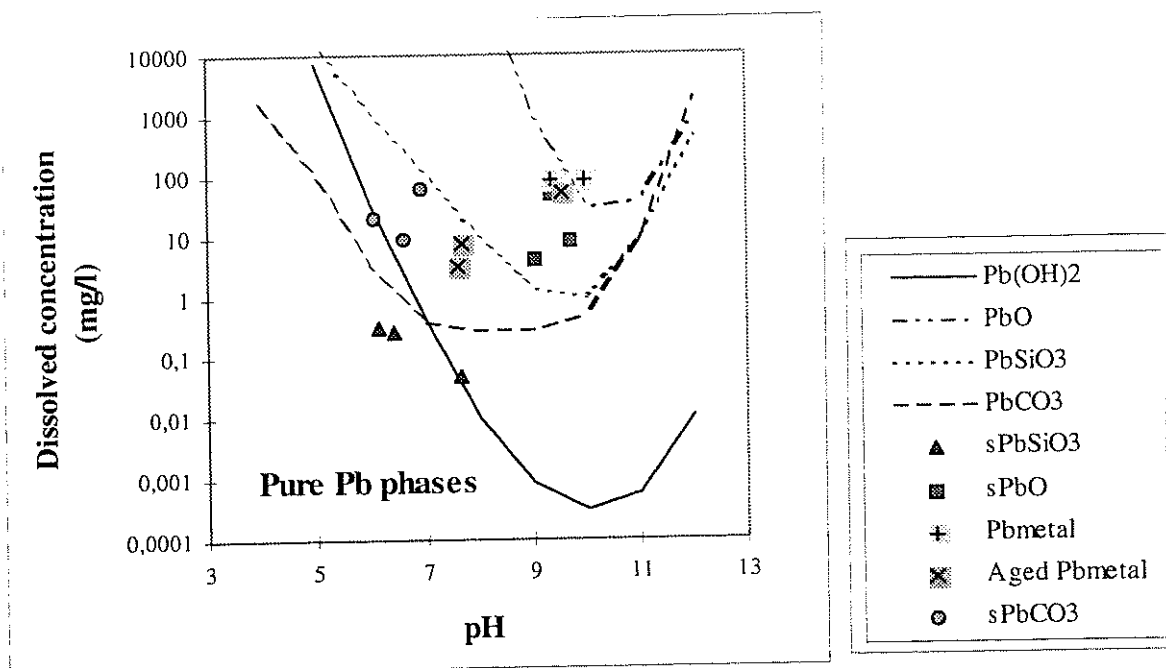


Figure 9. Modelling and measurements of Pb leaching from pure Pb phases

At Metaleurop leaching of pure Pb phases has been carried out using the French 3-step leaching test [3]. These data have been put into the graph for comparison. The leaching data for PbO correspond well with the leachability predicted for PbO, although the first two steps of the leaching test are undersaturated with respect to PbO solubility (slow kinetics of dissolution?). The leaching behaviour of Pb metal corresponds to that of PbO, which is not very surprising as Pb metal oxidizes relatively fast. Aged Pb metal matches in the first step with PbO, but in later steps the solubility moves in the direction of PbCO<sub>3</sub> solubility. The solid PbSiO<sub>3</sub> leachability does not correspond well with the PbSiO<sub>3</sub> solubility curve. It matches better with either Pb(OH)<sub>2</sub> (or PbCO<sub>3</sub>). The solid PbCO<sub>3</sub> solubility as measured in the leaching test corresponds reasonably well to the modelled PbCO<sub>3</sub> solubility (slightly supersaturated), except for the first leaching cycle that has a rather high concentration. The pure phases seldom remain pure as external influences may convert the surface of pure Pb phases to other forms, which may then become solubility controlling. The fact that pure PbSiO<sub>3</sub> corresponds closer to PbCO<sub>3</sub> than to the silicate, can be caused by a small contribution of leadcarbonate in the silicate. Since it is the least soluble phase, it may become the controlling phase. Based on these modelling and laboratory observations, the following mechanism can be derived. When metallic Pb droplets occur embedded in slag or as individual particles among slag, the leaching behaviour of Pb will initially reflect the behaviour of PbO as Pb oxidizes rapidly. This stage does not last in contact with the atmosphere, since due to interaction with CO<sub>2</sub> from the air PbO will be react to PbCO<sub>3</sub>. This is the more stable phase upon aging of slag. If this mechanism proves to be correct, the question can be posed whether testing the fresh reactive slag is representative for slag leaching behaviour in environmental exposure conditions. Due to the unknown progression of the oxidation/carbonation, the Pb leaching results on fresh slag must be quite variable. This is in agreement with the observations. It might be enlightening to verify for slag with a high Pb leaching level in relatively fresh slag the change in Pb leachability with time.

### 3.2.2 Geochemical modelling of slag leaching behaviour

Using the geochemical speciation model MinteqA2 [14], the leaching data obtained from the pH stat experiments on Pb and Zn slags have been modelled to identify the potential solubility controlling phases. This information is relevant for decisions on possibilities for modification to improve slag leaching characteristics. It also helps to identify the influence of the degree of amorphous glass versus crystalline phases. The leaching data obtained for major, minor and trace elements have been transformed to Mol/l concentrations and used to calculate saturation indices for all possible mineral phases. Based on the evaluation of the saturation indices, those phases that are likely controlling phases due to a good match between measured concentrations corrected for activity (Debye-Huckel) and solubility of specific phases over all or a part of the pH range studied have been selected. In figure 5 potential solubility controlling phases have been inserted.

*Lead* - The most relevant solubility controlling phase for Pb solubility from Pb and Zn slag appears to be cerussite -  $\text{PbCO}_3$ . This is consistent with the observations on pure Pb phases. Only in case of ISF Gran 3 solubility control of Pb by  $\text{PbO}$  and  $\text{PbSiO}_3$  matches better with the observed solubility curve than cerussite. XRD measurements have revealed the presence of metallic Pb droplets and  $\text{PbO}$  in this sample.

*Zinc* - The solubility of Zn is largely matched by the solubility dictated by zincite -  $\text{ZnO}$ .

### 3.2.3 Mineralogical aspects

The basicity of slags, which is reflected in the leachable lime content, dictates the final pH in the leachate to a large extent. As has been shown before pH is an important controlling factor of slag leachability. The mineral phases identified as solubility controlling phases are not the same as those identified as bulk mineral phases by XRD of the total slag samples. This illustrates the point that leachability is controlled by mineral phases at the surface of slag particles, which is not necessarily the same as the mineral composition within the slag particles. In the case of the Pb phases this is already clear, but for other elements the same applies (Table Ia and b).

Table Ia. Mineral phases identified in the slag bulk matrix

pH	SATURATION INDICES*							
	12.0	10.5	9.5	8.5	7.5	6.5	5.5	4
FRANKLINITE	4.14	6.77	8.10	14.72	10.60	7.72	10.72	9.28
P-WOLLSTANIT	-0.44	-2.31	-3.70	-5.20	-6.66	-8.22	-9.21	-10.55
GEHLENITE	-11.32	-12.89	-14.75	-18.30	-20.74	-25.30	-29.21	-33.18
WUSTITE	1.84	2.44	1.27	-0.50	-2.47	-4.47	-6.51	-9.71
WURTZITE	2.55	3.64	3.77	2.63	2.18	1.77	1.14	0.19
ANORTHITE	-6.51	-4.25	-3.77	-4.90	-5.10	-7.38	-9.13	-9.87
HERCYNITE	-2.13	1.83	2.11	0.26	-0.84	-3.92	-7.32	-10.86
FE $\text{CR}_2\text{O}_4$	9.29	12.81	12.26	9.49	8.29	5.02	0.30	-9.59

Tabel Ib. *Solubility controlling mineral phases based on geochemical modelling using leachate analysis data.*

pH	SATURATION INDICES*							
	12.0	10.5	9.5	8.5	7.5	6.5	5.5	4
Fe(OH) <sub>2</sub>	<b>0.04</b>	<b>0.84</b>	<b>-0.28</b>	-2.04	-4.01	-6.01	-8.05	-11.26
NORSTRANDITE	-2.08	<b>-0.51</b>	<b>0.20</b>	<b>0.15</b>	<b>0.58</b>	<b>0.05</b>	<b>-0.63</b>	-0.80
QUARTZ	-2.58	-1.60	-1.13	-0.67	-0.28	<b>0.08</b>	<b>0.67</b>	1.61
PB(OH) <sub>2</sub> (C)	3.49	2.51	<b>0.58</b>	<b>0.05</b>	<b>0.13</b>	<b>0.21</b>	-1.23	-3.50
CERRUSITE	-2.70	<b>-0.56</b>	<b>-0.95</b>	-0.36	<b>0.22</b>	<b>0.78</b>	<b>-0.58</b>	-2.98
ZN(OH) <sub>2</sub> (E)	<b>-0.51</b>	<b>-0.93</b>	-1.58	-0.92	<b>-0.92</b>	-2.09	-3.73	-5.97

\* Values close to zero indicate solubility control; indices are given in log-scale units.  
 Bold numbers indicate potential solubility control by the indicated mineral phase.

### 3.3 Prediction of long term release

In figure 10 the basic data - leachability as a function of LS and leachability as a function of pH - for the prediction of Pb and Zn release from slag are given. The lines in the plots of cumulative release against LS represent the modelled release curves for a constant K value. In table II the relevant data are given for the slags studied.

Table II. *Availability and K values for Pb and Zn slags*

Slag	Pb availability (mg/kg) [15]	Pb K value	Zn availability (mg/kg)[15]	Zn K value
Kivcet	2217	200	5329	4000
BFS lot2	327	9000	1175	9000
ISF lotC	231	50000	4827	110000
BZL slag	357	200	2232	100000

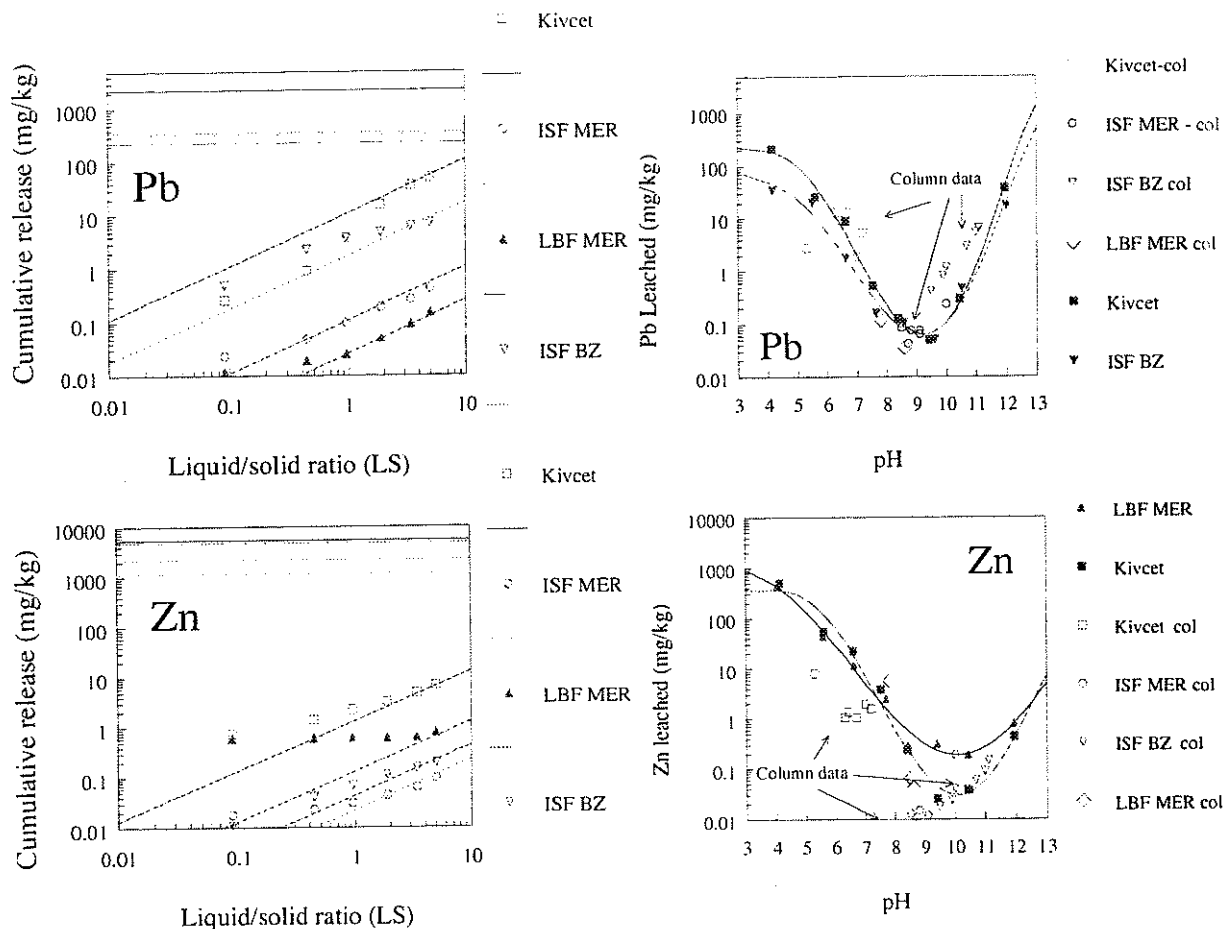


Figure 10. Relation between column test data and pH static leach test data for Pb and Zn, horizontal lines refer to availability test data

The value of the K value is largely dictated by the difference between the availability level and the actual leaching at any given pH. From the pH graphs, it is clear that the difference between availability ( $\approx$  leachability at pH=4) and leachability of Zn at pH = 9 covers 5 orders of magnitude. As optimized conditions the minimum leachability at pH 8 - 9 has been selected in combination with a low availability.

All calculations have been made for Pb and Zn only. These may not be the only elements that determine whether the application is environmentally acceptable. This type of calculation should be extended to other elements to verify that all constituents of concern meet requirements for use.

### 3.3.1 Utilization in road base

Using the data as specified above in the formulas presented in section 2.5. The release can be calculated over a time frame of 100 years. For a few combinations of release controlling parameters - K-value, availability, infiltration rate - this calculation has been made. The procedure is similar to that applied in the CROW study of roadbase applications of

stabilized coal fly ash and Municipal Solid Waste Incinerator Bottom ash [22]. The results are given in Appendix II.

Under optimized conditions the release of Pb and Zn can be controlled to a level which is below the regulatory levels currently used in the Netherlands in relation to the Building Materials Decree [18].

Without control, leachability may be unacceptably high, thus clearly prohibiting beneficial use of slags. Application under infiltration reduced conditions, such as under an asphalt top cover and well above groundwater level (> 0.5m) such as to prevent direct contact with groundwater, can reduce the release rate further to a level which meets criteria for use. In the case of untreated use of slags, it is important to be able to guarantee that the release is not changed with time as a result of changing pH conditions in the application (e.g. acidification). This condition can be fulfilled in different ways.

### 3.3.2 Utilization in embankment

As another specific example the calculation has been made for an embankment of 6 meter high, that can be used as base for an highway overpass. Data obtained from the calculation are presented in Appendix III. From the data it follows that for solubility controlled elements such as Pb and Zn the height is not a factor of concern as the release is identical for the 0.5 m and the 6 m high application. Obviously, the height makes a lot of difference for elements that show availability controlled leaching such as Mo, B and soluble salts.

## 3.4 Comparison of leaching data with related materials and regulatory criteria

### 3.4.1 Comparison with related materials

In figure 11 the pH dependent leaching data for Al are given for the Pb and Zn slags studied in comparison with phosphate slag, steel slag and mine-tailings from coal mining (rich in pyrite and other reduced Fe and Mn species) [1]. The general trend in the leaching behaviour is very similar. The difference in leaching levels is in part due to the alkalinity of slags.

A comparison between different materials is not easy [27,28], as the comparison can give a complete distorted picture of the reality. This difficulty is caused by the fact that the elements that are critical are not the same in each material. Consequently, a comparison on an element by element basis can be very misleading. What is needed is an objective measure to relate materials with different critical elements to one another. An option is available in the form of an environmental index [23], but the basis of reference needs to be defined.

Here a comparison of leaching behaviour is made with MSWI-bottom ash, which is now more and more utilized as road base construction material under specific precautions [18,25]. In figure 12 the leaching behaviour of Pb, Zn, Cd from Pb and Zn slag is compared with that of MSWI-bottom ash (IAWG study [24]). Since the data on MSWI-bottom ash were available in µg/l the data from the slags have been adjusted to these numbers. The horizontal lines reflect the Dutch regulatory limits related to the Building Materials Decree [18]. The Pb leachability is higher than that of MSWI-bottom ash, whereas Zn and Cd show a lower leachability than MSWI-bottom ash. Based on such a comparison, both materials could be utilized in similar applications, provided that the technical specifications of the material meet the requirements. It is recommended to measure the technical parameters required for road base application of aged or modified slag.



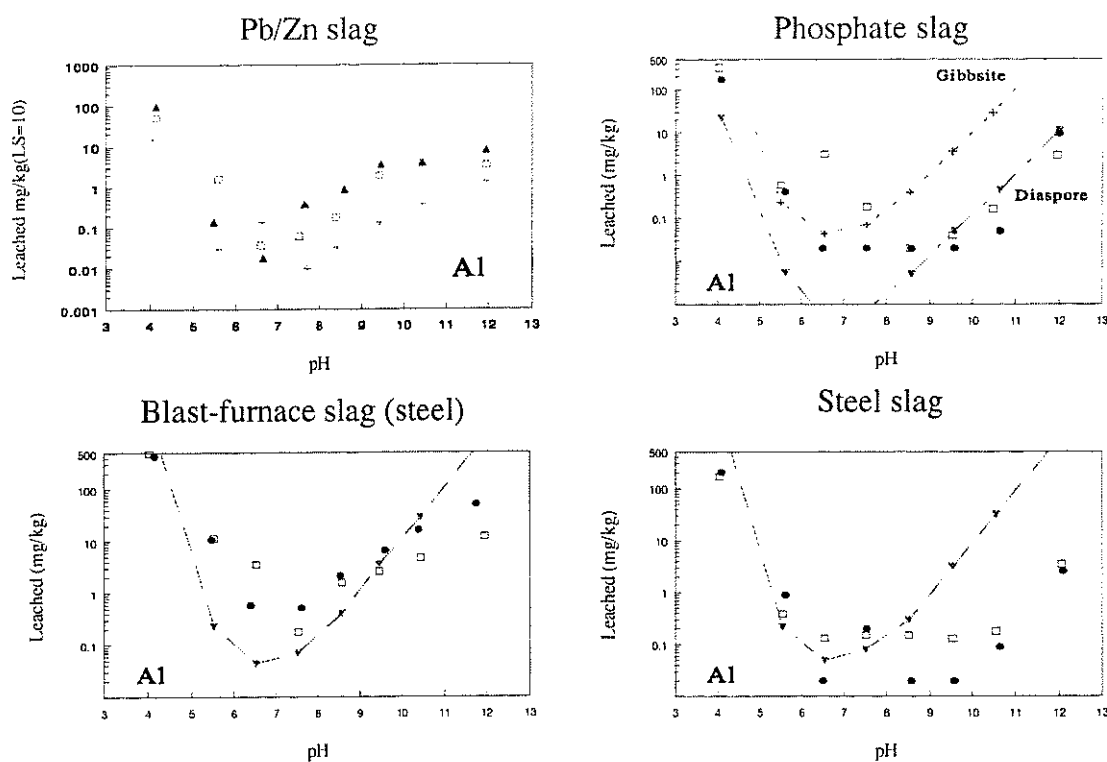


Figure 11. *Leaching of Al from Pb/Zn slag in comparison with that from phosphate slag, blast furnace slag and steel slag*

### 3.4.2 Comparison with regulations

Currently, the most extended regulatory limit values in practice are those specified in the Dutch Building Materials Decree [18]. The Decree is based on marginal burdening of the soil underneath an application of any type of building materials (conventional or derived from secondary materials). The starting point for the regulation is the release considered acceptable after 100 years of exposure. For comparison the release values for 100 years are given together with the mg/kg limits for leaching tests carried out on granular materials. The translation between release at 100 years and the leach tests data is based on an evaluation of release processes and actual average infiltration conditions. Recent field verification experiments [22] indicate that several assumptions made are valid.

In France limit values have been specified for utilization of Municipal Solid Waste Incinerator Bottom ash [20]. The latter has a much more limited scope than the Building Materials Decree (BMD) and the number of elements regulated is also limited.

In Germany, regulation for construction materials is in progress at the national level. Currently, the "Bundeslander" each have their own approaches. The most extended is the approach by North Rhein Westfalia. Here 4 levels are specified: Z0, Z1.1, Z1.2 and Z2. Below Z0 implies free use of material in all applications, Z1.1 and Z1.2 require additional measures and materials above Z2 are not allowed.

The data obtained from the slag leaching characterization using the pH static leach test, allow a comparison with the regulatory limit values. These are given in mg/kg for a granular material, but have been converted here to mg/l for practical purposes (all data were available for modelling in mg/l). (Limit in mg/l = Limit (in mg/s)/LS (in l/kg) (LS=10).)

In table III the actual values of the current regulations are given.

In de Building Materials Decree there are two limit values:

Category I : unrestricted utilization

Category II : utilization of > 10000 tons per application, 0.5 m above lowest groundwater level, under an infiltration reducing top cover (e.g. asphalt).

In the graphs presented in figures 13 the category I is indicated by a dashed line and category II by a dotted line. The results of the comparison with the BMD are specified in table III.

By providing a carbonate buffer and increasing the limited sorptive capacity of Pb/Zn slag, the leachability of Cd can be controlled to within the regulatory limits. Cd and Sb prove to be the most critical parameters due to the fact that they more than any other element define the upper and lower pH boundaries, where leaching is within regulatory acceptance. GRAN 3 is a sample that deviates in many respects and has a leachability beyond that of any of the other slags. The statements made in terms of acceptability are related to the Dutch limits, which are quite strict. The comparison provided in figure 13 gives a more solid long term projection than a single step extraction result as specified in most regulatory procedures. This is caused by the fact that the pH stat covers also potential long term changes in pH conditions to which materials may become exposed. A comparison with French regulations for MSWI bottom ash in road base (applicable??) and a much more limited number of parameters only excludes Gran 3 and leads to an acceptable pH domain of 7.5 to 10.5.

It is recommended to improve slag leaching behaviour by adding a small proportion of other industrial by-products. The proportion of which remains to be established. This can enhance the buffer capacity and provide sorptive capacity for several of the metals of concern in slag leaching. The regulatory testing protocols are too limited to verify the level of improvement attained.

Due to its relative simplicity, it is recommended to verify this option as significant reduction in leachability may be reached and the optimal pH range for use becomes wider.

Since the use of secondary raw materials in construction is increased in Europe, it is important that environmental criteria for utilization are developed at the European level.

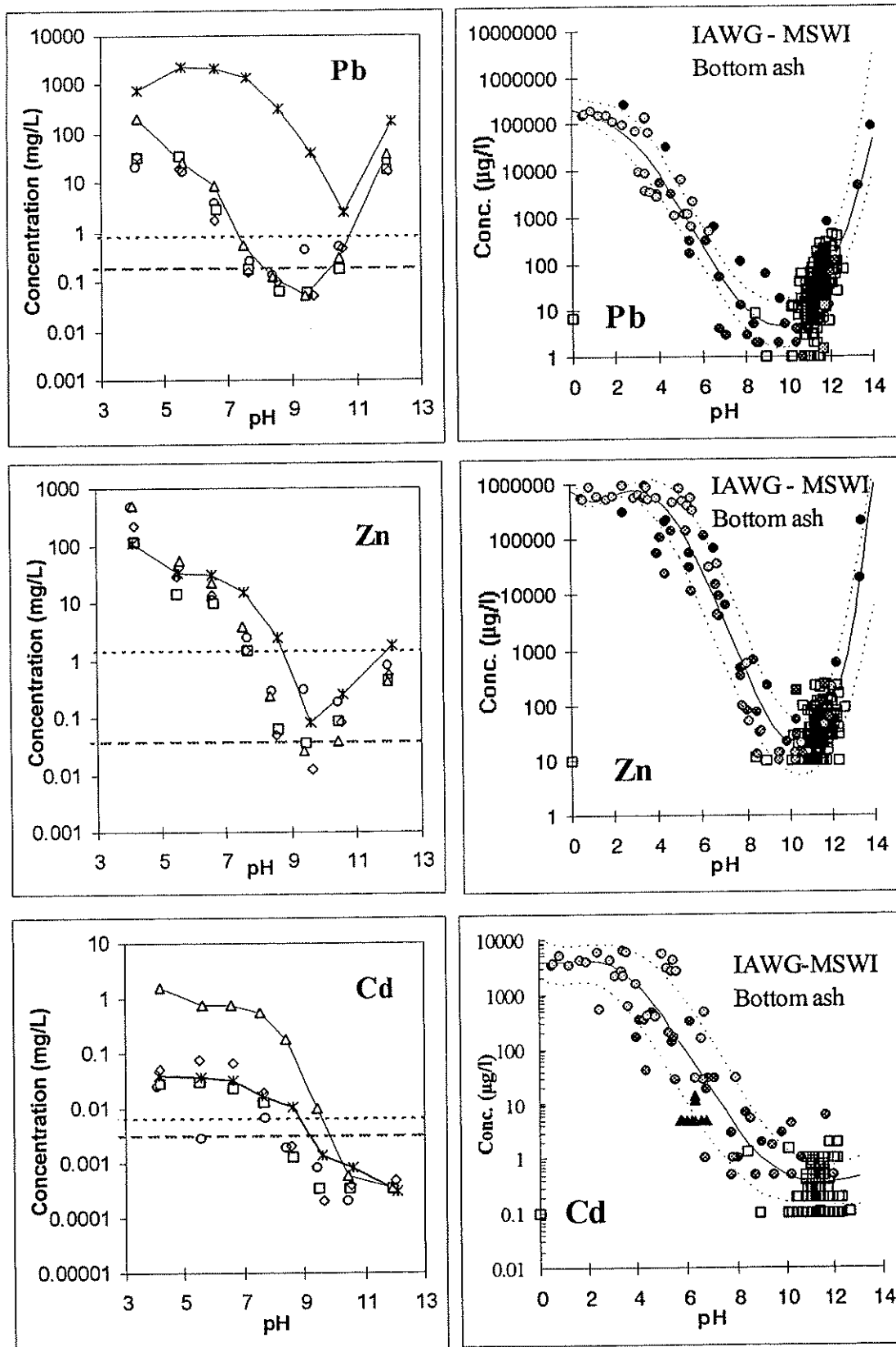


Figure 12. Comparison of Pb/Zn slag leachability with MSWI-bottom ash leaching  
 ○ LBF MER lot 2; □ ISF MER lot C; △ KIVCET 1; ◇ ISF BZ 2;  
 \* ISFMM Gran 3

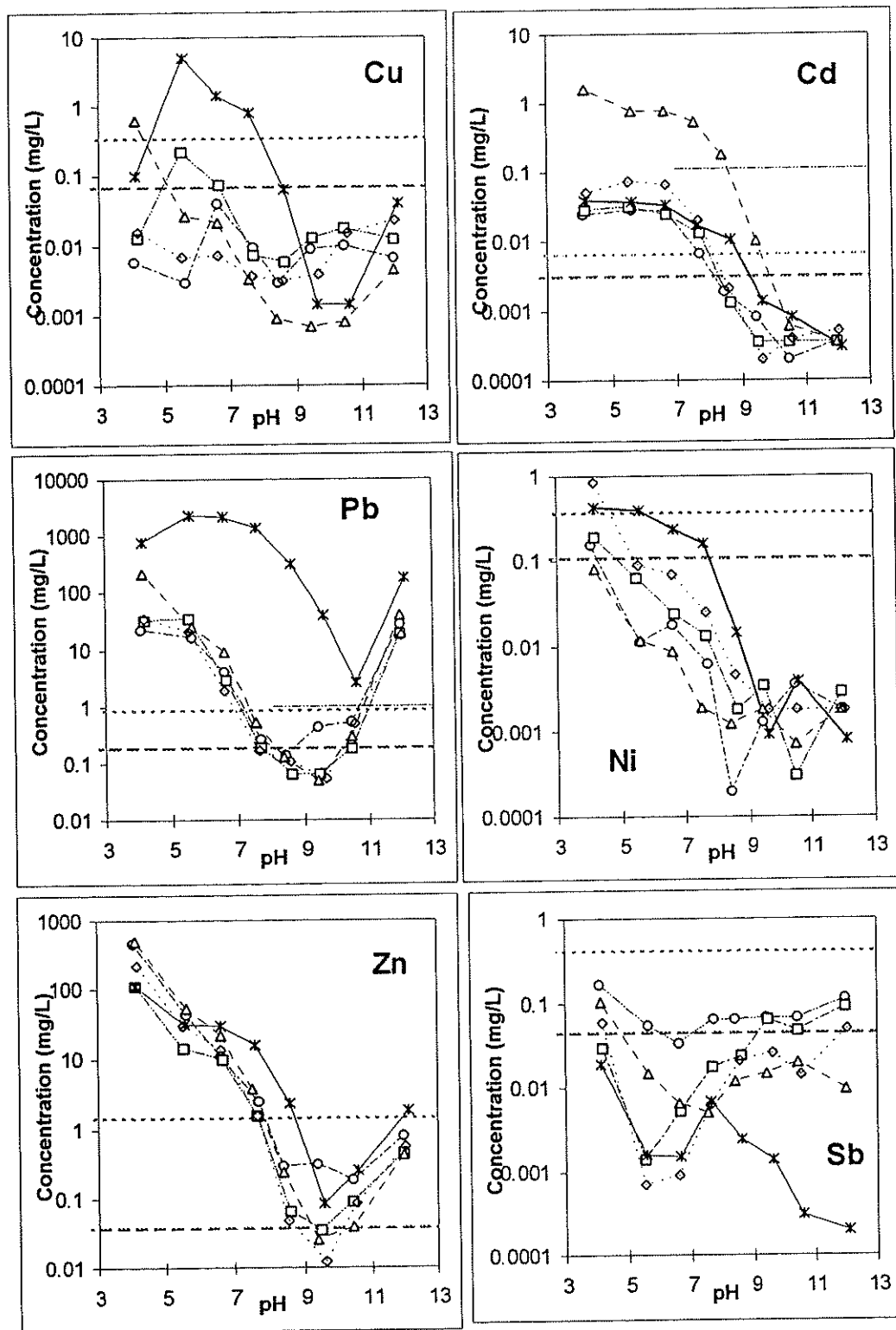


Figure 13. Comparison of Pb/Zn slag leaching with French, German and Dutch utilization regulations or guidelines (BMD Cat I: line; BMD Cat. II: line; FRMSWI: dot-dash) Circle: LBF lot 2; square: ISF Lot C; triangle: Kivcet 1; diamond: BZL ISF 2; star: QSL Gran C.

Table III. *pH domains per element meeting dutch regulatory criteria*

	Cat 2	Cat 1
Ba	all slags at pH > 6	ibid
Cd	all slags at pH > 7.5 - kivcet and Gran 3	all slags at pH > 8 - kivcet and Gran 3
Cr	all slags	all slags
Cu	all slags at pH > 6.5 - Gran 3	ibid
Mo	all slags	all slags
Pb	all slags between pH 7.5 and 10 - Gran 3	all slags between pH 8 and 10 - Gran 3
Ni	all slags at pH > 5	all slags at pH > 5, only Gran 3 at pH > 8
Sn	all slags	all slags
Zn	all slags between pH 8 and 11 - Gran 3	all slags between pH 8.5 and 10 - Gran 3
As	all slags between pH 5 and 11	ibid
Se	all slags	all slags
Sb	all slags	all slags between pH 5 and 9 - WJ lot2
F	all slags	all slags
V	all slags	all slags
S	all slags	all slags

### 3.5 Quality control aspects

#### - QA/QC approach

The issue of quality assurance and quality control is important for slag use in construction. The material to be used in construction must meet technical specifications as any other (natural) material used in construction applications. These criteria and associated tests are all available. Slag is a sand like material and can be tested according to procedures developed for sand. The environmental aspects are a separate issue, where guarantees are needed that the material provided has leaching properties within well defined boundaries. It must be possible to identify and isolate slag batches that do not meet specifications. In this sense, Pb and Zn producers become slag producers as well including a certain level of quality control to guarantee endusers of a constant product quality. The testing to be carried out for environmental quality should such as to ensure that undesired deviations from the basic characteristics of slag are identified. Test results of quality control should therefor always be placed in relation to the more extended basic characterization data generated in the framework of this project. This will allow to pick out deviations more easily and in addition to provide guidance into what management options are open to meet specifications in a second step or divert a batch to landfill. The hierarchy of testing associated with QA/QC should be based on the current distinction in levels of testing as specified in CEN TC 292. The frequency of testing is strictly related to performance in QC. When the slag produced meets the criteria all the time a relatively low frequency of testing can be agreed, as soon as an excursion takes place the frequency steps up until the system is under control again. The elements to be measured can be reduced to the ones identified as crucial from a regulatory perspective. At a low frequency the full range of elements needs to be verified to ensure that the slag is still produced with the same specifications on all counts.

After a certain period of data generation, product certification can be considered. It is the best indication that the issue of slag use is considered with the proper incentives. Not to get rid of slag with a minimum effort because dumping is becoming more difficult, but to make

an effort to treat slag as one of the products of the Pb and Zn production. This is very much an image aspect.

*- Compliance test and concise test*

For quality control purposes, it is important to have short procedures that allow a quick verification to determine that the material is consistent with a previous characterisation. In CEN TC 292 a compliance test for granular materials has been developed [12]. It consists of three extraction options. Here the two step option LS = 2 and LS = 2 - 10 has been applied to be able to relate the test results to the column test data. In addition, two pH controlled experiments were carried out as described in the proposed concise test for granular materials [13]. The pH conditions applied are pH 4 and pH 12 (LS=10). In figure 14, the data are plotted as a function of pH and compared with the pH static information for the five slags tested. The data show a good correlation between pH dependent leaching behaviour and the individual measurements in the CEN test and the added pH controlled tests for the concise test. The markedly different behaviour of GRAN 3 is also recognised in the concise test. For quality control purposes, the relevant condition for a given application can be selected.

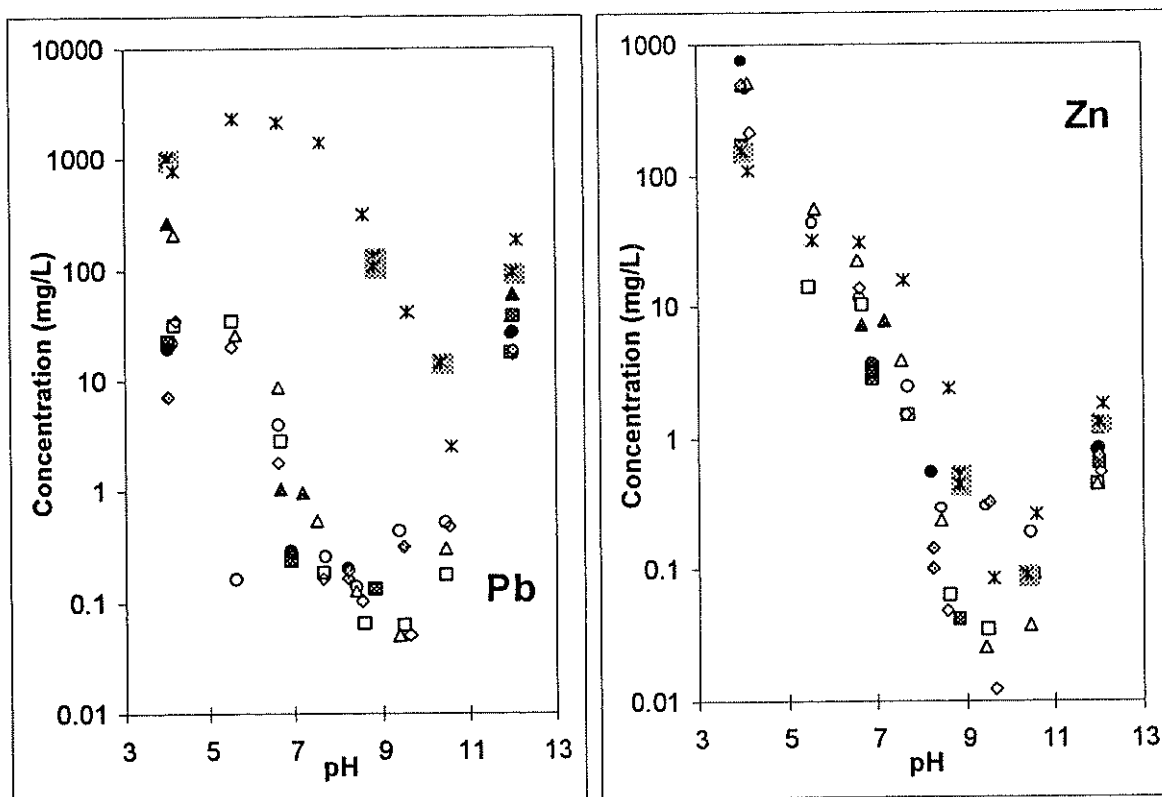


Figure 14. Correlation between CEN compliance test, concise test (closed symbols) and pH static leach test data for five different slags (open symbols).  
 ○ LBF MER lot 2; □ ISF MER lot C; △ KIVCET 1; ◇ ISF BZ 2;  
 \* ISF MM Gran 3