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Waste Materials in Construction: Putting Theory into Practice

VALORIZATION OF LEAD-ZINC PRIMARY SMELTERS SLAGS

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1. INTRODUCTION

Lead and zinc primary smelters in Europe produce and dump every year about 1 Mt of slag. The industrial objectives of the Brite Euram project on which we will report here are to valorize the primary lead and zinc slags, and to avoid their dumping through their use in safe construction and civil engineering materials representing high tonnages. To maintain its competitiveness regarding overseas competitors, the European non-ferrous metallurgy industry has to avoid the burden of dumping cost, and must hence develop beneficial uses for its slags. 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 work towards 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. And further to develop cost effective processes and techniques to use the non-ferrous slags in environmentally compatible construction and civil engineering materials, as a partial or total substitute to quarry raw materials. Slags from other industrial processes such as blast furnace slag, steelslag 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.

2. EXPERIMENTAL

2.1 Characterisation and leaching behaviour

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] .

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 and 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.
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 [10] 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. Slag has been exposed to the atmosphere for more than a year to observe changes in leaching controlling properties.

2.2 Improvement of the slags by metallurgical parameters

A better understanding of the factors controlling the slag leaching behaviour can lead to measures to improve the environmental properties of slag by controlling relevant parameters in the metallurgical process. For this purpose, the leaching data generated in the first part of the work are evaluated against the operating conditions of the different furnaces, as they do not run under the same operating conditions. Aspects addressed in this part are related to the basicity of slag, the occurrence of metallic Pb and to the level of crystallinity of the slags. In full scale operating facilities, tests have been performed in order to decrease the metallic lead content in the slags. In addition, experiments on slag cooling and granulation have been carried out, as these bear on the level of slag crystallinity.

2.3 Development of beneficial applications of slags

The following options for beneficial use of slags as substitute for natural raw materials have been evaluated:

- Aggregates for concrete (partial sand replacement)
- Structural fill in embankments and use as road construction materials
- Base materials for brick and tile manufacture

For different applications different specifications may apply. First the technical suitability of the slags for a given application needs to be determined. When this proves to be the case, the material can be prepared and its actual properties tested. Then the environmental aspects of use of the material in construction will be addressed. For the identification of technical properties end users are involved in the programme.

- Concrete

In the case of application in concrete, the concrete properties will be evaluated at sand replacement levels of 0 (reference), 10, 50 and 100 %. The durability of the concrete is evaluated through measurements of freeze-thaw resistance, alkali-aggregate reaction, long term and autoclave expansion. The leaching behaviour of slag-based mortars and concretes is evaluated using leaching tests focusing on the properties of the intact product rather than studying size reduced material. The major pollutants will be monitored (e.g. heavy metals, Ba, sulphate)as well as major elements or parameters relevant for the leaching behaviour of the material (Al, Ca, Na, K, pH).

- Application on embankment and road construction

In road construction secondary materials can be applied in different layers of the construction. The investigations have been carried out to compare the properties of the following mixes containing slag :

Road cover	° surface bitumen concrete with slag addition as gravel
Road base	° slag treated with cement and lime,
	° slag concrete with cement and gravel,
	° asphalt concrete with lime gravel.

Following the verification of the technical performance of the mix designs, field demonstration has been carried out at a level of 600 m^2 in 5 sections of different composition.

- *Application in bricks and tiles*

The possible application of slag as sand replacement in a special bricks and tiles manufacturing process is based upon transformation of a lime-sand mixture in an autoclave process. The performance has been studied at laboratory scale with various quantities of slag as a partial substitution of sand. After demonstration of satisfactory performance, an experiment on a larger scale has been performed at a sand lime bricks plant.

- *Study of environmental performance of slag containing construction products*

The environmental performance of the slag containing construction products is verified in long term laboratory leaching tests (3 months, 6 months, 1 year) under a number of exposure conditions, such as acid rains, alkaline waters, oxidizing and reducing conditions, salted and fresh water, water saturated testing and discontinuous exposure to water. Pilot scale tests have been designed and manufactured in close collaboration with the final product producers and users.

3. RESULTS

3.1. Slag characterisation and leaching behaviour

3.1.1 Physical and mineralogical properties of slag

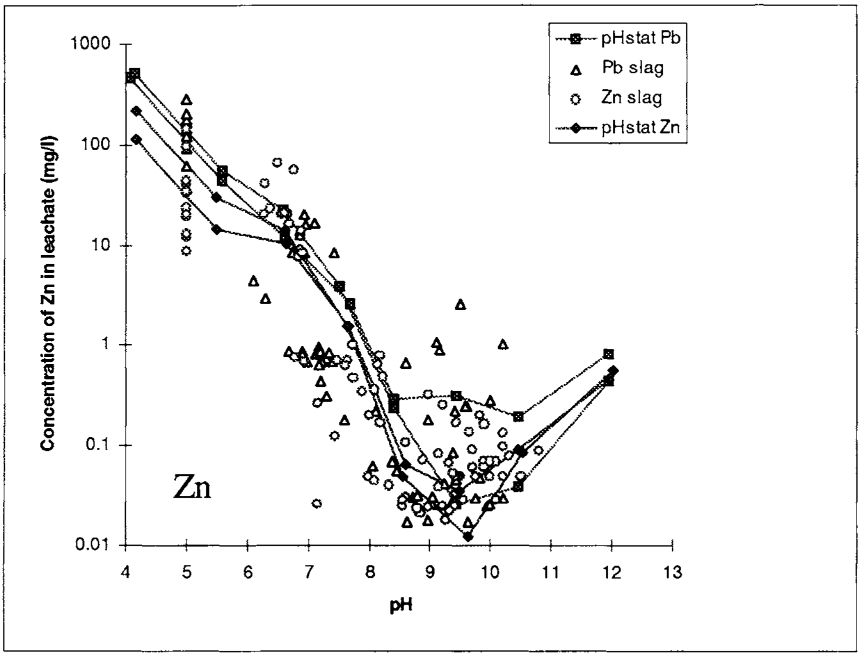
Through proper collection of 21 lead and zinc primary smelter slag samples from smelting installations in 4 European countries, it has been possible to cover a broad spectrum of slag qualities from both a chemical and mineralogical point of view. Zn assays ranging from 5 to almost 12 % and Pb assays 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 mm. This renders them similar to natural washed sands obtained in quarry operations. Mineralogical investigations have shown that granulated slag consist all largely of an Fe-Ca bearing aluminosilicate glass, as reflected by the presence of moderate amounts of SiO_2, FeO and CaO, together with minor amounts of Al_2O_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 CO_2 flushing or under acetic acid leaching, all analysed elements exhibit higher releases. In figure 1 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 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.

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 assessable 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 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 be avoided.



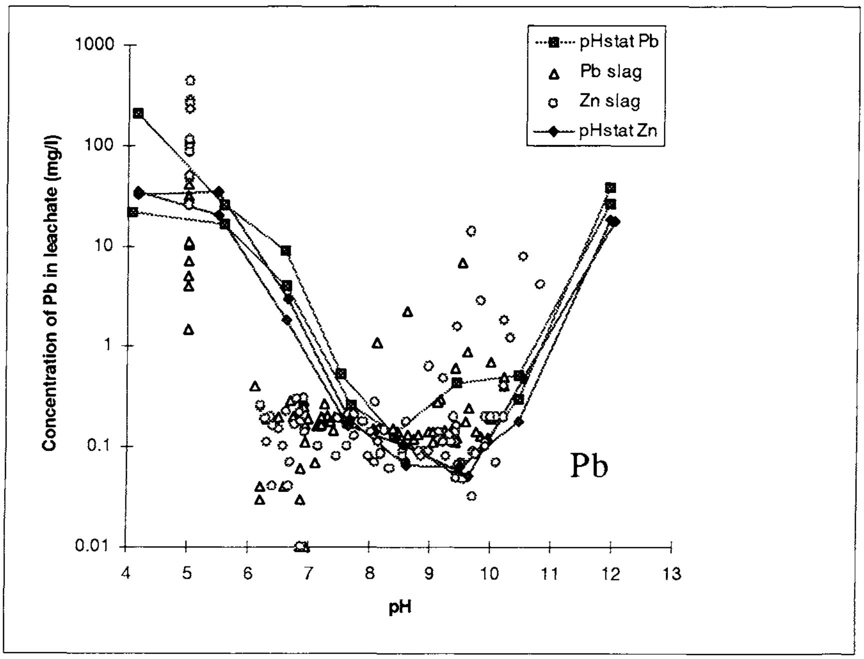


Figure 1. Results of pH dependent leaching behaviour for Pb and Zn from Pb and Zn slags in comparison with regulatory test data (X31-210, DEV S4, EP tox and TVA).

- *Reducing properties of Pb/Zn slag.* Using a recently modified procedure [12] 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- Eh curve for normal oxidised 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)[13]. 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[13], this is reflected in the measured reducing properties of the slag as a function of pH.

- *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_3 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 2 the pH dependent leaching behaviour of Al, Cu, Cr, Mn, Pb and Zn is given. 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, if necessary.

- *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 [14] 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 3 the column test results for Pb are graphically presented as a function of LS.

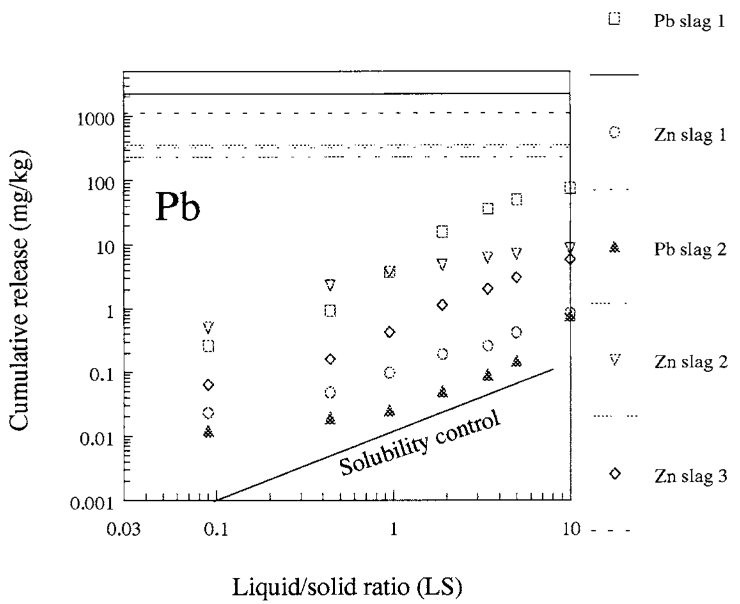


Figure 3. Column test data of Pb for four Pb and Zn slags showing cumulative release expressed in mg/kg covering the liquid to solid ratio 0.1 to 10. The availability test data are included as horizontal lines.

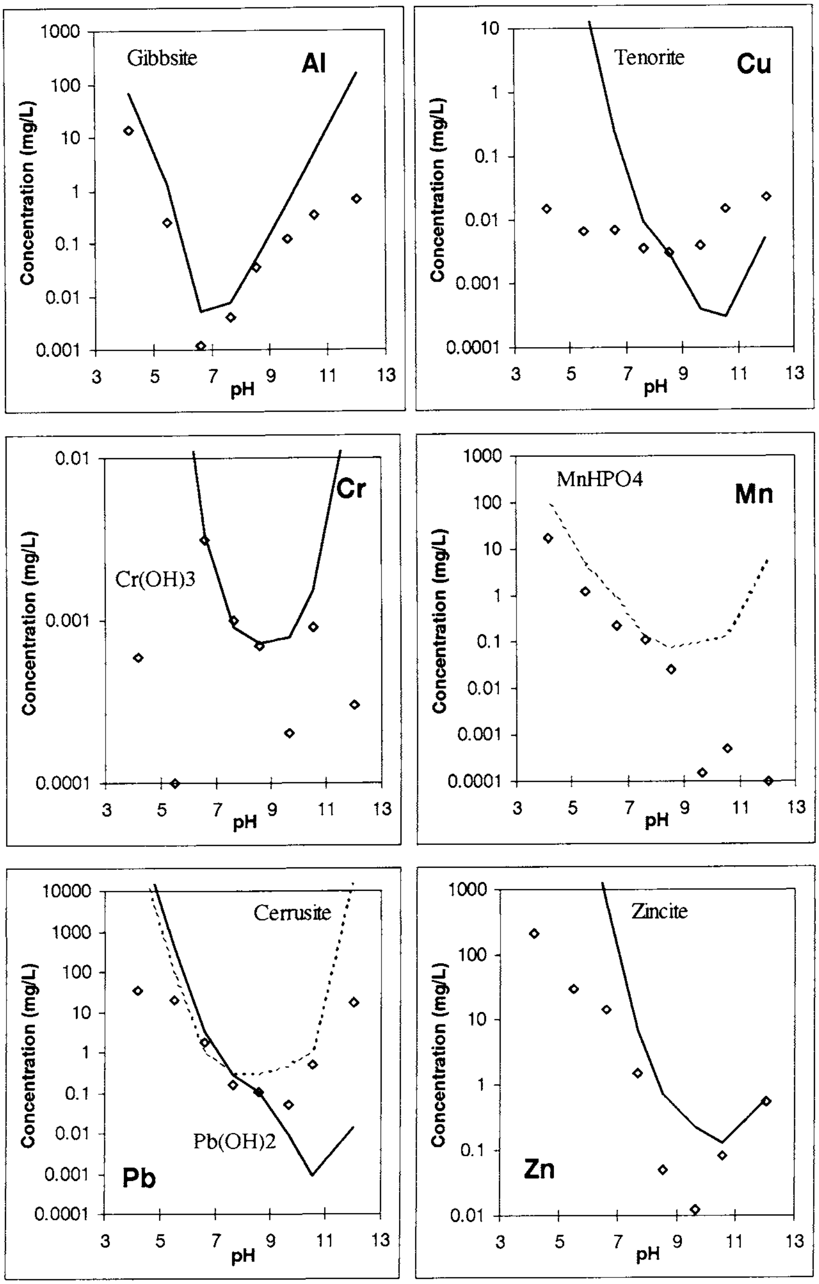


Figure 2. pH dependence of leaching and geochemical modelling of leaching behaviour from Pb/Zn slag (using MINTEQA2).

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. 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).

- *Leaching behaviour of pure phases.* The concentrations dictated by solubility pure Pb phases has been modelled. In figure 4 the modelling data are presented.

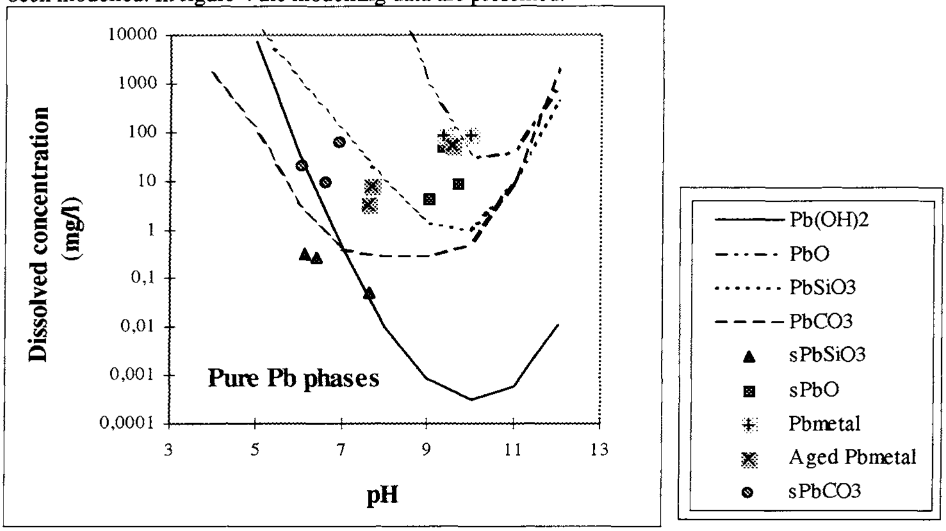


Figure 4. Modelling and measurements of Pb leaching from pure Pb phases.

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, allthough 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 $PbCO_3$ solubility. The solid $PbSiO_3$ leachability does not correspond well with the $PbSiO_3$ solubility curve. It matches better with either $Pb(OH)_2$ (or $PbCO_3$). The solid $PbCO_3$ solubility as measured in the leaching test corresponds reasonably well to the modelled $PbCO_3$ 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 $PbSiO_3$ corresponds closer to $PbCO_3$ 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 embeded 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_2 from the air PbO will be react to $PbCO_3$. 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 enlighting to verify for slag with a high Pb leaching level in relatively fresh slag the change in Pb leachability with time.

- *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 = 0.7m, Ø = 0.4 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 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. 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 consistency of the leaching data on aged slag with the pH-stat data is very promising.

- *Geochemical modelling of slag leaching behaviour.* Using the geochemical speciation model MinteqA2[10] , the leaching data obtained from the pH stat experiments on Pb and Zn slagshave 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 crystaline phases. The leaching data obtained for major, minor an 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 2 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 cerrusite - $PbCO_3$. This is consistent with the observations on pure Pb phases. Only in case of ISF Gran 3 solubility control of Pb by PbO and $PbSiO_3$ matches better with the observed solubility curve than cerrusite. XRD measurements have revealed the presence of metallic Pb droplets and PbO in this sample.

Zinc - The solubility of Zn is largely matched by the solubility dictated by zincite - ZnO.

- *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 off 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 element the same applies (Table 1a and b).

Table 1a. MINERAL PHASES IDENTIFIED IN THE SLAG BULK MATRIX

	SATURATION INDICES							
pH	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
FECR2O4	9.29	12.81	12.26	9.49	8.29	5.02	**0.30**	-9.59

Table 1b. SOLUBILITY CONTROLLING MINERAL PHASES BASED ON GEOCHEMICAL MODELLING USING LEACHATE ANALYSIS DATA

	SATURATION INDICES							
pH	12.0	10.5	9.5	8.5	7.5	6.5	5.5	4
Fe(OH)2	**0.04**	**0.84**	**-0.28**	-2.04	-4.01	-6.01	-8.05	-11.26
NORSTRANDITE	-2.08	**-0.51**	**0.20**	**0.15**	**0.58**	**0.05**	**-0.63**	-0.80
QUARTZ	-2.58	-1.60	-1.13	**-0.67**	**-0.28**	**0.08**	**0.67**	1.61
PB(OH)2 (C)	3.49	2.51	**0.58**	**0.05**	**0.13**	**0.21**	-1.23	-3.50
CERRUSITE	-2.70	**-0.56**	**-0.95**	**-0.36**	**0.22**	**0.78**	**-0.58**	-2.98
ZN(OH)2 (E)	**-0.506**	**-0.927**	-1.576	**-0.916**	**-0.916**	-2.086	-3.727	-5.97

Note: Values close to zero indicate solubility control; indices are given in log-scale units.

- *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[15]. 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[16]. The pH conditions applied are pH 4 and pH 12 (LS=10). In figure 5, 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.

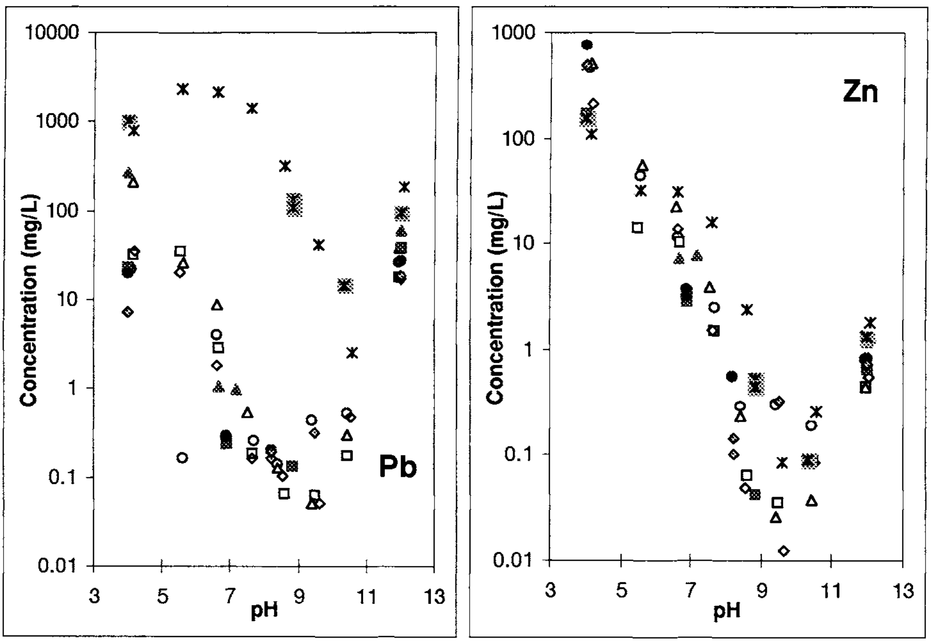


Figure 5. Correlation between CEN compliance test, concise test and pH static leach test data for five different slags.

3.2 Improvement of the slags by metallurgical parameters

The main goal of the work is to utilize the slags in civil engineering applications. This goal should preferably be reached without alteration of the process. However, if the leachability would prove to be too high for utilization of slag as a substitute to raw materials, it could be necessary to modify some aspects of the process. The leachability of Pb is considered most critical in this respect as metallic Pb will have an influence on leachability. The following measures have been tested to reduce the metallic lead content:

- selective settling of lead droplets
- transforming of lead in a more stable phase e.g. silicate
- diminishing the accessibility

The two experiments involving lead blast furnace slag must be considered as preliminary. The first focused on slag tapping at higher temperature and the second on re-melting and cooling at different speeds.

3.2.1 Slag tapping at higher temperature

Two forehearth operations have been conducted, each of them being achieved at full scale over a three shift period. The following results were obtained:

	Total lead release NFX31-210 (mg/kg)
Normal forehearth operation - slag temperature 1185 °C	5.4
Overheated forehearth operation - slag tapping temp. 1210 °C	1.3

The decrease in lead leachability is not directly linked to an improvement of lead droplet settling. It rather appears to be related to a modification in slag mineralogy.

3.2.2 Re-melting and cooling

The cooling mode has been studied at the laboratory. After re-melting the slag was submitted to three cooling modes: rapid cooling through water quenching , moderate cooling through tapping into ingot and slow cooling by controlling the temperature decrease at 2 °C/min. The following results were obtained:

Treatment	Reference slag	Rapid cooling	Moderate cooling	Slow cooling
Lead leachability (NF X 31-210)	4.0	0.7	0.4	0.2

To explain the observed leaching behaviour three mechanisms can be identified: settling of metallic lead, transformation of metallic lead in lead silicate and modification of the crystallinity of the slag. Experiments are underway to identify which mechanism is prevails.

3.3 Environmental assessment of utilization scenarios of slags

3.3.1 Materials and recipes

On the basis of technical and environmental criteria, a preliminary study allowed the choice of a substitution level of aggregates by slags for each type of material manufactured by the related industrial partners. The recipes retained for environmental evaluation are presented in the following table.

materials / recipes	concrete kg/m^3		breeze blocks kg/m^3		brick (%)		sand-cement (%)		sand -bitumen (%)	
reference	sand	792	sand	1197	sand	90	granulate	94.5	granulate	100
	gravel	1010	gravel	803	lime	10	road		bitumen	4.5
	cement	320	cement	200			binder	5.5		
	water	200	water	130						
	slags 11 %		**slags 15.2%**				**slags 47 %**		**slags 50%**	
ISF slags	slag	81.4	slag	164			slag	47	slag	50
	sand	732	sand	1075			granulate	46.5	granulate	47
Métaleurop	gravel	1010	gravel	803			road		filler	3
	cement	320	cement	200			binder	5.5	bitumen	4.5
	water	200	water	130						
					slags 8-15 %					
ISF slags					slags	8-15				
Britannia					sand	75-82				
Zinc					lime	10				
	slags 11 %		**slags 16 %**				**slags 47 %**		**slags 50 %**	
LBF slags	slags	81.7	slags	172			slags	47	slags	50
	sand	736	sand	1075			granulate	46.5	granulate	47
Métaleurop	gravel	1010	gravel	803			road		filler	3
	cement	320	cement	200			binder	5.5	bitumen	4.5
	water	200	water	130						

3.3.2 General presentation of the methodology

The environmental validation of the obtained materials was carried out by studying leaching behaviour of the materials under specified conditions. The methodology described in the French experimental standard X30-407 and the methodological guide of the WG6 of the CEN/TC 292 were used : The valorization scenarios were described in terms of influence factors. The parametric tests were used to measure the respective influence of these factors (pH) on the leaching behaviour of the materials (solubility, dynamics and release intensity).

The limits of our impact study are :

- The materials are observed in only one stage of their life cycle (that for which the materials were designed)
- migration in the immediate environment (soils, surface waters, underground water) of the leached constituants from the site of use is not followed up
- toxicity for man or ecological impact on the flora and fauna as a secondary effect is not evaluated

The aim is essentially to measure the flux of pollutants in the considered scenarios

3.3.3 Presentation of the study

The following table presents the scenarios and most probable use criteria for each material.

Materials	concrete		breeze blocks	brick	sand cement	sand bitumen
scenarios	wall	foundation	wall	wall	base layer	
in contact with the air			✔	✔		
flooded not in contact with the air		✔				
normal road					✔	✔
road in contact with underground water					✔	✔

3.3.4 Presentation of the experimental programme

Analysis of the scenarios allowed us to retain influence criteria whose effects were evaluated using the parametric tests presented in the following table :

parametric tests \ scenarios		**in contact with air**	**flooded not in contact with air**	**normal road**	**road in contact with underground water**
leaching on crushed samples	acid neutralizing capacity	*	*	*	*
	solubility according to pH	*	*	*	*
	test at equilibrium	*	*	*	*
carbonation		*		*	
leaching on monolithic material	with demineralised water	*		*	
	with a synthetic solution of porewater		*		*
	with acid solution	*		*	
	coupled with a wetting/drying cycle	*		*	

The programme consists of several levels of environmental evaluation.

Level 1 : Parametric tests in the laboratory to evaluate release while varying one influence parameter (e.g. solubility tests measure variation according to chemical context).

Level 2 : Pilot tests in real environmental exposure conditions integrating the variation of climatic factors. There are two sizes :

Level 2A :small size pilots ($1m^2$) for concrete, breeze blocks, bricks,

Level 2B: large size pilots (150 m^2) for road construction materials.

The levels of exposure tested for the different materials are summarized in the following table :

Materials / scenarios / experimental level	concrete		breeze blocks	bricks	sand cement		sand bitumen	
	wall	**foundation**	**wall**	**wall**	**normal road**	**flooded road**	**normal road**	**flooded road**
level 1	ISF MER LBF MER	ISF MER LBF MER	ISF MER LBF MER	ISF BZ	ISF MER LBF MER	ISF MER LBF MER	ISF MER LBF MER	ISF MER LBF MER
level 2A	ISF MER		ISF MER	ISF BZ				
level 2B					ISF MER		ISF MER	

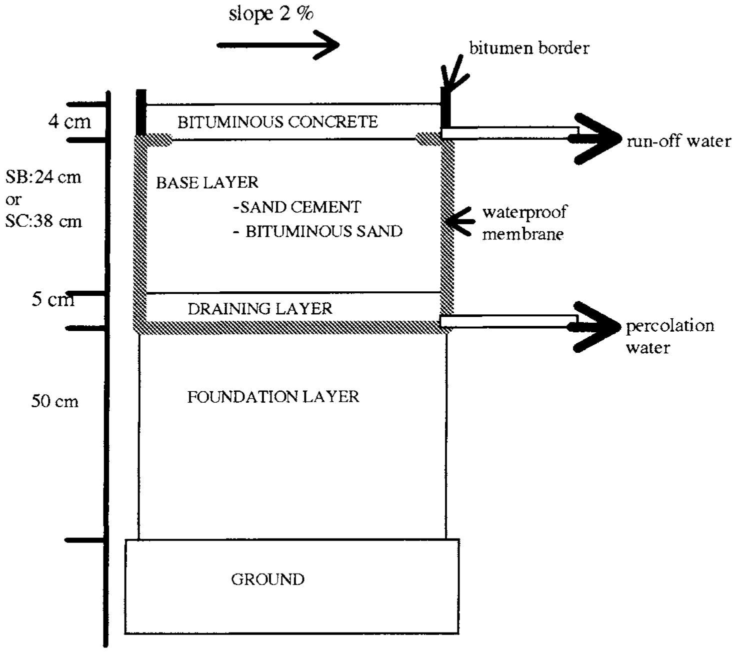
3.3.5 Presentation of the pilots

Level 2A : It concerns concrete, breeze blocks and bricks. For each material there is a reference recipe and a recipe with the slags ISF provided by Metaleurop (concretes, breeze blocks) or Britannia Zinc (bricks). The pilots have been installed since October 1996.The materials provided in monolithic form were assembled in a wall with a surface of $1m^2$ and arranged to slope at 30° in relation to the vertical. The lower surface of the wall is covered with a waterproof membrane. A system collects the run-off and percolation waters. Each sample, which is collected according to the arbitrary climatic conditions, is analysed (lead, zinc, calcium, sodium, potassium, filtered and the volume and pH are measured. The follow-up is in progress.

Level 2B : It concerns road construction material. For each material there is a reference recipe with slag ISF from Métaleurop. The four experimental surfaces were made in Béthunes (Pas de Calais) by Colas and have been in operation since May 1996. The tested materials form the base layer of the road structure (just beneath the road surface layer). Each experimental surface is of 158 m^2. The following diagramme shows the structure as a whole :

surface n° 1 ***sand bitumen reference***	***surface n°2*** ***sand bitumen and slags ISF MER***	***surface n°3*** ***sand cement reference***	***surface n°4*** ***sand cement and slags ISF MER***
surface layer draining bituminous concrete 0,04 m			
sand bitumen 0.24 m	**base** sand bitumen with slags 0.24 m	**layer** sand cement 0.38 m	sand cement with slags 0.38 m
drainage layer in 10/20 limestone 0.05 m			
foundation layer : red schist 0.50 m			

The following figure shows the collecting device of run-off and percolation waters.



The level 1 laboratory studies are also in progress. The results of these trials and those concerning the pilots will be available in autumn 1997.

4. CONCLUSIONS

The regulatory test methods can be placed in perspective by comparing the test results in relation to the pH static leaching test. The measurement of pH in leachates is rather critical due to the low buffer capacity of Pb and Zn slag. More strict control of the final pH in leachate analysis is needed for materials with very low buffer capacities as exposure to the atmosphere for even a relatively short time may bias the results in an unacceptable manner.

The leaching behaviour of elements from Pb and Zn slags is generally very consistent. Exceptions can be related to significant differences in slag properties, such as degree of ageing and degree of crystallinity.

If metalic Pb is present in slag or mixed with slag, fresh slag will show high Pb leachability due to high PbO solubility. Upon aging PbO converts to $PbCO_3$, which in the geochemical modelling has been shown to be the most important solubility controlling phase in most cases. These observations lead to the question whether testing of fresh slag is the appropriate way of judging slag leaching behaviour for Pb for environmental assessment purposes.

The geochemical modelling has revealed that solubility controlling phases are not the same as those observed in mineral analysis of bulk slag. The often new phases formed at the surface of a materials exposed to moist, atmospheric conditions dictate the leaching behaviour of the slag material in practice. An important difference has been observed for the controlling phase of Pb in ISF GRAN 3 where PbO and $PbSiO_3$ are the most likely solubility controlling phases in contrast to cerrusite (PbCO3) in the other slags.

Based on the present understanding of the leaching behaviour of slags, as produced, as a secondary raw material in construction, conditions for beneficial application can be identified. The conditions that need to avoided can be clearly identified and codes of practice for reuse can be defined.

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