Goumans/Senden/van der Sloot, Editors
Waste Materials in Construction: Putting Theory into Practice

Leaching of chromium from steel slag in laboratory and field tests - a solubility controlled process?

A-M. Fällman

Swedish Geotechnical Institute, S-581 93 Linköping, Sweden
e-mail: annfal@geotek.se

Abstract

Differences in concentrations in leachates and leaching conditions were found in laboratory and field tests on electric arc furnace steel slag. Solid phases were assumed to control the leachate concentrations of chromium and barium. Geochemical modelling was used to indicate solubility controlling solid phases. The mineral $BaSO_4(c)$ and solid solutions of $Ba(S,Cr)O_4$ were predicted to control the concentrations of barium and chromium in the leachates, respectively. These solids were not expected to be present as primary minerals in the steel slag and were rapidly formed, within 6 hours.

1. INTRODUCTION

Steel slags are utilised in roads, as construction and paving materials, since its physical properties are similar to natural materials like gravel. Around 77%, equal to 19 Mtonnes, of the electric arc furnace (EAF) steel slag produced world wide was utilised in civil engineering during 1990.[1] Environmental concerns regarding utilisation and landfilling of steel slag focus on the content of heavy metals and specially on the leachable quantities, where chromium have gained special attention due to its toxicity in the hexavalent state.[2]

The conditions under which the leachates are produced varies, depending on purpose, design and local conditions. Differences such as rate of infiltration, penetration of air through the material, and particle sizes of the material may influence the resulting concentrations of e.g. metals in the leachates.[3] Laboratory leaching tests represent conditions that may be different from the field situation.[4] Variations in concentration of more than one order of magnitude were found for chromium, vanadium and lead in leachates from EAF slag under different leaching conditions in field and laboratory tests (dilution was excluded). [3, 4] Interdependencies between the concentrations of chromium, barium, sulphur and calcium in leachates from steel slag were seen in an earlier study.[5] In addition, Fruchter et al.[6] found that solid solutions of barium, chromate and sulphate controlled the concentration of chromate in the leachates from fly ash (laboratory and field tests).

The objective of this study was to test if the concentrations of chromium and barium in leachates from EAF steel slag in different leaching systems could be solubility controlled.

2. MATERIALS AND METHODS

2.1 Material and sample preparation.

The material used was slag from scrap based production of low alloyed steel in electric arc furnace. The slag was emptied below the furnace, excavated, and transported while still hot to an intermediate storage for cooling (water sprinkling). The non-magnetic, screened 0-300 mm fraction (sampled at one occasion) was used in all tests reported in this paper. The total composition of the slag (average of two test samples) is presented in Table 1.[4] (Digestion in $LiBO_2$ melt as well as HNO_3 in a Teflon bomb;[7, 8] analyses by Inductively Coupled Plasma Emission Spectrometry (ICP-AES) for major elements and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for As, Cd, Co and Pb).

Table 1
Total composition (mg/kg) of the steel slag.[4]

Element		Element	
Fe	242000	Zn[1]	244
Ca	221000	Nb	198
Al	219000	Sr	178
Si	57700	Cu[1]	166
Mg	45200	Zr	55.2
Mn	39300	Ni[1]	45
Cr	7760	Pb[1]	21.5
P	4600	Mo	20.6
Na	3700	Sn	17.5
Ti	2800	Co[1]	5.8
S	1260	As[1]	5.3
V	1210	Cd[1]	0.45
Ba	728	Be	<1.2
K	460	Hg[1]	<0.41
W	410		

[1] Digestion in HNO_3 and Teflon bomb.

2.2 Laboratory Leaching Tests.

Leaching tests were carried out as column tests, pH static tests and single batch tests.[4, 5, 9] The laboratory samples were air dried at 50 °C and stored in closed containers until use. Oversized material, according to the specifications, was size reduced in a jaw crusher. Ultra pure water (<0.2 mS/m) and 0.1 mM HNO_3 (column test) were used as leachant. Bottles and beakers of polypropylene (PP) or polyethylene (PE) were used in the leaching tests and bottles of PE were used for storage of leachate samples. The column was made of polyacrylate.

Leachates were pressure filtered (N_2) in a polytetrafluoroethylene (PTFE) coated stainless steel filtering device through a 0.45 µm cellulose nitrate filter (D 100 mm).

Column tests were performed on test samples of grain size of 0-20 mm (columns with the diameter 0.1 m and height 0.9 m) with inflow in the bottom at a flow rate corresponding to a leachate to solid (L/S) ratio of 0.1 per day (maintained by a peristaltic pump, Gilson, Minipuls 3).[4] A 1.2 µm glass fibre filter was placed in the column at the outlet as a pre-filter. The outflow leachate was further passing through a 0.45 µm filter and accumulated in a closed bottle under N_2-atmosphere. Accumulated samples at L/S-ratios of approximately 0.1, 0.3, 0.7, 1.0, 2 and 4 were taken out.

The pH static tests were carried out at L/S=5 for 24 hours on test samples of grain size 0-4 mm (75-150 g) under continuous measurement and adjustment of pH by a titrator (Radiometer TIM 90) to ±0.05 units, with either 0.1-0.5 M HNO_3 or 0.5 M NaOH.[5] The leachates were mixed with a PTFE coated propeller. The beakers were covered but not air tight during the test.

Single step batch tests were carried out at L/S ratios 1.7 and 4.25 for 3, 6, 24, 48, 168 or 336 hours with end over end rotation (10 rpm) on grain sizes 0-1 mm and 0-8 mm.[9] Care was taken to minimise the head space in the bottles (100 or 250 ml). The tests were carried out in a two level factorial design[10] with the parameters L/S ratio, grain size and time. The factorial design was evaluated according to an additive model based on the saturation indices, defined below, and based on 2 standard deviations (SD).

2.3 Lysimeter.

A lysimeter of the size 3.0 x 3.0 x 1.2 m^3 made of plywood and covered with pre-formed HDPE liner was filled with approximately 10 m^3 slag corresponding to 21 tonnes of material.[4] The percolate was collected at the centre of the bottom. A geotextile attached to a synthetic draining layer on top of the bottom liner prevented particles from entering the leachate collecting system. The percolates were continuously flow measured and proportionally sampled by a tipping bucket system placed indoors in the basement of a nearby building. The sampled leachate was stored in a bottle under argon gas to prevent CO_2 uptake and oxidation.

2.4 Test Road.

The slag was used as road base material in a 50 m long section of an unpaved road (width 5 m and average height 2 m).[3] The test part was divided into two sections: one with the 0-300 mm size fraction and the other with the fraction 11-300 mm where material of grain size below 11 mm had been removed. Two leachate collection units (1x4 m^2 at 3% slope) were placed in each section at depths of 0.5 and 1.5 m below the road surface. The leachates were collected in a similar system as in the lysimeter but the leachates were stored open to the atmosphere. Samples for pH measurements were taken directly from the tipping bucket. The experimental program in this study was started 1.5 years after the test road was built.

2.5 Leachate Analysis.

Leachates were analysed with respect to pH, redox potential (Pt and calomel electrodes) and concentration of elements (ICP-AES, ICP-MS). Chromium was in some cases analysed by Atomic Absorption Spectrophotometer with Graphite Furnace (AAS-HGA). Sulphate was analysed by ion chromatography in the leachates from lysimeter, test road and batch tests. In the other leachates it was assumed that all sulphur were present as sulphate. Alkalinity was measured by titration with 0.1 M HCl (not in the batch test leachates).

2.6 Geochemical model.

The geochemical code MINTEQA2 version 3.11 was used for speciation calculations.[11] Saturation indices (SI) were derived from the calculated ion activity products (IAP) and solubility products (K_s) for the relevant minerals (SI=log IAP-log K_s). Input data were measured pH, Eh and concentrations of inorganic substances in the leachates (Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, SO_4^{2-}, Si, V and Zn). The pH measurements in the batch test leachates were not reliable due to disturbances of Na. The pH values for these leachates were instead obtained from the calculations (ion balance assumed). The redox potential and the pH were not allowed to change in the simulations and solids were not allowed to precipitate. Redox reactions were specified for Fe(II)/Fe(III), Mn(II)/Mn(III) and Cr(III)/Cr(VI). The state of oxidation was fixed for V(V), As(V), Cu(II) and S(VI). The temperature used was 25 °C. The thermodynamic data base provided by the code was used with amendments as shown in Table 2. Further changes in the data base were addition of Mo and revision of the constants for hydroxides of Cr(III) and Cu(II).[12-14]

Table 2
Selected stability constants amended or changed in the data base.[15]

Mineral	K_S
$Ba(S_{0.77}Cr_{0.23})O_4$	-10.13±0.07
$Ba(S_{0.96}Cr_{0.04})O_4$	-9.79±0.06
$BaSO_4$	-9.78±0.06

3. RESULTS AND DISCUSSION

The differences in leaching conditions between the tests are illustrated by the differences in pH, Figure 1. Leachates from the laboratory systems were alkaline, while neutral from the lysimeter. The test road showed pH values comparable to those from the laboratory tests in the 0-300 mm material while the 11-300 material gave pH values between the laboratory tests and the lysimeter.

The leachate compositions were also differing between the tests, see Table 3. Chromium concentrations were highest in the lysimeter and test road with 11-300 mm material, while barium concentrations were highest in the laboratory tests and the test road with 0-300 mm material. The conclusion was that different chemical conditions were dictating the leaching systems and that geochemical modelling was necessary to further understand the mechanisms controlling the leachate concentrations.

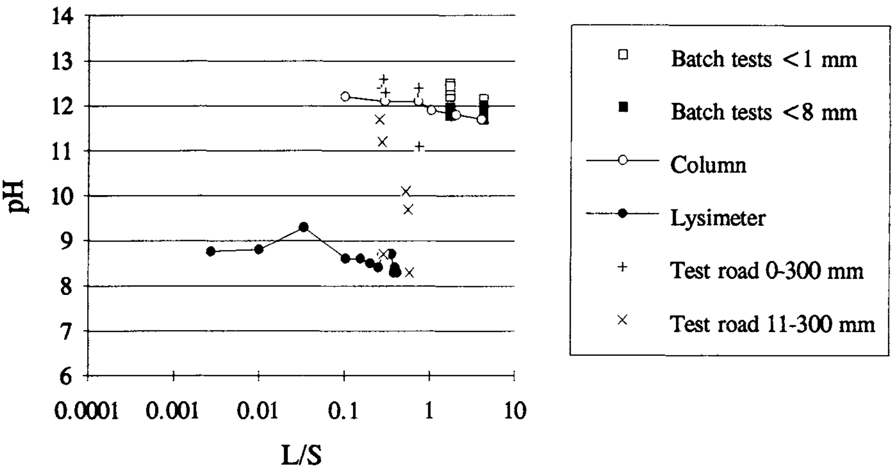

Figure 1 pH in the leachates from different tests on steel slag.

Table 3
Concentrations in leachates (mg/l) from the different laboratory and field tests. Parenthesis mark maximum values measured previously but not used in this study.[3]

Element	Ca	S(tot)	SO_4^{2-}-S	Ba	Cr
Batch test <1 mm	255-910	<0.16-2.62	<0.1-0.8	0.11-51	<0.0005-0.030
Batch test <8 mm	130-280	1.1-5.0	0.3-3.2	0.41-3.8	<0.0005-0.075
pH static	94.9-1900	3.08-10.5	NA	0.26-3.61	0.0031-0.060
Column	108-236	1.38-18.3	NA	0.32-1.21	0.013-0.13
Lysimeter	35.4-54.8	5.4-49	5-97	0.072-0.12	0.086-0.73
Test road 0-300 mm	350-900	NA(6.9)	0.2-13	7.2-15.6	0.024-0.048 (0.10)
Test road 11-300 mm	9.1-170	NA(30)	0.9-11	0.20-0.51	0.032-0.081 (0.66)

NA= not analysed

Results from the speciation calculations expressed as SI versus pH are given in Figure 2 for $BaSO_4$(c), gypsum, witherite, and in Figure 3 for $BaCrO_4$ and barium sulphate/chromate. The barium concentrations in the leachates appeared to be controlled by barium sulphate for all leachates except those from the batch test with grain sizes <1 mm. Gypsum did not limit sulphate. The steel slag is produced in a reducing system where sulphates are not likely formed.[16] Less than half of the sulphur content was analysed as sulphate in most (75%) of the leachates from batch tests. Sulphate minerals could be formed after oxidation and were likely formed as secondary minerals. The high SI values for $BaSO_4$ in some column and test road leachates could possibly reflect an overestimation of the SO_4^{2-}-S fraction. However, this was not confirmed. Co-precipitation with Sr was proposed by Fruchter et al.[6] to explain over saturation of $BaSO_4$. This could not be confirmed in this study since Sr was not analysed.

Barium carbonate (witherite) could be an additional candidate controlling barium. The SIs for witherite, see Figure 2, were pH dependent, and all the calculated systems were falling into the same pH dependency pattern. The high SIs for witherite in the test road with 0-300 mm material could be due to in-growth of carbonate during the exposure to the open air. The SIs for witherite in the column leachates were lower than for $BaSO_4$ and thus less likely to control the barium concentrations.

Barium chromate was the chromium mineral in the MINTEQA2 database showing SIs closest to zero. However, these were too low to indicate solubility control of the chromium concentrations (see Figure 3).

Rai et al.[15] found that solid solutions of barium, sulphate and chromate were obtained from over saturated solutions of these components. They also determined the stability constants and ratios between sulphate and chromate in the solid solutions. The introduction of these stability constants into the MINTEQA2 database resulted in calculated SIs close to 0 for all leachates except from the batch tests on <1 mm material, see Figure 3. The SIs of the $Ba(S,Cr)O_4$ solid solutions were close to those for barium sulphate, but different from the SIs for barium chromate. Neither of the solid solutions with 4% and 23% chromium, respectively, could be regarded as dominant in the control of chromium concentrations. Fruchter et al.[6] also found that these solid phases appeared to control the leachate concentrations of chromium in their studies on coal fly ash.

Chromium is likely found in Cr_2O_3 or Cr-(Fe,Mg)-oxides in the slag.[2] Chromates were likely formed after oxidation. The measured redox potential was used to assess the partitioning between Cr(III) and Cr(VI) in the leachates. The Cr(VI) activity at pH 4-6 was 23, 9 and 11 magnitudes lower, respectively, than the Cr(III) activity. In spite of these low modelled activities the calculated SIs for the $Ba(S,Cr)O_4$ solution with 4% chromium were close to saturation.

The factorial design evaluation of the SIs from the batch tests leachates gave as result that $BaSO_4$(c) and the $Ba(S,Cr)O_4$ phases might be solubility limiting (i.e. SI=0 within the confidence interval of 3 SD) for the tests on <8 mm samples (see Table 4). For the small grain size <1 mm samples only $BaSO_4$ (c) (only L/S=1.7) appeared to represent saturation. There was no time effect on SI for these solids.

Table 4
Predicted intervals for SI (3 SD) based on factorial design interpretation of the batch tests.

	Grain size 0-1 mm			Grain size 0-8 mm		
	No L/S effect	L/S 1.7	L/S 4.25	No L/S effect	L/S 1.7	L/S 4.25
$BaCrO_4$	[-3.40, -1.83]			[-2.79, -1.22]		
$BaSO_4$ (c)		[-1.81, 0.93]	[-2.93, -0.19]		[-1.72, 1.02]	[-1.81, 0.93]
$Ba(S_{0.96},Cr_{0.04})$	[-2.22, -0.21]			[-1.46, 0.55]		
$Ba(S_{0.77},Cr_{0.23})$	[-2.13, -0.25]			[-1.30, 0.58]		

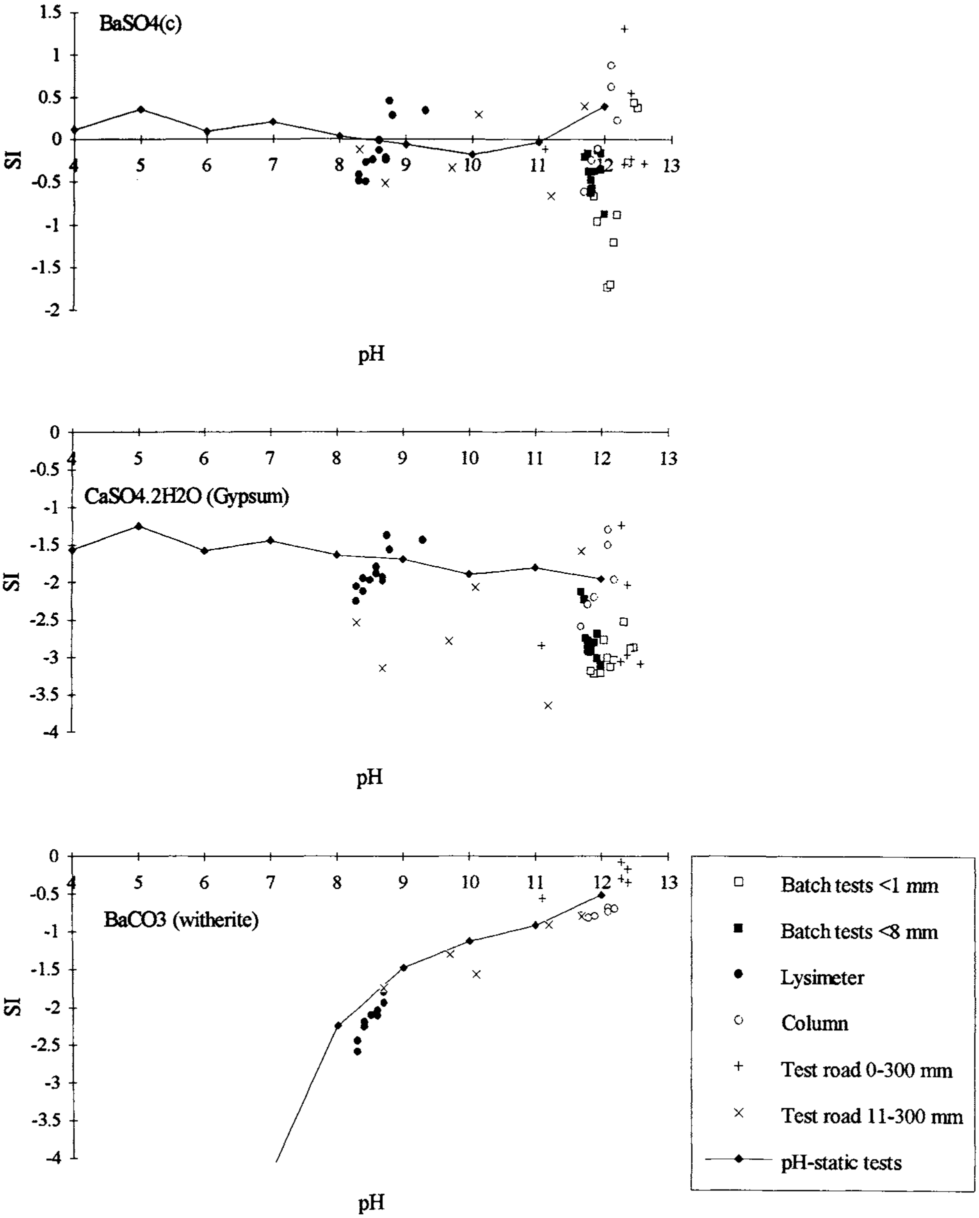

Figure 2. Saturation index (SI) versus pH for $BaSO_4$(c), $CaSO_4 \cdot 2H_2O$ (gypsum), $BaCO_3$ (witherite) in the leachates from different tests.

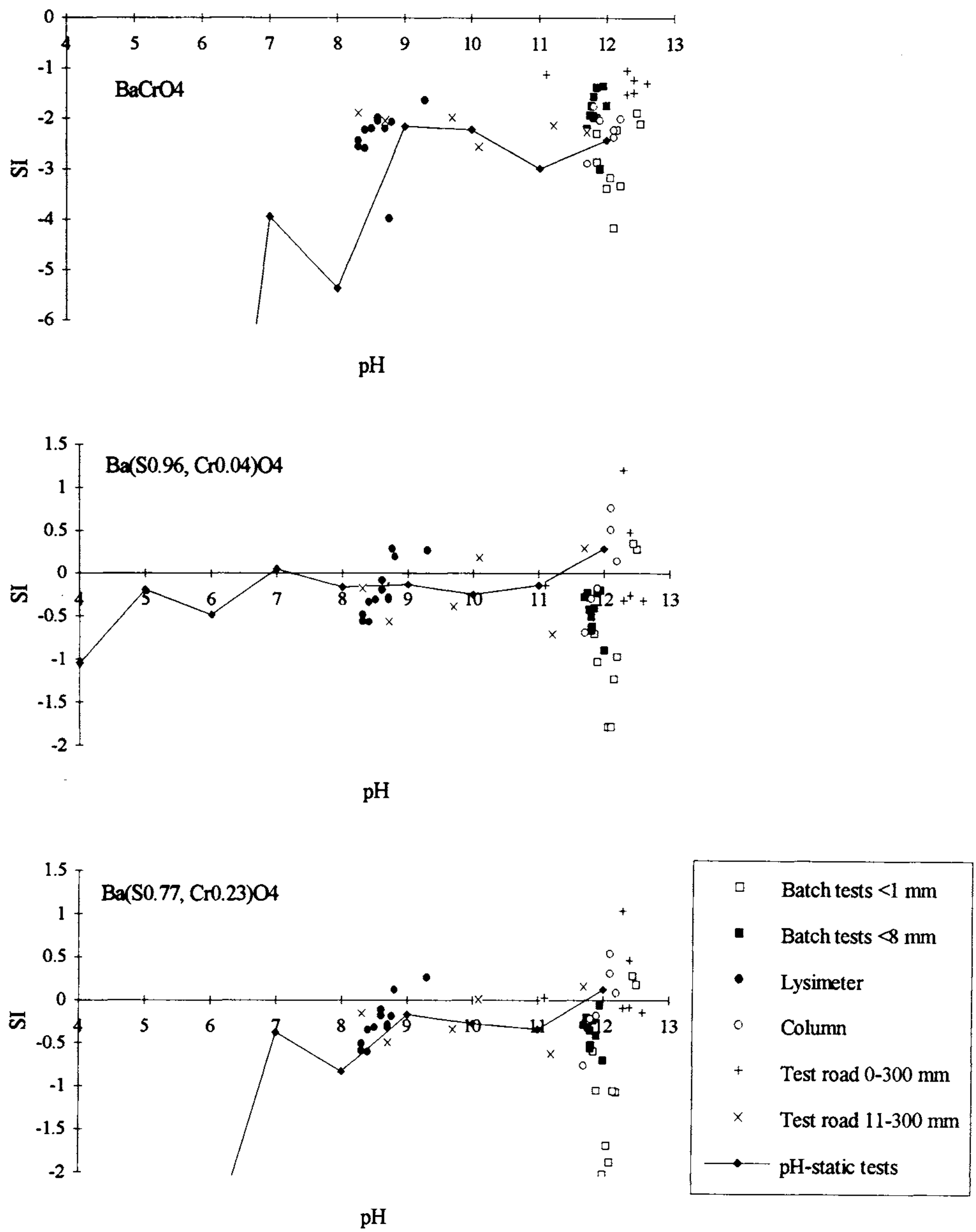

Figure 3. Saturation index (SI) versus pH for $BaCrO_4$, $Ba(S_{0.96}Cr_{0.04})O_4$ $Ba(S_{0.77}Cr_{0.23})O_4$ and in the leachates from different tests.

4. CONCLUSIONS

It is indicated from this study that concentrations of barium and chromium may be controlled by the solubility of well defined solid phases. The mineral $BaSO_4$ and solid solutions of $Ba(S,Cr)O_4$ were predicted to control the concentrations of barium and chromium in the leachates, respectively. Solubility controlled conditions were rapidly achieved, within 6 hours, in the batch test. None of these phases were expected to exist as primary minerals in the steel slag. However, the presence of these predicted solids associated with leached slags need to be verified.

ACKNOWLEDGEMENTS

This work was funded by the Swedish Waste Research Council under grants AFR Dnr 324/92 and 126/93 and in addition based on work funded by Fundia Special Bar AB.

5. REFERENCES

1 The Management of Steel Plant Ferruginous By-Products, International Iron and Steel Institute, Committee on the environmental Affairs and Committee on Technology, Brussels (1994).

2 Ye, G., Burström, E. and Fällman, A-M. Utilisation and Stabilisation of Steelmaking Slags. Swedish Waste Research Council, AFR-Report 57, Stockholm (1995).

3 Fällman, A-M. and Hartlén, J. Utilisation of electric arc furnace slag in road construction. In *Environmental Geotechnics*, M. Kamon (ed.), pp 703-708. Balkema, Rotterdam (1996).

4 Fällman, A-M. and Hartlén, J. Leaching of Slags and Ashes - Controlling Factors in Field Experiments versus in Laboratory Tests. In *Environmental Aspects of Construction with Waste Materials*. Goumans, J.J.J.M., van der Sloot, H.A., Aalbers Th.G. (eds.), pp 39-54. Studies in Environmental Science 60, Elsevier, Amsterdam (1994).

5 Fällman, A-M. and Aurell, B. Leaching tests for environmental assessment of inorganic substances in wastes, Sweden. *Sci. Total Environ.* **178:** 71 (1996).

6 Fruchter, J.S., Rai, D. and Zachara, J.M. Identification of solubility-controlling solid phases in a large fly ash field lysimeter. *Environ. Sci. Techn.* **24:** 1173 (1990).

7 ASTM D 3682-91 Standard Test Method for Major and Minor Elements in Coal and Coke Ash by Atomic Adsorption.

8 SS 02 81 83 Metal content of water, sludge and sediments - Determined by flameless atomic absorption spectrometry - Electrothermal atomization in a graphite furnace - General principles and guidelines; Swedish Standards: Stockholm, (1986).

9 Fällman, A-M. End point criterion in batch leaching tests for granular solid wastes. *Environ. Sci. Technol.* (submitted)

10 Box, G.E.P., Hunter, W.G. and Hunter, J.S. *Statistics for Experimenters*; John Wiley & Sons: New York, (1978).

11 Allison, J.D., Brown, D.S. and Novo-Gradic, K.J. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual. Environmental Research Laboratory; U.S. EPA: Athens, GA (1990).

12 Rai, D., Zachara, J.M., Schwab, A.P., Schmidt, R.L., Girvin, D.C. and Rogers, J.E. Chemical Attenuation Rates, Coefficients and Constants in Leachate Migration. Volume 1: A critical Review. EPRI EA-3356, Electrical Power Research Institute. Palo Alto (1986).

13 Rai, D., Zachara, J.M., Eary, L.E., Girvin, D.C., Moore, D.A., Resch, C.T., Sass, B.M. and Schmidt, R.L. Geochemical behaviour of Chromium Species. EPRI EA-4544, Electrical Power Research Institute. Palo Alto (1986).

14 Comans, R.N.J., van der Sloot, H.A. and Bonouvrie, P.A. Geochemical reactions controlling the solubility of major trace elements during leaching of municipal solid waste incinerator residues. In *Municipal Waste Combustion Conference*. Kilgroe, J. (ed.), pp 667-679. Air and Waste Management Association, Pittsburg, PA (1993).

15 Rai, D., Zachara, J.M., Eary, L.E., Ainsworth, C.C., Amonette, J.E., Cowan, C.E., Szelmeczka, R.W., Resch, C.T., Schmidt, R.L., Girvin, D.C. and Smith, S.C. Chromium Reactions in Geological Materials. EPRI EA-5741, Electrical Power Research Institute, Palo Alto (1988).

16 Rosenqvist, T. *Principles of extractive metallurgy*. McGraw-Hill, New York (1974).