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EVALUATION OF THE CHROMIUM SPECIATION IN ISRAELI COAL FLY ASHES

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Abstract

Upon the request of the Israeli National Coal Board the Cr speciation in Israeli coal fly ashes was evaluted. Six fly ashes - fresh ash, fly ash used in road application and fly ash collected from an embankment were tested. For this purpose, the ash leaching behaviour has been characterized as a function of the pH in a so-called pH dependence leaching test, which forms the basis for the evaluation of chromate leaching behaviour through modelling of solubility controlling phases. The Israeli coal fly ashes are not different from other coal fly ashes generated by coal in power plants from world wide coal sources. The chromium in coal fly ash is partially available as chromate (Cr^{VI}). This species is particularly relevant for leaching in the pH domain pH 5 – 12. At pH < 5 Cr^{III} is becoming a more predominant species. The fresh Israeli coal fly ash do not exceed 20 mg/kg leachable Cr^{VI}, which amouts to about 10 % of the total Cr in coal fly ash. Geochemical modelling has shown that a solid solution of $BaSO_4$-$BaCrO_4$ (S96%) is a dominant solubility controlling phase under oxidised conditions. The significantly reduced chromate levels in the aged roadbase material is possibly explained by adsorption of Cr^{III} on hydrated ironhydroxide at the neutral pH developing with time. This reaction will pull the equilibrium Cr^{VI} to Cr^{III} towards the Cr^{III} side. The in-situ transformation leads to a significantly reduced Cr leachability of less than 1 mg/kg leachable chromate, which amouts to less than about 0.5 % of the total Cr. Only by field verification under the roadbase leaching can be ruled out. In the embankment, the lack of measuring significant Cr levels under the Hadara embankment over the last 20 years would support in-situ transformation. However, the ash sample taken deep into the Hadeira embankment may well have a very different coal source for its production, which could explain the difference between the two samples analysed. Measuring CO_2 liberated by acidification would allow drawing conclusions on the different origin of the two ash samples.

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1. INTRODUCTION

In Israel concern was raised over the level of chromate in coal fly ash and its consequences for the environment in case fly ash is used in contruction applications. A concern was that chromate in Israeli coal fly ashes was higher than that in coal ashes in other parts of the world. ECN has been asked to evaluate the chromate level in a selection of Israeli coal fly ashes. For this purpose leaching tests and modelling work has been carried out, which allows the results to be placed in context with other relevant data from previous studies into the chemical speciation of chromium in coal fly ash [1] and comparable matrices [2].

2. EXPERIMENTAL

2.1 Materials selection

For the study coal fly ashes have been selected by the Israeli National Coal Board as shown in Table 2.1.

Table 2.1 *Materials tested*

No	Sample code	Origin	pH
2	FM2	3 months composite industrial ash	12.05
6	FR2	3 months composite industrial ash	11.85
1	JASR	Road base material Jasr-el-Zarka	9.00
5	D911	Same as JASR one year after placement 2 m	8.38
3	C3-5	Southern Embankment Hadera 1-1.5 m	10.75
4	C41	Southern Embankment Hadera 8 m	9.24

2.2 Test methods

All ashes have been subjected to the following leaching tests:

- pH dependence leaching test [3] covering the pH range from 3 – 12 using the draft procedure in development in CEN TC 292 WG 6 (“ANC mode”), LS=10 and 48 hours contact time. In the hierarchy of CEN TC 292, this is a characterization test (level 1 test). This test provides a basis for the chemical speciation modelling to identify the chemical speciation. The information is used as input to the geochemical modelling

- a reduced pH dependence leaching test of 4 pH conditions in the range from pH 6 -12.

- a batch leach test as specified in EN 12457 part 2 [4] modified to L/S=50 to verify depletion of soluble chromate by comparing the L/S=10 results from the pH dependence test with the L/S=50 data.

The following elements have been measured in all extracts by Induced Coupled Plasma Atomic Emission Spectrometry (ICP-AES): Cr, Ba, SO4 as S, K and Al. The experimental results are presented in standard format and in electronic form (EXCEL) to allow use of data for quality control purposes.

2.3 Geochemical modelling

Geochemical modelling is used to identify the controlling factors of the leaching processes. Release can be governed by salts or minerals that are more or less soluble, and by adsorption on mineral or organic surfaces. Identification of the processes responsible for leaching enables the assessment of the long-term leaching behaviour. The saturation indexes of known minerals, calculated for all the leachates, are used to identify whether the concentrations in the leachates are governed by mineral solubility.

In many cases, the leaching behaviour can be approximated by assuming equilibrium with certain minerals. If mineral equilibria govern the leaching behaviour it also elucidates the pH dependent behaviour on the long-term. In cases where the leaching as a function of pH is lower than predicted by mineral equilibria the mineral equilibria can give the upper limit to the solubility. In these cases the adsorption equilibria can be more important. In common with mineral equilibria, adsorption equilibria give the upper limit of the concentration that can be leached. In combination with the liquid-solid ratios the maximum amount leached can be calculated on the basis of the experimentally determined pH dependent solubility.

The speciation code Ecosat (Keizer and van Riemsdijk, 1998) [5] was used for geochemical modeling. The stability constants (K) from MINTEQA2 (Allison et al., 1991) [6] have been used. The activities were calculated using the Davies equation. The modeling approach consisted of calculating the saturation indices (SI) of all available minerals in MINTEQA2 (Allison et al., 1991) [6]. Potentially solubility controlling minerals were selected on the basis of the calculated saturation indices ($-1<SI<1$). The minerals that gave the best prediction of the experimental pH dependent solubility curve were selected. Lines have been drawn assuming equilibrium (c_{eq}) with minerals by calculating the quotient of the experimental concentration (c_{det}) of an element and the calculated saturation index as 10^{SI}: $c_{eq} = c_{det} / 10^{SI} = c_{det} (IAP/K)^{-1}$ (IAP is the calculated ion activity product on the basis of the experimental data).
It is assumed that the speciation does not change significantly for situations, where the saturation index is in the range of $-1<SI<1$ and $SI=0$, for which the equilibrium of a mineral is drawn as a line.

2.4 Data presentation

Leaching test results may be expressed either as

- Leachate concentration in [mg/l]
- Constituent release in [mg/kg of material] for granular materials or
- Constituent release in mg/m^2 for monolithic materials.

Leach test results are frequently expressed as eluate concentration, as this is the form in which results become available after eluate analysis. Subsequent data conversion may be necessary for different purposes. The eluate concentration as measured is used for geochemical modelling. Some regulations use concentrations expressed in mg/l. Others use leached quantities (mg/kg dry matter) or other derived units, such as mg/m^2.
Conversion of measured leachate concentrations into constituent release is necessary for the comparison of data obtained in different leaching tests at different liquid to solid (L/S) ratios.

Conversion formula:
Constituent release [mg/kg] = leachate concentration [mg/l] x L/S ratio [l/kg]

However, in comparing results from different leaching tests it is important to take other aspects that control release of constituents into account (e. g. pH value, L/S ratio)

Presentation of data as measured eluate concentrations or as constituent release can also be necessary for the determination of the general leaching mechanism (see Figure 2.1). Examples:

- Silicon (Si) represents a solubility controlled element. Here, presentation of leaching data in [mg/kg] leads to differences, whereas data presented in [mg/l] show the solubility control in the pH region of 3 to 8 (constant concentration irrespective of L/S).

- Chlorine (Cl) represents an availability controlled element. Data from tests at different L/S ratios expressed in [mg/l] lead to apparent differences, while data presented in [mg/kg] show that in all cases the whole fraction available for leaching is released.

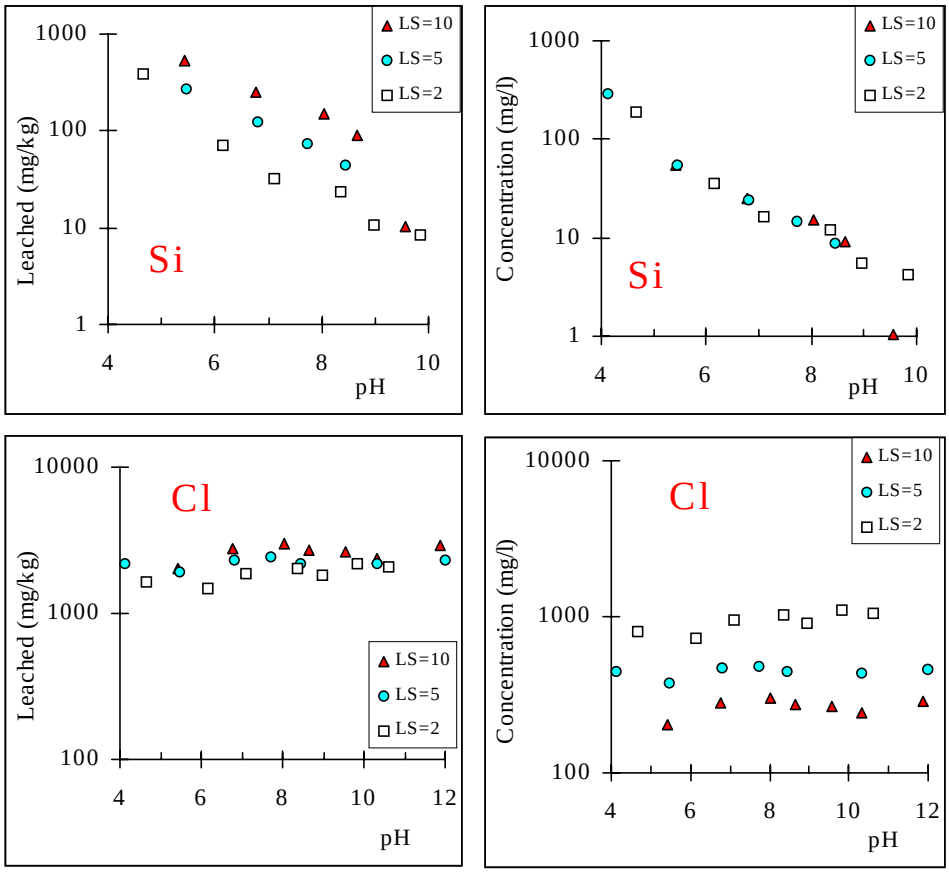

Figure 2.1 *Distinction between Solubility Control (Si) and Availability Control (Cl) in the Presentation of Leaching Test Results[7].*

3. RESULTS

3.1 Leaching test data

The raw data of the leaching tests carried out are given in Appendix A. A graphical presentation of the pH dependence test data is provided in Appendix B.

3.1.1 Acid neutralization capacity

The ANC data obtained from the pH dependence test for the different coal fly ashes are given in Figure 3.1. Only Fly ash FM2 has a relatively high acid neutralization capacity consistent with a fresh alkaline ash. Fly ash FR2 has a relatively low acid neutralization capacity. Apparently, the coal (blend) fired to produce FR2 has a moderate Ca content and produces a mildly alkaline ash. All samples from the road base and from the embankment have a rather low acid neutralization capacity, which implies that most of these ashes are largely carbonated. This is also apparent from the own pH of the ashes. The abundant calcite generated as a result of carbonation provides a buffer against further pH decrease. In the field situation, both in the roadbase as well as in the embankment, a moist unsaturated condition of the fly ash enhances neutralization by atmospheric and biologically derived CO_2, as the gas diffusion rate is about 5 orders of magnitude faster than the diffusion in water. The high pH imposed by the fresh fly ash on water films on the ash particles lead the moist ash to act as a CO_2 pump. The long term condition of the ash will be a neutral pH around 8.

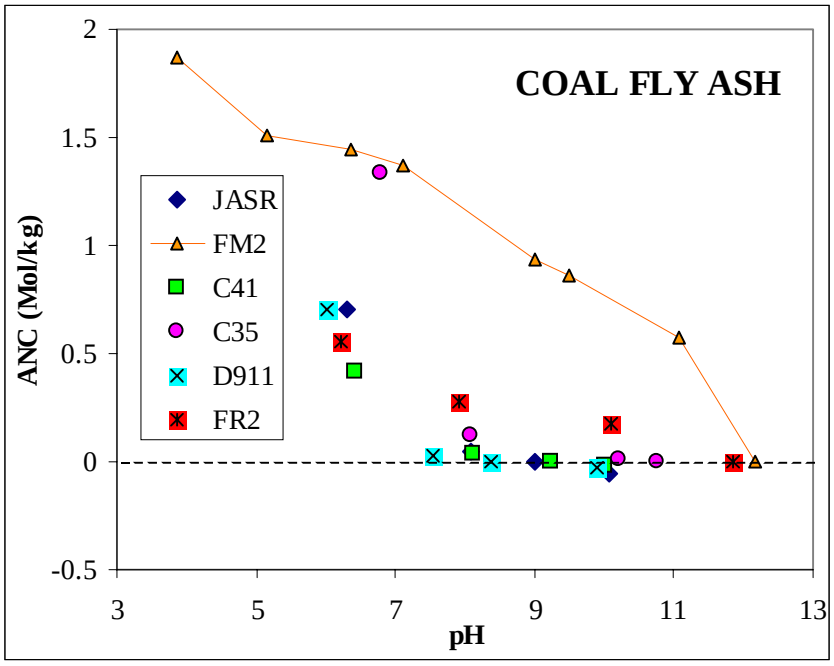

Figure 3.1 *Acid neutralization data obtained from pH dependence test on Israeli coal fly ash samples.*

3.1.2 pH dependence test

A graphical presentation of the pH dependence test data is provided in Appendix B. In Figure 3.2 a summary is given for Ba, Cr and sulfate, which are known to be relevant for chromate

leachability from other work [2,8,9]. The fresh collected ashes FM2 and FR2 show a very similar leaching behaviour (shape of the curve) as a function of pH for Ba, Cr and sulfate. The Cr and sulfate level at mild alkaline pH are about a factor of 2 lower for FR2 than for FM2. Both the the fresh roadbase ash (JASR) and the shallow sample from the embankment (C3-5) correspond well with the two fresh ashes in both level and behaviour. Only the Ba leaching behaviour is slightly different.

The deep sample from the embankment (C41) and the roadbase ash collected after 1.5 year after placement (D911) both feature significantly lower Cr leachability than the fresh ashes (factor 10 - 20). Both these ashes have reached an almost neutral pH (resp. 9.24 and 8.38). The fact that the sample taken deep into the embankment is largely carbonated or features a lower pH than the sample closer to the surface is counter to what one would expect. The leaching behaviour of Ba and sulfate from the aged roadbase material deviates most from all other samples. The question arises, what causes the Cr decrease: conversion of Cr^{VI} to Cr^{III} in the field or leaching?

To allow a better comparison, the Cr results are split into the origin of the materials (Figure 3.3). The L/S=50 data, expressed in mg/kg, match generally well with the L/S 10 data as applied in the pH dependence leaching test. This indicates that the leachable chromium fraction (chromate) has been leached out completely under these test conditions. This points at full reversibility of the chromate solubility control and makes it unlikely that more leachable Cr^{VI} is present in the ash than that reflected by the L/S=50 data.

The reason for the significant difference in Cr leachability for C41 and C3-5 cannot be identified with certainty. The deeper sample is lower in pH, which is not what would be expected. On the other hand, the ash sampled at 8 and 1.5 meter depth do not necessary originate from the same coal source. This may lead to a difference as can be seen in the 50 coal ashes from world wide origin studied before [11]. If this ash was a neutral or mildly alkaline ash after production, it may have largely maintained its character. As can be seen from Figure 3.4 (Cr, right graph) neutral or mildly alkaline ashes generally have a lower Cr leachability.

In the roadbase, it is likely that carbonation progresses fairly rapidly and that also hydrated ironoxide is formed capable of retaining Cr^{III}. As the Cr^{III} / Cr^{VI} equilibrium is shifted, slowly a significant portion of the Cr^{VI} is converted to Cr^{III}. At the observed level of release, it should be possible to distinguish between the two mechanisms – leaching and transformation. A measurement of total composition is useless, as the difference that needs to be quantified is about 5 mg/kg on a total Cr content of 160 - 200 mg/kg. Given the variability in total Cr composition in different fly ash charges, this is not feasible. If no Cr is found under the roadbase Percolate analysis in goundwater underneath the embankment have shown no significant increase in Cr levels (range: 0.008 – 0.088 mg/l) over the last 20 years [10], which implies that significant leaching can be ruled out. Transformation of Cr^{VI} to Cr^{III} can be identified as the most likely mechanism in the this field site, when it can be proven that Cr release to groundwater is non-existant.

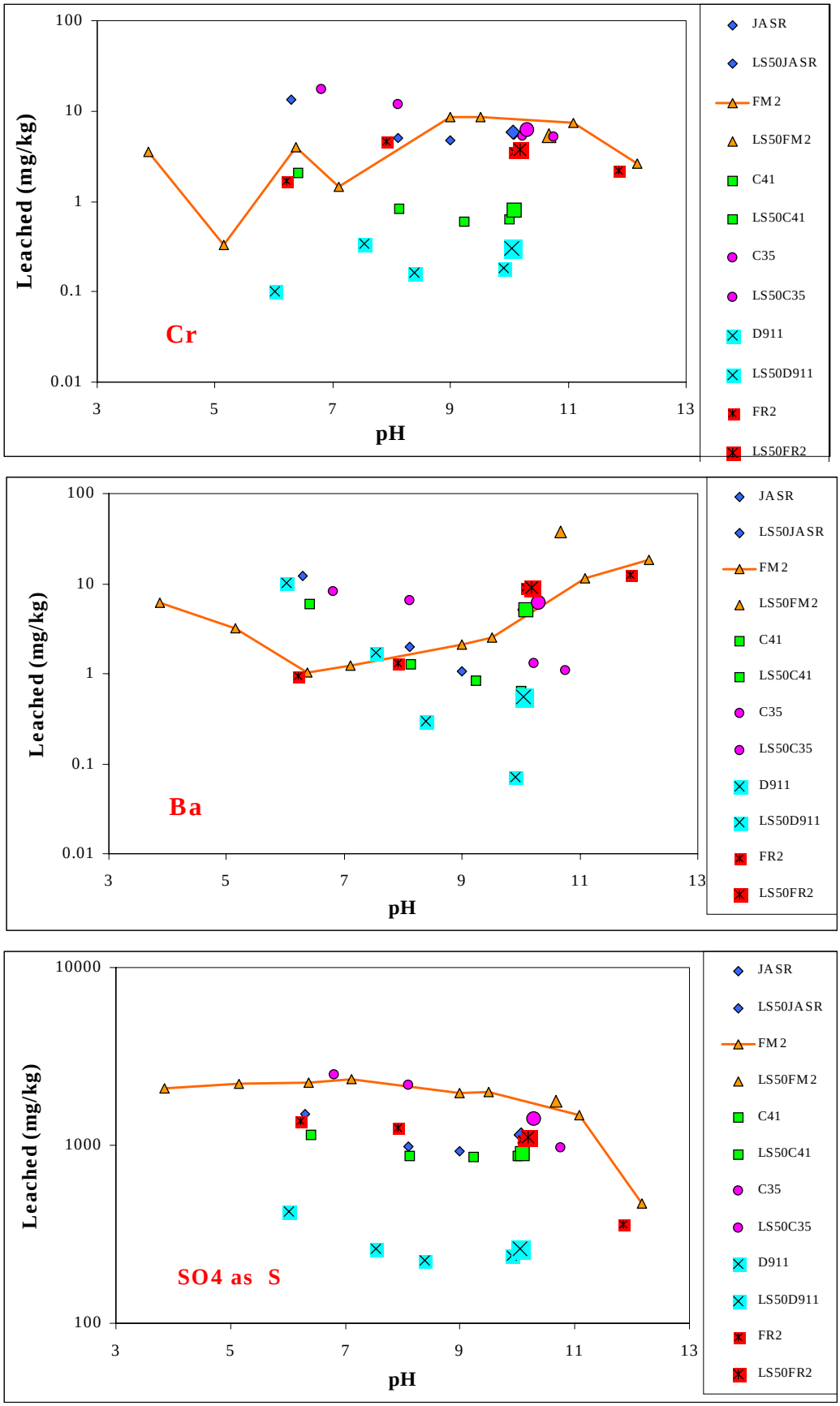

Figure 3.2 *pH dependence leaching test data of Cr, Ba and sulfate from Israeli coal fly ashes.*

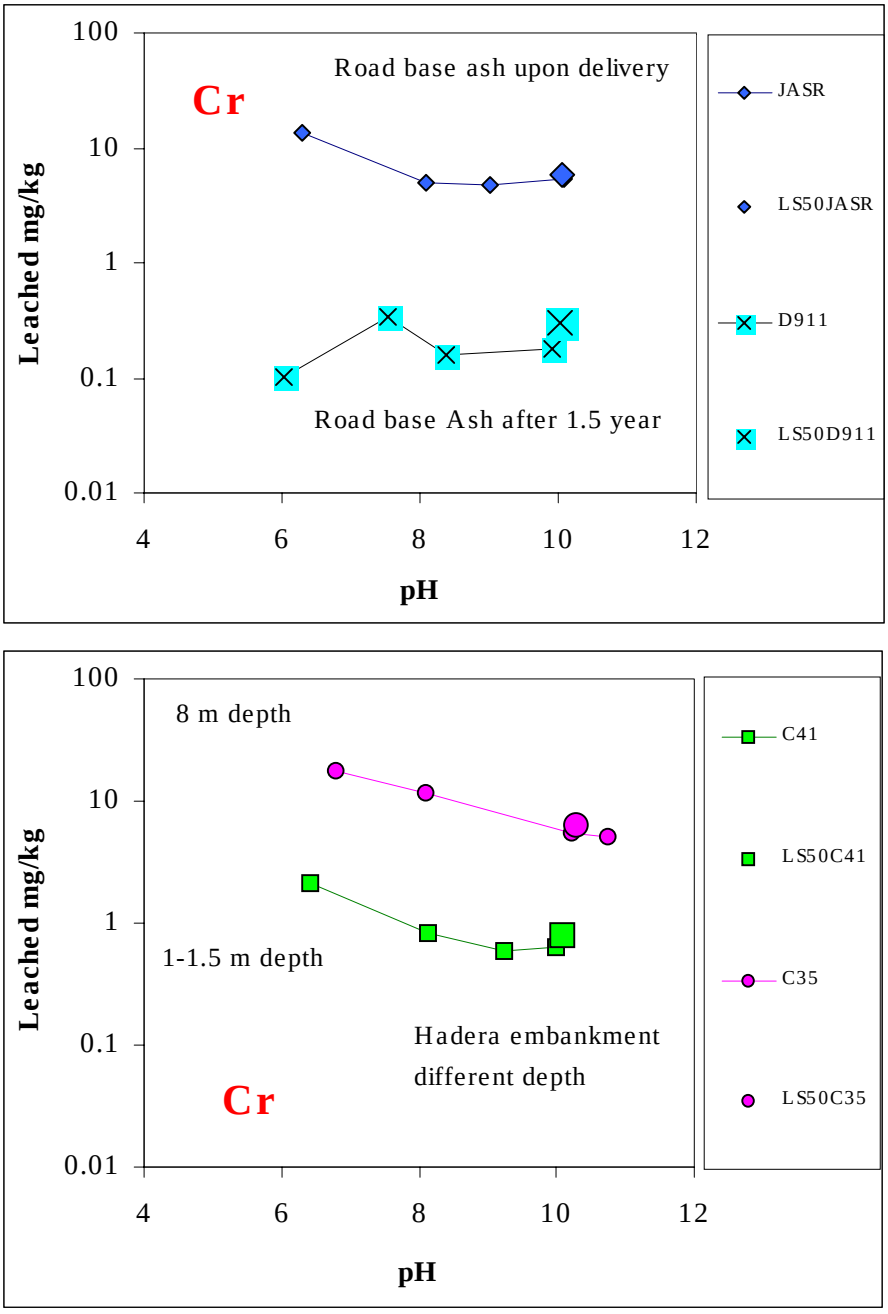

Figure 3.3 *Cr data for fly ashes sorted according to origin. The larger symbol denotes the L/S=50 data.*

A further illustration of the maximum amount of chromate is provided by plotting the experimental data as a function of L/S (Figure 3.5). The element K is a typical element representing wash out. All K is essentially leachable. The elements Ba and sulfate shown in this figure are examples of solubility control. Cr shows in most samples depletion, this implies that almost all leachable Cr is leached before L/S=10. This behaviour is typical for the very mobile Cr ^{VI}. This implies that the leachable Cr from fresh Israeli coal fly ash amounts to about 20 mg/kg, which is roughly 10 % of the total Cr content. After in situ conversion, the leachable Cr reduces to less than 1 mg/kg (about 0.5 % of the total).

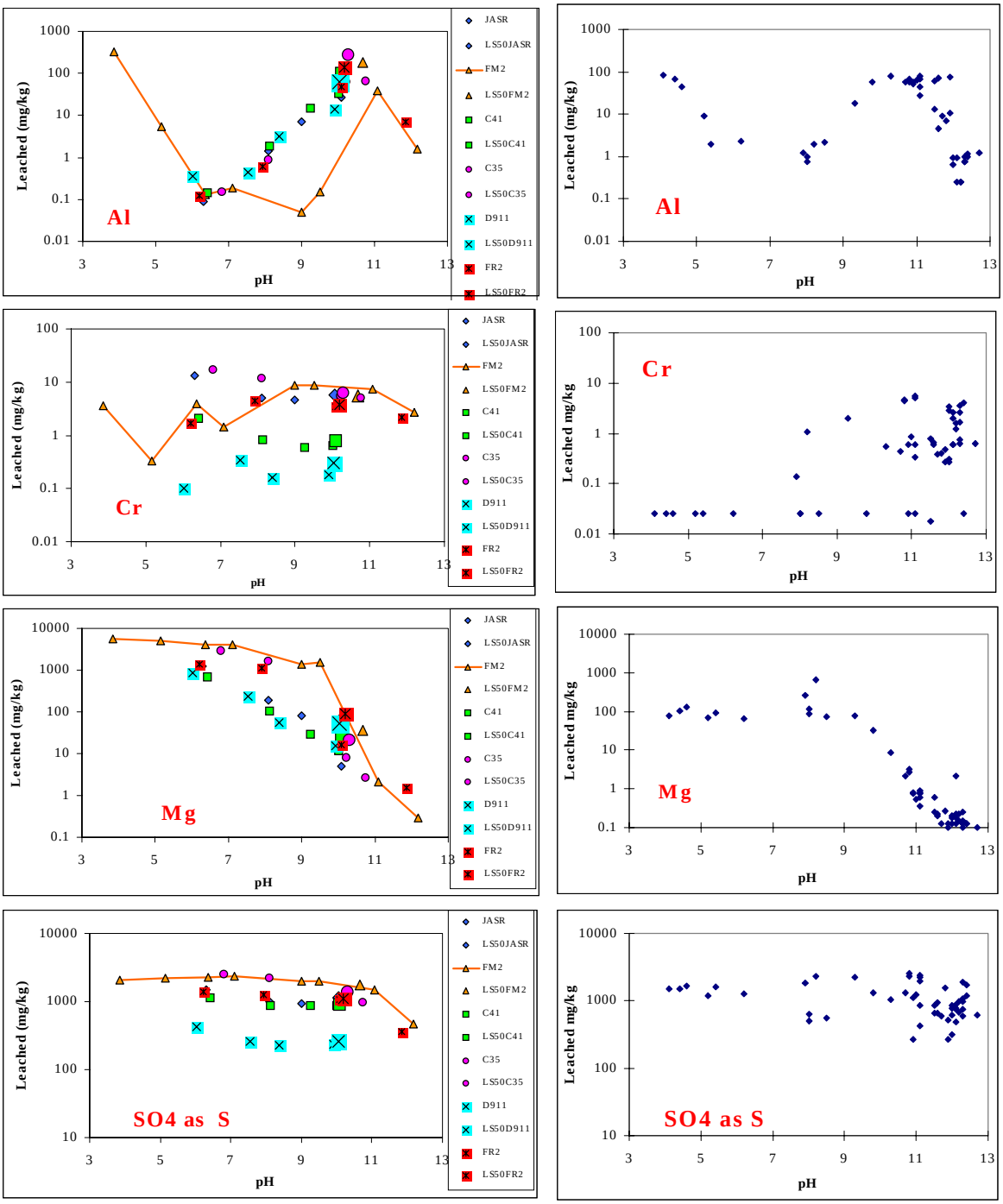

Figure 3.4 *Comparison between Israeli fly ashes and 50 world wide coal fly ashes.*

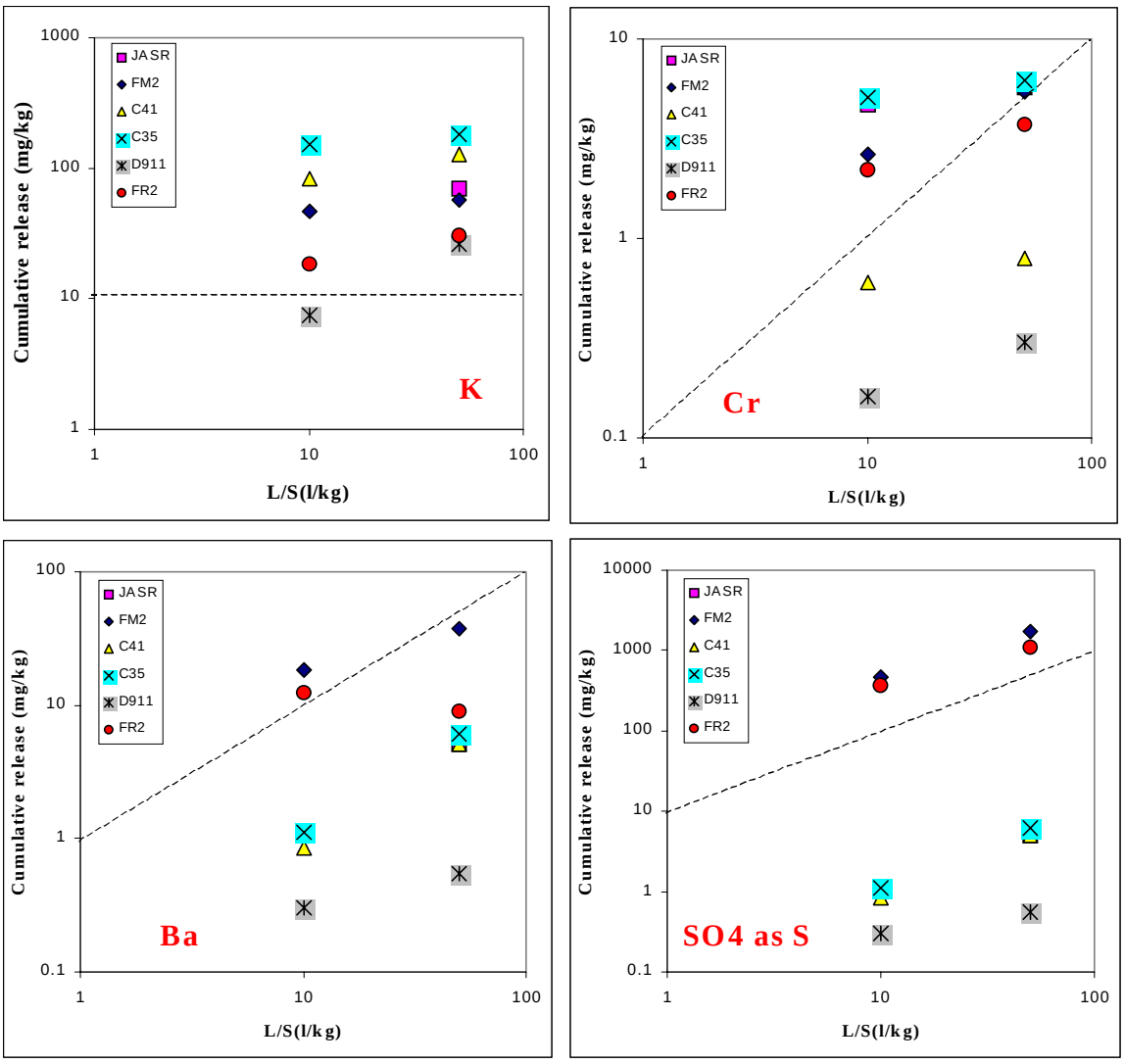

Figure 3.5 *Graphical presentation to identify solubility control or wash out. Dotted line (slope 1) represents solubility control. Slope 0 denotes wash out.*

3.1.3 Comparison with other data

The data obtained for the six Israeli ashes are compared with data from coal fly ashes from world wide origin [11]. In Figure 3.4 the comparison is given for Al, Cr, sulfate and Mg. The behaviour of Al is consistent throughout all ashes. A minimum leachability at pH 6-7 caused by gibbsite solubility control and low Al leachabilities at high pH caused by the pozzolanic properties of fly ash.
The Cr leachability is very consistent with that of cement mortars (Figure 3.9). Elevated leachability at low pH, a minimum at pH 5. Maximum leachability at mild alkaline pH and a reduced leachability at high pH. The low Cr leaching of acidic ashes is related to the low levels of Cr in such coals from fluvial origin (Australian, Indian). It is hypothized that in the kiln a small fraction of the Cr is converted to chromate. Low initial Cr levels in coal will then lead to low Cr ^{VI} levels. The data for the alkaline ashes are in agreement. Thus there is no significant difference in Cr leaching behaviour of Israeli coal ashes and ashes from other sources.

The Mg leachability is typically controlled by brucite. At low pH the avialbility for leaching is reached. Acidic ashes feature low Mg and Ca levels, which is refelcted in the individual Mg

leach test results shown in the right hand side of figure 3.5. The curve of FM2 would be obtained if an alkaline ash (pH>11) from the right hand graph was tested over the entire pH range.
The sulfate leachability is not very different between the Israeli ashes and ashes from other sources. This is more related to the process of coal firing, than to the coal source, as a major part of the initial sulfur in coal gets transformed to gaseous SO_3.

3.2 Geochemical speciation of chromium

Two approaches are followed:
- Geochemical modelling of speciation using MinteqA2 and/ or ECOSAT
- Development of chemical stability diagrams as function of Eh and pH.

The geochemical modelling is an important element in a scenario approach [12], which forms the basis for evaluating leaching test results. Presentation of the test results without placing them in the context of the question is not useful.

3.2.1 Geochemical modelling

The results of the geochemical modelling using ECOSAT [5] with the MINTEQA2 database [6] are presented in figure 3.6 and 3.7. The geochemical modelling data for Cr, Ba and sulfate are given. The calculated equilibrium concentrations are plotted in the graph with the pH dependence test data. When the curves coincide over a reasonable portion of the pH domain, that chemical phase may prove to be a relevant solubility controlling phase. In the case of Cr, $BaSO_4CrO_4$ solid solution appears to be the most relevant phase. In the top figure the saturation indices for this solid are given.

The leaching of Cr seems to be determined in almost all fly ashes by solubility control by a solid-solution of $BaSO_4$ and $BaCrO_4$.

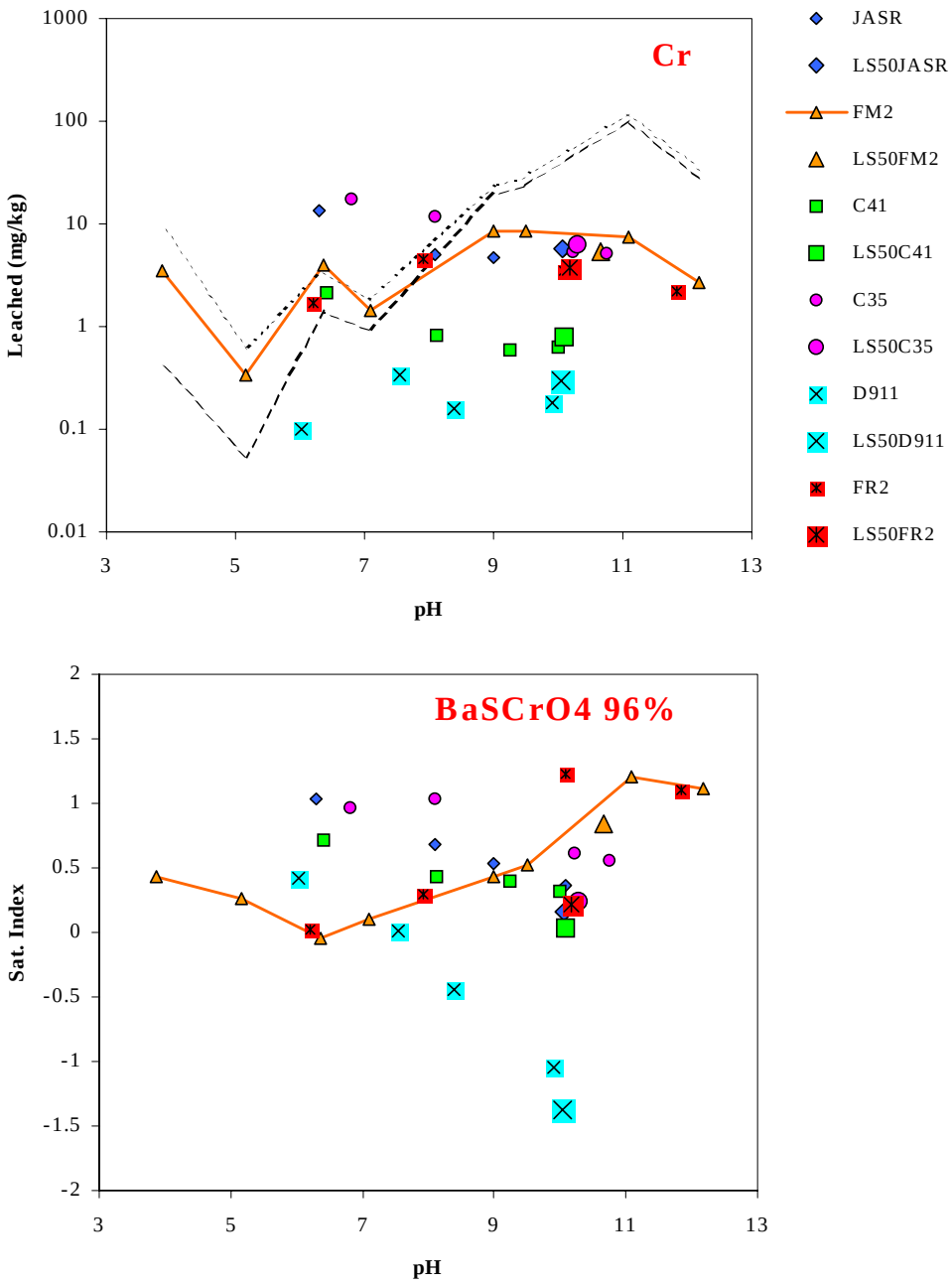

Figure 3.6 *Geochemical modelling data for Cr, Ba and sulfate in all coal ashes studied (top). In the top graph the saturation indices for Ba(S96Cr4)O4 are given for all pH stat eluates analysed.*

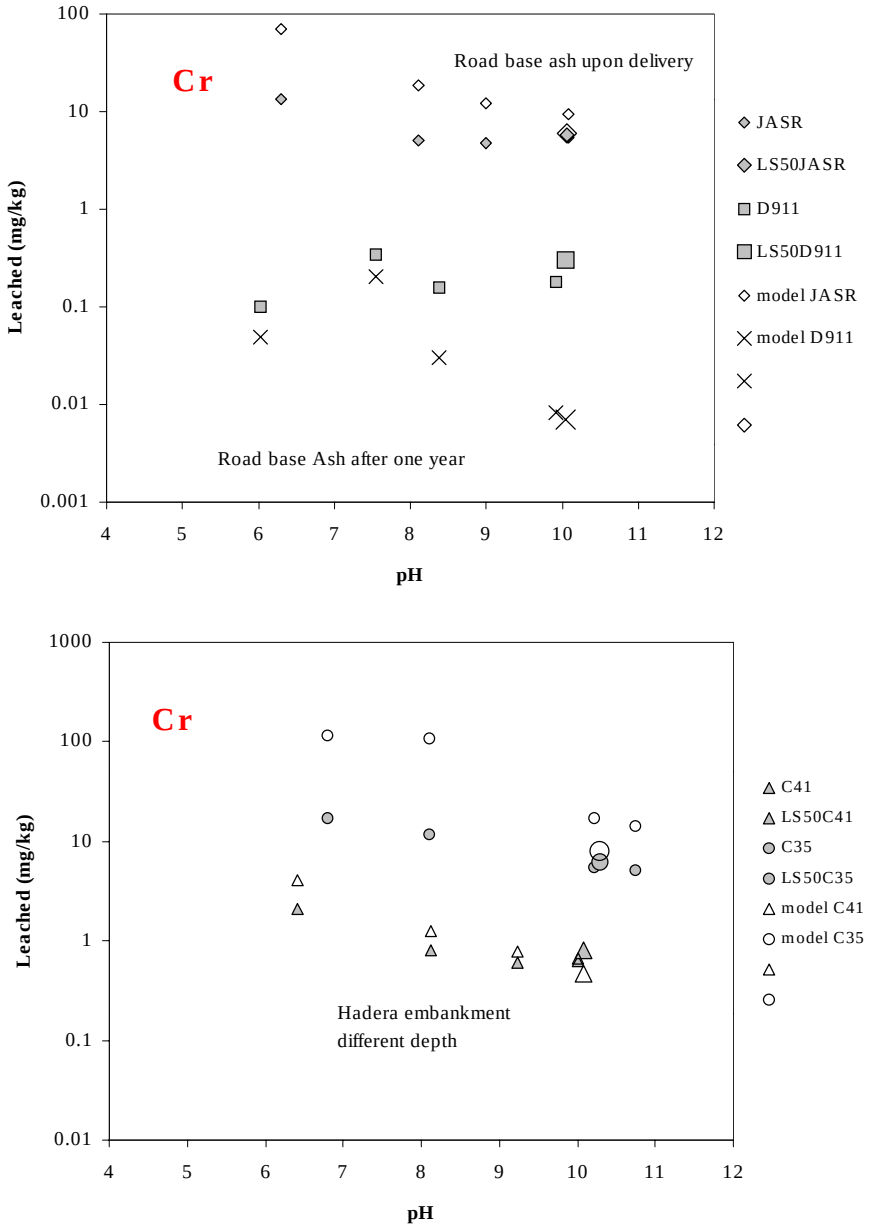

Figure 3.7 *Modelling data of Cr solubility control by Ba(S96Cr4)O4 for embankment and Hadera samples. Open symbols modelling data and solid samples measurements.*

3.2.2 Stability diagrams as function of Eh and pH

Using the program Geochemist's Workbench [13] stability diagrams for redox sensitive species can be calculated based on input data taken from the pH dependence leaching test. The elements, which served as input in the model, were Cr, Ba, Fe and S. Input concentrations are read from the pH dependence tests at pH values between 8 and 9 (Table 3.1). The diagrams are calculated assuming these concentrations represent molar activities, furthermore a temperature of 25 ^{o}C and pressure 1.013 bar is assumed.

Table 3.1 *Molar concentrations that served as input for the calculation of the stability diagrams.*

	FM2 (pH 9)	D911 (pH 8.38)	C41 (pH 8.12)
Ba	1.51e-6	2.19e-7	9.18e-7
Cr	1.60e-5	3.10e-7	1.56e-6
Fe	1.80e-8	1.80e-8	7.19e-8
S	6.08e-3	7.00e-4	2.72e-3

In Figure 3.8 the Eh-pH diagrams are shown for the solution (left) and for the solid phase (right) for fly ashes FM2, aged road base material D911 and embankment material C41. In the graphs the normal pH-Eh relation is inserted commonly found for oxidized conditions. This allows to conclude that Cr in the fly ash samples FM2, FR2, C3-5 and JASR is dominated by $Ba(S_{96}Cr_4)O_4$ solubility control, because of similar leaching behaviour as can be seen from fig 3.2. It also shows that in solution, Cr^{III} is only relevant at pH < 5. At pH > 5 chromate is by far the predominant species. This is consistent with data from cement mortars, in which blast furnace slag cement represents a reducing condition, in which no chromate can remain stable. The Cr leaching curve for blast furnace slag cement reflects Cr^{III} leachability (Figure 3.9). Any increase over the low Cr concentration at pH > 5 can be attributed to chromate., The firing conditions in kilns play a role for the Cr^{VI} formation and thus also in coal fired power plants dictate the degree of Cr conversion to Cr^{VI}. As mentioned before the Cr content in coal is hypothized to be related to the Cr^{VI} content. Introduction of biomass in coal fired units may increase the Cr^{VI} level in ash by increasing the Cr level and the exposure of that increased level by the finer particle distribution of biomass ash.[14].

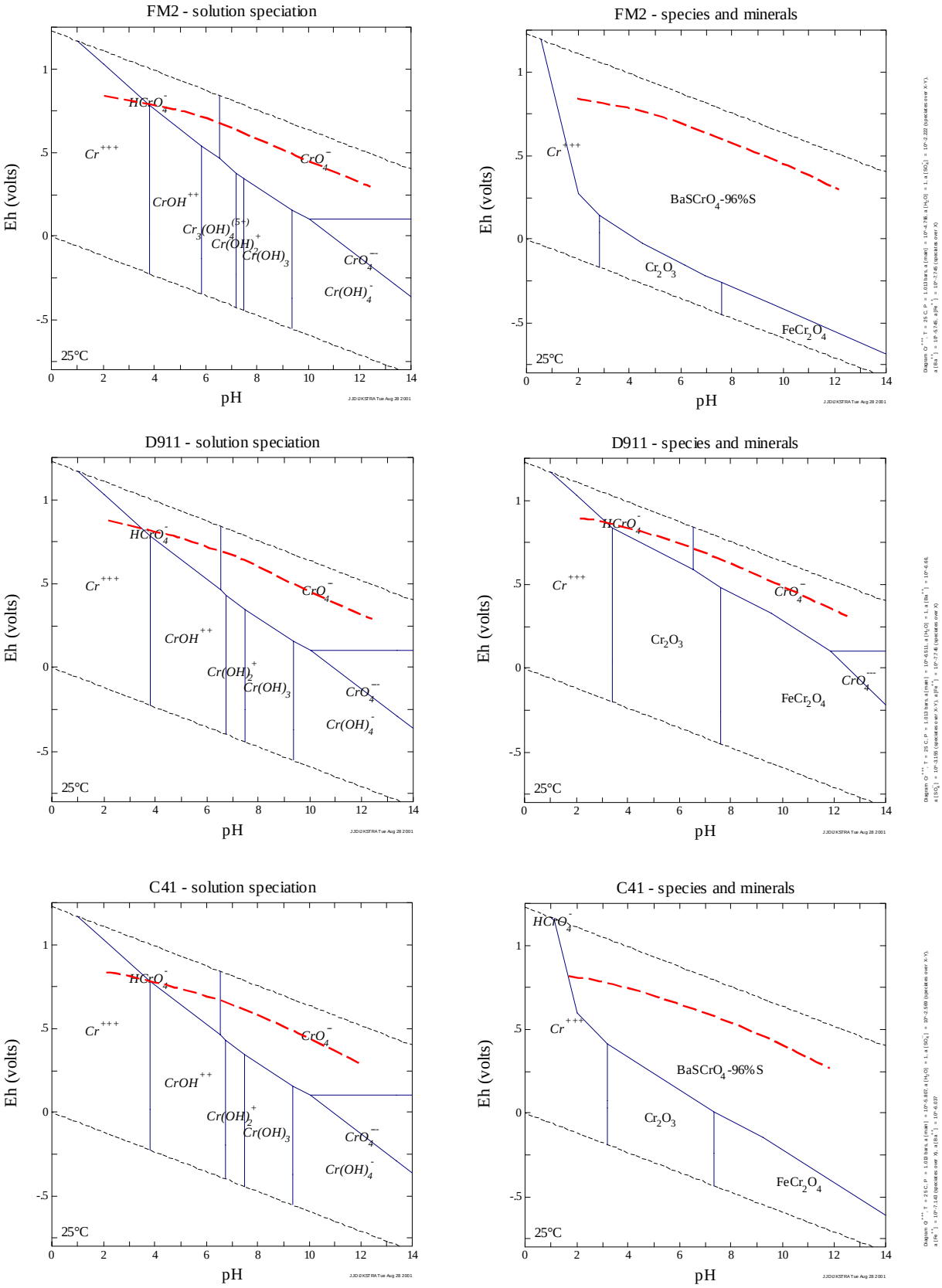

Figure 3.8 *Eh-pH diagrams for FM2, D911 and C41 fly ashes in comparison with the pH- Eh conditions relevant for normal oxidised condition (broken line). Left: solution; right: solid.*

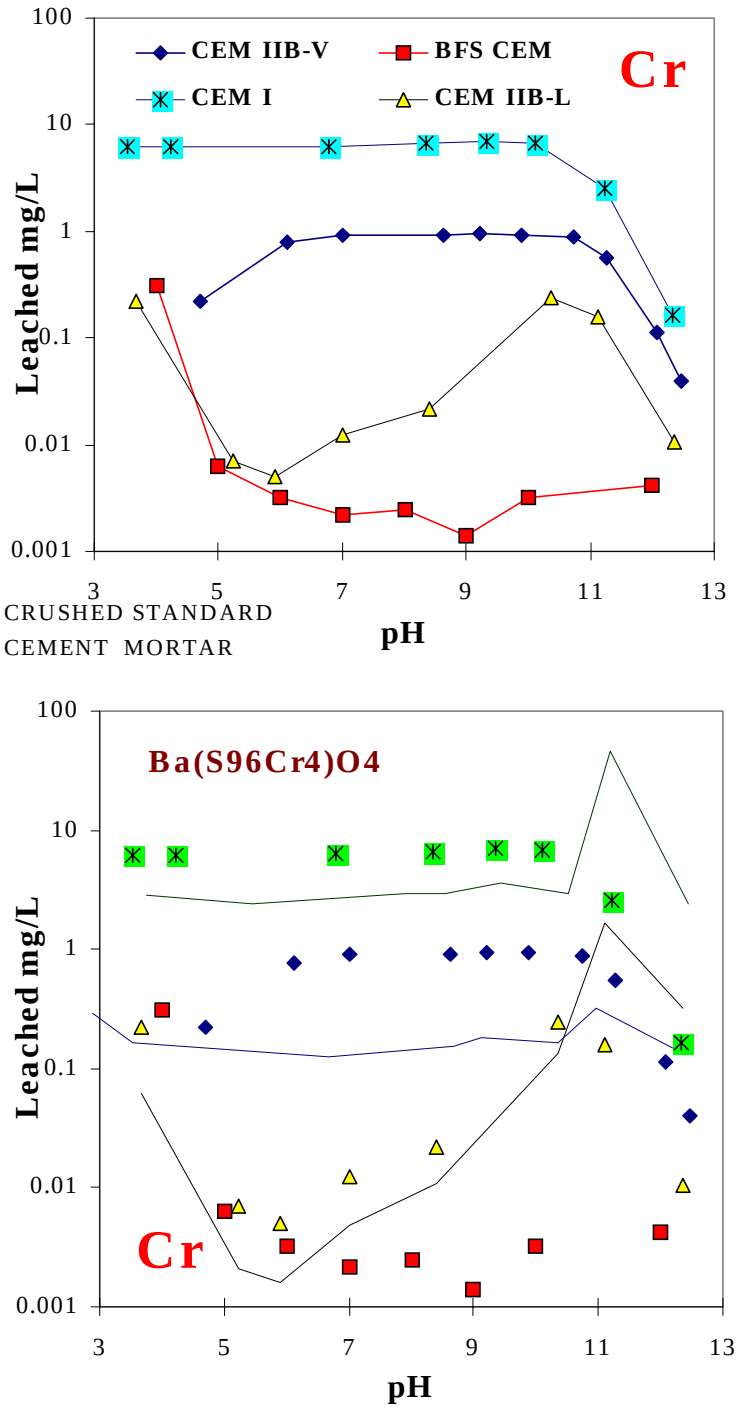

Figure 3.9 *pH dependence test data and modelling results for Portland cement mortars, blended cement mortar and a blast furnace slag cement mortar illustrating the relevance of* $Ba(S96Cr_4)O_4$ *as solubility controlling phase for cement mortar.*

4. CONCLUSIONS

General
Characterizing ash leaching behaviour as a function of the pH, in a so-called pH dependence test or ANC test is useful for:

- modelling of geochemical controlling phases (basis for long term prediction of release behaviour)
- to evaluate long term leaching behaviour and impact of external stresses on materials (carbonation)
- for comparison of leaching behaviour across fields to maximize use of information between fields.

Modelling forms the basis for long term leaching behaviour predictions, as identification of solubility controlling phases is crucial for understanding the processes governing leaching behaviour of coal ash. The characterization test presented – pH dependence test - provides the input parameters for such geochemical modelling. Scenario specific and site-specific parameters can then be introduced to take different applications of the same material and regional differences into account.

Chromate
The Israeli coal fly ashes are not different from other coal fly ashes generated by coal in power plants from world wide coal sources. The chromium in coal fly ash is partially available as chromate. This species is particularly relevant for leaching in the pH domain pH 5 – 12. At pH < 5 Cr^{III} is becoming more predominant.

The fresh Israeli coal fly ash do not exceed 20 mg/kg leachable Cr^{VI}, which amouts to about 10 % of the total Cr in coal fly ash.

Geochemical modelling has shown that a solid solution of $BaSO_4$-$BaCrO_4$ (S96%) is an important solubility controlling phase under oxidised conditions. If reducing conditions would develop in enclosed systems, any chromate would be readily converted to the less harmful reduced Cr^{III} species and most likely bound in hydrated ironoxide phases..

In the aged roadbase material significantly reduced chromate levels are observed. This may be attributed to leaching or to slow conversion of Cr^{VI} to Cr^{III}. The roadbase sample proves to be largely carbonated. Adsorption of Cr^{III} on hydrated ironhydroxide at the neutral pH developing with time will pull the equilibrium Cr^{VI} to Cr^{III} towards the Cr^{III} side. For this process reducing conditions are not needed. It may be just an equilibrium shift resulting form the formation of more stable adsorption complexes with iron. This is the most likely explanation today for the observed lower leachability of Cr in the field samples from the Jasr-el-Zarka roadbase. A verification of the groundwater under the roadbase will reveal if leaching or the in-situ transformation is the predominant mechanism.

The in-situ transformation would lead to a significantly reduced Cr leachability of less than 1 mg/kg leachable chromate and thus less than about 0.5 % of the total Cr. The binding of Cr^{III} to ironoxide is very stable and unlikely to change back again.

The situation in the embankment is not fully resolved. Although the lack of measuring significant Cr levels under the Hadara embankment over the last 20 years would support in-situ transformation, it can not be taken as proof, as the ash at 8 m depth may have another origin as the ash closer to the surface. A check to see if carbonation has occured in the deep sample would be to analyze for CO_2 after acidification. The amount of CO_2 can be recalculated to alkalinity and thus to the ANC of the original ash. If CO_2 is low, the ash is most likely from another coal source. The Mg, Ca, Sr and Ba levels are lower in the C41 sample relative to the

C3-5 sample. This might be related to carbonation. It may also point at a significantly lower level of all alkaline earth elements, which is a typical feature of neutral to acidic ashes.

Recommendation

CO_2 analysis of all ash samples to check the level of carbonation of all field samples. Fresh ash has a low carbonate level.

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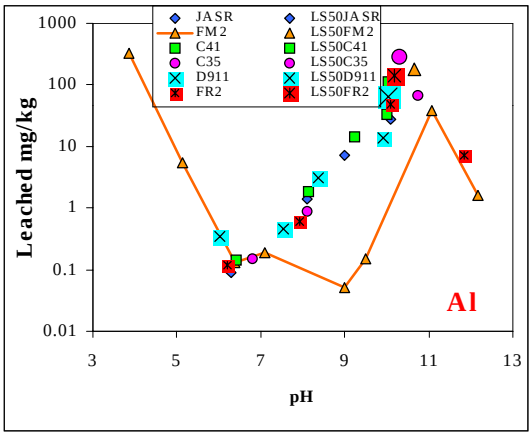
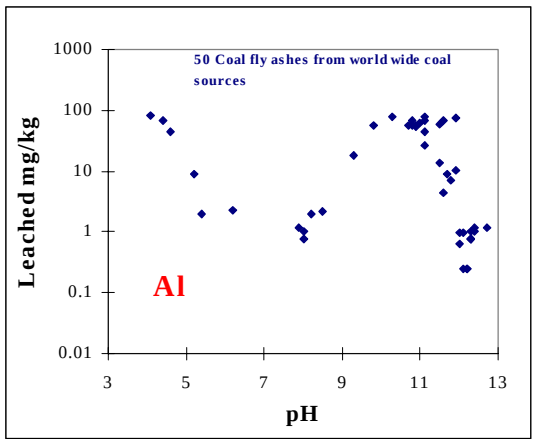
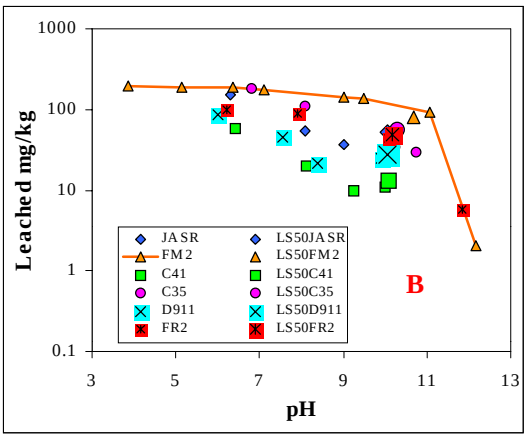
DATA							AL	AS	B	BA	CA	CD	CO	CR	CU	FE	K	LI
							mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
					1 M		5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01
Seq	**Code**	**Rep**	**pH**	**mS**	**ml**	**LS**	**0.0004**	**0.0138**	**0.0072**	**0.0001**	**0.1031**	**0.001**	**0.0054**	**0.0022**	**0.0012**	**0.0045**	**0.0512**	**0.001**
1	JASR	1	10.08		-1.2	10	2.693	0.004	4.283	0.057	10.332	0	-0.001	0.545	-0.002	0.015	10.1	0.227
2	JASR	2	8.10		1	10	0.138	0.022	5.386	0.195	242.35	0	-0.002	0.497	-0.003	0.004	11.129	0.475
3	JASR	3	6.30		1-14n	10	0.009	0.069	14.893	1.191	1725.83	0.001	-0.003	1.345	-0.005	0.004	27.729	1.155
4	JASR	4	9.00		0	10	0.713	0.003	3.623	0.106	102.028	0	-0.002	0.469	-0.002	0.001	8.649	0.358
29	LS50JASR	1	10.06	0.239	0	50	1.379	0.008	1.038	0.102	21.544	0	0.001	0.115	-0.002	0.005	3.072	0.108
					14.4 M													
5	FM2	1	12.18		0	10	0.162	0.001	0.202	1.854	662.301	0	-0.001	0.265	-0.004	0.001	4.695	1.329
6	FM2	2	11.08		0.8	10	3.849	-0.007	9.206	1.153	1204.79	0	0.001	0.734	-0.005	0.002	5.062	1.36
7	FM2	3	9.50		1.2	10	0.015	0.028	13.651	0.25	1628.43	-0.001	0.004	0.853	-0.006	0.001	5.728	1.522
8	FM2	4	9.00		1.3	10	0.005	0.036	14.126	0.207	1643.75	0	0.001	0.856	-0.007	0.001	5.896	1.552
9	FM2	5	7.10		1.9	10	0.019	0.619	17.584	0.123	2157.31	0.001	0.08	0.144	-0.005	0.008	7.058	1.764
10	FM2	6	6.37		2	10	0.013	0.819	18.384	0.101	2284.5	0.002	0.096	0.388	-0.006	0.005	6.404	1.825
11	FM2	7	5.15		2.1	10	0.525	0.697	18.655	0.313	2508.46	0.011	0.171	0.033	0.088	0.004	7.03	1.898
12	FM2	8	3.86		2.6	10	31.511	0.102	19.041	0.605	2725.54	0.015	0.209	0.35	0.938	0.035	8.594	2.057
30	LS50FM2	1	10.67	1.367	0	50	3.598	0.004	1.584	0.741	268.338	0	0	0.108	-0.001	0.003	1.153	0.273
					1 M													
13	C41	1	10		-0.4	10	3.29	0.016	1.082	0.064	36.04	0	-0.003	0.063	-0.001	0.003	9.403	0.135
14	C41	2	8.12		0.8	10	0.183	0.092	1.974	0.126	238.335	0	0.001	0.081	-0.002	0.004	11.573	0.233
15	C41	3	6.41		0.6-14n	10	0.014	0.219	5.74	0.597	1207.23	0.001	0.009	0.209	-0.004	0.002	21.777	0.591
16	C41	4	9.24		0	10	1.468	0.027	1	0.084	96.27	-0.001	-0.003	0.06	0	0.001	8.406	0.153
31	LS50C41	1	10.08	0.181	0	50	1.991	0.002	0.264	0.101	23.3	0	-0.001	0.016	-0.002	0.003	2.544	0.042
17	C35	1	10.22		0.2	10	6.38	0.002	3.41	0.131	190.363	0	0.002	0.538	-0.001	0.003	16.662	1.153
18	C35	2	8.1		2.4	10	0.085	0.037	10.92	0.64	1362.45	0	0.001	1.169	-0.003	0.002	25.16	1.976
19	C35	3	6.8		1.9-14m	10	0.015	0.032	17.769	0.82	2419.2	0	0.009	1.717	-0.002	-0.002	26.046	2.682
20	C35	4	10.75		0	10	6.718	-0.002	2.908	0.11	113.445	0	0.002	0.51	0.001	0.003	15.228	1.05
32	LS50C35	1	10.29	0.35	0	50	5.622	0.006	1.106	0.122	59.944	0	0	0.125	-0.001	0.003	3.629	0.265
21	D911	1	9.91		-0.6	10	1.394	0.066	2.476	0.007	11.092	0	-0.001	0.018	0.001	0.007	1.447	0.049
22	D911	2	7.54		0.6	10	0.045	0.145	4.498	0.172	261.581	0	0.003	0.034	0.001	0.001	3.343	0.118
23	D911	3	6.02		1-14m	10	0.035	0.119	8.587	1.005	1286.41	0	0.015	0.01	-0.003	0.001	5.605	0.24
24	D911	4	8.38		0	10	0.312	0.028	2.116	0.03	31.067	0	-0.002	0.016	-0.002	0.001	0.737	0.051
33	LS50D911	1	10.04	0.134	0	50	1.27	0.013	0.55	0.011	8.168	0	-0.001	0.006	-0.001	0.003	0.527	0.017
					14M													
25	FR2	1	10.09		0.25	10	4.793	0.001	4.321	0.902	501.054	0	-0.001	0.35	-0.003	0.002	2.414	1.051
26	FR2	2	7.92		0.4	10	0.059	0.261	8.94	0.13	739.943	0.001	0.011	0.452	0	0.001	2.874	1.217
27	FR2	3	6.21		0.8	10	0.012	0.698	9.949	0.095	950.86	0.002	0.061	0.167	-0.002	0.001	3.34	1.325
28	FR2	4	11.85		0	10	0.707	0.003	0.586	1.242	222.37	0	-0.002	0.221	-0.001	0.001	1.865	0.845
34	LS50FR2	1	10.18	0.652	0	50	2.857	0.017	0.973	0.179	108.157	0	-0.005	0.074	-0.002	0.002	0.612	0.217

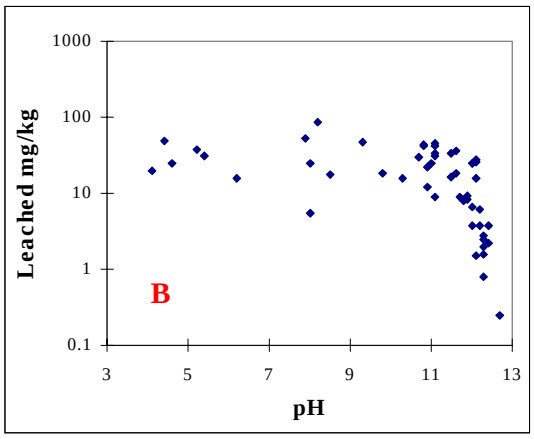
		MG	MN	MO	NA	NI	P	PB	S	SB	SE	SI	SN	SR	TI	V	ZN
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
		5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01	5/23/01
Seq	**Code**	**0.0107**	**0.0003**	**0.004**	**0.013**	**0.0049**	**0.0052**	**0.031**	**0.0454**	**0.0138**	**0.007**	**0.0214**	**0.01**	**0.001**	**0.0008**	**0.001**	**0.0005**
1	JASR	0.488	0	0.228	159.043	0	0.112	-0.007	103	0.016	0.026	2.943	-0.001	0.428	0	0.217	0
2	JASR	19.228	0.007	0.215	16.83	0.001	0.403	-0.013	98.697	0.014	0.025	2.912	0.002	5.344	0	0.055	0.002
3	JASR	121.015	0.399	0.395	25.046	0.04	3.135	0.001	149.5	0.024	0.118	41.345	-0.001	29.75	0	0.235	0.017
4	JASR	8.227	0.001	0.206	14.899	-0.001	0.083	0.024	92.323	0.003	0.015	1.359	0	2.662	0	0.046	0
29	LS50JASR	1.286	0.001	0.044	21.61	0.002	0.052	0.02	22.95	0.017	0.006	1.393	-0.001	0.803	0	0.05	0.001
5	FM2	0.029	0	0.284	8.958	0	0.016	-0.003	47.44	0.005	0.007	0.932	0.002	12.357	-0.001	0.007	0.002
6	FM2	0.207	0	0.404	9.372	-0.006	0.043	-0.004	146.817	0.011	0.043	2.108	-0.001	12.218	0	0.138	0
7	FM2	150.706	0	0.373	10.304	0.006	0.076	-0.023	199.094	0.017	0.076	32.054	0.002	14.907	0.001	1.014	0.001
8	FM2	137.998	0.007	0.358	10.245	0.034	0.115	-0.032	195.021	0.008	0.06	42.155	0.002	15.198	0	1.055	0.001
9	FM2	393.678	2.382	0.314	11.944	0.291	8.191	0.009	232.076	0.035	0.136	77.066	-0.001	21.711	0	1.669	0.004
10	FM2	403.678	3.773	0.289	11.489	0.32	27.876	-0.004	222.642	0.007	0.119	88.563	0	23.011	0.001	1.74	0.005
11	FM2	480.637	7.776	0.181	12.52	0.46	27.111	-0.036	219.431	0.014	0.122	212.244	0.002	28.946	0	1.444	0.368
12	FM2	536.701	9.031	0.023	13.388	0.544	3.793	0.033	205.453	0.009	0.063	315.363	-0.003	34.501	0.002	0.574	0.871
30	LS50FM2	0.712	0	0.086	2.935	-0.002	0.023	0	35.263	0.004	0.014	2.09	-0.004	2.91	0.001	0.119	0.001
13	C41	1.199	0.005	0.356	89.147	-0.002	0.055	-0.015	87.011	0.052	0.017	2.466	0.001	0.986	0	0.107	0.001
14	C41	10.492	0.009	0.379	20.14	0.002	0.482	-0.008	87.224	0.056	0.038	3.442	0	3.856	0.001	0.128	0
15	C41	70.218	0.526	0.674	27.998	0.09	1.573	0.004	113.871	0.02	0.091	33.674	0.002	16.319	0	0.471	0.015
16	C41	2.886	0.002	0.346	16.773	-0.001	0.066	-0.007	86.32	0.047	0.015	1.097	0.004	1.987	0	0.058	0
31	LS50C41	0.528	0	0.075	10.518	0.002	0.037	-0.012	18.063	0.019	0.01	1.334	-0.001	0.634	0	0.043	0.001
17	C35	0.818	0.002	0.204	26.353	0.001	0.052	-0.021	110.864	0.011	0.021	0.739	0.005	5.124	0	0.066	0
18	C35	157.903	0.059	0.406	33.18	0.007	0.894	-0.016	216.924	0.023	0.094	5.642	0.004	23.823	0.001	0.263	0.003
19	C35	288.989	0.641	0.523	36.502	0.094	1.612	-0.031	246.937	0.011	0.133	22.227	0.008	40.202	0.002	0.345	0.004
20	C35	0.257	0.001	0.198	26.27	0.002	0.041	-0.009	96.634	0.012	0.017	1.588	0	3.811	0.001	0.069	0.002
32	LS50C35	0.42	0	0.045	7.256	0.003	0.022	-0.026	28.182	0.009	0.013	0.919	0.002	1.688	0.001	0.054	0.001
21	D911	1.54	0	0.034	91.079	0.001	0.457	-0.001	23.705	0.02	0.016	3.768	0.004	0.194	0.001	0.464	0.001
22	D911	23.089	0.025	0.048	159.908	0.003	2.364	-0.013	26.258	0.029	0.051	12.887	0.001	4.349	0.002	0.537	0.002
23	D911	86.336	0.771	0.099	9.604	0.078	2.04	-0.022	42.055	0.022	0.083	59.351	0.005	19.515	0.001	0.508	0.015
24	D911	5.626	0.003	0.03	3.489	-0.001	0.315	0.011	22.592	0.019	0.005	2.729	-0.002	0.591	0	0.17	0.001
33	LS50D911	1.059	0	0.009	15.33	0	0.231	-0.016	5.256	0.012	0.009	2.523	-0.002	0.159	0	0.107	0.001
25	FR2	1.603	0.001	0.501	7.191	-0.002	0.057	-0.014	106.997	0.021	0.131	0.698	0.001	6.187	0	0.298	0
26	FR2	111.236	0.102	0.511	8.087	0.081	1.796	-0.006	125.949	0.036	0.196	32.335	0	7.086	0.001	1.37	0.001
27	FR2	137.845	0.938	0.469	8.709	0.229	29.577	-0.023	136.672	0.033	0.314	59.772	0.004	9.469	0	1.899	0.01
28	FR2	0.15	0.001	0.413	6.014	0	0.092	-0.027	35.922	0.002	0.035	4.721	0.001	5.465	0.001	0.058	0.003
34	LS50FR2	1.815	0	0.092	20.333	0.001	0.047	-0.024	22.258	0.009	0.044	1.565	0.002	1.273	0.001	0.201	0.001

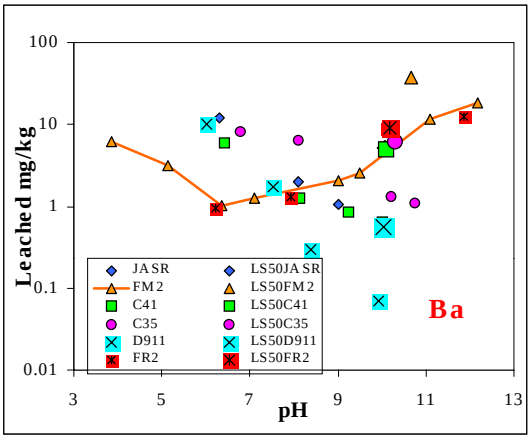
Annex B

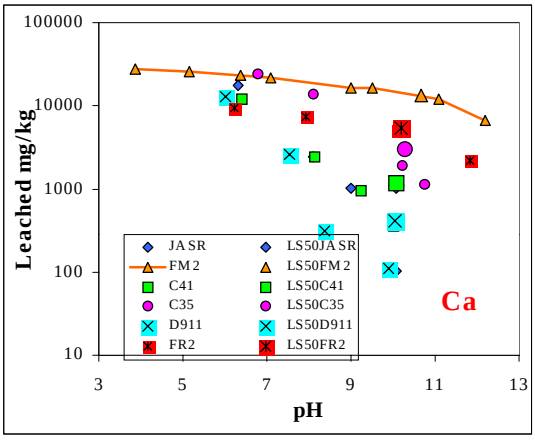

JA SR
FM 2
C41
C35
D911
FR2
LS50JA SR
LS50FM 2
LS50C41
LS50C35
LS50D911
LS50FR2
Al
Leached mg/kg
pH

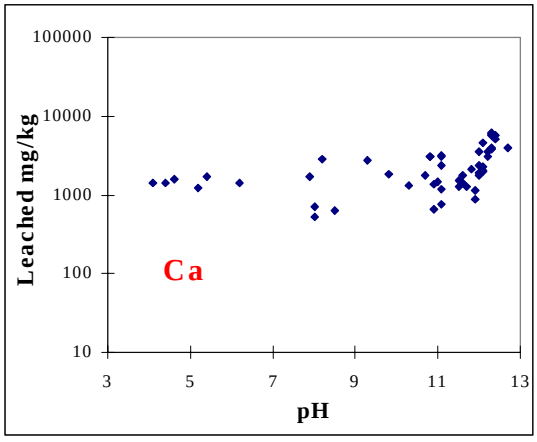

50 Coal fly ashes from world wide coal sources
Al
Leached mg/kg
pH


JA SR
FM 2
C41
C35
D911
FR2
LS50JA SR
LS50FM 2
LS50C41
LS50C35
LS50D911
LS50FR2
B
Leached mg/kg
pH

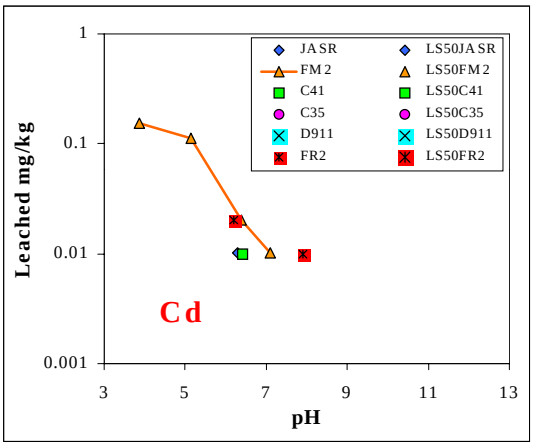

B
Leached mg/kg
pH

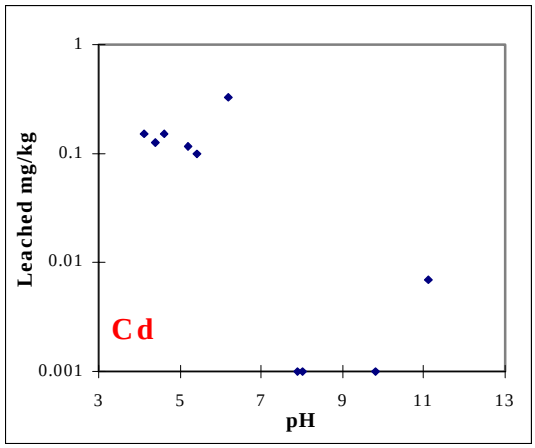

JA SR
FM 2
C41
C35
D911
FR2
LS50JA SR
LS50FM 2
LS50C41
LS50C35
LS50D911
LS50FR2
Ba
Leached mg/kg
pH

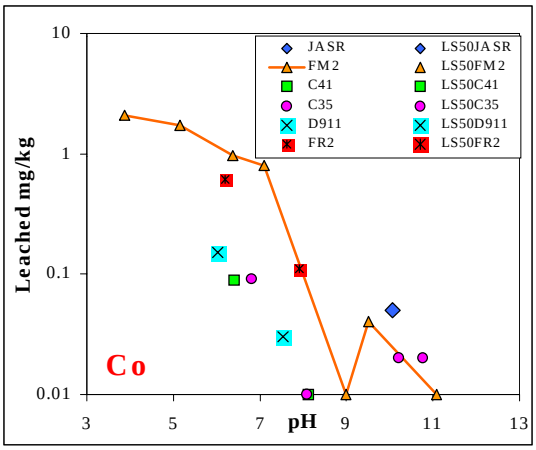

JA SR
FM 2
C41
C35
D911
FR2
LS50JA SR
LS50FM 2
LS50C41
LS50C35
LS50D911
LS50FR2
Ca
Leached mg/kg
pH

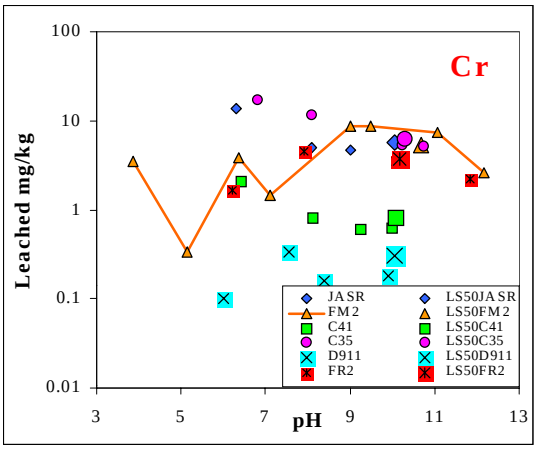

Ca
Leached mg/kg
pH

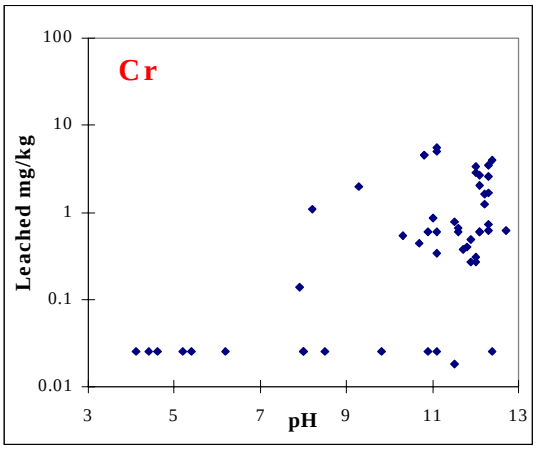
Annex B

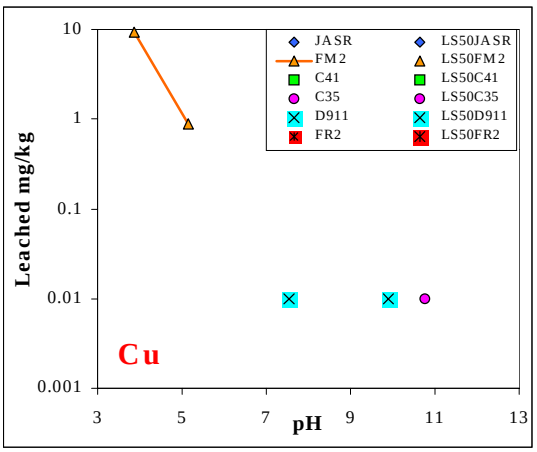

JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
Leached mg/kg
1
0.1
0.01
0.001
Cd
3
5
7
9
11
13
pH

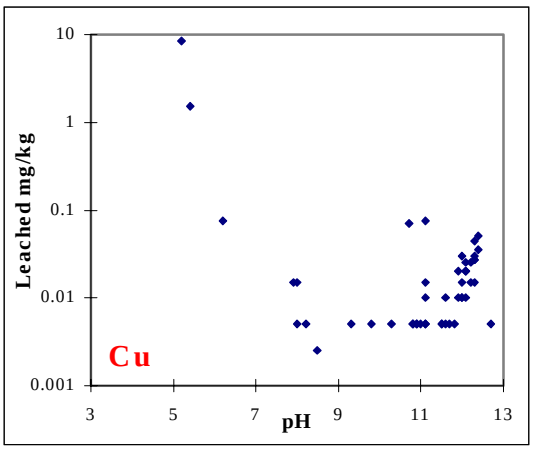

Leached mg/kg
1
0.1
0.01
0.001
Cd
3
5
7
9
11
13
pH


JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
Leached mg/kg
10
1
0.1
0.01
Co
3
5
7
pH
9
11
13

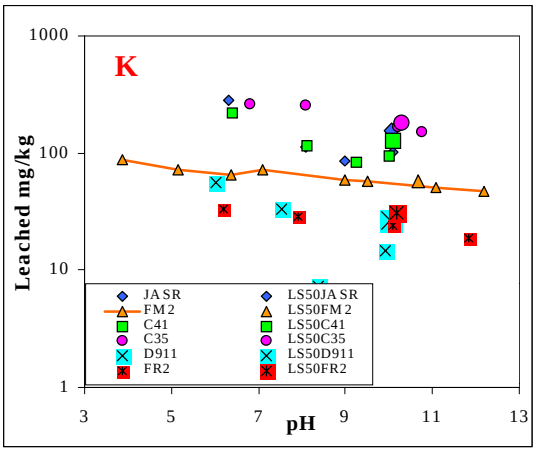

Cr
Leached mg/kg
100
10
1
0.1
0.01
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
3
5
7
pH
9
11
13

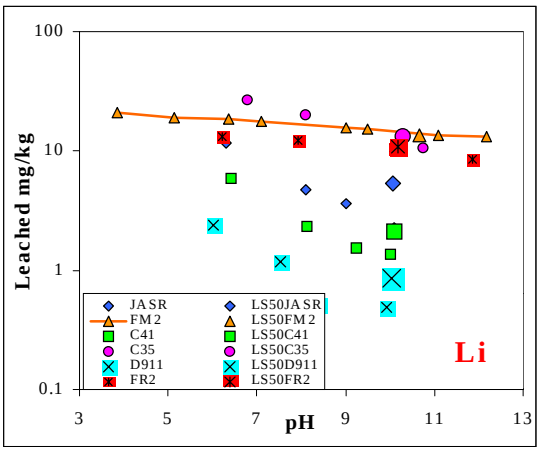

Cr
Leached mg/kg
100
10
1
0.1
0.01
3
5
7
pH
9
11
13

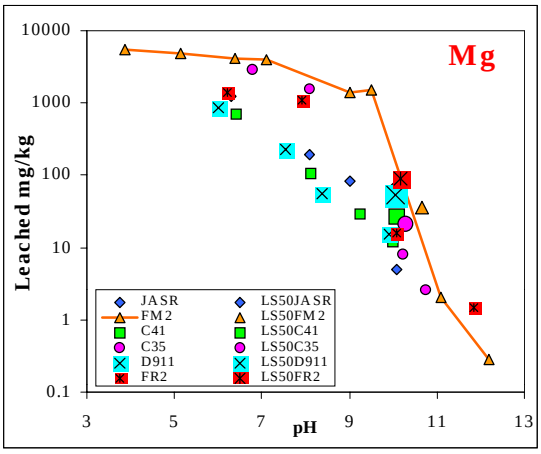

JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
Leached mg/kg
10
1
0.1
0.01
0.001
Cu
3
5
7
pH
9
11
13

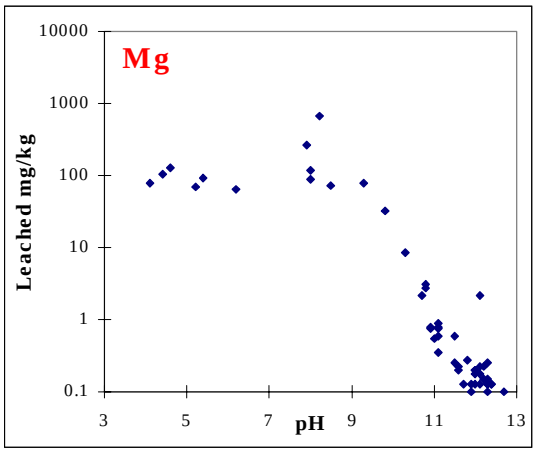

Leached mg/kg
10
1
0.1
0.01
0.001
Cu
3
5
7
pH
9
11
13

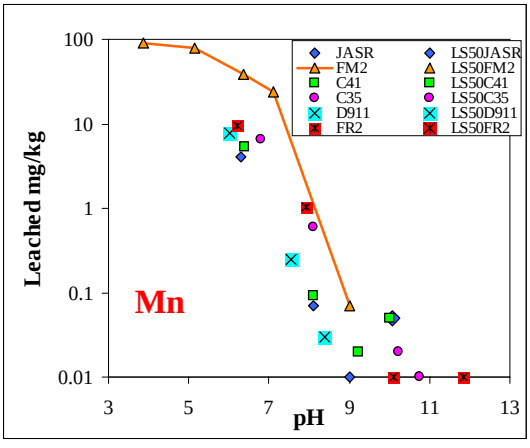
Annex B


K
Leached mg/kg
pH
1000
100
10
1
3
5
7
9
11
13
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2

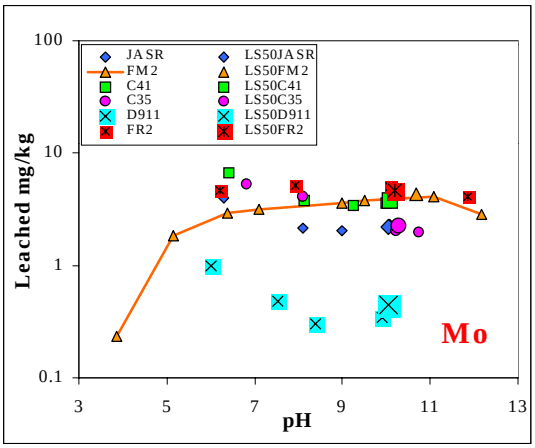

Li
Leached mg/kg
pH
100
10
1
0.1
3
5
7
9
11
13
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2

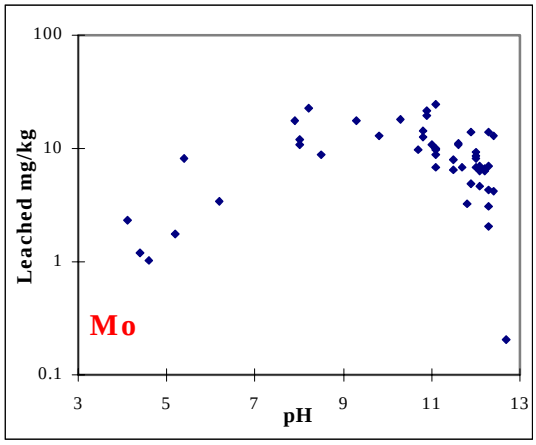

Mg
Leached mg/kg
pH
10000
1000
100
10
1
0.1
3
5
7
9
11
13
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2

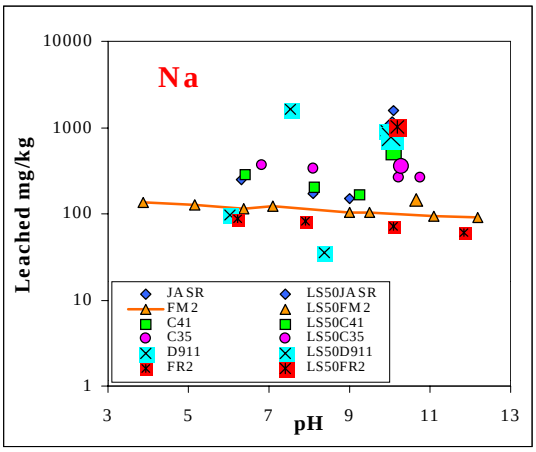

Mg
Leached mg/kg
pH
10000
1000
100
10
1
0.1
3
5
7
9
11
13

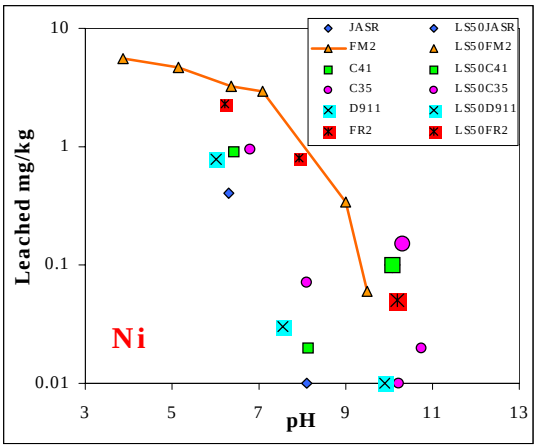

Mn
Leached mg/kg
pH
100
10
1
0.1
0.01
3
5
7
9
11
13
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2

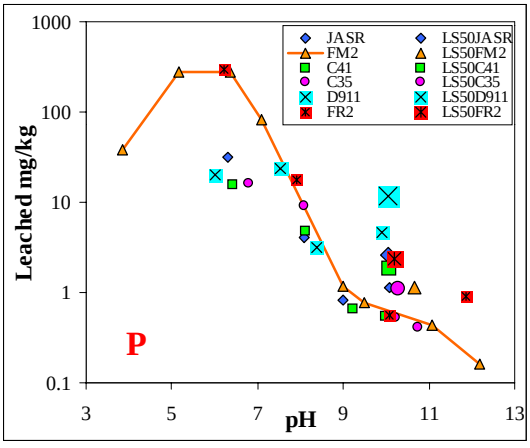
Annex B


JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
Leached mg/kg
pH
Mo

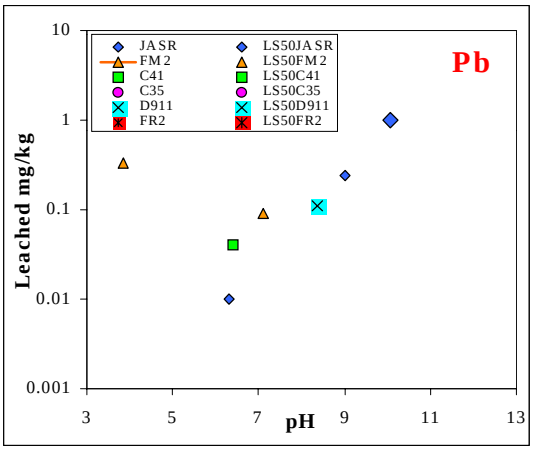

Leached mg/kg
pH
Mo

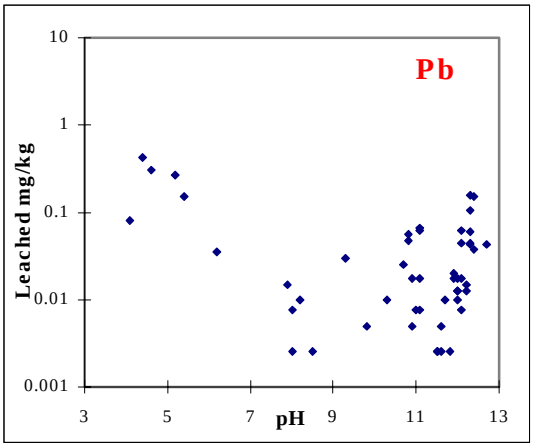

Na
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
Leached mg/kg
pH

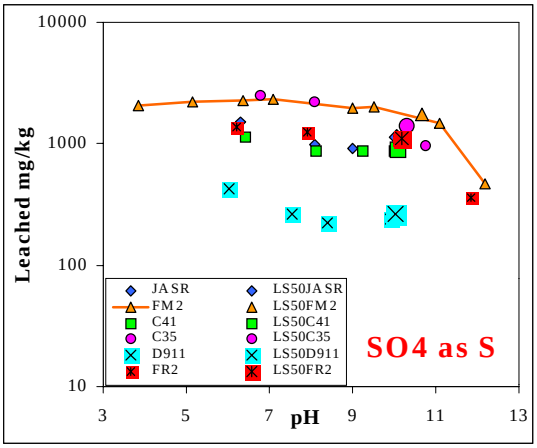

JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
Ni
Leached mg/kg
pH

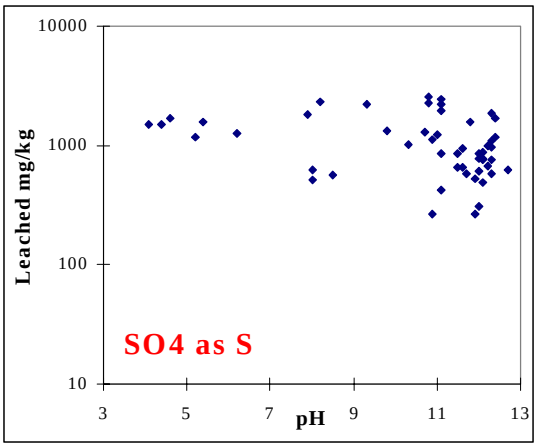

JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
P
Leached mg/kg
pH

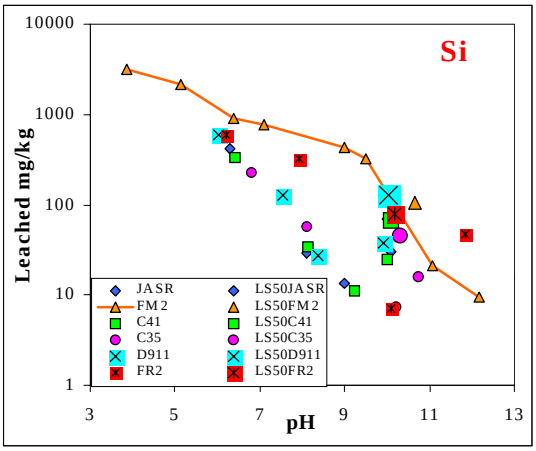
Annex B

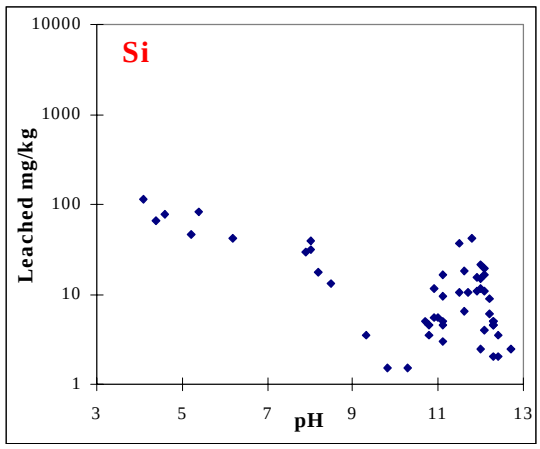

Pb
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
Leached mg/kg
pH
10
1
0.1
0.01
0.001
3
5
7
9
11
13

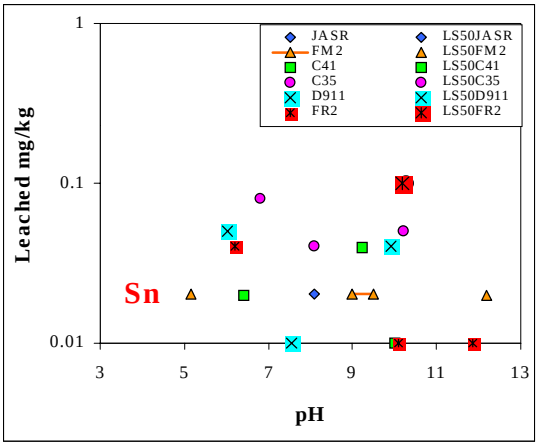

Pb
Leached mg/kg
pH
10
1
0.1
0.01
0.001
3
5
7
9
11
13


SO4 as S
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
Leached mg/kg
pH
10000
1000
100
10
3
5
7
9
11
13

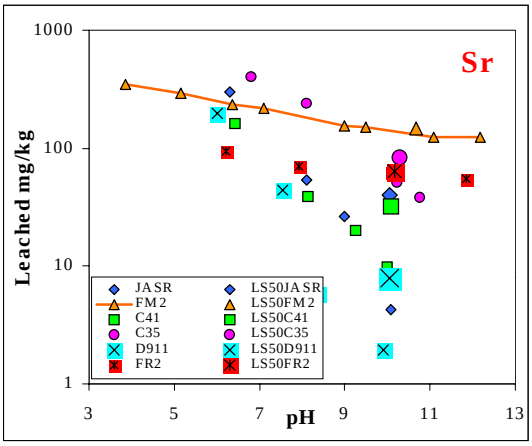

SO4 as S
Leached mg/kg
pH
10000
1000
100
10
3
5
7
9
11
13

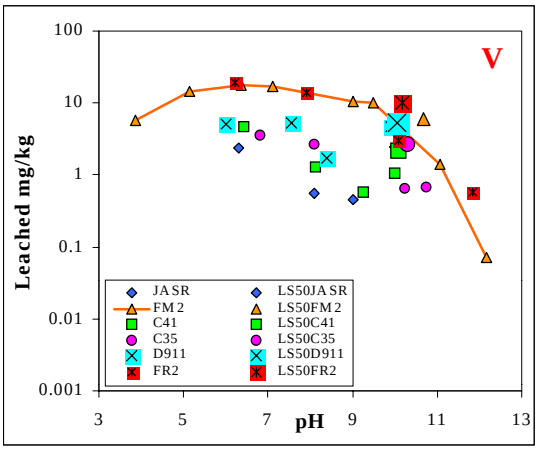

Si
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
Leached mg/kg
pH
10000
1000
100
10
1
3
5
7
9
11
13

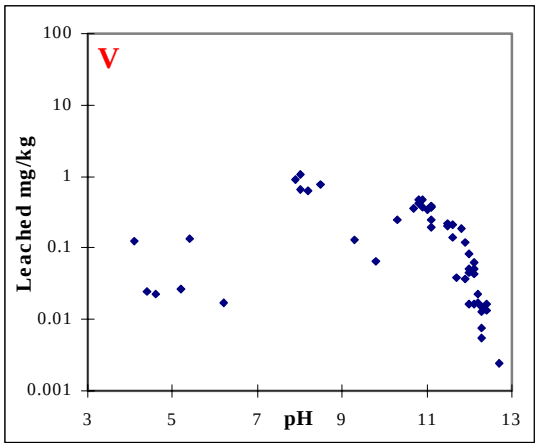

Si
Leached mg/kg
pH
10000
1000
100
10
1
3
5
7
9
11
13

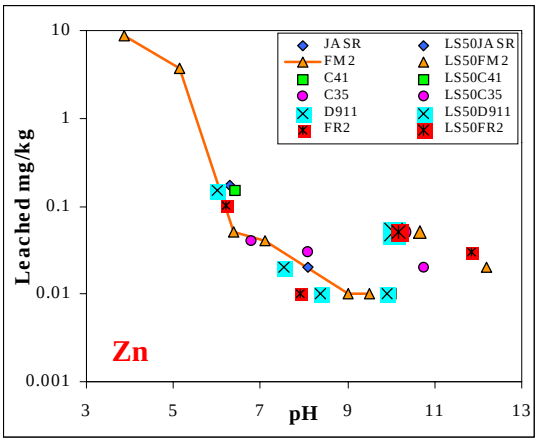

Sn
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2
Leached mg/kg
pH
1
0.1
0.01
3
5
7
9
11
13

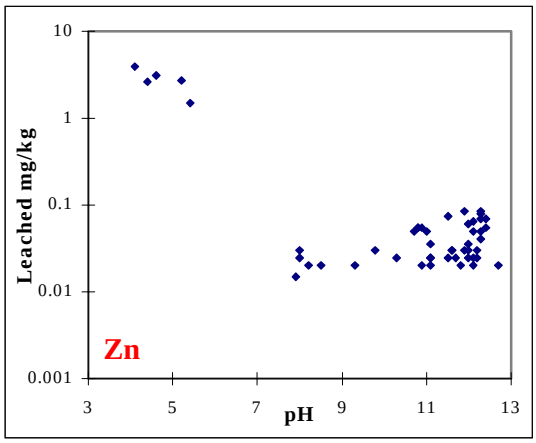
Annex B

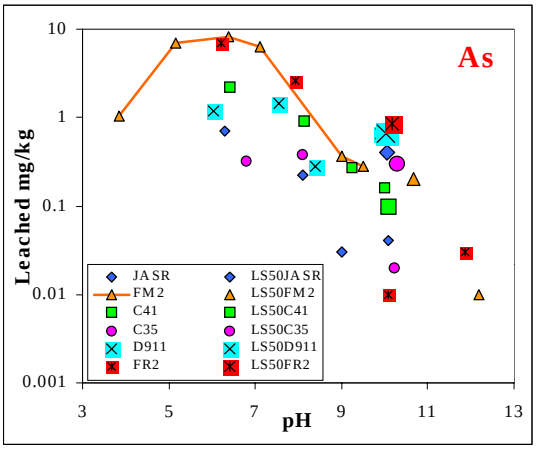

Sr
Leached mg/kg
1000
100
10
1
3
5
7
9
11
13
pH
JA SR
FM 2
C41
C35
D911
FR2
LS50JA SR
LS50FM 2
LS50C41
LS50C35
LS50D911
LS50FR2

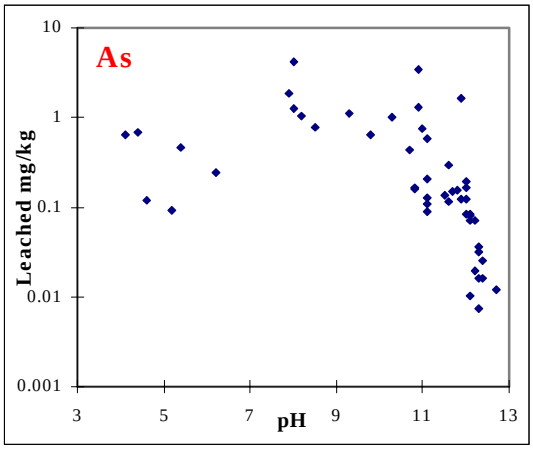

V
Leached mg/kg
100
10
1
0.1
0.01
0.001
3
5
7
9
11
13
pH
JA SR
FM 2
C41
C35
D911
FR2
LS50JA SR
LS50FM 2
LS50C41
LS50C35
LS50D911
LS50FR2


V
Leached mg/kg
100
10
1
0.1
0.01
0.001
3
5
7
9
11
13
pH

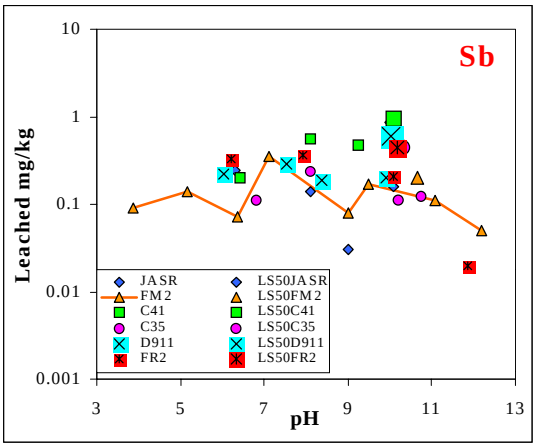

Zn
Leached mg/kg
10
1
0.1
0.01
0.001
3
5
7
9
11
13
pH
JA SR
FM 2
C41
C35
D911
FR2
LS50JA SR
LS50FM 2
LS50C41
LS50C35
LS50D911
LS50FR2

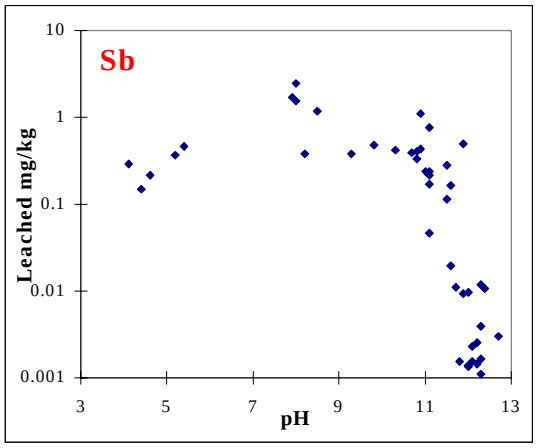

Zn
Leached mg/kg
10
1
0.1
0.01
0.001
3
5
7
9
11
13
pH

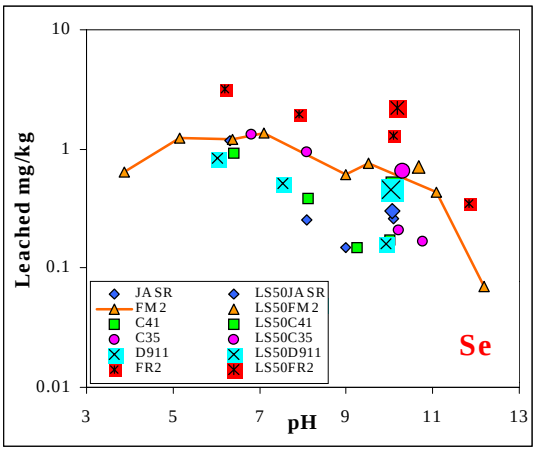

As
Leached mg/kg
10
1
0.1
0.01
0.001
3
5
7
9
11
13
pH
JA SR
FM 2
C41
C35
D911
FR2
LS50JA SR
LS50FM 2
LS50C41
LS50C35
LS50D911
LS50FR2

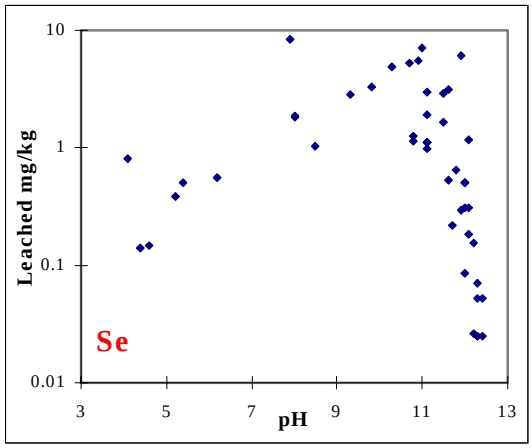

As
Leached mg/kg
10
1
0.1
0.01
0.001
3
5
7
9
11
13
pH

Annex B


Sb
Leached mg/kg
pH
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2


Sb
Leached mg/kg
pH


Se
Leached mg/kg
pH
JASR
FM2
C41
C35
D911
FR2
LS50JASR
LS50FM2
LS50C41
LS50C35
LS50D911
LS50FR2


Se
Leached mg/kg
pH