



# Use of characterisation leaching tests and associated modelling tools in assessing the hazardous nature of wastes

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## ABSTRACT

The evaluation of the hazardous nature of a waste is frequently based on total composition in many jurisdictions, while for most cases the chemical form of the constituents and the release pathways that may result in exposure of man and organisms under conditions of handling, transport, disposal or beneficial use are the most important factors controlling potential environmental impact. Thus, leaching assessment related to possible management scenarios rather than total content can provide a much more robust basis for evaluating health risks and environmental risks for waterborne pathways. Standardized characterisation leaching tests based on intrinsic characteristics of a material provide a new foundation for needed decisions. Chemical speciation modelling using characterisation testing results provides a means to identify mechanisms controlling constituent release, including mineral or sorptive phases, and thus insights into the long-term release behaviour of the material and approaches to reducing potential impacts.

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## 1. Introduction

A wide range of properties are relevant for the characterisation of the hazardous nature of a waste, including flammability, reactivity, carcinogenicity, and constituent leachability [1]. Multiple exposure pathways require consideration including waterborne, airborne contact and ingestion routes. In many cases, a central concern is the possibility of harmful substances being released from the waste, which may adversely affect natural resources and impact human health and ecology. In the Hazardous Waste Directive [1] the relevance of the chemical form of substances is recognized. Without clear guidance on how to assess the chemical form of substance, alternative options have been developed, which assume the total content fully consists of a critical form [2,3]. In particular with respect to large volume industrial waste streams, the approach to declare a waste Ecotoxic (H14) upon exceeding a total content limit is overly conservative and counterproductive in finding environmentally acceptable solutions for beneficial use of (parts of) such material streams.

This paper describes how a common set of characterisation leaching tests can be used to solve some of the major waste classification issues by appropriately including knowledge of the chemical responses to external influences (e.g. carbonation, oxidation, degra-

dation, mixing with other waste) and constituent release over various time frames. Evaluation of an industrial chemical sludge from nickel processing, identified under the hazardous waste catalogue classification code 11 01 09 (galvanic sludge) is used here to illustrate the approach. The selected characterisation leaching tests have been developed and demonstrated to be applicable to a wide range of wastes and environmental media, such as soil, sediments, sludge, treated wood, compost, extractive industry wastes, electronics industry wastes, a wide range of construction products, and many otherwise considered hazardous wastes. Since the criteria for Hazard criterion H13 are not designated, the methods specified here would be suitable tools to fill this gap in the assessment. As will be discussed below, the tools also will allow conclusions on other hazard criteria.

## 2. Experimental

### 2.1. Material

The material studied is an industrial sludge from electroplating activities with an enrichment of Ni. It falls under the hazardous waste catalogue classification code 11 01 09 (galvanic sludge).

### 2.2. Test methods

Total elemental composition of the material has been analyzed using aqua regia digestion following EN 13657 [4]. As internal ref-

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erences: NBS 1633A, NBS2704, and an internal soil standard STSoil 1 have been used.

The following characterisation leaching tests have been carried out on the samples:

CEN/TS14429 [5] pH Dependence Leaching Test (similar to ISO/TS21268-4 [6]; EPA preliminary Method 1313 [7] and automated method TS14997 [8]) over  $3 \leq \text{pH} \leq 12$  with liquid to solid ratio (L/S) of 10 L/kg, particle size ( $<0.5$  mm) and 48 h contact time. CEN/TS14405 [9] Percolation Test (similar to ISO/TS21268-3 [10]; EPA preliminary Method 1314 [11]) with L/S = 0.1–10 L/kg.

Total digestion and leaching test extracts were analyzed using induced coupled plasma atomic emission spectrometry (ICP-AES) for Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V and Zn. Total inorganic carbon (TIC), dissolved inorganic carbon (DIC), total organic carbon (TOC) and dissolved organic carbon (DOC) were determined using a Shimadzu carbon analyzer.

### 2.3. Chemical speciation modelling

Chemical speciation of the solid phases within the waste sample and leaching test extracts was simulated based on test results using the ORCHESTRA modelling framework [12] embedded in LeachXS<sup>TM</sup> [13,14]. Aqueous speciation reactions and selected mineral precipitates were taken from the MINTEQA2 database. Ion adsorption onto organic matter was calculated with the NICA-Donnan model [15], using the generic adsorption reactions as published by Milne et al. [16]. Adsorption of ions onto iron and aluminium oxides was modelled according to the generalized two layer model of Dzombak and Morel [17]. The input to the model consists of available metal content for leaching, selected possible solubility controlling minerals, active Fe- and Al-oxide sites (Fe- and Al-oxides were summed and used as input for hydrous ferrous oxides (HFO) as described in [18]), particulate organic matter, and a description of the DOC concentration as a function of pH (polynomial curve fitting procedure). Since the DOC analysis of the extracts does not represent the reactive part of the dissolved organic matter, a fixed fraction of the total DOC was used in modelling. The quantification of sorptive phases for modelling is now being standardized in ISO/TC190 [19]. As a starting point for the model calculations, the maximum value as obtained in the pH dependence leaching test (between pH 3 and 13) was used as the available elemental content for leaching, thus excluding elemental content that is strongly sequestered in, for example, alumina silicate phases. The mineral phases that were allowed to precipitate were selected after calculation of their respective saturation indices (SI) in the original pH dependence leaching test eluates and evaluating their suitability based on the prediction of all substances. The speciation of all major, minor and trace elements is calculated in one problem definition, which limits the degrees of freedom in selecting parameter settings considerable, as improvement of the model description for one element may deteriorate the outcome for other elements. Carbonate was estimated based on the TIC.

## 3. Results

### 3.1. Comparison of total elemental composition and leachability

Table 1 provides the total elemental composition of the Ni sludge. The material largely consists of calcium phosphate and calcium sulphate. The Ni content exceeds the 5000 mg/kg limit stated in the hazard criteria of the Hazardous waste Directive (1991), which renders the material potentially hazardous.

Fig. 1 compares the leaching behaviour of Ni and Mo to the total content present in the Ni sludge. Mo has been selected to show the release behaviour of an oxyanion. Release behaviour of additional elements can be found in the [Supplementary information](#). It is clear that a single step procedure, like the EN12457 series [20–22] and TCLP [23], are insufficient to address the wide range of possible exposure conditions of waste. Up to several orders of magnitude difference between leached content and total content exist as a function of pH, with leached content (release) approaching total content at pH 3. Over the pH domain relevant to field conditions, as indicated by the vertical sides of the box between pH 6.5 and 8.5, at least a difference of one order of magnitude exists between release and total content for both Ni and Mo. This pH domain is assumed on the basis of the neutral pH of the sludge (1.5 pH unit on either side of pH 7) and because there is no indication why in an environmental setting the material would become either acidic or alkaline. The cumulative leached quantity of Ni from the percolation test results (indicated as an open circle in Fig. 1) compares well with the release measured using the pH dependence test at the corresponding pH. From combined evaluation of the release as a function of pH from the pH dependence test, the cumulative release as a function of L/S from the percolation test and the concentration as a function of L/S from the percolation test, it can be concluded that Ni leaching is largely controlled by solubility limitations (i.e., saturated solution). Initially, pH in the percolation test eluate is low and the eluate concentration of Ni decreases as eluate pH increases (see also the inset graph of pH vs. L/S at the lower right of Fig. 1).

The release as a function of pH for Mo is completely opposite to that of Ni. Release of Mo is at a minimum around pH 4–5, while maximum release is observed at pH  $>8$ . The cumulative leached quantity of Mo from the percolation test results closely agrees with the release measured using the pH dependence test at the corresponding pH (again as indicated by an open circle in Fig. 1). From the release behaviour observed from the percolation test results, it can be concluded that Mo leaching is controlled by solubility limitations at the material's own pH.

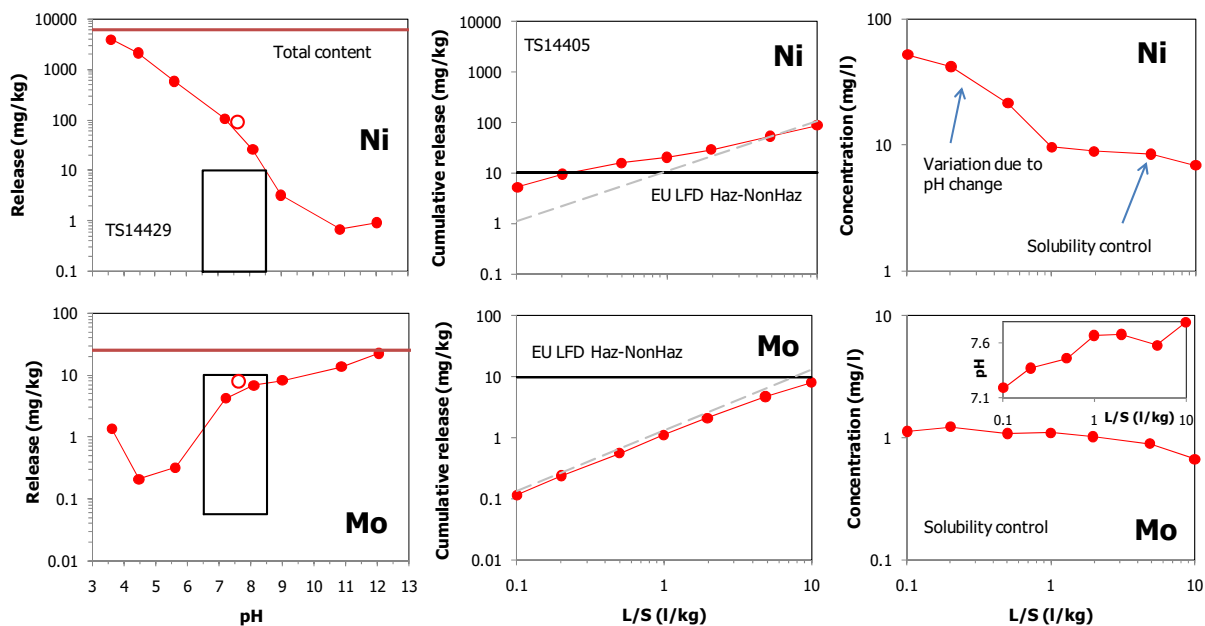
The comparison of leaching test results with EU Landfill Directive [24] criteria for hazardous versus non-hazardous classification indicates an exceeding of the limit value for Ni based on both release over the relevant pH domain from the pH dependence test and cumulative release measured using the percolation test. Mo results are close to but do not exceed the respective limit values. To be able to reduce or mitigate the expected release, it is important to understand the chemical phases that control the solubility of each constituent.

The combined use of the results from the pH dependence test and percolation test can provide additional insights into the expected behaviour of a material under a variety of possible disposal or use scenarios that are relevant to the H criteria. Fig. 2 illustrates which pH domain needs to be considered when evaluating possible exposure risks for cases of inhalation/ingestion, exposure of the material to an acidic environment (e.g. co-disposal with acidic waste), exposure to natural pH conditions or situations where the material becomes alkaline either by exposure to alkaline conditions (e.g. co-disposal with alkaline waste) or stabilisation with alkaline binders. In addition, from the percolation test, the initial leachate concentration in a disposal scenario (i.e., pore water concentrations) can be inferred based on eluate concentrations at low L/S (L/S 0.1–0.2 L/kg).

From the above discussion, it is clear that hazardous determinations based on total content can result in hazard estimates that are many orders of magnitude greater than will likely be realised and do not provide insights into management conditions that will reduce potential adverse impacts. The proposed characterisation based on leaching using the pH dependence test and percolation test will provide an improved understanding of release behaviour

**Table 1**  
The total elemental composition the Ni-sludge (all in mg/kg dry matter).

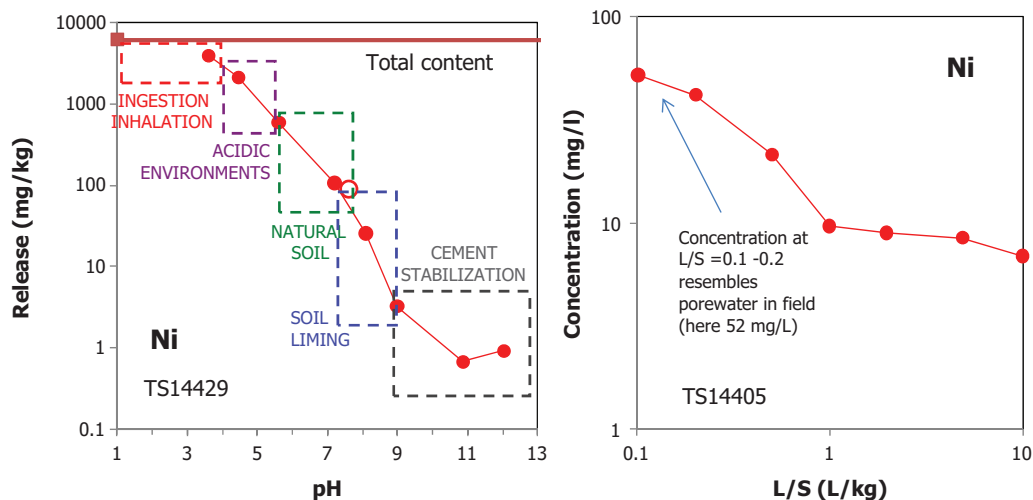
Element	Ni-sludge 1	Ni-sludge 2	Element	Ni-sludge 1	Ni-sludge 2	Element	Ni-sludge 1	Ni-sludge 2
Al	1639	1430	Fe	10,589	10,596	S	33,308	32,362
As	<4	<4	K	324	303	Sb	0.87	1.45
B	34.6	33.48	Mg	4405	3954	Se	1.2	1.8
Ba	6.6	6.3	Mn	917	912	Si	3202	3154
Ca	301,630	295,765	Mo	0.10	0.01	Sn	1.77	0.15
Cd	0.54	0.75	Na	4025	3901	Sr	151	149
Co	124	126	Ni	6124	6076	Ti	87	86
Cr	1592	1591	P	131,153	125,626	V	6.5	6.3
Cu	1174	1150	Pb	29.8	27.8	Zn	135	136



**Fig. 1.** Release behaviour of Ni and Mo from Ni sludge as obtained by pH dependence and percolation tests. Open circle in the two left hand graphs represent the cumulative release of Ni and Mo in the percolation test. The pH of the eluate from the column test is inserted in lower right graph.

that is beneficial for the entire category of Ni sludge's. Related testing of other materials and waste types has indicated that many if not most materials have common leaching behaviour within a class of materials (e.g., municipal solid waste incinerator bottom ash, sev-

eral types of coal fly ash, treated wood, bauxite waste; [25–32]). Major constituent chemistry within such matrices is controlling the release of constituents of potential concern. This allows implementation of a tiered approach to testing that does not require full



**Fig. 2.** Leaching behaviour as basis for judgement of exposure risk of Ni sludge.

**Table 2**  
Chemical speciation fingerprint for Ni-sludge.

Prediction case		Nickel sludge + kol2		DOC/DHA data	
Speciation session		Nickel sludge + kol2		pH	[DOC] (kg/L)
Material		Nickel sludge dry A (P,1,2)		1.00	4.000E–04
Solved fraction DOC	0.2			3.60	3.730E–04
Sum of pH and pe	15.0			4.46	3.310E–04
L/S (L/kg)	10.0			5.61	3.070E–04
Clay (kg/kg)	0.010			7.20	3.000E–04
HFO (kg/kg)	0.001			8.09	2.930E–04
SHA (kg/kg)	0.002			8.99	3.080E–04
Percolation material	Nickel sludge dry A (C,1,1)			10.86	3.230E–04
Avg L/S first perc. fractions (L/kg)	0.1517			12.03	3.450E–04
				14.00	4.000E–04
Polynomial coefficients for DOC					
C0	–4.361E+00	C3		1.280E–04	
C1	–2.925E–02	C4		0.000E+00	
C2	1.391E–04	C5		0.000E+00	
Reactant concentrations					
Reactant	mg/kg	Reactant	mg/kg		
Al	1500	Mg	3788		
Ba	2.4	Mn	136		
Ca	76,831	Mo	22		
Cd	0.011	Na	3374		
Cr	10.2	Ni	3886		
Cu	63	Pb	12		
Fe	821	PO <sub>4</sub> -3 as P	58,862		
H <sub>2</sub> CO <sub>3</sub>	5695	Sb	0.49		
As	0.13	Se	0.21		
B	11.5	SO <sub>4</sub> -2 as S	76,510		
Si	1444	Sr	43.7		
K	246	V	0.04		
Li	2.2	Zn	1.15		
Selected minerals					
3CaO·Al <sub>2</sub> O <sub>3</sub> ·[Ca(OH) <sub>2</sub> ] <sub>0.5</sub> ·[CaCO <sub>3</sub> ] <sub>0.5</sub> ·11.5H <sub>2</sub> O[s]				CSH <sub>2</sub> ECN	OCF
3CaO·Al <sub>2</sub> O <sub>3</sub> ·CaSO <sub>4</sub> ·12H <sub>2</sub> O[s]				Cu(OH) <sub>2</sub> [s]	PbMoO <sub>4</sub> [c]
Fe(OH) <sub>3</sub> [am]		Brushite[2]		Diaspore	Portlandite
Ba[SCr]O <sub>4</sub> [96%SO <sub>4</sub> ]		Ca <sub>2</sub> Cu[PO <sub>4</sub> ] <sub>2</sub>		Dolomite	Rhodochrosite
BaCaSO <sub>4</sub> [50%Ba]		Ca <sub>2</sub> Pb[PO <sub>4</sub> ] <sub>2</sub>		FCO <sub>3</sub> Apatite	Sepiolite[c]
Bixbyite		Calcite		Gypsum	
Brucite		CaMoO <sub>4</sub> [c]		Ni(OH) <sub>2</sub> [s]	Strengite

characterisation to be carried out over and over, but rather that characterisation of similar wastes or initial characterisation of a waste type can serve as a benchmark for a group of materials [33]. A similar characterisation of other waste types will help understand the hazardous nature of wastes better and provide an alternative to classification by definition or origin (hazardous waste list).

### 3.2. Chemical speciation aspects

The Hazardous Waste Directive (1991) recognizes the importance of the chemical form of substances. However, means to assess the chemical form of elements are limited particularly in complex mixtures of substances and at concentration levels that are often too low for instrumental techniques. This has led to the default approach to declare the chemical form of a substance based on total composition and subsequently treat a material as hazardous for lack of better knowledge. This is an undesirable result because more stringent management conditions are required for many materials than would be needed based on more thorough understanding. The pH dependence leaching test in combination with geochemical modelling provides a means to provide useful insights in the chemical behaviour of materials, enabling more informed conclusions about the short and long term behaviour of materials as well as consequences of different exposure conditions.

#### 3.2.1. Chemical speciation fingerprint

The results of chemical speciation modelling based on leaching test results is reported in terms of a chemical speciation fingerprint (CSF) that defines the relevant mineral phases and quantities, sorptive sites and other relevant speciation parameters based on the assumption of aqueous-solid equilibrium partitioning. Further results include the simulated leaching behaviour and phases controlling observed eluate concentrations for the leaching test results and estimates of expected leaching behaviour under different management scenarios. Table 2 provides the resulting CSF for the Ni sludge evaluated in this paper.

Fig. 3 provides the model description (simulation results) for 20 elements based on the CSF. At least in the relevant pH range (6.5–8.5) at L/S of 10 L/kg the CSF simulation (red dashed line) for Al, Ba, Ca, Si, sulphate, Cu, Mn, Ni, V, P, carbonate, and Mg reasonably represent the measured leaching behaviour (red dots), well within the uncertainty associated both with the testing results and with the thermodynamic parameters. The description of Cd also is reasonable considering the very low concentrations. For Cr and Mo, the experimental data reaches a minimum concentration around pH 5. The prediction at low L/S shows a pattern consistent with the release behaviour at L/S = 10. This could point at an identification of the proper release controlling phases, but incorrect thermodynamic constants for these phases. For Pb, the measured concentration is greater than the CSF simulation; this could be due

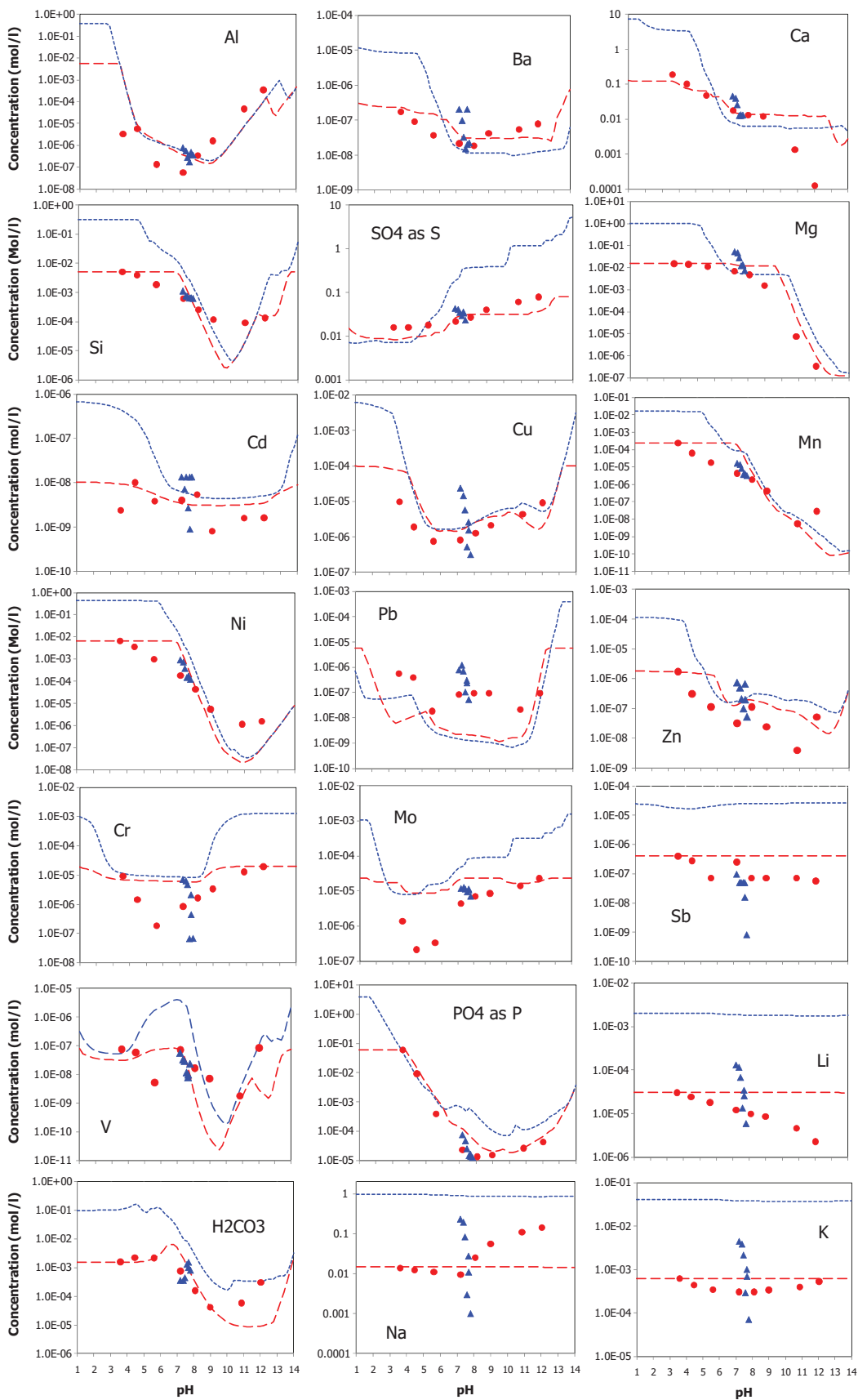


Fig. 3. Model description for Ni sludge based on CSF derived from pH dependence test data. Dots – pH dependence test data at L/S=10; triangles – column test data ranging from L/S 0.1–10; broken line – model for L/S=10; dotted line – model for L/S=0.2.



**Table 3**  
Ni association with specified mineral and sorptive phases at specified pH.

Phases at	pH 7.4	pH 6.5	pH 5.5
Solid humic acid	0.3%	0.4%	53%
Hydrated iron oxide phase	0.5%	0.9%	16%
Ni(OH) <sub>2</sub>	64%		
Ni <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	35%	98%	
Clay			31%

to the selection of a specific Pb-phosphate as a possible precipitating mineral. For Na, increasing concentration at pH >7 is a result of sodium hydroxide additions as part of the experimental test method.

Fig. 3 also provides percolation column test results (blue triangles) with  $0.1 \leq L/S \leq 10$  L/kg and CSF simulation at L/S of 0.2 L/kg (blue dotted line). For several elements (i.e., Al, Ca, Si, Mn, Ni, carbonate) the CSF simulation at L/S of 0.2 and 10 L/kg coincide at the pH between 7 and 8, and the experimental data from both the pH dependence test and the column test also agree well with the CSF simulations, indicating a aqueous concentrations controlled by saturation in equilibrium with a likely correctly identified mineral phase. Initially greater concentrations of Cu and Pb from column test results than predicted by equilibrium CSF simulation at L/S of 0.2 L/kg followed by decreasing concentrations suggest the presence of a small mobile fraction, which at present has not been identified. Complexation with DOC could be a candidate mechanism for this observation. However, the description at L/S of 10 L/kg does not show it as pronounced. Column test results for K, Li and Na indicate typical elution of a fully solubilised species but a lower concentration than the CSF simulations at L/S of 0.2 L/kg because of the extent of preferential flow (e.g., dual porosity) in the column. The column elution behaviour of Sb and Cr appear to be indicative of washout of the species, perhaps controlled by adsorption/desorption phenomena. As indicated in the paper by Dijkstra et al. [26], mass transfer and elution effects need to be coupled with local equilibrium modelling to more fully capture the elution phenomena observed from column tests, but presentation of such results for the nickel sludge is beyond the scope of this paper.

Fig. 4 presents the partitioning of nickel between solid phases, adsorption to iron oxide, binding to particulate organic matter (POM, solid phase) and binding to DOC (complexation in the aqueous phase). Complexation with DOC in solution is most prevalent at pH between 8 and 12. The association of Ni in the solid phase is very pH dependent with multiple phenomena rather than a single phase responsible for the observed solid liquid partitioning. In Table 3 this is illustrated for 3 pH conditions. Sharp changes in mineral association may occur as a function of pH (note situation at pH 6.1 and pH 7.4). Between pH 6 and 7, precipitation as Ni<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is the predominant Ni speciation while Ni(OH)<sub>2</sub> predominates at pH >7.5. Since phosphate is such a dominant phase in the sludge, it is likely that Ni is incorporated in a solid solution of phosphates rather than precipitation as a pure nickel phosphate phase. Since the solubility of a solid solution is generally less than a pure nickel phosphate, the discrepancy at around pH 6 between measurement and prediction can well be explained by such a mechanism. To the extent analytically possible, confirmation of the predicted phases using direct analytical measurements would be beneficial. The information gained and the associated complexity of elemental distribution amongst several solid phases and adsorbed states goes well beyond the phase association that can be inferred from sequential chemical extraction [34], which identifies single phases for a given extraction step and may be very misleading [35].

Understanding the distribution of an element between different solid and aqueous speciation also provides insights into possible exposure and uptake. Based on the work of Postma et al. [36], where

leaching was put into context with ecotoxicity testing, significant changes can occur in the solution composition and speciation obtained by leaching because of dilution and addition of nutrients during preparation for ecotoxicity testing. The role of complexation with DOC is very important because many organisms are not impacted when hazardous constituents are DOC-bound. The effect of reduced toxicity because of DOC complexation was apparent for Cu leached from treated wood and PAHs (polyaromatic hydrocarbons) leached from a gas works contaminated soil.

#### 4. Relevance of proposed characterisation for hazardousness properties

The pH dependence leaching test and the percolation test can provide the basis for evaluating the hazardous nature of materials in connection with different H criteria (Waste Management Act, 1996):

- The irritant or corrosive nature of a waste (H4, H8) can be evaluated based on the pH obtained without acid or base addition as part of the pH dependence test. If the resultant pH is <2 or >11 the criteria apply.
- The test provides a more detailed assessment of risk in case the total content exceeds limiting concentrations as specified in H4/H8 (total concentrations of 1, 5, 10 and 20% based on the risk phases or combined risk phases) and in H5/H6 (total concentrations of 0.1, 3 and 25% based on the risk phases or combined risk phases), as the total content of a substance is rarely completely leachable and it would have to be leachable (transferred to the water phase) to exert its hazard potential.
- The criteria for inhalation or ingestion risk (H5/H6) can be evaluated based on the amount of a constituent released at low pH (e.g., pH <2) as part of the pH dependence test.
- The criteria for gas formation (e.g., H3, category highly flammable substances that in contact with water or damp air produce H<sub>2</sub> gas – R15) can be based on gas evolution at either high (alkaline) or low (acidic) pH as part of the pH dependence test. At high pH, gas formed can be either NH<sub>3</sub>, or H<sub>2</sub>, when metallic parts are present in the waste. At low pH, formation of HCN, HF, H<sub>2</sub>S may occur. However, the most common gas evolved at low pH is CO<sub>2</sub>, which is liberated from calcite and other carbonate bearing minerals at pH <4. Therefore potential formation of HCN, HF and H<sub>2</sub>S is best assessed through the direct analysis of CN<sup>-</sup>, F<sup>-</sup> and S<sup>2-</sup>.
- The potential for formation of unacceptable concentrations in leachates after disposal (H13) can be evaluated using the pH dependence test and the first fraction of the percolation test. The pH dependence test provides the possible changes in constituent leaching in response to changes in pH (i.e., from other co-disposed wastes). The first fraction of the percolation test provides the maximum concentration of highly soluble species that can be anticipated for the initial leachate produced under landfill conditions (very low L/S condition). Leaching tests are carried out at L/S = 10 L/kg or greater fail to provide adequate indications of initial leachate concentrations when a substance is in a highly soluble form (for example, see Cu, Pb and V in Fig. 3).
- Additional insights into ecotoxicity testing responses (H14) can be provided by the pH dependence in combination with chemical speciation modelling. This approach may help avoid misinterpretation based on changes induced by the test conditions which are insufficiently understood.

##### 4.1. Proposed testing approach

The following general characterisation testing is proposed to achieve a better understanding of the hazards and environmental risks associated with management of mixed materials:

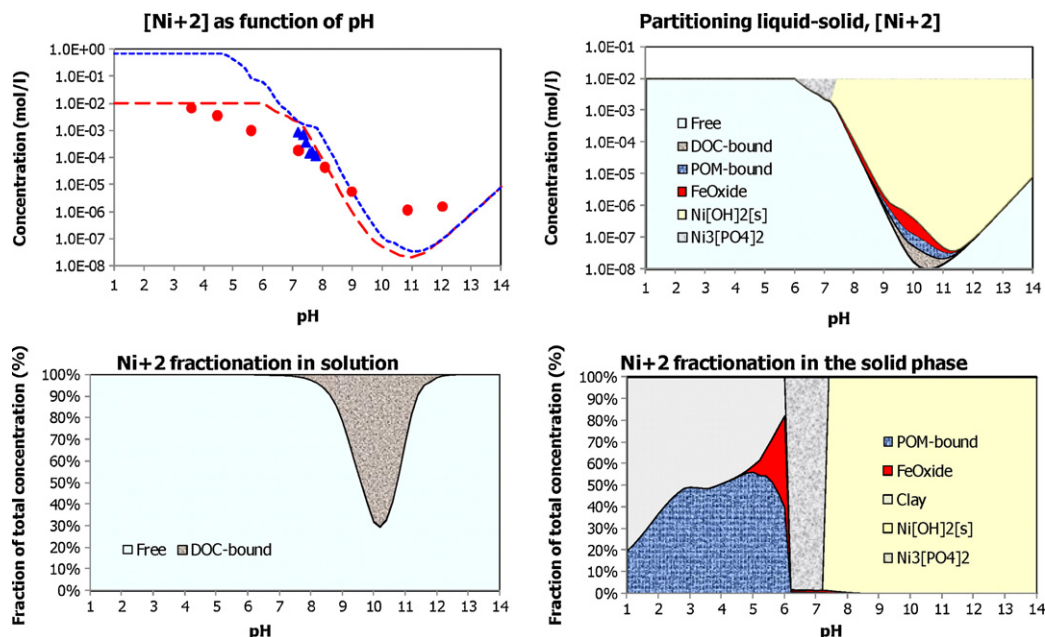


Fig. 4. Partitioning of Ni in Ni sludge between dissolved and solid phases. Legend for top left figure: dots – pH dependence test data at  $L/S = 10$  L/kg; triangles – column test data ranging from  $L/S$  0.1–10 L/kg; broken line – CSF model for  $L/S = 10$  L/kg; dotted line – CSF model for  $L/S = 0.2$  L/kg.

- pH dependence leaching test (TS14429 or equivalent) including (i) acid and base neutralisation capacity, (ii) determination of the pH, electrical conductivity (EC), and redox (Eh) without acid or base addition (own pH), (iii) identification of gas formation at high or low pH, and (iv) measurement of DOC;
- percolation test (TS14405 or equivalent), first fraction only, for porewater simulation, including (i) determination of the pH, EC and Eh, and (ii) measurement of DOC; and,
- modelling of chemical speciation based on pH dependence test data.

As part of the above characterisation, redox measurement provides an indicator for reducing (sulphidic) or oxidising conditions, DOC provides an indicator for mobilization of contaminants and degradability, and EC provides an indicator of total soluble salts (i.e., ionic strength).

The full characterisation should include measurement of elements or species of concern based on potential hazards or risks and also major constituents because the major constituents to a large extent control the release of minor and trace constituents. Current multi-element analysis methods like ICP-OES (Induced coupled plasma–optical emission spectrometry) allow measurement of almost any element at relevant concentration levels, thus allowing identification of the crucial substances for a given waste and subsequently through modelling identifying the likely chemical forms controlling release.

The type of proposed characterisation seems demanding, but in fact it is a form of initial characterisation, which characterises the release behaviour of the hazardous waste type. Other wastes from a similar origin or type will show very similar characteristic behaviour. In fact, even across different waste types behaviour of individual elements often is rather similar even though the release levels may differ. This is precisely the point that has caused the greatest confusion in the waste field. Why does the same waste at one time leach more or less than at another time? A simplified approach consists of the selection of a relevant pH condition for the material and presenting that test result in combination with earlier characterisation data of the material type. This lends much more

intrinsic value to the single step measurement, as it allows much more extended conclusions to be drawn. Only in case of substantial deviation from the reference data, further testing in this tiered approach would be required [33].

#### 4.2. Waste mixtures

Co-disposed wastes may show interactions that are undesirable from a stability point of view. For example, some wastes with metallic elements may lead to  $H_2$  gas formation when exposed to alkaline waste. When hazardous wastes are thrown together haphazardly in a waste deposit, the chance of creating such a situation is very likely and has caused spontaneous fires. A very simple test applied on municipal solid waste incinerator fly ash can be defined to assess this potential ( $H_2$  generation test). In other cases beneficial effects may occur, as substances through interaction with other wastes may be precipitated or adsorbed to reactive surfaces. Through chemical speciation modelling the resulting effect of mixing of wastes can be assessed, when the chemical speciation fingerprints for the constituting materials are available. First steps of this type of modelling have been realised with predominantly inorganic waste [37].

#### 4.3. Database

The material database contained in the LeachXS™ database/expert system already contains a considerable number of wastes containing entries in the Hazardous waste list (2000). The proposed characterisation of wastes would be most efficient, if the resulting characterisation data were publicly available (although with source identities protected) for comparison. The recently developed LeachXS Lite version [38] may provide the required functionality. Both the characterisation data and the simplified testing results can be imported in the system. This has the advantage that characterisation data for a given waste are also assessable to jurisdictions where elaborate testing for technical and economic reasons cannot get the highest priority.

## 5. Conclusions

As illustrated here for Ni sludge, substantially more information on the chemical properties and associated risks in relation to its hazards classifications based on the H categories and risk phases can be obtained from the testing protocols being adopted as standardized testing procedures in CEN, ISO and US EPA. Similar extended characterisation and modelling data as for the Ni sludge are available for several hazardous and non-hazardous wastes listed in the European Waste Catalogue. It is recommended to take advantage of developments in other fields (soil, construction) to improve the classification of waste by making optimal use of these new test methods and the associated geochemical modelling capabilities. This may not only be applied to find actual release controlling phases, but also to eliminate perceived mineral phases identified as critical in the Hazardous waste Directive by the mismatch they provide in geochemical modelling. By applying methods that are now being adopted in different fields, the switch from one field to another does not require that entirely new testing will be needed because the same test results for a waste can be used to decide on hazard classification, suitability for acceptance at landfills and suitability for beneficial use, which also links into criteria for End of Waste [39]. The current approach for testing End of Waste on the basis of a single step test is clearly inadequate to release a former waste to uncontrolled use in any type of product.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.03.119.

## References

- [1] Hazardous Waste Directive (91/689/EEC).
- [2] Handreiking Classificatie van (verontreinigde) grond in het kader van Eural (in Dutch), Municipality Dordrecht, 2002.
- [3] Technical Guidance WM2, Interpretation of the Definition and Classification of Hazardous Waste, 2nd ed., Environment Agency, 2005, version 2.2.
- [4] EN 13657, Characterization of Waste. Digestion for Subsequent Determination of Aqua Regia Soluble Portion of Elements, CEN, Brussels, 2002.
- [5] CEN/TS 14429, Characterization of Waste – Leaching Behaviour Tests – Influence of pH on Leaching with Initial Acid/Base Addition, CEN, Brussels, Belgium, 2005.
- [6] ISO/TS 21268-4, Soil Quality – Leaching Procedures for Subsequent Chemical and Ecotoxicological Testing of Soil and Soil Materials – Part 4: Influence of pH on Leaching with Initial Acid/Base Addition, ISO, 2007.
- [7] Preliminary EPA Method 1313, Leaching Test (Liquid–Solid Partitioning as a Function of Extract pH) of Inorganic Species in Solid Materials Using a Parallel Batch Extraction Test, US Environmental Protection Agency, 2009.
- [8] CEN/TS 14997, Characterization of Waste – Leaching Behaviour Tests – Influence of pH on Leaching with Continuous pH Control, 2005, CEN/TC292.
- [9] CEN/TS 14405, Characterization of Waste – Leaching Behaviour Tests – Up-Flow Percolation Test (Under Specified Conditions), CEN, Brussels, Belgium, 2004.
- [10] ISO/TS 21268-3, Soil Quality – Leaching Procedures for Subsequent Chemical and Ecotoxicological Testing of Soil and Soil Materials – Part 3: Up-flow Column Test, ISO, 2007.
- [11] Preliminary EPA Method 1314, Leaching Test (Liquid–Solid Partitioning as a Function of Liquid–Solid Ratio) of Constituents in Solid Materials Using an Up-flow Percolation Column, US Environmental Protection Agency, 2009.
- [12] J.C.L. Meeussen, ORCHESTRA: an object-oriented framework for implementing chemical equilibrium models, *Environ. Sci. Technol.* 37 (2003) 1175–1182.
- [13] H.A. van der Sloot, P. Seignette, R.N.J. Comans, A. van Zomeren, J.J. Dijkstra, J.C.L. Meeussen, D.S. Kosson, O. Hjelmar, Evaluation of environmental aspects of alternative materials using an integrated approach assisted by a database/expert system, in: *International Symposium on Recycling and Reuse of Materials*, University of Dundee, Dundee, Scotland, 2003, pp. 769–790.
- [14] H.A. van der Sloot, P.F.A.B. Seignette, J.C.L. Meeussen, O. Hjelmar, D.S. Kosson, A database, speciation modelling and decision support tool for soil, sludge, sediments, wastes and construction products: LeachXS™–Orchestra, in: *Second International Symposium on Energy from Biomass and Waste*, Venice, 2008.
- [15] D.G. Kinniburgh, W.H. van Riemsdijk, L.K. Koopal, M. Borkovec, M.F. Benedetti, M.J. Avena, Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency, *J. Colloids Surf. A* 151 (1999) 147–166.
- [16] C.J. Milne, D.G. Kinniburgh, W.H. van Riemsdijk, E. Tipping, Generic NICA–Donnan model parameters for metal-ion binding by humic substances, *Environ. Sci. Technol.* 37 (2003) 958–971.
- [17] D.A. Dzombak, F.M.M. Morel, *Surface Complexation Modeling: Hydrrous Ferric Oxide*, John Wiley & Sons, Inc., New York, 1990.
- [18] J.A. Meima, R.N.J. Comans, Application of surface complexation/precipitation modeling to contaminant leaching from weathered municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.* 32 (1998) 688–693.
- [19] ISO/DIS12782 parts 1–5, Soil Quality – Parameters for Geochemical Modelling of Leaching and Speciation of Constituents in Soils and Soil Materials – Part 1: Extraction of Amorphous Iron (hydr)oxides with Ascorbic Acid; Part 2: Extraction of Crystalline Iron (hydr)oxides with Dithionite; Part 3: Extraction of Aluminium (hydr)oxides with Ammonium Oxalate – Oxalic Acid; Part 4: Extraction of Humic Substances from Solid Samples. Part 5: Extraction of Humic Substances from Aqueous Samples, ISO, Geneva, Switzerland, 2010.
- [20] EN 12457-1, Characterisation of Waste – Leaching – Compliance Test for Leaching of Granular Waste Materials and Sludges – Part 1: One Stage Batch Test at a Liquid to Solid Ratio of 2 L/kg for Materials with High Solid Content and with Particle Size below 4 mm (without or with Size Reduction), 2002.
- [21] EN 12457-2, Characterisation of Waste – Leaching – Compliance Test for Leaching of Granular Waste Materials and Sludges – Part 2: One Stage Batch Test at a Liquid to Solid Ratio of 10 l/kg for Materials with Particle Size below 4 mm (without or with Size Reduction), 2002.
- [22] EN 12457-4, Characterization of Waste – Leaching: Compliance Test for Leaching of Granular Waste Materials and Sludges – Part 4: One Stage Batch Test at a Liquid to Solid Ratio of 10 l/kg for Materials with Particle Size Below 10 mm (without or with Limited Size Reduction), 2002.
- [23] Toxicity Characteristic Leaching Procedure (TCLP). Federal Register, 51(114), Friday, June 13, 1986, 21685 21693 (proposed rules). Federal Register (261), March 29, 1990 (final version).
- [24] EU Landfill Directive (1999) Council Directive 1999/31/EC and Council Decision 19 December 2002 on criteria. Hazardous and solid waste management system; identification and listing of special wastes; disposal of coal combustion residuals from electric utilities (2009) 40 CFR Parts 257, 261, 264, 265, 268, 271 and 302 [EPA-HQ-RCRA-2009-0640; FRL-] RIN – 2050-AE81. USEPA, Washington.
- [25] J.J. Dijkstra, J.C.L. Meeussen, R.N.J. Comans, Leaching of heavy metals from contaminated soils; an experimental and modelling study, *Environ. Sci. Technol.* 38 (16) (2004) 4390–4395.
- [26] J.J. Dijkstra, H.A. van der Sloot, R.N.J. Comans, The leaching of major and trace elements from MSWI bottom ash as a function of pH and time, *Appl. Geochem.* 21 (2006) 335–351.
- [27] J.J. Dijkstra, J.C.L. Meeussen, H.A. van der Sloot, R.N.J. Comans, A consistent geochemical modelling approach for the leaching and reactive transport of major and trace elements in MSWI bottom ash, *Appl. Geochem.* 23 (2008) 1544–1562.
- [28] J.J. Dijkstra, J.C.L. Meeussen, R.N.J. Comans, Evaluation of a generic multi-surface model for inorganic soil contaminants, *Environ. Sci. Technol.* 43 (16) (2009) 6196–6201.
- [29] D.S. Kosson, F. Sanchez, P. Kariher, L.H. Turner, R. Delapp, P. Seignette, Characterization of Coal Combustion Residues from Electric Utilities – Leaching and Characterization Data, USEPA EPA-600/R-09/151, 2009.
- [30] H.A. van der Sloot, A. van Zomeren, Leaching and chemical speciation modelling of wastes, in: J. Römbke, R. Becker, H. Moser (Eds.), *Ecotoxicological Characterization of Waste – Results and Experiences from a European Ring Test*, Springer Science+Business Media, Inc., Norwell, MA, 2009.
- [31] H.A. van der Sloot, L. Heasman, P. Quevauviller, Harmonization of Leaching/extraction Tests, Elsevier Science, Amsterdam, 1997.
- [32] C.M. Carter, H.A. van der Sloot, D. Cooling, A. van Zomeren, T. Matheson, Characterization of untreated and neutralized bauxite residue for improved waste management, *Environ. Eng. Sci.* 25 (4) (2008) 475–488.
- [33] D.S. Kosson, H.A. van der Sloot, F. Sanchez, A.C. Garrabrants, An integrated framework for evaluating leaching in waste management and utilization of secondary materials, *Environ. Eng. Sci.* 19 (3) (2002) 159–204.
- [34] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (7) (1979) 844–851.
- [35] H.A. van der Sloot, B. Susset, O. Hjelmar, U. Kalbe, J. Mehu, J. Galen, L. Chateau, B. Schnuriger, D.S. Kosson, A.C. Garrabrants, J. Steketee, H. Sakanakura, P. Nielsen, K. Lewin, J. Hyks, D. Guyonnet, R. Keren, D. Bendz, P. Suer, T. van Gerven, Evaluation of ruggedness testing needs for the percolation test, pH dependence leaching test and monolith leaching test based on existing information, in: 10th Draft of an Internal Report of the European Standardisation Organisation CEN/TC 292/WG 2 and 6, 2010.
- [36] J.F. Postma, H.A. van der Sloot, A. van Zomeren, Ecotoxicological response of three waste samples in relation to chemical speciation modelling of leachates, in: J. Römbke, R. Becker, H. Moser (Eds.), *Ecotoxicological Characterization of Waste – Results and Experiences from a European Ring Test*, Springer Science+Business Media, Inc., Norwell, MA, 2009.
- [37] H.A. van der Sloot, A. van Zomeren, J.J. Dijkstra, J.C.L. Meeussen, R.N.J. Comans, H. Scharff, Prediction of the leaching behaviour of waste mixtures by chemical speciation modelling based on a limited set of key parameters, in: A. Haarstricht, T. Reichel (Eds.), *Modelling Landfills*, IWWG, 2007.
- [38] LeachXS Lite, <http://www.vanderbilt.edu/leaching/downloads.html>, 2010.
- [39] L. Delgado, A.S. Catarino, P. Eder, D. Litten, Z. Luo, A. Villanueva, End-of-Waste Criteria Final Report EUR 23990, 2009.