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TECHNICAL ARTICLE

Characterisation Leaching Tests and Associated Geochemical Speciation Modelling to Assess Long Term Release Behaviour from Extractive Wastes

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Abstract A pH dependent leaching test (CEN/TS 14429) and a percolation leaching test (CEN/TS 14405) developed in CEN/TC 292 have been used for the first time to characterise the release behaviour of different sulphidic mining wastes. Geochemical speciation modeling using LeachXS Orchestra provides another type of partitioning between mineral and sorptive phases than is currently practised in the mining industry. Comparing new leaching test data for seven tailings and two waste rock samples with model predictions gives new insights into release behaviour. In leaching, mineral transformations on the surface of waste rock or tailings particles, rather than bulk mineral composition, dictate release, which implies that mineralogical examinations are not necessarily relevant from a leaching perspective. Kinetic aspects of release from sulphidic waste can be addressed by testing material in different stages of oxidation or exposure to atmospheric conditions.

Keywords Extractive wastes · Leaching · Characterisation · Geochemical speciation · Sulphidic waste · Impact assessment

Introduction

New developments in testing (Garrabrants et al. 2010; Van der Sloot et al. 2010) focus on obtaining the intrinsic properties of waste and (secondary) construction materials to improve the understanding of release controlling factors and thereby improve prediction of long-term release behaviour (Carter et al. 2008). As the testing methodology is applicable to a wide spectrum of materials and products (EN 12920 2008; Kosson et al. 2002; Van der Sloot et al. 2010), the same approach is suggested for characterisation of sulphidic mining wastes. Attempts to simulate practices in the laboratory will always be limited to the specific conditions of specific experiments and can seldom be transposed to other conditions. Geochemical modelling is practised to describe mine water quality (Maest et al. 2005), where most emphasis is obviously on the description of sulphide oxidation (Destouni et al. 1999; GARD Guide 2009; Price 2009), and much less on the consequences of release of substances in the neutral to mild acidic range (Foster et al. 2011). For some mine wastes, the release at neutral pH can already lead to undesired contaminant release (LPSDP 2007). Unlike the operationally defined sequential extraction (SCE) procedures (Dold 2001; Moricz et al. 2009), which define broad group associations, the approach proposed here aims at quantifying speciation between minerals, sorption, solid solutions, and factors influencing the leaching process (pH, liquid solid (L/S) ratio, and redox state). The results of this work are relevant for long-term prediction of contaminant release from extractive waste disposal sites, even if they do not turn acidic.

Methods

The sulphidic mining wastes that were subjected to leaching are specified in Table 1. The Pyhäsalmi sample was studied in a humidity test cell (Kaartinen 2007). These

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tailings and waste rock samples were studied in the framework of developing a static test for acid neutralisation behaviour (EN 15875 2011). The waste type, primary mined elements, the mineralogical composition, and the neutralisation potential (NP) were obtained from Punkkinen et al. (2009).

A pH dependent leaching test (CEN TS 14429 2005) was performed on 7 tailings (T1, T2, T3, T6, T8, T9 and Pyhäsalmi) and 2 waste rock samples (WR1 and WR2). The up-flow percolation test (CEN TS 14405 2004) was carried out on two tailings and one waste rock sample. A description of the broader use of these methods in soil, sludge, sediments, and construction products is given in Van der Sloot et al. (2010).

Independent estimates of the amount of reactive surfaces present in the samples, which are required for sorption modelling, were made by selective chemical extractions. The amount of amorphous and crystalline iron (hydr)oxides in the waste mixture was estimated by a dithionite extraction (Kostka and Luther III 1994). The amount of amorphous aluminum (hydr)oxides were estimated by an oxalate extraction (Blakemore et al. 1987). The extracted amounts of Fe and Al were summed and used as a surrogate for hydrous ferric oxides (HFO) in the model. The reactive component of the dissolved organic carbon (DOC; i.e. the sum of the fulvic and humic fraction) was assumed to be 20 % of the total DOC, as no data for the mining waste exist to date and similar values have been obtained in a study on bauxite residues (Carter et al. 2008) following a recently developed rapid batch method for DOC fractionation (van Zomeren and Comans 2007).

The leachates and extracts from laboratory tests were analysed 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 by induced-coupled plasma—optical emission spectroscopy (ICP-OES). The DOC and total inorganic carbon (TIC) were analysed with a Shimadzu TOC 5000a analyser. Cl, F, ammonium, and sulphate were analysed according to NEN-EN-ISO 10304-1using a Dionex IC25 ion-chromatograph with a Dionex AS18 column (250 × 4 mm) and a conductivity detector (Dionex DS3). The pH in the leachates was determined using a Mettler Toledo Inlab combination electrode with a polysulphone shaft and gel electrolyte. The analytical precision of the analysis methods is generally better than 10 %. The expected precision in the leaching test results (leaching test plus chemical analyses) is generally 10–30 %, depending on the element and the concentration level considered.

The mineralogical composition was determined using a mineral liberation analyser (MLA), which consists of a scanning electron microscope (SEM) and an energy dispersive X-ray analyzer with two detectors. The phase concentrations and associations of metallic elements were measured using the XBSE method, which produces an X-ray spectrum for each phase. A program compares the measured spectrum to a spectrum library and identifies the phases. The area fractions of the phases are then converted to mass fractions with densities given for the phases. The neutralisation potential (NP) was analysed according to the recently established European standard EN 15875 (2011).

Data Comparison and Geochemical Modelling

The release behaviour of different tailings and waste rock samples and the chemical speciation of the eluates obtained

Table 1 Sulfidic waste samples tested

Sample code	Type	Operation	Main minerals	NP (mol H^+/kg)
T1	Tailings	Zn, Pb, Ag, Cu, Au	Quartz 51 %, Biotite 7.8 %, Pyrite 7.3 %, Tremolite 4.9 %, Pyrrhotite 3.4 %, Chlorite 3.0 %	1.0
T2	Tailings	Zn, Pb, Ag	Quartz 25 %, Microcline 24 %, Biotite 12 %, Clinopyroxene 7.2 %, Garnet 4.4 %, Hyalophane 3.9 %	1.0
T3	Tailings	Zn, Pb	Quartz 60 %, Microcline 13 %, Calcite 8.2 %, Muscovite 4.2 %, Pyrite 3.6 %	1.9
T6	Tailings	Hard-coal	Illite 77 %, Quartz 8.7 %, Kaolinite 6.7 %, Siderite 4.2 %	0.14
T8	Tailings	Coal	Illite 85 %, Smectite 3.5 %, Dolomite 2.9 %, Ankerite 1.6 %, Quartz 1.4 %, Pyrite 1.3 %, Siderite 0.7 %	1.1
T9	Tailings	Ni, Cu	Serpentine 53 %, Chlorite 13 %, Anthophyllite 10 %, Goethite 4.3 %, Plagioclase 3.0 %, Tremolite 2.7 %	2.2
WR1	Waste rock	Au	Chlorite 37 %, Quartz 31 %, Plagioclase 19 %, Calcite 6.4 %, Muscovite 5.3 %	4.6
WR2	Waste rock	Zn, Cu, Au, Ag	Quartz 63 %, Muscovite 14 %, Pyrite 21 %, K-feldspar 1.3 %	0.82
Pyhäsalmi	Tailings	Zn, Cu	Talc	

from the pH dependent and percolation tests were compared with the LeachXS^{TM} ORCHESTRA expert system. LeachXS^{TM} (Van der Sloot et al. 2008) includes a database with an extended set of experimental data on different waste and building materials, including wastes from the extractive industry. The system facilitates data storage, data handling, graphical display, exporting data, and reporting. Within LeachXS^{TM}, ORCHESTRA (Meeussen 2003) is used as the geochemical speciation and reactive transport code for modelling experimental results and the chemical behavior of materials in specific application scenarios. ORCHESTRA can calculate chemical speciation in thermodynamic equilibrium systems using the same thermodynamic database format as other geochemical speciation programs (e.g. PHREEQC or MINTEQ) and contains state-of-the-art adsorption models for oxide and organic surfaces as well as solid solutions. Ion adsorption onto organic matter was calculated with the NICA-Donnan model (Kinniburgh et al. 1999) using generic adsorption reactions (Milne et al. 2003). Adsorption of ions onto iron and aluminum oxides was modelled according to the generalized two layer model of Dzombak and Morel (1990). The object-oriented ORCHESTRA chemical speciation module can be used in combination with previously established transport algorithms (modules) that calculate single or multi-phase diffusion or convection in single or multi-regime porous media models. Aqueous speciation reactions and selected minerals were taken from the MINTEQA2 database (Allison et al. 1991). The MINTEQA2 database is internally consistent; additional mineral reactions taken from literature were transformed into the same format by rewriting the reactions using primary entities in LeachXS-ORCHESTRA. More detail on the geochemical speciation code can be found elsewhere (Dijkstra et al. 2006, 2008; Meeussen 2003).

The input to the model consists of fixed element availabilities, selected possible solubility controlling minerals, active Fe-and Al-oxide sites, particulate organic matter, and a description of the DOC concentration as a function of pH (polynomial curve fitting procedure). Fe- and Al-oxides were summed and used as input for HFO as described by Meima and Comans (1998). The DOC analysis of the extracts does not represent the reactive part of the dissolved organic matter. Based on experience with other similar samples, where the quantification between the hydrophilic fulvic, and humic acid fraction in DOC was quantified, reactive fractions of DOC are defined as a function of pH (lowest proportion of reactive forms at neutral pH and increasing towards both low and high pH). A polynomial fit is created through eight data points to allow quantification of the reactive DOC at intermediate pH values in modelling. Basically, the speciation of all elements is calculated in one problem definition in the model with the same parameter settings. This limits the degrees of freedom in selecting parameter settings considerably, as improvement of the model description for one element may deteriorate the outcome for other elements. As a starting point for the model calculations, the maximum leached concentration obtained in the pH dependent leaching test (between pH 3 and 13) was used as the available concentration. Total carbonate is used as measure for leachable carbonate. The redox status of the material is specified as the sum of pe + pH and was assumed to be 10 (slightly reducing conditions in the laboratory test).

Results

Comparison of Different Sulphidic Wastes

One of the key questions to be answered is: how different are sulphidic mine tailings and waste rocks in terms of their leaching behaviour? In Fig. 1, eight elements (out of 25) are shown; additional information can be obtained from the authors. Despite significant differences in the mineralogical composition (see Table 1), the release behaviour of most elements as a function of pH is rather consistent. Similar behaviour is understood since the leaching curves are similar, indicating similar release-controlling phases for widely different waste samples and, for several substances, similar levels of release as well. This is most likely due to the fact that the surfaces of all sulphidic mine tailings and waste rocks have been changed by exposure to the atmosphere, which has resulted in alterations in the surface mineralogy and the formation of secondary minerals. These now dictate release behaviour rather than the core sulphidic minerals observed by XRD and similar mineralogical quantification methods. Similar observations have been made in other fields, e.g. MSWI bottom ash, soils, and cement mortars (Van der Sloot et al. 2010).

In the case of Ni, all tailings and waste rocks fall within one order of magnitude except T9, which is about a factor of 100 higher. T9 is being mined for Ni and Cu. The T9 Cu data correspond with other tailings originating from Cu mining (T1, T9, Pyhäsalmi), and the tailings showing elevated Zn levels correspond with tailings stemming from Zn mining (T1, T2, T3, Pyhäsalmi). Also, the behaviour of major elements, as shown for Mg, is very systematic. Tailings T9 (serpetinized ultra basic rock) are higher in Mg than any of the other tailings by about a factor of 10. Tailings T8 (dolomite, ankerite) and Pyhäsalmi (talc) tailings are elevated in Mg (factor 2–3) relative to all other tailings and waste rock samples, which together form a relatively narrow cluster with the same leaching pattern as a function of pH. The release behaviour of As is more variable between the different mine waste samples. It is

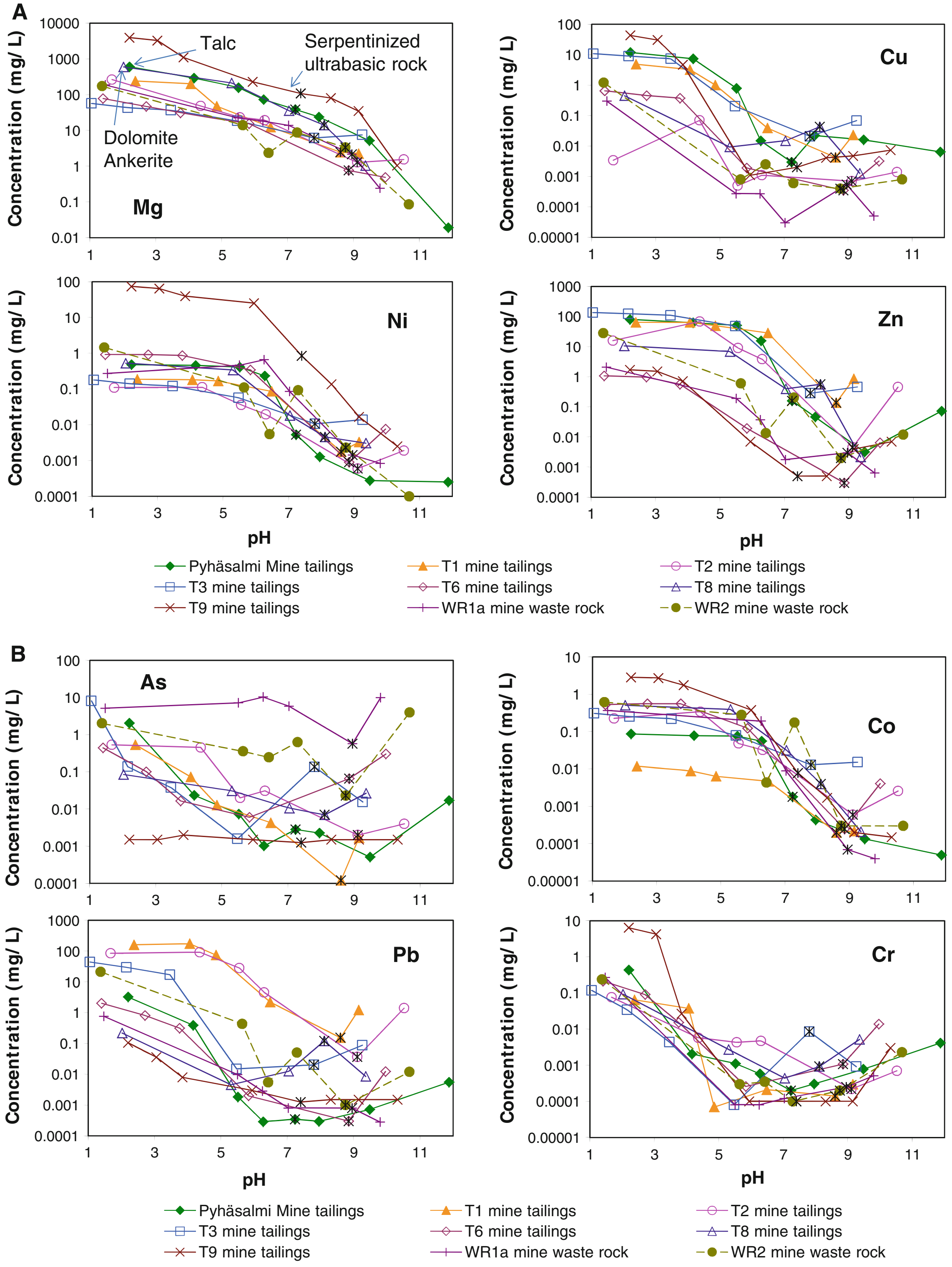

Fig. 1 Comparison of tailing and waste rock leaching behaviour of Mg, Cu, Ni, Zn, As, Co, Pb, and Cr as a function of pH, as obtained by the pH dependent test (CEN/TS 14429)

noticeable, however, that substantial release of As can occur at neutral pH, which can exceed acceptable release levels, i.e.1 and 10 mg/L at WR2 and WR1a, respectively. The relatively large variation in the leached As concentrations is probably due to oxidation of arsenopyrites. The release behaviour of Co is very consistent with release levels at low pH, with lower release levels for T1 and higher release levels for T9, compared to the other samples. The tailings from Pb mining (T1 and T2) stand out relative to the other mine waste samples. T3, which is also mined for Pb, is elevated but not as significantly as the previous two samples. Considering the relatively low release levels, Cr levels fall in a relatively narrow band with the exception of T9, which is 20–50 times higher at low pH than the other mine waste samples. Thus, the nature of the main ore components is reflected in the leaching behaviour. It is also clear that substances have their own specific behaviour, dictated more by their chemistry than by the specific source or location.

The pH dependent leaching of tailings from Cu mining activities (Pyhäsalmi, T1, T3, and T9) is shown in Fig. 2. Data from a humidity test cell study (Kaartinen 2007) and field data (Cidu et al. 2011; Druschel et al. 2004; GARD Guide 2009; Price 2009) are placed in perspective to the laboratory test data. The pH that is plotted on the x-axis is the natural pH of the leachate at the moment of sampling (for the field data). The humidity test cell experiment with Pyhäsalmi tailings (Kaartinen 2007) showed acidification (lowest pH close to 3); however, the Cu concentrations (as well as several other metals e.g. Al, Cd, Mn, Ni, Pb, and Zn) at pH values below 6 do not match with the pH dependent curve for the Pyhäsalmi tailings. This observation implies that the acid condition that developed was not taking place in the cell in contact with the waste, but outside the cell in the outlet of the humidity cell. If the pH 3 condition had developed within the cell, the Cu release would have been at least equal, but more likely would have exceeded the concentration at L/S = 10 and pH 3 (around 10 mg/L), as the L/S in the humidity cell is relatively low compared to the batch test. Field data (Price 2009) roughly follow the trend depicted by the leaching curves, although the concentrations from the field data are generally lower than the laboratory observations. The evolution of acidification shows results at a much lower L/S ratio than the pH dependent test, as reflected both by the Richmond mine data (Druschel et al. 2004) and seasonal variation data (GARD Guide 2009). The Richmond mine data (Druschel et al. 2004) concerns a very acidic mine leachate, with a pH ranging between 0.5 and 0.9, resulting in very high Cu levels. The lower values for Cu are for a sump and pool, which may have undergone some dilution. In the case of the seasonal variation of mine leachate (GARD Guide 2009), the pH dependent curve resulting from taking pH–Cu concentration combinations from the graphs shown in Fig. 3 shows a rather systematic trend as a function of the changing pH during acidification. The drainage data by Cidu et al. (2011) for an abandoned Pb, Zn mine are consistent with this pH dependent behaviour as well. This example shows that trends in Cu leaching found in the field are placed in perspective by comparing these results with laboratory characterisation test results.

In Fig. 3, the development of pH and Cu concentrations (taken from the GARD Guide 2009) are plotted as a function of time. Low pH results in high leachability, but not haphazardly, as one might think, but quite systematically and parallel to the pH curve for tailings from Cu mining. Whether this is purely an L/S effect (factor ≈20 between the low L/S leachate of around 0.5 and the L/S = 10 condition in the test) or whether the Cu release effect is not corresponding entirely with the observed pH (neutralisation effects) remains to determined. Figures 2 and 3 provide a different understanding of the same phenomenon. In Fig. 4, the effect of L/S is shown for an acidic abandoned mine waste soil. The first fractions of the percolation test (L/S = 0.2) are a factor of 10 higher than the L/S = 10 concentrations at the same pH. The flat portion of the pH dependent curve between pH 4 and 4.5 indicates almost full dissolution of Cu at that condition. The conclusion from these comparisons is that in spite of kinetic processes, there are systematic trends in the release behaviour of relevant substances that can provide a basis for predicting long term release.

Geochemical Speciation

Using LeachXS Orchestra, the chemical speciation of 30 elements using >650 minerals in the thermodynamic database were used to assess potentially relevant mineral phases for mine waste by calculating saturation indices (a

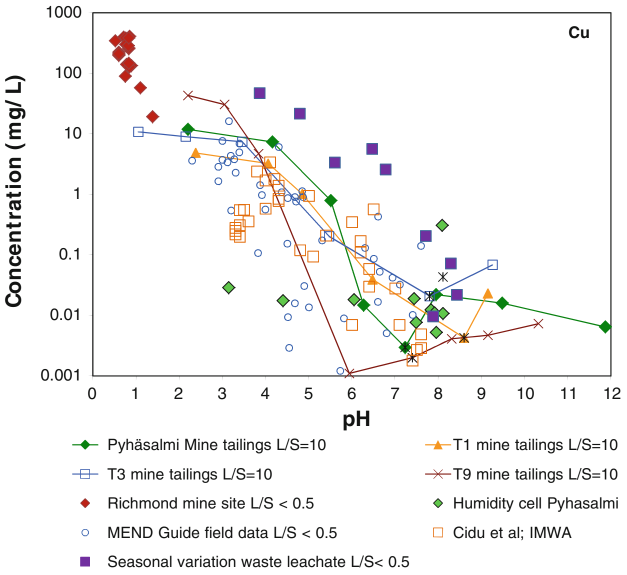

Fig. 2 Cu leaching as a function of pH for laboratory data from Cu mine tailings (T1, T3, T9, and Pyhäsalmi) and field data (Cidu et al. 2011; Druschel et al. 2004; GARD Guide 2009; Kaartinen 2007; Price 2009)

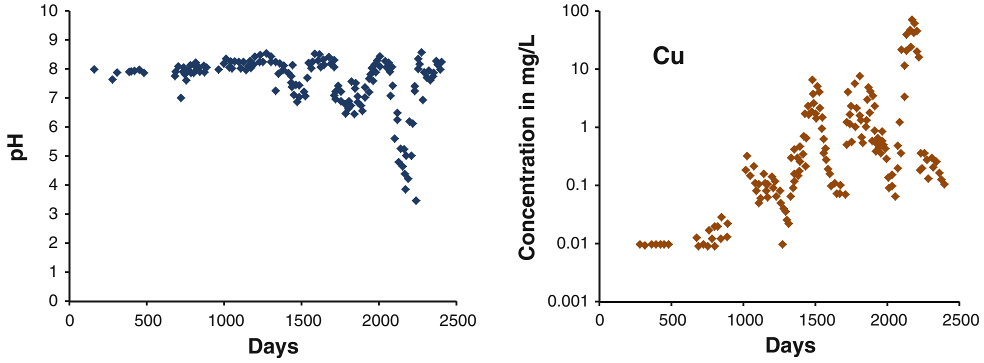

Fig. 3 Leachate monitoring data over a period of 6 years showing seasonal variation in pH development and associated Cu release (From GARD guide 2009); data for graph 2 taken from peaks and valleys in the curves

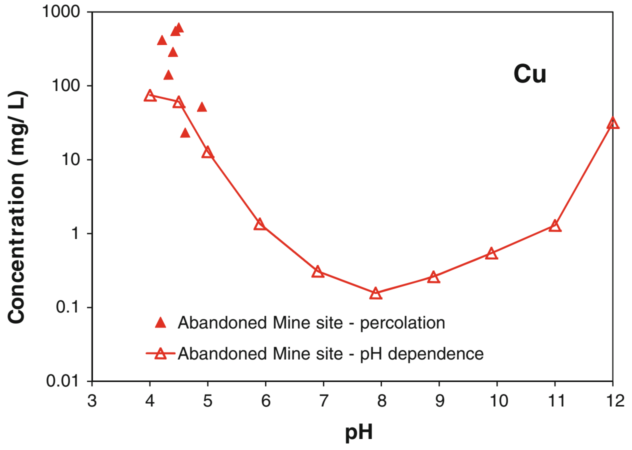

Fig. 4 Relationship between pH dependence test data (TS14429, L/S = 10) and percolation test data (TS14405, L/S = 0.1–10) for an acidic soil from an abandoned mine site (Van der Sloot et al. 2001)

SI value close to 0 points to potential relevance). Adding possibly relevant sulphide minerals for mine waste, some 80 minerals were selected based on experience from modelling a wide spectrum of wastes, soils, and construction products (Van der Sloot et al. 2010). Subsequent descriptive modelling of the pH dependent test results was carried out using minerals and reactive sorptive phases (clay, hydrated iron oxide and aluminum oxide, and dissolved and particulate organic matter). The resulting model description was verified against the measurements (CEN/TS 14429 data at L/S = 10) and optimized to provide the best fit for all major, minor, and trace elements. This iterative process results in a chemical speciation fingerprint (CSF), as shown in Table 2 for tailings T9. This CSF is subsequently used to predict release at low L/S (0.2), which can be compared with the concentrations in the first fractions of the percolation test. The low L/S reflects the concentrations in pore water seeping from landfills, particularly, in large fills and low infiltration rates. The results of the multi-element model description of release and the partitioning of Cu, Ni, Zn and Mg between dissolved and solid phases are given for T9 tailings (Fig. 5). As can be seen from the concentrations derived from the saturation indices, the match between specific minerals and the measured values is relatively poor in many cases, with the exception of $NiSiO_4$. For Cu, $Cu(OH)_2$ and chalcanthite seem to provide a reasonable fit in high and low pH domains, while cupric ferrite is way off. For Zn, none of the phases seem to fit well over the pH range of 6–11. In the case of Mg, brucite gives a good match at high pH. However, all of these minerals were selected (among others, see Table 2) to be possible solubility controlling minerals in the multi-element modelling assessment to predict the leached concentrations.

Models to calculate adsorption of elements to hydrous ferric oxide (HFO), organic matter (humic acid), and clay were also added to the model system. After the multi-element modelling (including reactive surfaces), it turned out that cupricferrite and $ZnSiO_3$ were the main phases of interest to predict Cu and Zn leaching (contrary to the observations made in Fig. 5). The different choice for solubility controlling phases is caused by the fact that counter-ions in a particular mineral may be incorporated in other phases as well, thus effectively lowering the “available” concentration for precipitation of specific mineral phases in the presence of other phases. The SI calculation based on the solubility of one mineral does not take that crucial aspect into account, whereas the multi-element modelling does. The model also takes competition with sorption sites into consideration. The conclusion is that SI calculations, which are used often for guidance, can be misleading; hence, discarding phases beforehand based on closeness of fit needs to be viewed with caution.

The agreement between model description and measurement for L/S = 10 data, as well as the match between prediction at low L/S and the first fractions of the column test are quite good considering the complexity of the multi-element, multi-phase interactions. This observation suggests that the same geochemical processes are relevant over a wide range of L/S conditions and might form the basis for estimating long-term release in an actual disposal scenario (where the L/S ratio will be low).

Table 2 Chemical speciation fingerprint for Mine tailings T9

Prediction case	Mining waste TG9 col		DOC/DHA data		
Speciation session	Mining waste NEN_EU2		pH	[DOC] (kg/l)	[DHA] (kg/l)
Material	Mining_waste_T9 (P,1,1)		1.00	5.0E−06	1.0E−06
			2.20	4.5E−06	9.0E−07
Solved fraction DOC	0.2		3.05	2.7E−06	5.4E−07
Sum of pH and pe	10.0		3.84	1.8E−06	3.6E−07
L/S	10.1 l/kg		5.94	2.9E−06	5.8E−07
Clay	1.7E−02 kg/kg		7.40	2.8E−06	5.6E−07
HFO	5.0E−04 kg/kg		8.31	2.9E−06	5.8E−07
SHA	1.0E−04 kg/kg		9.15	1.6E−06	3.2E−07
Percolation material	Mining_waste_T9 (C,1,1)		10.32	4.1E−06	8.2E−07
Avg L/S first perc. fractions	0.12 l/kg		14.0	5.0E−06	1.0E−06
		Polynomial coeficients for DOC			
		C0	−5.792E + 00	C2	2.493E−02
		C1	−2.147E−01	C3	−7.612E−04
Reactant concentrations					
Reactant	mg/kg	Reactant	mg/kg	Reactant	mg/kg
Al	1,735	Fe	20,683	Pb	1.07
As	0.02	H_2CO_3	60,000	S	3,985
B	24.5	K	2,160	Sb	1.4
Ba	19.3	Li	7.0	Se	0.31
Ca	2,455	Mg	39,572	Si	2,181
Cd	0.06	Mn	428	Sr	3.0
Cl	Not measured	Mo	0.035	V	4.9
Cr	65	Na	143	Zn	17.1
Cu	435	Ni	747		
F	Not measured	P	0.080		
Selected Minerals					
AA_Anhydrite	Bixbyite	$Cu[OH]_2[s]$	Hydcerrusite	$NiCO_3[s]$	Sb_2O_4*
AA_Brucite*	BlaubleiI	$CuCO_3[s]$	Illite[1]*	Nsutite	Siderite
AA_Calcite*	Boehmite*	CupricFerrite*	Laumontite	Otavite	Sphalerite
AA_Fe[OH]3[am]	Brochantite	Diopside*	Manganite	$Pb[OH]_2[C]$	Strontianite*
AA_Fe[OH]3[microcr]*	$Ca_2Cd[PO_4]_2$	Dolomite	$Mg_3[PO_4]_2{:}22H_2O[c]$	$Pb_2V_2O_7$*	V_2O_3
AA_Gypsum	$Ca_4Cd[PO_4]_3Cl$	$Fe_2[MoO_4]_3[1]$	Mg-Ferrite*	$Pb_3[VO_4]_2$	Willemite
AA_Magnesite*	$Ca_4Cd[PO_4]_3OH$	$Fe_2[MoO_4]_3[2]$	$Mn_3[AsO_4]_2{:}8H_2O$	$PbMoO_4[c]$	Wurtzite
Alunite*	$Cd[OH]_2[A]$	$FeCr_2O_4$*	$MnHPO_4[C]$*	Phlogopite	$ZnCO_3{:}H_2O$
$Ba[SCr]O_4[96\ \%\ SO_4]$*	$Cd[OH]_2[C]$	Fluorite	$MnSeO_3{:}2H_2O$	Portlandite	ZnS[A]
$BaCaSO_4[50\ \%\ Ba]$*	$Cd_4[OH]_6SO_4$	Galena	Monticellite	Pyrite	$ZnSiO_3$*
$BaSrSO_4[50\ \%\ Ba]$	Cerrusite	Goslarite	Morenosite	Pyrocroite	
Beta-TCP	Chalcanthite	Greenockite	Nesquehonite	Pyrolusite	
Bianchite	$Cr[OH]_3[A]$	H_2MoO_4-white	$Ni[OH]_2[s]$*	Retgersite	
Birnessite	Cr_2O_3	Hausmannite*	Ni_2SiO_4*	Rhodochrosite	

* Denotes mineral phases identified as providing a significant contribution to the mineral assemblage

Since T9 tailings stem from mining of Ni, this element is discussed in more detail. For Ni leaching from T9, the model description at L/S = 10 is compared with the pH dependent test measurements (top left graph of Fig. 6). In the same graph, the first two fractions from the percolation test are given, which match well with the pH dependent test data. This observation indicates that the same geochemical processes apparently control the leaching of Ni at both low (0.12 L/kg) and relatively high (10 L/kg) L/S ratios. The model prediction at L/S = 0.12, based on the same chemical speciation fingerprint as derived from the model description at L/S = 10, is given showing solubility

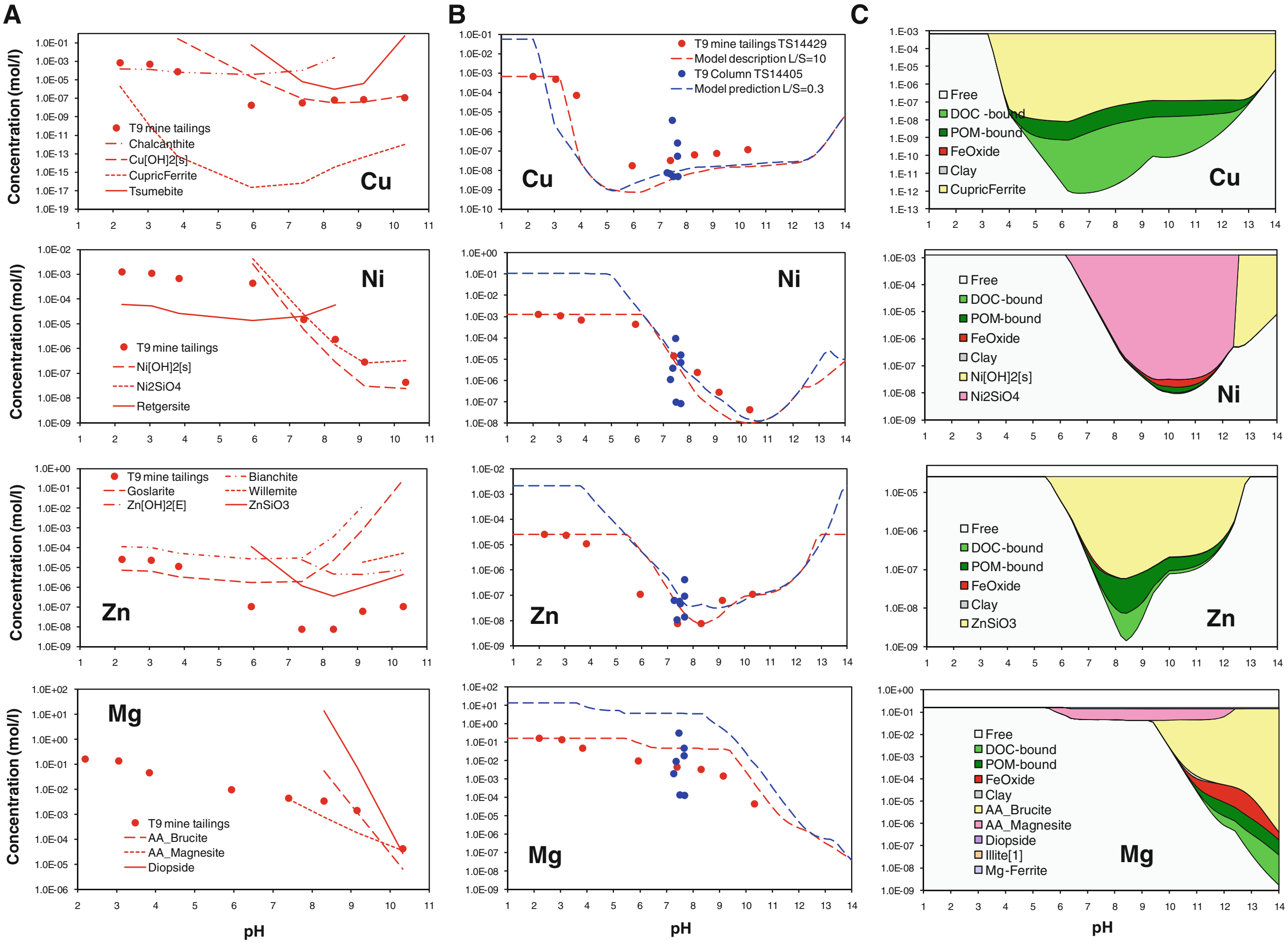

Fig. 5 Concentrations as derived from saturation indices (**a**), multi-element model description for L/S = 10 (TS14429 data) with model prediction (**b**) for L/S = 0.2 (first fraction TS 14405) and associated phase partitioning for Cu, Ni, Zn, and Mg in T9 tailings

control of Ni by Ni_2SiO_4 over a wide pH and wide L/S range. A separate run with $Ni(OH)_2$ as a possible solubility-controlling phase showed a poor match. Ni_2SiO_4 is formed at high temperatures and pressures (Robie et al. 1984). However, in view of the fact that the description of Ni behavior in a complex assemblage is described very well over a wide pH and L/S range (percolation test), it appears that the true mineral cannot differ very much from the stability constant of Ni_2SiO_4, which justifies the use of this phase until better information is available. The partitioning in solution and in the solid derived from the multi-element modelling is given in the second row of graphs. The partitioning in the solid is also shown using a log scale on the y-axis (third level of graphs). The model prediction for the percolation test is also provided, based again on the chemical speciation fingerprint derived from the model description at L/S = 10. At the fourth level, the pH prediction for the percolation test is compared with the measurements. The pH is somewhat underestimated (0.3 pH units) in the first fractions of the column test and starts to deviate more at the higher L/S ratios (0.8 pH units). In the percolation test, the highest Ni concentrations are released at a low L/S ratio and these concentration levels are adequately predicted by the model. The concentrations at higher L/S ratios are at the detection limit of the instrument and cannot be compared with the model results. However, it is concluded that the chosen assemblage of minerals to describe this system is probably a reasonable choice for this material since the pH and the Ni concentrations are adequately predicted until L/S = 2 L/kg.

In Table 3 the partitioning derived from the pH dependent test and speciation modelling is provided. Although limited organic matter is present, it does affect metal leachability, as about 8 % of Ni in solution is complexed at pH 10 as a DOC bound species. In comparison with the total content of 2,398 mg/kg of Ni in T9, an availability plateau is observed at 650 mg/kg, which means that of the total content, some 30 % is actually leachable under extreme conditions (size reduction, low pH, etc.). This modelling outcome implies that unless the phase becomes

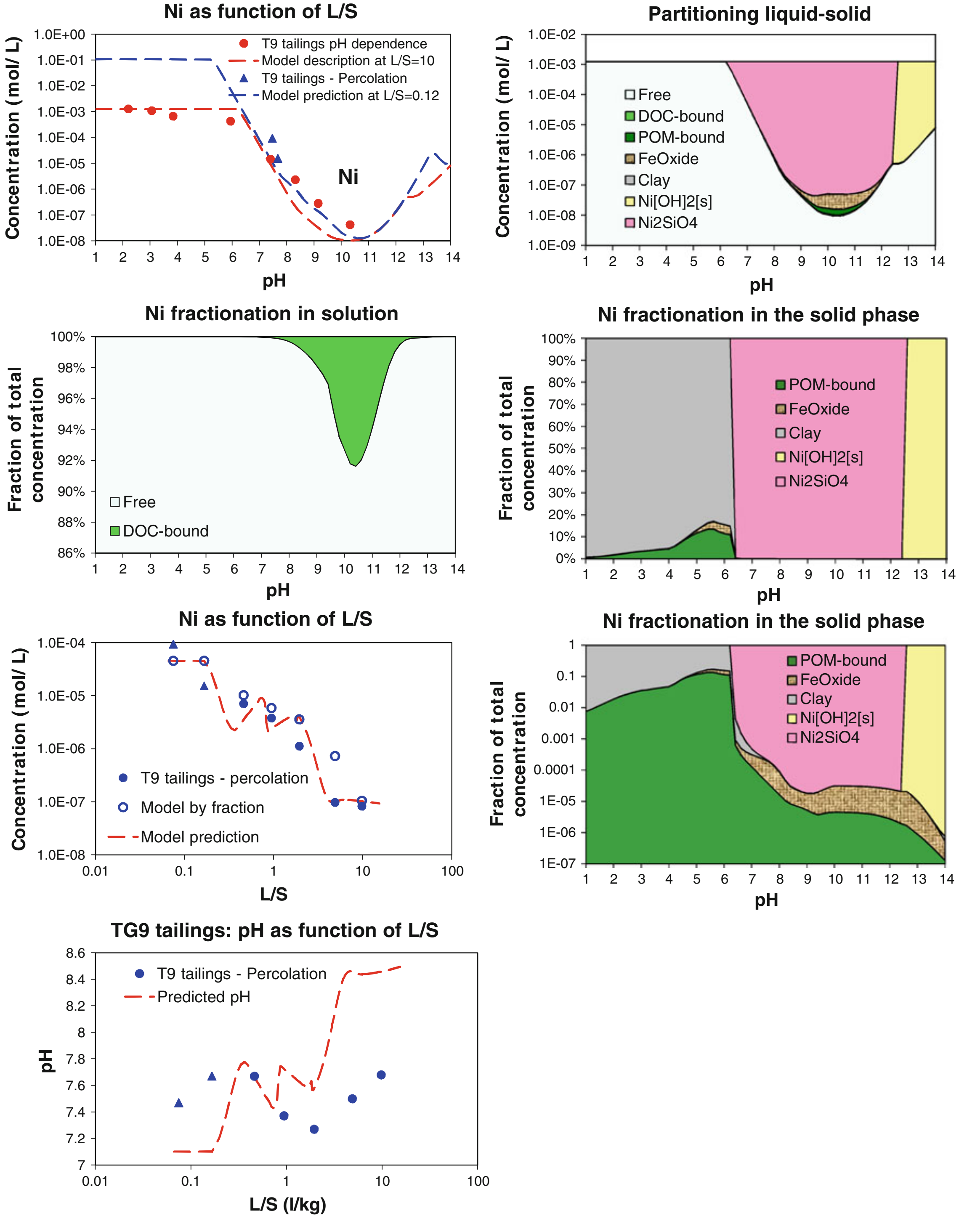

Fig. 6 Partitioning of Ni from mine tailings T9 with a description of release behaviour as a function of pH at L/S = 10, prediction at L/S = 0.2 and prediction of percolation test data, the *triangles* shown in the pH dependence test graph indicate the first two fractions of the percolation test (low L/S—pore water simulation)

depleted, the Ni concentration in solution is very well understood and can be used for predictions of other exposure conditions than these laboratory tests.

The model description of the pH dependent leaching behaviour using the same CSF with limited adjustments has been used for all of the other six mine tailings and the two waste rocks studied within the context of the work mandated by the European Commission to develop a static test for wastes from the extractive industry and guidance on dealing with potential acidification, as referenced in the

Table 3 Ni partitioning in T9 tailings

Phases	pH 8 (%)	pH 7 (%)	pH 5.5[a]	pH 2.5[a]
POM	0.002	0.01		
Clay		0.06		
Hydr Fe oxide	0.01	0.03		
Ni_2SiO_4	99.99	99.90		

[a] Full "available" fraction (650 mg/kg) dissolved

Mining Waste Directive (2006). Similar agreements between model description, low L/S prediction, and measurements in the pH dependent test were obtained for the other tailings and waste rock samples. The results of this assessment are very similar to those presented in Fig. 5. This implies that the processes that determine the leaching behaviour are generic and seem to be applicable to all mining wastes, despite the differences in their base mineralogy. It should be noted that the extent to which these processes are important determine the actual leached concentrations (see, also, the identified range in observed leached concentrations in Fig. 1). This can be understood by the fact that leaching is a process that takes place on the exposed exterior of particles. All studied sulphidic mining wastes apparently form similar phases upon oxidation that control release.

The predicted release behaviours in a column test, based on the CSFs obtained from the pH dependent test, are given for Ca, Mg, Si, sulphate, Zn, and pH in Fig. 7. The pH prediction is somewhat underestimated at the low L/S ratios and overestimated at high L/S ratios. Ca, sulphate and Si are described well, given the fact that the prediction of pH is not yet perfect. Mg is the most pH sensitive element in this pH range and is over-predicted at low L/S and high L/S, accordingly. The elements Ni (Fig. 6) and Zn (Fig. 7) are predicted quite well.

The pH dependent test is an equilibrium based test and hence does not capture kinetic release, such as sulphide oxidation. However, testing acid forming sulphidic waste at different stages of sulphide oxidation (and thus at different stages of pH decrease) will provide insight into the release controlling factors at these intermediate stages. Acidification using HNO_3, as applied in the leaching standard, will capture most of the release behaviour resulting from acidification by sulphide oxidation. Sulphate may not increase as much in the test when pH decreases as will occur in long term field exposure with continuing oxidation. This might be considered to affect the conclusions drawn from the test. However, few elements will be directly affected by the mobilised sulphate itself. Iron, which may be mobilised and oxidised might affect the reactive surface for sorption, but as pH decreases, its role for metal and oxyanion binding decreases rapidly. Consequently, the pH dependent test gives a rather good first estimate of possible effects on release. Since severe acidification is undesirable, mitigating measures are likely to be taken long before very low pH values are reached. This implies that the emphasis in modelling long term behaviour will lie in the neutral to very mildly acidic range, for which the pH dependent test is ideally suited.

Conclusions

Recently developed characterisation leaching tests, which are increasingly being applied in waste characterisation,

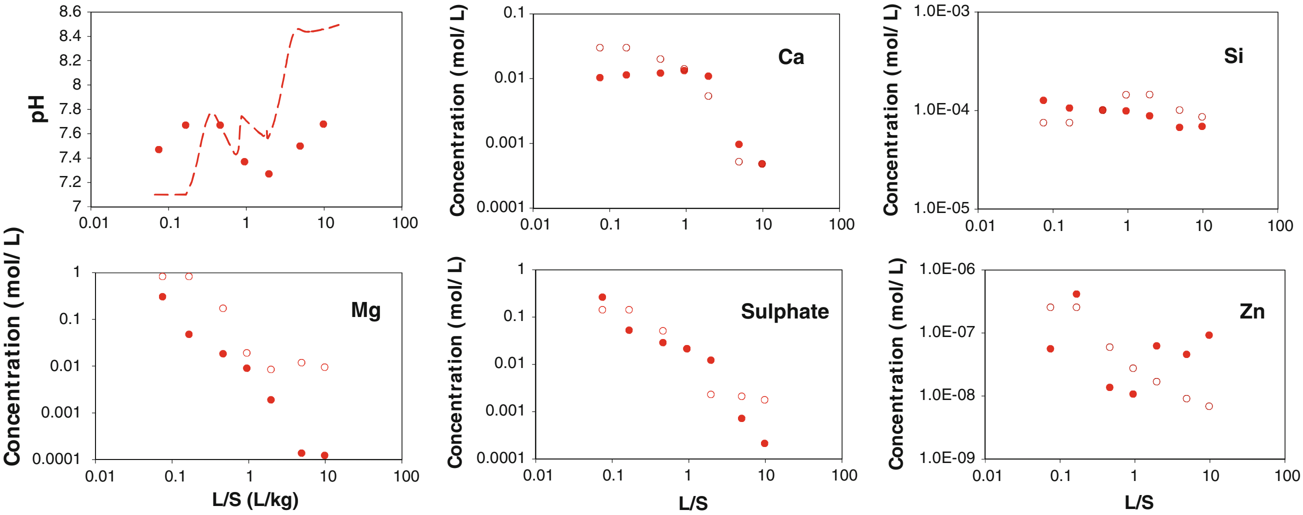

Fig. 7 Model prediction of percolation test data for T9 (*open circles* are average concentrations over the L/S interval corresponding with the intervals used in the test) in comparison with measurements (*dots*)

have been applied for the first time to sulphidic mine tailings and waste rocks. The comparison between release behaviour from the mine tailings and waste rocks shows more consistency between release behaviour than would be possible based on single step tests or kinetic tests applied to assess acidification. Although there is a strong emphasis on the acidification potential of these materials, the release under neutral and mildly acidic conditions should not be undervalued, as undesired leaching may occur under non-acidifying conditions (e.g. As).

Bringing data from different mine sites tested under the same experimental conditions (using the proposed characterisation test) together in a dedicated database will reveal consistency that is now lacking due to the wide variety of tests currently used. Linking such data with lysimeter studies, kinetic testing results, and field observations will provide valuable insight into release behaviour. Understanding that surface mineral coatings, formed by weathering and oxidation, control the release of substances implies that sulphide minerals analysed by XRD are not likely dictating leachate concentrations. Potential rate-controlling minerals defined by geochemical modelling may not be the mineralogically justified choice (Nordstom 2009), but when the identified phase describes release rates under a wide range of conditions well, the true phase cannot be too far off in terms of composition and thermodynamic properties, and thus is it a suitable choice for modelling until better thermodynamic data become available.

Multi-element multi-phase chemical reaction transport modelling can be a challenge, but it is rewarding when the behaviour of extractive wastes (including sulphidic wastes) in laboratory tests can be described. This is already quite an achievement as the complexity of a percolating system is high. Describing kinetically controlled oxidation of sulphidic waste in a multi-element, multi-phase context using available model descriptions for biologically mediated sulphide oxidation is the next step in model development (Mayer et al. 2002). For assessment of long-term release from wastes from the extractive industries, geochemical reaction transport modelling is the only way forward, as testing in the laboratory will not allow a prediction of what the water quality seeping from tailings and waste rocks will be under a variety of exposure conditions over the long term. This approach needs to proceed in steps, starting from an understanding of the leaching behaviour in controlled laboratory tests to kinetic testing, lysimeter studies, and ultimately field observations. It is crucial that verification of modelling output with experimental data provides the level of understanding needed along the way to move us to the next level of complexity.

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