Characterisation leaching tests and associated geochemical speciation modelling to assess long term release behaviour from extractive wastes

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Abstract The pH dependence leaching tests (CEN/TS14429 and the percolation CEN/TS 14405) developed in CEN/TC 292 have been applied for the first time to characterise the release behaviour of different sulfidic wastes. The comparison of the leaching test data for 7 tailings and 2 waste rock samples has given new insights in release behaviour. The geochemical speciation modeling using LeachXS-Orchestra provides another type of partitioning between mineral and sorptive phases than currently practised in the mining industry. In leaching, mineral transformations on the surface of waste rock or tailings particles dictate release rather than bulk mineral composition. Kinetic aspects of release from sulfidic waste can be addressed by testing material in different stages of oxidation or exposure to atmospheric conditions.

Key Words extractive wastes, leaching, characterisation, geochemical speciation, sulfidic waste, impact assessment

Introduction

New developments in testing (CEN/TC 292) focus on obtaining intrinsic properties of extractive wastes 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 (Kosson et al. 2002; van der Sloot et al. 2010), the same testing approach has been suggested for characterisation of sulfidic mining wastes. Attempts to simulate behaviour in practice in the laboratory will always be limited to the specific conditions in that specific experiment and can seldom be transposed to other conditions. Unlike the operationally defined sequential extraction procedures (Dold et al. 2001), which define broad group associations, the new proposed approach aims at quantification of partitioning between minerals, sorption, solid solutions and factors influencing the leaching process (pH, liquid solid ratio - L/S and redox).

Materials

In Table 1, the sulfidic mining wastes that were subjected to leaching are specified. The waste type, the primary mined elements, the mineralogical composition, and the neutralisation potential NP are given (Punkkinen et al. 2009). These tailings and waste rock samples were studied in the framework of developing a static test for acid neutralisation behaviour (EN 15875, 2011).

Leaching methods

The pH dependence leaching test (CEN TS 14429, 2005) was performed on 7 tailings and 2 waste rock samples. 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). 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 part of DOC is assumed to be 20% of the total DOC.

Chemical analysis

The leachates and extracts from laboratory tests were analysed for major, minor and trace elements by ICP (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, Zn). DOC (dissolved organic carbon) and TIC (total inorganic carbon) were analysed by a Shimadzu TOC 5000a analyser. Cl, F, ammonium and sulphate were analysed by ion-chromatography.

Geochemical modelling

Chemical speciation of the solutions was calculated with the ORCHESTRA modelling framework (Meeussen 2003). 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 (Kinniburgh et al. 1999), with the generic adsorption reactions as published by Milne et al. (Milne et al. 2003). Adsorption of ions onto iron and aluminum oxides was modelled according to the generalized two layer model of

***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
Pyhasalmi	Tailings	Zn, Cu	Talc	

Dzombak and Morel (Dzombak and Morel 1990). The database/expert system LeachXS was used for data management, as the system can handle pH dependent leaching data, percolation test data, lysimeter and field leachate data for visualization of the calculated and measured results (van der Sloot et al. 2008).

The input to the model consists of fixed element availabilities, selected possible solubility controlling minerals, active Fe-and Al-oxide sites (Fe- and Al-oxides were summed and used as input for HFO as described in (Meima and Comans, 1998), particulate organic matter and a description of the DOC concentration as a function of pH (polynomial curve fitting procedure). 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 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 the 8 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 value as obtained in the pH dependence leaching test (between pH 3 and 13) was used as the available concentration. Total carbonate is used as measure for leachable carbonate.

Results

Comparison of different sulfidic wastes - One of the key questions to be answered is: How different are sulfidic mine tailings and waste rocks in terms of their leaching behaviour? Despite significant mineralogical differences, the release behaviour of the various major, minor and trace elements is rather consistent. Similar behaviour is understood as the same shape of the leaching curve indicating similar release controlling phases as well as similar level of release for widely different waste samples. This is most likely a result of the fact that all sulfidic mine tailings and waste rocks have been changed on the surface due to exposure to the atmosphere. This has resulted in alterations in the surface mineralogy by formation of secondary minerals. These in turn dictate release behaviour rather than the core sulfidic minerals observed by XRD and similar mineralogical quantification methods. Similar observations have been made in other fields e.g. MSWI bottom ash, soils, cement mortars (van der Sloot et al, 2010). In figure 1, only 2 elements out of 25 are shown (additional information can be obtained from the authors). In case of Ni, all tailings and waste rocks fall within one order of magnitude except T9, which is about a factor of 100 higher. This is related to the fact that T9 is mined for Ni and Cu. Also the behaviour of major elements, as shown here for Mg, is very systematic. Tailings T9 are higher in Mg than any of the other tailings by about a factor of 10. Tailings T8 and Pyhasalmi tailings are elevated (factor 2 - 3) relative to all other tailings and waste rock samples, which together form a relatively narrow cluster. Thus, in the leaching behaviour, the nature of the main ore components is reflected. It is also clear that substances have their own specific behaviour, not as much dictated by a specific source or location but rather by their own chemistry.

Geochemical speciation - Using LeachXS-Orchestra, the chemical speciation of 30 elements using > 650 minerals in the thermodynamic database were used to assess relevant mineral phases (SI units). Subsequent descriptive modelling using a selection of some 20 - 40 minerals was carried out (available from the authors). The same model description with only minor adjustments has been used for all 7 mine tailings and 2 waste rocks studied within the context of the mandated work. This implies that a generic description seems applicable to all mining wastes despite the differences in their base mineralogy. As in the case of cement stabilised material, where carbonation leads to a pH decrease with time, it is not necessary to modify the pH by addition of CO_2 instead of HNO_3 to capture the release behaviour of most of the major, minor, and trace elements. Only a few elements would be affected directly by the CO_2, namely Ca, Ba, and Sr. Similarly, acidification using HNO_3 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 in long term field exposure. This might be considered to affect the conclusions to be drawn from the test, however, very 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 dependence test gives a pretty good first estimate of possible effects. 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 dependence test is ideally suited.

For Ni from T9, the model description at L/S =10 is given in comparison with the pH dependence test measurements (top left graph of figure 2). In the same graph, the first two fractions from the percolation test are given, which match well with the pH dependence test data. 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 control of Ni by Ni_2SiO_4 over a wide pH and wide L/S range. In the second row of graphs the partitioning in solution and in the solid derived from the multi-element modelling is given. The partitioning in the solid is also shown using a log scale on the y-axis (third level of graphs). Here also the model prediction for the percolation test is 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 shown in comparison with

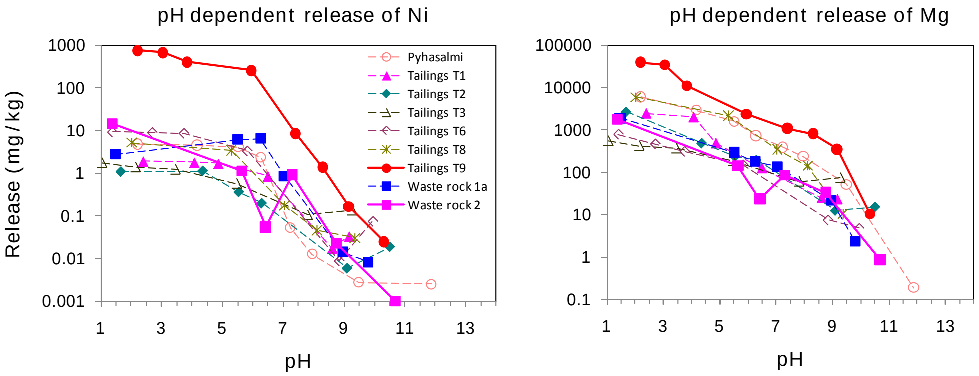
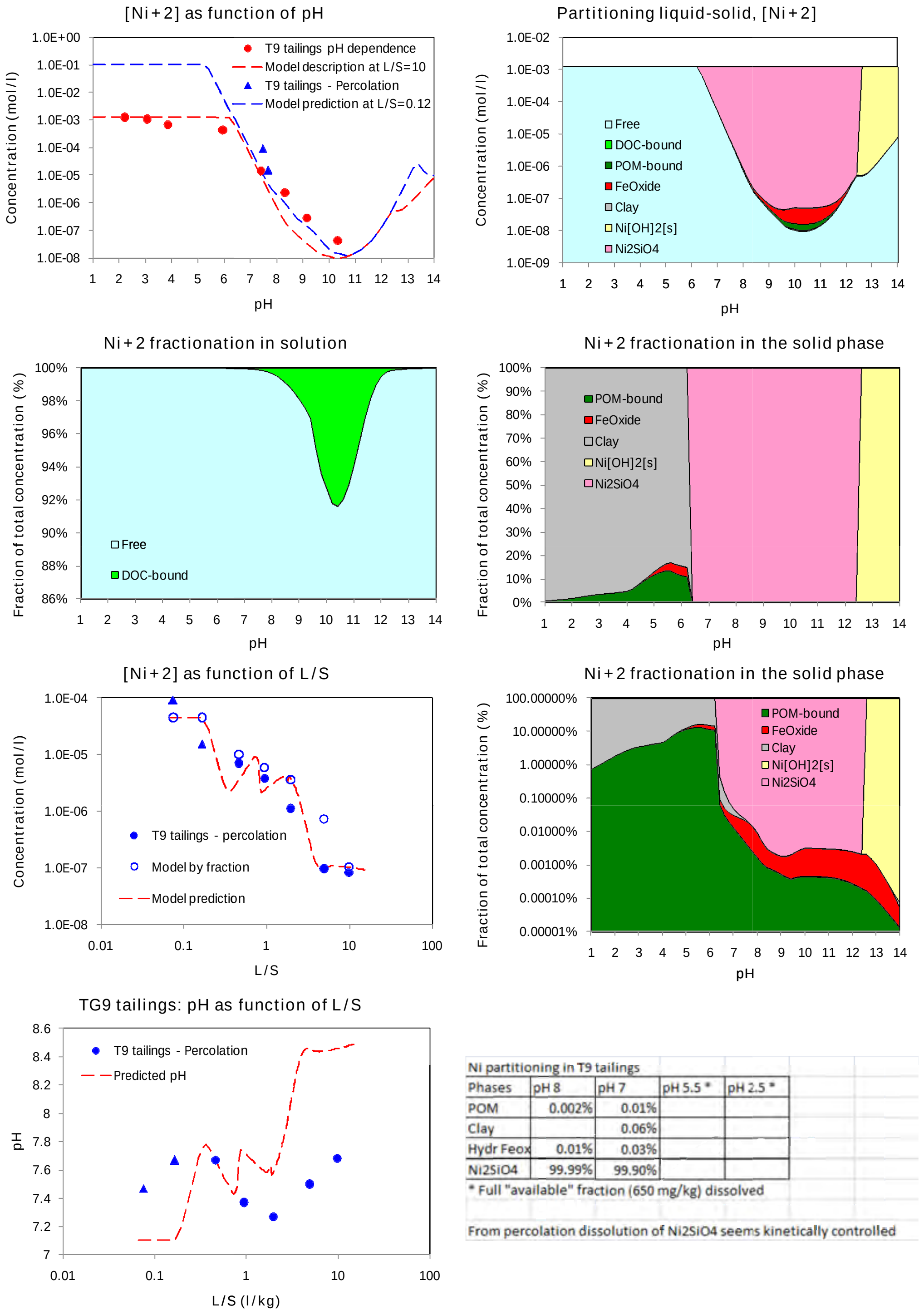


Figure 1 *Comparison of tailing and waste rock leaching behaviour of Ni and Mg as a function of pH showing very consistent leaching behaviour in spite of differences in mineralogical and elemental composition.*



Ni partitioning in T9 tailings

Phases	pH 8	pH 7	pH 5.5 *	pH 2.5 *
POM	0.002%	0.01%		
Clay		0.06%		
Hydr Feox	0.01%	0.03%		
Ni2SiO4	99.99%	99.90%		

* Full "available" fraction (650 mg/kg) dissolved

From percolation dissolution of Ni2SiO4 seems kinetically controlled

Figure 1 *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 measurements. This indicates that apparently the overall mineral assemblage is reasonably well described; otherwise the pH prediction would be way off. In the table, the partitioning derived from the pH dependence and speciation modelling is provided. Although limited organic matter is present, it does affect metal leachability, as at pH 10 about 8% of Ni in solution is complexed as a DOC bound species. In comparison with the total content of 2398 mg/kg of Ni in T9, an availability plateau is observed at 650 mg/kg, which means that of the total content, some 27% is actually leachable under extreme conditions (size reduction, low pH, etc). This modelling outcome implies that unless the phase becomes depleted, the Ni concentration in solution is very well understood and can be used for prediction of other exposure conditions.

Conclusions

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 in the long term. This approach needs to build up in steps starting from an understanding of the leaching behaviour in controlled laboratory test to kinetic testing, lysimeter studies, and ultimately observations in the field. It is crucial that along the way verification of modelling output with experimental data provides the level of understanding needed to move to the next level of complexity. Bringing data from different mine sites tested under the same experimental conditions (proposed characterisation test) together will reveal consistency that due to the variety of test used is now lacking. Linking such data with lysimeter studies, kinetic testing results, and field observations will provide valuable insight in release behaviour. Understanding that surface mineral coatings control release implies that sulphide minerals analysed by XRD will not dictate leachate concentrations. In addition, observed potentially controlling minerals through geochemical modelling may not be the mineralogical justified choice, but when the identified phase can describe release under a wide range of conditions well, it is the suitable choice for modelling until better thermodynamic data become available.

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