

# Review Of Laboratory Methodologies To Determine The Sorption And Release Of Metals Related To The Interaction Of Mine Drainage Water With Natural Media (Peat, Till And Bedrock). A Case Study From A Base Metal Mine In Arctic Finland.

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## Abstract

Mine waste storage facility seepage may be a groundwater contamination source. Contamination transport in the sub-surface is influenced by adsorption and/or exchange of metals from soil and rock surfaces. The quantitative determination of metal adsorption and exchange using laboratory testing is complex and site-specific. This study considered methods including partition coefficients ( $K_d$ ), upflow columns and batch tests to assess the long-term sorption/exchange behaviour in peat, till and bedrock at an Arctic Finnish base metal mine. Upflow columns provided empirical data to calculate sorption/release factors for input to contaminant transport models, potentially more representative information than  $K_d$  or batch tests methodology.

**Keywords:** Sorption, Contaminant transport, Mine waste, Ion exchange,  $K_d$

## Introduction

Seepage draining to ground from mine waste and tailings facilities may lead to metal rich mine drainage entering ground and surface waters. Prediction of this seepage quality, and the ultimate water chemistry following mixing with ground and surface waters is common, but the effect of adsorption or exchange on soil and rock surfaces along the flowpath on the downstream water quality may be missing or assumed to be nil for a conservative estimate. Deriving appropriate sorption or exchange characteristics can be difficult unless site specific data is available as numerous surfaces affect sorption or exchange reactions such as clays, metal oxides and hydroxides (particularly iron species), metal carbonates, phosphates and organic colloidal matter (Bradl 2004). Key variables controlling sorption and exchange include soil type, metal speciation, element concentrations, soil and water pH, liquid: solid mass (L:S) ratios and contact times.

This study looked at analytical options for deriving site-specific sorption or exchange data for a base metal mine in Arctic Finland. Ni and Co are the key metals of interest at this site, as high concentrations of Ni are seen in seepage water from mine waste and tailings, but elevated Co seen in potential downgradient water bodies. Underlying the mine waste and tailings facilities are a mixture of peat soils, till/moraine and weathered bedrock, each with noticeably different potential sorption and exchange capacities. Partition coefficient ( $K_d$ ) tests were completed on a range of sub-surface samples from the site. These tests are completed on relatively small sample sizes and are short duration. Additional batch and column tests were also completed on samples to better understand the mechanism and sorption capacity. All sub-surface samples were collected using drilling and trial pitting methods at the site and maintained in as close to in-situ conditions as possible prior to analysis, completed at Geochem Ltd, Pontypool.

## $K_d$ tests

The partition coefficient ( $K_d$ ) is a descriptor of the distribution of a species between a solid and aqueous phase after equilibrium. In groundwater assessments it represents the overall sorption of a specific species in liquid to the contact geological material.  $K_d$  is a critical parameter for modelling the potential retardation of specific solutes in geological materials.

The British Geological Survey (BGS) (BGS 2000) and Environment Agency of England and Wales (EA) (EA 2005) established an industry method for Kd testing. This method uses a known mass of geological material in a vessel with synthetic groundwater. The groundwater-geological material mix is left to equilibrate for 72 hours. A leachate containing the contaminant of interest is added to the mixture and equilibrated for 48 hours. The mass of contaminant added and the remaining contaminant in solution is used to calculate Kd using the following (where I = initial concentration (mg/L), F = final concentration (mg/L), V = liquid volume (l) and M = solid mass (kg):

$$K_d = \left(\frac{I-F}{F}\right) \times \left(\frac{V}{M}\right)$$

The studies main parameters of interest were Ni and Co, and the typical ranges found in the tailings storage facility (TSF) and waste rock storage facility (WRSF) seepage were used as the basis for the initial concentration. The concentration range for Ni was 1 mg/L – 10 mg/L, and for Co 0.1 mg/L – 1 mg/L. The synthetic groundwater was also based on site baseline measurements. The material used in the Kd testing included:

- Peat from the WSRF area and TSF area
- Weathered bedrock (as weathered bedrock coatings, likely metal oxides/hydroxides) from the WRSF
- Glacial till from the TSF area

A number of rounds of testing were completed aiming to provide validated results based on the standard method. The initial L:S ratio used for the peat samples was 25:1 and for the weathered bedrock coatings 5:1. For accurate Kd results the percentage of the contaminant absorbed within a test should be between 25–75% but the initial

results for both the weathered bedrock and peat showed very high adsorption (> 95%). The sorption capacity was not reached so the results of the first round do not provide accurate assessment of the  $K_d$  value, limiting the results. In subsequent testing rounds on the same materials, and also the TSF till and WRSF peat, higher L:S ratios were used aiming to reach sorption capacity. The concentration of the simulated seepage was also increased to aid in reaching sorption capacity. Overall, 33  $K_d$  tests were completed and only five were considered valid based on the standard methodology (Table 1).

The results for  $K_d$  are high, suggesting that Ni and Co are strongly adsorbed onto the material, and mobility of these elements from the material will be lower. These high values likely reflect the high organic carbon content of the peat and the high iron hydroxide content of the weathered bedrock coatings.

The WRSF peat material has a  $K_d$  for Ni ranging between 2992–611 L/kg, the TSF peat material 504–0817 L/kg, the TSF till 351–1052 L/kg and the WRSF weathered bedrock coatings 135–1430 L/kg. As the weathered bedrock coatings would need to be normalised to account for the bulk weathered bedrock mass and surface area, the peat appears to have a much higher and the till somewhat higher  $K_d$  and Ni will be adsorbed to the peat at a stronger level than the weathered bedrock. The WRSF peat material Co Kd ranges between 2582–4355 L/kg, for the TSF peat 103–26340 L/kg, for the TSF till 1195–4078 L/kg, and for the weathered bedrock coatings 452–6582 L/kg. The variation between the  $K_d$  is less distinct in rounds 1 between peat, till and the weathered bedrock coatings for Co, but the Co appears to be more mobile than Ni. However, in rounds 2, 3 and 4 the  $K_d$  is much higher and also higher than the Ni range, which contradicts the results from round 1 as it suggests that Co has a stronger affinity for the peat than Ni. However, it should be noted that no results from the peat material gave results within the method validity range (based on percentage adsorption). The variation could be linked to the variable L:S ratios and the difference between the spiked concentration of contaminant used and the final  $K_d$  calculated. The methodology

also assumes material can be easily milled or pulped, which was not possible on peat samples and thus the inherent heterogeneity of the peat is likely to be exacerbated by the low masses required. As a reference the K<sub>d</sub> range for Pb on a Cornish siltstone sample was calculated between 37–318 L/kg on spiked Pb concentrations between 10–100 mg/L (EA 2005).

The overall K<sub>d</sub> ranges are relatively similar between the two parameters, however the K<sub>d</sub> does appear to be limited by the initial concentration, as K<sub>d</sub> increases as the initial concentration increases. This is

also the case for L:S ratios as they increase the K<sub>d</sub> increases. The value of K<sub>d</sub> is sensitive to small changes in solute concentration if the ratio of the final/initial concentrations is small, which occurs when the K<sub>d</sub> for a material type is high and to derive a result a higher L:S ratio is needed. As the L:S ratio increases this typically increases the error within the K<sub>d</sub> measurement (BGS 2000).

Peat material typically has much higher K<sub>d</sub> values than weathered bedrock coatings or till, which can be expected by the nature of the material as peat has high organic carbon content compared with the other material.

**Table 1** K<sub>d</sub> test results – rounds 1 to 4.

Round of Testing	Sample	L:S Ratio	Contaminant (mg/L)	I (mg/L)	F (mg/L)	V (L)	M (kg)	Kd (L/kg)	% Adsorbed
Round 1	WRSF peat	25:1	Ni 10	10.03	0.033	0.025	0.001	7611	100
			Ni 1	0.72	0.006	0.025	0.001	2992	99
			Co 1	1.21	0.007	0.025	0.001	4355	99
			Co 0.1	0.12	0.001	0.025	0.001	2582	99
	TSF peat	25:1	Ni 10	10.5	0.132	0.025	0.001	1959	99
			Ni 1	0.75	0.035	0.025	0.001	504	95
			Co 1	1.25	0.032	0.025	0.001	948	97
			Co 0.1	0.12	0.023	0.025	0.001	103	81
	WRSF Bedrock	5:1	Ni 10	12.21	0.058	0.025	0.005	1044	100
			Ni 1	0.67	0.024	0.025	0.005	135	96
			Co 1	1.14	0.003	0.025	0.005	1818	100
			Co 0.1	0.14	0.002	0.025	0.005	452	99
Round 2	WRSF Bedrock	50:1	Ni 10	5	0.181	0.025	0.0005	1430	97
			Co 1	1	0.016	0.025	0.0005	3052	98
			Ni 10	5	0.407	0.025	0.00025	1217	92
			Co 1	1	0.015	0.025	0.00025	6582	99
	TSF Peat	125:1	Ni 10	5	0.081	0.025	0.0002	8113	98
			Co 1	1	0.012	0.025	0.0002	9961	99
			Ni 10	5	0.121	0.025	0.0001	10817	98
			Co 1	1	0.019	0.025	0.0001	12443	98
	TSF Till	25:1	Ni 10	5	0.188	0.025	0.001	687	96
			Co 1	1	0.02	0.025	0.001	1195	98
			Ni 10	5	0.465	0.025	0.00025	1052	91
			Co 1	1	0.046	0.025	0.00025	2012	95
Round 3	WRSF bedrock	500:1	Ni 20 *	22	10.65	0.25	0.0005	510	50
			Co 2 *	2	0.863	0.25	0.0005	716	59
	TSF peat	1000:1	Ni 20 *	22	8.86	0.25	0.00025	1429	59
			Co 2	2	0.219	0.25	0.00025	8580	90
	TSF Till	250:1	Ni 20 *	22	8.94	0.25	0.001	351	58
			Co 2	2	0.339	0.25	0.001	1299	84
Round 4 (Average Repeats)	TSF peat	2000:1	Ni 20 *	20	8.63	0.25	0.00025	1358	58
	TSF Till	500:1	Co 2	2	0.168	0.5	0.00025	26340	93
			Co 2	2	0.26	0.25	0.0005	4078	89

\* Denotes result valid according to methodology.

The till tends to show lower affinity for the Ni and Co, however, if the weathered bedrock is normalized for original sample surface area and mass then this is not the case when Ni is the contaminant.

**Alternative methods: batch tests**

An alternative method for assessing sorption and exchange mechanisms was assessed using batch leaching tests with spikes of key species (such as Cl, SO<sub>4</sub> and Na). The tests were completed on one sample of peat from the TSF area to determine sorption mechanisms and key controls and the effect on the key metals Co and Ni. The spiked desorption tests used the following desorbents: CaCl<sub>2</sub>, KCl, MgCl<sub>2</sub>, Na<sub>2</sub>HPO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>. The desorbents were leached at 2 different concentrations, one high (1M) and one low (0.1M). The aim of the batch leach tests was to leach a sample of the peat at a liquid to solid ratio of 20:1. An equivalent dry mass of the peat sample

(10 g) was used and 167 ml of each desorbent solution added, which made a total volume of 200 ml with the original pore water. The original volume and chemistry of pore water and the lixiviant was estimated to allow the calculation of net mass release or adsorption in the final leachate produced. The mixture was allowed to equilibrate, before the liquid and solid were separated and the resulting leached solution analysed for cations and metals. A blank deionized water was also analysed as a QA/QC measure.

Ca is net adsorbed and the pre-lixiviant concentration is higher than the post-leachate (net release is negative). Mg shows a similar trend to Ca, for most desorbents types there is net release of Mg. However, when Mg is the desorbent there is net absorption. For K and Na, the cations are typically net released when the desorbent does not contain the cation being measured, but the net release rates are much lower than for Mg

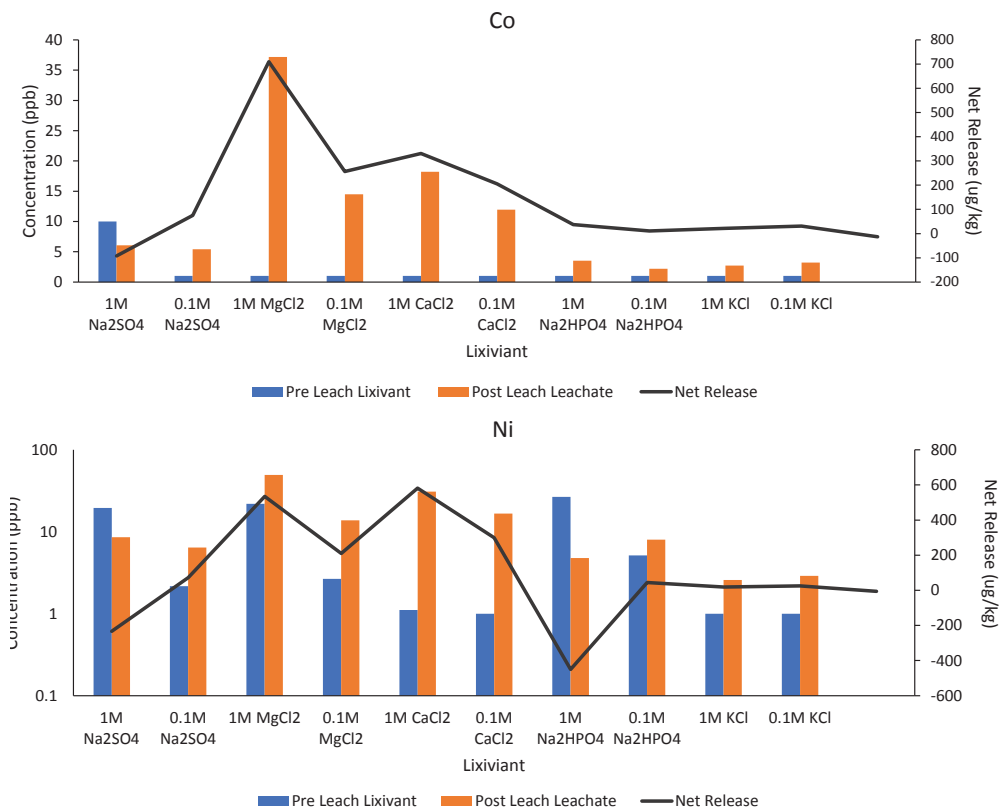


Figure 1 Co and Ni results in pre-leach lixiviant and post-leach leachate in the batch tests.

and Ca. When the desorbent contains either K or Na the net release rate tends to be highly negative. The behaviour of sodium in relation to sorption and desorption of other elements is important due to the high concentration of Na in tailings leachate. The sorption preference for these cations appears to be  $\text{Na} > \text{K} > \text{Mg} > \text{Ca}$ .

The results for Co and Ni are shown in Fig. 1. Co concentrations tend to be higher in post-leach leachate than pre-leach lixiviant. Net release tends to be positive for all desorbents, but particular for those containing Mg and Ca, so Co is readily released from the peat particularly by bivalent cations. Ni concentrations are also released at a relatively high net release ( $> 500 \mu\text{g}/\text{kg}$ ) by bivalent desorbents like Mg and Ca. However, in contrast sodium leachates, particularly at higher 1M concentrations, tend to show a higher Ni concentration in pre-leach lixiviant and the net release is negative suggesting adsorption of Ni rather than release.

### Alternative methods: column tests

A second alternative method for assessing sorption/exchange included in this study was kinetic upflow columns. A range of materials

from the site were tested but only the peat samples are discussed here. The columns were loaded with  $< 22 \text{ mm}$  size fraction peat (TSF peat (238 g) and WRSF peat (240 g)) and were not open to the atmosphere (fig. 2). Testing was completed in a cold room (8 and 10 °C) and irrigated at  $\sim 24 \text{ ml}$  per day using either tailings or waste rock leachate as influent feed. Following a break in testing a second version of influent feed was introduced, which was typically lower in metals than the initial feed. Outflow effluent volumes were measured weekly and collected in-situ analyses and bimonthly metals and major ion analysis.

Ni (fig. 3) has a high influent concentration (a maximum of  $\sim 2110 \mu\text{g}/\text{L}$  for waste rock and  $1320 \mu\text{g}/\text{L}$  for tailings), but post-hiatus the concentration of tailings influent lower than previously measured, with a notable drop from  $\sim 1320$  to  $\sim 50 \mu\text{g}/\text{L}$ . Even though the influent concentration is very low, it's higher than effluent concentrations suggesting that Ni is being actively sorbed by the peat. Ni in the waste rock influent peat column is also being sorbed effectively to the peat, as effluent values only reach a maximum of  $\sim 50 \mu\text{g}/\text{L}$ . Post-hiatus the effluent concentration remain high whilst the influent concentration remain low, suggesting a continuation of Ni sorption in the peat. The cumulative loading also suggest sorption as the influent rises continually, but the effluent's increase is far slower, although this is more pronounced pre-hiatus.

The tailings and waste rock peat columns show different Co concentration trends. Effluent Co concentrations from the tailings peat column is typically higher than the influent. Post-hiatus the influent reduces to the detection limit and the effluent concentration decreases to between  $3 \mu\text{g}/\text{L}$  and the detection limit. The waste rock influent Co concentration is always higher than that of the effluent released from the column. The influent reduces gradually from  $\sim 140$  to  $\sim 6 \mu\text{g}/\text{L}$  between the start and week 34 post-hiatus. The effluent is consistently lower than the influent throughout the testing from around  $40 \mu\text{g}/\text{L}$  at the start to  $\sim 2 \mu\text{g}/\text{L}$  post-hiatus. The cumulative mass loads clearly



*Figure 2 Peat column experiment set-up (Geochem Ltd).*

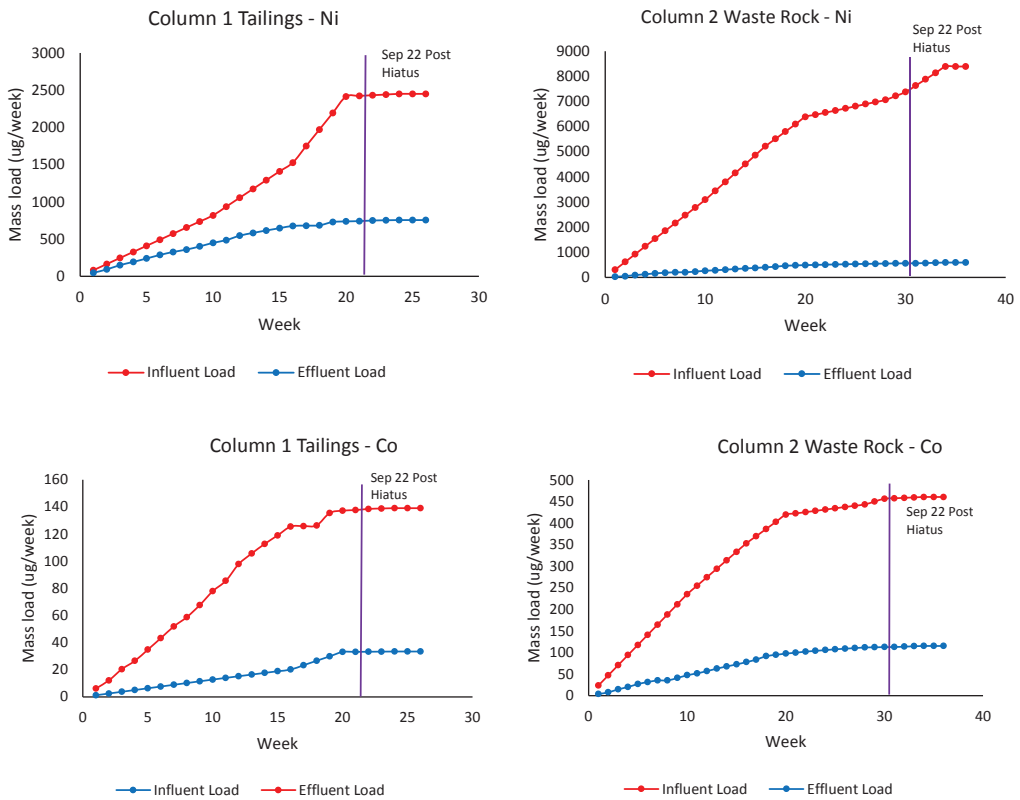


Figure 3 Upflow peat column Co and Ni

show a difference in the behaviour of Co between the two columns. In the waste rock peat column Co is net adsorbed by the peat, whereas in the tailings column, particularly pre-hiatus and to a lesser extent in post-hiatus, Co is net released from the peat.

A key advantage of upflow columns is they are carried out at L:S ratios representative of site conditions within a test environment and are run over a progressive and wide range of L:S ratios (0.1 to >20).

### Conclusions

$K_d$  testing is potentially a less valuable method for understanding the sorption capacity and material variation. There is potential for higher error at high concentrations and L:S ratios required to verify results, whereas the upflow columns appear to give more consistent results. Based on the valid results the peat has a higher  $K_d$  value than either the bedrock coatings or the till. The weathered

bedrock coatings, once normalised for bulk sample surface area and mass, have the lowest calculated  $K_d$ .

The batch testing aided understanding of sorption and exchange mechanisms. Monovalent cations (Na or K) and bivalent cations (Ca or Mg) showed differences in mechanism and behaviour, which is important for the mine site as tailings leachate has high process salt concentrations (Na and K). In the column tests, the Ni tends to be adsorbed in the peat material, whereas Co is released. The cumulative increase in L:S ratios with column progression allows assessment of metal sorption/exchange rates over differing conditions, and often shows similarities in overall results regardless of L:S ratio variation.

Although individual analytical methods with short timeframes and sample sizes can provide information on certain aspects of sorption and exchange (such as mechanisms

in the batch tests), to derive data which is realistic to the site-specific conditions, larger sample sizes and longer timescales used in the column tests are beneficial. As L:S ratio varies through the column tests the mechanism and action of sorption and exchange often maintains its rate, rather than the variation seen in the  $K_d$  tests, potentially making column tests a more useful analytical tool for deriving site-specific sorption and exchange data.

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