Use of Residues Generated from Construction and Fish Industries to Remediate Mine Drainage in Greenland

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Abstract
This study focuses on the development of low-tech remediation methods using local residue materials – shrimp shells from the fishing industry and crushed concrete from the construction industry. The mobility of selected trace elements was compared based on batch and column leaching studies, where the waste rock was mixed with the residue materials. The batch leaching results showed that both concrete and shrimps were able to decrease the leaching of Pb and Zn. The column study showed that concrete was not a satisfactory candidate to immobilize Pb and Zn from a long-term of view.

Keywords: Batch leaching test, Column leaching test, Concrete, Heavy metals, Mine Drainage, Shrimps, waste rock

Introduction
Cryolite has the chemical formula Na_3AlF_6 (sodium hexafluoroaluminate) and is used in the Hall-Héroult process for production of aluminum, where it works as a catalyzer and lowers the melting point of aluminum oxides from 2072 °C to 1012 °C. Ivittuut in southern Greenland had the biggest known cryolite deposit, which was mined from the middle of the 18th century until 1962, where the mine was closed, since artificial cryolite took over the market.

The mine pit is placed adjacent to a large fiord system, and a series of environmental site investigations in the early 80's revealed high concentrations of particularly lead and zinc in sediments, sea weed, blue mussels, dust and lichens, but not in samples of fish and shrimps. The most significant increases were found for lead and zinc in organisms living in the tidal zone (sea weed and blue mussels). The investigations showed, that waste rock used for building the quay area was the main source of leaching of metals. The area is highly influenced by tidal water with an amplitude of more than 4 m, and at each tidal cycle sea water is sieving through the quay area and dissolving lead and zinc minerals in the waste rock and leaching the metals to the fiord system. It was estimated that 1-3 kg of lead was entering the fiord every day giving an annual impact of the fiord of 400-1000 kg lead (Johansen et al. 1995; Bach et al. 2014).

In Greenland, logistics is challenging, due to climatic conditions and very limited road network. It also means that the mining industry in Greenland can be economically challenged, due to high transport costs, and the fact that most goods are shipped to Greenland from Denmark.

Shrimp shells generated from the Greenlandic fishing industry have been either discharged with the waste water, used for animal feed production or production of shrimp flour. Shrimp shells contains 40-50% proteins and 15-25% chitin. Chitin is a polysaccharide and is considered to be one of the most abundant renewable biopolymers (Anastopoulos et al. 2017). Several studies have shown that shrimp shells are capable of removing metals from aqueous solutions either by adsorption on chitin (Karthikeyan et al. 2005; Forutan et al. 2016; Karthik et al. 2015) or by precipitation with sulfide, where the chitin work as substrate for microbial reduction of SO_4^{2-} to S^{2-} which may precipitate a number of heavy metals: Me^{2+} (aq) + S^{2-} (aq) MeS (s) (Daubert & Brennan 2007, Robinson-Lora & Brennan 2008, Sinziana et al. 2001).

Concrete residue is generated from the construction industry when demolishing buildings, concrete structures etc. The concrete waste product is a basic material due to the presence of hydroxide ions, and its immobilization of heavy metals in the waste rock by the increase of pH due to cement amendment is well documented (Sephton and Webb 2017).

The purpose of this study was to investigate the use of local residue materials to minimize the leaching of metals from mining waste products. It was tested if amendment of waste rock with shrimp shells could decrease the leaching of metals, and it was tested if amendment of waste rock with crushed concrete would decrease the mobility of some metals.

Methods

Waste rock (WR) material was collected at the quay area in Ivittuut. The material was air dried and crushed to <4 mm. Shrimp shells were delivered by a local shrimp factory. The shells were freeze-dried. Crushed concrete was obtained from a recycle center in Denmark. The leachant was sea water collected from the Nuuk fiord system. Water was collected every 2 weeks at the same site and at a depth of 50 m. After collection the water was filtered to 1.2 µm and stored at 5°C with continuously air supply.

Batch leaching tests were performed as 24-h shake flask tests according to a modified ASTM D3987 method, using 250 mL PE bottles with 100 ml sea water and 10 or 10+1 g solid. The bottles were placed on a shaking table at room temperature (21 °C). Column leach tests were performed according to a modified ISO/TS 21268-3 standard method. The columns were constructed from acrylic plastic tubes (PPMA) with an internal diameter of 50 mm and a length of 35 cm. The leachant flowrate was set to 12 ml/h. pH, redox, conductivity, dissolved oxygen (DO) and temperature was measured using a YSI professional Plus multiparameter instruments. See table 1 for composition of the tests.

Chemical analysis were performed at an accredited laboratory (Eurofins, DK)

The directly measured elemental values in mg/L for the batch and column leaching results was converted to be mg/kg WR taking into account of the L/S ratio for further mass balance calculation.

The X-ray diffraction analysis (XRD) analysis was performed on a Panalytical X'Pert Pro diffractometer at a commercial laboratory Actlabs, Canada. The XRD analysis was performed for the raw WR, raw concrete, and 6 residues obtained from the column test (WR–C01, C02; shrimps amended WR samples – C03 vs C04; concrete amended WR samples – C05 vs C06. Top and bottom indicate the position in the column where the samples were taken for XRD analysis). A portion of each pulverized sample was mixed with corundum (as an internal standard). The amount of the crystalline minerals were recalculated based on a known percent of corundum.

Results and discussion

Raw materials

The chemical analysis showed that in the raw WR, Pb and Zn level was 0.06 % and 0.53 % of dry weight (DW), respectively (Table 2). The variation of these trace elements was typically high representing the heterogeneous of the waste rock. In shrimps the Pb and Zn level accounted for only <0.0003 % and 0.002 %, respectively when compared with that of the raw WR. The content of total organic carbon (TOC) in the shrimps was 22 %, which was more than 3000 times higher than that in the WR. The TOC level in the WR and concrete was low (0.4–0.7 %).

Table 1 *Composition of batch tests (n=3) and column test.*

Batch	W_{WR} (g)	$W_{shrimps}$ (g)	$W_{concrete}$ (g)	Column	W_{WR} (g)	$W_{shrimps}$ (g)	$W_{concrete}$ (g)
B01	10	-	-	C01+C02	1250	-	-
B02	-	1	-	C03+C04	660	70	-
B03	-	-	1	C05+C06	1120	-	125
B04	10	1	-				
B05	10	-	1				

Table 2 *Chemical composition of raw waste rock, shrimps and concrete samples.*

	DW (%)	Pb (mg/kg DW)	Zn (mg/kg DW)	TOC (%)
Waste Rock	100.0±0	600±286	5257±6798	0.68±0.09
Shrimps	91.3±0.6	3.0±0.0	20.0±1.7	22.0±0.0
Concrete	91±0	7.8±0.7	500±61	0.4±0.1

Batch leaching results

The eluate from WR was of neutral pH (B01), however the eluate from the shrimps and concrete was slightly alkaline (8.7–9.2) (Table 3). The eluate from amended samples (B04, B05) had slightly higher pH than that from the WR sample. Dissolved oxygen (DO) was much lower in the tests containing shrimps, which implies that degradation of organic matter was going on. The EC values in the raw samples was in quite similar level with respect to WR, shrimps and concrete.

The leached Pb and Zn from the WR samples was 13.3 mg/kg and 2.8 mg/kg, which accounted for 2.2 % and 0.053 % of the total content of Pb (600 mg/kg) and Zn (5257 mg/kg) in the WR (Table 1), respectively. The leached Pb and Zn from the raw shrimps and concrete was much lower than that from the raw WR. The leached Pb level from the raw WR was more than 200 times that of the Pb leaching from the shrimp amended WR sample and more than 300 times that of the concrete amended WR sample. Similarly, the leached Zn level from the raw WR was 15 and 44 times the leached zinc level from the shrimps- and concrete amended WR samples. The batch leaching results revealed the dramatic effect of shrimps and concrete in immobilization of Pb and Zn.

Column leaching results

The column tests showed that the cumulated level of Pb at L/S ratio 10 (v/w) in WR (C01 vs C02), shrimps amended (C03 vs C04) and concrete amended (C05 vs C06) samples was 42–55, 0.48–2.4 and 67–98 mg/kg, respectively (Figure 1).

The cumulated level of Zn at L/S 10 in the WR, concrete amended- and shrimps amended samples was 57–64, 2.4–7.6 and 140–220 mg/kg, respectively (Figure 1). The results clearly demonstrated a trend and plateau when the leachant was going through the materials packed in each individual column. Based on the column leaching test, amendment of the WR with shrimps showed a large effect on the immobilization of Pb and Zn. In contrast, the concrete amended WR samples showed higher leached level of Pb and Zn. Opposite to the batch leaching results, the column results suggested that the WR amended with concrete was not a promising method in the immobilization of Pb and Zn in the WR. An average leached Pb at L/S 10 in the columns was calculated to be 48.5, 1.44 and 82.5 mg/kg for the sole WR, shrimps amended WR and concrete amended WR sample, respectively, which was corresponding to 8.1 %, 0.24 % and 13.8 % of the total content of 600 mg/kg Pb (Table 1) in the raw WR. Similarly, the average leached Zn at L/S 10 was calculated to be 60.5, 5.0 and 80 mg/kg for WR, shrimps amended- and concrete amended sample, respectively, which was corresponding to 1.1 %, 0.1 % and 1.5 % of the total content of 5257 mg/kg Zn (Table 2) in the raw WR.

Eluate from the shrimp amended columns had a very low DO content and a very low ORP (Figure 2), compared to the other

Table 3 *Physicochemical characterization and mobilized elements in eluate from batch test.*

	pH	DO (mg/L)	EC (µS/cm)	Pb (µg/kg) (n=3)	Zn (µg/kg) (n=1)
B01 WR	6.5±0.0	5.1±0.1	42931±266	13333±577	2800
B02 Shrimps	8.7±0.1	0.2±0.3	44316±474	61.3 ± 51.1	200
B03 Concrete	9.2±0.0	4.0±0.3	44877±400	36.7±8.3	200
B04 WR + shrimps	7.7±0.4	0.0±0.1	37618±6122	209.4 ± 178.4	63.6
B05 WR + concrete	8.0±0.0	5.1±0.3	42904±674	136.4 ± 53.7	190.9

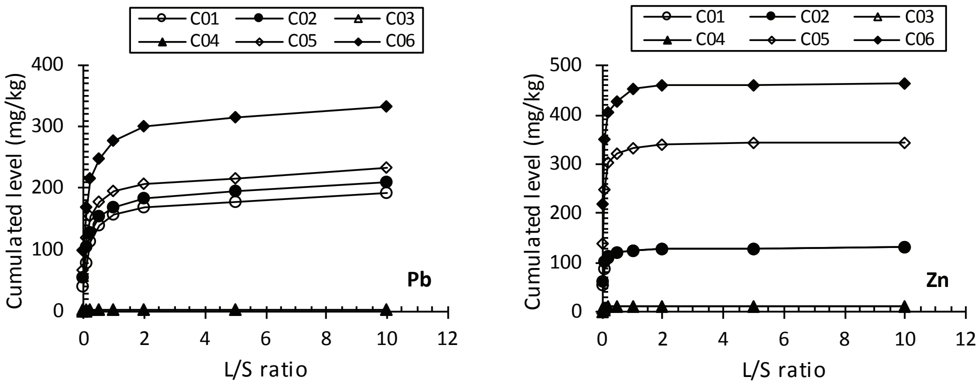

Figure 1 Cumulated leaching of Pb and Zn from the column test

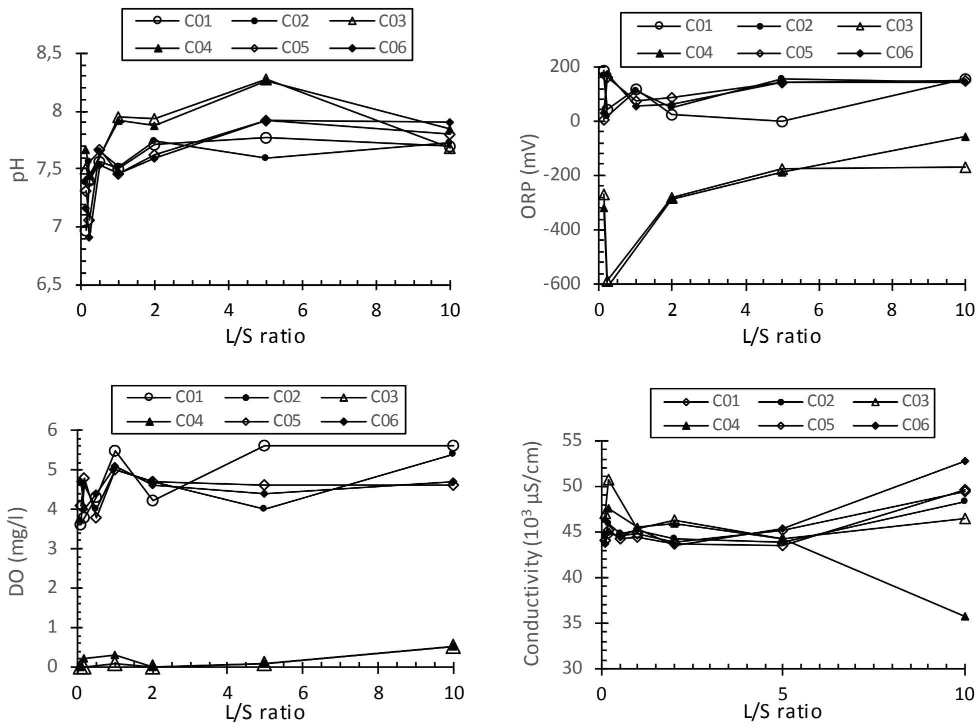

Figure 2 Physical/chemical parameters from the column test

columns, which as it was the case in the batch test implies degradation of organic material. For most of the measurements, the highest pH was found in the shrimp amended columns, while the amendment with concrete only had limited effect on the pH compared to the sole WR. The conductivity in the eluate was high, due to the use of sea water as leachant, and generally the measurements were relatively stable with a minor increase at L/S 10.

XRD results

The XRD analysis revealed that quartz (SiO2) (44.3–61.3 %, data not shown) and cryolite (31.2–41.9 %) were the most abundant minerals in all the tested samples. Siderite was detected in most samples (4.4–7.3 %) (Table 4). Muscovite $(KF)_2(Al_2O_3)_3(SiO_2)_6$ (0.9–2.0 %) was identified in the raw WR and a few amended samples. Plagioclase (3.0-6.9 %) was not detected in the control, shrimp- and con-

Table 4 Mineral abundances (%) for the raw materials and residues from column leaching test

Mineral	Cryolite	Siderite	Plagioclase	Sphalerite	Galena
Chemical formula	Na3AlF6	FeCO3	NaAlSi3O8 to CaAl2Si2O8	ZnS	PbS
Columns after L/S10					
CO1	39.3	7.1	n.d.	0.2	0.2
CO2	41.5	6.9	n.d.	0.2	0.1
CO3 top	37.5	7.3	n.d.	0.2	n.d.
CO3 bottom	36.3	7.1	n.d.	n.d.	n.d.
CO4 top	36.7	4.4	n.d.	n.d.	0.4
CO4 bottom	31.2	4.8	n.d.	n.d.	n.d.
CO5	34.6	6.2	3.0	trace	n.d.
CO6	38.2	6.5	3.2	n.d.	n.d.
Raw material					
WR	41.1	6.9	5.6	trace	n.d.
Concrete	n.d.	n.d.	6.9	n.d.	n.d.
WR + concrete	41.9	6.8	4.4	n.d.	n.d.
WR + shrimp	35.1	7.2	n.d.	0.2	n.d.

WR= waste rock. n.d. = not detected

crete amended WR. Sphalerite (≤ 0.2 %) and galena (≤ 0.4 %) was detected only in few samples. Amorphous mineral (26.1 %) was solely detected in the raw concrete sample (data not shown). Apatite $(Ca_5(PO_4,CO_3)_3(OH,F)$ (≤ 2.8 %) was detected only in one of shrimp amended column (data not shown), implying that microbial activities were on-going in the column, similar to that described by Briggs and Kear (1994). Calcite ($CaCO_3$) (6.4 %) was detected only in the raw concrete.

General consideration

Previously Johansen et al. (1995) reported that the WR in the mining area consists of trace amount (0.29 %) of pyrite (FeS_2), ZnS (0.3 %) and PbS (0.25 %). In the present study, however pyrite is not detectable in the raw WR. The sulfur containing minerals are ZnS and PbS (Table 4), which are non-acid producing sulfide minerals while pyrite is acid generating (Dold 2003).

At pH 6–8.5 and E_h in the range of -0.6 to 0.2 v (Figure 2) which are measured in the present study, following the geochemical behavior of elements between aquatic and solid phases (Takeno 2005), it finds that the predominant Pb species is Pb^{2+} or $Pb(OH)^+$, and the predominant Zn species is Zn^{2+} and $Zn(OH)_2$(aq).

The addition of nutrients e.g. P to WR due to amendment of shrimp with WR led to the formation of minerals, e.g. apatite, similar to that mechanism described by Porter et al. (2004). Ca compounds are abundant in concrete. The high level of Ca compounds is generally considered to be efficient for the Pb immobilization (Kumpiene et al. 2008). However, this was not the case for the concrete amended WR in the column test, and the reason remains unclear.

This study has shown, that shrimps can minimize the leaching of metals from waste rock. It was not determined, if it was due to adsorption on chitin or due to precipitation with sulfide, but the work is still ongoing. Future work will also investigate long-term capacity of the shrimp amended waste rock.

Conclusions

The batch leaching results showed that both concrete and shrimps were feasible to use in immobilizing of Pb and Zn. The column leaching results demonstrated clearly that shrimps was a good candidate in immobilization of Pb and Zn. However, the column study showed that concrete was not a satisfactory candidate to immobilize Pb and Zn from a long-term perspective, which might be due to the change of pH value in the system. The total chemical content of Pb (0.06 %) and Zn (0.52 %) in the raw WR sample agreed well with the XRD results, of which the mineral abundance of galena and sphalerite for the raw WR sample was undetectable, while it was in trace amount in some of the amended samples, which clearly showed a low level of these minerals. Low dissolved oxygen in the shrimps amended batch, and the formation of apatite in a column with shrimps amended sample implied that microbial activities were involved in the leaching process, though a more specific investigation is needed to confirm this.

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References

Anastopoulos I, Bhatnagar A, Bikiaris DN, Kyzas GZ (2017) Chitin adsorbents for toxic metals: A review. Int. J. Mol. Sci 2017, 18, 114, doi: 10.3390/ijms18010114

ASTM D3987-12 (2012) Standard Practice for Shake Extraction of Solid Waste with Water, ASTM International, West Conshohocken, PA, 2012, www.astm.org, DOI: 10.1520/D3987-12

Bach L, Asmund G, Riget F (2014) Environmental monitoring in 2013 at the cryolite mine in Ivittuut, South Greenland. Aarhus University, DCE – Danish Centre for Environment and Energy, 32 pp. Scientific Report from DCE – Danish Centre for Environment and Energy No. 105. dce2.au.dk/pub/SR105.pdf

Briggs DEG, Kear AJ (1994) Decay and Mineralization of Shrimps. Palaios 9:431-456, doi: 10.2307/3515135

Daubert LN, Brennan RA (2007) Passive Remediation of Acid Mine Drainage Using Crab Shell Chitin. Env. Eng. Sci. 24 (10), 1475-1480.

Dold B (2003) Basic concepts of environmental geochemistry of sulfide mine-waste, in: Geochemistry and geomicrobiology of mine water formation. Universitė de Genève, Lisbon, pp 1–36

Forutan R, Ehsandoost E, Hadipour S, Mobaraki Z, Saleki M, Mohebbi G (2016) Kinetic and equilibrium studies on the adsorption of lead by the chitin of pink shrimp (Solenocera melantho). Entomol. Appl. Sci. Lett. 2016, 3, 20–26.

Johansen P, Asmund G, Riget F (1995) Environmental investigations at Ivittuut 1982-1992. Report no. 7, Greenland Environmental Investigations, March 1995. (In Danish)

Karthik R, Meenakshi S (2015) Chemical modification of chitin with polypyrrole for the uptake of Pb(II) and Cd(II) ions. Int. J. Biol. Macromol. 2015, 78, 157–164.

Karthikeyan G, Andal NM, Anbalagan K (2005) Adsorption studies of iron(III) on chitin. J. Chem. Sci. 2005, 117, 663–672.

Kumpiene J, Lagerkvist A, Maurice C (2008) Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. Waste Manage 28:215–225, doi: 10.1016/j.wasman.2006.12.012

Porter SK., Scheckel KG, Impellitteri CA, Ryan JA (2004) Toxic metals in the environment: thermodynamic considerations for possible immobilisation strategies for Pb, Cd, As, and Hg. Crit Rev Environ Sci Technol 34:495–604, doi: org/10.1080/10643380490492412

Robinson-Lora MA, Brennan RA (2008) Evaluating crab-shell chitin, lactate, and spent mushroom compost for acid mine drainage remediation in Central Pennsylvania. Proceedings America Society of Mining and Reclamation 2008, 911-926, doi: 10.21000/JASMR08010911

Sephton MG, Webb, JA (2017) Application of Portland cement to control acid mine drainage generation from waste rocks. Appl Geochem 81:143-154, doi: 10.1016/j.apgeochem.2017.03.017

Sinziana VM, Werth CJ, Sanford RA (2001) Evaluation of Different Polymeric Organic Materials for Creating Conditions That Favor Reductive Processes in Groundwater. Bioremediation Journal 5(1):1-13, doi: 10.1080/20018891079267

Takeno N (2005) Atlas of Eh-pH diagrams. Intercomparison of thermodynamic databases. Geological Survey of Japan Open File Report 419