Leaching dynamics of Pb, Zn, and F: Laboratory and field leaching of waste rock from cryolite mining at Ivittuut, South Greenland

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Extended Abstract

Pollution from mining can have substantial environmental and health effects on nearby communities. Understanding the weathering processes of mining waste and related release of pollutants allows the identification of appropriate environmental remediation methods. At Ivittuut, situated in Arsuk Fjord, South Greenland, cryolite has been mined for approximately 130 years. The generated waste rock (WR) was disposed along the coastline in Ivittuut and contains sulfides, including pyrite (FeS_2), galena (PbS), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$), and minor amounts of arsenopyrite (FeAsS) and molybdenite (MoS_2). Moreover, there are substantial quantities of siderite ($FeCO_3$) and cryolite (Na_3AlF_6) in the WR that are exposed to weathering after the mine was closed in 1982. Base metals, primarily Pb and Zn, are leached from the waste rock. Over the past four decades, a monitoring project has estimated the annual release of dissolved Pb into the Arsuk Fjord to be 133–333 kg (Johansen et al. 1995, 2010). The monitoring of the site also showed that the release of Pb and Zn is decreasing. Since 1982, Pb release has decreased by up to 3 times, whereas Zn release has decreased at a lower rate (Johansen et al. 1995, 2010; Bach et al. 2014).

The current study focuses on long-term humidity cell test (HCT) leaching experiments on WR from Ivittuut using seawater and natural precipitation as leaching solutions. The HCTs were performed at: 1) room temperature, 2) in a 5 °C refrigerated room, and 3) outdoors. The WR, composed of 44.3% quartz, 41.1% cryolite, 6.9% siderite, 5.6% plagioclase and 2% mica, was exposed over 40 weeks in duplicates to natural precipitation (outdoor experiments, HCT 5–6) and seawater (room temperature and 5 °C, HCT 1–4 on Fig. 1) with a weekly rinsing cycle for the laboratory experiments. Each cell was loaded with 1 kg of crushed WR with a grain size of less than 4 mm and the flushing water volume was set to 1 L for the laboratory experiments. The outdoor experiments aimed to replicate natural weathering processes (HCT 5 and 6 on Fig. 1). The room temperature (HCT 1 and 2) and 5 °C experiments (HCT 3 and 4) were run with a liquid-to-solid ratio of 1, while the outdoor experiments (HCT 5 and 6) ran with the precipitation amount entering the cells during the test period, leading to a constrained collection of leachates adequate for chemical analyses. The physicochemical parameters of the leachates were measured weekly, and the chemical composition of the leachate samples collected at weeks 0, 1, 2, 6, 11, 16, 17, 22, 26, 31, 36 and 40 was analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The concentrations of the leachates are compared to the Greenland Water Quality Criteria (GWQC) for seawater and freshwater (Fig. 1).

Substantial differences were observed between leaching experiments conducted at different temperature settings (Fig. 1). Higher temperatures resulted in higher concentrations of Pb and Zn leached compared to the lower-temperature HCTs. Room temperature experiments resulted in concentrations approximately 10 times higher than those in the 5 °C experiment. The experiments conducted at room temperature showed low Pb and Zn concentrations in leachates sampled in the first weeks, reaching a maximum at week 17, with gradually decreasing concentrations toward week 40 (Fig. 1 a and b, HCT 1 and 2), but with an increasing trend of Zn concentration at week 40.

Fluorine concentrations were only determined in the room temperature experiments (Fig. 1c). The F leaching pattern was opposite to that for Pb and Zn. The F concentrations in leachates were elevated (approx. 20 mg/L) at week 0, decreased (approx. 12 mg/L) at week 17 and increased (approx. 15 mg/L) again at week 40 (Fig. 1c).

The 5 °C experiment showed Pb concentration in leachate reaching a maximum at week 26 (Fig. 1 a, HCT 3 and 4). The leaching pattern for Pb and Zn showed decreasing trends at week 40, with Zn concentrations lower than in leachates sampled at week 0 (Fig. 1b).

Throughout the duration of the laboratory experiments, the pH of the leachates remained constant with minimal fluctuations. Leachates from HCT 1 and 2 maintained a pH of 7.8 ± 0.1, while those from HCT 3 and 4 exhibited a slightly lower pH of 7.7 ± 0.1.

The outdoor leaching experiment (HCT 5 and 6) with precipitation water (rain and snow) showed more fluctuating concentrations of Pb and Zn in leachates compared to those in the room and 5 °C temperature experiments (Fig. 1 a and b). The concentrations of Pb and Zn in leachates decreased at week 17 and increased again at week 27. This is most likely due to concentrations of Pb and Zn in leachates correlating with precipitation amounts. During winter and freezing conditions no water ran through the outdoor columns, and therefore, no leachate samples could be collected. During spring and summer, there was a variation in the volume of precipitation entering the columns. Weeks with higher volume of precipitation entering the columns resulted in higher concentrations of Pb and Zn, while weeks with lower precipitation resulted in lower element concentrations leached from the WR.

The pH values in leachates from the outdoor experiment show greater variability and tend to be lower compared to those from the laboratory experiments (HCT 1, 2, 3 and 4), averaging at 7.1 ± 0.4.

The observed variations in leaching rates due to precipitation (HCT 5 and 6 in Fig. 1) and temperature (HCT 1, 2, 3 and 4) suggest that the release of Pb and Zn from Ivittuut WR will vary during the different seasons of the year. Our results show an enhanced leaching rate of Pb from WR when using seawater compared to freshwater.

The data from week 40 indicate (Fig. 1 a and b) that the weathering rates of the Pb and Zn bearing minerals (galena and sphalerite) did not change over the time period of the experiment and that the experiments would need to be continued for a longer period to potentially see a change in leaching rates of Pb and Zn. A 40-week HCT duration is relatively short, and concentrations and pH values have been shown to increase and decrease over longer periods (Maest and Nordstrom 2017).

The pH values in the leachates from all experiments typically indicate neutral conditions. The relatively lower pH values in the leachates from the outdoor experiment are likely due to the lower pH in precipitation water used for the experiment (mean value of 4.7 ± 0.1). Conversely, the slightly higher pH values from the laboratory experiments are likely because of the higher pH in seawater (mean value of 8.0 ± 0.1). This suggests that regardless of the initial pH in precipitation being low and the slightly elevated pH in seawater, the leaching of the WR tends to cause relatively neutral pH values.

Ongoing experiments involve mineralogical analyses of leached WR material to determine the extent of mineral surface weathering and potential formation of

secondary minerals. These observations will be used to determine if secondary minerals could modify the release of metals.

Our results showed that the concentrations of Pb and Zn in leachates are substantially higher than the GWQC for seawater and freshwater (up to 2 orders of magnitude), whereas the fluorine concentration in leachates is about 10–15 times higher than the GWQC. Colder temperatures lowered the leaching rate of Pb and Zn compared to room temperature experiments. This implies that the arctic environment may in some cases decrease the leaching rates of contaminants from pollution sources.

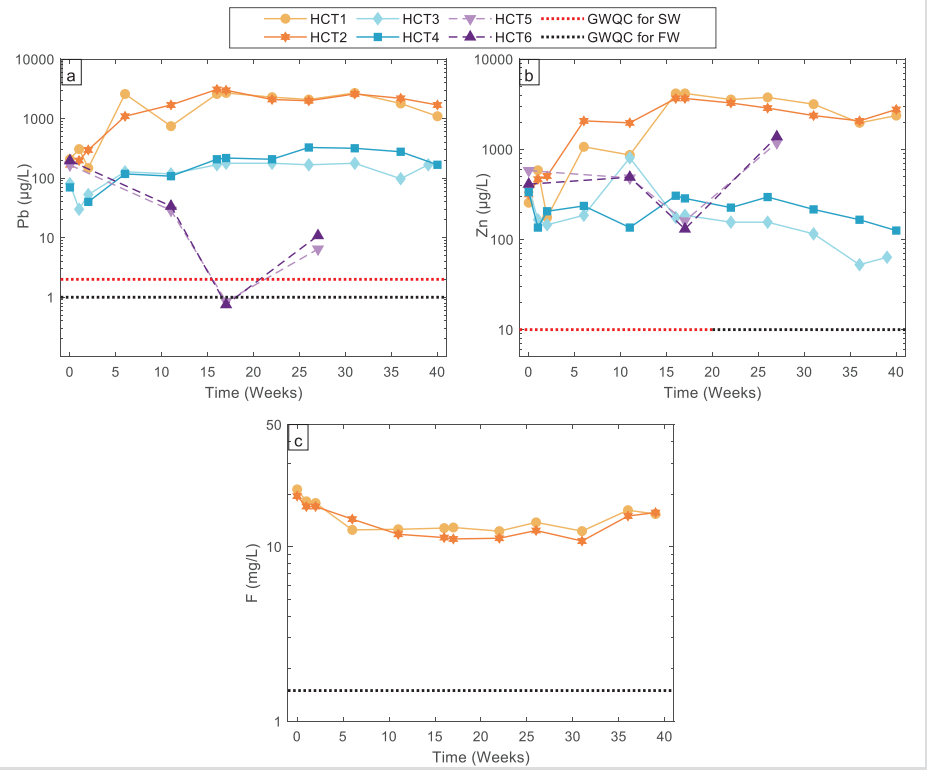

Figure 1 *Concentrations of (a) Pb (µg /L), (b) Zn (µg/L) and (c) F (mg/L) in leachates (log scale) from HCT experiments vs time. HCT 1 and HCT 2 represent the cells at room temperature, HCT 3 and HCT 4 were conducted in a 5 °C room, and HCT 5 and HCT 6 were outdoor experiments. Also indicated are the Greenland Water Quality Criteria (GWQC) for seawater (dashed black line) and freshwater (dashed red line) for filtered water for mining activities (MRA 2015). The GWQC for Zn in seawater and freshwater are identical*

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