Heterotrophic leaching of LD-slag – Formation of organic ligands

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Abstract Heterotrophic leaching of LD-slag with aspen wood shavings as carbon source mobilises several priority elements, including vanadium. In aerobic systems the initial production of DOC (450 mg/L) is significantly higher than in reference systems with only aspen wood (50 mg/L). Alkaline hydrolysis of the wood in combination with microbial activity produces a wide spectrum of potential metal complexing agents. The DOC in both LD and references systems contains dominating species with number average molecular weights below 1200 D. Carboxylic acids make up a few percent of this material. Among them, isosaccharinic acid was positively identified which indicates that other polyhydroxy carboxylic acids also can form.

Key Words LD-slag, DOC, carboxylic acids, molecular weight distribution, Aspen wood

Introduction

Environmental impact from solid alkaline waste materials has received relatively little attention in comparison with acid generating refuse. Large amounts are, however, produced from several industrial sectors and processes where steel production is just one. Other segments include for instance the lime production industry as well as cement production. In 2010 some 4900 metric tonnes of crude steel was produced in Sweden (www.jernkontoret.se/english/steel_industry/statistics). During the steelmaking process, the formation of slag is close to or even exceeding the amount of steel. The steel to slag ratio varies between the different processes but the annual production of alkaline slag from all iron refinement processes has been estimated to some 1.5 M tonnes. The quality of the slag such as solid phases and hence alkalinity and amount of metals also differs. The generally high content of alkalinity has made it an interesting option for amendment of acid waste. Recently, also the high content of some priority elements illustrates its potential use as a source for them. Unfortunately, many of the steel slags are very resistant to dissolution. In an effort to better understand the properties of this kind of solid alkaline waste, its biogeochemistry and potential use as a source for priority elements and alkalinity we have initiated several systematic studies. The studies include technologies for element recovery as well as release of elements to the environment. Here, we present some recent experience from the properties of slag from the Lintz-Donnawitz process.

LD-slag is best described as a high temperature oxide (Ca, Fe, Si) with different amounts of silicates and its high content of calcium oxide is the major alkaline component. During outdoor storage of the material it undergoes carbonatisation. This is a continuous process between carbon dioxide from the air that results in the formation of notably calcium carbonate. The material also reacts with water to produce calcium hydroxide. The resulting phase has a complex composition where the surface properties are best described as calcium oxide/hydroxide/carbonate, often in non stoichiometric proportions. The solid phase in general contains some 80% of CaO, FeO and SiO (SSAB Merox 2006) but the surface properties are different after contact with air and water. Depending on the process LD-slag contains rather high amounts of priority elements such as Cr, Mo, Ni and V. Just the vanadium content of up to 3% (d.w.) (Macsik & Jakobssen 1996) makes it an economically interesting material if a reasonable cheap process was available. The content of these elements is also a potential environmental risk since they all are toxic.

Previous studies have demonstrated that chemical dissolution of LD-slag requires a laborious procedure that involves crushing/milling, size fractionation and salt roasting (NaCl, Na_2CO_3, Na_2SO_4) at temperatures around 1000 °C, which is quite expensive. Another way of extracting the elements of interest would be to take advantage of the natural biogeochemical processes of such high alkalinity oxide materials. Heterotrophic leaching of LD-slag with aspen wood shavings as carbon sources have been demonstrated to yield up to 10% of the acid vanadium content in two to three months (Grandin, 2011). Unfortunately rather little is known about the mechanisms that are involved in such processes. The reasons are not clear but are probably related to the fact that this fresh (oxide) material gives an aqueous pH around 12—13 and extremophiles would be involved in any biological interaction. In general our understanding of both the element chemistry and biology/ecology is limited in systems with such high pH. It is without any doubts, however, that we need to understand them much better. One possible strategy to increase the release of elements bound in highly alkaline solids would be to take advantage of heterotrophic activity of the microbial community that occurs naturally (c.f. Willscher and Bosecker 2003). Under the circumstances in the waste heterotrophic activity would result in a local production of organic acids as well as formation of a number of potential ligands that would enhance metal mobilisation.

The hypothesis was tested by adding shavings of aspen (*Populus tremula*) to crushed LD-slag and incubating the systems aerobically at room temperature. Since focus was put on the redox sensitive vanadium both water saturation and field capacity were evaluated. During the incubation the release of elements, general hydrochemical parameters (pH, principal inorganic anions) and total dissolved carbon were followed. Further, the quality of the organic material was monitored with respect to molecular size, production of low molecular weight carboxylic acids and isosaccharinic acid as a proxy for polyhydroxy carboxylic acids.

Methods

LD-slag that had been stored dry was crushed and sieved (0.25—0.56 mm) where after layers of slag and shavings (5x5 mm) were put in 50 ml polycarbonate test tubes. To the systems 18.2 MΩ water was added to reach the field capacity of the materials and the tubes were then put in a humidor to ascertain a constant water vapour pressure. Samples were collected by adding 50 ml 18.2 MΩ water and collecting the sample as the water drained from the material. For a more complete description of the procedure see Sjöberg *et al.* (2011). Data discussed here also include reference systems that only contained aspen wood shavings at its water holding capacity and open to the air. Both series were made in quadruplicate.

Sub-samples for organic analysis were frozen immediately after sample collection (Karlsson *et al.* 1999) and pH was measured within 30 minutes after sampling. Principal anions (F^-, Cl^-, NO_3^-, SO_4^{2-}) were measured with ion chromatography (Column Dionex AS-12A, bicarbonate buffer) on filtered solutions (0.20 µm). Metal analyses were made with ICP-MS (Agilent 7500 cx). The dissolved organic carbon (TOC) and inorganic carbon (IC) were quantified with a Shimadzu TOC-V. Gel permeation chromatography (Pettersson *et al.* 1989) on pre filtered sample solutions (0.20 µm) provided information on the size distribution of dissolved constituents. These samples were diluted with the running buffer in order to minimize the impact of pH and ionic strength on the apparent volumes of the analytes. Capillary electrophoresis was employed to quantify the low molecular weight organic acids, including isosaccharinic acid as a proxy for polyhydroxy carboxylic acids (Dahlén *et al.* 2000). Interpretation of the electropherograms was made by the use of corrected peak area and external calibration functions.

Results and discussion

In the reference systems with only aspen shavings the pH showed limited variation within the range 5—6 which indicates that the buffering of the systems was not subjected to any acid production from the potential mineralisation of the wood (figure 1). For the LD-systems the starting pH indicated that the material was partly carbonised. A pH around 10 indicates that the surface contains a hydroxide/carbonate mixture since a calcium oxide surface would give a pH around 12. The rather pronounced decrease in pH during the first six weeks would be expected if heterotrophic acid production took place.

The drop in pH coincided with a lowering of the DOC concentrations in the LD-systems. In the reference system no statistically different DOC concentrations were found during the whole incubation period. Some relation between pH and DOC would be expected at high pH where there are finite pools of both alkalinity and wood. The wood is readily undergoing alkaline hydrolysis which results in a large number of low molecular

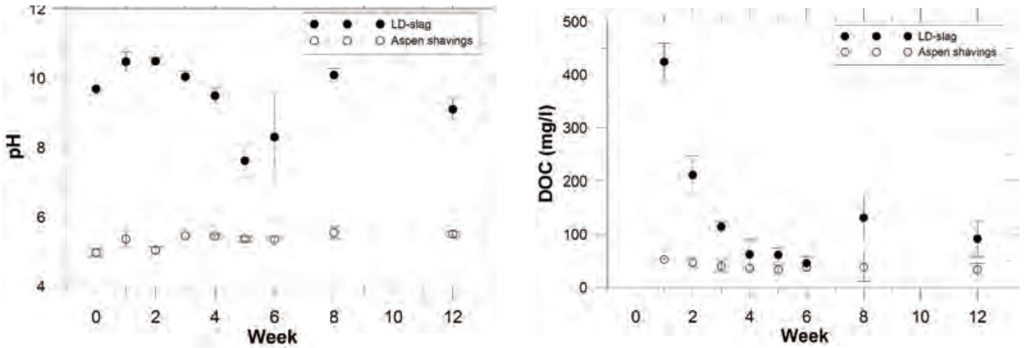

Figure 1 *Average values and standard deviations (n = 4) for pH and concentrations of dissolved organic carbon (mg/L) during the incubation.*

weight organic substances, including several carboxylic acids (c.f. Pavasars *et al.* 2003; Klinke *et al.* 2002).

The concentrations of aqueous DOC would remain essentially constant in a system that is controlled by hydrolysis, once the kinetics of the processes are established. This was evidently not the case since the DOC in the LD-systems slowly approached those of the references (figure 1). It seems therefore likely that the initial products from the hydrolysis are mineralised and carbon dioxide was formed. Although quantification the carbon dioxide production was not included in the study for practical reasons the formation of H_2CO_3 would have such an impact. Further, pH in both systems seems to stabilise within the buffering region of bicarbonate/carbonate. Production of (carboxylic) acid intermediates would increase the acidification of the system.

There was a substantial production of carboxylic acids in the LD-systems although the analyses was restricted to the simple low molecular weight acids (malonic, oxalic, fumaric, lactic, maleic, formic, succinic, tartaric, L-tartaric, glutaric, adipic, acetic, propionic, butyric, valeric, citric). Acetic acid was the most frequently found acid in the LD-systems (figure 2) and its concentrations were positively correlated to the DOC. The sum of dissolved carbon from the quantified carboxylic acids is, however, just a few percent of the DOC in the aqueous phase (figure 2). This implies that other forms of soluble carbon species were present. The concentration changes of the carboxylic acids during the incubation as well as the development of DOC clearly indicate that the original hydrolysis species are mineralised.

During the beginning of the incubation of the LD-systems the sum of adipic and glutaric acids was of the same concentration magnitudes as acetic acid, and with an identical development in time. Unfortunately, the matrix conditions did not allow for a complete separation of ISA why it could not be quantified with indirect UV detection. ISA co-migrated with adipic acid, as evidenced by the UV/Vis spectrum in this particular peak in the electropherogram. A positive separation can be made by electrokinetic injection of the sample in the capillary and hence can ISA be identified even in these complex matrices. This approach isr not rational for routine analysis because of its narrow linear concentration ranges for quantification why mass spectrometric quantification is the only reasonable alternative (Hagberg 2003). However, merely the presence of ISA indicates that this class of organic molecules with extremely stable metal complexes at high pH are formed in the LD-systems.

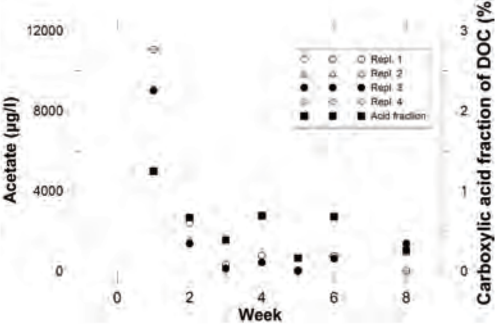

Figure 2 *Concentrations of acetic acid (µg/L) and the fraction of carbon in the carboxylic acids in relation to DOC concentrations (%) in the LD-systems.*

With time, the proportions of the carboxylic acids in the LD-systems changed (figure 3) and resembled qualitatively those in the reference systems. In no samples were lactic, valeric or butyric acids detected at concentrations that exceeded 3 µg/L why there are reasons to believe that the systems remained aerobic, although the presence of micro anaerobic environments cannot be excluded. The changes in concentration as well as in carboxylic acid composition are both taken as indications on microbial mineralisation. The presence of diverse assemblies of fungi and bacteria were confirmed by light microscopy and it is presently being investigated. Probably, the initial alkaline hydrolysis products are available for mineralisation. If this process is continuous cannot be concluded from the present experiment but unless the surface of the LD-slag is passivated by adsorption of dissolved species or secondary precipitates there are reasons to expect a continued production of microbial available dissolved organic species through the hydrolysis.

In the reference systems the composition of carboxylic acids was quite constant over time. Acetic acid was dominating, malonic, succinic, adipic and citric acids sometimes reach limit of detection but not the limit of quantification. As for the LD-systems there was no indication of anaerobic conditions. The micro flora developed but at lower densities than in the LD-systems which supports that alkaline hydrolysis plays an important role to supply the system with a pool of easily accessible carbon.

The majority of the components in the DOC could not be identified with capillary electrophoresis. Analysis with gel permeation chromatography supported the general time trend for DOC in the LD-systems since the low molecular weight fraction was lowered with time. This analysis indicated the presence of a bi-modal size distribution with a clearly dominating fraction of small molecules. The dissolved carbon fraction has on average a number average molecular weight (M_n)

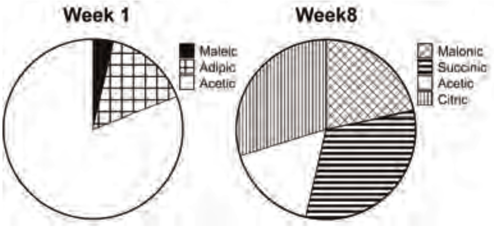

Figure 3 Relative distribution of the dominating low molecular weight carboxylic acids in the LD-systems after aerobic incubation with aspen wood shavings for two and eight weeks, respectively (n=4).

below 1200 D and a weight average molecular weight (M_w) below 1650 D. The polydispersity is in the range of 1.3—1.6 why the material is rather heterogeneous with respect to apparent size. In the majority of samples the distribution was biased towards the low molecular weight region. The samples were diluted in the running buffer before analysis in order to minimize the impact of pH and ionic strength on their volumes. In the high molecular weight region there were occasional observations of species within the range of 4 kD to 6 kD. Their more or less random presence was taken as an indication of cell ruptures, fragmentation of the wood or other artifacts. These results were not investigated further.

Also in the reference systems the molecular weight distribution was dominated by the low weight fraction. The average distribution was not different from the LD-systems. There was however a tendency towards an increased abundance in the higher molecular weight region. This difference was not statistically significant. Also in these samples there were a few observation of high molecular weight material but they were excluded from further evaluation for the same reasons as above. To conclude, these observations strongly indicate that the dominating fraction of dissolved organic matter has average molecular weights below 1200 (M_n). Further, this fraction is not dominated by low molecular weight carboxylic acids why further investigations should be directed towards with t seems therefore reasonable to conclude that

Conclusions

Upon contact with the alkaline LD-slag aspen wood shavings are undergoing hydrolysis. The pool of mobilised dissolved carbon species serves as a carbon source for the establishment of complex microbial communities. The majority of the organic species are mineralised. These processes result in a fraction of dissolved carbon that has a number average molecular weight below 1200 D. Up to some 3% of this fraction is made up by low molecular weight carboxylic acids where acetic and adipic acids dominate during the initial decomposition. After some 6—8 weeks, the population of carboxylic acids produced in the LD-systems are similar to those in the reference systems with aspen wood. Among them isosaccharinic acid was identified, which forms very strong complexes with di- and multivalent cations at high pH.

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