

# BIOCHAR FOR THE IMPROVEMENT OF SOIL AND ROCK WITH ACID POTENTIAL

Erlend Sørmo <sup>1\*</sup>, Erika Kämäräinen <sup>2</sup>, Matilda Edvardsson <sup>2</sup>, Christian Maurice <sup>2,3\*</sup>

<sup>1</sup> Norwegian Geotechnical Institute (NGI), Oslo, Norway.

<sup>2</sup> Ramböll Sverige, Luleå, Sweden

<sup>3</sup> Luleå University of Technology, Luleå, Sweden

**Abstract.** Biochar is a carbonaceous material generated by the heating of organic matter under limited access to oxygen (called pyrolysis). While pyrolysis is applied to dry feed, hydrothermal carbonization can be used for wet materials such as sludge. Application of biochar to soil is considered inherent climate friendly since biochar remain stable in the soil for a long time, and thus removing carbon from the short-term carbon cycle. Biochar has the ability to adsorb trace elements and raise pH, when added to soil or/and water. Geomaterials, both soil and rock, containing sulphur in the form of sulphide minerals have the potential to harm the environment. Lowering groundwater in sulphide rich soils and disposal of excavated sulphide rich soil and rock in piles are example of situations where measures have to be taken to mitigate the formation of acid leachate. This presentation aims at presenting the results from two studies where biochar's capacity to adsorb trace elements is investigated. In the first study, the adsorption capacity of several biochars was compared with leachate generated from the oxidation of sulphide soil, showing a significant decrease of the concentration of elements such as copper and zinc. In the second study, the ability of waste timber biochar to stabilize the leaching from sulphide rich gneisses containing readily soluble, oxidized secondary mineral crusts was investigated. Preliminary results show that the acidity of the oxidized gneisses exceeds the buffer capacity of the biochars, resulting in an acidic, metal rich leachate. Rather reducing metal leaching through sorption and pH control, metals from the biochar matrix are released, resulting in an increased release of metals compared to the control.

## 1. Introduction

Biochar is the product of heating biomass in the absence of or with limited air to above 250°C, a process called charring or pyrolysis also used for making charcoal [1]. The International Biochar Institute, IBI [2], defines biochar as: 'A solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment, designed to be used for environmental management. Biochar can be used as a product itself or as an ingredient within a blended product, with a range of applications as an agent for soil improvement, improved resource use efficiency, remediation and/or protection against particular environmental pollution and as an avenue for greenhouse gas (GHG) mitigation [1]. Biochars are generally considered non-degradable and are thus classified as carbon sinks if they e.g. are added to soils [1]

A defining feature of biochars, similar to charcoal, is a certain level of organic C in the form of fused aromatic ring structures that are formed during pyrolysis [1]. The degree of aromaticity, which increases with pyrolysis temperature, is related to porosity and internal surface area (SA) and is hence a deciding factor determining the

sorption properties of the biochar [3, 4]. Furthermore, biochar made from woody materials generally are alkaline due to a certain ash content, and it has been shown that such biochars improve the quality of acidic soils by increasing soil pH upon application [1].

Hydrochar is the solid product of hydrothermal carbonization (HTC) or liquefaction (some-times referred to as HTC material) and is distinct from biochar due to its production process and proper-ties [5]. The organic material is converted into a carbon rich material which is more or less degradable, has a high adsorption capacity and is alkaline. Various materials can be used as raw material in the manufacture of HTC biocarbon, for example food residues, manure or sludge of various kinds [6, 7].

As biochar has shown to have both a capacity to buffer acid soils and sorb metals [1], it was hypothesized that biochar could stabilize sulphide rich materials with potential for acid rock drainage (ARD).

This article aims at presenting the results from two studies where biochar's capacity to limit the release of trace elements is investigated. In the first study, the adsorption capacity of several biochars was compared with leachate generated from the oxidation of sulphide

\* Corresponding author: [ers@ngi.no](mailto:ers@ngi.no), [christian.maurice@ltu.se](mailto:christian.maurice@ltu.se)

soil. In the second study, the ability of waste timber biochar to stabilize the leaching from sulphide rich gneisses containing readily soluble, oxidized secondary mineral crusts was investigated.

## 2. Materials

### 2.1 Biocarbons

The following five char materials were used for the adsorptions test:

- Charcoal: Two charcoal are produced in Finland by BIOCORE, of birch and pine wood, respectively, which are referred to as Birch-char and Pine-char. The charcoal was produced in a retort in batches, for 15 hours. The highest temperature during the process is 450 °C and the raw material (pine or birch wood) is kept at that temperature for about 3 hours. The remaining time, 12 hours, is needed to heat the material and cool it. The charcoal is at last stored in an oxygen-poor environment for 20 hours. These materials are originally not aimed for soil amelioration and formally not biochar

- Biochar: A biochar manufactured by Carbofex, in Tampere, Finland, using mainly spruce branches and rest wood as a raw material. The process is continuous with a rotary oven where the raw material is heated to about 600 °C.

- HTC-biocarbon: Two HTC-biocarbon produced by Processum (Örnsköldsvik, Sweden) using biosolides (sludge). The operating parameters during manufacture were 18 bar and about 200 °C. Outgoing HTC slurry contained a large amount of water which, after settling, was removed by filter press.

- Waste Timber (WT) Biochar: Made from a feedstock of waste timber – disposed uncontaminated wood materials, such as wood panels, furniture, and hard- and soft board. WT was shredded, and the wood chips pyrolyzed at approximately 600 °C in a Pyreg® unit with after combustion features at Verora GmbH, Switzerland. The WT biochar has properties such as a relatively high surface area (SA) and C-content, suggesting that it is potentially a good sorbent [8]. A pH of  $7.9 \pm 0.1$  and an ash content of  $9.4 \pm 3.8$  % suggest that it has alkaline properties suited for buffering acidic leachate. However, the WT-biochar has a high content of metals, such as Cu ( $50 \pm 130$  mg/kg), Pb ( $120 \pm 70$  mg/kg) and Zn ( $2100 \pm 2800$  mg/kg), making it unsuited for agricultural soil improvement use [8]

### 2.2 Sulphide bearing geomaterials:

#### 2.2.1 Sulphide soil

The coastal areas of Finland and Sweden, along the Bothnian bay, and a clayey/silty soil containing organic matter and iron sulphide mineral (iron mono and disulphide, up to 25 000 mg/kg dw) was formed in the sediment of the ancient *Littorina Sea*.

In natural state, moist sulphide soils do not affect surrounding nature. When the groundwater table is

lowered, or soil is excavated and disposed in piles, the Sulphur-containing minerals oxidize, generating an acid and aluminium rich leachate toxic to most water organisms, especially fish. Sulphide soil oxidation has a direct environmental effect on water quality when not managed properly and it also create an aggressive corrosive environment for infrastructure.

The sulphide soil used in this experiment contained  $S_{tot} = 10\ 000$  mg/kg d.w.

#### 2.2.2 Sulphide rich gneiss

The bedrock in Southern Norway mainly consists of gneisses, and in some areas these gneisses contain elevated levels of sulphide minerals [9]. The ARD potential of these rocks came to attention in the aftermath of a large road construction project where disposal sites for rock masses of blasted gneiss were created without proper protective barriers [9]. Characterization of the sulphide bearing gneisses is challenging, as total sulphur alone has not been a good predictor to ARD potential [10]. Furthermore, these gneisses contain little or no buffering minerals, such as calcite, leading to a quick drop in pH and subsequent ARD when secondary minerals from deep weathering zones, such as jarosite, are present in blasted rock material [10].

The gneiss used in this experiment was collected in the municipality of Lillesand on May 3rd at a site where the rock masses previously had been described as a gneiss with plagioclase, quartz and biotite as primary minerals (>10%) and muscovite, potassium feldspar, carbon and pyrite as subordinate minerals (1-10 %) [10]. It had a red crust of secondary minerals from weathering on the surface and the total sulphur ( $S_{tot}$ ) level was  $0.8 \pm 0.1$  % and total inorganic carbon (TIC) <0.01%. Heavy metal contents were as follows: Al  $8.9 \pm 0.4$ %, Cd  $0.37 \pm 0.04$  mg/kg, Cr  $59 \pm 6$  mg/kg, Cu  $73 \pm 12$  mg/kg, Ni  $30 \pm 7$  mg/kg, Pb  $7 \pm 1$  mg/kg and Zn  $161 \pm 3$  mg/kg.

## 3. Methods

### 3.1 Sulphide soil

Leaching/adsorption-tests were used to assess the ability of the of the biochar to adsorb trace elements.

Leaching: Sulphide soil leachate was obtained using a five-centimetre layer of material covered with five-centimetre water and left to oxidize for one month in contact with air and water. To generate a leachate with higher concentrations of trace elements, a similar setup was used, adding a pH-sensitive slag from a copper smelter containing e.g. copper and zinc.

Adsorption tests: The collected leachate was filtered prior to adsorption test. Biochar and leachate, at a L/S ration of 10, were kept in a bottle for one week before the elate was filtrated through suction filtration.

Analysis with regard to trace elements was done by ALS Scandinavia. The eluate was preserved by acidifying with 1 cm<sup>3</sup> nitric acid per 100 cm<sup>3</sup> of sample.

The analyses were performed according to a modified version of EPA Procedure 200.7 using ICP-AES and a modified version of EPA Procedure 200.8 using ICP-SFMS (US EPA 1991).

### 3.2 Sulphide rich gneiss

Leaching from the crushed gneiss material mixed with 3 different dosages of biochar was studied using an unsaturated column experiment, similar to the setup described by Pearce (2018). The rock samples were crushed to <10 mm using a jaw crusher. The crushed rock material contained 62 % grains < 2 mm and a relatively high number of fines, with 11 % of the grains < 0.125 mm.

Glass columns with an internal diameter of 100 mm, open at the top and with an acrylic wool particle filter and a plastic cap in the bottom were used. The bottom of the column was drained by a 0.2 mm PE tube into pre-cleaned PE bottles (500 ml). A control column (gneiss only) and dosages of 1, 2.5 and 5 % biochar (d.w.) were set up by pre-mixing/homogenization then loading of columns with packing according to standard setup for column leaching tests (CEN/TS 14405).

The columns were watered with ultra-pure water (18M $\Omega$ , 100 ml) once a week for 8 weeks, and samples collected from the leachate bottles after 4 and 8 weeks. The first two weeks additional water (100 ml extra each week) was added to saturate the field capacity of the columns. The leachate samples were analysed for pH (potentiometry, ISO 10523), sulphate (ion chromatography, ISO 10304-1), and metals (Al, Cd, Co, Cr, Cu, Ni, Pb and Zn; ICP-SFMS/ICP-AES, ISO 17294-1,2/ISO 11885).

## 4. Results and discussion

### 4.1 Sulphide soil

The results of two series of adsorption tests with oxidised sulphide soil are presented in Table 1. The tests indicated that the trace element content in the sulphide soil leachate decreases upon contact with the materials. The variation between the materials was large. The biochar, produced at the highest temperature, showed the best adsorption capacity reducing the levels of Cu, Mn, Ni, Zn and Al, which is probably due to a larger porosity and surface area created at high pyrolysis temperature biochar (Hao et al, 2013, Hale et al, 2016).

The sulphur content was marginally affected by the addition of char materials, showing some increase with the HTC-materials. HTC-1 adsorbs/reduces the content of Cu, Mn, Ni, Zn and even Al but release of sulphur took place from the material. The aluminium content decreased for all materials except HTC-2 where there is a clear increase. The levels of Cu, Mn and Ni decreased for all char materials. The Zn levels decreased for three materials and increased with Birch-char and HTC-2.

HTC-2 reduced the levels of copper and nickel, although the effect was not as clear as for the other materials.

HTC-2 showed opposite results regarding aluminium and zinc. The high aluminium and zinc leaching observed with HTC 2 was observed in all tests performed, where the levels of these elements increased during the tests (see also Table 1, Table 2).

All the materials had the ability to reduce the levels of Cu, Ni and even Mn from the sulphide soil leachate with high levels of Cu, Ni and Zn (Table 2). The concentrations of Zn were also significantly reduced with all materials except for HTC-2, where concentrations of Zn and also Al increased during the test. As with the first sulphide soil water, the sulphur content was marginally affected by the addition of char materials, with an increase from HTC materials. Elevated residual Zn levels were observed with the birch charcoal, although a significant adsorption effect was observed.

The results of the tests indicate that char materials have the ability to mitigate the effect of the oxidation of sulphide soil and decrease the concentration of trace elements in the acid leachate. The char materials neutralised the acid leachate and adsorbed the metal ions, the biochar being the most efficient. The capacity of the material has not been assessed. Over time, the char's buffering capacity may be consumed by acidity, altering the adsorption. Further, the ability of the materials to withstand degradation should be controlled.

**Tabell.1** Trace element concentration in the sulphide soil leachate before and after the adsorptions test with different biochar. After one week.

Element	Unit	Leachate	Pine-char	Birch-char	HTC 1	HTC 2	Biochar
S	mg/l	117	111	109	185	226	111
Al	µg/l	570	<200	<200	<200	2 830	<200
Cu	µg/l	53	<10	<10	12	<50	<10
Mn	µg/l	19 500	11 600	11 200	2 480	11 300	8430
Ni	µg/l	216	62	81	68	<200	44
Zn	µg/l	149	<10	453	42	2 630	<10

**Tabell 2.** Trace element concentration in the sulphide soil iron sand leachate exposed to before and after the adsorptions test with different biochar. After one week.

Element	Unit	Leachate	Pine-char	Birch-char	HTC 1	HTC 2	Biochar
S	mg/l	47	48	53	123	173	47
Al	µg/l	<200	<200	<200	<200	17 000	<200
Cu	µg/l	6 020	25	74	167	270	20
Mn	µg/l	7 430	1 890	6 950	1 510	6 140	705
Ni	µg/l	650	129	359	158	354	71
Zn	µg/l	594	13	164	58	6 400	<10
pH		5.4	8.5	9.2	7.2	5.2	10.1

## 4.2 Sulphide rich gneiss

pH in the control column was low (2.8) at the first sampling (4 weeks) and had not changed at the second sampling (8 weeks) (Table 3). Leachate with such a low pH is expected as the material contained secondary minerals from weathering that produce acid when they dissolve in water [10]. The leaching of several metals, such as Al, Cd, Co, Cu, Ni and Zn, were all relatively high, as was expected from the low pH, as the acid dissolves metals with low solubility from secondary minerals as well as from the primary minerals of the gneiss. Leachate concentrations are shown in Table 3. The high potential for ARD is observed here is in accordance with measurements made in previous ex situ experiments [10] and documented in field from waste rock piles [9].

Biochar treatment did not reduce the leaching of metals from the gneiss. Rather, the concentrations of most of the measured metals in the leachates from the gneiss and biochar mixtures were higher than in leachates from the control (Table 3). The pH increased proportionally with biochar dosage, but only by half a pH unit, from 2.8 in the control to 3.3 in the column dosed with 5 % biochar (Table 3). At the same time, the leachate concentration of Zn was 10 times higher in the 5 % biochar column

than in the control. Similar relationships were observed for Cu, Co, Cd, and Ni.

These observations are explained by the biochar not having high enough buffer capacity to counter the acid producing potential of the gneiss. pH increases with biochar dosage, but only by half a unit with 5 % biochar, resulting in a pH of 3.3, which still allows for a high leaching of metals from the gneiss. Furthermore, the low pH also mobilises metals from the biochar matrix. The biochar contained high concentrations of Zn, which increases the total leaching of Zn from the gneiss and biochar mixtures far beyond that of the control. So instead of adsorbing metals and countering sulphide oxidation, the biochar becomes an additional source of metal leaching in this context.

It is plausible that a higher dosage of biochar would buffer the leachate to higher pH that would inhibit such a high leaching, but if one assumes a linear relationship between biochar dosage and pH increase, it would be necessary to add approximately 45 % biochar to increase the pH to >7. Most likely, using such a high dosage would not be feasible due to practical and economical constraints.

**Table 3.** Leachate pH, sulphate and metal concentrations at 4- and 8-week samplings.

Parameter	Weeks	Dosages				Parameter	Weeks	Dosages			
		0 %	1 %	2.5 %	5 %			0 %	1 %	2.5 %	5 %
pH (-)	4	2.8	3.1	3.1	3.3	SO <sub>4</sub> <sup>2-</sup> (mg/l)	4	3300	4700	4900	8900
	8	2.8	2.9	3.0	3.3		8	4260	6100	7470	9430
Al (mg/l)	4	405	530	482	787	Cu (mg/l)	4	1.70	2.89	3.44	4.89
	8	586	811	697	690		8	1.93	2.79	3.39	2.09
Cd (µg/l)	4	163	265	311	660	Ni (mg/l)	4	8.60	13.2	14.9	28.8
	8	189	387	404	662		8	9.02	18.6	18.5	26.8
Co (mg/l)	4	3.29	4.87	5.41	9.99	Pb (µg/l)	4	2.61	1.55	2.34	10.1
	8	3.05	6.13	6.25	9.01		8	2.52	<2.0	<2.0	3.33
Cr (µg/l)	4	26.4	35.8	34.1	53.0	Zn (mg/l)	4	25.2	79.6	107	267
	8	44.6	53.6	41.9	28.5		8	35.1	126	147	292

## 5. Conclusion

The results from the tests with sulphide soil showed that all tested materials (both HTC and wood-based pyrolysis char) were able to deplete the metal ions present in the leachate. This means that the char materials could be used to mitigate the effect of the sulphide oxidation. The biochar produced at the highest temperature, generally showed the best results, thanks to high porosity, surface area and high buffer capacity. Even the HTC 1 and the two wood-based charcoal produced at medium-high temperature showed similar results. HTC char was acidic, with a low acidification potential that could easily be buffered (result not shown). HTC materials differed in terms of leaching properties. For example, significant levels of zinc were leached from HTC-2, which had the lowest pH. The pyrolysis charcoal was alkaline, with limited buffer capacity.

The results from the test with sulphide rich gneiss demonstrated that biochar should not be used to stabilize weather gneiss with a high ARD potential. At least, biochar should not be used in this context without making sure the buffer capacity of the biochar will be

exceeded by the acidifying potential of the gneiss. If this happens, the biochar will just make the problem worse, by increasing the amount of metals leached. To explore the biochar's potential sorption effect or effect on reduction of sulphide oxidation, one would therefore need to use an additional material with a higher buffer capacity along with the biochar. In addition, the potential effect of biochar for stabilising unweathered, sulphide bearing gneisses should be investigated.

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