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Applying industrial side streams in the neutralization of acid generating sulfide-rich sediments – The impact on pH and leaching of harmful elements

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ABSTRACT

Acid sulfate soils can cause severe environmental harm due to a low pH and mobilization of harmful elements. Acid sulfate soil material is formed when oxidation of sulfide minerals causes a drop in pH to <4.0 for mineral oil materials and <3.0 for organic soil materials or when the soil materials contain enough sulfide to potentially do so.

Two dredged, acid sulfate soil materials from Finland were used in this laboratory study. Chemical analyses were performed to determine the pre-incubation characteristics of both fresh dredged sediment samples and oxidized samples after 23 weeks of incubation. Total element concentrations were determined after digestion in aqua regia by ICP-MS or ICP-OES. The leachable concentration of elements was determined by using the two-stage shaking test (method SFS-EN 12457-3). The leaching of harmful elements (Cd, Co, Ni, Mn, and Zn) was high in the acidified dredged spoil samples. Also, the leaching of S was high. The soluble concentration was dependent on total concentration, pH, and the mobility of the elements.

During a 23-week oxidation period, the impact of various amounts of industrial side streams (alkaline ashes, industrial lime residues) as neutralizing agents on the acid-generating dredged sediments was investigated in the laboratory. Calcite was used as a reference material. pH measurements were carried out during the incubation period. The leaching of elements was determined with a modified method based on the SFS-EN 12457-2 standard before and after oxidation.

The untreated dredged spoils and the samples treated with too low amounts of neutralizing agents, acidified to pH < 4 during the oxidation period. Thus, harmful elements were leached out. However, the 100 % theoretical calculated neutralization need was suitable to prevent acidification and thus the leaching of harmful substances from the neutralized acid-generating dredged spoils. However, the leaching of Mo increased at neutral pH values. The results showed that industrial side streams can be applicable for the neutralization of acid sulfate soil materials. However, the legislation must also be considered.

1. Introduction

Dredging is necessary for deepening and maintaining waterways and port areas. Sometimes dredging is necessary for removing contaminated sediments near shorelines. Dredged material, excluding contaminated sediments, has usually been deposited in the sea. In Finland, the Finnish Environment Institute has published guidelines for selecting suitable areas for deposition at sea (Ympäristöministeriö, 2015). However, today

it is hard to find good deposition sites from sea areas close to some major cities. In addition to that, dredging and dumping of dredged material at sea can have negative effects on the aquatic environment. Thus, there is more and more interest to deposit dredged material on land. The dredged material can be used e.g., in port structures, landscaping, and as growing media.

Unfortunately, the physical and chemical properties of dredged material are in many cases not optimal for application in infrastructure

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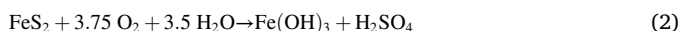
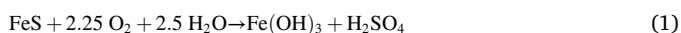
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building, agriculture, or for application as raw material on land. While the dredged sediments are usually organic-rich and fine-grained (clay and silt), stabilization is often needed before the material can be used for the building of various earthworks. In some cases, the dredged material contains elevated concentrations of potentially harmful elements and compounds. In the Baltic Sea countries, sediments deposited in the Littorina Sea phase, and the post-Littorina Baltic Sea may be rich in acid-generating sulfides. When the sulfide-rich sediments are disposed on land, the sulfides within, usually metastable iron sulfide (e.g., mackinawite and greigite; denoted FeS in [reaction 1](#)) and pyrite (FeS₂) (e.g., [Boman et al., 2008, 2010](#)), start to oxidize ([reactions 1 and 2](#)) and it will lead to the formation of sulfuric acid and subsequent release of harmful elements.



If the pH, during the soil forming process (soil ripening), drops below 4 due to the oxidation of sulfide minerals, an actual acid sulfate soil is formed. An acid sulfate soil may consist of either or both actual acid sulfate soil material or potential acid sulfate soil material. The definition of active acid sulfate soil material is soil material with a pH below 4 in mineral soil or pH below 3 in organic soil materials (such as peat or gyttja; LOI > 20 %). Whereas potential acid sulfate soil material is a soil material with a mass fraction of sulfur in sulfide form over 0.01 % and displays a pH drop below 4 in mineral soil materials or pH below 3 in organic soil materials after a soil incubation procedure ([Creepier et al., 2012](#)). Waterlogged or subaqueous sulfide-rich sediments may usually be classified as potential acid sulfate soil materials (subaqueous acid sulfate soils) and in the event of dredging and deposition and subsequent oxidation, these usually form actual acid sulfate soils. Acid sulfate soils are often considered the nastiest soils in the world ([Dent and Pons, 1995](#)) and internationally their known extent is estimated to be about 50 million ha ([Michael et al., 2017](#)). The total extent of acid sulfate soils in Finland is about 1 million ha ([Auri et al., 2022](#)). Acid sulfate soils often pose a risk to the environment due to their high acidity (actual acid sulfate soils) or high acidification potential (potential acid sulfate soil material). Actual acid sulfate soils usually leach large amounts of metals into recipient watersheds and may ruin productive farmlands if managed poorly (e.g., [Åström and Björklund, 1995](#); [Palko, 1996](#); [Åström and Björklund, 1997](#); [Edén et al., 1999](#); [Österholm and Åström, 2002](#); [Mosley et al., 2014](#); [Mattbäck et al., 2017](#)). The leachate formed in the landfill area is the most important environmental threat. Leaching from the oxidized layer significantly increases the metal, sulfate, and chloride concentrations in the runoff. Changes in water quality can be very rapid, for example after long dry periods. In addition to that, low pH on the surface can limit the growth of plants on the deposition site. Oxidation and acid generation will make a challenging corrosive environment for infrastructures. The general poor geotechnical properties in the acid sulfate soils are related to the high amount of organic matter in the sediments leading to e.g., low shear strength, high consolidation, and settlement, and easy disturbance during dredging. A special characteristic of the acid sulfate soil materials in infrastructure buildings is nevertheless their capability to produce a highly corrosive environment for steel and concrete structures. The water containing dissolved sulfate can diffuse into cement and cause cracking, expansion, and loss of bondage between cement and gypsum, which results in loss of concrete strength ([Prasad et al., 2006](#)). The factors behind the corrosive environment can be diverse and they act in different environments of the soil profile, including the oxic and anoxic (reduced) environment and the boundary between them. Principal factors acting in the oxic environment are low pH, high sulfate content/electrical conductivity, and differences in local oxygen concentrations. The anoxic conditions and the available sulfate in the soils enable the activity of sulfate-reducing bacteria (SRB) leading to the formation of sulfides and H₂S which can be corrosive, especially to steel structures ([Muyzer and Stams, 2008](#);

[Enning and Garrelfs, 2014](#)). The transitional boundary between the oxic and anoxic environments can be even more corrosive than a single environment alone. In the boundaries, there can be a high amount of sulfate available and the differences in the local electrical potential are high.

Acidification of the potential acid sulfate soil materials can be prevented by e.g., covering the disposed masses, stabilization, or neutralization. By covering the sulfide-rich masses immediately with low permeability and compacted landfill, the oxidation of the material will cease and prevent the decrease in pH and thus the leaching of the harmful metals. Even more efficiently, the acidification can be prevented by placing the spoil into waterlogged reducing conditions under the groundwater level.

Stabilization is used for weakly load-bearing soil materials that are not suitable due to their poor load-bearing capacity for construction. Stabilization makes the soil hard, thus making it useful for construction grounds. After stabilization, harmful substances can be bound, and the high pH prevents acid formation in sulfide-containing soils. Cement has typically been used for stabilization. It is possible to stabilize the soil to sufficient strength by using industrial waste and side streams (e.g., slag, ash, and lime residues) as part of the stabilization mix, while significantly reducing climate emissions compared to stabilization with cement alone ([Firoozi et al., 2017](#); [Zhang et al., 2020](#); [Jarva et al., 2021](#)).

Liming is an economical and effective method to neutralize and thus prevent the pH of the soil from dropping to the acidic side. Liming agents can be utilized for the dual purpose of acidity neutralization as well as soil fertilization. The application of liming materials has been found to improve soil structure, reduce the solubility of heavy metals, and enhance the availability of phosphorus to plants ([Mench et al., 1994](#)). The most commonly used liming agents are limestone (CaCO₃) and dolomite (CaMg(CO₃)₂). In addition, other Ca- and Mg-containing oxides, hydroxides, carbonates, and silicates have also been used as liming agents. Chemical composition, especially Ca and Mg content, particle size, and moisture influence the neutralization behaviour. Several industrial side streams, such as ashes and lime residues, can also be considered potential liming agents since they contain large amounts of calcium and magnesium ([Muse and Mitchell, 1995](#); [Zhang et al., 2002](#); [Pöykiö and Nurmesniemi, 2008](#); [Skousen et al., 2013](#); [Drapanauskaitė et al., 2021](#); [Drapanauskaitė et al., 2022](#)).

The legislation regulates the controlled use of different stabilization and liming agents, especially when using industrial waste and side streams. There are also several guidelines and limits for the disposal of masses. It is difficult to find common guidelines for the deposition and modification of excavated and dredged masses since the legislation is very country specific. Legislation can be an obstacle to using otherwise suitable industrial side streams ([James et al., 2012](#); [Vassilev et al., 2013](#); [Silva et al., 2019](#)). In the legislation, e.g., the limits of the maximum and soluble concentrations of harmful metals, are specified and threshold and lower guideline limits are given.

In this study, the neutralizing ability of alkaline ashes and industrial lime residues on two potential acid sulfate soil materials has been investigated in laboratory by incubating the materials treated with different concentrations of neutralizing agents for 23 weeks and measuring pH, incubated acidity and leachability. Pre-incubated properties of the soil materials (e.g., chemical composition, sulfide specification, and leachability) and the neutralization agents (e.g., chemical composition, leachability, and neutralizing ability) were also determined before the neutralization tests.

2. Materials and methods

2.1. Studied soil materials

The neutralization studies were carried out with two very different types of dredged soil materials, which were assumed to have a significant difference in acid production and acidification rate (Soil A and Soil

B).

Soil A was an organic-rich silty clay typically found in the coastal area of southern Finland (Matalahti in Naantali, Finland). Naantali is situated on the shore of the Baltic Sea. Dredging was used to deepen and maintain the waterways of a narrow bay called Matalahti, and dredged material was deposited on land close to the bay. Both the dredged material from the bay bottom and the topmost sediments bordering the bay consist of clay and silt with strongly humidified organic matter (gyttja). The gyttja clays are underlain and surrounded by older clay deposits that contain less organic matter.

Soil B was a coarse-grained sulfide material (Rantatoppila in Oulu, Finland) most often found in the North Ostrobothnia region. Rantatoppila is located in the River Oulujoki estuary. A small marina for 300 boats will be built in the area. Rantatoppila and its surrounds have been an important port, warehouse, and industrial area and the sediments have been partly contaminated by high concentrations of heavy metals from past industry activities (Auri et al., 2022). The dredging was carried out as a dry dredging operation, whereby the harbour basin was sealed with an extension of the breakwater headwall. The land surface around the dredging site is mainly coarse sand and fill soils.

The samples from the Matalahti site (Soil A) were taken from a test pit dug with a spade in the dredge spoil area. The samples were taken from the oxidized and unoxidized horizon, which were identified by pH measurements and visual inspection. The samples from Rantatoppila (Soil B) were collected directly from the unoxidized dredge material. All the samples were preserved in tightly sealed containers in a cold room (+5 °C) before the analyses.

2.2. Chemical analysis of the soil materials

Chemical analyses were carried out for the soil materials in two phases: pre-incubation characteristics from fresh dredged sediment samples and characteristics of oxidized samples after 23 weeks of incubation. Soil incubation is a way of 'letting the soil speak for itself' (Dent, 1986) where the main idea is to keep the soil material moist and have it oxidized at room temperature to simulate what would happen in nature during soil ripening. This study followed an approach like Creeper et al., 2012 in which the soil was incubated for >19 weeks in a 2–10 mm thick layer. To obtain the required amount of incubated material for the leaching tests, the soil samples were incubated in aerated plastic boxes (about 25 × 40 cm in size) and were kept moist using deionized water. Parallel samples were incubated in chip trays (28 × 24 × 45 mm) for monitoring the drop in pH during incubation (Creeper et al., 2012). The measurements were made in about 2 weeks intervals.

The pre-incubation pH was determined by using the potentiometric method after CaCl₂ leach. pH and electrical conductivity (EC) were measured from the two leachates from the two-stage shaking test method (SFS-EN 12457-3) at Eurofins Labtium Oy, Finland. EN 12457-3 consists of two extraction steps. The sample is first agitated with deionized water for 6 h at a liquid-to-solid ratio (L/S) of 2. The eluate and the solid are separated by filtration (0.45 μm). In the second step, the solid is subsequently mixed for 18 h with new water at L/S 8 and the eluate is separated by filtration. The concentrations of leached components in both collected eluates are then measured. The results are reported in mg/kg DM at a cumulative liquid-to-solid ratio of 10 l/kg. The pH monitoring during incubation was made with a pH-electrode on sample surfaces that were moisturized with deionized water.

Total carbon was determined by using method SFS-EN 13137 (method A, Determination of total organic carbon, TOC, in waste, sludges, and sediments). The same method was used to determine separately inorganic and organic carbon by Eurofins Labtium Oy. Loss on ignition (LOI) was determined by the gravimetric method at 550 °C. The humus content was determined spectrophotometrically. Dissolved organic carbon (DOC) was measured from the two leachates from the two-stage shaking test (method SFS-EN 12457-3, L/S-ratio 10 l/kg).

The total sulfide (total reduced sulfur, TRS) content of the samples

was determined with a simplified distillation method for sulfur speciation (Dalhem et al., 2021). The dredged spoil samples were placed in an airtight bag and frozen to prevent oxidation. Avoiding oxidation is important, as oxidation may lower the sulfide content. The samples were thawed in a nitrogen gas atmosphere before being transferred to the reactor (50 mL centrifuge tube). Then 6 M HCl and 3 M CrCl₂ were added to the reactor converting iron sulfides and elemental sulfur into hydrogen sulfide (H₂S). The hydrogen sulfide was precipitated in the form of zinc sulfide and the amount of zinc sulfide was determined after distillation. The total sulfide amount (TRS) was measured for both untreated soil samples and the treated samples of Soil A.

The total-S was determined by using the combustion technique S-analyzer and sulfidic S by combustion technique S-analyzer at a temperature of 810 °C, at Eurofins Labtium Oy, Finland. The total S concentration was determined from aqua regia extraction by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a modified ISO 11466 method, SO₄ was measured from water extraction by using ion chromatography (IC) technique, and the cumulative leachable S and SO₄ (L/S ratio 10 l/kg) was determined by using the two-stage shaking test (method SFS-EN 12457-3) at Eurofins Labtium Oy, Finland.

The total concentrations of metals or metalloids were determined from aqua regia digestion of dried (40 °C) and sieved (<2 mm size fraction) samples by inductively coupled plasma-mass spectroscopy (ICP-MS) and ICP-OES at Eurofins Labtium Oy laboratory in Finland. Hg assay was done pyrolytically using a method comparable to US EPA method 7473. The leachable concentration of elements (L/S-ratio 10 l/kg) was determined by using the two-stage shaking test (method SFS-EN 12457-3) at Eurofins Labtium Oy, Finland.

Quality control was assessed by using duplicate samples (every tenth sample) except for TRS where all samples were analysed in duplicate. The average analytical error for all measured parameters mentioned above was below 10 %. Additionally, the accredited laboratory Eurofins Labtium Oy, Finland used internal standards for their quality control procedures.

The oxide composition of the dredged soils and neutralizing agents were determined with a scanning electron microscope, SEM (LEO Gemini 1530 with Thermo Scientific Ultra Dry Silicon Drift Detector SDD) coupled to an elemental X-ray detector (EDS, Energy Dispersive X-Ray Spectroscopy, Thermo Scientific). The mineral phases in the soil materials were determined with X-ray diffractometry, XRD (Empyrean, Malvern Panalytical), and quantified with the Rietveld refinement method. The Powder Diffraction File (PDF®) database from International Centre of Diffraction Data (ICDD) was used in the analysis of the crystalline phases. The particle size distribution of the dredged spoils was determined using Sedigraph and sieving methods.

2.3. Neutralizing tests

Five alternative materials were chosen as neutralizing agents. Two alkaline ashes from fluidized bed combustion. The ash, FBC ash A, was received from a plant using a mixture of biomass (60–75 %), coal (25–40 %), peat (1–2 %), and refinery gas (1–2 %) as fuel. The other ash, FBC ash B, was from a plant using a mixture of wood (65–80 %; wood chips, forest residue, bark and sawdust), peat (20–30 %), and deinking sludge as fuel. Industrial lime residues were obtained from two different production plants. Lime kiln dust A was collected from the lime kiln in lime production. Lime kiln dust B was collected from the lime kiln in pulp and paper production. Commercial biochar (Bioproffa Nero, Carbolex Oy) was also used in the neutralization studies. Biochar is completely different, with no neutralizing ability, compared to the other materials used. Biochar was used to test if its known property of binding soluble metals can be utilized in acid sulfate soil materials to reduce harmful leachate (Wang et al., 2018; Kinnunen et al., 2021). Calcite, CaCO₃ (Nordkalk Oy), was used as a reference material to which other alternative materials were compared.

The amount of acid production of a soil sample can be evaluated by

determining the acidity concentration, which indicates the acid production capacity of the soil sample, i.e., the load. The theoretical acidity, and at the same time the theoretical amount of neutralizing agent needed, can be calculated from the total sulfur content of the soil sample (Visuri et al., 2021) because the load of the acidic sulfate soil is usually directly proportional to the sulfur content. However, this calculation usually exaggerates somewhat the actual acidity. The determination is based on the acid production process, where two moles of hydrogen (acidity) are formed from one mole of sulfur. The theoretical acidity can be calculated from Eq. (1), where a is the theoretical acidity (mmol H^+ /kg), c_1 is the sulfur content (g) or sulfur (%) $\times 10,000$ and, m_1 is the molar mass of sulfur

$$a = \frac{c_1}{m_1} \times 2 \quad (1)$$

The theoretical liming need can be calculated from the sulfur content according to Eq. (2), where m_2 is the theoretical liming need (kg $CaCO_3$ /t), c_1 is the sulfur content (g) or sulfur (%) $\times 10,000$, m_1 is the molar mass of sulfur and c_2 is the molar mass of $CaCO_3$.

$$m_2 = \frac{c_1}{m_1} \times \frac{c_2}{1000} \quad (2)$$

The acidity of Soil A, according to the total sulfur content, was about 1150 mmol/kg. Calculated from this, the theoretical need for liming was 55 kg/t of calcite. Correspondingly, the theoretical acidity of Soil B was 91 mmol/kg and thus the theoretical need for liming was 4.6 kg/t.

Traditionally, the calcium carbonate equivalent (CCE) value has been calculated to determine the neutralizing value of a liming material compared to pure calcium carbonate. A CCE of 100 % indicates that the material will neutralize the same amount of acidity as pure calcium carbonate. CCE is determined by acidifying the sample with HCl, followed by a back titration to pH 5 with NaOH. In this study, the relative neutralization ability of the different liming materials was determined by titrating 10 g of the material with 2.5 M sulfuric acid to pH 5.5. Titration with sulfuric acid was chosen as it is also generated when the acid sulfate soil materials acidify. The neutralizing ability of calcite was used as a reference and the amounts of other substances were proportional to its amount.

Three different theoretical neutralization need (TNN) levels were used in the experiments; 100 %, 50 %, and 10 % of the total calculated neutralization need of the neutralization agents, of which 100 % corresponds to the theoretical liming need. The quantities of the reference material Calcite in Soil A were therefore 55 kg/t, 27.5 kg/t, and 5.5 kg/t (calculated as dry mass). The amount of the other neutralizing agents needed was calculated from the results of the titration with sulfuric acid compared to the result of Calcite. The corresponding liming requirement of Soil B was about one-tenth compared to Soil A. Accordingly, the required amount of calcite in Soil B was 4.6 kg/t, 2.3 kg/t, and 0.5 kg/t. The amount of biochar could not be determined by titration, because the pH immediately dropped below 6. The amount of biochar (275 kg/t, 100 % dry) was chosen because this level still mixed well into the dredged sediments.

To be able to calculate the amount used in the laboratory experiments, the wet density (Soil A = 1304 g/l, and Soil B = 2013 g/l) and the water content (Soil A = 59.7 %, Soil B = 19.3 %) were first determined. After this, the final recipes for the laboratory experiments were calculated (Table 1). One litre (or dm^3) of dredging spoil and the required amount of neutralizing agent were mixed with a Hobart mixer for a total of 3 min. After mixing, triplicate samples were put in chip tray boxes for monitoring of the pH. At the same time, samples were collected for solubility measurements.

The pH of untreated and treated samples was measured as triplicates during the incubation period and the calculated median values were used as the result. The pH monitoring was carried out for a total of 161 days (about 23 weeks). The procedure for the treated samples followed the same method as for untreated soil samples (Creepers et al., 2012).

Table 1

Amount of neutralizing agents used in proportion to wet soil [g/l] for Soil A and Soil B with three different theoretical neutralization need (TNN) levels.

TNN	Soil	Calcite	FBC ash A	FBC ash B	Lime kiln dust A	Lime kiln dust B	Biochar
	g/l	g/l	g/l	g/l	g/l	g/l	g/l
Soil A							
100 %	1304	28.9	117.1	16.5	23.1	15.6	144.5
50 %	1304	14.5	58.5	8.2	11.6	7.8	72.3
10 %	1304	2.9	11.7	1.7	2.3	1.6	14.5
Soil B							
100 %	2013	7.4	30.1	4.2	6.0	4.0	37.2
50 %	2013	3.7	15.1	2.1	3.0	2.0	18.6
10 %	2013	0.7	3.0	0.4	0.6	0.4	3.7

During the incubation, acid-generating oxidation will occur due to reactions with atmospheric oxygen; and if the amount of acid produced during oxidation exceeds its acid-neutralizing capacity, the soil will acidify which results in a pH drop and mobilization of various elements. The incubation of the treated samples was made in larger boxes (25 \times 40 cm) than in the chip tray boxes (28 \times 24 \times 45 mm) normally used for soil samples. About 2 kg of the treated samples were spread on the bottom of the sample boxes into a 1–2 cm thick layer so that the oxidation was efficient and would happen as simultaneously as possible in all samples. The pH was measured by inserting a Hamilton Flatrode pH-electrode directly into the moistened sample. The pH was measured about every two weeks for at least 19 weeks or so until there was no further change in pH. The samples were kept moist throughout the incubation adding deionized water to them if necessary.

The acid producing potential, or the incubated acidity of the samples, was determined from incubated samples by acidity analysis. The acidity of the sample refers to its ability to neutralize a strong base to a certain pH value. The acidity measured after incubation reliably describes the natural potential amount of acid produced in a soil sample upon oxidation and is generally highly correlated with the solubility of metals (Visuri et al., 2021). The acidity was determined from untreated and treated samples by titrating an aqueous solution from the sample with sodium hydroxide to pH values of 5.5 and 6.5 (Österholm and Nystrand, 2016). The amount of acid was calculated from the consumption of sodium hydroxide and the unit was indicated as mmol H^+ /kg.

2.4. Solubility measurements of neutralization agents and neutralized materials

The effect of the neutralizing agents on the solubility of metals and metalloids was measured after the incubation period. The solubility measurements were carried out using a modified method based on the SFS-EN 12457-2 standard (Mattbäck et al., 2022). The incubated samples were mixed, and the pH was measured as triplicates. The pH value was compared to the incubation pH value, and if the sample was completely oxidized, the solubility measurement was continued. The sample for the solubility measurement was put into a plastic test tube and dried in a freeze-dryer. Dried samples were stored in a desiccator. The dried sample was mixed well, and two parallel samples were taken for the solubility measurement. The leaching method presented in Mattbäck et al., 2022 was specifically developed and tested to be used on large sample series where there is a low amount of available sample material, and was based on similar methods presented in Åström and Björklund (1997) and Fang and Wong (1999); but further modified to bear more resemblance to the standard one-step 10:1 liquid-solid leaching method EN 12457-2 which consist of the same extraction methodology as the two-step EN 12457-3. The procedure consisted of

weighing in approximately 4 g (dry weight) of sample material and adding deionized water to a liquid-solid ratio of 10:1. The test tubes were placed in a flat shaker for 24 ± 1 h, after which the samples were centrifuged for 15 min at a speed of 4000 g. After the extraction, the liquid was filtered through a 0.2 μm pore size filter. A pore size of 0.2 μm (instead of 0.45 μm) was used to minimize potential clay colloids passing through the filter, causing an overestimation of metal concentrations (Mattbäck et al., 2022; c.f. Nystrand and Österholm, 2013). Electrical conductivity and pH were measured from the filtered sample, and a 20 ml sample was taken for elemental analysis. The sample was preserved with nitric acid and the metal and metalloid concentrations were determined with ICP-MS equipment. The leachate of metals (L/S-ratio 10 l/kg) in the neutralization agents was determined using the two-stage shaking test (SFS-EN 12457-3:2002) at Turku University of Applied Science. Quality control of the leaching tests was performed by using five method blanks and 26 duplicate samples. The average analytical error for the presented parameters was below 10 %.

2.5. Legislation

Guideline values for the concentrations of harmful substances in the soil have been set in most countries, which are used in decision-making related to areas suspected of being contaminated or soil protection (Carlon, 2007). These concentration values are commonly called soil guideline values or soil criteria. Guideline values are used by comparing them with the concentrations of harmful substances measured in the soil. Guideline values can serve, e.g., as general target values for soil protection or restoration, as threshold values that trigger the need for additional research or investigation, or as values, when exceeded, the soil must be cleaned. The guideline values can be intended for certain land use or as general guidelines independent of land use. The legal status and binding nature of the guideline values usually vary between different countries (Carlon, 2007). Guideline values for harmful substances in e.g., soil, ground buildings, raw materials, and industrial side streams, have been established.

In this study, legislation in Finland was used to verify the risks of the total and soluble concentrations of the dredged spoils, industrial side streams, and treated dredged spoils. In Finland, there are several governmental acts and decrees that can be applied to dredged spoils when deposited on land and recycled as material for new building grounds. The provisions of the Environmental Protection Act (YSL 527/2014) regarding soil pollution and the decree on the assessment of soil contamination and remediation needs (PIMA decree 214/2007) apply to dredged soil materials that have been placed on land (Finlex, 2007, 2014). Among other things, the regulations prohibit activities that cause or may cause soil pollution and obligate the polluter to find out the state of the area and to clean the area if necessary. In addition, the annex to the PIMA decree specifies 52 environments or threshold values and guideline values for substances harmful to health, which can be used to support a case-by-case risk assessment when assessing the state of the area and the need for risk management measures. The threshold and lower guideline values for the total concentration of harmful metals set in the PIMA decree are shown in Table 2.

Waste materials (e.g., ash, slag, and lime) that can be used in earthworks are specified in the Finnish Government decree on the recovery of certain wastes in earth construction (MARA, 843/2017) (Finlex, 2017). The purpose of the decree is to promote the recovery of waste by specifying the conditions under which, if fulfilled, the use of waste referred to in this decree in earth construction does not require an environmental permit by the Environmental Protection Act (527/2014). This enables the use of recycled materials in construction projects, e.g., when replacing natural materials with recycled materials. The solubility limits can also to some extent be applied to determine environmental risks when stabilizing or neutralizing soils with industrial side streams. The limit values for the soluble concentration of harmful metals for a covered and paved field structure set in the MARA decree are shown in

Table 2

The threshold value and lower guideline value for sensitive land use from the decree on the assessment of soil contamination and remediation needs (214/2007). The maximum permitted limit values of the soluble concentration in the decree on the recovery of certain wastes in earth construction (843/2017). Maximum limit values for the total concentration of harmful metals in the MAF decree (1784/12/2011).

Substance	Threshold	Lower guideline	Covered field limit value	Paved field limit value	Limit value
	decree 214/2007		decree 843/2017		decree 1784/12/2011
	Total conc.		Soluble conc.		total conc.
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Antimony (Sb)	2	10	0.3	0.7	No limit
Arsenic (As)	5	50	0.5	1.5	25
Barium (Ba)	No limit		20	60	No limit
Cadmium (Cd)	1	10	0.04	0.06	1.0
Cobalt (Co)	20	100	No limit		No limit
Chromium (Cr)	100	200	0.5	5	1.8
Copper (Cu)	100	150	2	10	300
Lead (Pb)	60	200	0.5	2	600
Molybdenum (Mo)	No limit		0.5	6	No limit
Mercury (Hg)	0,5	2	0,01	0,03	100
Nickel (Ni)	50	100	0,4	1,2	100
Selenium (Se)	No limit		0,4	1	No limit
Zinc (Zn)	200	250	4	12	1500
Vanadium (V)	100	150	2	3	No limit

Table 2.

Legislation of liming agents is in many countries included in the legislation of fertilizer. The task of the Finnish Fertilizer Products Act (711/2022) is to ensure that the fertilizer products put on the market are safe and suitable for crop production. The goal is also to promote the safe utilization of industrial side streams as fertilizer. The act has recently been updated to match the new European fertilizer regulation (EU Fertilizing Product Regulation (FPR) 2019/1009). In addition, the [decree of the Ministry of Agriculture and Forestry of Finland \(MAF\)](#) on Fertilizer Products (1784/12/2011) has included limits for liming agents that also could be applied to industrial side streams when used as neutralizing agents (MAF, 2011). The limit values for the total concentration of harmful metals set in the MAF decree are shown in Table 2.

3. Results and discussion

3.1. Properties of dredged sediments

The pH of unoxidized Soil A sediment was 6.7 and during incubation, the pH dropped to 3.4. The material was fine-grained as the particle size <2 μm , corresponding to the clay content, was 49.6 %. Based on the particle size distribution, Soil A was classified as silty clay. The amount of organic matter was quite high as the measured loss on ignition (LOI) was 9.8 % and the humus content was 10 %. The total sulfur content of the unoxidized material, measured after digestion in aqua regia, was 1.9 % and the sulfide (TRS) content was 1.7 %.

The pH of the unoxidized Soil B sediment was 7.4 and during incubation, the pH dropped to 3.1. Thus, both Soil A and Soil B sediments can be defined as acid sulfate soil materials. Soil B was a coarser material with a clay content of only 4.9 % and was classified as fine sand. The organic matter was low, loss on ignition (LOI) was 0.7 % and the humus content was only 0.1 %. The total sulfur content of the unoxidized material was 0.10 % and the sulfide (TRS) content was 0.14 %.

The oxide composition of the soils was calculated from SEM/EDS

measurements (Table 3). Both soil materials contained the same elements. The main difference was that Soil A contained more sulfur and iron. In addition, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was higher in Soil B.

Both soils consisted of the same mineral phases (Table 3, Fig. 1). However, there were clear differences in the mineral composition. The clay content (illite) of Soil B was very low, and the soil material consisted mainly of feldspar and quartz. In Soil A, the proportion of illite was much higher, about 30 %. In addition to this, Soil A also contained about 10 % chlorite (Clinochlore). A layered sheet mineral often found in clay-graded sizes. The sulfur content of Soil A compared to Soil B was significantly higher, calculated as oxide (1.6 % vs 0.3 %) and as pyrite (FeS_2) mineral (2.1 % vs 0.1 %); i.e., corresponding quite well with TRS.

The total concentrations of potentially harmful metals and metalloids in Soil A and Soil B were determined with ICP-MS after digestion in aqua regia (Table 4). Overall, the measured total concentrations were much higher in Soil A than in Soil B. However, the total concentrations of the harmful elements were lower than the threshold and lower guideline values mentioned in the PIMA decree 214/217 (Table 2). Only the concentration of arsenic (8.2 mg/kg) in Soil A was higher than the national threshold value (5.0 mg/kg). Geologically, Naantali belongs to the arsenic province of southern Finland, where concentrations of about 10 mg/kg are common in soil materials. Thus, a regional baseline value for arsenic in fine-grained sediments of 11.7 mg/kg has been set (Tarvanen and Auri, 2019). The concentration of arsenic in Soil A was lower than this baseline value. Thus, both Soil A and Soil B can be considered non-contaminated soil materials. Soil B was a sandy material, consisting mainly of quartz and feldspar compared to the more clayey Soil A. The higher surface area of clay particles and the organic matter provides active sites for the adsorption of metals, thus the concentration of harmful metals was much higher in Soil A. Median metal concentrations have been recorded in fine-grained sediments in western Finland: 13 mg/kg Co, 27 mg/kg Cu, 48 mg/kg Cr, 448 mg/kg Mn, 31 mg/kg Ni, 90 mg/kg Zn and 50 mg/kg V (Åström and Björklund, 1997). In Soil A, the total concentrations are higher than the average in western Finland, and in the coarser Soil B much lower.

3.2. Solubility of harmful elements from the dredged sediments

The leaching tests of the fresh and incubated dredged spoil samples were carried out using a modified method based on the SFS-EN 12457-2 standard. The measured soluble concentrations were compared to the Finnish decree on the recovery of certain wastes in earth construction (MARA, 843/2017) (Finlex, 2017). In this study, the soluble concentrations were compared to the maximum permitted solubility in covered and paved field structures (Table 2). A covered field means protecting a structure containing waste with a layer of uncontaminated natural soil or aggregate of at least 10 cm in thickness in roadway and field structures. A paved field means protecting a structure containing waste with asphalt with a maximum void of 5 %, or some other material so that the seepage of rainwater into the structure does not exceed 5 %.

The soluble concentrations of the fresh, unoxidized Soil A and Soil B

samples were low (Table 4). Most of the soluble concentrations in the studied potentially acid-producing soils, when not oxidized and acidified, were below the maximum limit values specified in the MARA decree. The only exception was molybdenum (Mo) in Soil A. The soluble concentration of molybdenum (0.62 mg/kg) exceeded the limit value for a covered field (0.5 mg/kg). When compared to the total concentration of Mo, the soluble amount corresponds to 24.3 % of the total content in Soil A. The percentage of soluble Mo (31.9 %) was even higher in Soil B but because of the low total concentration, the limit values were not exceeded. The soluble percentage of antimony (Sb) in Soil A was also quite high (14.2 %). In Soil B, the percentage of soluble Sb could not be determined as the soluble content was less than the detection limit (< 0.010 mg/kg) of the analyses. The leaching of some other elements, Al, Co, Fe, Mn, and S, not mentioned in the MARA decree was also measured. The leaching of Al, Co, Fe, and Mn was low (0.0–0.3 %) in the fresh, unoxidized samples. The leaching of S was in Soil A 1.9 % and in Soil B higher at 9.6 %. The total concentration was based on the aqua regia extractable fraction for all elements. If bulk concentrations, including insoluble elements not dissolved in aqua regia, were considered, the percentual leaching would probably be smaller for most elements.

In the oxidized (incubated) dredged spoil samples, the leaching of the elements was generally higher than in the unoxidized samples. In Soil A, the amounts of leachable Ni (11 mg/kg), Cd (0.29 mg/kg), and Zn (30 mg/kg) were much higher than the permitted maximum limit values for both a covered and field structure. In Soil B, only the amount of soluble Ni (0.69 mg/kg) exceeded the maximum limit of a covered field structure. Part of the reason is the low total concentration of harmful metals in Soil B compared to Soil A (Table 4). As an example, the total concentration of cadmium in Soil B was 0.022 mg/kg, while the limit values for the soluble concentration in the MARA decree is 0.04–0.06 mg/kg. Another reason is the lower content of clay minerals. The fine-grinded clay sediments bind metals easier than coarser soil materials (Deng et al., 1998). The order in which the harmful elements percentually were leached out during the incubation period was in Soil A; Cd > Co > Ni > Mn > Zn and in Soil B; Cd > Mn > Co > Ni > Zn. The leaching of the other harmful elements was quite low. However, the leaching of S was about 50 % in both soil materials. The leaching of sulfur is high since sulfides oxidize to soluble sulfates when pH decreases below 4 during incubation (Ward et al., 2004). As much as 74.6 % of Cd was leached out from Soil A. In Soil B, it was almost halved to 40.9 %. The same trend was found for most other high soluble metals, the leaching (as %) of the harmful metals in Soil A was about doubled compared to Soil B (Co; 35.6 vs 17.4 %, Ni; 26.2 vs 11.3 %, Zn; 19.8 vs 10.2 %). The leaching of manganese differed from the other high-soluble metals. The leaching (as %) was almost the same in both soil materials (23.6 vs 18.6 %). The leaching of the other elements measured was much lower (0.0–2.5 %). Copper (Cu) showed a slightly higher solubility (3.2–8.0 %). Although the percentual leaching of Al was low, the amount leached out was reasonably high since the total concentration was high in the soil materials. The leaching of Cu, Ba, and Se was higher in Soil B

Table 3
The oxide and mineral composition (wt%) of Soil A and Soil B.

Oxide	CaO	MgO	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	FeO	S	TiO ₂
	%	%	%	%	%	%	%	%	%
Soil A	1.5	4.0	57.4	18.3	4.4	2.3	9.1	1.6	0.9
Soil B	2.9	2.2	67.8	13.7	2.8	3.5	5.9	0.3	0.9

Mineral phase	Illite	Chlorite	Albite	Orthoclase	Quartz	Hornblende	Pyrite
	%	%	%	%	%	%	%
Soil A	30.1	10.7	31.9	8.2	15.3	1.7	2.1
Soil B	0.7	1.0	51.7	5.8	32.4	8.3	0.1

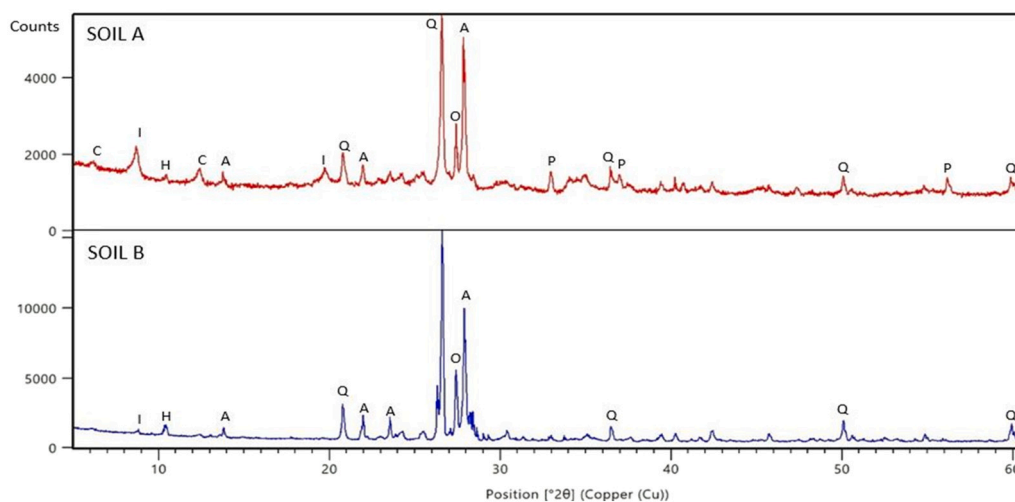


Fig. 1. X-ray diffractograms of Soil A and B. Q = Quartz, I = Illite, A = Albite (Na-feldspar), O = Orthoclase (K-feldspar), C = Chlorite (Clinochlore), H = Hornblende, P = Pyrite.

Table 4

Total concentration (aqua regia digestion) of untreated dredged sediments Soil A and Soil B. The soluble concentration (mg/kg) and percentage (%) leached of fresh and incubated sediments Soil A and Soil B. * = below detection limit.

Element	Soil A	Soil A fresh pH = 6.7		Soil A incubated pH = 3.4		Soil B	Soil B fresh pH = 7.4		Soil B incubated pH = 3.1	
	Total mg/kg	Soluble mg/kg	of total %	Soluble mg/kg	of total %	Total mg/kg	Soluble mg/kg	of total %	Soluble mg/kg	of total %
Antimony (Sb)	0.19	0.027	14.2	< 0.01	0*	0.050	< 0.01	0*	< 0.01	0*
Arsenic (As)	8.2	0.097	1.2	0.068	0.8	1.2	0.017	1.4	0.0055	0.5
Barium (Ba)	77	0.25	0.3	0.12	0.2	27	0.14	0.5	0.68	2.5
Cadmium (Cd)	0.39	< 0.005	0*	0.29	74.6	0.022	< 0.005	0*	0.0088	40.9
Chromium (Cr)	67	0.032	0.0	0.21	0.3	15	0.013	0.1	0.015	0.1
Copper (Cu)	40	0.040	0.1	1.2	3.2	4.5	0.059	1.3	0.36	8.0
Lead (Pb)	16	0.018	0.1	0.013	0.1	2.1	0.034	1.6	< 0.003	0*
Molybdenum (Mo)	2.5	0.62	24.3	0.0027	0.1	0.38	0.12	31.9	0.088	0.0
Nickel (Ni)	42	0.072	0.2	11	26.2	6.1	0.013	0.2	0.69	11.3
Selenium (Se)	1.2	0.0050	0.4	< 0.001	0*	0.21	< 0.001	0*	< 0.001	0*
Zinc (Zn)	155	0.033	0.0	31	19.8	15	0.15	1.0	1.5	10.2
Vanadium (V)	73	0.21	0.3	0.091	0.1	20	0.028	0.1	< 0.01	0*
Aluminium (Al)	30,367	13	0.0	1658	5.5	3970	4.9	0.1	63	1.6
Cobalt (Co)	18	0.010	0.1	6.3	35.6	3.0	0.010	0.3	0.52	17.4
Iron (Fe)	51,167	5.8	0.0	266	0.5	10,800	4.6	0.0	6.8	0.1
Manganese (Mn)	428	0.38	0.1	100	23.6	98	0.23	0.2	18	18.3
Sulfur (S)	18,767	355	1.9	8994	47.9	1000	96	9.6	481	48.1

compared to Soil A. Whether it is the result of the different soil types, particle size distribution, or measurement procedures was not determined in this study.

Earlier studies have shown that an appreciable amount of Al, Co, Cd, Cu, Mn, Ni, and Zn are dissolved from the oxidized layer of acid sulfate soils (Åström and Björklund, 1995; Åström, 1998; Peltola and Åström, 2002; Sohlenius and Öborn, 2004; Fältmarsch et al., 2008; Mattbäck et al., 2022). These metals are all known to be abundantly leached from acid sulfate soils (Österholm and Åström, 2004; Nordmyr et al., 2008). In contrast, metals that are not abundantly leached from acid sulfate soils, i.e., Cr, Fe, and V showed consistently low soluble concentrations from the studied dredged spoils (Deng et al., 1998; Österholm and Åström, 2004). Zn, Ni and Co are likely released from iron sulfides (Volkov and Fomina, 1974). Zn, Cu and Cd can be associated with organic matter (Scholz and Neumann, 2007) and also Al (Nordmyr et al., 1990). Cr and V are connected to weathering-resistant fractions or to organic matter and the small losses of Fe are thought to be due to precipitation of iron hydroxides (Åström, 1998). The percentual amounts of elements leached out from acid sulfate soils in mid-western Finland have been studied earlier (Österholm and Åström, 2002). In the study, the

total concentrations were as follows: S (40–50 %), Mn (25–35 %), Ni←Co (approx. 10 %), Zn (5–10 %), Cu-Al-Fe (< 5 %), and Ba-Cr-V (< 1 %). The leaching of Cd was not possible to determine because of a low concentration below the detection limit. Another study showed even lower leaching percentages (Peltola and Åström, 2002). In the present study, the leaching of the low-soluble elements (Ba, Cr, V, Cu, Al, and Fe) and S was on a similar level and the leaching of Mn was lower as in the earlier findings. However, the percentual leaching of Ni, Co, and Zn was much higher in Soil A. In Soil B, the leaching of Co was higher, and Ni and Zn were on the same level as in the previous study. The amount of elements mobilized depends on the degree of acid formation, the total amount of elements present in the sediment, and the stability of the material containing the elements (Sohlenius and Öborn, 2004; Åström and Rönnback, 2005). Thus, grain size, mineral distribution and composition, concentration of organic matter and where the ground-water table is located also affect the geochemistry of acid sulfate soil materials. All this must be taken into account when comparing the leaching of different types of sediments or soil materials in different regions and countries.

Interestingly, there are no limitations on the leaching of Al, Co, and Mn in the legislation. All three can be toxic in higher concentrations. For

Co, there are limits on the total concentration when deposited on land when defining contaminated materials, but not for the leaching. For Al, there are no limitations. Aluminium exists mainly as inorganic, soluble and/or organic forms in soil environment. Inorganic Al is exchangeable in soil but can also be bound to silicate clays, hydrous oxides, sulfates, and phosphates (Violante et al., 2010). In Finnish acid sulfate soils, Al occurs in aluminosilicate and probably also as Al-hydroxide (Deng et al., 1998; Fältmarsch et al., 2008). Aluminium is one of the most enriched elements in drainage water from acid sulfate soils. The rate of dissolution of Al-bearing minerals is pH-dependent and thus Al ions tend to increase with decreasing soil pH below 5 (Violante et al., 2010). The low pH promotes aluminosilicate weathering and Al-hydroxide dissolution and thus Al mobilization (Fältmarsch et al., 2008). As the pH decreases below 5, Si is leached leaving the Al in the solid form of Al-oxyhydroxide. This unstable form releases the phytotoxic specie Al^{3+} into the soil (Abate et al., 2013). The trivalent Al^{3+} is dominant in soil solutions when the soil pH is <5. The most common and immediate toxic effect of Al^{3+} in plants is the inhibition of root growth (Barcelo and Poschenrieder, 2002). Soluble Al can also affect aquatic life (e.g., Exley et al., 1991; Hudd, 2000; Sutela et al., 2012). An increased level of Al can affect some species' ability to regulate ions, like salts, and inhibit respiratory functions, like breathing e.g., when accumulated on the surface of a fish's gill.

The leaching of Mo was almost zero in the incubated soils (0.1 vs 0.0). The leaching of molybdenum from solid minerals to soil solution depends on e.g., soil pH, soil content of Fe, Mn, Al-oxides, clay minerals, and organic carbon (Rutkowska et al., 2017). The maximum adsorption of Mo onto positively charged metal oxides occurs between pH 4 and 5 (Xu et al., 2013). In acidic soils, molybdate anions (MoO_4^{2-}) are adsorbed onto positively charged Fe, Mn, and Al-oxides as well as clay minerals and organic colloids. The solubility of Mo increases with increasing soil pH as the solubility of MoO_4^{2-} increases about 100-fold for each unit of pH increase above 3. This explains why the leaching of Mo was high in the unoxidized soil materials and the treated samples where the pH remained neutral. In the acidified samples, the leaching was very low.

3.3. Neutralization experiments

3.3.1. Chemical properties of the neutralization agents

The oxide composition of the neutralization agents was calculated from SEM/EDS measurements (Table 5). A liming material usually contains Ca and/or Mg compounds capable of neutralizing soil acidity. The highest calculated CaO content (> 90 wt%) was measured in Calcite and Lime kiln dust B, followed by FBC ash B and Lime kiln dust A (about 65 wt%). The CaO content of FBC ash A was only 23 wt%. The MgO content varied between 1.5 and 3.4 wt%. FBC ash A was a typical low calcium biomass ash and FBC ash B is a high Ca wood-based ash. The alkaline ashes are a mixture of oxides, hydroxides, carbonates, and silicates. The burning of coal, gas, oil, or other low-Ca biomass fuels in industrial boilers results in an ash material that is less alkaline than wood ash. Thus, different ashes can vary considerably in calcium carbonate equivalent (CCE) values. Biochar consisted of carbon, 99.8 wt% calculated as CO_2 , and all other oxides each <0.08 wt%.

Total carbon and separately the inorganic and organic carbon were determined by using method SFS-EN 13137. The highest carbon content (about 11 %) was determined in Calcite and Lime kiln dust B (Table 5). Almost all carbon was also in the carbonate form. Together with the high CaO content, this confirms that they mainly consist of (> 90 %) calcium carbonate ($CaCO_3$). Most carbon was also determined as carbonate in FBC ash B (2.6 %) and Lime kiln dust A (7.1 %). In FBC ash A, the carbon was mainly in a non-carbonate form.

The total element concentration of the neutralizing agents was measured with ICP-OES after digestion in aqua regia. The total concentrations were compared to the limits set for liming agents in the decree MAF 1784/12/2011 (Table 2). The element concentrations of all neutralizing agents used, except FBC ash A, were below the limit values

Table 5

Trace metal concentration (mg/kg), oxide composition (wt%) and carbon content (%) of the neutralizing agents.

	Calcite	FBC ash A	FBC ash B	Lime kiln dust A	Lime kiln dust B	Biochar
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Antimony (Sb)	0.041	3.2	2.2	0.54	< 0.02	0.11
Arsenic (As)	1.8	40	15	5.3	0.33	0.50
Barium (Ba)	4.6	83	319	223	305	41
Cadmium (Cd)	0.041	5.2	0.99	0.22	0.94	0.067
Chromium (Cr)	< 1.0	52	26	8.4	5.2	1.5
Copper (Cu)	1.3	144	100	5.0	< 1.0	4.0
Lead (Pb)	1.3	72	52	13	0.79	1.1
Molybdenum (Mo)	0.10	9.1	5.2	2.2	0.058	0.12
Nickel (Ni)	< 2.0	44	11	7.3	< 2.0	2.9
Selenium (Se)	0.061	1.2	0.35	0.27	< 0.02	0.12
Zinc (Zn)	3.6	788	364	31	141	23
Vanadium (V)	< 1.0	66	18	17	1.5	1.7
Aluminium (Al)	1190	46,700	39,500	8960	403	582
Cobalt (Co)	< 1.0	16	3.3	3.3	< 1.0	2.1
Iron (Fe)	1210	24,300	8070	5440	263	790
Manganese (Mn)	69	2730	653	386	410	180
Sulfur (S)	40	19,300	3730	4590	364	338
	%	%	%	%	%	%
CaO	90.2	22.9	65.3	65.3	92.2	
MgO	3.4	3.2	1.9	3.3	1.5	CO_2
SiO_2	4.4	33.2	15.2	16.3	0.6	99.8 %
Al_2O_3	1.1	13.7	9.9	6.9	0.3	Others
K_2O	0.3	5.2	1.0	1.3	0.0	< 0.08 %
Na_2O	0.0	3.4	0.4	0.5	2.0	
Fe_2O_3	0.5	0.0	0.0	2.3	0.0	
SO_3	0.0	9.4	2.1	2.9	0.0	
P_2O_5	0.0	1.9	0.6	0.0	2.3	
C	11.5	2.9	2.8	7.2	11.1	80.2
C carb	11.5	0.5	2.6	7.1	11.1	< 0.05
C non carb	0.06	2.4	0.14	0.09	< 0.05	81.3

given in the decree (Table 5). The concentrations of As (40 mg/kg) and Cd (5.2 mg/kg) in FBC ash A were too high. However, in the decree, there is another limit of 15 mg/kg of Cd allowed, when the material is used as forestry fertilizer. The higher limit has made it possible to use, especially wood ashes as forest fertilizers. Otherwise, the high concentration of harmful metals has been the reason why, e.g., certain ashes from multi-fuel power plants do not have been used as fertilizers or liming agents (Nieminen et al., 2005; Maresca et al., 2018; Silva et al., 2019). For all other neutralizing agents used in this study, the measured metal concentrations were below the maximum limit set in the decree and thus could be used as a liming agent.

The leaching of the neutralizing agents was determined with the two-stage shaking test (SFS-EN 12457-3). The leaching of selected elements was compared to the maximum limit values in the MARA decree (843/2017). The soluble concentrations of the neutralizing agents were overall quite small (Table 6). The soluble Cr from FBC ash A and Lime kiln dust A exceeded the limit value of a covered field (Cr 0.5 mg/kg). However, the concentrations were clearly below the limit value of a paved field (Cr 5 mg/kg). The soluble concentrations of biochar were, due to the porosity of the biochar, determined only with a 1-stage shaking test using an extraction time of 24 h and an extraction ratio L/S of 10 l/kg.

3.4. pH and acidity of neutralized samples

3.4.1. Soil A

The pH values of Soil A samples during the incubation period are

Table 6
Leaching (mg/kg) of selected elements in the neutralizing agents.

Element	Calcite mg/kg	FBC ash A mg/kg	FBC ash B mg/kg	Lime kiln dust A mg/kg	Lime kiln dust B mg/kg	Biochar mg/kg
Arsenic (As)	< 0.04	0.12	< 0.04	0.05	< 0.04	< 0.04
Barium (Ba)	< 0.2	0.93	34	4.4	6.5	0.70
Cadmium (Cd)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001
Chromium (Cr)	< 0.2	1.3	< 0.2	1.1	0.29	0.20
Copper (Cu)	< 0.2	0.47	0.32	0.30	0.24	< 0.04
Lead (Pb)	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.1
Nickel (Ni)	< 0.2	< 0.2	< 0.2	< 0.2	0.20	< 0.04
Zinc (Zn)	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 0.04
Aluminium (Al)	0.58	11	1.5	2.2	0.81	< 0.04
Iron (Fe)	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.50
Manganese (Mn)	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	1.4

shown in Fig. 2a (100 % TNN), Fig. 2b (50 % TNN), and Fig. 2c (10 % TNN). The pH of untreated Soil A (pH 6.7) increased to between 7.0 and 10.1 after the addition of the neutralizing agents. The highest pH (>9) was measured for FBC ash B (100 % and 50 %) and Lime kiln dust A

(100 %). In the other samples, the pH increased slightly or remained the same. After five days, the pH was around 8. However, for the untreated Soil A and the biochar sample, the pH had already decreased.

After one week, the pH of the untreated Soil A sample decreased

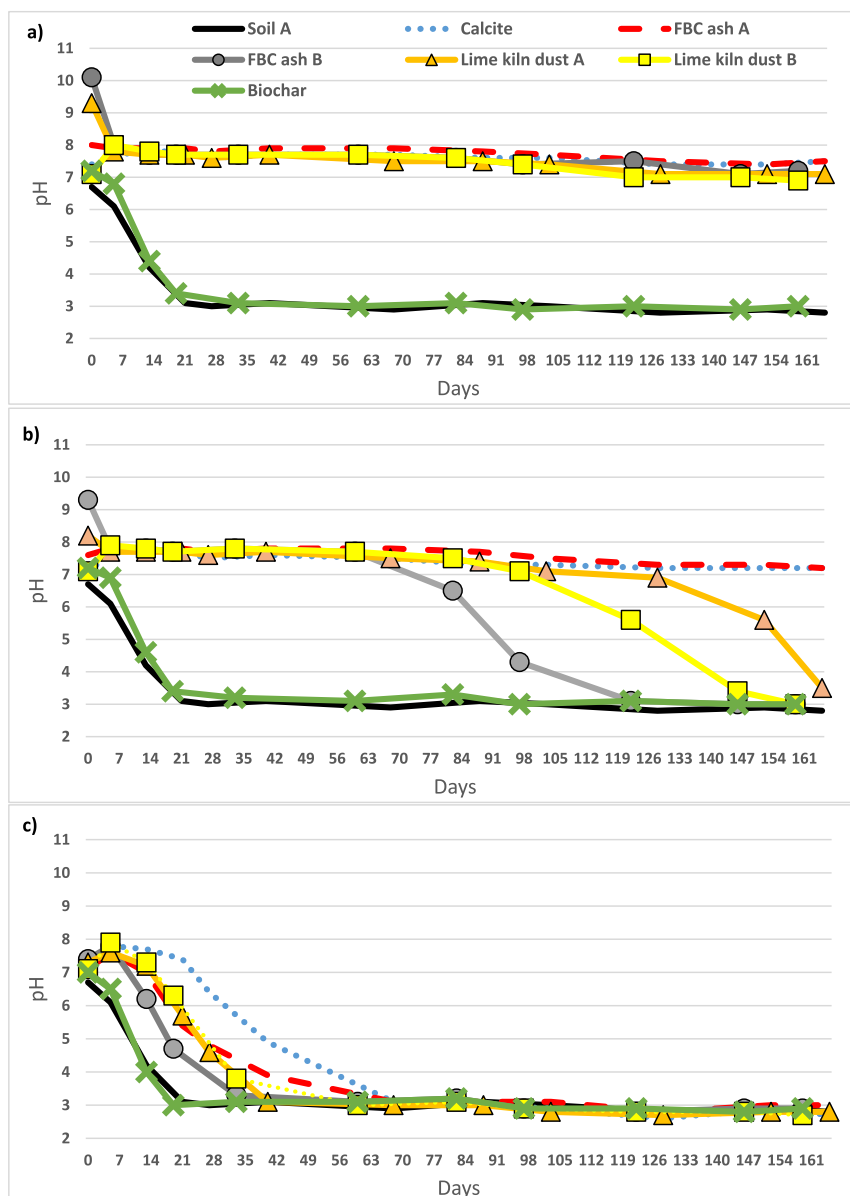


Fig. 2. Soil A, measured pH as a function of days during the 23-week incubation period: a) 100 % theoretical neutralization need (TNN), b) 50 % TNN, c) 10 % TNN.

strongly and was after two weeks 4, and after three weeks <3.5. After this, the pH dropped to about 3 or slightly below and remained at this level throughout the measurement period. At the 100 % TNN, the pH remained neutral at around 7 for all treated samples, except when biochar was added, throughout the whole measurement period. At 50 % TNN, the pH decreased to <4 after 17 to 23 weeks, in samples treated with FBC ash B, Lime kiln dust A, and Lime kiln dust B. In the samples, treated with Calcite and FBC ash A, the pH was still above 7 at the end of the measurement period. At 10 % TNN, the pH decreased to <4 within four to seven weeks in all treated samples. First, the pH started to decrease in FBC ash B, and last, in the Calcite sample. Generally, the pH dropped in all these samples to the same level as the untreated Soil A and remained there during the rest of the measurement period. As expected from the titration results, the used biochar did not show any neutralization ability in any sample. A similar drop in pH was noticed for all treatment levels of biochar as for the untreated soil sample.

The incubated acidity of untreated Soil A was 522 mmol H⁺/kg (Table 7). The value is very high and exceeds the limit of 100 mmol H⁺/kg, defined as a high risk of acidification (Visuri et al., 2021). When the incubated acidity exceeds 100 mmol H⁺/kg in fine-grained soil materials, the acid production can be assumed to be related to sulfide-derived acid production. In all treated samples, where pH decreased below 4, the acidity was very high (> 350 mmol H⁺/kg).

At the 100 % TNN, the pH did not drop below 6.5 for any neutralizing agent used in this study. Thus, it was not possible to titrate, and the incubated acidity was estimated to be zero. However, in the samples treated with biochar, the acid production was high (394–423 mmol H⁺/kg) at any treatment level. At 50 % TNN, the incubated acidities were high (337–422 mmol H⁺/kg) for FBC ash B, Lime kiln dust A and B. In these samples, the pH was below 4 at the end of the measuring period. However, the measured incubated acidity was 20–30 % lower than in untreated Soil A. For Calcite and FBC ash A, the incubated acidity was zero, as the pH still was neutral. At the 10 % TNN, all the incubated acidities were between 414 and 525 mmol H⁺/kg. In practice, the difference to the untreated soil was so small that the 10 % level of neutralization agents do not have a significant effect on acid production.

The total sulfide (TRS) content after incubation was determined for the untreated and treated (100 % TNN) Soil A samples. The sulfide content was very low (0.07 %) in the incubated untreated Soil A. This was expected as sulfides are oxidized to sulfates when pH decreases during incubation. The sulfide content of the incubated, treated (100 % TNN) samples varied between 0.96 and 1.23 %, except for the one

Table 7

The incubated acidity (at pH 6.5) of the untreated Soil and the samples treated with the 100 %, 50 % and 10 % theoretical neutralization need (TNN) of Calcite and the industrial side streams.

Neutralizing agent and TNN	Soil A	Soil B
	mmol H ⁺ /kg	mmol H ⁺ /kg
Calcite 100 %	0	0
Calcite 50 %	0	0
Calcite 10 %	414	27
FBC ash A 100 %	0	0
FBC ash A 50 %	0	0
FBC ash A 10 %	395	28
FBC ash B 100 %	0	0
FBC ash B 50 %	362	0
FBC ash B 10 %	474	26
Lime kiln dust A 100 %	0	0
Lime kiln dust A 50 %	422	1
Lime kiln dust A 10 %	525	32
Lime kiln dust B 100 %	0	0
Lime kiln dust B 50 %	337	0
Lime kiln dust B 10 %	484	27
Biochar 100 %	394	29
Biochar 50 %	423	29
Biochar 10 %	421	30
Untreated soil sample	522	34

treated with biochar, where the sulfide content was only 0.06 %. The sulfide content of the treated samples was quite high, about half of the sulfide content of the untreated sample (1.7 %). This indicates that the activity of iron and sulfur oxidizing microorganisms is inhibited due to maintaining a high pH in the 100 % TNN treated samples (see Boman et al., 2008 and references therein) and that sulfide oxidation has not gone to completion (sulfate). With the TRS method, also elemental S is being quantified and it is likely that high TRS values in the 100 % TNN treated samples reflects this fraction as elemental S is an intermediate S-species in sulfide oxidation (cf. Boman et al., 2008). Speciation of elemental S was however not performed in this study. The total water-soluble sulfur concentrations in the treated (100 % TNN) samples (excluding biochar) were 0.40–0.74 %. The result describes probably the concentration of water-soluble sulfate and combined with the total sulfide remaining in the samples, the result corresponds to the original total sulfur content of the dredged spoil sample (about 1.8 %). Based on this, it can be estimated that at the 100 % level neutralizing agent added, the majority of the sulfur binds to the sample. However, a considerable part also dissolves into the aqueous solution as sulfate. At the other treatment levels (50 % and 10 % TNN) the sulfides oxidize probably almost completely to sulfate as a result of the decrease in pH. However, part of the sulfate can bind in low pH conditions (pH below 4) to less soluble sulfate minerals, such as jarosite and to schwertmannite, and thus not all of the sulfate will dissolve in the water shaking test (e.g., Burton et al., 2007; Vithana et al., 2013).

3.4.2. Soil B

The pH values of Soil B samples during the incubation period are shown in Fig. 3a (100 % TNN), Fig. 3b (50 % TNN), and Fig. 3c (10 % TNN). The pH of untreated Soil B was 7.4 at the beginning of the experiment. After the addition of neutralizing agents, the highest pH (9.4–10.7) was measured for samples treated with FBC ash B and Lime kiln dust A (100 % and 50 % TNN). The pH of the sample with FBC ash A (100 % TNN) also increased to almost 9. However, one week later, pH of all these samples had decreased to about 8.

After one week, the pH of the untreated Soil B sample had decreased to about 4.5, and after two weeks to about 4. After this, the pH further decreased to about 3 and remained there until the end of the measurement period. At the 100 % TNN, pH of the treated samples remained neutral throughout the measurement period. However, biochar did not show any neutralization ability in Soil B either. The drop in pH showed a similar profile as the untreated Soil B for all treatment levels added. At 50 % TNN, the pH of the samples treated with FBC ash B and Lime kiln dust A started to decrease after seven weeks, and the sample with Lime kiln dust B after 11 weeks. The pH decreased to about 4 for these samples during the measurement period. The samples treated with Calcite and FBC ash A remained neutral until the end of the measurement period. At 10 % TNN, the pH of all samples dropped below 4 in five to eleven weeks. The pH decreased first in the samples treated with FBC ash B, followed by samples with Lime kiln dust A and Lime kiln dust B, and last in samples with Calcite and FBC ash A.

The incubated acidity of untreated Soil B was 34 mmol H⁺/kg (Table 7). The value is low compared to Soil A. However, it is quite high for this type of coarse-grained soil material and also reflects the low total S in the soil. According to the risk classification of coarse-grained soil materials, values higher than 20 mmol H⁺/kg refers to a high risk of acidification (Visuri et al., 2021). In all samples treated with the 10 % TNN and in all samples treated with biochar, the incubated acidity was higher than 20 mmol H⁺/kg. In the samples treated with 100 % TNN, the acidity was zero. The incubated acidity was also very low (0–1) for samples treated with 50 % TNN of FBC ash B, Lime kiln dust A, and Lime kiln dust B, although the pH values during incubation in the chip trays decreased below 4.5.

3.4.3. Comparison of neutralization behaviour of Soil A and B

Both Soil A and Soil B showed similar behaviour during the

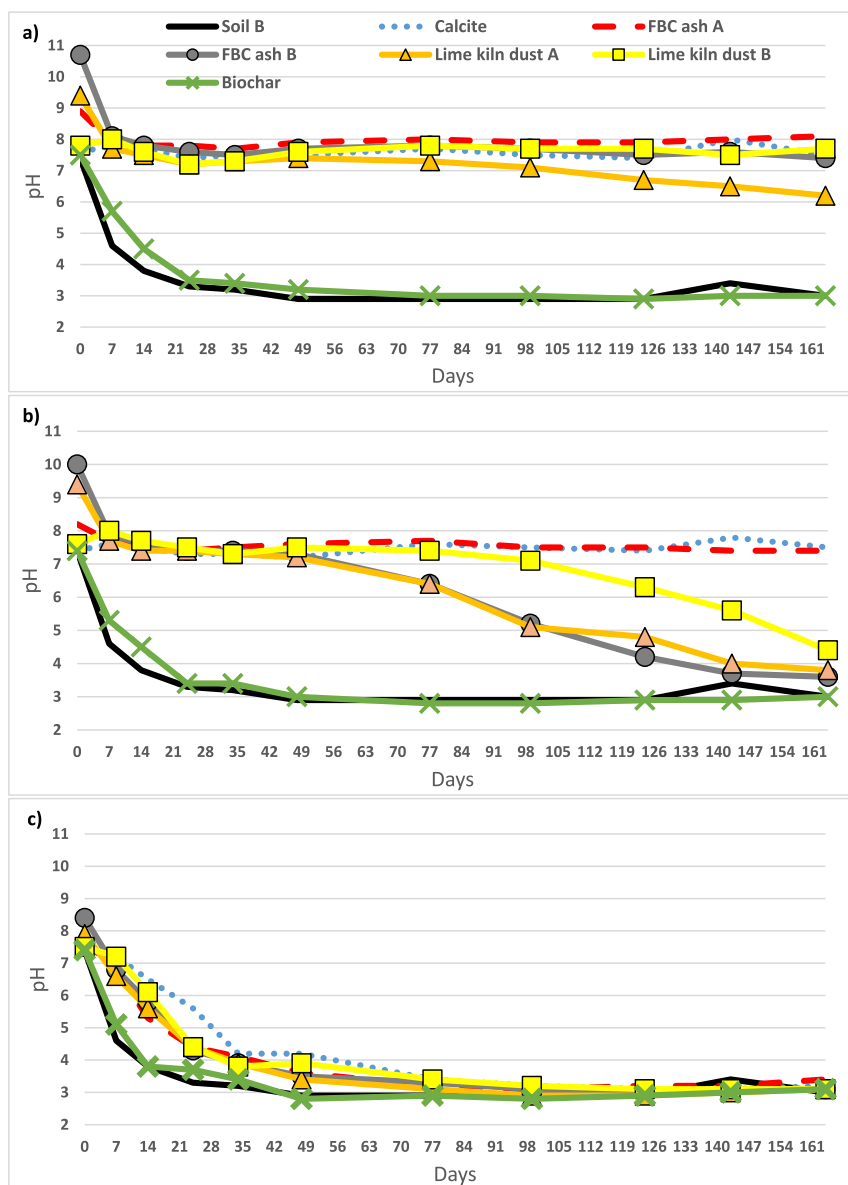


Fig. 3. Soil B, measured pH as a function of days during the 23-week incubation period: a) 100 % theoretical neutralization need (TNN), b) 50 % TNN, c) 10 % TNN.

measurement period. In the untreated soil samples and samples treated with biochar, the pH dropped below 4 very quickly and quite simultaneously. In the laboratory tests, oxidation was enhanced by using thin sample layers. In addition, the temperature and humidity conditions were optimized. Soil B contained coarser soil materials and thus the soil materials may behave very differently at construction sites. In coarser soil materials, oxygen can penetrate the spread layer more easily and evenly and passes water better. On the other hand, in Soil A-type (silty clay), drying cracks, and crumb structures usually are formed, which greatly enhances the oxidation of the soil material. Coarse-grained low-sulfur (mass fraction of S in the range 0.01–0.1 %) acid sulfate soil materials have been found to acidify below pH 4 during oxidation because of a poor buffering capacity for this type of soil material (Mattbäck et al., 2017). This can explain the similar acidification behaviour although the chemical properties (e.g., S content) of the dredged spoils were quite different.

In the samples treated with FBC ash B and Lime kiln dust A, the pH increased at the beginning of the experiment in both Soil A and B. In Soil B, the pH also increased for FBC ash A. However, the pH quickly recovered close to neutral in both soils. These industrial side streams are

very alkaline and will initially increase the pH. The neutralizing capacity is a function of the rate of reaction in the soil that is controlled by the fineness of the particles. Wood ash has been shown to react faster than agricultural lime, resulting in higher initial increases in pH, which are generally maintained for shorter periods in ash-amended soil materials although, in some cases, the application of wood ash can result in long-term pH changes (Vance, 1996). Lime kiln dust from lime production (as Lime kiln dust A) usually contains both CaCO_3 and CaO . A higher CaO content makes the reactions faster and initially, the pH will increase. The slight increase in pH for the other samples can be explained by a proper dissolution of the neutralizing agents and an intensification of the reactions during the days following the mixing.

The 100 % TNN was sufficient for all industrial side streams in both Soil A and Soil B to keep the pH neutral during the 23-week monitoring period. The incubated acidity was also zero for these samples. This was also quite predictable, as the theoretical acid production used to calculate the 100 % TNN (Soil A, 1150 $\text{mmol H}^+/\text{kg}$; Soil B, 91 $\text{mmol H}^+/\text{kg}$) was more than double compared to the proven acid production capacity (Soil A, 522 $\text{mmol H}^+/\text{kg}$; Soil B, 34 $\text{mmol H}^+/\text{kg}$). Presumably, the acid production of the neutralized samples will not increase from

this even in longer times, and this amount can be considered safe in terms of neutralization. Even though the acid production potential of both untreated Soil A and B was found to be high, relative to the soil type, it is worth noting that the acidity of Soil A is about 10 times higher than Soil B. In practice, this is likely to be seen as a higher long-term acidity load in Soil A-type silty clays, while the acidity can be washed away quickly from the sandy material of Soil B-type. The acidity caused by fine grain ($< 63 \mu\text{m}$) is reported to usually be 10–100 times higher than coarse-grained ($> 63 \mu\text{m}$) soil materials (Mattbäck et al., 2017).

At 50 % TNN, the samples treated with Calcite and FBC ash A, prevented acidification. The samples treated with FBC ash B, Lime kiln dust A, and Lime kiln dust B were acidified in both soil materials. In Soil B, the first samples started to acidify after about 50 days, and in Soil A after about 60 days. However, in Soil B, the pH did not drop to quite low readings and, especially with FBC ash B, the acidification was slower. However, it is not possible to assess what will happen to the samples in the long term and whether the pH difference between the samples will even out. For Calcite and FBC ash A, the results showed that the theoretical neutralization requirement of 50 % was sufficient to keep the material neutral during the monitoring period. For the other neutralizing agents used in this study, the 50 % TNN was not sufficient to neutralize the material in the long term but could probably keep the pH close to neutral for a shorter period. The need for a short-term neutral pH could be interesting, e.g., if short-term interim storage for the soil is needed. However, based on the acidification rates of the thin sample layers used in the study, it is not possible to reliably assess the acidification in high-volume soil masses.

At 10 % TNN, all treated samples were quite simultaneously acidified below pH 4 in both soil materials and the incubated acidity was of the same order as in the untreated soil samples. This indicates that the 10 % TNN is not sufficient to neutralize the soil materials. In practice, an amount between the 50 and 100 % TNN used in this study, is sufficient to neutralize acid generating sulfide-rich sediments.

The TNN was calculated from the total sulfur content in the dredged spoil samples. The calculated theoretical acidity was more than doubled compared to the actual acidity measured in the samples (Soil A; 1150 vs 533 mmol H^+ /kg, Soil B; 91 vs 34 mmol H^+ /kg). This indicates that the TNN was lower than the calculated amount used in this study. However, the neutralizing agents would work the same, only lower amounts would be needed to neutralize the acid sulfate soils.

The amount of the industrial side streams used was calculated from the results of the titration with sulfuric acid. The amount of sulfuric acid needed to reach pH 5 was measured and the results for the industrial side streams were compared to the amount needed for Calcite. To reach the same neutralization ability as Calcite, about four times more FBC ash A must be used. The other industrial side streams could be used in lower amounts than Calcite; FBC ash B (57 %), Lime kiln dust A (80 %), and Lime kiln dust B (54 %). Titration with sulfuric acid was chosen as acid sulfate soils are acidified mainly from the release of sulfuric acid. The titration results might differ from the results obtained by using the calcium carbonate equivalent (CCE) method, where the material is first titrated with hydrogen chloride and then back titrated with sodium hydroxide.

A small amount of uncertainty in the results could have arisen when mixing the samples, especially due to the very small amounts of neutralizing agents needed for Soil B. At the 10 % level, only a few grams of the substance were mixed into roughly 2 kg of dredged soil material. However, it seems that the mixing has been successful. To confirm the results, field tests are still needed to study how these neutralizing agents behave in practice.

3.5. Leaching of harmful elements from the treated samples

The leaching of selected elements from the treated samples after the incubation period was analysed with ICP/OES. The leachate was prepared by using a one-step 10:1 liquid-solid leaching method modified

from EN 12457-2. The leaching of the harmful elements in the samples treated with the neutralizing agents correlated well with acidification (Tables 8–11). In the samples that were acidified, the leaching of the elements was of the same order of magnitude as in the oxidized untreated soil materials. The biochar treatment did not affect the leachability. The soluble concentrations were quite similar to those measured in the incubated soil material samples. Thus, the proposed binding of leached elements was not found for the biochar used in this study.

In the treated samples where the pH remained neutral during the incubation period, the leaching of elements was overall very low (< 1 %). However, the leaching of Mo was high (20–30 %) and exceeded the maximum limit value set for a covered field in all neutral samples, except for sample Calcite 50 % TNN in Soil A. Also, in Soil B the leaching of Mo was higher in the neutral samples, but it did not exceed the limit values set in the decree. In the neutral samples treated with FBC ash A and FBC ash B, the soluble concentration of Mo was even higher than in the untreated soil samples. This indicates that a part of the Mo content in the ashes also was leached out in these conditions. The total concentration of Mo in FBC ash A was 9.1 % and in FBC ash B it was 5.2 %. Also, the slightly higher pH in the treated samples compared to the untreated soil material samples enhanced the leaching of Mo. The leaching of Sb is also lower in acidic conditions and is enhanced when pH is neutral (Cappuyns et al., 2021). However, the soluble concentrations of Sb were below the limits set in the decree.

In the treated samples in Soil A that acidified, the amounts of leachable Ni (7.3–12 mg/kg), Cd (0.18–0.24 mg/kg), and Zn (22–34 mg/kg) (Table 8) were much higher than the maximum limits set in the MARA decree (Table 2). Also, the concentration of soluble Cu (3.3 mg/kg) in the sample treated with FBC ash B exceeded the maximum value for a covered field (2 mg/kg). If the reason is a more soluble Cu content in FBC ash B or a higher Cu content in this soil sample was not studied. In Soil B, the soluble concentrations were low (Table 10), as the total concentration of harmful elements was very low in the sample (Table 4). Only the amount of soluble Ni (0.41–0.79 mg/kg) in the acidified samples exceeded the maximum limit of a covered field. However, at the 50 % TNN, the leaching was very low also for the neutralized samples (FBC ash B, Lime kiln dust A and B) in Soil B that acidified to below pH 4 in the pH measurement tests. The pH of these treated samples in the leaching tests remained neutral and also incubated acidity was low. One explanation could be that the oxidation in the thinner layer in the chip trays of the coarser soil B in the chip trays was faster. This could suggest that 50 % TNN is enough to prevent a significant increase in solubility. However, the neutralizing need level of 50 % is probably not sufficient to keep the pH at a neutral level and thus an increase in solubility in the long term is very possible.

The leaching of Al, Co, Fe, Mn, and S in the treated acidified samples was similar to the leaching behaviour in the untreated acidified samples. The order in which the elements percentually on average leached out in the acidified samples was in Soil A: Cd (58 %) $>$ Co (30 %) $>$ Mn (21 %) $>$ Ni (21 %) $>$ Zn (16 %) and in Soil B; Cd (42 %) $>$ Mn (19 %) $>$ Co (17 %) $>$ Ni (10 %) $>$ Zn 10 %. Compared to the untreated dredged spoil samples, the leaching (as %) was lower in treated Soil A and remained roughly the same in treated Soil B. The leaching of S in the acidified samples was 49 % in Soil A and 58 % in Soil B. The leaching of the other measured metals was low (< 2 %), and only the leaching of Cu was a little higher (Soil A = 3 %, Soil B = 7 %). The solubility of Cu, Ba and Se was again slightly higher in Soil B compared to Soil A. The leaching was strongly dependent on pH. The amount of leachable Co, Ni, and Zn even showed a correlation to modest pH change (3.1 to 2.7), as leachable values were notably higher in the lower pH samples.

The total concentration of As and Cd in FBC ash A was too high compared to the limits in decree 1784/12/2011 in FBC ash A and the soluble concentration of Cr of FBC ash A and Lime kiln dust A exceeded the maximum limit set in decree 843/2017. However, in the treated neutralized samples where the pH remained neutral, the leaching of these elements was below the maximum limits set in the decree. It is not

Table 8

Soluble concentration (mg/kg) of metals and metalloids in treated samples (Soil A). 100 %, 50 % and 10 % theoretical neutralization need (TNN) of Calcite and the industrial side streams used. Soil pH was measured after incubation.

Sample	pH	Sb	As	Ba	Cd	Cr	Cu	Pb	Mo	Ni	Se	Zn	V	Al	Co	Fe	Mn	S
		µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	mg/kg	µg/kg	mg/kg	mg/kg	mg/kg
Calcite 100 %	7.2	14	17	515	0.57	2.4	32	0.095	725	35	3.5	21	37	0.083	15	0.23	0.85	4049
Calcite 50 %	7.0	9	14	526	0.50	2.1	34	0.15	461	34	3.5	24	22	0.073	13	0.27	0.81	5160
Calcite 10 %	3.1	2.2	60	200	185	100	596	15	2.4	8270	< 1.0	19,547	45	897	4311	256	91	8871
FBC ash A 100 %	7.5	23	48	1102	1.4	2.9	50	0.040	1403	29	4.0	25	94	0.24	6.5	0.36	0.87	7415
FBC ash A 50 %	7.4	25	48	1153	1.3	3.3	54	0.13	1153	38	6.5	35	120	0.25	11.0	0.31	1.9	6115
FBC ash A 10 %	3.2	1.4	17	340	235	66	1099	13	2.4	7493	< 1.0	21,481	20	844	4496	49	110	7893
FBC ash B 100 %	7.2	17	21	641	0.89	3.1	52	0.14	1101	32	3.0	22	62	0.14	8.0	0.36	0.70	4754
FBC ash B 50 %	3.1	2.4	31	401	231	66	939	47	2.0	7344	< 1.0	24,654	27	734	4878	252	82	9707
FBC ash B 10 %	2.7	2.5	23	20	241	578	3268	0.55	3.3	12,068	< 1.0	34,192	171	2313	7039	278	116	11,564
Lime kiln dust A 100 %	7.1	10	14	602	0.74	2.2	34	0.075	712	33	2.0	24	38	0.082	10.5	0.34	0.82	5720
Lime kiln dust A 50 %	3.1	2.1	23	245	211	71	854	1.2	3.2	7630	1.6	23,644	67	639	4652	259	83	8875
Lime kiln dust A 10 %	3.0	2.2	57	135	196	156	988	8.5	3.4	9333	1.5	23,583	56	1254	5269	261	94	9484
Lime kiln dust B 100 %	6.9	12	15	560	0.56	2.2	31	0.24	635	36	3.0	31	34	0.083	15.0	0.25	0.89	4751
Lime kiln dust B 50 %	3.1	2.2	27	353	222	74	902	27	1.9	7558	< 1.0	22,173	25	650	4837	192	89	9725
Lime kiln dust B 10 %	2.9	2.6	43	91	207	267	1613	5.7	2.8	10,081	< 1.0	28,226	116	1562	6250	398	111	10,081
Biochar 100 %	3.0	1.6	32	32	200	255	1453	0.96	2.3	9018	< 1.0	25,049	58	1403	5411	230	103	8266
Biochar 50 %	3.0	2.3	54	66	230	215	1201	3.2	2.9	9661	< 1.0	24,027	86	1301	5556	325	100	8459
Biochar 10 %	3.1	2.2	52	135	195	160	867	6.0	3.6	9668	1.5	25,046	99	1202	5560	406	95	8415

Table 9

Soluble concentration (%) of the total concentration of the treated sample (Soil A). 100 %, 50 % and 10 % theoretical neutralization need (TNN) of Calcite and the industrial side streams used. Soil pH was measured after incubation. 0* = below detection limit.

Sample	pH	Sb	As	Ba	Cd	Cr	Cu	Pb	Mo	Ni	Se	Zn	V	Al	Co	Fe	Mn	S
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Calcite 100 %	7.2	7.4	0.2	0.7	0.3	0.0	0.1	0.0	28.7	0.1	0.2	0.0	0.1	0.0	0.1	0.0	0.2	21.6
Calcite 50 %	7.0	4.7	0.2	0.7	0.3	0.0	0.1	0.0	18.2	0.1	0.2	0.0	0.0	0.0	0.1	0.0	0.2	27.5
Calcite 10 %	3.1	1.1	0.7	0.3	56.1	0.2	1.6	0.1	0.1	19.6	0*	12.6	0.1	3.0	27.0	0.5	21.3	47.3
FBC ash A 100 %	7.5	11.6	0.6	1.4	0.3	0.0	0.1	0.0	55.5	0.1	0.3	0.0	0.1	0.0	0.0	0.0	0.2	39.5
FBC ash A 50 %	7.4	13.2	0.6	1.5	0.3	0.0	0.1	0.0	45.6	0.1	0.6	0.0	0.2	0.0	0.1	0.0	0.5	32.6
FBC ash A 10 %	3.2	0.5	0.2	0.4	71.2	0.1	2.9	0.1	0.1	17.8	0*	13.9	0.0	2.8	25.3	0.1	25.7	42.1
FBC ash B 100 %	7.2	8.4	0.3	0.8	0.3	0.0	0.1	0.0	43.5	0.1	0.2	0.0	0.1	0.0	0.0	0.0	0.2	25.3
FBC ash B 50 %	3.1	1.1	0.4	0.5	70.0	0.1	2.5	0.3	0.1	17.4	0*	15.9	0.0	2.4	27.4	0.5	19.1	51.7
FBC ash B 10 %	2.7	1.1	0.3	0.0	73.0	0.9	8.7	0.0	0.1	28.6	0*	22.1	0.2	7.6	39.5	1.1	27.0	61.6
Lime kiln dust A 100 %	7.1	0.5	0.2	0.8	0.3	0.0	0.1	0.0	28.1	0.1	0.2	0.0	0.1	0.0	0.1	0.0	0.2	30.5
Lime kiln dust A 50 %	3.1	1.1	0.2	0.3	63.9	0.1	2.3	0.1	0.1	18.1	0.1	15.3	0.1	2.1	26.1	0.5	19.5	47.3
Lime kiln dust A 10 %	3.0	1.1	0.7	0.2	59.4	0.2	2.6	0.1	0.1	22.1	0.1	15.2	0.1	4.1	29.6	0.5	22.0	50.5
Lime kiln dust B 100 %	6.9	5.8	0.2	0.7	0.3	0.0	0.1	0.0	25.1	0.1	0.2	0.0	0.0	0.0	0.1	0.0	0.2	25.3
Lime kiln dust B 50 %	3.1	1.1	0.3	0.5	67.3	0.1	2.4	0.2	0.1	17.9	0*	14.3	0.0	2.1	27.2	0.4	20.8	51.8
Lime kiln dust B 10 %	2.9	1.1	0.5	0.1	62.7	0.4	4.3	0.0	0.1	23.9	0*	18.2	0.1	5.1	35.1	0.8	25.9	53.7
Biochar 100 %	3.0	0.5	0.4	0.0	60.6	0.4	3.9	0.0	0.1	21.4	0*	16.2	0.1	4.6	30.4	0.5	24.1	44.0
Biochar 50 %	3.0	1.1	0.7	0.1	69.7	0.3	3.2	0.0	0.1	22.9	0*	15.5	0.1	4.3	31.2	0.6	23.4	45.1
Biochar 10 %	3.1	1.1	0.6	0.2	59.1	0.2	2.3	0.0	0.2	22.9	0.1	16.2	0.1	4.0	31.2	0.8	22.2	44.8

Table 10
Soluble concentration (mg/kg) of metals and metalloids in treated samples (Soil B). 100 %, 50 % and 10 % theoretical neutralization need (TNN) of Calcite and the industrial side streams used. Soil pH was measured after incubation.

Sample	pH	Sb	As	Ba	Cd	Cr	Cu	Pb	Mo	Ni	Se	Zn	V	Al	Co	Fe	Mn	S
		µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	mg/kg	µg/kg	mg/kg	mg/kg	mg/kg
Calcite 100 %	7.7	0.50	23	542	0.030	1.6	19	0.48	85	3.4	5.0	< 0.50	69	0.33	0.40	0.24	0.023	271
Calcite 50 %	7.6	0.40	16	555	0.031	1.4	19	0.43	65	3.3	4.0	< 0.50	40	0.32	0.50	0.25	0.036	303
Calcite 10 %	2.8	0.50	8.2	644	9.7	17	533	0.55	< 0.50	674	< 1.0	1611	0.91	52	523	14	19	634
FBC ash A 100 %	8.0	< 0.20	57	1112	< 0.03	< 0.2	< 0.2	< 0.03	202	< 0.1	8.1	< 0.50	121	1.3	< 0.1	0.049	0.030	647
FBC ash A 50 %	7.9	< 0.20	48	875	0.070	1.6	20	0.13	141	2.9	6.0	< 0.50	121	0.79	0.60	0.073	0.059	372
FBC ash A 10 %	3.7	0.70	5.6	883	8.9	1.9	37	0.69	0.90	411	< 1.0	1304	1.4	2.1	341	13	18	532
FBC ash B 100 %	7.9	0.40	42	390	0.090	2.8	37	0.36	240	4.9	5.0	6.0	200	0.59	1.7	0.36	0.014	250
FBC ash B 50 %	7.2	0.50	10	713	0.11	1.7	16	0.53	110	3.3	3.0	< 0.50	49	0.42	0.90	0.23	0.021	271
FBC ash B 10 %	2.9	0.40	12	673	10	17	385	0.42	1.3	637	3.0	1.487	1.2	48	514	17	19	524
Lime kiln dust A 100 %	7.2	0.40	9.4	712	0.050	1.2	11	0.32	71	2.8	2.0	< 0.50	29	0.26	0.50	0.16	0.092	361
Lime kiln dust A 50 %	6.9	0.50	7.0	815	0.050	1.4	15	0.48	81	4.2	3.0	11	18	0.21	0.91	0.15	0.052	372
Lime kiln dust A 10 %	3.0	1.5	10	708	8.7	9.6	263	1.5	0.61	597	< 1.0	1416	0.81	24	486	38	21	607
Lime kiln dust B 100 %	7.8	0.40	27	511	0.060	1.6	22	0.45	120	3.6	4.0	< 0.50	90	0.36	0.70	0.2	0.018	261
Lime kiln dust B 50 %	7.7	1.7	24	472	0.060	2.9	31	1.7	91	4.4	3.0	5.1	90	1.1	1.2	0.9	0.048	186
Lime kiln dust B 10 %	2.9	0.20	5.6	584	11	17	338	0.21	0.61	758	< 1.0	1741	0.92	72	574	6.9	18	686
Biochar 100 %	3.0	< 0.20	7.3	586	9.2	14	303	0.12	1.2	788	< 1.0	1819	1.0	29	547	32	22	566
Biochar 50 %	3.0	< 0.20	7.3	598	7.4	15	335	0.13	0.60	629	< 1.0	1420	0.71	36	497	15	15	487
Biochar 10 %	2.8	< 0.20	11	543	10	17	402	0.10	< 0.50	735	< 1.0	1610	1.0	56	553	4.9	18	574

quite clear which legislation and decree to apply when neutralizing acid-generating sulfide-rich sediments with industrial side streams. To clarify this, the Ministry of Environment in Finland is preparing a new decree (MASA decree). The aim of the Masa decree (utilization of soil material waste from construction) is to further promote the appropriate, safe, ecological, and economic utilization of construction surplus materials, recycled materials, and waste in land and infrastructure construction. Regulation will also apply to e.g., stabilization of excavated and unexcavated soil materials using recycled waste materials. Hopefully, this will clarify legislation and increase the use of recycled acid sulfate soil materials in a sustainable way.

4. Conclusion

The two investigated dredged spoils showed highly dissimilar chemical and physical properties; one (Soil A) being mud (gyttja-bearing silty clay) with a high sulfur content (1.9 %) and the other (Soil B) being fine sand with a low sulfur content (0.1 %). Both dredged spoils were acidified during the incubation (oxidation) to a pH below 3.5 in two to three weeks. Thus, both acid generating sediments can be classified as acid sulfate soil materials. Being acid sulfate soils means that the dredged spoils have a high potential to leach out significant amounts of harmful substances when deposited on land and exposed to air. This could be prevented e.g., by neutralizing the deposited acid generating dredged spoils.

The total concentration of harmful elements in both dredged spoils was low and thus they were considered non-contaminated soil materials. The soluble concentrations of the fresh, unoxidized dredged spoil samples were low, well below the permitted maximum limits set in the Finnish MARA decree. However, Mo was leached out in neutral pH conditions and exceeded in Soil A the limit value set in the decree. Generally, the leaching of elements was much lower in Soil B as the total concentration of the elements also was much lower than in Soil A. In the incubated dredged spoil samples, the leaching of harmful elements was higher. Percentually, the leaching of Cd, Co, Mn, Ni and Zn was high. The amount of leached Al and S was also high. In soil A, the soluble concentration of Cd, Ni and Zn was much higher than the permitted maximum limits in the decree. In soil B, only the leaching of Ni exceeded the maximum limit.

The neutralization experiments showed that industrial side streams (alkaline ashes and lime residues) were able to prevent the acidification of the two different types of acid generating dredged spoils during the 23-week oxidation period. The calculated 100 % theoretical neutralization need (TNN) was able to both prevent acidification as well as leaching of harmful substances. The treated samples with lower levels of neutralization agents started to acidify. The leaching of harmful metals in the acidified (pH < 4) treated samples was roughly at the same level as in the oxidized, untreated reference dredged spoils. The investigated biochar did not have a neutralizing effect, nor was it able to bind harmful substances and metals that became soluble due to acidification.

Based on the results, alkaline side streams such as ashes and lime residues can be used as neutralizing agents for acid sulfate soil materials to prevent the leaching of harmful substances. In addition, industrial side streams give a good opportunity to treat acid sulfate soil materials in a sustainable way. However, the legislation must be considered, and it would be recommended to verify the correct neutralization amount with field tests to achieve the right level of neutralization agents needed.

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Table 11

Soluble concentration (%) of the total concentration of the treated sample in Soil B. 100 %, 50 % and 10 % theoretical neutralization need (TNN) of Calcite and the industrial side streams used. Soil pH was measured after incubation. 0* = below detection limit.

Sample	pH	Sb	As	Ba	Cd	Cr	Cu	Pb	Mo	Ni	Se	Zn	V	Al	Co	Fe	Mn	S
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Calcite 100 %	7.7	0.0	1.9	2.0	0.0	0.0	0.4	0.0	22.6	0.0	2.4	0*	0.3	0.0	0.0	0.0	0.0	27.1
Calcite 50 %	7.6	0.0	1.3	2.0	0.0	0.0	0.4	0.0	17.3	0.0	1.9	0*	0.2	0.0	0.0	0.0	0.0	30.3
Calcite 10 %	2.8	0.0	0.7	2.3	45.5	0.1	11.8	0.0	0*	11.0	0*	11.0	0.0	1.3	17.4	0.1	19.4	63.4
FBC ash A 100 %	8.0	0*	4.7	4.0	0*	0*	0*	0*	53.7	0*	3.8	0*	0.6	0.0	0.0	0.0	0.0	64.7
FBC ash A 50 %	7.9	0*	3.9	3.2	0.0	0.0	0.4	0.0	37.5	0.0	2.9	0*	0.6	0.0	0.0	0.0	0.1	37.2
FBC ash A 10 %	3.7	2.0	0.5	3.2	40.9	0.0	0.8	0.0	0.3	6.7	0*	8.9	0.0	0.1	11.4	0.1	18.4	53.2
FBC ash B 100 %	7.9	0.0	3.4	1.4	0.0	0.0	0.8	0.0	63.8	0.1	2.4	0.0	1.0	0.0	0.1	0.0	0.0	25.0
FBC ash B 50 %	7.2	0.0	0.8	2.6	0.0	0.0	0.4	0.0	29.3	0.0	1.4	0*	0.2	0.0	0.0	0.0	0.0	27.1
FBC ash B 10 %	2.9	0.0	1.0	2.4	45.5	0.1	8.6	0.0	0.3	10.4	0.5	10.1	0.0	1.2	17.1	0.2	19.3	52.4
Lime kiln dust A 100 %	7.2	0.0	0.7	2.6	0.0	0.0	0.2	0.0	18.9	0.0	1.0	0*	0.1	0.0	0.0	0.0	0.1	36.1
Lime kiln dust A 50 %	6.9	0.0	0.6	3.0	0.0	0.0	0.3	0.0	21.5	0.1	1.4	0.1	0.1	0.0	0.0	0.0	0.1	37.2
Lime kiln dust A 10 %	3.0	4.0	0.8	2.6	40.9	0.1	5.8	0.1	0.3	9.8	0*	9.6	0.0	0.6	16.2	0.4	21.6	60.7
Lime kiln dust B 100 %	7.8	0.0	2.2	1.9	0.0	0.0	0.5	0.0	31.9	0.1	1.9	0*	0.5	0.0	0.0	0.0	0.0	26.1
Lime kiln dust B 50 %	7.7	4.0	2.0	1.7	0.0	0.0	0.7	0.1	24.2	0.1	1.4	0.0	0.5	0.0	0.0	0.0	0.0	18.6
Lime kiln dust B 10 %	2.9	0.0	0.5	2.2	50.0	0.1	7.5	0.0	0.3	12.4	0*	11.8	0.0	1.8	19.1	0.1	18.7	68.6
Biochar 100 %	3.0	0*	0.6	2.1	40.9	0.1	6.7	0.0	0.3	12.9	0*	12.4	0.0	0.7	21.6	0.3	22.6	56.6
Biochar 50 %	3.0	0*	0.6	2.2	31.8	0.1	7.4	0.0	0.3	10.3	0*	9.7	0.0	0.9	16.6	0.1	15.5	48.7
Biochar 10 %	2.8	0*	0.9	2.0	45.4	0.1	8.9	0.0	0*	12.0	0*	11.0	0.0	1.4	18.4	0.0	18.4	57.4

CRediT authorship contribution statement

Thomas Kronberg: Writing – original draft, Conceptualization, Methodology, Investigation, Visualization. **Timo Tarvainen:** Writing – original draft, Conceptualization, Methodology. **Jaakko Auri:** Writing – review & editing, Investigation, Methodology, Visualization. **Jan-Erik Eriksson:** Writing – review & editing, Conceptualization, Methodology, Investigation. **Stefan Mattbäck:** Writing – review & editing, Methodology, Investigation. **Anton Boman:** Writing – review & editing, Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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