

# STABILIZATION OF SULFIDE-RICH SEDIMENTS WITH INDUSTRIAL SIDE STREAMS

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## KEYWORDS

Acid sulfate soils, Stabilization, Industrial side streams, Leaching.

## ABSTRACT

The dredged spoils in the coastal areas of Finland are very likely potential acid sulfate soils that, when spread on land, begin to oxidize and form sulfuric acid. The drop in pH dissolves harmful elements from the clay that are transferred to the environment with the runoff water.

Chemical analyses were performed to determine the pre-incubation characteristics of the fresh sample and the sample after 19 weeks of incubation. The total concentration of the elements in the spoil was analyzed after digestion in aqua regia. The leaching of metals and metalloids was determined by using the two-stage shaking test method.

Seven recipes with industrial side stream (ash, blast furnace slag and lime residues) additions were developed, with an emphasis on reducing the amount of cement needed for clay stabilization. Both laboratory and field tests were performed. The unconfined compression strength (UCS) was determined after 7, 28 and 91 days. The leaching of elements from the stabilized samples was determined.

The measured strength development and successful immobilization of harmful elements suggest that sulfate-rich sediments can be used as building ground materials. Industrial side streams can substitute part of the cement traditionally used for stabilization. Accordingly, a significant reduction in carbon footprint, calculated as CO<sub>2</sub> emissions, can be achieved.

## 1. INTRODUCTION

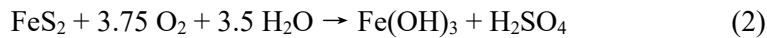
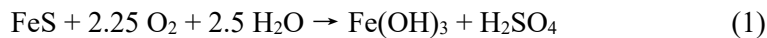
Dredging is necessary for deepening and maintaining waterways and port areas. However, disposing of the large amounts of dredged sediment is challenging. Dredging and dumping the sediments at sea can negatively affect

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the aquatic environment. Thus, increasing interest is paid in utilizing dredged spoils for land construction. However, the beneficial use of dredged spoils requires the stabilization of clays in the sediment. Legislation must also be considered to determine the risks of the total and soluble concentrations of elements or compounds leaching from the dredged spoils, industrial side streams, and treated dredged spoils.

In the Baltic Sea countries, sediments deposited in the Littorina Baltic Sea may be rich in acid-generating sulfides. When the sulfide-rich sediments are disposed on land, the sulfides in the usually metastable iron sulfide, denoted FeS in reaction 1) and pyrite (FeS<sub>2</sub>) in reaction 2), start to oxidize, leading to the formation of sulfuric acid and subsequent release of harmful elements [1].



If the pH drops below 4 due to the oxidation of sulfide minerals, an actual acid sulfate soil is formed.

In geotechnical engineering, stabilizing different clays is widely applied [2-5]. Stabilization solidifies soil materials otherwise unsuitable for construction due to their poor load-bearing capacity. Stabilization hardens the clay soil, thus making it suitable for construction grounds. Stabilization immobilizes harmful substances and prevents the acid formation characteristic of sulfide-containing soils. Cement is typically used for stabilization. However, cement production negatively impacts the environment due to high CO<sub>2</sub> emissions and energy consumption. Thus, using industrial waste and side streams (e.g., slag, ash, and lime residues) as part of the stabilization recipes significantly reduces CO<sub>2</sub> emissions compared to stabilization with cement alone.

In this work, industrial side streams were used to stabilize sulfide-rich sediments. The amount of cement was reduced by using a high amount of fly ash in combination with blast furnace slag, bottom ash, and lime residues. Another goal was to prevent the dissolution of harmful metals from the stabilized soil, thus enabling the safe use of sulfide-rich sediments in the soil underlying the construction foundations. The work was carried out both in the laboratory and in field experiments.

## **2. MATERIALS AND METHODS**

The dredged spoil used in this study was an organic-rich silty clay typically found in the coastal area of southern Finland. Dredging was used to deepen

and maintain the waterways of a narrow bay called Matalahti (Naantali, Finland). The dredged sediments were deposited on land close to the bay.

Chemical analyses were performed to determine the pre-incubation characteristics of fresh dredged sediments and oxidized samples after 19 weeks of incubation. Titratable incubated acidity (TIA) was determined by mixing the soil with KCl and then titrating it with NaOH to a pH of 5.5 [6]. Total element concentrations in the sediments and side streams used for the stabilizations were determined after digestion in aqua regia by ICP-MS or ICP-OES. The leachable concentrations of elements were determined by using the two-stage shaking test (method SFS-EN 12457-3).

Cement (Plus, CEM II/B-M S-LL 42,5N, Finnsementti Oy) was used as a reference binder in the stabilization tests. The Plus cement is a blended cement consisting of 65-79% clinker and 21-35 % blast furnace slag and calcite. Fly ash and three alternative stabilizing materials were chosen: 1) A commercial ground granulated blast furnace slag (GGBFS) product (KJ 400, Finnsementti Oy). 3) Fly ash received from a combined heat and power (CHP) plant using a mixture of biomass (60-75%), coal (25-40%), peat (1-2%), and refinery gas (1-2%) as fuel. 4) Lime kiln dust (LKD) collected from the lime kiln in lime production (Nordkalk Oy). 5) Municipal solid waste incineration bottom ash (MSWI), received as a 0-2 mm fraction from Suomen Erityisjäte Oy.

Laboratory experiments were first performed to optimize the stabilization recipes for the field test. In the field tests, the dredged spoil was spread on the test area and left to dry for 6 months before mixing with the binders. The area was divided into squares and in each square, the fly ash was spread and mixed with the spoil. The following day, the other binders were mixed into a depth of 1 meter (Figure 1). Samples were taken from each test square and test cylinders for unconfined compression strength (UCS) measurements were prepared.

The stabilization recipes were calculated as the mass of binders in 1 m<sup>3</sup> of spoil (Table 1). In total, 350 kg binders, including an ash content of 100-200 kg/m<sup>3</sup> were added to 1 m<sup>3</sup> spoil. In one recipe (R7), only 600 kg ash per 1 m<sup>3</sup> spoil was added. The raw materials were weighed and mixed in a Hobart mixer for two minutes. Small, compacted cylinders, 56 mm in height and 28 mm in diameter (2:1) were prepared by tapping the tube against the table. The sample cylinders were tightly plugged at both ends. The samples were stored for 2 days at room temperature (23 ± 1°C) and then moved to a refrigerator (6 ± 1°C) to wait for the compression strength measurements. The UCS was measured after designated curing times of 7, 28, and 91 days.

UCS was measured using a universal testing machine (L&W Crush tester) operated at a speed of 1 mm/min. The maximum load (N) at the breaking point was used to calculate the strength (kPa). The average strength was based on

triplicate measurements/cylinders for each mixture. The mixed samples from each test area in the field tests were directly put into cylinders for the strength measurements as given above.

The two-stage shaking method was used to measure the leachable concentration of the elements from the stabilized samples after 91 days.



Figure 1. Field test: a) dredged spoil before stabilization, b) adding binders, c) mixing, and d) test field ready.

Table 1. Stabilization recipes calculated for 1 m<sup>3</sup> wet sediment with the average mass of 1300 kg.

Recipe	Ash	Cement	GGBFS	LKD	MSWI
	kg/m <sup>3</sup>	kg/m <sup>3</sup>	kg/m <sup>3</sup>	kg/m <sup>3</sup>	kg/m <sup>3</sup>
R1	200	150	0	0	0
R2	200	50	100	0	0
R3	100	150	0	0	100
R4	100	50	100	0	100
R5	200	50	50	50	0
R6	200	25	75	50	0
R7	600	0	0	0	0

### 3. RESULTS AND DISCUSSION

#### Properties of dredged sediment

The pH of unoxidized dredged spoil was 7.8 but decreased to 2.7 during the incubation for 19 weeks. The material was fine-grained, with clay particles < 2  $\mu\text{m}$  around 52%. The measured loss on ignition (LOI) was 5.1%. For the unoxidized material, the total sulfur and sulfide contents were 1.9% and 1.6%, respectively. The incubated acidity (TIA<sub>pH5.5</sub>) was 158 mmol H<sup>+</sup>/kg. This value exceeds the limit of 100 mmol H<sup>+</sup>/kg, which is defined as a high risk of acidification in fine-grained soil materials, thus being classified as acid sulfate soil material.

The total concentrations of elements in the fresh dredged spoil after digestion in aqua regia and the leaching of harmful metals are shown in Table 2. Element leaching from the fresh unoxidized dredged spoil was very low; only molybdenum (0.9 mg/kg) showed significant leaching. However, several harmful elements leached from the oxidized spoil sample with a pH of 3.4. The measured soluble element concentrations were compared to the Finnish decree on the recovery of certain wastes in earth construction (MARA, 843/2017) [7]. The solubility limits in the decree can be used to assess whether stabilizing or neutralizing soils with industrial side streams possesses environmental risks. The soluble concentrations were compared to the maximum permitted solubility in covered and paved field structures. The leachable concentrations of Cd (0.20 mg/kg), Ni (6.4 mg/kg), and Zn (27.7 mg/kg) exceeded the maximum limits given in MARA decree (Cd 0.06 mg/kg, Ni 1.2 mg/kg, and Zn 12 mg/kg) for a paved field structure.

#### Stabilisation results

Strength, given as the UCS values, for the laboratory and field samples after 7, 28, and 91 days are shown in Figure 2. The average UCS for the different stabilized field samples varied between 750 kPa and 2500 kPa after 91 days. These values were doubled compared to those received for the samples sediments stabilized in the laboratory (400 to 1200 kPa). The standard deviation was relatively high (400 -700 kPa) for the field stabilization samples but clearly lower (< 100 kPa) for the laboratory stabilization samples. The high standard deviation implies that mixing the binders with the sediment was not homogeneous in the field tests. The significantly higher strength values in the field tests compared to the laboratory tests can be explained in different ways. The inhomogeneous mixing and lower water content of the dredged spoil in the field test likely influenced the results. Binders on top of the soil and mixing from above did not provide a homogenous material in the depth direction but probably gave a higher content of binders close to the surface. The dredged spoil had time to dry before adding the binders. Thus, the relative

share of binders was likely higher in the field tests than in the laboratory tests. The water content had decreased from 280% when deposited on land to around 110% after 6 months. Most likely, the water content varied locally in the field squares. In the laboratory experiments, the water content was more even, about 130%, thus explaining the higher strengths in the field experiments. It was assumed that the exact location of the sampling point for the field tests affected the results, as suggested by the relatively high standard variation of the measured strengths.

The laboratory experiments were assumed to describe better the impact of the different side streams on stabilization. Substituting slag GGBFS (recipes R1 vs R2 and R6) for about 65% of the cement provided similar strength values after 91 days. In contrast, a slower early strength development was measured for the slag mixtures. GGBFS has been successfully used to substitute cement in concrete and, together with limestone, in blended types of cement [8]. Substituting MSWI bottom ash for 100 kg/m<sup>3</sup> fly ash (stabilization recipes R5 and R6) did not affect the strength. R8, with the lowest cement content, showed the lowest strength. The strength of the test area with ash as the stabilizer (R7) was about 100 kPa. However, the dredged spoil mixed with 600 kg/m<sup>3</sup> fly ash was hard enough to enter even with a caterpillar after 14 days, most likely due to the drying and compaction of the mixture.

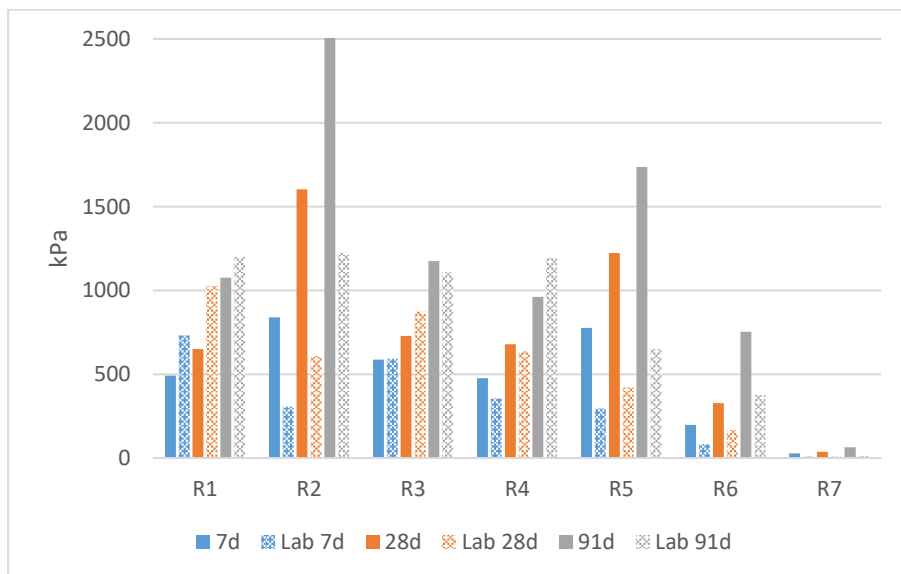


Figure 2. The unconfined compression strength (UCS) of the soil and binders mixed in the laboratory and in the field.

The leaching experiments were performed for the field test samples. The leaching of elements after stabilization was generally low. Cd, Ni and Zn leach from acid sulfate soils upon oxidations. However, the concentrations of

these elements leaching from the stabilized samples was low. In contrast, the solubility of Mo increases with increasing pH; thus, the leaching of Mo increased from the stabilized samples and exceeded the limit allowed for a covered field structure (0.5 mg/kg). The industrial side streams used as binders affected the leaching results. The total concentration of copper (1730 mg/kg) was very high in MSWI. However, only a small part of copper (2.7 mg/kg for sample R3) was leached out, but yet exceeding the limit for a covered field (2 mg/kg). On the other hand, the value was below the limit of a paved field structure (6 mg/kg). The release of vanadium for mixtures containing slag (GGBFS) exceeded the MARA limits. The total concentration of vanadium in GGBFS was 396 mg/kg. As vanadium concentration was very low in the dredged spoil, the leached vanadium must come from the slag used for the stabilization.

Table 2. Total concentration of the dredged spoil, leaching of elements from the dredged spoil fresh and incubated for 19 weeks and from the field stabilisation recipes after 91 days.

Element	Total conc.	Leaching								
	Sediment			Recipes						
	Fresh mg/kg	Frsh mg/kg	incu- bated mg/kg	R1 mg/kg	R2 mg/kg	R3 mg/kg	R4 mg/kg	R5 mg/kg	R6 mg/kg	R7 mg/kg
Sb	0.62	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
As	9.9	0.1	<0.05	0.1	0.1	<0.05	0.1	0.053	0.051	0.1
Cd	0.33	<0.05	0.20	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cr	81	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cu	47	<0.5	0.5	2.2	1.8	7.2	0.9	2.2	1.8	<0.5
Pb	17	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Mo	2.4	0.9	<0.05	1.2	1.3	2.7	0.7	1.4	1.1	1.3
Ni	51	0.1	6.4	0.8	<0.07	0.8	<0.07	0.8	0.6	<0.07
Se	3.6	<0.05	<0.05	<0.05	0.1	<0.05	0.1	0.1	0.1	0.1
Zn	181	<0.6	27.7	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
V	86	0.4	<0.2	0.6	2.2	0.5	3.3	2.0	3.0	0.7

#### 4. CONCLUSIONS

The presence of acid sulfate soils and potential acid sulfate soils should be identified and considered in land construction at an early stage, preferably even before excavating or dredging. Acidic sulfate soils are challenging for land construction because of poor geotechnical properties, e.g., high water content and organic matter. Notably, such soil oxidation might lead to the release of potentially harmful elements in run-off waters. The dredged sediment studied contained acid sulfate soil material. Thus, harmful elements (Cd, Ni, and Zn) leached from unstabilized sediments during incubation.

Four industrial side streams were tested as stabilizers: blast furnace slag, ash, lime kiln dust and MSWI bottom ash. The field and laboratory tests showed that dredged sediment could be stabilized with cement and industrial side stream mixtures. This implies that cement can partly be replaced with the side streams, depending on their composition. All mixtures achieved good geotechnical properties. The stabilization effectively neutralized the acid-producing capacity of the sediment. Thus, leaching of harmful substances from the stabilized masses was minor. The amount of industrial side stream needed suppressing the leaching must be optimized for each side stream and sediment to fulfill the limits in legislation for a particular application.

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