UDK 69.004.8:658.567.1
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 47(3)353(2013)

DREDGED MUD FROM THE PORT OF KOPER – CIVIL ENGINEERING APPLICATIONS

MULJ IZ LUKE KOPER – UPORABNOST V GRADBENIŠTVU

Ana Mladenović[1], Željko Pogačnik[2], Radmila Milačič[3], Anica Petkovšek[4], Franka Cepak[5]

[1]Slovenian National Building and Civil Engineering Institute, Dimičeva 12, 1000 Ljubljana, Slovenia
[2]Salonit Anhovo, Joint-Stock Co., Vojkova 1, 5210 Deskle, Slovenia
[3]Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
[4]University of Ljubljana, Faculty of Civil Engineering and Geodesy, Jamova 2, 1000 Ljubljana, Slovenia
[5]Luka Koper, d. d., Vojkovo nabrežje 38, 6501 Koper, Slovenia
ana.mladenovic@zag.si

Prejem rokopisa – received: 2012-10-02; sprejem za objavo – accepted for publication: 2012-11-08

The Port of Koper, one of the biggest and the most important ports in the Northern Adriatic Sea, is constantly faced with the problems caused by the accumulation of marine sediments inside the port, disturbing some of the port's crucial operations. However, these sediments can be viewed as a potential raw material and, in order to define the best way of using them in the civil-engineering field, an extensive research project has been launched. The preliminary results of this project are presented and discussed in the paper. So far the project has given two main results: first, the concentration of heavy metals in the aqueous leachates is low and, secondly, in their present state, the sediments are too wet, so that there are only limited possibilities for drying them out naturally. For this reason additional technological treatment will be needed.

Keywords: dredged mud, civil-engineering applications

Luka Koper, kot eno najpomembnejših pristanišč v severnem delu Jadranskega morja, se nenehno spopada s težavo akumulacije sedimentov na plovnih poteh, kar povzroča težave pri najbolj kritičnih delovnih zmogljivostih pristanišča. Po drugi strani ta material lahko obravnavamo kot potencialno surovino v gradbeništvu. V prispevku so podani preliminarni rezultati interdisciplinarnih raziskav, ki kažejo naslednje: prvič, koncentracija težkih kovin v izlužkih je nizka in drugič, v stanju, kot je, je sediment preveč vlažen, da bi ga bilo mogoče osuševati z naravnimi postopki in je zato potrebna dodatna tehnološka obdelava.

Ključne besede: mulj, uporaba v nizkih gradnjah

1 INTRODUCTION

The Port of Koper is one of the biggest and the most important ports in the Northern Adriatic Sea, and it is primarily transit oriented. It is a multi-purpose port with two piers, 26 berths, and 12 specialized terminals. One of its main problems is related to a constant accumulation of marine sediments inside various parts of the port, resulting in disturbances to some of its most crucial operational capacities. A total of 80000 m^3 of sediments have to be removed annually. The sediment found in the Port of Koper is a mixture of clay and silt (henceforth referred to as mud) and represents the kind of waste, for which there is insufficient disposal space along the Slovenian coast (**Figure 1**). According to the slogan "No waste here, just resources!" this sediment can be viewed as a potential raw material. In order to define the best way of using it in civil-engineering applications, an extensive research project is under way. Some of the preliminary results are presented and discussed in the paper.

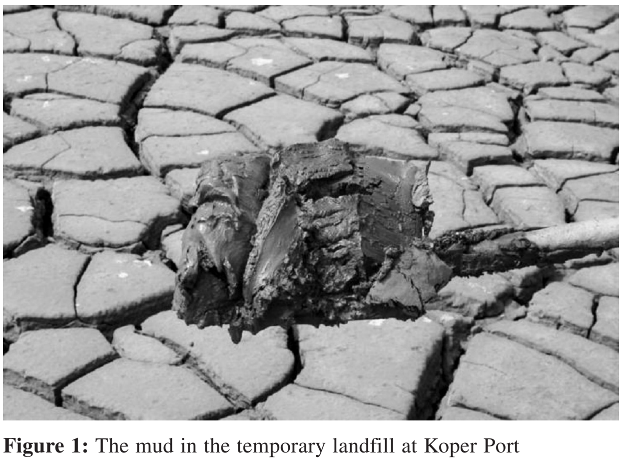

Figure 1: The mud in the temporary landfill at Koper Port
Slika 1: Mulj na začasni deponiji v Luki Koper

2 EXPERIMENTAL WORK

2.1 Materials and methods

In January 2012 several batches of mud were taken from the temporary deposits at the end of Pier I (the mud from Basin 1) and Pier II (the mud from Basin 2). All the material was homogenised and divided into subsamples for the targeted analyses – except for the chemical analyses, which were performed on the mud from each location separately and, additionally, on the sample from Basin 3. Quantitative mineralogical compositions were determined using X-ray diffraction (Phillips PANalytical

X'Pert PRO equipment with Cu Kα radiation). Powdered samples were scanned at a rate of 2 °/min, over the range of 2–70 ° (2θ). A particle-size analysis was performed using a Cilas 920 laser granulometer in the water as a suspension media. The samples for the thermal testing were heated in cylindrical pots, made of inert materials, by applying a temperature scan of 10 °C/min at room temperature, up to 1400 °C. A STD 2960 Simultaneous DTA-TGA analyser was used, complemented with the Universal Analysis for Windows 95/98/NT software tool, edition 2.5H.

Several geomechanical tests were performed in order to evaluate the basic properties and behaviour of the mud under loaded conditions. The most crucial test was the edometer test carried out according to SIST/ISO/TS 17892-5:2004.

In order to evaluate the environmental impact, the extent of pollution was estimated by determining the total metal concentrations, by identifying the most hazardous, highly mobile metal fractions and by partitioning the metals into easily, moderate soluble, and sparingly soluble fractions. For this purpose various sequential extraction procedures were applied.[1–3] Special attention was paid to the estimation of the content of the highly mobile, biologically available fractions of metals in the sediments. The total metal concentrations in the sediments and in various stages of the sequential-extraction procedure were determined using inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7700x ICP-MS. A CEM Corporation CEM MARS 5 Microwave Acceleration Reaction System was used to digest the sediments. Mechanical shaking of the samples was performed with a Vibromix 40 elliptical, orbital shaker. The samples were centrifuged using a Hettich Universal 320 Centrifuge, and a WTW 330 pH meter was used to determine the pH values.

2.2 Reagents

Merck suprapur acids and Milli-Q water (Direct-Q 5 Merck suprapur acids and ultrapure water) were used for the preparation of the samples and standard solutions. All the other reagents were of the analytical reagent grade. A Stock IV CertiPUR ICP Multi Element Standard Solution containing (1000 ± 10) mg L^{-1} element concentrations in 1 mol L^{-1} HNO_3 was obtained from Merck. Sartorius 0.45 µm cellulose nitrate membrane filters with 25 mm diameters were used in the filtration procedure.

2.3 Determination of the total metal and aqueous leachate concentrations

0.2 g of a dry homogenised sediment was weighed in a Teflon tube, and microwave-assisted digestion using a mixture of HNO_3, HCl and HF was applied according to the procedure proposed by Ščančar et al.[3] All the analyses were performed in triplicates. In order to determine the element concentrations of the aqueous leachates, 10 g of each sample were shaken for 24 h with 100 mL of water, centrifuged and filtered through 45 µm membrane filters. The elements in the aqueous leachates were determined by ICP-MS.

3 RESULTS AND DISCUSION

3.1 Particle-size analysis

The results of the particle-size analysis showed that the majority of the grains had a dimension of less than 2 mm, and that the quantity of the grains with a size of 63 µm or less varied between 75 % and 97 % by mass. About 40 % by mass of the grains were under 5 µm, i.e., within the clay size range.

3.2 Mineralogical composition

The quantitative mineral composition of an average sample of the mud determined by XRD is presented in **Table 1**. The results show that clay minerals, i.e., illite, chlorite and Ca montmorillonite, made up more than 40 % of the investigated mud. These results are in good correlation with those obtained by Ogorelec[4].

Table 1: Quantitative mineral composition of the mean sample of mud
Tabela 1: Kvantitativna mineralna sestava povprečnega vzorca mulja

Mineral	% by mass
Illite/muscovite	25
Chlorite	20
Quartz	21
Calcite	19
Feldspar	9
Dolomite	3
Pyrite	2
Ca montmorillonite	1

3.3 Thermal analysis

Within the range between 200 °C and 450 °C a strong exothermic peak was observed. This peak represents an oxidation of organic matter and dewatering of clayey mineral assemblages and probably some amorphous Fe-Al oxide gels (**Figure 2**). Within the temperature interval between 400 °C and 500 °C the $S + O_2 \Leftrightarrow SO_2$ reaction takes place, which is due to the decomposition of pyrite into pyrrhotite and free oxygen, which reacts at the same time with H_2^+; $H_2 + 1/2O_2 \Leftrightarrow H_2O$ within the temperature range of 530–580 °C, producing another exothermic peak.[5] At a temperature of about 580 °C the $\alpha \rightarrow \beta$ inversion of quartz and a likely dehydroxylation reaction of kaolinite[6] occur. In the same endothermic interval, illite loses its constitutive water, which is caused by dehydroxilation of the octahedral sheet, as the hydroxyl groups of the tetrahedral sheet are gradually removed up to a temperature of 850 °C.[7] The second endothermic peak at about 600 °C and another, smaller one, at around 700 °C can be attributed to chlorites.[3] The third and

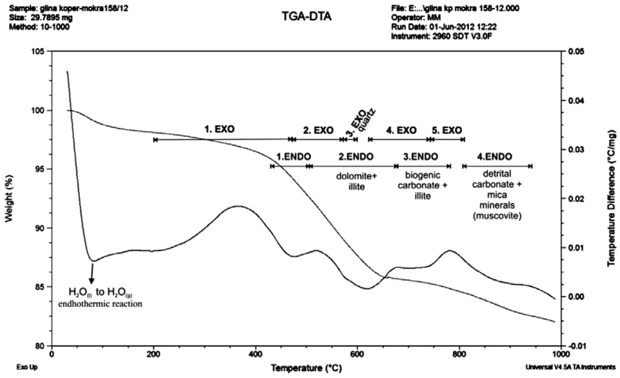

Figure 2: TGA-DTA analysis
Slika 2: TGA-DTA analiza

fourth endothermic peaks form a decarbonatization interval: (a) calcium carbonate derived from marine fauna skeletons, i.e., a biogenic carbonate; (b) dolomite; and (c) terrigenic carbonate.[8] The final exothermic peak, at approximately 800 °C, belongs to various phase transformations of amorphous Fe-Al minerals.[6]

3.4 Geomechanical parameters

The initial research was focused on determining the basic physical and mechanical parameters that are crucial for evaluating a possible stabilization of the mud. It was concluded that the content of the water in the mud is extremely variable (from 55 % to 95 % by mass) and that the density of the untreated material is very low so that it is not possible to stabilise it in its existing form. It can be seen, from the edometer curves, that, at an effective normal pressure of 200 kPa, it is possible to achieve a pore coefficient of between 0.9 and 1.1, which corresponds to the moisture content of between 33 % and 40.7 %. Only at such moisture contents (i.e., between 33 % and 40 %) the material is close to the state when a

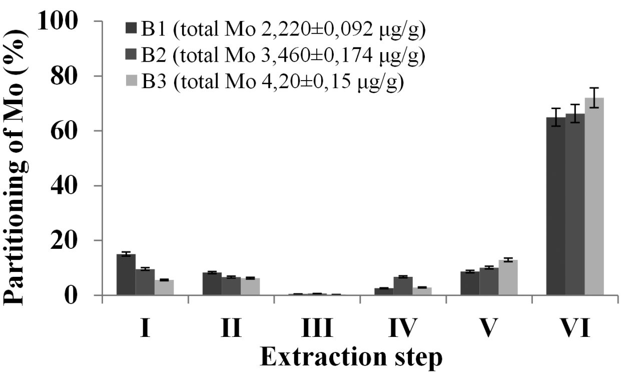

Figure 3: Partitioning of Mo between various phases (I: Water-soluble, II: Exchangeable, III: Bound to carbonates, IV: Bound to Fe and Mn oxides, V: Bound to organic matter, VI: Residual fraction) in sediments (B1, B2 and B3) from Luka Koper
Slika 3: Porazdelitev Mo med različne faze sedimenta (B1, B2 in B3) iz luke Koper: (I: vodotopni, II: izmenljivi, III: vezan na karbonate, IV: vezan na Fe in Mn okside, V: vezan na organsko snov, VI: težko topni ostanek)

chemical stabilization by means of inorganic binders, e.g., fly ash, lime, cement and their various combinations, is technically and technologically feasible.

3.5 Environmental analysis

In order to estimate the extent of pollution, the total element concentrations and the concentrations in the aqueous leachates were determined. From the results of these analyses and a comparison with the limiting values prescribed by the existing legislation for the inert and non-hazardous waste, it is clear that the highest total element concentrations were found in the sediment from Basin 3. The elevated total element concentrations were observed in the case of Cr (within the range from 200 mg/kg to 380 mg/kg), Ni (within the range from 140 mg/kg to 175 mg/kg) and As (within the range from 15 mg/kg to 40 mg/kg), i.e., the concentrations that are higher than those found in the sediments elsewhere in the Slovenian costal area.[3] In general, the concentrations in the aqueous leachates are also the highest for the sediment from Basin 3, but still lower than the limits set by the legislation for the inert waste leachates.[9] In order to estimate the partitioning of the elements between the easily and sparingly soluble sediment fractions, a 6-step sequential-extraction procedure was also performed. The data obtained indicated that the measured concentration of the elements in the easily soluble fractions was, in general, very low. The only exception was Mo. The partitioning of Mo is presented in **Figure 3.** It is clear that the easily soluble fraction (i.e., the water-soluble fraction and the exchangeable fraction) makes up about 25 % of the sediment from Basin 1 and about 10 % of the sediment from Basins 2 and 3. It can be concluded that, with regard to the total heavy-metal concentrations, the concentrations in the aqueous leachates and the partitioning of the elements between easily and sparingly soluble sediment fractions, the sediments from the basins of the Koper Port can be used as a secondary material in civil engineering.

4 CONCLUSIONS

Preliminary results show that the mud from the Port of Koper does not represent a threat to the environment with regard to heavy-metal pollution. However, due to its salt content it is not possible to plan the use of this mud in the areas outside the Port of Koper. It is planned to use an appropriate treatment to fix the chlorides within the building composite. Due to a high quantity of water in the mud, it will be more economical to stabilize it with a drying-out process, using suitable technology.

Acknowledgments

The results were obtained within the ARRS project "Sediments in aquatic environments: their geochemical and mineralogical characterization, remediation and use as secondary raw materials", 2011–2014.

5 REFERENCES

[1] A. Šömen Joksič, S. A. Katz, M. Horvat, R. Milačič, Comparison of single and sequential extraction procedures for assessing metal leaching from dredged costal sediments, Water, Air and Soil Pollution, 162 (**2005**), 265–283

[2] R. Milačič, J. Ščančar, S. Murko, D. Kocman, M. Horvat, A complex investigation of the extent of pollution in sediments of the Sava River, Part 1, Selected elements, Environmental Monitoring and Assessment, 163 (**2010**), 263–275

[3] J. Ščančar, T. Zuliani, T. Turk, R. Milačič, Organotin compounds and selected metals in the marine environment of Northern Adriatic Sea, Environmental Monitoring and Assessment, 127 (**2007**), 271–282

[4] B. Ogorelec, M. Mišič, J. Faganeli, P. Stegnar, B. Vrišer, A. Vukovič, The recent sediment of the Bay of Koper (Northern Adriatic), Geologija, 30 (**1987**), 87–121

[5] G. Locher, Mathematical models for the cement clinker burning process, ZKG International, 55 (**2002**), 29–50

[6] R. C. Mackenzie, The differential thermal investigation of clays, Mineralogical Society (Clay Minerals Group), London 1957, 456

[7] J. H. Araújo, N. F. da Silva, W. Acchar, U. U. Gomes, Thermal decomposition of illite, Material Research, 7 (**2004**), 359–361

[8] Ž. Pogačnik, J. Pavšič, A. Meden, Geological records as an indicator of the thermal characteristics of mudstones within the temperature range of decarbonatisation, Mater. Tehnol., 43 (**2009**) 3, 157–163

[9] Official Gazette of the Republic of Slovenia, No. 61/11, 2011