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SOIL-WASHING AND THERMAL PLASMA TREATMENT FOR DECONTAMINATION OF DREDGED MARINE SEDIMENTS FROM THE MIDIA PORT – ROMANIA

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Abstract

The aim of this paper is to show the results of two methodological approaches applied for decontamination of the Midia Port dredged sediment to assess their potential reusability. Firstly, the sediment samples were defined in physical, chemical, microbiological and ecotoxicological terms. The results were compared to the limit values established by environmental regulations for dredged sediment management. Some sediment samples exposed a very high concentration of hydrocarbons; the sediments were classified in three categories on the basis of their level of organic/inorganic pollutants. The polluted sediment samples were subjected to the soil-washing treatment. The post treatment analysis revealed that the coarse silty and sandy fractions resulted unpolluted. The soil-washing induced the physical concentration of pollutants (*i.e.* C>12) in the silty-clay fraction. The wastewater from the treatment plant, once treated, showed no critical issues. After soil-washing treatment, the sediment samples were exposed to a laboratory scale 30kW RF thermal plasma source. Two types of plasma assisted treatments have been performed: the carbothermal process (to evaluate the technical feasibility of silicon extraction during material inertization) and the vitrification process (only for material inertization). Scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS) with X-ray fluorescence (XRF) and leaching tests were used to investigate the obtained material. The acquired results revealed a decontamination of the collected sediments with leaching test results below legal limits. EDS analysis showed the increment of silica (SiO₂) content by about 5-7 % after the plasma treatment and that the localized extraction of silicon by the carbothermal reduction process has been obtained.

Key words: Midia Port, plasma treatment, remediation, sediment management, soil-washing

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1. Introduction

At the European level, the total quantity of the dredged sediments reaches 200 million cubic meters per year (SEDNET, 2011). Mostly, the dredged materials are directly transferred to the corresponding

basins and associated water is discharged into the surrounding environment, sometimes without paying particular attention to the entire suite of environmental risk associated with the waste management. The process linked to dredged materials represents one of the most important subjects regarding the coastal zone

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management and it is obvious that its environmental sustainability should be enhanced.

A sustainable approach in relation to the management of dredged material requires a change of focus: rather than considering dredged material as a waste, dredged sediment needs to be seen as a resource. Issues of perception remain one of the biggest challenges to those promoting sustainable dredged material management (SEDNET, 2014).

In actual fact, sediment treatment benefited from much reinforcement. Considerable exploration and experimentation plans are mainly designed to promote technical knowledge for managing and treating contaminated sediments from aquatic environments (marine and freshwater). Several programs have been developed in different countries of the world (Germany, Belgium, Netherlands, Japan, Canada and the United States), (Averett et al., 1990; Averett, 1994).

Recently, a tendency of increasing the environmental awareness corroborated with a more restrictive legislation concerning the dredging operations, dredged sediment management and beneficial use of dredged material has been recorded. Sediments represent an essential element of a marine aquatic system, sustaining a diversity of habitats and ecosystems, playing a determinant role related to the global environmental quality of the investigated area. Since dredging operations and stocking dredged materials inherently cause environmental perturbation, they possibly hold a significant environmental impact. In order to maximize the awareness and limit the extent of this environmental impact, several international conventions have occurred lately. The main subject of the conventions is organizing a profound assessment of the ecological impact before the dredging implementation, in order to predict the potential effects and reduce the uncertainties referring to the levels of impacts (PIANC, 2008).

The beneficial reuses of dredged materials represents a good option to classical "dredge and dispose" concept for many coastal environmental management programs. The present study focuses on the experimental methodologies tested to decontaminate the polluted sediments collected from the Midia Port, aiming their reuse as future

opportunities in industrial and economic development applications. This research is part of the SEDI.PORT.SIL. project ("Recovery of dredged SEDiments of the PORT of Ravenna and SILicon extraction"), conceived to demonstrate an integrated approach for the sustainable management of sediments dredged from ports; co-financed by the European Commission through LIFE+ funds (LIFE09/ENV/IT/00158) and the Port Authority of Ravenna; the project aimed to assess the efficiency of physical, chemical and biological treatments for the decontamination of polluted sediments and associated water, and the technical feasibility of the extraction of Ferrosilicon alloy (FeSi) through a thermal plasma treatment of sediments (Ulazzi et al., 2012).

2. Experimental

2.1. Description of the area

The port of Midia is located at an essential point of the Romanian coastal area, namely the Cape Midia (in the city of Năvodari), at the intersection between the northern and southern units of the Romanian Black Sea coastline (see Fig. 1a). It is one of the subordinated harbors to the main Constanța Port located at a distance of 25 km far away from this.

The port was mainly designed and built to support petrochemical industry activities, founded in the course of the Second World War. Its infrastructure was developed during the late 1970's, in order to be one of the major commercial sea port operators for hydrocarbons along the Black Sea coastline. For a relatively long-lasting interval it has functioned as an important marketing center of the commercial activity in the area. After 1990, it went through a time of low commercial marine activity; currently, it acts as an oil and a general merchandise terminal, serving the largest oil refinery in the southeastern Europe (Petromidia) and the adjacent industrial platform. Covering a total area of 834 ha, of which 234 ha is represented by land, and 600 ha of water, the port of Midia is bordered to the north and south by breakwaters, having a total length of 6.97 km. The area has been subject to many historical and anthropic pollution sources located in the port surrounding area (Fig. 1b).

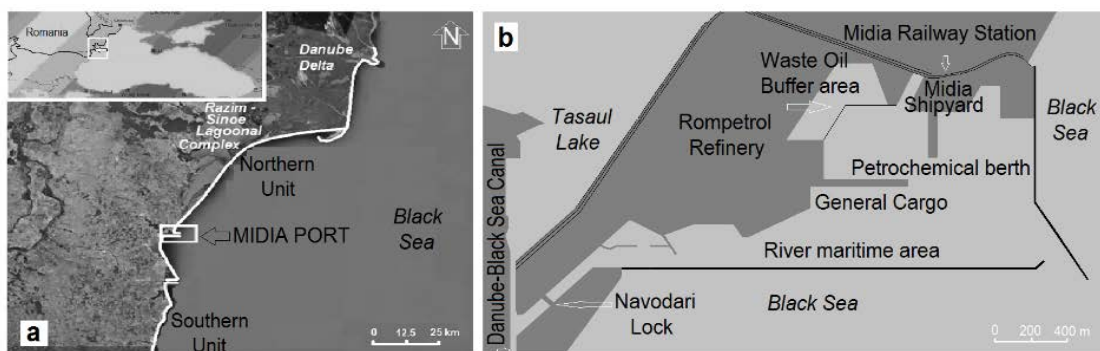


Fig. 1. Illustration of the Black Sea coastline (a), and the graphical representation of the Midia Port area (b), (updated upon [http:// www.google.com/earth/index/html](http://www.google.com/earth/index/html); [http:// www.portofconstanza.com](http://www.portofconstanza.com))

The collected sediment samples were subjected to a methodological evaluation process, to determine their prospective ability to be reused after decontamination treatment. Consequently, the soil-washing technology and thermal plasma treatment were used to decontaminate the Midia Port sediments.

The sediment samples were gathered from the Midia Port perimeter during 2011. Many of the sampling stations were established in the transit area of ships (MDA11-15, MDA11-20, MDA11-21, MDA11-22 and MDA11-23), based on the idea that the most significant accidental oil spills and/or hazardous material from a vessel in traffic or during cargo transfer operations take place in this area. Another sampling station (MDA11-16) was located near the Waste Oil Buffer area (local point source of residual flow) and the other one (MDA11-14) was situated in the Marine area (shipping activities around the port) (Fig. 2).

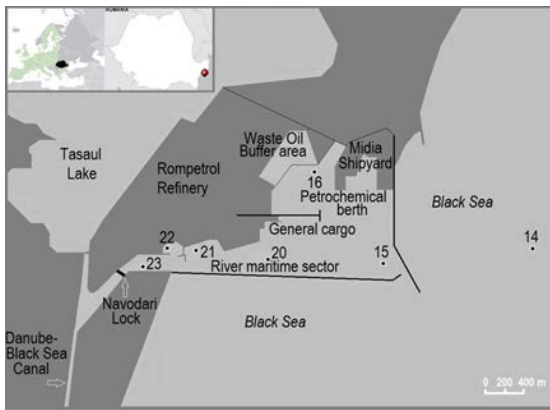


Fig. 2. The sediment sample location in the Midia Port area

The surface sediment sampling was classically conducted using a Van-Veen bodengreifer. The collected sediments were stored in glass jars (1000mL) and placed in a freezer at 4°C prior to distribution to the laboratories.

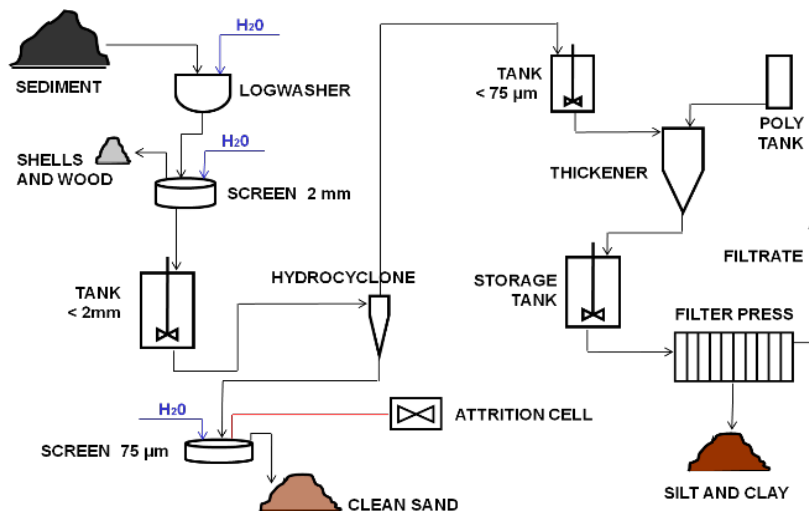


Fig. 3. Illustrative flow diagram of the Soil-Washing lab-scale plant used for treatment tests (sketch-draft accomplished by Diemme Enologia SpA – Italy)

2.2. Material and methods

2.2.1. The Soil - Washing sediment treatment scope and methodology at laboratory scale

The soil-washing is a water-based physical separation process that relies on traditional physical and chemical extraction and separation processes for removing a broad range of organic, inorganic, and radioactive contaminants from soil (Mann, 1999). It's fundamentally a volume reduction, waste minimization treatment technology process, where the following results are achieved on sediments:

- separation of sediments fine particles, as clay, which “host” the contamination from the coarse bulk sediment fractions, such as, sand;
- contaminants dissolution or solubilisation into liquid phase and subsequent removal of the contaminants from the liquid phase.

The soil-washing sediment treatment was accomplished through a Soil Washing Pilot Plant at laboratory scale at Diemme Enologia SpA laboratories (Italy). The incoming sediments for lab-scale plant test (Fig. 3), are combined with water and owing to a dynamic interaction of liquid and solid phases (turbulence) they become completely resuspended.

The resuspended sediment is screened at 2 mm mesh size for the first grain size dissociation. The rejected overscreen mainly composed of organic materials and waste, as wood and shell fragments are disposed, while the underscreen composed of water, solid fraction below 2 mm, as well as contaminants, is pumped through the hydrocyclone (used to separate the solid-liquid suspension phases) for clean sand recovery.

The hydrocyclone separator's rejected fraction, composed of clay (the finest grain-size dimension), water and any residual contaminants, is passed through a clarifier-decanter (solid separation), where the suspended solids are coagulated and sedimented to group into a thick sludge cake form.

Then, the sedimented sludge is sent through a plate filter press for mechanical dewatering. The plate filter press is suitable to reach the minimum possible level of the residual humidity in the final compressed cake. The waste water coming from the Soil-Washing plant and sludge mechanical dewatering techniques is treated within a purification process to reduce contaminants below the specified legislative limits. As soon as the contaminants are separated together with the fine particles, the residual products and waste could be processed through biological post operations adequate to degrade the organic contaminants (assuring a total recovery of this fraction), or, could be disposed.

2.2.2. The laboratory scale thermal plasma treatment: experimental set-up

Thermal plasma technology (Boulos et al., 1994) has been successfully employed in a wide range of industrial applications and in the past decade, it has also become a prominent technology in the field of waste treatment (Gomez et al., 2008; Heberlein and Murphy, 2008). Among several benefits with respect to conventional technologies we specify: high process control, low off-gas flow rates, melting of high temperature materials and rapid decomposition of hazardous substances, together with the possibility of obtaining a final recyclable product.

Thermal plasmas are generated at atmospheric pressure by heating a working gas to temperatures around 10^4 K, in order to achieve partial ionization of the species, and are sustained through ohmic heating by passing or inducing an electric current through the gas. These types of plasmas are characterized by local thermodynamic equilibrium (LTE), meaning that the temperatures of electrons and heavy particles approach each other and the chemical species fractions are close to the equilibrium composition.

Using the plasma technology treatment of contaminated sediments several major advantages could be achieved:

- the high plasma temperature and energy density (up to 10 kW/cm^3) leads to the destruction of all organic contaminants present in the sediments;
- the high heat transfer rate facilitates rapid melting of the heavy metals and mineral phases leading to the formation of a stable non-leaching vitreous matrix;
- the opportunity of yielding marketable co-products when halogens are not present in the waste products;
- the absence of combustion and the use of electric energy to generate the plasma allows the selection of a wide range of process gases (*e.g.*, air, oxygen, argon) lowering the gas flow rate and the off-gas treatment requirements, featuring control over the chemistry of the process.

The most widely used methods for the generation of thermal plasmas are by means of high intensity arc direct current (DC) discharge (Gleizes et al., 2005) and by inductively coupled radio frequency

(RF) discharge (Bernardi et al., 2005; Boulos, 1997). While DC arcs are commonly used in mid and large scale industrial applications due to their higher energy efficiency, RF discharges provide a more stable plasma plume, lower flow velocity and turbulence fluctuations and a higher flexibility in terms of choice of operating gas. The Inductively Coupled Plasma Torch (ICPT) generates a plasma discharge through the ohmic dissipation of currents induced in the plasma by an external RF coil that surrounds the confinement tube. The ICPTs is used as a high enthalpy plasma source whose applications include material treatment, spraying, powders spheroidization, nanoparticles synthesis (Barton and Mordy, 1984; Colombo et al., 2006; Deegan et al., 2006; Drouet et al., 1995). For these reasons the experimental activities (presented in this paper) have been performed using a flexible lab-scale ICPT installation in order to provide a small scale plasma testing environment, reducing the operational costs and the amount of material fluxes needed to perform tests, knowing that eventually the industrial upscale of the process should be performed using a DC plasma torch. The experimental trials have been performed using the 35 kW lab-scale ICPT (Tekna Plasma Systems inc. - model PL-35) available at the Department of Industrial Engineering (DIN) by the University of Bologna (Italy), to provide in a smaller scale the same high temperature and high heat exchange conditions that can be found in an industrial scale installation. Sediment samples have been placed in a graphite crucible and exposed to the RF plasma jet inside a cooled stainless steel chamber in a controlled atmosphere.

The off gases produced during the plasma treatment pass through a cyclone to separate the largest particles and then through a dry collector (Colombo et al., 2012). In Fig. 4, a simplified outline of the inductive plasma reactor system is given. Two different experimental applications were considered:

- the carbothermal reduction procedure, that implies the addition of carbon to the untreated Midia Port sediments, in order to investigate qualitatively the technical feasibility to separate the metallurgical pureness degree silicon (Si) from the silica (SiO_2) content (the technology used allows the extraction of silicon, metallurgical pureness degree silicon and ferrosilicon from the sediment under test);
- the vitrification (inertisation) of contaminants present in sediments.

In the extraction of silicon alloys by means of carbothermal reduction, the main challenge is represented by the choice of the ratio between the amount of treated sediment and the carbon to be added in order to obtain an accurate reduction reaction without the formation of silicon carbide. Although it is well known that this process requires several procedures (Abdellatif, 2011; Enger et al., 1975), particularly due to the different temperature zones inside the reaction chamber, the overall formula reduction reaction is summarized in Eq. (1):

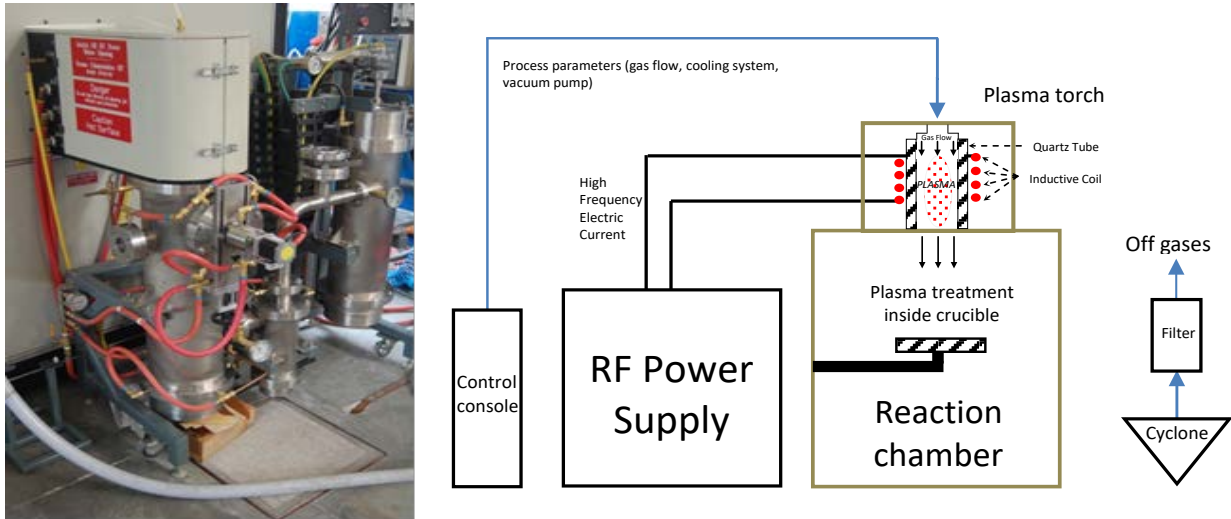
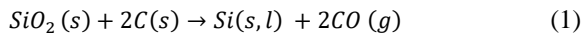
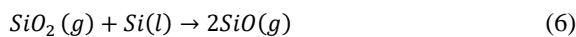
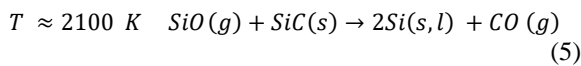
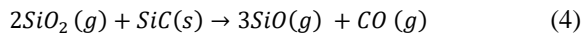
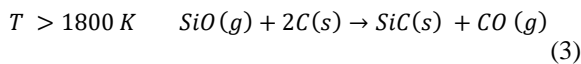
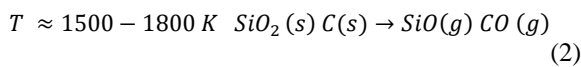


Fig. 4. Picture and schematic of the inductive plasma reactor system (Colombo et al., 2012)



Considering only a Si-C-O system, the general formula reduction sub-reactions and their respective temperature taken into consideration to establish the different amounts of sediments and carbon to treat are summarized in Eqs. (2-6):



The presence of other sediment constituents, such as calcium oxide (CaO), aluminium oxide (Al₂O₃), magnesium oxide (MgO) and hematite (Fe₂O₃), that could definitely change the development of the global reaction regarding the silicon separation, have been neglected.

The other group of tests has been aimed at treating directly with the thermal plasma source the as-received sediments in order to vitrify them and analyze the resulting material to check out the leaching properties. The amount of the Midia Port sediment material requested to achieve the vitrification test was not enough in order to demonstrate the feasibility of this technology, during this stage of the experiment. Instead, the relevant data were obtained from other sets of sediment samples (e.g., sediment collected from the Port of Ravenna, that represents another case study within the above

mentioned project; for more information please visit the website, On line at: <http://www.lifesediportsil.eu>.

All the samples have been analyzed by means of SEM (scanning electron microscopy), EDS (energy dispersion spectroscopy) and XRF (X-ray fluorescence) in order to characterize their composition and microstructure and verify the feasibility of silicon separation. In addition, the leaching tests were performed in order to evaluate the pollutant stabilization process in the resulting material.

3. Results and discussion

3.3. Soil-Washing efficiency

Overall, three cycles of treatment were conducted in order to obtain recovered sediments relevant for possible reuses (e.g., artificial beach nourishment, infrastructure or environmental engineering etc.).

The sediment treatment activities on laboratory scale performed at Diemme Enologia Spa (Italy) related to soil washing, was foreseen within the Midia port sediment as a progressive sediment cleaning, for coarse inert silty and sandy fractions remediation and recovery with a consequent progressive concentration of contaminants into the finest fractions of clay. Soil washing in short terms is a waste minimization, waste reduction remediation process. The sediment coarse fractions composed of inert materials as sand and gravel can be totally remediated and recovered to be used as secondary raw materials. This process applies on both heavy metals and hydrocarbons contaminated sediments. The sediments gathered from the Midia Port area showed a variable grain-size, being composed of a mixture of different class types, fluctuating from sand, sandy silt, silty sand, clayey silt etc. and varying degrees of contaminations in

connection with the sampling collection area (Table 1).

Table 1. Mass balance on Midia Port sediments, categories "yellow and red"

Particle size diameter:	Midia Port sediment category: yellow	Midia Port sediment category: red
>2mm	<1	<1
0.125<mm<2	43.7	50.0
0.075<mm<0.125	44.7	15.4
<0.075mm	11.5	34.2

Note: All data are expressed as percent (w/w on dry solid)

The sediment characterization was carried out in conformity with the established Italian Legislative Decree 152/06 as amended for contaminated soil management; this approach was adopted since the Romanian elaboration and approval of the specific framework law concerning soil protection is still in the process of implementation in accordance with regulations of EU environmental legislation. According to the obtained results, the sediments were classified in three categories depending on their levels of contamination: "green" (no polluted sediments), "yellow" (moderately polluted sediments) and "red" (highly polluted sediments). The analysis results indicated that the sediments show high levels of organic compound contamination: hydrocarbons (expressed as mineral oils) - C>12, polycyclic aromatic hydrocarbons - PAH's and polychlorobiphenyls - PCB's. Oppositely, the heavy metal content is not so high, incidentally registering some elevated values for As and Hg. The parameters exceeding the limits are presented in Table 2.

After the soil-washing process, the sand fraction is found to be unpolluted and that represents an important development of this study, leading also to the possibility of reusing this type of material (see Table 3). As expected, the soil-washing process leads to pollutant concentration into the clay fraction, that at the end of the process presented high levels of hydrocarbons (C>12). This type of pollutant could be purified using bioremediation (Bamforth and Singleton, 2005) but, due to the limited amount of available sediments, this technique could not be experienced during this study.

One of the main goals of this stage of treatment was also the reduction of the existing contaminants of process water, in order to obtain a proper quality without any negative ecological impact. The post treatment analysis of residual water confirmed that the investigated parameters (microbiological and ecotoxicological), were generally under the admissible limits established by the current standards. The investigated samples are included in very low toxic and nontoxic category.

Conversely, the ecotoxicological results of the test indicated a negative feedback (a potential toxic response) manifested by the *Vibrio fischeri* bacteria in this type of aqueous medium. The contaminated sediment treatment through the soil-washing process indicates as a main environmental benefit, the recovery of coarse fractions totally remediated and suitable to be reused.

The marginal residual finest fractions could be remediated via landfarming with biological degradation of hydrocarbons or via thermal plasma treatment.

Table 2. Determination of the chemical composition for each category of sediments ("yellow" and "red")

Method	Sediment Parameter	u.m.	Italian regulation (DLgs 152/06 Appendix 5)			Midia Port sediment category: yellow	Midia Port sediment category: red
			Tab. 1A recreational use	Tab. 1B industrial use	Other (DM367/2003 Table 2)		
Heavy Metals							
EPA 3051A 2007+EPA 6020A 2007	Cd	mg/kgss	2	15	0.3	<0.2	0.4
EPA 3051A 2007+EPA 6020A 2007	Hg	mg/kgss	1	5	0.3	0.3	0.4
PAHs							
EPA 3550C 2007+EPA 8270D 2007	Benzo (g, h, i) perylene	mg/kgss	0.1	10	0.055	<0.03	0.05
EPA 3550C 2007+EPA 8270D 2007	Crysene	mg/kgss	0.1	50	-	<0.03	0.17
Aliphatic Hydrocarbons							
ISO16703:2004	Total Hydrocarbons (C>12)	mg/kgss	50	750	-	35	241
Anions							
UNI EN ISO 10304-1:2009	Chloride	mg/L	100	-	-	342	498
UNI EN ISO 10304-1:2009	Fluorides	mg/L	1.5	-	-	0.16	4.1
Other parameters							
APAT CNR IRSA 5130 Man 29 2003	COD	mg/L	30	-	-	24	60

Note: Only exceeding values are shown; the complete set of analysis is available at the website, On line at: <http://www.lifesediportsil.eu>

Table 3. Analytical values after sediment washing treatment

Particle size diameter	Heavy metals (ppm ds)				Aliphatics hydrocarbons (ppm ds)		Sum BTEXs (ppm ds)	Sum PAHs (ppm ds)
	Ni	Pb	Cd	Hg	C<12	C>12		
Midia Port sediment category: yellow								
>0.075 mm	<12	<10	<0.2	<0.2	<1	<20	<0.1	<0.03
<0.075mm	20	13	<0.2	<0.1	<1	<20	<0.1	<0.03
Midia Port sediment category: red								
>0.075 mm	<12	<10	<0.2	0.2	<1	<20	<0.1	<0.03
<0.075mm	34	37	<0.2	<0.1	<1	980	<0.1	1.2

Note: All data are expressed as ppm on a dry solids basis

Briefly, soil-washing treatment of contaminated sediments means, saving resources, less energy consumption with consequent lower CO₂ emission, and:

- reduction of raw material excavated from quarries;
- lower industrial water consumption;
- reduction of road transport;
- reduction in energy consumption;
- reduction on disposal of contaminated materials.

The advantages of the soil washing process are several: *e.g.*, operates near the port area, provide very low energy consumption, and complete treatment of the residual waste water too, eliminating the risk of surrounding water contamination. Landfarming operate in close monitored builds and strict air purification treatment is foreseen, avoiding any potential ambient contamination. Soil washing process provides a complete solution for contaminated sediment, on an industrial scale, suitable to be easily implemented on an existing port area. Remediation of dredged sediments is unavoidable; their uncontrolled disposal is no longer acceptable.

Analysis of long-term sustainability, among other things, was able to demonstrate the soil washing process applicability on contaminated dredged sediments, for pollutants treatments and raw materials recovery. After the soil washing process contaminated sediments became useful, valuable products suitable for many different industries and no more only a waste to be disposed. Recovering products from this waste means less natural raw material to be extracted and transported, less land consumption, less energy consumption, less requirement for landfill and confined disposal facility (CDF) and less illegal activity. Dredging sediments is not avoidable, inactivity is not an alternative, ports and rivers need dredging.

This work provides a high visibility for environmental and economic management of dredged contaminated sediments. Large scale industrial process plant in the Midia Port is feasible, including all aspects related, as waste water and air treatment. Creating a green approach and environmental responsible mentality between all actors involved in managing this specific waste, will generate valuable products, job opportunities and further research and advancement on the efficiency and recovery. Structural poly-functional sediments processing platform, could act as central treatment facility

covering needs for large area or large customer base of small harbors. A different mental attitude must be built, considering and operating the ports dredging as standard maintenance to be performed every year; benefits are several, including always a perfect ports deepness and economical solution to the massive environmental problem. The actual ports dredging activities based on the spot emergency isn't sustainable any longer. The environmental benefit is evident in all communities, in short, this experimental treatment process can create from contaminated sediments value added products; contaminated sediments are not strictly considered only a waste.

3.2. Thermal plasma treatment efficiency: vitrification and silicon extraction

Two major sediment classes (yellow and red), the most polluted fractions due to their high hydrocarbon content, have been processed by means of the ICPT after treatment with soil-washing technique. Each category was subdivided into three categories based on their particle size diameter: sand (0.125-2 mm), silt (0.075-0.125 mm) and clay (< 0.075 mm). Therefore, in order to determine the amount of carbon requested to separate the silicon (Si) from silica (SiO₂), XRF analyses were conducted: results are presented in Table 4.

After that, the investigated sediments were placed in a graphite crucible inside the reaction chamber and treated by the high temperature plasma discharge at controlled atmosphere. Under these conditions, six experimental tests were performed: operating conditions of an optimized carbothermal reduction and vitrification tests are presented further on (Tables 5 and 6).





Material resulting from plasma treatment of carbothermal reduction and vitrification processes have been analyzed with different characterization techniques: (i) X-Ray Fluorescence (XRF) to determine the main compounds of the sediments after the thermal treatment (Test 1 and Test 5), (ii) SEM/EDS to check out the silicon extraction from all the other compounds (Test 3 and Test 6), and (iii) leaching tests (Test 3 and Test 6) to check the capability of the sample to retain the embedded elements. With respect to the vitrification tests (Test 2 and Test 4), it is assumed that the inadequacy of these trial tests is mainly due to insufficient amount of

sediment subjected to the thermal plasma treatment. Unfortunately, it wasn't anticipated the loss of the material during the experiments. We were forced to summarize to these outcomes because we did not have the opportunity to collect other samples. At first it was assumed that the unfavorable outcome was owed to the poor compaction of the untreated material. However, in the following trials, even if the material was very well compacted by conventional techniques, the amount of material was not enough to vitrify it. Under these circumstances, it is supposed that the carbon added to the sediments can play a basic role to compact the mixture, allowing it to remain inside the crucible after plasma treatment. Therefore, we conclude that vitrification of such a low amount of sediments is not possible with this technique even in a lab-scale ICPT.

Table 4. The quantification of the chemical components (%) of the investigated material (yellow and red) before the plasma treatment by XRF technique



Compound	Midia Port sediment category: yellow	Midia Port sediment category: red
SiO ₂	64.7	60.97
TiO ₂	0.6	0.58
Al ₂ O ₃	9.03	9.85
Fe ₂ O ₃	2.93	3.77
MnO	0.11	0.11
MgO	3.06	2.99
CaO	8.03	8.9
Na ₂ O	1.53	1.43
K ₂ O	1.46	1.76
P ₂ O ₅	0.15	0.18
LOI	8.39	9.48
Total	99.99	100.01

Table 5. Operating conditions of a carbothermal reduction and vitrification tests (Test 1, Test 2 and Test 3)

Test 1 - CARBOTHERMAL REDUCTION			<i>Mixture of material before thermal plasma treatment</i>	Final Result	
Mixture: 25g YELLOW sand fraction of sediments + 3.1g C (75% of the stoichiometric) = 28.1g Crucible dimensions: 80mm x 30mm (diameter x height)				Material measured after the experiment: 18.3g Corresponding percentage = 65% <u>Observations:</u> One third of the material was found inside the crucible after the treatment, using the 75% of the stoichiometric amount of carbon.	
Plasma Treatment					
Gas plasma	Argon	15 slpm			
Gas sheat	Argon + Hydrogen	30 slpm Ar + 30 slpm H ₂			
Gas carrier	Argon	3 slpm			
Plate power	28 kW				
Pressure	95kPa				
Treatment parameters	Exposure time: 8 min	*Crucible position: 92 mm from torch outlet			
Test 2 - FIRST VITRIFICATION ATTEMPT			<i>Yellow silt fraction before thermal plasma treatment</i>	Final Result	
Mixture: 30g YELLOW silt fraction of sediments Crucible dimensions: 80mm x 30mm (diameter x height)				Material measured after the experiment: 0g Corresponding percentage = 0% <u>Observations:</u> no material was found after plasma treatment. This unexpected result could be the result of a poor compaction of the untreated material.	
Plasma Treatment					
Gas plasma	Argon	15 slpm			
Gas sheat	Argon + Hydrogen	30 slpm Ar + 30 slpm H ₂			
Gas carrier	Argon	3 slpm			
Plate power	28 kW				
Pressure	95kPa				
Treatment parameters	Exposure time: 5 min	*Crucible position: 92 mm from torch outlet			
Test 3 - CARBOTHERMAL REDUCTION			<i>Yellow clay fraction before thermal plasma treatment</i>	<i>Yellow clay fraction after thermal plasma treatment</i>	Final Result
Mixture: 18.5g YELLOW clay fraction of sediments + 2.5g C (80% of the stoichiometric) = 21g Crucible dimensions: 80mm x 30mm (diameter x height)					Material measured after the experiment: 13.7g Corresponding percentage = 65% <u>Observations:</u> As well as in the first test, the 65% of the material remaining in the crucible after thermal plasma treatment. The surface of the material shows vitreous traces.
Plasma Treatment					
Gas plasma	Argon	15 slpm			
Gas sheat	Argon + Hydrogen	30 slpm Ar + 30 slpm H ₂			
Gas carrier	Argon	3 slpm			
Plate power	28 kW				
Pressure	95kPa				
Treatment parameters	Exposure time: 8 min	*Crucible position: 92 mm from torch outlet			

Note: *Crucible position that was chosen after many simulation laboratory activities (Colombo et al., 2012)

Table 6. Operating conditions of a carbothermal reduction and vitrification tests (Test 4, Test 5 and Test 6)

<i>Test 4 - SECOND VITRIFICATION ATTEMPT</i>			<i>Final Result</i>	
Mixture: 21.4g RED sand fraction of sediments Crucible dimensions: 80mm x 30mm (diameter x height)			Material measured after the experiment: 0g Corresponding percentage = 0% <u>Observations:</u> once again, no material was found in the crucible after the experimental test. The material was compacted as much as possible, using conventional techniques, but it was not enough to vitrify it.	
<i>Plasma Treatment</i>				
Gas plasma	Argon	15 slpm		
Gas sheat	Argon +Hydrogen	30 slpm Ar + 30 slpm H ₂		
Gas carrier	Argon	3 slpm		
Plate power	28 kW			
Pressure		95kPa		
Treatment parameters	Exposure time: 8 min	*Crucible position: 92 mm from torch outlet		
<i>Test 5 - CARBOTHERMAL REDUCTION</i>			<i>Material after applying plasma discharge</i>	<i>Final Result</i>
Mixture: 20g RED silt fraction of sediments + 2.9g C (90% of the stoichiometric) = 22.9g Crucible dimensions: 80mm x 30mm (diameter x height)			 <p>Material measured after the experiment: 13.9g Corresponding percentage = 61% <u>Observations:</u> adding the 90% of the stoichiometric amount of carbon, the percentage of material measured after the treatment was 61%, slightly lower in comparison with the tests 1 and 3.</p>	
<i>Plasma Treatment</i>				
Gas plasma	Argon	15 slpm		
Gas sheat	Argon +Hydrogen	30 slpm Ar + 30 slpm H ₂		
Gas carrier	Argon	3 slpm		
Plate power	28 kW			
Pressure		95kPa		
Treatment parameters	Exposure time: 8 min	*Crucible position: 92 mm from torch outlet		
<i>Test 6 - CARBOTHERMAL REDUCTION</i>			<i>Red clay fraction after plasma treatment</i>	<i>Final Result</i>
Mixture: 19.5g RED clay fraction of sediments + 3g C (95% of the stoichiometric) = 22.5g Crucible dimensions: 80mm x 30mm (diameter x height)			 <p>Material measured after the experiment: 13g Corresponding percentage = 58% <u>Comments:</u> with the 95% of the stoichiometric amount of carbon, the percentage of material found in the crucible after plasma treatment was 58%, even lower than the test 5. This fact allows us to assume that the more carbon is added to the sediments, the more reactions take place and consequently, more gases are produced and evaporated from the mixture, and less material remains in the crucible. In the adjacent figure it can be appreciated the brilliant and luminous surface of the final material.</p>	
<i>Plasma Treatment</i>				
Gas plasma	Argon	15 slpm		
Gas sheat	Argon + Hydrogen	30 slpm Ar + 30 slpm H ₂		
Gas carrier	Argon	3 slpm		
Plate power	28 kW			
Pressure		95kPa		
Treatment parameters	Exposure time: 8 min	*Crucible position: 92 mm from torch outlet		

Note: *Crucible position that was chosen after many simulation laboratory activities (Colombo et al., 2012)

3.2.1. XRF characterization of plasma treated sediments

Test 1 and Test 5 have been analyzed by wavelength dispersive XRF after plasma treatment. The obtained results are presented in the next table (see Table 7).

By comparing these XRF results after the plasma treatment, with the preceding ones (the XRF analyses before the treatment), we can state that some of the elements that persisted in the final material (and consequently their oxides), have significantly

increased their percentages, for example the Si (between 5,6 and 8%) and Ca (between 2,6 and 3,3%). Nevertheless, the percentage of Fe has decreased from 3-3,8% to 1,8-2,4%, that represents a percentage of the 35-40% of the initial amount of iron. The amount of other chemical elements as Ti, Al and Mg has maintained almost the same. A first important finding is inferred from these results, namely that the percentage of silica (% SiO₂) not only that remains in the final material after the plasma treatment, but also its percentage increases. These outcomes are possibly

a consequence of the internal conditions as the partial evaporation of some volatile chemical elements and the formation of other chemical compounds due to high temperatures during the plasma treatment.

3.2.2. SEM/EDS characterization of plasma treated sediments

The chemical analyses and imaging of a variety of micro-zones by using the SEM/EDS microscopy were performed (Fig. 5), on the leftover material obtained from the Test 3 and Test 6. The results are shown in Table 8. The analysis indicates that the most prevalent element is silicon. We noticed that its proportion fluctuates from one point to another. For instance, in the framework of the Test 3 there are points that reach up to 80% silicon, while another spot regions have only a proportion of 3%.

Under these circumstances, it is remarkable to note that by using thermal plasma treatment, it is possible to capture a significant number of small spot areas that can range from 0% silicon and up to 50-77% silicon. It is possible that this silicon could be attached to one or two atoms of oxygen (or even with iron), and in some scanning microscope observations, they represent more than 85% of the material. These qualitative results show that it is possible by means of

plasma treatment to obtain a carbothermal reduction of the sediment Si compounds leading to the generation of aggregates of high-grade-Si material.

We expect that using large amount of sediments a more efficient separation between high-grade-Si and the rest of the material will be achieved due to different material density. Such separation phenomenon is used for metal recovering from incinerator fly-ash using plasma treatment reactor (Heberlein and Murphy, 2008).

3.2.3. Leaching tests on plasma treated sediments.

Leaching test was applied to the materials resulted from the Test 3 and Test 6. The results, summarized in Table 9, show that the amount of heavy metals and hydrocarbons released from the samples is below the legal limit, so that these materials can be classified as inert, showing that plasma treatment is a very reliable technique to completely decontaminate and inerting dredged polluted sediments, regardless their origin and their amount of hydrocarbons and heavy metals. Unfortunately, the amount of sediments available to carry out these tests has been not enough to perform well vitrification tests, and in both attempts not material was found inside the crucible after the trial.

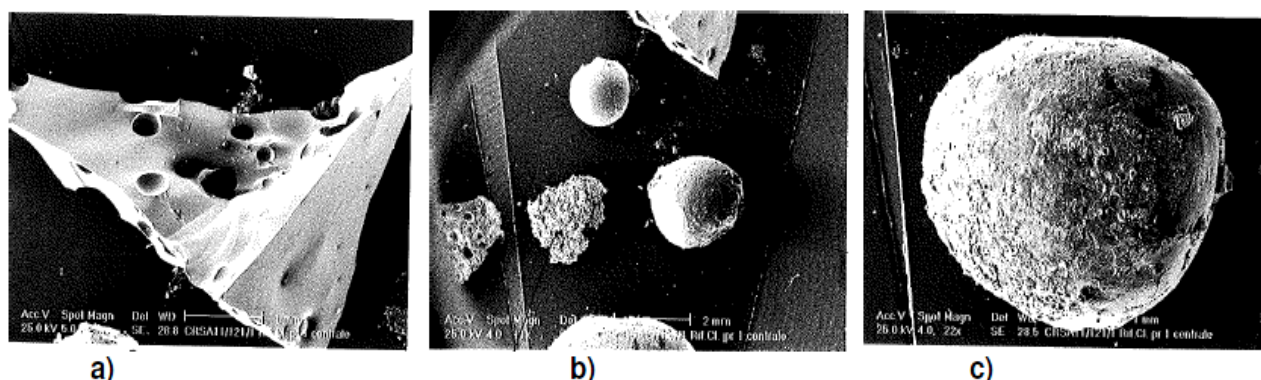


Fig. 5. SEM investigation on extracted silicon (enlargements, a) 44x, b) 13x and c) 26x), (picture taken during the SEM analysis, performed at CRSA MED Ingegneria S.r.l. laboratory) (Colombo et al., 2012)

Table 7. The quantification of the chemical components (%) of the investigated material (yellow and red) after the plasma treatment by XRF technique

Compound	Test 1 (after treatment), (Midia Port sediment category: yellow)	Variation (compared with yellow class before treatment)	Test 5 (after treatment), (Midia Port sediment category: red)	Variation (compared with red class before treatment)
SiO ₂	72.7	+8.00	66.6	+5.63
TiO ₂	0.6	0.00	1	+0.42
Al ₂ O ₃	8.6	-0.43	11.5	+1.65
Fe ₂ O ₃	1.8	-1.13	2.4	-1.37
MnO	0.1	-0.01	0.1	-0.01
MgO	3.1	+0.04	3.8	+0.81
CaO	10.6	+2.57	12.2	+3.30
Na ₂ O	1.3	-0.23	1.2	-0.23
K ₂ O	1.3	-0.16	1.1	-0.66
P ₂ O ₅	0.1	-0.05	0.1	-0.08
Total	100.01		100	

Table 8. The elemental composition in different points of the investigated material within Test 3 and Test 6

Element	Points of analysis									
	a	b	c	d	e	f	g	h	i	j
Test 3										
C	5.6	6.4	0.0	9.6	0.0	32.4	9.3	64.6	26.6	5.3
O	28.2	25.1	36.1	27.1	19.8	16.4	38.1	20.7	20.0	21.2
Mg	1.3	7.5	0.6	0.7	0.0	1.8	2.5	0.6	0.7	0.7
Al	12.5	13.4	2.5	2.2	3.5	8.1	12.8	1.5	3.3	13.6
Si	38.6	31.1	58.7	52.4	76.8	16.4	26.9	3.1	25.1	46.0
K	4.1	0.7	1.0	0.3	0.0	0.8	1.2	0.0	2.9	6.3
Ca	1.5	12.0	0.0	5.7	0.0	19.0	3.5	2.7	14.4	2.7
Ti	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fe	4.1	3.9	0.0	2.0	0.0	5.5	3.4	6.9	7.6	1.3
Na	4.2	0.0	1.1	0.0	0.0	0.0	0.0	0.0	0.0	2.9
V	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Test 6										
C	0.0	0.0	4.3	0.0	12.4	11.2	58.9	9.7	6.4	0.0
O	3.8	36.0	37.5	31.4	40.7	30.4	1.2	44.9	29.4	26.2
Mg	1.3	2.7	2.4	2.0	3.6	3.8	0.0	3.9	2.3	1.4
Al	1.8	1.3	0.0	0.9	20.7	24.1	0.0	17.0	11.8	4.6
Si	61.7	51.3	54.3	65.7	14.7	18.6	8.4	16.5	27.2	61.8
K	1.2	1.3	0.7	0.0	0.0	0.0	0.0	0.0	3.0	1.7
Ca	0.0	0.9	0.0	0.0	8.0	11.9	31.5	8.0	7.2	4.2
Ti	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fe	2.2	5.8	0.9	0.0	0.0	0.0	0.0	0.0	11.9	0.0
Na	0.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.0
V	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Note: a, b, c, d, e, f, g, h, i, and j indicates the investigated spot regions; respectively, C, O, Mg, Al, Si, K, Ca, Ti, Fe, Na and V represent the distribution of these elements within the spot regions

Table 9. The overall leaching trial results (mg/l) of the experiment 3 and 6

Test Methods -Leaching	Reference Limits - DM 27/09/2010 Tab. 2 Inert Waste	Reference Limits - DM 27/09/2010 Tab. 5 Non Hazardous Waste	Experiment 3	Experiment 6
Al	-	-	1.89	3.17
As	0.05	0.2	<0.005	0.006
Ba	2	10	<0.1	<0.1
B	-	-	0.25	0.30
Cd	0.004	0.1	<0.0005	<0.0005
Cr tot	0.05	1	<0.005	<0.005
Cr VI	-	-	0.004	0.24
Fe	-	-	0.001	<0.001
Mn	-	-	<0.001	<0.001
Hg	0.001	0.02	0.0004	<0.001
Ni	0.04	1	<0.001	0.001
Pb	0.05	1	<0.005	<0.005
Cu	0.2	5	<0.005	<0.005
Se	0.01	0.05	0.002	0.012
Sn	-	-	<0.001	<0.001
Zn	0.4	5	<0.04	<0.04
Total hydrocarbons (C>12)	-	-	<10	<10
Organics screening	-	-	<10	<10

However the important finding is that even without vitrification the treated sediments can be considered as inert material, so that the after treatment residue can be easily disposed after Si content separation.

4. Conclusions

The application of the proposed technologies for the treatment of contaminated sediments leads to

the estimation of the potential beneficial reuse of the Midia Port dredge material. The soil-washing allowed to obtain sandy fractions, free of pollutants, still saline, which can be reintroduced in the form of the environmental restoration as beach nourishment, and a final fraction of clays where pollutants have accumulated. This portion of sediments, once dehydrated, can be treated with thermal plasma. In this respect, the experiments carried out at lab-scale have

shown promising results to qualitatively assess the feasibility to extract metallurgical pureness degree silicon related to Midia Port sediments and to make them inert, representing also an important contribution to sediment management.

The methodological approach designed can be considered as a good prediction for assessing the reusability of Midia Port sediments, which is very significant for this area.

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