

Recycling contaminated marine sediments as filling materials by pilot scale stabilization/solidification with lime, organoclay and activated carbon

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Abstract

Nowadays, stabilization/solidification (S/S) applied to the treatment of contaminated marine sediments (CMSs) represents a key technology for the production of new materials for civil engineering. Literature has shown the feasibility of CMSs recycling, although sediment needs pre-treatments for the removal of organic matter and to improve the mechanical properties of the product post S/S. In view of the full-scale applicability where it is essential to reduce any additional phase (i.e., pre-treatments), this study is aimed at demonstrating the technical feasibility of recycling CMSs as filling materials by S/S treatments with lime, organoclay and activated carbon. The original sediments are contaminated with heavy metals, PCBs, and PAHs, exceeding limits values prescribed by law. Different mixtures were tested on the STABSOL-P pilot scale plant. The absence of specific CMSs pre-treatments resulted in failure to comply with the 28-days leaching test only for copper; greater air curing with 56-days allowed it to be complied with for all the investigated metals. The organic contamination, while slowing down the process of chemical stabilization, allowed in any case to get a product environmentally compatible. The unconfined compression strength tests showed values (>28 kPa) that would allow potential CMSs recycling for environmental enhancement. The mass balance of the case study of the Mar Piccolo of Taranto (Southern Italy) showed potential recycling of marine sediments (the production of 974 kg filling materials per 1000 kg of dredged sediment) with a consequent missed disposal in landfills of 0.65 m³/1000 kg of sediment.

1. Introduction

Solidification and stabilization are probably the most mature technologies for the remediation of contaminated soils/sediments, with both in-situ and ex-situ applications (Lofrano et al., 2017). The U.S. Environmental Protection Agency (EPA) defines solidification as “a process that encapsulates waste to form a solid material” (US EPA, 1997); the process reduces the surface area of the solidified materials and coats them with low-permeability materials, thus reducing contaminant mobility. Stabilization, like solidification, reduces the leachability of contaminants through the addition of chemical binders (RaCenović et al., 2019). Solidification/stabilization (S/S) is typically used to immobilise metals, although S/S may be effective for low levels of organic contaminants (Woo et al., 2019).

Nowadays, the concepts of the circular economy are giving a new perspective to S/S treatments. No longer as a simple technology of remediation aimed at the immobilisation of the contaminant and disposal in landfills of the final solid product, but as a key technology for the production of new materials to be used in civil engineering (Shubbar et al., 2019).

The binders commonly used are Portland cement and lime. Early research concerned the recycling of dredged sediments for the construction of road foundations or base layers using cement based S/S (Pinto et al., 2011). Rather than the feasibility of the product obtained, they had highlighted several bottlenecks. The organic matter in the sediment, after complexing with calcium by buffering the pH increase, slowed the hydration of the cement from

Abbreviations		Al	Albite (NaAlSi ₃ O ₈)
AC	Activated carbon	An	Anorthite (CaAl ₂ Si ₂ O ₈)
CaO	Calcium oxide or Lime	C	Chlorite ((MgFeAl) ₈ (SiAl) ₈ O ₂₀ (OH) ₁₆)
CMSs	Contaminated marine sediments	Ca	Calcite ((Ca,Mg)CO ₃)
EDS	Energy Dispersive X-ray Spectrometry	D	Dolomite (MgCa(CO ₃) ₂)
LOD	Limit of Detection	G	Gypsum (CaSO ₄ *2(H ₂ O))
M1-M4	Mixtures	H	Halite (NaCl)
OC	Organoclay	I	Illite ((K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ (H ₂ O)])
PAHs	Polycyclic Aromatic Hydrocarbons	I/S	Illite-Smectite (K _x Al ₂ [AlSi ₃]O ₁₀ (OH) ₂)
PCBs	PolyChlorinated Biphenyls	K	Kaolinite 1A (Al ₂ Si ₂ O ₅ (OH) ₄)
q _u	Unconfined compressive strength	L	Lime (CaO)
SEM	Scanning Electron Microscope	M	Montmorillonite (Na, Ca) _{0.3} (Al, Mg) ₂ Si ₄ O ₁₀ (OH) ₂ *n(H ₂ O)
S/S	Stabilization/solidification	P	Portlandite (Ca(OH) ₂)
W/S	Water-to-Solid ratio	Pe	Periclase (MgO)
XRPD	X-Ray Powder Diffraction	PW	Pseudowollastonite (CaSiO ₃)
<i>Symbols</i>		Q	Quartz (SiO ₂)
A	Aragonite (CaCO ₃)	S	Sanidine ((KNa)(Si, Al) ₄ O ₈)
		Z	Zeolite (SiO ₂)

producing calcium silicate hydrate (CeSeH) and calcium hydroxide (CH) for the development of resistance (Wang et al., 2015a). Chlorides, sulphates (Zentar et al., 2012), and non-negligible

amounts of clay (Fernandes et al., 2007) also compromise strength as well as the durability of cement products. Subsequent studies have made it possible to overcome these barriers by highlighting the technical feasibility of producing fill materials, partition blocks, and paving blocks (Todaro et al., 2018).

Wang et al. (2015a) showed that the 28-days compressive strength of cement, coal fly ash and lime sediment blocks allowed the blocks to be used as filler material for construction. The marine sediment was pre-treated by advanced oxidation and thermal processes, favouring the volatilization of the organic content of the sediment. The carbon dioxide (CO₂) curing of the sediment blocks and their subsequent oven-drying made it possible to increase the compressive strength to values of the order of 6e7 MPa. In a second study, Wang et al. (2015b) demonstrated the technical feasibility of adopting a cement based S/S for the construction of load-bearing/ non-load-bearing masonry blocks as well. The mixtures consisted of contaminated marine sediment, first thermally pre-treated and then re-hydrated with freshwater, coarse aggregates, supplementary binders and Portland cement. The obtained blocks were characterised by 28-days compressive strengths greater than 10 MPa. Subsequently, Wang et al. (2017) made paving blocks using S/S based on the binary use of magnesium oxide cement and Portland cement, employing CO₂ curing. A later assessment of costs and benefits suggested that the production of paving blocks achieved the highest potential profits, whereas the production of filling materials had an advantage in saving most of the disposal fee (Wang et al., 2018). In a further study, Wang et al. (2019a) assessed the influence of Si-rich minerals on the formation of magnesium silicate hydrate (M-S-H) gel in reactive magnesium oxide (MgO) cement used S/S treatment of sediment. Other hot topics of research concern the development of new binders and additives as well as the definition of appropriate mixes design. Concerning the binder, Shubbar et al. (2018) developed a low carbon binder from the ternary blending of cement, ground granulated blast furnace slag, and high calcium fly ash. Additives (e.g., activated carbon or clays) are added to avoid any interference with the formation of the sediment block caused, for example, by the presence of organic matter in the sediment. Concerning additives, the use of phosphates in combination with hydraulic binders helps to reduce lead

mobility, even at acidic pHs (Hale et al., 2011). Fly ash, in combination with cement or calcium oxide, acts both as a filler and as an artificial pozzolana, increasing the effectiveness of the treatment (Colangelo et al., 2012). Kadir Aeslina et al. (2016) showed the effective combination of cement and seashell powder in treating lead-contaminated soils while Wang et al. (2019b) experimented with wood-based biochar. Li et al. (2019) investigated the organo-clay, a permeable hydrophobic clay, very effective in adsorbing organic substances and in immobilising metals. With reference to the selection of the mix design, it depends on the final product desired. In the case of high values of mechanical parameters, it is possible to add different aggregates. Limeira et al. (2010) used raw limestone aggregates, while Wang et al. (2015b) experimented on several wastes such as recycled glass cullet and coal combustion ash.

It emerges from the above that the production cycle of the sediment block becomes much more complex and sediments before their use are subject to pre-treatment that is not always economically viable on a full scale, such as their drying. The literature (see Table 1S, Supplementary data) shows how few studies concerning environmental applications of contaminated marine sediments based on lime as a binder are available. This recycling path is characterized by lower mechanical strengths than those of building materials. It may require a simplified production cycle and given the low compressive strengths to be achieved, binders other than the commonly used Portland cement could be used.

In this context, the study aims at demonstrating the technical feasibility of recycling contaminated marine sediment as filling materials through a S/S treatment process based on mixes of sediment, lime, organoclay, and activated carbon.

In view of the full scale applicability where it is important to reduce any additional phase, there was no pre-treatment of the collected sediment. No addition of coarse aggregates has been made; this leads to a lower compressive strength of the filling materials than that of the cited studies, but in any case higher than the values expected for a filling material with acceptable mechanical properties for environmental reuse (Smith et al., 2017). In the chosen mix, the function of the activated carbons and the organoclay is to control the organic substance present in the starting sediment, which otherwise could affect the stabilization/ solidification processes. Lime was chosen for its low cost and environmental impact compared to the cement.

The experiment, part of a larger project promoted by the Italian Government for the remediation of the Mar Piccolo of Taranto (Southern Italy), was conducted using a S/S pilot plant with the intent of simulating as much as possible the phases of a real dredging-S/S treatment.

2. Materials and methods

Sediment sampling (i), construction of representative samples for S/S tests (ii), sediments and reagents chemical-physical and mineralogical characterisation (iii), conduction of S/S treatment at

pilot scale (iv), execution of leaching tests (v), chemical-physical and mineralogical characterisation of the mixtures following the curing phase (vi), execution of the unconfined compressive tests for the determination of compressive strength (vii), were the main phases of the experimental plan (see also Fig. 1S, Supplementary data).

2.1 *Sampling, conservation, representative sample construction and characterisation of polluted sediments*

Contaminated marine sediment samples were taken in the first basin of the Mar Piccolo of Taranto at the sampling points of Fig. 1a. The sediment was sampled using a continuous drilling machine that has been installed on an offshore platform. For each sampling point, the core barrel was inserted until it reached the aquitard: basic less-permeable geological formation (20e30 m below the seafloor). 1.5 m long polycarbonate liners, acting as a container to avoid phenomena of cross-contamination of the sediment, were placed inside the core barrel tube along the entire vertical line (Fig. 1b). Each liner containing the sediment was stored in a wooden crate, which was placed in a refrigerated container at +4 °C, in order to avoid both loss and alteration of sediment physical-chemical properties. The sediment in each liner was sub-sampled to create homogeneous samples representative of the whole layer 1.5 m long; samples were subjected to chemical- physical characterisation and particle size analysis, after the removal of particles larger than 2 cm. The standard protocols of ISPRA (the Italian Institute for the Environmental Protection and Research) and U.S. EPA were used for determining grain-size, moisture content, and organic matter of sediments (ICRAM-APAT, 2007). The concentrations of metals were obtained by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) in accordance with EPA method 200.8 (EPA, 1994). For the determination of the total Polycyclic Aromatic Hydrocarbon (PAH) and PolyChlorinated Biphenyl (PCB) concentrations as well as each compound or homolog group, a Gas Chromatograph - Mass Spectrometer (GC-MS) and EPA method 8275A was used (Table 1). In order not to alter the integrity of the sediment, each liner was repositioned in the refrigerated container at +4 °C.

The most contaminated sediment was found to be that of the surface liner (0e1.5 m) (Barjoveanu et al., 2018). The characterisation allowed the mapping of homogeneous areas from particle size and a chemical-physical point of view; at equal grain size, it was possible to identify areas with different levels of organic and inorganic contamination (Fig. 1c). The representative samples for the subsequent pilot plant S/S tests were constructed by mixing the sediments of the surface liners of several homogeneous areas (Fig. 1d). The samples were characterised by the composition and chemical-physical properties reported in Table 2.

They were essentially fine-grained sediments, for which silt fraction varies between 42.8% and 43.2%, clay fraction between 37.4% and 37.8% and sand fraction ranges from 19.3% to 19.4%.

The pH, moisture, and organic matter content was on average 8.7, 44.9% and 14.4%, respectively; the electrical conductivity was 3.4 mS/cm on average.

Table 1

Methods used for the characterisation of the water and soil matrix.

Parameter	Matrices	Unit	Standard
Moisture content	Soil	%	EPA 24 (1993)
Organic content	Soil	%	EPA 160.4 (1971)
Particle size distribution	Soil	%	ICRAM-APAT (2007)
pH	Soil and water	u. pH	EPA 150.1 (1982)
Conductivity	Soil and water	$\mu\text{S}/\text{cm}^2$	EPA 120.1 (1982)
Inorganic pollutants	Soil and water	mg/kg	EPA 200.8 (1994)
Organic pollutants	Soil and water	mg/kg	EPA Method 8275A (1996)

The chemical characterisation showed that they were polluted by heavy metals, PAHs and PCBs (see Table 2). The contents of contaminants in the table were compared with the corresponding limits defined by both site-specific law (ICRAM, 2004) and the Italian National Law (L.D., 2006). Regarding inorganic contaminants, copper and lead exceed the corresponding ICRAM (2004) limit values. Cumulative PAHs and PCBs largely exceed the limit values for organic contaminants. The most common compounds in PAHs were Anthracene, Pyrene, Benz(a)anthracene, Crysene, Benzo(k)fluoranthene and Benzo(j)fluoranthene (Fig. 2S, Supplementary data). Instead, the PCB 101, PCB 110, PCB 118, PCB 146, PCB 151, PCB 153, PCB 180 and PCB 183 were the most common ones in PCBs (Fig. 3S, Supplementary data). Although the dry sediment was characterised by values of copper and lead higher than the limit values, the contaminants seemed not to be bio-available; the concentrations found in the eluates after the leaching test (carried out

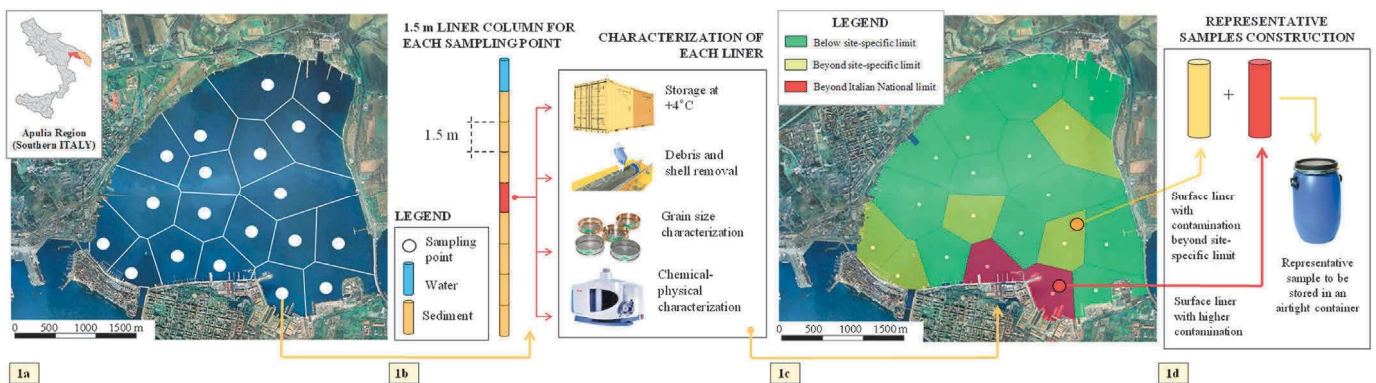


Fig. 1. (a) Sample area in the Mar Piccolo of Taranto (Southern Italy); (b) conservation and characterization of liners for each sampling point; (c) mapping of homogeneous areas in terms of particle size and pollution load (metals and organics); (d) preparation of representative samples for S/S tests on the pilot plant.

Table 2

Chemical-physical and particle size characterisation of representative sediment samples.

Parameter	Unit ^a	Values				Average \pm St. Dev.	Limit value
		Sample 1	Sample 2	Sample 3			
Physical parameters							
pH	pH unit	8.73	8.77	8.75	8.75 \pm 0.02	e	
Redox potential	mV	-101.02	-101.15	-101.10	-101.09 \pm 0.07	e	
Conductivity	mS/cm	3.31	3.48	3.45	3.41 \pm 0.09	e	
Moisture	%	44.94	44.85	44.94	44.91 \pm 0.05	e	
Solid	%	55.06	55.15	55.06	55.09 \pm 0.05	e	
Organic matter	% solid	14.36	14.49	14.47	14.44 \pm 0.07	e	
Ash	% solid	85.64	85.51	85.53	85.56 \pm 0.07	e	
Particle size distribution							
Sand fraction	%	19.32	19.48	19.44	19.41 \pm 0.08	e	
Silt fraction	%	43.09	42.76	43.18	43.01 \pm 0.22	e	
Clay fraction	%	37.59	37.76	37.38	37.58 \pm 0.19	e	
Chemical parameters - Inorganic contaminants						ICRAM (2004)	
Arsenic	mg/kg	11.91	11.99	11.89	11.93 \pm 0.05	20.00	
Barium	mg/kg	e	e	e	e	Not defined	
Beryllium	mg/kg	0.99	1.02	0.97	0.99 \pm 0.03	Not defined	
Boron	mg/kg	e	e	e	e	Not defined	
Cadmium	mg/kg	0.73	0.70	0.71	0.71 \pm 0.02	1.00	
Chromium	mg/kg	57.12	57.76	57.43	57.44 \pm 0.32	160.00 ^b	
Cobalt	mg/kg	7.14	7.03	7.09	7.09 \pm 0.06	Not defined	
Copper	mg/kg	81.02	79.25	80.08	80.12 \pm 0.89	45.00	
Iron	mg/kg	e	e	e	e	Not defined	
Lead	mg/kg	83.12	83.52	83.31	83.32 \pm 0.20	50.00	
Mercury	mg/kg	<0.01	<0.01	<0.01	<0.01	0.80	
Nickel	mg/kg	37.88	39.66	38.75	38.76 \pm 0.89	100.00 ^b	
Selenium	mg/kg	e	e	e	e	Not defined	
Thallium	mg/kg	e	e	e	e	Not defined	
Vanadium	mg/kg	56.61	56.81	57.25	56.89 \pm 0.33	Not defined	
Chemical parameters - Organic contaminants						ICRAM (2004)	
S PAHs ^c	mg/kg	5042.84	5048.23	5045.01	5045.36 \pm 2.71	4000.00	
S PCBs ^d	mg/kg	1819.87	1832.69	1824.74	1825.77 \pm 6.47	190.00	
Chemical parameters - Leaching test						Italian D.M. 5/2/98	
Arsenic	mg/l	0.004	0.017	0.015	0.012 \pm 0.007	0.05	
Barium	mg/l	e	e	e	e	1.00	
Beryllium	mg/l	e	e	e	e	0.01	
Boron	mg/l	e	e	e	e	e	
Cadmium	mg/l	e	e	e	e	0.005	
Chromium	mg/l	e	e	e	e	0.05	
Cobalt	mg/l	e	e	e	e	0.25	
Copper	mg/l	0.008	0.001	0.004	0.004 \pm 0.004	0.05	
Iron	mg/l	e	e	e	e	0.20	
Lead	mg/l	e	e	e	e	0.05	
Mercury	mg/l	e	e	e	e	0.001	
Nickel	mg/l	e	e	e	e	0.01	
Selenium	mg/l	e	e	e	e	0.01	
Thallium	mg/l	e	e	e	e	0.002	
Vanadium	mg/l	0.019	0.030	0.025	0.025 \pm 0.006	0.25	

^a Dry-basis.^b For sediments with a pelitic fraction (clay + silt) > 20%.^c Further information in terms of PAHs composition is reported in Fig. 2S of Supplementary data.^d Further information in terms of PCBs composition is reported in Fig. 3S of Supplementary data.

according to the EN standard 12457-2 (EN standard 12457-2, 2002)) were well below the limit values reported in the Ministerial Decree 05/02/1998 (see Table 2). After characterization, the representative sample 3 was used for the S/S tests, described below.

2.1. Lime and additives characterization

The sediments were treated by adding different contents (by dry soil weight) of lime, organoclay (OC), and low-cost activated carbon (AC). Calcium oxide (CaO), commonly known as quicklime, was the type of lime used during the investigation, instead of the more environmentally impacting Portland cement. The stabiliser was commercially produced finely ground with 99% passing 75 mm

sieve and 97% passing 45 mm sieve. The product was obtained from Unicalce S.p.A (Italy).

Organoclay PM 199 (CETCO, Hoffman Estates, IL) was a bentonite-originated element modified with quaternary amines that exchanges the surface cation charges of bentonite for organic molecules.

A low-cost adsorbent such as coconut shell-based activated carbon (LIQPRO CS 1100) replaced conventional activated carbon. It has efficient micro-porosity with makes it suitable for high flow rate applications; the high surface area ensures superior adsorption of low molecular weight organic compounds.

OC and AC were obtained from Maccaferri S.p.A. (Italy). The physical properties of these adsorbents are shown in Table 3.

The chemical-physical characterisation in Table 4 showed lower values than the ICRAM (2004) limit values for lime, AC, and OC. The leaching test showed a release of Barium and Thallium

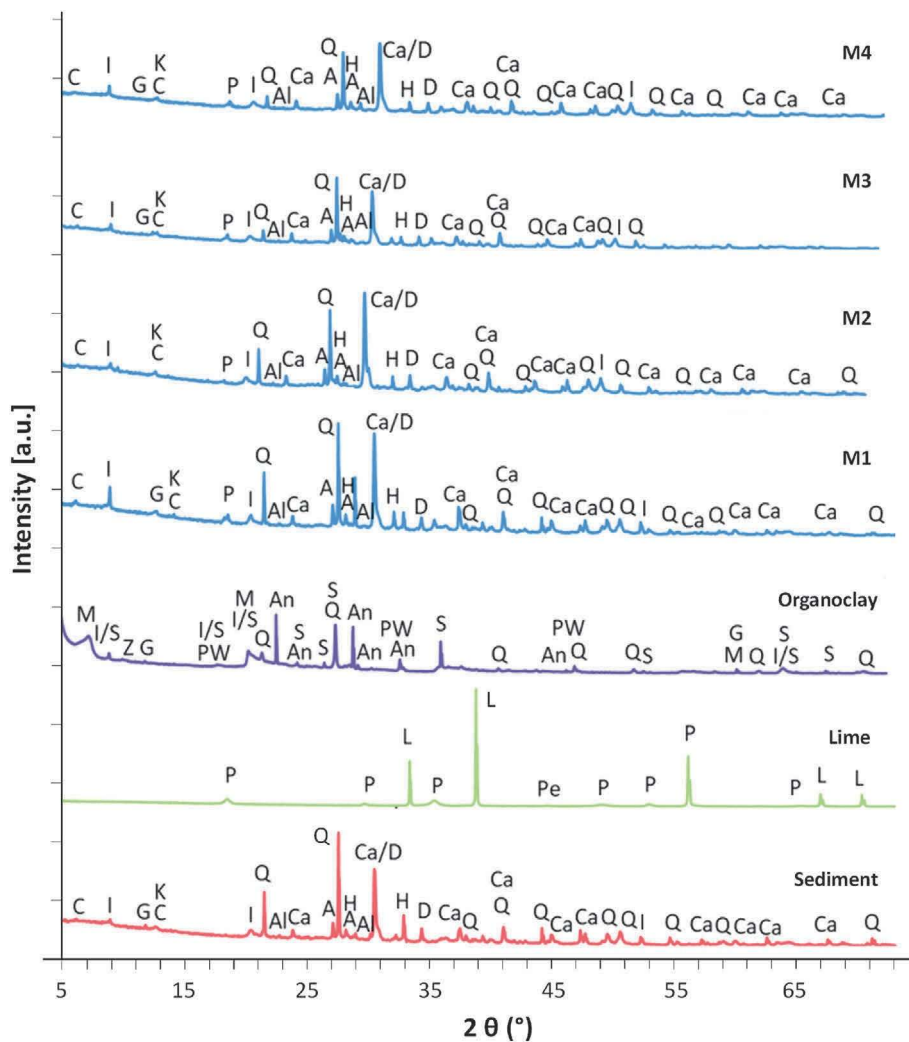


Fig. 2. XRPD patterns.

above the corresponding limit values for lime. No exceedances were observed for AC and OC.

2.2. S/S treatment

The four mixtures (labeled M1 e M4) were prepared by using different contents (by dry soil weight) of lime, AC, and OC (Table 5).

In all mixtures, the percentage lime was set at 10 wt% while the water-to-solid (W/S) ratio was kept at 0.7.

S/S experimentation involved the use of the STABSOL-P pilot plant (Hextra S.r.l.) made available by Unicalce S.p.A. The main component of the plant was the mixing chamber, consisting of a cylinder containing the material to be treated and mixed by blades attached to a shaft, driven by a motor-gearbox unit. The mixing blades, as well as the entire plant, were made of stainless steel.

Each S/S treatment test (4 in total) was conducted using samples of 2 kg of sediment, in line with the reactor capacity (about 2e4 kg). The plant was operated in the following main phases: (i) mixing of the sediment in the reactor with the set amount of additive (AC, OC) for 5 min; (ii) adding the lime (and water) and mixing for 10 min. The amount of water was determined on site in relation to the moisture content of the sediment as it is. The resulting mixtures were stored in suitable containers for solidification of the material for the next 56-d, a value well above the minimum of 28-d set in

literature. The samples were kept at 20 ± 5 °C and 80% moisture content in the curing phase; samples for the analytical characterisations were taken after 1, 7, 14, 21, 28, and 56-d from treatment.

The testing program consists of chemical (i.e. leaching tests), physical, mineralogical, and mechanical investigations as herein described.

2.3. Leaching test

The prepared mixtures underwent leaching tests according to the EN standard 12457-2 (EN standard 12457-2, 2002), taken in by EN 12457e2:2002. A 40 g portion was sampled and transferred to a polyethylene bottle. Demineralized water was added with a solid-liquid ratio of 1:10 by weight, and the bottles were kept in rotation at 12 rpm for 24 h using Rotax 6.8 (Velp Scientifica). To end of the 24 h, a short retention time was given to the extraction vessels for the

settlement of suspended coarse solids; the leachate was filtered for the removal of suspended solids. This test procedure produces an eluate that has been characterised physically and chemically according to appropriate standard methods. Eluates were divided into an appropriate number of parts for the different chemical analysis, after having been acidified at a pH = 2, through nitric acid. The soluble concentrations of heavy metals of interest were analysed using ICP-OES. For each leaching test, 3 sediment samples were taken (120 g total). The leaching test values shown in this study are the average ones.

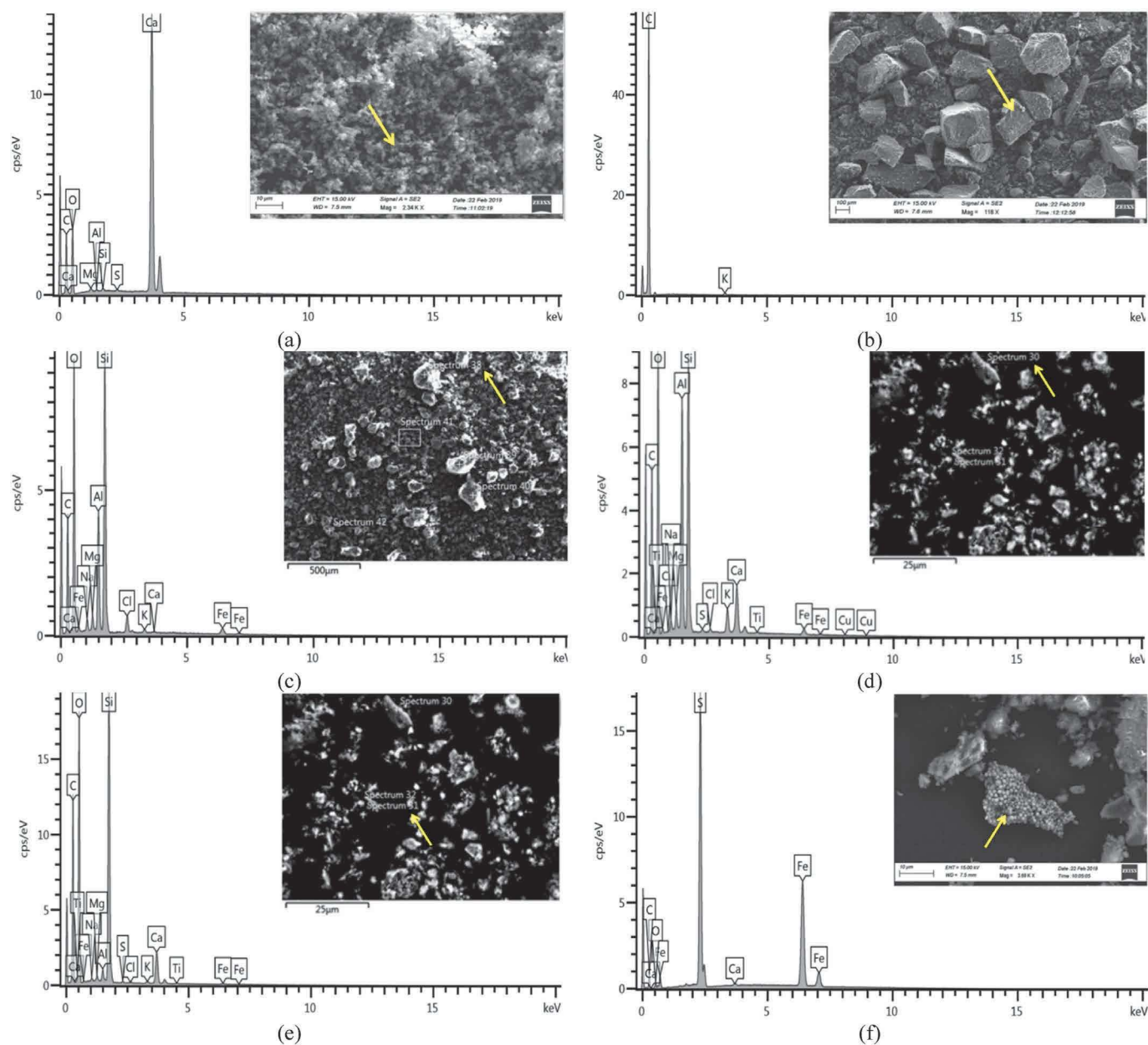


Fig. 3. EDS spectra of (a) lime, (b) AC, (c) OC; (d) phyllosilicate and (e) quartz grains in the untreated sediment; (f) pyrite grain of the M1 mix treated sediment.

Table 3
Main properties of additives.

Additive	Mesh	Density (kg/m ³)	Specific surface area (m ² /g)
Organoclay PM 199	1.00 mm/0.15 mm	800 ± 100	0.5 kg per kg of OC is absorbed; surface area is not relevant
LIQPRO CS 1100 Activated carbon	2.36 mm/0.60 mm	480 ± 30	1150

2.4. SEM-EDS and XRPD analysis

The mineralogy of the investigated samples and starting materials was also studied by Scanning Electron Microscope (SEM) images, acquired with secondary electrons (SE) and/or backscattered electrons (HDBSD) and confirmed by Energy Dispersive X-ray Spectrometry (EDS) analysis. In total, 69 images and 45 EDS spectra were acquired, although only the most relevant data were reported in this study.

X-ray Powder Diffraction (XRPD) data on selected samples were collected in air using a PANalytical Empyrean X-ray diffractometer with Bragg-Brentano geometry, large beta filter-Nickel, PIXcel3D detector and CuK α radiation ($\lambda = 1.5418 \text{ \AA}$), operating at 40 kV/ 40 mA. The incident beam path was collimated using Soller slits of

0.02 rad, a fixed incident beam mask of 10 mm, an anti-scatter slit of $\frac{1}{2}^\circ$, and a divergence slit of $\frac{1}{4}^\circ$. The diffraction patterns were collected considering (i) for lime and AC, 5 scans in the interval of 2θ between 5° and 85° for a total scan time of 90 min, (ii) for OC, 4 scans in the interval of 2θ between 3° and 80° , for a total scanning time of 106 min, (iii) for the sediment and M1-M4 mixtures, 4 scans in the interval of 2θ between 3° and 70° , for a total scan time of 92 min. The samples were ground to obtain a homogeneous powder. Lime was ground with an agate; AC with a Retsch vibromulin in a ZrO₂ jar at a frequency of 10 Hz for 2 min. In both cases, the obtained powder was inserted into the sample holder by standard loading. The OC, the sediment and the M1-M4 mixtures were ground using the same operating conditions as the AC, but the powders were inserted into the sample holder by lateral loading to prevent the preferred orientation of the crystallites of the clay phases, which would alter the relative intensity of the peaks obtained by diffraction.

The powder from lime, AC, OC, sediment, and M1-M4 mixtures samples, recovered after the XRPD analysis, was adhered to a double-sided graphite adhesive disc, which was placed on a stab that was shaken to remove the excess powder. Except for AC, all remaining samples were sputtered in order to metallise the powder using an incandescent graphite filament. A total of 8 samples were analysed using a Zeiss Sigma 300 VP, with acceleration voltages of 15.00 kV and a working distance of 7.5 mm.

Table 4

Chemical characterisation and leaching behaviour of lime and additives.

Parameter	Unit	Values			
		Lime	Activated carbon	Organoclay	Limit value
Chemical characterisation					ICRAM (2004)
Arsenic	mg/kg ^a	e	<0.010	<0.010	20.00
Barium	mg/kg ^a	e	e	e	Not defined
Beryllium	mg/kg ^a	e	<0.010	0.094	Not defined
Boron	mg/kg ^a	e	e	e	Not defined
Cadmium	mg/kg ^a	e	<0.010	<0.010	1.00
Chromium	mg/kg ^a	e	<0.010	0.876	160.00 ^(b)
Cobalt	mg/kg ^a	e	<0.010	0.233	Not defined
Copper	mg/kg ^a	e	18.151	1.133	45.00
Iron	mg/kg ^a	e	<0.010	<0.010	Not defined
Lead	mg/kg ^a	e	<0.010	4.951	50.00
Mercury	mg/kg ^a	e	<0.010	<0.010	0.80
Nickel	mg/kg ^a	e	4.433	0.650	100.00 ^(b)
Selenium	mg/kg ^a	e	<0.010	<0.010	Not defined
Thallium	mg/kg ^a	e	<0.010	<0.010	Not defined
Vanadium	mg/kg ^a	e	<0.010	0.828	Not defined
Leaching test					Italian D.M. 5/2/98
Arsenic	mg/l	<LOD	0.013	0.003	0.05
Barium	mg/l	1.345	e	e	1.00
Beryllium	mg/l	<LOD	<LOD	<LOD	0.01
Boron	mg/l	0.031	e	e	e
Cadmium	mg/l	<LOD	<LOD	<LOD	0.005
Chromium	mg/l	0.039	0.001	0.001	0.05
Cobalt	mg/l	<LOD	<LOD	<LOD	0.25
Copper	mg/l	<LOD	0.002	<LOD	0.05
Iron	mg/l	<LOD	e	e	0.20
Lead	mg/l	0.043	0.001	<0.001	0.05
Mercury	mg/l	<LOD	<LOD	<LOD	0.001
Nickel	mg/l	<LOD	<LOD	<LOD	0.01
Selenium	mg/l	<LOD	<LOD	0.002	0.01
Thallium	mg/l	0.003	<LOD	0.001	0.002
Vanadium	mg/l	<LOD	<LOD	<LOD	0.25

^a Dry-basis; ^(b): for sediments with a pelitic fraction (clay + silt) > 20%; ^(c): Limit of Detection (LOD) = 0.001 mg/l.

Table 5

Mixture design for S/S testing (values in wt.%).

Mix	Lime (A)	Additives (B)		Sediment (C)	Total reagents (A + B)	Total (A + B + C)	W/S ratio ^a (adim)
		AC	O C				
M1	10	0	0	90	10	100	0.7
M2	10	5	0	85	15	100	0.7
M3	10	2.5	2.5	85	15	100	0.7
M4	10	0	5	85	15	100	0.7

^a Water/Solid ratio.

2.5. Unconfined compressive test

A cylindrical soil sample (with a length/diameter ratio of 2), without any confining pressure, was subjected to an axial compressive load until failure occurred. The specimen was located in a triaxial load frame (Tritech 50 kN, Controls S.p.A.) where a load cell of Imperial College type can measure the axial force applied to the specimen. Axial displacements were measured by a Linear Variable Displacement Transducer (LVDT). The standard displacement transducer had a

maximum travel length of 50 mm; its body was fixed to the loading ram, while the piston allowed to move jointly to the cell and measures its movement. The accuracy of such displacement measurements was about 0.05%.

Unconfined Compressive (UC) tests were performed in accordance with [ASTM D2166/D2166M-16, 2016](#) D2166 for the natural and treated sediments at 28-d of curing time. UC testing was

performed at a 5 mm/min rate until failure as the maximum deviator stress observed during testing. The unconfined compressive strength (q_u) is defined as the ratio of Failure Load (P) to the cross-sectional area of the sediment sample (A_c) if it is not subjected to any lateral pressure (1):

$$q_u = P/A_c \quad (1)$$

The changed average cross-sectional area at a particular deformation during the test was calculated using the following equation (2):

$$A_c = A_0 / (1 - \varepsilon) \quad (2)$$

where ε was the axial strain ($\varepsilon = DL/L$). For each compression test, 3 replicas were performed.

3. Results and discussion

3.1. Sediment, lime, additives and mixtures phase composition

The mineralogical composition of the sediment, as derived by XRPD investigations, is shown in Fig. 2. It corresponds to that of the sub-Apennine clays (Dell'Anna and Laviano, 1991). The main mineralogical phases were clay minerals, quartz, carbonates, plagioclases, and feldspars. The clay minerals were found to be a mixture of illite, chlorite, and kaolinite. Differently from previous literature, smectite is not detectable in the XRPD pattern as a separate mineralogical phase, but as an illite-smectite (IeS) mixed layer phase.

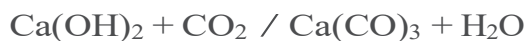
The mineralogical characterisation of the lime sample showed the presence of lime, portlandite, and periclase. The XRPD pattern of the OC sample showed that it consisted of a mix of polycrystalline phases, specifically: sanidine, Na-rich anorthite, montmorillonite, smectite, illite-smectite, quartz, and pseudowollastonite. The background profile evidences the occurrence of two amorphous bands, centred at $2\theta \approx 25^\circ$ and at $2\theta \approx 45^\circ$, indicating the presence of nanocrystalline carbonaceous (graphite) material in the mixture (Todica et al., 2014). As a consequence, OC was a mix of amorphous material (presumably anthracite), clay minerals (montmorillonite and smectite), and feldspars. The simultaneous presence of carbon material and clay minerals confers the OC sample significant adsorbing and exchanging properties, classifying it as suitable for the capture of polluting metals from the contaminated sediment (Addy et al., 2012).

The AC diffractogram (Fig. 4S, Supplementary data) did not show sharp Bragg peaks but broad bands in the same position as found in the OC sample, confirming the poorly crystalline nature of the sample.

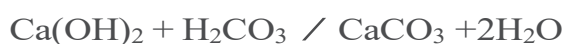
The analysis of the XRPD pattern of the M1 mix indicated the occurrence of aragonite, chlorite, illite, portlandite, quartz, halite, calcite, and albite (Fig. 2, M1 mix). This composition is similar to that of the untreated sediment. The main difference was the presence of portlandite (Ca(OH)₂), absent in the untreated sediment. Portlandite comes from the addition of lime to the sediment; however, in the diffractogram there were no peaks attributable to lime (CaO) and periclase (MgO), as registered in the diffraction pattern of the pure binder (Fig. 2, Lime). This inconsistency can easily be explained by the reaction of lime and water to yield portlandite (3):



It cannot be excluded that part of the calcite (CaCO₃) present in the mix resulted from the reaction between portlandite and carbon dioxide present in the atmosphere, according to the following reaction (4):



However, the reaction did not take place between a solid and a gas, but in the aqueous solution, because of the water present in the wet sediment. Therefore, the calcium hydroxide and the carbon dioxide dissolved in water formed the H₂CO₃ carbonic acid, which, by acid-base reaction, yields the low-soluble salt: calcium carbonate (5):



The mineralogy of the M2 mix was very similar to that of the M1 mix. The M2 mix also showed the characteristic peak of the portlandite centred at $2\theta \approx 18^\circ$, although the intensity of this reflection seems lower than the M1 mix (Fig. 2, M2 mix). AC, being amorphous, did not produce diffraction peaks in the diffractogram; it did not even contribute significantly to the background of the diffraction pattern, which was therefore very similar to that found

for the M1 mix. A weak signal ($2\theta \approx 9.5^\circ$) attributable to a zeolitic phase was identified in the M2 diffraction pattern, although its attribution is doubtful and further analysis had to be conducted.

Except for the sorosilicate ilvaite, the phases identified in the M3 mix (Fig. 2, M3 mix) were the same as those described for the previous diffractograms. In the M3 mix diffractogram, no evidence of the montmorillonite (present in the OC sample) was detected.

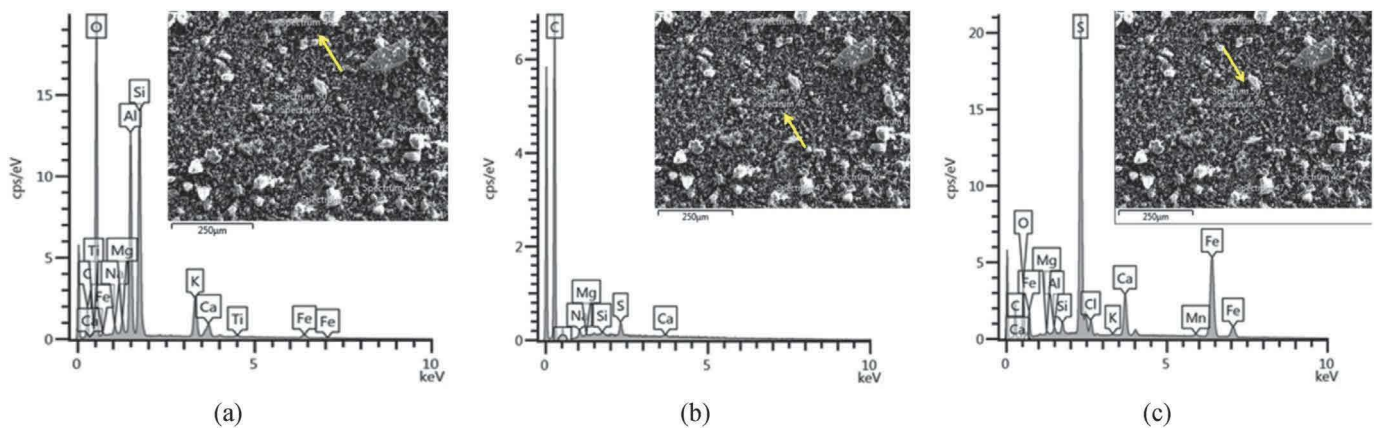


Fig. 4. EDS spectra of (a)

Probably, the small amount of OC used in the mixture and the compression treatment, which could have partly amorphized the clay minerals, can explain this result. Similar behavior was also found in the diffraction pattern produced by the M4 mix, shown in Fig. 2. Although the OC content was twice as that of the M3 mix, the characteristic peaks of montmorillonite were not identified even for the M4 mix diffractogram.

Fig. 3a shows the EDS spectrum executed on a grain from the lime powder sample. The sample shows grains of morphology varying from prismatic to irregular but has homogeneous chemistry, consistent with the mineralogic composition from XRPD analysis.

Fig. 3b shows the typical AC EDS spectrum, where only the carbon signal was observed. The morphology and particle size of the sample was similar to that of the granular activated carbon, which has a smaller external surface than that of powdered activated carbon (De Gisi et al., 2016). The diffusion of adsorbate was therefore an important factor for these substrates, suitable for the absorption of gases and vapors and appropriate for water treatments.

Fig. 3c shows the typical EDS spectrum measured for OC. The elemental composition of the selected grain was consistent with the chemistry of the smectite and/or montmorillonite crystalline phase. Chemical maps (Fig. 5S, Supplementary data) were also acquired on one region of the sample, illustrating how it is made up of alumina-silicate minerals compatible with the mineralogy expected after XRPD analyses.

The EDS analyses of the illite/smectite aluminosilicate mineral and sediment quartz grains are shown in Fig. 3d and e, respectively. The chemical maps (Fig. 6S, Supplementary data) of the same region as the sample in Fig. 3d and e showed a consistency of the sample's chemistry with the XRPD mineralogy.

The SEM on the treated sediments produced results comparable to each other and to those of the untreated sediment. All the findings showed that the samples are formed by the phases that make up their initial products. No newly formed phases were identified. As an example, the results obtained on the M3 mix are shown: the phases identified by SEM were alumino-silicates (probably phyllosilicates), feldspars (Fig. 4a), carbonaceous material (Fig. 4b) and gypsum (Fig. 4c). The chemical maps (Fig. 5) of the region showed expected signals.

It was noted that in the M1 mix the SEM investigations had revealed the presence of pyrite, FeS₂ (see Fig. 3f). Although the presence of pyrite is undetected based on the results of the XRPD analyses, it is known from Dondi et al. (1992) that small amounts of it could be present in the study sediments. The apparent discrepancy between SEM and XRPD results was due to the variability of the mineralogical composition of the natural sediments. Marine sediments, depending on the sampling point, could show variations in the relative abundances of the crystalline phases that constitute them.

3.2. Leaching tests

The tests carried out on the treated marine sediment have shown no release value higher than the limit imposed by the Ministerial Decree 05/02/1998 for metals.

With regard to the variation of the pH of the eluates as the reaction time of the stabilization process increases, descending trends of the pH were observed (Fig. 6a). The pH reached values in the range 9e11 after a reaction time of 28-d, an interval that corresponded to the minimum values of transfer of metals from the sediment by leaching, or the range of pH at which the minimum solubility of salts and hydroxides of heavy metals contaminants was achieved. In all the M1-M4 mixtures there was a significant initial release of the toxic metal ions retained by the sediment (Fig. 6beh). For some metals such as cobalt, chromium, and lead the released amount was below the limit of the Ministerial Decree 05/02/1998. For other metals, such as nickel and copper, values were initially observed above the legal thresholds and they decreased with time. This phenomenon could be attributed to the mixing operations and the associated bond breaking, resulting in a release of contaminating metal ions from sediment.

The values found could support the applicability of the S/S treatment used for the considered sediment in line with Couvidat et al. (2016) and Pinto et al. (2011). Except for copper, all ion concentration values were below the legal limits at the end of the 28-d. 56 days after treatment also copper had values below the legal limits. In addition, the presence of adsorbent agents (AC and/or OC) added to the binder (CaO) improved the immobilisation of the polluting ions.

The above results indicated that, despite the total concentrations of heavy metals in the marine sediments studied, the release of contaminants after contact with deionised water was very

limited. This was due to the low solubility of metals and to the stability of their solid phases under slightly basic conditions (Couvidat et al., 2016). Mobility of the metals appeared to be governed by pH; however, the addition of lime appeared to increase the leaching of copper. The latter, in turn, was most probably due to the organic contamination (PAHs and PCBs) of the untreated sediment. The results in Fig. 7 show how organic contaminants interfered with the hydration chemistry of the binder; at 28 days they compromised the effectiveness of metal stabilization and hardening development, delaying the hydration reaction (Wang et al., 2015a).

3.3. Unconfined compressive strength

Fig. 8 show the results of the UCS tests carried out on specimens of treated mixtures after 28-d curing times.

The first consideration that can be made is that, although the untreated sediments have a liquid consistency ($q_u = 0$), after treatment the soil consistency rises, irrespective of the additive or reagent used. The maximum value of q_u is obtained for lime and AC treated specimens (28.1 kPa). Based on the experimental results, the use of AC could produce a material that is not only strong enough for land reclamation, but it could also do so in a shorter time.

The high clay content (37.6%) of the marine sediment could be the primary reason for the reduction of compressive strength; the high content of fine size particles probably weakened the granular skeleton leading to a low compressive strength (Meddah et al., 2010). It should be stressed that the results are relative to sediments with a high content of organic matter, heavy metals and pore water salinity (35 g/l). The aspects are coupling in interfering with binder hydration chemistry and influencing the mechanical properties (Pandey et al., 2012).

The compressive strength was compared with the criteria for reuse as fill materials for site formation (i.e., ground leveling/stabilization to the design formation level before construction works) to validate the applicability of sediment recycling. Vahedifard et al. (2015) performed a slope stability analysis to establish minimum q_u values for feasibility considerations. The results showed that q_u values of 18 and 24 kPa would satisfy a minimum factor of safety equal to 1.5 for 3.5 and 5.0 m slopes, respectively.

3.4. Impact of research and future trends

Since the S/S chemistry is already established, the scale-up from pilot-scale to full-scale implementation is focused on the materials-handling aspects of the S/S process.

The absence of specific pre-treatments of sediments (i.e., dewatering) involves the absence of the additional water for the treatment. For M2, M3, and M4 mixtures, each ton of wet sediment involves 55 kg of lime and 27.5 kg of additives, for a total of 82.5 kg of chemicals; for the M1 mixture, only 55 kg of lime is added (Table 7 and Fig. 9). These dry reagents are typically fed from the storage silos using a screw auger.

Compared to the fresh product, an approximate decrease of 10% is possible to observe after 56-days curing in terms of respective mass loss during the curing phase. (Table 6)

The results showed a total recovery of dredged sediments and a consequent absence of waste production. One of the most interesting implications is to avoid landfilling, estimated in 0.65 m³ per ton of dredged sediment. Considering that the production scheme sediments contaminated by metals and organic compounds (PAHs and PCBs) by stabilization/solidification treatments based on lime, organoclay, and activated carbon for the production of filling materials for environmental applications. The experimental investigation, carried out on marine sediments in one of the most contaminated areas of Italy (Mar Piccolo of Taranto), was characterized by the absence of any pre-treatment of the sampled sediments as well as by the use of a S/S pilot plant, whereas most of the experiments in literature are at laboratory scale.

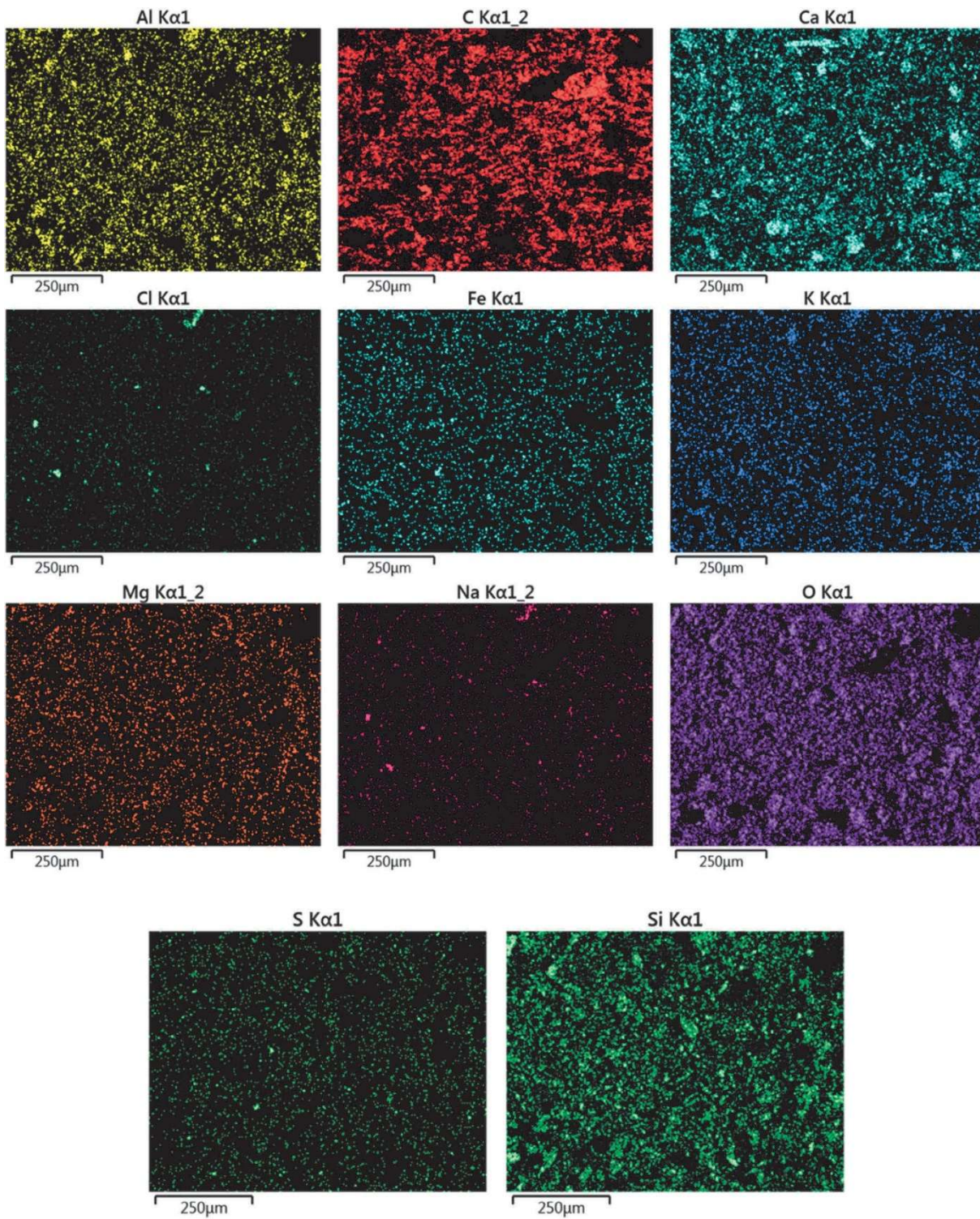
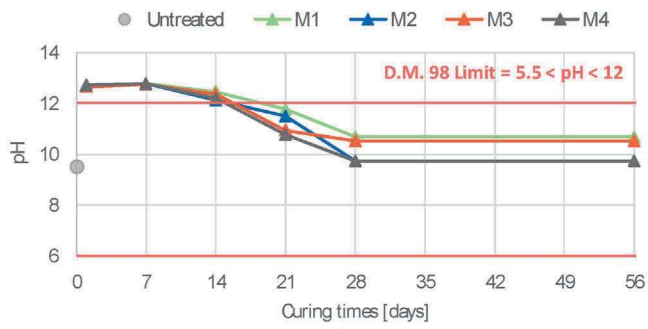
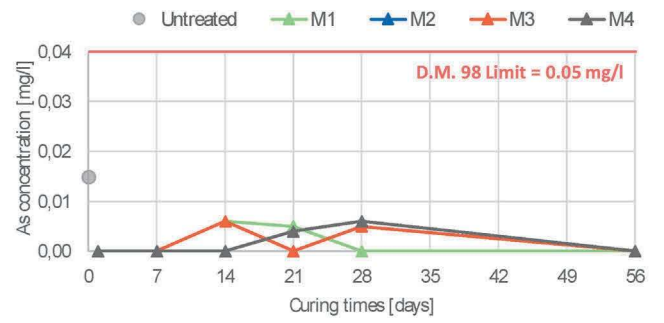


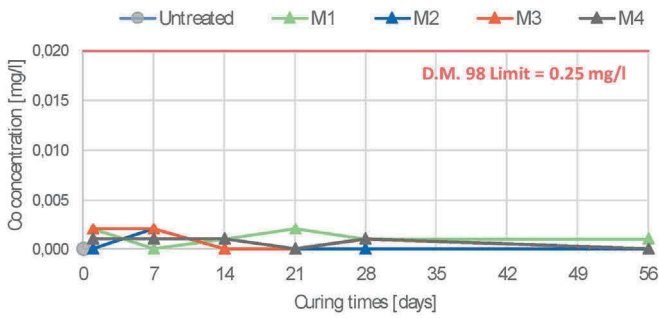
Fig. 5. Chemical maps of the M3 mix treated sediment.



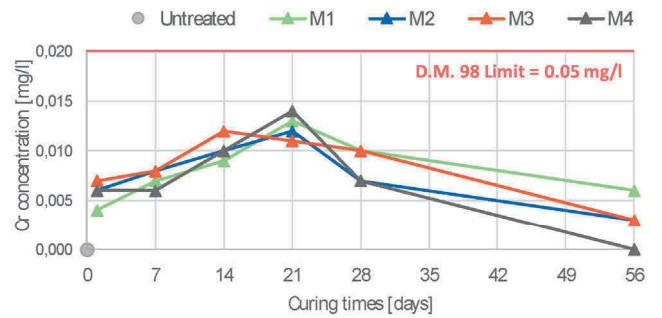
(a)



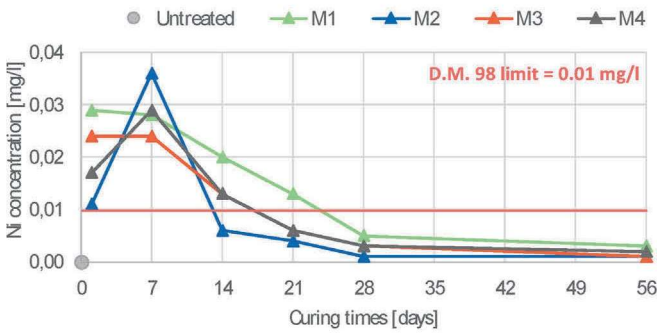
(b)



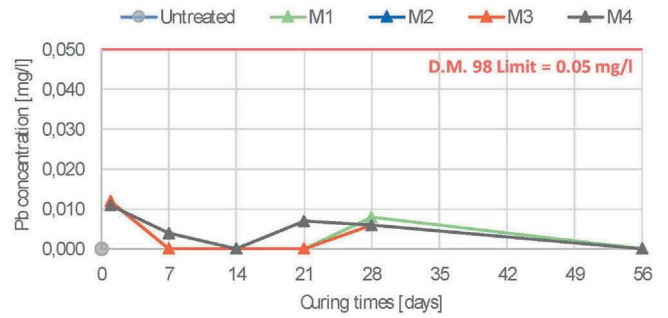
(c)



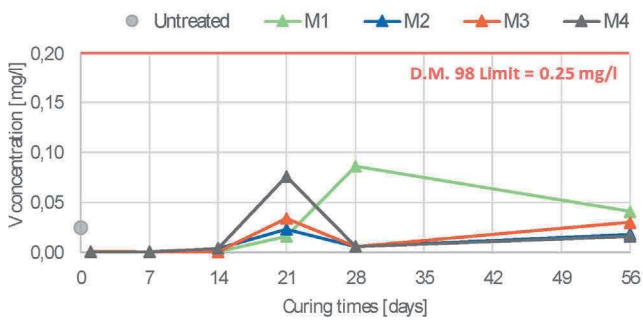
(d)



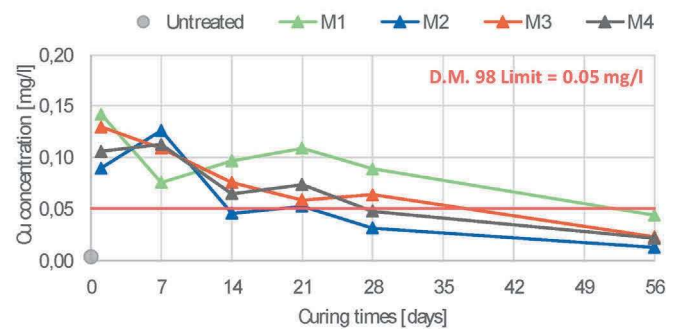
(e)



(f)



(g)



(h)

Fig. 6. S/S average parameters variation at different curing times: (a) pH; (b) arsenic; (c) cobalt; (d) chromium; (e) nickel; (f) lead; (g) vanadium; (h) copper. The legal limit values for the leaching test refer to the Italian 5/2/98 Law.

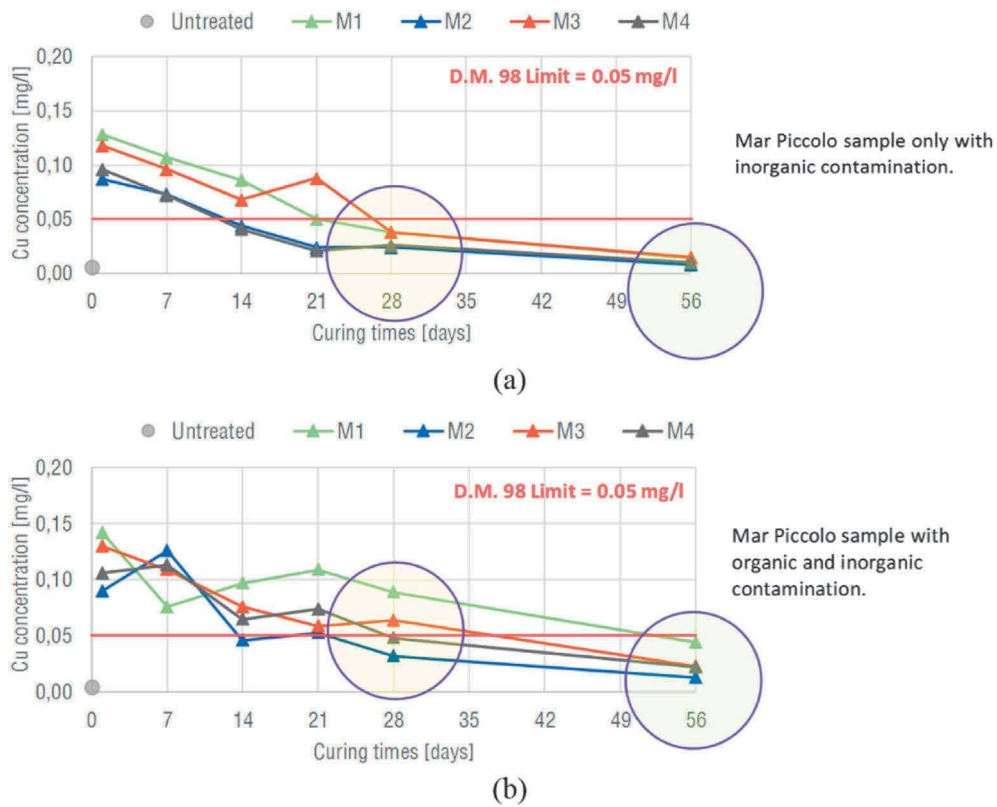


Fig. 7. Comparison of performance in terms of copper (Cu) immobilisation for a sample contaminated with (a) only inorganic compounds and (b) both organic and inorganic compounds (average values).

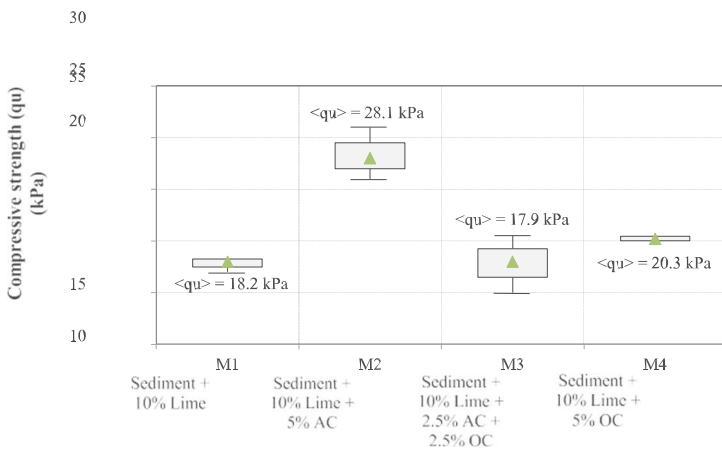


Fig. 8. Unconfined compressive strength of specimens treated with lime + additives.

The results showed how the main mineralogical phases in the investigated sediments were clay minerals, quartz, carbonates, plagioclases, and feldspars; the clay minerals, in turn, were found to be a mixture of illite, chlorite, and kaolinite. All the findings showed that the samples were formed by the phases that make up their initial products, so no newly formed phases were identified in the investigated mixtures. The absence of specific sediment pre-treatment aimed at removing organic contaminants resulted in

for sediment-based materials is simplified, full scale intervention could have a positive impact on the local economy; the products thus obtained could cover the demand for inert materials for environmental applications in the surrounding area.

Future research should focus primarily on strengthening the obtained results. It will be interesting to deepen the consolidation phase of the dredged sediment after the recycling - varying its duration - as well as to improve the curing phase (CO₂-assisted) and the compressive mechanical strength by adding inert aggregates directly into the mixture.

4. Conclusions

The study showed the technical feasibility of recycling marine failure to comply with the 28-d leaching test only for copper. However, greater air curing with 56-d allowed it to be complied with for all the investigated metals. The organic contamination properly treated with the considered mix designs, while slowing down the process of chemical stabilization, in any case allowed to obtain a product environmentally compatible. The unconfined compression strength tests carried out on specimens of treated mixtures after 28-d curing times showed values (>28 kPa) which would allow potential recycling of the sediment for environmental enhancement such as site remediation and land formation. Besides the possibility of technically recycling sediments, one of the most interesting implications has been to avoid dredged sediments being landfilled. The mass balance of the case study of the Mar Piccolo of Taranto (Southern Italy) showed potential recycling of marine sediments of 974 kg per 1000 kg of dredged sediment with a consequent missed disposal in landfills of 0.65 m³/1000 kg of sediment.

Table 6

Comparison of the crystalline phases identified by XRPD in the raw materials and the S/S products.

Mineral and symbol	Formula	Material							
		Lime	OC	AC	Sed ^a	M1	M2	M3	M4
Albite	Al	NaAlSi ₃ O ₈			x	x	x	x	x
Anorthite	An	CaAl ₂ Si ₂ O ₈	x						
Sanidine	S	(KNa)(Si, Al) ₄ O ₈	x						
Halite	H	NaCl			x	x	x		
Aragonite	A	CaCO ₃			x	x	x	x	x
Calcite	Ca	(Ca,Mg)CO ₃			x	x	x	x	x
Dolomite	D	MgCa(CO ₃) ₂			x	x		x	x
Kaolinite 1A	K	Al ₂ Si ₂ O ₅ (OH) ₄			x	x	x	x	x
Chlorite	C	(MgFeAl) ₈ (SiAl) ₈ O ₂₀ (OH) ₁₆			x	x	x	x	x
Illite	I	[K,H ₃ O][Al,Mg,Fe) ₂ (Si,Al) ₃ O ₁₀ [(OH) ₂ .(H ₂ O)]			x	x	x		
Illite-Smectite	I/S	K _x Al ₂ [AlSi ₃]O ₁₀ (OH) ₂	x					x	x
Montmorillonite	M	(Na, Ca) _{0.3} (Al, Mg) ₂ Si ₄ O ₁₀ (OH) ₂ *n(H ₂ O)	x						
Lime	L	CaO	x						
Portlandite	P	Ca(OH) ₂	x				x	x	x
Periclase	Pe	MgO	x						
Quartz	Q	SiO ₂		x			x	x	x
Zeolite	Z	SiO ₂		x					
Gypsum	G	CaSO ₄ *2(H ₂ O)		x					
Graphite	e	C			x				
Pseudowollastonite	PW	CaSiO ₃			x				x

^a Sed = untreated sediment.

Table 7

Mass balance results of the tested mixes for 1000 kg of sediment fed into the S/S plant.

MIX	Water [m ³]	Lime [kg]	AC [kg]	OC [kg]	Energy [kWh]	Product 0-days [kg]	Product 56-days [kg]	Not disposed [m ³]
1	0.00	55.00	0.00	0.00	25	1055.0	949.5	0.65
2	0.00	55.00	27.50	0.00	25	1082.5	974.3	0.65
3	0.00	55.00	13.75	13.75	25	1082.5	974.3	0.65
4	0.00	55.00	0.00	27.50	25	1082.5	974.3	0.65

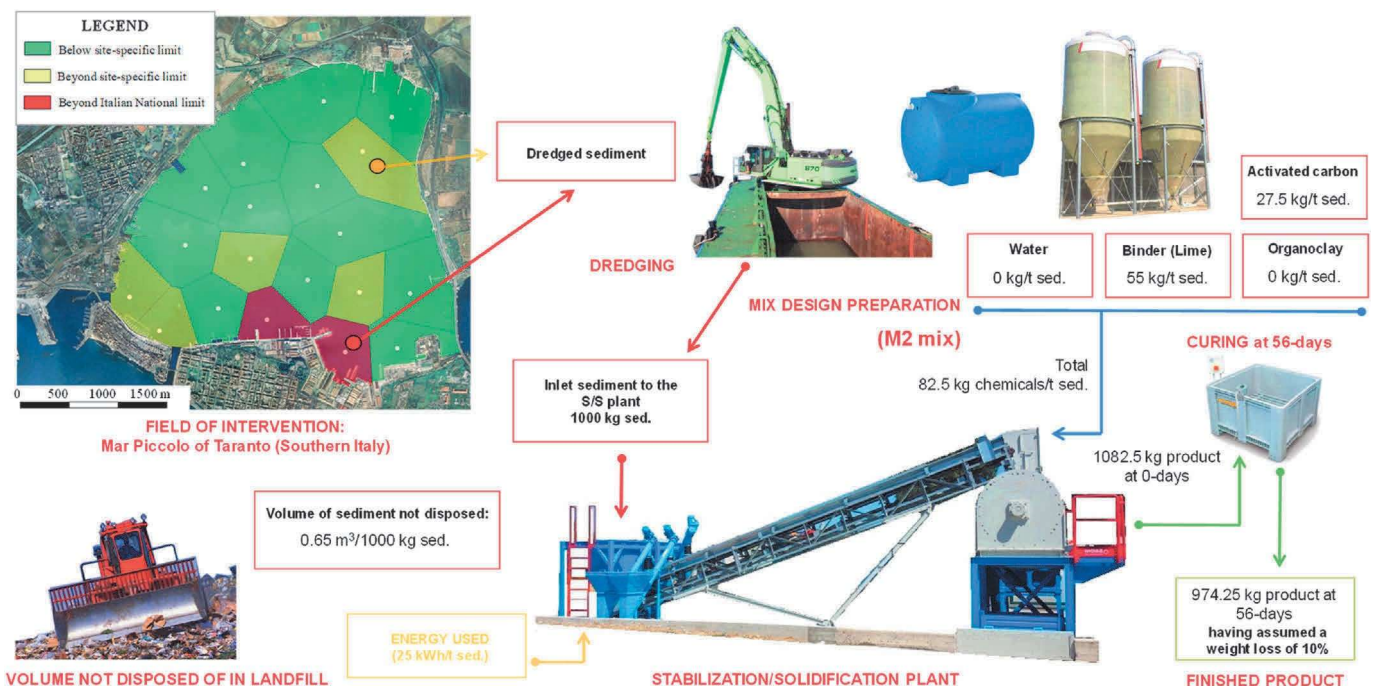


Fig. 9. Potentially recyclable sediments as a result of mass balance relating to the boundaries of the study area.

CRedit authorship contribution statement

Sabino De Gisi: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft. Francesco Todaro: Conceptualization, Methodology, Investigation, Writing - original draft. Ernesto Mesto: Methodology, Formal analysis, Investigation, Writing - original draft. Emanuela Schingaro: Validation, Writing - review & editing, Supervision, Funding acquisition. Michele Notarnicola: Conceptualization, Validation, Writing - review & editing, Supervision, Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2020.122416>.

References

- ASTM D2166/D2166M-16, 2016. *Standard Test Method for Unconfined Compressive Strength of Cohesive Soil*. ASTM International, West Conshohocken, PA.
- Addy, M., Losey, B., Mohseni, R., Zlotnikov, E., Vasiliev, A., 2012. Adsorption of heavy metal ions on mesoporous silica-modified montmorillonite containing a grafted chelate ligand. *Appl. Clay Sci.* 59e60, 115e120. <https://doi.org/10.1016/j.clay.2012.02.012>.
- Barjoveanu, G., De Gisi, S., Casale, R., Todaro, F., Notarnicola, M., Teodosiu, C., 2018. A life cycle assessment study on the stabilization/solidification treatment processes for contaminated marine sediments. *J. Clean. Prod.* 201, 391e402. <https://doi.org/10.1016/j.jclepro.2018.08.053>.
- Colangelo, F., Cioffi, R., Montagnaro, F., Santoro, L., 2012. Soluble salt removal from MSWI fly ash and its stabilization for safer disposal and recovery as road basement material. *Waste*

- Manag. 32, 1179e1185. <https://doi.org/10.1016/j.wasman.2011.12.013>.
- Couvidat, J., Benzaazoua, M., Chatain, V., Bouamrane, A., Bouzahzah, H., 2016. Feasibility of the reuse of total and processed contaminated marine sediments as fine aggregates in cemented mortars. *Construct. Build. Mater.* 112, 892e902. <https://doi.org/10.1016/j.conbuildmat.2016.02.186>.
- De Gisi, S., Lofrano, G., Grassi, M., Notarnicola, M., 2016. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review. *Sust. Mater. Technol.* 9, 10e40. <https://doi.org/10.1016/j.susmat.2016.06.002>.
- Decree, Ministerial, 1998. Identification of not-hazardous waste subjected to simplified recovery procedures (in Italian). Italian Official Journal No 88, 16/04/1998.
- Dell'Anna, L., Laviano, R., 1991. Mineralogical and chemical classification of Pleistocene clays from the Lucanian Basin (Southern Italy) for the use in the Italian tile industry. *Appl. Clay Sci.* 6, 233e243.
- Dondi, M., Fabbri, B., Laviano, R., 1992. Characteristic of the clays utilized in the brick industry in Apulia and Basilicata (Southern Italy), 35A. *Mineralogica et Petrographica Acta*, Bologna, pp. 181e191.
- EN standard 12457-2, 2002. Characterization of waste - leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: one stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction). Italian National Unification. UNI EN 12457-2:2002.
- EPA 120.1, 1982. Method 120.1: Conductance by Conductivity Meter. Official Name: Conductance (Specific Conductance, Umhos at 25 °C). http://www.caslab.com/EPA-Method-120_1/.
- EPA 150.1, 1982. Method 150.1: pH in Water by Electrometric Method. Official Name: pH, Electrometric Method. http://www.caslab.com/EPA-Method-150_1/.
- EPA 160.4, 1971. Method 160.4: Volatile Residue by Muffle Furnace. Official Name: Residue, Volatile (Gravimetric, Ignition at 550 °C). http://www.caslab.com/EPA-Method-160_4/.
- EPA 200.8, 1994. Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry. Revision 5.4. Cincinnati, OH. <http://www.caslab.com/EPA-Methods/PDF/EPA-Method-2081.pdf>.
- EPA 24, 1993. Method 24: Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coating. <http://www.caslab.com/EPA-Method-24/>.
- EPA Method 8275A, 1996. Semivolatile organic compounds (PAHs and PCBs) in soils/sludges and solid wastes using thermal extraction/gas chromatography/mass Spectrometry. U.S. Environmental Protection Agency, Washington, D.C.. TE/GC/MS). <https://www.epa.gov/sites/production/files/2015-12/documents/8275a.pdf>
- Fernandes, V.A., Purnell, P., Still, G.T., Thomas, T.H., 2007. The effect of clay content in sands used for cementitious materials in developing countries. *Cem. Concr. Res.* 37, 751e758.
- Hale, B., Evans, L., Lambert, R., 2011. Effects of cement or lime on Cd, Co, Cu, Ni, Pb, Sb, and Zn mobility in field contaminated and aged soils. *J. Hazard Mater.* 199e200, 119e127. <https://doi.org/10.1016/j.jhazmat.2011.10.065>.
- ICRAM, 2004. Values of Intervention for Sediments of Areas Strongly Anthropized with Reference to the Site of Reclamation of National Interest in Taranto (In Italian). Central Institute for Scientific and Technological Research applied to the Sea, Rome, Italy.

- ICRAM-APAT, 2007. Handbook for Dredging Marine Sediments (In Italian). Central Institute for Scientific and Technological Research applied to the Sea, Rome, Italy (Available at: this link: <http://www.isprambiente.gov.it/contentfiles/00006700/6770-manuale-apat-icram-2007.pdf>).
- Kadir Aeslina, A.K., Mohamad, R.I., Mohd, M.A.B.A., Noor, A.S., Haqem, H., 2016. The usage of glass waste as cement replacement. *Key Eng. Mater.* 673, 95e104.
- L.D., 2006. Legislative decree No. 152/2006, Environmental regulations (in Italian). *Ital. Off. J.* 88, 04/04/2006.
- Li, D., Seaman, J.C., Kaplan, D.I., Heald, S.M., Sun, C., 2019. Pertechnetate (TcO₄—) sequestration from groundwater by cost-effective organoclays and granular activated carbon under oxic environmental conditions. *Chem. Eng. J.* 360, 1e9.
- Limeira, J., Agullo, L., Etxeberria, M., 2010. Dredged marine sand in concrete: an experimental section of a harbor pavement. *Construct. Build. Mater.* 24, 863e870.
- Lofrano, G., Libralato, G., Minetto, D., De Gisi, S., Conte, B., Todaro, F., Calabro', D., Notarnicola, M., 2017. In situ remediation of contaminated marine sediment: an overview. *Environ. Sci. Pollut. R.* 24, 5189e5206. <https://doi.org/10.1007/s11356-016-8281-x>.
- Meddah, M.S., Zitouni, S., Belaabes, S., 2010. Effect of content and particle size distribution of coarse aggregate on the compressive strength of concrete. *Construct. Build. Mater.* 24, 505e512.
- Pandey, B., Kinrade, S.D., Catalan, L.J.J., 2012. Effects of carbonation on the leach- ability and compressive strength of cement-solidified and geopolymer- solidified synthetic metal wastes. *J. Environ. Manag.* 101, 59e67.
- Pinto, P.X., Al-Abed, S.R., Barth, E., Loftspring, C., Voit, J., Clark, P., Ioannides, A.M., 2011. Environmental impact of the use of contaminated sediments as partial replacement of the aggregate used in road construction. *J. Hazard Mater.* 189, 546e555.
- RaCenovi'c, D., Kerkez, D., Pilipovi'c, D.T., Dubovina, M., Grba, N., Kr'cmar, D., Dalmacija, B., 2019. Long-term application of stabilization/solidification technique on highly contaminated sediments with environment risk assessment. *Sci. Total Environ.* 684, 186e195.
- Shubbar, A.A., Jafer, H., Dulaimi, A., Hashim, K., Atherton, W., Sadique, M., 2018. The development of a low carbon binder produced from the ternary blending of cement, ground granulated blast furnace slag and high calcium fly ash: an experimental and statistical approach. *Construct. Build. Mater.* 187, 1051e1060.
- Shubbar, A.A., Sadique, M., Kot, P., Atherton, W., 2019. Future of clay-based construction materials e a review. *Construct. Build. Mater.* 210, 172e187.
- Smith, B.T., Howard, I.L., Vahedifard, F., 2017. Lightly cemented dredged sediments for sustainable reuse. *Environ. Geotech.* 5 (6), 324e335. <https://doi.org/10.1680/jenge.16.00019>.
- Todaro, F., De Gisi, Notarnicola, M., 2018. Sustainable Remediation Technologies for Contaminated Marine Sediments: Preliminary Results of an Experimental Investigation. *Environ. Eng. Manag. J.* 17 (10), 2465e2471.

- Todica, M., Stefan, T., Simon, S., Balasz, I., Daraban, L., 2014. UV-Vis and XRD investigation of graphite-doped poly(acrylic) acid membranes. *Turk. J. Phys.* 38, 261e267. <https://doi.org/10.3906/fiz-1305-16>.
- US EPA, 1997. Innovative Site Remediation Technology, Solidification/Stabilization. Design and Application, vol. 4. US EPA, Washington, DC, USA. EPA-542-B-97-007.
- Vahedifard, F., Howard, I.L., Bazne, M., Smith, B.T., Barksdale, M.A., 2015. Sustainably Enhancing Intermodal Freight Operation of Ports Using Geotextile Tubes. National Center for Intermodal Transportation for Economic Competitiveness and US Department of Transportation. Report NCITEC 2013-05.
- Wang, L., Kwok, J.S.H., Tsang, D.C.W., Poon, C., 2015a. Mixture design and treatment methods for recycling contaminated sediment. *J. Hazard Mater.* 283, 623e632. Wang, L., Tsang, D.C.W., Poon, C.-S., 2015b. Green remediation and recycling of contaminated sediment by waste-incorporated stabilization/solidification. *Chemosphere* 122, 257e264.
- Wang, L., Yeung, T.L.K., Lau, A.Y.T., Tsang, D.C.W., Poon, C.-H., 2017. Recycling contaminated sediment into eco-friendly paving blocks by a combination of binary cement and carbon dioxide curing. *J. Clean. Prod.* 164, 1279e1288.
- Wang, L., Chen, L., Tsang, D.C.W., Li, J.-S., Baek, K., Hou, D., Ding, S., Poon, C.-S., 2018. Recycling dredged sediment into fill materials, partition blocks, and paving blocks: technical and economic assessment. *J. Clean. Prod.* 199, 69e76. <https://doi.org/10.1016/j.jclepro.2018.07.165>.
- Wang, L., Chen, L., Cho, D.-W., Tsang, D.C.W., Yang, J., Hou, D., Baek, K., Kua, H.W., Poon, C.-S., 2019a. Novel synergy of Si-rich minerals and reactive MgO for stabilisation/solidification of contaminated sediment. *J. Hazard Mater.* 365, 695e706.
- Wang, L., Chen, L., Tsang, D.C.W., Kua, H.W., Yang, J., Ok, Y.S., Ding, S., Hou, D., Poon, C.S., 2019b. The roles of biochar as green admixture for sediment-based construction products. *Cement Concr. Compos.* 104, 103348.
- Woo, H.E., Tran, T.V., Lee, I.C., Kim, J.O., Hibino, T., Nohara, H., Kim, K., 2019. Remediation of contaminated sediment originating from wastewater at T harbor areas using slaked lime e fly ash e cement mixture. *Estuar. Coast Shelf Sci.* 227, 106340. <https://doi.org/10.1016/j.ecss.2019.106340>.
- Zentar, R., Wang, D., Abriak, N.E., Benzerzour, M., Chen, W., 2012. Utilization of siliceous aluminous fly ash and cement for solidification of marine sediments. *Construct. Build. Mater.* 35, 856e863.