

## USE OF MUSSEL SHELLS FOR MECHANICAL STABILISATION OF DREDGED MARINE SEDIMENTS: SOME GEOTECHNICAL ISSUES

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### Abstract

The note shows some results concerning an experimental activity conducted on marine sediments dredged and conferred in the Taranto port fill-in basin. This study is part of a PON RI 2018-2021 PhD project that included the collaboration between Politecnico di Bari, Italcementi S.p.A. and ETH-Zurich aiming to promote the reuse of two waste products from port and coastal areas (marine sediments and mussel shells) and define eco-sustainable solutions to mechanically stabilise the sediments. Specifically, the proposed solutions entail the mixing of the sediments in their natural state with mixtures of hydraulic binders and mussel shell powder, where the mussel powder partially replaces the binder in the mixture.

### 1. Introduction

The sustainable use of resources is a fundamental aspect in a world where there is an exponential increase in the demand for them to sustain the constant economic and societal growth. This requires new strategies that have to be centred on the transformation of waste into recycled resources for use in other applications. This approach, inspired by the fundamentals of the circular economy, can be applied to different fields of Civil and Environmental Engineering, including the management and the reuse of marine sediments which are dredged periodically (in Europe about 100-200 million m<sup>3</sup>/year) in harbour areas either for the port effectiveness or for the site remediation (SedNet, 2011). In this context, several research studies in geotechnical engineering entail the mechanical stabilisation of sediments by commercial binders such as cements and lime (Federico et al. 2015; Chang et al., 2007). Cements are the most widely used materials in the building industry (according to the WWF, concrete production could reach 5 billion tonnes by 2030) but they are also among the most harmful: the concrete production process requires large amounts of energy and releases pollutants, i.e., for every ton of clinker produced, one ton of CO<sub>2</sub> is released into the atmosphere. For this reason, in the most recent years, some solutions have been proposed making use of more sustainable binders that reduce the CO<sub>2</sub> consumption and accomplish with the so-called green new deal (Latifi et al., 2018; Yoobanpot et al., 2018; Roque et al., 2022). This note is part of this research, and it reports some results about an experimental study comparing solutions for the stabilisation of sediments making use of commercial and new binders. The new binders have been obtained by partial substitution of the commercial ones

with mussel shell powder. The powder has been obtained by recycling mussel shells, i.e., another bio-waste currently produced in large quantities (about 230.000 ton/year in Europe) and dumped in landfills with complex and expensive disposal procedures.


Some recent projects promote the use of mussel shells for numerous applications from the cosmetic to the fertiliser industry and as additives to traditional binders. However, in none of these projects, mussel shells are used as partial substitute for binders to mechanically and/or chemically stabilise fine grained marine sediments. The note presents some laboratory results of geotechnical tests carried out on both the new binders when mixed to sediments and commercial binder-sediment mixtures.

## 2. Materials and methods

### 2.1 Untreated sediment

The untreated sediment (US) has been dredged from the Taranto port in the south of Italy. It is a clayey silt of negative consistency ( $CI = (w_L - w_0)/PI = -0.73$ ) that can be classified as high plasticity soil, CH (USCS, ASTM 2011) (Table 1). As suggested by both standards and literature (e.g., BS 1337; Sollecito et al., 2019), the water content  $w$  and the Atterberg limits were corrected to take account of the pore fluid salinity. Moreover, Atterberg limits have been determined on the total sample instead of on the material passing on the ASTM sieve n. 40. This allowed considering the effect of the presence of algae and other organic materials that actively interact with the soil particles (e.g., Roque et al. 2022). Table 1 also reports the specific gravity of the soil solid ( $G_s$ ) and the amount of organic matter measured in US by total organic carbon (TOC). The chemical characterisation of the sediment (ISPRA, 2010) showed that heavy metals and organic pollutants are present in lower quantities than law limits (Column B Table 1 Annex 5 to Title V of Part IV of Legislative Decree 152/06).

Table 1. Untreated sediments: US – Physical and plasticity properties. Key:  $w_L$ : liquid limit;  $w_P$ : plastic limit;  $\gamma_s$ : weight of soil solids per unit volume;  $w_0$ : water content; SF: sand fraction; MF: silt fraction; CF: clay fraction; TOC: total organic carbon;  $G_s$ : specific gravity of soil solids; \*modified procedure.

Material	$w_L$ [%]	$w_P$ [%]	$\gamma_s$ [kN/m <sup>3</sup> ]	$w_0$ [%]	SF [%]	MF [%]	CF [%]	TOC [%]	$G_s$ [-]
 Untreated sediment, US	53.40	25.24	15.95	74.08	5.80	63.80	30.40	1.52	2.68
Standard used	ASTM D 4318*	ASTM D 854-14	ASTM D 2216-D4542	ASTM D 422				DIN EN 15936	-

### 2.2 Cements

Three types of cements were used: from the traditional type I Portland Cement 52.5R (P), to a more sustainable commercial binder, such as the type III Termocem green blast furnace cement (T), to the most recent Sulphoaluminate cement (CS), i.e., cements resulting from a Core process with < 550 kg / t CO<sub>2</sub> emissions and at least 30% of pre- or post-consumption recycled material. The main differences among the chemical composition of the three cements are the high percentages of SO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> in CS, high CaO content in P and CaO and SiO<sub>2</sub> in T (Table 2).

### 2.3 Limestone and Mussel shells

Usually, cements are made mainly by calcining a mixture of about 75% limestone and 25% clay to form a calcium silicate clinker which is then ground and mixed with a small amount of gypsum. The choice of the ingredients for the new binder (hereafter referred to as CemShell) was guided by the comparison between the mixtures formed by dredged sediments, commercial cements, and powdered

Limestone (LST) with those where dredged sediments were treated with commercial cement and the

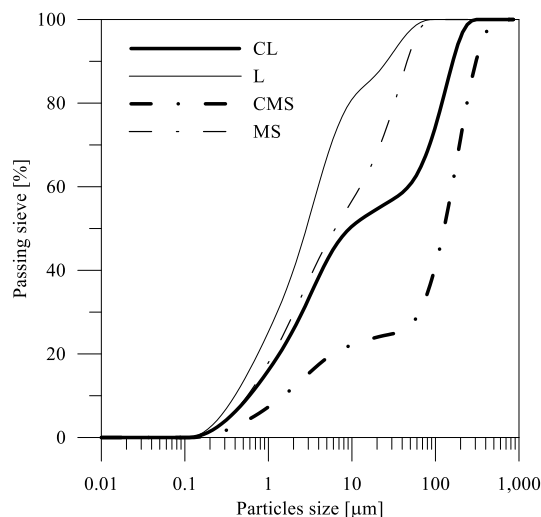


Fig 1. Particle size distribution of limestone (L, CL) and mussel shell powder (MS, CMS).

same quantity of mussel shells powder in place of LST, as greener source of calcium carbonate. Traditional Limestone was crushed and sieved to have two grain particle size distributions: i) L, that is characterised by  $D_{50} = 2.84 \mu\text{m}$  and uniformity coefficient  $C_u = D_{60}/D_{10} = 2.409$ ; ii) CL, coarser than the previous one, with  $D_{50} = 9.38 \mu\text{m}$  and  $C_u = 5.548$  (Fig 1).  $D_{10}$ ,  $D_{50}$  and  $D_{60}$  are the grain sizes corresponding to the 10, 50 and 60% of passing sieve, respectively. The shells used in this study are of the type *Mytilus galloprovincialis*. For the production of the mussel shell powder (MS), the mussel shells underwent the following treatment: i) washing with hot water for about 10 minutes and oven-drying at  $105^\circ\text{C}$  for 48 hours to remove impurities and organic matter from the shells (Othman et al. 2013); ii) milling in a Retsch jaw crusher; iii) sieving to obtain two different particle size distributions, CMS and MS (Fig 1). The first one is coarser and characterised by

$D_{50} = 127 \mu\text{m}$  and  $C_u$  equal to 0.754, the second one, MS, has  $D_{50} = 6.32 \mu\text{m}$  and  $C_u = 2.213$ . Moreover, Table 2 shows that chemical composition of mussel shells is similar to that of limestone, mainly consisting of calcium oxide (CaO), with small fractions of other oxides.

Table 2. Chemical composition of the mussel shell powder, MS, and cement (Portland cement, P; Termocem green cement, T, Sulphoaluminate cement, CS).

Oxides [% mass]	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SrO	MnO	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	Sr [PPM]	Ni [PPM]	Cu [PPM]	LOI
P	63.06	3.92	4.51	18.09	1.59	0.5	0.93	4.13	0.11	0.03	0.07	0.22	-	-	-	-	2.64
T	44.99	8.25	1.48	32.81	5.79	0.52	0.81	3.61	0.05	0.09	0.15	0.38	-	-	-	-	1.27
CS	40.19	23.64	1.37	7.57	2.75	0.89	0.49	20.03	0.09	0.16	0.11	0.35	-	-	-	-	0.75
MS	53.605	0.02	0	0.038	0.239	0.355	0.034	0.197	0.034	-	-	0	0.002	812	48	118	45.58

Fig 2 shows the SEM analyses performed on mussel shells by Ballester and coauthors (Ballester et al., 2007). Differently from limestone, where  $\text{CaCO}_3$  aggregates consist mainly of rounded particles, the fabric of mussel shells is made up of elements of similar average size ( $2\text{--}6 \mu\text{m}$ ) but more elongated shape. Moreover, as reported in the literature, the structure of mussel shells, like all bivalves, can be divided into three parts: the outer layer, periostracum, the middle layer, i.e., the prismatic layer (Gènio, 2014), and the inner layer referred to as nacre (Martínez-García et al., 2017). Elongated shapes characterise both prismatic layer and nacre. The first part of the experimental programme entailed the comparison between mixtures formed by sediments, cements and limestone powder and the same mixtures where limestone was replaced by mussel shell powder (MS). Both the powders were tested with the fine (i.e., MS and L) and a coarser (CMS and CL) grain sizes. For each Cement used (i.e., P, T or CS type), the sediment-mixtures were prepared by replacing  $1/3$  or  $1/2$  of cement with either mussel shell or limestone powder, for both fine and coarse-grained sizes. Finally, also traditional sediment-cement control mixtures were prepared and tested. The content of binders added to the sediment was adjusted according to the dry weight of the sediment, which was determined from the natural water content ( $w_0 = 74.08\%$ ). The virgin material was first homogenised in a mechanical mixer for 10 minutes at medium speed (285 RPM). Subsequently, the binder was added, and the material was further mixed for 5 minutes at lower speed (140 RPM). After 7 and 28 days of curing in marine water,

the following determinations were carried out on the mixtures: Atterberg Limits, Texturometer pressure and pH of curing water. The Texturometer is a new recording instrument for the measurement of mechanical textural parameters (hardness, cohesiveness, viscosity, elasticity, adhesiveness, brittleness, chewiness, and gumminess) and usually is used on food and for quick determinations on hydraulic binders. Although frequently used for cements, it has been originally applied to natural and treated sediments to verify their state and quantify their strength in a quick way. The principle of the Texturometer is similar to that of CPT tests and is the measurement of the force (in Newton) opposed to the driven penetration of a probe into the material at constant rate. In this case, the test was performed on a cylindrical probe with a contact surface area of 3 mm.

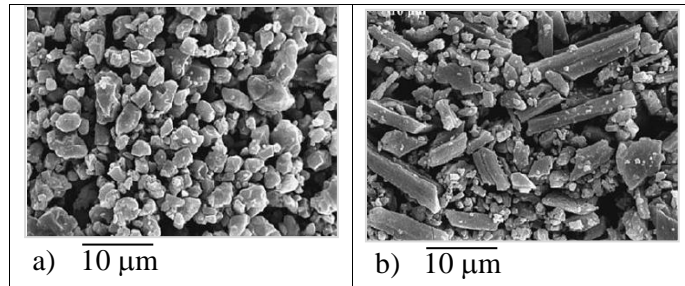
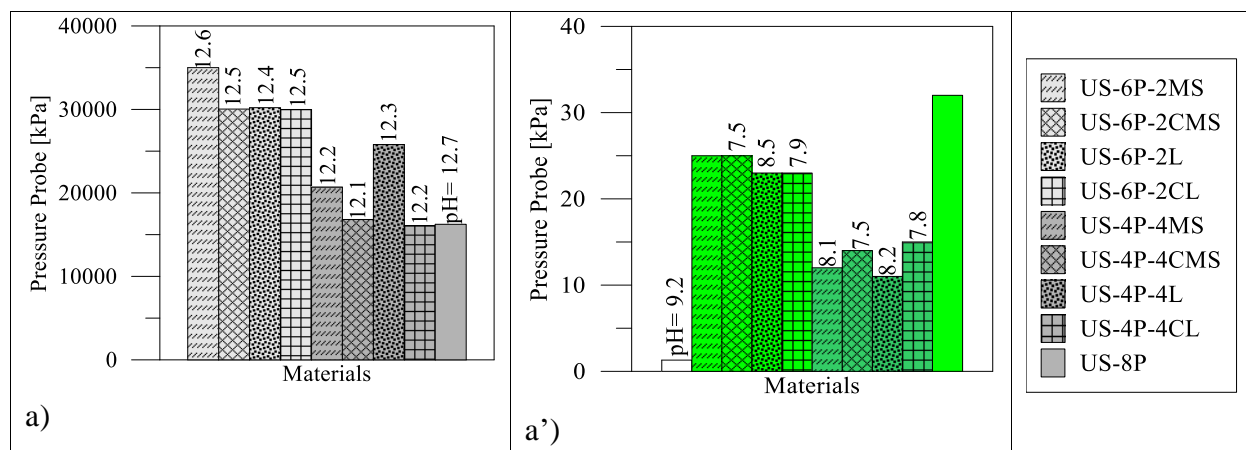


Fig 2. SEM images of (a) quarry limestone aggregate and (b) mussel cannery industry (Ballester et al., 2007).

### 3. Results

In order to define the mix design of CemShell, the results of Texturometer and Atterberg limit tests after 7 days of curing of sediments treated with cement and L and with cement and MS were compared (Fig 3). The pH values of curing water were also determined. Moreover, Fig 3 shows the results obtained when mixing the sediments with just commercial cement in the same total percentage. The first general consideration that can be made is that P sediment-mixtures with 1/3 replacement ratios with MS or L show higher CI, pH and strengths than the corresponding ones with ratios 1/2 (i.e., 4% cement and 4% additive). All the mixtures including L or MS exhibit better performances than US8P mixture. Specifically, for P replacement ratios equal to 1/3 (i.e., 6% P and 2% additive), both MS and L-mixtures exhibit far higher values of CI and texturometer pressure than the relevant control mixture (US8P). Comparing columns a and a' in Fig 3, it can be observed that CS-mixtures exhibit texturometer pressures, CI and pH values of curing water much smaller than the corresponding P-mixtures. Specifically, higher average values of pH (about 12, ASTM D4972-01) have been measured for P-treated sediments, whereas pH values about 8 are typical of CS-sediment mixtures. Consistently, the CI values of the CS-mixtures remain negative except for the control mixture which has CI about zero (Fig 3b').



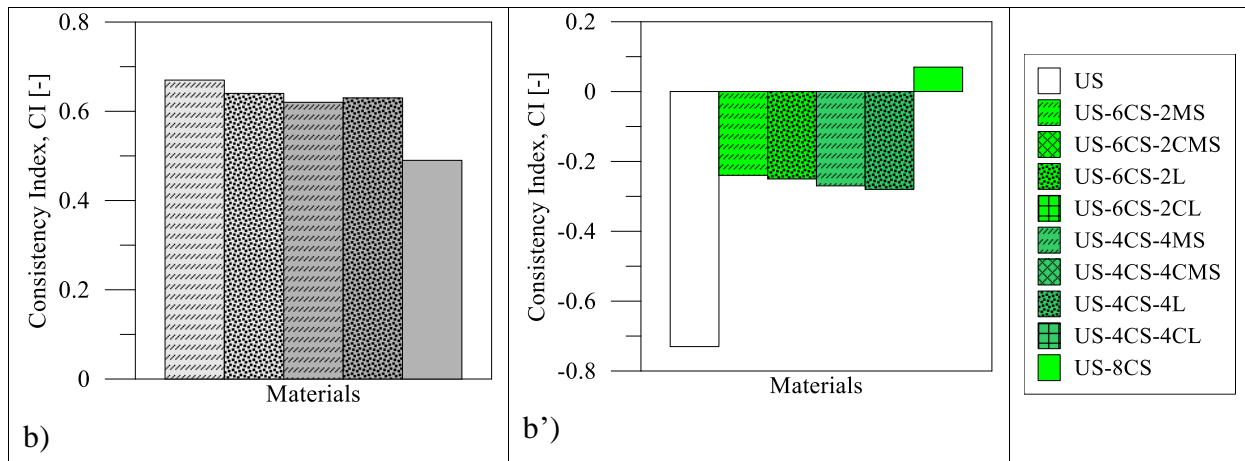
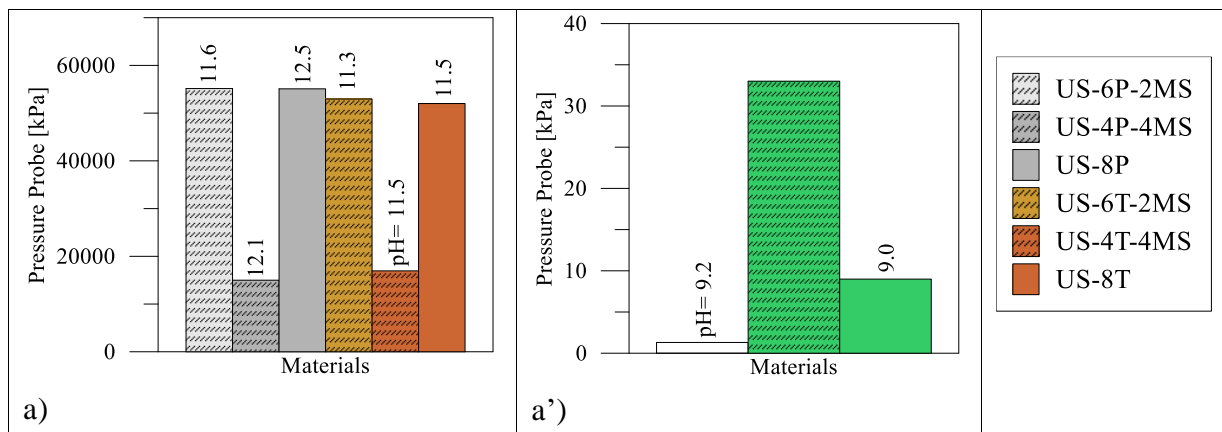


Fig 3. a-a') Pressure probe of Texturometer apparatus and pH (number in the Figure), b-b') CI for natural sediments (US) and mixtures after 7 days of curing.

Moreover, the partial replacements of CS with either L or MS seems to further reduce both texturometer pressure and consistency of the mixtures. However, the CS-mixtures exhibit texturometer strength and CI values always higher than those of the untreated sediment, US (Fig 3a'-b'). It has to be noted that, both consistency and texturometer strength of the sediment-cement mixtures including CMS or MS are generally higher than the corresponding ones with L. Moreover, treated sediments including finer powders with replacement ratio 1/3, either of MS or L, exhibit higher or at least comparable strength than those with coarser ones, i.e., CMS or CL, irrespective of the type of cement. For 1/2 replacement ratios the opposite is recorded only when CS is used. For those mixtures exhibiting higher consistency and strength values after 7 days of curing, the effect of curing time was monitored by performing the same tests after longer curing time (28 days, Fig 4). New determinations were also carried out on blast furnace slag (i.e., T) cement-sediment mixtures, i.e., US6T2MS and US4T4MS, and the corresponding control mixture (US8T). Fig 4 shows that the CI, texturometer strength and pH values of the T-cement mixtures are similar to those of the corresponding one obtained by using Portland cement. Moreover, longer curing times make the consistency and the texturometer strength increase for both the MS-mixtures and the control ones. As expected, CS-mixtures exhibit much lower performances. As far as the MS content is further increased to 1/2 replacement ratio, a decay in all the targeted parameters is recorded in the mixtures (Fig 4). Regarding the curing water, the results reported in Fig 4a-a' show that the maximum pH values were exhibited by mixtures of sediment treated with 8P and 8T (pH is about 12). The mixtures with CS show the lower pH values (pH about 8-9).





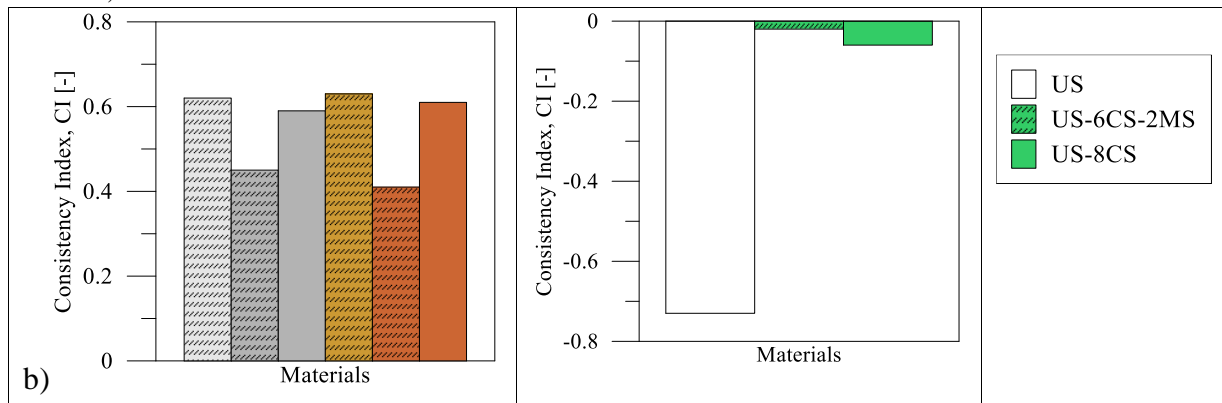


Fig 4. a-a') Pressure probe of Texturometer apparatus and pH (number in the Figure), b-b') CI for mixtures after 28 days of curing.

#### 4. Conclusions

The note shows some experimental results regarding the mix design phases of new binders for dredged sediments stabilisation. The preparation of the new binder has been guided by the comparison between the mixtures formed by dredged sediments, commercial cements, and powdered limestone with those where dredged sediments were treated with commercial cement and the same quantity of mussel shell powder, as greener source of calcium carbonate. The sediment used for the stabilisation treatment is a silt with clay of medium plasticity, fluid consistency and high organic matter content. The reported data appear to be consistent with each other and show that, after 7 and 28 days of curing, the finer MS powder has to be preferred to the coarser one. Moreover, the MS powder is better performing than the same quantity of limestone powder. Finally, irrespective of the cement used, if one third of cement is replaced by MS the performance of the mixture MS-sediment-cement is comparable to that sediment-cement both in terms of texturometer pressure and in terms of consistency index. All the mixtures sediment-CS show low mechanical performance. This could be caused by the nature of the hydration products of this type of cement and the presence of high amounts of soluble sulphates.

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