Stabilization of marine soil with alkali-activated slag for deep-mixing columns

Claver Pinheiro, Sara Rios, António Viana da Fonseca
CONSTRUCT-GEO, Faculty of Engineering, University of Porto, Porto, Portugal

Nuno Cristelo
CQ-VR, School of Science and Technology, University of Trás-os-Montes e Alto Douro, Vila Real, Portugal

Ana Fernández-Jiménez
Instituto Eduardo Torroja (IETcc) – CSIC

ABSTRACT: In the last decade, the use of the Deep Soil Mixing (DSM) technique to improve low bearing soils has been growing consistently. Usually, the construction of the DSM columns involves large volumes of cement, whose production increases the exploitation of natural resources and CO2 emissions, justifying the development of alternative binders. In the present work, an industrial slag, activated by sodium hydroxide and sodium silicate, was used to stabilize a marine soil, dredged from the Portuguese coast. The mechanical behaviour was assessed, using flexural and compression tests, and the results were compared with the same soil stabilized with high-performance Portland cement. The specimens were cured under saltwater, at a temperature of 18ºC, for 7, 14 and 28 days. The marine soil presented a pH of 3 and it was contaminated with heavy metals like chromium and lead and oxides like sulphur trioxide which with water can become sulphuric acid. This, together with the submerged curing conditions, formed a problematic, although realistic scenario for the application of the alkaline activation technique. The results showed that the alkali-activated slag developed better performances than the Portland cement.

KEYWORDS: Deep Soil Mixing, slag, alkali activation, stiffness tests, flexural strength, compressive strength.

1 INTRODUCTION

Soil Mixing (SM) is a generic term applied to soil improvement methods in which binders, usually lime or cement, are mechanically mixed with the soil to improve its strength, permeability and compressibility characteristics (Larsson, 2003). The SM technique can be subdivided into two general methods: Deep Mixing Method or Deep Soil Mixing (DMM or DSM), and Shallow Mixing Method (SMM).

The mixing of soils in-depth with lime and cement has been used in Sweden since the mid-1970s as a breeding technique and in Japan for more than 40 years.

The application of the DSM technique extends to several areas of geotechnics, such as reinforcement of foundation soils, slope stability, liquefaction mitigation and earth retaining structures (Bruce & Bruce, 2001). The range of soils where the DSM can be applied is wide, ranging from softer soils to granular soils, although for silty and clayey soils the most suitable constructive solution is different from that suitable for granular soils.

For the application of the DSM technique, large volumes of binder (usually Portland cement) are necessary. Since cement production requires a significant amount of raw materials and releases carbon dioxide to the atmosphere it is not very environmentally friendly.

The growth of concrete production has led to a need to increase cement production to quantities never attained. Cement production increases exponentially and is expected to reach the top of the emissions produced by human activity along with the energy and transport sector (Rattanasak & Chindaprasirt, 2009). For this reason, research aiming the development of binders based on waste materials, that were previously discarded, has been growing fast. A significant advantage of these new materials is that it is environmentally friendly in comparison with traditional Portland cement whose production generates CO2 emissions (Rios et al., 2015).

Alkaline activation (AA), can be described as a reaction between aluminosilicate materials and alkali or alkali-based earth substances, namely, ROH, Ca $(OH)_2$, R_2CO_3, R_2S, Na_2SO_4, $CaSO_4 \cdot 2H_2O$, $R_2 \cdot (n)SiO_2$, in which R represents an alkaline ion, such as sodium (Na) or potassium (K), or an alkaline-earth ion, such as calcium (Ca) (Rios *et al.,* 2015). This technique is particularly adequate to create binders (Alkaline activated cements or AAC) based on residues, such as fly ash or slag, which constitute very effective options due to their amorphous aluminosilicate microstructure (Rios *et al.,* 2018). The reactions begin with destruction of the covalent bonds Si-O-Si, Al-O-Al and Al-O-Si present in the glassy phase of the original. The alkali cations, which depend on the activator used, act in the construction of the structure, compensating for the excess of negative charges during the dissolution phase. The products precipitate and reorganize into more stable and ordered structures of Si-O-Al and Si-O-Si (Fernandez-Jimenez et al., 2005). When calcium is present in the mixture in significant amounts, dissolved Al-Si will propagate from any newly formed solid surface, consequently favouring the production of a dominant C-S-OH gel phase. If this does not occur, the Si and Al ions will accumulate around the nuclei points, sharing all the oxygen ions forming Si-O-Al and a three-dimensional structure of Si O-Si. The result is an amorphous aluminosilicate gel (sometimes designated as N-A-S-H gel), which evolves, with curing time and crystallization, from an Al-rich phase to a Si-rich phase (Fernandez-Jimenez *et al.,* 2006). In some circumstances, both types of cementitious gels are present and interacting leading to structural and compositional changes in the process (Garcia-Lodeiro *et al.,* 2011).

In this work, an alkali activated slag was used to create a binder that was mixed with a soil sampled from an experimental field located in Vila do Conde - Portugal. The soil was characterized in situ by Cone Penetration Tests (CPTU) (Rios e*t al.*, 2018) and its characteristics were used to prepare the laboratory specimens that could reproduce the application of Deep Soil Mixing in this site. The soil-binder specimens were submerged in saltwater for curing. At ages of 7, 14 and 28 days these samples were tested for flexural and compressive strength to evaluate the evolution of the material. Reference cement specimens were used and passed through the same tests. To a allow a better comparison, the cement content and water content of those reference specimens were defined using the proportions found in the literature (Bruce & Bruce (2001); Bruce (2000); Bruce *et al.,* (2013)).

2 MATERIALS CHARACTERISATION

The slag used in this study was collected in the Megasa steel industry, in Maia, Portugal. In this case, the material used is white slag, still without commercial application outside the steel industry facilities. It is very rich in calcium, ideal for processes of alkali activation as shown in Table 1. To make this material suitable for its use in this work, the material needed to undergo a milling process in cycles of 15h in a Micro-Deval mill. After milling, more than 50% of the slag had a size of less than 10 μm, as shown in the grain-size curve of Figure 1. The increase of the specific surface of the material, enhanced the chemical reactions with the activator, creating a binder that could solidify under these specific curing conditions.

The soil of the study was collected in an area that is close to the centre of Vila do Conde, in the North of Portugal, located on the left bank of the Ave River and very close to the river mouth suffering from the tidal influence. The tides in this region of the Atlantic coast are very wide, often reaching 4 m difference in height between low tide and high tide. The site presents a coastal or estuarine situation, subject to sedimentation predominantly due to the sea agitation, but also by the effect of tidal currents and fluvial inflows. The soil grain-size after the process is showed in Figure 1.

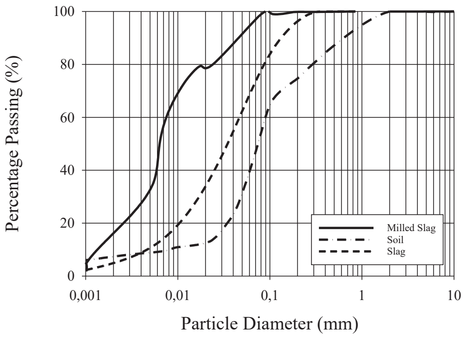

Figure 1. Particle size distribution of Slag, before and after milling, and Soil.

In the site where the soil was dredged the activity of shipbuilding and repair is relevant (Dias et al., 2011). In the last decade of 20th century, a new modern shipyard was installed in another place, and the old services and surroundings of the shipyard were abandoned. In 2003, it was decided to re-qualify the area, installing a shipbuilding museum, using new facilities in the old yard area and the old customs building. The legacy of this old activity is the soil contamination (Santos-Ferreira et al., 2015). The actual composition of the soil is showed in Table 1.

It is clear from the analysis presented in Table 1 that the soil has a serious contamination problem especially in terms of the amount of SO_3 which in contact with water can form H_2SO_4 - very dangerous for the environmental and for the material. Contaminated water and sediments are the cause of various physical and chemical processes of degradation of cementitious materials and the area is a preferred site of deposition of sediments, not only from the Ave River, but also of another small stream that converges to the Ave River in this specific point. On the other hand, it was a place of deposition of dredged sediments from the Ave River in the past, due to the current necessity to guarantee the navigability of the river. The geotechnical properties of the slag and soil are showed in Table 2.

Table 1: Composition of the slag and the soil (wt%).

Slag		Soil			
Element	(wt%)	Element	(wt%)	Element	(wt%)
CaO	54.9000	Y_2O_3	0.0015	Cl	0.2480
SiO_2	23,.000	Ga_2O_3	0.0020	CaO	0.6230
MgO	8.5000	Nb_2O_5	0.0020	MgO	0.8330
Al_2O_3	6.6000	PbO	0.0050	TiO_2	0.8520
Fe Total	1.1000	SrO	0.0127	Na_2O	1.1200
MnO	0.4000	Rb_2O	0.0241	SO_3	2.7300
Cr_2O_3	0.0000	MnO	0.0282	Fe_2O_3	3.3550
Others	5.0000	ZnO	0.0312	K_2O	3.9800
-	-	BaO	0.0380	CO_2	6.2200
-	-	Cr_2O_3	0.0486	Al_2O_3	12.4000
-	-	ZrO_2	0.0649	SiO_2	67.2200
-	-	P_2O_5	0,1660	-	-

The alkaline activator solution was a combination of sodium hydroxide and sodium silicate. Sodium hydroxide, originally in flake form, with a specific gravity of 2.13 at 20ºC and 95-99% purity, was dissolved in distilled water up to the desired concentration.

The specimens were cured under sea water collected in Porto. The most important characteristics of the distilled water and sea water used in this work are summarized in Table 3.

Table 2: Geotechnical properties of slag and soil.

Property	Slag	Soil
Plastic Limit	NP	NP
Liquid Limit	NP	NP
D_{50}	0.01 mm	0.07 mm
Specific gravity	3.34	2.61
Fines fraction (sieve Nº 200)	98.05%	50.52%
Uniformity Coefficient	1.81	10.02
Curvature Coefficient	1.03	2.72
pH	12.52	3.11

Table 3: Properties of sea and distilled water.

Property	Distilled water	Sea water
pH	5.40	7.34
Conductivity	1.21 µS/cm	10.8 µS/cm
Total Dissolved Solids (TDS)	0.81 ppm	7.24 ppm
Salinity (ppm)	0.00031 ppm	0.0034 ppm
Chloride (ppm)	0.18 ppm	1.92 ppm

3 OPTIMIZATION OF THE MIXTURE

The first step was to define the best ratio between binder and aggregate (slag/soil). These mixtures were named Soil + AAC. Mixtures with 1:4, 1:3 and 1:2 binder/soil mass ratios were tested for curing under water to understand its hardening properties. Qualitative analysis concluded that the mixtures with 1:4 and 1:3 proportions still had a soft surface at the end of the first day, while the mixture with a 1: 2 ratio was hard by touch at the end of the first day. At this stage of the material recognition, it was not yet defined which form of application of the DSM would be simulated. For the first tests, the wet version of DSM was used, where the paste was prepared with a defined liquid/solid ratio and then mixed with the saturated soil. When the 1:2 mixture was submerged in seawater, it stood integral for the first 3 days and after it crumbled. Following Bruce & Bruce (2001), Bruce (2000) and Bruce *et al.,* (2013) precepts, for marine soils, wet DSM was replaced by dry DSM. In this later case, the final water content in the mixtures results only from the water present in the soil in situ used at the laboratory to prepare the activator solution being the soil added dry (Rios *et al.,* (2018b); Pinheiro *et al.,* (2018); Pinheiro *et al.,* (2019)). This leads to lower values liquid contents in the final mixture.

The next step was to define the amount of sodium hydroxide (NaOH) and sodium silicate that would be used in the mixture. A study of various mixtures was performed, keeping the 1: 2 binder/soil ratio constant, and varying the sodium silicate amount and the molar concentrations of NaOH, to define which mix would stay intact for 7 days under water and consequently the samples that could be tested for flexural and compressive strength.

The results of this study were presented in Pinheiro *et al.,* (2019) where the CPTu tests performed by Rios *et al.,* (2018a) were used to define the soil void ratio. Equation 1 was used, for a degree of saturation (*S*) of 1, and the void ratio (*e*) was assumed to be 0.8, based on the CPTu data. From this, a water content value of 30.55% was obtained which was kept constant throughout the experimental plan. By this way, the dry version of the Deep Mixing Method was simulated in the laboratory, using a water content corresponding to 30.55% of the weight of dry soil (this water was used in the activator). The final molar concentration of the sodium hydroxide after mixing with sodium silicate is calculated taking into account the number of moles of NaOH (X_{NaOH}), derived from the Na_2O present in both the sodium silicate solution and in the sodium hydroxide flakes, with the total quantity of water present in the mixture in grams (w_t) – equation 2:

$$w = \frac{S \cdot e}{G_s} \tag{1}$$

$$NaOH_{molal} = \frac{X_{NaOH} x1000}{w_t} \tag{2}$$

Molar concentration of NaOH ranging from 6.5 to 8.0 and amounts of sodium silicate that comprised 0% to 50% of the total weight of the alkaline activator were used. Results showed in Pinheiro *et al.,* (2019) evidence that, at the optimum molar concentration of sodium hydroxide is 6.5 mol, the mechanical strength increases with the silicate content. This mixture was initially adopted as the best mixture so that it could be compared with the group that would be made with ordinary Portland cement. As these first tests were done at 7 days, there was no idea how the material would behave at older ages. When specimens for longer tests were prepared, the mixture began to show cracks and lost integrity at 14 days of age. To solve this problem, the mixture was re-evaluated, and the amount of slag was increased until the binder/soil ratio reached 1: 1. The specimens with 1:1 mixture remained intact until 28 days and flexure and compressive strengths were evaluated. To better comprehend the process illustrated above, Figure

2 shows the Soil + AAC and Soil + PC before submerged curing and, after, submerged.

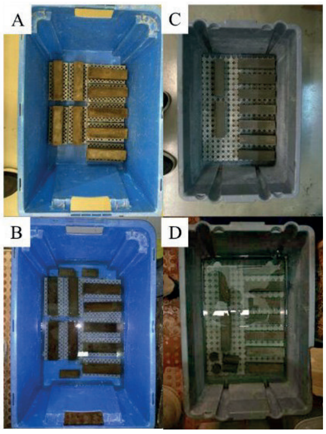

Figure 2. The submerged curing process where: (A) Soil + AAC before submerged curing and (B) Soil + AAC submerged. (C) Soil + PC before submerged curing and (B) Soil + PC submerged.

For the control group (Soil + PC), a mixture of Portland cement and soil were mixed, and the amount of cement was defined according to Bruce (2000). For dry methods (in soils of 60 to over 200% moisture content), typically 100–300 kg of dry materials per cubic metre of treated soil are used, providing strengths of 0·2– 20·0 MPa, depending very much on soil type. The control group was constituted by CEM I 52,5R cement, which is a grey cement of very high performance and fast curing, recommended to produce special concrete for major engineering works. The proportion binder: soil followed the precepts of EN (2005), Bruce & Bruce (2001) and Bruce (2000). In this case, a value of 300 kg per 1m^3 of soil was chosen and the ratio used was 1:6.5 (cement/soil). Table 4 shows the constitution of the mixtures tested.

An important point to keep in mind is that the amount of water was higher in the Soil + PC because this parameter varies with the amount of the soil. Since the amount of soil is bigger in the Soil + PC mixture than in the Soil + AAC mixtures, and the quantity of water to add is calculated to have the soil saturated then, the mixture with more soil should have more water.

Table 4: Experimental group (Soil + AAC) and Control Group (Soil + PC) with amounts of each constituent.

Constituent	Soil + AAC	Soil + PC
Soil (g)	397.06	784.07
Slag (g)	397.06	-
Cement (g)	-	120.63
NaOH (g)	17.70	-
Silicate (g)	31.76	-
Water (g)	121.30	239.54
Liquid / Solids	0.14	0.26
Binder* / Soil	1	0.15

(*) binder refers to the amount of slag or cement

4 FLEXURAL AND COMPRESSIVE STRENGTH

The evaluation of the flexural and compressive strength were made according to EN 196-1 (2016). The flexural strength was made by concentrated load method in the middle of the specimen. The semi-prisms were conserved until the moment of the compression test and the flexural strength F_s was calculated by equation 3.

$$F_s = 1{,}5 \; x \; F_f \; x \; l / b^3 \tag{3}$$

where:

- F_s is the flexural strength (MPa);
- b is the side of the square section of the prism (mm);
- F_f is the load applied to the centre of the prism at rupture (N);
- l is the distance between the supports (mm).

The compressive strength test was performed on both parts of the failed prism. The compressive strength C_s was by equation 4:

$$C_s = F_c / 1600 \tag{4}$$

where:

- C_s is the compressive strength (MPa);
- F_c is the maximum load (N);
- 1600 is the area of the plates or auxiliary plates (mm^2). Normally 40 mm × 40 mm and can be adjusted.

The result of the flexural strength test was calculated as the arithmetic mean of three individual results while the compressive strength is the arithmetic mean of six individual results. Figure 3 shows the machinery used for compressive and flexural strengths tests and the sides of the Soil + AAC after the test.

The results of the flexural and compressive strength tests are shown in the Figure 4 for 3, 7, 14 and 28 days of curing time. It is noticeable that the Soil + AAC mixture has a better performance over time compared to the Soil + PC mixture. This is especially clear in the compressive strength results.

At 3 days of age, all the specimens have already enough strength to perform the test. Table 5 shows the evolution of each mixture between 3 and 28 days. The UCS evolution of the slag-based mixtures is very significant, especially in terms of flexural strength.

The growth rate of the improved soil with the slag addiction in flexural strength tests is much higher compared to the same improved soil with Soil + PC. Even starting with lower values at 3 days of age, at 28 days the value of Soil + AAC is 65% higher than the Soil + PC. In the compressive strength, the strength increase is not so significant, but for 3 days of age, the Soil + AAC is better compared to the cement mixture and remained higher up to 28 days.

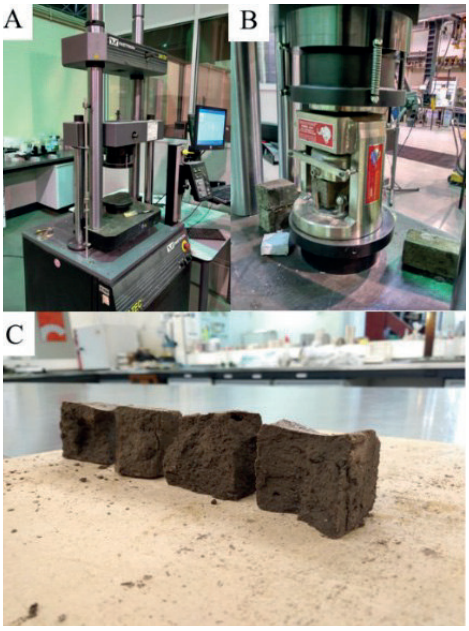

Figure 3. The compressive and flexural strength tests: (A) The machinery for the tests, (B) The test performed at Soil + AAC sample and (C) Sides of Soil + AAC sample after the compressive strength test.

At 28 days, the slag mix has doubled the compression strength values compared with 3 days of the same mixture. Comparing the two mixtures at 28 days the Soil + AAC has more than twice the strength than the Soil + PC.

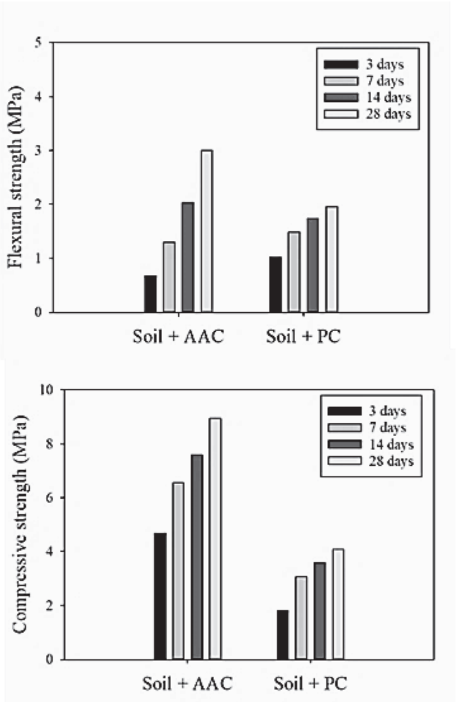

Figure 4. Flexural and compressive strength of improved Soil + AAC and Soil + PC tested at different ages.

Table 5: Strength evolution for each material.

Age/Test	Soil + AAC	Soil + PC	Growth rate	
			Soil + AAC	Soil + PC
3 days/Flexural	0.68	1.02	77%	48%
28 days/Flexural	3.00	1.96		
3 days/Compressive	4.69	1.81	48%	56%
28 days/Compressive	8.95	4.08		

5 CONCLUSIONS

The paper presents the behaviour of one soil improved with Soil + AAC and Soil + PC cured in seawater and tested for flexural and compressive strength at different ages. The slag's use in soil improvement is quite recent, demanding still additional studies to have a good knowledge of the final product. Portland cement is the most widespread construction material in the world and the knowledge about its behaviour is well stablished. Alkaline activated cement (AAC) is generally performed with fly ash or metakaolin but the slag used in this work proved to reach very good results for this specific case. These promising results should encourage further tests. The quantity of slag was very high compared to the quantity of cement but this should not be a problem, since the slag is an industrial by-product and so its production does not involve more environmental impacts, conversely to what happens with Portland cement. The use of slag for soil improvement proved to be very versatile even with contaminated soil and with low pH. It has been shown in the definition process that the AA application is very dependent on the type of material that will be used together with the alkaline activated binder. Thus, formulations must be well adapted to the mix material conditions. So, the AA technique can be applied in diverse conditions providing that the materials are well characterized, and an optimization is performed for each case.

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