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Cosa-Martínez, J.; Soriano Martínez, L.; Borrachero Rosado, MV.; Paya Bernabeu, JJ.; Monzó Balbuena, JM. (2020). Stabilization of soil by means alternative alkali-activated cement prepared with spent FCC catalyst. *International Journal of Applied Ceramic Technology*. 17(1):190-196. <https://doi.org/10.1111/ijac.13377>



The final publication is available at

<https://doi.org/10.1111/ijac.13377>

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Additional Information

Stabilization of soil by means alternative alkali activated cement prepared with spent FCC catalyst

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Received: date; Accepted: date; Published: date

Abstract: Alkali-activated cements are widely studied as alternative and sustainable binder in soil stabilization. In this research work, a mold was designed and constructed, which allowed small cubic specimens to be made (40x40x40 mm³). With the newly designed mold, cubic samples of soil stabilized with Portland cement (OPC) and alternative AAC (based on spent fluid catalytic cracking catalyst FCC) were prepared from which compressive strength was obtained. Cylindrical specimens were also prepared using the same binders as in the previous case to obtain their compressive strength. The results obtained in both cases were compared. Greater resistances for cubic samples were achieved. The cubic specimens were selected for being better in terms of standard deviation of compressive strength for AAC stabilized soil. The obtained compressive strength and standard deviation results were compared between the soil specimens stabilized with different stabilizers cured at 7, 14, 28 and 90 days. The method allows small-sized cubic specimens to be prepared. It improves ergonomics. It also facilitates a large number of specimens being obtained with a small amount of sample. Soil stabilized with AAC yielded higher compressive strength after 90 days compared to that with OPC.

Keywords: Sustainable construction materials, Waste reuse, Alkali-activated cement, Soil stabilization.

1. Introduction

Large-sized and heavy cubic or cylindrical specimens are normally used to study stabilized soils for their use on road surfaces UNE 12390-1 [1] and in compressed earth blocks (CEB), where even the same block is used, as in UNE 41410 [2]. In some standards, smaller sized cylindrical specimens are used; e.g. ASTM STP 479 [3]. In this study, the Harvard miniature mold was used (see Fig. 1), but cylindrical samples have some problems as cubic ones do, such as possible buckling when some compression is exercised. They do not usually have the same base (\varnothing 3.8 cm) and height (7.6 cm) dimensions, and thus presents certain slenderness, and possibly defects on the upper face that do not guarantee total flatness. When utilizing soil stabilization with alkali-activated cement (AAC), we may come across very plastic optimum dry density, which causes specimens to deform while unmolding at the end of compaction, an effect that is more pronounced in cylindrical specimens (see Fig. 2)



Figure 1. Mold used for cylindrical specimens.



Figure 2. Cylindrical specimen deformed when unmolding by sample plasticity.

A mold was designed and constructed for a sample size of $40 \times 40 \times 40 \text{ mm}^3$ because it is a size that is suitable for the load cell of the compressive strength test (Fig. 3) usually employed for OPC mortar testing (UNE-EN 196- 1 [4]).



Figure 3. A cubic specimen in a compressive strength test.

Apart from solving the raised problems, the use of specimens with these characteristics helps many specimens to be obtained with small material samples because it is possible to use many specimens for some studies. Indeed we have even accounted for more than 700 in some studies. This specimen type allows numerous variables to be studied, and a little raw material to be used to manufacture specimens, which also cuts economic and environmental costs by reducing the generated material and waste. Besides, ergonomics in handling is improved by reduced weight.

Different soil stabilizer types exist. The most commonly used one is Portland cement (OPC) [5]. As an alternative to it, several solutions are used, including blends of lime-pozzolana [5]. Can be found plenty of documents about using stabilizers for soils with OPC, lime, or with both, along with the methodology followed to prepare large-sized specimens in Standards NLT -310/90 [6] and UNE EN 13286, parts 50, 51, 52 and 53 [7]. Finding bibliography on the stabilization of soils with AAC is less common [8-13], where sodium silicate is frequently used as an activator. What is even less common is using AAC, whose activator is obtained from waste [14-17], where sodium silicate can be synthesized from mixtures of rice husk ash and sodium hydroxide and can, thus, considerably reduce CO₂ emissions [18,19].

To fulfill the research objectives, a mold for the cubic specimens was designed specifically and made with a central filling gap that allows layers of the material to be placed and their subsequent compaction.

In this article, the results of soils stabilized with AAC and those stabilized with OPC were compared to determine a simple protocol to prepare small-sized cubic specimens as a step prior to preparing the larger specimens normally used in current standards. The dispersion of the results

was studied by calculating the standard deviation for each employed stabilizer, and for the two studied specimen types: cubic and cylindrical.

2. Experimental Section

2.1. Mold design and compaction procedures

Mold height must exceed 40 mm to be able to contain the soil volume before being compacted, with a cubic steel cube of 39x39x39 mm (dice) whose weight was 464 g. As shown in Figure 4, a removable cubic mold of 100x80x100 mm was designed with four screws on its front and two on its lower part, and with a central filling gap (40x40 mm base and 100 mm high) that allows layers of the material to be placed and serves as a guide for the cube. The mold base was made of a 10 mm-thick steel sheet. The steel employed for mold construction was ST.37-2 according to EN 10025 and was supplied by ThyssenKrupp Materials Iberica.



Figure 4. Mold design of variable height.

When performing the AAC cylindrical specimens according to ASTM STP 479 [3], humidity was above optimum in these specimens. This behavior may be attributed to the difference of rheology of material compared to soil or OPC stabilized soil. An error due to deformation occurred when unmolding, and sometimes the specimen buckles in the simple compressive strength test. The upper face of specimens does not offer the desired flatness and is inclined due to deformation (see Fig. 2). For this reason, a decision was made to design a mold for the specimens measuring 40x40x40 mm³ following a procedure to manufacture similar specimens to cylindrical specimens, and with the

same dimensions on all sides to solve flatness and slenderness problems. This size of 40x40x40 mm³ are usually used for mortars specimens. The choice of this specimen size makes it easier to obtain compression strength values with the equipment available in the laboratory.

Standard UNE 103 501 [20] (which corresponds to ASTM D 1557 [21]) was used as the basis for all the experiences. The aims here were to specify the method to determine the dry and wet density ratio in soil for compaction energy of 2632 J/cm³, and to define the maximum dry density and its corresponding or optimal humidity, which can be obtained in the laboratory. The 1.5 Kg weight rammer strike was used in cylindrical and cubic specimens' preparation.

The cylindrical specimens were made in five layers of filling. By following Equation 1, it was possible to apply an approximate energy of 2632 J/cm³ by dropping a 1.5-kilogram mass from 20 cm in height and with 15 blows as indicates ASTM C 1557.

$$\frac{\text{Blows (15)} \times \text{Layers (5)} \times \text{Rammer weight (1.5 kg} \times 9.81) \times \text{Rammer fall (0.20 m)}}{\text{Vol. (86 cm}^3)} \approx 2632 \text{ J/cm}^3$$

Equation 1. Compaction of cylindrical specimens.

The cube specimens were made in three layers of filling, as seen in Table 1, following a similar procedure to that used in the modified proctor (ASTM C 1557). With Equation 2, which allows the energy applied while preparing cubic specimens to be calculated, a 1.5-kilogram mass was dropped from 20 cm in height and with 19 blows.

$$\frac{\text{Blows (19)} \times \text{Layers (3)} \times \text{Rammer weight (1.5 kg} \times 9.81) \times \text{Rammer fall (0.20 m)}}{\text{Vol. (64 cm}^3)} \approx 2632 \text{ J/cm}^3$$

Equation 2. Compaction of cube specimens.

To cure samples, a temperature of 22°C and 50% relative humidity [23] were chosen for all curing times (7, 14, 28 and 90 days)

Step 1-	Introduce a layer of mixture soil with the stabilizer
Step 2-	Introduce the dice in the mold
Step 3-	Apply 15 blows with the 1.5-kilogram weight, moving the rammer strike at different parts of dice surface
Step 4-	Turn 180 degrees the mold and remove the dice by gravity

|
Repeat steps 1 to 4 to complete the three layers of soil mixture

Step 5-	Loosen the mold's screws by completely removing the two lower screws
Step 6-	Remove the lower plate
Step 7-	Press the dice to remove the specimen from the bottom of the mold

Table 1. Cubic mold, the specimens manufacturing diagram.

2.2. Materials

The Spanish company PAVASAL, S.A. supplied the soil used to prepare the samples. This soil is that normally used to produce road surfaces. Thermogravimetry (35 to 1000 ° C) of a soil sample was carried out to determine its nature. Figure 5 shows the TG and DTG soil curves. Here we observe loss of mass in the curve starting at 700°C, which indicates the presence of dolomite (two mass loss steps overlapped in the range 700-950°C).

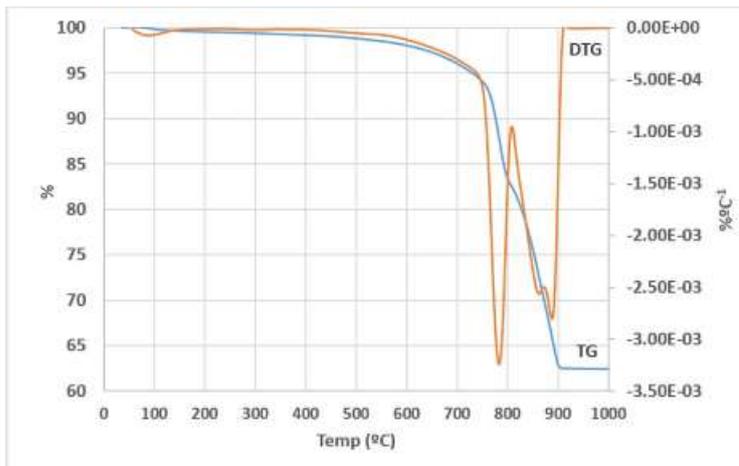


Figure. 5 Thermogravimetric curves (TG and DTG) for used soil.

For the thermogravimetric analysis, a Mettler Toledo TGA 850 module was used, along with an alumina crucible with a 30mg soil sample, at a heating rate of 20°C/min in an air atmosphere (gas flow 75 mL/min).

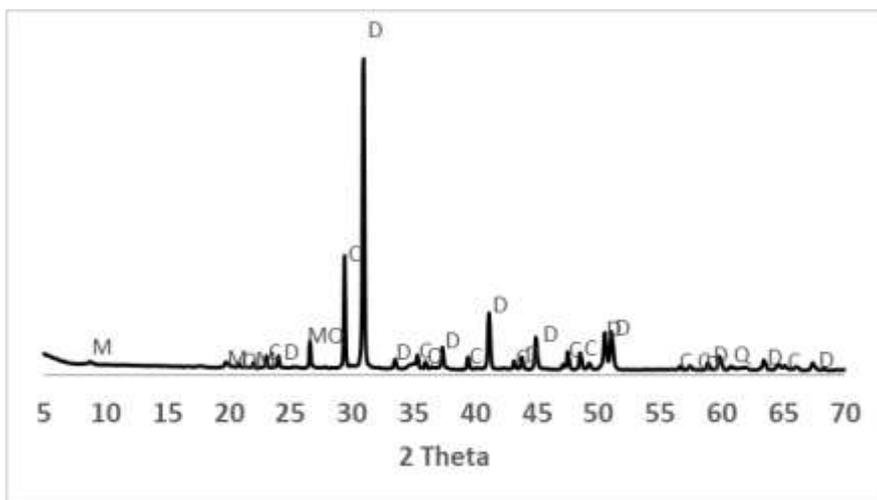


Figure. 6 XRD of soil. Q: Quartz (SiO_2) (pdfcard 331161; C: Calcite (CaCO_3) pdfcard 050586; D: Dolomite ($\text{CaMg}(\text{CO}_3)_2$), pdfcard 360426; M: Muscovite Mica ($\text{KMgAlSi}_4\text{O}_{10}(\text{OH})_2$) pdfcard 210993

XRD analysis were performed in a Bruker AXS D8 Advance device, from 10 to 70 2θ (2s accumulation time in a 0.02 angle step). The diffractogram of the soil sample (figure 6) shows that the majority mineralogical compound is dolomite, with small proportions of calcite. Traces of quartz

and phyllosilicates as muscovite mica are also detected. We can consider that it is mostly a dolomitic soil.

The water used to prepare samples came from the drinking water distribution network of the Universitat Politècnica de València (UPV), Spain.

The employed Portland cement (OPC) was gray cement type CEM I-52R, whose chemical composition is provided in Table 2. It was supplied by the company Lafarge Asland (Spain). The classification of this cement corresponds to that referred to in Standard UNE-EN 197-1 [22].

The spent catalyst from the catalytic cracking process (FCC), whose chemical composition is provided in Table 2, was petrochemical industry waste. The company OMYA Clariana S.A. (Tarragona, Spain) supplied it.

% Mat.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	LOI*
OPC	20.4	4.5	4.7	64.5	1.2	1.6	1.0	0.09	-	-	2.0
FCC	47.76	49.26	0.6	0.11	0.17	0.02	0.02	0.1	0.01	1.22	0.5

Table 2. Chemical compositions of OPC and FCC. * Loss on ignition determined at 950°C.

To prepare the alkaline/activating solutions in order to produce alkali-activated binders, sodium hydroxide pellets were used. They were supplied by the company Panreac S.A. with a purity of 98%. The utilized waterglass (sodium silicate), composed of 28% SiO₂, 8% Na₂O and 64% H₂O, was supplied by Merck.

The 25-kilogram soil sample to be used was taken and homogenized by quartering. Then the fraction to be passed through the 4-mm opening sieve and dried in an oven at 60°C was selected.

2.3. Method

We used a Harvard miniature mold to make the specimens, to obtain the optimum dry density and to know its compressive strength with no other stabilizers. A modified proctor test was run with soil without a stabilizer (Fig. 7) according to Standard UNE 103 501 [20]. Secondly (Fig. 8), a modified proctor was made to stabilize soil with OPC because it is the most widely used stabilizer. Finally (Fig. 9), a modified proctor was performed to stabilize soil with AAC by taking FCC as the precursor and a sodium silicate-NaOH solution as the activator [18].

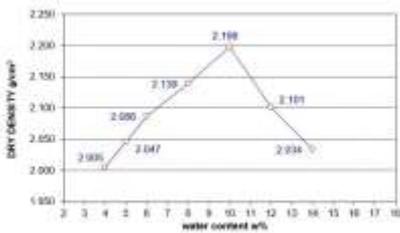


Figure 7. Soil-modified proctor curve

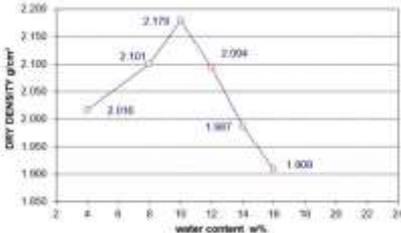


Figure 8. Soil OPC-modified proctor curve

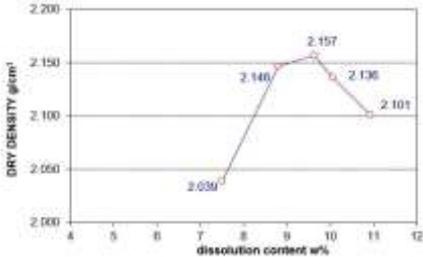


Figure 9. Soil AAC-modified proctor curve

From the optimum dry density obtained by the modified proctor, soil mixtures were prepared with these stabilizers to compare their compressive strengths.

The mixture was made with the compacted soil with no stabilizer, the soil stabilized with 10% OPC, and the soil stabilized with AAC by adding 10% of FCC activated with the sodium silicate solution. The alkali solution consisted of 60.8% of Na_2SiO_3 , 26% of H_2O and 13.22% of NaOH , was prepared 30 minutes before and was used in an ambient temperature. The alkali solution/FCC ratio was 1.73 by mass.

To make the mixture with no stabilizer, we placed 1000g of soil in the mixer for 1 minute before adding water (97g) and finally mixing for another 2-minute period. The water/solid ratio content was 0.097.

To make the mixture with OPC, we placed 1000g of soil in the mixer for 1 minute before adding OPC (100g) and mixing for another 1-minute period, and finally adding water (110g) and mixing for 2 minutes. The water/solid content was 0.1.

To make the mixture with AAC, we placed 1000g of soil inside the mixer for 1 minute before adding the precursor (FCC, 100g) and mixing for another 1-minute period, and finally adding the activating solution (sodium silicate+NaOH+water, 107 g) and mixing for 2 minutes. The solution/solid ratio was 0.097 and the water/total solids ratio was 0.064.

To avoid the mixture from drying when making specimens, which can take a considerable time, all the mixture was placed inside a bag with an airtight seal. Then the amount of soil mixture, which corresponded to each layer to make up specimens, was placed inside smaller sealed bags. To prepare specimens, the process described in the "Experimental process" section was followed.

3. Results and Discussion

We compared the cylindrical and cubic specimens. As Figure 10 shows, the standard deviation was more pronounced in the AAC cylindrical specimens because its consistency was more plastic. Therefore, as shown in Figure 2, some cylindrical specimens hardly met the perpendicularity values of the different standards. However, the compressive strength data were fulfilled in both the cylindrical and cubic specimens, with minimum values for using the soil for both road surfaces and CEB.

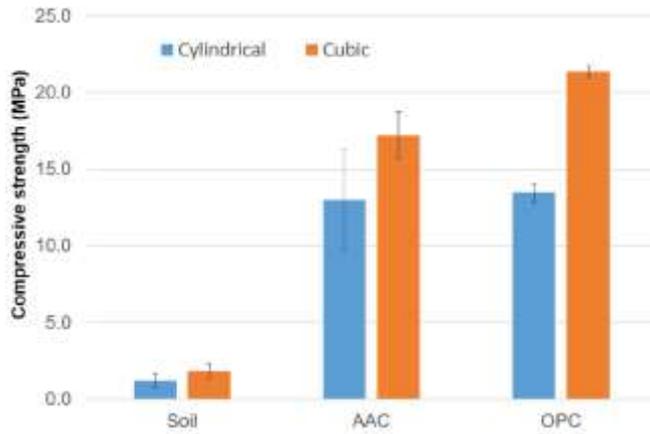


Figure 10. Cubic and cylindrical specimens: soil without stabilizer, soil stabilized with OPC and soil stabilized with AAC at 7 days.

We also compared the cubic specimens with no stabilizer and those with the different stabilizer types. Figure 11 shows how the compressive strength of the soil with no stabilizer was approximately 3MPa. When stabilizing with OPC, a better compressive strength was observed at earlier curing times. Approximately 24MPa was achieved with the soil stabilized with OPC. When stabilizing with AAC, the increase in compressive strength became more progressive, with lower compressive strength compared to OPC at earlier curing times, but with better compressive strength at 90 days compared to OPC, with compressive strength coming close to 30MPa. This means that the development of the alkali-activated binding matrix is slower but much more effective than that for OPC.

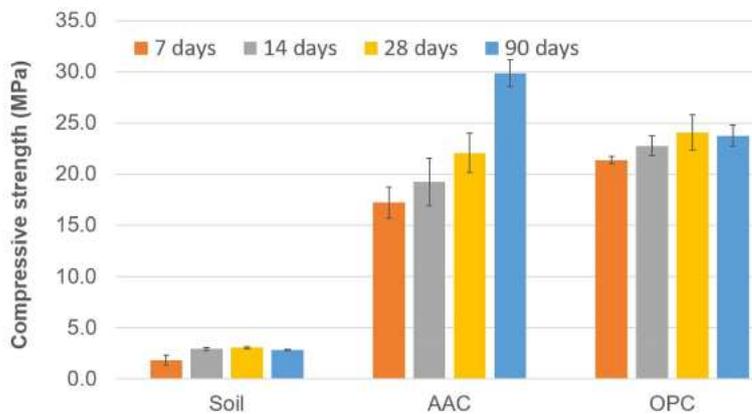


Figure 11. Compressive strength at 7, 14, 28 and 90 days. Cubic specimens of soil with different stabilizations.

4. Conclusions

With a simple system, the method allows small-sized cubic specimens to be prepared to mitigate the problem of high standard deviation in the specimens stabilized with AAC, and the shape factors by the buckling and flatness of load faces. It improves ergonomics in handling by reducing weight. It also facilitates a large number of specimens being obtained with a small amount of sample, and allows many variables to be studied using only a little raw material to produce them, which cuts economic and environmental costs due to the reduction in the generated material and waste.

Thanks to its mechanical behavior, and compared to the soil without stabilizers, with both stabilization by OPC and AAC, it proves effective and notably increases compressive strength. In the soil stabilization with AAC, the compressive strength progressively grows, with better values than that for OPC stabilized systems at 90 days. A different trend is observed between the soil stabilized with OPC and the soil stabilized with AAC. When we stabilize with OPC, there are no differences between 28 and 90 days of curing time. This fact is due to the fact that a total hydration of the OPC has practically occurred. In the case of stabilization with AAC, the chemical system is different and the chemical reactions are slower so that between 28 and 90 days of curing there is an increase in compression strength.

Acknowledgments

The Spanish Ministry of Economy and Competitiveness for the support granted to the APLIGEO Project (BIA2015 70107-R) and FEDER funds, which includes this research work. PAVASAL for its collaboration and for supplying soil. The Concrete Science and Technology University Institute (ICITECH) of the Universitat Politècnica de Valencia (UPV) for allowing us to use its facilities to undertake the experimental part. BP OIL España S.A. for supplying FCC.

Authors Contributions: José María Monzó, Maria Victoria Borrachero and Jordi Payá conceived and designed the experiments; Juan Cosa and Lourdes Soriano performed the experiments; Juan Cosa analyzed the data; Juan Cosa wrote the paper, which was reviewed by all the authors.

Conflicts of Interest: The authors declare no conflict of interest.

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