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Experimental analysis of enhanced cement-sand-based geothermal grouting materials

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Abstract

Nowadays, Ground Source Heat Pumps (GSHP) are achieving significant efficiencies, mostly because of the development of their electromechanical components. However, concepts such as the technical performance of the grouting materials deserve more profound analysis, as becoming essential in areas where good potential thermal performance of the GSHP and serious risks of groundwater contamination exist. In this paper, several fluid mortars with enhanced characteristics have been evaluated. Results show improved mechanical and thermal properties compared to conventional grouting materials. Likewise, mortars exhibited good performance after being subjected to durability treatment. For now, the cost of some mortars may constitute a barrier.

Keywords: grouting material, fluid mortar, cement, graphite, durability.

1. Introduction

The use of fluid mortars for grouting is widespread in construction. In fact, besides all the very well-known applications in the fields of the civil and building engineering, another application can be highlighted in the last few years that requires the development of specific admixtures: ground source heat pumps (GSHP). Due to its very favourable features, including lower energy consumption and GHG emissions, renewable and clean energy or independence of supply, this technology, widely implemented in countries such as Sweden or Germany for more than 30 years, has also become very popular in countries such as Spain, where other renewable technologies such as solar or wind energies are much more developed [1]. Moreover, the significant thermal efficiencies achieved are removing typical barriers to the evolution of this technology, such as the high initial investment required. Closed-loop GSHPs with vertical boreholes acting as ground heat exchangers are the most common geothermal installation worldwide, with depths ranging from 90 to 200 m. Between the heat carrying fluid flowing through the pipe and the ground a backfill material normally known as grouting material is placed, which provides thermal coupling, borehole wall stability and environmental ground protection [2]. This is indeed a very important element of the GSHPs, not only due to its influence on the system's thermal efficiency, but also because of the potential problems of contamination of aquifers that a poor-quality grouting material might cause [3,4,5].

Although the research done in the last few years is not extensive, some investigations can be highlighted, such as those where the thermal conductivity of different bentonite-based grouts with different types and quantities of sands and graphites is evaluated [6,7]. A more thorough characterization was carried out in [8-13], where mechanical strength, thermal performance and permeability of bentonite-based grouts were analysed before and after they were subjected to freezing damage and heating-cooling cycles. The favourable influence of the graphite on the thermal performance of the grouting materials, its adverse effect on the mechanical behaviour and the negative impact of the high w/s (water/solid) ratios of the very workable admixtures, are some of the important conclusions of these investigations. As for cement-based materials, thorough research was done in the early 2000s [2,14-17] throughout which a superplasticized cement-based grout was designed that resulted in better thermal and mechanical performance than neat cements or bentonite-based grouts. In [18] and [19], the authors incorporated other materials such as electric arc and blast furnace slags, construction and demolition waste or steel fibres with the aim of achieving higher thermal conductivities and improved mechanical behaviour as well as permeability, respectively. The durability of cement-based grouts was evaluated in [20,21] by means of testing mechanical and thermal performance of several admixtures mainly made up of cement and natural and recycled sands, respectively. Lately, other investigations have been published that deal with problems arising during mixing, placement or with residence time, such as the decreasing values of conductivity when there is poor control of water content [22] or when the level of saturation changes [23].

Thus, little research has been done so far on the suitability of this type of materials. However, new applications related to GSHP systems are showing up, such as deep borehole heat exchangers [24], geothermal District Heating [25,26] or Smart Grids using geothermal energy [27]. At the same time, the research on the use of advanced (nano-) materials in conventional construction materials like mortars or concretes [28,29] is rapidly increasing. All in all, it seems that further research about grouting materials is required, especially for GSHP installations where the risk of contamination of groundwater is higher and so the use of enhanced materials

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is a must. To that end, an analysis of the characterization of several types of cement-sand-based fluid mortars with different sands and additives has been carried out in this paper. In addition, their performance has been evaluated when they are subjected to wet-dry cycles, something very common in situations when water table and heat play a role.

2. Materials and methods

Materials and properties

Four types of mortars with different mix proportions have been designed that are made of cement, water, superplasticizer , two types of aggregates (limestone and silica) and two different carbon-based additives: flake graphite and expanded graphite. The cement type CEM II-B (V)/32.5R (EN 197-1 [30]) was selected simply for availability reasons. The main criteria for the selection of the aggregates were local availability of the limestone and the considerably better thermal properties of silica sand [14]. As for the additives, the former is a naturally occurring form of graphite with purity over 94%, which is typically found as flat, plate-like crystals with angular edges. The nanosized expanded graphite is produced from natural graphite by chemical oxidation and expansion at high temperature, reaching expansion ratios of 200-300 and purities over 99%. As well as the well-known properties of flake graphite (e.g. thermal and electrical conductivity or chemical stability) worm shaped expanded graphite was assumed to contribute with its higher surface area and sealing properties, among others. Neither of the additives are water soluble so, in contrast to what occurs with heavy metals, toxic substances are not expected to be generated in the groundwater. In addition, they are not bioavailable and have very low chemical reactivity. The different morphology of the two additives can be identified in Figure 1.

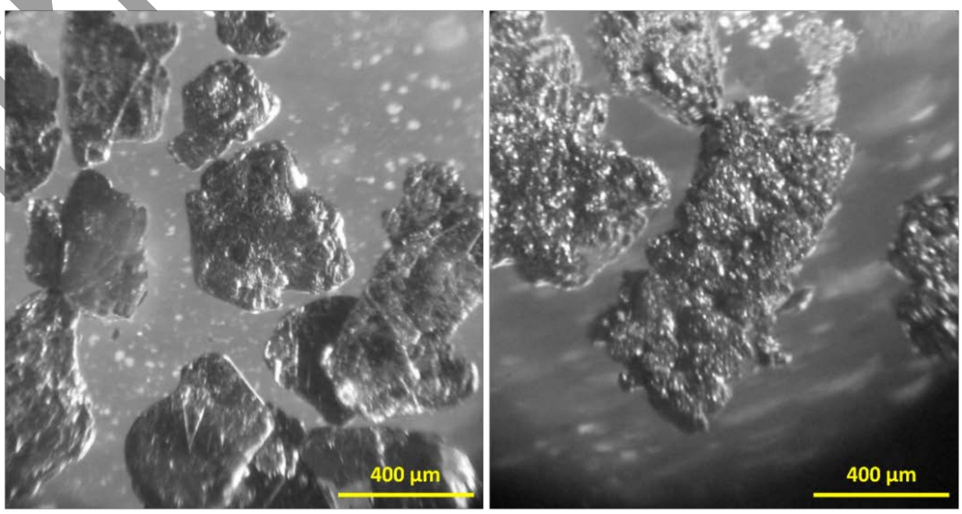

Fig 1.- Optical micrographs of the flake graphite (left) and expanded graphite (right) used in the research

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Finally, a powdered superplasticizer and cohesion promoter (MasterCast 205 MA) with bleeding prevention effect was used, which is especially recommended for the design of good quality self-levelling mortars with improved flowability. Table 1 shows the specific gravity and water absorption of the aggregates and graphites used, as well as their particle size distribution. Sands with a maximum aggregate size less than 2 mm were used for workability purposes.

Table 1. Main properties of the aggregates and additives used

	Limestone (L)	Silica (S)	Flake graphite (Fg)	Expanded graphite (Eg)
Specific gravity	2.725	2.638	2.250	0.040
Water absorption (%)	0.50	0.16	N/A	N/A
Sieve size (mm)	% Passing			
4	100	100	100	100
2	91	100	100	100
1	59	99	100	100
0.5	39	90	99	100
0.25	26	30	36	100
0.125	19	4	1	42
0.063	14	2	0	0

In Table 2 the nine different mix proportions (M1 to M9) are shown. The amount of water used for the design of the mortars was determined based on the flow table consistency test (EN 1015-3 [31]). Given the application studied here, diameters over 300 mm were desired resulting in mortars having good fluid properties yet retaining suitable mechanical and thermal properties. The amount of superplasticizer used was kindly suggested by the provider.

Table 2. Mix proportions of all the cement-sand mortars designed

Mortar	M1	M2	M3	M4	M5	M6	M7	M8	M9
w/c	0.35	0.39	0.46	0.40	0.40	0.44	0.44	0.42	0.51
L/c	2.00	0.60	0.00	1.94	1.91	1.88	1.85	1.98	1.97
S/c	0.00	1.40	2.00	0.00	0.00	0.00	0.00	0.00	0.00
Fg/c	0.00	0.00	0.00	0.06	0.09	0.12	0.15	0.00	0.00
Eg/c	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.015	0.030
sp/c	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025

w: water; c: cement; L: limestone sand; S: silica sand; Fg: flake graphite; Eg: expanded graphite; sp: superplasticizer.

Methodology for characterization

A conventional 1500W mortar mixer with speed regulation was used that ensured the proper mixing of the different materials involved. Three specimens per mix proportion and type of test

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were prepared for characterization purposes. After the mixing process, fresh samples were cured at ambient temperature until moulds could be removed. Then, the mortars were immersed in water at 20±2 ºC and left for curing for 28 days.

For the characterization of the different admixtures, fresh densities were obtained based on the European standard EN 1015-6 [32]. After the curing period, different thermal and mechanical properties of the mortars were evaluated. Thus, hardened densities, thermal conductivities and compressive and flexural strengths were determined as defined in the well-known standards EN 1015-10 [33], ASTM 5334-08 [34] and EN 1015-11 [35], respectively. For the conductivity tests, the Hukseflux TPSYS02 device with the TP02 Non-Steady-State Probe was used, which enables analysis in temperature and conductivity ranges from -55 to 180 ºC and 0.1 to 6.0 W/mK, respectively, with an accuracy of ±3%. Based on the hard nature of the material, very thin hollow steel bars had to be placed inside the fresh samples to enable the introduction of the needle. Moulds employed for the different tests were like those in [11], as required by the standards followed.

In addition, one more test was carried out for the evaluation of the pipe-mortar bond strength. The importance of this test derives from the potential debonding effects, which may lead to a loss of thermal efficiency and to environmental problems such as cross contamination between aquifers. As detailed in [21], the test is based on a cylindrical gap that has to be created between a 32x2.9 mm high-density polyethylene (HDPE) pipe embedded in the mortar specimen and the bottom of the specimen (Figure 2).

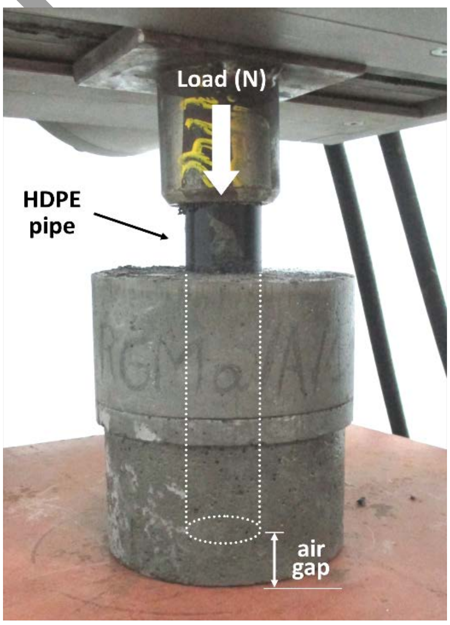

Fig 2.- Schematic view of the test for the evaluation of the pipe-mortar bond strength

The gap allows the pipe to go downwards when the load applied by a general-purpose testing machine, on the part of the pipe that sticks out of the mortar, reaches a certain threshold. This value defines the bond strength and corresponds to the maximum load registered during the test. The mechanical tests were carried out until the specimens' failure, whereas for the thermal conductivity tests three measurements were performed per sample. Results of fresh and hardened density, thermal conductivity, compressive and flexural strength and bond strength were determined as the mean of the values obtained for the specimens tested.

Methodology for durability

After the characterization stage, all the mortars except M4 and M5 (those with lower amounts of natural graphite and therefore, less representative for the durability analysis) were subjected to a durability test that consisted of 11 wet-dry cycles. As mentioned before, in situations where heat is exchanged with soils subjected to variable water-table levels, the durability assessment of the filling materials is very relevant. Thus, the same four laboratory tests were carried out on the mortars after the 11 wet-dry loads were applied.

The duration of each cycle was 72 hours (three days): the specimens were submerged in a water tank at 20±2 ºC for 24 hours and for the remaining 48 hours they were dried in ambient air. Three extra specimens per mix proportion and type of test were fabricated for durability purposes. Note that all the specimens per type of mortar, both for characterization and durability purposes, were from the same batch to avoid altering the comparison between the results obtained before and after they were subjected to the wet-dry cycles. This comparative analysis will contribute to the quality assessment of the materials proposed.

3. Results and Discussion

In Figure 3, the thermal conductivity results of the nine mortars are shown together with those of hardened density and the w/s ratios. Considering M1 as a reference mortar, it can be seen that the others, with either more conductive sands or carbon-based additives, achieve higher thermal conductivities. Mortars M2 and M3 achieved very good results merely by using increasing quantities of silica sand, something to be considered in situations where this aggregate is highly available. The higher w/s ratio of M3 can also be highlighted as it leads to better workability, although reducing the potential increase in thermal conductivity. Slightly lower results were obtained in [15] and [18] for similar cement-sand admixtures, probably due to the greater use of mixing water and/or the addition of bentonite. When silica sand is not

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available or not desired, thermal enhancing additives such as those analysed in this paper might be used to improve the efficiency of GSHP installations with soils having very good thermal properties. In this sense, the influence of the flake graphite is shown in Figure 3 as the difference between the increasing trend of thermal conductivities in mortars M4 to M7 and the corresponding flat trend of the hardened densities.

It should also be mentioned that values of conductivity 22% and 26% higher than the reference mortar were obtained for M8 and M9, regardless of their low values of hardened density. Thus, the use of expanded graphite (particularly in M9) made possible the increase of the w/s ratios while improving the thermal properties of the mortars. This is relevant as the workability is a critical property when selecting the grouting materials for geothermal purposes. On the other hand, the use of excess water in the admixture would lead to mortars with poorer mechanical properties as compared to the reference sample.

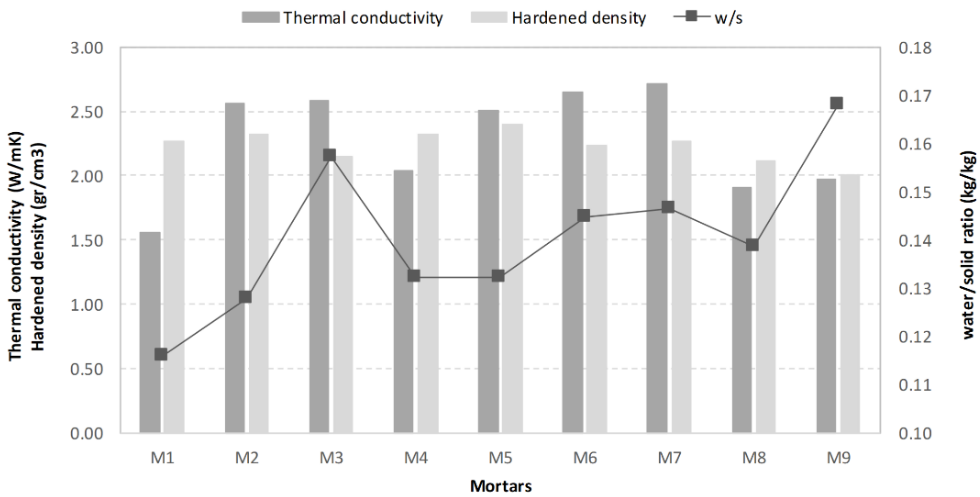

Fig 3.- Thermal conductivity, hardened density and w/s ratios of the mortar specimens

In line with previous results, the values of thermal conductivity of mortars M8 and M9 stand out, considering the low additive/cement ratios used (Figure 4). This is very important given the significant price of expanded graphite in relation to natural flake graphite (≈70 times more expensive according to the particular provider used for this research). The linear increase in the mortars' conductivity with the increase in their additive/cement ratios should also be highlighted (Figure 4), as well as the maximum values measured, with mortars reaching values of conductivity 30-74% higher than for the reference admixture by adding 3.0-7.5 %wt flake graphite with respect to sand (1.7-4.3 %wt with respect to mortar). Therefore, the high availability of this additive is an asset due to its suitable thermal enhancing properties. However,

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the hydrophobic nature of the flake surface and the bubbling effect when mixed with water, makes the manufacturing process a little more difficult than desired. As seen in Figure 5, a crust is formed at the top of the samples due to the flotation of the graphite, part of which is attached to the air bubbles, thereby being separated from the admixture. This issue has to be further considered in order to minimize the loss of flake graphite when filling the moulds.

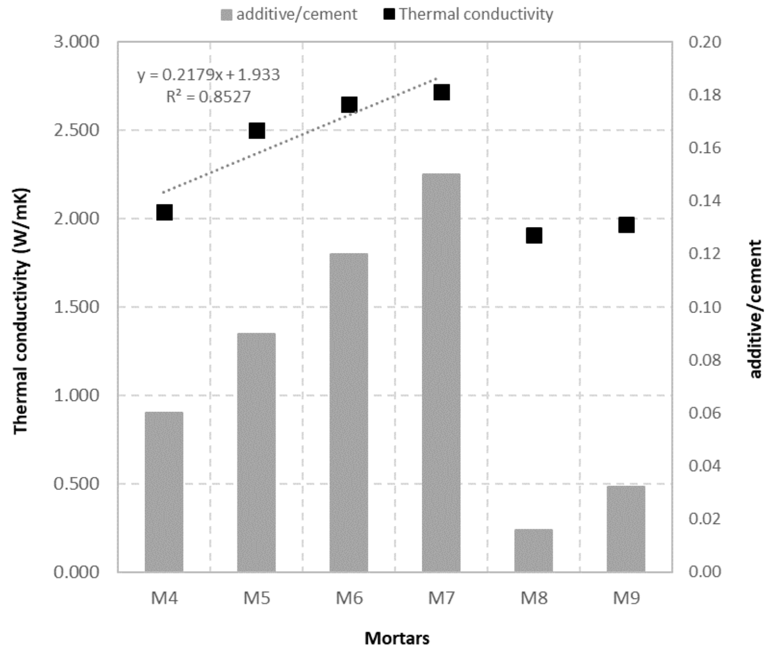

Fig 4.- Thermal conductivity of the mortar specimens as a function of their additive/cement ratios

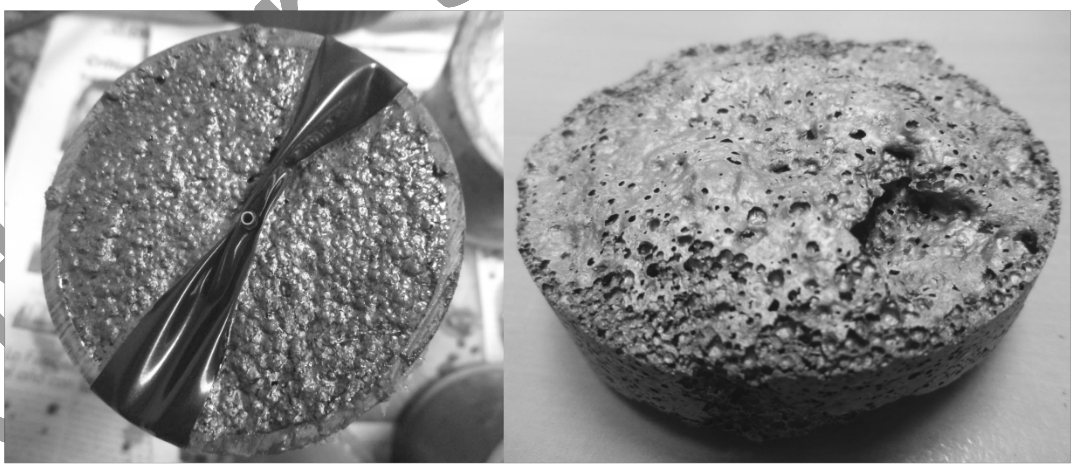

Fig 5.- Crust formed at the top of the specimen when flake graphite is added to the mortar

Finally, the values of thermal conductivity measured before and after the durability treatment are shown in Figure 6. According to the graph, there is hardly any variation between the values obtained, which means that the wet-dry cycles to which the seven admixtures were subjected, did not have any influence on their thermal behaviour. The visual inspection of the specimens confirmed the lack of any substantial damage that could have affected this behaviour. Something similar was noticed in [21]: analogous silica-based and limestone-based cement-sand mortars were not affected at all by a durability treatment based on the application of freeze-thaw cycles. This seems to demonstrate the thermal resilience of this type of mortars.

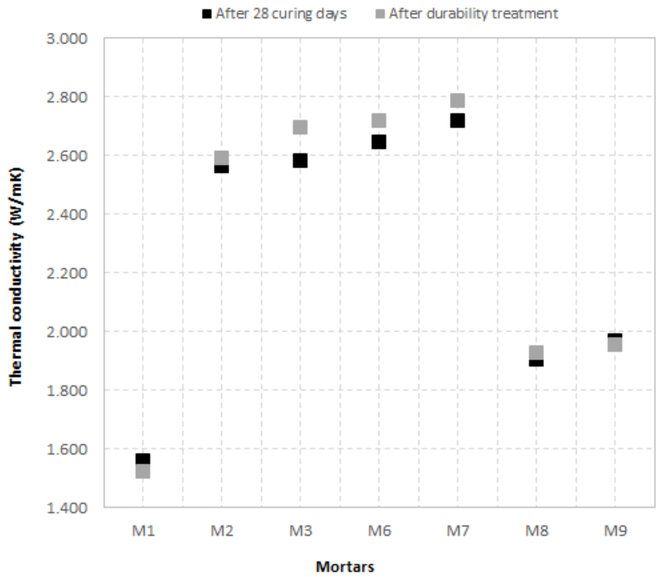

Fig 6.- Results of thermal conductivity before and after the durability treatment

As for the mechanical characterization of the mortars, the results of compressive and flexural strength compared to their w/c (water/cement) ratios are shown in Figure 7. All the mortars except M2 presented lower resistances to compressive and flexural loads than the reference mortar, but on the other hand, the increasing w/c ratios suggest improved workability.

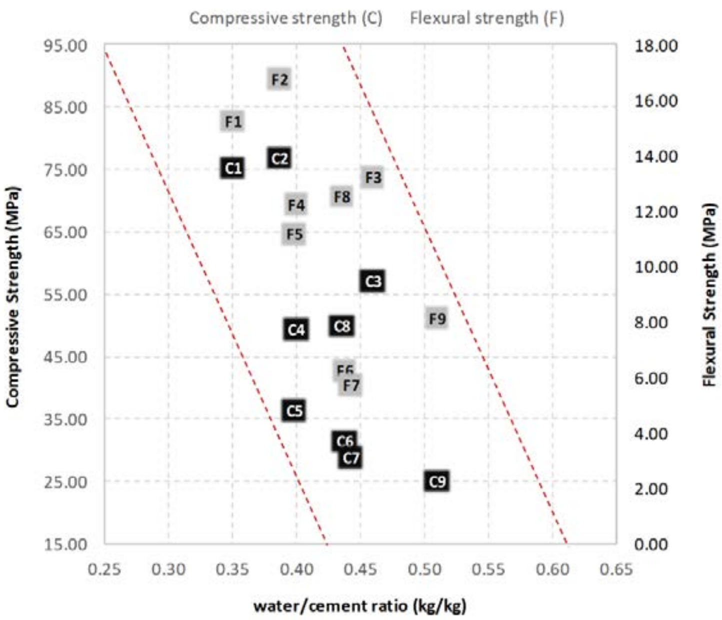

Fig 7.- Compressive and flexural strength of the mortars as a function of the water/cement ratio

Values of compressive strength in the same range were obtained in [18] and [21] for mortars with limestone or silica sand, whereas smaller values were measured in [15] and [19], probably due to the use of higher volumes of mixing water. When comparing with conventional grouts [9,11], the difference is one order of magnitude. Therefore, given the specific area of application, suitable combinations of mechanical and thermal behaviour have been obtained for the mortars studied, including those with the two different types of graphites. The difference between the results for M6 and M7, with 3.5%wt and 4.3%wt flake graphite, respectively, and M8, with 0.5%wt expanded graphite, is also interesting. Although similar w/c (and w/s) ratios were used, considerably higher values of compressive and flexural strength have been obtained for M8, which suggests the influence of the nanosized graphite on the admixture.

Although the comparison is not statistically appropriate because of the different compositions of the admixtures, a relationship might be assumed (as suggested by the red-dashed lines) between the amount of mixing water and the mechanical strength of the resulting mortars. In the case of mortars M4 to M9, the w/c ratios are likely related to the higher water absorption requirements of admixtures incorporating graphites. The fact that the w/c ratios remains crucial for their design whatever other elements are involved is illustrated by the results of the two mortars with expanded graphite. Thus, despite the above mentioned positive influence of the additive, the compressive and flexural strengths were substantially reduced (50% and 35%, respectively) after doubling the amount of additive, something which clearly correlates with the significant difference in the w/c ratios of the two mortars. All in all, regardless the adverse effect of excess water in the mix, the mechanical performance of M9 can be considered to fulfil the requirements for geothermal groutings.

The compressive and flexural strength results before and after the durability treatment are presented in Figure 8. It can be clearly observed that the influence of the wet-dry cycles on the mechanical behaviour of the mortars was almost negligible, no matter the type of sand or additive incorporated, and only two mortars lost certain flexural resistance (M1 and M2). In order to confirm whether the mortars were statistically affected by the durability treatment or not, the p-p plots of flexural and compressive strength for all the data (with no treatment distinction) have been plotted (Figure 9). As can be seen, both samples follow a normal distribution, which indicates that the variations of the results are a product of the inherent variability of the materials and the uncertainty of the test procedure. Likewise, a Two-Sample T-Test has been carried out with Minitab software. As expected, this test provided p-values of 0.541 and 0.721 for the results of compression and flexural strengths, respectively. As p-values are greater than the significance level (α=0.05), the null hypothesis (H0: μ1 = μ2) cannot be rejected, hence it can be concluded that the average flexural and compression strengths of mortars subjected to durability treatment are not statistically different to those of mortars not subjected to treatment.

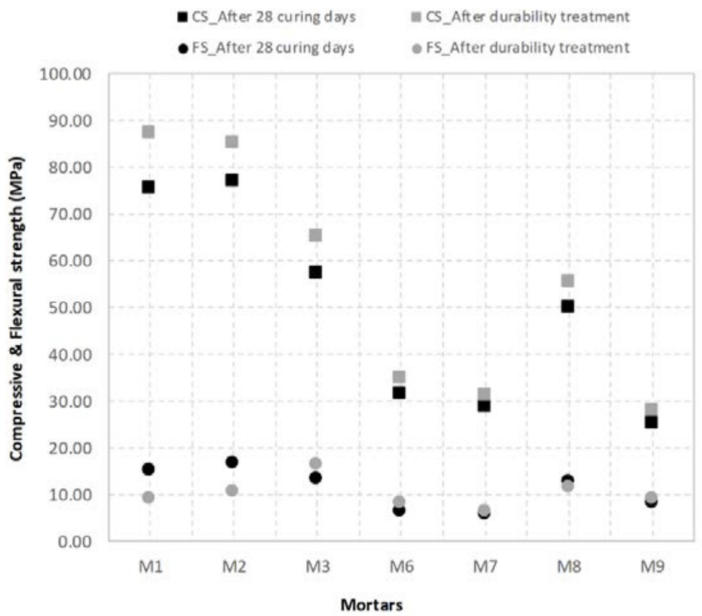

Fig 8.- Results of mechanical resistance before and after the durability treatment

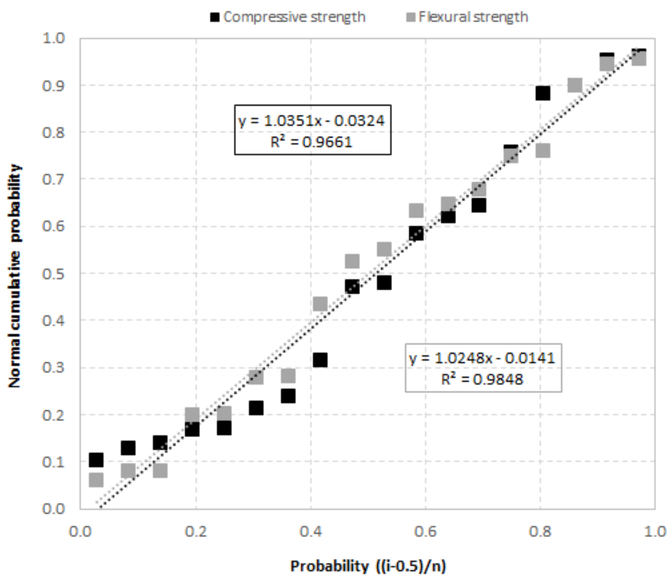

Fig 9.- P-P plot for the values of compressive and flexural strength measured

The results of the evaluation of the pipe-mortar bond strength for the nine admixtures are shown in Figure 10. Comparable adherence loads in the range between 0.6 and 0.8 kN were measured for all of them except one, the mortar with highest amount of expanded graphite (M9). Mortars

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with increasing amounts of flake graphite (M4-M7), with adherence loads over 0.7 kN, did not improve the value achieved by the reference mixture. On the other hand, the large standard deviations obtained for most of the average loads are very noticeable, which preclude drawing conclusive statements on this question other than the analogous behaviour already stated. In further studies, more specimens per mortar and test should be used for accuracy purposes.

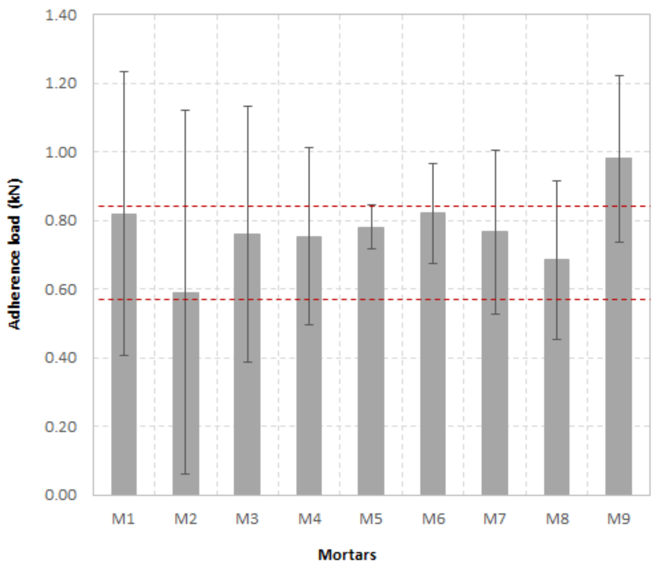

Fig 10.- Results of the adherence test after the 28 days' curing

For the same reason, caution should be exercised with the retained resistance data shown in Figure 11. According to these results, all the mortar-pipe specimens undergo some loss of adherence, which leads to a retained resistance that is always in a narrow range between 56 and 72% except for one of the mortars, with most of them having retained resistances over 60%.

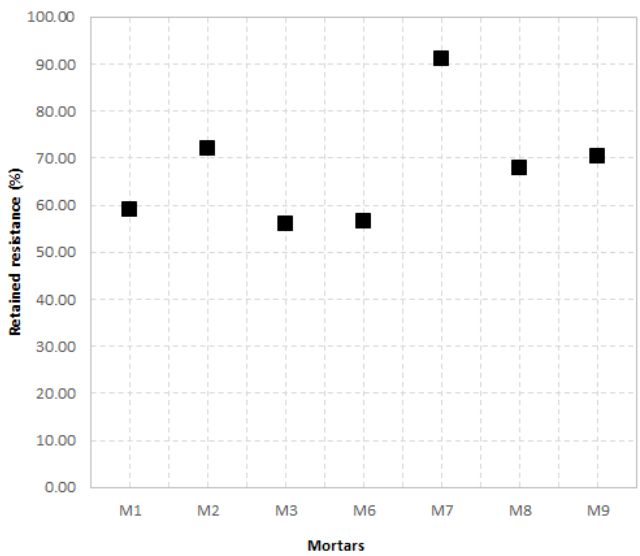

Fig 11.- Retained bond strength after the durability treatment

As for the larger deviation of M7, since none of the common technical factors (mixing process, type of sand, amount of additive, etc.) seems to explain it, the only reason for this seems to be the wide scattering of the data, which causes the large standard deviations already mentioned.

Finally, the cost of the different mortars are displayed in Table 3. These costs are exclusively based on the very well-known prices of the raw materials, also included in the table, whereas concepts such as their transport or the mixing process are not considered. Sources of the prices are local construction materials' stores, local quarries and the provider of the graphites used.

Table 3. Cost of the cement-sand mortars based on the price of the materials

Price of materials (€/kg)					
Cement	Limestone	Silica	Fg	Eg	SP
0.14	0.009	0.010	27	1900	1.60

Cost of the mortars (€/kg)								
M1	M2	M3	M4	M5	M6	M7	M8	M9
0.06	0.06	0.06	0.49	0.77	0.99	1.23	8.89	17.27

According to the figures in the table and the results of thermal and mechanical characterization as well as the durability aspects previously discussed, it seems that using advanced materials like expanded graphite in mortars for geothermal purposes is still far from being cost-effective, even though the properties of the resulting fluid mortars are indeed improved when this product is employed. As for the more conventional flake graphite, thermal conductivity results showed that for specific situations (e.g., when soils have very good thermal properties), it might be worth using it despite the lower cost of the silica sand mortars. For comparison purposes, it should be said that the cost of mortars M4, M5, M6 and M7 is similar to or less than those of commercial grouts with enhanced thermal properties.

4. Conclusions

In this paper, the mechanical and thermal characterization of nine different cement-sand mortars for geothermal purposes has been carried out and their durability has been assessed after being subjected to wet-dry cycles. Based on the results of the different tests, the following main conclusions can be drawn:

- The use of small quantities of flake and expanded graphite clearly increases the thermal conductivity of the mortars even when considerable w/c ratios are used. Likewise, the use of silica sand instead of (or in combination with) limestone substantially improves it. Nevertheless, the enhancing capacity of the graphites seems to be superior if the low quantities used in this research (< 5 %wt) are considered.

- Despite the different mix proportions and materials involved, all the mortars showed adequate to very good values of mechanical strength, significantly higher than those of conventional geothermal grouts. More importantly, good mechanical to thermal performance ratios were obtained for mortars with suitable workability.
- Similar values of pipe-mortar bond strength were obtained for mortars M1 to M5, which means that using flake graphite did not have any influence on this parameter. As for the higher value of bond strength achieved by M9, the large standard deviations obtained in the test did not allow a positive effect to be inferred from using expanded graphite.
- The durability of the mortars under wet-dry cycles has been proved, as hardly any damage was noticed in terms of thermal conductivity or mechanical strength. As for the pipe-mortar adherence, some damage has been measured in all the mortars after the durability treatment, even though most of them have retained at least 60% of the bond strength.
- The cost of the different mortars designed, as well as the mechanical and thermal characterization results suggest that using advanced materials such as expanded graphite in GSHP installations is not cost-effective yet. However, the current development of the graphite technology and the resulting future decrease in prices might help to change this in the near future.

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