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Nanoreinforced concrete composites for possible nuclear waste confinement - a preliminary study

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Abstract— **Cementitious materials are the most abundant building materials even nowadays. Similarly, in the nuclear industry, concrete is the most used material for the confinement of radioactive waste, it has favorable properties, both chemical and physical, making it a desirable matrix for the encapsulation of radioactive and toxic wastes. Cemented wastes are preferred for the storage of a large varieties of fission products, such as low and intermediate level radioactive waste e.g., β—emitter ^{90}Sr. Anyway, because of the intrinsic fragility of ordinary Portland Cement (OPC) a lot of efforts have been spent to enhance his mechanical resistance.**

Graphene Oxide (GO) represent an opportunity to overcome this problem. In fact, there is much evidence that GO can influence the toughness and the strength of the cement composites by regulating the morphology of the cement hydration products.

^{90}Sr, the main strontium isotope in radioactive waste, is a by-product of the fission of uranium and plutonium in nuclear reactors. In this study we investigate the effects of strontium on mechanical properties of cement (OPC) and GO-reinforced cement. Different samples have been prepared with fixed concentration of GO. It has been observed that small quantities of GO, significantly [1] increases the compression strength of cement composites. The addition of Sr (65.0, 67.6 and 70.2 ppm) resulted in an increase of the compressive strength of 6.78%, 3.02% and 0.70% for those samples respectively, in comparison to OPC.

Compression strength in samples of OPC with GO remained quite constant even in presence of Sr.

Keywords: **Radioactive waste, Graphene Oxide, Compressive strength, Strontium.**

I. Introduction

Due to its favourable chemical and physical properties, cement is extensively utilized in the nuclear industry for confining low and intermediate-level radioactive waste, such as those containing β-emitter ^{90}Sr. However, the traditional Ordinary Portland Cement (OPC) possesses inherently brittle characteristics, and numerous efforts have been made to enhance its mechanical strength. In recent decades, fibre-reinforced and nanoreinforced concretes have been developed. However, significant progress has not been achieved in addressing the brittle performance of this material. Graphene Oxide (GO) provides an opportunity to overcome this issue by influencing the toughness and strength of cement composites through the regulation of cement hydration products morphology. This study investigates the combined effects of GO and stable strontium, the latter being used as a simulant for ^{90}Sr (a radioactive isotope), on the mechanical properties of OPC. It is noteworthy that ^{90}Sr is a by-product of uranium and plutonium fission in nuclear reactors and is considered a chemical analogue for ^{226}Ra in performance assessment studies for cements in radioactive waste repositories [2-3]. The cement specimens were characterized using various techniques, including mechanical tests, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). This study provides new insights into the use of concrete in radioactive waste storage by investigating the influence of GO and stable strontium on the mechanical properties of OPC. The synthesis of GO has been approached with the goal of developing and optimizing the synthesis process, considering economic and environmental sustainability by improving the efficiency of the different process stages.

II. Materials and Methods

The synthesis of GO has been addressed using the Hummers method [4] as a reference base, as well as modified versions [5–13], with variations to enhance the overall efficiency.

Modified Hummers method starts from a commercial graphite powder upon which is performed a chemical oxidation using sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2).

The GO, once produced, was mixed to the cement in solution form, obtained dispersing a fixed quantity in distilled water and exposing the solution in an ultrasonic bath at the frequency of 37 kHz with a power of 100 W for 30 minutes.
Increasing concentrations of strontium (67.6, 70.2 and 71,6 ppm) were added to the GO solution and then mixed with cement. The concentrations used were chosen in a range close to the maximum solubility limit of the strontium in cement [14]. To realize 1 cm^3 cubic specimens was used OPC CEMII/BLL 32.5R. The water cement (w/c) ratio have been of 0.5. The GO was added to the cement in a fixed quantity equal

to 0.03% w/v. In Fig. 1 is shown the flow sheet of the cubic specimen preparation.

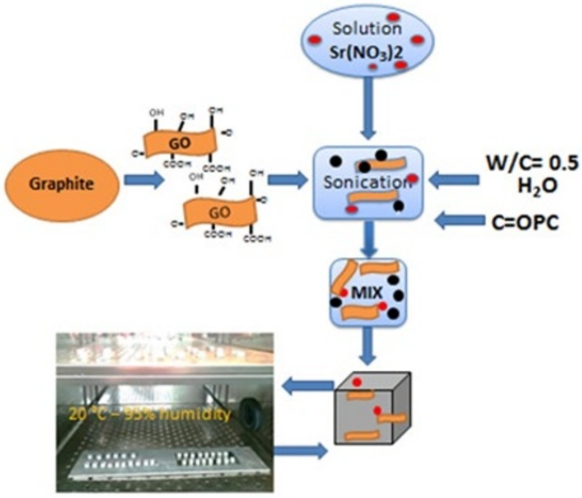

Fig. 1. Flow sheet of the cubic specimen preparation with and without GO and/or stable strontium.

After the preparation, the samples were cured in an environmental testing chamber at 20° C and 95% of relative humidity following a standard 28-day procedure Fig. 2 [1].

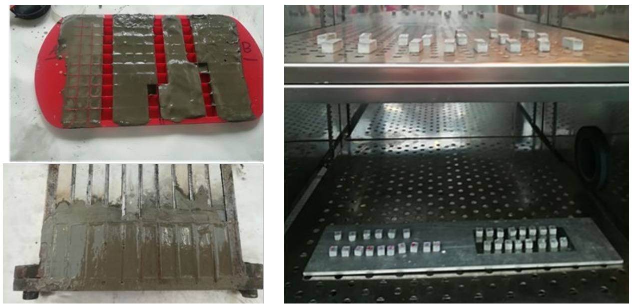

Fig. 2. Sample preparation and curing environmental test chamber.

The compressive strength test was performed using a uniaxial press (Fig. 3). Initially, several tests were conducted to optimize the compression speed based on the geometry of the prepared samples. The chosen speed was 5 mm/min. Fig. 3 shows the setup of the Tecnotest® equipment used for the compression tests, while Fig. 4 shows a sample between the plates of the press.

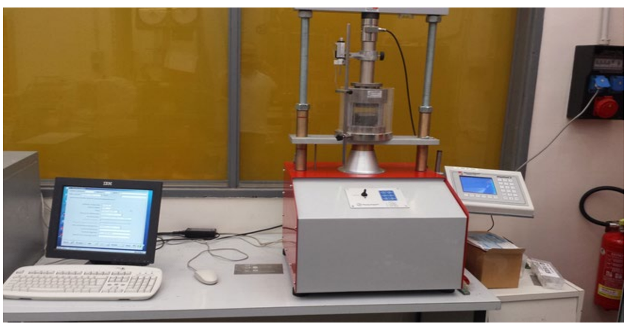

Fig. 3. Set-up of the TECNOTEST T051/B65 equipment used for compression tests.

To investigate the effects of GO and Sr on cement hydration products have been performed the thermogravimetric analysis (TGA). Thermal analyses were run on a Simultaneous TG/DTA NETZSCH STA Jupiter. at 10 °C/min from 25 °C to 1200 °C in 100 cm^3/min of air flow, in order to study the effect of Sr and 0.03% GO addition on the hydration characteristics of concrete matrix.

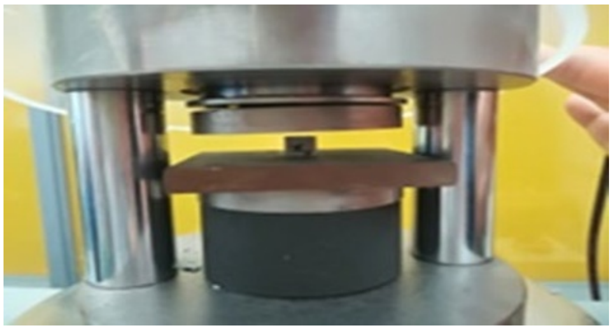

Fig. 4. Specimen before the compression test.

The microscopic analysis of the samples, following the mechanical tests, was carried out using a Zeiss MA 15 scanning electron microscope (SEM).

III. Results and Discussion

A. Scanning electron microscopy

The microstructure of concrete with the Sr and GO addition has a significant effect on mechanical characteristics. The SEM analysis was used to identify the relation between microstructure and the improvement of the compressive strength. The SEM image of representative sample I (OPC + 0.03% GO + 71.5 ppm Sr) in Fig. 5 reveals the hydration products. The analysis confirmed the intimate connection of the GO with the cement hydration products (Fig. 5-6).

The GO's layers are positioned as bridge to the cement hydration products endorse the hypothesis the role on the structural effects of the cement-GO composite.

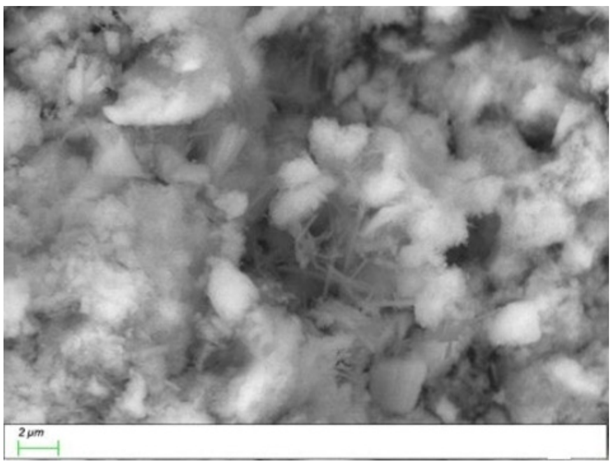

Fig. 5. SEM image of sample (I) prepared modifying OPC with 0.03% of GO and 71.6 ppm of Sr (▬ 2 µm).

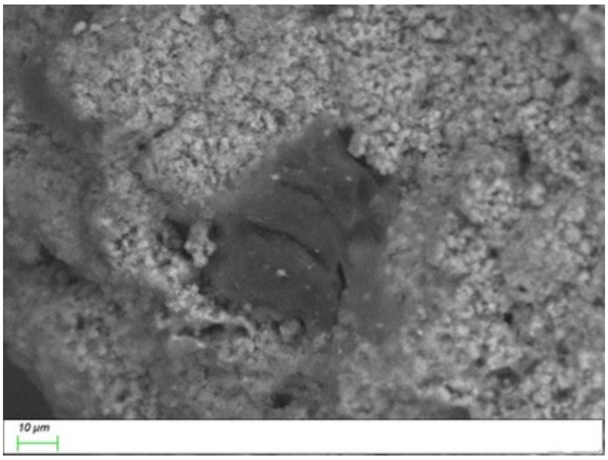

Fig. 6. Sem image of sample (F) prepared modifying OPC with 0.03% of GO (▁▁▁ 10 µm).

B. Thermogravimetric analysis

The thermogravimetric and derivate thermogravimetric curves of concrete (OPC) and OPC added with Sr and Sr + GO are shown in Fig. 7 and Fig. 8 respectively.

At 120 °C, a weight loss of approx. 5wt% are attributed to water desorption. Subsequent mass losses between 120-650 °C are attributed to water from the decomposition of the C-S-H (450-550 °C) and dihydroxylation of the $Ca(OH)_2$. Finally, between 650-900 °C the mass loss is attributed to the decarbonation of carbonate.

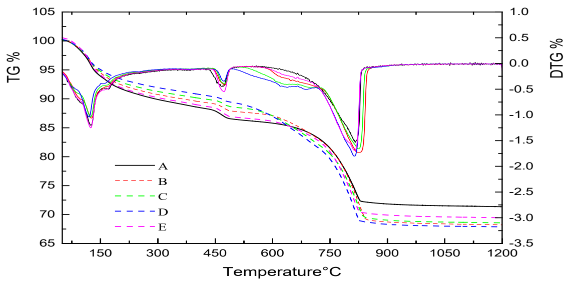

Fig. 7. TG/DTG curves of samples hydrated for 28 days at 25°C: A (OPC), B, C, D, E (OPC + %Sr) concrete specimens.

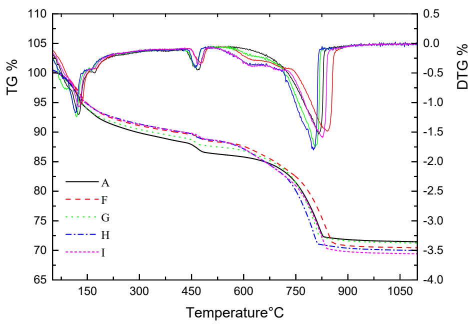

Fig.8. TG/DTG curves of samples hydrated for 28 days at 25 °C: A (OPC), F (OPC + 0.03% GO), G, H, I (OPC + 0.03% GO + %Sr) concrete specimens.

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The effect of the Sr at different concentration and of the 0.03 w% GO content on the degree of hydration of the samples (α) was determined using Eq. (1) α(%) = WB/0.24; where WB is non evaporable water content of the samples [15].

The values of hydration degree of the different samples are shown in Fig. 9.

The data demonstrate that the addition of Sr (65.0, 67.6, 70.2 and 71.6 ppm) improved the hydration degree of 24.71%, 23.07%, 20.58% and 18.13% in comparison to the concrete OPC. The degree of hydration for OPC is 35.41%. While hydration degree in samples of OPC with 0.03% of GO is 14.5% and decreases anomalously at 4.5% for sample G (GO + 67,6 ppm Sr) and remained quite constant at 23% for sample H and I with GO + 70.2 ppm Sr and GO + 71.6 ppm Sr respectively. The findings demonstrate that the 0.03% of GO improved by 29% the degree of hydration of the sample E with the highest concentration of Sr 71.6 ppm.

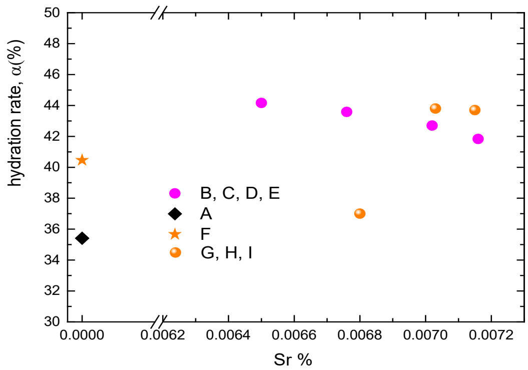

Fig. 9. Hydration rate versus %Sr of: A (OPC), F (OPC + 0.03% GO), B, C, D, E) (OPC + %Sr) and G, H, I (OPC + 0.03% GO + %Sr) concrete specimens.

C. Compressive strength test

The preliminary results of the compressive strength test showed performed by composite GO specimens showed only a partial enhancement of the mechanical properties capable to hinder the decline of mechanical performances induced by the increasing amounts of strontium. In Table I are displayed the results of compressive strength test of the specimen and the corresponding density.

TABLE I
COMPRESSIVE TEST STRENGTH AND DENSITY OF SPECIMENS

Sample symbol	Description	Compressive strength test (MPa) (µ±SD)	Density (g/cm^3)
A	OPC	69.3 ± 5	1.68
B	OPC + 65.0 ppm Sr	74.1 ± 6	1.70
C	OPC + 67,6 ppm Sr	71.5 ± 4	1.66
D	OPC + 70,2 ppm Sr	69.9 ± 6	1.63
E	OPC + 71,6 ppm Sr	67.8 ± 6	1.61
F	OPC + 0.03% GO	70.5 ± 4	1.68
G	OPC + 0.03% GO + 67.6 ppm Sr	69.0 ± 3	1.68
H	OPC + 0.03% GO + 70.2 ppm Sr	70.4 ± 6	1.67
I	OPC + 0.03% GO + 71.6 ppm Sr	70.4 ± 3	1.66

OPC = Ordinary Portland Cement CEMII/B-LL32.5R Sr = $Sr(N0_3)_2$ GO = Graphene Oxide.

The specimens, once compressed as illustrated in Fig. 10, take on a distinctive hourglass shape upon fracture.

Fig. 11 presents the graphic depicting the relationship between the applied compression on the specimen (N/mm^2) and the elapsed time (s) with specific emphasis on the breaking point.

Fig. 10. Sample after compression

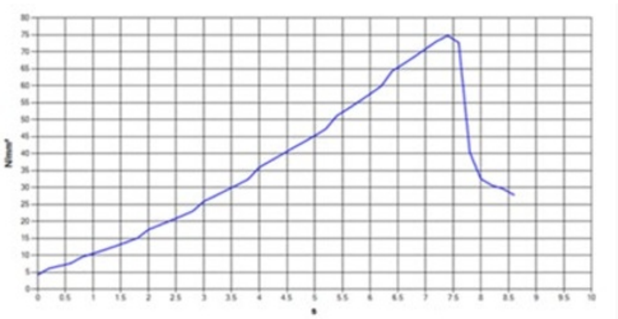

Fig. 11. Compression diagram

The bulk density decreased with the increasing amount of Sr in the mixture. for Sr = 71.6 ppm the decrease of density is by about to 7% to OPC.

The addition of 0.03% of GO decreases the density by 3% compared to OPC, while adding the same amount of GO to OPC + Sr samples induces an increase the density of about 2% (Fig. 12).

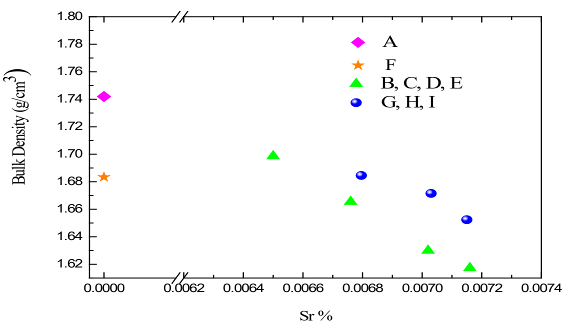

Fig. 12. Bulk density versus %Sr of: A (OPC), F (OPC + 0.03% GO), B, C, D, E (OPC + %Sr) and G, H, I (OPC + 0.03% GO + %Sr) concrete specimens.

The addition of Sr (65.0, 67.6 and 70.2 ppm) resulted in an increase of the compressive strength of 6.78%, 3.02% and 0.70% for B, C, D samples respectively, in comparison to OPC. While at higher concentrations of Sr (71.6 ppm) a reduction of 2.24%, in sample E, has been observed. Compression strength in samples of OPC with GO remained quite constant even in presence of Sr (Fig. 13).

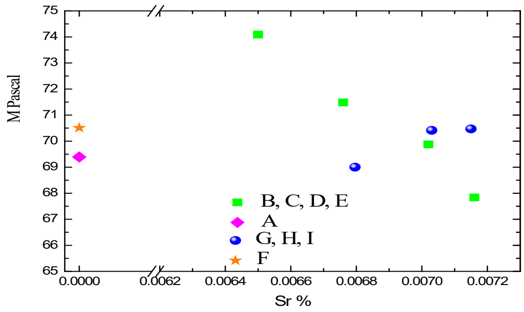

Fig. 13. Compressive strength versus %Sr of: A (OPC), F (OPC + 0.03% GO), B, C, D, E) (OPC + %Sr) and G, H, I (OPC + 0.03% GO + %Sr) concrete specimens.

IV. Conclusions

Confinement of nuclear wastes requires new research activities focused on stable and reinforced matrixes for allowing the entrapment of low and intermediate level radioactive isotopes. The addition of graphene oxide (GO) to cement CEMII/B-LL32.5R has been found to increase the compressive strength. The addition of increasing concentrations of strontium to cement CEMII/B-LL32.5R resulted in a decrease of the compressive strength. However, it appears that the addition of GO stabilizes compressive strength in cements with strontium, potentially mitigating the negative effect of strontium on such a parameter. These initial results are promising; however, further work is required to add to the obtained data and investigate the effect of different concentrations of Sr and GO on migration of Sr in cementitious materials.

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