Experiment Proposal

Experiment number GP2024034

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Experiment title	3D printable eco-sustainable composites containing marble dust waste

MRF Instrument	**XRD TOMOGRAPHY**	**Days requested:**	2
Access Route	Direct Access	**Previous GP Number:**	no
Science Areas	Chemistry, Materials	**DOI:**	-
Sponsored Grant	None	**Sponsor:**	-
Grant Title	-	**Grant Number:**	-
Start Date	-	**Finish Date:**	-
Similar Submission?	-		
Industrial Links	-		

Non-Technical Abstract

The extraction and processing of stone and marble, playing a major role in the Italian economy, involves the production of large amounts of CaCO3 by-products during the crushing and washing operations. Considering the importance of developing green and low-impact products, several solutions have been proposed in the last years, mostly focused on the preparation of a wide range of composites, including polymer-based formulations and cement matrices. In this research, we investigated some innovative and eco-friendly 3D printable formulations enriched with large amounts of CaCO3. In particular, we focused our attention on Alginate/CaCO3 composites, based on the incorporation of marble dust in a polymeric matrix, and MSH/CaCO3 composites, based on the incorporation of marble dust waste in a cementitious matrix. These formulations were used to 3D print some objects, and RIGAKU Nano3DX X-ray microscope could provide crucial information about their porous structure.

Publications -

ISIS neutron and muon source — **E-platform:** No

Instruments		**Days Requested:**	
Access Route		**Previous RB Number:**	
Science Areas		**DOI:**	
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ISIS@MACH ITALIA

Science and Technology Facilities Council
ISIS Neutron and Muon Source

Sample record sheet

Principal contact Dr Monica Tonelli, University of Florence, ITALY
MRF Instrument **XRD TOMOGRAPHY** **Days Requested:** 2
Special requirements:

SAMPLE

Material	polymeric composites	2 cementitious composites	-
Formula	(C6H8O6)n + CaCO3 for the polymeric composites	(MgO)x(SiO2)y(H2O)z + CaCO3 for the cementitious composites	-
Forms	Solid	Solid	
Volume	1 cc	1 cc	
Weight	mg	mg	
Container or substrate	none	none	-
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

Temperature Range	room temperature - K	room temperature - K	-
Pressure Range	atmospheric pressure - mbar	atmospheric pressure - mbar	-
Magnetic field range	- T	- T	-
Standard equipment	None	None	-
Special equipment	none	none	-

SAFETY

Prep lab needed	No	No	-
Sample Prep Hazards	no	no	-
Special equip. reqs	no	no	-
Sensitivity to air	No	No	-
Sensitivity to vapour	No	No	-
Experiment Hazards	no	no	-
Equipment Hazards	-	-	-
Biological hazards	no	no	-
Radioactive Hazards	no	no	-
Additional Hazards	-	-	-
Additional Details	-	-	-
Sample will be	Removed By User	Removed By User	-

1. Background and Context

The valorisation of wastes is fundamental towards the development of green and low-impact products. The case of calcium carbonate waste is particularly relevant in Italy, since the total Made in Italy exports of marble, natural stones, travertine, and granites involves the production and export of tens of millions of tons of materials, playing a major role in the economic growth. The extraction and processing of stone and marble involves the production of large amounts of $CaCO_3$ by-products during the crushing and washing operations. Thus, the identification of new methods for managing the impact of this waste has resulted in a large scientific interest towards the recovery and use of stone by-products, either as slurry or dust. $CaCO_3$ has been employed for the preparation of a wide range of composites, including polymer-based formulations and cement matrices. For example, several recent research used marble waste in combination with polyethylene, polypropylene, and epoxy resins, to increase the density and reduce the cost of these composite.[1] At the same time, $CaCO_3$ is a well-known filler for cementitious materials, and can be used to influence several physico-chemical properties, while reducing the consumption of cement, which in turns reduce the cost and the environmental impact of these pastes.[2] In this framework, we investigated some innovative and eco-friendly 3D printable formulations containing large amounts of $CaCO_3$. This research involves the work of a PostDoc and two master students. The research is supported by The National Recovery and Resilience Plan of Italy "3A-Italy Circular and Sustainable Made in Italy" (PNRR, 3A-ITALY - B83C22004890007)

2. Proposed experiment

To thoroughly characterize some selected 3D printed composites, the porous structure of these systems should be investigated. To this purpose, RIGAKU Nano3DX X-ray microscope, available in the ISIS@MACH ITALIA infrastructure, could be crucial, allowing for the visualisation, upon reconstruction, of some dry objects. These data will be complemented with gas porosimetry analyses, to gain a complete picture of the porous structure of the systems, both at the nano- and -micro-scale. Finally, compressive strength tests will be used to correlate the mechanical properties of these samples with their pores' distribution.

3. Summary of previous experimental proposals or characterisation

We investigated various formulations containing large amounts of marble dust waste, towards the preparation of 3D printed eco-sustainable composites. To this purpose, we focused our attention on two classes of composites:

- Alg/$CaCO_3$ composites: these formulations were prepared enriching a water dispersion of alginate biopolymer (Alg) with several amounts of marble dust, in presence of different concentration of $CaCl_2$. Alginate is a polysaccharide able to chelate di- and trivalent cations (e.g., Ca^{2+}), resulting in physically cross-linked hydrogels. The reinforcement of Alg paves the way towards several fields of application, and the development of Alg/$CaCO_3$ composites could allow the obtainment of hybrid organic-inorganic composites with anisotropic properties, able of shape-morphing in response to external stimuli, such as humidity variation.[3]
- MSH/$CaCO_3$ composites: these systems were prepared by mixing MgO/SiO_2 powders with several amounts of marble dust in presence of water, also including some additional additives. As already well known, MgO/SiO_2 react with water to produce magnesium silicate hydrate eco-sustainable cements (MSH). The printability of such formulations was already demonstrated in

the literature.[4] Here, we enriched these matrices with large amounts of $CaCO_3$, to obtain 3D printable systems to be used as substrates for coral reef growth. In fact, less environmentally friendly concretes were already used to assist the regeneration of the marine environment, and the use of $CaCO_3$ perfectly suits this field of application, mimicking the natural composition of corals.[5]

The investigated formulations, either based on biopolymer of cementitious matrices, were characterized in terms of homogeneity, fluidity, extrudability and hardening properties. Then, several 3D printing tests were performed, to adjust the processing parameters and to assess the printability of some selected formulations, towards the preparation of specifically designed objects. According to the preliminary results (see Figure 1), we developed two new 3D printable formulations containing large amounts of marble dust waste.

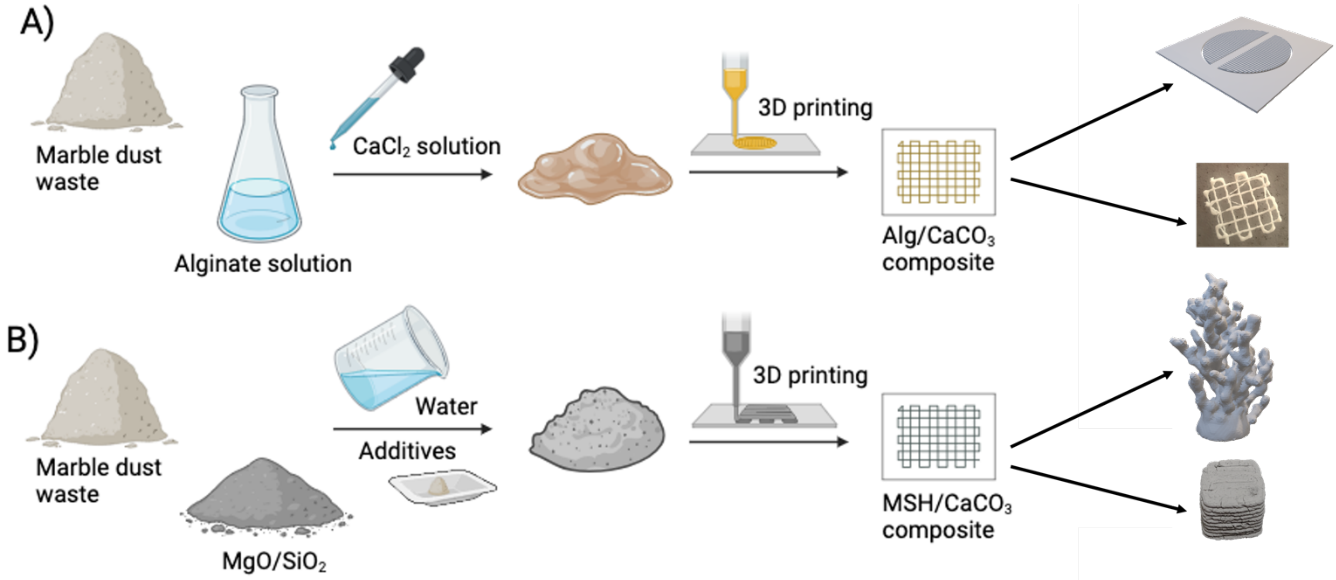

Fig 1. Schematic diagram of samples' preparation.

4. Justification of experimental time requested

The opportunity to use the RIGAKU Nano3DX X-ray microscope will provide paramount information about the inner structure of the 3D printed systems (cubic samples of about 1 cm^3). These experiments will allow to unravel the total porosity at the microscale and eventually evidence the presence of cracks, to be correlated with the formulations' composition and mechanical properties. We plan on investigating 4 systems: 2 Alg/$CaCO_3$ 3D printed samples, and 2 MSH/$CaCO_3$ 3D printed samples. To this purpose, a working time of 2 days is expected to be needed to collect the data, to be further used to reconstruct the structure upon image processing and calculation of the total porosity (either in volumes of interest or in the entire investigated specimens).

[1] Awad et al., *Construction and Building Materials*, **2019**, 228, 116766.
[2] Aliabdo et al., *Construction and Building Materials*, **2014**, 50, 28-41.
[3] Lai et al., *Materials & Design*, **2021**, 205, 109699.
[4] Tonelli et al., *JCIS*, **2021**, 598, 24-35.
[5] Su et al., *Cement and Concrete Composites*, **2022**, 140, 105059.