Alternative Cementitious Binders Using Mineral Wastes

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Abstract. The present study discusses preliminary findings on the potential of upcycling mine tailings into an alternative source of supplementary cementitious materials. Thermal and mechanical activation mechanisms were used to alter the highly crystalline microstructure of the raw tailings. Scanning and transmission electron microscopy and X-ray diffractometry were used to investigate morphological and microstructural features. The R3 test was used to assess the chemical reactivity of the processed mine tailings and benchmark their behaviour against widely used supplementary cementitious materials such as microsilica and fly ash. The results showed that indeed the followed activation mechanisms have gradually amorphized the raw tailing, yielding it eligible to participate in chemical reactions within a cementitious matrix.

Keywords: meta supplementary cementitious materials; upcycling; mineral wastes; binders; cement.

1 Introduction

1.1 The Traditional Civil Infrastructure

The United Nations predict a rapid urbanisation growth rate for the next 25 years. According to the data the world's urban population has grown a four-fold since post the second world war, reaching approximately 4 billion people today. The projection for 2050, indicates an estimated global population of 9.7[1] billion people of which 7 billion people are expected to be living in urban habitats [2]. To sustain this increase of the urban population, civil infrastructure is also estimated to grow, delivering the necessary assets for future urban societies. This will require significant increase in the construction materials need, with concrete being the most dominant and widely used construction material.

Undoubtedly the manufacture of cements and concrete have a heavy carbon footprint and heavy reliance on supply of pristine natural resources. Nonetheless, shifting away from cement and concrete is perceived as an idealistic possibility for several reasons amongst which are the ease and low cost of construction compared to alternatives (e.g., steel), the global availability of raw materials to produce cement and concrete and of course the very good mechanical performance of concrete. To satisfy this vast demand for concrete production globally, approximately 27 billion tonnes of natural aggregates and nearly 3 billion tonnes of fresh water are required [3]. To address this enormous environmental impact the European Cement Association and the International Energy Agency have recently highlighted the importance of transitioning to alternative sources for raw materials and switching to alternatives binders [3], [4].

Over the last three decades the efforts of reducing the environmental impact of concrete focused on the reduction of cement content through the utilisation of supplementary cementitious materials (SCMs). Such compounds are now widely used in the manufacture of blended cements and hence used in the production of concretes. Nonetheless, the use of SCMs does not come without issues. Although their use is quite extensive their contribution on emissions reduction is not more than 10%, something that signals the need for utilising higher volumes in a more efficient way [5]. Another major issue with SCMs is that they rely heavily on specific waste streams which are associated with industrial process that are gradually either heavily reformed or about to seize (e.g., incineration processes) to meet the global carbon emissions reduction targets. There is therefore an immediate need to investigate the possibility of alternative cementitious materials and binders, something which is highlighted in the Institution of Civil Engineers low carbon concrete route map, published in April 2022 [6]

1.2 Mineral Wastes

Currently there are billions of tones of minerals wastes from mines, excavations and quarries that are produced globally every year. Considering only the mineral wastes produced from the mining sector alone, this figure is in the range of 5 to 7 billion tones per year [7]. The global mining data shows significant increase in the extraction of mining products the last 35 years [8]. To make things worse, the mining activities are expected to grow significantly in the years to come to support the increasing demand for the so called low-carbon technologies. Therefore, the road to a low-carbon sustainable future will be a very mineral intensive road, which inevitably will lead to substantial increase in the volumes of associated mineral wastes. The disposal and management of such wastes is a major challenge that creates environmental and social challenges.

Mineralogically, mineral wastes consist typically of SiO_2, Al_2O_3, CaO and Fe_2O_3. This chemical composition makes them very attractive candidates to be used in the production of construction materials, as these oxides are also the main constituents of cement as well as of key alkali-activated binders. The potential of upcycling mineral wastes for the manufacture of cement or concrete can provide a natural solution to a growing major problem while at the same time alleviate some of the environmental impact these wastes have. Recent reports from the World Business Council for Sustainable Development, the World Economic Forum and the Organisation for Economic Co-operation and Development have highlighted the need for large scale utilisation of such wastes [9], [10]. In fact, these organisations predict that there will be a growing market for these materials and their recycling is expected to grow considerably by 2060.

Mineral wastes besides having a favourable chemical composition, they are also highly crystalline. This impairs their ability to participate in any chemical reactions within the cementitious matrix and in their raw form cannot be considered as potential binders. Therefore, thermomechanical, and chemical treatments are necessary to rearrange the highly ordered crystal structure of tailings to an amorphous arrangement of atoms. Such processing will lead to the formation of extensive distortions in the crystalline lattices of mining wastes which will enable their participation in chemical reactions.

The present study discusses the potential of using mine tailings as supplementary cementitious materials. The performance of the raw mine tailing is compared with mine tailings that have been thermally and mechanically activated.

2 Materials

The mine tailing (MT) used in this study is a by-product of graphite mining processes. Its chemical composition consists mainly of silicates, comes in dry powder format and Table 1, shows its XRF analysis. Potassium hydroxide, of 85% extra pure flakes, calcium hydroxide of 98% purity, and granular potassium sulphate of 99% purity from Acros organics were used in anhydrous form for R3 tests along with calcium carbonate precipitate in powder form from Fisher. Isopropyl alcohol was used for dispersion and cleaning to avoid contamination during analytical studies (SEM, TEM, and XRD). Commercially available fly ash and silica fume were used for benchmarking purposes.

Table 1. Chemical composition of the graphite mine tailing used in this study

Oxide	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	MgO	K_2O	CaO	SO_3	TiO_2
%	58.3	14.6	5.3	5.0	3.8	1.8	1.7	0.4	0.6

3 Experimental Procedures

3.1 Activation of Mine Tailings

The mine tailings used in this study were processed using, separately, thermal, and mechanical activation mechanisms. Thermal processing of mineral compounds (also known as calcination) is known to modify crystalline structures in two ways: dehydroxylation of hydroxides in minerals such as kaolinite at ~580 ºC and mica at ~700 ºC [11]and decarbonation in carbonate minerals such as calcite, dolomite, etc. [12], [13].The calcination temperature was determined based on the minerology and recommendations from existing literature. As the mine tailing studied here is rich in kaolinite and phlogopite, the calcination temperature was chosen to be above 650ºC. Literature suggests that heating above 900ºC leads to formation of new crystalline alumino silicate mineral phases which may reduce the reactivity of the activated mine tailing [14]. Therefore, in this case calcination temperature of 750 ºC was adopted and the samples calcined at this temperature are designated MTCT750. Temperatures in the range of 700 - 850 ºC shall be achieved using conventional rotary kilns, flash calcination units, fluidized bed, roller hearth kilns or even by static calcination in tunnel or shuttle kilns[15]. A Carbolite laboratory chamber furnace was used. The sample was placed on a tray shaped fused alumina crucible (of internal dimensions 217x95x60 mm and a wall thickness of 16 mm). To ensure uniform heating of the sample, this was evenly spread to a height of 1.5cm. A ramp up rate of 300ºC/ hour was used to comply with the thermal expansion of crucible and prevent fracture due to thermal shock. The samples remained at set temperature for 2 hours to ensure complete calcination. The sample was allowed to cool gradually in the furnace to avoid thermal shock due to sudden exposure to the atmosphere and removed when it reached room temperature.

Mechanical activation on the other hand, utilizes the application of mechanical actions on samples to induce changes on the microstructure of minerals. Mechanical processing leads to the reduction of the particle size and to the increase of the surface area. The most common mechanical activation technique is grinding where literature suggests that such processing leads to the formation of defects in the crystal lattice and phase transformation that improve the reactivity of crystalline mineral compounds [16], [17]. Such intense milling can be achieved by high energy milling using planetary ball mill, nutating mill, vibratory ball mill, stirred ball mill, motor mill, jet mill and disc mill. These mills vary in range of milling energy input from 13 – 165 kJ/g[18]. This makes it possible to choose the most suitable mill pertaining to the desired output such as particle size, crystallinity, hardness of the raw material etc. [19], [20]. The tailing used in this study was grinded using a Fritsch Pulversiette 6 planetary ball mill. Tungsten carbide balls and jar were used for this purpose to prevent contamination of the tailing sample. Grinding time of 30 mins was adopted and the sample is designated MTBM30. The kinetic energy imparted during milling is directly proportional to the diameter of the balls raised to the power four [21]. As the maximum particle size of the material used for grinding is expected to be less than

600 microns after sieving, the maximum suitable size of 10 mm balls were used, to optimize the diameter and the imparted collision energy (kinetic energy) [21].

3.2 Microstructural Analysis and Chemical Reactivity

Mine tailing samples were observed for morphological changes before and after thermal and mechanical processes. These observations were done using a scanning electron microscope (SEM) (JSM-5700F, JEOL) operated at 20kV. The samples were secured on carbon tape and sputter coated with gold.

Transmission electron microscopy (TEM) was performed at 200 kV using a JEOL JEM-1400F for observations of physical and morphological changes in the individual particles with the applied treatment. Isopropyl alcohol was added to 1 g of mine tailing sample in a test tube till it formed a colorless suspension. This suspension was subjected to ultrasonication for 1 minute at a frequency of 20 kHz. A drop of this dispersed sample was mounted on a holey carbon grid using a micropipette. The grid was allowed to dry at a drying chamber at 27 ºC for 3 hours allowing the isopropyl alcohol to evaporate completely. Following this, the grids were placed in the TEM chamber for analysis.

X-ray diffractometry was performed using a Bruker D8 Advance X-ray diffractometer (XRD), with Cu-Kα radiation of wavelength 1.540549 Å and radiation energy of 8.04 keV to study the mineralogy. Prior to measurements, mine tailing samples were passed through 150 μm sieve to avoid any preferred orientation and to achieve a smooth surface. The fine powder was spread on the sample holder and a glass plate was used to strike of the excess material and achieve a flat and smooth surface.

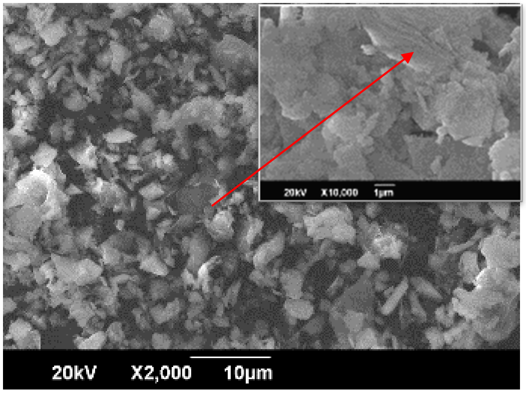
The chemical reactivity of the treated mine tailings as well as of the benchmarking samples, was performed following the provisions of the R3 test. The experimental procedure for R3 test is provided in the ASTM C1897(2020). The experimental procedure involved producing a mix containing 10g mineral waste, 30g calcium hydroxide, 5g calcium carbonate and 54g solution of potassium hydroxide and potassium sulphate (4 g potassium hydroxide and 20 g potassium sulphate in 1L water) . The heat of hydration of this mix was monitored, using an I-Cal HPC - High Performance Calorimeter, for a period of 7 days under the constant temperature of 60 ºC. The first 75 minutes of the tests were not taken into consideration due to temperature differences as recommended [22]–[25]. Cumulative heat, at the end of three and seven days, per gram of material was reported. The higher heat of hydration indicates a higher degree of reactivity. To minimize the difference in temperature all the materials and the containers used were conditioned at 60 ºC for 24 hours prior to the start of the procedure. In addition to the tailing samples, for benchmarking purposes the R3 test was performed to silica fume and fly ash which are known for their reactivity in cementitious systems.

4 Results and Discussion

4.1 Morphological Observations

Fig. 1 below shows the morphology of the samples under the SEM. The unprocessed mine tailing samples (MTR) were highly crystalline with dense particles of size ranging from about 1 µm to 70 µm. The particles were angular with sharp edges and with an uneven particle size distribution. The smaller particles were found adhered to the surface of the larger particles. Sheet like layers were also observed indicating the presence of phyllosilicate crystals (Fig. 1a inner image).

a) MTR



b) MTCT750 **c) MTBM30**

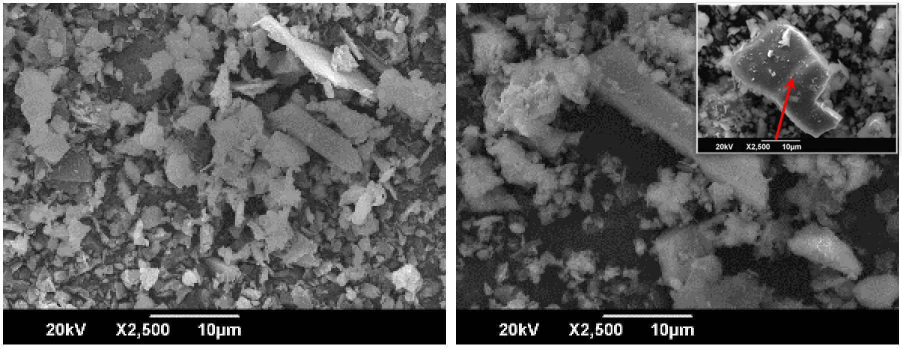
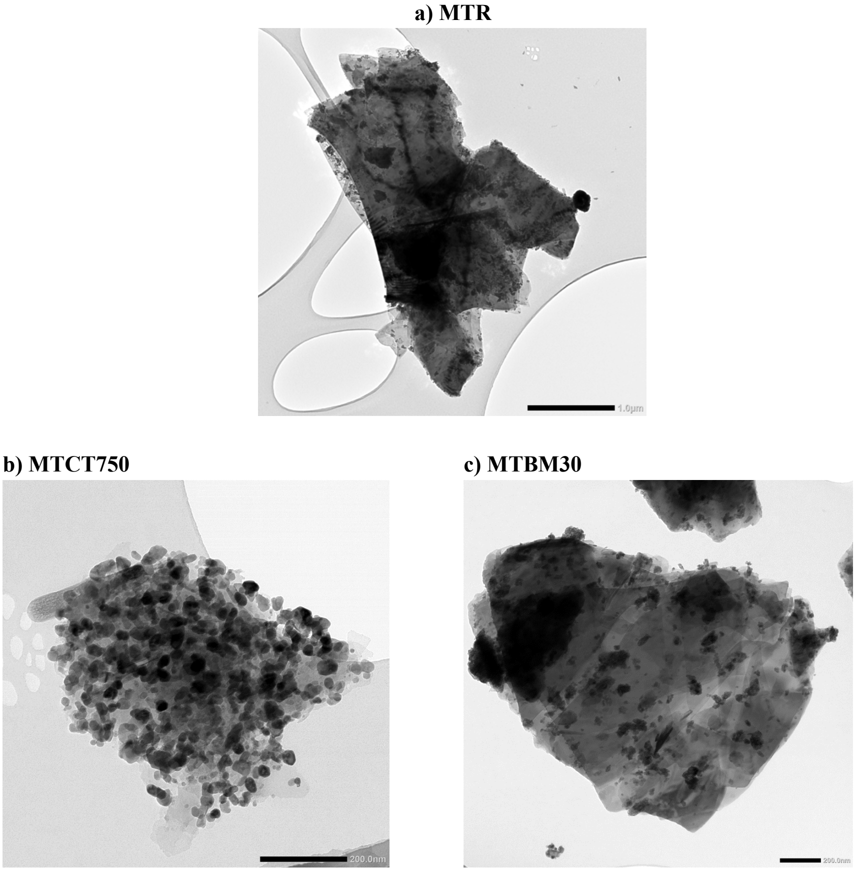


Fig. 1. SEM images of samples used in this study. a) Inner image - Sheetlike appearance of phyllosilicates in MTR samples; Red arrow points at the layered appearance of phyllosilicates b) Appearance of flocculant particles MTCT750; e) inner image - SEM image showing the development of cracks in particles of MTBM30.

The calcined sample shows the formation of particles of flocculant appearance, something that agrees with similar observations reported in the literature [23]In addition, there is indication of partial vitrification and melting which signals that further heating could lead to fusing and melting of certain phases as reported in previous studies [24]The ball milled sample does not show any agglomeration of particles while at the same time there are indications that the sample exhibits reduction in its particle size as well as that cracks start appearing on the particles' surface. The individual crystals were also observed with TEM (see Fig.2). The primary particle observation indicated that mine tailing particles were polycrystalline. The mine tailing particles had sharp angular edges. Though the mine tailing particles appeared crystalline after calcination at 750°C, some particles exhibited signs of aggregation and sinter necks. This could be due to the primary crystallites forming solid bridges during calcination process [25]. However, it is evident that with increasing temperature particles' morphology changes to something less hierarchical and ordered. The originally solid angular MTR crystals gradually transition to an amorphous material. Similar observations are made for the grinded sample, where the particles appear to lose the highly angular edges transitioning to a smoother texture.



a) MTR

b) MTCT750

c) MTBM30

Fig. 2. TEM images of samples used in this study

4.2 Microstructural Analysis and Chemical Reactivity

Figure 3a below shows the X-ray diffractograms for the samples investigated in this study. The XRD data shows that the raw mine tailing is highly crystalline with several phases being identified. The processing of the tailing has resulted in structural changes that have led to the widening of the peaks as well as peak shifting for biotite, phlogopite, quartz and plagioclase as shown in Fig. 3b. These changes can be attributed to the mechanical and thermal treatment and signal the initiation of amorphization of the material.

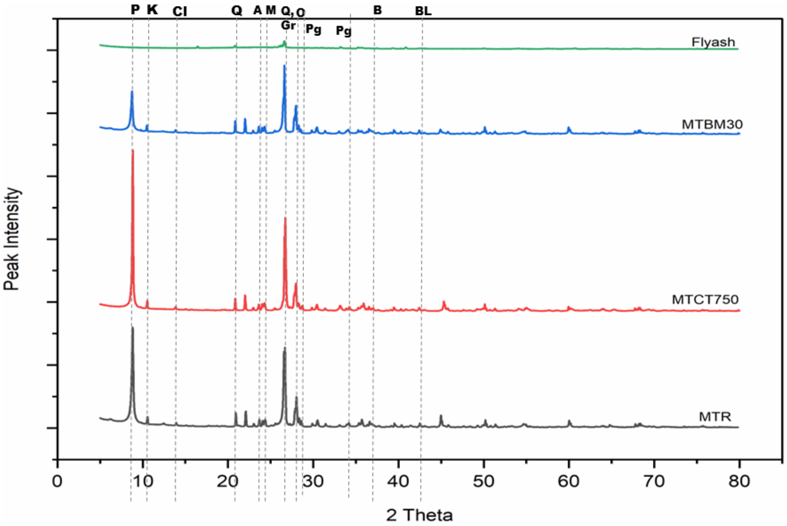
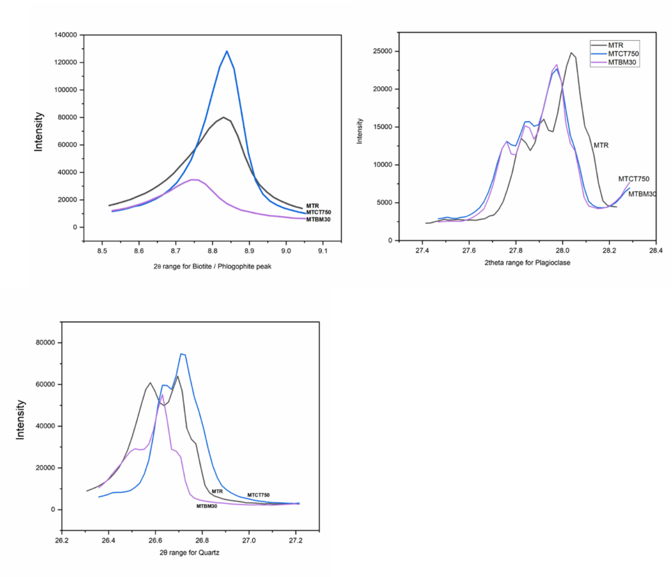


Fig. 3a. XRD phases of mine tailing before mechanical and thermal treatment (Note: P – Phlogopite; K – Kaolinite; Cl – Chlorite; Q – Quartz; M – Muscovite; A – Albite; B – Biotite; Pg – Plagioclase; Cr – Chromite; BL – Berlinite).



The measured heat of hydration during the R3 test is reported in Fig. 4 below. The data shows that the initial high heat of hydration followed by slower or almost no heat of hydration shows a typical trend of a highly reactive supplementary cementitious material as reported in the literature. It can be seen from the figure that the silica fume exhibits a similar trend [26], [27]From the data it is evident that the raw mine tailing (MTR) does not seem to produce much heat of hydration, which means that it does not contribute to the evolving chemical reactions. Nonetheless, the two processed samples appear to exhibit significant increase the measured heat of hydration. This indicates that both processed mine tailings have contribution in the evolution of the hydration reactions. In fact, the trend that each shows resembles the trend of the heat evolution observed for fly ash.

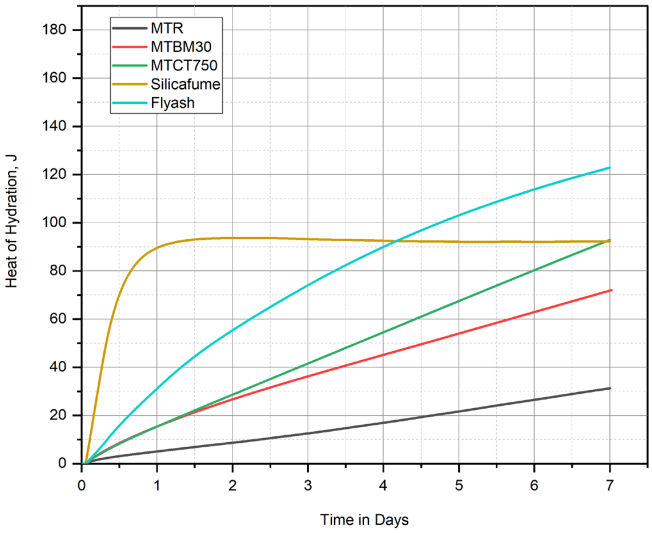


Fig. 4. Heat of hydration from R3 test for raw mine tailing, processed tailing and silica fume and fly ash.

5 Conclusions

The present study discussed preliminary data on the potential of upcycling mine tailings into supplementary cementitious materials. The data showed that thermal and mechanical processing can indeed convert the highly crystalline microstructure of raw tailings, yielding them eligible to participate in the hydration reactions within a cementitious binder. This indicates the feasibility of exploring the use of minetailing as an SCM for use in cementitious binder. However, both the mechanical and thermal activation processes are energy intensive. This necessitates the need of detailed Life Cycle Assessment study on cradle to gate basis to quantify the achieved environmental benefits.

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