Environmental-chemical compatibility of granitic-mining waste for liner material

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ABSTRACT: Mining waste is generated from extracting mineral resources and, without proper disposal, can lead to negative environmental impacts because it can contain pollutants. Emerging studies of alternatives valorizing and reusing the residue through sustainable practices. Therefore, this research investigated the potential of granitic mining waste for waterproof liner materials, considering that most used liners, clays and geosynthetics, are increasingly scarce and costly solutions, respectively. This paper aims to analyze chemical compatibility, and microscopic structure of a granitic-mining mud to produce alternative material for liner construction. It was mixed in a clay at 25% and 50% ratio to develop a waste-based geocomposites. European limits for pollutants were respected for all mixtures, and the permeability remained less than 10^{-9}m/s, which appears to be feasible for liners production. Thus, the valorization of mining waste as liner material arises as solution for creating new waste-based added-value product in the scope of circular economy.

1 INTRODUCTION

Mining waste (MW) is a by-product of mining activity, generated from crushed rocks, soils and processes of ore's extraction, usually called muds, sludges, tailings, or wastes. The main properties of MW are in accordance with the bedrock and the desired ore, although due to several physic-chemical and hydromechanical processes used during this activity, it can be considerable different from the original material. All mining activities and processing methods have several negative environmental impacts associated to large excavation, vegetation-cover removal, and possibly contamination of soil and water due to incorrect disposal of the produced wastes. Usually, mining tailings are disposed in piles or dams located nearby the mine. According to its characteristics of successive elevations from a departure dike, these structures may be subject to variations in methodologies constructive throughout its useful life. Tailings arranged in dams generally use three constructive methods, massifs with elevations by downstream, or by upstream, or by the central line method (Silva *et al.,* 2014), although it is important to reiterate that the first method has been prohibited in many countries because of its high chance of accidents.

Soil is the raw material of landfills, slopes, roads, dams, ponds, and canals. They are geotechnical interventions that aim to improve urban infrastructure. For hydraulic barriers, clays are normally used, and basically are associated with high volumetric variation and plasticity, and low compressive strength, as well as very low permeability. Liners are basically made of compacted-clay liner (CCL) or geosynthetic-clay liner (GCL), made of clay layers without or with, respectively, medium to high-density polyethylene geomembrane embracing it. CCL and GCL must have low hydraulic conductivity (k) to prevent soil and groundwater contamination.

The valorization and reuse of industrial by-products can lead to new products within the scope of the circular economy, as the reuse of these waste materials, such as waterworks sludges, thermal industry fly ashes, and several mining tailings, among other residues have shown their potential for varied applications, from liners to soil reinforcement (Marchiori *et al.,* 2020; 2022b). The k of MW has been studied during the past decade, and promising values were found for liner application. Bareither *et al.* (2016) found k around 10^{-8} and 10^{-10} m/s for pure tailings of rock wastes and Fall *et al.* (2010) had to incorporate 4-8% of bentonite into the residue to achieve 10^{-9} m/s and reduce the costs of typical barriers. Otherwise, Hu *et al.* (2017) observed a difference when measuring k for copper and iron tailings, k values for the respective materials were 10^{-4} and 10^{-6} m/s, as the organic tailings present larger k. Besides, Patiño *et al.* (2006) tested copper tailings in comparison with silty sands inside triaxial membranes to obtain the flow ration within confining stresses between 50 and 300 kPa, values of k decreased with load increment, and achieved 10^{-9} and 10^{-10} m/s for minimum and maximum confining.

USEPA (1994) highlighted the importance of site evaluation, field exploration and laboratory tests of MW for a safe disposal, along site and field exploration, being recommended geological and geotechnical foundation's recognition within drilling tests and hydrologic aspect of the area. Laboratory tests should comprehend particle size distribution, Atterberg limits, and consolidated undrained triaxial shearing test, specifically for the fine portion of the tailings, as this portion could contribute for lowering the overall permeability. Moreover, Rubinos *et al.* (2021) and Maritsa *et al.* (2016) alerted for the chemical and environmental aspects of using MW as containment structures like liners, stressing the importance of x-ray fluorescence (XRF) for oxide analysis determination, scanning electron microscope (SEM) for microstructure evaluation, and x-ray diffraction (XRD) for mineral compounds. Especially due to the fact of waste rock may potentially be acid-forming, which is not suitable for embankment construction, although necessary to evaluate each waste rock, as they may have varied chemical composition and reactivity.

Therefore, the objective of this research is to get a better understanding of the chemical, mineralogical and microstructure of granitic mine waste (GMW) within soils to evaluate its application in earthworks, such as liners materials. In addition, it can be produced new waste-based materials in the scope of circular economy (Marchiori *et al.,* 2020; 2022c). Thus, GMW is a promising candidate for environmental geotechnics and environmental sanitation applications, namely for producing alternative liner material or other possible applications, such as soil reinforcement.

2 MATERIALS AND METHODS

The soil was collected at a construction site at Castelo Branco (Portugal) and the GMW was provided by João Tomé Saraiva's construction company from a mine called "Pedreira da Devesa", which is an extractive unit of rock, granite, located in Santana de Azinha, Guarda (Portugal). The geomechanical main parameters are presented in Table 1 and were published in (Marchiori *et al.,* 2022a). Two mixtures of GMW and soil were developed based on dried masses in temperatures of 60-65°C for 24h, with the following ratios as previously performed by (Marchiori, 2022a): 50:50% (50% of GMW and 50% of soil); 25:75% (25% of GMW and 75% of soil).

Table 1. Main geomechanical parameters of GMW, soil, and mixtures (Marchiori, 2022a).

Parameter	G_S	w_L	w_P	PI	w_{opt}	$\rho_{d,max}$	C_C	c'	ϕ''
Unit	[-]	[%]	[%]	[%]	[%]	[kN/m^3]	[-]	[kPa]	[º]
Soil	2.78	38	29	9	20	17.2	0.100	10	25
25:75%	2.70	34	24	10	19	16.7	0.150	0	27
50:50%	2.61	34	19	15	20	15.7	0.120	0	30
GMW	2.50	34	12	22	21	14.7	0.110	0	33

G_s. specific gravity; w_L. liquid limit; w_P. plastic limit; PI. Plastic index; w_{opt}. optimal water content; $\rho_{d,max}$. maximum dry density; C_C. compressibility coefficient; c´. cohesion; ϕ''. Internal friction angle

Chemical characterization was done through x-ray fluorescence (XRF), for oxide analysis determination, scanning electron microscope (SEM), for magnified images, using a S-2700 Hitachi equipment and Axios by Malvern Panalytical, respectively and X-ray diffraction (XRD), for mineralogical characterization, using a Phillips Analytical X-Ray B.V and X'Pert-Pro MPD by Malvern Panalytical. Oxides values, obtained through XRF, were normalized without loss on ignition (LOI) value, to have the value of each oxide in the treated samples' composition.

3 RESULTS AND DISCUSSION

3.1 *XRD and SEM*

XRD of GMW and the soil can be observed in Figure 1 and Figure 2, respectively. Soil's mineral activity is characterized by mainly quartz (SiO_2), muscovite ($KAl_2Si_3AlO_{10}(OH,F)_2$), and kaolinite ($Al_2Si_2O_5(OH)_4$). GMW consists mainly of quartz, muscovite, anorthoclase ($(Na,K)AlSi_3O_8$), and biotite ($K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$), which are minerals that generally appear associated mainly in the Bowen series during cooling over time in granitic rocks, while the mixtures present these above-mentioned minerals. Figures 1 and 2 below represent the XRD of GMW and the soil, respectively, exposing quartz in both their composition and kaolinite within the soil.

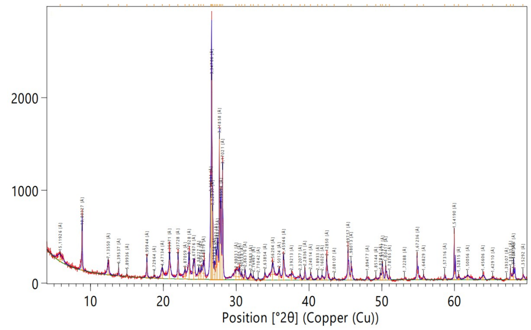

Figure 1. XRD of GMW

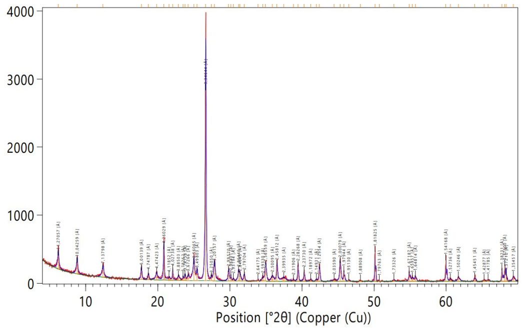

Figure 2. XRD of soil

SEM of GMW, the soil, 50%, and 25% mixtures can be observed in Figure 3 to Figure 6, respectively. SEM images for GMW and mixtures are presented in a magnification of 300x. For the GMW analysis, a higher amount of the material was analyzed compared to the mixtures, to observe if the mixtures suffered intense chemical reactions and consequent alterations in its microscopic structure based on the GMW introduction. That behavior was not observed, exposing that the mixtures between soil and granitic mining wastes were each material´s respective raw composition in different ratios, depending on the added GMW amount. Also, as highlighted in red in all Figures, GMW and soil's particles are found both in the 50% and 25% mixtures. Thus, SEM analysis seem to corroborate with a homogeneous mixture of both materials according to the added GMW ratio.

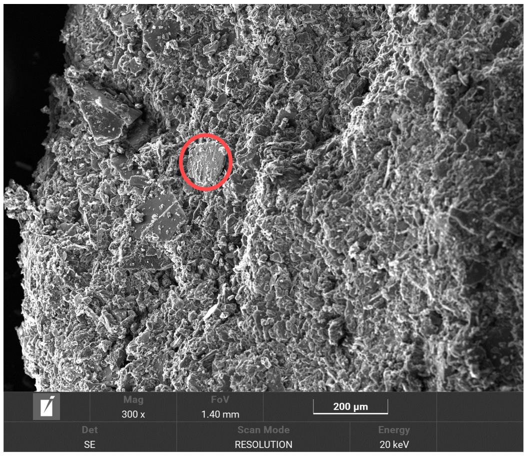

Figure 3. SEM of GMW

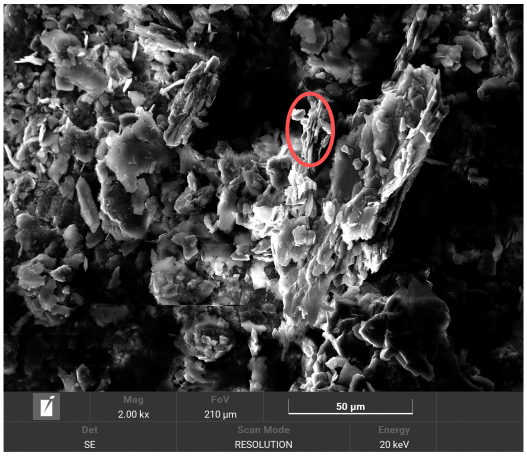

Figure 4. SEM of soil

Figure 5. SEM of 50:50%

Figure 6. SEM of 25:75%

3.2 *Chemical composition*

Oxides composition is presented in Table 2. All materials showed very similar chemical characteristics, mainly composed by SiO_2 (~60%) and Al_2O_3 (~25%), with lower percentages around 5% of Fe_2O_3 and K_2O, and low ratios of calcium, sodium, and magnesium. Usually, natural tailings originate from hard magmatic rocks and are characterized by the dominance of sulphide minerals, mostly (pyrite), quartz and paragonite (Fall, 2009). Also, it is important to reiterate that the quartz presence means that a desulphurized natural material will be mainly made of quartz, containing considerable amount of silica. According to (ASTM C618, 2003), the pozzolanic activity potential can be measured when summing the content of Al_2O_3, SiO_2 and Fe_2O_3 oxides. If the obtained value is equal to 70% or more, which is the case of GMW that reach approximately 90.5%, the potential for pozzolanic activity can be considered high for the material alone and for the mixtures (the sum of the three oxides reaches approximately 88.8% and 90.5% for mixtures 50:50% and 25:75%, respectively). High amount of SiO_2 and Al_2O_3 can be explained by the hydrogeology of the material's region (Guarda and Branco, Portugal). This location consists in residual reliefs, quartzite, and granitic profiles, which have created detrital sediments (Dias, 1998). Maritsa *et al.* (2016) analyzed spitilic mining waste and found that its chemical composition showed significant similarities with the local bedrock, which was the same case as the granitic mining waste here analyzed.

In addition, all chemical compounds respected regulatory limits (Diário da República, 2020) for liner construction, not showing contamination potential. Corroborating with this research and evaluating GMW as liner material due to low k, other authors have found interesting results. Rubinos *et al.* (2021) analyzed copper tailing and highlighted the attention to the levels of some pollutants like Cu, As, Mo, and Pb, although necessary to evaluate their leachability levels as the found amounts could be encapsulated within the material itself, respecting regulations. If leaching values are more than the stablished through the regulatory limits, then it represents potential environmental and health risk, exposing the need of its suitable disposal. Maritsa *et al.* (2016) has found in nickel tailings the same mineralogy observed here – quartz and muscovite – and other minerals, such as albite, chlorite, and augite, highlighting that the last two could contribute to decrease hydraulic conductivity, which was circumvented by adding 3% of bentonite, enhancing k value overall and reaching 10^{-9} m/s values.

Portuguese regulatory limits for environmental barrier (Diário da República, 2020) established values for heavy metals, which GMW has attended to such limits, being the chemical composition of all tested materials exposed in Table 1 below. This behavior varies among authors, Bevandic *et al*. (2021) found high contents of Pb and Zn when analyzing different mining wastes, while Kazmierczak *et al.* (2019); Leite *et al.* (2019); and Longhi *et al.* (2016) found no significant concentration of heavy metals among the analyzed mud wastes from the granitic extraction. Portuguese directive defines different specifications depending on the geological barriers and its materials, considering inert liners as those with materials that have k value lower than 10^{-7} m/s (10^{-9} m/s if it is a non-hazardous material) and with more than 1 m thickness, while a liner using hazardous wastes should have more than 5m thickness and a k value lower than 10^{-9} m/s. Hydraulic conductivity of the analyzed materials were determined by Marchiori *et al.,* (2022a) and can be used as low permeability liner due to k values lower than abovementioned ones. Previous research indicated reduction in the weight for a new material development due to lower G_S, increase in plasticity, stabilized compressibility, and greater shear strength, when incorporating GMW into soils.

Table 2. Chemical composition of GMW, soil, and mixtures.

Oxides (%)	GMW	50:50%	25:75%	Soil	Detection Limits (DL)
Na_2O	2.66	3.51	2.07	0.58	0.01
MgO	1.38	1.41	1.64	2.28	0.01
Al_2O_3	25.0	24.3	24.8	27.4	0.01
SiO_2	59.6	60.3	60.4	56.1	0.01
K_2O	4.39	4.00	4.64	4.45	0.01
TiO_2	<DL	1.25	0.43	0.93	0.01
CaO	1.11	0.98	0.71	<DL	0.01
Fe_2O_3	5.85	4.19	5.32	8.30	0.01

4 CONCLUSIONS

The main conclusions of this research are that GMW ‘s mineralogy is based on quartz, muscovite, anorthoclase, and biotite while the chemical compounds are very similar to the region’s soil, exposing high silica and alum, and less significative ratios of iron, calcium, sodium, and magnesium. XRD and SEM images exposed the presence of quartz and kaolinite and no intense chemical reaction within the composites. GMW and mixtures respected Portuguese’s regulatory limits for heavy metals. Therefore, GMW has potential to be a substitute of clays and geosynthetics as a hydraulic barrier layer – liner, while also presenting interesting values for soil reinforcement. In addition, as it is continuous research, several tests should be performed to assess GMS, namely around hydraulic behavior as cracking and wet-dry cycles and leaching potential of pollutants. A small-scale field construction should also be done to assess and confirm its permeability, and mechanical evaluation. Thus, GMW within clayey soils can be considered a possible path to produce a new liner material with mining by-products.

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