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Recycled red mud as an useful geotechnical material

La boue rouge recyclée comme matériau géotechnique utile

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ABSTRACT: Red mud (RM) is an extractive waste from Bayer process in alumina production. The most conventional methods of RM disposal are tailing dams, or dry storage, both of which raise environmental concerns due to the high alkalinity of RM and the presence and leaching of potentially hazardous elements (PTEs). Due to its fine-grained nature and poor mechanical properties, as well as leaching of potentially hazardous substances, RM cannot be used by itself. Properties of the RM can be improved, by mixing it with hydraulic or pozzolanic binders, such as calcareous ashes or steelmaking slag, to produce mechanically stable and durable composites for earthworks. On the other hand, RM can also serve as an immobilization additive for remediation of contaminated soils. Two different approaches for useful utilization of RM are presented based on results of laboratory research and a real case study, opening of new possibilities for conserving natural resources and reducing environmental hazards of RM deposits.

RÉSUMÉ: La boue rouge (RM) est un déchet extractif issu du procédé Bayer de production d'alumine. Les méthodes les plus conventionnelles d'élimination des MR sont les barrages à résidus ou le stockage à sec, qui tous deux soulèvent des préoccupations environnementales dues à l'alcalinité élevée des RM et au lessivage d'éléments potentiellement dangereux (PTEs). En raison de sa nature à grains fins et de ses mauvaises propriétés mécaniques, ainsi que de la lixiviation de substances potentiellement dangereuses, la RM ne peut pas être utilisée seule. Les propriétés du résidu de la RM après extraction peuvent être améliorées, en le mélangeant avec des liants hydrauliques ou pouzzolaniques, tels que des cendres calcaires ou des scories sidérurgiques, pour produire des composites mécaniquement stables et durables pour les travaux de terrassement. D'autre part, la RM peut également servir d'additif d'immobilisation pour l'assainissement des sols contaminés. Deux approches différentes pour une utilisation utile de la RM sont présentées sur la base des résultats de recherches en laboratoire et d'une étude de cas réel, ouvrant de nouvelles possibilités pour la réduction des dépôts de la RM conservant ainsi les ressources naturelles et réduisant les risques environnementaux liés aux gisements problématiques de la RM.

Keywords: Red mud; recycling; geotechnical composites; environment.

1 INTRODUCTION

Red mud (RM) is an extractive waste from Bayer process in alumina production. The process is based on digestion of the bauxite ore in a hot NaOH solution. The alumina-rich solution is then separated from the solid residues, which consist of Fe and Al (hydr)oxides and are referred to as RM. Production of RM worldwide amounts to more than 160 million tonnes annually (Zalar Serjun et al., 2018, Zeng et al., 2020, IAI, 2022). The large amount of generated RM creates several disposal problems due to the absence of appropriate storage methods (Jha et al., 2020). The most conventional methods of RM disposal are to pump the slurry into ponds behind “tailing dams”, or disposal of dewatered RM by dry stacking. In both approaches, large areas of land are needed (Samal, 2021), posing a threat related to potential instability and collapsing of RM deposits and raising environmental concerns due to the high alkalinity of RM, the presence and leaching of PTEs, and alkaline airborne dust emissions (Jha et al., 2020, Samal, 2021). Potential applications for the utilisation of RM need to be explored to minimise the associated negative environmental impacts (Zalar Serjun et al., 2018, Jha et al., 2020). However, the chemical and physical properties of RM vary considerably, reflecting their different sources (differences in bauxite composition and processing plant operation). This means that the potential recycling of each deposit of RM has to be considered separately, in its own case study (Oprčkal et al., 2020). RM is not only a source for recovery of metals, such as Fe, Ti, Mn, Na, K and also rare earth elements, such as Sc, Y, Hf, Zr, and Ti (Samal, 2021), but can also be a valuable construction material (Jha et al., 2020, Samal, 2021). Due to its fine-grained nature and poor mechanical properties, as well as the environmental concerns, RM cannot be used as construction material by itself.

The properties of the RM residue can be improved, by mixing it with hydraulic or pozzolanic binders, such as calcareous ashes or steelmaking slag, to produce mechanically stable and durable composites for earthworks. On the other hand, RM can also serve as an immobilization additive for remediation of contaminated soils (Zalar Serjun et al., 2018, Oprčkal et al., 2020).

Two different approaches for the useful utilization of RM are presented, based on the results of laboratory research and a real case study, opening new possibilities for the reduction of RM deposits.

2 RED MUD AS AN ADDITIVE FOR REMEDIATION OF CONTAMINATED SOILS

Data presented in the literature show that RM's high sorption capacity for PTEs is due to the large specific surface area of its constituent mineral phases, which enables two main immobilization mechanisms: (a) surface complexation of PTEs with Fe and Al ox/hydroxides, and (b) adsorption by alumosilicates. The RM was used as an immobilisation additive for the preparation of a stable, technically and environmentally acceptable geotechnical composite. It was intermixed to contaminated soil (CS) from one of Slovenia's largest heavily contaminated areas (Zalar Serjun et al., 2018, Oprčkal et al., 2020).

2.1 Materials

The RM was sampled from an open disposal site nearby alumina plant in Podgorica, Montenegro. The RM was dried at 105 °C in a convection oven and ground to a particle size below 2 mm. The mineralogical analysis showed that the RM is composed of calcite, hematite, gibbsite, boehmite and a phase that belongs to the feldspathoid group of minerals (cancrinite / vishnevite). Goethite, quartz, ilmenite, illite/muscovite, perovskite, rutile and dolomite present its minor constituents.

Samples of contaminated soil (CS) were obtained from a 17 ha large brownfield at the Old Zinc-Works site, which is located in the central part of the town of Celje, in eastern Slovenia. According to the European Union's List of Waste (EC, 2014), excavated soil from this location was regarded as a hazardous waste. The CS consisting of silty-sandy gravel was sampled, and then crushed in a jaw crusher to a grain fraction below 16 mm.

2.2 Experimental

The geotechnical composite was prepared by blending the CS with 25 wt.% of the RM and optimal water content, followed by subsequent compaction. The optimal water content was determined by means of the Modified Proctor Compaction Test (SIST, 2013), in order to achieve maximum dry density of the composite. Monolithic test specimens of the composite were cured in a climatic chamber (20°C and 98% humidity) for 3, 7, 28, and 56 days for subsequent analyses.

To investigate the immobilization properties and efficiency of the RM, the characterisation of the RM and the CS by surface area and microstructure by X-ray fluorescence (XRF), X-ray powder diffraction (XRD), and scanning electron microscopy equipped with energy dispersive spectroscopy (SEM/EDS), as well as changes in leachate composition were studied. The BET surface areas of the RM and the CS were determined by N_2 sorption tests. Their total elemental composition was studied by XRF and corresponding phase and microstructural analyses were performed by XRD, and SEM/EDS.

The tank leaching procedure (SIST, 2002), was applied to the test specimens of the RM, CS, and composite (CS/RM). Selected PTEs in the eluates were determined by an inductively coupled plasma mass spectrometer (ICP-MS), whereas the content of Cl^- and SO_4^{2-} were investigated by the UV-Vis absorption spectrophotometry.

In addition to the basic characterization and leaching tests for environmental acceptability studies, also some basic geotechnical properties of the CS/RM composite were evaluated, namely unconfined compressive strength (SIST, 2004) and water permeability (SIST, 2019a).

2.3 Results and discussion

The most abundant PTE in the CS was Zn, which was present in concentrations of up to 15 %, whereas Si was the second most abundant element (11%), followed by Fe, Ca, Al, S, and Mg. The most problematic parameters in the eluate of the CS were water soluble Cd, Pb, and Zn, and SO_4^{2-}, which concentrations exceeded the limit values according to the present Slovenian landfilling legislation (GS, 2016) by factors of 10.5, 2.0, 16.6, and 1.35, respectively. The CS therefore has to be regarded as hazardous waste.

For the used RM a large BET specific surface area was determined, i.e. 20.1 m^2/g. According to the results of the XRF total elemental analysis, the most abundant constituent in the RM is Ca, which makes up almost 15 %. Other major constituents are Fe, Al, Si and Ti, followed by an array of minor constituents. The results of the performed chemical analysis of the eluate indicated that, according to the present Slovenian landfilling legislation (GS, 2016), this RM is a non-hazardous waste.

The phase composition of the CS/RM composite reflects the combination of minerals from the RM and the CS, since no new mineral phases were identified by the XRD. The eluates from the CS/RM composite show a time-dependent decrease in conductivity. The measured concentrations of the PTEs in the eluates from the CS/RM were all below the limit values for inert materials (GS, 2016), which shows the immobilization effectiveness of the used RM. The immobilization of the PTEs in the investigated composite was attributed to the fact that the goethite and gibbsite mineral phases, as well as the hematite from the RM, provide numerous adsorption sites due to their large specific surface areas, resulting in the high adsorption capacity.

The unconfined compressive strength of the CS/RM composite was determined after 3, 7, 28, and 56 days of curing, and amounted to 0.5 to 0.7 MPa with no time-dependent trends. This is in agreement with findings that no new mineral phases formed in the composite that could contribute to the binding of grains. Water permeability (SIST 2019a), determined after 28 days of curing on intact monolithic test specimens, amounted to 7.88×10^{-8} m/s.

3 RED MUD AS CONSTRUCTION MATERIAL

Relatively few attempts have been made on the effective utilization of RM for the geotechnical application alone or, its combination with several chemical and waste stabilizers (Jha et al., 2020). Recycling of the RM for the production of geotechnical composite construction materials was studied. Since the applied RM residue was in a form of slurry, it needed to be treated with the addition of binder to obtain solidified, mechanically stable and the environmentally acceptable geotechnical composite material with properties suitable for use in earthworks.

3.1 Materials

In this case the RM from the Podgorica pond was first processed with gravitational and magnetic large-for extraction of metal phases, which are used as raw materials in metallurgy. The residue or the RM after extraction was in the form of slurry with a 42 wt.% of solids. The mineralogical analysis showed that it is composed of hematite, gibbsite, cancrinite, calcite, boehmite and aluminium fluoride.

Ash (PA) was obtained from a paper mill VIPAP Videm Krško, Slovenia. It is a waste that can be used as a binder with hydraulic or pozzolanic properties for soil remediation, solidification and stabilization. It is a highly alkaline material that contains a latent hydraulically active phases. The composition and properties of PA are highly dependent on the type of fuel burned, the combustion technology used, and the combustion conditions.

3.2 Experimental

The geotechnical composite (RM/PA) was prepared by mixing the RM with the PA. The amount of the PA required to achieve the appropriate consistency for compaction was determined on basis of laboratory trials. To prepare the RM/PA, 0.75 kg of PA was added to each 1 kg of RM residue slurry with a water content of 139 wt.% and homogenized. Prior to the RM/PA specimen preparation, the mellowing period of 24 hours was required to allow the chemical reactions to take place and to achieve a suitable consistency - workability of the mixture. During the mellowing period, the mixture was stored in an airtight plastic container at ambient temperature and then homogenized again. The test specimens were prepared by compaction in the molds (SIST, 2005) using the standard Proctor compaction effort (SIST, 2013). The specimens were cured at 22 °C and 98% humidity for 2, 7, and 14 days. The prepared specimens were used to determine the geotechnical, mineralogical and chemical properties of the investigated geotechnical composite at selected curing times.

Basic geotechnical properties of the composite were determined, such as unconfined compressive strength - UCS (SIST, 2004), consolidation properties - oedometer test - E_{oed} (SIST, 2017), water permeability - k (SIST, 2019a) and shear strength - ρ', c' (SIST, 2019b). Mineralogical composition was determined by XRD, while environmental acceptability by PTEs concentrations in leachate (SIST, 2002), which were determined with ICP-MS.

3.3 Results and discussion

According to the results of the XRD analysis the PA consists of calcite, lime, amorphous phase, quartz, portlandite, magnetite, gehlenite, anhydrite and feldspars. Leachate analysis of the PA showed that concentrations of all selected PTEs are below permissible levels (GS, 2022).

Mineral phase of the RM/PA composite was analysed at different time intervals, after 2, 7, and 14 days. The XRD analysis showed that during the curing new mineral phase – ettringite was formed. This phase is a member of the typical hydration products mineral group, formed in systems with latent hydraulic active materials (i.e., the used PA).

Geotechnical properties of the composite are time dependant and are presented in Table 1

Table 1. Geotechnical properties of the RM/PA composite.

Parameter	After 2 days	After 7 days	After 14 days
UCS (kPa)	144	3548	4939
E_{oed} at 100kPa (MPa)		79.4	
k at 100kPa (m/s)		5.5×10^{-11}	
ρ', c'(°, kPa)		51.5, 0,0	

From the point of view of the evaluated geotechnical properties, the investigated composite shows similar geotechnical properties as high quality natural silts, sands or gravels, that confirms its applicability as construction materials in earthworks. The results of the chemical analyses showed that the geotechnical composite RM/PA is environmentally acceptable and does not pose any risk to the environment when used as a construction material for earthworks (GS, 2022).

4 CONCLUSIONS

Two applications of the RM in construction were studied. It was shown that the RM can be effective immobilizer for PTEs in contaminated soils, thus transforming contaminated soils in useful construction material. On the other hand, the RM can also be used as construction material when stabilized with paper mill fly ash. In both cases prepared composites exhibits adequate geotechnical properties for earthworks, as well as environmental acceptability according to the Slovenian legislation.

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