

# The Potential Use of Residual Soil from Ribeira Valley (Brazil) in Mitigating Metal Contamination: A Geotechnical Characterization

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## Abstract

The incorrect disposal of hazardous waste causes serious problems around the world. For instance, mining waste is one of the main sources of potentially toxic metals in the environment. In the Ribeira Valley region of Brazil, residues generated during lead ore smelting were improperly deposited in the Ribeira de Iguape River and on the soil's surface without protection. An alternative solution for mitigating local contamination is verifying whether a local residual soil is appropriate to use as a mining waste landfill liner. The soil is sandy silty clay, with a plasticity index of 24%, an optimum water content,  $w_{opt}$ , of 26.3% and a maximum dry density,  $\rho_{dmax}$ , of 1.515 g/cm<sup>3</sup> from the Standard Proctor test. Specimens molded at an optimum compaction condition showed hydraulic conductivity of 10<sup>-9</sup> m/s and effective shear strength parameters of  $c' = 22$  kPa and  $\phi' = 26.8^\circ$ . The soil is acidic (pH 4.6), exhibits low CEC (41.4 mmol<sub>c</sub>/dm<sup>3</sup>) and presents a predominance of negative charges on the particle surface (PZSE 3.6 < pH), favoring cation retention. The hydraulic and mechanical characteristics together with the chemical properties suggest that this soil is a candidate for use as a liner. Further studies are underway to characterize its chemical contaminant retention and to complete the analysis about its suitability for the desired purpose.

## Keywords

Tropical soil • Liner • Metal contamination

## 1 Introduction

Inadequate disposal of hazardous waste causes serious problems around the world. Substances present in such waste can be released into the environment and affect its quality. For instance, potentially toxic metals can be absorbed by and accumulate in various lifeforms and persist for decades in the environment (Lester 1987; Alloway 1995).

Potentially toxic metals originate in natural or anthropic processes, and their toxic effects depend on the quantity of the ions available for cation exchange (Sparks 1995; Sposito 1984). One of the main sources of metals in the environment is the incorrect disposal of mining waste that contains these elements. In the Ribeira Valley of Brazil, residues generated during the lead (Pb) ore smelting process were improperly deposited in the Ribeira de Iguape River. Between 1991 and 1995, waste was deposited directly onto the soil surface without base or cover protection. Thus, the river and soil were contaminated by metals such as Pb and cadmium (Cd) (Kasemodel et al. 2016).

An alternative to minimize mining waste contamination is the deposition of residues in a waste containment facility with liner and cover systems. A liner's function is waterproofing and contaminant retention (Daniel 1993; Rowe et al. 1995). Besides low hydraulic conductivity and adequate shear strength, the material selected for the construction of a sealant barrier must have favorable characteristics to retain the contaminants, and resistance to chemical elements and to the erosive process (Bradl 2004). In the context of the Ribeira Valley problem, an alternative is the use of local soil as a liner. It's a residual soil formed under tropical climate, for which there is still little information related to its contaminant retention ability. Thus, the purpose of the current study is to characterize a residual soil collected in the Ribeira Valley, to verify whether it presents suitable properties to be used as a sealant barrier in mining waste containment facilities.

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## 2 Materials and Methods

The studied soil is a residual soil from the municipality of Eldorado Paulista, in the Ribeira Valley of Brazil. Figure 1 shows an overview map of the region.

The soil was collected in the superficial portion of the profile (0–40 cm). It was a highly weathered pink and white colored soil. It is a residual soil resulted from shale rock alteration. The soil was collected in the coordinates S 24° 31' 12" e W 48° 04' 37". The samples were shade dried, quartered and homogenized. This study includes measuring soil geotechnical properties and characteristics. The properties and characteristics considered were particle size distribution, according to Brazilian standard NBR 7181/2016 (ABNT 2016); consistency limits [NBR 6459/1984 from ABNT (1984) and NBR 7180/1984, also from ABNT (1984)]; and Standard Proctor compaction test [NBR 7182/1986 from ABNT (1986)]. Subsequently, three compacted cylindrical specimens of 5 cm in diameter and 10 cm in height were prepared under the optimum conditions for measuring hydraulic conductivity and shear strength. The hydraulic conductivity tests were conducted using triaxial cells as flexible wall permeameters (Head 1998). Shear strength tests were consolidated undrained (CU) with consolidation stresses,  $\sigma'_3$ , of 50, 100 and 200 kPa. The failure was indicated by the peaks in the curves  $\sigma'_1/\sigma'_3$  against axial strain. Mohr-Coulomb criterion yielded shear strength parameters

for both total and effective stresses, according to Eqs. (1) and (2), respectively:

$$\tau = c + \sigma \cdot \tan(\varphi) \quad (1)$$

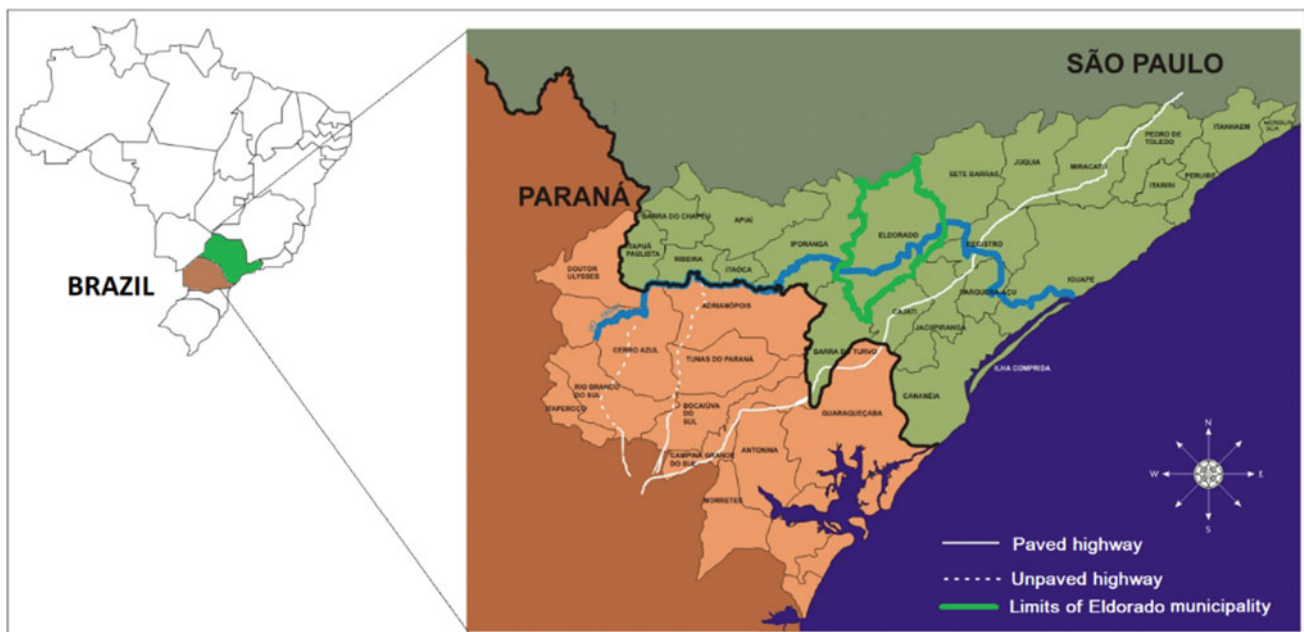
$$\tau = c' + \sigma' \cdot \tan(\varphi') \quad (2)$$

In these equations,  $c$  and  $\varphi$  are the total cohesion and shear strength angle,  $c'$  and  $\varphi'$  are the effective cohesion and shear strength angle.

The study also included soil chemical tests following geotechnical tests. Soil pH measurement were taken in distilled water and in KCl solution as described by the Brazilian Agricultural Research Corporation (EMBRAPA) (Empresa Brasileira de Pesquisa Agropecuária 2011). The procedure was performed in triplicate and the pH readings were taken with a Digimed DH21 pHmeter with a glass electrode. The results allowed for the calculation of  $\Delta\text{pH}$  ( $\text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$ ), providing information about the surface electrical charges of the particles.

The PZSE—Point of Zero Salt Effect was measured through a potentiometric titration (Alleoni et al. 2016). HCl was used as an acid, NaOH as a base and KCl as the electrolyte.

The organic matter (OM) content was determined through oxidation with a potassium dichromate solution in the presence of sulfuric acid (Camargo et al. 2009). Cation exchange capacity was obtained through the sum of the bases method (Embrapa 1997).



**Fig. 1** Overview map of the Ribeira Valley region, highlighting Eldorado municipality. Adapted from Vale do Ribeira Program, Federal University of Paraná (UFPA)

### 3 Results and Discussion

Table 1 shows the results from soil geotechnical characterization tests. A predominance of fines (54.5% clay and 20.4% silt) was observed, which is a favorable characteristic, since the natural materials adsorption capacity is strongly influenced by its surface area exposed to reactions and therefore by the particle size (Langmuir 1997). Also, these proportions satisfy the recommended literature suggestions for the use of clayey soil as liners that are a minimum of 20% clay (Rowe et al. 1995) and 30% fines (silt + clay) (Benson et al. 1994).

Also from Table 1, the soil LL is 58% and the PI is 24% that classifies the soil as CL in the Unified Soil Classification System (American Society for Testing and Materials 2000), i.e., an elastic clay of low plasticity, lean clay. PL and PI values obtained for the residual soil comply with the literature recommendations for a good performance as sealant barrier, since typical recommendations indicate a minimum PL of 20% and a minimum PI of 7% (Benson et al. 1994).

Figure 2 shows the compaction curve of the soil that presented an optimum water content,  $w_{opt}$ , of 26.3% and a maximum dry density,  $\rho_{dmax}$ , of 1.515 g/cm<sup>3</sup> through a Standard Proctor test. Table 2 shows the conditions of the compacted specimens used in the hydraulic and triaxial shear tests. The hydraulic conductivity was  $6.5 \times 10^{-9}$  m/s. This result is in the same order of magnitude of the recommendations found in literature about soils to be used as liners (Daniel 1993; Rowe et al. 1995; Benson et al. 1994; United States Environmental Protection Agency 1989).

Figure 3 shows the shear strength envelopes. For total stress, cohesion was 34 kPa and the friction angle was 13.5°. Effective parameters were cohesion of 22 kPa and friction angle of 26.8°, figures consistent to those typically observed for soils classified as CL in the Unified Soil Classification System (Carter and Bentley 1991).

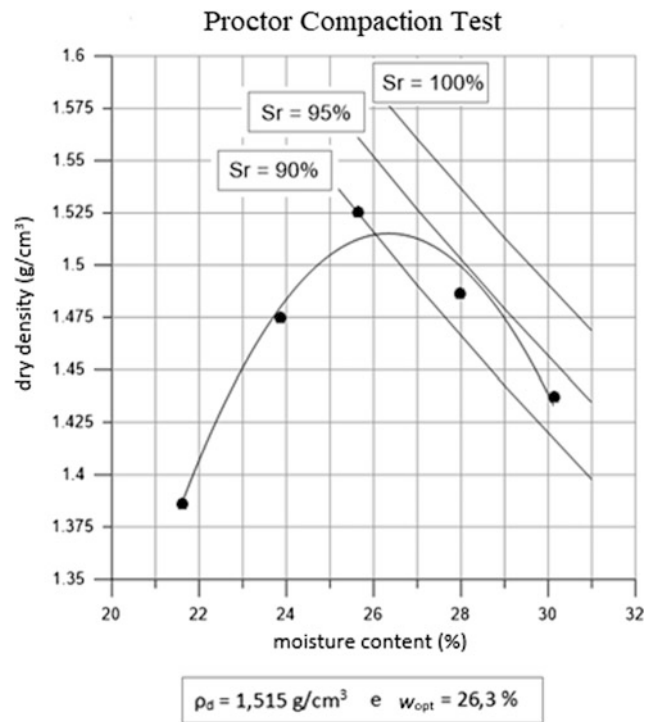


Fig. 2 Proctor compaction curve of the Ribeira Valley soil

Table 3 summarizes the results of hydraulic conductivity and shear strength tests.

Finally, Table 4 gathers the chemical test results. The soil CEC is 41.4 mmol<sub>c</sub>/dm<sup>3</sup>. CEC demonstrates a soil's ability to retain and exchange positively charged ions on the colloidal surface. Therefore, it is important in soil characterization, mainly for studying contaminant retention. The CEC value obtained for the studied soil suggests a predominance of low activity non-expansive clay minerals such as kaolinite, and a possible presence of Fe oxides. The typical range of CEC values for kaolinite is 50–150 mmol<sub>c</sub>/dm<sup>3</sup>,

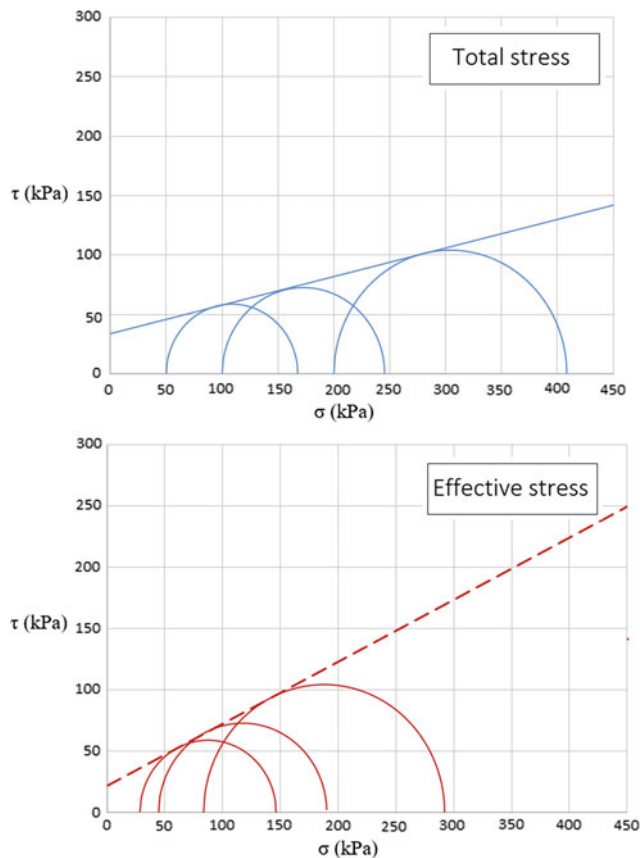
Table 1 Geotechnical characteristics of the Ribeira Valley residual soil

Parameter	Unit	Average value
Clay content	%	54.4
Silt content	%	20.4
Fine sand content	%	13.4
Medium sand content	%	7.0
Coarse sand content	%	3.8
Gravel content	%	1.0
Liquid limit LL	%	58
Plastic limit PL	%	34
Plasticity index PI	%	24
Optimum water content $w_{opt}$	%	26.3
Maximum dry density $\rho_{dmax}$	g/cm <sup>3</sup>	1.515

**Table 2** Conditions of the compacted specimens used in the triaxial shear tests

Specimen	$w_m$	$w_m - w_{opt}$	$\rho_d$ (g/cm <sup>3</sup> )	RC	$e$	$\eta$ (%)	Sr (%)
1	25.8	-0.5	1.514	99.9	0.799	44.4	87.9
2	25.7	-0.6	1.513	99.9	0.800	44.4	87.5
3	24.9	-1.4	1.526	100.7	0.785	44.0	86.4

Obs.:  $w_m$ —molding water content; RC =  $100 \cdot \rho_d / \rho_{dmax}$ —Relative compaction;  $e$ —void ratio;  $n$ —porosity; Sr—degree of saturation

**Fig. 3** Determination of strength parameters of the soil from Ribeira Valley (Brazil) by Mohr-Coulomb failure criterion

and for Fe oxides is 20–50 mmol<sub>c</sub>/dm<sup>3</sup> (de Mello et al. 1983). Kaolinite and Fe oxides are common in intensely weathered soils formed in tropical environments, especially in near the surface (Fookes 1997).

The soil's organic matter content is 9 g/kg. Soil organic matter plays an important role in its metal retention capacity.

The pH of the soil measured in water is 4.6. This condition favors metal mobility because it allows the metals to remain free in the solution (Sparks 1995). In addition, pH influences the surface charge of Al, Fe, Mn and Si oxides and hydroxides, and clay minerals like kaolinite (Langmuir 1997). The soil pH measured in the KCl solution is 3.7. Thus,  $\Delta pH$  is -0.9, a negative value that indicates a predominance of negative charges on the surface of colloidal particles of soil. PZSE also provide information about the

**Table 3** Results of hydraulic conductivity and shear strength tests

Parameter	Unit	Average value
Hydraulic conductivity, $k$	m/s	$6.5 \times 10^{-9}$
Total cohesion $c$	kPa	34
Total shear strength angle $\phi$	°	13.5
Effective cohesion $c'$	kPa	22
Effective shear strength angle $\phi'$	°	26.8

**Table 4** Parameters obtained from the Ribeira Valley residual soil characterization tests

Parameter	Unit	Average value
CEC	mmol <sub>c</sub> /dm <sup>3</sup>	41.4
OM	g/kg	9
pH <sub>H<sub>2</sub>O</sub>	–	4.6
pH <sub>KCl</sub>	–	3.7
$\Delta pH$	–	-0.9
PZSE	–	3.6

charge of soil particles. The soil PZSE is 3.6. The value is lower than the pH measured in water. This is more evidence that the particles' surface charges are predominantly negative. These negative charges favor the retention of cations, such as potentially toxic metals (Sparks 1995; Sposito 1984).

## 4 Conclusion

The predominance of negative charges at the soil surface and the geotechnical characteristics suggest that this is a soil appropriate for composing a landfill liner, considering its texture, low permeability, low clay activity (indicating non-expansive clay) and shear strength. Thus, the use of the local soil as a liner to mitigate contamination is a feasible alternative for the recuperation of the region. For this reason, complementary chemical tests are underway to address the contaminant retention capacity of this tropical soil.

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## References

- Alleoni, L.R.F., Mello, J.W.V., Rocha, W.S.D.: Electrochemistry, adsorption and ion exchange in soils. In: Melo, V.F., Alleoni, L. R.F. (eds.) *Soil Chemistry and Mineralogy—Part II—Applications*. Sociedade Brasileira de Ciência do Solo, Viçosa (2016) (in Portuguese)
- Alloway, B.J.: *Heavy Metals in Soils*, 2nd edn. Blackie Academic & Professional, London (1995)
- American Society for Testing and Materials (ASTM): ASTM D2487. Standard Classification of Soils for Engineering Purposes (Unified Soil Classification System). ASTM International, West Conshohocken (2000)
- Associação Brasileira de Normas Técnicas (ABNT): NBR 7181. Standard test method for granulometric analysis of soils. ABNT, Rio de Janeiro (2016) (in Portuguese)
- Associação Brasileira de Normas Técnicas (ABNT): NBR 6459. Standard test method for liquid limit. ABNT, Rio de Janeiro (1984) (in Portuguese)
- Associação Brasileira de Normas Técnicas (ABNT): NBR 7180. Standard test method for plastic limit. ABNT, Rio de Janeiro (1984) (in Portuguese)
- Associação Brasileira de Normas Técnicas (ABNT): NBR 7182. Standard test method for soil compaction. ABNT, Rio de Janeiro (1986) (in Portuguese)
- Benson, C.H., Zhai, H., Wang, X.: Estimating hydraulic conductivity of compacted clay. *J. Geotech. Eng.* **120**(2), (1994)
- Bradl, H.B.: Adsorption of heavy metal ions on soils and soil constituents. *J. Colloid Interface Sci.* **277**, 1–18 (2004)
- Camargo, O.A., Moniz, A.C., Jorge, J.A., Valadares, J.M.A.S.: Methods of chemical, mineralogical and physical analysis of soils - Instituto Agronômico de Campinas. *Boletim Técnico* **106** (2009)
- Carter, M., Bentley, S.P.: *Correlations of Soil Properties*. Pentech Press, London (1991)
- Daniel, D.E.: *Geotechnical Practice for Waste Disposal*. Chapman & Hall, London (1993)
- Embrapa: *Manual of methods of soil analysis*. Centro Nacional de Pesquisa de Solos. Rio de Janeiro (1997) (in Portuguese)
- Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA): *Methods of Soil Analysis* (in Portuguese) (2011)
- Federal University of Paraná (UFPA): Vale do Ribeira Maps. Available in: <http://www.valedoribeira.ufpr.br/mapas.htm> (in Portuguese)
- Fookes, P.G. (ed): *Tropical Residual Soils: A Geological Society Engineering Group. Working Party Revised Report*. The Geological Society, London (1997)
- Head, K.H.: *Manual of Laboratory Testing*, vol. 3, 2nd edn. Wiley, Chichester (1998)
- Kasemodel, M.C., Lima, J.Z., Sakamoto, I.K., Varesche, M.B.A., Trofino, J.C., Rodrigues, V.G.S.: Soil contamination assessment for Pb, Zn and Cd in a slag disposal area using integration of geochemical and microbiological data. *Environ. Monit. Assess.* **188**(698)
- Langmuir, D.: *Aqueous Environmental Geochemistry*. Prentice Hall, New Jersey (1997)
- Lester, J.N.: Heavy metals in waste water and sludge treatment process, vol. 2. In: *Treatment and Disposal*. CRC Press, Boca Raton, FL (1987)
- Rowe, R.K., Quigley, R.M., Brachman, R.W.I., Booker, J.R.: *Clayey Barrier Systems for Waste Disposal Facilities*. Chapman & Hall, London (1995)
- Sparks, D.L.: *Environmental Soil Chemistry*. Academic Press, London (1995)
- Sposito, G.: *The Surface Chemistry of Soils*. University Press, Oxford (1984)
- United States Environmental Protection Agency.: *Requirements for hazardous waste landfill design, construction and closure*. Seminar publication EPA (1989)
- de Mello, F.A., Brasil Sobrinho, M.O.C., Arzolla, S., Silveira, R.I., Cobra Neto, A., de Kiehl, J.C.: *Soil Fertility*. Nobel, São Paulo (1983) (in Portuguese)