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## Geotechnical characterisation for landfill disposal of phosphoric acid production residues

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### ABSTRACT

The case study of a dismissed petrochemical plant located in Southern Italy is presented, wherein phosphoric acid production residues have to be transformed through a series of on-site treatment procedures into non-reactive stabilised wastes, which can be accepted for disposal in a non-hazardous solid waste landfill according to the regulations in force. Oedometric compression, triaxial shear, torsional ring shear and column leaching tests were carried out with the aim to determine the strength and deformability parameters of the stabilised residues, as well as to investigate the long-term mobility of water-soluble contaminants under a confining stress level that simulates the final disposal conditions. Such a characterisation of the coupled chemo-hydro-mechanical behaviour allowed the effectiveness of such treatment procedures in producing a waste stream that does not pose threats to the landfill geotechnical stability to be ascertained.

**Keywords:** non-reactive stabilised waste, stabilisation treatment, geotechnical characterization, landfill stability

### 1 INTRODUCTION

The decommissioning of the phosphoric acid production facilities within a petrochemical plant located in Southern Italy raised the issue of the final disposal of residues that originated before the cessation of the production activities. Such residues are markedly acidic (pH < 3.5), may contain traces of naturally occurring radionuclides<sup>1</sup> and are characterised by a significant concentration of fluorides, chlorides, phosphates, sulphates and heavy metals. In view of the above, the production residues were classified as hazardous wastes and, hence, the development of adequate on-site treatment procedures was required in order to stabilise the original hazardous waste streams and to obtain non-reactive stabilised wastes, which are able to maintain their stability even in the long term and therefore are suitable for disposal in a non-hazardous solid waste landfill according to the Italian Decrees D.M. 27/09/2010 and D.M. 24/06/2015.

In particular, the planned on-site treatment procedures consist of a first *neutralisation* stage, which

is performed through the addition of quicklime or hydrated lime to the fluidised waste (Lewis and Boynton, 1976) and causes the pH to increase until reaching a value in the 6 to 11.5 range, a second *filtration* stage, which allows the solid phase to be separated from the liquid phase and a slurry with a dry solids content higher than 25% by weight to be obtained, and a third *stabilisation* stage, whose objective is to enhance the stiffness and strength properties of the densified slurry through the addition of chemical binders.

A testing programme was defined with the aim to evaluate the effectiveness of the aforementioned treatment procedures in achieving long-term chemical and mechanical stabilisation of the hazardous wastes. Such a testing programme was divided into a first stage that simulated, at the laboratory scale, the treatment procedures which are planned to be performed during the decommissioning of the production facilities, with the purpose of obtaining representative samples of the stabilised residues, and a second stage that allowed conformance of the stabilised residues with respect to the requirements for disposal in a non-hazardous solid waste landfill to be verified. In addition to the chemical conformance tests, a series of geotechnical tests were carried out in order to ascertain that the stabilised

<sup>1</sup> Due to the natural content of U-238, Th-232 and their decay products, phosphorites (the ore used in the wet-process phosphoric acid production) are classified as NORM (*Naturally Occurring Radioactive Materials*).

residues show “adequate physical stability and load capacity”, as well as a “long-term leaching behaviour that is not subject to negative alteration in the landfill disposal conditions” (D.M. 24/06/2015).

Due to the lack of established protocols for the execution of the latter geotechnical tests, the objective of this paper is to present the testing apparatuses, the experimental procedures and the results interpretation that led to a thorough characterisation of the residues mechanical behaviour, which is needed in order to optimise the waste placement and compaction phases, the safety during landfilling activities, the mechanical stability of the waste body, the volume capacity of the landfill and the final closure and land reclamation operations (Manassero and Shackelford, 1994).

## 2 MATERIALS AND METHODS

### 2.1 Specimen preparation

The phosphoric acid production residues underwent two different laboratory-scale treatment procedures.

According to the first treatment procedure (Sample N.1), the *neutralisation* was achieved by mixing the residue with an aqueous suspension of hydrated lime (12.5 g of hydrated lime per kg of residue), until a pH value equal to 10.2 was obtained at equilibrium. The material densification, or *filtration* stage, was performed by means of a consolidometer, which allows a vertical pressure to be applied through a pneumatically controlled piston under null horizontal strain conditions. As water is drained by porous disks located at the specimen ends, a consolidation process occurs and different densification degrees can be reached by varying the applied pressure. A dry solids content equal to 65.27% was obtained, corresponding to a water content equal to 53.21%. Finally, the material *stabilisation* was performed through the addition of 3% by weight of sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ), which reacts with soluble calcium salts contained in the pore solution leading to the formation of insoluble calcium silicates: the latter compounds represent the binding agents within the pores of the stabilised residue (Hurley and Thornburn, 1971).

According to the second treatment procedure (Sample N.2), upon achieving the *neutralisation* similarly to Sample N.1, 0.5% by weight of activated carbon was added in order to reduce the content of Dissolved Organic Carbon. The *filtration* was simulated through oven drying and, as such, the reduction in the water content (or increase in the dry solids content) was associated with a decrease in the saturation degree, while maintaining a high porosity. The *stabilisation* consisted in the addition of 0.1% by weight of Actifluo, a commercial product containing the coagulant Aluminum polychloride for the removal of fluorides from the pore solution, 10% by weight of powdered sodium bentonite and 3% by weight of Portland cement 32.5. The geotechnical tests were carried out on the

stabilised residue after a 28 days long curing period.

### 2.2 Testing apparatus and procedures

The geotechnical characterisation of both Sample N.1 and Sample N.2, after stabilisation according to the previously illustrated treatment procedures, was based on the results of the following laboratory tests:

- oedometric compression (OED) tests;
- isotropically consolidated drained triaxial (CID-TX) tests;
- isotropically consolidated undrained triaxial (CIU-TX) tests;
- torsional ring shear (TRS) tests;
- column leaching (CL) tests.

The stress-controlled OED tests were carried out in order to determine the deformability parameters of the stabilised residues, following a geometric progression of the applied load as specified by the standardised test method that is described in ASTM D2435 (2020). The physical properties of the tested specimens at the initial stage are reported in Table 1.

Table 1. Initial physical properties of the specimens subjected to the OED tests.

	Sample N.1	Sample N.2
Bulk unit weight, $\gamma$ (kN/m <sup>3</sup> )	17.66	16.18
Water content, $w$ (%)	51.04	72.6
Dry unit weight, $\gamma_d$ (kN/m <sup>3</sup> )	11.69	9.37
Void ratio, $e$ (-)	1.266	1.827

The strain-controlled CID-TX tests were carried out on three specimens of the stabilised residues, each one consolidated under a different isotropic effective stress, with reference to the standardised test method that is described in ASTM D7181-20 (2020). The specimen properties at the end of the consolidation stage are reported in Table 2.

Table 2. Physical properties of the specimens subjected to the CID-TX tests, at the end of the consolidation stage.

	Specimen N.1	Specimen N.2	Specimen N.3
Isotropic effective stress, $p'$ (kPa)	30	60	90
Sample N.1 void ratio, $e$ (-)	1.088	0.975	0.903
Sample N.2 void ratio, $e$ (-)	1.640	1.450	1.310

The strain-controlled CIU-TX tests were carried out on three specimens of the stabilised residues, with reference to the standardised test method that is described in ASTM D4767-11 (2020). As a difference from the CID-TX tests, the isotropically consolidated specimens (Table 3) were loaded to failure under undrained conditions, and the effective stress path of each specimen was derived from the excess pore pressure measurements.

Table 3. Physical properties of the specimens subjected to the CIU-TX tests, at the end of the consolidation stage.

	Specimen N.1	Specimen N.2	Specimen N.3
Isotropic effective stress, $p'$ (kPa)	50	150	250
Sample N.1 void ratio, $e$ (-)	0.890	0.863	0.956
Sample N.2 void ratio, $e$ (-)	1.708	1.724	1.540

Three specimens of the stabilised residues were then subjected to the TRS tests, with reference to the standardised test method that is described in ASTM D6467-13e1 (2013). While TX tests allowed the peak and critical state values of the angle of shearing resistance to be assessed, the residual shear strength was evaluated through the interpretation of the TRS test results. The specimen properties at the end of the consolidation stage are reported in Table 4.

Table 4. Physical properties of the specimens subjected to the TRS tests, at the end of the consolidation stage.

	Specimen N.1	Specimen N.2	Specimen N.3
Vertical effective stress, $\sigma'_v$ (kPa)	30	60	120
Sample N.1 dry unit weight, $\gamma_d$ (kN/m <sup>3</sup> )	11.86	11.84	12.10
Sample N.2 dry unit weight, $\gamma_d$ (kN/m <sup>3</sup> )	10.53	10.94	11.39

Finally, the CL tests were performed on the stabilised residues with the aim to investigate the effectiveness of the treatment procedures in reducing the long-term mobility of water-soluble contaminants (Shackelford and Glade, 1997; Kamon et al., 2000). The testing apparatus consists of a triaxial cell that allows the specimen to be consolidated under a known isotropic effective stress, in such a way that the state of stress representative of the landfill disposal conditions can be simulated. A volumetric liquid flux of distilled water is generated through the specimen in response to an applied hydraulic head difference, which is kept constant in time. Liquid flow rate is measured at the specimen exit side, and the collected permeate stream can then be analysed for the determination of the contaminant concentrations and other chemical parameters (e.g. pH and electrical conductivity, EC). The physical properties of the tested specimens at the end of the consolidation stage are reported in Table 5.

Table 5. Physical properties of the specimens subjected to the CL tests, at the end of the consolidation stage.

	Sample N.1	Sample N.2
Isotropic effective stress, $p'$ (kPa)	200	300
Void ratio, $e$ (-)	0.922	1.538

### 3 RESULTS AND DISCUSSION

#### 3.1 Oedometric compression tests

The measured variation in the void ratio as a function of the vertical effective stress (Fig. 1) allowed the compression index,  $c_c$ , and the swelling index,  $c_r$ , to be determined for both Sample N.1 and Sample N.2 (Table 6). Evidently, the lower values of the elastic and elasto-plastic deformability parameters that were observed for Sample N.1 are to be related to the higher density that was achieved through filtration within the consolidometer.

Table 6. Compression index and swelling index values as derived from the OED test results.

	Sample N.1	Sample N.2
Compression index, $c_c$ (-)	0.279	0.484
Swelling index, $c_r$ (-)	0.021	0.024

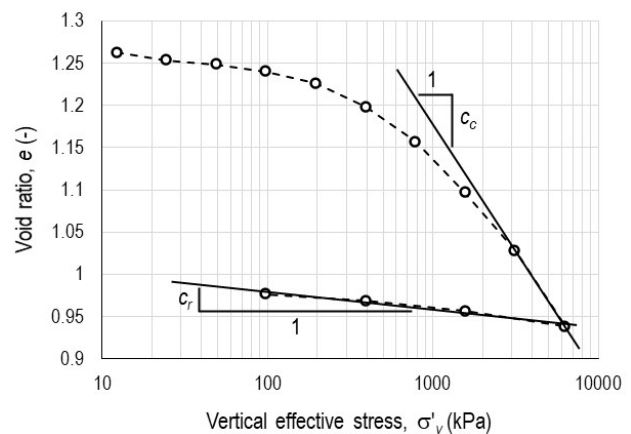


Fig. 1. Change in the void ratio as a function of the vertical effective stress during the OED test performed on Sample N.1.

The shape of the experimental curves that represent the variation in the void ratio as a function of time, as illustrated in Fig. 2 for Sample N.1 in correspondence of an increase in the vertical effective stress from 392.4 to 784.8 kPa, suggested that the measured volumetric strain was mostly caused by creep phenomena.

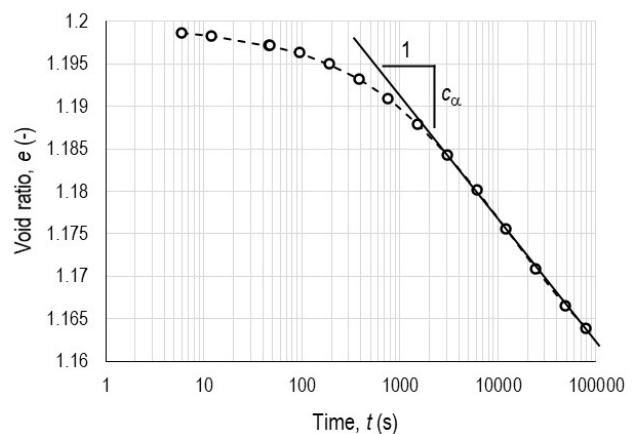


Fig. 2. Graphical determination of the secondary compression index for Sample N.1, at the load increment step  $\sigma'_v = 784.8$  kPa.

Therefore, with respect to Sample N.1, the tails of the  $e - \log(t)$  curves were further interpreted assuming that settlements were occurring at constant effective stress (i.e. primary compression virtually complete), in order to estimate the secondary compression index,  $c_{\alpha}$ , which is defined as the change in the void ratio per logarithmic cycle of time. An increase in the  $c_{\alpha}$  parameter was noticed as the vertical effective stress was increased during the OED test (Fig. 3), similarly to overconsolidated clayey soils (Lancellotta, 2009).

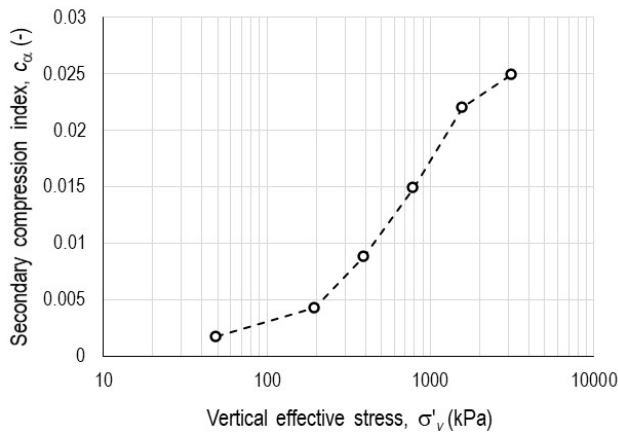


Fig. 3. Secondary compression index for Sample N.1 as a function of the vertical effective stress.

### 3.2 Triaxial shear tests

The results of the CID-TX tests showed a dilatant behaviour of the stabilised residues, with negative volumetric strains (i.e. increase in specimen volume) being observed when failure was approached. Such a behaviour was responsible for the mobilisation of peak shear strength values significantly higher than the values that were measured at the critical state condition, which was considered to be reached when shearing occurred without further changes in the effective stress state and void ratio.

If the maximum shear stress,  $t$ , is plotted against the mean normal effective stress,  $s'$ , as illustrated in Fig. 4 for Sample N.1, the stress-paths followed during the CID-TX tests can be visualised and interpreted through the Mohr-Coulomb failure criterion, where the cohesion is assumed to be null and the angle of shearing resistance,  $\varphi'$ , is selected so as to ensure the best fitting of the experimental data. While the shear strength locus at the critical state is well represented by a straight line in the  $t - s'$  plane and, as such, its interpretation through the aforementioned failure criterion allows the angle of shearing resistance at constant volume,  $\varphi_{cv}'$ , to be determined, a number of literature studies have shown that the peak strength locus of dense sands and heavily overconsolidated clays is curvilinear (Wood, 1990). Nevertheless, interpretation of the peak strength data of both Sample N.1 and Sample N.2 via the Mohr-Coulomb criterion demonstrated that the peak

strength locus of the stabilised residues could be approximated as a straight line, whose slope in the  $t - s'$  plane is given by the sine of the peak angle of shearing resistance,  $\varphi_p'$ . The values of the strength parameters, which were determined according to the previously illustrated approach, are reported in Table 7, showing that both the laboratory-scale treatment procedures led to a similar behaviour at failure.

Table 7. Constant volume and peak values of the angle of shearing resistance as derived from the CID-TX test results.

	Sample N.1	Sample N.2
Angle of shearing resistance at constant volume, $\varphi_{cv}'$ (°)	42.57	40.25
Peak angle of shearing resistance, $\varphi_p'$ (°)	45.68	46.99

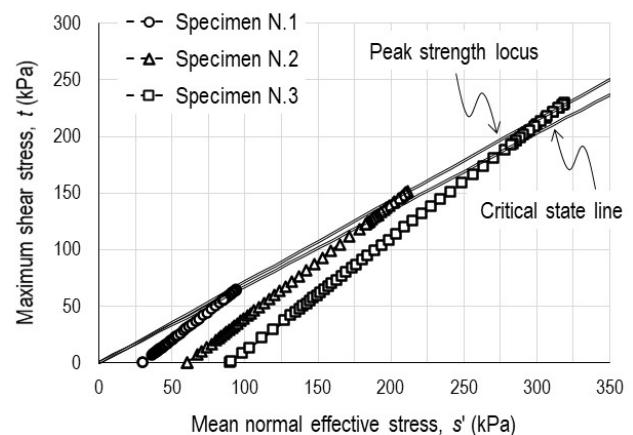


Fig. 4. Stress-paths followed by the specimens subjected to the CID-TX tests (Sample N.1), and interpretation through the Mohr-Coulomb failure criterion.

This good correspondence between the observed behaviours of Sample N.1 and Sample N.2 at the ultimate state also emerged from the interpretation of the results of the CIU-TX tests. The measured  $t$  monotonically increased during the tests until the critical state condition was reached, as expected for densely packed porous media that are loaded under undrained conditions. Furthermore, after an initial phase wherein positive excess pore pressures were measured upon an increase in the axial strain, negative excess pore pressures subsequently built up as a result of dilatancy of the stabilised residues.

As illustrated in Fig. 5 for Sample N.1, the stress-paths followed during the CIU-TX tests were influenced as well by the occurrence of dilatancy under null volumetric strain conditions, since the horizontal deviation of the undrained stress paths from the virtually drained ones had to be equal and opposite in sign to the excess pore pressure. In such a way, undrained yielding entailed that the stress-paths moved along the intersection between the constant void ratio plane and the peak strength locus, whose shape could then be visualised on the  $t - s'$  plane. Despite an

appreciable non-linearity of the peak strength locus when approaching the critical state condition, the linear approximation results to be certainly acceptable for the tested material and the confining stress levels that are encountered in landfills.

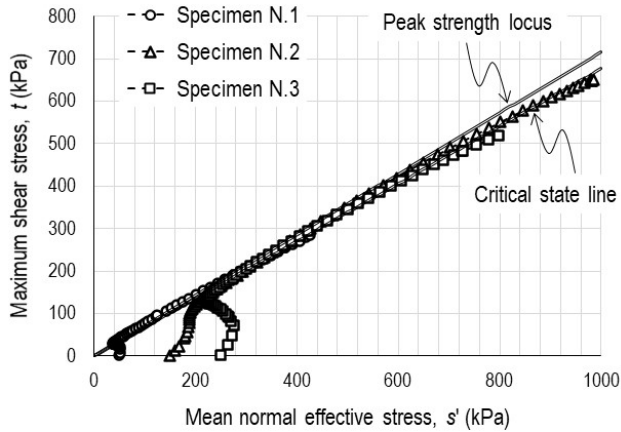


Fig. 5. Stress-paths followed by the specimens subjected to the CIU-TX tests (Sample N.1), and interpretation through the Mohr-Coulomb failure criterion.

### 3.3 Torsional ring shear tests

The residual shear strength was fully mobilised, for all the specimens subjected to the TRS tests, at relative displacements along the shear band of the order of a few centimetres. Under the hypothesis that the couple of shear stress,  $\tau_n$ , and vertical effective stress,  $\sigma_v'$ , acting on the horizontal plane coincides with the couple of stresses acting on the failure surface, the angle of shearing resistance at the residual state,  $\phi_r'$ , was determined through a linear regression of the experimental data on the  $\tau_n - \sigma_v'$  plane, as illustrated in Fig. 6 for Sample N.1.

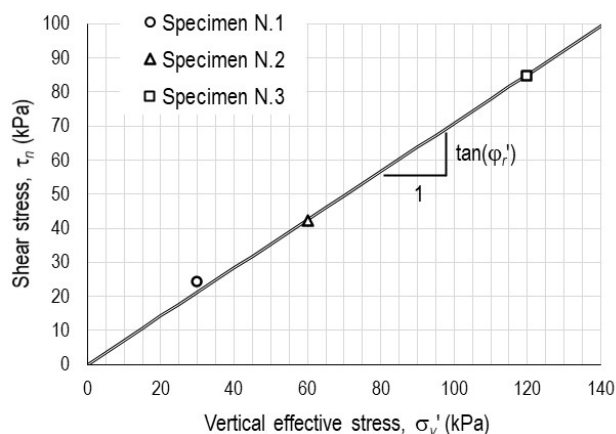


Fig. 6. Residual shear strengths measured during the TRS tests (Sample N.1), and interpretation through the Mohr-Coulomb failure criterion.

The estimated values of the  $\phi_r'$  parameter, which are reported in Table 8, pointed out that the residual shear strength of Sample N.2 was considerably lower than

that of Sample N.1. This evidence was explained by referring to the stabilisation treatment performed on Sample N.2, as the residue had been mixed with powdered bentonite: indeed, when shear strains are sufficiently large, plate-like clay particles on both sides of the failure surface become oriented parallel to the shear band, thus causing a measurable reduction in the mobilised friction at the macroscale. The latter effect is then expected to be more relevant in the case of the bentonite-amended residue if compared to the unamended residue.

Table 8. Residual state values of the angle of shearing resistance as derived from the TRS test results.

	Sample N.1	Sample N.2
Angle of shearing resistance at the residual state, $\phi_r'$ (°)	35.33	31.48

### 3.4 Column leaching tests

The measured liquid flow rate during the CL tests allowed the hydraulic conductivity,  $k$ , of the stabilised residues to be determined. The  $k$  values that are reported in Table 9 show that the addition of powdered bentonite resulted in a slightly lower permeability of Sample N.2, consistently with the decrease in  $k$  that is usually observed when the bentonite content of slurry cut-off walls is increased (Manassero et al., 1995).

Table 9. Hydraulic conductivity values as derived from the CL test results.

	Sample N.1	Sample N.2
Hydraulic conductivity, $k$ (m/s)	$9.2 \cdot 10^{-9}$	$3.0 \cdot 10^{-9}$

Furthermore, the chemical parameters (i.e. EC, pH and concentrations of a series of target analytes) that were measured on samples of the collected permeate stream were plotted against the pore volume of flow, which was calculated assuming that the void ratio did not change during permeation with respect to the end of consolidation value (Fig. 7 and Fig. 8).

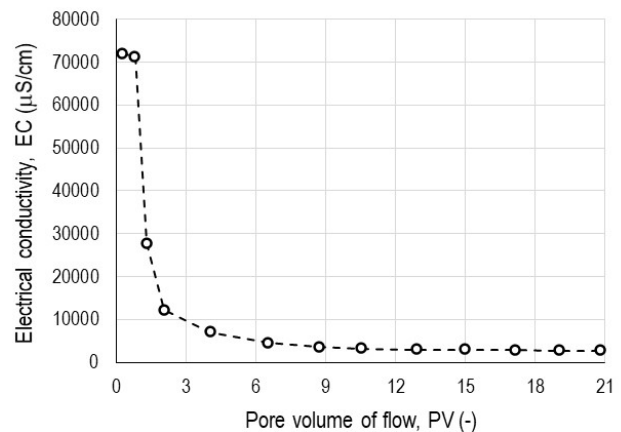


Fig. 7. Measured electrical conductivity as a function of the pore volume of flow during the CL test performed on Sample N.1.

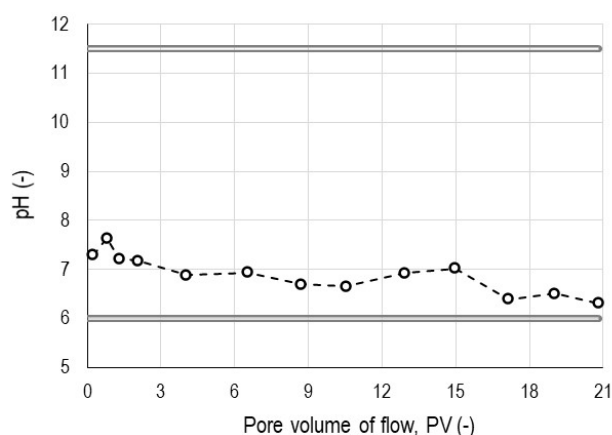


Fig. 8. Measured pH as a function of the pore volume of flow during the CL test performed on Sample N.1, and comparison with the upper and lower threshold values (grey double lines) which are specified by the regulations in force.

All the determined chemical parameters exhibited a stable behaviour, with long-term values that fell within the acceptance range for disposal of non-reactive stabilised wastes in non-hazardous solid waste landfills.

#### 4 CONCLUSIONS

In light of the elasto-plastic work-hardening model proposed by Manassero and Shackelford (1994) with a view to describe the stress-strain response of structured particulate materials, the stabilised industrial residues showed a ductile-softening behaviour, which is typical of porous media with weak cementing bonds and initial density higher than the value corresponding to the critical state. Such a mechanical behaviour, which resembles that of heavily overconsolidated soils, allowed undrained instability phenomena that may occur in high water content treated sludges to be excluded (Arroyo et al., 2006; Gens, 2019). Indeed, as a consequence of the open skeletal and highly porous microstructure, high water content treated sludges may be prone to exhibit large compressive volumetric strains upon collapse of the fragile bonds, and to accumulate positive excess pore pressures under undrained conditions until a complete loss of shear strength is reached.

Besides the chemical conformance tests, which consisted in leaching tests for quantifying the release of water-soluble compounds and the acid neutralisation capacity in accordance with standardised methods, the column leaching tests also allowed the gradual decrease in the release of contaminants to be ascertained, until a stable steady-state condition was reached in all cases. As a result, the performed tests have shown a stable behaviour of the treated residues in the long term.

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