Final Disposal of the Wastes Associated to the Oil Spill of the Tanker P*restige* through its Stabilization with Quicklime and Granite Fines [1]

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Abstract

The sinking of the tanker *Prestige* produced a large oil spill that affected a wide coastal area of the NW corner of Spain. Cleaning operations were performed on the sea and the shores and the waste recovered waste is a mélange of fuel, water, sand and pebbles, algae, plastic bags and boxes, cleaning tools, contaminated dresses and boots,…. which, at the time of writing this contribution, is still pending of its final disposal. Waste mass balances show that, while the total amount of recovered fuel is close to the amount spilled by the vessel (~43000 metric tons) the total amount of waste sums up to more than 4 times this quantity (~170000 metric tons). In order to help to design a cost effective management strategy we have undertaken a comprehensive study aimed at: a) finding stabilization agents; b) to characterize the geotechnical behavior of the stabilized mass and c) to recycle it through its incorporation to the production cycle of prefabricated concrete and mortar elements. This paper focuses in the two first aspects while the third one is treated in a companion paper. The incorporation of lime and granite fines as stabilizing agents transforms the fluid waste into a dry and dusty material amenable of safe compaction and landfill disposal. Moreover, the properties of the mixture enhance the separation of extraneous materials (plastic, rock pebbles, etc.), pass the currently accepted leaching tests (i.e. EN 12457) and show a good geotechnical performance.

Keywords: oils spill, oily waste, waste stabilization, geotechnical characterization

Introduction

On the morning of November, 19th of 2002, the convenience flag tanker *Prestige* collapsed into two parts that subsequently sank to more than 3000 m at the west margin of the Galician trough. The sinking of the vessel was the final act of a series of large oil spills that, starting on November 13th, affected the Atlantic and Cantabrian shores of Spain, Portugal and France. Immediately after the disaster, tens of thousands of people volunteered for weeks in

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the cleaning and decontamination operations of the shores, particularly in Galicia, the region that suffered the worst impact.

Cleaning operations were performed on the sea and the shores. Far from what one could expect, the major part of recovered waste is a mélange of fuel, water, sand and pebbles, algae, plastic bags and boxes, cleaning tools, contaminated dresses and boots,… which, in the hurry of the operations, were located in transitory storages awaiting a final destiny.

Waste mass balances (Table 1) show that, while the total amount of recovered fuel is close to the amount spilled by the vessel (~43000 metric tons) the total amount of waste sums up to more than 4 times this quantity (~170000 metric tones). This is not unusual in oil spills as demonstrated in previous accidents like the *Exxon Valdez*, *Katina* and *Erika*.

Operations scenario	Total waste	Fuel/waste ratio	Pure fuel	Non-fuel waste
Galician coast	67883	0.18	12219	55664
Cantabrian coast	21855	0.16	3497	18358
French coast	25470	0.16	4075	21395
Sea recovery	55543	0.42	23388	32155
Total	170751	0.25	43179	127572

Table 1. Waste mass balances (in tons) associated to the oil spill of the tanker *Prestige*. Source: CEDRE (2005)

Although oil spill catastrophes occur more often than desirable, there is a small body of literature concerning the management of the oily wastes. In addition, the treatment of heavily mixed materials (Figure 1), like the ones produced along the cleaning activities after the spill of *Prestige* complicates any simple solution. In relation to the *Prestige* disaster, IPIECA (2004) states that "*The failure to rigorously implement a comprehensive waste management plan meant collected wastes were deposited together in lined pits with no segregation for recycling or final disposal; the disposal process for this mixed waste is ongoing and will be expensive and time consuming*". A similar situation took place a few years earlier after the sinking of the *Erika* tanker (Ansell et al., 2001).

As far as the cleaning operations of the Galician shores proceed, different provisional collection points were allocated. Typically they were simple, unconditioned, trenches and shallow excavations although in some cases the material was stocked in old clay quarries. Along the few months after the disaster, the wastes contained at the provisional storage sites were transferred to two specially conditioned safety ponds within the facilities of the CTRIG

(Galician Center for the Treatment of Industrial Wastes), near the locality of As Somozas (A Coruña). At present, ~75000 tons of the oily wastes of the Prestige await a decision concerning its final management and disposal.

Stabilization is the solution more frequently used in order to get rid of oily wastes after a major oil spill. This technique seeks to facilitate the disposal of the waste by improving its behavior through the mixing with adequate materials prior to the final disposal in landfills. Within that context, quicklime has been extensively used in some past pollution incidents such as the *Amoco Cadiz* grounding at French coasts in 1967 or the *Erika* in 1999.

Following the sinking of *Prestige*, different research teams addressed investigations aimed at finding selected materials amenable of fuel dispersion and/or coagulation in order to facilitate its recovery or elimination prior to the arrival to the coast. Among them, are worth noting the contributions by García Frutos et al. (2002) and Agüero et al. (2003) whom used vegetal carbon and sepiolite, respectively. Their results suggest a better coagulating potential for carbon in the ocean waters rather than sepiolite. However, their line of research concentrated on the recovery of oil from the sea and not in the stabilizing potentials of the coagulants in relation with the oily wastes.



Figure 1. General view of *Prestige's* wastes stored in a safety pond of the CTRIG. Note that rather complex nature of the waste material

Due to the large amount of materials that need to be processed, the selection of stabilizing agents is a matter of economic concern so that, added to the industrial costs

(machinery, man work, energy consumption,…), a comprehensive analysis should also include the commercial value of the stabilizers, their transportation costs and their immediate availability. The cost-effectiveness of the overall process depends on that.

This paper focuses on an integrated stabilization approach by which the wastes of *Prestige* are combined with given amounts of quicklime and a local inert waste produced by the dimension stones industry. The stabilized product, an earth-like material, has been then studied from the geotechnical point of view in order to define its behaviour prior to landfill disposal. In a parallel research line, which are covered in a separated paper, some mixtures of the stabilized material have been used as an addition to cementitious materials (mortar and concrete) as a prior step to develop non-structural construction elements (i.e. interlocking concrete pavement, small precast pieces,…) within a waste recycle perpective.

Materials and Methods

Oily Wastes

Prestige's wastes were kindly supplied by SOGARISA, the Galician society in charge of the management of the CTRIG. As mentioned before, the waste is a mélange (Fig. 1) of fuel, sea water, sand, pebbles, algae, wood, plastic bags, cleaning tools and dresses. The ratio fuel/non-fuel (F/NF) waste is close to 0.25, that is, about the fourth part of the raw waste is pure fuel.

In the stabilization studies we considered the use of two batches of waste. In a preliminary stage, we selected a fuel-rich fractions (~0.3 m^3 of batch-type 1) with a F/NF ratio higher than 0.75. That waste incorporates a small amount of impurities (i.e. materials different from fuel) being the most significant sea water. In a second stage, we worked with the raw waste (~1.5 m^3 of batch-type 2) taking into account that, attending to the nature of the waste "as is", any classification within the context of the industrial stabilization process would be costly and complicated. The approximate F/NF ratio is ~0.25 with a wide variety of impurities (mainly sea water, sand and pebbles, plastic bags and cleaning dresses). Working with such a kind of waste implies the manipulation of an important amount of stabilizers and care has to be paid in order to screen out those particles with larger sizes.

Granite Fines

The elaboration of dimension stone typically includes mechanical processes like sawing of size-normalized rock blocks, polishing of the sawed slabs, etc. As a result of all these activities, an important quantity of dusty material (granite fines) are produced (Fig. 2). The Porriño area, in the south of Galicia, is worldwide renowned by its dimension stone industry and, only there, the production of granite fines adds up to ~350000 m^3 every year.

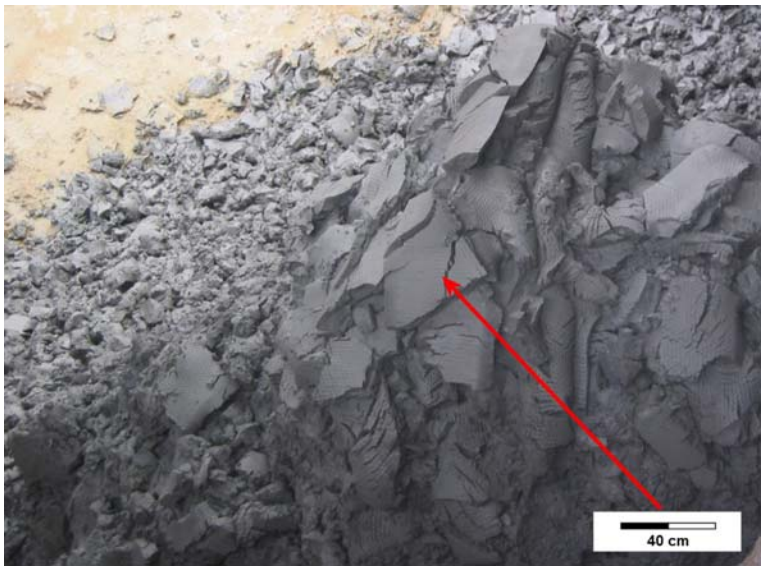


Figure 2. Cakes of granite fines released by a filter press from a elaboration natural stone workshop of Porriño (S. Galicia)

Far from it would appear, granite fines are not just crushed granite particles but a very homogeneous silt-sized granitic material mixed with significant amounts of steel grit and calcite resulting from the carbonation of lime added to water along the sawing process. Figure 3 shows a typical granulometric curve of the granite fines and Table 2 the corresponding chemical composition. More details on Galician granite fines are given in Barrientos et al. (2004) and Delgado et al. (2005).

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	MgO	P_2O_5	MnO	C_{tot}	C_{org}	C_{inorg}	CO_3
M1	66.1	13.0	6.60	5.40	4.70	3.01	0.52	0.13	0.082	0.41	0.12	0.29	1.45
M2	66.0	14.4	6.00	4.20	4.80	3.22	0.50	0.37	0.071	0.40	0.10	0.30	1.50
M3	67.5	13.6	5.30	3.60	5.00	3.00	0.39	0.23	0.069	0.49	0.20	0.28	1.40
M4	69.7	15.8	1.59	1.80	4.50	4.00	0.50	0.20	0.031	0.48	0.47	0.02	0.10

Table 2. Chemical composition (in weight %) of typical granite fines. C_{tot}: total carbon; C_{org}: organic carbon; C_{inorg}: inorganic carbon; CO_3: equivalent carbonate content from C_{inorg}

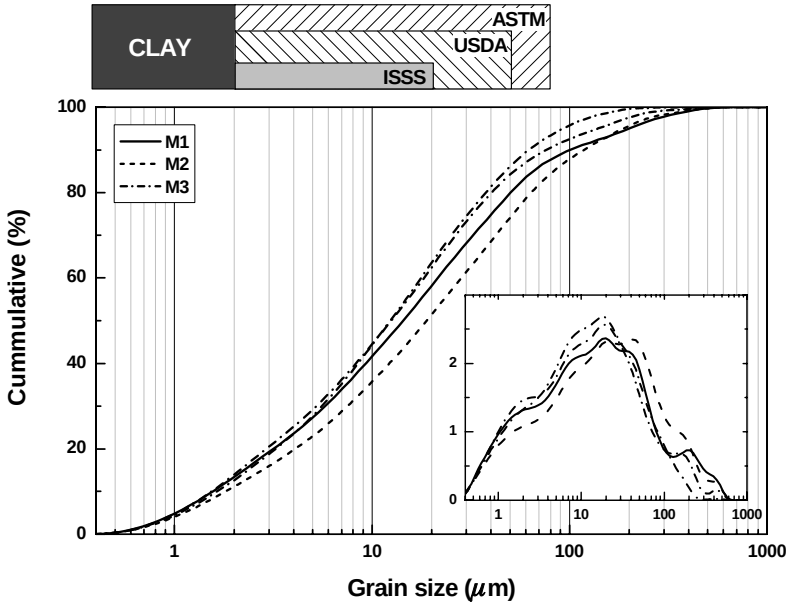


Figure 3. Typical grain size cumulative distribution curves associated to granite fines from gangsaws (M1, M2, M3) and from disk saws (M4). The plot also indicates the conventional limits for silty particles, according to major soil classification systems. The inset shows the distributed grain size population

Granite fines for the stabilization study were kindly provided by the Galician Granite Association.

Quicklime

Commercial, industrial/agricultural-grade quicklime (77 % CaO purity; >92 % with grain size < 6 mm) manufactured by CEDIE was employed in our study. A typical X-ray diffraction of the material is shown in figure 4. Apart from lime, the rest of mineral phases present in the quicklime are dolomite, dicalcium silicate (Ca_2SiO_4) and a certain amount of portlandite ($Ca(OH)_2$). In the preliminary assays to use the stabilized product with a cementitious material, expansive reactions developed in the mortar test samples. Analyses of the source of the expansive reaction let us identify the presence of small chunks o partly hydrated lime that, along the setting process of the mortar hydrate and generate important stresses around them. In order to eliminate these mortar/concrete deterioration mechanisms, it was decide to sieve the raw quicklime to a grain size smaller than 0.4 mm. The X-ray diffraction associated to the sieved quicklime (Fig. 4) reveals that portlandite has been effectively removed by the screening process. Thus, since using sieved quicklime, no expansive reactions have been identified in any cement-based test sample.

Reaction time is also enhanced with the sieved material. This obeys to the fact that smaller particles react more effectively (higher specific surface) and because non-reactive portlandite has been previously eliminated.

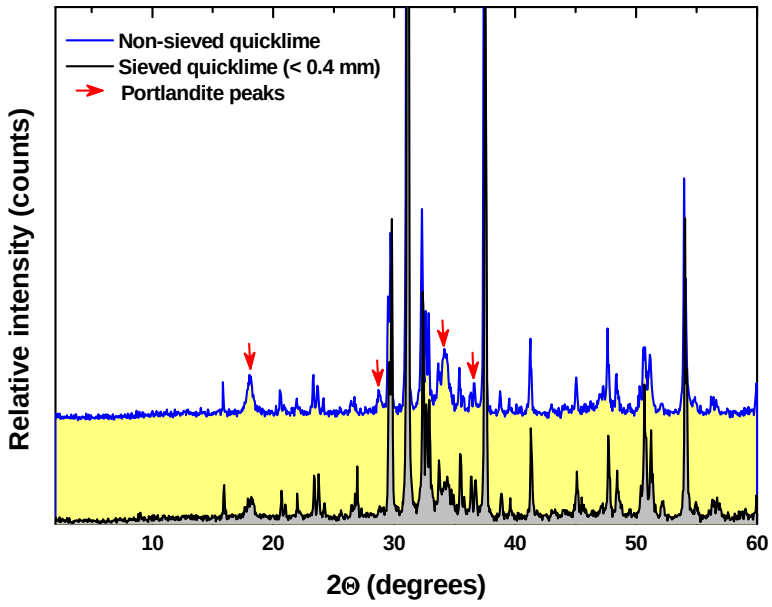


Figure 4. X-ray diffractograms of a raw sample of commercial quicklime (non-sieved) and sieved to a grain size smaller than 0.4 mm. Typical mineralogy include lime, dolomite and dicalcium silicate (Ca_2SiO_4). Arrows point towards the portlandite ($Ca(OH)_2$) in the non-sieved quicklime material

Experimental Techniques

The characterization of the waste included the determination of mineralogy, composition and physical properties. Thus a complete series of experimental techniques have been applied. They include X-ray diffraction (DRX), X-ray fluorescence (FRX), electron microscopy (SEM-EDS), thermogravimetry coupled to thermal differential analyses and the infrared spectroscopy of released gases (TDA-TG+FTIR), BET specific surface, elemental analyses, density, moisture content, and batch-leaching tests). In addition, stabilized products were assayed following conventional geotechnical tests (compaction, consolidation, direct shear and CBR). Not all the samples were analyzed for the complete panoply of tests and, because some of them are still on going, in the present paper illustrate only a part of the results obtained.

The mineralogical characterization was performed over pulverized, dry-grounded samples (<50 μm) and a SIEMENS D5000 X-ray diffractometer scanning a 2Θ angle between

2 and 60º, steps of 0.05º and 2.5 seconds for data acquisition. Wavelength employed was Cu-K_α (1.54 Å) and graphite monochromator. Characteristics related to the shape of particles were identified with the aid of a JEOL JSM-6400 scanning electron microscope.

For the simultaneous determination of TDA and TG we employed a TA Instruments SDT 2960 analyzer. Samples were analyzed inside alumina furnaces under oxic (i.e. air) and non-oxic conditions (N_2). The programmed heating ramp, up to 1050 K, was of 5 K min^{-1}. For selected samples, the gases released were collected and transferred to a BRUKER VECTOR 22 infrared spectrophotometer for their identification.

Specific surfaces were determined with N_2 through the BET technique (Brunauer et al., 1938) using a Thermo Finnigan SORPTOMATIC 1990 system for 20 hours per sample.

Each one of the stabilized products and the Prestige's fuel itself was tested against conventional batch-leaching assays (UNE-EN 12457-2, 2003). The corresponding eluates where filtered with a MILLEX HN sieve of 0.45 μm and then analyzed with an ICP-MS VGElemental, Quadrupolar PlasmaQuad-II S-option model.

Table 3 shows a relation of the relevant UNE-EN European standards used in order to obtain corresponding geotechnical parameters of interest of the stabilized products. It must be acknowledged that, due to the intrinsic characteristics of the stabilized products –that cannot be considered in many ways as a typical soil– some of the geotechnical assays performed had to be modified according to the reasons explained in the following sections.

Parameter	UNE-EN standard	Parameter	UNE-EN standard
Moisture content	103300 (1993)	CBR	103502 (1995)
Modified Proctor test	103501 (1994)	Direct shear test	103401 (1998)
Standard Proctor test	103500 (1994)	Consolidation	103405 (1994)

Table 2. UNE-EN European standards used in the determination of selected properties and parameters of the granite fines studied in this work. CBR stands for California Bearing Ratio

For the consolidation tests, we used a battery of oedometric frames able to attain maximum normal loads of up to 1800 kPa. Vertical displacements were monitored with the aid of a data acquisition system (DAS) that recorded the signal of a series of Linear Variable Displacement Transducers (LVDT). The loading/unloading path for the consolidation tests

was 80:150:300:600:1000/600:150 kPa and each load actuated for no less than 24 h. Due to the nature and origin of the material, all the samples –cylindrical, with 50 mm diameter and 20 mm height– were dry-remolded.

Direct shear tests were performed with a shear box able to attain up to 400 kPa normal stress. Each sample that, like in the rest of the assays performed was dry-remolded, was submitted to normal loads of 100, 200 and 300 kPa. After performing a series of preliminary tests and the analysis of the corresponding results, a shear rate of 0.25 mm min^{-1} was decided to be adequate for the stabilized waste. Horizontal and vertical displacements were recorded with a DAS associated to a couple of LVDTs that monitored the sample along each test.

Mixing Protocol

All the mixtures have been performed on a hand-made basis. However, due to the different amounts of materials (waste and stabilizers) needed in the case of fuel-rich and fuel-poor wastes, scaled tools (trowel or showel, drawer or conditioned floor, …) need to be employed. Figure 5 shows the typical starting point of the mixtures performed with the fuel-rich fraction of the waste.

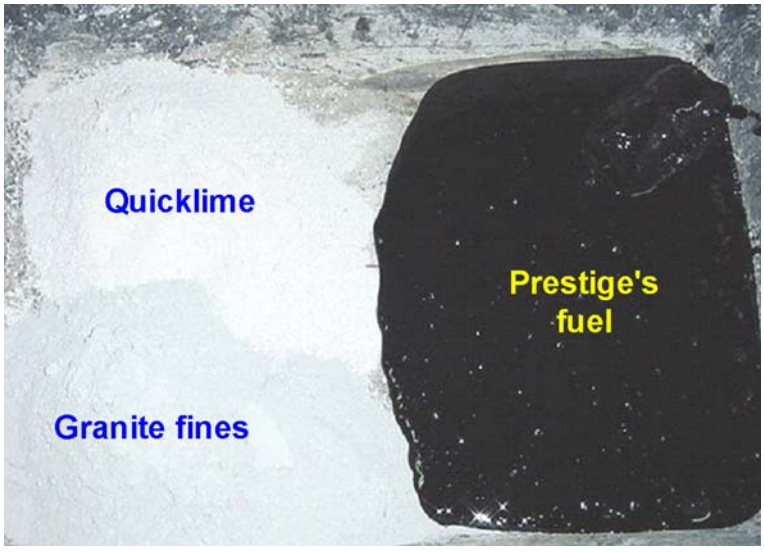


Figure 5. Stabilizing agents and *Prestige's* fuel prior to manual mixing in a drawer. The length of the picture represents the ~50 cm of the bottom of the drawer

For each mixing batch, the different materials (stabilizers and fuel) were gently kneaded for a time that ranged from 15 to 30 minutes. Then, the product was left to seat for, at least, 2 to 3 additional hours and the appearance, eventual transformations and any other

relevant aspect was conveniently recorded for ulterior analyses. Figure 6 illustrates the transformation of the fuel-rich-waste into an earth-like material typical of the stabilized products obtained in the study.

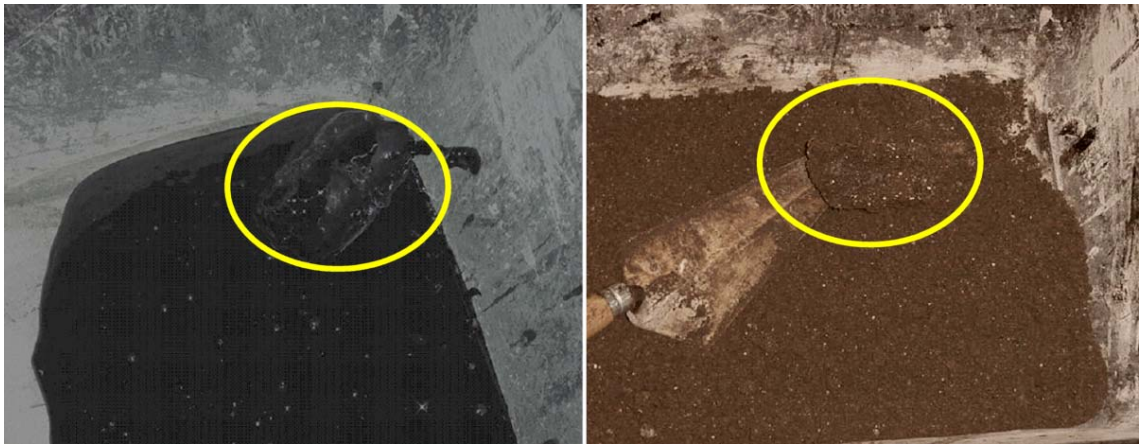


Figure 6. Result of the stabilization process with quicklime and granite fines. On the left, observe a large particle of oily EPS (expanded polyestirene) and its easy manipulation and separation upon stabilization (right picture). The size of the trowel blade is 20 cm.

Results

Figure 7 presents in a triangular coordinate diagram the different fuel/quicklime/granite fines dosifications used in our study. The grey-shaded areas of the plot have been identified as cost-excessive and non-feasible mixtures. Such a categorization is based on the consideration that a low-fuel content stabilized material (i.e. less than 30 % waste) would demand a large amount of stabilizers and will produce a big amount of stabilized material that needs to be managed. Under these circumstances, the costs associated to such a stabilization procedure are expected to be high. In turn, according to our experience, it is very difficult to mix more than 50 % fuel with the stabilizers and to get an acceptable stabilized product. Thus, we have determined that our technical upper fuel dosification limit stands around that value. Although our categories are based in a very broad criteria, we believe that they might be important as an aid to keep in mind the multiple scales of the processes involved in the stabilization of the wastes (environmental, economical, societal, etc.).

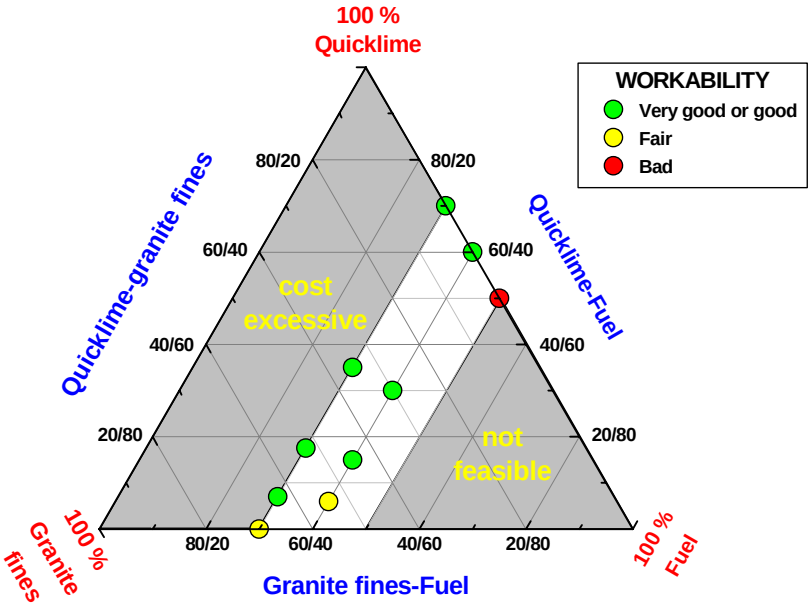


Figure 7. Triangular diagram showing different proportions of fuel, granite fines and quicklime used in the stabilization tests. Workability in terms of that explained in table 3.

The appearance of stabilized waste is of that of an earth-like, granulated material of variable color. This typically is a function of the dosifications and when they have higher fuel contents they also have a darker color. In general, all of them range from dark to light brown (Figure 8) and, in some cases, we have detected a turn into lighter tonalities as a function of time. All the samples smell due to the presence of hydrocarbons although odor is not a striking feature of the stabilized waste.



Figure 8. General appearance of different stabilized materials.

The touch of the stabilized product mainly depends on the proportions of stabilizers. The more dusty material has a touch that, in contrast to silty/clayey soils, is a little bit sticky and persists in the fingers even thought their water content is low (Table 5). In fact, one of the striking features of all the stabilized materials is that they are hydrophobic. This behavior constrains its geotechnical characterization as far as many of the standard tests have been designed to run under moist or saturated conditions. Hence, aspects like soil classification based on Atterberg limits, standard or modified Proctor tests, saturated bearing capacity (CBR) or the consolidation behavior under saturated conditions cannot be performed or need to be adapted. Moreover, conventional mechanical sieving is non-efficient for the smaller pore sizes as far as they tend to clog due to the adherence of particles.

Sample	% Fuel	% Quicklime	% Granite fines	Workability	Comment
M1	30	70	0	Very good	Fine grained and brown dust after ~2 h. Sticky mass before
M2	40	60	0	Good	Earth-like, dark aspect after ~2 h. Sticky mass before
M3	30	17.5	52.5	Very good	Similar to M2
M4	30	35	35	Very good	Similar to M1 but not sticky after kneading. Grain size < 5 mm
M5	30	7	63	Good	Dry earth-like, dark aspect. Lumps of fuel and granite fines develop
M6	40	30	30	Good	After kneading, lumps of 10-50 mm are present. After 3-5 h, the appearance is dark earth-like
M7	30	35	35	Very good	Color is clearer than for the rest of mixtures. Dry earth-like, dusty material in ~2 h. higher sand content
M8	30	35	35	Very good	Color is clearer than for the rest of mixtures (light grey). Dry earth-like, dusty material in ~2 h. Higher sand content and includes a wide variety of material other than fuel that can be easily screened
M9	50	50	0	Bad	For up to 2-3 months, sticky and plastic mass. Then transforms into a lumpy clay-like material
M10	30	0	70	Fair	After kneading, lumps of 20-70 mm develop. After ~15 days air exposure they become loose and crumble in the fingers
M11	40	15	45	Good	After kneading, lumps of 20-100 mm remain for up to 5 days. After that, lumps may be crumbled with the fingers to a grain size of 0-10 mm

Table 3. General description and characteristics of the stabilized materials. We relate workability to the capacity of the stabilized product to develop an earth-like, dusty aspect amenable of eventual reuse or easy land filling

Table 3 summarizes the most relevant aspects relative to the description of the stabilized products find using quicklime and granite fines as stabilizer agents. It is interesting to observe that many mixtures change their texture after setting for a variable period of time.

The most typical transformation is the change from a sticky mass into an earth-like, dusty material that remembers in several aspects a natural soil. However, as we will show later, the stabilized product cannot be considered as a natural soil. Depending on the nature of the mixture, setting times may vary from a few hours (~2) to several weeks (> 8).

On the other hand, stabilization products can be divided into three major categories: dusty, lumpy and sticky (Table 4). This is important as far as depending on that, their use as concrete addition might be compromised (Carro et al., 2005). Furthermore, the sticky product might be more difficult to compact for land filling.

Category/Type	Mixtures	Summary and Purpose
1	M1, M3, M4, M7, M8	After 2-5 h reaction time a dusty material develops which is amenable of screening in order to separate particles larger than ~1 cm in diameter. Used as an addition to mortar/concrete waste recycling
2	M2, M5, M6	After 2-5 h reaction time a lumpy material develops which is amenable of screening in order to separate any particle larger than ~5 cm in diameter. They can be used to separate the different types of waste materials (plastic, tools, pebbles, wood,...)
3	M9, M10, M11	After 5-60 days of reaction time, lumps formed may be easily crumbled. Amenable of landfill disposal

Table 4. Categories of stabilized waste, attending to their general characteristics, behavior and eventual uses given in our research

It is interesting to observe that stabilization with the products considered in our study makes possible the separation of the different types of materials present in the waste mélange. We have seen that, once passed the setting time of the mixture –type 1 products–, the major part of extraneous elements can be collected by hand and stored for ulterior classification/ treatment. The separation process is enhanced by the presence of granite fines. This is an added value to their use in the stabilization process. The separation is so effective that some elements (in particular plastic pieces) appear clean and free of fuel. This is of the greatest importance because it would be easy –and cost effective– to set up a screening system by which separate the fuel-rich, stabilized fraction from the non-fuel, water-free fraction.

The hydrophobicity of the stabilized material makes not possible to measure the specific gravity of their solid particles by pycnometry with water and this fluid was replaced by alcohol and acetone in the determinations. It is acknowledged that both liquids may dissolve to some extent the hydrocarbons of the fuel. However, its heavy nature and the short

contact time between the liquid and waste allow us to make an acceptable estimate of the specific gravity of each stabilized material.

	M1	M2	M3	M4	M5	M6	M7	M8
ω (%)	0.15	0.38	2.04	1.08	15.7	1.02	-	-
ρ_s	1.98	2.32	2.09	2.05	2.07	1.96	2.11	2.11
C_C	0.27	0.37	0.43	0.53	0.34	0.47	0.28	0.22
C_S	-4.6E-04	2.0E-02	5.4E-03	6.2E-03	2.0E-03	-1.0E-03	-1.5E-03	-9.8E-04
E_m	7.94	5.02	4.17	3.31	4.7	4.08	5.04	7.71
m_V	0.19	0.33	0.35	0.48	0.3	0.41	0.25	0.17
ϕ	32	34	32	32	31	30	32	32
c'	19	0	14	14	17	25	28	24
% fuel	30	40	30	30	30	40	30	30
% quicklime	70	60	17.5	35	7	30	35	35
% granite fines	0	0	52.5	35	63	30	35	35

Table 5. Summary of relevant geotechnical parameters (average values): Moisture content (ω), in weight %; solid density (ρ_S), in Mg m^{-3}; compression index (C_C); swelling index (C_S); edometric module (E_m), in MPa; index of volumetric compressibility (m_V), in MPa^{-1}; ϕ: friction angle, in degrees; c': cohesion, in kPa

Table 5 summarizes the most significant results obtained from the preliminary geotechnical survey. It is interesting to observe that there is some sort of relationship between moisture content and the proportion of quicklime and granite fines (Fig. 9) by which, the greater the amount of granite fines, the greater moisture content of the product. With respect to quicklime, the opposite is observed.

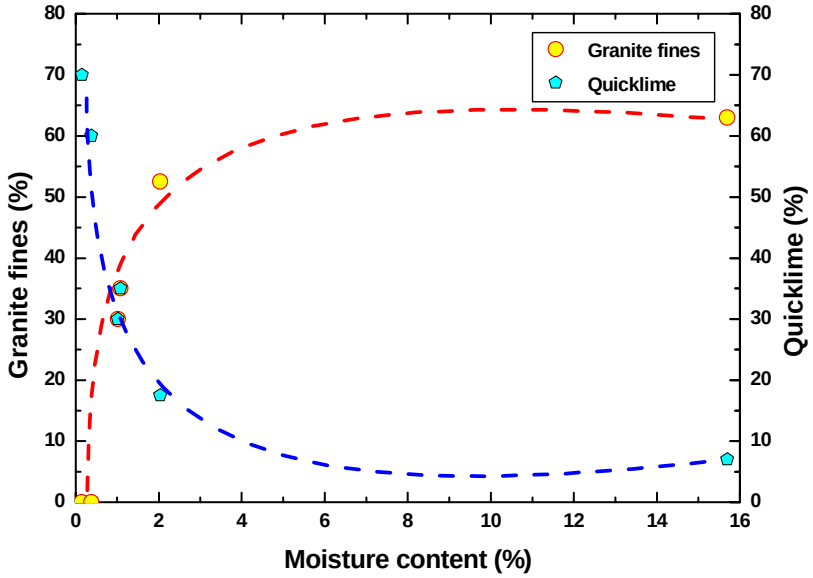


Figure 9. Moisture content (in weight %) of the stabilized materials M1 to M6, as a function of the amount of quicklime and granite fines. Note that higher moisture contents are obtained for the samples with higher proportion of granite fines.

This tendency might be explained by the fact that the fuel-rich fraction employed in the stabilization tests is, in fact, an emulsion of seawater and fuel. When this is mixed with quicklime, water hydrates lime (giving pass to portlandite) and, in part, evaporates attending to the highly exothermic nature of the lime hydration reaction. Thus, according to the data provided by CALCINOR, temperatures may be raised to more than 70 ºC within 10 minutes of reaction with the waste. When more granite fines are added replacing quicklime, kneading temperatures become smaller and, depending on the amount of water present, there might be not enough quicklime to exhaust it (via hydration or evaporation).

The results of the oedometric assays are presented in Table 5 and figures 10, 11 and 12. On the other hand, figure 13 shows a typical picture of a test sample after performing a consolidations assay. It is interesting to note that, for all the samples studied, the virgin consolidation line is nearly the same and that, upon unloading, there is no significant change of volume.

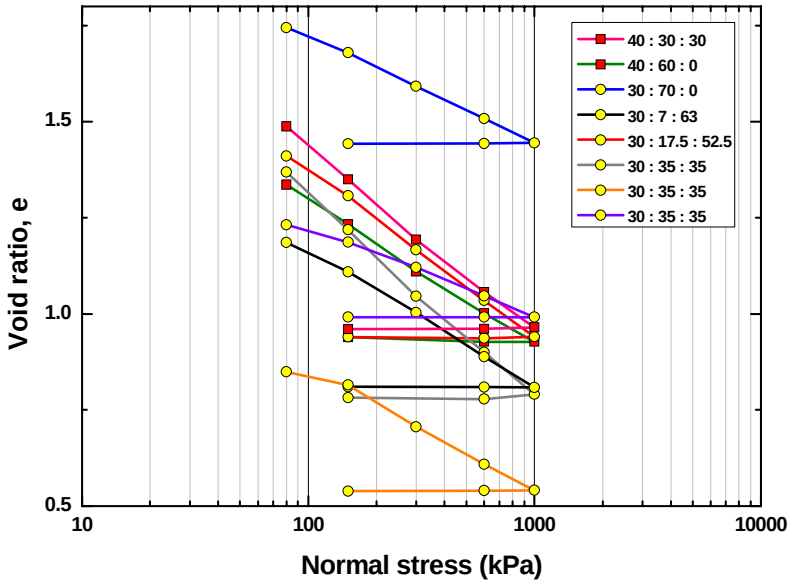


Figure 10. Change of the void ratio with respect the logarithm of the normal stress applied.

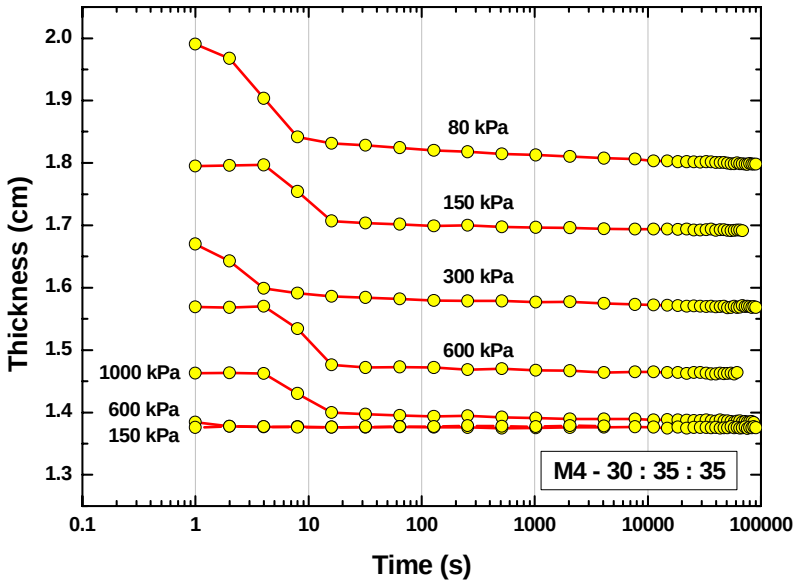


Figure 11. Typical consolidation curves of the M4-type material (30 % fuel). Note that fast reduction of volume at the beginning of the loading step and the virtual absence of swelling along the unloading steps.

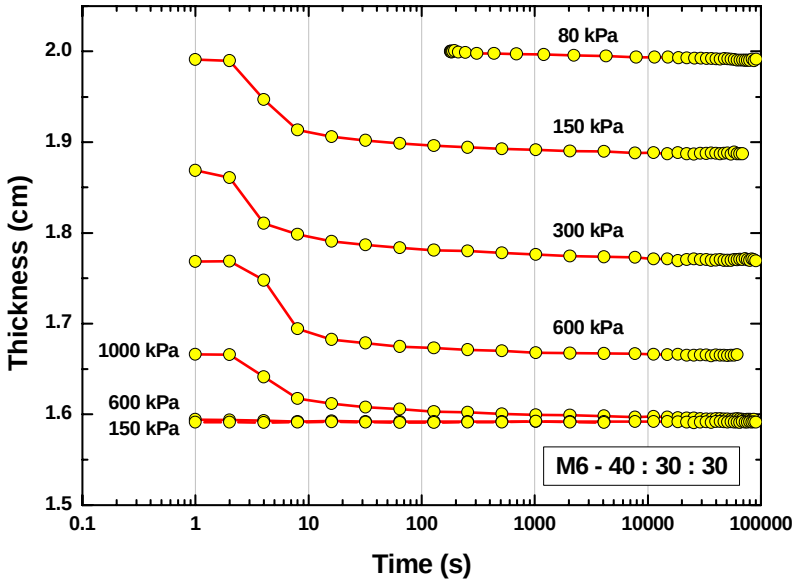


Figure 12. Typical consolidation curves of the M6-type material (40 % fuel). Note that fast reduction of volume at the beginning of the loading step and the virtual absence of swelling along the unloading steps.

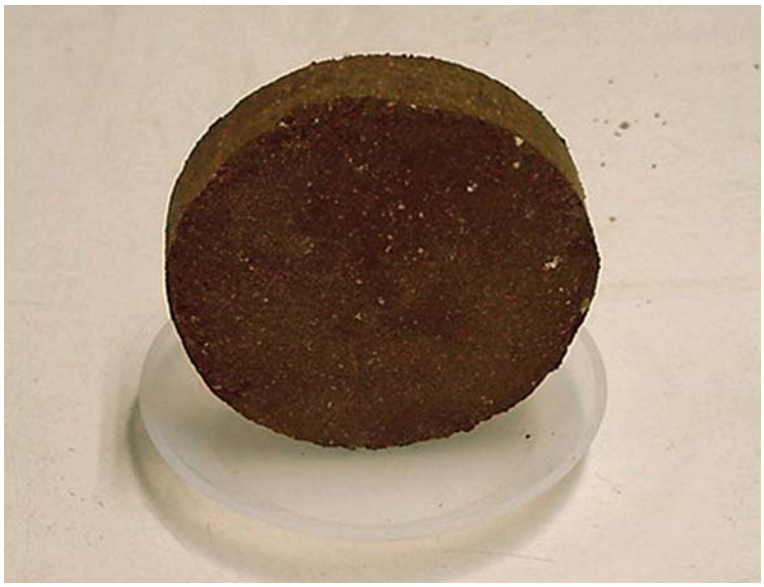


Figure 13. Sample of stabilized waste (fuel-rich fraction) after completing an oedometer test

The shape of the consolidation curves conforms to the ones typical of many soils. However, it must be stressed that, in contrast to the typical geotechnical determination, our load/unload sequence was performed in the absence of water. Hence, the apparent fast consolidation of the material appearing in figures 11 and 12 (which are representative of all the samples) obeys to the fact that, in contrast to the well established consolidation theory, when loading, there would not be an increase in pore water pressures and the concomitant volume reduction due to their dissipation.

Although pore water pressures are not determinant in the consolidation behavior of the stabilized material, it is not clear in the change in void ratio occurs as a result of particle re-organization or due to the deformation of the "solid" skeleton of the material. Hence, if we assume that the stabilized waste is conformed by drops of a more or less fluid fuel encapsulated by a mineral, non-cohesive, carapace, we should expect that when the sample is loaded, deformation will occur at the expenses of porosity.

The maximum normal stress applied to the test samples was 1000 kPa. This is a practical upper limit considering that waste managers consider the possibility of land filling with a maximum thickness equivalent to a normal stress of less than the 1000 kPa of our tests.

Figures 14 and 15 show some results related to the direct shear tests performed with the products of waste stabilization. All the samples analyzed how a consistent slope in a hear stress vs. normal stress plot.

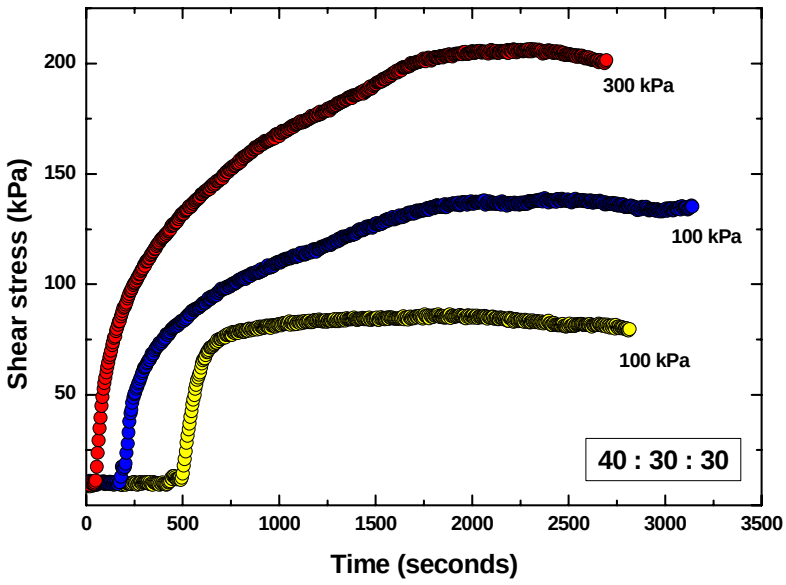


Figure 14. Representative shear stress v. time plot corresponding to sample M6 for three different normal stresses (100, 200 and 300 kPa)

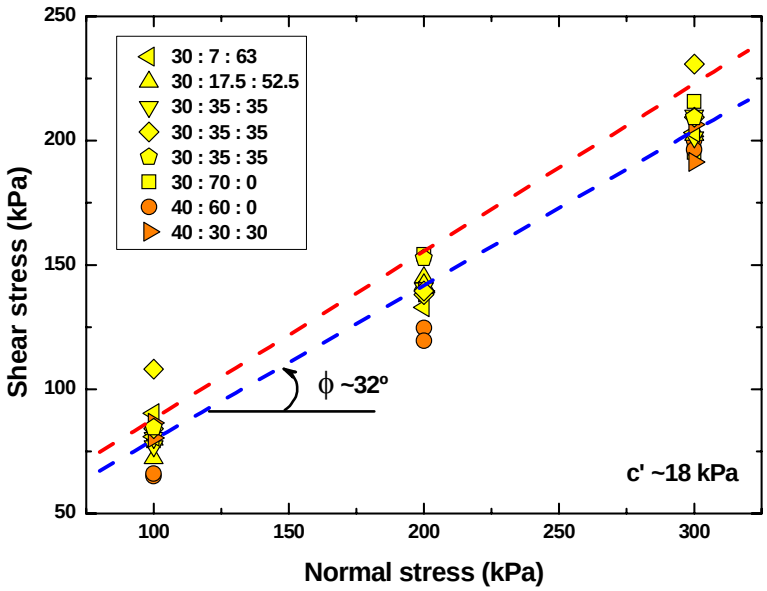


Figure 15. Results of the direct shear tests performed. In the plot, shear stress vs. normal stress for the eight samples tested. The average friction angle is ~32º while average cohesion is ~18 kPa. Note that lower cohesions are obtained for mixtures with the higher fuel content (orange symbols). Blue dashed line represents an average fit to the experimental data. Red dashed line represents the behaviour of pure granite fines.

The friction angle of the studied materials is ~32º, a value typical of many soils and, in particular, virtually identical to the one associated to pure granite fines (Barrientos et al., 2004). On the other hand, the average cohesion is small (~18 kPa) although there is a clear affinity in the way that those materials with the higher fuel content tend to have lower values of cohesion than in the opposite case.

Figures 16 and 17 represent the results obtained in the compaction tests performed applying compaction energy and following an experimental procedure analogue to the standard Proctor test. As we mentioned before, the hydrophobicity of the stabilized products prevent their kneading with water. However, because we have used different dosifications of fuel, quicklime and granite fines, it is possible to asses the compaction behavior or the material attending to the relative amount of the different stabilizers. The results show that there is a general trend in the samples that remembers the shape of typical compaction curves (dashed blue line). However, samples M7 and M8 (grey symbols) are clearly out of the tendency. It is interesting to observe, however, that, in contrast to samples M1 to M6, which are based on the fuel-rich fraction of the waste, samples M7 and M8 have been made with the raw, non-fuel rich waste.

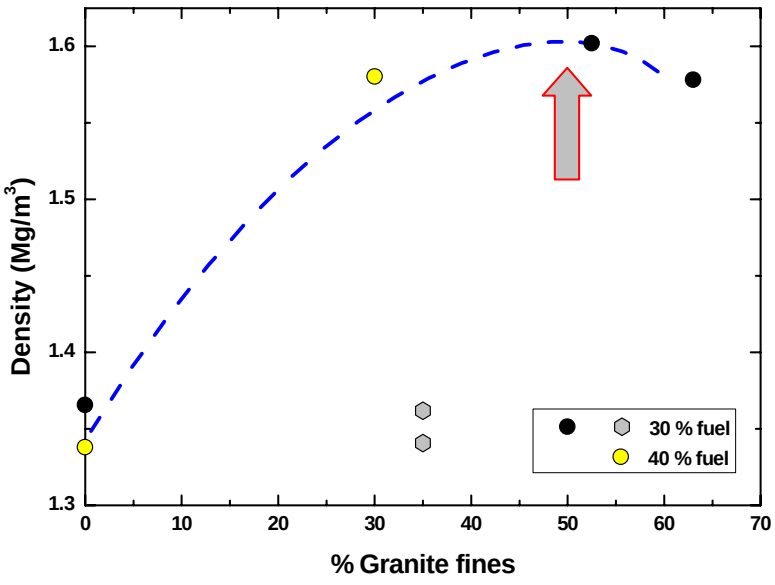


Figure 16. Dry-density vs. the % of granite fines in some of the stabilized products assayed. Black and grey points correspond to samples with 30 % fuel while the yellow ones have 40 %. Samples associated to grey symbols have a higher sand content (what is typical of the raw waste) and this lowers the associated dry density upon compaction. Arrow indicates, from the compaction point of view, optimal proportions.

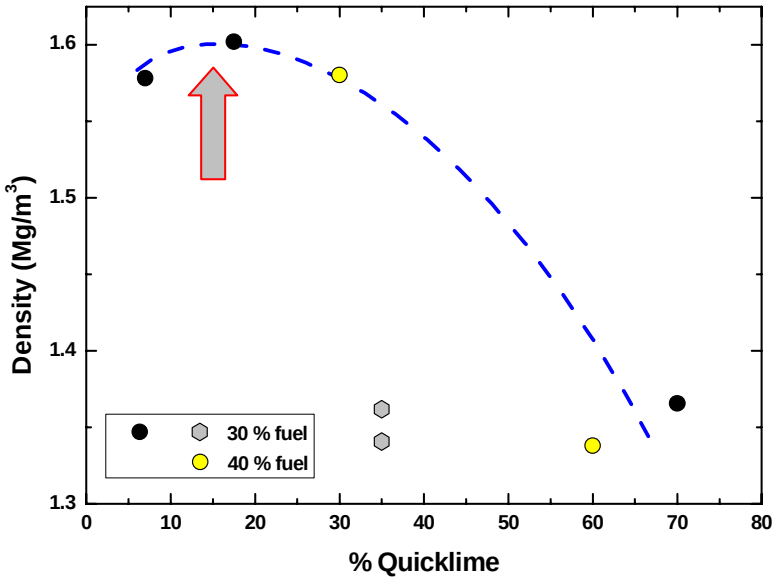


Figure 17. Figure complementary to figure 16 where dry-density is plotted against the % of quicklime. Arrow indicates, from the compaction point of view, optimal proportions

Thus, because the more sandy nature of these last materials, the maximum attainable dry density is smaller than for the rest of samples and are, therefore, not comparable.

The grey arrows drawn in figures 15 and 16 illustrate the optimum amount of quicklime and granite fines in order to achieve the highest compaction level, according to the compaction energy supplied in our tests. These preliminary values appear to be about 50 % granite fines, 15 % quicklime and 35 % fuel. It must be stressed, however, that the raw waste may have a different behavior and more data is still needed.

It is interesting to note that the optimum compaction is related with higher granite fines content. In turn, high contents of granite fines are associated to higher water contents. Therefore, we speculate that higher moisture contents and the hydrophobic nature of the waste may cooperate in order to obtain a better package when compacted.

Table 6 and figure 18 shows the preliminary and partial results of dry CBR tests performed with the waste stabilized products. They indicate that, when comparing quicklime-rich and granite fines-rich mixtures, the higher bearing capacities are associated to the first one. Such a behavior may be related to the nature of fuel/stabilizer interaction. Thus, in the

case of quicklime, the stabilization reaction would be associated to its chemical reactivity (hydration of lime and heat release associated to the pozzolanic reaction) while in the case of granite fines would be related to surface interactions. Apart from that, although more data is on the course of elaboration, the results presumably illustrate the extreme behaviors of the stabilization products which appear to be, in any case, acceptable for earth embankments and land filling.

Sample	% Fuel	% Quicklime	% Granite fines	# Blows	Dry density (Mg/m^3)	$CBR_{2.5}$ (%)	$CBR_{5.0}$ (%)
1	30	70	0	60	1.44	60	55
				30	1.42	55	52
				15	1.32	23	15
5	30	7	63	60	1.91	11	13
				30	1.91	21	25
				15	1.69	20	19

Table 6. Partial results of CBR tests performed with fuel stabilized products. $CBR_{2.5}$ and $CBR_{5.0}$ correspond to the standard 2.5 and 5.0 mm punch penetration of the CBR test. 1 blow is equivalent to a compaction energy of 26.5 kJ m^{-3} supplied by a modified Proctor rammer of 4.54 kg falling from an height of 457 mm



Figure 18. Sample of stabilized waste (M5-type) after performing a CBR test

Table 7 shows the results of batch-leaching tests performed with some of the stabilization products of the fuel-rich waste. They are compared in the same table with the reference values given by the existing European Union directives. We can see that any element or parameter surpass the maximum concentrations established even for inert wastes.

These important results inform us on the efficiency of the stabilization process, at least for a waste with the characteristics of the fuel of the *Prestige's* tanker.

	M1	M2	M3	M4	M5	M6	Inert waste	Non-dangerous waste
pH	11.94	12.26	11.82	11.79	11.98	11.83	-	> 6
Conductivity	8.69	8.95	7.85	8.11	5.56	8.80	-	-
As	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.5	2
Ba	6.93	4.48	0.99	1.48	0.73	1.27	20	100
Cd	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	1
Cr	0.15	0.19	<0.15	<0.15	<0.15	<0.15	0.5	10
Cu	0.06	0.07	<0.02	<0.02	0.06	0.04	2	50
Hg	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.01	0.2
Mo	0.02	0.03	0.16	0.04	0.15	0.08	0.5	10
Ni	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	10
Pb	0.46	0.45	0.07	0.21	0.03	0.16	0.5	10
Sb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.06	0.7
Se	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.1	0.5
V	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	-	-
Zn	0.3	0.34	<0.2	<0.2	<0.2	<0.2	4	50
F^-	14.4	15.7	12.4	10.9	10.9	15.9	10	150
Cl^-	3277	3311	3544	1756	3230	4391	800	15000
SO_4^{2-}	88.1	129	94.1	122	31.6	83.3	1000	20000

Table 7. Results of UNE-EN 12457-2 leaching tests performed with a selection of the products of fuel stabilization. All the components are given in mg/kg of dry material; Conductivity in mS cm^{-1}. Reference values for inert waste and non-dangerous wastes (L/S = 10 L /kg) correspond to the Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste and the Council Decision 2003/33/CE of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills

Summary and Conclusions

Our experiments show that it is possible to transform the waste into a dry and fine grained material amenable of compaction using conventional machinery. Moreover, the properties of the mixture enhances the separation of extraneous materials (plastic, etc.) what is of great aid in the waste classification scheme. In order to identify the most relevant geotechnical properties of the stabilized fuel, we have performed a series of tests including density, shear strength, compaction, consolidation and CBR. In addition, a series of batch-leaching tests (EN 12457) have been addressed to identify the environmental hazard that the stabilized fuel represents to the environment.

The results obtained so far indicate that fuel stabilized with the adequate proportions of quicklime and granite fines develop an acceptable geotechnical behavior that allows it to be disposed and compacted in earth fill and embankments without the need of high-performance low-permeability barriers.

It is not clear, at present, the nature of the stabilization reactions happening among fuel, quicklime and granite fines. Although the effectiveness of the stabilization with quicklime is not a matter of debate, it would be interesting to address if stabilization mechanisms imply the encapsulation of fuel drops or if there is some sort of reaction-enhanced phase transformation in the fuel by which this fluid transforms into a solid-like material. In the same way, the intrinsic nature of the stabilization with quicklime (pozzolanic reaction and encapsulation) and granite fines (surface reaction) needs to be addressed.

Synergy of quicklime with granite fines cooperates positively in the stabilization process. Hence, the use of that stabilizer: a) result in better separation of extraneous materials from the raw waste than when using only quicklime; b) provides higher densities upon compaction; c) reduces costs associated with the use of commercial quicklime; d) takes advantage of an inert waste generated by the local dimension stone industry. Within the context of the design of future contingency plans against oil spills in Galicia, taking into account the positive contribution of granite fines to the management of oily wastes, we suggest their use as a liner material in temporary trenches at or near the shores.

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