Solidification/Stabilization of Refinery Sludge in a Pozzolan-Cemented Clay Matrix

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A project involved solidification/stabilization of a hydrocarbon sludge in a silty clay matrix cemented with a pozzolanic lime-fly ash admixture. The compactable mixture can harden as a dimensionally stable landfill monolith that minimizes contaminant mobility. The solidification/stabilization product has more than 50 percent porosity to contain the sludge in the available airspace. This limits the strength to that of a firm cohesive soil, and mass behavior is evaluated by traditional geotechnical methods. Customary influences on fine soil permeability apply as well, with compactive effort alone affecting results over a range from 10^{-5} to 10^{-7} cm/sec. The solidification/stabilization process retards hydrocarbon mobilization primarily by physical microencapsulation. Less than 5 percent of the carbon was mobilized in 10-pore volumes of throughput in column leaching tests. This solidification/stabilization method appears to be suitable to allow reuse of the surface for industrial purposes as long as cap integrity is maintained. Consequently, the potential use of cemented clay solidification/stabilization for hydrocarbon-contaminated soils in highway rights of way is also indicated.

Many highway projects encounter soil contaminated with petroleum products in the right of way. Time and land use constraints often limit in situ remediation options, so excavation and offsite landfilling is a common solution even though only a fraction of the mass is the contaminant, and excavated soil must be replaced. An alternative method combines traditional soil stabilization with additives (*1*) and waste solidification/stabilization (S/S) methods (*2*), for treatment and redeposition under the roadway, as shown in Figure 1. S/S processes can be optimized for mechanical properties and the pavement section performs the same functions as a landfill cap: isolation of its subgrade from the surface environment.

S/S often uses cements and inexpensive byproducts as reactants to mechanically improve waste materials and immobilize contaminants (*2–4*). However, S/S may appear to be inappropriate for organic materials because they often interfere with hydration (*5*). Also, regulations often specify arbitrary values of material properties such as an unconfined compressive strength of 340 kN/m^2 or 50 psi (*6,7*), but lower strengths are certainly capable of bearing loads.

Treatment and onsite redeposition in capped landfill monoliths can be thought of as an extreme case of an organic conventional highway subgrade stabilization. Ground modification to meet deformation criteria for pavements is similar to providing mechanical support to maintain the integrity of the landfill cap. Analysis of the S/S product response to the in situ environment is the appropriate approach (*8*). Cap surfaces settle and distort because of post-closure compression of the treated waste, which depends on both the gravity (self-weight) loads and the material compressibility, shown conceptually in Figure 2.

PROJECT DESCRIPTION

Acidic hydrocarbon sludges from petroleum processing have been stored in lagoons for several decades. Although little impact has been detected, permanent disposal was desired. Studies indicated that recycling, biodegradation, incineration, or offsite disposal were all unfeasible for technical, economic, or social impact reasons. S/S and onsite landfill deposition was seen as a viable alternative. A potential additional benefit is that the former lagoon "footprints" could be reclaimed for light industrial use.

Sequential pit-by-pit remediation was desired to allow adjustments to variations in sludge consistency variations, and to preserve the existing surface drainage system. The "air space" above the sludge surface in each lagoon is roughly equal to the sludge volume, so a maximum volumetric swell of 100 percent is allowed. Assuming that the sludge would be encapsulated without contributing to mechanical strength, this can be expressed as a requirement that the S/S product have an oil-filled volumetric fraction of at least 50 percent.

In a laboratory investigation, S/S with portland cement or lime-fly ash mixtures (*4*) at this porosity gave unsatisfactory results, barely meeting self-support and freely expelling the sludge liquid. Codisposal of the sludge with a very plastic spent clay (absorbent from refining operations) showed promising results, but the spent clay was difficult to handle. With the feasibility of using a fine-grained soil "skeleton" to encapsulate the sludge, S/S with the local clayey silt and a pozzolanic lime-fly ash additive was studied. Hardened samples display self-support, low permeability and favorable leaching results. The geotechnical properties of the stabilized mixture are comparable to that of a compacted clayey silt, so it is inferred that the admixture compensates for weakening effects of remolding and high porosity. Optimization of the proportioning, mixing method, and deposition technique is described elsewhere (*8–10*).

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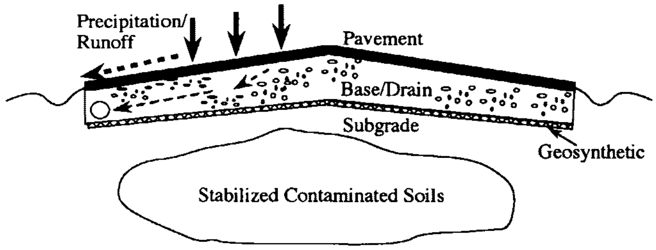

FIGURE 1 Treated soil burial under subgrade.

Monolith Performance

The ultimate goal of the stabilization component of S/S is to minimize transport of contaminants from the deposited mass. Contaminant movement requires three elements:

1. The contaminant must be mobile, in erodible particle, vapor, free liquid, or solute form;
2. There must be a pathway for movement; and
3. There must be a gradient to induce and sustain transport.

The engineering problem is to restrict these elements by a combination of S/S and external containment. The latter, as in conventional landfills, isolates the mass from surrounding surface and subsurface environments. The solidification component of S/S, especially the pore structure microencapsulation, restricts internal transport by mechanical means (i.e., it fosters resistance to deterioration, distortion, and seepage effects of the internal mechanical, hydraulic, and biochemical environment shown in Figure 2).

The internal pathway for seepage advection is often indexed by the saturated permeability. If the deposit is unsaturated, the effective permeability to liquids is lower still, but the ease of vapor movement is increased. Optimization of pathway restriction might involve having a degree of saturation in which the pair pores are occluded.

Some transport restrictions cannot be affected by S/S. It does not restrict hydraulic gradients, so the cap must shed rainfall to keep infiltration and seepage gradients intermittent and limited. Concentration gradients driving diffusion are not controllable at all. Other concerns such as durability and erodability are problematical, as a cemented oily clay does not resist freeze-thaw or wet-dry cycling or erosion. A thick, impermeable cap is necessary for climatic isolation. Matrix deterioration by biodegradation was not studied, although restriction of oxygen penetration and a high pH should retard aerobic activity.

Slope stability and bearing capacity (for vehicles) analyses show generous factors for safety at unconfined compressive strengths well below 100 kN/m^2 (15 psi). Consolidation indexes are the more relevant mechanical properties. For the site monoliths up to 15 m thick, the maximum overburden pressure anticipated is about 250 kN/m^2. The strain in the lower portion (Figure 2) caused by primary consolidation is computed to be about 5 to 6 percent. A similar amount of secondary consolidation over 50 years is expected (*11*). It is also desirable that the mixture be unsaturated to complete primary consolidation before cap installation and to minimize liquid expulsion.

Materials

Sludge

The sludge was deposited over several decades, during which there were process changes and ongoing volatilization and separation of the heavier fractions, resulting in variations in sludge composition and consistency between lagoons. An analysis of the sludge from the freshest, least viscous deposit (used in this S/S study) was conducted in 1987, with results for general characterization only. The sludge is primarily long-chain aliphatics, as expected with the residue from processing crude oil into lubricants. Constituents classified at that time as hazardous volatiles (boiling point <100°C) were not detected above the micrograms/liter (ppb) range. Sulfur, semivolatile and nonvolatile hazardous constituents are present up to several hundred ppm.

The studied sludge has a consistency of a slow-curing asphalt, an ash content of 4.5 percent and a total organic carbon

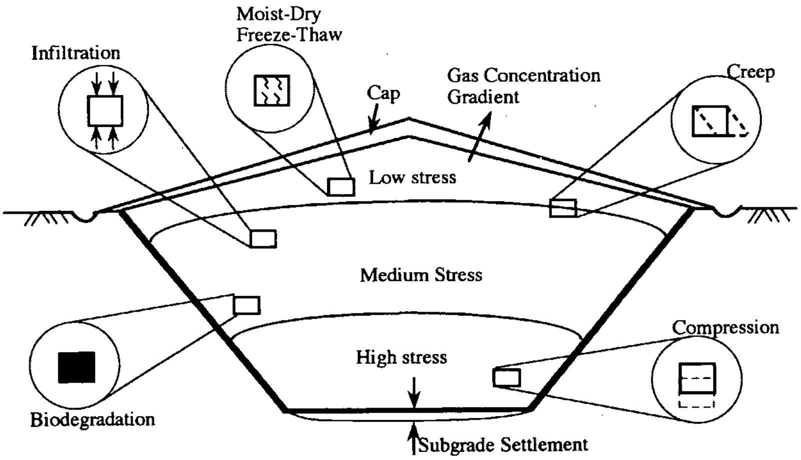

FIGURE 2 Internal and boundary stress environment of a landfill.

content of 35.3 percent. The sludge was divided into "solid" and "liquid" portions, based on the loss from a mixture oven-dried at 105°C for 24 hr.

Silty Clay

The onsite clayey silt is derived from weathering on the gneiss bedrock. X-ray diffraction tests indicate that kaolinite is the predominant clay mineral. The cation exchange capacity was measured at 49 meq/100gm and specific gravity was 2.72. Other indexes include a liquid limit of 31 percent and a plasticity index of 11, 86 percent fines and 8 percent clay-sized material. The soil is classified as ML by the Unified system. The Standard Proctor maximum dry unit weight is 17.3 kN/m^3, with an optimum moisture content of 16 percent.

The natural soil exists in loamy peds or aggregations, but is readily pulverized. An array of structures can be formed, depending on compaction effort and moisture content. As the clayey silt is the skeleton of the S/S product, its hydraulic and mechanical properties indicate the expected values of the final solidified product. Undisturbed samples tested in a flex-wall permeameter at low confining stresses had a permeability of 4.5×10^{-5} cm/sec, and the natural structure displayed high compressibility. Compaction at 90 percent standard proctor unit weight, slightly wet of the optimum moisture content, reduced the permeability to 3×10^{-8} cm/sec. One-dimensional compression tests on the compacted samples showed a compression index (C_c) of 0.20 and a recompression index (C_r) of 0.04. Unconfined compression tests on compacted samples in the 15 to 20 percent moisture range showed thixotropy, with as-compacted strengths about 83 kN/m^2 (12 psi), increasing 50 percent over 30 days.

Additives

Lime neutralizes the sludge, appears to allow the emulsion to coalesce as globules, reduces clay plasticity, and is a component in the pozzolanic reaction. It also appears to condition the clay to immobilize the sludge. Reduced carbon solubility with lime was observed only in the presence of a fine-grained soil. Hydrated dolomitic lime was used to minimize heat and volatilization.

Bituminous coal fly ash was obtained from a nearby power plant, with a specific gravity of 2.54 and a median grain size (d_{50}) of 0.03mm. It met Type *F* criteria, except for excess carbon content, which was measured as 14.6 percent by the loss on ignition test. The fly ash serves as an absorbent to improve the blending of sludge and clay, and then participates in the pozzolanic cementing. It also appears to be a source of alkalinity during permeation with acidic solvents, thus improving the S/S longevity.

Lime-fly ash proportioning was varied over a range of water contents. Unconfined compressive strengths of 517 kN/m^2 (75 psi) and higher at moisture contents of 25 percent to 35 percent were obtained in 30 days. A lime-fly ash blend in the ratio of 1:3 was chosen for the stabilization. Addition of small amounts of cement to this blend substantially increased strength.

Mixtures

The properties of the sludge-clay-pozzolan mixtures depend on component proportioning, moisture content, age, sludge consistency, and compactive effort. The premise is that the soil structure is expanded and held at high porosity by a lime conditioning and inclusion of fly ash. With time, pozzolanic reactions improve strength. The resulting structure is conceptually illustrated on Figure 3, showing different pore channels between and within the cemented peds. The optimum mixture proportioning (by weight) for the high-viscosity sludge using a soil moisture content slightly below its optimum moisture content was found to be

1.0 sludge / 0.75 clayey silt / 0.75 fly ash / 0.25 lime

The fresh mixture had a "moisture" content of 11 percent after 24 hr of drying at 105°C, with losses including both water and organics. Compaction at 100 percent and 50 percent standard proctor effort yielded moist unit weights of 15.4 kN/m^3 (98 lb/ft^3) and 14.8 kN/m^3 (91 lb/ft^3), respectively. The volumetric proportioning, using constituent specific gravities, is computed as shown in Figure 4. This does not account for water produced by neutralization. It can be seen that the goal of a 50 percent sludge content was met, and there is a finite air content.

TYPICAL RESULTS

Samples for unconfined compression tests were compacted at 100 percent proctor effort in teflon molds, extruded, and cured in sealed containers. Lower compaction effort did not yield consistent results. A typical initial strength was about 69.0 kN/m^2 (10 psi), increasing to 110.3 kN/m^2 (16 psi) at 30 days, and 151.7 kN/m^2 (22 psi) at 60 days. Samples cured in molds showed 40 percent higher strength, indicating a confinement effect, which is expected to occur in the field.

One-dimensional compression results with the spent clay, at clay moisture contents bracketing the optimum moisture content and including a replication set are shown in Figure 5. Samples were obtained by pressing a cutter ring into a proctor mold of the prepared mixture. As expected, the wetter clay was softer, indicating that the mechanical skeleton is indeed the modified soil. Similar results and compression indexes were obtained with the main (Figure 4) native mixture.

Permeability results also showed effects of the fine-grained matrix structure. Samples were compacted at different levels of effort in fixed-wall, falling-head permeameters. Tests began after 14 days of curing. Permeability or hydraulic conductivity of 2×10^{-5} cm/sec was obtained with light compaction, decreasing to 3.5×10^{-7} cm/sec for samples compacted with 100 percent proctor effort. Results were insensitive to hydraulic gradient.

Permeation tests also yielded effluent samples. Both permeability and effluent quality were similar with dilute sulfuric acid, dilute acetic acid, and distilled water permeants (pHs of 2.5, 4, and 6, respectively). Thereafter, only distilled water was used, yielding effluent pH about 8.

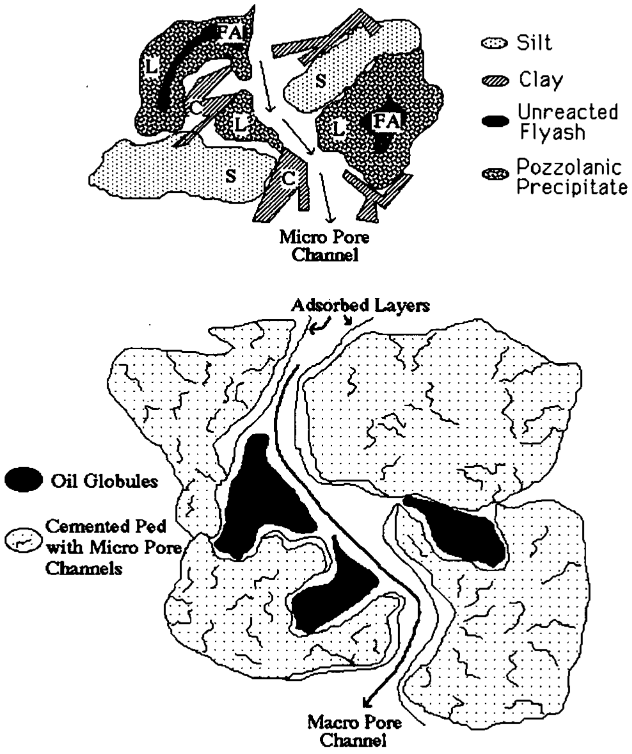

FIGURE 3 Conceptual model of stabilized product structure.

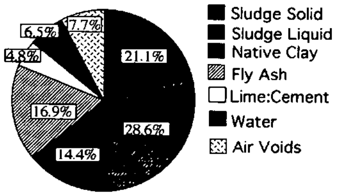

FIGURE 4 Volumetric proportions.

Illustrated in Figures 6 and 7 are the results of total organic carbon analysis on the effluent. Sample *EK* was a test with the spent clay, whereas curves 1*A* and 1*B* are results on the main mixture with the native clayey silt, but permeated at different gradients.

Although there was no phase separation in the effluent, it can be seen by Figure 6 that there is a "first flush" effect of

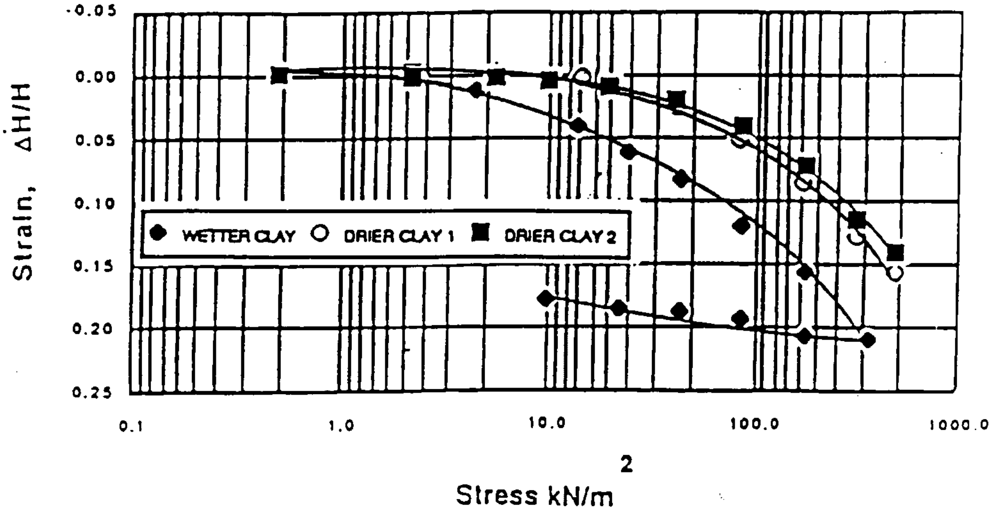

FIGURE 5 Compressibility sensitivity to soil moisture content.

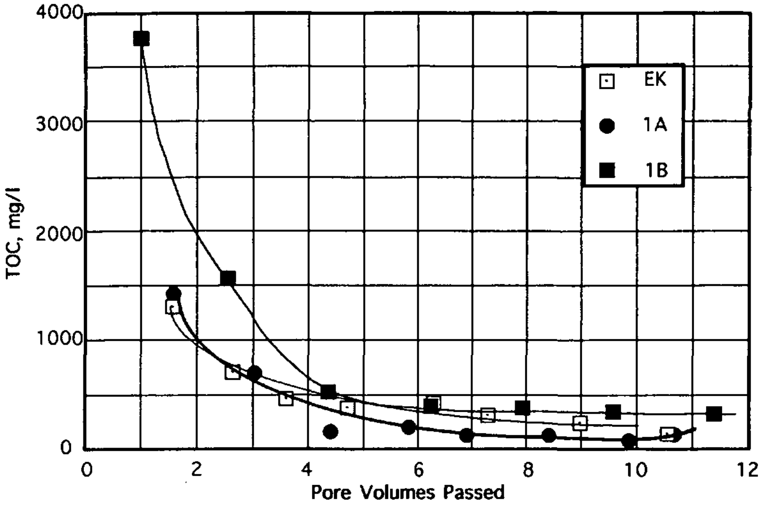

FIGURE 6 Permeameter effluent quality versus throughput.

very high carbon content. A better perspective on effectiveness is shown in Figure 7, indicating the accumulated percent of the sample carbon content mobilized. It can be seen that the less than 5 percent of the carbon was mobilized at throughputs that could represent many decades of infiltration. The difference between the No. 1*A* and No. 1*B* curves is a hydraulic detention time effect. The former was run at an average gradient of 60 cm/cm, and the latter at 10 cm/cm. The implication is that the rate-determining step in contaminant release is carbon transport from where it is entrapped or absorbed in the pore structure (see Figure 3) to the main interconnected channels.

STRENGTH IMPROVEMENT

The experimentation previously described was done with a composite sludge sample from the prototype lagoon. In tests with the more liquid sludge component, lower strengths and higher permeabilities were obtained. Drier clay improved initial strength, but the rate of strength gain was limited, perhaps because of a deficiency in moisture to complete the pozzolanic reactions. To increase strength, Type II portland cement was substituted for the lime, keeping the proportioning of the other constituents constant. Results are illustrated in Figure 8, expressed in terms of relative lime and cement percentages (e.g., 100/0 represents no cement substitution, whereas 50/50 represents 50 percent replacement of the lime). It can be seen that the latter mixture had much higher strength.

A pilot set of permeation and consolidation tests on the higher cement content mixture indicated more carbon mobilization with higher cement replacement of the lime and no variation in the stiffness. This confirms that the clayey silt skeleton dominates compressibility and that lime-clay interaction dominates the immobilization. Consequently, the 85/15 lime/cement ratio was selected, giving a net proportioning (by weight) of

1.0 Sludge / 0.75 Clayey Silt / 0.75 Fly Ash /
0.21 Lime / 0.04 Cement

CONCLUSIONS

This laboratory project demonstrated the feasibility of solidifying a hydrocarbon sludge in a very porous, cemented fine-grained soil matrix. The mixtures usually do not meet the

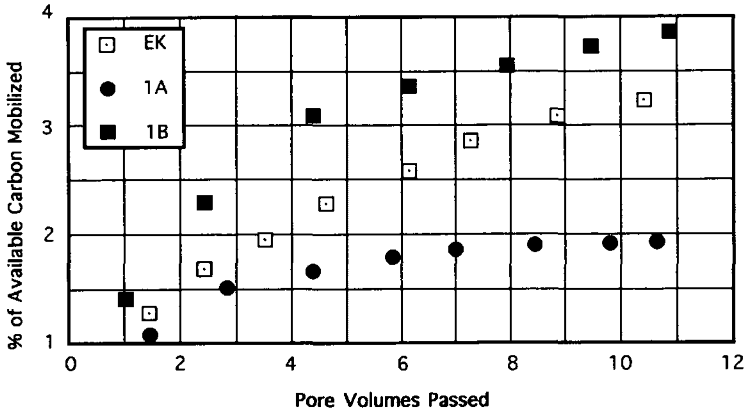

FIGURE 7 Accumulated quality of permeation effluent.

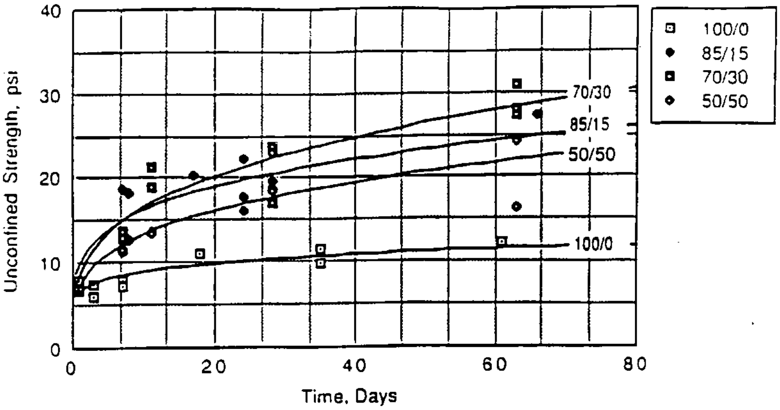

FIGURE 8 Effect of cement addition on strength gain.

mechanical values often specified for hazardous materials, but engineering analysis shows that the results are adequate for dimensionally stable and impervious capped landfill monoliths. The underlying point is that field performance depends on the in situ conditions as well as material properties. Compressibility and unconfined compressive strengths were acceptable when the overburden stress is accounted for and the deformation criteria are expressed as slope stability, zero liquid expulsion, and uniform cap support.

In this investigation, a soil-like texture was readily obtained. Depending on the factors that would be expected to be influential (clay moisture content, compactive effort, sludge consistency, additive proportioning, etc.), hardened material properties vary up to an order of magnitude. Permeability was the most sensitive property, as would be expected for a fine-grained soil. Compressibility was the least sensitive, possibly because of the pozzolanic cement compensating for factors that soften the soil skeleton. The shear strength was most sensitive to sludge consistency, but this could be compensated for by the addition of portland cement.

Exactly what happens to the microencapsulated hydrocarbons distributed through the porous matrix is not well understood, but the contrast between immobilization with and without a fine-grained soil matrix was dramatic. Hydrocarbon mobility was radically decreased. Similar results were obtained with two fine-grained soils of different index properties. The slow internal transport to advective channels during permeation implies a potential for immobilization mechanisms such as sorption on particle surfaces or an organic layer, and possibly embedment in pozzolanic precipitates. The extent to which the stabilization component of S/S can be considered a success depends on regulatory requirements.

S/S of a viscous hydrocarbon sludge with cemented silty clay implies feasibility for onsite improvement of subgrades contaminated with similar highly viscous organic materials.

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