Reactive Barriers for Containment of Metals-Contaminated Dredged Materials: Diffusion Studies

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ABSTRACT

Heavy metals are a prevalent and tenacious contaminant in many sediments and dredged materials. Traditionally these contaminated sediments are moved to secure locations and capped with clean sediment materials in a confined aquatic disposal (CAD) cell. This technique relies upon the tortuosity and reactivity of the overlying clean sediments to inhibit metal diffusion. The use of reactive barriers in sediment caps offers the opportunity to actively precipitate and adsorb contaminants as they migrate from contaminated sediments, thus improving overall cap performance. Apatite minerals, such as fluorapatite ($Ca_5(PO_4)_3F$), were evaluated as reactive barriers in a series of laboratory-scale diffusion experiments that took place over a period of 600 days. It was hypothesized that surface adsorption and precipitation would effectively bind diffusing heavy metals, preventing them from migrating past the reactive barrier. Diffusion models were used to determine barrier effects on effective diffusion coefficients (D_e). Decreases in diffusivity are attributed to adsorption/precipitation reactions in the presence of the apatite barriers. Reductions in average diffusivity for the most effective phosphate barrier (Florida apatite), when compared to a conservative control, were 91% for Pb, 99.8% for Zn, 37% for Cr, and 57% for Cu. After diffusion, mineralogical analysis revealed several of the metal phosphate minerals in the reactive barrier material were highly stable apatite and tertiary metal phosphates including: $Pb_4O(PO_4)_2$, $ZnCr_{0.85}(PO_4)_2 \bullet xH_2O$, $Pb_3Cr(PO_4)_3$, $Pb_3Fe(PO_4)_3$, $Cd_5(PO_4)_3OH$, and $CaZn_2(PO_4)_2 \bullet 2H_2O$. The presence of such metal phosphate minerals further indicates that Pb, Cd, and Zn had adsorbed to the reactive barrier mineral surfaces and reprecipitated as metal phosphates. The use of reactive barrier sediment caps may reduce the environmental concerns associated with dredged material disposal.

INTRODUCTION

The magnitude of dredging projects in the U.S. is enormous. Over the past ten years, an average of 270 million cubic yards of sediment has been dredged each year from our nation's navigable waters with a peak in 1994 of 302 million cubic yards. In 1999 alone, 284 million cubic yards of sediment were dredged in the U.S. at a cost of $812 million.[1] There is much interest in trying to beneficially use these dredged materials.

Heavy metals are one of the more prevalent contaminants in sediments and are problematic with respect to dredge material management.[2,3,4,5,6,7] They impact sediment restoration activities in the Coastal Zone Management system and some of the estuaries and waterways adjacent to the National Estuarine Research Reserve System (NERRS).[3,4] Indicative of the widespread nature of this contamination, the Coastal Sediment Database (COSED) reports that 12 – 16% of all sediments surveyed from around the U.S. contained heavy metal concentrations above background levels.[5]

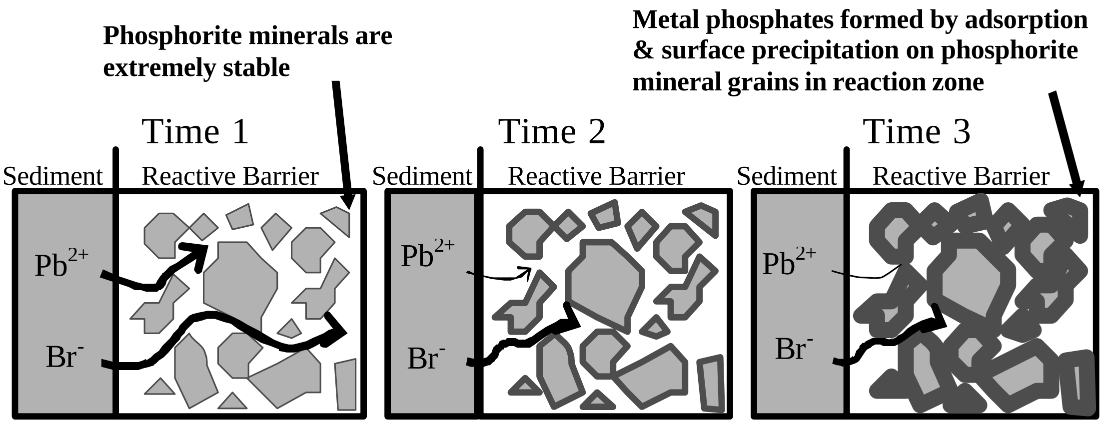
Contaminated Sediment Capping

Cap designs are site specific, based upon locally available material and site requirements. Often confined aquatic disposal (CAD) cell caps of 1 meter thick are required because of factors which reduce cap effectiveness including: (i) settling/dewatering of the material after cap placement, (ii) erosion of the cap over time by local currents, (iii) bioturbation, and (iv) variation in cap placement thickness.[8] The only portion of a capping system that can be considered to inhibit diffusion of contaminants from the sediments below is the effective cap depth after these factors are accounted for. *In situ* capping systems are often composed of many different types of layers (e.g. armor stone, geofabric). This is because they may be located in areas of higher erosion potential. Reactive barriers could be useful in either of these capping scenarios to extend the life of a cap, reduce the required cap thickness, and replace clean sediment caps.

Reactive Barrier Concept

The reactive barrier is a novel technique that has been developed for use in landfills and terrestrial applications to create a contaminant migration barrier that actively precipitates diffusing ions.[9,10,11] It also holds promise for marine and estuarine subsurface applications, potentially with sediment reuse scenarios. With conventional capping systems, contaminant migration is inhibited "passively", primarily by the high tortuosity and natural chemical reactivity of the capping layers. With reactive barrier systems, contaminant migration is inhibited by both direct precipitation within the barrier and by any increase in tortuosity associated with this precipitation within the reactive barrier. Figure 1 shows the diffusion of reactive Pb^{2+} and non-reactive Br^- through a reactive barrier material. Time 1 shows contaminants present in the sediment layer only. Time 2 shows the beginning of diffusion of these contaminants into the reactive barrier, with Pb^{2+}diffusion being inhibited because of sorption/precipitation reactions with phosphorite barrier material. Time 3 shows an accumulation of Pb^{2+}at the interface due to significant surface sorption/ precipitation reactions, while Br^- diffusion continues only inhibited by increases in tortuosity.

Figure 1. Diffusion into a reactive barrier over time



There is a reactive component to conventional capping systems and ion exchange and specific adsorption reactions will occur with components of these sediments.[13] These reactions will take place with iron and manganese oxides, clay minerals, and organic complexing ligands (humic acids). The use of phosphorites is perhaps more robust than clean sediments because the nature of the surface precipitates are geochemically more stable. Natural apatites have been tested in laboratory studies to determine their ability to precipitate heavy metals from solution in a flow-through column.[12] Here reductions in solution Pb concentrations of 99% were observed.

Phosphate Minerals as Reactive Barriers

Apatites, particularly simple fluoroapatites ($Ca_5(PO_4)_3F$) and carbonate fluoroapatites ($Ca_5(CO_3,PO_4)_3F$) are the predominant mineral phases in marine sedimentary phosphorite deposits.[14,15,16] Their solubilities are extremely low and their geochemical stabilities are high at typical pH, ionic strength, and organic ligand levels associated with sedimentary deposits.[17,18,19,20,21] The wide predominance field of apatites with respect to pH and Eh add to their stability even under varying environmental conditions. Apatites are geochemically stable as they are the most common diagenic product of sedimentary accretion of phosphate in marine sediments[14,15,16] and are found in sediment environments ranging from highly oxidized to moderately reducing.[22] There has been extensive research on the sorption of metals to hydroxyapatite surfaces[16,20,21,23,24,25,26] as well as the formation of surface precipitates [19,23,24,27,28] on apatites. It is these immobilizing features of apatites that we exploit in the reactive barrier concept.

Diffusion

The primary mechanism for contaminants escaping from an established subsurface containment system, in the absence of upwelling groundwater, is by diffusion as described by Fick's second law.[29] The nature of the solid matrix affects the diffusion because of different diffusion path lengths and the physical and chemical reactions with the particle surfaces. The effective diffusion coefficient (D_e) is used to quantify these effects and is specific to each individual solid matrix and its chemical (i.e. retardation) and physical (i.e. porosity and tortuosity) environment as they relate to the sorption/precipitation of the diffusing ions.[29]

There are many possible solutions to Fick's second law, each dependent upon the specific diffusional situations (i.e. initial and boundary conditions). In a system that contains two saturated sediments sharing a common boundary, one contaminated with an initial concentration (C_o) of solute species i and the other with a concentration ($C = 0$ at time zero), the following solution to Fick's second law can be used to determine the effective diffusion coefficient.[29,30]

$$C_{i(x,t)} = \frac{1}{2} C_o \mathrm{erfc}\left[\frac{x}{2\sqrt{D_e t}}\right] \qquad (1)$$

In this equation, values of C_i in the x direction over time t can be calculated. Here *erfc* is the complementary error function and D_e is the effective diffusion coefficient of the diffusing ion.

The use of phosphorites as a reactive barrier offers several potential economic benefits under different capping scenarios including reductions in the quantity of clean sediment required to cap the contaminated sediment, a reduction in the amount of stabilizing material required, and a reduction in the amount of sediment handling. The extremely stable nature of the phosphorite materials means that a properly design reactive barrier could outperform conventional capping systems and help promote beneficial use.

EXPERIMENTAL METHODS

Our group at the University of New Hampshire (UNH) and Louisiana State University (LSU) used multiple analytical techniques to understand immobilization/stabilization mechanisms and reaction products formed during reactive barrier diffusion studies. This multifaceted approach uses many complimentary analytical techniques to determine bulk and surface chemical characteristics of phosphate barriers. Elemental composition of the sediments and phosphates were determined by neutron activation analysis (NAA) and x-ray fluorescence (XRF). Bulk sample crystalline mineralogy before and after treatment or diffusion was determined by x-ray diffraction (XRD). Scanning electron microscopy was used to determine changes in barrier mineral morphology due to diffusion of reactive elements.

Raw Materials

Well characterized contaminated sediment collected from the Newtown Creek in New York was selected for use in the experiments.[31,32] Heavy metal salts were added to the sediments to raise total sediment metal concentrations to 2000, 4000, or 6000 mg/kg and sediments were stored at 4°C until use. The spiked samples were split between the UNH and LSU diffusion experiments to ensure materials being used at both locations were treated identically. A reference clean (low concentration of heavy metals) control sediment from Rhode Island was also collected for the purpose of monitoring diffusion through a clean sediment barrier.

Three natural phosphate materials were used for reactive barriers in the diffusion experiments. Two of these materials were unprocessed mineral phosphates, one from central Florida and one from Soda Springs, Idaho. The third material was a waste mine tailings taken from an Idaho phosphate fertilizer processor. The two Idaho phosphate sources contained high concentrations of Cr, Cu, and Zn, making them less desirable capping materials. For comparative purposes two synthetic phosphate standards (Himed Hitemco Medial Applications Inc., NY) that best reproduced the natural apatite chemistry were also used (fluorapatite ($Ca_5(PO_4)_3F$), carbonate fluorapatite ($Ca_5(PO_4,CO_3)_3F$).

Reactive Barrier Diffusion Studies - LSU

X-ray fluorescence (XRF) conducted at the Center for Advanced Microstructures and Devices (CAMD) was used to monitor the diffusion of heavy metals at 0, 30, 80, 200, and 400 days. XRF measurements of diffusion tubes can monitor the progress of the metals through the various barriers without sacrificing any of the tubes. The experiments used a non-reactive tracer, Br, which has a peak location that does not interfere with the metal signals taken from the XRF.

Kapton®-coated tubes measuring 1 x 1 x 7 cm were used for the main diffusion experiments. Plexiglas racks containing the tubes were placed on their sides and filled half-way with a measured quantity of Newtown Creek sediment. The remaining portion of the tube was filled with either a reactive phosphate material, or a non-reactive clean sediment. The tubes were kept in a dark horizontal position at 100% humidity and 25°C during the long diffusion period.

Reactive Barrier Diffusion Study - UNH

Experiments conducted at UNH consisted of diffusion tubes established for diffusion monitoring through 4 reactive barrier types and one non-reactive barrier material (clean sediment). Tube and sediment storage conditions were identical to those at LSU. Diffusion analysis consisted of quick freezing and sectioning the tubes into wafers. These slices were treated with acid digestion and subsequent analysis by inductively coupled plasma spectroscopy (ICP). This provided a concentration gradient for Pb that could be compared between phosphate and control tubes and allowed for the calculation of effective diffusion coefficients. These tubes were also used to analyze phosphate barriers exposed to diffusing metals by XRD and SEM for the presence and chemical structure of heavy metal phosphate precipitates.

Spectroscopic Methods

The total composition of the sediments and phosphate materials were quantified for 35 elements using Neutron activation analysis (NAA) and X-ray fluorescence (XRF) at the University of Texas. Details for NAA/XRF measurements are described elsewhere.[33,34]

X-ray diffraction (XRD) was used to identify crystalline mineral phases at the sediment/barrier interfaces that may have formed as a result of the metal diffusion. Details of XRD spectroscopy are described elsewhere.[35,36]

RESULTS AND DISCUSSION

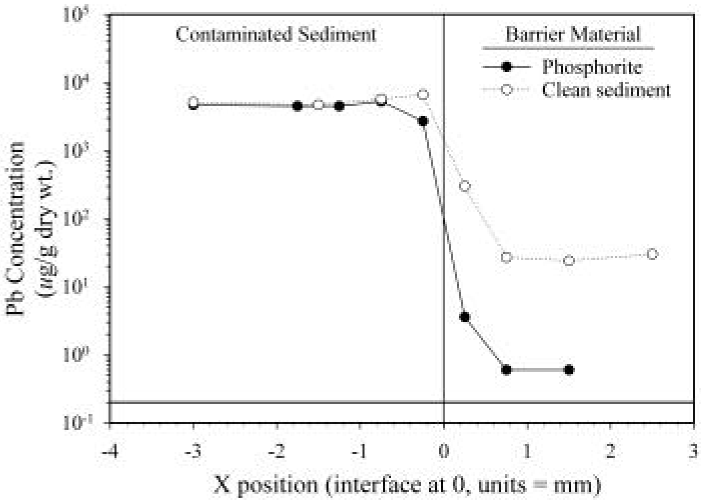
Characterization of Natural Phosphates Minerals

High concentrations of heavy metals were present in the Idaho samples and made their utility as reactive barriers questionable. Major elements (>10,000 mg/kg) present in the three different apatite minerals included Ca, Si, P, Al, Fe, and K. Potassium was only present as a major element in the Idaho samples. Minor elements (<10,000 mg/kg and >1,000 mg/kg) present in the apatite minerals included S, Na, Ti, Cr, Sr, and Zn. Cr and Zn were present in trace concentrations in the Florida apatite sample. Many trace elements (<1,000 ppm) were observed in the apatite samples as is common with natural apatite formations including: Zr, V, Mg, Cl, Ba, Ni, Mn, Sn, Cd, Cu, Mo, Rb, and U. Florida phosphate barrier material contained the highest phosphate concentration (14%). XRD analyses of the Florida phosphate showed it consisted mostly of fluoro- and carbonate- apatite minerals as well as fluorellestadite (an apatite mineral that has silicon substituted into its structure for phosphorus).

Diffusion Analysis

Diffusion studies were conducted both at LSU and UNH. An example diffusion profile from the work at UNH is shown in Figure 2. In this figure the contaminated sediment (4000 mg/kg Pb and Zn) is located left of zero and various barrier materials right of zero. Effective diffusion of lead was lower through synthetic apatite barriers ($3.9 \times 10^{-14} m/s^2$), than clean sediment barriers ($4.5 \times 10^{-13} m/s^2$) over a period of 400 days.

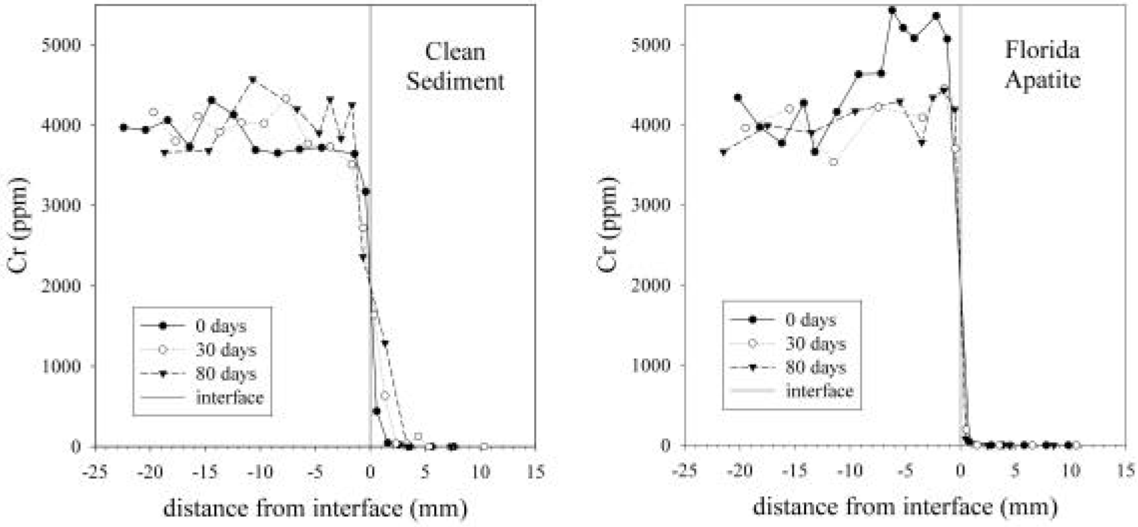
Figure 2. Diffusion of lead through reactive and non-reactive barriers



Multiple diffusion profiles taken from LSU are presented in Figure 3. One of the advantages of using XRF to monitor heavy metal diffusion through the tubes was the ability to noninvasively obtain concentration profiles. The diffusion over the 80-day period of time for Cr through the clean sediment barriers and the Florida phosphate barrier tubes showed the higher rates of diffusion in the clean sediment material.

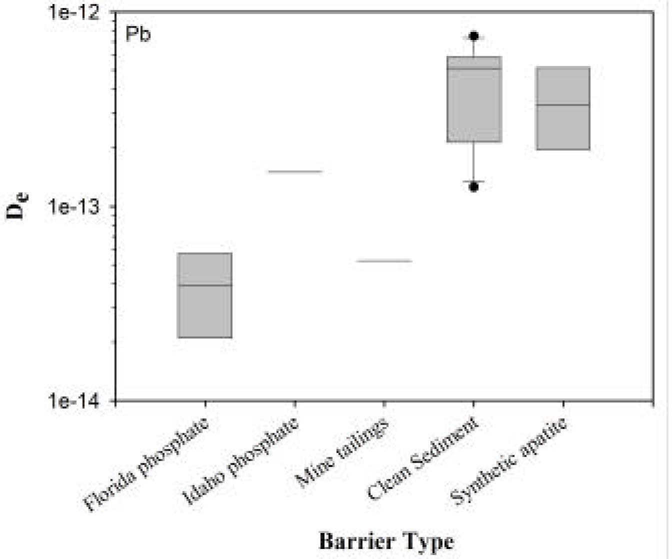
Bromine was the non-reactive tracer present in the samples and as such indicated the relative tortuosity of the barrier material. For Br, effective diffusivity was lower in the clean sediment than in the various phosphate materials. This trend was consistent with the grain size analysis of these materials, but statistical analysis could not show significant differences in Br diffusivity between the clean sediment and the Florida phosphate barriers.

Figure 3. Diffusion of chromium through reactive and non-reactive barriers



Florida phosphate inhibited Pb diffusion by approximately one order of magnitude over the clean sediment materials despite the fact that it had a lower tortuosity (Figure 4). Other elements were analyzed and are summarized in Table 1. The synthetic and Florida phosphate minerals inhibited Zn diffusion by several orders of magnitude over the clean sediment material. The synthetic and Florida phosphate minerals also inhibited Cr diffusion by an order of magnitude over the clean sediment material.

Figure 4. Comparison of Pb effective diffusion coefficients



However, there was very little difference between the barrier materials in how they affected the diffusivity of Cu. This may be explained by the relatively weak affinity of Cu for the apatite structures as compared to other metals such as Pb, Cd, and Zn.[24]

Among all of the natural phosphate barrier materials, Florida phosphate performed best at lowering the effective diffusivity of Pb, Zn, and Cr. Synthetic apatite minerals performed

Table 1. Effective diffusion coefficients for reactive and non-reactive barriers (m/s^2)

Barrier	Pb	(n)	Zn	(n)	Cr	(n)	Br	(n)	Cu	(n)
Florida Phosphate	$3.89x10^{-14}$	2	$3.81x10^{-13}$	2	$3.88x10^{-14}$	5	$3.15x10^{-12}$	5	$1.28x10^{-13}$	5
Idaho Phosphate	$1.50x10^{-13}$	1	$1.27x10^{-12}$	1	$4.65x10^{-12}$	4	$5.91x10^{-12}$	3	$1.76x10^{-13}$	4
Mine Tailings	$5.26x10^{-14}$	1	$1.35x10^{-12}$	1	$1.21x10^{-12}$	3	$9.28x10^{-14}$	2	$1.62x10^{-12}$	3
Sediment	$4.50x10^{-13}$	6	$2.29x10^{-10}$	6	$1.83x10^{-13}$	3	$6.85x10^{-14}$	1	$2.97x10^{-13}$	3
Synthetic Fluorapatite	$4.53x10^{-13}$	2	$4.85x10^{-13}$	2	$7.89x10^{-14}$	2	$9.96x10^{-11}$	1	$1.90x10^{-13}$	2
Synthetic Hydroxyapatite	$1.52x10^{-13}$	1	$7.83x10^{-14}$	1	NA	-	NA	-	NA	-

equally well or better than the Florida phosphate in reducing the effective diffusivity of Zn, Cr and Cu. Statistically, the Florida phosphate significantly outperformed clean sediment materials in reducing the effective diffusivity of Pb. The clean sediment material appeared more effective at inhibiting Cu diffusion than the phosphate materials, but was not statistically significant.

X-ray Diffraction Analyses

XRD analyses of the diffusion tubes, following 600 days of diffusion were conducted to identify heavy-metal phosphate adsorption/precipitation reactions products occurring within the reactive barrier materials. The Florida phosphate barrier materials, exposed to diffusing Cd, Cr, and Cu, showed the presence of several metal phosphate reaction products including: $Cd_5(PO_4)_3OH$, $MgFe_2(PO_4)_2(OH)_2 \bullet 8H_2O$, $AlPO_4$, and $Al_5(PO_4)(SO_4)(OH)_{10} \bullet 8H_2O$. No copper or chromium phosphate reaction products were observed. This could be because metal accumulations were below XRD detection limits, precipitants were amorphous in character, or because of a low reaction rate with the barrier material. The Florida phosphate barrier materials exposed to diffusing Pb and Zn showed the presence of several metal phosphate reaction products including: $Pb(H_2PO_2)_2$, $Pb_4O(PO_4)_2$, $Pb(PO_2)_2$, $Pb_5P_4O_{15}$, $ZnH_2P_2O_7$, and $ZnCr_{0.85}(PO_4)_2 \bullet xH_2O$.

CONCLUSIONS

The use of phosphate minerals as a reactive barrier material shows potential for effectively inhibiting the migration of Pb, Zn, Cr, and Cd as well as other elements from metal contaminated sediments. Naturally occurring apatite minerals from Florida effectively immobilized Pb and Zn during a 600-day diffusion test. However, diffusion for other elements such as Cu and Cr were not inhibited significantly more than by the clean, silty sediments. The higher solubilities of their respective metal phosphate phases and the relative inability of these elements to compete with Pb and Cd in phosphate minerals could explain this behavior as well as the chemical reactivity of the clean sediments. The sorption of Pb, Zn, and Cd during diffusion involves the formation of several metal apatite phosphate phases, which are highly insoluble and resistant to changes in pH and Eh. Further modeling of the barrier materials has shown that the observed reductions of more than an order of magnitude in Pb diffusion through the reactive barriers indicates that this material is an excellent candidate for developing an *in situ* reactive barrier system for the long-term containment of heavy metals, possibly in beneficial use applications.

The specific implications of this modeling for cap design is that a reactive barrier can decrease the effective diffusivity of a capping system by one order of magnitude and will significantly improve cap performance with respect to Pb and Zn contaminant sequestration. As an alternative to conventional capping systems a clean sediment cap required to be one meter thick, to inhibit metal diffusion, could possibly be reduced to only the depth required for bioturbation and erosional factors, with a thin layer of reactive phosphate underneath. There are also many beneficial use applications for contaminated dredged materials in which phosphate based reactive barrier technologies could be used.

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