

# Alkaline Leachate and Calcareous Tufa Originating from Slag in a Highway Embankment near Baltimore, Maryland

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A series of springs located along the lower contact of a slag bed 3 to 7 m thick sandwiched within an embankment for Interstate 695 in Baltimore County, Maryland, discharges water with a pH of 12.5 to 13 and a dissolved calcium concentration of roughly 1000 mg/L. Further reactions with atmospheric CO<sub>2</sub> cause this leachate to precipitate copious quantities of calcite (CaCO<sub>3</sub>) in the form of surficial tufa, interstitial cement within the fill, or fine powdery sediment in surface water. Because of its high pH, the leachate is classed as a hazardous waste, and the Maryland State Highway Administration has been required to construct a fenced enclosure and containment pond for the springs and to haul away the leachate or treat it before discharge. The cost of remediation had reached \$1,000,000 by early 1994, when a treatment plant using hydrochloric acid to neutralize the leachate was about to begin operation. This case history demonstrates that great caution should be exercised in use of industrial by-products as construction materials. Although other recent studies have clarified the mechanism of tufa formation, unanswered questions remain regarding the mobility and fate of labile constituents other than calcium. Such questions must be answered before such reactive materials are dispersed into the environment in the name of recycling.

During April 1986 the Maryland Department of the Environment (MDE) notified the State Highway Administration (SHA) of a suspected chemical spill on the right-of-way for Interstate 695 (Baltimore Beltway) near North Point Boulevard. The spill consisted of a wet white solid on the face of an embankment below one of the ramps. SHA hired a contractor to remove this material. However, in October 1987, MDE found more of the material and requested further action. When the contractor again attempted to scrape up the deposit, its apparent source was exposed—a spring on the embankment. Since the effluent from this spring had a pH greater than 12.5, it was classified as a hazardous waste, and MDE directed SHA to contain the discharge. SHA responded by constructing a lined containment pond in November 1987. Water from this pond was periodically pumped out by a tank truck and hauled to a secure permitted disposal site in another state. The cost of this procedure (about \$7,000/week) prompted a search for a more cost-effective system and motivated a hydrogeologic study to determine the source of the caustic discharge and identification of any other responsible parties.

## INVESTIGATION

Six alkaline springs have been found in the problem area; two are perennial; the others flow only following precipitation events. The

springs can be located even when they are inactive because they are all marked by patches of unvegetated soil and distinctive white mineral deposits (often forming plumes that can be traced upslope to a point source), which range from loose powdery sediment to rigid crusts 20 mm or more in thickness. The crusts contain numerous pores—molds of grass stems and other debris trapped by the growing crust. On the basis of petrography, chemical analysis, X-ray diffraction, and strong effervescence in dilute hydrochloric acid, the crust has been determined to be largely calcite (calcium carbonate). It resembles calcareous tufa, a deposit that forms around some natural springs. Calcite also occurs in the fine sediment that carpets the bottom of the containment pond as paper-thin rafts (like miniature ice floes) or a continuous skin on the surface of the pond and as an interstitial cement that has lithified the soil of the embankment near the perennial springs to a depth of at least 300 mm.

The embankment in the study area is composed mostly of sandy soil obtained by stripping native material from a large area immediately east of the embankment, where aerial photographs record a history of agricultural land use with no evidence of industrial waste generation or disposal. Discontinuous clay lenses occur, mostly in the lower part of the embankment. Sandwiched within this natural material is a layer of slag that is apparently continuous for hundreds of meters but varies greatly in thickness. The slag consists mostly of sand to gravel-sized fragments of dark gray rocklike material, which often contains vesicles (round voids) formed by gas bubbles trapped within the molten slag. Most of the slag fragments have softer, light gray weathered "rinds" that effervesce in hydrochloric acid, indicating the presence of calcite. The slag also contains varying amounts of silt- to clay-sized material, which is not readily identifiable, although it resembles the slag in color. It may be residue formed by weathering and leaching of slag or some other industrial waste.

The slag layer is believed to be the source of the alkaline seepage for the following reasons:

1. Samples of slag from borings and surface exposures on the embankment gave reaction pH values of 12 to 13 when mixed with distilled water. When leached with nitric acid, they yielded very high concentrations of dissolved calcium and magnesium. In contrast, soil samples of the nonslag embankment materials have reaction pH values closer to neutral (5.5 to 8.0) and calcium concentrations averaging only 0.2 percent of those in the slag samples.

2. All the observed alkaline springs are located along the line where the bottom of a slag bed intersects the embankment surface.

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3. The greatest volume of alkaline seepage is observed near the area where the slag is thickest.

4. The major chemical constituents of the seepage occur in proportions consistent with an origin by leaching of slag.

There is some doubt regarding the exact nature of the material within the slag bed that is responsible for the high pH of the leachate. The reaction pH of blast furnace slag is normally in the range of 9 to 11; in one study, blast furnace slag from eight different sources yielded reaction pH values ranging from 9.4 to 11.7, with an average of 10.6 (1). This suggests that blast furnace slag alone could not be responsible for the high pH observed in the present study. However, there are published references to other steel industry wastes that are more strongly alkaline, for example, arc furnace dust (reaction pH 11.7 to 12.8), ladle refining slag (11.0 to 12.7), A.O.D. converter dust (11.5 to 12.25) (2), an "alkaline sludge" from coal tar processing with a pH of 14.0 and high concentrations of phenols (3), and steel slag and slacker aggregate (4). According to the contractor, the slag was "borrowed" from an abandoned railroad spur fill constructed 40 years ago. The contractor believes that the material may have been blast furnace slag, open hearth slag (a type of steel slag), or "plant refuse" described as "a conglomerate of residual slag and debris from pit operations and refuse from plant operations after primary extraction of metallics by crane magnets."

## HYDROGEOLOGY

The mostly likely conceptual model for groundwater flow within the embankment is shown in Figure 1. The model assumes that direct precipitation or stormwater runoff readily infiltrates the sandy natural soil above the slag. The groundwater then moves downward through the slag until it encounters the less permeable clayey layers (aquiclards) beneath the slag, which cause formation of one or more perched water lenses that spread vertically and laterally until they reach the surface of the embankment and erupt as springs. If these lenses are not replenished by infiltration, they will eventually shrink or totally disappear as water seeps down and out of the embankment; this explains why most of the alkaline

springs are ephemeral and cease flowing in a downward sequence. The peculiar shape of the slag layer serves to funnel groundwater from a large catchment area toward the perennial springs on the east side of the embankment.

The hydrogeologic model assumes that slag is the most permeable material within the embankment. Available data on hydrologic parameters of slag are very limited. The coefficient of permeability (hydraulic conductivity) of compacted granulated slag is reported to be roughly equal to that of "clean" sand and gravel (5). It is somewhat puzzling that a suspected high-conductivity perched aquifer should exhibit slow protracted drainage through perennial springs. However, there are several factors that could explain this. First, slag may have unusual aquifer properties. Because the surface of slag particles is rough and vesicular, a layer composed of such particles should have an intergranular pore geometry different from that of, for example, a typical quartzose sand or gravel. Also because of the vesicles, a slag bed should have intragranular as well as intergranular porosity. The result could be that a slag layer would have a higher specific yield and a more protracted period of gravity drainage than many natural aquifer materials whose particle size distribution (as determined by sieving, for example) is similar. Another factor could be that seepage from the overlying less permeable natural soil recharges the slag aquifer at a rate roughly balancing the rate of spring discharge. Finally, it is possible that aquifer discharge is choked by progressive carbonate cementation of areas where seepage might otherwise occur, thereby ponding leachate within the slag.

## GEOCHEMISTRY

The major chemical species found in inorganic chemical analyses of water from the main perennial spring are shown in Table 1. The water is characterized by high concentrations of calcium, hydroxyl, chloride, sodium, and potassium ions. When the analysis is recalculated as milliequivalents per liter, it becomes evident that  $\text{Na}^+$  is almost exactly balanced by  $\text{Cl}^-$ , and  $\text{Ca}^{2+}$  is approximately balanced by  $(\text{OH})^-$ . The most likely explanation for this pattern is that the leachate forms mainly by dissolution of two solids,  $\text{NaCl}$  and  $\text{CaO}$  [or  $\text{Ca}(\text{OH})_2$ ].

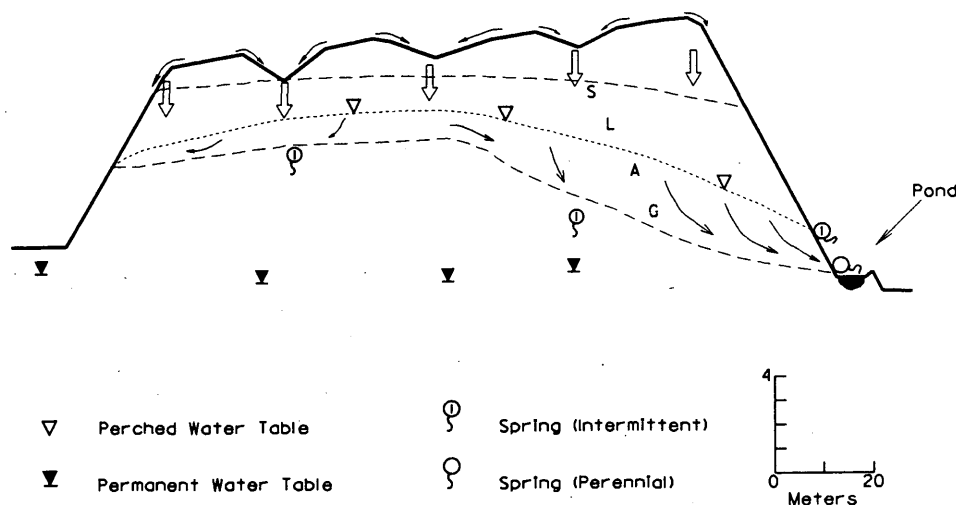


FIGURE 1 Cross section of embankment with conceptual groundwater flow model.

TABLE 1 Concentration of Major Ions in I-695 Slag Leachate

Units	Ion					
	Ca <sup>2+</sup>	OH <sup>-</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	K <sup>+</sup>	Al <sup>3+</sup>
Mg/l <sup>a</sup>	1137	1048	557	859	50 <sup>c</sup>	13.5
Meq/l <sup>b</sup>	56.74	61.62	24.23	24.24	1.28	1.50

<sup>a</sup>Milligrams per liter<sup>b</sup>Milliequivalents per liter<sup>c</sup>Estimate based on a different analysis

Recent studies (4) have identified free lime (CaO) as the source of the high calcium levels in steel slag leachate. Free lime (also known as quicklime) cannot coexist with liquid water because it irreversibly hydrates to portlandite, Ca(OH)<sub>2</sub>, at earth-surface conditions. This suggests that, given sufficient contact time, the solubility of portlandite could set an upper limit on the concentrations of Ca and (OH)<sup>-</sup> in slag leachate if the system is isolated from CO<sub>2</sub>. The slag layer at North Point is largely protected from contact with atmospheric CO<sub>2</sub> by the relatively thick blanket of overburden, the cemented soil zones, and the presence of perennially water-saturated conditions in part of the slag. These factors favor generation of a leachate dominated by calcium and hydroxide ions. Once this leachate comes into contact with air, however, CO<sub>2</sub> will begin to dissolve into the leachate, forming H<sub>2</sub>CO<sub>3</sub>, most of which will quickly dissociate to form (CO<sub>3</sub>)<sup>2+</sup>, which in turn will react with Ca<sup>2+</sup> to form CaCO<sub>3</sub> (calcite). The solubility of portlandite is roughly 2 orders of magnitude greater than that of calcite at room temperature. This means that uncarbonated slag leachate will reach supersaturation with respect to calcite even if only tiny amounts of CO<sub>2</sub> dissolve into it, because the Ca<sup>2+</sup> content has built up to very high levels as the result of prior exclusion of CO<sub>2</sub>. Thus, steel slag leachate is unlike many natural waters in that it can precipitate calcite without having the solubility of calcite reduced by heating, evaporation, or degassing of CO<sub>2</sub> from the so-

lution, although these factors can increase the degree of supersaturation and thereby speed up precipitation.

Because the North Point leachate was not analyzed for carbonate and bicarbonate, published analyses from Ohio (6), which did include these important species and were otherwise similar to the North Point analyses, were used as input to WATEQ4F, a computer program that calculates degree of saturation of a solution with respect to various mineral species (7). The results (Table 2) confirm that the most alkaline Ohio underdrain slag leachate is a solution that is nearly saturated with respect to portlandite and supersaturated with respect to calcite even at a cool springtime temperature (13°C) and even though it has absorbed very little CO<sub>2</sub> (as much as water at equilibrium with a partial pressure of 10<sup>-11.2</sup> atm CO<sub>2</sub>). This concentration is far below the atmospheric concentration of CO<sub>2</sub> (10<sup>-3.5</sup> atm) and even farther below those found in many soils, where plant and microbial respiration produces CO<sub>2</sub>. The result is that slag leachate not only will continue to absorb and react with CO<sub>2</sub> whenever it contacts the open air in drainpipes or surface slopes, as is well known (4), but also will react with CO<sub>2</sub> in soil pores. This property may explain the origin of the case-hardened soils observed at North Point.

Further evidence that precipitation of calcite from carbonate-poor slag leachate requires only addition of CO<sub>2</sub>, not heating or evaporation, was provided by a simple experiment conducted in

TABLE 2 Log<sub>10</sub> of Activity of Chemical Species in Solution and Saturation Indexes of Calcite and Portlandite

Species	Type of Solution		
	H <sub>2</sub> O @ Equilibrium With Ca(OH) <sub>2</sub> , No CO <sub>2</sub> , 25° C	Steel Slag Leachate, Ohio, 13° C <sup>a</sup>	H <sub>2</sub> O @ Equilibrium With CaCO <sub>3</sub> & Air, 25°C
H <sup>+</sup>	-12.5	-12.8	-8.4
OH <sup>-</sup>	- 1.5	- 1.6	-5.6
Ca <sup>2+</sup>	- 2.1	- 2.4	-3.7
CO <sub>3</sub> <sup>2-</sup>	(Not present)	- 3.8	-4.7
HCO <sub>3</sub> <sup>-</sup>	"	- 6.1	-2.9
H <sub>2</sub> CO <sub>3</sub>	"	-12.5	-5.0
P <sub>CO2</sub>	"	-11.2	-3.5
S. I. <sup>b</sup>	"	2.3	0.0
Calcite			
S. I.	0.0	- 0.6	-9.7
Portlandite			

<sup>a</sup>Concentrations from analysis in Reference (6); converted to activities using (7)<sup>b</sup>Positive S.I. indicates supersaturation, negative S.I. indicates undersaturation, zero indicates saturation

the Maryland SHA chemistry laboratory. Pure  $\text{CO}_2$  from a pressurized tank was bubbled into a sample of North Point leachate, causing a rapid precipitation of calcite accompanied by a steady decline in pH. This process is in dramatic contrast to carbonate precipitation in most natural environments, which is often triggered by a rise in pH or a loss of  $\text{CO}_2$  from solution.

Magnesium was not detected in the North Point leachate, and very low levels of magnesium have also been reported in slag leachate in other areas (6). This lack of magnesium is surprising, since magnesium is a major constituent of most slag and is a common cation in natural groundwater. Either magnesium is not dissolving from the slag or it is dissolving and then reprecipitating within the slag layer or somewhere between the slag and the spring. Computer manipulation of leachate analyses suggests that both of these alternatives are plausible. A published analysis of slag leachate from Ohio (6), which contained a relatively high level of magnesium (4.4 mg/L) and was otherwise similar to the North Point leachate, was used as input to WATEQ4F. Since no data were available on dissolved silica, various assumed contents of silica were added to the analysis. The results indicated that if the Ohio slag leachate contained as little as 0.01 ppm dissolved silica (a level several orders of magnitude below that found in most natural surface and groundwaters), it would be strongly oversaturated with respect to several high-temperature alkaline-earth (Ca- or Mg-bearing) silicates that have been reported to occur in fresh blast furnace slag or are similar to silicates known to occur in slag (e.g., forsterite,  $\text{Mg}_2\text{SiO}_4$ , and diopside,  $\text{CaMgSi}_2\text{O}_6$ ). This finding suggests that these minerals, which do weather (albeit slowly) in normally acid natural groundwaters, are unlikely to decompose in the alkaline environment of slag leachate, and it tends to support the conclusion of other reports (4) that the solutes in slag leachate are largely derived from other sources, such as free lime (CaO). The WATEQ4F results also indicate that if slag leachate did originally contain even small quantities of dissolved silica and magnesium or acquired them by mixing with natural water, the resulting solution could be supersaturated with respect to several Mg-bearing silicate minerals (talc and sepiolite), which are known to form at relatively low temperatures. Even without dissolved silica, the Ohio leachate is supersaturated with respect to several low-temperature magnesian carbonate and hydroxide minerals, including artinite,  $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ , and brucite,  $\text{Mg}(\text{OH})_2$ . Formation of brucite at earth-surface conditions is quite plausible. In fact, standard laboratory methods for titration of calcium hardness call for raising the pH to 12 to 13 (the same range observed in some slag leachates) in order to eliminate magnesium interference by precipitating all Mg as  $\text{Mg}(\text{OH})_2$  (8). If the slag leachate contained dissolved aluminum (as the North Point leachate does) in addition to low levels of silica and magnesium, the resulting hypothetical solution would be strongly supersaturated with respect to chlorite, a common product of natural low-temperature weathering of magnesian rocks. Although chlorite and other layer silicates are difficult to synthesize directly from solution at low temperatures, they are readily formed by modification of preexisting clays (9).

The above discussion indicates that there are a number of plausible mechanisms that could be expected to scavenge Mg from slag leachate. It also points to the need for research into the mobility and fate of silica, alumina, and other constituents of slag. Although calcitic tufa is the most conspicuous chemical product of steel slag leachate, many other less obvious reactions are possible. For example, the chemical environment in slag leachate is

quite similar to that within water-saturated cement paste, which suggests that the alkali-silica reaction could occur (especially when deicing salt is present) or that cementitious minerals could form in or near buried slag. Such reactions could be beneficial or deleterious, depending on site-specific conditions and design goals.

The most important inorganic chemical constituents in the alkaline seepage that cannot be readily explained by leaching of slag are sodium and chloride. These two ions occur in roughly the same 1:1 molar ratio as in common salt (NaCl). Some industrial wastes contain NaCl brine, but a more likely source is highway deicing salt. A rough estimate of the amount of NaCl deposited on I-695 in the probable catchment area of the springs is about 27 000 kg/year. Much of this salt dissolves and infiltrates the embankment. Although not all of it reaches the alkaline springs, enough probably does to account for the roughly 680 kg/year of NaCl discharged to the containment pond.

Ions not directly involved in carbonate equilibria may have significant effects on the precipitation of calcite. If water temperature and concentrations of  $\text{Ca}^{2+}$  and  $(\text{CO}_3)^{2-}$  are the same in two solutions but one solution has a higher concentration of other dissolved ions, that solution will be less saturated with respect to calcite because the activity coefficients of  $\text{Ca}^{2+}$  and  $(\text{CO}_3)^{2-}$  will be reduced. The most significant of these "passive" ions at North Point and in typical highway underdrain water are  $\text{Na}^+$  and  $\text{Cl}^-$ ; since concentration of these ions varies greatly depending on weather conditions and time of year, they may be important influences on seasonal variations in tufa precipitation.

If the flow rate and dissolved solids content (excluding NaCl) of the springs are extrapolated, the embankment is losing roughly 1000 kg of solids in solution every year. The long-term effect of this process on embankment stability is unknown.

The containment pond in which the spring water accumulates often has a peculiar turquoise color. This was a cause of concern, because some heavy metal ions (copper, chromium, and vanadium) can produce blue or green colors in solution. However, these elements are not present in detectable amounts in the pond or spring water. The color is believed to have a benign origin. The water of many natural springs fed by carbonate (limestone or dolomite) aquifers also has a blue or blue-green appearance. There are at least eight springs named Blue Spring in Missouri alone (10), and Maryland has the Potomac Blue Spring south of Cumberland. The cause of this color is probably the differential scattering of white light by particles of suspended carbonate minerals less than 1  $\mu\text{m}$  in diameter. This "Tyndall scattering" is basically the same mechanism that makes the clear daylight sky appear blue.

Water from the main perennial spring contains two semivolatiles organic compounds (29 ppb naphthalene and less than 10 ppb methyl-naphthalene). Furthermore, the strong mothball-like odor of naphthalene is evident in some boring samples of the slag bed, and all slag samples tested averaged about 1.5 percent organic matter, which is significantly higher than the results for the nonslag soil samples. The semivolatiles polycyclic aromatics detected are coal-tar derivatives, produced when coal is converted to coke, which is then used to fuel the same furnaces that produce slag as a by-product. The prime contractor for the I-695/North Point Boulevard complex is also a major supplier of slag aggregate and has a contract to do hauling at the giant Bethlehem Steel Sparrows Point plant. This coincidence makes it more likely that the contractor emplaced within the embankment slag contaminated by coal-tar sludge and possibly other industrial wastes from Sparrows Point.

## REMEDIATION

Capping the spring is not a valid solution. Even if the conspicuous perennial discharges could be sealed, the groundwater would simply back up until new outlets were established; the effect would be cosmetic at best. Furthermore, it is undesirable to impede drainage in an embankment, because this could increase pore pressures to the point that slope failure occurs.

Removing the slag would entail excavating hundreds of lane-feet of pavement and thousands of cubic yards of overburden, as well as the slag itself, which might then have to be disposed of as a hazardous waste. The monetary and other cost (traffic disruption, etc.) of rebuilding the embankment would be out of proportion to any benefit to be obtained.

Various techniques for encapsulating or isolating buried wastes to prevent interaction with groundwater are possible (e.g., slurry walls, grout injection). However, the volume and areal extent of the slag would make this strategy expensive, and introducing impermeable materials into an embankment would produce complex and probably adverse effects on groundwater drainage.

Reducing leachate generation by minimizing infiltration into the top of the embankment offers a reasonable first solution, and one that could be pursued incrementally. Relatively inexpensive measures include repairing distressed ditch pavement, paving ditches, and installing rebuts to catch pavement runoff before it can flow onto grassy surfaces and infiltrate. As an extreme measure, the entire top of the embankment could be capped with impermeable material. However, since drainage control could not guarantee a total absence of spring flow, management chose to have the leachate treated and discharged. A pilot study indicated that bubbling CO<sub>2</sub> gas through the leachate rapidly reduced the pH to non-hazardous levels, but this technique was never employed on a full-scale basis because of concern about the large quantities of calcite sludge that it would have generated. Instead, a temporary treatment plant housed in a truck trailer used HCl to neutralize the leachate. Continuing problems with vandalism and corrosion of the trailer by HCl fumes caused a return to pump-and-haul disposal while a permanent treatment plant, also using HCl, was constructed. Doubts remain about the suitability of a system that will require repeated skilled maintenance and monitoring and that involves leaving a hazardous acid substance in a vandal-prone unmanned structure.

## CONCLUSIONS

Slag leachate acquires its high pH and calcium content through hydrolysis of a man-made metastable compound (quicklime) in a microenvironment largely closed to CO<sub>2</sub>. Once it moves out of this environment and becomes subject to buffering by atmospheric CO<sub>2</sub>, it dissolves CO<sub>2</sub>, precipitates calcite, and exhibits a decline in pH. This process could be accelerated by bubbling CO<sub>2</sub> or air through the leachate.

On the basis of the contractor's account of its provenance, the slag may have experienced decades of exposure before emplace-

ment in the I-695 embankment, which is itself over 20 years old. This suggests that aging or weathering of some slags does not guarantee their inability to generate troublesome leachate.

Conspicuous tufa is not the only form of calcite precipitated from slag leachate. Cemented soils also form, affecting drainage and vegetation of the subgrade. Precipitation of other minerals, including carbonates, hydroxides, and silicates, is thermodynamically favorable.

The caustic seepage from the I-695 embankment teaches an expensive lesson; costs of remediation had reached \$1,000,000 by early 1994. Whatever the original motive for its use, slag has certainly not turned out to be cost-effective in this instance. Highway agencies are coming under increasing pressure to use industrial wastes in construction. Some of these materials are attractive from the standpoint of initial cost, performance specifications, and availability, but they may involve risks that must be carefully studied before these materials are accepted. More research needs to be done on the mobility and fate of weathering products and leachate constituents before industrial waste products are widely dispersed into the environment in the name of recycling.

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