

AN ELEMENTAL IRON REACTOR FOR ARSENIC REMOVAL FROM GROUNDWATER

Dimitrios Vlassopoulos (dimitri@sspa.com), Joy Pochatila, Arthur Lundquist, and Charles B. Andrews (S.S. Papadopoulos and Associates, Bethesda, Maryland)
Michael T. Rafferty, Ken Chiang, and Dominique Sorel
(S.S. Papadopoulos and Associates, San Francisco, California)
Nikolaos Nikolaidis (Technical University of Crete, Chania, Greece)

ABSTRACT: A prototype in-situ flow-through reactor was constructed and operated to treat groundwater affected by arsenic at a former pesticide manufacturing site in New Jersey. Elemental iron is employed as the reactive medium. Perched groundwater beneath the site is affected by arsenic at concentrations of up to 10 mg/l.

A series of field treatability tests using flow-through vessels packed with a mixture of iron and quartz sand were performed. Constant flow rate tests were conducted over periods of one to several days with residence times ranging from 1 minute to 5 hours. The mean influent arsenic concentration was 3.0 mg/l. Steady-state effluent concentrations were generally less than 0.01 mg/l for retention times greater than 40 minutes, and increased with decreasing residence time. In the treatability tests, more than 99.8% of the influent arsenic was removed. Arsenic removal in the reactors follows pseudo first-order kinetics, but actually depends on the rate of iron corrosion.

A full-scale reactor was designed to treat up to 10 gallons per minute of shallow groundwater collected from railroad sub-drains at the site. An in-situ, passive (gravity flow) system was designed that is capable of isolating the flow stream from surrounding groundwater for performance monitoring. The reactor consists of a concrete-walled vessel in which a 1.8 cubic meter reactive zone is emplaced between upstream and downstream gravel chambers. The reactor also is equipped with an influent-side CO₂ injection system for pH control. The treatment unit was operated between July and November 2001. More than 280,000 gallons of perched groundwater were treated and 3 kg of arsenic were removed over a 16 week period. Arsenic removal, initially greater than 99%, began to decline after the first month, eventually leveling off at 94% removal by the third month.

INTRODUCTION

In recent years, elemental or zero-valent iron (ZVI) has received considerable attention as a reactive medium for treatment of a wide variety of contaminants in water, including chlorinated hydrocarbons, chromium, nitrate, and radionuclides (United States Environmental Protection Agency, 2002, and references therein). One of the chief advantages of ZVI-based treatment technologies is their adaptability to passive flow-through applications, which can be significantly less costly to operate and maintain than traditional pump-and-treat systems.

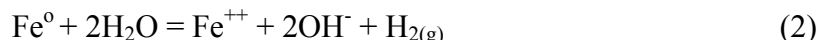
Although ZVI-based technologies are presently available for some contaminants (e.g. chlorinated hydrocarbons), many other potential applications are still under development and testing. Technologies for arsenic removal based on ZVI are of particular

interest, in view of the potential savings in treatment costs relative to existing alternatives such as chemical precipitation/coagulation and ion exchange. Recent studies by Lackovic et al. (2000), Su and Puls (2001), and Ferrell et al. (2001), have demonstrated arsenic removal by ZVI in batch and flow-through laboratory systems. These studies have shown that the arsenic removal mechanism is closely linked to iron corrosion reactions.

Aqueous corrosion of elemental iron proceeds by oxidative dissolution, both aerobically (coupled to oxygen consumption):



as well as anaerobically (coupled with hydrogen evolution):



These reactions result in an increase in pH and dissolved iron concentrations and a decrease in the redox potential of the water. Other electron acceptors (nitrate, sulfate, bicarbonate, etc.) may also promote iron corrosion. Depending on the type and concentration of electron acceptors, ferrous ions can also be further oxidized to ferric iron. Solid-phase corrosion products can include $\text{Fe}(\text{OH})_2$, mixed Fe(II/III) oxides (magnetite, maghemite) and hydroxides (green rusts), and FeOOH polymorphs. Arsenate (As(V)) and, to a lesser extent, arsenite (As(III)) species are adsorbed by ferric oxyhydroxides (Fuller et al., 1993; Waychunas et al., 1993) and green rusts (Randall et al., 2001). Green rusts are intermediate products of iron oxidation that eventually transform to ferric oxyhydroxide phases where arsenic can ultimately be sequestered by co-precipitation. Furthermore, solid-phase spectroscopic and solution-phase speciation evidence indicates that As(V) does not directly participate as an oxidant in iron corrosion and therefore reduction of As(V) to As(III) by iron corrosion alone is not expected to be significant (Ferrell et al., 2001). The co-precipitation of arsenic with iron corrosion products is thus a potentially viable removal mechanism.

We present a field evaluation of the arsenic remediation technology (AsRT) described by Nikolaidis et al. (2000). The prototype unit was constructed at a former pesticide manufacturing site in New Jersey where shallow groundwater in a perched zone is affected by arsenic at concentrations of up to 10 mg/L. Pilot operation of the prototype began in July 2001 to evaluate long-term performance and maintenance requirements and gather information to be used in developing cost comparisons with other treatment options. This paper summarizes the design and construction of the reactor, and presents a preliminary performance evaluation.

MATERIALS AND METHODS

The ZVI used in this study was a scrap iron aggregate supplied by Connelly-GPM (Chicago, IL). This variety of iron was selected because of its fairly uniform grain size (-8+20 mesh), relatively high specific surface area ($1.8 \text{ m}^2/\text{g}$), and high reactivity towards arsenic (Lackovic et al., 2000). The iron was mixed 50% by weight (approximately 1:3 by volume) with coarse quartz sand. The porosity of the mixture was ~50%.

Field Treatability Studies. Field treatability tests were conducted to evaluate arsenic removal kinetics. Three flow-through vessels were used (15-gallon and 20-gallon canisters, and a 10-cm diameter by 60-cm long PVC column). A known volume of the

iron/sand mixture was packed between layers of pea gravel and the vessels were sealed. Site groundwater was pumped to an equalization tank, from where it was pumped to the reactor vessel. Each of the tests consisted of pumping groundwater through the reactor at a constant flow rate, which was varied between tests. This allowed the hydraulic residence time within the reactive zone to be varied between 1 minute and 5 hours. Each test was carried out for between one and several days, depending on the flow rate.

Influent and effluent water quality parameters (temperature, pH, and specific conductance) were continuously monitored and effluent ferrous iron and arsenic concentrations were screened in the field. Automatic samplers were used to collect influent and effluent water samples at regular intervals. Water samples were analyzed for arsenic and iron.

Full-Scale Prototype Design and Construction. The purpose of the construction and operation of the full-scale prototype was to collect data from long-term operation, in particular to measure expected removal rates, arsenic loading rates on the iron bed, breakthrough rates, and to identify potential operational problems to be mitigated in a full-scale operation. Kinetic information obtained from the field treatability data were used for design of the full-scale reactor. The full-scale system was designed to treat up to 10 gpm of water containing dissolved arsenic at an average concentration of 3 mg/L.

The water is collected from a railroad sub-drain which provides a preferential pathway and discharge zone for perched groundwater at the site. The collected water is piped to the reactor unit through an in-ground, gravity flow system that is capable of isolating the flow stream from surrounding groundwater for performance monitoring. Water flows from the sub-drain through a flow meter into the reactor and from the reactor into a limestone gravel exfiltration trench. A gas injection port fitted with a diffuser on the influent-side piping between the flow meter and the reactor is designed to allow for influent pH adjustment as necessary by injection of CO₂. The reactor, constructed from a 3.5 m³ concrete box, was installed between 7 and 11 feet below ground surface. Treatment occurs within a 1.8 m³ zone containing approximately 3400 kg of the iron/sand mixture. Gravel chambers are located at each end of the concrete box to distribute the flow across the treatment bed. Sampling ports are installed in the influent and effluent piping, and multilevel monitoring points are installed at four locations within the reactor.

Performance Monitoring. Reactor performance is monitored by collecting and analyzing water samples from the influent, effluent, and interior (multilevel) monitoring points. Sampling is carried out with a peristaltic pump and disposable polyethylene tubing using low-flow techniques. Field measurements include temperature, specific conductance, pH, dissolved oxygen, redox potential (ORP) and turbidity, as well as dissolved arsenic and ferrous iron. Influent, effluent, and interior monitoring point water samples are analyzed for total and dissolved metals (arsenic, iron, manganese, and aluminum), major cations, anions, silica, and sulfide.

RESULTS AND DISCUSSION

The treatability tests provided information on initial arsenic removal kinetics, which was used for the scale-up to full-scale system. An overview of the treatability study

findings is presented below, followed by full-scale design considerations, and an account of the full-scale treatment unit performance.

Field Treatability Studies. A total of nine test runs were performed. Operating conditions and results for each test are summarized in Table 1. Influent arsenic concentration remained fairly constant with a mean value of 3.0 mg/L. Influent iron concentrations averaged 0.9 mg/L. Mean (steady-state) effluent concentrations are summarized in Table 1. Effluent arsenic concentrations were generally less than 0.01 mg/L for tests in which the residence time was longer than 45 minutes, but longer residence times (up to five hours) did not result in significant further decrease in effluent arsenic concentration (Figure 1).

TABLE 1. Pilot test conditions and results.

| <i>Test</i> | <i>Pore Volume (L)</i> | <i>Residence Time (min)</i> | <i>Volume Treated (L)</i> | <i>pH_{influent}</i> | <i>pH_{effluent}</i> | <i>Fe_{effluent} (mg/L)</i> | <i>As_{effluent} (mg/L)</i> |
|-------------|------------------------|-----------------------------|---------------------------|------------------------------|------------------------------|-------------------------------------|-------------------------------------|
| 1 | 28.6 | 290 | 687 | 7.23 (0.16) | 9.13 (0.07) | 10.9 (1.88) | 0.005 (0.002) |
| 2 | 19.3 | 260 | 500 | 6.76 (0.12) | 8.37 (0.87) | 0.66 (0.19) | 0.004 (0.001) |
| 3 | 28.6 | 81 | 2078 | 6.90 (0.10) | 9.20 (0.21) | 19.8 (1.74) | 0.004 (0.000) |
| 4 | 28.6 | 47 | 2330 | 6.85 (0.06) | 9.76 (0.15) | 11.7 (0.89) | 0.008 (0.002) |
| 5 | 28.6 | 28 | 2984 | 7.42 (0.06) | 9.25 (0.08) | 17.5 (2.69) | 0.078 (0.025) |
| 6 | 28.6 | 15 | 4516 | 7.13 (0.07) | 9.37 (0.06) | 7.50 (1.05) | 0.061 (0.005) |
| 7 | 28.6 | 4.9 | 625 | 7.60 (0.02) | 7.77 (0.02) | 5.74 (0.52) | 0.217 (0.016) |
| 8 | 2.0 | 1.8 | 1980 | 7.07 (0.03) | 7.76 (0.05) | 9.65 (0.55) | 0.051 (0.007) |
| 9 | 2.0 | 1.0 | 2645 | 7.35 (0.13) | 7.62 (0.16) | 5.80 (0.33) | 0.104 (0.005) |

Values in parentheses represent 1 standard deviation

Full-Scale Design. Retention time was the primary design parameter used to scale-up to the prototype treatment unit. The necessary retention time and flow rate determine the required size of the reactor. A minimum retention time of 40 minutes was considered necessary to achieve adequate arsenic removal (Figure 1). Historical data indicated that the average flow rate from the sub-drain discharge was on the order of 2 gpm, and could range from less than 1 up to 10 gpm. To achieve the minimum required retention time under the relatively wide range of variation in flow rates, a safety factor of 3 was applied to the mean flow rate. The required pore volume of ~240 gallons corresponds to a treatment zone volume of 480 gallons (1.8 cubic meters). Assuming an influent arsenic concentration of 3 mg/L, initial effluent arsenic concentrations less than 0.01 mg/L would be expected under average flow conditions. The prototype was therefore constructed with a 1.8 cubic meter treatment zone.

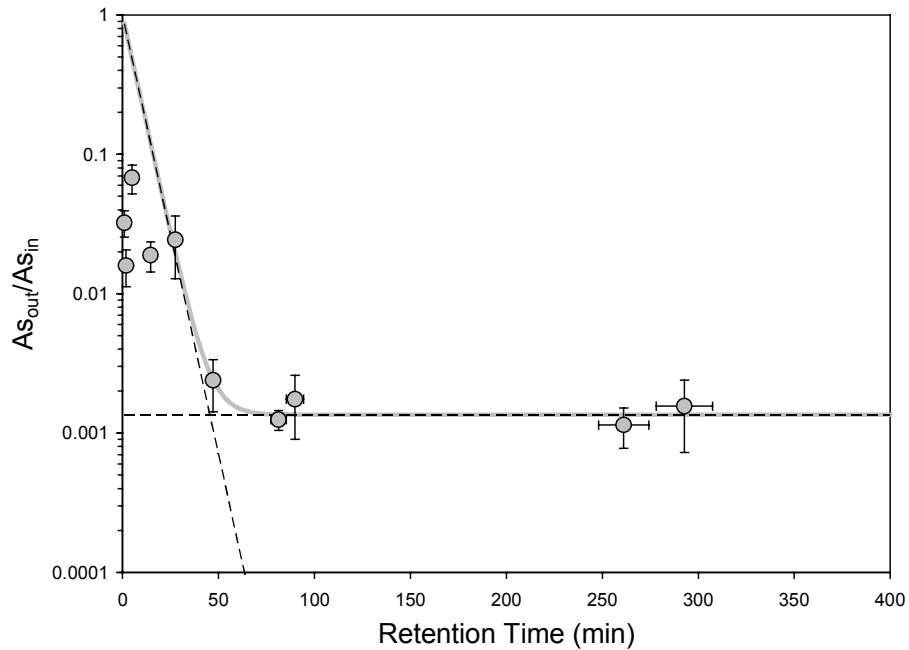


FIGURE 1. Steady-state arsenic removal as a function of residence time.

Performance of the Prototype System. The full-scale treatment unit was operated initially for a period of sixteen weeks between July and November 2001. Operation was suspended because of insufficient groundwater discharge from the sub-drain due to a particularly dry Fall season in New Jersey. Table 2 summarizes influent and effluent arsenic concentrations, flow rates, cumulative volume treated and arsenic removed during the first 16 weeks of operation. During this period, a total volume of approximately 280,000 gallons of perched groundwater was treated, and approximately 3 kg of arsenic removed. The average influent dissolved arsenic concentration was 2.8 mg/L. Effluent dissolved arsenic concentrations ranged from below detection limits (0.0066 mg/L) to 0.342 mg/L, generally increasing over time.

Dissolved oxygen concentrations decreased from an average of 5.9 mg/l in the influent to negligible levels in the effluent. The oxidation-reduction potential (ORP) decreased from an average of -24 mV in the influent to -143 mV in the effluent. Average influent pH was 7.2 and increased to 9.4 in the effluent. These observations are consistent with the expected effects of iron corrosion. The average effluent dissolved iron concentration (0.28 mg/L), however, is only slightly greater than the average influent concentration of 0.19 mg/L. The lack of elevated dissolved iron concentrations in the effluent (contrary to what was observed during the treatability study) implies that most of the dissolved iron released by corrosion reactions in the treatment zone is precipitated within the downstream gravel bed before exiting the reactor. This observation is consistent with several other applications of zero-valent iron in-situ treatments (Gu et al. 1999; Sass et al., 1998; Warner et al. 1998) where effluent concentrations of dissolved iron are typically less than 1 mg/L. Gu et al. (1999) indicate that under these typically

alkaline conditions (pH>8 and presence of dissolved carbonate), dissolved iron concentrations are expected to be less than 0.01mg/L.

TABLE 2. Summary of prototype reactor performance.

| Day | Flow Rate (gpm) | | Volume Treated (gallons) | Arsenic Concentration (mg/L) | | Arsenic Removal (%) | Cumulative Mass Removed (kg) |
|-----|-----------------|------------------|--------------------------|------------------------------|----------|---------------------|------------------------------|
| | Measured | Interval Average | | Influent | Effluent | | |
| 2 | 2.0 | 2.0 | 5,530 | 3.00 | 0.042 | 98.6 | 0.06 |
| 5 | 1.7 | 1.6 | 12,500 | 2.08 | 0.0095 | 99.5 | 0.12 |
| 10 | 1.9 | 1.5 | 23,700 | 3.12 | <0.0066 | >99.8 | 0.25 |
| 16 | 2.1 | 1.3 | 35,100 | 3.45 | <0.0066 | >99.8 | 0.40 |
| 24 | 2.8 | 5.8 | 102,000 | 2.01 | 0.0723 | 96.4 | 0.89 |
| 32 | 1.6 | 1.9 | 124,000 | 2.48 | 0.0343 | 98.6 | 1.09 |
| 48 | 2.2 | 0.9 | 146,000 | 3.77 | 0.342 | 90.9 | 1.36 |
| 65 | 2.6 | 2.6 | 213,000 | 3.28 | 0.0856 | 97.4 | 2.19 |
| 83 | 1.5 | 1.8 | 261,000 | 3.17 | 0.201 | 93.7 | 2.73 |
| 96 | 0.6 | 0.9 | 277,000 | 2.36 | 0.130 | 94.5 | 2.86 |
| 109 | 0.1 | 0.3 | 283,000 | 1.85 | 0.113 | 93.9 | 2.91 |

Figure 2 shows dissolved arsenic concentrations in influent, effluent and within the treatment zone (30 cm from the upstream end), and flow rate versus time. Arsenic concentrations in both the effluent and within the treatment zone gradually increased during the first nine weeks, but appear to have stabilized since. The spikes in effluent concentration during the fourth and seventh weeks of operation coincide with period of higher than average flow related to significant precipitation events. Although the reactor discharge pipe is normally at a higher elevation than the local groundwater, during such events groundwater levels can rise to the point which groundwater may temporarily enter the gravel bed on the effluent side of the reactor unit. Under these conditions, the effluent can be contaminated by the untreated groundwater, and this appears to be a likely explanation for the spikes.

Relationship of arsenic removal rates to iron corrosion rates. More than 99% of the influent arsenic was removed initially, but after the ninth week, the reactor appears to have stabilized at around 94% removal. It was hypothesized that decreasing iron corrosion rates and slower production of new sorption sites were responsible for the decline in performance. To evaluate this, pseudo first-order arsenic removal rates were calculated according to:

$$k_{As} = \frac{-\ln(As_{effluent} / As_{influent})}{RT} \quad (3)$$

where $As_{effluent}$, $As_{influent}$, and RT are effluent and influent dissolved arsenic concentration and residence time, respectively. These were compared to apparent iron corrosion rates, as approximated by the net rate of dissolved iron production:

$$k_{Fe} = \frac{(Fe_{max} - Fe_{influent})}{RT} \quad (4)$$

where $Fe_{influent}$ and Fe_{max} refer to influent and maximum dissolved iron concentrations (at the column effluent for the treatability tests or within the iron media for the full-scale system). Figure 3 shows arsenic removal rates as a function of iron dissolution rates for both column and full-scale systems. The arsenic removal rate is strongly correlated with iron corrosion rate, which suggests that continued long-term performance of the arsenic treatment unit is dependent on maintaining high iron corrosion rates.

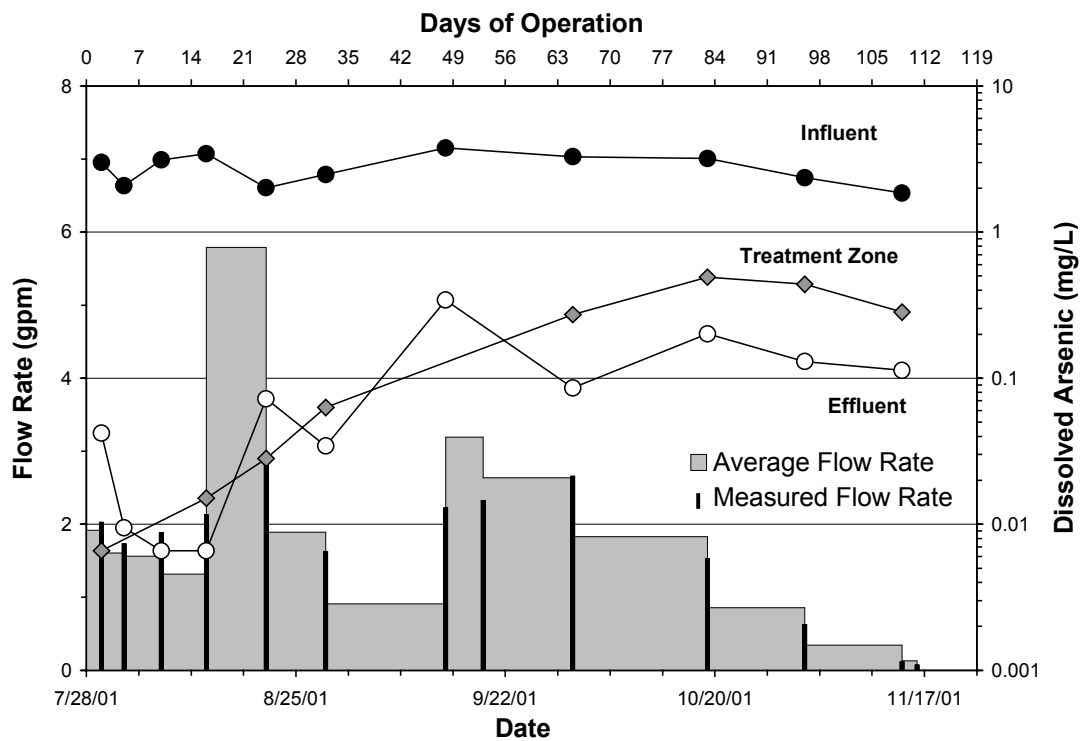


FIGURE 2. Flow rate and arsenic concentrations versus time.

There are several possible explanations for the observed decrease in arsenic removal, all linked to the overall rate of iron corrosion and production of sorption sites in the reactor, including: (1) initially higher rates of sorption site generation due to corrosion of high surface area fines which were completely dissolved over time; (2) decrease in effective surface area available for corrosion due to coating of iron surfaces by corrosion products, (3) passivation of iron surfaces due to an increases in influent pH over time.

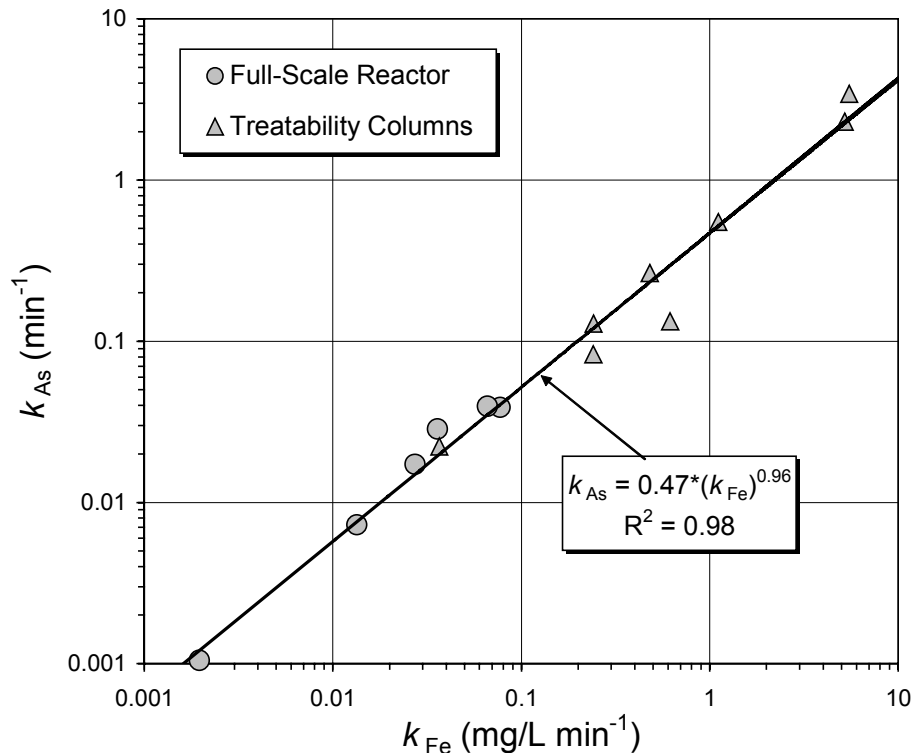


FIGURE 3. Correlation of arsenic removal rates with iron dissolution rates.

CONCLUSIONS

A prototype in-situ treatment unit for arsenic removal was constructed and operated for sixteen weeks. More than 280,000 gallons of perched groundwater were treated and 3 kg of arsenic were removed during this period. The reactor removed >99% of influent arsenic initially but appears to have stabilized at 94% removal after the ninth week. The technology holds promise for both in-situ and above-ground applications, but additional understanding of factors determining the long-term performance of the reactive media is still needed.

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