POSTER PRESENTATION: 1c. Remediation technologies and approaches

ISCO APPLICATION IN A SALTMARSH AREA CONTAMINATED BY FUEL IN SOUTHERN SPAIN (BIOXISOIL PROJECT)

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INTRODUCTION

In situ chemical oxidation (ISCO) is an effective technology for clean up site contaminated by organic compounds. This remediation involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming groundwater or soil contaminants into less harmful chemical species. Commonly applied oxidants are permanganate, hydrogen peroxide (with or without iron), ozone and persulfate. For ISCO to be effective, the oxidant must contact the contaminant. This can be difficult in many soils and aquifers where natural heterogeneities can result in flow bypassing around lower permeability zones or where the presence of natural compounds can generate non-productive reactions that consume oxidant compromising the adequate oxidant transport and distribution.

This case study describes the remediation of hydrocarbon in a complex site in a southern of Spain. Site soils are the result of an accumulation of earthy anthropogenic materials on marsh deposits, showing important constraints for ISCO development such as a temporary shallow water table and an irregular vertical and horizontal distribution of contamination as well as a high calcium carbonate content and salinity.

OBJECTIVES

The overall objective of the project is to evaluate, in real conditions, an ISCO application in a saltmarsh area contaminated by fuel in southern Spain, hydraulics and hydrogeochemicaly heterogeneous, by ISCO technique using as oxidant catalyzed hydrogen peroxide (Fenton's reagent).

This objective will be addressed by the partial achievement of the following objectives:

- Conduct a thorough site characterization in order to evaluate soil and water pollution as well as pedological and hydrological properties.
- Study the impact of the physical and chemical subsurface heterogeneities in the success of the ISCO technique.
- Evaluate and validate the effectiveness of the modified Fenton reaction in terms of TPH reduction and oxidation product formation.

METHODOLOGY

The initial direct-push technologies were used to make a complete site characterization. A total of 25 soil pits were realized with pedological criteria including corresponding soil sampling and the soil profile description. Hydraulic parameters like flow pattern or hydraulic conductivity were obtained by topographical survey of the site and by pumping tests in soil pits and pre-existing boreholes.

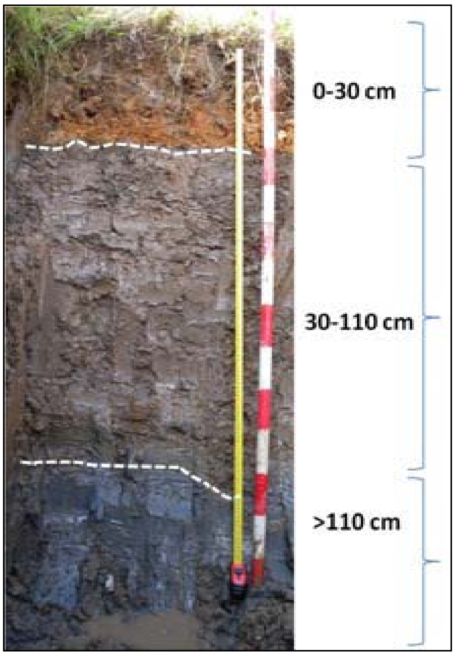
In order to study the impact of the physical and chemical subsurface heterogeneities and to design the injection program a more detailed characterization of soil and groundwater, consisting on well drilling in a selected area of 900 m^2 (figure 1) and the continuous monitoring of the underground water level evolution by the installation of automatic Diver type registration systems were realized.

Monitoring wells were pumped, to evacuate of a minimum of three volumes of water, prior to collecting a groundwater sample with a 12 V to take a representative sample. Ground-water sample collection took place 24 hours following well purging with bailers made of Teflon®. Sampling occurred in a progression from the least to the most contaminated well. Likewise, measurements for temperature, pH, ORP, conductivity and O_2 were taken at the time of the sampling.

Figure 1. Site layout and the monitoring network.

RESULTS

Based on one of the test pits performed, the characteristics of the materials constituting the zone of action are summarized in the Figure 2,



Anthropogenic fill level. Coarse grain size, basic pH; abundant CaCO3; moderate organic matter content;
variable salinity generally low; well rooted; well oxygenated
(reddish colours).

Shells level. level shells. Fine-grained (clayey-sandy) trend
laminar structure. Abundant presence of traces of astreidos, pectinides and others, occasionally cobble and

Figure 2. Conceptual Site Soil Model.

This conceptual model indicate that, from a hydraulically point of view, so-called "shell level" located within a depth, between 0.20 and 1.20 m., is limited in high by a anthropogenic fill more permeable and in depth by a sludge level, rich in clay, compacted and very impermeable. This physical heterogeneity can difficult oxidant distribution and transport capacity in the subsurface and consequently the efficiency of the treatment. Chromatographic soil analysis showed presence of TPH in the shells level.

Water analysis in monitoring wells showed high content of natural scavengers (inorganic carbon, chlorides and sulphates) that could affect the natural oxidant demand, that is an expression of how much oxidant is consumed, due to the fact that they compete with the contaminants of concern for hydroxyl radicals.

These findings (subsurface heterogeneities, preferential flow paths and presence of scavengers that consume oxidant) had implications for the program design injection:

A. To cushion the impact of physical heterogeneities and presence of preferential flow paths:

- Injections wells were constructed of polyvinylchloride (PVC) pipe with the screen interval placed in the vertical section intended for treatment. Injections well are constructed with slot well screens and coarse sand pack located to the same depth or slightly deeper than, the bottom of shell level (the most contaminated level).
- Affected level was isolate by packers (figure 3).

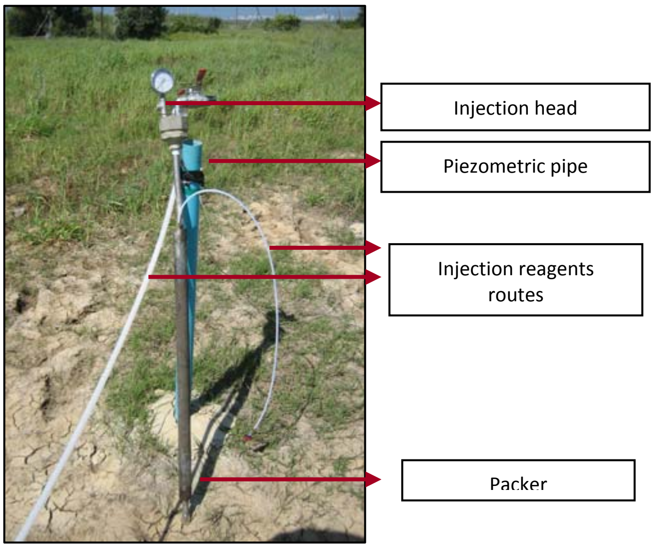


Figure 3. Head injection and packer used to isolate shell level

B. To cushion the impact of presence of natural scavengers:

- Hydrogen peroxide stabilizers were used.
- Hydrogen peroxide and catalyst solution with iron and hydrogen peroxide stabilizer were injected separately in order to increase the radius of influence.

Assuming these design characteristic, the reagents injection in a selected area started in January 2013. After injection of 9000L, by the help of an Automated injection device by Aitemin, that allowed to work in four injection wells simultaneously, and with the help of injection heads attached to a plug are arranged inside wells (Figure 4 and 5), a new groundwater sampling were realized in order to evaluate the efficiency of oxidation (TPH removed). Injection volumes, the concentration of TPH removed (g / L) and oxidation performance survey for each injection wells are shown in Table 1.

Figure 4. Details of the automated injection device

Figure 5. Head injection detail

Table 1. Injection volumes, the concentration of TPH removed (g / L) and oxidation performance survey for each wells.

Wells	Volume of oxidant (L)	[TPH] removed (ug/L)	Performance(%)
ZA1.1	0	-7440	-96%
ZA1.2	148	-1188	-80%
ZA1.3	0	-1329	-76%
ZA1.4	126,33	-23520	-99%
ZA1.5	0	-1329	-63%
ZA2.1	0	-1869	-76%
ZA2.2	148	-54264	-98%
ZA2.3	0	-45155	-99%
ZA2.4	150	-43210	-92%
ZA2.5	1442	-12006	-92%
ZA2.6	606	-1074	-72%
ZA2.7	0	-20808	-97%
ZA3.1	80	-57	-4%
ZA3.2	0	-689	-34%
ZA3.3	140	-1280	-62%
ZA3.4	392	-1778	-64%
ZA3.5	0	-652	-34%
ZA4.1	88	-712	-32%
ZA4.2	577	444	42%
ZA4.3	689	10	1%
ZA4.4	166	-174	-11%
ZA4.5	0	-403	-21%
ZA5.1	170	287	21%
ZA5.2	0	-530	-18%
ZA5.3	0	-606	-28%
ZA5.4	73	-933	-40%
ZA5.5	138	274	28%
I1	228	224	32%
S21	0	-1265	-32%
S22	294	-9939	-86%
S23	0	-1380	-63%
S24	10	286	47%
S15	0	532	93%
S26	605	-20924	-91%
S27	227	-1250	-45%
S28	110	1320	183%

Legend	
(green)	Inyected and [TPH] reduction
(red)	Inyected and [TPH] increase
(blue)	No Inyected and [TPH] reduction
(yellow)	No Inyected and [TPH] increase

Based on performance results, four types of cases were distinguished:

- Wells where Fenton reagent was injected and TPH dissolved concentration was reduced (ZA1.2, ZA1.4, ZA2.2, ZA2.4, ZA2.5, ZA2.6, ZA3.1, ZA3.3 , ZA3.4, ZA4.1, ZA4.4, ZA5.4, S22, S26 and S27). The greatest reduction occured in those wells with a higher preoperational TPH concentration, ZA2.4 ZA1.4.The presence of byproducts (alcohols, aldehydes and ketone), absents prior to the start of injection, indicated that the decrease was due to hydrocarbons oxidation and not to a dilution effect resulting from the injection of reagent solutions.
- Wells where Fenton reagent were injected but TPH concentration increased (ZA4.2, ZA4.3, ZA5.1, ZA5.5, I1, S24 and S28), phenomenon known as "rebound" (induced by TPH desorption from soil or solubilization of FLSN). Presence of byproducts confirmed the hydrocarbons oxidation. However, TPH increase would indicate soil areas untreated.
- Wells where Fenton's reagent wasn´t injected but TPH concentration decreased (ZA1.1, ZA1.3, ZA1.5, 2.1, ZA2.3, ZA2.7, ZA3.2, ZA3.5, ZA4.5, ZA5.2, ZA5.3, S21, S23, PC4). This finding, coupled with the byproduct presence in adjacent wells, demonstrated the correct reagent distribution through the subsurface.
- Wells where Fenton reagent wasn´t injected and the concentration of TPH increased (S15). This situation is attributed to the same phenomenon of solubilization or desorption from untreated areas.

Conclusions

An effective site characterization that allows the development of a valid conceptual site model (CSM) is essential for the design of ISCO technology and to determine treatment goals and operating conditions. A conceptual site model should incorporate the location and mass of contaminant of concern, an understanding of the pedology, geology and hydrogeology, aquifer geochemistry, major migration pathways for the contaminants of concern, groundwater flow direction/gradient, and the identification of surface and subsurface structures and underground utilities.

In this study area, a deep knowledge of site conditions (pedologic, geochemical and lithologic characteristics of the site, flow and mass transport) and its resulting conceptual site model (CSM) were fundamental tools to ensure the success of ISCO.

The injection program has been based on two strategies; the use of hydrogen peroxide stabilizers and the special oxidant delivery strategy (target level isolation and pressure injection). Both strategies were designed in order to solve some limitations that could have endangered the contact between the oxidant and TPH. These limitations are, on the one hand, hydrogeochemical conditions that limit the persistence of the oxidant in the subsoil by quickly reacting to this via catalysis (high pH and high content of anions -carbonates, sulphates and chlorides-), and on the other hand, hydraulic conditions that hinder the distribution of oxidant in the basement (high heterogeneity of soil horizons, low permeability of the target horizon and shallow, spatial and temporal variability of the water table).