INOVATIVE IN SITU REMEDIAL TECHNIQUES – KNOWLEDGE TRASFER AND PRACTICAL EXPERIENCE

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Abstract

In situ chemical oxidation (ISCO) is one of promising remediation technologies applied within the Central and Eastern Europe. Type and extent of contamination, as well as treated matrix and an application method are driving parameters for determining, which of oxidation agents or their combinations are the best choice for set site conditions. Laboratory experiments of Fenton's reagent, potassium permanganate and sodium persulphate (activated and non-activated) plus conclusions of selected pilot-scale tests are discussed. Information on a possible combination of ISCO with surfactants is further given.
Biologically enhanced reductive dechlorination (bio-ERD) offers a potential for destruction of chlorinated ethenes by an addition of a suitable electron donor directly to a contaminated ground. Organic by-products or processing waste of a food industry (e.g. beet molasses, stillage, whey) represent suitable as well as low-cost alternative electron donors for boosting this process. Results of laboratory experiments and a pilot-scale test performed on site heavily contaminated by chloroethylenes are presented.
Nano zero-valent iron (nZVI) has 20 to 30-times higher reactivity then conventional ZVI, and thus this aspect is often stated as a main advantage of its usage (as a contrariety to its high price). Stoichiometry and passivation of nZVI active surface by reaction by-products are closely associated together and this fact directly influences practical efficacy this material. Experimental testing of various nZVI reactivity on Cr(VI+) and results of a pilot-scale on a site polluted by chlorinated hydrocarbons and petroleum substances are discussed.
Moreover, bio-ERD and nZVI can be successfully combined in order to speed up remedial process, stabilise its performance and to cut clean-up financial costs. During this remedial train, nZVI generally accelerates establishment of anaerobic conditions in the ground and makes the first decomposition step (chemical reduction) of targeted pollutants. Later, the bio-ERD process finishes contamination treatment and, in general, returns back natural conditions onto a remediated site.

Keywords: Chemical Oxidation, Enhanced Reductive Dechlorination, Nano Zero-Valent Iron, Abiotic Chemical Dehalogenation, Biodegradation, Pollution, *In Situ*

1 Introduction

Practical applications of *in situ* remedial technologies are very promising today. Optimization of engineering measures (no need to excavate or to pump) and remedial costs are considered as their main advantages. A major disadvantage is seen in the fact that these approaches are locally specific and, therefore, it is necessary to thoroughly evaluate site conditions and to deeply consider technical feasibility of these methods before their usage.
The paper refers to practical knowledge obtained during a transfer of three innovative technologies (i.e. ISCO, bio-ERD, nZVI) from laboratory to company remedial practice. Principles of these methods are generally described at Wimmerova et al., 2010 and Svab et al., 2010.

2 Experimental part

2.1 In Situ Chemical Oxidation (ISCO)

ISCO was tested on various samples coming from selected contaminated sites located in the Czech Republic and Poland. The sites were contaminated by chlorinated ethenes (mainly PCE, TCE) and total petroleum hydrocarbons (TPH). The applied *in situ* method was pre-selected based on available information on the site's local conditions, type of contamination and a demand to complete proposed remedial work in shortest time (Wimmerova, 2009). Three oxidation agents (potassium permanganate, Fenton's reagent and sodium persulphate) were tested in bench laboratory conditions. For activation of hydrogen peroxide and sodium persulphate ferrous sulphate heptahydrate was used.

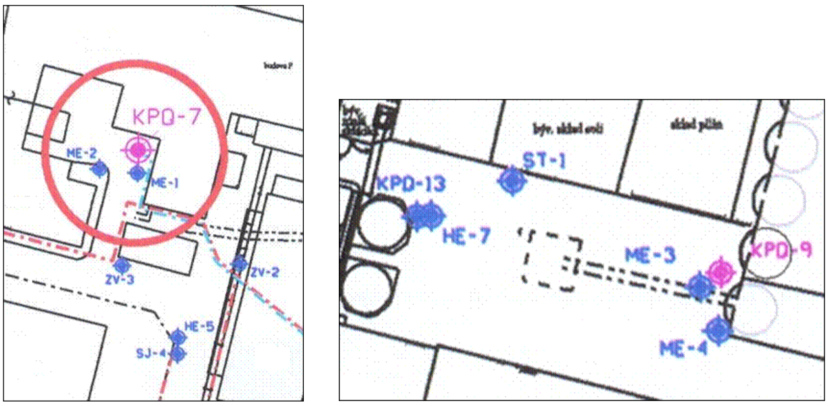

Fig. 1: *ISCO pilot-scales' set up (left – permanganate; right – Fenton)*

The pilot-scale tests presented were performed on two separate plumes of a former tannery site located in the Czech Republic. In both cases, one well was used for an oxidant gravitation injection and other three for process monitoring (***Fig. 1***).

2.2 Biologically enhanced reductive dechlorination (bio-ERD)

The presented experiments were carried out on samples taken from a contaminated site located in the Czech Republic. Stillage, beet molasses and whey were tested as alternative electron donors in laboratory reactor vessels (***Fig. 2***). Detailed analyses of chemical and physical properties of the used food-processing substrates were carried out before own experimental work.

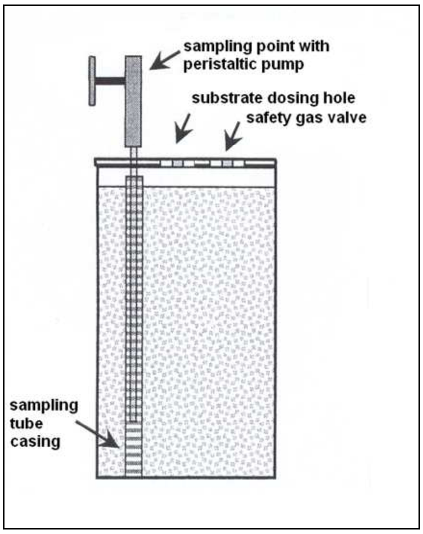

Fig. 2: *Bio-ERD laboratory reactors*

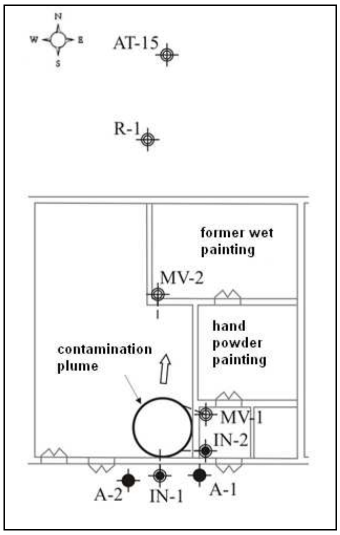

Fig. 3: *Bio-ERD pilot-scale*

A pilot-scale test was carried out on the above-mentioned site at the same time. As an electron donor was used whey mixed with beet molasses (w/w ratio 100:1). During the pilot test, whey was injected into four application wells and the process was monitored in other three wells (***Fig. 3***).

2.3 Nano zero-valent iron (nZVI)

Experimental testing of four nZVI samples' reactivity (coming from different suppliers) on Cr(VI+) and chlorinated hydrocarbons (CLHs) was carried out. The main idea of these experiments was to compare migration properties of the commercially available samples of nZVI in the highly-permeable model porous matrix and to check possibilities of improving these migration properties.
Based on achieved results a pilot-scale application was performed on a site polluted by CLHs and TPH due to air transportation. The process was observed in one application wells and three monitoring wells. A special device was used for nZVI injection (***Fig. 4***).

Fig. 4: *nZVI pilot-scale set up (left – wells' layout; right – an injection device)*

2.4 Combined Nano-Bio

This approach combines chemical reduction of Cr(VI+) by nZVI with biological reduction of the same metal. The first part (nZVI) is recommended for hotspot remediation of high Cr(VI+) concentrations, a prevention of this metal migration and to lower toxicity for bio-ERD. The second step (bio-ERD) is generally used for reduction and fixation of Cr(VI+) or for final treatment of plumes.
Batch experiments were performed on samples taken from a site contaminated by Cr(VI+) located in the Czech Republic. As substrates whey, lactates and vegetable oil were tested; nZVI of a Czech commercial producer was used. Further, column tests were also carried out. Different nZVI and Cr(VI+) concentrations and simulation of a system after organic substrate depletion were observed (***Fig. 5***).

Fig. 5: *Nano-Bio experimental columns*

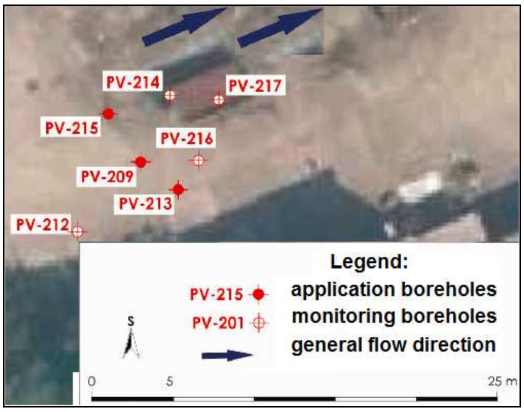

Fig. 6: *Nano-Bio pilot-scale*

A pilot-scale experiment has been on-going on the same site, where the Cr(VI+) contamination was caused by a potassium dichromate production. Three application and four monitoring boreholes have been used during this test (**Fig. 6**).

3 Results and discussions

3.1 Chemical oxidation

In general, all tested oxidants were approved to be effective for pollution reduction. Decrease of chlorinated ethenes up to 100% was achieved with 1.5w/v% potassium permanganate. Maximal speed of this oxidant consumption was observed within the first 150 hours of oxidation. Fenton (17.5v/v% hydrogen peroxide) was also highly effective for PCE and TCE destruction (up to 99.9%). Oxidation reaction was faster and more vigorous. Some of the oxidized soil contained high levels of iron (up to 140 g/kg) usable as a catalyst for hydroxyl radical formation.
The selected results from sodium persulphate experimental work showed, that the oxidant is a bit faster consumed in the case of use of activator. But, contaminant analyses did not indicated higher decrease of TPH in this case. Thus, the obtained results did not confirm a positive effect of ferrous ion on the TPH oxidation process.
During the pilot-scale test with potassium permanganate approx. 20 m^3 of 2w/v% permanganate solution was injected at a speed of 50 l/h. The results confirmed contaminant decrease below their detection limits. One month after finishing the infiltration, slight increase of chlorinated ethylene concentration was observed (i.e. rebounding effect). One month later additional increase up to 31% of the starting concentrations took place, but further increase was not observed. Similar results were achieved with Fenton. Due to problematic oxidant spreading, the peroxide was infiltrated at a higher speed (70 to 100 l/h). Slight rebounding effect was also observed (***Fig. 7***).

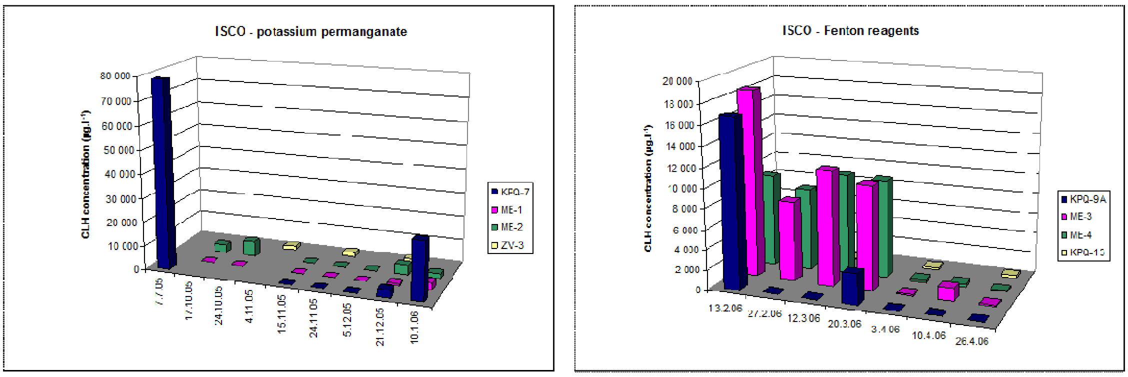

Fig. 7: *ISCO pilot-scales’ results*

Currently, DEKONTA researches dealing with the ISCO technique have been concentrating on elimination of two basic operational problems of this method: i) restricted contamination availability for oxidation process, and ii) inability of common oxidants to migrate on larger distances. Feasibility of further combination of surfactants with modern oxidants (persulphates, percarbonates, simple or activated) has been experimentally tested.

3.2 Biological dechlorination

Results of the laboratory part confirmed that is possible to use all tested substrates as alternative electron donors. Ethene and ethane were not detected, but high concentrations of methane were measured in all samples. The most significant changes were observed in the reactors with added stillage (up to 94%), followed by beet molasses and whey.
During the pilot testing approx. 8 m^3 of the substrate mixture was applied. At first stage, PCE and TCE significant decrease (below 40 mg/l and 22 mg/l) and massive increase of *cis*-1,2-DCE and VC (up to 240 mg/l and 60 mg/l) were observed. At second stage, ethane and methane (up to 4 mg/l and 2.5 mg/l) were detected. Increase of anaerobic and sulphate reducing bacteria contents (up to 10^4 CFU/ml and 10^3 CFU/ml) was also seen. Degree of dechlorination varied during the pilot test; it increased from 10-20% to 50-60% (***Fig. 8)***. Based on experiences obtained during the pilot test operation parameters were elicited for the model site.

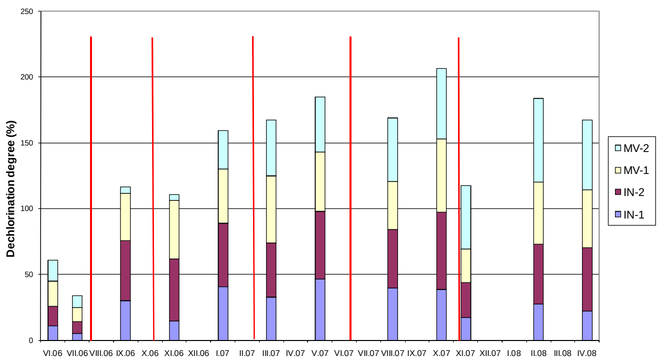

Fig. 8: *Dechlorination degree at the bio-ERD pilot (red lines indicate injection)*

3.3 Nano Iron

The detailed results of the laboratory part are available at Svab et al., 2010. These results confirmed the commonly known fact that reactivity of nZVI goes against its migration ability. But, it is important to mention the observed formation of a self-mixed pocket of nZVI in sand layers, which can cause significant discrepancy in experimental conclusions (***Fig. 9***).

Fig. 9: *The self-mixed pocket causing formation of a preferential way*

During the pilot-scale test, nZVI was injected three times via a specially developed apparatus. The results obtained confirm ability of the applied nZVI to reduce CLHs. After the first iron application 50% decrease of DCE in the injection well was observed as well as TCE. At the same time, increase of ethene, ethane and methane concentrations were detected.

Backward increase of CLHs in the injection well was observed two months later. This increase was supposedly caused by new contamination feeding (probably coming from unsaturated zone). Thus, the second application of nZVI was carried out. Again, the analogical trend of CLHs behaviour was observed. The monitoring wells showed also pollution fluctuations. The measured decrease levels were 24% and 44%.

3.4 Nano-Bio

During the batch test, rapid decrease of Cr(VI+) was measured for whey and lactate. Similar reduction rates were observed – 0.38 and 0.49 mg Cr(VI+)/l/day. Bioreduction was dominant process rather than chemical reduction; reduced chromium was bound mainly to Fe and Mn oxides (more then 60%). Effective reducing capacity was quantified as 80 to 160 mg Cr(VI+)/g of nZVI (depending on Cr(VI+) and nZVI concentration in soil). Natural attenuation capacity varied from 2.7 to 20.7 mg Cr(VI+)/kg of soil, depending again on Cr(VI+) concentrations.

The pilot nZVI injection resulted in rapid decrease of redox potential of the site and increase of groundwater pH up to 7 m from injection wells. After 7 months, groundwater remains under strongly reducing conditions in the area of injection wells, whereas further downgradient of the injection, the redox potential gradually restores to original level. Also, effect of nZVI injection was detectable in monitoring well situated at a distance of 7 m from the injection wells. 7 months later, Cr(VI+) concentrations stays below the detection limit in injection areas and monitoring well located at the distance of 3 m (***Fig. 10***).

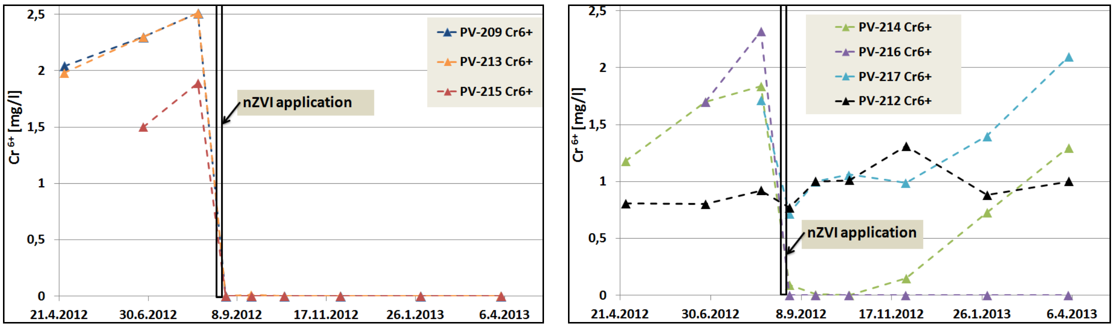

Fig. 10: *Concentration of Cr(VI+) during the pilot-scale tests*

Concentrations of total Cr correspond to concentrations of Cr(VI+), which implies that reduced chromium precipitates readily and its solubility is minimal under site pH.

4 Conclusions

The modern *in situ* remedial technologies are very promising for various contaminant treatments. Although they have many advantages, it is necessary to consider their limitations as well.

The technological knowledge obtained during R&D activities and numbers of pilot-scale applications of selected innovative *in situ* techniques helped to develop internal company guidelines and to establish company's professional confidence in applications of these methods.

Further, this achievement helped to broaden and optimise treatment measure, not only in the Czech Republic but also in other Central and Eastern European countries.

Acknowledgement

Authors would like to acknowledge for financial supports the Ministry of Industry and Trade of the Czech Republic, the Technology Agency of the Czech Republic and the 7th Framework Programme of the European Community (grants no. FD-K3/025, FI-IM2/086, FI-IM4/143, FR-TI3/244, TA01021792, and UPSOIL 226956).

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