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In situ chemical oxidation/reduction using the jet grouting technique (HaloCrete®)

Oxydation/Réduction chimiques sur site à l´aide de la technique de jet grouting (HaloCrete®)

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ABSTRACT: In 2018, after more than 8 years of development, Keller realized the first remediation work according to the new HaloCrete® remediation technique. Following some preliminary tests to prove the general applicability, in 2012 first extensive research work started with a series of laboratory experiments examining basic behavior of contaminant, binder and reductant as well as the leaching behavior of the simulated columns. As a consequence of the promising results, large-scale field test using standard jet grouting equipment were executed. In addition to the challenging test setup, e.g. the management of a constant ground water flow, the development of verification procedures suitable for on-site usage was one of the most important tasks. The main research process was completed by applying the new technique to a former laundry in Austria, where the soil was heavily contaminated with chlorinated hydrocarbons. HaloCrete® was designed to be a part of a combined solution of soil decontamination and retaining structure. In addition to the preparatory works, also safety, logistic and legal challenges due to working on a narrow site with potential harmful materials are described in the paper. Other key aspects discussed are the possibilities and limitations of extensive quality control to verify the success of remediation works.

RÉSUMÉ: En 2018, après plus de 8 années de développement, Keller a exécuté le premier travail de remédiation second la nouvelle technique de HaloCrete®. De suite de tests préliminaire pour éprouver l´applicabilité générale, le premier travail de recherche extensive a commencé avec une sérié d´expériments laboratoires qui examinaient le comportement de base de contaminant, de liant et de réducteur ainsi que celui du comportement de lessivage des colonnes simulées. En conséquence des résultats promettants, on a exécuté des tests sur une grande échelle en appliquant l'équipement de jet grouting. En plus de la mise en place compliquée de tests p. ex. celui de la gestion du flux constant d´eaux souterraines, le développement de procédures de vérification favorable à l´usage sur site était l`une des tâches la plus importante. La procédure principale de recherche a été complétée en appliquant la nouvelle technique à une ancienne blanchisserie en Autriche, où la terre était contaminée considérablement par des hydrocarbones chlorées. HaloCrete® a été projeté d´être une solution combinée de décontamination de la terre et de structure de support. En plus des travaux préparatoires, la sécurité, la logistique et des défis légaux dus à la construction sur un site étroit avec des matériels probablement nuisibles ont été décrits également dans le document. D´autres clés aspects discutés sont les possibilités et limitations du contrôle extensif de qualité pour vérifier le succès des travaux de remédiation.

KEYWORDS: jet grouting, DNAPL, site remediation, ISCO, ISCR

1 SITUATION

Chlorinated solvents (CS) like Tetra- and Trichloroethene (PCE/TCE) enjoy a widespread use in various application, especially chemical laundries and metalworking industries. They possess properties which, if they are used improperly, might cause problems to the environment. Sadly, this has often been the case in the past.

They behave as so called Dense Non-Aqueous Phase Liquids (DNAPL) seeping into the subsoil and through ground waterbodies forming pools on top of impermeable layers (Schwille, 1988). With time they intrude into these layers where they cannot be effectively treated with conventional remediation techniques i.e. injections. Due to their low solubility, they stay there for centuries causing cancerogenic plumes in the groundwater. Combined with the fact that users i.e. laundries often have been situated in urban areas further complicates the situation. Typical urbanized boundary conditions, e.g. heterogeneities due to manmade interactions (water, power and other lines, backfilling, etc.) make remediation works even more difficult.

1.1 *Remediation*

A possible approach to remediate CS-contaminated sites is oxidation or reduction using various chemical agents. This has proven to be very successful using nanoscale zero valent iron (nZVI) and Potassium Permanganate ($KMnO_4$) under laboratory conditions (Kueper et al., 2014). Here the contact between the reacting chemicals can be controlled sufficiently good. In the field the mixing required can be assured only by using the jet grouting or deep soil mixing techniques.

2 HALOCRETE® RESEARCH PROJECT

Similar to most other applications, binders can't be omitted for JG due to statical reasons. Therefore, the interaction between binders and remediation agents needs to be understood, hence examined. The research project HaloCrete® was set up for this purpose. A three phased approach was chosen, consisting of (1) batch testing, (2) column experiments and (3) a large scale field experiment. As a remediating agent nZVI was chosen. All experiments were designed to reflect the installation of a jet grouting column as close as possible.

2.1 *Batch experiments*

During the batch experiments six binders have been tested for suitability. It could be shown that hydraulic (ordinary Portland cement, OPC) and latent hydraulic binders (fly ash and slag sand) did not interfere negatively the ongoing reactions. Clays even exhibited catalytic effects.
Another finding was that that H_2 evolving from unwanted side reaction can be used to determine the suitability of a binder. Except for a tested zeolite, all other binders formed stable slurries which could be used in further experiments. Preliminary tests with mixtures of two binders indicated no negative interaction.

2.2 *Column experiments*

After the conclusion of phase 1 column experiments were conducted in phase 2 to take groundwater flow and real soil behavior into account. The high vapor pressure of TCE led to problems during the setup of the experiments. To circumvent them an approach similar to tremie concreting was chosen. A hard impermeable core was placed in glass columns, surrounded by a permeable annulus. To monitor the effectiveness of the reaction, treated as well as untreated tests were performed. The results presented in Figure 1. show significantly lower contamination concentrations in the treated columns.

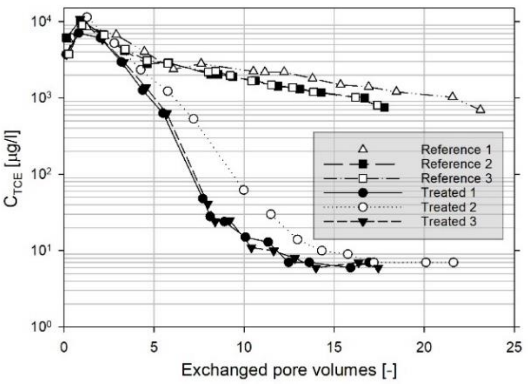

Figure 1. TCE concentration in column effluents (Logarithmic scale). After reaching a peak shortly after experiment start, they begin to decrease. The gradient differs significantly between treated and reference columns

2.3 *Large scale experiment*

The results of phase 2 justified the final phase, large scale testing under defined soil and hydraulic conditions. They took place at the Austrian Institute of Technology facilities were a four chamber (2m x 2m x 3m) lysimeter was available. The goal of this phase was to check if the various slurry recipes designed during phase 2 are applicable in the field. One of the criterions was to achieve an even distribution of nZVI across the whole cross section of the columns.

The chambers were built up using sandy materials with different permeabilities. The middle, relatively high permeable layer, was spiked with TCE. A steady groundwater flow was established by using levels at the influx and efflux respectively (Figure 2.).
TCE-Concentrations were measured in the efflux. After reaching steady state conditions, the JG column was executed.

After the treatment, the measurement of the concentrations was continued until no significant changes were observed. The columns were excavated, and samples were taken across the cross sections at various depths. As the TCE had been colored with β-carotene it was possible to correlate contents of colorant and contaminant (Figure 3.).

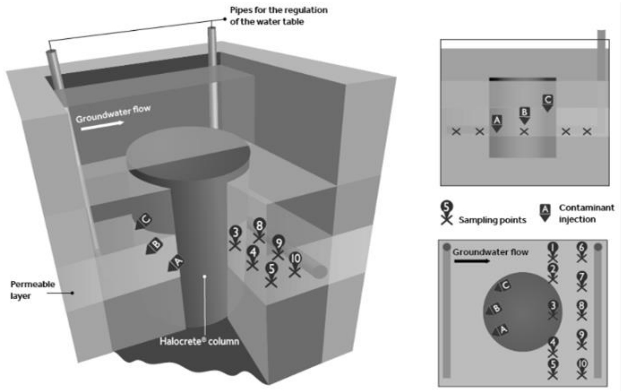

Figure 2. The large scale experiment setup. Groundwater flows through the middle layer which is TCE spiked (point A, B, C). Samples are taken at points 1-10.

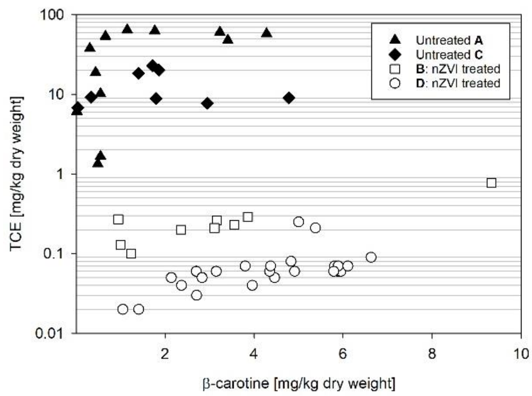

Figure 3. Results of the correlation between β-carotene and TCE (logarithmic scale).

The results confirmed the expectations to achieve low TCE concentrations in the treated columns whereas the untreated tests led to higher TCE concentrations. Regarding the mechanical parameters, the slurry was designed to achieve a strength of ca. 1 N/mm², matching approx. the soil strength before treatment. Using a Schmidt hammer on site during the excavation works, the strength requirements were confirmed successfully.

3 TEST APPLICATION / KOMBO RESEARCH PROJECT

The next step was to test the technique on a real-world site (technology readiness level 6). "N69 Putzerei Alaska", a former laundry, located in Zwölfaxing close to Vienna, constituted such a site. PCE was used there in the past which led to a heavily contaminated subsoil below and next to the main building.

The follow-up research project named KOMBO consisted of several work packages, starting with a detailed site investigation, large-scale experiments and finally the actual remediation works of the location. The source zone of the contamination was located using membrane interface testing (MIP). The testing principles are as follows: the compounds are picked up at a heated, hydrophobic membrane at the tip of a CPT tool. From there they are transported via an inert carrier gas stream to a gas chromatograph. Different detectors enable a classification and to some degree a qualitative determination (Figure 4.).

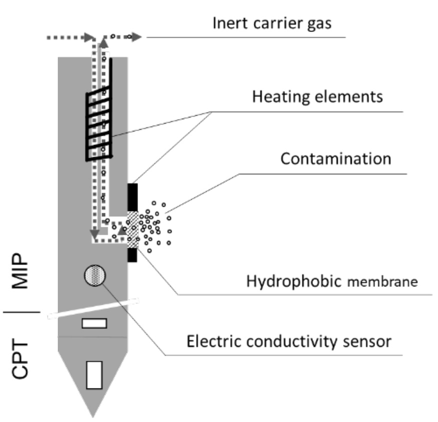

Figure 4. MIP probe (schematic)

In this way, the highest concentrations of CS were detected at a depth of ca. 8.0 m bGL., just on top of a silt layer into which they had penetrated partly over the years. Information on the soil type were also derived from the readings of the electric conductivity sensor.

The parameters for the JG works as well as the basic slurry design were selected based on the results of the large-scale tests of the Halocrete® research project (Freitag et al., 2014). Due to the oxidizing nature of the groundwater and soil conditions, Potassium permanganate ($KMnO_4$) was chosen as oxidizing agent. The actual remediation was done with the so-called Super triplex JG technique where two high pressure pumps are used in parallel. This allows for a simultaneous precutting- and jetting process. The approach was chosen in order to produce only one type of backflow slurry.

3.1 *Waste disposal*

The question of waste disposal had arisen early during the project. Although it was expected that degradation reactions will continue in the slurry, this assumption needed to be proofed. During KOMBO the backflow was collected and stored until chemical analyses confirmed the suitability for deposition according to legal regulations (Table 1.). During this examination $KMnO_4$, which intensively colored the slurry purple, caused problems, as it complicates chemical analyses. Many of them are based on photometry and therefor influenced by heavily dyed liquids and the dilution required. Chromium, a common OPC compound, is one of the affected components. pH and electric conductivity were high as expected because cement was used for the slurry.

Table 1. Excerpt of the chemical analysis, exceeded parameters in bold.
C&DWL…Construction and Demolition Waste Landfill
MWL…Mass waste Landfill

Eluate Analysis		**Result**	**Limit Values**	
Parameter	**Dim.**		**C&D WL**	**MWL**
pH	-	12,4	6,5-13	6-13
Conductivity	mS/m	983	**300**	
Evaporation Residue	mg/kg	30600	**25000**	100000
Chrome total as Cr	mg/kg	0,68	2	70
Chrome VI as Cr	mg/kg	**<10**	**0,5**	20
AOX as Cl	mg/kg	9,0	**3**	30
TOC as C	mg/kg	59	500	2500
Phenols as Index	mg/kg	<5		1000

The chemical analyses confirmed the initial assumption of the continuation of the degradation reactions. No compounds which would lead to a classification of the backflow as dangerous waste were detected.

The wastewater on site was also analyzed prior to disposal. The results conformed to the analyses of the solid waste, allowing a discharge into public sewage.

3.2 *Proof of success*

Usually, a remediation work is considered to be successful if concentrations and freight limits are reached in a defined monitoring well. Source zone remediation techniques like HaloCrete® strongly depend on a reliable localization of hot spots. Every undetected hot spot reduces the chances of a successful remediation dramatically. For the KOMBO project, the hot spots were well known, however, due to time and space constraints it was not possible to treat them all.

As only low strength requirements had to be met by the JG body, the slurry was designed to result in UCSs which allowed CPT soundings in the jetted subsoil zones. Figure 5. shows the results of a repeated MIP sounding at the same spot pre and after treatment. The DELCD signal - an indicator for chlorinated compounds - was reduced significantly. As a side effect of the OPC the electric conductivity was raised in the treated zone indicating the top and bottom of the JG column.

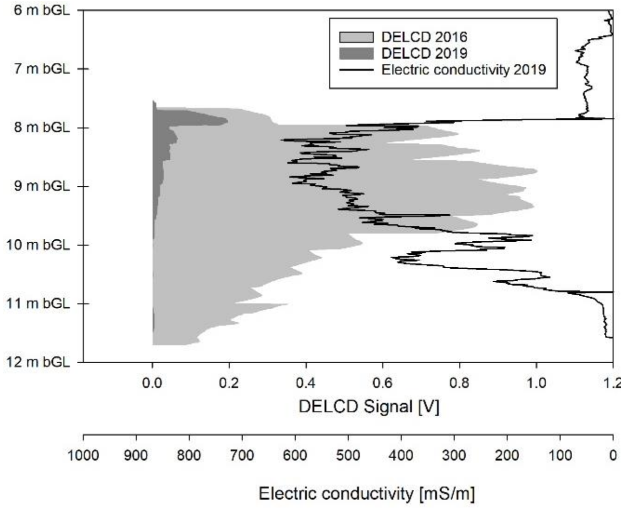

Figure 5. Comparison of MIP soundings from 2016 and 2019 indicating reduction of TCE in the subsoil. Electric conductivity shows top and bottom of the column.

4 FIRST APPLICATION

After concluding the research projects, the first real-world application was a former chemical laundry in Graz, Austria. The site "ST 25 Putzerei Plachy" is situated prominently, adjacent to the Central park. A plume originating from the laundry was detected right below this park (Moser, 2013).

Keller was contracted for retaining works for a construction pit using bored piles, but during the detail planning process two difficulties emerged. Firstly, the neighboring street was too narrow to allow for access with the large drilling rigs and secondly the contamination reached below the existing building and below the street. For both reasons, the intended solution was not possible. Keller was involved early enough in the project to suggest an alternative solution. Together with geotechnical and environmental consultant of the owner of the site, JG was designed for the structural support works and HaloCrete® for the remediation works of the contaminated areas.

4.1 *Preparatory tests*

When working under oxidizing conditions the question of natural oxidant demand (NOD) arises. The NOD needs to be known precisely, because an underestimation of this soil parameter would lead to insufficient oxidant and consequently an incomplete dechlorination.

During this stage of the project, also possible oxidants were tested for suitability under the given soil conditions. Mainly $KMnO_4$ as well as Sodium permanganate ($NaMnO_4$) were examined. The advantage of the latter is that it is available as a highly concentrated liquid, however, the disadvantage of the higher cost was even more critical. For the final formulation of the slurry recipe both, the NOD values and the PCE concentration in the field were taken into considerations. Figure 6. summarizes the results of NOD tests.

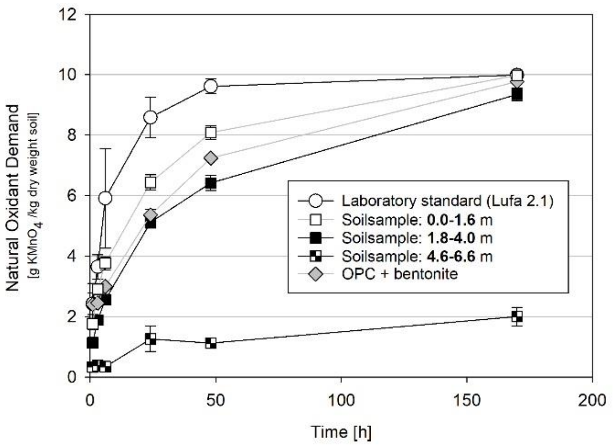

Figure 6. Results from experiments determining NOD of subsoil and binder. Note the difference depending on depth in the soil samples.

4.2 *Execution of works*

After finishing the planning stage, the duration of actual execution on site was comparably short. Along the narrow street ("Kirchengasse") and under the existing building HaloCrete® columns were installed (Figures 7. and 8.). Those columns hat to fulfill the same mechanical requirements than the non-HaloCrete® columns. Available space on site was very confined, a part of the site installation had to be placed in adjacent gardens. The organic compounds in the soil, detect during preliminary tests, caused problems of the hardening of the cement for the conventional JG. This issue was solved using C_3A free cement.

The waste logistics was handled by a specialized contractor. Apart from a separated collection of the possibly contaminated HaloCrete® backflow and the pure JG backflow, no additional measures were required. Chemical analyses proofed that no toxic compounds were found in both types of backflow.

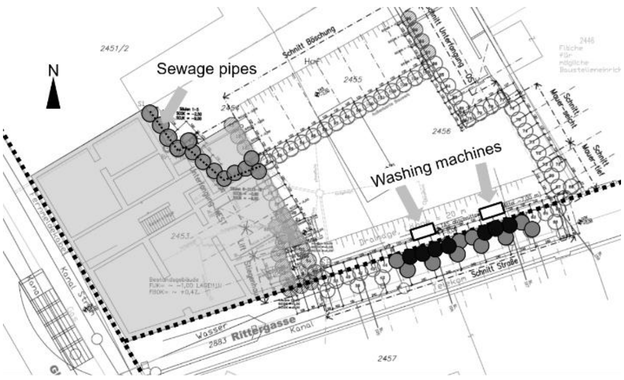

Figure 7. The site Rittergasse / ST25 Putzerei Plachy. Grey and black circles show columns enriched with $KMnO_4$. next to the washing machines and below the sewage lines. The grey area to the left indicates the existing buildings.

4.2.1 *Personal safety precautions*

As CS are cancerogenic, appropriate personal safety gear, gloves and facemasks with particle and active coal filters had to be used during the works on site. A detailed emergency plan was established, with various levels of escalation in case CS were detected. Most of the measures planed realized only after the excavation had begun.

The oxidant itself is classified as OPC and handled accordingly.

Figure 8. Picture of the site. The direction is towards central park, with a view into the partially demolished building. The Rittergasse is situated to the left.

4.3 *Proof of success*

At the Rittergasse site the HaloCrete® columns were part of the excavation pit support. Therefor the UCS required was too high to allow for soundings in the columns. The success of the remediation measures was proven by means of core drillings taken from the jet grouting wall at different depths (Figure 9.). According to the contract with the client, a decrease of concentration related to a predefined reference value had to be achieved. The reference concentration was defined by the environmental consultant based on measurements on site as well as experience from previous projects.

Figure 9. Core drilling being taken from the jet grouting wall at the Rittergasse site. The upper level at -2.0m bGL is shown. The location is directly below the eastern washing machine as shown in Figure 7.

The samples were examined at an independent laboratory. The results indicated a decrease in concentration by a factor of $1x10^6$. Assuming that the reference concentration was rather conservative, an actual decrease of $1x10^5$ seems realistic. So, the HaloCrete® application was considered to be successfully by all parties involved.

5 SPECIFIC CHALLENGES FOR REMEDIATION PROJECTS

5.1 *Personnel safety*

Although obvious, it must be mentioned that remediation projects require high personnel safety standards and measures. This is even more true when dealing with cancerogenic substances with high vapor pressures.

During all the works reported in this paper, dedicated H&S personal was involved to define the safety measures required by the type of chemical exposure.

5.2 *Conceptual site model*

Especially the KOMBO project demonstrated the importance of a detailed site investigation for source zone remediation projects. A second hot spot was identified during an additional MIP campaign with reduced spacings between the soundings. This hot spot would have been overlooked and could have caused potential problems and costs later on (Freitag et al., 2018).

5.3 *Logistics and legal*

The question of backflow treatment is a very special one in this context and influences logistics on site tremendously. According to Austrian law, excavation material from registered, heavily contaminated sites is declared to be “dangerous”. This classification leads to the necessity of storing the material on site until it has been reclassified as “not dangerous” by an accredited chemistry lab. This can be circumvented by dedicated interim storage areas, but the material must remain separated until reclassification. Figure 10. shows the storage on site at Zwölfaxing.

Figure 10. Transport skips as backwash storage. They had to remain on site for over a month.

To reduce the time span for storing the backwash on site, it was considered to be a waste stream. For such a solution continuous chemical testing is required. Additional costs for these tests need to be compared to the reduced effort for the storage of the skips on site. Of course, all these considerations need to comply with local legal requirements and restraints.

5.4 *Quality assurance / Proof of success*

For many remediation projects, the proof of success is not a simple task and needs to be addressed together with the selection of the remediation method. Although, single values for contamination concentrations are not commonly used any more, also (daily) freights allowed are difficult parameters to proof the success of a source zone remediation.

First of all, a single hot spot overlooked during the exploration campaign, can – if situated unfavorable – influence significantly a control well. Only a fine meshed site investigation can prevent such misinterpretations.

In addition, sampling in a hot spot treated with JG is a challenging task. If the JG material is too hard for soundings, core drillings need to be done. For the interpretation of results coming from core drilling samples, the effect of temperature and transportation losses need to be taken into account. If the JG body rather soft, MIP soundings as presented in this paper are a suitable measure for in situ testing. This method also has the advantage of providing continuous values instead of single results obtained with core drillings.

6 CONCLUSIONS AND OUTLOOK

This paper can only give a brief overview of the work being conducted over the course of more than eight years. As of now, the authors are convinced that HaloCrete® is a sound treatment technology for source zone remediations on sites contaminated with chlorinated hydrocarbons. All advantages of the jet grouting technique are fully sustained which allows for synergies between the execution of remediation works and excavation pit support or foundation elements.

Furthermore, the application of the HaloCrete® technique can be extended to other contaminant substances, like polycyclic aromatic hydrocarbons and mineral oils. For the second group, research work has already started, first results are expected for autumn 2021.

7 ACKNOWLEDGEMENTS

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