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HOMBRE

"Holistic Management of Brownfield Regeneration"

D 4.2: Testing of principles and description of critical design parameters of technological and process aspects of the technology trains

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Summary

Preventing sites from becoming brownfields (BFs) and regenerating existing BFs is key to tackling urban sprawl and ensuring a more sustainable built environment as was laid out at the start of the EU FP7 project HOlistic Management of Brownfield REgeneration (HOMBRE). However, real and perceived barriers make stakeholders choose for the development of greenfields rather than redeveloping BFs. The Technology Train (TT) concept contributes to smoothen the transition from BFs to its new functional use by offering a structured way to select technological and non-technological interventions to create optimized added value for the stakeholders and the community at large. Three examples of technology trains are worked out in the domains of sustainable energy production, sustainable water use, sustainable reuse of waste materials and improvement of soil and groundwater quality. These are basic domains that are at stake in many of Europe's redevelopment areas. In this report, the performances of three specific technology trains are presented, namely:

TT1) Aquifer thermal energy storage (ATES) combined with bioremediation of chlorinated ethenes;
TT2) Stabilization and Solidification of heavy metal contaminated soils and use of secondary raw materials from infrastructures;
TT3) In-situ Ecogrout (calcite stabilization) in aquifers

The link between selected technology trains and HOMBRE cases was weak as the cases that were included within the HOMBRE project were not in a stage that an initial development plan was defined. Besides, the pre-defined TTs are very specific and did not match the needs and situation of the sites. Therefore, except for TT2, testing the TTs by using materials from HOMBRE sites and mimicking local predicted conditions was not possible. Although the testing of TTs was not possible on application level, considerable progress was made on the understanding of the technological aspects of the TTs, which helps the implementation of the TTs in other real cases.

For TT1 this resulted in an increased understanding of the relation between the local characteristics of the subsurface like the redox chemistry of the subsoil, and the possibilities to enhance the capacity for attenuation of contaminants in the groundwater. Further, the relation between design of the buildings and its operation on the performance of the ATES system showed that the technology is technically very robust. For TT2 this resulted in an increased understanding of the relation between initial soil characteristics and additives on the mechanical (strength) and chemical (leaching of metals) properties of the produced aggregates. For TT3 this resulted in the understanding of applicability criteria to employ Ecogrout on large scale for soil improvement.

The elaboration of the three technology trains to assess critical design parameters revealed that many technical parameters are available that can be adjusted to optimize its functioning. In general it can be stated that the proposed technology trains can all function within a wide range of technological boundary conditions. All technology trains can be adjusted in order to meet the required quality of specific end-points. Therefore the technology trains provide an excellent ground to build on within the field of BF redevelopment. Here in this study it is shown that the technology trains can function in a wide variety of environmental and technological boundaries. In fact the developed technology trains can in principle deliver goods and services to meet the basic needs at BFs regarding energy, building materials and water quality.

Contents

1. Introduction: aim of technology trains

Preventing sites from becoming brownfields (BFs) and regenerating existing BFs is key to tackling urban sprawl and ensuring a more sustainable built environment as was laid out at the start of the EU FP7 project HOlistic Management of Brownfield REgeneration (HOMBRE). However, real and perceived barriers make stakeholders choose for the development of greenfields rather than redeveloping BFs. The Technology Train (TT) concept contributes to smoothen the transition from BFs to its new functional use by offering a structured way to select technological and non-technological interventions to create optimized added value for the stakeholders and the community at large.

The strategy upon TTs starts with the definition and exploration of available resources at a specific BF. In parallel an inventory is performed on the possible future demands that will show up in the new land use of the BF site and the surrounding areas. With the information that was obtained by assessing the resources and demands of the BF and its surroundings, a first iterative exercise can be done to estimate the level at which self-sufficiency can be obtained for the different goods and services. Together with the local ambitions regarding (for instance) renewable energy, water management, materials use, environmental quality, and an indication of the timescale at which the redevelopment is implemented, a generic exploration of preferred options can be made: the operating windows within which TTs should be designed. The design of TTs for BF redevelopment itself, however, needs study for each specific technology to smoothen the transition of the land use at a specific BF into a new land use after redevelopment. Such study can be performed by either focusing on technology push by showing that a specific technology train can be applied widely, or by technology pull in which specific technologies are initially discarded. Within the technology pull type of development the demands and boundary conditions at a specific BF site are dominant in the technology development.

In the HOMBRE project three examples of technology trains are worked out in the domains of sustainable energy production, sustainable water use, sustainable reuse of waste materials and improvement of soil and groundwater quality. These are basic domains that are at stake in many of Europe’s redevelopment areas. In this report, the performances of three specific technology trains are presented, namely:

TT1) Aquifer thermal energy storage (ATES) combined with bioremediation of chlorinated ethenes;
TT2) Stabilization and Solidification of heavy metal contaminated soils and use of secondary raw materials from infrastructures;
TT3) In-situ Ecogrout (calcite stabilization) in aquifers

Whereas in deliverable 4.3 ”Description of Operating Windows for successful implementation of the Technology Trains uptake” (Smit *et al.*, 2014) the focus was set on technology pull, the focus in this deliverable is set on technology push. Here, the technological principles of the three specific technology trains are elaborated, based on laboratory experiments. From these principles, critical design parameters of technological and process aspects are discussed.

2. Testing of principle of the technology trains

The principle of TTs was ideally tested on relevant HOMBRE cases. Except for TT 2 (stabilization and solidification of heavy metal contaminated soils and use of secondary raw materials from infrastructures), the link between selected technology trains and HOMBRE cases was weak as the cases that were included within the HOMBRE project were not in a stage that an initial development plan was defined. Besides, the pre-defined TTs are very specific and did not match the needs and situation of the sites. Therefore, testing the TTs by using materials from HOMBRE sites and mimicking local predicted conditions was not possible. However, although the testing of TTs was not possible on application level, considerable progress was made on the understanding of the technological aspects of the TTs, which helps the implementation of the TTs in other real cases.

2.1 TT1: ATES and bioremediation

TT on water and energy (TT1) combines the issue of contaminated groundwater as an obstacle for BF redevelopment with the possibility to decrease the primary energy demand by storing thermal energy in the aquifer below the BF site by Aquifer Thermal Energy Storage (ATES). Groundwater contamination is generally seen as a major liability risk during the redevelopment of BFs as the exact location and size of contaminant sources and plumes are difficult to assess. Furthermore, in many (former) industrial locations, contaminants originating from different sources mix, which makes the process to identify responsible polluters challenging. As the size of individual and merged contaminant plumes can be large, costs for active remediation can be large as well. Next to the problem of contaminated groundwater, the attractiveness for using a location is related to costs of using that location. In this, energy costs are expected to become increasingly important as energy prices increase at higher rates than inflation. Increasing energy prices and legislation on the energy performance of buildings (e.g. European Directive 2002/91/EC: Energy Performance of Buildings Directive (EPBD)) accelerate the desire to make use of aquifers for the supply of heat and cold (ATES). ATES is a technology that proved to be cost effective with reasonable pay-back times of 5-7 year when cooling is provided. The presence of contaminants in aquifers hampers the application of ATES systems in many cases as mobilization of contaminants has to be avoided.

TT1 targets to supply an improved aquifer quality and renewable (thermal) energy which are both services that are valuable for the new BF sites use. These services are also known as ecosystem services (van Wensum, 2013). In the following paragraphs, the technological knowledge-gaps are discussed as well as the approach to fill in these gaps and the results that were obtained by laboratory experiments and modelling.

2.1.1 Identified knowledgegaps of the combination ATES and bioremediation

The individual technologies that were linked in the TT1, ATES and bioremediation, are currently widely applied in the Netherlands (ATES and bioremediation) and in Europe (bioremediation). From these applications and the underlying scientific knowledge it is known that the redox chemistry (availability of electron donors and acceptors), the indigenous microbial community, the availability of contaminants and nutrients, and the environmental conditions (e.g. pH, temperature) play a crucial role in the success of bioremediation to mitigate identified risks. Also, it is expected that the flow-rates of ATES systems and the temperature shift of infiltrated water from 5 °C in winter and above 15 °C in summer affect the bioremediation compared to traditional bioremediation. Although the potential benefits of both technologies, and the combination of them, have been recognized by many stakeholders, lack of experiences prevents a wider application. In order to reduce this barrier we addressed the following knowledge gaps:

- what are the effects of ATES on biological degradation of chlorinated ethenes?
- will the reduction of (insoluble) Fe(III)species to soluble Fe(II) by the mobilized electron donors lead to an increased risk of well clogging?

- what are the actual energy savings by using ATES?
- design strategies to optimize the performance of ATES systems: maximizing aquifer energy storage versus maximizing individual systems performance.

These knowledge gaps are addressed in the following paragraphs 2.1.2 - 2.1.5. For each knowledge gap, a brief problem definition, the methodology, and the results is described. Finally, in paragraph 2.1.6, the main conclusion is given for TT1.

2.1.2 Effect of ATES on biological degradation of chlorinated ethenes

The results of the research on this knowledge gap is (partly) published as Ni, Z *et al.* (2014)

2.1.2.1 Problem description

Reductive dechlorination of tetrachloroethene (PCE) and its daughter products in aquifers is often hampered by Fe(III) reducing conditions. Rigorous treatment to adjust the redox potential and stimulate dechlorination may be costly and potentially have negative effects on other aquifer functions (e.g. bio-chemical clogging in for example groundwater extraction wells or transport pipelines). Considering these possible negative interferences with other aquifer utilizations, and the targeted application in large volumes of contaminated aquifer, we applied a step-wise approach, to estimate the minimum amount of electron donor needed for improving the redox potential of the aquifer to initiate PCE reductive dechlorination. Added to this, the potential of increased groundwater flow on the mobilization of Soil Organic Matter (SOM) by increased shear stress might contribute to the enhanced conditions under which dechlorination can take place. If indeed the mobilized (activated) SOM could reduce competing electron acceptors, such as Fe(III) species, the combination of ATES and bioremediation would demonstrate a valuable synergy.

2.1.2.2 Methodology

In summary the following experiments were performed to test the effect of ATES on the biological degradation of chlorinated ethenes (PCE and its daughter products):

1) Assessing the biodegradation of PCE in a system with original aquifer materials without any additions (baseline) using samples from Utrecht (the Netherlands) which are reported to be under Fe(III) reducing conditions. Experiments were performed in serum bottles (120 ml) in which 20 grams of aquifer sample and 60 ml of anaerobic tapwater was added under a head space of 99% N_2 and 1% CO_2. In regular intervals the headspace was sampled using Solid Phase Micro Extraction (SPME) followed by analyses on a GC-FID to quantify the concentration of PCE and its daughter products. Experiments were performed at a temperature of 25 °C.
2) Redox titrations with electron donor to estimate the minimum amount of electron donor needed to achieve redox potential values theoretically suitable for reductive dechlorination of PCE to occur (sulfate reducing or methanogenic conditions: < -400 mV). In several steps, either Ascorbic Acid (AA) or Sodium Lactate (SL) were added to a mixed batch that contained aquifer material from Utrecht and anaerobic tapwater under an atmosphere of 99% N_2 and 1% CO_2.
3) PCE reductive dechlorination in different combinations of pre-treatment and subsequent stimulation scenarios (figure 1).
4) Assessing the effect of shear stress on the mobilization of SOM. Using different shaking methods, the redox potential of a maxture of aquifer material from Utrecht and anaerobic tapwater was continuously monitored. On a regular time interval chemical analyses were performed to quantify the Chemical Oxygen Demand (COD), the Total Organic Carbon (TOC), and redox parameters (Fe, SO4).

An overview of experiment 3 is given in figure 1. After pre-treatment of aquifer material with either AA or SL, 4 conditions were selected to explore the effect of added stimulants (extra electron donor ED) (SL), bio augmentation with Dehalococcus Ethenogens (Bio), and ED + Bio). For each condition the concentration of chlorinated ethenes, volatile fatty acids, Fe (II), SO4, and ethene was monitored.

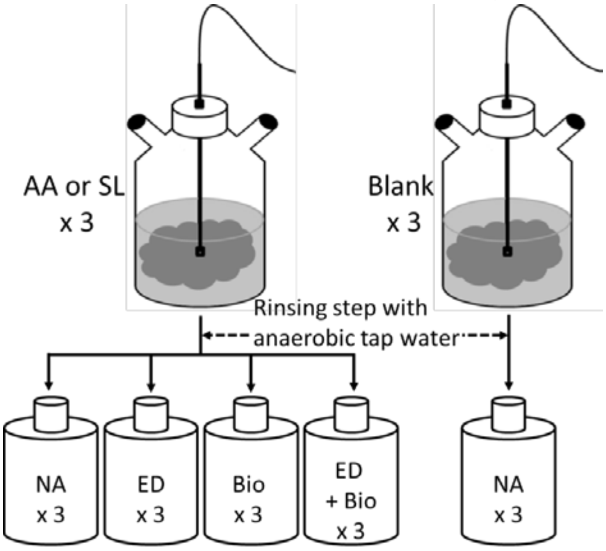


Figure 1: Experimental set-up for the reductive dechlorination batch tests after pre-treatment with AA or SL. NA: natural attenuation; ED: stimulation with electron donor; Bio: stimulation with inoculum.

2.1.2.3 Results

The natural attenuation (NA) potential of untreated aquifer material from Utrecht is limited if not absent. In figure 2 this can be seen as the constant PCE and Fe(II) concentration over a period of 100 days. After adding 20 mM of acetate, reduction of Fe(III) to Fe(II) species was found as an increase of Fe(II) concentration but no degradation of PCE was observed. It was concluded that the presence of available Fe(III) outcompeted PCE as most suitable electron acceptor. Therefore a pre-treatment with ED is needed to reduce competing electron acceptors such as Fe(III). The effect of the stepwise addition of AA or SL on redox potential is shown in the bottom of figure 3. ΔRedox potential is the difference between the average of the blanks and the average of treatment replicates, using the smoothed redox potential value at the moment just before reductant was added.

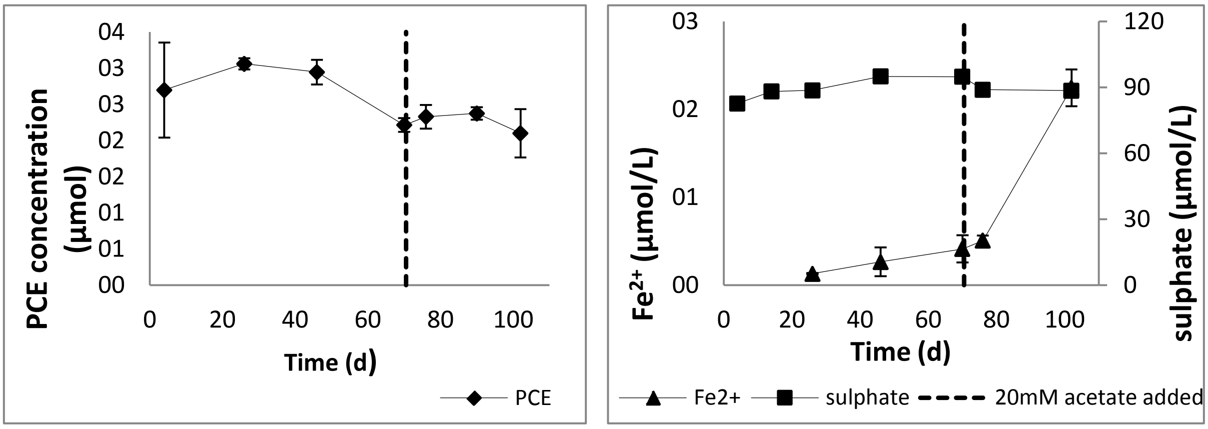


Figure 2: PCE concentration (left) and Fe(II) and SO_4 concentration (right) in time of untreated aquifer material. The dotted line at day 72 days indicate the addition of acetate (20 mM).

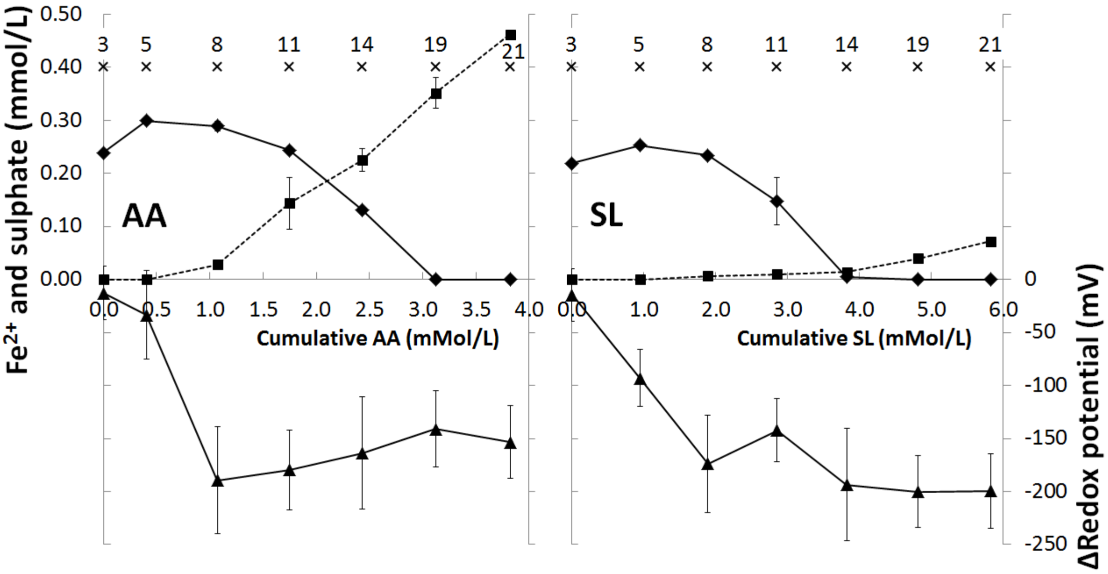


Figure 3: Fe^{2+} and sulphate evolution (top) and Redox change (bottom) in experimental system with titration of AA (left) and SL (right) respectively, compared to blank. Error bars represent standard errors or duplicates. In some points, error bars cannot be seen as they are smaller than symbol size. Numbers with crosses indicate the time of measurement and subsequent electron donor additions.

Results from the redox titration revealed that, for the selected PCE contaminated aquifer that was initially under Fe(III) reducing conditions, a minimum addition of 75 µMol electron eq/g dry mass of aquifer material was needed to obtain suitable redox conditions. Additionally, the type of electron donor that provides this amount of electron equivalents seems not to be specific, as AA and SL showed a similar final redox potential of -450 mV. Interestingly changes in Fe^{2+} and SO_4^{2-} could only be observed after the redox potential had been lowered. A possible explanation for this observation is provided by Christensen et al. (2000) who stated the reduction of ferric aqua ions to ferrous aqua ions is rapid while the reduction of structural Fe(III) to form ferrous aqua ions is a much slower reaction. The observed, initially rapid decrease of redox potential in our study might thus be related to the reduction of a limited amount of aqueous electron acceptors. The slow increase of Fe^{2+} which was observed after the 2nd addition of AA or SL then relates to the reduction of structural Fe(III).

After the redox potentials stabilized at -450 mV for more than 5 days, the pre-treated aquifer materials were rinsed as described in the methods section, and PCE reductive dechlorination tests started. For the aquifer material that was previously conditioned with AA or SL, in the natural attenuation (NA) tests without stimulation by either additional electron donor or inoculum, a lag phase of at least 30 days was observed before PCE started to degrade. The degradation was incomplete during the experiment and stopped at cis-DCE in AA1 and TCE in SL1 (see figure **4**). Without any pre-treatment no degradation of PCE was observed (data not shown; similar to figure 2)

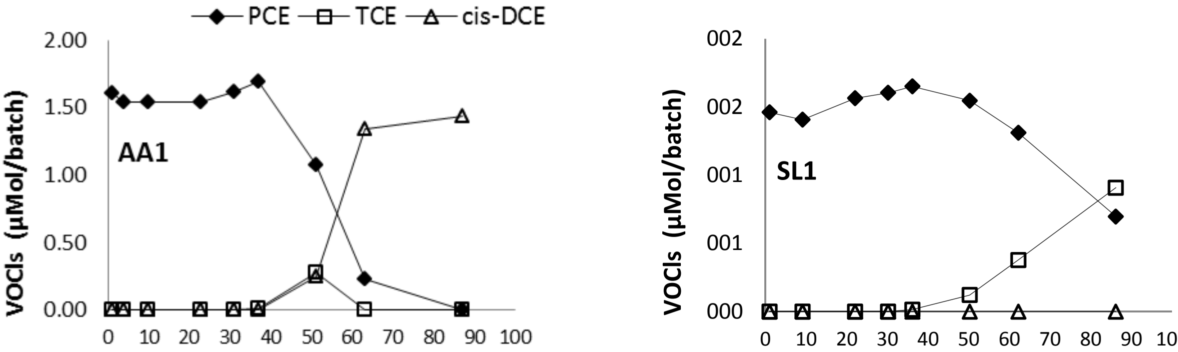


Figure 4: PCE reductive dechlorination in pre-treated aquifer materials. Concentration of chlorinated ethenes in time (days).

In the electron donor (ED) stimulation tests, AA2 and SL2 in figure 5, showed a shorter lag phase compared to the data in figure **4**. Complete degradation of PCE to ethene was only observed when an active enrichment of Dehalococcus Ethenogens was added (AA3 and SL3). In these conditions also the initial lag-phase was much shorter.

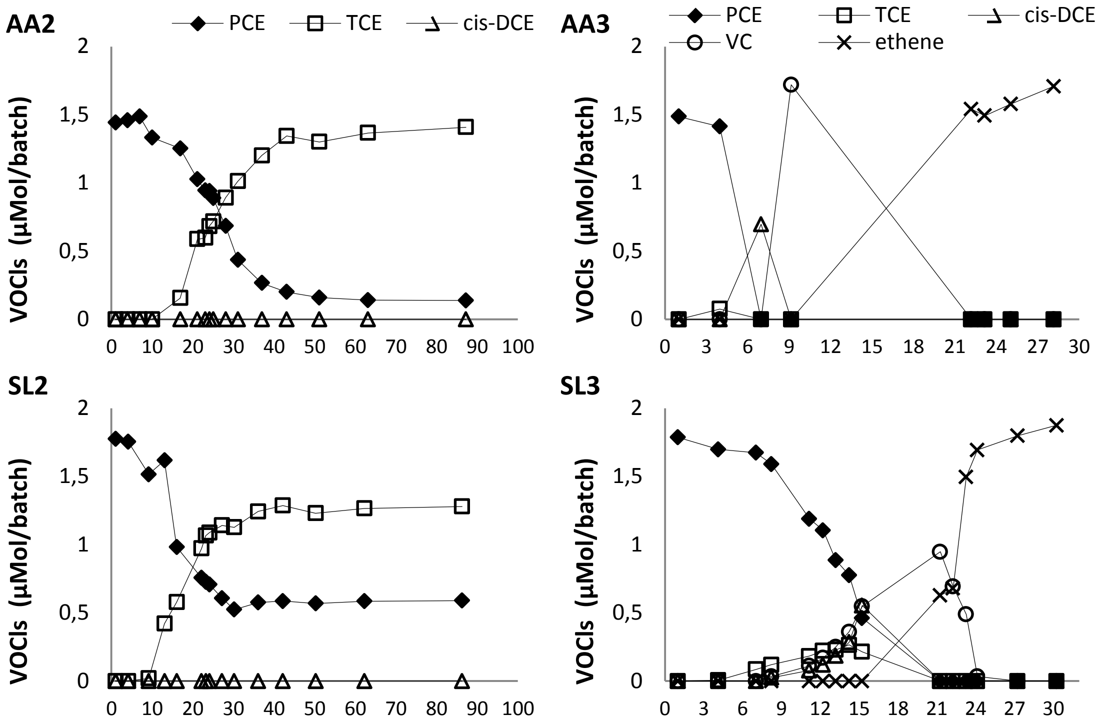


Figure 5: PCE reductive dechlorination in pre-treated aquifer materials with addition of extra electron donor (AA2 and SL2) and dechlorinating bacteria (AA3 and SL3). Time is in days.

In the ED + bioaugmentation tests, PCE was degraded within 7 days without a lag phase (figure 6). A second PCE spiking was also removed within 5 days and complete conversion to ethene was found in all batches at day 28.

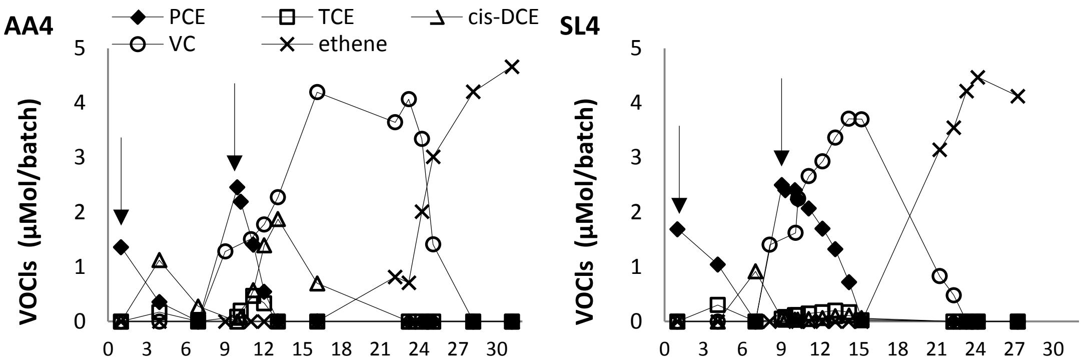


Figure 6: PCE reductive dechlorination in pre-treated aquifer materials with addition of extra electron donor and dechlorinating bacteria. Time is in days.

Results of the biodegradation experiments showed that it is essential to reduce competing electron acceptors (e.g. Fe(III)) before degradation of PCE starts. Addition of ED during the biodegradation increased the conversion rate of PCE to cis-DCE. However, the indigenous bacteria could not convert the DCE that was produced into harmless compounds such as ethene. Only after addition of an active enrichment of Dehalococcus Ethenogens, complete degradation of PCE was found. Adding extra ED to the bioaugmented samples led to a further increase of conversion rates. It was concluded that conditions that are originally not suitable for complete degradation of PCE to ethene required both the addition on ED to reduce competing electron acceptors and the introduction of suitable bacteria. However, as the experiments were performed in a closed system we cannot estimate the potential of natural augmentation in real ATES systems. Therefore our findings are a worst case estimate.

Finally, the potential of the aquifer material to supply electron donors by mobilizing SOM through the enhanced groundwater flow was tested. In two experiments the effect of shaking on the redox potential and the effect of shaking and temperature on TOC and COD release was tested. Three differences in physical forces was tested by use of horizontal shaking, orbital shaking and no shaking (static) (figure 7).

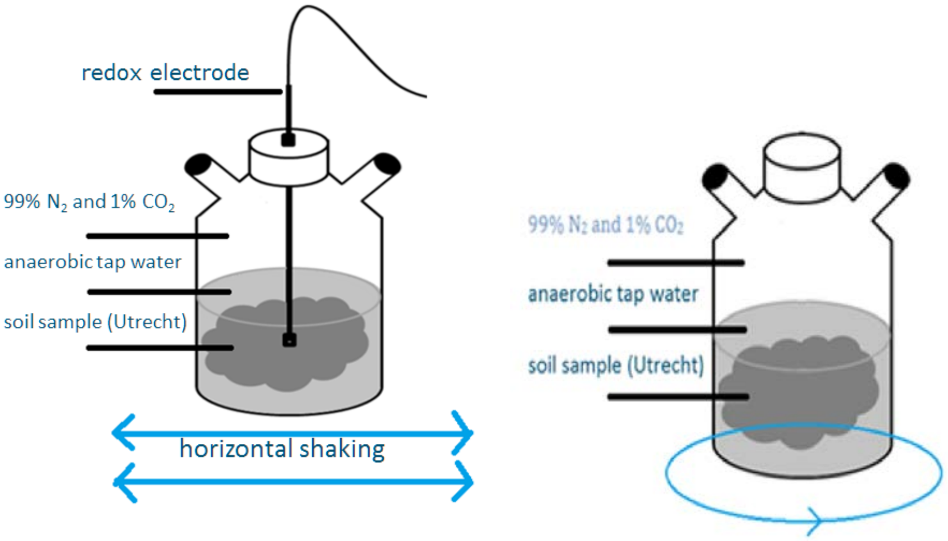


Figure 7: applied forces to test the mobilization of SOM as electron donor.

Clearly, as can be seen in figure 8, a disturbance in the form of shaking mobilizes organic matter. The effect can be seen already in a couple of days. The relation between energy input and COD release to the liquid is visible in such a way that the highest chance of collision (horizontal shaking) lead to the highest rate of COD release. Therefore, the application of ATES might indeed lead to improved conditions for reductive dechlorination when mobilized SOM can reduce competing electron donors such as Fe(III).

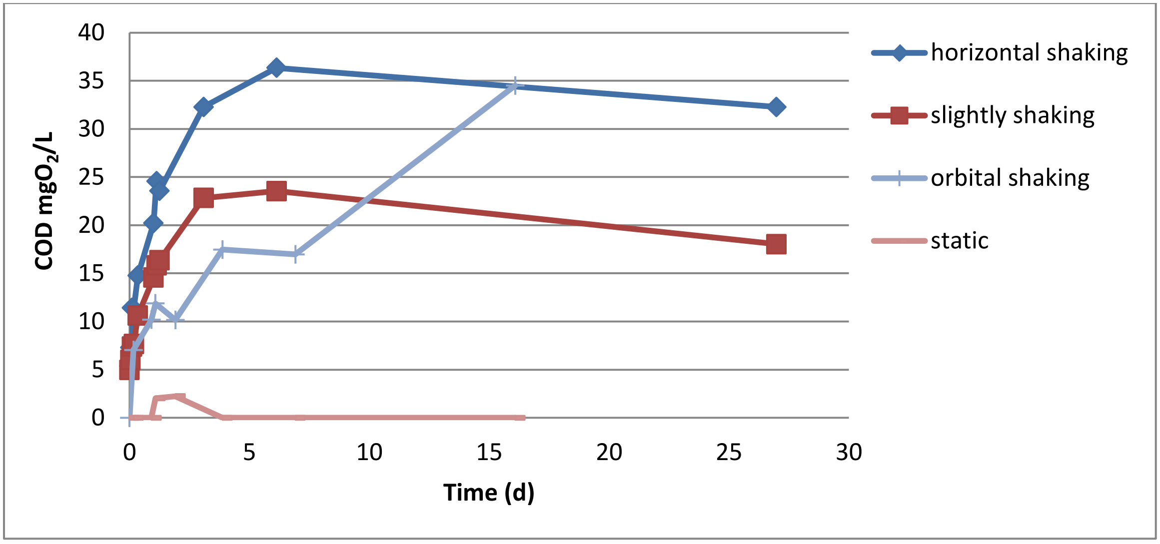


Figure 8: effect of shaking on the release of electron donor (indicated as chemical oxygen demand) in time.

2.1.2.4 Discussion and conclusion

The findings of these experiments on the effect of ATES on biological degradation of chlorinated ethenes are relevant for improving the cost-effectiveness of the design and operation of in-situ bioremediation. The redox potential of an aquifer can be used as a general indicator to evaluate the potential of PCE reductive dechlorination. The result from our step-wise experiments can be meaningful for dealing with in-situ bioremediation and for applications in large volumes of contaminated aquifer. For achieving specific goals of in-situ bioremediation projects on different VOCls contaminated sites with various environmental conditions, the balance between cost and profit, and potential risks (e.g. bio-chemical well clogging due to bacteria growth and precipitation of metals) should be estimated before the design and operation. From a technological perspective, the operating window of this technology train can be enlarged by the addition of electron donor, the addition of an active enrichment of suitable bacteria, and an increased flow rate of groundwater. Compared to traditional bioremediation, especially the positive effect of mobilizing SOM as electron donor is interesting as costs related to the buying of substrate (ED) can be reduced.

2.1.3 Effect of aquifer remediation technologies on ATES functioning

The results of the research on this knowledge gap is unpublished data. The research is described in the master thesis of Andrea Bigoni (WU) to be available at the sub-department of Environmental Technology.

2.1.3.1 Problem description

Wells are crucial parts within an ATES system and therefore it is essential that wells operate without problems that can limit their injection/recovery performance. One of the most frequent technical problems that occur in water wells of ATES systems is clogging. Clogging is defined as the obstruction of the pores of the well screen and gravel pack by solid material (Andersson, 2007). Usually, pump inlets and screen slots are the parts of a well that are interested by clogging because in there the highest rates of particles deposition are usually found. The processes that are responsible for the impairment of wells are categorized as physical, biological and chemical (Jenne et al., 1992 ; Andersson, 1990).

Although in most cases the physical, biological and chemical clogging can be prevented by proper design of the ATES systems, in some cases, for example during active remediation of contaminants, the risk of clogging emerges during the operation of the ATES system. Injection and production wells can be clogged by precipitates that are induced by the variation of three environmental factors: groundwater temperature, redox potential and pH (Jenne et al., 1992), which are typically manipulated to enhance degradation of contaminants. Experiences of ATES plants as well as laboratory experiments show that specially Fe and Mn oxides are the minerals usually encountered in wells (Griffioen & Appelo, 1993 ; Jenne, 1990 ; Jenne et al., 1992). According to a survey performed by the DVGW (German Technical and Scientific Association on Gas and Water) in order to quantify the main reasons of wells clogging, on 281 clogged wells the most prominent issue was clogging by incrustations (95%). Carbonates, biological clogging and clay swelling were the most negligible ones with 3.2%, 1.4% and 0.4% , respectively.

Currently the kinetics of well clogging due to the formation of metal precipitates is not clear. The applicability to combine ATES and bioremediation hampers from this knowledge gap as few stakeholders are willing to take the risk of ATES malfunctioning due to enhanced bioremediation.

2.1.3.2 Methodology

In order to study the kinetics of Fe-hydroxides precipitation, a two stage experimental procedure was designed. First a preliminary test was done in order to develop a temporal scheme so that the kinetics of Fe hydroxide could be studied. Then, using this information, an experiment was performed in which we monitored the hydraulic resistance over time of a column containing anoxic aquifer material which is being percolated with either anoxic or aerated water.

The devices used to perform the clogging experiments were: vertical column, one peristaltic pump and two 1 l water flasks as depicted in figure 9. One flask was used to continuously recycle the water into the vertical column and the other one was used to supply the vertical column in order to keep a constant water level.

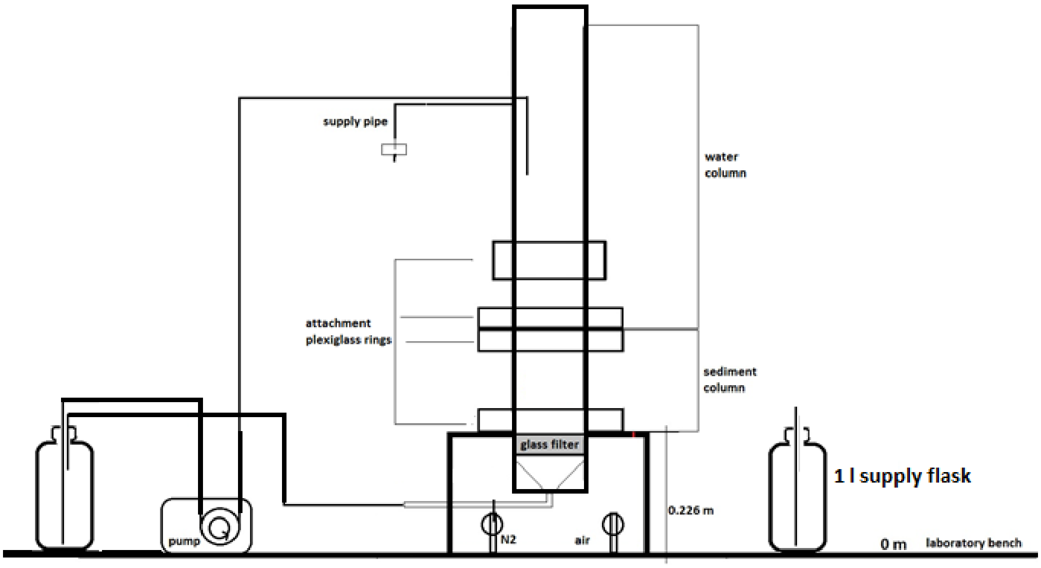


Figure 9: experimental set-up to analyse kinetics of clogging due to Fe(III) precipitation

Below the sediment a glass filter was installed. The glass filter is thick 0.005 m; the surface is 0.0037 m2; volume of 18.7 cm3 and the porosity is Φ=0.55. The porosity was determined by imbibition method. It is expected that clogging will initiate on the glass filter as the diameter of pores in the glass filter is smaller than pores in the sample.

Water and sediment level were monitored regularly. The flow rate (Q_{out}) was semi-continuously monitored by measuring the volume of water coming out from the bottom pipe of the filtering system in one minute using a 5 ml graduated cylinder. According to the Darcy's equation, the water flow is induced by a difference of pressure ΔP and the latter is directly proportional to the differential hydraulic head ΔH. Therefore, knowing that the ΔH between the vertical column and the flask was $\Delta H = 0.377$ m,

After measuring Q_{out}, the water was sampled for Dissolved Oxygen, pH, and metal composition. At the end of each experiment, the sediment column and glass filtered were inspected by microscopy.

2.1.3.3 Results

The effect of recirculating aerated and non-aerated water over the anoxic sediment column is depicted in figure 10. A rapid increase of hydraulic resistance was seen for the recirculation of aerated water while a more constant hydraulic resistance was observed for non-aerated water.

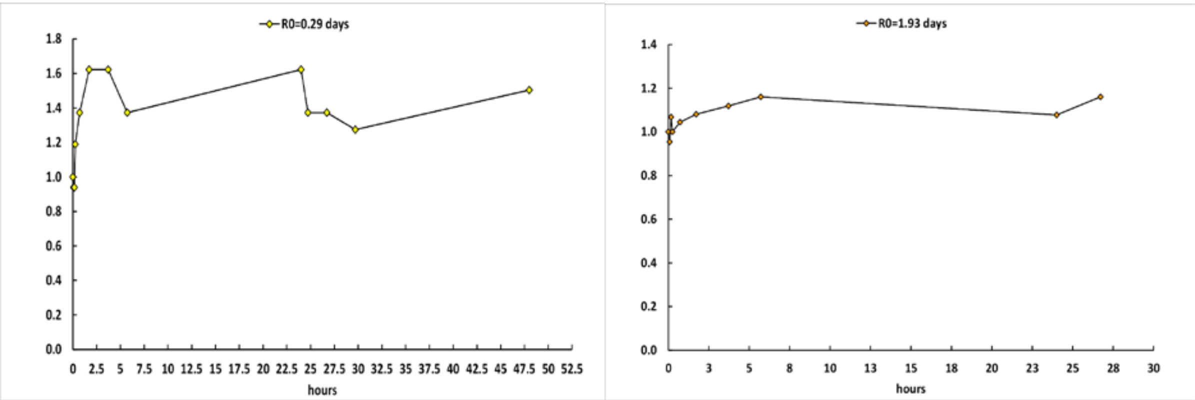


Figure 10: normalized measured hydraulic resistance in time (hours) for aerated (left) and non-aerated (right) conditions.

The rapid increase of hydraulic resistance in the aerated experiment coincided with a rapid decrease of Fe(II) that was dissolved in the water (data not shown). In cases where hydraulic resistance was more stable, also the (normalized) aqueous concentration of metals was constant.

Microscopic analyses showed that incrustations were mainly found in the glass filter, confirming the hypothesis that clogging initiate where pore diameters were smallest. The formed precipitates were too small to block pores in the soil matrix itself. However, the time in which experiments were performed was not sufficiently long to exclude the possibility that in time clogging of pores in the soil matrix will occur. Besides, the variability of results was too high to draw conclusions.

2.1.3.4 Discussion and conclusion

The findings of this experiment demonstrate the risk of clogging due to air (oxygen) entry within an anoxic aquifer. These conditions are possibly met in case of in-situ treatment of contaminants with advanced oxidation treatment such as fenton's reagents or air sparging. As the combination ATES-bioremediation is mainly focused on the remediation of plumes, often additional techniques are required to control (mitigate) sources of contaminants. The operating window of ATES-bioremediation is reduced in cases where strong electron acceptors are being introduced. However, as recent work of Sutton (2014) put forward, electron acceptors will quickly be reduced in situ. Therefore, prior to installing an ATES system there are sufficient techniques available to remove sources of contaminants (when needed). A comprehensive understanding of the contaminant situation and the need to mitigate risks is needed before a decision is made regarding the feasibility of (any) remediation effort.

2.1.4 Optimization strategies for thermal energy storage

The results of the research on this knowledge gap is submitted as Sommer *et al.* (2015).

2.1.4.1 Problem description

Two important reasons for applying ATES are 1) to reduce costs for heating and cooling, and 2) to reduce CO_2 emissions with respect to conventional heating and cooling systems. To facilitate optimal use of the subsurface, some municipalities in the Netherlands have issued master plans that regulate the positioning of the wells for storing thermal energy. Common zonation patterns used for positioning wells for cold and heat storage are the „checkerboard‟ and „lane‟ pattern (figure 11). These patterns can be applied for multiple ATES systems or for the wells of individual systems. From superposition of the drawdown at each well, it follows that the checkerboard pattern minimizes the hydraulic impact of the well field on hydraulic head. The lane pattern, on the other hand with R2/2<R1, is thermally more efficient, because neighbouring wells that store a similar temperature reduce dissipative heat loss to their surroundings (positive thermal interference). Finally, from a spatial economic perspective, the distance between the cold and warm well can be varied, leading to the overarching question: how much (in terms of) decreased economic benefits from individual ATES systems is acceptable to maximize the overall storage capacity on a site? Reducing the distance between warm and cold wells decreases the energetic capacity of each doublet system but will increase the energetic capacity of all systems.

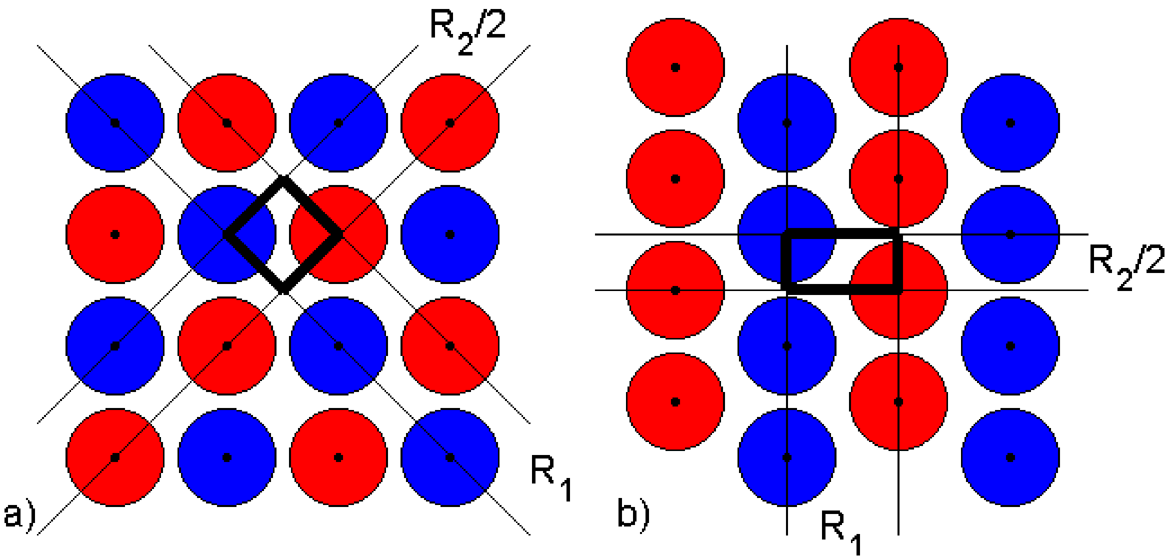


Figure 11: a) Checkerboard and b) lane zonation patterns to arrange ATES wells. The coloured circle around each well indicates 1 Rth distance for heat storage (red) and cold storage (blue). By using axes of symmetry, each pattern can be modelled by considering the square (indicated in bold) in each respective subfigure.

2.1.4.2 Methodology

To test the thermal performance of large-scale application of ATES a simplified hydrogeological model which is representative for the aquifer used for thermal storage in Amsterdam, The Netherlands was used. In this model, different zonation patterns and well-to-well distances were tested with respect to economic and environmental perspectives. Using a sensitivity analysis we identified key factors that determine optimal well-to-well distances and quantify the impact of these factors on the amount of energy that is supplied and on the reduction of costs and CO_2 emissions.

The dimensions of our model are based on geohydrological conditions of the aquifer used for ATES in Amsterdam, The Netherlands. Analysis of 36 permitted ATES systems (105 wells) in Amsterdam shows that well screens are generally constructed at a depth between 70 and 180 m. The average well screen length is 64.8 meters. The aquifer at these depths belongs to the Peize formation that consists of course sand (grain size 210-2000 µm). The aquifer is simplified to a confined aquifer with a thickness of 60 meters with its base at 180 m and a realistic hydraulic conductivity of 30 m/d. The groundwater flow velocity in this aquifer is neglected in order to enable the use of symmetry axes so that the performance of a doublet system in a large-scale application of ATES can be modelled with the boxed volume in figure 11. Boundary conditions comprise of no flow and zero heat flux along the boundaries of the boxed volume. The wells are modelled with a fixed flow rate and injection temperature. Heating and cooling loads in our simulations are simplified to a 4 month heating period in winter and a 4 month cooling period in summer, with a period of 2 months in between when the system is not running, similar to the seasonal variation observed in an existing ATES system in the Netherlands. To calculate the equivalent annual cost and CO_2 emission associated with the energy provided by the ATES system, a reference system was selected that consists of a gas boiler heating system (efficiency 85%) and electrical compression cooling (with a coefficient of performance (COP) value of 3.5). In our analysis we assume that all energy provided by the ATES system is used and should otherwise be produced by the conventional system. Energy, costs and CO_2 emissions in our analysis are calculated for a doublet in a large-scale application of ATES.

2.1.4.3 Results

Thermal efficiency of a doublet ATES system in the lane pattern (figure 11b) was determined for a distance between lanes (R_1) and wells within a lane (R_2) that are independently varied between 0.3 and 5 R_{th}. The simulated well temperature is presented for the first year of simulation in figure 12 for the specific case where $R_1 = 3\ R_{th}$ and $R_2 = 0.5\ R_{th}$.

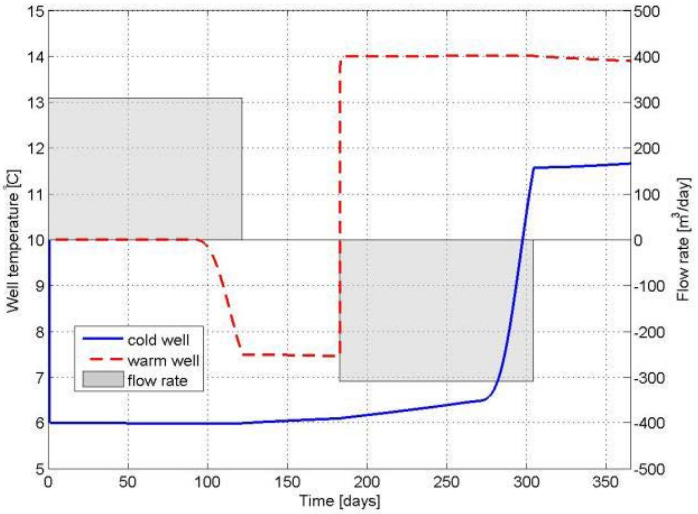


Figure 12: Modelled well temperatures in the first year of operation (R_1=3 R_{th}, R_2=0.5 R_{th})

The simulation starts at t=0 day with injection of cold water in the cold storage well for 121.5 days. During this period the temperature in the well is equal to the injection temperature (6 °C). The temperature in the warm well remains equal to the initial aquifer temperature (10 °C) until breakthrough of the cold water appears around t=100 days. After the initial injection phase there is a 61 day period in which the system is inactive. At t=182.5 days the system switches to cooling mode (extraction from cold storage well) and the temperature in the warm storage well becomes equal to the injection temperature (14 °C). Again after approximately 100 days a breakthrough of injected warm water appears at the cold storage well, apparent from the increase in temperature in the cold storage well from 6.5 to 11.5 °C at t=280 days. The thermal efficiency of a doublet ATES system can then be calculated by dividing the calculated energy that was extracted in a period of 30 years with the extracted energy over the same period assuming no energy losses. For the example of R_1=3R_{th}, R_2=0.5R_{th} the thermal efficiency of a single well is calculated to be approximately 80%. The relation between well distances on the thermal efficiency of a single doublet is illustrated in figure 13a and the energy ratio for multiple doublets in a specified area is illustrated in figure 13b. Obviously, decreasing well distances lead to lower efficiencies of single ATES doublet systems while the energy efficiency of energy storage in a specified area becomes larger.

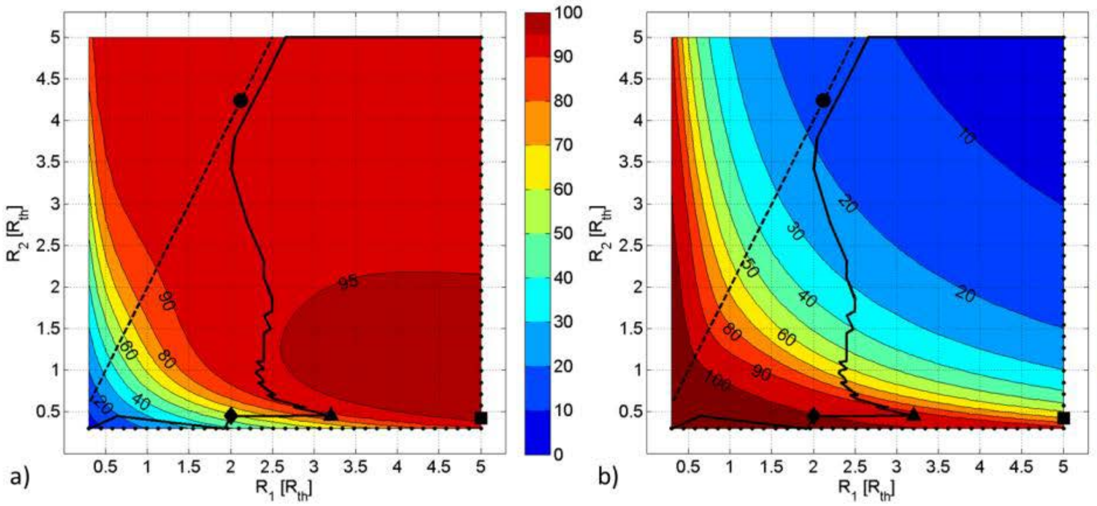


Figure 13: a) average thermal efficiency for individual doublets (ηt) [%] and b) average energy ratio for a chosen area with multiple doublets (ηe) [%]

Using the results that are depicted in figure 13b, an estimation was made with respect to cost reduction and CO_2 emission reduction compared to a reference system as function of well distances. The results are visualized in figure 14 and expressed per year per m^2 surface area per meter aquifer thickness per °C difference in injection temperatures. Cost reduction increases from 0.0012 €/yr/m^2/m/°C at maximum well distance (R_1,R_2) = (5,5) R_{th} to a maximum of 0.019 €/yr/m^2/m/°C at (R_1,R_2) = (3.2,0.45) R_{th}. For very small well distances severe thermal interference reduces the well performance such that it is not economically feasible to apply ATES (a cost reduction smaller than 0). Reduction in CO^2 emissions compared to a conventional heating/cooling system range from 0.017 kg/yr/m^2/m/°C at (R_1,R_2) = (5,5) R_{th} to a maximum value of 0.27 kg/yr/m^2/m/°C at (R_1,R_2) = (3.4,0.3) R_{th}.

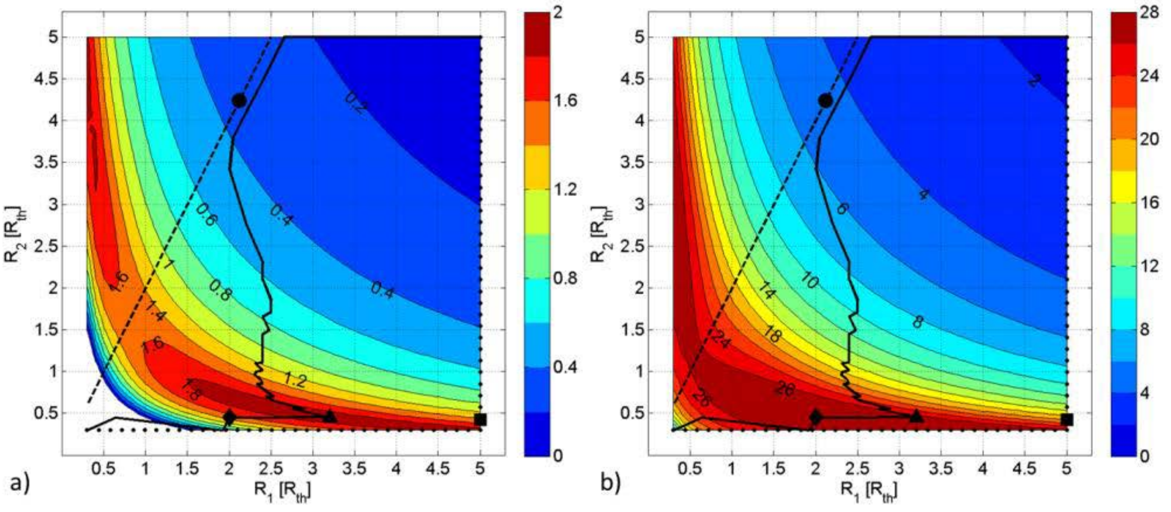


Figure 14: a) cost reduction [0.01 €/m2/yr/m/°C], and b) CO2 emission reduction [0.01 kg/m2/yr/m/°C].

The sensitivity analyses showed that the optimal well distances, energy ratio and associated cost and CO_2 emission reduction are all most sensitive to variations in gas price and temperature difference over the cold and warm storage. Regarding cost reduction, first-order and total-effect indices are similar, indicating that parameters act independently on the model output. For the other performance indicators, first-order indices are generally lower than the total-effect indices, indicating parameter interactions.

Our optimization shows that in case of large-scale application of ATES 30 to 40% more energy can be supplied by allowing negative thermal interference between systems compared to the case in which all negative interference is avoided. This decreases the performance of individual doublets, but as more doublets can be realized, total energy delivered per aquifer volume, and associated cost reduction is higher than in the case that all negative thermal interference is avoided.

2.1.4.4 Discussion and conclusion

The energy that can be supplied by large-scale application of ATES is limited by thermal interference between the warm and cold storage. The thermal performance of individual well doublets is optimal when negative thermal interference is avoided. However, in this case, each doublet occupies an unnecessary large aquifer volume, which limits the number of ATES systems that can be realized in a given area, although a larger potential exists. By including more advanced design methods based on local conditions and allowing a limited amount of thermal interference, we have shown that the number of systems can be increased, such that the total benefits of ATES in an area are larger.

Optimal distance between lanes was between 2.8 and 3.3 R_{th} and optimal distance between the wells within a lane was between 0.41 and 0.56 R_{th}. While optimal well distances are only to a minor extent sensitive to variations in hydrological and economic conditions, the absolute reduction in costs for heating and cooling and reduction in CO_2 emissions show large variation. They are especially sensitive to the gas price and the temperature difference between the cold and warm storage. Therefore, future efforts on sustainability and optimization of ATES would benefit greatly from availability of more accurate and extensive data on the economic aspects of ATES and integrated assessment of ATES as part of the heating and cooling system.

When systems in a large-scale application have different owners, it is for the individual owners more favourable to avoid all negative thermal interference. It is therefore important to identify areas with a high energy demand, considering the available aquifer volume, so that the authorities can influence energy savings that can be achieved by introducing regulations. As suggested in Bloemendal *et al.* (2013), another approach is to consider the subsurface as a common resource pool and apply self-organization or self-governance as possible governance tools to approach optimal and sustainable use of the subsurface.

Investment costs for ATES can vary between locations due to different hydrogeological conditions (e.g. presence of clay layers increases drilling cost due to slow drilling, low aquifer hydraulic conductivity requires a larger well diameter, larger well screen length or more wells to produce the same amount of energy), location specific conditions (permits, infrastructure that is present) and economy of scale. Although optimal well distances seem only for a limited degree sensitive to this variation, economic benefits of ATES are. Therefore, future efforts on sustainability and optimization of ATES would benefit greatly from availability of more accurate and extensive data on the economic aspects of ATES. Integrated economic assessments of low temperature ATES systems in literature are scarce. However, the economic analysis presented in Vanhoudt *et al.* (2011) enables comparison of our results. Vanhoudt *et al.* report on a monitoring study of a low temperature doublet ATES system that supplies cooling and heating to a hospital in Belgium over a three years period. For the ATES system they report total investment (695 k€) and annual fuel costs (28.7 k€). For a reference system, that consist of gas-fired boilers and cooling machines, total investment costs and annual fuel costs are estimated 241 k€ and 82.4 k€ respectively. Assuming a lifetime of both systems equal to 30 years, as in our study, results in an estimated cost reduction by using ATES of 43% compared to the reference system. This is similar to the cost reduction of 45% that is obtained in our study.

2.1.5 Energy savings from ATES

The results for this part are unpublished data. The research is described in the master thesis of Svetla Kirkova (2013) and Barbara van Gulick (2014) which are available at Wageningen Universities library.

2.1.5.1 Problem description

Integrated economic assessments of low temperature ATES systems in literature are scarce. However, the performance of an ATES system can be evaluated using several criteria, such as energetic performance, and economic and environmental considerations. It was stated by Dincer (2002) that a generally accepted basis on how to evaluate and compare the energy performance of different TES systems is yet to be developed. The lack of an existing, objective basis to evaluate the energetic, economic and environmental performance affects the application of TES systems negatively as decision makers are uncertain to what extend TES systems will contribute to their ambitions.

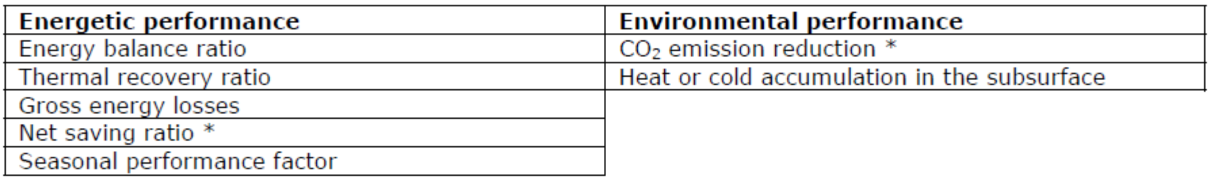
2.1.5.2 Methodology

The performance of an existing ATES installation, in combination with the heating, ventilation and air conditioning system of a building with mixed functions in the Netherlands was analysed. The performance assessment limits itself to the analysis of energetic and environmental aspects. Elements that were considered in the performance analyses are:

1) the source of energy. This can be thermal energy from a Thermal Energy Storage (TES) system or natural gas from the grid. This energy then needs to be
2) converted into a form of energy that can be used to heat or cool the building. This conversion step can be done by heat pumps, air conditioners or boilers before
3) the heat or cold is distributed throughout the building by radiators, ventilation air or by floor heating or concrete core activation. The energy is then delivered to the user, who might or might not be satisfied by the provided service.

An overview of the heating and cooling system of the buildings that were studied is provided in figure 15. The arrows indicate the direction of energy flow where red coloured arrows refer to heat and blue coloured arrows refer to cold. In table 1 the selected performance indicators are summarized. These indicators provide insight in the performance of the ATES system itself and allows comparison of the performance of the system over time, and with the performance of other systems (Hastings 2010).

Table 1: Performance indicators for assessing the energetic and environmental performance



Energetic performance	Environmental performance
Energy balance ratio	CO_2 emission reduction *
Thermal recovery ratio	Heat or cold accumulation in the subsurface
Gross energy losses	
Net saving ratio *	
Seasonal performance factor	

*: comparison to a reference case needed.

The Energy Balance Ratio (EBR) shows the ratio between heat and cold that is extracted from the wells of the ATES system. The ratio equals 0 when the amount of extracted heat and cold in balance. When extracted heat is larger than extracted cold, the ratio is negative while in the opposite case the ratio is positive. For calculation of the EBR, summer was defined as the period between April 1st and September 30th. The period between September 30th and April 1st was defined as winter.

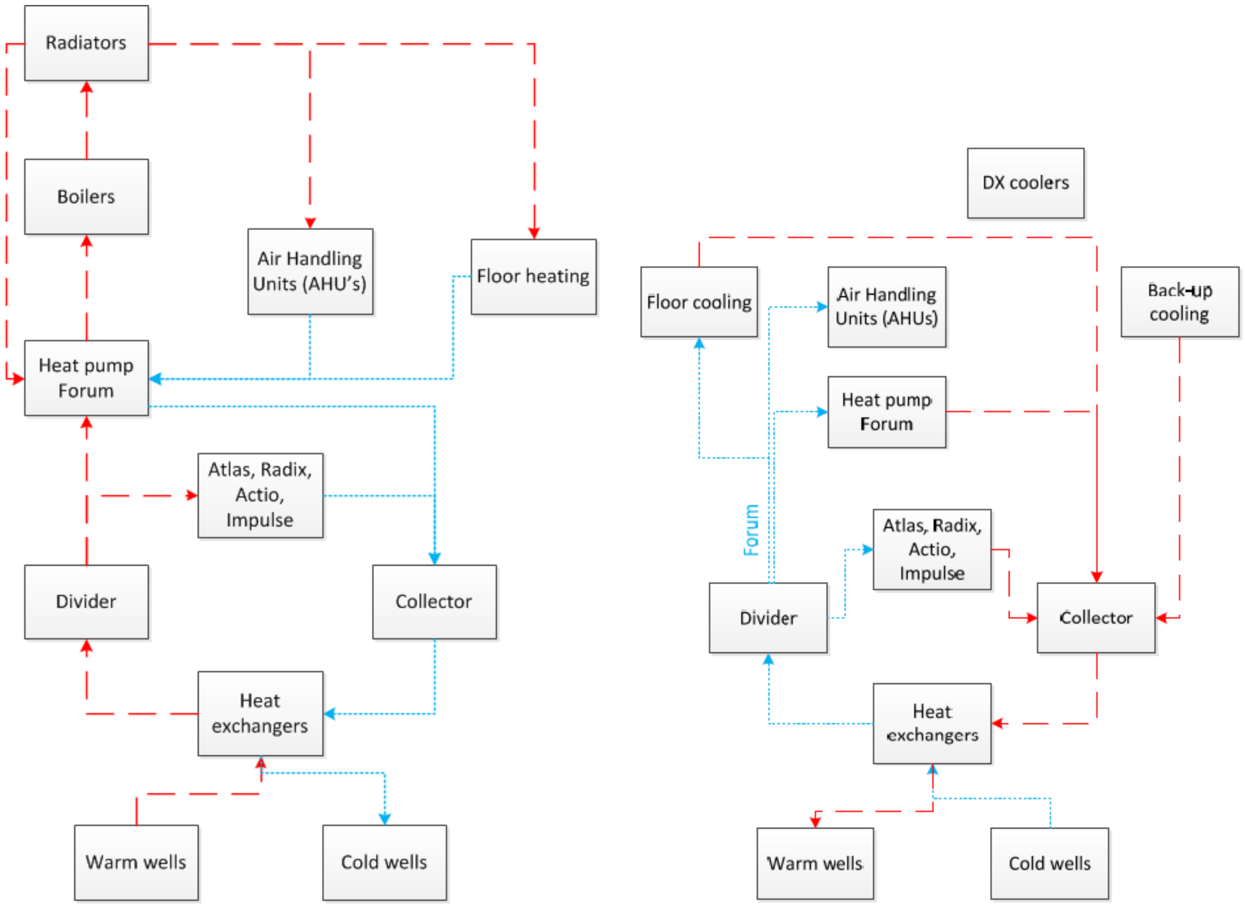


Figure 15: Schematic overview of the ATES-HVAC system in heating mode (left) or cooling mode (right)

The Thermal Recovery Ratio (TRR) shows how much of the energy that is injected into the wells is extracted in the following season. Due to conduction and convection of thermal energy, some energy that is stored is inevitably lost out of reach of the well pumps. A TRR of 1 indicates that all energy that has been injected is also extracted in the following season, which is favourable. In the case that not all thermal energy that has been injected is extracted in the following season, the TRR lies between 0 and 1. When the TRR is negative thermal interference between warm and cold wells had occurred.

The Net Saving Ratio (NSR) shows how much energy is conserved by making use of the ATES as a source for the HVAC system. The NSR can be negative or lie between 0 and 1. A NSR of 1 would mean that there is an ATES system in place, but its operation does not cost any energy, which is not possible. If the NSR lies between 0 and 1, this indicates that the ATES system consumes less energy than a reference system. A NSR that is negative indicates that the operation of the ATES-HVAC system costs more energy than the operation of a reference HVAC system.

An essential, but complex indicator is the Seasonal Performance Factor (SPF). Guidelines for calculating the SPF were drafted in the SEPEMO project (Zottl, Nordman et al. 2012). The SPF depends strongly on the systems boundaries as visualized in figure 16. The heat pump (or cooling unit) is considered to be the central element of the ATES system, indicated as heating/cooling scale 1. Larger scales show additional systems that are installed to provide sufficient heating and cooling power to the buildings users.

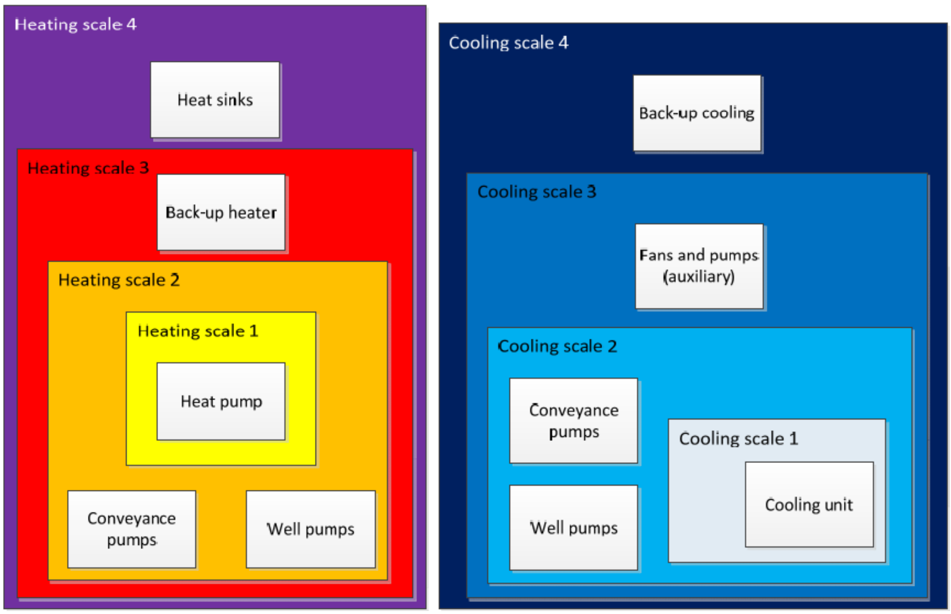


Figure 16: Schematic overview of the system boundaries as defined by the SEPEMO project.

Data that are used to stipulate the performance indicators in table 1 are summarized in table 2. These data were mostly available in the data logs of the building. In some cases, data was deduced from other related data that were available.

Table 2: Data needed to calculate performance

Energetic indicators	Environmental indicators
Electricity consumption well pumps	CO_2 emissions reference case
Gas consumption	CO_2 emissions current system
Pumping rates	Temperature of injected water
Natural groundwater temperature	Temperature of extracted water
Temperature of injected water	Pumping rates
Temperature of extracted water	
Electricity and gas consumption in reference case	
Electricity consumption heat pump	
Energy delivery heat pump	

For the energetic performance indicators intervals of one hour were used. However, the seasonal performance which is of interest by Dutch regulations that prescribe that all thermal energy that has been injected should also be extracted from the aquifer within a period of five years (Ministerie van Infrastructuur en Milieu 2013) are reported per year. For the economic and environmental performance, it is less interesting to know the performance of the system per hour. Therefore, the time intervals used for these indicators are larger, typically one year.

2.1.5.3 Results

The energy balance ratio demonstrates a clear relation with the seasons: in wintertime warm water is extracted while in summertime cold water is extracted. At a higher temporal resolution large (hourly scale) large variations are visible that could be attributed to the outside temperature and the opening hours of the building. Over a period of 4 years, an energy balance was achieved, which is visible by the intersection of the cumulative energy extraction with the 0-line. Clearly, the energy balance related strongly to the climate conditions, indicating that an energy balance is not feasible within too short periods of time.

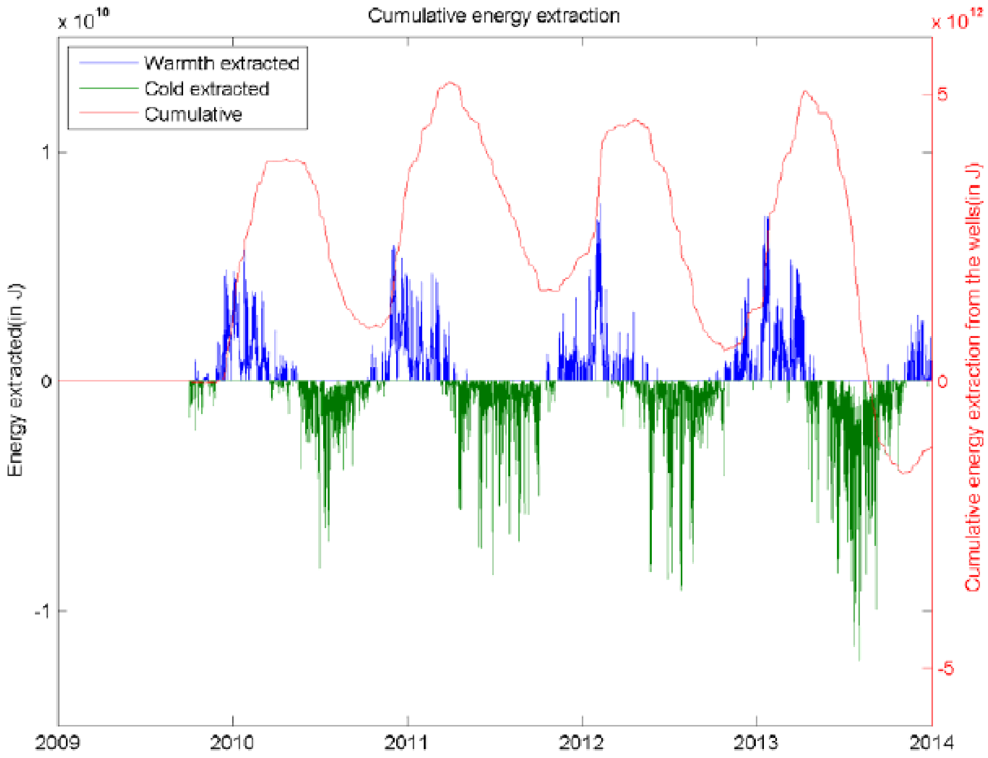


Figure 17: extracted energy from ATES wells (heat and cold) and cumulative energy extraction

We conclude that the use of the EBR provides added value to assess the long term effect of ATES systems on the temperature of the aquifer but has limited value to assess the energetic performance of the building.

In figure 18 the TRR for the warm and cold wells are presented. Negative values of the warm wells suggest thermal interference between warm and cold wells. Closer inspection to the positioning of temperature sensors revealed that these influenced the temperature data in a negative way as they were influenced by the (cold) outside temperature. The TRR data can therefore not be used in this case as performance indicator. For the cold wells, only wells 1 and 2 have a negative TRR in the first year of evaluation. The TRR of the cold wells indicates that 12 to 58% of the thermal energy that has been injected in the past years, is recovered in the following season, for wells 3 and 4. The recovery ratio of wells 1 and 2 is much lower: only up to 31% of the injected thermal energy was recovered. The difference in TRR between the wells 1 and 2 and wells 3 and 4 was unexpected since the amount of energy extracted from the two well groups did not differ significantly. An explanation for this phenomenon is yet to be found. Another remark that can be made regarding the TRR of the cold wells is that the TRR increases over the years which can either be attributed to a change in underground processes or to the fact that more energy extraction was intended in the first place. As the volume of water extracted from the wells has not increased over the years we suspect that the TRR rises due to more efficient energy storage in the aquifer.

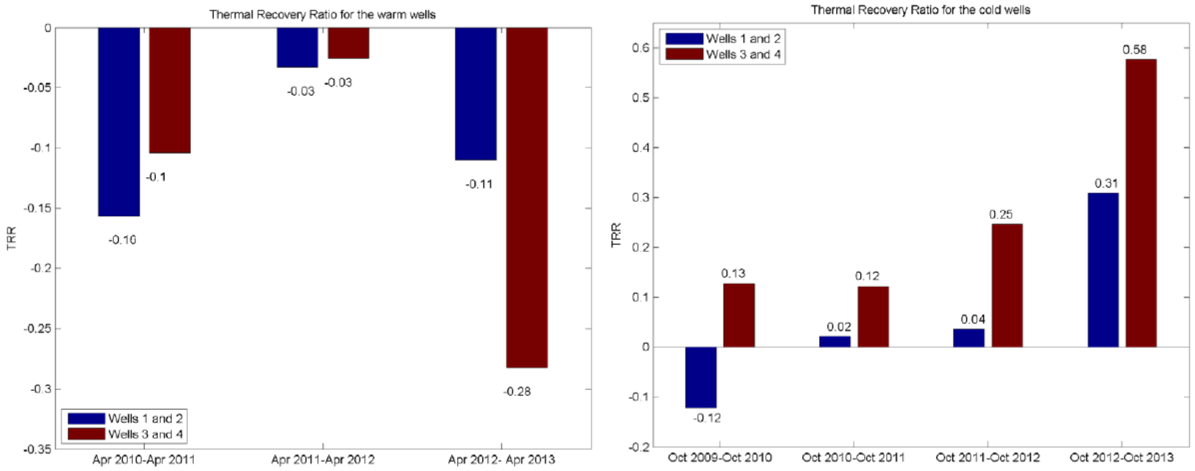


Figure 18: TRR of the warm (left) and cold (right) wells

We conclude that the TRR provides additional information regarding the energy storage efficiency of the aquifer when reliable data can be obtained. However for the assessment of energy performance of buildings this indicator has limited value.

The NSR is shown in figure 19 for the period from April 2010 to the January 2014. It can be seen in the figure that the NSR can have negative values, mainly in the winter months. Negative values indicate that the energy consumed by the current system (including ATES) is higher than the estimated energy consumption of the reference system. This is mostly related to electricity consumption of the well pumps for the extraction of heat from the wells in winter time.

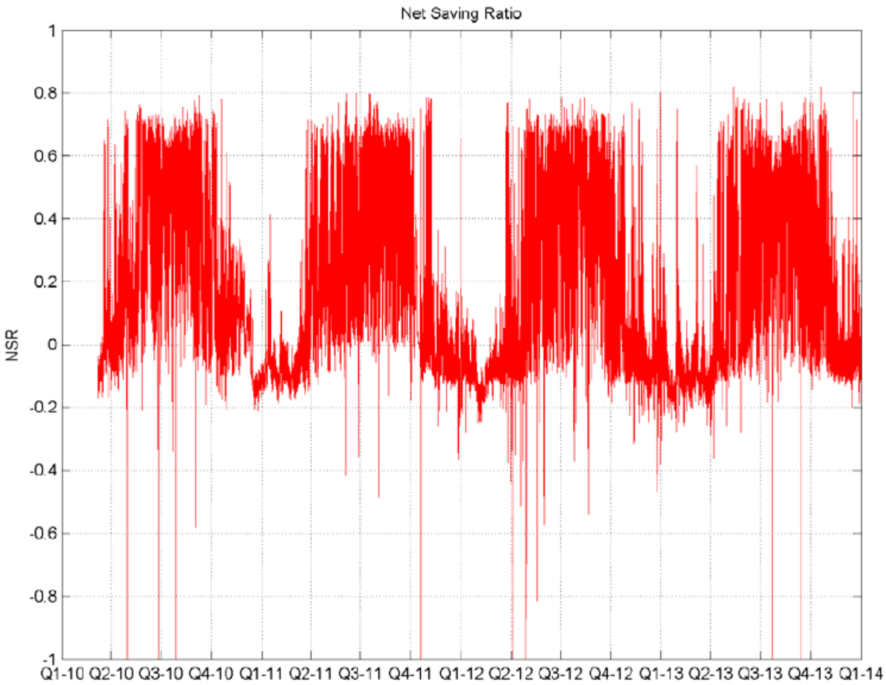


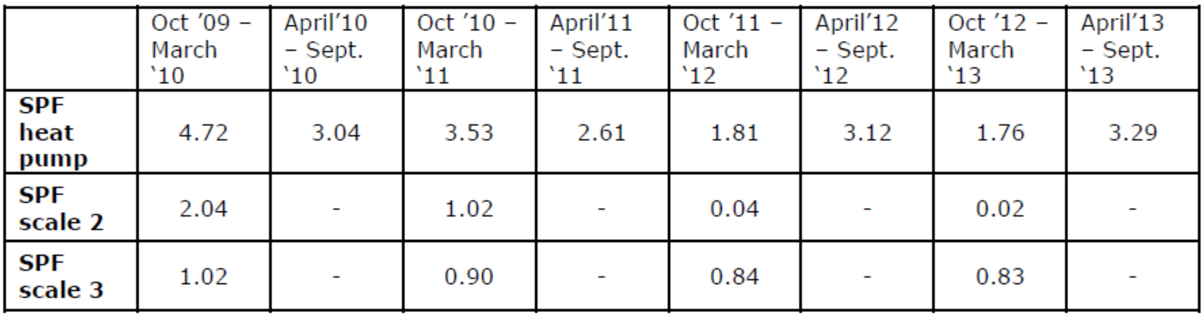
Figure 19: Net Saving Ratio of the ATES –HVAC system on an hourly basis for the period between April 2010 and January 2014

These wells served a total of five buildings. As we lacked data to attribute a portion of the electricity consumption to the building of interest, the electricity consumption was overestimated and the Net Saving Ratio was a weak indicator to assess the performance of the ATES-HVAC system of interest. If the NSR is positive and the closer the ratio is to 1, the higher are the energy savings are by incorporating an ATES system in the HVAC system. To our surprise, the NSR varied strongly on an hourly resolution, probably because of day/night temperature variation. Over the period that was considered, the ATES system helped to decrease energy consumption with a NSR of 18%. It should be mentioned that this relates only to the heating of the building. For cooling the NSR is expected to be higher but as we had limited data on the cooling of the building we could not quantify the NSR.

As the NSR needs the inclusion of a reference system, this indicator has limited value to compare buildings with different functions. The added value can be found by comparing the actual energetic performance with the design specs, thereby helping the buildings operator to improve the buildings energetic performance.

The SPF for three different scales were calculated from available data and presented in table 3. The SPF for the cooling seasons (April to September) could not be calculated for scale 2 and 3 due to a lack of data on cold that was delivered to the buildings and the electricity consumption that is associated with this energy delivery.

Table 3: SPF of each season for three scales as indicated in figure 16



	Oct '09 – March `10	April'10 – Sept. `10	Oct '10 – March `11	April'11 – Sept. `11	Oct '11 – March `12	April'12 – Sept. `12	Oct '12 – March `13	April'13 – Sept. `13
SPF heat pump	4.72	3.04	3.53	2.61	1.81	3.12	1.76	3.29
SPF scale 2	2.04	-	1.02	-	0.04	-	0.02	-
SPF scale 3	1.02	-	0.90	-	0.84	-	0.83	-

The SPF of the heat pump declined (even halved) in the winter seasons over the years that were studied. When searching for possible reasons for this decline, it was found that the pattern of electricity consumption of the heat pump changed significantly after 2010. At that time, the operational conditions of the heat pump changed and the focus shifted from using the heat pump for heating to cooling. This resulted in a reduced performance of the heat pump in winter months as partial utilization of the heat pump reduces the Coefficient of Performance (COP).

The SPF of scales 2 and 3 follow the same behaviour as the SPF of the heat pump. As electricity consumption by the well pumps and the distribution system continued unchanged after 2010, the drop in SPF was also seen at these scales, although the numbers are exaggerated as part of the electricity consumption can be attributed to other buildings. From table 3 we can conclude that the ATES system has sufficient potential to reduce the consumption of primary energy for heating purposes (SPF scale 2 > 1 in winters of 2010 and 2011) but operational conditions influences the performance to a large extend. Unfortunately no data was available for the cooling seasons. As ATES systems can especially reduce electricity consumption for cooling (thus increasing SPF scale 3) the picture is distorted.

Although the performance of the ATES system is not as high as was expected, even at low SPFs the emission of GHG was reduced compared to a reference system as can be seen in figure 20. However, this is mainly due to the production of electricity by wind power.

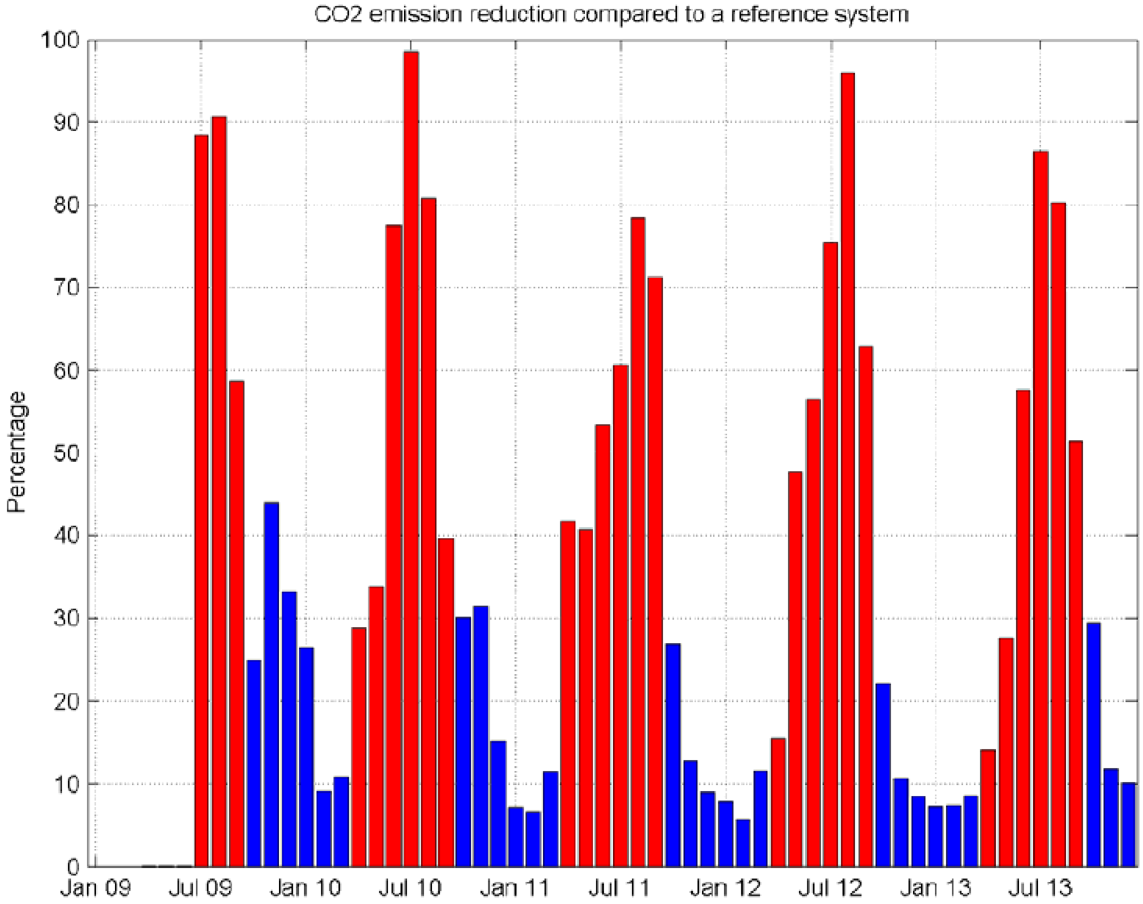


Figure 20: CO_2 emission reduction as a percentage of the CO2 emissions of a reference system

2.1.5.4 Discussion and conclusions

At the start of the research, an evaluation framework for ATES systems was sought. However, this framework does not exist (Dincer 2002). Review of 9 studies (van Mourik 1992; Marseille, Armstrong et al. 1993; Paksoy, Gürbüz et al. 2004; Hoes, Desmedt et al. 2006; Andersson 2007; Desmedt and Hoes 2007; Vanhoudt, Desmedt et al. 2011; Kranz and Frick 2013; Ghaebi, Bahadori et al. 2014) has yielded a collection of six different indicators. The most used performance indicator found in literature is the performance factor, seasonal performance factor or the coefficient of performance (either of the three used in 89% of the reviewed studies). Also, the amount of energy saved by making use of an ATES system was a much used indicator (67% of the reviewed literature). Furthermore, CO_2 emission reduction, pay-back time, load fraction covered by the ATES system and energy recovery from the wells have been used to analyse ATES performance. Two of the reviewed studies used five indicators, thereby using more indicators than other studies (Marseille, Armstrong et al. 1993; Hoes, Desmedt et al. 2006). When examining the use of the performance factor, seasonal performance factor or the coefficient of performance, it can be noticed that the studies make use of these indicators in different ways. The indicators are used to indicate performance of the heat pump or the entire system and are evaluated for different time intervals, namely seasonal or yearly.

In comparison to the reviewed studies, the research performed in this study has made use of a broader set of indicators and has used more detailed spatial scales and time intervals. The evaluation has included seven indicators, all providing insight in the performance of a specific part of the system or the ATES-HVAC system as a whole in the domains of energy and environmental impact. Also, multiple spatial scales and several different time intervals were used for the performance evaluation. The spatial scale of evaluation can be inherent to the indicator, such as the Thermal Recovery Ratio, but for some indicators the scale of evaluation can be defined. This is the case with the Seasonal Performance Factor. The conclusions that can be drawn from the results of the calculations differ per analysed scale. The method of using different spatial scales for evaluation is similar to that proposed by Bejan (2002) when he proposes exergy accounting to be performed in smaller and smaller subsystems to detect the areas that destroy exergy the most (Bejan 2002). In the case of this research, exergy accounting is substituted by performance analysis on the basis of energy. This method is of added value to the performance evaluation, as it provides knowledge on areas for improvement.

2.1.6 Critical design parameters for TT 1

Using the research that was described in the previous sections it becomes clear that the individual technologies (bioremediation and ATES) and the combination of these two technologies in a technology train provide large flexibility to tweak the performance in such a way that it can link the available resources and the estimated demand. This flexibility allows application of the TT in many cases where ambitions regarding energy savings or re-use of energy, as well as improvement of aquifer quality exist. In this, seperate design parameters of the ATES-bioremediation combination can be identified regarding 1) optimal performance of groundwater remediation, 2) optimal performance of energy system, and 3) optimal performance of groundwater remediation and energy system.

1) For the optimal performance of TT1 for groundwater remediation, key parameters that define the chance of succesfull remediation of groundwater that were identified in this reserach are:

1. intrinsic degradability of the contaminants;
2. environmental conditions (availability and characteristics of electron acceptors and donors, including soil organic matter (redox potential), pH, and temperature);
3. microbial population that is present in the aquifer;
4. required groundwater quality / risk level;
5. available time to reach the required groundwater quality / risk level.

From a technological perspective, both the environmental conditions and the microbial population are parameters that can be modified in order to meet the required groundwater quality / risk level at a predefined time. For optimizing the aquifers temperature to stimulate biological activity it can be beneficial to extract more cold groundwater. In cases where the natural conditions are not feasible for bioremediation, a step wise approach for adding electron donors/acceptors and microorganisms can be followed to minimize the level of intervention (thus costs). From a design perspective, the spatial configuration can be adjusted in order to make the best use of the groundwater flow for mobilizing SOM as electron donor, and temperature to stimulate biodegradation. In cases where contaminants mass removal is not required, it can be an option to optimize the infiltration and extraction rates, allowing for net hydrological containment. Drawbacks of these adjustments of parameters are the increased risk of clogging due to precipitation reaction originating from redox changes or the growth of a biofilm. In laboratory experiments, especially the precipitation reactions were found to be relevant.

2) For the optimal performance of TT1 to supply renewable (thermal) energy, key parameters which define the efficiency of the ATES system as were identified in this research are:

1. energetic performance and installation of the buildings to be served by the ATES system including the local climate conditions;
2. geohydrological parameters (permeability and thickness of the aquifer);
3. distance between warm and cold wells;
4. energy balance of the aquifer;
5. price of gas and electricity.

From a technological perspective, the energetic performance and installation of the buildings can be adapted to maximize the value of the ATES system. These aspects will directly influence the required groundwater extraction (and infiltration) rates and the energy balance. In order to maintain an energy balance, the addition of either heat or cold can be required. This energy balance sustains the beneficial use of the ATES system. From a design perspective, the spatial configuration of wells can be adjusted in order to maximize energy storage for individual systems (large distance), to maximize energy storage in a specific area (small distance between similar wells, larger distance between opposing wells), or to minimize effects on hydraulic head (small distance between opposing wells).

3) For optimal performance of the combined bioremediation and energy storage, key parameters are:

1. distance between warm and cold wells
2. energy and groundwater balance
3. environmental conditions (especially redox states)

The influence of these parameters towards either bioremediation or energy storage is opposing. For example, a decreasing distance between wells might stimulate the mobilization of SOM by increased groundwater flow, it reduces the efficiency of thermal energy storage as negative interferences become more realistic. Similar opposing relations were identified for the energy balance and redox conditions. A net flux of heat into the aquifer will stimulate the biological activity due to a temperature increase but hampers the supply of cold for cooling purposes which is considered the main benefit of ATES systems. Also the adjustment of environmental conditions to stimulate biodegradation will introduce an increased risk on well clogging which negatively affects the ATES operation. Optimizing the groundwater balance seems to be beneficial for both the groundwater quality and energy storage as hydrological containment might be combined with an improved energy balance.

2.2 TT2: Stabilization and Solidification of heavy metal contaminated soils for aggregates production and use of secondary raw materials from infrastructures

The technology train for building materials and soil (TT2) addresses the issue of managing potentially large volumes of industrial soil and construction and demolition waste (C&DW) that may arise from redeveloping a BF site. To this aim, ex-situ and on-site technologies may be possibly applied, depending on the soil characteristics, quality of C&DW recycled material, site specific conditions and on the regeneration pathway chosen for the specific BF case. In order to assess the applicability of ex situ treatments of industrial soil in a BF redevelopment context, a specific tailored TT was selected and tested at lab scale. For the reuse of C&DW, we focussed on the possibilities of on-site recycling, promotion of reuse and recycling of these materials, and selection of high quality recycled aggregates for use in structural and non-structural concrete in buildings and infrastructure.

For the industrial soil, TT2 was based on stabilization/solidification (S/S) and granulation of a metal contaminated BF soil and was aimed at producing aggregates with suitable physical, mechanical and environmental characteristics to allow their reuse in civil engineering applications. This possibility is of particular interest in a BF regeneration framework as there is generally a demand for construction materials such as aggregates and/or fillers. This is elaborated in section 2.2.1.

For C&DW, TT2 focussed on determination of C&DW quality in order to prove the suitability of the technology for the upcoming performances at real scale works. The objective of testing building materials is to contribute in the decision of how to improve the aggregates quality and how to apply the maximum percentage of these materials, optimizing the re-use and recycle of C&DW for BF regeneration.

Both for S/S and C&DW reuse, the possibility of replacing virgin raw materials with site-excavated material presenting specific properties could be an interesting asset, both from an economical and environmental point of view.

2.2.1 Technology Train on Industrial Soil

The results addressing this knowledge gap were published as Capobianco, O. *et al.,* 2014a and Capobianco, O. 2014.

2.2.1.1 Problem description

The selected TT consisted in a grain size screening step in which the material was separated into two size fractions, followed by the treatment of the fine fraction (d < 2 mm) by the combination of stabilization/solidification with granulation. Recently, a few studies focused on coupling of the above-mentioned techniques in order to obtain aggregates from the treatment of several waste material (see e.g. Cioffi et al., 2011; Scanferla et al., 2009), proving that such a treatment may be effective in obtaining pellets exhibiting sufficient mechanical strength and a decreased release of toxic elements, such as As, Pb, Cd and Hg (Scanferla et al., 2009). However, a systematic study of the influence of operating conditions and the type of binder on the properties of the final product is still missing.

In order to fill this gap, lab-scale tests were first performed on a non-contaminated natural soil, by varying the operating conditions and the type and amount of binders and additives, so to identify the preliminary operating windows of the process.

Subsequently, a second set of experiments was carried out on a moderately contaminated industrial soil collected at the Gruber site, a former wool manufacturing plant located within the national priority site of Terni-Papigno, in the municipality of Terni (Italy), in order to assess the influence of soil properties on the characteristics of the obtained aggregates.

The main aim of this work was to evaluate the applicability of the proposed process to treat a metal-contaminated BF soil in terms of the effects exerted on the physical and mechanical properties, as well as on the leaching characteristics of the produced aggregates in comparison with those observed for the untreated soil. In the following paragraphs the main findings obtained as a result of the experimental activities are reported and discussed and the conditions of applicability of TT2 as well as its main criticalities are highlighted. Hence, a perspective for the further investigation of the proposed treatment is provided.

2.2.1.2 Methodology

The S/S-granulation experiments were performed in a laboratory scale granulator operated at 24 rpm for 5-10 minutes, with a tilt of 66°. The rotation speed, the granulator inclination, as well as the duration of the tests were selected by performing preliminary optimization experiments on the natural soil, the results of which are not reported in this report.

The experiments were performed on the fine fraction of the natural non contaminated soil by testing a high resistance Portland cement (CEM I 52.5R) and a Portland composite cement (CEM II/A-LL 42.5 R) and sulfonate-based (A1) or acrylic-based (A2) superplasticizer additives. For both cements, cement to total solid material (C/S) ratios of 0.2, 0.25, 0.3 and 0.35 kg/kg were tested, whereas for the superplasticizers additives to cement (A/C) ratios of 0.01 and 0.02 kg/kg were employed. A few of the mixture formulations that provided the best results in terms of mechanical strength in the preliminary tests were subsequently selected to treat the BF soil sampled a the Gruber site within the Terni-Papigno priority site.

In order to investigate the effects of the proposed TT on industrial soil with different initial properties, and hence to better characterize the operating windows of the process, the S/S-granulation tests were performed on three soil samples collected at the site, hereafter termed Q1, Q2 and Q3, whose main physical and chemical characteristics are reported in Table 4.

As shown in Table 4, appreciable concentrations of As, Cu, Hg, Pb, Sn and Zn were observed for the tested samples. Specifically, Cu, Pb, Hg and Sn concentrations in sample Q1 exceeded the respective Italian threshold values for residential use. The fraction of organic carbon (foc) of the industrial soil was around 1.2 wt. % for sample Q1, while the samples Q2 and Q3 as well as the natural soil seemed to be free of organic matter, exhibiting a foc below the instrumental quantification limit.

The suitability for reuse of the produced aggregates was evaluated in terms of their physical properties (particle size distribution, ASTM D422), resistance to compression (Aggregate Crushing Value - ACV, BS 812-110) and environmental behaviour (leaching behaviour, EN 12457-2). The description of the employed set-up as well as of the adopted experimental procedure for material testing and analysis is reported in Capobianco et al. (2014a).

Table 4: Main characteristics of the fine fraction (d < 2 mm) of the three samples of industrial soil collected at the Terni Gruber site (Italy). Bold values refer to concentrations exceeding regulatory limits.

	Q1	**Q2**	**Q3**	**Residential use limits (It. LD 152/06)**
Physical characteristics				
Particle with d < 2mm (% wt.)	49	48	94	-
Chemical characteristics				
As (mg/kg)	8.7	3.6	6.1	20
Ba (mg/kg)	153	58.0	78.7	-
Cr (mg/kg)	34.4	7.65	10.7	150
Cu (mg/kg)	**475**	6.03	20.0	120
Hg (mg/kg)	**1.02**	0.48	0.52	1
Pb (mg/kg)	**105**	36.2	43.5	100
Sn (mg/kg)	**43.8**	**62.2**	**56.3**	1
Zn (mg/kg)	129	38.4	43.8	150
foc (% wt.)	1.2	< 0.05	< 0.05	-

2.2.1.3 Results

Screening tests on natural soil

The main results obtained from the S/S – granulation treatment carried out on the natural soil in terms of the particle size distribution of the obtained granules as a function of the different mixture formulations tested are reported in Figure 21.

The obtained granules showed an average d_{50} between 6 and 10 mm, one order of magnitude greater than that of the untreated natural soil (about 0.5 mm). The average particle size increased with increasing water content, confirming the results of previous studies on granulation processes, which reported that the granulation rate and the mean size of the granules product increases with increasing water content (Iveson et al., 1996; Salman et al., 2007). For both cements, the average diameter of the granules varied proportionally with the binder content, while the use of the additives allowed to obtain finer aggregates, in accordance with the results of previous studies indicating that a more viscous binder generally leads to the reduction of the granules consolidation rate and subsequently of the compaction and growth of the granules (Iveson et al., 1996). However, an increase of the A/C amount from 0.01 to 0.02 kg/kg did not imply any appreciable modification of the particle size distribution of the obtained granules, regardless of the type of cement used as a binder.

The main results in terms of the mechanical resistance of the final product are reported in Figure 22. A different behaviour of the granules was noted, depending on the type of cement used as binder in the S/S - granulation tests. Specifically, lower ACV, i.e. higher strengths, were obtained for the granules manufactured with cement R 52.5 in 9 cases out of 11, most likely due the better intrinsic performance of this type of cement in comparison with cement R 42.5. Making reference to cement R 52.5, the best ACV results were obtained at a C/S ratio equal to 0.25 kg/kg, for which an average ACV of about 21% was achieved, which is comparable to that typically obtained for natural gravel presenting a similar particle size distribution. It should be noted that the use of either type of superplasticizers did not imply any relevant improvement of the mechanical performance of the granules, regardless of the type of cement employed as binder. Anyhow, it should be pointed out that for both types of cement the use of the additives allowed to reduce the water to total solid material (W/S) ratio down to 0.14 l/kg, this value also being the minimum value for which appreciable increases of the granules resistance were achieved.

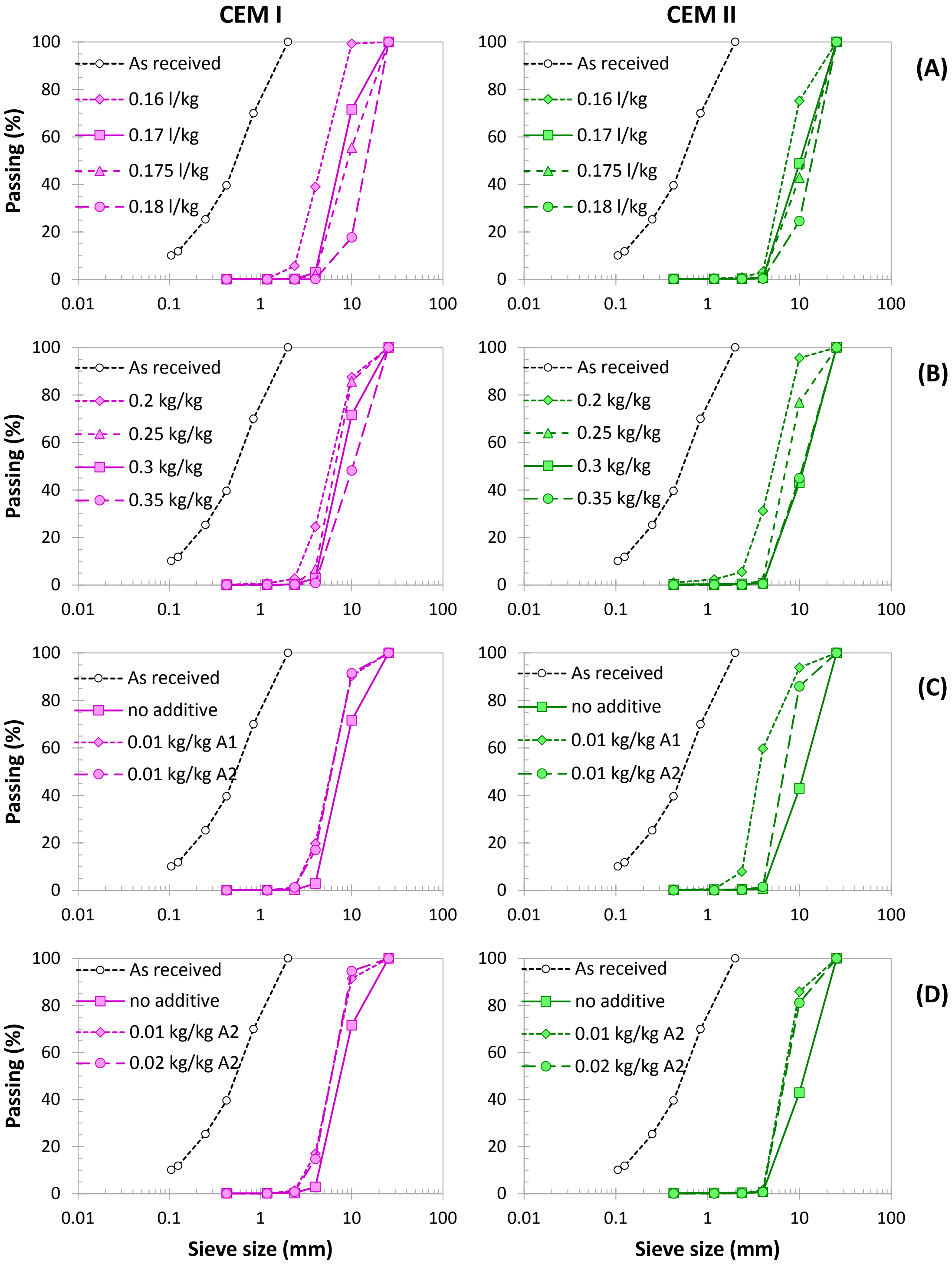


Figure 21: Comparison of the particle size distribution curves of the as received natural soil and of the granules obtained after the S/S-granulation treatment for cement R 52.5 and cement R 42.5 as a function of: a) water content (C/S=0.3 kg/kg); b) cement content at optimum water content; c) additive type at optimum water content (C/S=0.3 kg/kg); d) additive content at optimum water content (C/S=0.3 kg/kg).

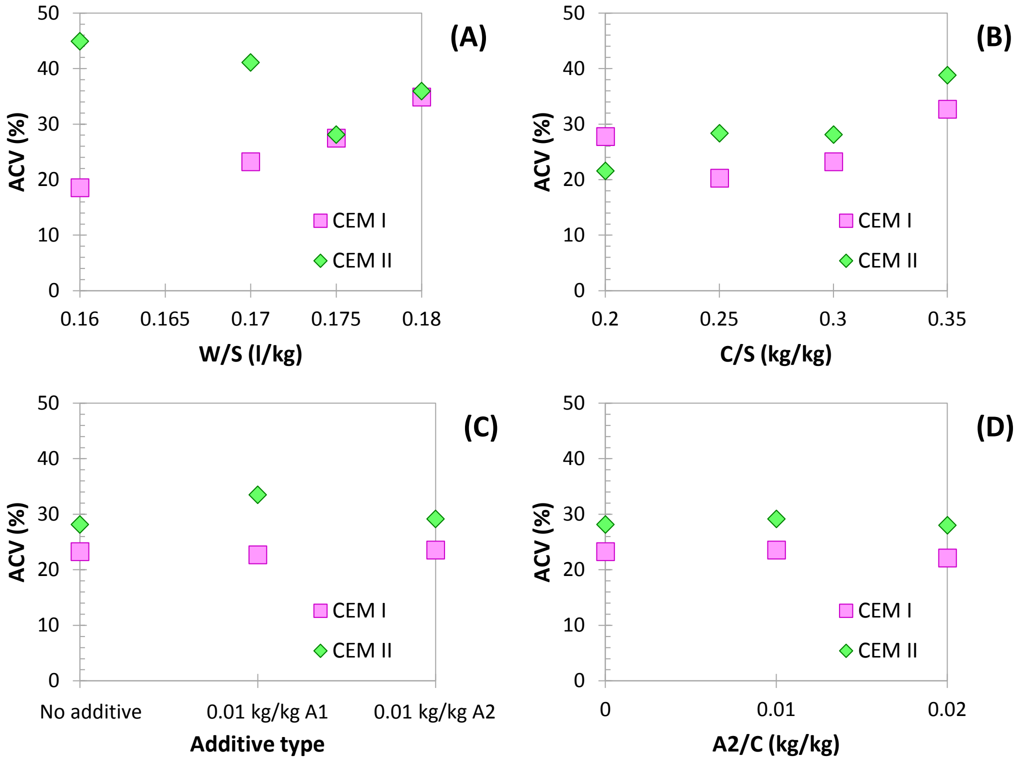


Figure 22: Results of the Aggregate Crushing Value (ACV) test for cement R 52.5 and cement R 42.5 as a function of: a) water content (C/S=0.3 kg/kg); b) cement content at optimum water content; c) additive type at optimum water content (C/S=0.3 kg/kg); d) additive content at optimum water content (C/S=0.3 kg/kg).

Tests on industrial soil

A few of the mixture formulations for which aggregates with a suitable mechanical performance for use in construction were obtained from the natural soil were selected to test the S/S - granulation treatment on the three samples of industrial soil. Specifically, cement R 52.5 was used and two concentrations C/S were tested: 0.25 and 0.3 kg/kg. In addition, for each cement concentration, the effect of the addition of the acrylic-based superplasticizer (A2) at a A2/C ratio of 0.02 kg/kg was also investigated. The results in terms of the particle size distribution and the mechanical strength of the produced granules are reported in Figure 23a and Figure 23b, respectively.

As for the natural soil, the cement-based granulation treatment applied to the industrial soil allowed to obtain aggregates with an average diameter one order of magnitude greater than that of the untreated soil. As expected, the minimum water to solid ratio which allowed the soil particles to grow and nucleate was found to be strictly particle size-dependent, i.e. a higher W/S ratio was needed to granulate finer particles (Salman et al., 2007). In addition, similarly to the natural soil, the use of a more viscous liquid obtained by adding the acrylic-based superplasticizer, generally allowed to produce slightly finer pellets. Differently from the natural soil, no major effect of the binder content on the average diameter of the granules was noted.

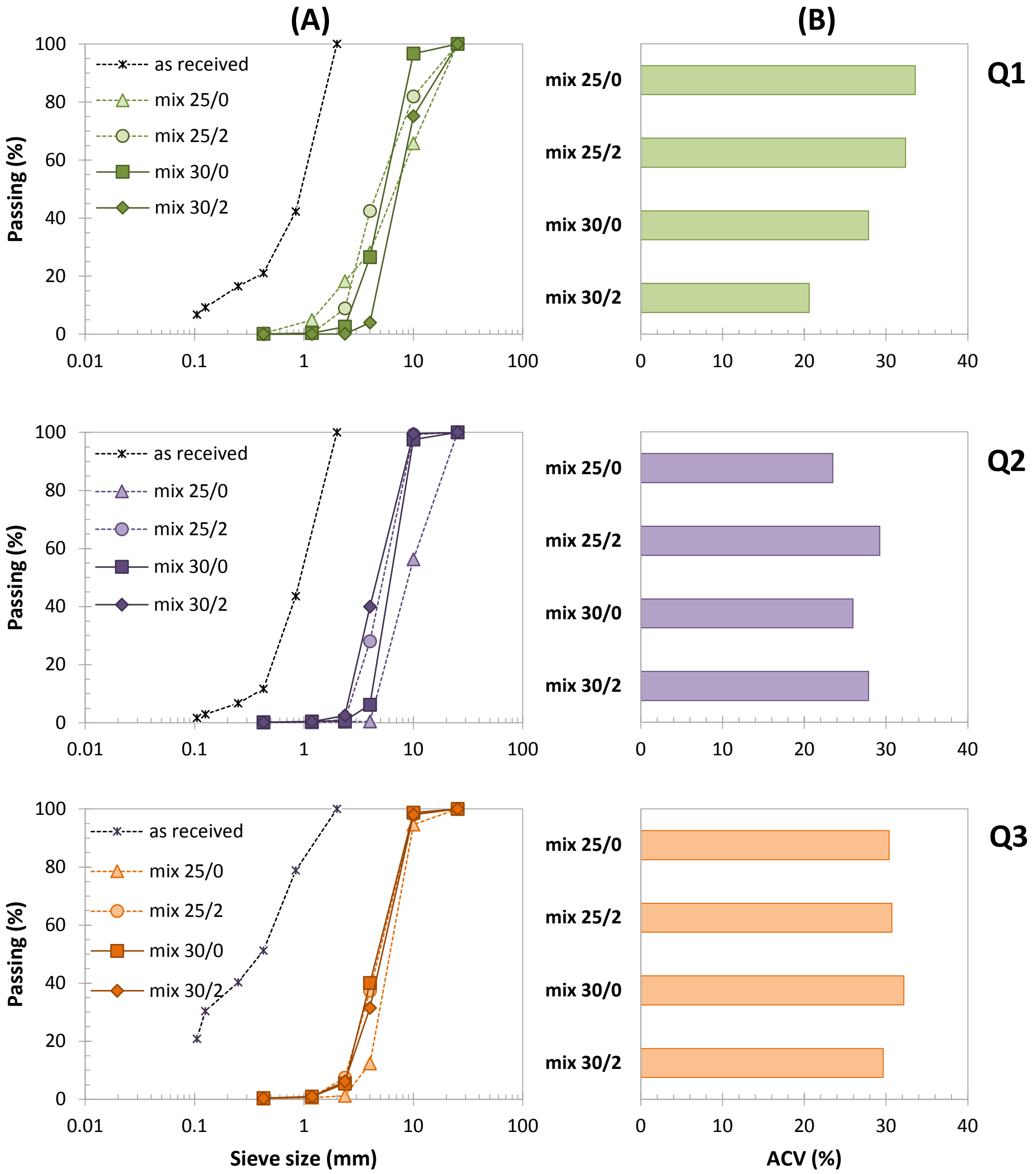


Figure 23: Effects of the S/S-granulation treatment on the properties of the three samples of the industrial soil for four mixture conditions in terms of: a) Particle Size Distribution and b) Aggregate Crushing Value (ACV). The first number after the term mix indicates the percentage of cement R 52.5 employed (25 or 30%) over the total solid material, while the second the content of superplasticizer A2 with respect to the cement (0 or 2%).

With regard to the resistance to compression of the produced granules, an average ACV approaching that of argillaceous limestone (≈ 29 %) was obtained as a result of the S/S - granulation treatment. As expected, the ACV resulted strongly influenced by the size of the obtained granules. Indeed, granules with a similar particle size distribution showed a similar resistance to compression, this behaviour being particularly evident for sample Q3. Besides, the product resulting from the treatment of sample Q3 also exhibited a relatively high ACV, i.e. a lower strength, probably due to the finesses of this soil; indeed it is commonly recognized that coarser particles generally yield a particles-cement paste product characterized by a higher mechanical performance (Meddah et al., 2010). The effect of the additive A2 was appreciable only for sample Q1, for which an optimum ACV of 20% that is between that of carboniferous limestone and mixed gravel, was achieved for mix 30/2. The differences noted on the effects of the binder composition may be tentatively related to the higher foc content of sample Q1 (≈ 1.2 % wt.) compared to that of the other tested soils, which was found to be negligible. In fact, previous works regarding the S/S of waste materials have reported that a foc greater than 1% can interfere with the solidification of the cementitious binder as well as with the mechanical resistance of the final product (Stegemann and Zhou, 2009).

The main results of the EN 12457-2 test performed on both untreated soil and cured granules in terms of eluates pH and release of critical metals are reported in table 5. In the same table, the results of the compliance leaching test performed on cement R 52.5 are reported for comparison together with the limits imposed by the Italian regulation for groundwater quality (It. LD 152/06), material reuse (It. MD 186/06) and final disposal in inert waste landfill (It. MD 27/09/10).

Table 5. EN 12457-2 leaching test results for the as received industrial soil and the granules obtained after the S/S-granulation treatment. Concentrations are expressed in µg/l.

		pH	Ba	Cu	Cr_{tot}
Q1	as received	8.6	15.73	85.15	< 3
	mix 30/0	12.9	799	86.01	9.18
	mix 30/2	11.6	171	105	16.64
Q2	as received	8.8	14.05	5.86	< 3
	mix 30/0	12.8	800	18.97	9.09
Q3	as received	8.6	15.09	8.45	< 3
	mix 30/0	12.9	960	45.41	12.07
	mix 25/0	12.9	613	42.50	11.05
	CEM I	13.1	4030	20.94	10.27
	Reuse (It. MD 186/06)	5.5 – 12	1000	50	50
	Inert Waste Landfill (It. MD 27/09/10)	-	2000	200	50
	Groundwater quality (It. LD 152/06)	-	-	1000	50

In order to assess the leaching behaviour of the granules produced from the different soil samples collected at the BF site, the leaching test was performed on the aggregates obtained employing a C/S ratio equal to 0.3 kg/kg without the use of the acrylic-based superplasticizer (mix 30/0). Results highlighted an increased mobilization of Ba, Cu and Cr as a result of the treatment. This effect was ascribed for Ba to the characteristics of the cement used as binder, which showed to release significant concentrations of this metal, and for Cu and Cr to the highly alkaline conditions produced as a result of the combined process, which may lead to the formation of more soluble phases containing these metals, especially Cu (Voglar and Leštan, 2010). Moreover, Cu eluate concentrations were found to be proportional to the starting soil concentrations of this metal, with a negligible effect of the combined treatment, neither positive nor negative, on the granules manufactured from sample Q1, which showed the highest Cu concentration, i.e. 475 mg/kg wt.

As for the effects of the superplasticizer addition on the leaching behaviour of the final product, the results of the leaching test performed of the granules produced from sample Q1 by employing 0.3 kg/kg of cement and 0.02 kg/kg of A2 showed a negative effect of the additive on the release of Cu and Cr, regardless of the achieved pH decrease to a value of 11.9 in comparison to the eluates pH of the aggregates produced with water only.

Finally, the leaching test was performed on the products attained as a result of the cement-based granulation of sample Q3 applying a C/S ratio of 0.25 kg/kg, in order to assess the effect of decreasing the cement content on the leaching of contaminants from aggregates showing similar size and mechanical strength. As shown in table 5, a decreased release with decreased cement content from 0.3 to 0.25 kg/kg was observed for Ba, while no relevant effects were noted for Cr and Cu. Besides confirming the effect of cement on the release of metals from the recycled aggregates, especially for Ba, the obtained results highlighted the major influence on the release of Cu and Cr of the eluate pH, which was found to be around 12.9, regardless of the cement content employed.

The effect of the granulation S/S process on the leaching behaviour of the material is different from the results obtained by Scanferla et al. (2012), who found that the leaching of metals from the granulated material was sensibly reduced with respect to the contaminated soil. Nevertheless, it is important to highlight that the leaching conditions applied by Scanferla et al. (2012) were quite different from the ones used in our work. Namely, they used as leaching agent a solution of magnesium sulphate, characterized by acidic pH. This probably contributed to reducing the final pH of the leachate to 8.8 against 11.6-12.9 of the leachates obtained in our work, thus affecting the release of metals as copper and chromium, whose solubility is greatly increased when the pH is increased to alkaline values.

2.2.1.4 Discussion

Operating windows provide an indication of the ranges of applicability of a process by identifying its critical parameters and for each of these the conditions that may lead the technology to fail or prove ineffective. To this aim, extreme conditions need to be tested at lab scale in order to define the optimum operating windows of the process. The application of the combined S/S-granulation to the BF soil collected at the Gruber site within the Terni-Papigno priority site allowed to obtain the following significant (although partial) results in terms of the conditions of applicability of the proposed process:

- Contamination by metals: the results of the experimental phase showed how the S/S-granulation process may be affected by the presence of relevant concentrations of Cu, although only minor considerations can be made for other potentially hazardous elements, due to the low metals concentrations observed for the tested soil, especially for samples Q2 and Q3;
- Fraction of total carbon: the influence of the superplasticizer addition on the mechanical properties of the granules produced as a result of the S/S-granulation treatment of sample Q1 was tentatively attributed to the higher foc of this soil sample in comparison to the other tested samples. This suggests that, based on the outcome of the experiments performed, the addition of a superplasticizer may be required for soils characterized by foc values indicatively higher than 1%;
- Particle Size Distribution: the presence of a higher fraction of fine particles was observed to lead to slightly lower mechanical properties of the obtained granules (see sample Q3), regardless of the applied operating conditions.

Hence, the following specific scientific gaps related to the factors outlined above should be possibly assessed in future experimental investigations:

- The feasibility of the combined S/S-granulation process to treat a highly and multi metal contaminated soil, in order to assess the influence of the contamination type and contamination degree of the starting material on the properties of the final product, especially in terms of leaching of metals from the obtained aggregates;

- The treatability of soils with a considerably higher foc than those observed for the Gruber soil samples, in order to better assess the effect of the soil foc on the strength and leaching behaviour of the manufactured granules;
- The testing of soils with different particle size distributions, in order to better assess the influence of the initial particle size distribution of the soil on the process performance.

Another issue that was not possible to investigate during this project for lack of suitable soil samples concerns the effect of the S/S - granulation technology on soil contaminated by organic contaminants. The application of S/S technologies to immobilize organic compounds has always been controversial. In fact, organic compounds tend to have a detrimental effect on the properties of the treated material and they may be leached out from the cementitious matrix with time. The testing of the S/S-granulation process on BF soils contaminated by organic compounds may possibly elucidate this point, allowing to enlarge the operating windows of the proposed technology train. In this regard, it would be also useful to treat soil samples contaminated by both organic and inorganic compounds, in order to assess also the influence of organic contaminants on the performance of the process with regards to inorganic contaminants immobilization.

Together with the scientific gaps just mentioned, the obtained results suggested that specific issues may possibly affect the application of the S/S-granulation treatment in a BF regeneration context. Such issues, both technological and non-technological, seem to be strictly related to the use of cement as binder in the combined process, as briefly outlined below:

- Environmental issues: the increased mobilization of Cu, Ba and Cr was mainly ascribed to the characteristics of the cement used as a binder, which showed to release significant concentrations of these metals. In addition, the leaching of the above mentioned elements is pH dependent and can increase in the alkaline environment produced as a result of the cement-based treatment. Besides, although the combined S/S-granulation treatment may potentially allow to save virgin raw materials and avoid landfilling, the greenhouse gas emissions related to the cement production process should be accounted for, to allow for a fair comparison with standard regeneration strategies.
- Economic issues: the costs of the proposed technology train, mostly related to the cement and additives needed, was estimated to be slightly lower than that of traditional ex situ S/S applications (Scanferla et al., 2009). However, the cost of the process should be compared also with standard regeneration strategies such as excavation and landfilling of the contaminated soil, to obtain a fair assessment of this technology train in different contexts;
- Social issues: the acceptance by public authorities and the community of a technology option that implies to leave the contaminated soil in the site, although properly stabilized, is not guaranteed in every national context.

2.2.1.5 Critical design factors

The results obtained from the experimental activities performed within the project showed that S/S-granulation techniques may represent a feasible opportunity for increasing the role of ex situ technologies within remediation and BF redevelopment projects. Nevertheless, the success of the proposed technology is very strongly depended upon the operating conditions applied and the properties of the starting materials. Specifically, the use of a high clinker containing cement (R 52.5) seemed to be the most prominent requirement for obtaining granules with mechanical properties approaching those of natural gravel (ACV ~20%). Moreover, results showed that the use of cement to solid ratios higher than 0.3 kg/kg may lead to a significant decrease of the strength of the final product. In addition, soil texture and composition play a relevant role in obtaining granules with satisfactory physical, mechanical and environmental characteristics. Table 6 briefly summarizes the main factors which were found to mainly influence the S/S-granulation treatment together with those that showed only minor effects on the process under the tested operating conditions.

Table 6. Factors influencing the performance of the combined S/S-granulation process

Macro categories	Key factors	Secondary factors
Characteristics of the mixture	Type of cement Amount of cement	Type of additives Amount of additives
Characteristics of the soil	Texture Type of metal Content of metals	foc

2.2.2 Technology train for re-use of C&DW materials

Results on this knowledge gap were not published.

2.2.2.1 Problem description

Construction and demolition waste (C&DW) forms a group of many constituents and the composition of the waste streams depend on the building structure and type of demolition process. In general, most of the wastes generated are managed by authorized corresponding operator and some parts are disposed to landfill. The most common valorisation of conventional demolition waste and, particularly the stony fraction derived from concrete, bricks and tiles are traditionally used as filling material in construction sites. However, recycled concrete aggregates are suitable for using in concrete. Some studies have been focused on this issue and indicated that the optimum application of these products depends on the quality of C&DW recycled material. Mixed waste (concrete, brick, gypsum and organic fraction) is generally suitable for use in low quality application while concrete waste is suitable for high quality applications.

A common feature of brownfield sites is the presence of redundant buildings. These structures represent many types of buildings and former industrial facilities. In many brownfield reclamation concepts complete highway layouts, utility service networks and drainage systems are destroyed and replaced by new infrastructure. In the worst case, this may include the disposal of the materials arising from infrastructure removal and the use of primary raw materials to construct replacements.

For this part the focus was on the recovery of stony fraction and use of recycled aggregates in BF regeneration, providing its insertion in the land management cycle and improving the grade of recycling material moving toward a more sustainable and environmentally friendly BF regeneration. We focussed on the possibilities of on-site recycling, promotion of reuse and recycling of these materials, and selection of high quality recycled aggregates for use in structural and non-structural concrete in buildings and infrastructure.

The objective of testing building materials is to contribute in the decision of how to improve the aggregates quality and how to apply the maximum percentage of these materials, optimizing the re-use and recycling of C&DW for BF regeneration. For this, a Construction and Demolition Waste (C&DW) flowchart tool is develop in order to support stakeholders in waste management decisions and to assess and promote reusing and recycling C&DW materials in BF regeneration. This flowchart has been develop as tool in the Brownfield navigator.

2.2.2.2 Methodology

Several tests were performed regarding building material to determine C&DW quality in order to prove the suitability of the technology for the upcoming performances at real scale works. The demolition of an old railway station located in Vigo, Northwest of Spain (figure 24) was selected as site. Samples of the aggregates from C&DW generated were characterized and further research on optimal dosage for structural concrete was developed and tested to compare its resistance, behaviour and characteristics.

Figure 24: Old railway station Vigo (Spain).

The first step of the railway station demolition was the dismantling of roof structures and elimination of asbestos (elimination of hazardous waste by selective demolition). A selective demolition of building structure and platforms was performed. Different organic fractions were managed by a specialized waste operator.

The management of construction and demolition waste in the railway station area is presented below and follows the construction and demolition waste flowchart developed and included in the Brownfield Navigator (developed in HOMBRE, D 3.1 Decision support framework for successful regeneration of Brownfields, Maring et al., 2014). The first step of the railway station demolition was the dismantling of roof structures and elimination of asbestos (elimination of hazardous waste by selective demolition). A selective demolition of building structure and platforms was performed. Different organic fractions were managed by a specialized waste operator.

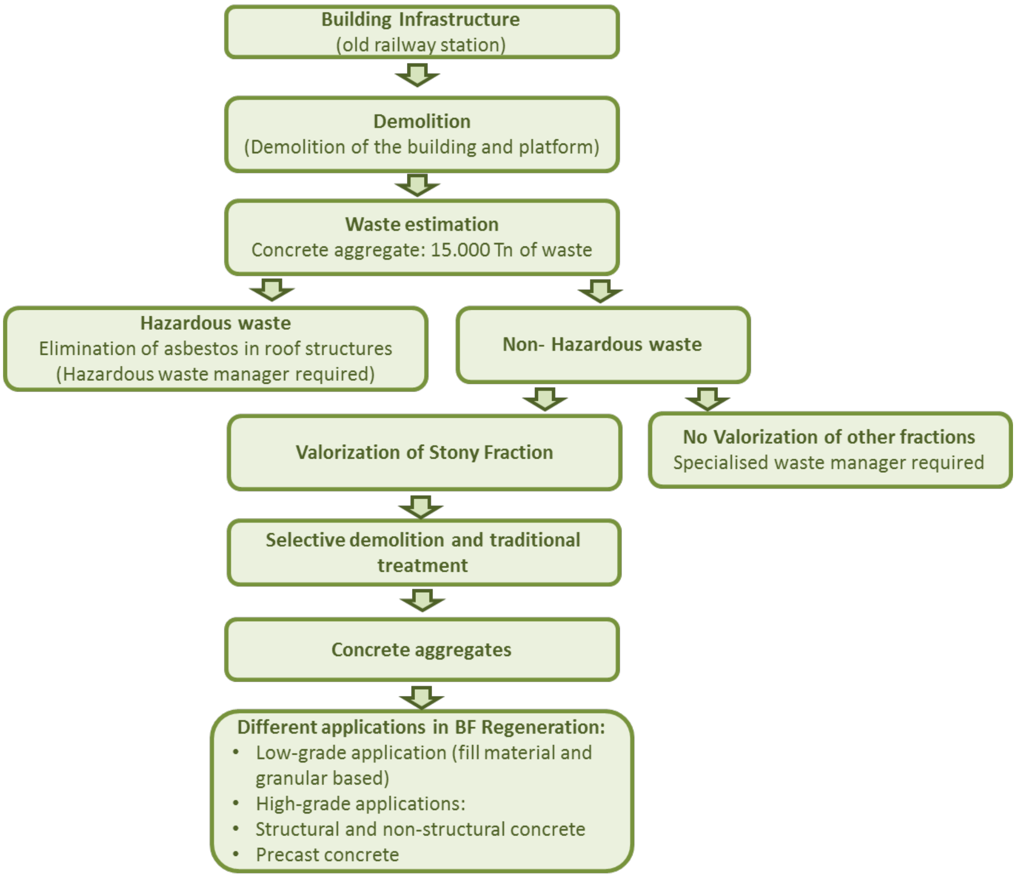


Figure 25: Flowchart of Construction and Demolition Waste management

Regarding the stony fraction, an on-site crushing plant was installed. A first visual characterization of the C&D waste materials (figure 26) showed that most of the aggregates were composed by concrete fractions and it showed low fractions of bricks and other waste materials. In addition, some samples were characterized in the laboratory.

Figure 26: Stony fraction recovered from the demolition works

Table 7 summarizes the tests that were performed in the laboratory in order to characterize the geometrical, chemical, mechanical and physical properties of the aggregates obtained from the stony fraction.

Table 7: Aggregates characterization

GEOMETRICAL PROPERTIES OF AGGREGATES	
EN 933-1	Determination of particle size distribution. Sieving method
EN 933-3	Flakiness Index
MECHANICAL AND PHYSICAL PROPERTIES OF AGGREGATES	
EN 1097-2	Resistance of Fragmentation
EN 1097-3	Determination of loose bulk density and voids
EN 1097-6	Determination of particle density and water absorption
CHEMICAL PROPERTIES OF AGGREGATES	
EN 1744-1	Part 7. Determination of water-soluble chloride salts
	Part 11. Total sulfur content
	Part 12. Determination of acid soluble sulfates
	Part 15. Organic compounds

Determination of particle size distribution

This test determines the proportion of particles of different sizes within a particular aggregate product. To determine the granulometry, aggregates are divided and sieved using different apertures that decrease in size from top to bottom. The used aperture sizes were: 31.5, 22.4, 16, 8, 4, 2, 0.5, 0.25 and 0.063 millimetres.

Assessment of fines

This test determines proportion index of fines aggregates. For this purpose, the sample was introduced in a graduated cylinder with a flocculent solution, which separated the finer fraction of the material.

Flakiness index

This test is used to determine the proportion of slabs, which are those arid rocks characterized by a flattened shape and low thickness. To calculate the Flakiness Index, the arid was sieved with sieves of size 40, 25, 20, 12.5, 10 and 6.3 mm. Subsequently, the arid was sieved again using a bar sieve for weighing the aggregate fraction passing through the sieve of each size range. The arid obtained a low Flakiness Index, reaching the value of about 4% in all fractions.

Resistance to fragmentations

The arid sample is introduced into a rotating drum, together with an abrasive load (in our case 11 steel balls) in the Los Angeles Abrasion Machine. After making it spin for 20 minutes, the percentage of the initial material retained by the sieve of 1.6 mm was calculated.

Determination of loose bulk density and porosity

Density is the weight per unit of volume of aggregates. The porosity is the percentage of total volume of the aggregates occupied by its voids. The test was performed by weighing the dry aggregates, with which a container with cylindrical shape had been filled, to calculate the bulk density. The porosity was calculated from the bulk density and particle and filler density.

Determination of particle density and water absorption

Density is the weight per unit of volume of aggregates. This test is a rapid procedure for determining the percentage of free or surface moisture in both fine and coarse aggregate, and the percentage of water absorption for aggregate of less than saturated surface dry (SSD) condition.

Chemical properties of aggregates

Chemical properties were analysed in order to ensure long-term durability of concrete. Water-soluble chloride salt, total sulphur content, acid soluble sulphate and organic compounds were analysed.

2.2.2.3 Results of characterization

The following picture shows the cumulative particle size distribution curves. Due to its source and characteristics the recycled aggregates obtained did not present the granulometric regularity that is presented in natural aggregates. The size obtained is highly variable and ranges from 2 to 20.

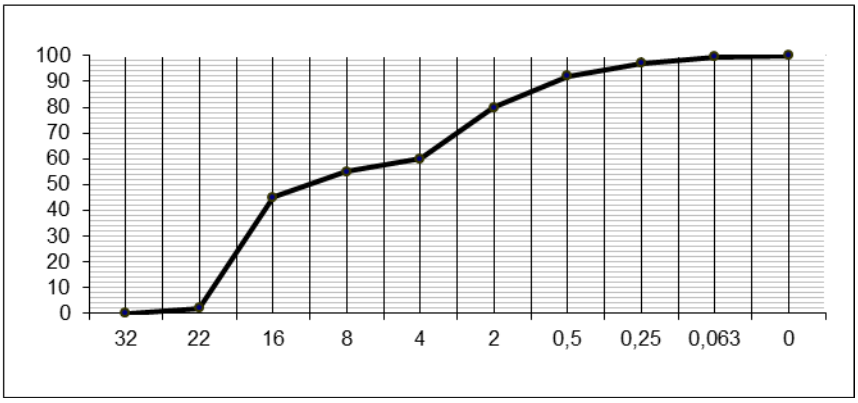


Figure 27: Particle size distribution

The results of properties characterization are presented in table 8. Taking the European legislation related with the use of different type of aggregates into account (table 9), the characteristics of the aggregates that were obtained is within the limits for using this type of aggregate in non-structural concrete. However, water adsorption was above the allowed limit for using this material in structural concrete.

Table 8: Aggregate characterization results

Property test	**Result**
Assessment of fines	4%
Resistance to fragmentation (%)	20%
Determination of loose bulk density (g/cm3)	1.40
% of Voids	46%
Determination of particle density (g/cm3)	2.62
Water adsorption (%)	7.5%
Flakiness index	4.43%
Determination of water-soluble chloride salts	0.006%
Total sulphur content (%)	0.3%
Determination of acid soluble sulphate (%)	0.9%
Organic compound (%)	0%

Table 9: Limit values for application of recycled aggregates in concrete in selected countries

	Ceramic Recycled Aggregate			Mix Recycled Aggregate			Concrete Recylced Aggregate
	Belgium	**UK**	**Germany**	**UK**	**Brazil**	**Germany**	**Spain EHA-08**
Bulk Density (kg/m^3)	> 1600	-	≥ 1800	-	-	≥ 2000	
Water Adsortion (%)	≤ 18%	-	≤ 20%		≤ 12%	≤ 15%	≤ 7%
Resistance of Fragmentation (%)	-	-	-	-	-	-	≤40 %
Chloride content (%)	<0.06%	-	<0.15%		≤1%	<0.04%	≤0.05%
Total sulfur content (%)	≤1%	≤1%	-	≤1%	≤1%	-	≤0.8%

The determination of particle size distribution is one of the most important characteristic regarding the utilization of aggregates in concrete. Not only does it influence the material's mechanical properties but also durability aspects are affected. The internal pore characteristics are very important properties of aggregates. The size, the number, and the continuity of the pores through an aggregate particle may affect the strength of the aggregate, abrasion resistance, surface texture, specific gravity, bonding capabilities, and resistance to freezing and thawing action. Absorption relates to the particle's ability to take in a liquid. Porosity is a ratio of the volume of the pores to the total volume of the particle. If the rock pores are not connected, a rock may have high porosity and low permeability.

To determine the effect of using recycled aggregates in concrete, different dosages of concrete were created by replacing different percentages of the natural aggregates by recycled aggregates (0%, 20% 50% and 100% of aggregates from recycled sources). The different dosages in term of Kg/m^3 are reported in table 10.

Table 10: Dosage of recycled concrete per m^3

	0%	**20%**	**50%**	**100%**
Cement AV CEM II 42,5 N (Kg)	295	295	295	295
Water (Kg)	165	165	165	165
Virgin fine aggregates 0-4(Kg)	855	855	855	855
Virgin coarse aggregates 5-12 (Kg)	766	579	364	0
Virgin coarse aggregates 12-20 (Kg)	218	182	103	0
Recycled aggregates 2-20(Kg)	0	185	460	818
w/c	0.55	0.55	0.55	0.55
Additive (%)	0.68	0.9	1.8	1.9

As there is no recommendation for using a specific type of cement for recycled aggregates, the cement used was AV CEM II 42,5 N with a range between 80 and 94% of clinker and addition of fly ash with limestone origin. The systematic of dosage and manufacturing has been the same than the one for traditional concrete manufacture. Recycled aggregates have been introduced as a raw material.

Figure 28: Laboratory for concrete manufacture

The workability obtained varied from 7.5, 7, 9.8, 10 cm from 0%, 20%, 50% and 100% respectively. This result is directly related with the percentage of applied additives and these dosages taking into account workability obtained can be used for concrete that require both pumping and non-pumping.

The hardness of concrete was evaluated by compressive strength of the mixtures for ages of 7 and 28 days. The results show that the addition of aggregates decreases the final compressive strength at 28 days (figure 29).

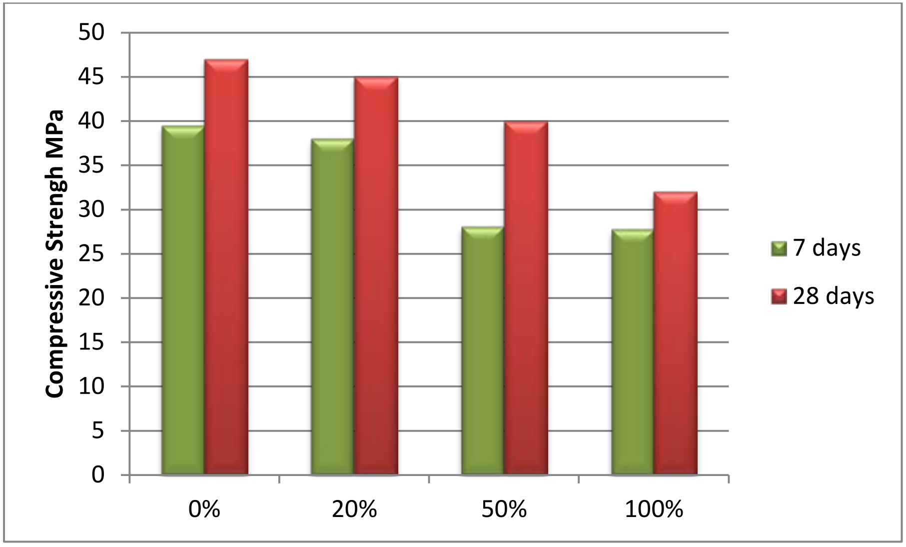


Figure 29: Compressive Strength

The characterization of the aggregates has shown that some parameters are not under the limits values defined in the normative for the use of recycled aggregates in concrete. However, concrete made with recycled aggregates (20%, 50%, and 100% replacement) high fresh workability and can achieve the same compressive strength of concrete made by natural aggregates in the range of 30–45 MPa at 28 days.

2.2.2.4 Critical design factors

The correct management of C&DW allows the reuse of waste materials for hard use in BF regeneration and therefore their integration in the life management cycle. Optimal application of recycled materials in BF regeneration is influenced by several parameters. The most important parameters that define the optimal application and treatment of the C&DW materials are:

- Type of demolition: selective and intensive
- Type of waste treatment: advance or traditional
- Quality of the recycled aggregates
- Quantity of the C&D waste generated will define the different recycling strategies: on-site vs. off-site recycling.

Apart from these parameters that will define the use of C&D waste from the technical point of view, legal, social and economic parameters determine the potential to reuse and recycle C&DW in BF regeneration. It should be noted that recovering recycled concrete aggregates reduces the use of virgin aggregate and its associated environmental costs of exploitation and transportation and reduces unnecessary landfill of valuable materials that can be recovered and redeployed. Recycling C&DW in BF regeneration can achieve several benefits: conservation of natural resources, reduction of energy consumption, preservation of the environment and decrease of waste disposal in management. However, one of the main barriers to on-site recycling the stony fraction of C&D waste for concrete manufacture, is that virgin materials are often easily and locally available and produced at low cost.

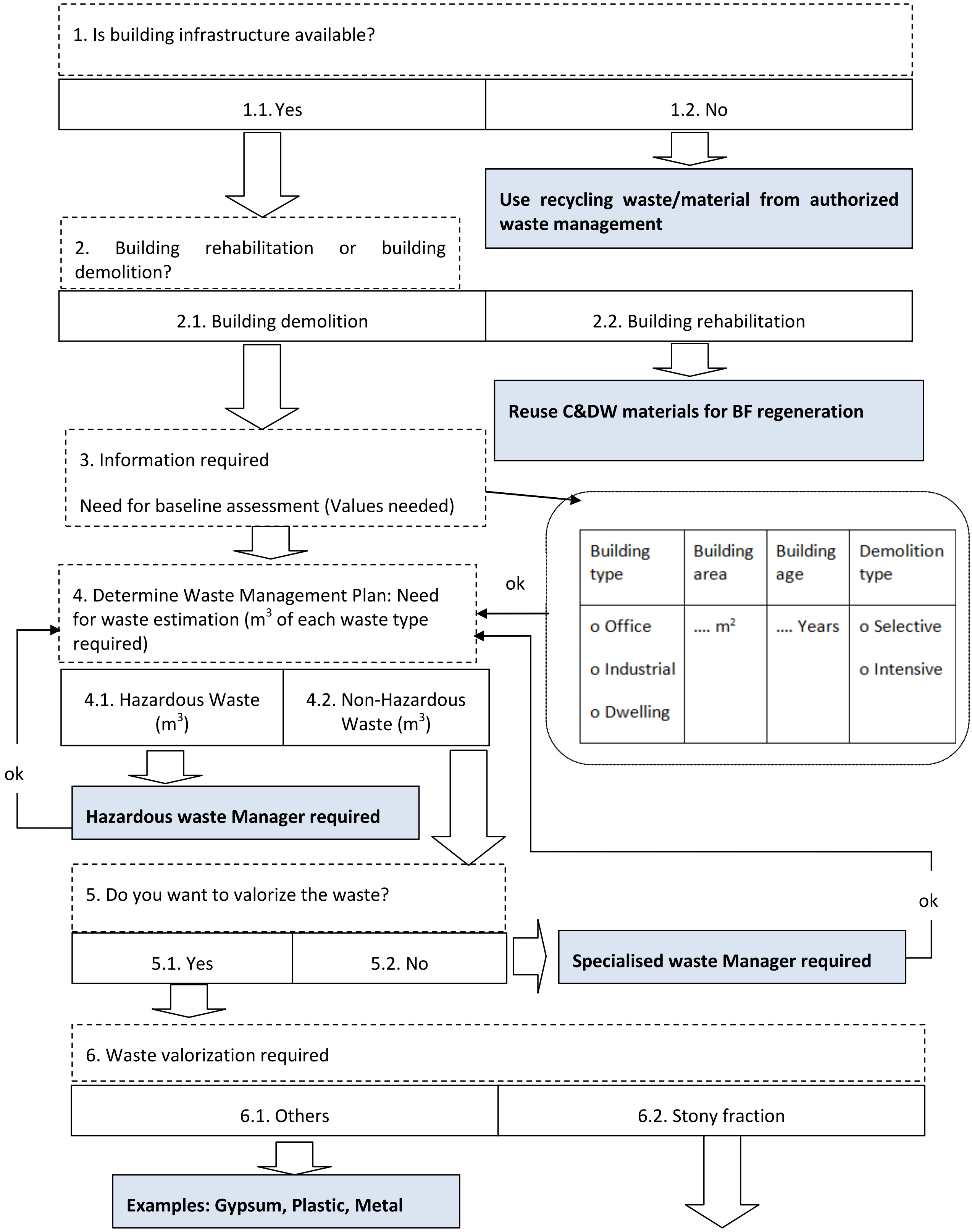
2.2.2.5 C&D waste flowchart tool

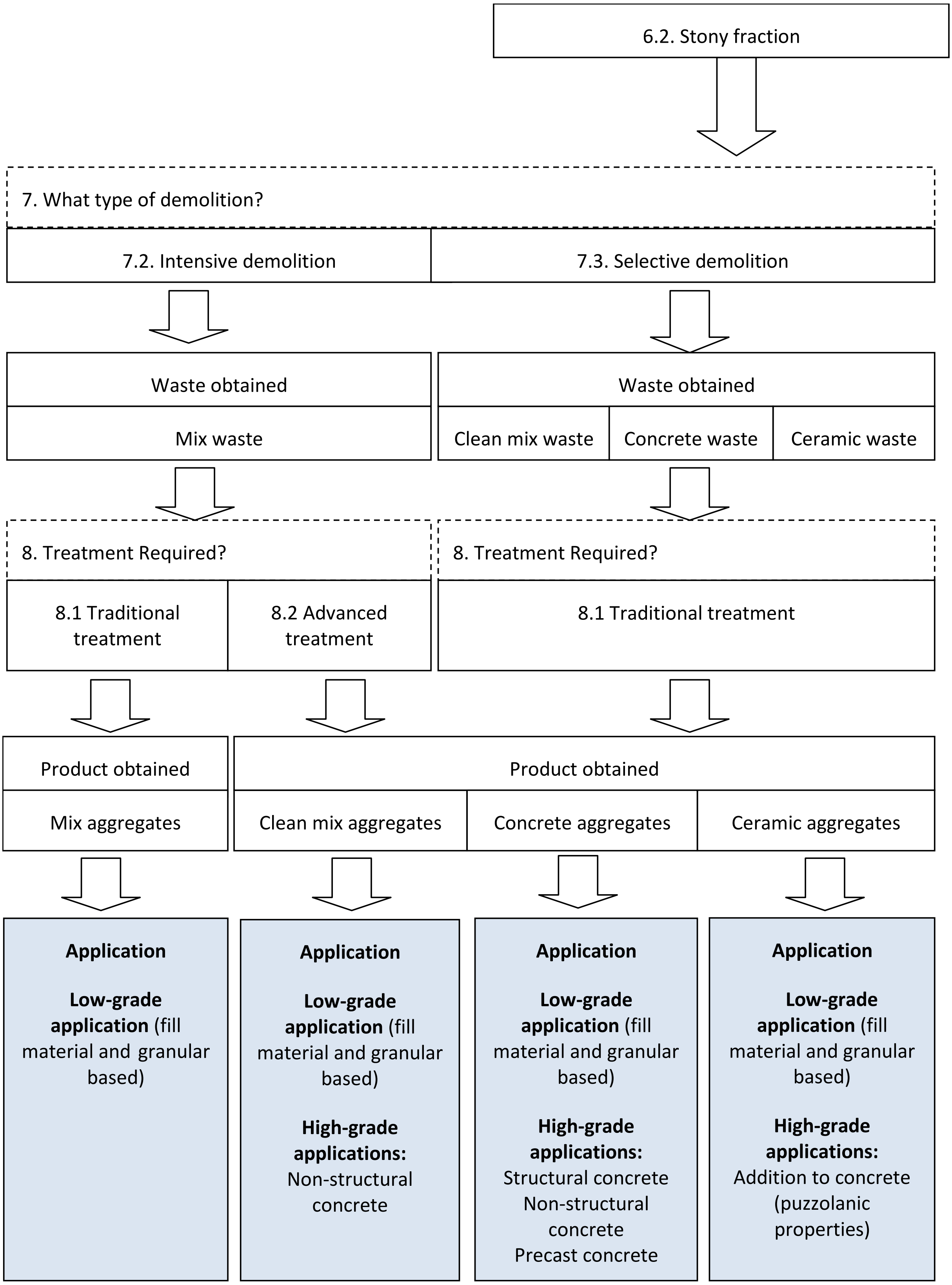
The main objective of C&D waste flowchart tool is to support stakeholders in waste management decisions and to assess and promote reusing and recycling C&DW materials in BF regeneration. This flowchart has been developed as a tool and has been integrated as part of the Brownfield Navigator (The Brownfield Navigator (BFN) RED LINE DOCUMENT).

The C&DW flowchart integrates the critical parameters and structures the assessment that is needed to decide on reusing and recycling C&DW material by addressing the correct application for each waste material generated.The flowchart is presented below in order to understand the different management strategies and to promote reuse and recycling of the different waste generated in brownfield areas taking into account the final scope of the brownfield regeneration project.

The results of the flowchart propose different applications for the different types of stony fraction generated from the demolition of the infrastructures that could be presented in brownfield areas.

Flow-chart Construction and Demolition Waste




6.2. Stony fraction
7. What type of demolition?
7.2. Intensive demolition
7.3. Selective demolition
Waste obtained
Mix waste
Waste obtained
Clean mix waste
Concrete waste
Ceramic waste
8. Treatment Required?
8.1 Traditional treatment
8.2 Advanced treatment
8. Treatment Required?
8.1 Traditional treatment
Product obtained
Mix aggregates
Product obtained
Clean mix aggregates
Concrete aggregates
Ceramic aggregates
Application
Low-grade application (fill material and granular based)
Application
Low-grade application (fill material and granular based)
High-grade applications: Non-structural concrete
Application
Low-grade application (fill material and granular based)
High-grade applications: Structural concrete
Non-structural concrete
Precast concrete
Application
Low-grade application (fill material and granular based)
High-grade applications: Addition to concrete (puzzolanic properties)

2.3 TT3: Ecogrout

TT3 on soil and water combines the issue of contaminated groundwater as an obstacle for BF redevelopment is the case in TT3 with the possibility to adapt the soil strength and stiffness. In those BF where soil stability is an issue, a soil stabilization method that would have positive effects on groundwater quality would be a considerable asset. The need for remediation and soil improvement are –when considered separately- often processes that lead to considerable (and often prohibitive) cost investments.

The Ecogrout process involves the reaction between calcium chloride and dissolved sodium carbonate according to Eq.1.

$$CaCl_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2NaCl + CO_2 \qquad \text{Eq. 1}$$

The reaction produces calcium carbonate and carbon dioxide in an equimolar ratio. The precipitation of calcite may cause an in-situ increase in stiffness and strength of the soil and a decrease in permeability while the produced CO_2 may potentially allow the in-situ stripping of volatile organic contaminants (VOCs) from groundwater.

The ecogrout process was explored as a technology train: the process is based on the principle of calcium carbonate (calcite, or vaterite) precipitation in the soil which leads to an increase of strength and stiffness. Carbon dioxide (CO_2), which is released as a side product of the calcium carbonate production reaction, evolves as a gas and serves as the agent for the stripping of contaminants in the groundwater.

2.3.1 Identified knowledgegaps for the ecogrout process

Classical grouting methods (e.g. jet grouting) use high pressures to pump highly viscous fluids into the ground. The resulting structure is a hardened grout mixture with a diameter of 0.1-1 meter. The systems used require cement or water glass (with a hardener) as their main components. The advantages of classical systems are their reproducibility and the high level of knowledge available by contractors to apply the system. The small diameter of the product, and the requirement to use high amounts of material are disadvantages, in combination with its large carbon footprint.

In the past 10 years, several systems have been developed aimed at overcoming these disadvantages. So called „microbial induced calcium precipitation" (or: biogrout) processes are aimed at strengthening soil over a much larger distance and with lower pressures by injecting liquids with a viscosity which is similar to water. The solutions react in the soil to form calcium carbonate, a process which is catalized by microorganisms. Most knowledge is available on a biogrout process using urea and calcium chloride, catalyzed by urease. An overview of the development of that process is shown in figure 30.

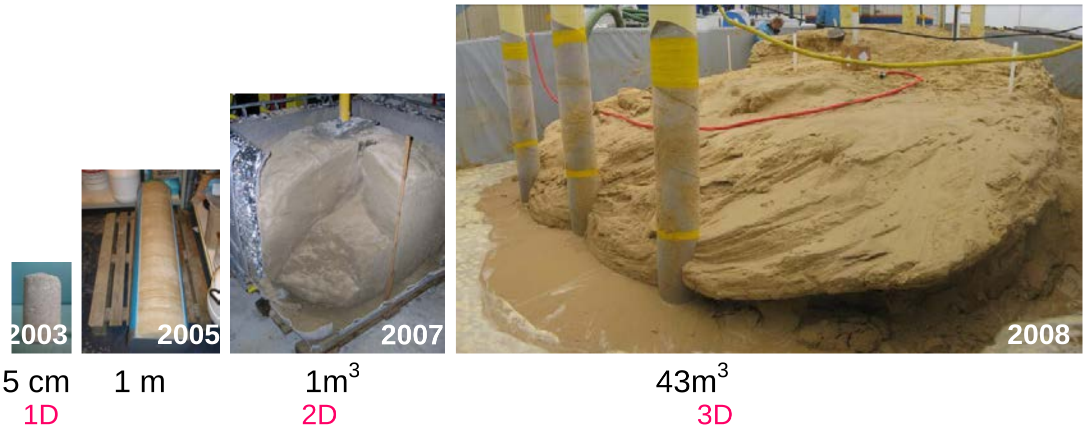


Figure 30: scale up of the urea-based microbial induced precipitation process.

Although technically the application of the process has developed from 1 D lab scale to 3D (pilot) scale, the use of microorganisms (that have to be cultured separately) forms a disadvantage. The system would furthermore solely have a positive impact on on soil strength and not on water quality.

The knowledge gained with this process formed the basis for the development of a new process that fits in the soil water technology train. Requirements for such a process are

- Injection pressures should be low (easy application);
- Gas should be produced that could optimally strip contaminants;
- No requriement for addition of microorganisms;
- Application possible over >1 m.

Based on these requirements, the Ecogrout process was selected: a process in which calcium chloride and sodium (bi)carbonate are injected in the soil to produce calcium carbonate and CO$_2$. The CO$_2$ can subsequently be used for removal of contaminants from the soil. The following knowledge gaps were defined, reformulated as research questions:

- Does the produced calcium carbonate strengthen soil?
    - The proposal of a completely new process for soil strengthening calls for a proof of principle test: is soil improvement possible with the proposed materials? In answering this question, the we focussed on „showing that it works" and identifying which parameters would be of critical importance
- Can the produced CO$_2$ be used to remove contaminants?
    - In combining the produced CO$_2$ with two typical contaminants in BFs (trichloroethylene and toluene)
- Does the applicability vary with depth of application?
    - The application range is not only governed by the distance between injection points, but also by the range of depths at which the process was applied. Pressure (as a result of depth) has a strong effect on the CO$_2$-CaCO$_3$-HCO$_3^-$ equilibrium and its effectswere evaluated through matematical modeling.
- Is injection possible at sufficiently high rates?
    - The answer regarding distance was answered by a scale up approach in which application distances were increased in each step. Special attention was given to the effect of gas formation on injection flows.

These 4 knowledge gaps are addressed separately in paragraphs 2.3.2 - 2.3.5.

2.3.2 Does the produced calcium carbonate strengthen soil?

Tests were performed in PVC columns of short (18cm) and long (1m) length under the three types of conditions described below.

2.3.2.1 Methods

PVC columns (internal diameter 6.6 cm, height 18.0 cm) were packed with gravel (figure 31; d_av=2 mm) under water: water was first added to the column, after which gravel was added in batches of circa 10 grams, immediately followed by manual compaction. The PVC columns were fitted at the bottom with connections for the entrance of two fluids, which met directly under the centre of the column. Fluids were passed through the column from bottom to top with a peristaltic pump (Master Flex). pH and electric conductivity (EC) were measured continuously in the outflow which and logged every 30 seconds (multi parameter analyser C864; Consort). In addition, selected samples were taken from effluent periodically to measure calcium ion concentrations. After the test, the column was stored into a drying oven at 55 °C for one day. Then material treated with cementation was removed from the column. All tests were performed at the temperature of 20 ±2 °C. Table 11 shows the test cases.

Figure 31: Gravel used in the tests

Table 11: Short column test case and initial conditions

Column	Fluids	pH	EC (mS/cm)	Flow rate (L/h)	Dry density (g/cm^3)	Porosity (%)
T	375 mM $CaCl_2$ 750 mM $NaHCO_3$	11 7.9	64.4 42.5	0.6 0.6	1.58	41
U	112.5 mM $CaCl_2$ 225 mM $NaHCO_3$	10.8 8.1	24.1 16.1	0.6 0.6	1.65	38
V	375 mM $CaCl_2$ + 125 mM HCl 750 mM $NaHCO_3$	0.3 8.1	98.6 44.8	0.6 0.6	1.02	61
W	375 mM $CaCl_2$ + 125 mM HCl 750 mM $NaHCO_3$	0.9 8.1	97.8 40.9	2.4 2.4	1.59	40
X	375 mM Ca-acetate + 125 mM HCl 750 mM $NaHCO_3$	5.2 7.5	34.2 42.3	0.6 0.6	1.61	39
Y	188 mM $CaCl_2$ + 188 mM Ca-acetate + 125 mM HCl 750 mM $NaHCO_3$	4.6 7.9	49.6 41.0	0.6 0.6	1.61	39
Z	375 mM $CaCl_2$ 750 mM $NaHCO_3$	3.8 8.0	61.2 43.1	0.6 0.6	1.55	41
AA	375 mM $CaCl_2$ + 125 mM HCl + 4.9M NaCl 750 mM $NaHCO_3$	0.2 8.0	-	0.6 0.6	1.56	41

(- Out of the range of the data logger)

During the tests different ratios of calcium and bicarbonate were tested, as well as the effect of using different calcium salts (calcium acetate and calcium chloride). Furthermore, the effect of the addition of NaCl was tested. A detailed overview of test conditions (and characteristics of the used fluids) can be found in Table 11.

1m column test

For selected columns, the system was scaled up to 1 meter (without further changing conditions) to evaluate if also cementation at higher strengths was achievable. The columns (internal diameter 6.6cm, height 100cm) were tested by same way with short column test. Table 12 shows the test case and initial conditions.

Table 12: 1m column test case and initial conditions

Column	Fluids	pH	EC (mS/cm)	Flow rate (L/h)	Dry density (g/cm^3)	Poro-sity (%)
L1	375 mM $CaCl_2$ + 125 mM HCl 750 mM $NaHCO_3$	0.8 7.8	103.2 42.8	0.6 0.6	1.58	40
L2	375 mM $CaCl_2$ + 125 mM HCl 750 mM $NaHCO_3$	1.0 8.1	96.4 47.2	2.4 2.4	1.53	42

2.3.2.2 Results

General behaviour

The general behaviour of the columns is illustrated in figure 32. After start of the injection, the production of CO_2 can be immediately seen as formation of gas bubbles, which are partly retained in the column and partly removed from the column through the top. After circa 20 minutes calcium carbonate precipitation can be seen on the gravel. The outflow has a milky character due to the suspended $CaCO_3$ carried out of the column.

Figure 32: Gravel packed column IV (beginning, 30min, 60min, 100min, 240min later and end)

After 5-20 hours, the column was fully clogged and pumping in of liquids was impossible. pH in the columns was always between 5.8 and 7 and stabilized in the first hour after starting the injection. The conductivity-signal decreased strongly, but this could always be fully attributed to sensor drift (probably as a result of precipitation on the sensor). The cemented column was always more cemented on the bottom (near the injection) than on the top, although the length of the cemented part varied considerably (figure 35).

Figure 33: Gravel treated with cementation (column W)

Results at different conditions

An overview of results at the used conditions can be found in table 13. Significant length was achieved at columns V, W, Y, Z and AA. All those columns had in common, that the pH of the influent was strongly lowered and that at least 50% of the calcium was provided in the form of calcium acetate. When the flow rate was increased from 0.6 to 2.4 L/min (corresponding to 0.9 and 3.4 m/h respectively) the full length of the column was cemented.

Table 13: The results of short column test

Column	Duration until clogging occurred	Cemented length
T	5.5	0
U	17	0
V	7	7
W	6	16
X	14	0
Y	20	5.5
Z	17	7
AA	12	7

Results 1m column test

Under the most promising conditions (column W) a 1 meter column cementation test was performed. Visual cementation was visible in circa 30 cm (figure 34), while calcium carbonate measurements indicated precipitation along circa 50 cm (figure 35).

The length of 30 cm out of 100 cm was cemented and visually showed considerable strength.

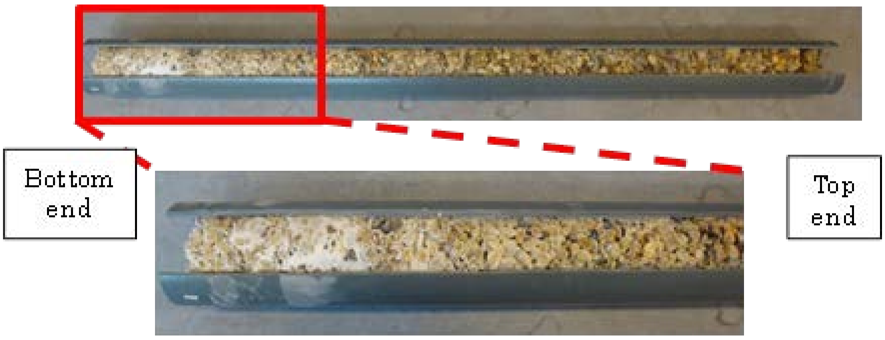


Figure 34: Cemented sample after removed from column

Calcium carbonate concentration over the length of the column was also performed, both by measurement of the increased density and by calcium carbonate concentration determination via acidification (figure 35). Significant calcite content is observed until at least 50 centimetres.

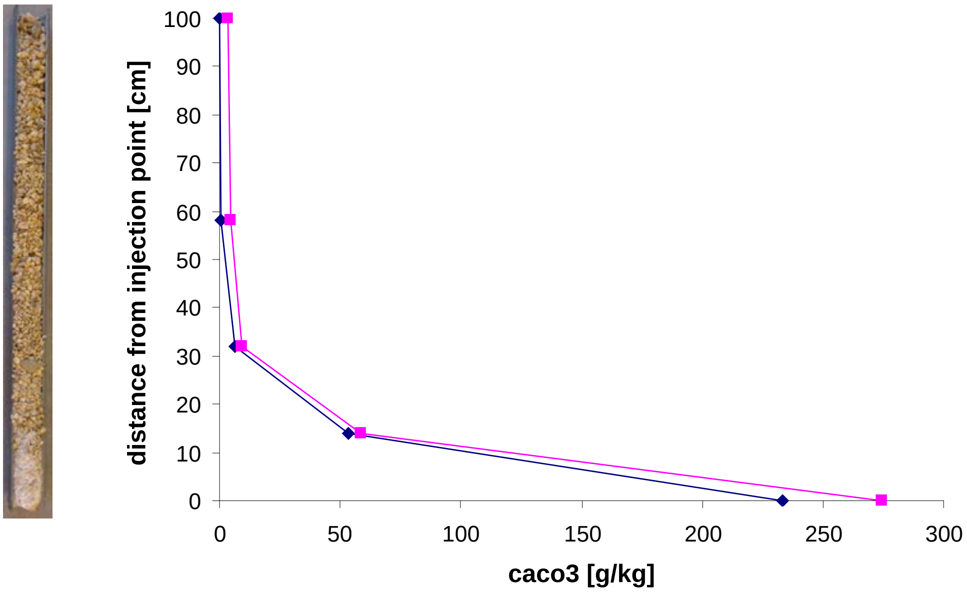


Figure 35: Calcium carbonate content (from weight measurement (■), from carbon dioxide measurement (♦))

2.3.2.3 Discussion

The research showed calcium carbonate precipitation by Ecogrout can strengthen soil. The calcium carbonate precipitation induced by combining of calcium ions with sodium bicarbonate results in strength; as long as the counter ion for calcium is not acetate. The experimental work immediately points to an important practical and experimental concern: the reaction rate is high and in combinatin with gas formation leads to clogging. For this reason in this setup, only satisfactory results could be obtained with gravel; which –because of its high permeability- allows the CO2 to be removed more easily.

2.3.3 Can the produced CO_2 be used to remove contaminants?

Based on literature review it was expected that the escape of CO_2, generated in the ecogrout process, will increase the volatilization of the contaminants. The relationship between stripping with CO_2 and different process conditions is evaluated in two experiments:

1. Pressure experiments were performed in order to evaluate if the stripping of toluene and TCE followed Henry's law, e.i. whether it was proportional to gas pressure
2. Evaluation of stripping potential of toluene and TCE in CO_2.

2.3.3.1 Effect of Pressure

Figure 36 shows the effect of pressure partitioning of TCE (top) and toluene (bottom). The concentration in the gas phase is linear for both chemicals, and thus a Henry's law can be used.

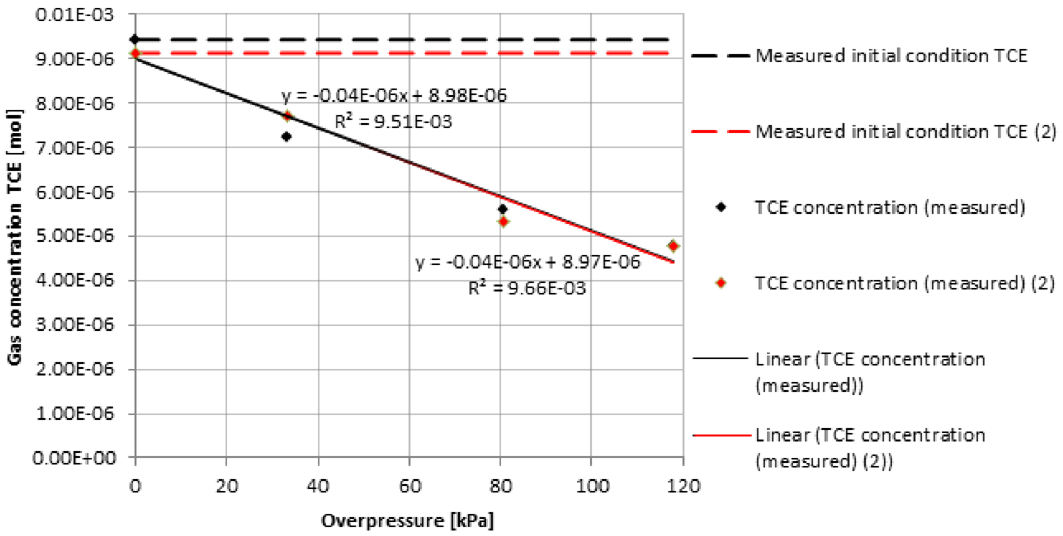


Figure 36: Pressure influence on phase transition, TCE, 20.6°C.

2.3.3.2 Stripping potential TCE and toluene with CO_2

The uptake of toluene and TCE in air and CO_2 respectively is shown in figure 37. Both the uptake rate and the total uptake seems to be not significantly different between air and CO_2. As is known from literature, the equilibrium gas concentration is roughly 2 times higher for TCE than for toluene.

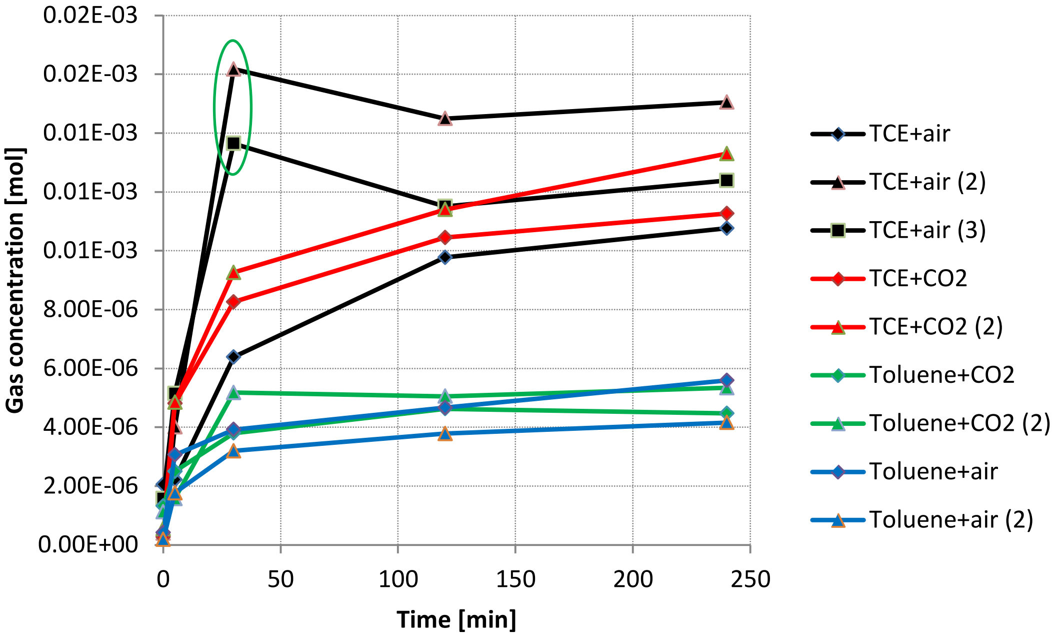


Figure 37: Uptake volatile organic contaminants by air and CO2, different temperatures.

2.3.3.3 Conclusion

It is concluded the Ecogrout process can be used to remediate volatile organic contaminated groundwater at brownfields. Both TCE and toluene have potential for stripping with CO_2 from the Ecogrout reaction. The parameter stripping velocity is increasing with increasing CO_2 production. The increase of stripping velocity compared with the volatilization rate was higher for more volatile compounds but may have been influenced by a pure phase layer for toluene.

.

2.3.4 Does the applicability vary with depth of application?

As depth is a parameter which is hard to evaluate experimentally, a mathematical model was created capable of predicting the gas formation at higher pressure and under different operating conditions. This modelling study explores the conditions under which precipitation amounts and rates can be controlled and prevent clogging in the vicinity of the injection point, whilst ensuring sufficient radii of influence for the Ecogrout treatment. To analyze this EcoGrout process, a model for multiphase flow of multiple gas-components and water (STOMP-WNE) with a reactive batch chemistry module (ECKEchem) is used. This model is extended to account for porosity and permeability alteration over time during calcite precipitation. Also a kinetic equation for degassing of CO_2 proposed by Zhao et al. (2011) is implemented. Simulation of an injection pulse with an EcoGrout solution at calcite equilibrium at a pCO_2 of 5.1 bar was done to investigate the behavior of CO_2 degassing in the porous medium and its effect on calcite precipitation. Several cases with different mechanical properties, kinetic properties or EcoGrout solution configurations are presented to investigate its sensitivity on CO_2 degassing and calcite precipitation.

2.3.4.1 Results

The model was built to obtain insight into different aspects of the EcoGrout process and its influence on the properties of the unconsolidated soil. In this study an Ecogrout solution is injected into the porous medium for 5 seconds at an injection pressure of 10 atm. The used EcoGrout solution is initially in equilibrium with calcite at a high pCO_2 value (figure 38). The calcite concentrations during the simulation are shown in figure 39.

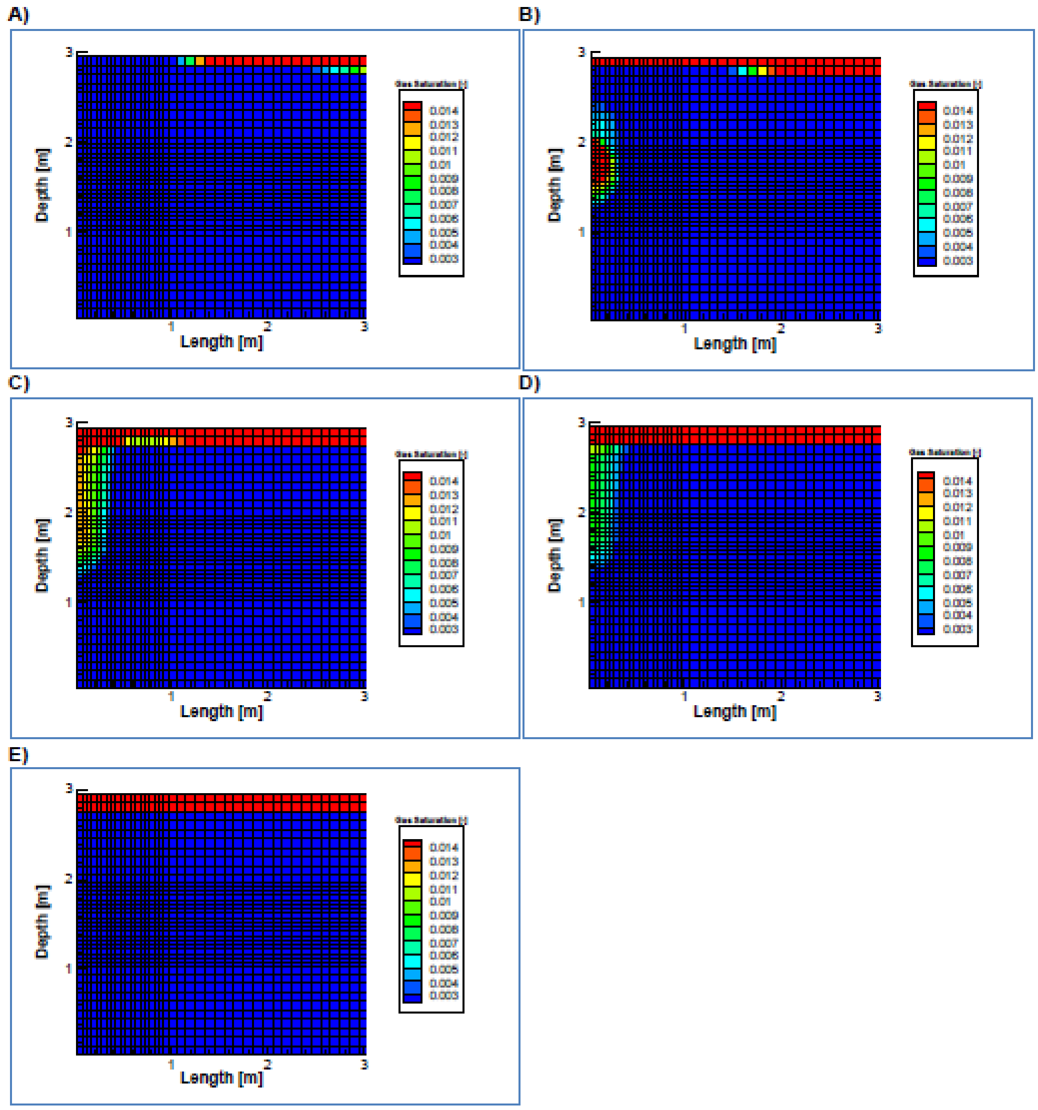


Figure 38: (CO2) Gas saturations at respectively: A) 5 s, B) 3 min, C) 20 min, D) 50 min and E) 600 min.

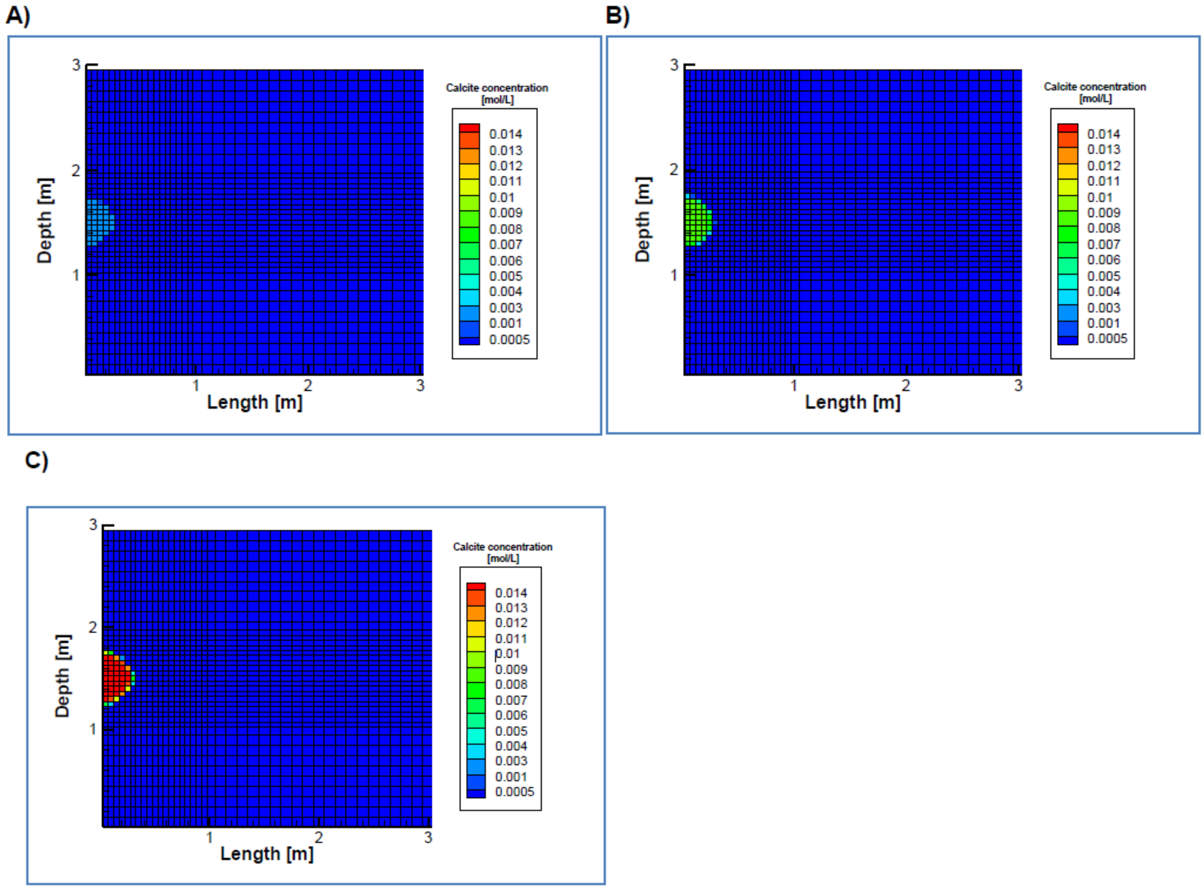


Figure 39: Calcite concentrations [mol/L] at respectively: A) 20 min, B) 50 min and C) 600 min.

Due to high injection pressures, no degassing occurs during injection. When the injection pulse stops the kinetic degassing of CO_2 starts. The model results show that during the kinetic degassing of CO_2 the pH and thereby the carbonate concentration increase. Consequently, the solution becomes supersaturated with respect to calcite and fast calcite precipitation kinetics occurs. Calcite precipitation from a solution in equilibrium with calcite at a pCO2 of 5.15 without and with taken into account the salinity (Case 1 and Case 2 respectively) and from a solution slightly undersaturated with calcite at a pCO_2 of 11 atm (Case 6) were modelled. This resulted in low calcite precipitation concentrations of respectively 1.49e-2, 2.05e-2 and 2.17e-2 mol/L for an injection pulse in porous medium with at an initial porosity of 0.4. These results imply that multiple injection pulses are required to attain the desired cementation of the soil in the field.

2.3.4.2 Conclusion

Injections at higher pressure (and thus at higher depth) are possible as long as the injection pressure is sufficiently high not to allow too much gas formation (and resulting well clogging). Only after the pressure is removed precipitation can take place. It will be critical –when performing at higher pressures- that the influence zone (the zone at which elevated pressure is created) is sufficiently large to allow a „delay" of the CO_2 formation.

2.3.5 Is injection possible at sufficiently high rates?

To evaluate whether sufficiently high rates can be achieved over a sufficiently high distance, a three dimensional experiment was developed using separate injection and extraction lances.

2.3.5.1 Methods

A polycarbonate reactor was built to perform the experiments (figure 40). The reactor had an internal diameter of 0.94 m, height of 0.46 m and an empty volume was thus 322 L. The injection and extraction wells were 40 cm stainless steel rods, in which 42 holes (D_{int}= 5 mm) at a distance of 5 mm from each other formed the well screen. Experiments lasted for 8 hours. At the bottom of the reactor there were two drainage valves: one in the center and another one more external (figure 41).

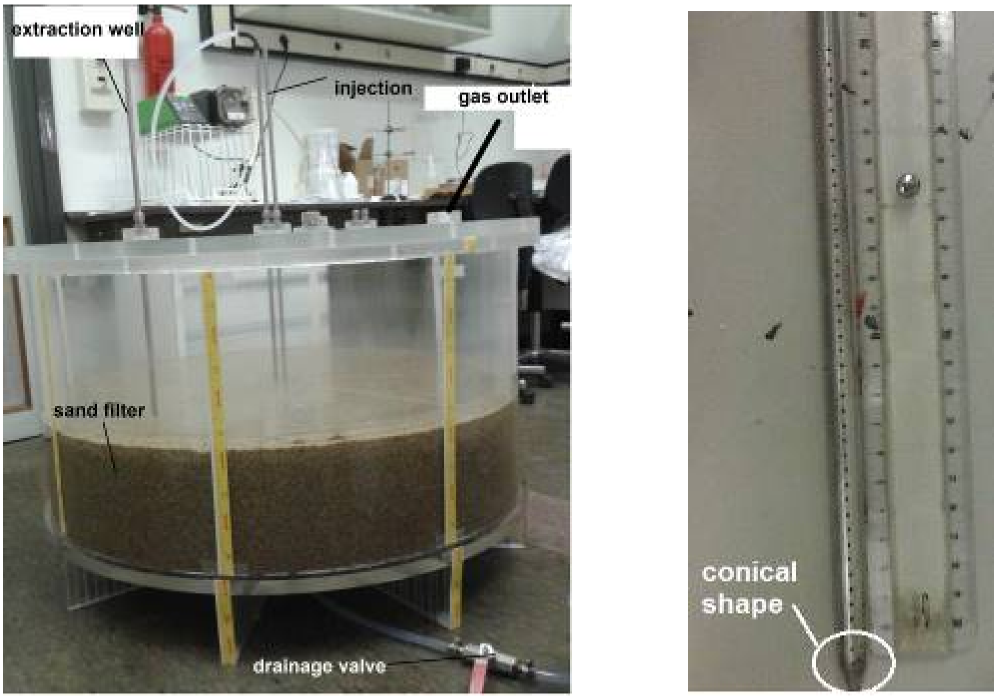


Figure 40: Reactor in which the experiments were performed (left), using 2 injection and 1 extraction points (right).

Experiments were performed using separate injection lances for calcium carbonate and for sodium bicarbonate.

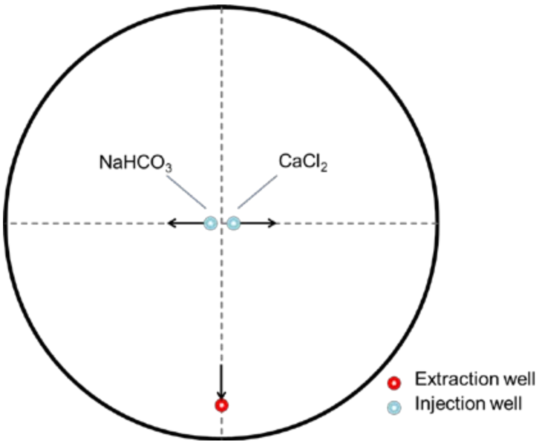


Figure 41: Top view of the reactor showing the injection and extraction wells, as well as the orientation of the holes in the well.

Experiments were performed using fine sand and coarse sand with concentrations of 0.375 mole/L $CaCl_2$ and 0.750 mole/L $NaHCO_3$ respectively.

2.3.5.2 Results

The experiments could be performed for 8 hours. Although injection flow rates reduced during the experiment due to the limited increase in pump pressure that the peristaltic pumps could handle, flow rates never decreased to more than 50% of their original rate. Immediately after the start of the experiment gas bubbles could be identified at different locations during the experiment. Gas bubbles mainly appeared in quadratns III and IV, the part of the reactor where sodium bicarbonate was injected (figure 42).

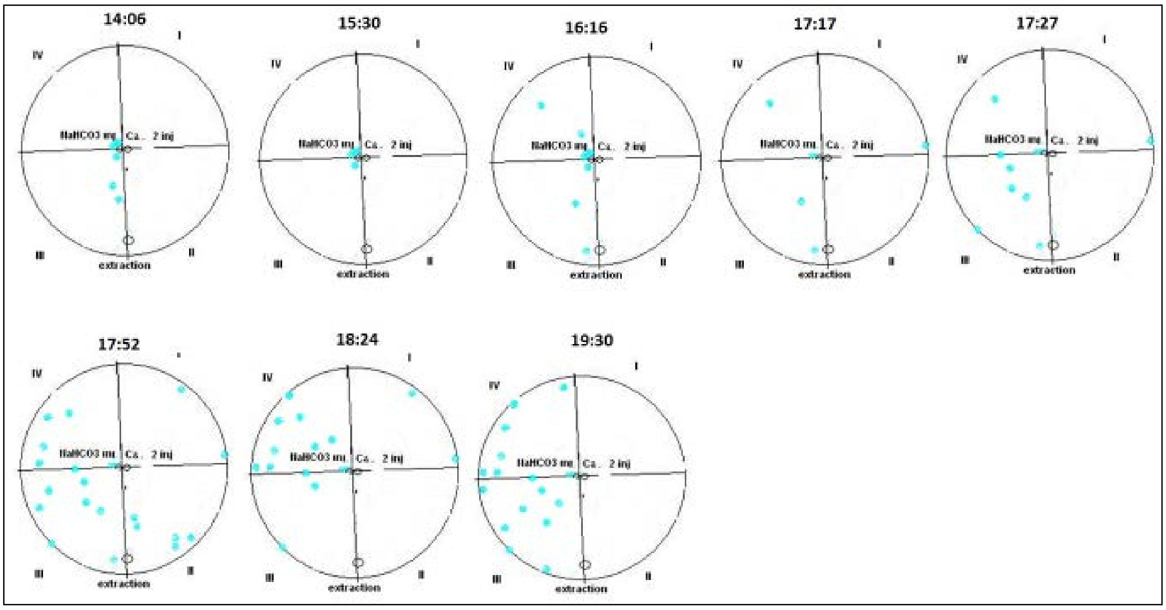


Figure 42: Locations where gas left the top of the gravel.

Regular injection of colorant resulted in the appearance of coloured liquid on top of the sand package, which shape varied in time (figure 43). While initially the colour (and thus the direction of the flow) was directed towards the extraction point, already after 10 minutes different (and strongly varying) flow parts were followed, which seem to indicate that two different (groups) of flow paths can be distinguished: 1 away from the injection point, and one in the direction of the injection point, but not following a straight line.

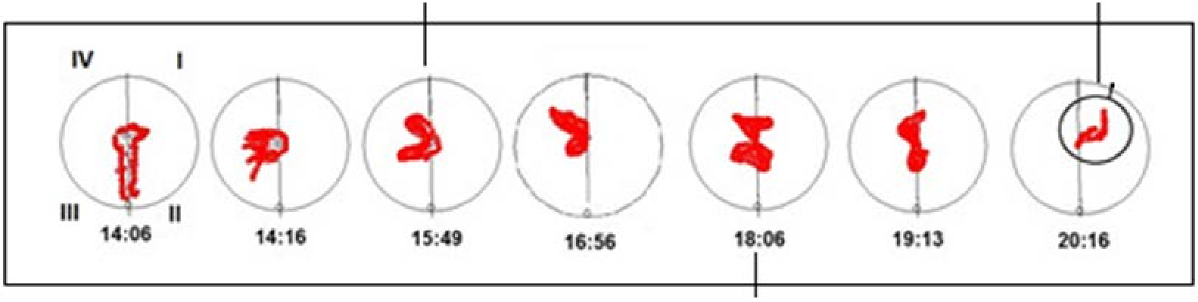


Figure 43: Locations where gas left the top of the sand/gravel.

During experiments with sand, injection fluids immediately moved up and disturbed the sand package, probably due to the lower permeability of the sand. After the experiment, calcite contents were determined at several locations. Results are shown in figure 44. The concentration of calcite was not homogeneous and much lower than expected based on the amount of calcium chloride added, suggesting much of the calcium must have remained unreacted.

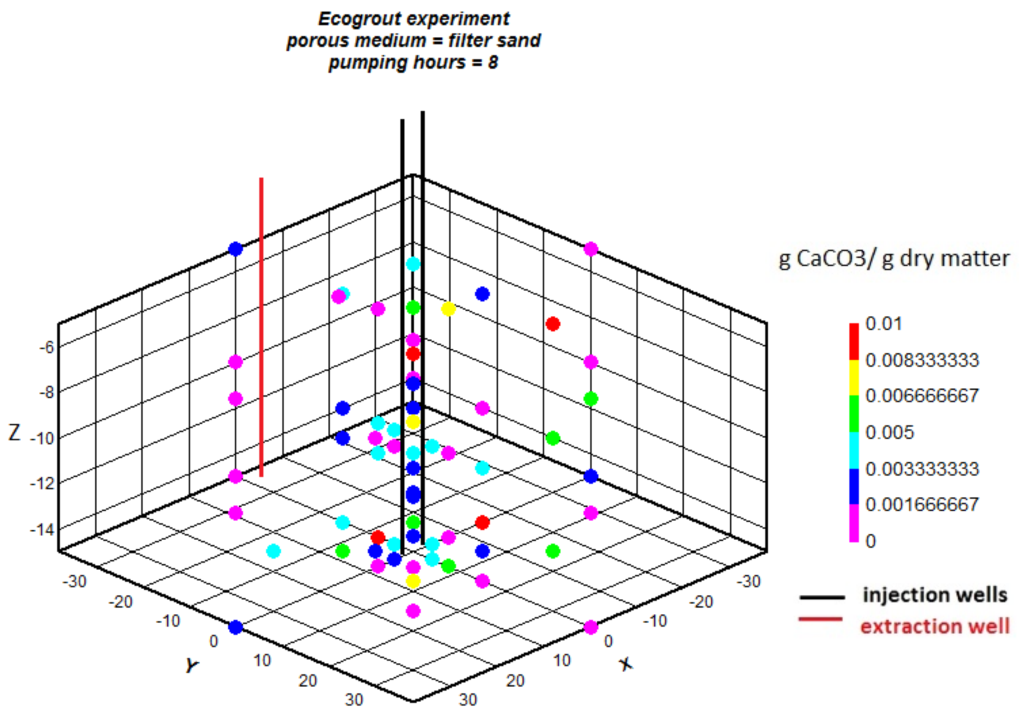


Figure 44: CaCO3 content at different locations

2.3.5.3 Discussion

Surprisingly perhaps, in the coarse sand experiment, clogging was much less an immediate concern than it was during the batch experiments. This probably has to do with the distance between injection points of sodium bicarbonate and calcium chloride, which allowed the two chemicals to stay separate for a sufficiently long period. The downside of this longer „window of operation” with regards to clogging, is that calcite precipitation is low; and no visible strength increase could be observed. A change in the orientation of the injection wells (towards eachother) would probably give rise to easier contact between the liquids and thus a higher reaction rate. Such a higher reaction rate will however likely come with an increase in clogging. The experiments in sand (where even at the flow rates used, permeability was too low immediately after start of the experiment) show indeed, that the risk too low permeability, and whence the loss of material to the top of the sand is a real one.

The low calcium carbonate content and its inhomogeneous distribution render the ecogrout system unsuitable to strenght increase used to increase bearing capacity (e.g. for foundations). However, in those locations where inhomogeneous and small strength increase is already useful (for example in liquefaction prone areas) the system may have potential. Additional experiments equiped to measure such small increases in strength (and more importantly: stiffeness) are necessary to evalute the potential of the Ecogrout system for those applications.

2.3.6 Conclusions

The Ecogrout-research was aimed at answering critical questions regarding the applicability of the process in BF. The research showed that the produced calcium carbonate could strengthen soil, as long as the counter ion for calcium is not acetate. The experimental work immediately points to an important practical and experimental concern: the reaction rate is high and in combinatin with gas formation leads to clogging. For this reason in this setup, only satisfactory results could be obtained with gravel; which –because of its high permeability- allows the CO_2 to be removed more easily.

Injections at higher pressure (and thus at higher depth) are possible as long as the injection pressure is sufficiently high to prevent excessive gas formation (and resulting well clogging). Only after the pressure is removed precipitation can take place. It will be critical –when performing at higher pressures- that the influence zone (the zone at which elevated pressure is created) is sufficiently large to allow a „delay" of the CO_2 formation.

The Ecogrout process can be used to remediate volatile organic contaminated groundwater at brownfields. Both TCE and toluene have potential for stripping with CO_2 from the Ecogrout reaction. The parameter stripping velocity is increasing with increasing CO_2 production. The increase of stripping velocity compared with the volatilization rate was higher for more volatile compounds but may have been influenced by a pure phase layer for toluene.

2.4 Combined Technology Train (TT2 + TT3): In situ carbonation of alkaline material by the combined Ecogrout-carbonation process

This combination of technology trains (thereby forming a new train) relies on the coupling of increased carbonation with the Ecogrout process. The precipitation of calcite may cause an in-situ increase in stiffness and strength of the soil and a decrease in permeability while the produced CO_2 may potentially allow the in-situ stripping of volatile organic contaminants (VOCs) from groundwater. In addition, the upward CO_2 flow produced by the Ecogrout process may stimulate the carbonation of an overlying layer of alkaline material, eventually present in the site as a result of past inappropriate disposal, resulting in the improvement of its environmental properties as well as in CO_2 storage. As an example, the carbonation reaction of calcium silicate is reported in Eq. 2.

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \qquad \text{Eq. 2}$$

Hence, the application of a combined Ecogrout – carbonation process at a Brownfield site may represent an opportunity for treating different matrices present in the Brownfield while achieving several benefits. The Ecogrout process was in this project tested focusing on the improvement of the structural properties of gravel by means of calcite precipitation and on CO_2 stripping potential for different types of VOCs.

A schematic overview of the combined Ecogrout-carbonation process is depicted in figure 45.

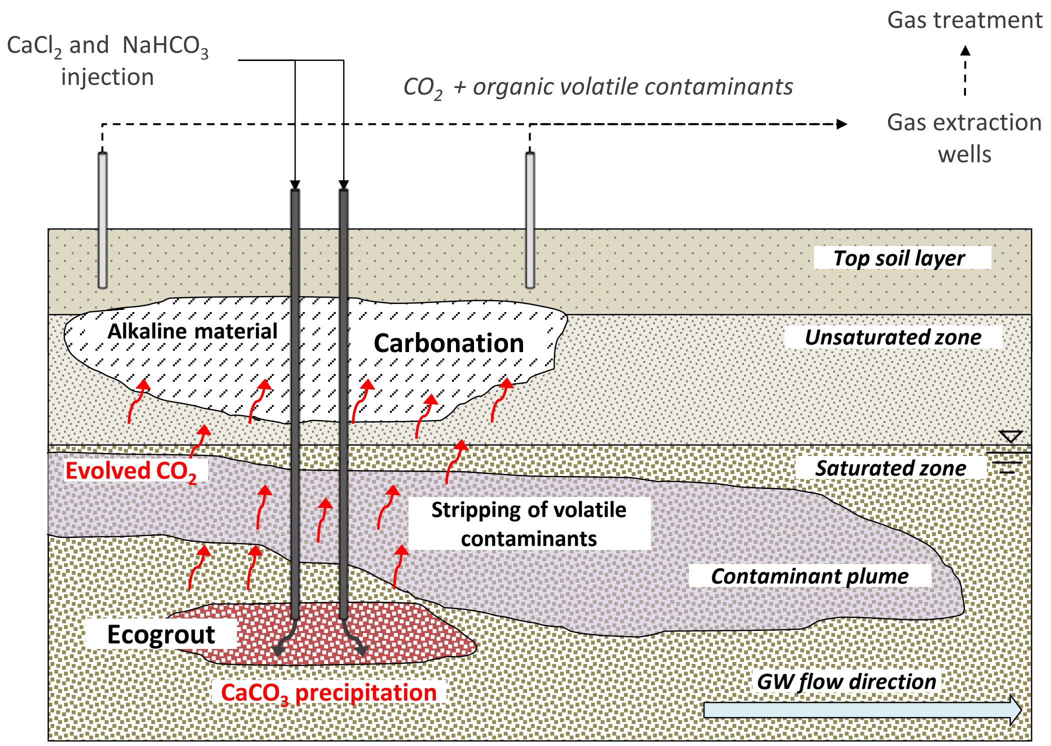


Figure 45. Schematic overview of the combined Ecogrout-carbonation process (adapted from Capobianco et al., 2014b)

2.4.1 Identified knowledge gaps

The effects of a combined Ecogrout-carbonation process on the properties of alkaline residues had not been evaluated yet. The assessment of the combined Ecogrout-carbonation process at lab scale was a first step towards the assessment of the applicability of the combined process in a BF regeneration context and was mainly aimed at evaluating the effects exerted on the achieved CO_2 uptakes of a selected alkaline material as a function of the conditions induced by the Ecogrout process.

2.4.2 Methodology

In order to evaluate the potential of the coupled process, a 3-stage sequential experimental investigation was carried out.

In stage 1, preliminary batch Ecogrout tests and column carbonation tests were performed at laboratory scale. The Ecogrout tests were carried out by employing the set-up shown in Figure 46a to estimate the CO_2 flow evolved during the reaction as a function of the injection regime and stirring conditions. In each test, the $NaHCO_3$ solution was manually poured into the reactor whereas the $CaCl_2$ solution was injected with a peristaltic pump set at 10 ml/min, after tight closing of the vessel. During each experiment, the pH and the CO_2 flow rates data were recorded. The tests were performed at $CaCl_2$ and $NaHCO_3$ concentrations of 125, 250, 300 mM and 250, 500, 600 mM, respectively.

The carbonation tests (set-up shown in figure 46b) were aimed at evaluating the degree of carbonation of the selected alkaline material, i.e. stainless steel (SS) slag, as a function of different parameters. Prior to perform the carbonation tests, the SS slag was divided into size classes (Fraction A: d < 0.84 mm, Fraction B: 0.177 < d < 0.84 mm, Fraction C: d < 2 mm, Fraction D: d < 10 mm) and each size class was characterized in terms of its environmental behaviour (leaching test EN 12457-2).

The size fraction A, which included the finest and most reactive portion of the SS slag (d < 0.177 mm) was also characterized in terms of its chemical (alkali fusion with $Li_2B_4O_7$ at 1050 °C followed by dissolution with 10% HNO_3) and mineralogical (XRD analysis) properties. The obtained results are reported in table 14. The major constituents of Fraction A included Ca, Si, Cr, Fe, Al and Mg. Appreciable concentrations of V and Ni were also observed. The XRD results showed that the analysed residues were mainly characterized by Ca-bearing phases, i.e.: dicalcium silicate, calcium-aluminium silicates and calcium-magnesium silicates. Some Fe phases, including iron sulphide, iron oxide and calcium oxide were also identified.

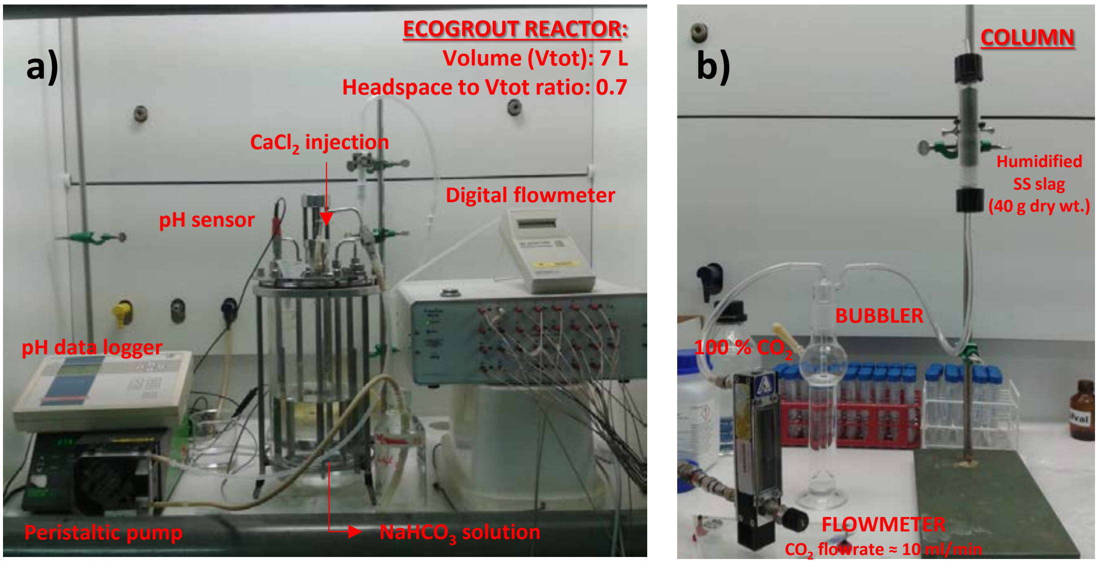


Figure 46. Set-ups used to perform the batch Ecogrout (a) and the column carbonation (b) experiments.

Table 14. Main chemical and mineralogical characteristics of Fraction A (d < 0.84 mm) of the SS slag.

Major elements (% wt.)		Trace elements (mg/kg wt.)		Mineralogy	
Ca	32.2	Na	0.13	Dicalcium silicate [Ca_2SiO_4]	**
Si	10.1	V	0.097	Aluminum calcium silicate [$CaAl_2SiO_6$]	**
Cr	4.09	Ni	0.10	Portlandite [$Ca(OH)_2$]	**
Fe	3.26	Ba	0.04	Melilite ($Ca_2(Mg_{0.5}Al_{0.5})(Si_{1.5}Al_{0.5}O_7)$)	**
Al	2.24	Mo	0.0051	Calcium Oxide (CaO)	*
Mg	1.79			Iron Sulfide (FeS)	*
Mn	1.17			Iron Oxide (Fe_2O_3)	*

The column carbonation tests were carried out by varying the following parameters: reaction time (from 1 to 24 hours), SS particle size (Fraction A, Fraction B, Fraction C, Fraction D), water to solid ratio (0.1 and 0.2 l/kg), water addition method (water added by mixing, water added by percolation). In order to possibly simulate the conditions expected at BFs as a result of the Ecogrout process, each column carbonation test was performed at ambient temperature (T = 22-25 °C) and pressure (P_{CO2} = 1 bar) and employing 100% CO_2 obtained from a gas bottle. The description of the experimental procedure adopted to perform the column carbonation tests are reported in Capobianco et al. (2014b).

At the end of the experiments, slag samples were collected from the top, middle and bottom level of the column and analysed to determine their carbonate content (EN 13137) and leaching behaviour

(EN 12457-2) as reported in Capobianco et al. (2014b). Selected slag samples were also collected to perform the CEN/TS 14429 pH-dependence leaching test, in order to better analyse the effects of the tested column carbonation treatment on the leaching behaviour of the slag and to identify the main mechanisms governing the release of major and regulated elements in a long-term scenario. In addition, to assess the reactivity of the material with CO_2, batch carbonation tests were also carried out under enhanced conditions. The results of the pH dependence leaching test as well as of the batch carbonation experiments are presented and discussed in Capobianco et al. (2014b).

In stage 2 combined tests were performed by assembling the set-ups used in the previous phase, as shown in Figure 47a, applying the operating conditions which gave the best results in the preliminary tests and subsequently evaluating the carbonate content and the leaching behaviour of the carbonated SS slag.

Finally, in stage 3, a combined test was performed using the set-up shown in figure 47b, designed in order to simulate field conditions so to estimate the effect of the injection mode on calcite precipitation in the gravel layer as a result of the Ecogrout process, as well as the differences in the degree of carbonation occurring in the slag layer. A reactor with an internal diameter of 94 cm and an internal height of 46 cm was poured with approximately 70 L of deionized water. Subsequently, about 300 kg of a uniform fine gravel (d_{95} = 2 mm) were inserted and compacted with a proper device. A blank test was performed by continuously injecting for 8 h 375mM $CaCl_2$ and 750 mM $NaHCO_3$ solutions at 100 ml/min along the entire height of the gravel by means of two different injection wells positioned at the centre of the reactor. The level of the water inside the reactor was kept constant by means of an extraction well located at 40 cm from the injection wells. During the test, the produced gas was conveyed to a CO_2 sensor connected to a data logger. The combined test was performed applying the same procedure and employing Fraction D of the SS slag, i.e. all the bulk material available. For the combined test, a properly designed layer of an inert porous material was located above the gravel to prevent the direct contact of the slag with water while the slag (about 7.5 kg) was placed on top of the layer and homogenously spread along the entire cross section of the reactor, providing a final height of the SS layer of about 2 cm.

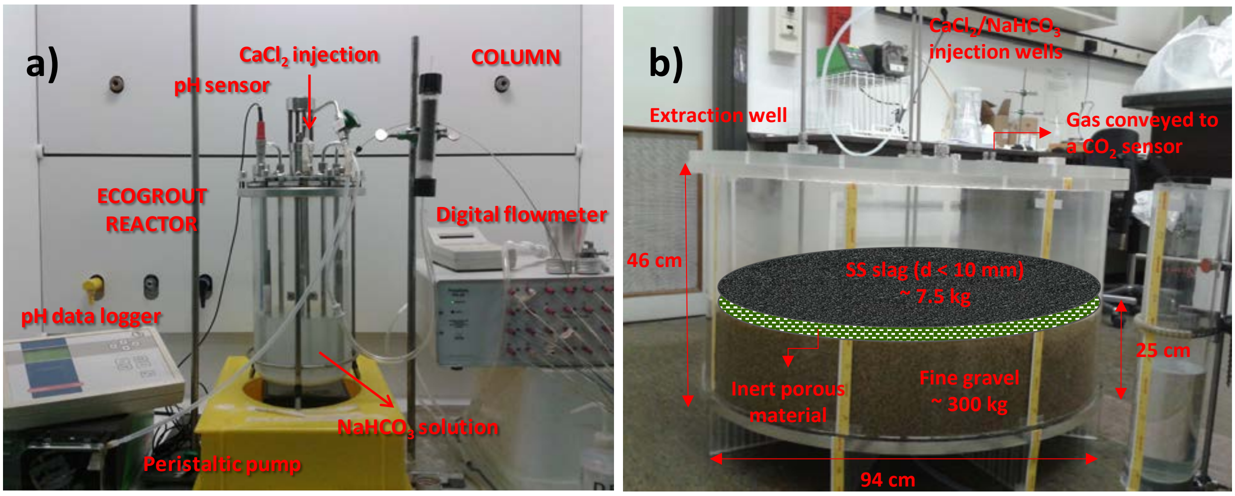


Figure 47. Set-ups used to perform the combined Ecogrout – carbonation tests at a) small scale and b) large scale.

2.4.3 Results

2.4.3.1 Ecogrout tests

The main results of the Ecogrout tests are reported in figure 48. Specifically, figure 48a reports the results of two duplicate tests performed employing 250 mM of $CaCl_2$ and 500 mM of $NaHCO_3$ in terms of pH of the Ecogrout solution and of the measured CO_2 flow rates as a function of time. During the first 20 minutes of the test, the gas flow rates were found to increase sharply with time while the pH values progressively decreased to a minimum value of about 5.5, achieved at 20 minutes. At this time, a corresponding maximum gas flow rate equal to 420 ml/min was obtained. The Ecogrout reaction seemed to reach completion after about 60 minutes; indeed for longer times a relevant modification of the pH as well as of the gas flow rates did not occur, with negligible CO_2 production and pH values variations after 90 min.

Figure 48b reports the obtained CO_2 flow rates as a function of the $CaCl_2$ and $NaHCO_3$ injection concentrations. The average CO_2 volume produced as a result of the Ecogrout reaction, estimated from the measured flow rates, was found to be around 7.5 and 9.5 L for the 250, 300 mM $CaCl_2$ tests, respectively. This result was not really in line with the stoichiometric CO_2 volumes potentially achievable, estimated by assuming CO_2 as a perfect gas and a constant temperature of 22 °C, which were found to be of around 6 and 7.2 L for the 250, 300 mM $CaCl_2$ tests, respectively. The differences between the estimated CO_2 volumes and the stoichiometric ones could be due to the combination of several factors, among others the assumptions made as well as the possible errors in the measurements of the actual CO_2 flow rates. Regarding the 125 mM $CaCl_2$ test, the achieved CO_2 flow rates did not allow to obtain a sufficient CO_2 volume to replace completely the air volume of the headspace. Indeed, the estimated CO_2 volume was found to be lower than the headspace volume and around 2 L.

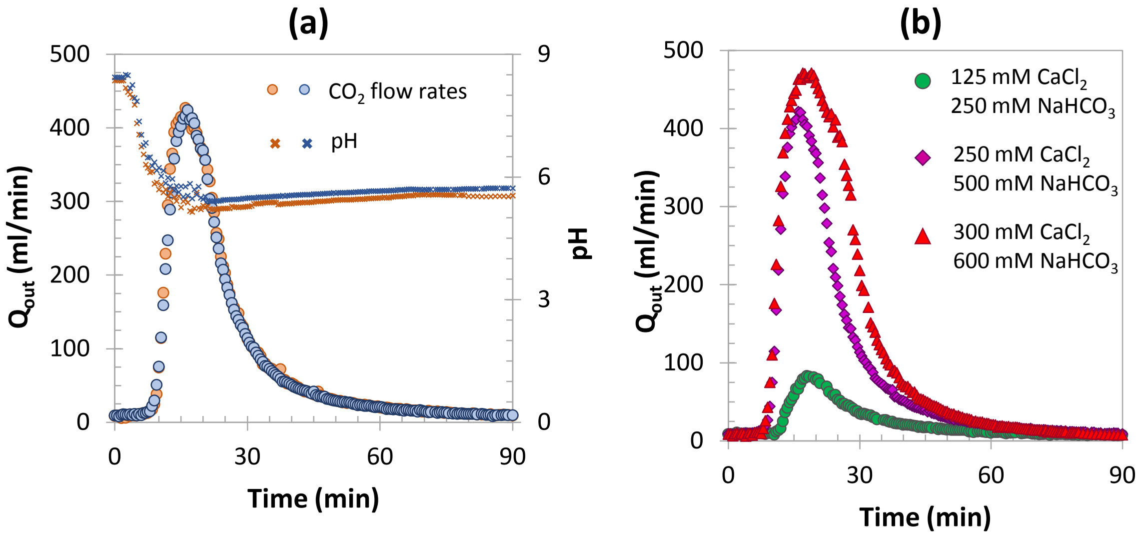


Figure 48. Results of Ecogrout tests in terms of: a) pH and CO_2 flow rates for the test performed at 250 mM $CaCl_2$ and 500 mM $NaHCO_3$; b) CO_2 flow rates as a function of $CaCl_2$ and $NaHCO_3$ injection concentrations.

2.4.3.2 Column carbonation tests

The obtained CO_2 uptakes, derived from the carbonate content analysis of the untreated and carbonated SS samples according to the equation reported in Capobianco et al. (2014b), for the finest (Fraction A) and coarser (Fraction D) size classes of the SS slag as a function of reaction times and sampling depth inside the column are reported in figure 49. Further findings concerning the other size classes investigated as well as the effects of changing the water to solid (L/S) ratio and the water addition method are reported in Capobianco et al. (2014b) and Capobianco (2014).

As can be observed in Figure 49, the highest CO_2 uptakes were attained for Fraction A (< 0.84 mm) of the SS slag, probably due to the fact that these size classes included the portion < 0.177 mm of the SS slag, which resulted to be highly reactive with CO_2 (Capobianco et al., 2014b). In fact, a maximum CO_2 uptake of 11.3 % was obtained at a reaction time of 24 hours for this size fraction. The finest portion of the SS slag seemed to exert a relevant influence also on the flow of CO_2 through the column. In fact relevant differences in the CO_2 uptake values obtained at different heights were particularly evident for Fraction A for the 1 h and 2 h tests. In spite of this, no pressure drop through the column was observed and for reaction times longer than 8 h the material appeared to react homogeneously with CO_2. The size Fraction D of SS slag showed to react homogeneously with CO_2 already after 1 h, i.e. no significant differences of the CO_2 uptakes were noted at different column depths. Furthermore, despite the presence of coarse SS particle (> 2 mm), accounting for 25% of the bulk material, a maximum CO_2 uptake similar to that obtained for Fraction B was achieved after 24 h (see Capobianco et al., 2014b and Capobianco, 2014), highlighting the relevant influence of the finest portion (< 0.177 mm) on the global reactivity of the SS slag and suggesting that the use of coarse SS particles may be feasible in field scale applications of the proposed process.

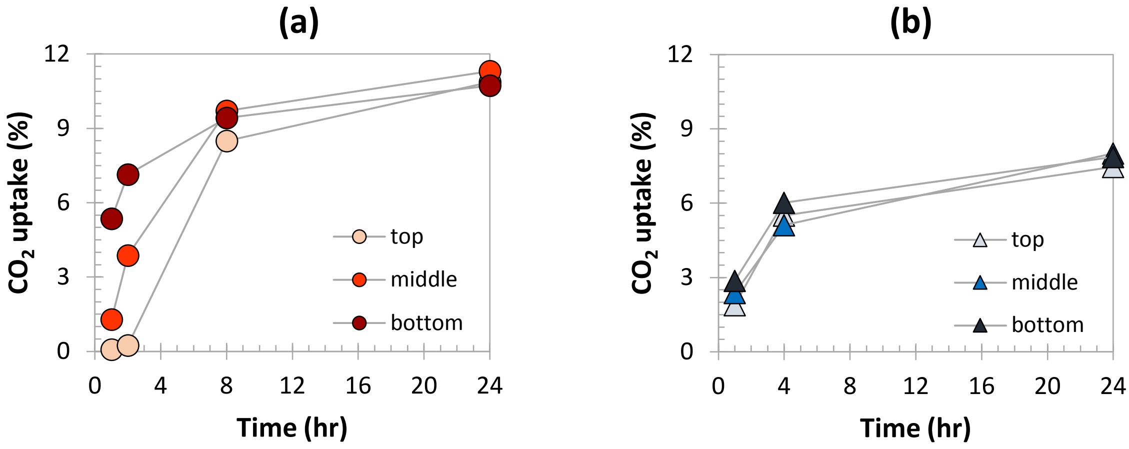


Figure 49: CO_2 uptake of SS slag as function of particle size at different column depths (T = 23-25 °C, P = 1 bar, L/S = 0.2 l/kg, water added by mixing); a) Fraction A: d < 0.84 mm; b) Fraction D: d < 10 mm.

2.4.3.3 Combined Ecogrout-carbonation tests performed at small scale

The combined Ecogrout-carbonation tests were performed at small scale by varying the $CaCl_2$ and $NaHCO_3$ concentrations as for the batch Ecogrout tests and employing Fraction A of the SS slag, since this size fraction showed the best results in the column carbonation tests in terms of the achieved CO_2 uptakes. Each test was performed at a set reaction time of 90 minutes, since this value was observed to lead to the complete depletion of the CO_2 production as a result of the Ecogrout reaction (see results of the Ecogrout tests in paragraph 2.3.3). Results showed that the CO_2 uptakes obtained from the test performed at the lowest concentrations of $CaCl_2$ and $NaHCO_3$ were appreciable only at the bottom of the column (figure 50a), confirming the results of the Ecogrout tests, i.e. an insufficient CO_2 volume to completely replace the headspace of the Ecogrout reactor and flow through the SS slag inside the column. Conversely, for the highest $CaCl_2$ and $NaHCO_3$ concentrations, the CO_2 released from the Ecogrout reaction seemed to react quite homogenously with the SS slag, allowing to achieve an average CO_2 uptake of 7.2 and 7 % for the 250 and 300 mM $CaCl_2$ tests, respectively (see Figure 50a). Furthermore, the achieved CO_2 uptakes were found to be significantly higher than those obtained as a result of column carbonation tests performed on the same SS size fraction at similar reaction times with 100% CO_2 from a gas bottle (see Figure 50b). Moreover, this result suggested that appreciable CO_2 uptakes may be possibly achieved at low contact times between CO_2 and SS slag. Indeed, the estimated contact times between CO_2 and the SS slag for the 250 and 300 mM $CaCl_2$ tests were around 8 and 10 times lower than those observed for the column carbonation tests, respectively.

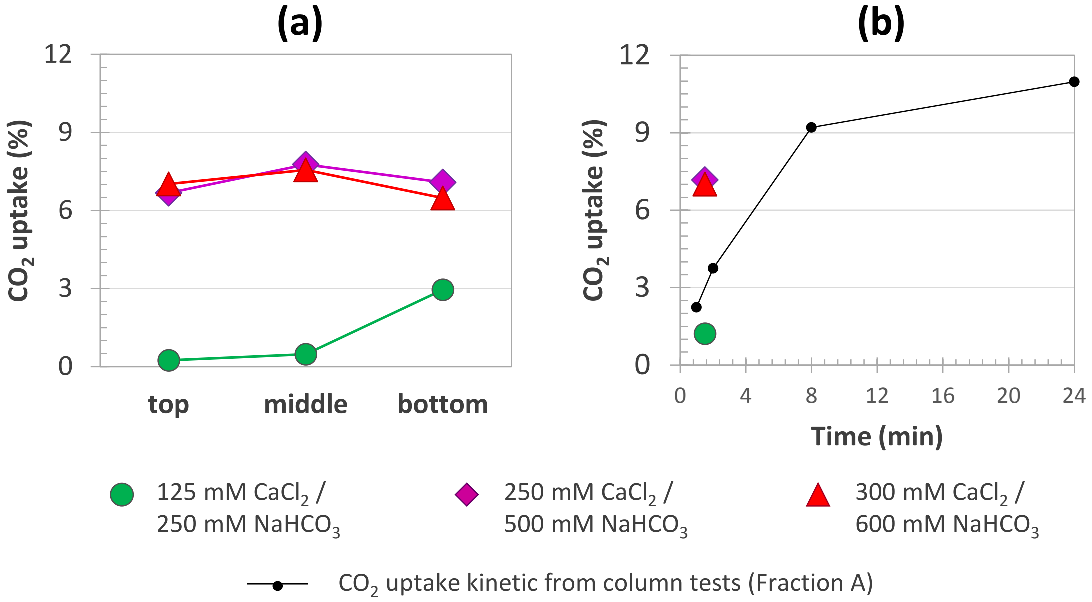


Figure 50. CO_2 uptakes resulting from the combined Ecogrout - carbonation tests as a function of $CaCl_2$ and $NaHCO_3$ concentrations at different column heights (a) and comparison with the average CO_2 uptakes kinetic obtained as a result of the column carbonation tests carried out with 100% CO_2 (b).

The significant carbonation degree of the slag was confirmed by the standard compliance leaching test performed on the carbonated SS slag obtained from the 300 mM $CaCl_2$ test, whose main results are shown in Figure 51. The combined process allowed a decrease of the eluate pH from 12.4 to 11 in 90 minutes, as well as the modification of the leaching behaviour of both major and regulated elements, providing similar qualitative effects to those found as a result of the column carbonation tests performed on the same size fraction and at similar reaction times (compare pink and red bars in figure 51). Nevertheless, the effects of carbonation were more pronounced for the SS slag resulting from the combined process. As far as major elements are concerned, the elements which resulted to be mainly influenced by carbonation were Ca and Si (see Figure 51a). Ca concentrations in the eluates of the carbonated slag were significantly reduced, up to one order of magnitude, revealing the formation of less soluble phases, e.g. calcite, than that characterizing the untreated slag (Baciocchi et al., 2010; van Zomeren et al., 2011). Conversely, Si leaching concentrations increased upon carbonation, due to the conversion of the original silicate minerals into more soluble phases (Huijgen and Comans, 2006). The release of regulated elements (figure 51b) was positively affected by the combined process, allowing to cut down the leaching concentrations of Al, Ba and Mo fairly below the Italian regulatory limits for material reuse (It. MD 156/06), disposal in inert waste landfill (It. MD 27/09/10) and groundwater quality (It. LD 152/06). Besides, the combined process showed to exert a significant immobilization effect also on Cr, leading to a 79% reduction after 90 minutes, at a value slightly lower than the established regulatory limits.

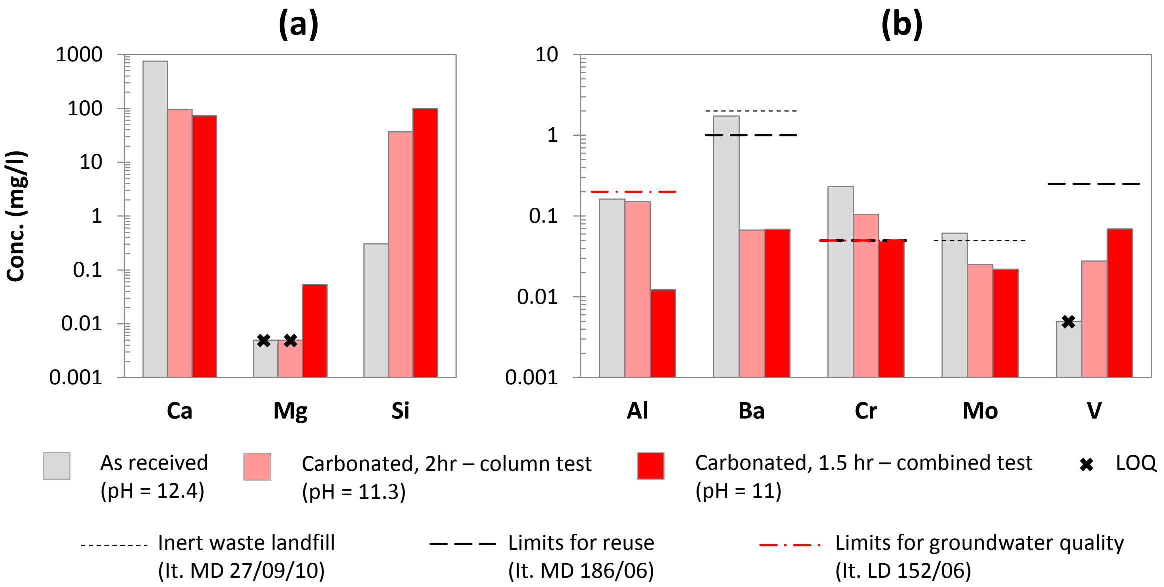


Figure 51.Comparison of the results of the leaching test on Fraction A (d < 0.84 mm) of the as received slag and carbonated slag from both column (T = 23 °C, P = 1 bar, L/S = 0.2 l/kg) and combined Ecogrout – carbonation (300 mM $CaCl_2$; 600 mM $NaHCO_3$) tests in terms of: a) major elements and b) regulated elements. Black stars refer to the limit of quantification (LOQ) of the specific element.

2.4.3.4 Combined Ecogrout-carbonation tests performed at large scale

Regarding the test performed in the larger reactor, the theoretical CO_2 volume releasable as a result of the Ecogrout reaction at the set $CaCl_2$ concentration (375 mM) was estimated to be around 440 L, this amount being sufficient to replace the headspace volume (147 L) up to three times. However, the CO_2 concentrations measured at the outlet of the reactor during both the blank and the combined test were around 700 ppm only, i.e. very far from pure CO_2 and only slightly higher than the CO_2 concentration in air. As far as the carbonation of SS slag is concerned, negligible CO_2 uptakes were obtained for all the collected samples, regardless of the distance of the sampling points from the injection wells as well as of the analysed size fraction, i.e. the bulk material (Fraction D) and the SS slag showing d < 0.84 mm (Fraction A).

2.4.4 Discussion

The results obtained from the combined Ecogrout-carbonation experiments performed at small scale suggested that an in-situ carbonation process which exploits a CO_2 upward flow at mild operating conditions may be a feasible option for the improvement of the environmental properties of alkaline residues at BFs. However, the combined Ecogrout - carbonation tests performed at larger scale highlighted that the poor mixing of the $CaCl_2$ and $NaHCO_3$ solutions within the porous medium may hinder the Ecogrout reaction to a relevant extent. In order to better elucidate the influence of the injection conditions of the $CaCl_2$ and $NaHCO_3$ solutions into the subsoil on the Ecogrout reaction, further Ecogrout tests should be possibly performed at large scale. Namely, in order to assess the potential of the Ecogrout process to produce calcite and release CO_2, the effects of the following conditions may be examined:

- $CaCl_2$ and $NaHCO_3$ solutions injection flow rates;
- Relative position of the $CaCl_2$ and $NaHCO_3$ injection and extraction wells;
- Depth of the $CaCl_2$ and $NaHCO_3$ wells;
- Injection mode of the reagents (continued or pulsed).

Once the influence of the above mentioned parameters on the Ecogrout reaction is evaluated, the process may be possibly optimized in terms of the Ecogrout radius of influence as well as CO_2 release.

Together with the above mentioned scientific gaps that should be possibly elucidated in future experimental investigations, it should be highlighted that the applicability of the combined Ecogrout-carbonation process in a BF regeneration context is considerably constrained by site-specific conditions. Namely, the application of the combined process entails the contemporary presence at the site of a proper amount of residues with alkaline properties, as well as of a soil with a low bearing capacity that has to be enhanced according to the specific regeneration project. In addition, the increased groundwater salinity due to the production of NaCl as a result of the Ecogrout reaction may be an issue, especially if the groundwater is used for municipal and agricultural supply. Finally, it should be considered that both calcium chloride and sodium bicarbonate show a higher density than water, thus possibly leading to the stratification of calcite at the bottom of the groundwater table rather than to its homogeneous production along the entire water height if sufficient regent flow rates are not ensured.

2.4.5 Conclusions

As for the possibility of applying in situ technology trains within a BF regeneration context, the findings obtained from the application of combined Ecogrout-carbonation process to industrial residues with alkaline properties suggested that the subsoil texture is one of the key factors which mainly influence the performance of the combined process in a real scale scenario and that its application in the presence of a soil with a fine texture may not be recommended. As for the alkaline material, together with the mineralogy and composition, the material texture may strongly influence the effectiveness of the proposed technology train. Indeed, the formation of preferential pathways through the slag layer for CO_2 escape may occur when a considerably coarse material is employed. Table 15 lists the key factors that need to be investigated in order to assess the applicability of the combined Ecogrout-carbonation process at BFs, which are mainly related to the alkaline residues and subsoil characteristics. In addition, site-specific conditions, mostly concerning groundwater flow rate and depth, should be carefully evaluated before applying the train at real scale. Indeed, although the transport of reagents through the water phase should be enhanced by applying proper flow rates in injection and extraction wells, the groundwater hydraulic gradient also may play a relevant role in ensuring the suitable mixing and transport of reagents. Besides, the feasibility of the combined Ecogrout-carbonation process within sites characterized by a deep groundwater table may be an issue, due to the rising costs for the Ecogrout equipment installation as well as to the dilution of CO_2 occurring in the pores of the unsaturated zone that may result in a negligible effect of carbonation on the overlying layer of alkaline material.

Summarizing, the possibility of applying the carbonation concept, especially in the framework of the Ecogrout process, is surely intriguing and the proof of concept was positive, but more efforts are eventually required to make it ready for field application and the conditions for its application need to be further investigated.

Table 15. Factors influencing the performance of the combined Ecogrout-carbonation process

Macro categories	Key factors	Secondary factors
Characteristics of the alkaline material	Mineralogy Texture	Total composition
Characteristics of the subsoil	Texture	
Site-specific conditions		Groundwater depth Groundwater flow rate

3. Application of the technology trains on BFs: conclusion and discussion

The elaboration of the three technology trains to assess critical design parameters revealed that many technical parameters are available that can be adjusted to optimize its functioning.

For TT1 this resulted in an increased understanding of the relation between the local characteristics of the subsurface like the redox chemistry of the subsoil, and the possibilities to enhance the capacity for attenuation of contaminants in the groundwater. Further, the relation between design of the buildings and its operation on the performance of the ATES system showed that the technology is technically very robust. For TT2 this resulted in an increased understanding of the relation between initial soil characteristics and additives on the mechanical (strength) and chemical (leaching of metals) properties of the produced aggregates. For TT3 this resulted in the understanding of applicability criteria to employ Ecogrout on large scale for soil improvement.

In general it can be stated that the proposed technology trains can all function within a wide range of technological boundary conditions. All technology trains can be adjusted in order to meet the required quality of specific end-points. Therefore the technology trains provide an excellent ground to build on within the field of BF redevelopment. Here in this study it is shown that the technology trains can function in a wide variety of environmental and technological boundaries. In fact the developed technology trains can in principle deliver goods and services to meet the basic needs at BFs regarding energy, building materials and water quality. Therefore these technologies could be advocated at BF sites and can in principle be regarded as fit for technology push.

In deliverable 4.3 of the HOMBRE project (Smit et al., 2014) it is shown that the technological aspects for the three TTs were not limiting the Operating Window for application of the concept of these TTs. The success of the application of technology trains was shown to be dependent rather on economic, environmental and social aspects than of technological boundary conditions. This is in line with the findings for the three TTs that are described in chapter 2 of this deliverable (D4.2). Therefore it is concluded that technology trains can be most successful when they are introduced via a technology pull mechanism which states the requirements for technology solutions.

Successful application of technology trains in BF redevelopment can only take place when both technology push and technology pull factors are considered within a comprehensive group of stakeholders. Technology push is essential to increase the awareness of possibly relevant technologies that can contribute to the redevelopment of BFs. However, the introduction of a new technology as such does not seem to be a strong driver for redevelopment of a BF. To tackle this phenomenon the aim of the HOMBRE project is to include new technologies in integrated solutions that allow for the valorisation of wider effects as is described in deliverable 5.1 “Valuation approach for services from regeneration of Brownfields for soft re-use on a permanent or interim basis; Creating opportunities from synergies between environmental, economic and social improvements” Menger et al., 2012. Within this approach, technological solutions are integrated in wider solutions aiming at wider benefits as monetary assets on BF redevelopment.

The awareness within the HOMBRE team that a balance should be found for technology push and technology pull strategies to successfully redevelop BFs was growing in the evaluation of multiple workshops that were organized with stakeholders of individual HOMBRE cases (e.g. Solec-Kujawski (PL), Terni (I), Markham Vale (UK)). From these workshops it can be concluded that technological aspects were not the determining issue for (problems of) redeveloping the respective BFs. Instead, the process of identifying beneficial functions for BFs in their new use phase was seen as main priority. Stakeholders realize that this identification is strongly related to economic and demographic conditions and developments on a larger spatial scale (regional/municipal) rather than local conditions on BF scale. It is expected, though not formally assessed in this study, that once a development direction for a BF site is chosen, the link between ambitions of stakeholders and barriers found at the BF site that hamper achieving those ambitions becomes more prominent, and technological requirements gain importance. To aid the process of defining future beneficial functions and link them to the introduction of technology trains the Golden Questions (elaborated in deliverable 4.4 of the HOMBRE project) were developed. These Golden Questions allow a structured search for beneficial use of the future site based on all available knowledge from all stakeholders. They aim at to come to the optimal development directions for BFs with the help of technology trains if needed.

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