

NanoRem is a four year, €14 million research project funded through the European Commission FP7.

Introduction

Within the NanoRem project Carbo-Iron® was introduced as new composite material where nanoiron structures are embedded in colloidal activated carbon grains ($d_p \approx 1 \mu\text{m}$). The carbon framework acts as spacer between the built-in iron and thus prevents the iron-iron interactions driven by the magnetic forces and known from bare NZVI. Particle agglomeration is therefore largely suppressed for Carbo-Iron particles. The composite material inevitably unifies properties of both components. The carbon component in Carbo-Iron® is responsible for the formation of stable suspensions over longer times, acts as strong sorbent for contaminants and support the performance of the reagent at the same time. The hydrophobic, porous carbon grain has the ability to enrich organic contaminants by several orders on magnitude in concentration and easily supplies them to the reactive metal sites.

Carbo-Iron® was subject of investigations at different scales and its application was prepared in terms of i) optimization of material production, ii) development of analytical methods for particle tracing in natural environments and iii) understanding and controlling particle migration by transport studies in column to large-scale experiments (flume and field application) and iv) screening of its reactivity towards a variety of organic water contaminants. The poster presents a selection of achievements and lessons learnt using the material which reach from upscaling of the production process to finding specific analytical methods for Carbo-Iron® tracing in field sediment samples. Distinct application modes were found for either selectively placing the particles near contaminant sources or forming broad plume-treatment zones. The most important results of the work carried out during the project period is summarized and insight is given into the progress of the tailored design of the colloidal *in-situ*-“microreactors”.

Migration in porous media

I) Optimization of suspension recipe for tailored reactive zone design – concept of „meta-stable suspensions“

Table 1: CMC partitioning between sorbed and free state for Carbo-Iron® suspensions with various CMC concentrations and $c_{\text{particulate}} = 20 \text{ g L}^{-1}$

c_{CIC}	c_{CMC}	$c_{\text{CMC, free}}$	ρ
[g L ⁻¹]	[g L ⁻¹]	[mg L ⁻¹]	[wt-%]
20	4	20	2600
20	2	10	600
20	1.5	7.5	180
20	1	5	100
20	0.2	1	50

Data calculated from sorption isotherm; ρ = maximum sorption capacity

- Sorption of carboxymethyl cellulose (CMC) to outer colloid surface (sorption isotherm)
- Dominant particle fraction (> 80 wt-%) can be stabilized over several hours
- $c_{\text{CMC, free}}$ and ρ as crucial parameter for „meta-stable suspensions“

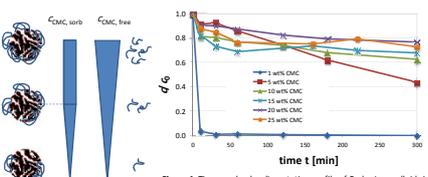


Figure 4: Time-resolved sedimentation profile of Carbo-Iron colloids in static suspensions ($c_{\text{particulate}} = 20 \text{ g L}^{-1}$; GWII; pH = 8.5, $v_{\text{settling}} = 0.3 \text{ mL at } h = 1 \text{ cm}$ below water table; c_{CMC} at 5 g L^{-1} ranging from 1 to 25 wt-% referred to $c_{\text{particulate}}$).

Table 2: Column test conditions for 1-m-columns

Test conditions	Value
$c_{\text{particulate}}$ [g L ⁻¹]	20 ($d_{50, \text{particulate}} = 1.3 \mu\text{m}$)
$c_{\text{CMC, free}}$ [g L ⁻¹]	1 - 4
$c_{\text{CMC, total}}$ [g L ⁻¹]	102
d [cm]	1.5
d [cm]	52
v_{in} [m d ⁻¹]	0.23
ρ_s [g L ⁻¹]	PM-8 (medium sand) ($d_{50} = 0.63 \text{ mm}$)
Fluid	pH 8.1
Water hardness [mg CaCO ₃ L ⁻¹]	123
Alkalinity [mg CaCO ₃ L ⁻¹]	77
Electric Conductivity [$\mu\text{S cm}^{-1}$]	440

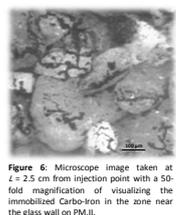


Figure 6: Microscope image taken at $z = 2.5 \text{ cm}$ from injection point with a 50-fold magnification of visualizing the immobilized Carbo-Iron in the zone near the glass wall on PM-8.

Experimental design for column tests

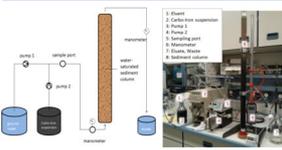


Figure 5: Setup for targeted particle deposition using 3 intermittent injection cycles (porous media: PM-8; injection volume: 52 m³ d⁻¹; subsequent resting time >24 h at $v_{\text{in}} = 0.25 \text{ m d}^{-1}$; model water according to the drinking water composition given by the Drinking Water Supply Association "Lake Constance" (ZVBWV).

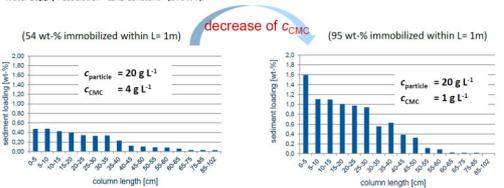


Figure 7: Sedimentation profiles after 3 intermittent injection cycles with spatially-resolved particle loading on PM-8 at different c_{CMC} ($c_{\text{particulate}} = 20 \text{ g L}^{-1}$; $c_{\text{CMC}} = 1.4 \text{ g L}^{-1}$; pH = 8.1; $v_{\text{in}} = 52 \text{ m}^3 \text{ d}^{-1}$; subsequent resting time >24 h at $v_{\text{in}} = 0.25 \text{ m d}^{-1}$).

II) Particle migration under groundwater-relevant conditions 3, 8

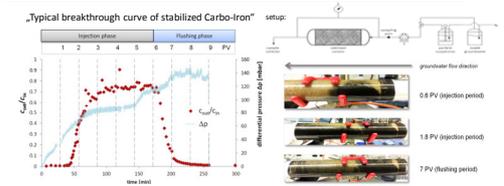


Figure 8: Left: Breakthrough curve of mobile Carbo-Iron colloid fraction under groundwater relevant conditions ($c_{\text{particulate}}/c_{\text{CMC}}$ - relative particle concentration normalized to c_{CMC} ; Δp - differential pressure between inlet and outlet) Right: Migration of Carbo-Iron colloids ($c_{\text{particulate}} = 15 \text{ g L}^{-1}$; $c_{\text{CMC}} = 1.5 \text{ g L}^{-1}$) performed in field site groundwater ($v_{\text{in}} = 10 \text{ m d}^{-1}$; pH 8.1; alkalinity 250 mg CaCO₃ L⁻¹; electric conductivity 1306 μS , total water hardness 680 mg CaCO₃ L⁻¹) and porous media from Hungarian site (Balsagyarmat, sieve fraction of sediment $d_s < 2 \text{ mm}$)

References:
 1 Jurischka, M. (2015): Process optimization of the industrial synthesis of Carbo-Iron® - A reagent for groundwater remediation. Bachelor Thesis, University of Technology Cottbus - Senftenberg, Germany.
 2 Ernst, M. (2014): Contribution to the preparation of a safety data sheet for Carbo-Iron and the characterization of the material regarding to suspension stability and mobility in sediment columns. Master Thesis, RWTH Aachen University, Germany.
 3 Wünsche, S. (2015): Investigation of stability and migration of Carbo-Iron in saturated porous media in 1D-column studies. Internship report, Otto-von-Guericke-University, Magdeburg, Germany.
 4 Zauner-Wieczorek, M. (2015): Development of an analytical method for tracing carbonaceous colloids in natural sediment matrices. Bachelor Thesis, Martin-Luther-University Halle-Wittenberg, Germany.
 5 Bleyl, S., Kopinke, F.-D., Mackenzie, K. (2012): Carbo-Iron® - Synthesis and stabilization of Fe(0)-doped colloidal activated carbon for in-situ groundwater treatment. Chem. Eng. J. 191, 588-595.
 6 Mackenzie, K., Bleyl, S., Georgi, A., Kopinke, F.-D. (2012): Carbo-Iron® - an Fe/Carbon composite - as alternative to nano-iron for groundwater treatment. Water Res. 46, 3817-3826.
 7 Mackenzie, K., Bleyl, S., Kopinke, F.-D., Doose, H., Bruns, J. (2015): Carbo-Iron® as improvement of the nanoiron technology: From laboratory design to the field test. Sci. Total Environ. 563-564, 641-648.
 8 Bleyl, S., Wünsche, S., Bianco, C., Tosco, T., Georgi, A., Mackenzie, K. (2017): Modeling of Carbo-Iron transport in water-saturated natural porous media. In preparation.

Concept of Carbo-Iron as subsurface “microreactor“

Material Synthesis - from lab-scale to industrial production 1

Thermal reduction of Fe-oxide/ AC

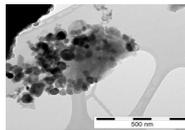
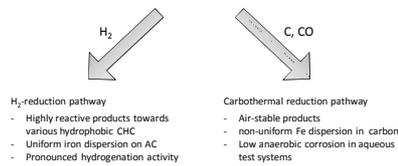


Figure 1: Bright field TEM image of Carbo-Iron (taken by UPOC).



Figure 2: Scale-up reactor for Carbo-Iron production (photo: SCIDRE).

“Mode of action“

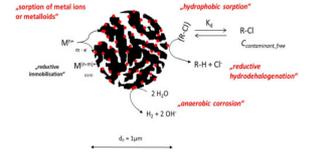


Figure 3: Transformation pathways of potential contaminant types at Carbo-Iron

- Results:**
- Two suitable synthesis pathways at lab-scale were developed
 - The carbothermal production was evaluated as the most appropriate for up-scaling and industrial production
 - Air stable products enable easy handling
 - The material quality strongly depends on the reduction mechanism and process temperature

Analytical tool for particle tracing in sediments by TPO-IR

Temperature-programmed oxidation coupled with infrared detection (TPO-IR) of solid sediment samples utilizes the fact that the immediate chemical environment of the carbon in different carbonaceous materials has an effect on the carbon-specific oxidation temperature, which can be analyzed temperature-resolved. In case of Carbo-Iron, the embedment of iron decreases the incineration temperature significantly in comparison to pure powdered activated carbon.^{4,5} One can take advantage of this temperature shift to detect carbon-based particles within a complex matrix containing a natural carbon background. The limit of detection was found to be 0.03 wt-% ($m_{\text{particle}}/m_{\text{sediment}}$).



Figure 9: Soil samples from Hungarian field site (Balsagyarmat); core samples taken at a distance of 0.5 m downstream to injection well (A) - from left to right going downwards from ground level, marked core samples represent the depth 12 - 14 m below ground level, where particles have been injected and obviously are present; (B) sandy and gravel raw material from well CMT 9; homogenized soil samples (ball milled and dried at 110°C).

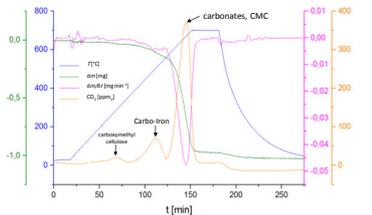


Figure 10: Temperature-programmed oxidation coupled with IR gas analysis (TPO-IR) of a model quartz sand loaded with CMC-stabilized Carbo-Iron and carbonate in a thermogravimetric balance (TGA-50 Shimadzu; air flow rate 50 mL/min; $m_{\text{sample}} = 47 \text{ mg}$; $\Delta T: 10 \text{ K/min}$; $T_{\text{max}} = 700^\circ\text{C}$).

- Scope and limits:**
- low particle loadings traceable
 - applicable in complex matrices (e.g. natural sediments)
 - low analytical effort
 - not applicable as on-site or in-situ method

Results:

- Particle-to-CMC-ratio is identified as key parameter for tuning suspension stability and deposition profile
- The so-called „meta-stable“ suspension was suitable for targeted particle deposition (used in large-scale flume - LSF, USTUTT)
- Particle suspensions can be effectively stabilized in a broad concentration range (to 30 g L⁻¹)
- Tests under groundwater-relevant conditions reveal a complex deposition pattern. A mobile fraction was found to pass porous media from the field site (breakthrough at 2 exchanged pore volumes in 25-cm-column)
- The commercial CMC used at the field site was only applicable in a pre-treated form (filtered over membrane < 0.2 μm) in column tests with site material, otherwise pore clogging in field site sediment occurred.

Summary & Conclusion

- Two thermal synthesis pathways with distinct material quality (regarding Fe dispersion on AC carrier) are developed. Both materials have been tested at lab-scale.
- Carbothermal Carbo-Iron® production was evaluated as feasible for industrial up-scaling.
- Suspension stability can be tuned ($c_{\text{particle}} \leq 30 \text{ g L}^{-1}$) to match the different particle deposition requirements for Plume or Source treatment
- Successful transfer of lab results to large-scale flume injection
- Carboxymethyl cellulose is suitable as colloid stabilizer, but appropriate specification (molecular weight, polymerization degree etc.) is essential for generation of a permeable reactive zone within the framework of field applications
- A new analytical tool has been developed for tracing carbonaceous particles in natural sediment matrices using TPO-IR method.

