METHODOLOGY OF COLUMNS TESTS FOR DESIGN OF ELECTRIC ENHANCED SYSTEM FOR IRON PARTICLES

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Abstract

The effectiveness of the reactive properties of zero-valent iron nanoparticles (nZVI) increases by the application of a direct current (DC). The saving of reactive agent and prolongation of the longevity of nanoparticles in the subsurface are the main advantages of DC application, which render in-situ chemical reduction by nZVI considerably more economical. During the support of nZVI remediation by an electric current, the synergic effect of the electric current close to the cathode is expected. There is a subsidy of electrons and production of H^+ during the process. nZVI is protected against oxidation and has a higher reactivity with the contaminants.

Keywords: Iron particles, reduction, reactive column, electric current
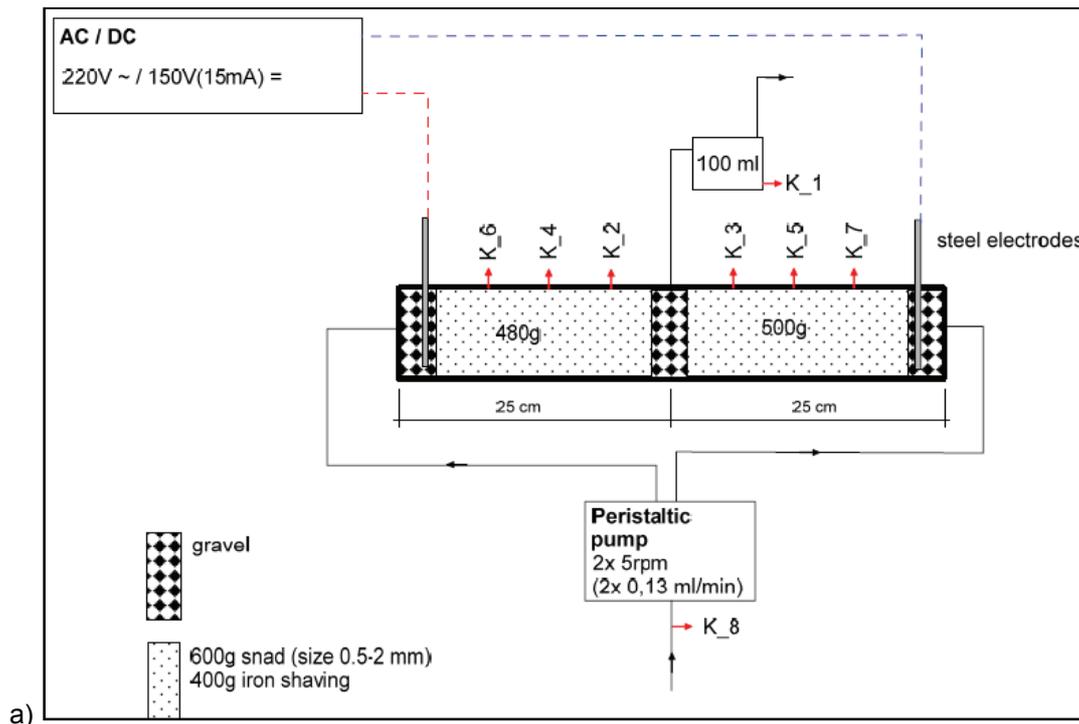
INTRODUCTION

The laboratory experiment in the flow arrangement is designed to study the synergic effect of iron particles supported by an electric current in detail. This test enables the processes close to the electrodes and their surroundings to be observed. The experimental arrangement and its boundary conditions were designed for a possible simulation of the real processes taking place at the sites.

The submitted paper presents a methodology of laboratory tests and selected results obtained from its use. The aim of the presented laboratory tests was to define in detail the physical and chemical properties and electric conditions, which may improve the efficiency of the chlorinated hydrocarbon (CHC) reduction process by zero-valent iron nanoparticles (nZVI). A procedure is presented, which enables the behaviour of the system to be described by a known water composition (geochemical model) and which can be used for controlling the support system by electric current.

1.   LABORATORY TEST METHODOLOGIES

When the electric support system is applied on site, the opposite electrodes are placed at a sufficient distance apart, which leads to a very small mutual influence of the surroundings of the electrodes. A configuration in the form of a cylinder with the reactive filling and two electrodes placed at the ends of the column was used in order to simulate the effects within one column test. Both ends of the column were used as inputs. The output is the same for both sites and is placed in the middle of the column. There are six sampling ports installed in the column, which enable the sampling of water and its subsequent analysis. The column output is connected to a 100-ml stainless-steel cell and an overflow below the water level. The output water is possible to be sampled without decreasing the contaminant concentration due to volatilisation. A block diagram and photograph of the column test is included at **Figure 1**.

The contaminated input water (mainly contaminated by volatile CHCs) is stored in a stainless-steel container placed in a refrigerator at a constant temperature (5 °C). In order to minimize the volatilization of CHCs, the container is hermetically sealed and a small overpressure is kept inside using inert gas (N_2). The water is distributed from the container to the peristaltic pump by stainless-steel capillaries. The peristaltic pump controls the flow rate through the system and subsequently to the column.

Figure 1 Configuration of column test: a) block scheme of reactive column (K_1-8: sampling ports); b) preparation of reactive column

A mixture of glass silica sand (grain size 0.5-2 mm) and iron shavings (size approximately 3-5 mm) was used as a reactive material for the test. The mixture was created in a mass ratio of 60% sand and 40 % iron shavings. It is possible to use any kind of iron particles for this column test; however, it is necessary to adapt the material of the rock environment to the chosen form of iron particles (micro, nano) in order to fix these particles in the environment and prevent their migration inside. The flow rate (duration of delay) has to be adapted to the final hydraulic conductivity of the system.

The column was prepared by filling the material in a dry state layer by layer, as shown in the block diagram in **Figure 1 a)**. The steel electrodes were placed in gravel. Subsequently, the reactive mixture was filled into the column. Half of the column (output) was filled with a further layer of gravel to serve as an output drain. The total column porosity was 45% and the volume of free pores was 283 ml. The column was placed horizontally and the double-headed peristaltic pump, which controls the flow rate through the system, was connected to both inputs. The speed of the peristaltic pump, the size of the tubes used and the connected capillaries were chosen in order for the duration of delay in the system to be approximately 1 day (corresponding to the reactivity of the material). Low flow rates were used when filling the column with water in order to ensure

sufficient time for the water to infiltrate the whole column and remove the maximum amount of air from the pore space. After filling the column with water, the flow rate in each of the input branches was set at 0.026 ml/min. During the experiment, the flow rates corresponding the flow velocity through column of 0.7-2 m/d were mainly used.

The following sampling plan was used for the column sampling. In order to prevent the sampling influencing subsequent samples, the samples were taken in a direction from the output port to the input port. Output port K_1 was sampled first, followed by K_2, K_3 and finally K_8. A glass syringe was used for sampling to minimize the effect of sorption. A volume of 11 ml was taken from each sampling port. The water was immediately analysed for CHC concentrations by GC, followed by the measurement of the physical and chemical properties (pH, ORP, and conductivity).
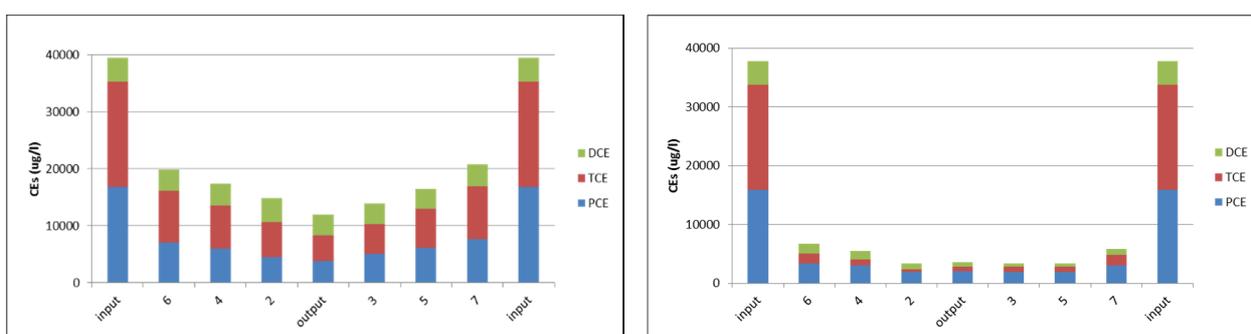
2.   RESULTS

Real water from a site contaminated by a mixture of chlorinated hydrocarbons (CHCs) was used for the experiment. The sum of CHCs was 50 mg/l and was mainly represented by PCE (40 %) and TCE (40 %), followed by 1,2-cis-DCE (10 %) and then other CHCs.

In the first phase of the test (system stabilisation) the column was left in a running mode with a low flow rate (m/d). Sampling was performed at the end of the test phase, which showed a low concentration of CHCs at the level of 10% of the input concentration. Subsequently, the flow rate through the column was increased (2 m/d), which led to a 4-fold increase in the concentration of output CHCs. In this mode the column was sampled twice to obtain the initial state of the distribution of CHC concentrations without the electric support system, and then the source of the direct current was connected.

The same current density values were used as for real applications of the set-up of the electric field support system -units of A/m^2. Due to the fact that a relative high flow velocity was used in the column compared to most sites (2 m/d), a current density around the upper boundary of this interval was chosen (approximately 7 A/m^2). The value of the current is given by the electrode areas (transitional resistance), the electric conductivity of the used water and the applied voltage. In order to achieve the chosen value of current density for the used column system (steel electrodes with a diameter of 5 mm, length of 35 mm and water conductivity of 800 µS/cm), it is necessary to apply a direct current of 150V. In this case the current passing through the column is approximately 8 mA.

Twelve sampling runs were performed during the column experiment. Five of them were performed without the electric current and seven with the direct current. The sixth run (without DC) and seventh run (with DC) were used to evaluate the influence of the electric current on the dechlorination process. There were four days between these sampling runs in order to minimise changes in the column due to material aging. The following series of diagrams presents the measured concentrations and the physical and chemical profiles in the column.

Figure 2 Concentration of CEs in column: left - without DC; right - with DC connection
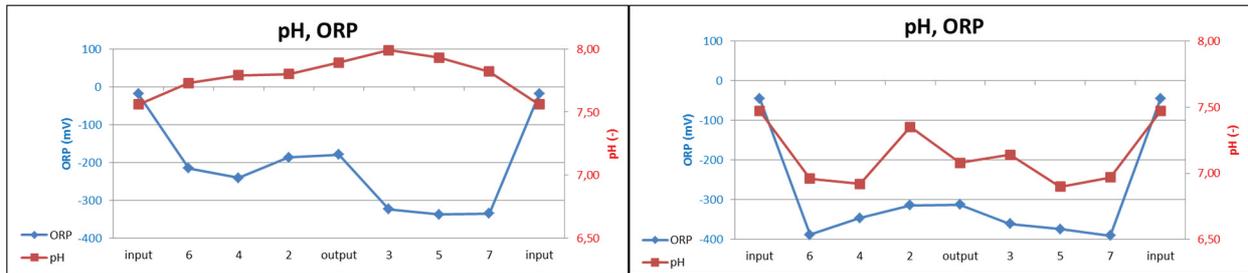
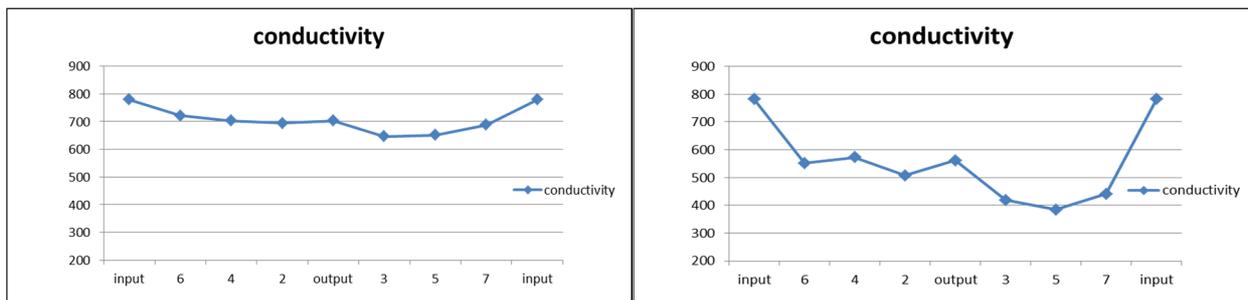**Figure 3** ORP and pH in column: left - without DC; right - with DC connection

Figure 4 Conductivity in column: left - without DC; right - with DC connection

Forms of Fe based on the measurement of pH/Eh

A reduction in CHC using Fe particles can be observed only if an active form of Fe (i.e. Fe^0 or Fe^{2+}) is present in the system. The form of Fe in the reactive system can be determined for a given water composition using a geochemical model. A geochemical model was created for the water used in column tests describing the forms of Fe, which is illustrated in **Figure 5**. In simple terms, if the point according to the measurement of pH-Eh is above the dashed brown line, then the conditions of Fe occurrence correspond to the trivalent state (non-reactive), or the active state if it is below the line ($^{2+}$ or ^{0}). This can be expressed by the distance of a given point from the transition area. This distance is expressed on the graph as $L\_Fe^{2+>>3+}$, the smaller this distance, the more reductive the conditions for the given pH-Eh, when the Fe is in a zero valent state at the lower limit of water stability.
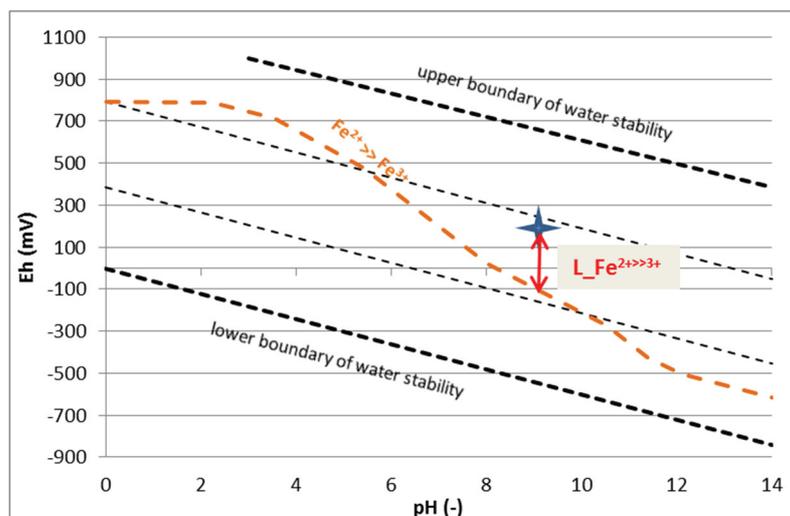

Figure 5 Distribution diagram of Fe for used water

Subsequently, the results of the measurement in the column profile were interpreted at the individual measuring points (for different pH/Eh values), the column was discretized along the sampling ports. The

measured and corresponding calculated values are plotted in the following tables. **Table 1** shows the values for the anode side, and **Table 2** for the cathode side.
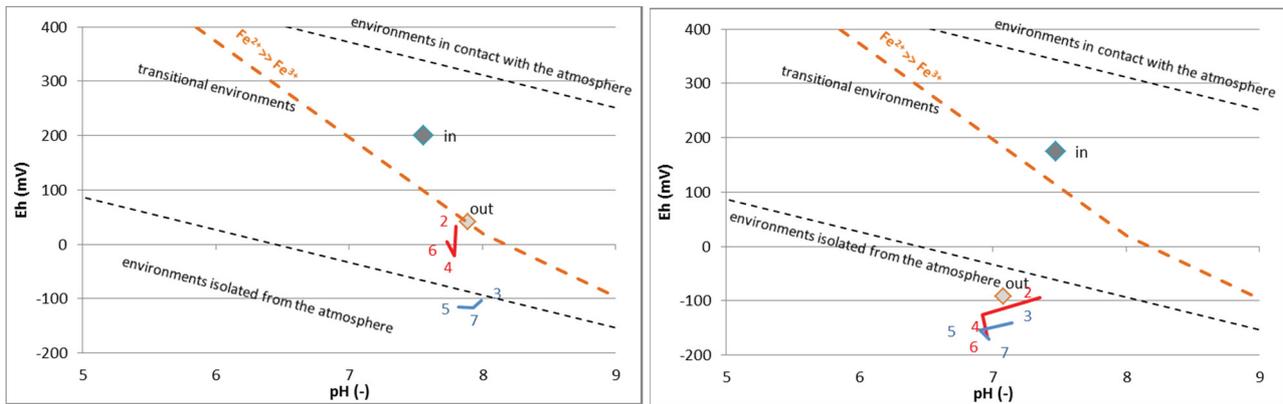
Table 1 Anode site of column, 6 Fe = without DC, 7 Fe+DC = with DC connection

	Port >>	input	6	4	2	output
ORP (mV)	6-Fe	-19	-215	-241	-187	-179
	7-Fe+DC	-45	-388	-346	-314	-312
pH (-)	6-Fe	7.56	7.73	7.79	7.80	7.89
	7-Fe+DC	7.47	6.96	6.92	7.35	7.08
Conductivity (uS/cm)	6-Fe	779	721	703	695	703
	7-Fe+DC	782	552	573	508	562
L_Fe$^{2+ >> 3+}$ (mV)	6-Fe	80	-88	-104	-49	-26
	7-Fe+DC	39	-388	-353	-250	-293
DCE (ug/l) / (%)	6-Fe	4 176	3 792 / **9%**	3 814 / **-1%**	4 243 / **-11%**	3 576
	7-Fe+DC	3 949	1 642 / **58%**	1 525 / **7%**	953 / **38%**	769
TCE (ug/l) / (%)	6-Fe	18 438	8 988 / **51%**	7 581 / **16%**	6 103 / **20%**	4 529
	7-Fe+DC	17 955	1 691 / **91%**	994 / **41%**	461 / **54%**	784
PCE (ug/l) / (%)	6-Fe	16 842	7 105 / **58%**	6 014 / **15%**	4 564 / **24%**	3 860
	7-Fe+DC	15 834	3 371 / **79%**	2 986 / **11%**	1 907 / **36%**	2 004
Sum_CEs (ug/l) / (%)	6-Fe	39 456	19885 / **50%**	17410 / **12%**	14909 / **14%**	11 965
	7-Fe+DC	37 738	6704 / **82%**	5504 / **18%**	3321 / **40%**	3 557

Note: The percentage degree in the given element is calculated from the difference of input/output concentration for each element.

Table 2 Cathode site of column, 6 Fe = without DC, 7 Fe+DC = with DC connection

	Port >>	input	7	5	3	output
ORP (mV)	6-Fe	-19	-335	-337	-323	-179
	7-Fe+DC	-45	-390	-374	-361	-312
pH (-)	6-Fe	7.56	7.82	7.93	7.99	7.89
	7-Fe+DC	7.47	6.97	6.90	7.14	7.08
Conductivity (uS/cm)	6-Fe	779	688	651	647	703
	7-Fe+DC	782	441	385	419	562
L_Fe$^{2+ >> 3+}$ (mV)	6-Fe	80	-193	-177	-154	-26
	7-Fe+DC	39	-389	-384	-332	-293
DCE (ug/l) / (%)	6-Fe	4 176	3 841 / **8%**	3 528 / **8%**	3 499 / **1%**	3 576
	7-Fe+DC	3 949	1 001 / **75%**	586 / **41%**	632 / **-8%**	769
TCE (ug/l) / (%)	6-Fe	18 438	9 254 / **50%**	6 808 / **26%**	5 305 / **22%**	4 529
	7-Fe+DC	17 955	1 793 / **90%**	871 / **51%**	844 / **3%**	784
PCE (ug/l) / (%)	6-Fe	16 842	7 679 / **54%**	6 141 / **20%**	5 072 / **17%**	3 860
	7-Fe+DC	15 834	3 070 / **81%**	1 960 / **36%**	1 929 / **2%**	2 004
Sum_CEs (ug/l) / (%)	6-Fe	39 456	20 774 / **47%**	16 477 / **21%**	13 875 / **16%**	11 965
	7-Fe+DC	37 738	5 865 / **85%**	3 417 / **42%**	3 405 / **1%**	3 557

Figure 6 Comparison of distribution diagrams: left - without DC; right - with DC connection

Column without electric current support system connected

From the point of view of the physical and chemical parameters, the two halves of the column behaved differently prior to connecting the electrical current. The anode side showed a lower reactivity of the fill material, which resulted in a lower pH and higher ORP. The lower reactivity of the anode side was also shown by the course of the conductivity, with a faster reduction of sulphates and nitrates on the cathode side leading to a higher decrease in conductivity.

Similarly, the lower average reactivity of the anode side was shown by the CHC concentration profile, whereby the anode side had a lower reduction efficiency. Both halves of the column achieved a good reduction efficiency for more chlorinated hydrocarbons (PCE, TCE), while the 1,2-cis-DCE concentrations were virtually unchanged. This indicates a short residence time in the column, where PCE, TCE and subsequently DCE are reduced (or DCE is formed as an intermediate product by gradual dechlorination and the absolute value of the concentration does not change). This was confirmed by adjusting the column run at the beginning of the experiment, whereby the DCE also effectively degraded when a longer delay time was used.

The values of the coefficient L_Fe$^{2+>>3+}$ were calculated for all of the measurements. To simplify the evaluation of the reduction conditions, the relationship between it and the effectiveness of the CHC reduction was sought. In terms of CHC reduction, positive values represent inactive conditions, where Fe is $^{3+}$. Negative values correspond to the active form of Fe in the state of ^{0} a $^{2+}$. For the cathode side with multiple reduction conditions, the coefficient L_Fe$^{2+>>3+}$ was lower by an average of approximately 100 mV (see the distribution diagram **Figure 6 - left**).

Column with the electrical current support system connected

The typical behaviour observed both on-site and in the laboratory during reactor tests when the electrical particle support system is engaged is as follows: (i) a rapid and massive decrease in ORP and increase in pH around the cathode; (ii) pH stabilization at 6-7 (for a steel electrode) and a slight decrease in ORP can be observed close to the anode for most water types.

After connecting the electrical support system to the column, a different effect on the physical and chemical parameters was observed to the assumptions. In both parts of the column there was a decrease of pH in the entire profile of approximately 1 unit. It was possible to observe a decrease in ORP of approximately -50 mV on the cathode side and a significant decrease of approximately -150 mV on the anode side. The physical and chemical parameters showed very similar conditions on both the anode and cathode side of the column, with an average pH of approximately 7 and ORP of approximately -350 mV. These values are also computed by the calculated coefficient L_Fe$^{2+>>3+}$, which shows that after connecting the electrical current the reduction conditions increase by approximately 200-300 mV in all of the points of the column, which also corresponds

to the distribution diagram **Figure 6 - right**). These conditions led to a greater decrease in conductivity across the entire column profile. However, it is still possible to observe a slightly higher reactivity on the cathode side.

After connecting the electrical current, the CHC concentration profiles changed on both sides of the column, where in terms of the CHC concentrations there was an approximately two-fold increase in the reactivity on all of the parts of the column. The main improvements can be observed on the parts of the column nearer the electrode, where the effect of the electrical current was more pronounced as expected. The improvement in reduction was more pronounced for the less chlorinated DCE, which is more difficult to reduce by Fe alone. On the anode side, the efficiency of the reduction compared to the state prior to connecting the electrical current increased by 49% for DCE, 40% for TCE and 21% for PCE. On the cathode side the efficiency increased by 65% for DCE, 40% for TCE, and 27% for PCE.
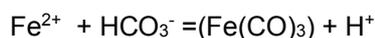
In contrast to the original assumption that there would be a synergistic effect of the electrical current only near the cathode, it was shown that the improvement also occurs near the anode. In the future, this could be used in the design of polygons at sites.

Interpretation with the geochemical model

For a deeper understanding of the processes occurring inside the column, the results were further interpreted using the geochemical model. It was determined that the bicarbonates present have a major influence on the behaviour of the entire system, which also controls the course of the reactions forming crystalline phases based on the amount of dissolved iron present in the solution. In addition, calcium and magnesium (and of course iron) are also involved in the precipitation of the mineral phase. Pyrite precipitates in a sufficiently reductive medium, and ammonium ions also form the dominant form of nitrogen in this environment. Sodium, potassium and chloride compounds do not enter the reaction.

Prior to connecting the electrical current, magnesium carbonate and calcium carbonate precipitate inside the column in areas with higher pH. Ferrous carbonate begins to precipitate after the dissolution of a sufficient amount of iron. After connecting the electrical current, these minerals continue to precipitate but the conditions in the system change and they begin to shift to areas with a lower redox potential, where the system is controlled by the reaction due to the formation of ferrous disulphide and precipitation of sulphates from the solution.

The physical and chemical profile of the column shows that connecting the electrical current leads to a drop in pH to approximately the same value on both sides. This is inconsistent with the results of the previous laboratory tests and field observations, where there is an increase in pH due to electrolysis in the area of the cathode. In the case of the reactive column, the physical and chemical parameters and chemical composition of the inlet water are controlled by the equilibrium between the dissolved ions HCO_3^-, Fe^{2+} and the mineral siderite (ferrous carbonate) due to a release of H^+ to the solution according to equation

$$Fe^{2+} + HCO_3^- = (Fe(CO)_3) + H^+$$

The presence of H^+ ions in solution decrease pH value around the cathode. This explanation was confirmed also with the fact, that in the cathode space of column at the end of experiment This is also explained by the fact that the port near the cathode in the cathode space of the column clogged up at the end of the experiment, which may be the result of precipitation of the siderite.

3.   CONCLUSIONS

The presented laboratory test methodology was very useful for studying the processes of the remedial application of iron particles supported by an electric current. The tests provided several new facts that were previously unknown or were subsequently clarified. The methodology was successfully used for the verification

of the remedial technique on other waters with a different geochemical composition and different types of contamination (organic and inorganic).

Compared to the original assumption, whereby a synergic effect of the electric current support on the reactivity of the iron particles was expected only close to the cathode, this effect was also shown to happen in the same size close to the anode. However, for the given type of real water the results were slightly better close to the cathode.

Furthermore, the results showed that for the method of iron particles supported by an electric current, a universal and simple set up of the electric system cannot be formulated for all sites. For each environment it is necessary to know its geochemical (water composition) and hydrological conditions (flow velocity as the main factor), which have a basic influence on the ongoing reduction. This fact was also shown in our case. With respect to the flow velocity and the chemical composition of the water, it is possible to regulate the delivered electrical power on the basis of laboratory tests with specific water so that, at a sufficient distance from the electrodes, the reduction conditions are in the area of stability Fe^{2+}, whereby the applied iron is most efficiently used for the reaction with the contamination.

ACKNOWLEDGEMENTS

REFERENCES

[1]   BENEŠ P., HRABAL J., NOSEK J. et al., 2016: Project report TAČR TA04020431 - Advanced in situ remediation technologies supported by electric field.