

RESULTS OF A PILOT-TEST FOR IN-SITU GROUNDWATER REMEDIATION OF ALKYLLEAD COMPOUNDS IN THE GROUNDWATER

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ABSTRACT

Air-injection-well remediation (AIW) is a innovative technique combining air-lifting and stripping. During AIW operation groundwater circulation is induced and used for remediation. The AIW technique is simple and low in investment and operating costs and a remediation technique which can be used for stripping volatile components as well as for supporting biodegradation (resp. oxygen, nutrients). The AIW method was used in a pilot test at a former chemical plant which produced Alkyllead as anti-knock compounds in gasoline. The technique gives good results for degradation highly toxic organolead compounds in the saturated zone and transforming into inorganic lead. Ideal conditions for in-situ groundwater remediation are hydraulic transmissivities $>10^{-6}$ m/s and low gradients. Technology limitations are higher iron content, high groundwater flow gradients and deep aquifers.

1. INTRODUCTION

The use of leaded gasoline in automobiles for many years, anti-knock compounds like mainly Tetraalkyllead (TEL) or Tetramethyllead (TML) were manufactured in Germany until the end of the 1980's. At a former chemical plant in Germany organolead compounds (Tetraalkyllead, TAL) were spilled during the production process and causes a groundwater contamination. The future use of the land as an industrial area and legal demands required planning an effective remedial design.

Common available remediation techniques like pump-and-treat resp. on-site UV-Light Oxidation could not be used for remediation of organolead by reasons of the high costs and the special behavior (chemical and physical properties) of the contaminants resp. reaction products. Also excavation of the contaminated soil and on-site thermal or biological treatment leads to extremely high remediation costs and/or costintensive constructional requirements. Additionally any exposure of organolead contaminated soil or groundwater requires health and safety measures to an unpayable extent.

Under this circumstances an innovative and simple in-situ-method was applied for groundwater remediation of organolead compounds enforcing the conversion of toxic Akyllead compounds into inorganic lead. The risk potential of inorganic lead is much lower since immobilisation takes place in aquifers with higher carbonatic content.

2. THE AIW PRINCIPLE AND GROUNDWATER CIRCULATION FLOW

The AIW is a combination of two common constructional or remediational techniques, the air-lift pump and a strip reactor. With an air lift pump water can be pumped in a vertical tube using pressurized air injected at the basis of the tube. Due to the buoyancy the air moves upwards and transports water in the same direction (Rautenberg 1972). In the case of an AIW the well tubing is screened below the groundwater table. It is not the aim to pump the water out of the aquifer but to create a groundwater

circulation cell in the aquifer (Fig. 1). The driving force of the groundwater flow is the difference in hydraulic head between the AIW and the surrounding aquifer. It is induced by the air injection.

Before starting the air injection, the pressure at the base of the AIW corresponds to the (hydrostatic) conditions in the aquifer. Regarding the situation immediately after starting the air injection, the table of the water-air-mixture rises above the surrounding groundwater table. At this time water flows out of the AIW along its whole vertical screened section. Reaching transient conditions and assuming, that the table of the air-water-mixture inside the AIW stays at the same level, the water inflow and outflow rate must be the same due to mass continuity. This results in a pressure reduction at the base of the AIW ($\Delta h_{B \text{ base}}$) until the marked areas A_1 and A_2 in Fig. 1 have approximately the same size.

The second technique, stripping, is a common method used for removing volatile compounds from water. The contaminated water is aerated and due to the difference in equilibrium concentrations the volatile compound is transferred to a certain amount into the air (Spindler 1983). For these reasons the injected air is not only the driving force for the groundwater circulation but also the stripping medium for volatile hazardous substances. To visualize the water flow in an AIW a small scale model was assembled with glass spheres and a tracer. Fig. 2 shows the water flow in this container around an AIW in different aquifer types. In a homogenous aquifer a) the water flows out the AIW in the upper section and returns to it at the lower part. In a partly layered aquifer b) a radial displacement of the streamlines occur. In this case the influence increases and the circulation cell widens up.

In the layered aquifer c) type two streamlines are induced, one in each layer. This phenomena means in nature, that contaminant transfer between different layers does not exist. The oxygen concentration around the circulation flow increases due to the air input. In addition liquid nutrients can be used as well to support biological activity inside the circulation flow.

Fig. 1: AIW differences in hydraulic head between the well and the surrounding aquifer due to air injection.

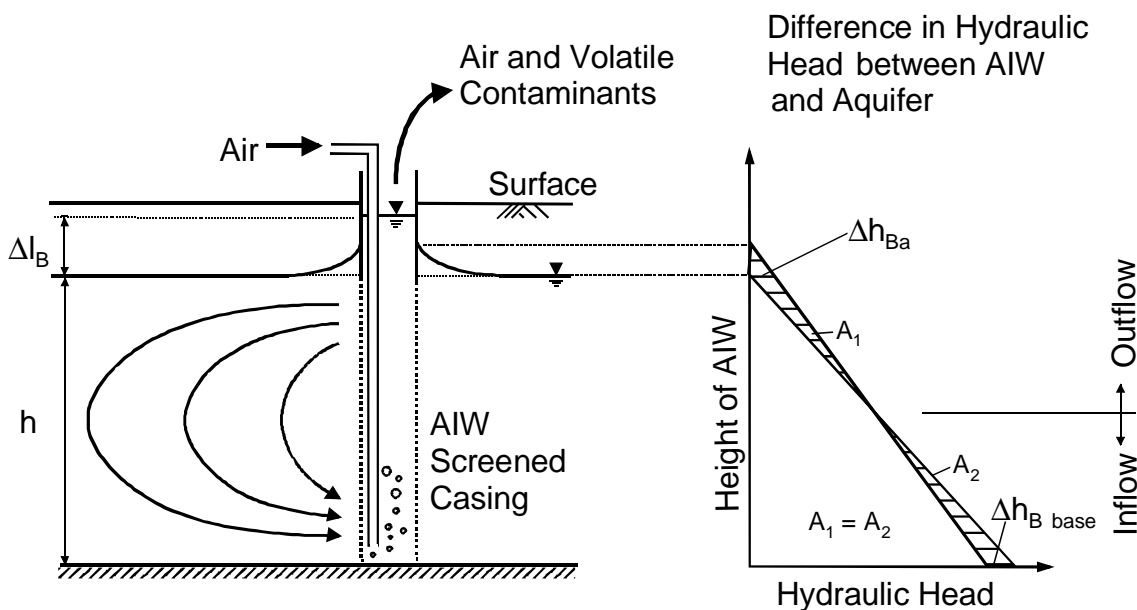
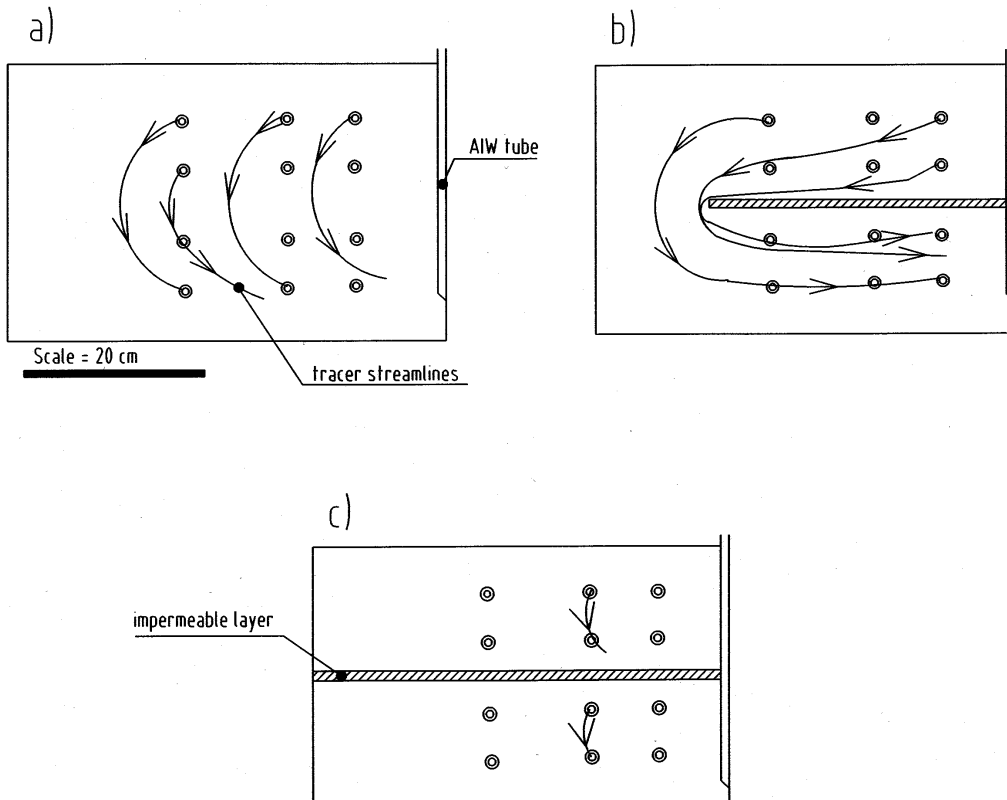


Fig. 2 Streamlines around an AIW (small scale experiment), a) above left: homogenous aquifer, b) above right: partly layered aquifer, c) bottom: layered aquifer.



3. AIW DESIGN

The AIW consists mainly of low cost components. A screened metal tube with a diameter of 2 inches is used in the saturated zone. The air is injected at the bottom of the tube with the use of an oil-free air-compressor. Additional standard periphery components for cleaning the stripped contaminants are standard remediation devices:

A water separator and activated carbon filters or other cleaning devices as well as a flow meter. The hydraulic design and the required air injection rate for the AIW is found in Luber 1999.

4. FIELD STUDY

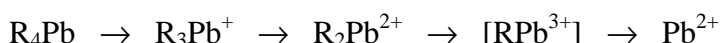
4.1 Basic observations at the site

At the site the original products TEL (Tetraethyllead) and TML (Tetramethyllead) were infiltrated into the saturated zone together with hydrocarbons which were used also during the production processes. Due to the density of TAL it was likely that the groundwater contamination took place throughout the whole aquifer thickness of approximately 50 meters. The presence of hydrocarbons caused fortunately a distribution pattern of the contaminants only in the upper aquifer zone.

Tetraalkyllead is a toxic agent and may be injurious to health if affected directly to skin or incorporation. Therefore a higher risk potential is predicted.

At the site several investigations showed that natural degradation of TAL takes place. The degradation of TAL during time formed mixed soluble alkyllead compounds like Trialkyllead- and Dialkyllead-mixtures, which are spreaded out with the groundwater flow. At the end of the transformation cycle of the organolead compounds inorganic lead is formed. Small scale laboratory tests by Mulroy & Oy (1998) proofed the transformation of TEL by the presence of oxygen. There probably exist two ways of degradation processes, microbiological transformation and hydrolytic reactions.

The decomposition of alkyllead compounds are simply described as follows:



Radojevic and Harrison (1987) concluded that Tetraalkyllead is less stable than Trialkyllead, but the decomposition rates and the mechanisms are not yet well understood.

The solubility of TEL itself is low and so TEL is found in higher concentrations in the soil samples only. Additionally downstream observations in the groundwater showed a very stable diffusion of the groundwater contamination where soluble Alkyllead compounds disappear at the outer downstream edge of the plume. According to the lack of oxygen in the contaminated groundwater plume and the presence of the transformation mixtures it was assumed that microbiological degradation takes place in the whole area. Teeling & Cypionka (1997) underline this findings in a laboratory study that aerobic soil microbes lead to a TEL degradation of high rates.

On the other hand it was observed during demolition work and hydraulic pumping tests on the site that any mechanical or hydraulical influence, ground movements or disturbance of chemical equilibrium release higher amount of organolead from the pore matrices.

In summary it can be assumed, that in this case a remediation technique has to be applied which supports natural biological degradation mechanisms an which does not disturb any equilibrium in a wide range.

4.2 Preliminary investigations and AIW testing

The distribution of the organolead contamination of the soil in the unsaturated and in the saturated zone was well investigated during the past years. According to small diameter drillings and groundwater sampling in different depths the contaminated area now is well known for planning further remediation activities. The subsoil at the site consists of fluvial sand deposits with an hydraulic conductivity of $3,5 \times 10^{-4}$ m/s and a very low gradient of $i = 1$ ‰. The groundwater table is low at approximately 3 m depth. Natural groundwater flow was specified with a tracer test to 70 m per year.

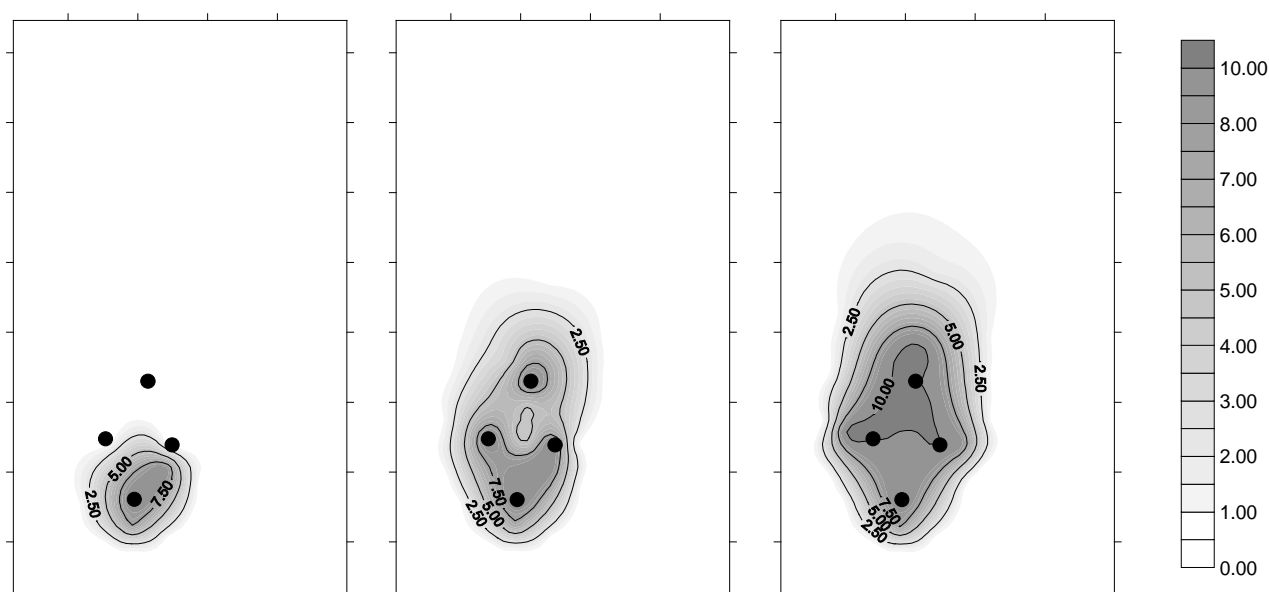
On the basis of the investigation results an AIW testing field with 4 wells and several monitoring wells were installed in an area of higher organolead concentration in the saturated zone. Fig. 3 shows the arrangement of the AIW field (black dots). Groundwater flow is from bottom to the top in fig. 3. The screen casing of the wells are 4 m each, preliminary hydraulic calculations yielded optimal AIW distances of 5 m from each other.

The injected air flow of $1,5 \text{ m}^3$ per hour into each AIW causes a „slight“ water flux through the AIW field of $8,2 \text{ m}^3$ per day. The groundwater table is lifted around the well tubes in consequence of the AIW operation up to $\Delta h = 0,33$ m depending on the air flow rate. For the first four weeks only one AIW

was in operation in order to monitor its influence alone. The whole AIW field was monitored continuously, at least every month. The following monitoring parameters were measured:

- pH value, redox potential, electrical transmissivity, temperature
- bacteria count, hydrogen carbonat and carbon dioxide content (off and on)
- oxygen content
- alkyllead compounds

Fig. 3 Arrangement of the AIW testing field, oxygen enrichment [mg/l] in the groundwater at three different times (left: 27 days, 1 AIW in operation; middle: 63 days, four AIW in operation; right: 272 days, 4 AIW for 245 days in operation).



5. RESULTS

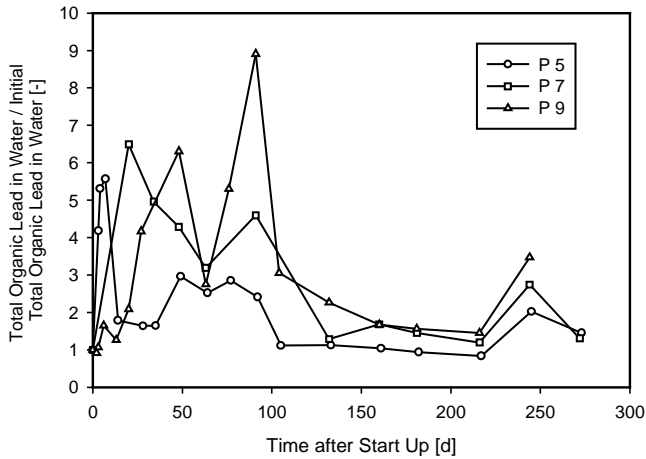
The main aim of the AIW testing field was to enrich oxygen content in the groundwater in order to accelerate natural biological activity and support Alkyllead transformation into inorganic lead. On the other hand it was important to have the operation field under control and keep water flow inside a certain circulation cell, so that no mobilisation occurs.

Fig. 3 shows the oxygen enrichment in the groundwater during maximum operation for 272 days. If the natural oxygen content of about 0,2 – 0,5 mg/l in advance of the AIW operation is considered it is clearly shown with the test that oxygen enrichment in the groundwater takes place continuously up to saturation content of about 10 - 11 mg/l. The oxygen enriched groundwater plume spreads out and moves slightly downstream.

The degradation process started immediately after AIW operation. Whereas the low soluble TEL had appropriate low and more or less constant concentrations before and after the operation of the AIW. The content of the better soluble Trialkyl and Dialkyl compounds increased significantly due to the changed flow situation around the AIW and the degradation process. Fig. 4 shows that during the first 100 days of operation organolead in dead end pores is released significantly to an higher content and is afterwards continuously degraded with further AIW operation. Making stored organolead available inside the circulation cell results also in increasing Tri- and Dialkyllead concentrations (see fig. 5).

Considering monitoring well P5 which is situated in the middle of the AIW field (see fig. 4) this phenomena can be proved.

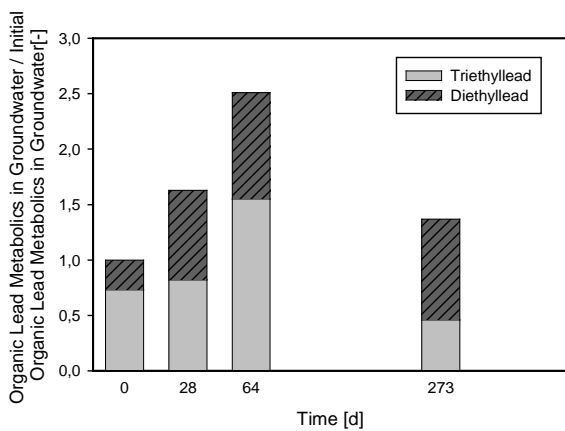
Fig. 4 Total organic lead concentrations in the groundwater versus time.



Running the AIW field for nearly 300 days the concentrations are reduced to a certain level around the starting level, and the released organolead content dissappeared. A further reduction of the concentrations can be expected at the time when adsorbed TEL supply or TEL from dead end pores decreases further.

Furthermore all monitoring wells downstream the AIW field show no arising organolead concentrations nor oxygen enrichment although one would expect this regarding the groundwater velocity of 70 m per year.

Fig. 5 Concentration of organic lead compounds in the groundwater at a monitoring well in the center of the AIW field.



6. CONCLUSIONS

The results of the AIW testing field at the organolead contaminated site showed good oxygen supply to the groundwater and causes Alkyllead transformation in a sense of enhanced natural attenuation. In addition it was shown that the AIW remediation works inside the circulation cell and downstream mobilisation of contaminants does not occur in a risky manner.

AIW groundwater remediation can be used for volatile components as well as for supporting biodegradation. Low investment and operation costs compared to conventional remediation methods (resp. pump and treat, on-site/off-site treatment) is a further advantage. Limitations of AIW are hydraulic conductivities higher than 10^{-6} m/s and higher iron content which affords nitrogen instead the use of air. This increases the operating costs. The use of AIW in aquifers with higher gradients and in deep aquifers is not recommended.

7. REFERENCES

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