Theme: A: Restoration
Thematic Session (LeS): ThS_A21: Non conventional concepts (1)

REMEDIATION OF PESTICIDE CONTAMINATION BY *IN SITU* ALKALINE HYDROLYSIS – A NEW SOIL REMEDIATION TECHNOLOGY

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Summary
A novel remediation technology consisting of a treatment train of enclosure, *in situ* alkaline hydrolysis and pump-and-treat has been proposed to clean-up a large, pesticide-contaminated site in Denmark. The site was in the 1950'ies and 1960'ies a large chemical dumpsite. Today, the area is heavily contaminated by 200-300 tons of primarily organophosphorous pesticides, mainly the highly toxic parathion. A new remediation technology is now being developed to remediate the site to a point where the threat to the aquatic environment is eliminated. In 2007-2008, an *in situ* pilot-scale experiment with alkaline hydrolysis was performed. The experiment included the construction of a 4 x 4 meter test field, infiltration of 30 m^3 of diluted caustic soda into the subsurface and 15 monitoring wells to assess the progress of the alkaline hydrolysis of parathion. Furthermore, the sediment's buffer capacities and geochemical changes due to high pH-values were investigated. The results of the experiments indicate that *in situ* alkaline hydrolysis may be a suitable low-cost technology for full-scale remediation of the site; however, further assessment of the efficacy of the method is required.

Introduction and background information

Soil degradation is a serious problem in Europe. The soil is subject to a number of threats such as erosion, floods, landslides, decline in organic matter, sealing, compaction and contamination. The European Commission estimated in 2006 that the number of potentially contaminated sites in Europe is 3.5 million.

In the Soil Framework Directive from 2006, it is proposed that Member States should establish an inventory of contaminated sites in Europe, and in addition that the Member States should over time ensure remediation of contaminated sites that may pose a risk to human health or the environment. Member States are encouraged to develop new research-based remediation technologies and to work on methods to decide on restoring to a level of functionality.

Cleaning up contaminated water and soil is a desirable part of any obsolete pesticide disposal operation. But dealing with contaminated soil is a costly, technically complex and difficult task. Limited funds for remediation usually focus first on removal or containment of the source of contamination and decontamination of soil and water is generally addressed on the basis of risk analysis when additional funds are available.

The site called "Groyne 42" in Denmark is an old pesticide dumpsite, heavily contaminated with 200-300 tons of chemicals, mainly the organophosphorous insecticide parathion.

The deposition period was from 1953 – 1962 where chemical waste was deposited between two sand dunes close to the North Sea. The chemical waste was dumped at the site mainly by the agrochemical company Cheminova situated nearby, but some deposition was also made by the state.

In 1971 and in 1981, the site was exposed by erosion and partial remediation was carried out. In 1971 after a huge storm had exposed the site, 1250 m^3 contaminated sand was removed, and the rest of

the site was covered by an asphalt cap. In 1981, another storm damaged the asphalt cap. At that time, 1200 tons of chemicals situated above groundwater level were removed. The remaining of the contamination at the dumpsite was now located under the groundwater level. It was covered with sand, and it was at the time concluded that the remaining contamination no longer posed a problem.

In 2000, it was discovered, however, that a heavy odour came from the site. New investigations with drillings and chemical analysis of soil and groundwater samples showed that the dumpsite still posed a threat to the environment and that 200-300 tons of pesticides and other chemicals remained in the soil and groundwater.

A detailed investigation to identify the exact location of the contamination in the saturated zone and the amount of contaminants remaining was completed in 2005. Following several years of characterization, it was decided that the site should be placed under hydraulic control as a temporary measure by installing a sheet piling enclosure and a membrane cap. The purpose of the enclosure was to prevent further leaching of toxins to the seawater. A treatability study involving six potentially viable remediation technologies was carried out concurrently. A novel treatment train consisting of *in situ* alkaline hydrolysis and pump-and-treat was selected for pilot-scale testing.

Figure 1 shows a principle sketch of the contaminated area as it looks today.

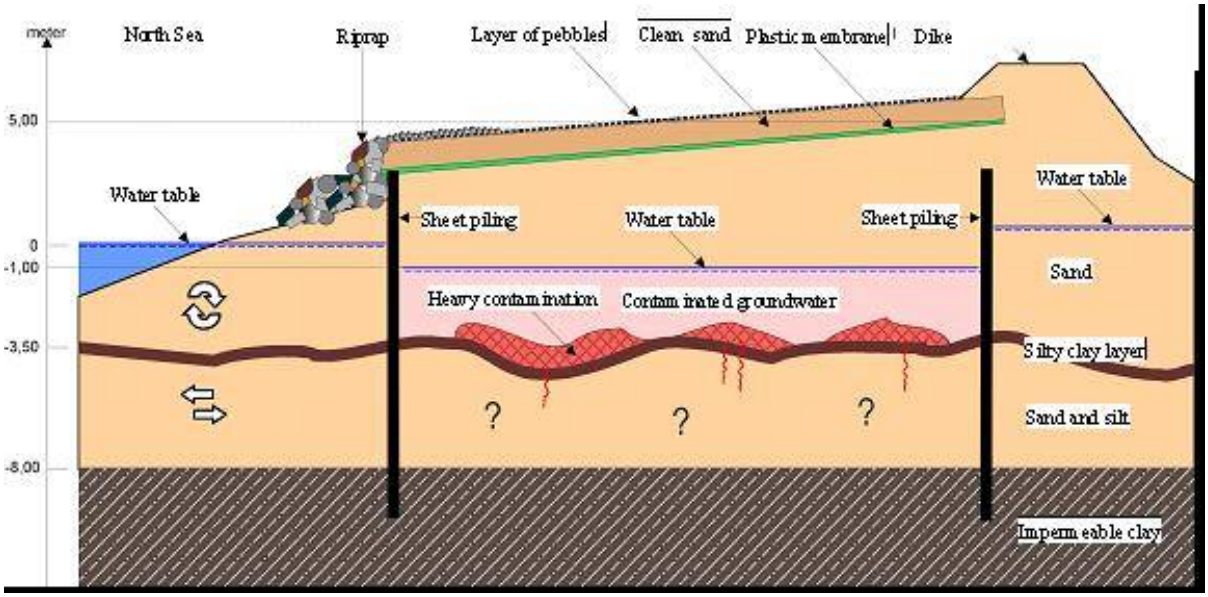

Figure 1: principle sketch of the enclosed site.

The photos in Figure 2 show the geographical location of the site.

Figure 2. Photos of the location of the site in Denmark. The former chemical dumpsite is located right on the beach close to the North Sea. In the lower right photo is seen the iron sheet piling enclosing the contamination.

The principles of *in situ* alkaline hydrolysis

The chemistry

The site is heavily contaminated with 200-300 tons of the highly toxic organophosphorous insecticides parathion, methyl parathion and similar compounds. The compounds have low water solubility and absorbs strongly to the soil. Increasing pH in the subsurface to about pH 12, by infiltration of diluted caustic soda, induces alkaline hydrolysis of the organophosphorous compounds (Figure 3). The major hydrolysis products *p*-nitrophenol (PNP) and O,O-dimethyl-thiophosphoric acid (MP2) or O,O-diethyl-thiophosphoric acid (EP2) have relatively low toxicity, are water soluble and can be removed from the subsurface by pump-and-treat.

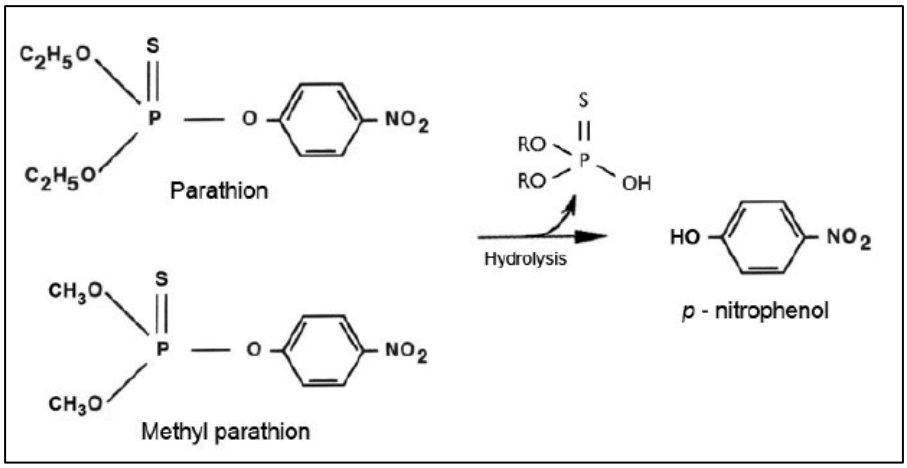

Figure 3. Chemical reaction showing the principle of the alkaline hydrolysis of organophosphorous pesticides.

It is well described in the scientific literature that alkaline hydrolysis can be used to degrade organophosphorous insecticides such as ethyl-parathion, methyl-parathion, sulfotep and malathion to less toxic and water soluble metabolites. The method has been used for many years by agrochemical companies that produce organophosphorus pesticides to neutralise the compounds upon accidental spills, but also as a pre-treatment of wastewater containing organophosphates before it is led to the biological wastewater treatment plant.

However, *in situ* alkaline hydrolysis has not previously been used as a technology to remediate groundwater and aquifer sediments contaminated with organophosphorous insecticides.

The treatment:
The envisioned strategy for full-scale remediation is shown in Figure 6 and involves an initial lowering of the groundwater table within the sheet piling. This is possible, since leakage from the surrounding areas into the encapsulated 20,000 m^2 area is less than 3 m^3/day. The next step is infiltration of diluted caustic soda through injection points. The geometry of these injection points for the delivery of caustic soda must be carefully planned to maximize contact in the hot spots. The progress of the alkaline hydrolysis is then monitored for several months. The groundwater containing the mobilized water soluble hydrolysis products is then pumped from the aquifer, neutralized and treated in a nearby wastewater treatment plant. Due to the sheet piling this pumping cause the water table to fall as the enclosed area is drained. Infiltration of caustic soda followed by pump-and-treat is then repeated as necessary. The full-scale treatment of the site will probably take 4-5 years.

When hydrolysis is complete, the aquifer is refilled with buffered water to ensure neutralization of any remaining caustic soda in the aquifer.

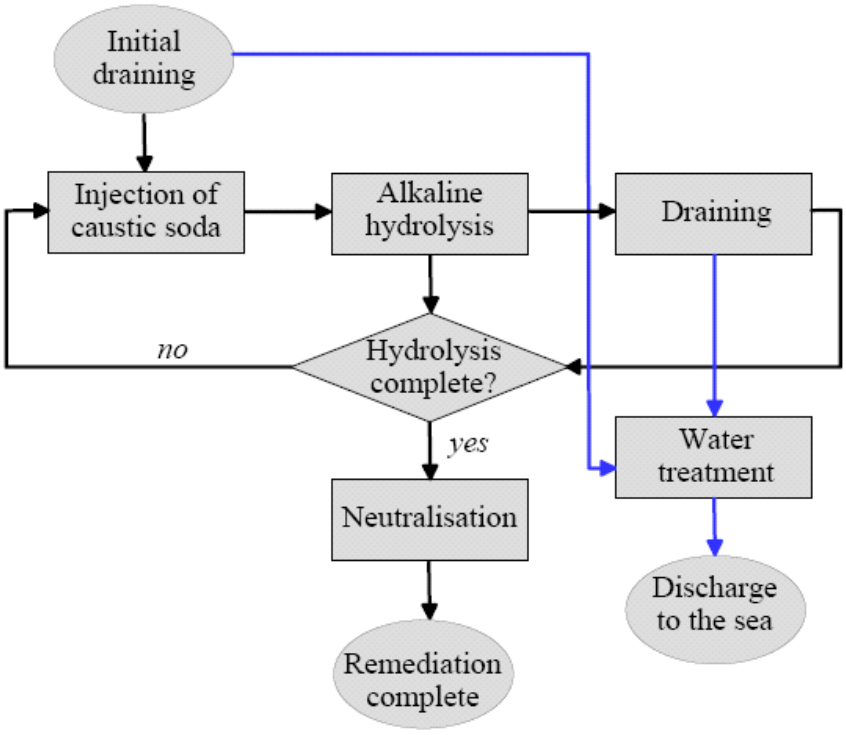

Figure 4. The proposed strategy.

Experiments carried with alkaline hydrolysis:

In 2005-2006 a series of laboratory test was carried out at pH 10 and 13 to determine the treatability of the contamination (Ramsay and Elkjær, 2006). Based on these results, it was decided to design a larger *in situ* experiment with alkaline hydrolysis in order to test the technology under field conditions.

Thus, in 2007-2008, Central Denmark Region and the Danish Environmental Protection Agency carried out a small-scale field study testing the method *in situ*.

The aims of the field test were:

- To demonstrate *in situ* that a solution of diluted caustic soda can be delivered effectively subsurface, and that pH aquifer sediments can be raised and kept at pH >11 for a prolonged period of time.

- To demonstrate *in situ* that alkaline hydrolysis is a suitable method to remediate soil and groundwater contaminated by organophosphorous pesticides.

The test field consisted of a central well and 5 well clusters surrounding the central well at a distance of 2 meters. Each cluster is composed of 3 separate wells, screened at different depths. A cross-section of the test field is shown in Figure 5. A sonic well-drilling method was used to enable the collection of undisturbed cores for detailed geological evaluations and sampling.

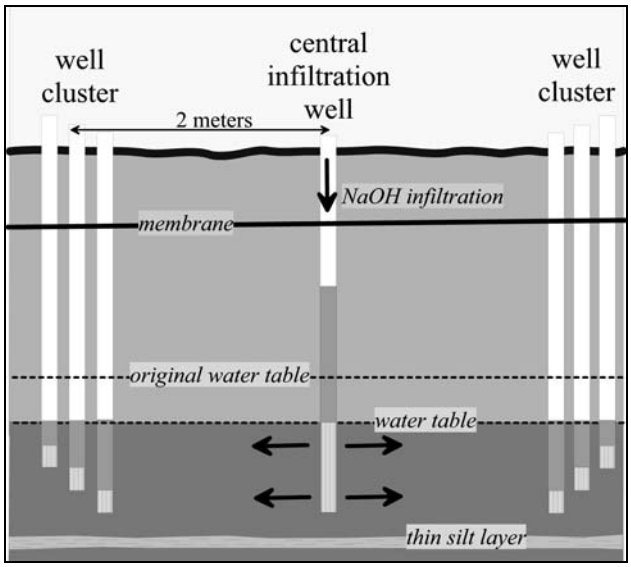

Figure 5: Design of field experiment with alkaline hydrolysis

Prior to the design of the field experiment, studies on the geochemistry and the buffer capacity of the sediment were carried out. The results of these studies are described by Hvidberg *et al.* (2008).

Results

In summary the field experiment with *in situ* alkaline hydrolysis demonstrated that:

- pH in of water sampled from the screens just above the thin silt layer (where the contamination is located) was raised to >11, and kept at this level for over 20 months (Figure 6).

- The concentration of the parathion hydrolysis products (EP2 and PNP) in the water of the observation wells increases gradually for 17 months after NaOH injection, whereafter a stagnation is observed (Figure 7 and 8).

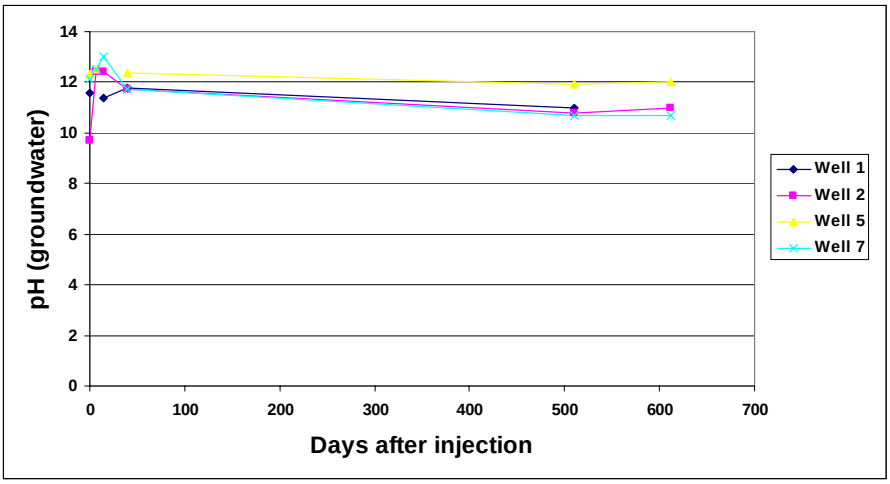

Figure 6. pH in the observation wells after NaOH injection

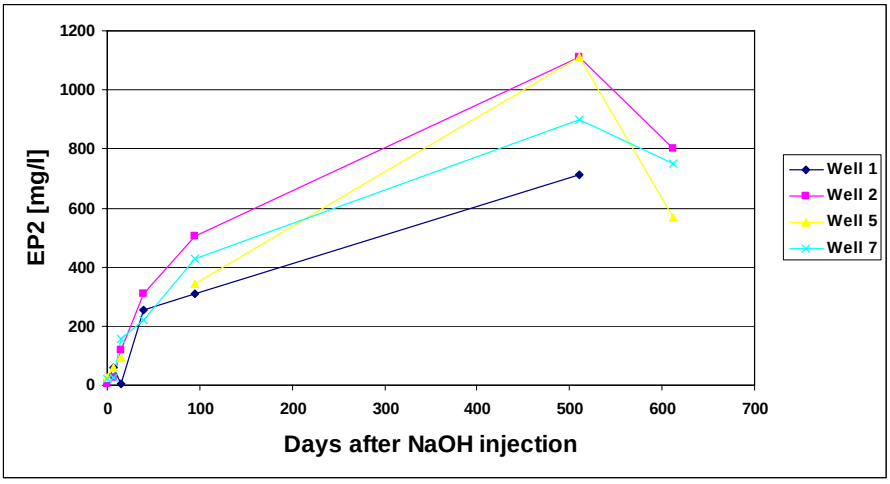

Figure 7. Concentration of the ethyl-parathion breakdown product "EP2" in the observation wells after injection with NaOH.

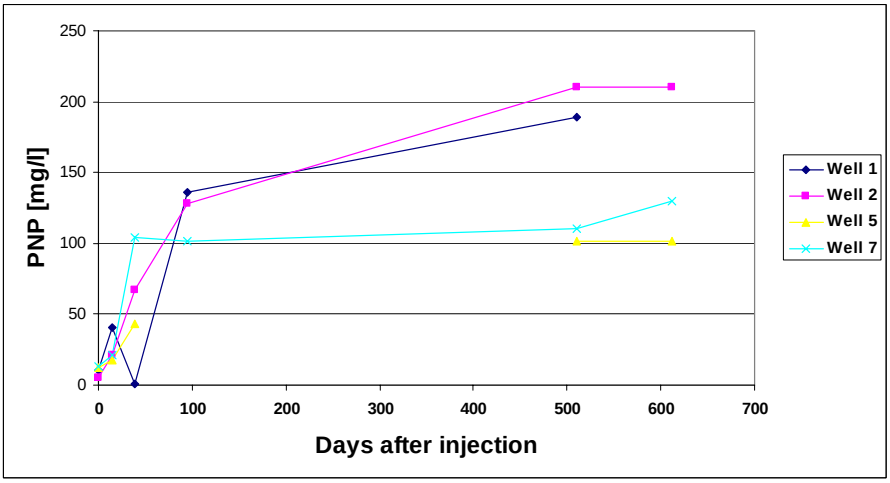

Figure 8. Concentration of the ethyl-parathion breakdown product "PNP" in the observation wells after injection with NaOH.

Conclusion
The field experiment generally indicates that a treatment train consisting of *in situ* alkaline hydrolysis and pump-and-treat may be suitable for remediation of contamination at the Groyne 42 site. However, before decision on full-scale remediation using this technology can be taken, the effectiveness of the method (mass removal) needs to be quantified in more detail.

Perspectives
The technology "*in situ* alkaline hydrolysis" tested in this study can potentially be used as a cost-effective method to remediate certain pesticide contaminated areas, although further development of the method is required. The technology can prove to be inexpensive compared to traditional remediation technologies and may potentially facilitate a decrease in the cost of the implementation of the Soil Framework Directive, and at the same time improve soil restoration and environmental protection.

In a new project named "NorthPestClean" running from 2010-2014 Central Denmark Region and the Danish Environmental Protection Agency will continue to develop the *in situ* alkaline hydrolysis technology.

The objectives of the new project are:

- The effectiveness of *in situ* alkaline hydrolysis will be quantified in field studies. The field studies will be carried out in four new pilot test cells (each 100 m^2) constructed as areas encapsulated by a 14m deep steel sheet piling.

- So-called enhancement technologies will be tested side-by-side in the four test cells with the purpose of improving delivery of the diluted caustic soda in the soil and enhancing contact between the contaminants and the alkaline solution post delivery.

- Measurable remediation stop-criteria will be established based on an environmental risk assessment.

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Enclosure, Alkaline Hydrolysis and Bioventing.