

# Co-treatment of Groundwater Contaminated by Hexacyanoferrate and Domestic Waste Water

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## INTRODUCTION

In many places in the Netherlands, soil and groundwater are polluted by hexacyanoferrate. The main sources of soil and groundwater pollution by hexacyanoferrate are former coal gasification sites. Sources of minor importance are: (former) land fill sites, chemical industries, pesticide industries, photo industries and depots of road de-icing salts. Rehabilitation of these sites through treatment of soil and groundwater often includes the removal of groundwater.

Polluted groundwater will normally be discharged to surface water, either directly or indirectly via a sewer system and a sewage treatment plant. Water quality boards require that this groundwater be treated before being discharged to a sewer system or to surface waters, which commonly demands expensive solutions. As far as discharge to surface water is concerned, on-site treatment can be considered as inevitable and reasonable. However, when groundwater is to be discharged into a sewer system, the necessity of on-site pre-treatment is not always obvious. Waste water collected by a sewer system, and therefore also groundwater, will be treated in a sewage treatment plant anyhow. Combined treatment of polluted groundwater and domestic waste water can be an interesting and cost saving alternative. However, pre-treatment is often officially required because of uncertainties about:

- the possible toxic effects of the pollutants on the biological sewage treatment processes;
- the amount of pollutants removed in the sewage treatment plant;
- the possible deterioration of sludge quality.

Up to now not much effort has been made to quantify these aspects. This seems strange, because only when this kind of information is available, discharge of polluted groundwater with or without pre-treatment can be compared with respect to both environmental and economical impacts.

In this research project the possibilities of a combined treatment of groundwater polluted by hexacyanoferrate and domestic waste water were investigated in bench-scale treatment systems. The bench-scale water treatment systems consisted of either an activated sludge treatment or an activated sludge treatment with simultaneous chemical phosphate removal and effluent filtration. The research was focused on biological treatment systems as 99% (by volume) of domestic waste water is treated in such systems in the Netherlands. Digestion of surplus sludges, incineration of dried sludges

and extraction of hexacyanoferrate from dried sludges by leaching were also part of this research project.

The results of this research help to answer the question of whether combined treatment of groundwater polluted by hexacyanoferrate and domestic waste water is an alternative to be considered in the practice of soil sanitation.

## EXPERIMENTS

Three bench-scale activated sludge reactors – completely mixed, continuous flow, with internal sludge recirculation – were used as experimental biological sewage treatment plants. These reactors were fed with domestic waste water to which hexacyanoferrate(II) was dosed. For simultaneous chemical phosphate removal, a solution of ferrosulphate was dosed into the aeration chamber. Samples of influent, effluent and activated sludge were collected and analyzed.

A bench-scale dual media filter was used as an experimental effluent filtration plant. Filtration experiments were carried out with and without a dosage of hydrochloric acid and ferrosulphate into the filter influent. The purpose of this dosage was to improve the removal of cyanide compounds in the filter by the formation of a Prussian blue-like mineral. Samples of filterinfluent and effluent were collected and analyzed. During filtration the pressure in the filterbed was measured.

Sludge digesting experiments were carried out in a two-stage sludge digester. Only the first stage of the digester was heated. Surplus sludges originating from both the conventional activated sludge treatment and the activated sludge treatment with simultaneous chemical phosphate removal were digested.

Dried surplus sludges originating from the activated sludge treatment with simultaneous chemical phosphate removal, from the digester and from the filter were incinerated for one hour at a temperature of 800°C.

Experiments to investigate the amount of hexacyanoferrate that can be leached out of dried sludges were carried out with acidified distilled water and artificial groundwater as leaching fluids. The same dried sludges were investigated as in the incineration experiments.

## RESULTS AND DISCUSSION

The average removal of hexacyanoferrate in an activated sludge process without simultaneous chemical phosphate removal varies from 17% to 45%. This variation in the removal of hexacyanoferrate is mainly caused by variation in

the sludge loading (0.98 to 0.25 kg COD/kgSS.day). The influence of the cyanide loading (4.1 to 34.3 g CN/kgSS.day) on the removal of hexacyanoferrate is of less importance.

The average removal of hexacyanoferrate in combination with simultaneous chemical phosphate removal is much better. In this case, the average removal is 61% (sludge loading: 0.19 kgCOD/kgSS.day and cyanide loading: 1.9 to 6.4 gCN/kgSS.day).

As most of the hexacyanoferrate in the effluent of activated sludge process with simultaneous chemical phosphate removal is dissolved, effluent filtration without a dosage of hydrochloric acid and ferrosulphate into the filter influent leads not to significant removal of hexacyanoferrate in the filter.

With a dosage of hydrochloric acid and ferrosulphate into the filter influent, the average removal of hexacyanoferrate in the filter is 95%. The overall average removal of hexacyanoferrate in the entire treatment system – activated sludge process with a simultaneous chemical phosphate removal and effluent filtration – is 98%, which leads to an average content of total cyanide in the final effluent of 0.18 mg CN/l when the average content of total cyanide in the influent of the treatment plant was 8.9 mg CN/l. Activated sludge treatment with simultaneous chemical phosphate removal and effluent filtration both remove half of the content of hexacyanoferrate in the influent.

With a dosage of hydrochloric acid and ferrosulphate into the filter influent the removal of hexacyanoferrate takes place mainly on the surface and in the upper part of the filterbed.

The cyanide content of the filter sludge is very high, up to 330 gCN/kg, being mostly Prussian blue. This figure heavily exceeds the Dutch standard (0.05 g CN/kg) for chemical cyanide wastes (up to 6600 times). The Dutch standard is based on the extreme toxicity of free cyanide (HCN and  $CN^-$ ). However, the toxicity of hexacyanoferrate and Prussian blue is negligible. Hence, the situation is not as bad as it seems.

The presence of hexacyanoferrate in the influent of the activated sludge process has no adverse effects on the biological sewage treatment processes. Due to the presence of hexacyanoferrate in the influent, the efficiency of the simultaneous chemical phosphate removal decreases about 15% in comparison with the phosphate removal in an activated sludge treatment with simultaneous chemical phosphate removal without hexacyanoferrate in the influent.

The amount of hexacyanoferrate bonded to the solid phase of the sludge increases during sludge digesting. The total cyanide concentration in the sludge water decreases as a consequence.

The observations during the digesting experiments do not deviate from the characteristics of a sludge digester in practice. However, since the experiments were carried out with one sludge digester only, it is not possible to make soundly based statements concerning the influences of hexacyanoferrate on the digesting process.

Incineration during 1 hour at a temperature of 800° C of dried sludges produces ashes with a cyanide content below the detection limit (0.05 mg CN/kg). Before incineration, the cyanide content of the dried sludges varied from 18 000 to 104 000 mg CN/kg.

The leaching experiments resulted in small loads of leached total cyanide. No influence was observed regarding the used leaching fluid (acidified distilled water or artificial groundwater). Although the leached loads are small, the total cyanide concentrations in the leaching fluid are high. Hence, dumping, without precautions, of dried sludges containing hexacyanoferrate, cannot be tolerated.

## CONCLUSIONS

The main conclusion of this research project is that combined treatment of groundwater polluted by hexacyanoferrate and domestic waste water in an ordinary treatment plant is possible, provided that effluent filtration with a dosage of hydrochloric acid and ferrosulphate into the filter influent is part of the treatment system. With a total cyanide concentration of about 10 mg CN/l in the influent, a 98% removal of hexacyanoferrate is realizable. Higher total cyanide contents in the mixture of polluted groundwater and domestic waste water are unlikely in the Netherlands. Simultaneous chemical phosphate removal as such is not really necessary. However, simultaneous chemical phosphate removal relieves the filter, removing about 50% of the hexacyanoferrate from the influent.

In the event that effluent filtration forms no part of the sewage treatment system, on-site filtration of the polluted groundwater with a dosage of hydrochloric acid and ferrosulphate into the filter influent is a realistic alternative. When hexacyanoferrate is the only pollutant, direct discharge of the filtered groundwater to the surface water will be acceptable.

When hexacyanoferrate is not the only pollutant, then the filtered groundwater may better be discharged into the sewer system, receiving further treatment in the sewage treatment plant.

Other conclusions regarding the investigated water treatment processes are:

- the presence of hexacyanoferrate in the influent has no adverse effects on the biological sewage treatment processes;
- in activated sludge treatment plants with simultaneous chemical phosphate removal, the removal of phosphate will be reduced about 15% when hexacyanoferrate is present in the influent.

Conclusions regarding the produced sludges are:

- the bonding of hexacyanoferrate to the solid phase of the sludge increases during digesting;
- incineration of dried sludges produces ashes which do not contain cyanide;
- leaching of dried sludges produces small loads, but high concentrations, of total cyanide in the leaching fluid.

Dumping, without any precautions, of dried sludges containing hexacyanoferrate is not generally acceptable.

## BIBLIOGRAPHY

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