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MODELEXPERIMENTS ON THE BEHAVIOUR OF CYANIDE AND BARIUM IN A LANDFILL AND IN THE SOIL

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ABSTRACT

On several locations in The Netherlands cyanide- and bariumcontaining waste has been dumped. In order to study the behaviour of cyanide and barium in a landfill and the soil beneath it, column experiments were set up in the laboratory. Six columns were filled with a sand layer, on top of which a layer of domestic waste was placed. In the waste layer bariumcyanide was introduced at different heights. The groundwater level in the columns was different. From the results it is concluded that most of the cyanide was converted. 4 to 22% of the cyanide leached out. Barium was mostly adsorbed on organic matter and partly precipitated as carbonate and sulphate, while 18 to 39% leached out. Leaching of cyanide is minimized when the cyanide and barium containing material is placed on top of a thick layer of domestic waste. Under these circumstances leaching of barium is initially small but increases rapidly in a later stage.

INTRODUCTION

On several locations in The Netherlands waste containing cyanide and barium from metal processing firms has been dumped. From investigations in Deurne, The Netherlands (Stuurgroep Cyanide Deurne, 1977) and from publications (Stiff, a.o., 1976, and Newton, 1977), it appeared that little is known about the behaviour of cyanide and barium in the landfill and the soil beneath it. Therefore column experiments were set up to investigate the behaviour of cyanide and barium under controlled conditions.

Table 1. Cyanide balance

Percent cyanide found in	high groundwaterlevel salt 'high'	high groundwaterlevel salt 'low'	low groundwaterlevel salt 'high'	low groundwaterlevel salt 'low'
Gas phase	2%	0%	0%	0%
Waste layer	11%	4%	11%	5%
Salt layer	0%	0%	0%	0%
Sand layer	0%	6%	0%	2%
Percolate	4%	17%	14%	22%
Recovery	16%	27%	25%	29%
Conversion:				
to NH_4^+, org-N	95%	22%	6%	13%
to N_2	-	51%	69%	58%

Table 2. Barium balance

Percent barium found in	high groundwaterlevel salt 'high'	high groundwaterlevel salt 'low'	low groundwaterlevel salt 'high'	low groundwaterlevel salt 'low'
Waste layer	31%	19%	22%	8%
Salt layer	9%	11%	15%	28%
Sand layer	18%	30%	2%	12%
Percolate	22%	39%	23%	18%
Recovery	80%	99%	62%	66%

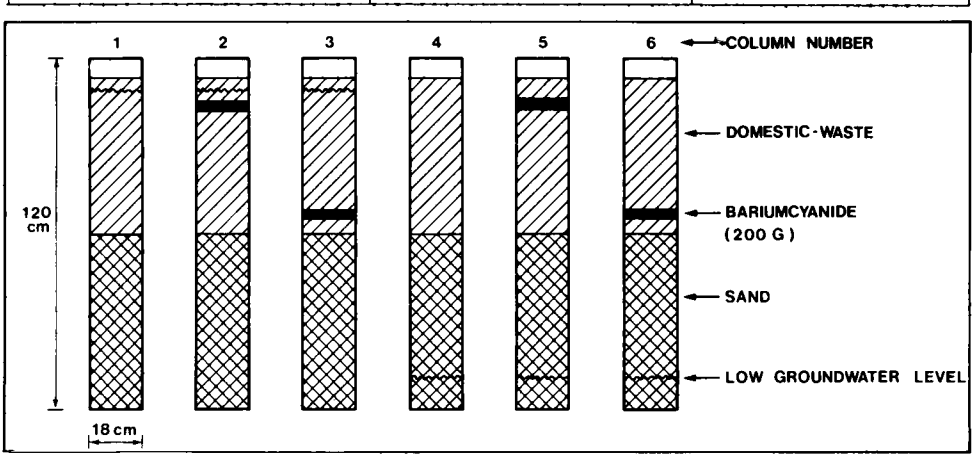

Figure 1. Composition of the 6 columns

THEORETICAL ASPECTS

In the landfill- and soil material the cyanide ion can undergo the following reactions:

- conversion to HCN (volatile) at pH < 9.2
- conversion to NH_4^+, org-N (or NO^-_3, NO^-_2, N_2)
- complexation with Fe^{2+} or Fe^{3+} : $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$
- precipitation of $Fe_4\left[Fe(CN)_6\right]_3$ (Prussian blue)
- conversion to SCN^- or OCN^-
- complexation with trace elements

The barium ion can undergo the following reactions:

- precipitation with carbonate : $BaCO_3$
- precipitation with sulphate : $BaSO_4$
- adsorption on organic matter or clayminerals
- complexation with fatty acids : $BaAc^-$, $BaAc^\circ_2$

MATERIALS AND METHODS

Six columns, each with a diameter of 18 cm, were filled with a sand layer of 60 on top of which a layer of 50 cm of ground domestic waste was placed. In order to investigate the influence of the groundwater level, a high waterlevel was maintain in three columns and a low waterlevel in the remaining three fig. 1.
In both cases one column contained 200 g of $Ba(CN)_2$ applied as a layer in the upperpart of the waste layer, a second column contained 200 g of $Ba(CN)_2$ introduce as a layer in the lower part of the waste layer and a third column without $Ba(CN)_2$ was used as a check. The columns were percolated with demi-water with a flux of 10 mm/day.
The percolate and the gasphase above the columns were periodically sampled and chemically analysed. After a percolation period of 7 months the soil and waste material was sampled and chemically analysed.

RESULTS

The cumulative quantities and percentages of cyanide (mainly free cyanide) that leached out of the columns are given in Figure 2.
The results indicate that large quantities of cyanide are leached mainly in the beginning of the experiments.
The cyanide balance (see Table 1) shows that 71 to 84% of the applied cyanide has converted to nitrogen compounds, because no cyanate or thiocyanate was found in th percolate.
Leaching of cyanide was least in the column with a high groundwaterlevel, the salt being placed in the upper part of the waste layer, probably because of the long

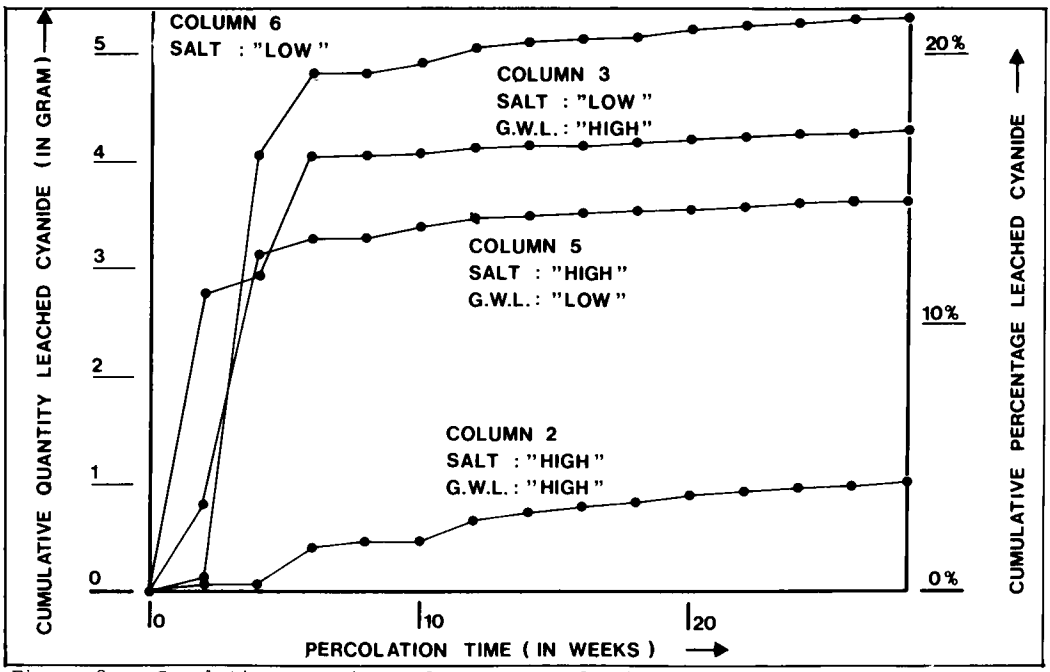

Figure 2. Cumulative quantity and percentage leached cyanide vs percolationtime. 25 gram of cyanide was applied to the column

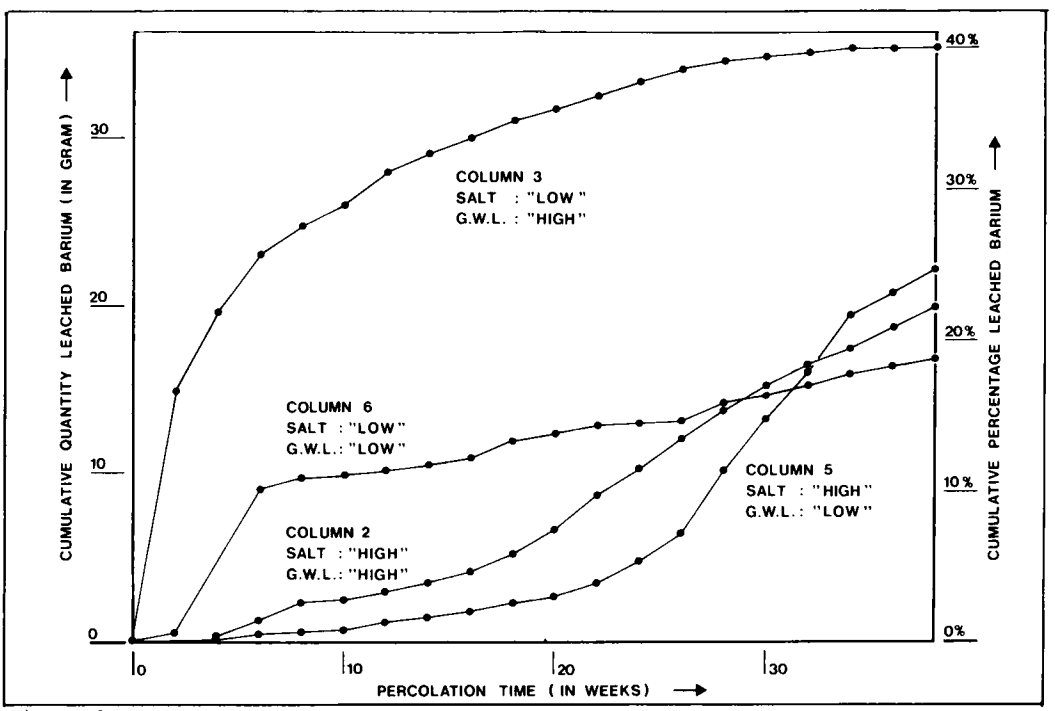

Figure 3. The cumulative quantities and percentage leached barium vs the percolation-time. 90 gram of barium was applied to each column

contact time of cyanide ions with domestic waste.

The cumulative quantities and percentages of barium that leached out of the columns are given in figure 3.

Leaching of barium is delayed substantially when it is introduced in the upper layers of the waste, but towards the end of the percolation time leaching slowly increased. The place where the bariumcyanide is introduced in the waste layer appears to be of great importance.

The barium-balance is given in Table 2. Barium, that was found on the place where the salt was introduced, was shown to be converted to bariumcarbonate. In the waste layer barium was adsorbed for a large part at organic matter and for a small part precipitated as carbonate and sulphate.

CONCLUSIONS

Cyanide leached out of the column for 4 to 22%, mainly as free cyanide ion; precipitated, probably as Prussian blue, for 7 to 13% while the remainder must have been converted to nitrogen. Barium leached for 18 to 39% and was partly adsorbed on organic matter and partly precipitated as carbonate and sulphate.

The least leaching of cyanide occured in the column with high groundwater level where the bariumcyanide salt was put in the upper part of the column.

A substantial amount of barium leached out of all columns, but leaching was delayed when the salt was introduced in the upper layers of the waste. Monitoring of the cyanide and bariumconcentrations in the groundwater beneath the landfill, is recommended for a long time after the dumping under all circumstances investigated.

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