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Geochemical interactions of a saline leachate with Molasse at a landfill site: A case study

CATHERINE MARTINSON

Key words: Molasse, toxic waste, groundwater

ABSTRACT

The impact of the toxic waste repository of Kölliken (AG) on groundwater has been studied for eight years. The landfill lies in the aquitanian Molasse, which is composed primarily of fractured marls interlayered with calcareous sandstone banks. Highly saline leachate migrates into the groundwater through preferential flowpaths. Part of the interpretative work done on field data includes the assessment of the Molasse as a geochemical barrier. The goal of this study is to determine what are the possible reactions controlling the geochemical interactions between the Molasse and the leachate. Based on the observation of a breakthrough of the leachate into the groundwater, a simplified input (leachate) / output (contaminated groundwater) system was modelled using MINTEQA2, a geochemical speciation model. Modelling results show that: the leachate can dissolve calcite and dolomite (which make up to 30% of the mineral composition of the Molasse); part of the attenuation of manganese and carbonate concentrations are probably controlled by the precipitation of rhodochrosite; the concentrations of calcium and magnesium in the contaminant plume are controlled by cation-exchange (aqueous sodium and potassium present in the leachate exchange with calcium cations occupying the majority of the exchange sites in the Molasse); gypsum precipitates along the flowpath (which was also documented by mineralogical analyses).

RESUME

L'impact de la décharge de Kölliken (AG) sur les eaux souterraines a fait l'objet d'études intensives depuis 1985. Les déchets sont entreposés dans la molasse aquitanienne, qui se compose principalement de marnes fracturées et de bancs de grès (cimenté par de la calcite). Des jus de décharge de salinité élevée migrent dans la molasse de long de chemins préférentiels. Une partie du travail d'interprétation des résultats de mesures et d'analyses chimiques comprend l'évaluation de l'effet de «barrière géochimique» de la molasse. Sur la base d'observations sur le terrain de l'évolution des concentrations dans les eaux souterraines à un point de mesure particulier, un système simplifié comprenant le jus de décharge (input), la molasse (milieu réactif) et l'eau souterraine contaminée (output) est modélisé au moyen de MINTEQA2 (un modèle de spéciation géochimique), afin de déterminer quelles sont les réactions géochimiques dominantes affectant le jus de décharge lors de sa migration à travers la molasse. Les résultats montrent que: la calcite et la dolomite (pouvant représenter jusqu'à 30% de la composition minéralogique de la molasse) peuvent se dissoudre au contact des jus de décharge; l'atténuation du manganèse et les concentrations d'hydrogénocarbonate sont probablement contrôlées en partie par la précipitation de la rhodochrosite; les concentrations de calcium et de magnésium dans les eaux souterraines contaminées sont contrôlées par des échanges ioniques (les cations de sodium et de potassium présents en hautes concentrations dans le jus expulsent le calcium et le magnésium fixés sur les sites échangeurs de la molasse); enfin, la précipitation du gypse dans la molasse à la suite de la migration du jus de décharge riche en sulfates est rendue possible par l'augmentation des concentrations de calcium dans les eaux souterraines contaminées. Ce phénomène a également été documenté par des analyses minéralogiques.

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Introduction

The goal of this paper is to present some results of the interpretative work that has been conducted lately on geochemical and chemical data gathered during groundwater monitoring campaigns at the site of the toxic waste repository Kölliken (Fig. 1). So far, very little geochemical work has been conducted on existing landfill sites in the Molasse. The available data are often complex (the chemistry of leachate and groundwater varies in time and location) and are not always suited to precise geochemical interpretation. In the case of Kölliken, the observation of a complete breakthrough of contaminants into the groundwater allowed a better understanding of the geochemical reactions affecting the composition of the leachate as it migrates through the Molasse. A simplified "input (leachate)/output (contaminated groundwater) system", with Molasse as reacting medium, was modelled to assess the effects of the Molasse as a natural geochemical barrier.

Geological setting and mineralogy of the Molasse

The toxic waste repository of Kölliken lies in a former clay pit dug in the aquitanian Molasse, which is composed essentially of marls and variegated clays interlayered with sandstone banks. The average mineralogical composition of the Molasse varies greatly and is summarized in Table 1.

Mineral	Percentage in the molasse
Quarz	9 - 40 %
Feldspars	0 - 60 %
Calcite	0 - 35 %
Dolomite	0 - 20 %
Clay minerals	5 - 85 %

Tab. 1. Average mineralogical composition of the aquitanian Molasse at the site of Kölliken (Peters 1993).

The clay minerals are composed essentially of illite (30–60%), smectite (5–35%) and iron-rich chlorite (20–40%).

The heterogeneity of the Molasse is not only due to its varying mineralogy, but is also caused by its architectural sedimentary features (channels, flood-banks, etc.) and deformation structures (faults, fractures).

The bottom of the landfill is mainly composed of clays and marls, but also of two outcrops of important permeable sandstone banks linked to the groundwater system. Contaminants leak out of the landfill mainly through the sandstone banks and migrate through fractures and zones of sandstones of higher permeability in a fingering pattern into the groundwater (Fig. 2).

Hydrogeology

Three aquifers are recognizeable at the site of Kölliken: (1) deep, old Na-HCO_3 Molasse groundwater, (2) shallower, more recent Ca-HCO_3 or Ca-Na-HCO_3 Molasse ground-

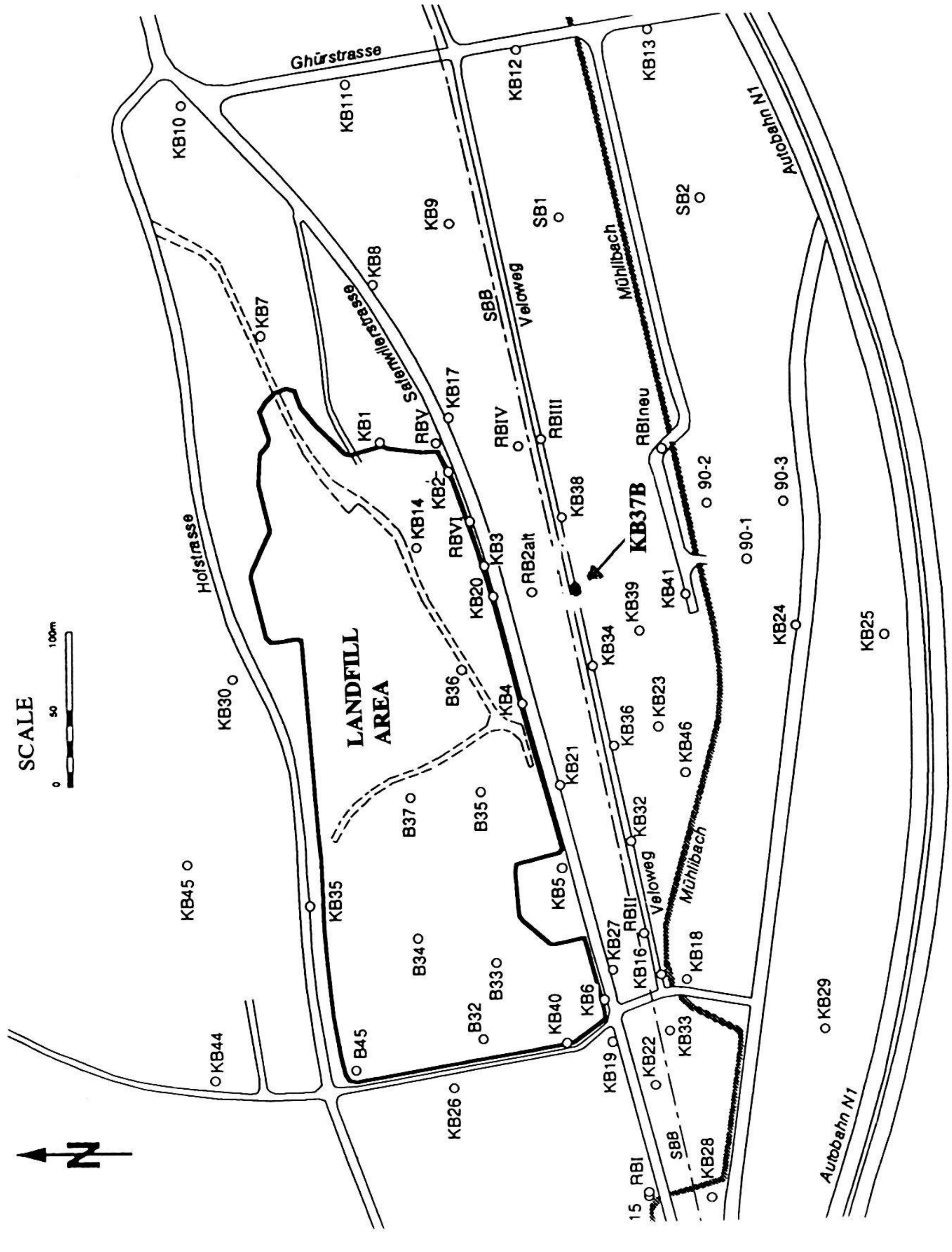

Fig. 1. Map view of the landfill and situation of the monitoring point KB37B

water, and (3) a shallow aquifer in quaternary gravels (Ca-HCO_3 groundwater). The deeper aquifer is partially confined. The hydrological relationship between the quaternary aquifer (which is exploited about 5 km downgradient from the site) and the Molasse aquifer is still unclear: both aquifers are separated by an impermeable till layer, but local connections through discontinuities of the layer are infered because typical tracers (e.g. bromide) from the landfill leachate were detected in the quaternary groundwater. The contaminant plume has reached both levels of the Molasse aquifer. Two channels of

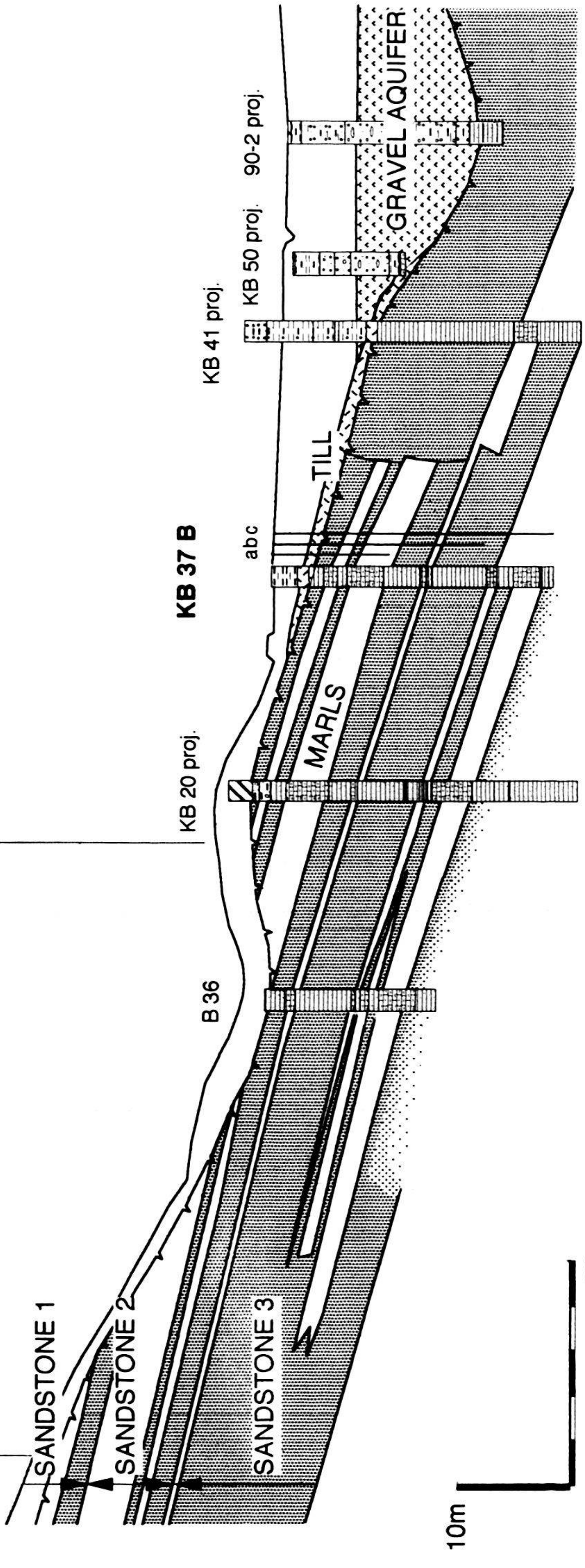

Fig. 2. Cross-section of the local stratigraphy in the Molasse (SMDK 1993)

permeable sandstone cross the Molasse under the landfill and act hydrogeologically as drainage. Groundwater flows to the south-east in the Molasse and to the east-north-east in the gravel aquifer (Fig. 2).

Chemistry of leachate and groundwater

The chemical composition of the leachate (salinity and pH) has evolved over the years, reflecting the various changes on the landfill due to remediation work and due to the most soluble salts being dissolved and washed out. Most of the leachate is collected in a drainage system, from which it can be sampled for analysis. Table 2 shows the chemistry of leachate sampled from the drainage system. The monthly variations of the concentrations can be sometimes very large (± 50%), as they are influenced by several factors such as precipitations, temperature and the leaching out of a very heterogeneous body of waste. General trends are nevertheless recognizable. In a general way, the leachate typically contains high amounts of chloride, sodium, potassium, bromide (a good tracer in slightly polluted groundwater), ammonium, manganese, sulfate, carbonate and organic carbon. The main organic contaminants are chlorinated and non chlorinated hydrocarbons.

Contaminated groundwater shows varying ranges of concentrations of salts and chlorinated organic compounds, depending on the dilution and the filtering effect of the Molasse along the flowpath. In strongly contaminated zones, the concentrations of calcium and magnesium can be very high, whereas the carbonate concentrations remain normal. Potassium and ammonium are always strongly attenuated because of adsorption on clays and ion-exchange (K^+ and NH_4^+); manganese can precipitate as carbonate and oxide/hydroxide upon redox changes along the flowpath.

Uncontaminated groundwater can be either of $Na\text{-}HCO_3$ (Tab. 2) or $Ca\text{-}HCO_3$ types, with pH values lying typically between 7.5 and 8.3. Sodium-carbonate waters are older, deeper groundwaters, and their composition reflects a long residence time within marls and clays where ion-exchange removed most of the dissolved calcium. Calcium-carbonate waters are generally in equilibrium with calcite. The chemistry of uncontaminated groundwater of $Na\text{-}HCO_3$ type is represented on Table 2. In the uncontaminated zones the variations of the concentrations are small (± 5%).

The monitoring point KB37B

The monitoring point KB37B (Fig. 1) is a borehole located in a zone of permeable sandstone corresponding to one of the sedimentary channels. At this point, the breakthrough of the contaminants into the Molasse was followed from its beginning (March 1990) to a plateau of maximum concentrations (Fig. 3a). The plateau was reached at the end of 1990 and since then, the maximum concentrations vary without changing the horizontal trend. Background values of groundwater in its uncontaminated state are therefore available (Tab. 2). During the breakthrough, several phenomena were observed:

(1) As the concentration of chloride increased dramatically from 5 to 12,000.00–15,000.00 mg/l, so did the concentration of calcium (20 to 2,000 mg/l) and magnesium (10 to 1,000 mg/l) (Fig. 3a). The molar ratio Ca/Mg remained constant (about 1.5). The

Parameter	**KB37B (10.89) background**	**KB37B (2.92) contaminated**	**Leachate (2.87) sector 6**
T (°C)	11.6	10.9	14.1
pH	8.06	6.71	6.66
Conductivity (μS/cm)	325	28'000	33500
Chloride (mg/l)	5.4	14330.0	12700.0
Bromide (mg/l)	-0.5	37.0	-50.0
Sulfate (mg/l)	18.0	1083.0	1400.0
Nitrate (mg/l)	-0.5	-5.0	-5.0
Ammonium (mg N/l)	0.01	3.1	564.0
DOC (mg C/l)(1)	1.2	18.0	225.0 (TOC)(2)
Carbonate (mg/l)	215.0	170	449.5
Calcium (mg/l)	19.0	2859.0	317.0
Magnesium (mg/l)	10.0	1403	83.0
Sodium (mg/l)	52	3251	6500.0
Manganese	-	2.1	480.0
Potassium (mg/l)	1.9	40	3450.0
AOX (μg Cl/l)(3)	-1.0	167	-

(1) Dissolved organic carbon
(2) Total organic carbon
(3) Adsorbable halogenated organics

Tab. 2. Measured concentrations in contaminated and uncontaminated groundwater and in leachate. (– indicates no measurement, negative values are the below detection limit. The values are discrete).

maximum concentrations of calcium and magnesium at KB37B are higher by an order of magnitude than in the leachate.

(2) The breakthroughs of potassium, ammonium and manganese at KB37B are comparatively slower and the concentrations are small compared to the concentrations in the leachate.

(3) The carbonate concentration slightly decreased during the breakthrough (Fig. 3b)

(4) The pH decreased from 8.2 (October 1989) to 6.7 (February 1991) to 6.5 (August 1993) (Fig. 3b).

(5) The maximum chloride concentrations in KB37 are higher than any of the recently measured concentrations in the leachate collected on the landfill. Likewise, the pH is lower than measured values in the recently collected leachate. Leachates collected between 1986 and 1987 also show high salinities and lower values of pH. This period corresponds to the early phase of the evolution of the landfill: the loads of salts being

washed out from the waste are high, and the pH is lower due to the production of organic acids through decomposition of organic matter. At the time, the landfill was not completely covered and the leachate was more directly influenced by precipitations. The drainage system of the landfill does not collect the entire volume of leachate; it is therefore possible that older, uncollected leachate stagnates at the bottom of the landfill before it migrates through fractures or zones of higher peremeabilities.

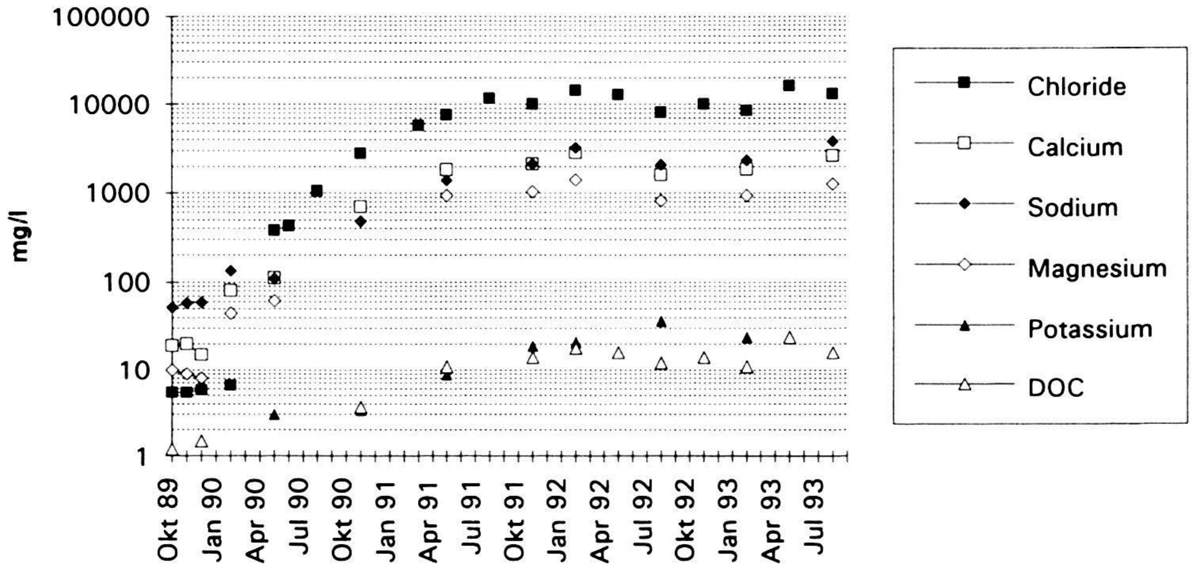

Fig. 3a. Breakthrough of the contaminants in the monitoring point KB37B.

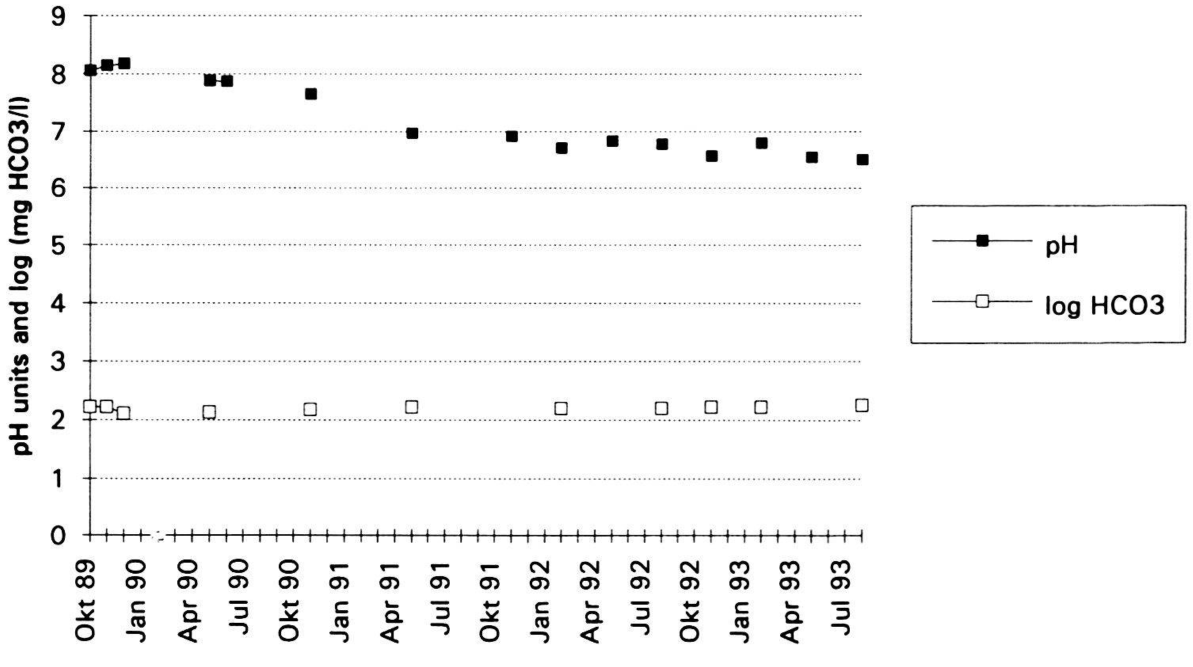

Fig. 3b. Evolution of pH and carbonate concentrations during the breakthrough of contaminants in KB37B.

The chemistry of contaminated groundwater at the point KB37B will be used as output (i.e. as a reference to which the modelling results will be compared to) in the modelling system for three reasons:

(1) the maximum concentrations are so high that the effect of dilution can be neglected;
(2) the chemical differences between leachate and contaminated groundwater are distinct enough to allow geochemical reactions to be inferred;
(3) the background chemistry of the groundwater (uncontaminated state) at this point is known.

Geochemical modelling

Modelling the geochemistry of a complex heterogenous system in great detail is beyond the scope of this work. Such modelling studies have been performed in various types of work, mostly to model laboratory experiments (e.g. Pavlik & Runnels 1991). However, the observed data are sufficient to elaborate a simplified model to determine the types of reactions affecting the chemistry of the leachate as it interacts with the Molasse, and to evaluate the impact of the leachate on the Molasse itself. A simplified model composed of an input (leachate), a reactive medium (Molasse) and an output (contaminated groundwater) allows a general evaluation of the principal mechanisms controlling leachate-rock interactions.

Chemical simulation modelling.

The chemical speciation model MINTEQA2 (Allison, J. et al. 1991) was used to simulate geochemical reactions that are likely to occur as leachate interacts with various mineral phases of the Molasse. The following, stepwise approach was used;

(1) Mesured concentration are entered into the model. The chemical speciation of leachate and contaminated groundwater was calculated. The concentrations are converted into activities (used to calculate selectivity coefficients, as shown below) and molarities. Saturations indices are calculated.
(2) The leachate (input) is allowed to equilibrate with calcite and dolomite respectively. This results in the dissolution of both mineral phases and in the net transfer of dissolved calcium and magnesium the final composition of the modelled solution.
(3) The leachate is then allowed to react with illite, which is entered into the model as a set of exchanging surfaces with given concentrations of exchangeable cations. Calcium, sodium and magnesium are assumed to be the main exchanging cations. Selectivity coefficients are taken from the literature or calculated (best fit). The calculated cation concentrations resulting from ion-exchange in the modelled solution are compared with the concentrations measured in contaminated groundwater.

Input

It was mentioned that high salinities and pH lower than 7 were measured in leachates collected between 1986 and 87. The chemistry of leachate collected in 1987 from a particular sector of the landfill showed great similarities with the contaminated groundwater in KB37B and was used as the input (see exact composition on Tab. 2).

Output

It is assumed that the modelling results should compare with the measured concentrations of contaminated groundwater in KB37B.

Reactive medium

The Molasse is a very heterogeneous medium. The most probable reactive fractions in the Molasse are assumed to be carbonates (calcite and dolomite) and clay minerals (mostly illite) as ion-exchangers and adsorbents. Exact data on the distribution of exchangeable cations in the Molasse of Kölliken are not available, but it is possible to estimate a plausible distribution based on published values (Peters 1991), cation-exchange capacities being known from laboratory measurements.

Selectivity coefficients can be calculated from background concentrations in groundwater and an assumed distribution of exchangeable cations. To be rigorously compatible with MINTEQA2 the selectivity coefficients must be calculated from the mass action expression (Morel 1991) as follows:

$$0.5\ \mathrm{Ca}_{(\mathrm{clay})} + \{\mathrm{Na}^+\} \rightleftarrows 0.5\ \{\mathrm{Ca}^{++}\} + \mathrm{Na}_{(\mathrm{clay})} \text{ and}$$

$$\mathrm{K}_{(\mathrm{Na/Ca})} = \{\mathrm{Ca}^{++}\}^{1/2} \cdot \mathrm{Na}_{(\mathrm{clay})}/\mathrm{Ca}_{(\mathrm{clay})} \cdot \mathrm{Na}^+$$

where $\{Ca^{++}\}$ is the activity of the aqueous concentration of the cation and $Ca_{(clay)}$ is the molarity of the adsorbed species (the activity coefficient is assumed to be 1), and $K_{(Na/Ca)}$ is the selectivity constant.

The following ion-exchange reactions were assumed to control the concentrations in the contaminant plume (Bjerg 1993):

Governing reactions

$$0.5\ \mathrm{Ca}_{(\mathrm{clay})} + \mathrm{Na}^+ \rightleftarrows 0.5\ \mathrm{Ca}^{++} + \mathrm{Na}_{(\mathrm{clay})}$$

$$0.5\ \mathrm{Ca}_{(\mathrm{clay})} + \mathrm{K}^+ \rightleftarrows 0.5\ \mathrm{Ca}^{++} + \mathrm{K}_{(\mathrm{clay})}$$

$$\mathrm{Mg}_{(\mathrm{clay})} + \mathrm{Ca}^{++} \rightleftarrows \mathrm{Mg}^{++} + \mathrm{Ca}_{(\mathrm{clay})}$$

$$\mathrm{Na}_{(\mathrm{clay})} + \mathrm{K}^+ \rightleftarrows \mathrm{Na}^+ + \mathrm{K}_{(\mathrm{clay})}$$

Proton-exchange was not considered in this model for lack of data. The proton saturation of the Molasse is probably low, because of the neutral pH of the background groundwater.

The concentrations of exchangeable cations per liter of water was calculated for an average water saturation of 87% (Institute of Geotechnics, Zürich 1991). The estimated average mass of rock in contact with 1 liter of water is 15 kg (value calculated from porosity and water saturation). The average concentrations of exchangeable cations in the Molasse per liter of water are calculated on the basis of this rock/water ratio.

A reasonable cation distribution in the exchanging sites of the Molasse was assumed (Peters personal communication 1993) for an average cation-exchange capacity of 10 meq/100 g (Tab. 3, data set 1).

Data set 1:

Cation	**meq/100g**	**Selectivity coefficients**
Calcium	8.0	$K_{Na/Ca} = 0.73$
Magnesium	1.0	$K_{Mg/Ca} = 3.41$
Sodium	0.5	$K_{K/Ca} = 38.09$
Potassium	0.5	$K_{K/Na} = 52.00$

Data set 2 (best fit) :

Cation	**meq/100g**	**Selectivity coefficients**
Calcium	4.8	$K_{Na/Ca} = 0.55$
Magnesium	2.1	$K_{Mg/Ca} = 0.51$
Sodium	1.4	$K_{K/Ca} = 109.20$
Potassium	1.7	$K_{K/Na} = 59.70$

Tab. 3. Values used for modelling of ion-exchange

A second set of parameters was used in a best-fit type of approach (Tab. 3, data set 2), based on data taken from the literature. The distribution of exchanging cations was either assumed or back calculated from assumed values of selectivity constants. The selectivity constants for calcium/sodium and sodium/potassium can be similar for a wide range of concentrations of aqueous species and ionic strengths (Peters 1991). Selectivity constants for calcium/sodium and sodium/potassium in the second set of data were then taken from the literature and the other constant were back calculated based on the background activities of the aqueous species.

The average carbonate content (calcite and dolomite) of the Molasse is 16 weight % of the rock. Infinite supply of carbonate was assumed for the reactions of dissolution.

Results and discussion

1) Carbonate dissolution

Leachate was allowed to react successively with calcite and dolomite, causing the dissolution of these minerals. The pH was fixed at the leachate value (6.66), because practically no buffering was observed in KB37B. The loss of buffering capacity could occur if all of the carbonate fraction has been dissolved along the flowpath ("channeling"), limiting the alkalinity supply. This implies the formation of secondary porosity as the carbonate cement dissolves. This hypothesis cannot yet be confirmed on the basis of the available geological and hydrogeological data. The calculated concentrations resulting from the dissolution of carbonates by the leachate are compared with measured values in KB37B on Table 4.

	Measured values		**Predicted by MINTEQA2**	
Parameter	**Leachate sector 6, 1987**	**KB37B 1992**	**Leachate in eq. with calcite and rhodochrosite**	**Leachate in eq. with calcite, dolomite and rhodochrosite**
pH	6.66	6.71	6.66	6.66
CO^2 (mol/l)	4.99E-2	3.14E-2	5.9E-2	8.9E-2
Ca^{++} (mol/l)	9.7E-3	7.3E-2	1-9.0E-2	1.3E-2
Mg^{++} (mol/l)	3.5E-3	5.9E-2	3.5E-3	1.5E-2
Mn^{++}	9E-3	3.9E-5	3.2E-4	2.1E-4
TIC (1) (mol/l)	7.9E-3	6.8E-3	9.4E-3	1.4E-2
SI (2) calcite	-0.385	+0.394	0.000	0.000
SI dolomite	-1.267	+0.578	-0.808	-0.789
SI rhodochrosite	-1.108	-0.112	0.000	0.000
SI gypsum	-0.467	+0.188	-0.112	-0.170
Na/Ca	30	2	14	22
Na/Cl	0.79	0.34	0.79	0.79

(1) TIC: total inorganic carbon (representative of carbonate concentration)

(2) SI: Saturation index. Positive values indicate supersaturation and tendency for the mineral to precipitate. Negative values indicate undersaturation and tendency for the mineral to dissolve. Zero values indicate equilibrium conditions. SI = IAP/Ksp, where IAP is the measured activity product and Ksp is the thermodynamic solubility constant.

Tab. 4. Comparison of the calculated and measured values as leachate is allowed to equilibrate with carbonates.

The results show that

a) the concentrations of calcium and magnesium in the contaminated groundwater are not controlled by calcite and dolomite dissolution alone,
b) the concentrations of hydrogen carbonate are probably determined by the precipitation of rhodochrosite ($MnCO_3$): upon dissolution of calcite or dolomite, the solution becomes supersaturated with respect to rhodochrosite. This could explain why the concentrations of hydrogen carbonate decrease slightly during the breakthrough.

Manganese is probably also attenuated by adsorption, because the equilibrium concentrations of manganese are still higher than the measured concentrations. The solution resulting from carbonate dissolution as predicted by MINTEQA2 is undersaturated with respect to manganese oxides and hydroxides. The calculations were run at an assumed redox potential of 200 mV, which might not be adequate to predict manganese speciation and attenuation.

2) Ion-exchange

Modelling results show that cation-exchange between leachate and Molasse play a greater role than carbonate dissolution in controlling the cation concentrations in the contaminated groundwater. The leachate was allowed to equilibrate with a substrate represented by three exchanging surfaces with calcium, magnesium and sodium as exchangeable cations; their concentrations were assumed to be a fraction of the cation exchange capacity of the substrate (10 meq/100g). As mentioned above, the model was run with two different sets of ion-exchange data and the results were compared with the chemistry of contaminated groundwater in KB37b (Tab. 5).

	Concentrations predicted by MINTEQA2		**Measured concentrations**
Parameter	**Modelling results data set 1**	**Modelling results data set 2 (best fit)**	**KB37B (2.92)**
Calcium (mol/l)	5.9E-2	7.3E-2	7.3E-2
Sodium (mol/l)	7.8E-2	1-3E-2	7.3E-2
Magnesium (mol/l)	1.02E-1	6.3E-2	5.9E-2
Potassium (mol/l)	4.7E-4	2.3E-4	1.1E-3
SI (gypsum)	0.13	0.25	-0.47
SI (rhodochrosite)	0.25	1.09	-0.11

Tab. 5. Comparison of results of ion-exchange modelling with measured values in KB37B.

Considering the uncertainties pertaining to the evaluation of the reactive medium and the simplifying assumptions required to elaborate the ion-exchange model, the modelled reactions can be considered as representative of the rock-leachate interactions at the site of study. The results show that:

a) the calcium concentration in the contaminated groundwater results from sodium and potassium from the saline leachate expelling calcium from the exchange sites and being adsorbed on the Molasse,
b) the attenuation of sodium and potassium in the contaminant plume can also be explained by ion-exchange reactions. In both approaches, the calculated concentrations of potassium are smaller by almost an order of magnitude than the measured concentrations, which indicates that potassium could also be adsorbed on clays,
c) the concentration of magnesium in the contaminant plume cannot be modelled satisfactorily by ion exchange between magnesium and calcium. The question as to which processes do control the concentrations of magnesium in the contaminated groundwater remains open. The discrepancies could also be caused by insufficient data on the concentrations of exchangeable magnesium in the Molasse. Meanwhile, modelling the reactions on the basis of best-fit data can show that ion-exchange could control the magnesium concentrations in the contaminated plume if the selectivity constant is low enough, which implies that the distribution of exchangeable calcium and magnesium does not correspond to the first assumption.

d) the modelled solution is supersaturated with respect to rhodochrosite and gypsum. Mineralogical analyses revealed the presence of gypsum in a fracture that was in contact with contaminated water, which confirms the modelling results. The final concentrations of calcium, sulfate, hydrogen carbonate and manganese after allowing the precipitation of gypsum and rhodochrosite are listed in Table 6 and compared with measured values in KB37B. The concentrations of sulfate and hydrogen carbonate predicted by MINTEQA2 are in good agreement with the measured values in KB37B.

	Concentrations predicted by MINTEQA2		**Measured concentrations**
Parameter	**Modelling results with data set 1**	**Modelling results with data set 2**	**KB37B (2.92)**
Sulfate(mol/l)	5.9E-2	7.3e-2	7.3E-2
Carbonate (mol/l)	7.8E-2	1.3E-1	1.4E-1
Manganese (mol/l)	4.7E-4	2.3E-4	1.1E-3

Tab. 6. Calculated conentrations after precipitation of gypsum and rhodochrosite.

Conclusions

Modelling results show that cation-exchange between the migrating, saline leachate of the Kölliken repository and the Molasse is the dominant process controlling the concentrations of calcium, magnesium, sodium and potassium in the contaminant plume at the monitoring point KB37B. Dissolution of calcite and dolomite are possible reactions, but they seem to play a minor role in the rock-leachate interactions. Formation of secondary porosity in the Molasse could take place as a result of carbonate dissolution, but they could be compensated by the precipitation of gypsum and rhodochrosite in fractures or in the pore space.

Further research on the Molasse as a reactive medium and natural geochemical barrier should be conducted in order to make predictions on the fate of contaminants in this type of sedimentary rock. This would give a support to geochemical modelling, which should be integrated in risk assessment studies. Within the framework of the present work, several questions could not be answered and require further study:

(1) What reactions do control the release of magnesium in the contaminant plume?
(2) What is the role of iron-oxide in attenuation of contaminants in the Molasse?
(3) How does the leachate affect silicates and alumino-silicates?
(4) Can the geochemistry of weakly contaminated zones be modelled?
(5) What ist the role and the behavior of dissolved carbon dioxide as the leachate migrates through the Molasse?

Further interpretative work should involve laboratory experiments to support the geochemical interpretation.

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