C. A. J. APPELO (*) - W. GEIRNAERT (*)

PROCESSES ACCOMPANYING
THE INTRUSION OF SALT WATER

SUMMARY

Salt water intrusion and conversely refreshening of water bearing strata are often accompanied by cation exchange processes in which $CaCl_2$ or $NaHCO_3$ type water is formed. In the refreshening process $CaCO_3$ solution also takes place. On salinization the deposition of $CaCO_3$ is prevented by simultaneously occurring sulphate reduction.

In various parts of The Netherlands no clear manifestation is found of these cation exchange processes; on a Piper diagram analyses plot on the mixing line between $CaHCO_3$ and $NaCl$ type water.

Equilibrium between cations in the salinization or refreshening front and exchangeable cations of the aquifer material was calculated using the Gapon equation. Whether cation exchange is visible in water analyses depends on Cation Exchange Capacity (CEC) of the sediments and concentrations in water. In a refreshening process, the pore volume needs to be flushed a number of times before water composition is unaffected by cation exchange; seawater intrusion gives faster salinization of a fresh aquifer with the same CEC. Mixed water is generally limited to situation where the pore volume has been flushed a number of times by the same water. These above processes are discussed with reference to a borehole in the western Netherlands, where the CEC of soil samples has been determined and compared with groundwater analyses.

(*) Institute of Earth Sciences, Free University, Amsterdam (The Netherlands).

1. INTRODUCTION

Glaciation induced sea level changes in the Pleistocene period have caused alternations of transgressions and regressions in most coastal basins. During periods of low sea level erosion took place and coarse material was deposited, these sediments being covered by marine clays in the interglacial periods. The aquifers also experienced different phases of salinization and of refreshing.

The last glacial period (Weichselian) and the rapid Holocene sea level rise still decisively influence the fresh-salt distribution in coastal areas. Infiltration of sea water and the replacement of salt- by fresh water are generally accompanied by cation exchange processes, which in turn can be used for reconstructing the events which caused an often complex fresh-salt distribution in groundwater bodies.

2. CATION EXCHANGE PROCESSES

In cation exchange processes the solid phase of the aquifer interacts with the groundwater. The negative charge of clay minerals, due to substitutions in the lattice, is balanced by adsorption of cations from the groundwater. Absorbed cations are in equilibrium with the ions in solution according to:

$$Na^+ + K^+\text{-clay} \rightleftarrows Na^+\text{-clay} + K^+$$

with the equilibrium constant K being given by:

$$K = \frac{[Na^+\text{-clay}] \cdot [K^+]}{[K^+\text{-clay}] \cdot [Na^+]}$$

The brackets indicate « activity » of the species, i.e. moles/l for the ion in solution, and mequivalents of the absorbed ion/100 gr soil.

Cations of higher charge are preferred in exchange reactions, but ion size can also be decisive. Ca is about 1.2 times stronger adsorbed than Mg. Specific adsorption of K results from the good fit of K in the interlayer space of clay minerals and the ion is about 5 times stronger adsorbed than Na.

The definition of an exchange equation is generally easy for exchange between ions of the same charge, but is difficult for ions of differing charge. In the latter case, definition of the exchanger-phase becomes an important, still unresolved problem. BOLT [1]; also BOLT and BRUGGENWERT [2], suggests use of the Gapon-equation for Na/Ca-exchange when detailed information on the exchanging material is lacking. This equation is also commonly used in ir-

rigation practice for estimating the Exchangeable Sodium Ratio (ESR) in soils. For Na/Ca-exchange the Gapon-equation reads:

$$\frac{[\,Na\text{-clay}\,]}{[\,Ca\text{-clay}\,]} = K_G \cdot \frac{[\,Na^+\,]}{\sqrt{[\,Ca^{2+}\,]}}$$

where K_G is the Gapon-constant (≈ 0.5 (mol/1$^{-\frac{1}{2}}$)). It should be noted that VAN DER MOLEN [7] found a certain discrepancy for Dutch soils when using this
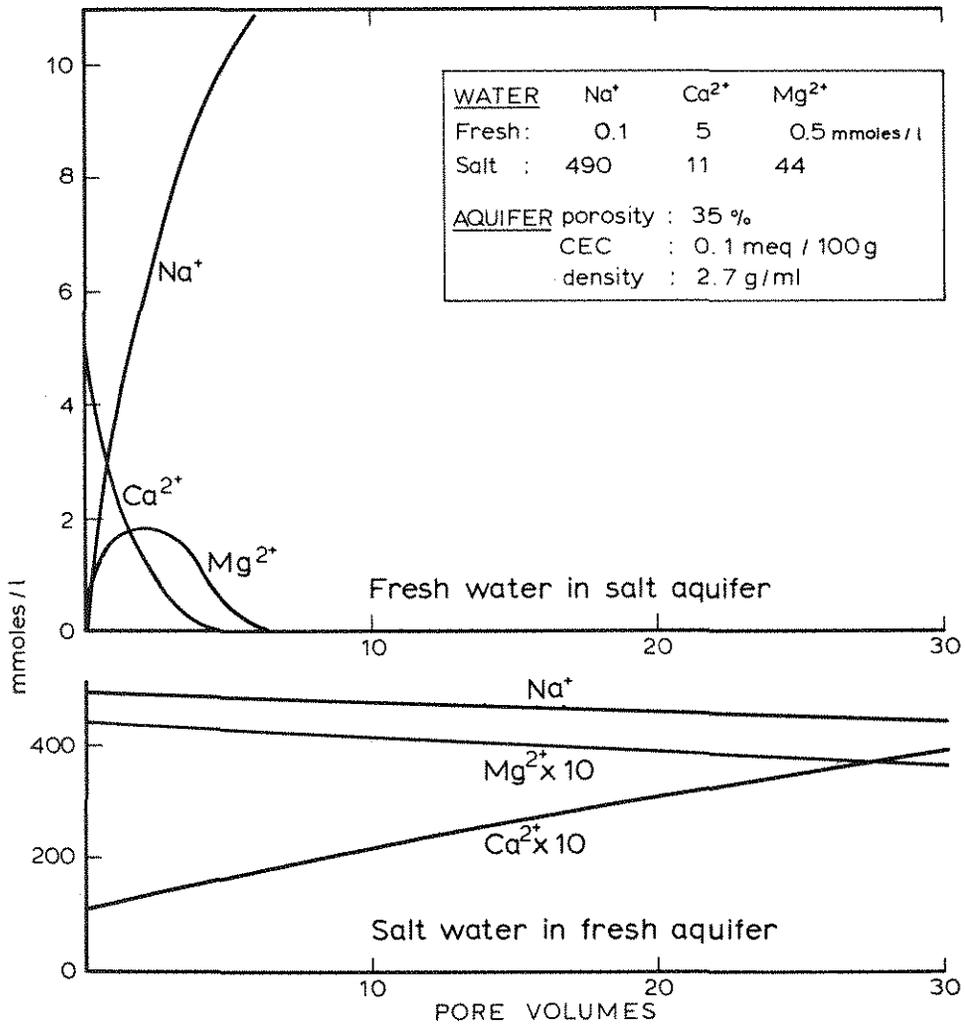

Fig. 1 – Change in water composition by cation exchange in the intrusion front: fresh water in salt aquifer and salt water in fresh aquifer. Composition change is shown as a function of passed pore volumes, using the Gapon formula and zero selectivity for Ca/Mg-exchange.

equation, and as such it must be considered as only an approximation when describing the equilibrium between a solution and the aquifer solid material.

Equilibrium will be disturbed when composition of the solution changes. When seawater infiltrates an aquifer containing fresh water, Na ions present in seawater will be exchanged against Ca ions adsorbed on the clays. Seawater thus becomes $CaCl_2$-type water. The reverse process occurs when fresh water replaces salt water in an aquifer. The fresh water will then change into $NaHCO_3$-type water. Figure 1 shows composition of the groundwater at an intrusion and replacement front as calculated from the Gapon-formula. It is evident that an increase of Ca in the salinization front is limited, since calcite will be deposited. In the refreshing process decrease of Ca will lead to a renewed dissolution of $CaCO_3$. Ca may then be further exchanged for Na, and HCO_3^- increases to often high values.

2.1. Observed water qualities

The reactions are visible in a number of water-analyses plotted in the Piper-diagram of figure 2. Groundwater-analyses are from Zeeland and Western Brabant in The Netherlands, where inundations have often occurred in the past centuries. A mixing-line is drawn on the Piper-diagram to represent conservative mixing of seawater and fresh water. The mark given with each plotted point is directed towards the location on this mixing line based on chloride content of the water samples.

It is clear from Fig. 2 that reactions with $CaCO_3$ occur upon refreshing of the aquifer, but are less for salinization. In fact, it seems that water composition evolves in a direction opposite to that which would be expected for an exchange of Na for Ca accompanied by $CaCO_3$-deposition. It is possible that $CaCO_3$-deposition (though occurring) is masked (as a reaction) in the Piper-diagram by SO_4-reduction, since it lowers the % $[SO_4 + Cl]$. SO_4 reduction also produces CO_2 by:

$$SO_4^{2-} + 2CH_2O \rightarrow S^{2-} + 2CO_2 + 2H_2O .$$
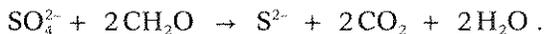
When S^{2-} precipitates with Fe into FeS or FeS_2 (pyrite), the CO_2 can make the water agressive towards $CaCO_3$, so that $CaCO_3$ deposition is actually prevented. Sulfate-reduction may still be active in the intruded seawater-analyses plotted in Fig. 2, since many of the samples are from shallow depth, taken after the great flood of 1953. Table 1 illustrates some typical examples of $CaCl_2$-type and $NaHCO_3$-type groundwater.

However such a clear manifestation of the cation exchange process not always is found. In various parts of The Netherlands where refreshening and salinization are taking place analyses plot on the mixing line between $CaHCO_3$ and NaCl type water. This cannot originate from a lack of exchangeable cations since the lithology of formation is not different.

2. 2. «Mixed-water»

Cation-exchange is dependent on the amount of cations to be exchanged in water and the available cations at exchange sites of the solid aquifer material. For a relatively low CEC of 0.1 meq/100 gr used in figure 1, the fresh water composition is little affected (less than 10% of Na- and Ca-concentrations) when 3 pore volumes have flushed the aquifer. For sea water on the other hand, less than 1/10 of a pore volume is sufficient to salinize the exchange complex of a fresh water aquifer with the same CEC. This low CEC of 0.1 meq/100 gr has been found in coarse sandy Pleistocene sediments in The Netherlands Veluwe area, and is used here to obtain an indication of minimum effects of cation exchange. With an increase in silt-content or organic material, CEC increases. Values of 0.5 to 2 meq/100 gr have been found in the sandy Pleistocene aquifers, leading to more prolonged exchange-effects than shown in Figure 1.
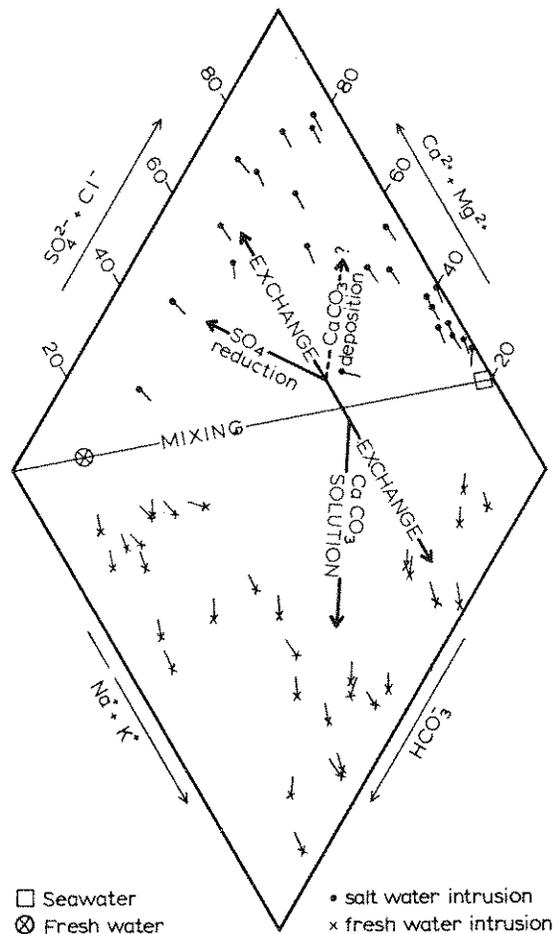

Fig. 2 – Piper plot showing compositions of groundwater from Zeeland and Western Brabant, The Netherlands, in which cation-exchange is visible. Mark at plotted points is directed towards position on mixing line based on Cl concentration of the groundwater sample.

□ Seawater
⊗ Fresh water

• salt water intrusion
× fresh water intrusion

A substantial intrusion of sea – or fresh water must show a compositional change from the intrusion-front to inner zones which are not affected by cation-exchange. Mixing of water from a spasmodic sea water intrusion with residing fresh water gives water with an intermediate chloride concentration, but also with signs of cation-exchange as in Zeeland and Western Brabant, provided that the CEC's of sediments are large enough. «Mixed water» with a composition that falls on the mixing line given in the Piper diagram is limited to the situation where the pore volume has been flushed a number of times by the same water.

Flushing situations with brackish water can be expected in estuaries where inundations take place with regular intervals, or at salt/fresh water interfaces where groundwater flow is active. These are the environments among others, where «mixed water» is presently observed: under polders directly north of the Nieuwe Waterweg (the Rhine-estuary west of Rotterdam), and the fresh/salt water interface under the Wadden island Ameland. Typical analyses are shown in Table 1.

TABLE 1 – Groundwaters showing « mixed water » composition, and composition influenced by cation exchange («$CaCl_2$» and «$NaHCO_3$»-types). Values in mmoles/l.

seawater		mixed water		$CaCl_2$ water		$NaHCO_3$ water		fresh water
pH	8.22	7.5	7.2	6.91	6.6	8.7	8.3	7.37
Na	485	24.5	54.3	341	124	40	2.0	0.48
K	10.6	0.82	1.42	2.8	2.4			0.05
Mg	55.1	2.93	7.1	27.9	30.7	2.8	1.1	0.07
Ca	10.7	3.04	7.86	39.6	47.2	0.7	0.65	1.31
Cl	566	27.2	73.0	440	271	25.6	1.4	0.73
HCO_3	2.4	9.03	15.3	7.0	3.8	14.4	4.0	2.48
SO_4	29.3	0.07	0	18.8	4.7	2.7	0.2	0.11
% seawater		5	13	78	48	5	0	0
Location		Ameland		48E	48H	48E	48A	49A
(RID-code)				45-1	35-1	69-1	3-3	48-1

In the two analyses given, Na and Mg are within 5% of concentrations expected from conservative mixing of fresh- and sea water based on Cl-concentrations. Ca and HCO_3 have increased however, as a result of calcite dissolution activated by reduction of sulphate.

3. POLDER GROOT MIJDRECHT

An example of using cation-exchange processes to obtain paleo-hydrological information can be given for the Polder Groot Mijdrecht.

In this polder in the western part of The Netherlands (Fig. 3), upconing of salt groundwater due to upward seepage has already been studied by GEIRNA-ERT [5]. A new deep borehole of The Netherlands Geological Survey could be used for taking undisturbed soil samples. The samples were taken with a coring device under the (hollow) drill bit preventing contamination with the drilling fluid.
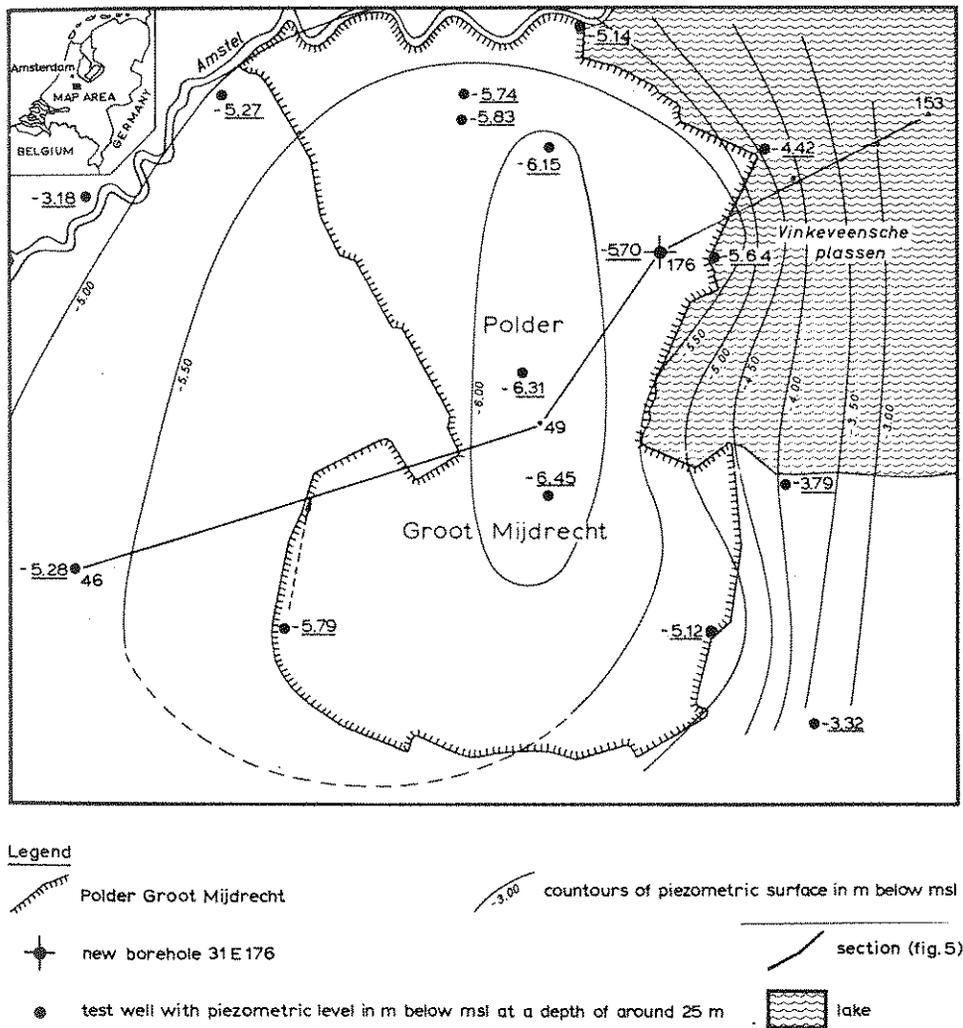

Fig. 3 – Location of new borehole in the polder Groot Mijdrecht with groundwater potentiometric surface.

A hydrological schematization of this borehole is given in figure 5 and shows covering layers of Holocene age, water bearing strata of fluvial Pleistocene sediments and a hydrological base at the change to marine deposits (Maassluis Formation). In the western Netherlands the Holocene is of marine origin, with the transition to fluvial sedimentation lying on the eastern border of the polder. In the aquifer to the West of the polder Groot Mijdrecht covered by marine Holocene deposits, $NaHCO_3$ type groundwater is found showing that the aquifer was subjected to a salinization phase and is now in the process of refreshening.
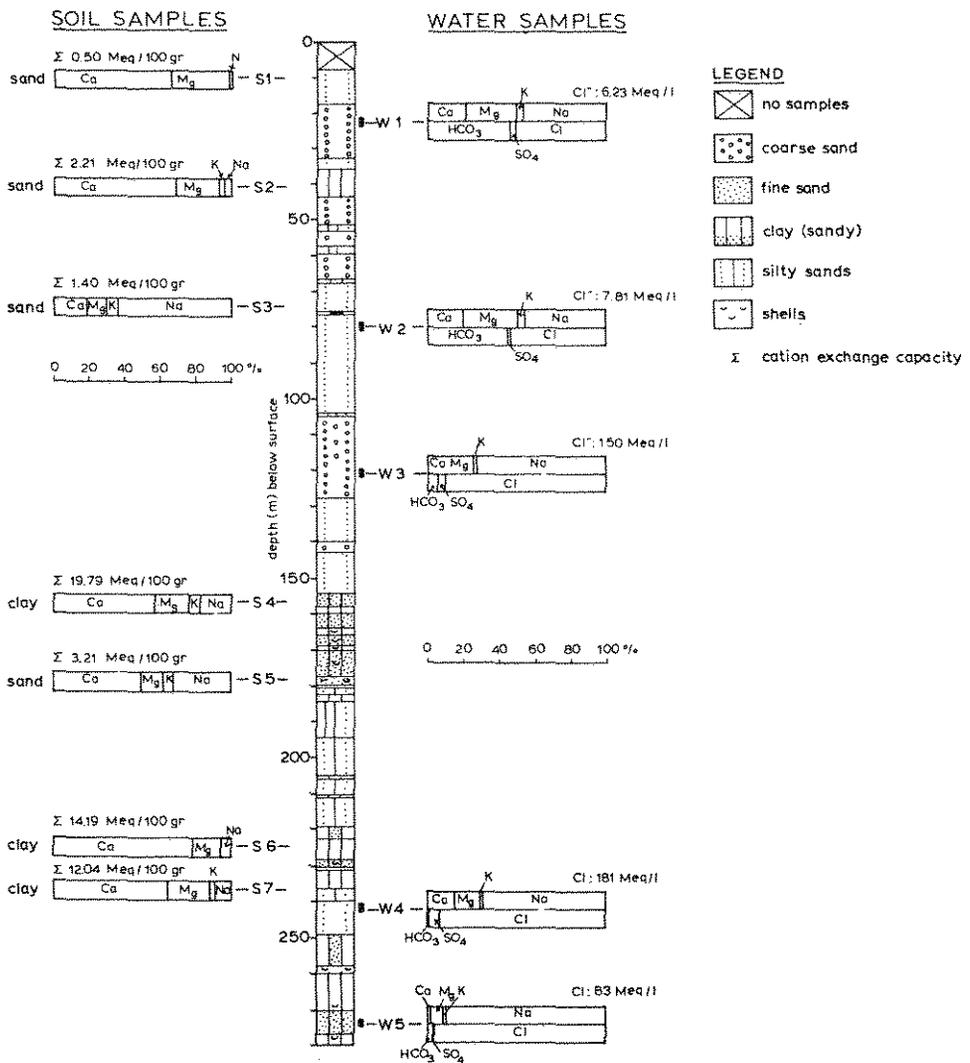

Fig. 4 – Lithology of the new borehole 31E 176, showing lithology and ion percentages in water and soil-samples.

In the polder Groot Mijdrecht, however, upconing of salt groundwater occurs which is of mixed-water type. This upconing is related to the difference in water level (about 3 m) between the polder canals and lake level at the eastern polder border.

Since the Holocene and the Maassluis Formation are the only marine sediments found in the area, the salinization of the aquifer must have occurred at the onset and during Holocene transgression.

The new borehole was located on the eastern flank of the salt-water cone. It was equipped with 5 piezometer tubes from which water samples were taken on different occasions. The cation exchange complex was determined from 8 soil samples (Fig. 4). Borehole water analyses fit the regional picture. Water from the bordering lake is found to a depth of 80 m, indicating deep infiltration and groundwater flow towards the polder. Samples 3, 4 and 5 show mixed water. The Cl concentration in sample 5 at a depth of 270 m was 83 meq/l, and is surprisingly lower than the 181 meq/l found in sample 4 at a depth of 240 m. Water sample 3 has a composition that is almost exactly comparable with those taken at shallow depth in other parts of the polder. The soil samples show different compositions. The exchange complex is compared with water compositions in table 2, using the Gapon equation. Soil samples S1 and S2 are in equilibrium with water samples W1 and W2. Soil samples S3 is somewhat «saltier» (contains relatively too much Na) when compared with water samples W3 and W4. Samples S4 to S7 are from the marine Maassluis and Oosterhout formations, but show a fresh water composition; only the (saltier) sand sample S4 is in equilibrium with water samples W3 and W4.

TABLE 2 – Comparison of water composition and exchange complex of Groot Mijdrecht samples with a Gapon-type equation.

water sample & ratio (*) $\dfrac{([Ca] + [Mg])}{[Na]}$		soil sample & ratio $\dfrac{[Na]}{([Ca] + [Mg])}$		K_G (**)
W1	7.94	S1 (sand)	0.04	0.32
		S2 (sand)	0.048	0.38
W2	7.76	S2 (sand)	0.048	0.37
		S3 (sand)	2.15	16.7
		S3 (sand)	2.15	1.9
W3	0.883	S4 (clay)	0.24	0.21
		S5 (sand)	0.52	0.46
		S5 (sand)	0.52	0.46
W4	0.887	S6 (clay)	0.061	0.054
		S7 (clay)	0.102	0.09
		S5 (sand)	0.52	0.34
W5	0.657	S6 (clay)	0.061	0.04
		S7 (clay)	0.102	0.07

(*) [ ] denotes activity in water (moles/l.), or meq/100 gr.
(**) $K_G \approx 0.5$ (moles/l.)$^{-\frac{1}{2}}$. Deviations point to non-equilibrium: a lower value to salinization, a larger value to freshening of the aquifer.

3.1. Groundwater flow pattern

By combining the water analyses and adsorption complex a picture emerges of flow patterns in the Groot Mijdrecht polder (Fig. 5). Seepage occurs from the eastern lakes towards the low lying polders. This lake water penetrates to depths of at least 80 m, and in amounts which are sufficiently large to flush the adsorption complex and bring it to equilibrium with the lake water.

Sample S3 at a depth of 75 m, does not fit this picture however, and still has too much Na. It may be that the sandy layer from which the sample is obtained is shielded by clay, and therefore not affected by the different lake water quality. The exchange complex is also too salt for the deeper water, and might represent a still older (more Na-rich) situation.

Mixed water is found beneath the lake water, and also in central parts of the polder at shallower depth. This water has Cl-concentrations of 150-160 meq/l, and suggests former salt water intrusions in the fluviatile deposits. Beneath the «mixed water», a chloride-inversion (lowering) is evident in marine formations at a depth of 280 m.
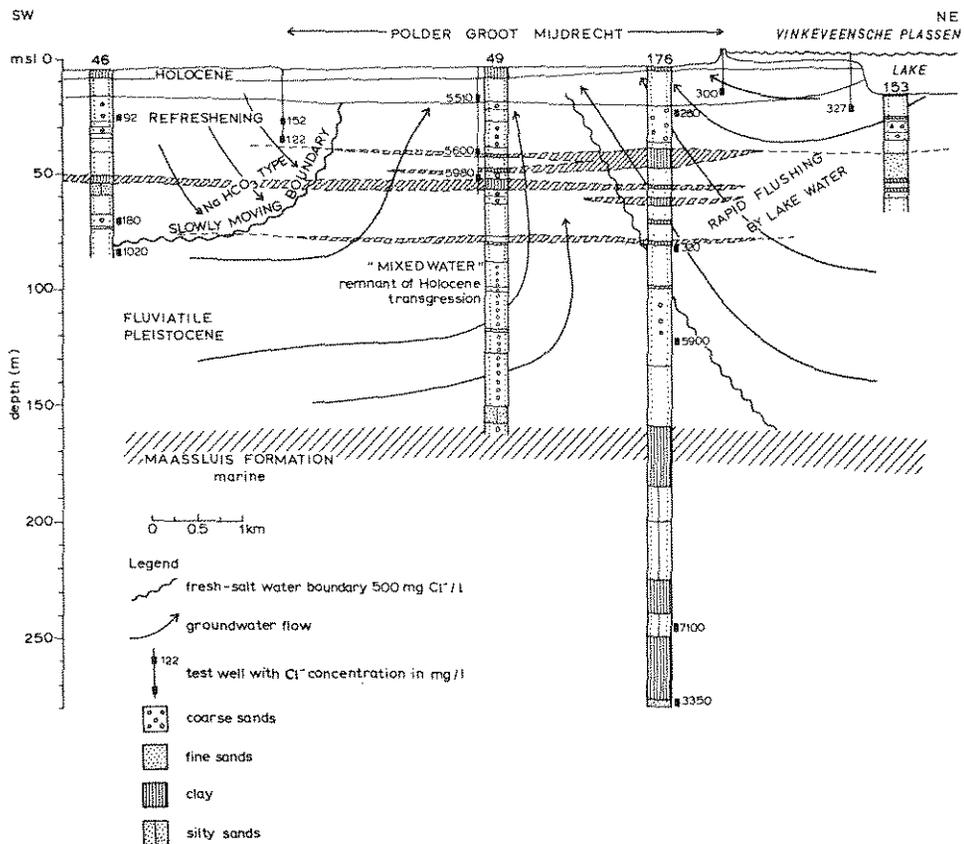

Fig. 5 – Profile over the polder Groot Mijdrecht with groundwater flow pattern.

The adsorption complex of these layers at present has a fresh-water composition, thus showing that refreshing of the marine Maassluis formation has taken place. This may have occurred during deposition of the overlying fluviatile deposits.

The CEC's for sand and clay material of the aquifers vary from 0.5 to 20 meq/100 gr. If the sandy aquifer has on average 0.5 to 1 meq/100 gr CEC, the pore volume needs to be flushed 2 to 3 times before the water composition becomes constant, and within 10% of the measured, mixed concentration in which no cation exchange is visible. The chloride concentration is very uniformly 150-160 meq/l in the mixed water (water sample W3 and older samples at shallow depth in the polder).

This might be obtained by mixing through dispersion of original water and a single pulse of intruded water. The amount of flushing, needed to equilibrate the exchange complex, is a number of pore volumes, however. It seems therefore, that the mixed water is a remnant of a brackish flow through the aquifer that was sufficiently continuous to give one water type to a depth of at least 120 m, and also flush the pore volume 2 to 3 times. This flow of large brackish water volumes means that the fluviatile (pleistocene) aquifer became totally saline during the Holocene transgression. The existing variation in salt, fresh and brackish water is thus relatively young, and the result of groundwater flow induced by polder reclamation at different levels over past centuries.

In the marine Maassluis formation clay layers have a fresher composition than sandy layers. Water sample W5 has lost Ca in return for Na, indicating that this water freshens the aquifer. Comparison with the exchange complex of clayey samples S6 and S7 points to salinization however, with a calculated value of $K_G \approx 0.05$ (table 2). This cannot be explained with the sample obtained in the present investigation. Reactions in the Maassluis formation will be more complex, since this formation was subjected to at least one refreshening and salinization phase more than the overlying fluviatile deposits.

4. CONCLUSIONS

In the subsurface of The Netherlands alternating fresh, salt and bracking water types are found. In the western part of the country these are the result of sea level changes in Pleistocene and Holocene times. Indications of past and present flow patterns can be obtained from cation exchange reactions which are reflected in water composition. A sea water intrusion front shows, $CaCl_2$ type water, while refreshening gives $NaHCO_3$-water. The exchange rections are accompanied by other reactions, notably dissolution of $CaCO_3$ and reduction of SO_4. Mixed water may be found behind the front when sufficient water has flushed the aquifer to equilibrate the exchange complex.

The comparison of water samples with the exchange complex of soil samples obtained from a borehole in the polder Groot Mijdrecht suggest that the fluviatile Pleistocene aquifer was completely salinized during the Holocene transgression. The present pattern of water types indicates large water

flows from the Vinkeveensche Plassen (lake) east of the polder, and slower refreshening from higher lying polders lying more to the west. In groundwater originating from the lake, cation exchange is no longer apparent and the water is in equilibrium with the exchange complex. In the western part there is still $NaHCO_3$-water present at the fresh/salt boundary, indicating a lesser flow.

The water types can be explained by the present distribution of land surface and groundwater levels, with salt water «bleeding out» of the deep lying polder [6]; the rate of «bleeding» depends on local conditions. In the lake to the east of the polder deep sandpits have been dug which permit the rapid infiltration of large amounts of water [4]. The polders to the west have a Holocene clay layer which impedes the fresh water flow towards the polder Groot Mijdrecht. The distribution of water types in the upper fluviatile aquifer is therefore relatively young and is the result of polder reclamation at different levels in the past few centuries. It confirms the qualitative genetic model proposed by DE VRIES [3] based on Holocene landscape evolution.

ACKNOWLEDGEMENTS

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