Quality of Groundwater, **Proceedings of an International Symposium, Noordwijkerhout, The Netherlands, 23–27 March 1981, W. van Duijvenbooden, P. Glasbergen and H. van Lelyveld (Eds.),**
***Studies in Environmental Science*, Volume 17**

RESULTS OF SOME LABORATORY MODEL EXPERIMENTS ON THE MANGANESE MIGRATION IN ALUVIAL SANDS

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ABSTRACT

A laboratory column study was performed to investigate the behaviour of manganese(II) during the passage of polluted groundwater through aluvial sands and so to simulate the transport (migration) under conditions of groundwater pollution from some rivers in Bulgaria. The parameters of the migration were calculated according to the method of the "three characteristic points" from the experimental curves. The migration forms of Mn(II) were mainly with positive charge.

The relatively high retention capacity of the sands is only slightly dependent on the lithology and filtration characteristics of the aluvial sands. The physico-chemical process, related with the retention, is not completely reversible sorption, complicated by precipitation of Mn(II)- basic compounds, in which no change of its oxidation state is to be presumed.

INTRODUCTION

This paper describes briefly two kinds of experiments on the manganese(II) migration, which may occur from some polluted rivers in Bulgaria in the groundwater accumulated along them. We have already carried out experiments with the same sand columns to simulate the migration of other pollutants in the field and the schematic plan of the set-up as well as the methodic of interpretation have also been described (refs. 1, 2).

A more detailed picture of the different conditions, under which the present study has been performed, is evident in Table 1. The polluting agent studied was prepared dissolving $MnCl_2 \cdot 4H_2O$ a.r. in drinking water of Sofia and the analyses were made using the standard atomic absorption spectrophotometric and polarographic procedures. Before the experiments the sand columns were watersaturated.

RESULTS

The change of Mn(II) output concentration is shown in nondimensional coordinate system c^*/t^* in Figure 1. Figure 2 shows the change in the volume (W) (or t^*) of the manganese polluted water, which has passed through, as a function of the time. The Eh-change was relatively small and in the limits +160 - +210 mV. (In the same time 5.8(5.9) < pH < 6.5.) The Mn(II) migration forms have been found to be almost 95% with

TABLE 1

Conditions of the laboratory experiments on the manganese migration

Conditions and parameters	Dimension	Experiment 1	Experiment 2
Probe	-	Sand Q^{al}	Sand Q^{al}
Effective diameter(d_{10})	mm	0.19	0.04
Coefficient of uniformity(d_{60}/d_{10})	-	4.53	6.01
Permeability	darcy	18.70	4.25
Porosity(n)	-	0.24	0.25
Total volume of the sample(V′)	cm^3	3375	324
Bulk mass density of the sample(ρ)	g/cm^3	2.00	2.10
Volume of the pore space(W_p)	cm^3	890	80
Organic C in the sample	%	<0.1	<0.1
Length of the column(x)	cm	39	16.5
Velocity of the filtration(V)	cm/min	0.336	0.347
Potential gradient	-	0.22	1.00
Flow through of the polluting agent	-	by impulse	continiously
Duration of the impulse	h	35	-
Input Mn(II) concentration(c_o)	mg/l	20	20
pH of the synthetic solution	-	5.9	5.8

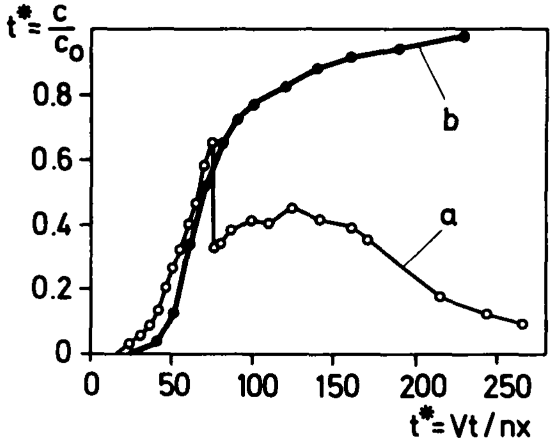

Fig. 1 Change of the Mn(II) output concentration as a function of time. Curve a: impulsive input of polluting agent - experiment 1; Curve b: continuous input of the manganese polluted water - experiment 2.

positive charge (presumably $Mn^{2+}(aq)$, $MnCl^+$, $MnHCO_3^+$, $MnOH^+$) and the rest - with no charge ($Mn(OH)_2^o$, $MnCl_2^o$).

The parameters of the migration were calculated according to the method of the "three characteristic points" - by $t^*_{0.16}$, $t^*_{0.5}$, and $t^*_{0.84}$ (refs. 1-3) - and are shown in Table 2. The following end formulas were used:

$$\varkappa = \frac{V}{x} t^*_{0.5} - n \; ; \quad \lambda = \frac{x}{8}\left[\frac{1-t^*_{0.16}/t^*_{0.5}}{\sqrt{t^*_{0.16}/t^*_{0.5}}} - \frac{1-t^*_{0.84}/t^*_{0.5}}{\sqrt{t^*_{0.84}/t^*_{0.5}}}\right]^2 ; \quad \theta = \frac{t^*_{0.5}\, c_o\, W_p}{V\, \rho\, E_{Mn}} \; ;$$

where $\varkappa$ - the distribution coefficient, λ - the parameter of the longitudinal dispersion (dispersivity), θ - the retention capacity, E_{Mn} - the equivalent mass of Mn(II).

TABLE 2

Migration parameters for the Mn(II)

Experiment	$t^*_{0.16}$	$t^*_{0.5}$	$t^*_{0.84}$	Migration parameters			
				$\varkappa$	θ /mgeq/g/	λ /cm/	Pe[a]
1	43	66	96[b]	15.6	0.0032	3.06	12.75
2	51.2	68.1	124	16.8	0.0029	3.85	4.29

[a] Peclet number; [b] after extrapolation of the experimental curve before the maximum

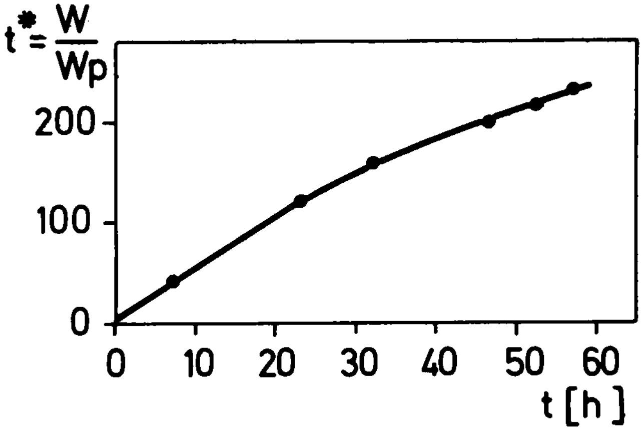

Fig. 2. Change in the volume (W) (resp. t^*) of the solution, which has passed through, as a function of the time in experiment 2.

CONCLUSIONS

The high retention capacity of the aluvial sands is evident. (The manganese midconcentration point is retarded relative to the bulk model groundwater flow by a factor of about 70.)

The almost equal parameters ($\varkappa$, θ and λ) for experiments 1 and 2 show, that the processes of retention (sorption and precipitation) are hardly dependent on the litology and filtration characteristics of the sands.

The low values of the Peclet number show, that in the cases studied the role of the molecular diffusion is important, but the convective diffusion prevails.

The character of the curve "a" in Fig. 1 after the impulse may be explained by quicker desorption (the minimum), followed by the slow dilution of the different basic precipitates of Mn(II) and/or the flush out of the contaminant from the "dead pores" (the second, large maximum with the long "tail"). This kind of experiments simulate well the situation, by which a contaminant "wave" comes from a river to an aquifer.

The conclusion, that the retention is due also to another physicochemical reaction (precipitation) is confirmed by the experimental curve, shown in Fig. 2, which proves colmatation (decrease of the permeability). The analyses of the extracted residue in the column (with 1:1 HCL) as well the small redox potential variation during the experiments are also significant in this direction. So one can say, that the sorption is not completely reversible in any of the studied cases.

The present study seems to be useful for the prediction of the manganese contamination rate in field conditions. It would be worthwhile to investigate the Mn(II) migration in strongly anaerobic conditions, in the presence of other heavy metals with or without Eh-change.

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