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## REMOVAL OF NITRATE AND AMMONIUM IONS FROM WATER BY ION EXCHANGE

The efficiency of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions' removal by ion exchange is presented. During investigations the influence of the competitive ions and the hydraulic loading value on the operating capacity of the resins tested was also established. The experiments showed that the efficiency of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions' removal depended mainly on the type of ion exchanger and chemical composition of feedwater. The presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (competitive ions) decreased the removal of ammonium ions. The course and efficiency of nitrates exchange were changed especially by sulphate ions.

### 1. INTRODUCTION

Groundwater from many areas in Poland contains nitrates and ammonium ions in higher concentration than their maximum contaminant levels (MCL) in drinking water. These levels are equal to  $10 \text{ g N-NO}_3^-/\text{m}^3$  and  $0.5 \text{ g N-NH}_4^+/\text{m}^3$ . In winter time, surface water can also be polluted by excessive amount of ammonium ions.

The processes traditionally used in water treatment plants do not remove these nitrogen compounds. Because of this some additional, more effective processes should be completed with water treatment system. This problem can be solved by the application of ion exchange, which up to the present has not been used in Poland for drinking water treatment. Practical application of ion exchange is possible provided that the ion exchangers used obtain Polish hygienic certificate.

Nowadays in Poland a few ion exchangers can be used for drinking water treatment; among them is nitrate selective resin Imac HP 555. This anion exchanger was tested in the investigation.

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## 2. BACKGROUND INFORMATION ON INVESTIGATION

The objective of the laboratory test was to investigate:

- the efficiency of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions removal,
- the influence of the competitive ions on the resins' operating capacity.

The experimental solutions were polluted with  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions ( $C_0$ ) by adding to water the known amounts of their salts:  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HCO}_3$  and  $\text{NaNO}_3$ .

The following ion exchangers were tested:

*For  $\text{NH}_4^+$  removal*

1. Ammonium selective exchanger: natural zeolite clinoptilolite (in  $\text{Na}^+$  form).
2. Ammonium non-selective exchangers:

- SAC resins: Relite C 250 (in  $\text{H}^+$  form),  
Purolite S 940 (in  $\text{Na}^+$  form).
- WAC resin: Amberlite IRC 50 (in  $\text{H}^+$  form).

*For  $\text{NO}_3^-$  removal (SBA resins)*

nitrate selective exchangers: Imac HP 555 (in  $\text{Cl}^-$  form),  
Purolite A-520 E (in  $\text{OH}^-$  form).

In order to obtain better results, countercurrent regeneration of resins was applied.

Operating exchange capacity ( $Z_{w,r}$ ) of the ion exchangers tested and the volume of water treated efficiently ( $V$ ) were calculated for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  effluent concentrations ( $C_k$ ) which are equal to:  $0.5 \text{ g N-NH}_4^+/\text{m}^3$  and  $10.0 \text{ g N-NO}_3^-/\text{m}^3$ , respectively.

## 3. THE INVESTIGATION RESULTS

### 3.1. AMMONIUM IONS' REMOVAL

The usefulness of the cation exchangers tested was different which was proved by their operating capacity values (meq  $\text{N-NH}_4^+/\text{dm}^3$  wet volume resin):

- Clinoptilolite: 2.35–16.80.
- Relite C 250: 13.6–138.2.
- Purolite S 940: 11.1–129.4.
- Amberlite IRC 50: 11.5–105.1.

Although the selectivity sequence for clinoptilolite: ( $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ ) shows preference for  $\text{NH}_4^+$  ions, the efficiency of this natural cation exchanger is

the worst. It should be attributed to strong competition of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions with  $\text{NH}_4^+$  ions.

Such a phenomenon was also observed for residual synthetic resins, but it was not so strong, but compatible with the selectivity sequence which in this case was arranged in the following ascending order:  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+$ . The influence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ion concentrations in feedwater on ammonium ions removal is shown in figure 1.

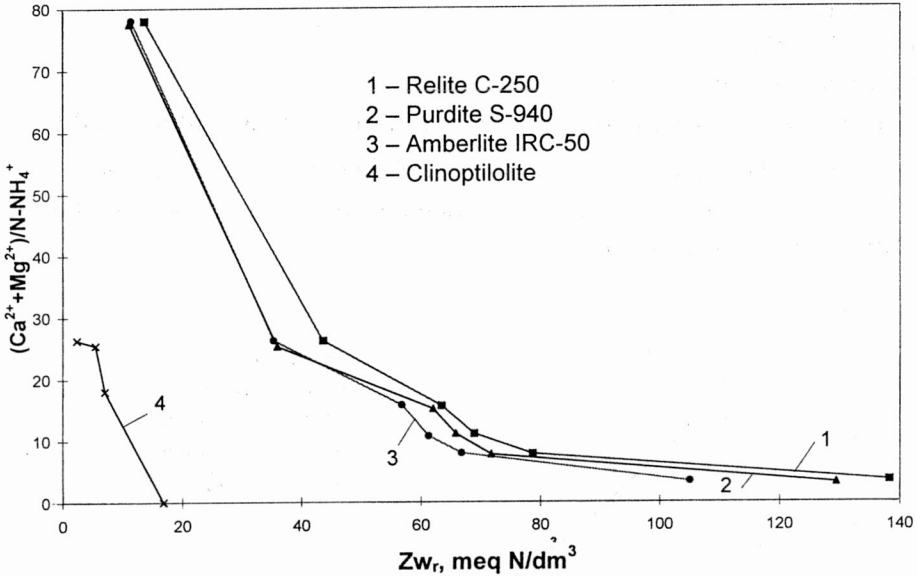


Fig. 1. Effect of the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ion concentrations on the resins' operating capacity

Table 1

Effect of  $O_h$  value on the volume of the water treated efficiently ( $V$ );  $V_B$  – bed volume

$O_h$ (m <sup>3</sup> /m <sup>2</sup> h)	$V/V_B$		
	Relite C 250	Purolite S 940	Amberlite IRC 50
5	140	114	108
10	170	152	127
20	143	135	116
30	102	119	–

In all experiments, the  $\text{Ca}^{2+}$  ion was most preferred, and the series representing the amounts of the ions exchanged was compatible with the selectivity sequence for synthetic resins.

The efficiency of all synthetic cation exchangers depended on the hydraulic loading rate ( $O_h$ ) value, and the optimum was 10.0 m/h. This influence is presented in table 1.

### 3.2. NITRATE IONS' REMOVAL

The results obtained showed that nitrate-selective resin Imac HP 555 was much better than Purolite A-520E. Their calculated operating capacities (meq N- $\text{NO}_3^-/\text{dm}^3$  wet volume resin) were:

- Imac HP 555: 651–1014.
- Purolite A-520E: 186–531.

In both cases, sulphate ions were removed from solutions and affected the  $\text{NO}_3^-$  ions exchange. The effect of  $\text{SO}_4^{2-}$  ions was different for two resins tested.

Variations of sulphate, nitrate and chloride ion concentrations in the effluent from Imac HP 555 are presented in figure 2.

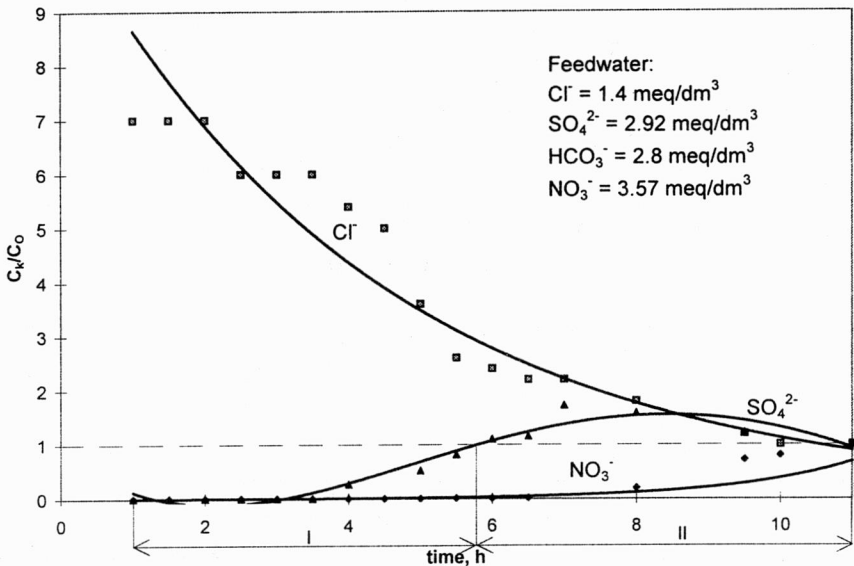
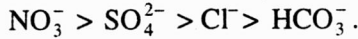


Fig. 2. Variation of sulphate, nitrate and chloride ion concentrations in the effluent from Imac HP 555

Taking into account these concentrations, this nitrate-selective resin runs can be divided in two stages:

- I: exchange of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  for  $\text{Cl}^-$ ,
- II: exchange of  $\text{NO}_3^-$  for  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  (mainly).

Such a course of ion exchange for the nitrate-selective resin is possible because the less preferred sulphate ions exit the resin in concentration exceeding their influent level more quickly than the most preferred nitrate ions, which is in agreement with Imac HP 555 selectivity sequence:



Such a phenomenon can explain why the operating capacity of this anion exchanger increased with the increase in sulphate ion concentration in feedwater (table 2).

Table 2

Effect of the quotient of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  influent concentrations on  $Z_{w,r}$  value for Imac HP 555

$\text{SO}_4^{2-}/\text{NO}_3^-$	$Z_{w,r}$ (meq N- $\text{NO}_3^-/\text{dm}^3$ )
0.41	651
0.82	691
1.00	704
1.36	726

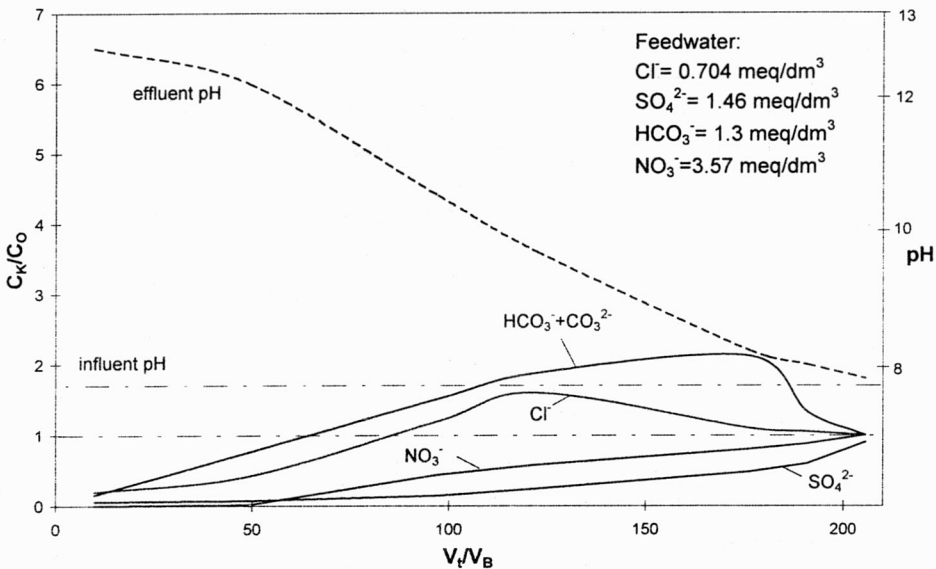
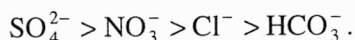


Fig. 3. Variations of anion concentrations and pH value in the effluent ( $V_e$ ) from Purolite A-520E

The effect of the  $O_h$  value, which changed in the range of 6–22 m/h, was small and equal to about 5%. Both anion exchangers tested were characterized by its best value of 12 m/h.

The application of Imac HP 555 brought about a 10% decrease in bicarbonate ions, and the effect of  $\text{HCO}_3^-$  ions on nitrate removal was very slight. A different situation arose when the second nitrate selective resin (Purolite A-520E) was used. In this case,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  (at  $\text{pH} > 8.3$ ) and also  $\text{Cl}^-$  ions acted as  $\text{SO}_4^{2-}$  ions during the second stage of Imac HP 555 runs. The process of anion exchange for Purolite A-520E is shown in figure 3 which proves that the selectivity sequence for this resin can be arranged in the following descending order:



The comparison of the water volumes treated effectively ( $c_k = 10 \text{ g N-NO}_3^-/\text{m}^3$ ) confirms better usefulness of Imac HP 555.

#### 4. CONCLUSIONS

1. Ion exchange can be used for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions' removal from water and the efficiency of this technique depends on chemical composition of feedwater, especially on the competitive ion concentrations and a type of ion exchanger.

2. Most often before ion exchange water pretreatment is needed, and ion exchangers required a hygienic certificate.

3. The efficiency of nitrate-selective resin Imac HP 555 is very high and the use of this anion exchanger can solve problem of nitrate ions' removal from drinking water.

4. Cation exchangers' efficiency can be improved by the application of two resins' system:

WAC + SAC.

Such a solution is important when feedwater is characterised by a strong bicarbonate alkalinity.

5. The main disadvantages of ion exchange are the following:

- very high concentration of  $\text{H}^+$  or  $\text{Na}^+$ ,  $\text{Cl}^-$  or  $\text{OH}^-$  ions (according to the type of the resin used) in effluent at the beginning of resin operation and high concentration of  $\text{SO}_4^{2-}$  anions during the second stage of Imac HP 555 runs,

- removal of not only  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions from water,
- generation of troublesome wastes; spent-regenerate solutions.

Two first problems can be solved by applying ion-exchange method in the treatment of water volume required and mixing it with the rest of untreated water.

#### USUWANIE JONÓW AMONOWYCH I AZOTANOWYCH Z WODY W PROCESIE WYMIANY JONOWEJ

Przedstawiono wyniki badań skuteczności wymiany jonowej w usuwaniu jonów amonowych i azotanowych z roztworów modelowych. Sprawność usuwania badanych jonów zależała przede wszystkim od rodzaju jonitu oraz obecności i stężenia jonów konkurujących w wykorzystaniu zdolności wymiennej jonitów, a w mniejszym stopniu od obciążenia hydraulicznego złóż jonowymiennych. Obecność jonów wapnia i magnezu w oczyszczanych roztworach zmniejszała ilość usuniętych jonów amonowych, a o przebiegu i skuteczności wymiany azotanów decydowało głównie stężenie jonów siarczanowych.

