

APPLICATION OF HYDROGENCARBONATE CYCLE ANION EXCHANGE FOR NITRATE REMOVAL FROM WATER

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Abstract

Contamination of natural waters with nitrate could not be stopped yet, so technologies to remove nitrates are urgently needed. In the present paper the sources of nitrate contamination are outlined, and the attempts made and technologies developed for nitrate removal are described.

At present mainly biological and chemical — first of all ion exchange — methods are used for this purpose.

The hydrogencarbonate cycle anion exchange method developed by MÉLYÉPTERV Consulting Engineering enables nitrate concentration to be reduced to as low as 2–3 mg/l. The advantage of the technique is that it restores the original natural state of the water. Nitrate is replaced by an ion the concentration of which is not limited by drinking water standards.

The procedure has been patented in Hungary, Austria, Belgium, Spain, Italy and Switzerland.

Using the procedure developed for strongly basic anion exchange resins, the IMAC HP 555 type nitrate selective anion exchange resin can be used to advantage for treating waters with high sulphate content.

1. Introduction

The nitrate content of surface and ground waters increases continuously all over the world, in our country as well. This increase is caused by the agricultural development, and by the increasing amount of waste water and sewage sludge which can be ascribed to the urbanization [1]. The contamination of the soil and ground water is further increased by the fact that as traditional animal keeping declines, the supply of the soil by humic substances is reduced [2].

The present importance of the nitrate contamination problem is reflected by the fact that in a significant proportion of the papers presented at the XIVth Congress of the International Water Supply Association devices was dealt with the problem of nitrate contamination. The conclusion drawn was that denitrification should be installed since on the long run ground waters cannot be protected from contamination [3].

As shown by the literature, the degree of contamination of ground waters is higher than that of surface waters.

The nitrate introduced into the human body with drinking water is not very poisonous, but it may be reduced to nitrite which is much more dangerous than nitrate. Nitrite reacts with haemoglobin to produce methaemoglobin, thus causing infant methaemoglobinemia, and with secondary and tertiary amines introduced with food to give nitrosamines which have a proved carcinogenic effect.

Foreign regulations usually specify limiting values between 20 and 50 mg/l nitrate, the WHO recommendation gives 10 mg/l $\text{NO}_3\text{—N}$ (44.2 mg/l NO_3) [4].

According to the Hungarian standard (450/1–78) a nitrate concentration below 20 mg/l is acceptable, concentrations between 20 and 40 mg/l are tolerable. The limiting value for separate wells is 80 mg/l, but it is strictly forbidden to give waters with a nitrate concentration exceeding 40 mg/l to infants.

We have to do everything to prevent nitrate contamination of our waters. However, if we have to use contaminated water, methods are to be sought for to remove nitrates.

2. Methods for nitrate removal

2.1. Biological denitrification

A number of attempts have been made to use biological methods for nitrate removal. In the majority of experiments the methods used for biological waste water purification were adapted to drinking water. Bringmann and Kühn used bacteria for nitrate removal in 1963 [5]. The principle of the method is that some bacteria (*Bacillus denitrificans*, *Bacterium nitrovorum*) are capable of reducing nitrate to nitrogen and nitrogen oxides in the presence of a hydrogen donor and carbon source. Gases thus formed can be purged from water. Bringmann and Kühn used gaseous hydrogen as hydrogen donor and carbon dioxide as carbon source.

Klotter used powdered milk or sugar [2], St. Amant and McCarty methanol as source of hydrogen and carbon [6]. Several other authors used methanol, however, they were aware of the danger of using this chemical [7–9].

Biological denitrification experiments have been made in Hungary, too. In one method apathogenic fungi were used, whereas water from food industry served as nutrient. In the case of a nitrate concentration of 150 mg/l in the raw water a residence time of 50–60 min was necessary to the reduction of the nitrate concentration below the limit value [10]. In another procedure the bacteria on a carrier were conditioned (nutrient: saccharose) before being used for nitrate removal [11]. When biological denitrification is used the

chemical oxygen demand and germ number of the water also increase, and, in addition to the nutrients, the metabolic products of bacteria get into the water. Accordingly, biological denitrification must be followed by a purification.

Biological denitrification may be considered for use in high-capacity plants where the precise and expert treatment necessary in biological purification may be ensured. The first biological plant for drinking water denitrification was installed in France in 1983 according to the literature [12]. The denitrification device was constructed according to the procedure of the firm O.T.V./Omnium de Traitement et de Valorisation, subsidiary company of the Compagnie Generale des Eaux), with a capacity of 1600 m³/d. The nitrate content of the raw water is 100 mg/l, that of the purified water 25 mg/l.

In the GFR an apparatus with a capacity of 100 m³/h (2400 m³/d) was installed in 1986 (DENITROPUR procedure, Sulzer Wasser- und Abwassertechnik). The nitrate concentration of the water was 80 mg/l before, and below 1 mg/l after purification. Hydrogen and carbon dioxide were used as hydrogen and carbon source [13].

2.2. Chemical methods

Nitrates are all readily soluble, so they cannot be removed in the form of precipitates. Chemical reduction of nitrates has been dealt with by several authors. The results of experiments have shown that under the usual conditions (in neutral solution, at room temperature) no appreciable nitrate reduction can be expected [14]. If, however, the reduction is carried out in strongly acid or strongly alkaline solution in the presence of a catalyst [15], the water produced cannot be used as drinking water, the less so as the main reduction product under the condition applied is ammonia, the limit value for which is by orders of magnitude smaller than that of nitrate.

The literature on the use of ion exchangers for water treatment is wide. A number of experiments and even plant technologies have been described [14, 16–24] with use of ion exchangers.

In the majority of works strongly basic anion exchangers in the chloride form are used for nitrate removal. Such procedures are described in the catalogues of companies producing ion exchangers [17–24, 26–29].

In Hungary Levárdy and Sellyey described experiments for removing nitrate using an anion exchanger in the chloride form in 1973 [25]. Buelow made detailed studies on the nitrate-chloride ion exchange process [23]. In a U.S. Environmental Protection Agency Report [24] the results of a thorough comparative study of the efficiency of anion exchanger produced in the U.S. in nitrate removal are presented. The study shows that chloride cycle anion exchange is used most widely for nitrate removal, deionization by ion exchange

or other methods (evaporation, reverse osmosis, electro dialysis) is much more expensive, and not used at present for nitrate removal.

In chloride cycle anion exchange — as nitrate selective anion exchanger was not available — the sulphate and part of the hydrogen carbonate is also exchanged for chloride. This, in addition to binding part of the resin capacity, is unfavourable for other reasons, too. At high salt concentrations the chloride content of the treated water may exceed the allowable limit for drinking water, and the water may become corrosive.

In order to eliminate these adverse effects, a hydrogen carbonate cycle ion exchange nitrate removal procedure was developed by MÉLYÉPTERV Consulting Engineering which has been patented in Hungary, Austria, Spain, Belgium, Italy and Switzerland. (Patent application in progress in France, the Netherlands and GFR). The advantage of the method is that it introduces an ion into the water which is a natural component and the concentration of which is not limited by drinking water standards.

The principle of the method is that the exhausted anion exchanger is regenerated in two steps: first with a chloride solution, then with hydrogen carbonate. In our experience the efficiency of the direct exchange of the nitrate for hydrogencarbonate is not sufficient.

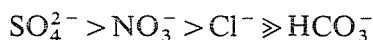
The procedure has been thoroughly studied by the author of the present paper in his thesis [30], and some of the findings will be mentioned later.

The procedure has been tested on the plant scale, and the results have been good [31, 32]. The consumption of chemicals in the regeneration was smaller even in plant experiments.

The introduction of hydrogencarbonate cycle nitrate removal was considered to be desirable by Gros and Kyburz [33] and by Höll and Kiehling [34]. The latter authors used limestone (CaCO_3) and carbon dioxide under pressure for regenerating the ion-exchange resin. However, they have found that the efficiency of regeneration was not sufficient and the nitrate-removal capacity of the resin was low. Starting from these experiments, a new procedure has been developed (CARIX) which, by using cation and anion exchanger in the same apparatus, simultaneously reduces the nitrate content and hardness. Carbon dioxide was used for regeneration, the excess was recycled [35].

The most recent result is the development of nitrate selective ion exchange resins.

For the usual, strongly basic anion exchangers the order of binding strength is



According to studies by Buelow this order is true for raw waters with medium salt concentration (about 400 mg/l), but at high salt contents (about 20 000 mg/l) nitrate and sulphate change places [23].

Recently nitrate selective ion exchangers have been developed by the Rohm and Haas Company under the trade name IMAC HP 555 and the VEB Chemiekombinat Bitterfeld (GDR) under the trade name Wofatit SN35L and SN36L which bind nitrate favourably to sulphate even at high sulphate concentrations in the case of raw waters with medium salt content [36–40].

These ion exchangers enable the drawbacks inherent in chloride cycle nitrate removal to be eliminated and offer special advantages [38].

Literature data concerning the evaluation of biological and ion exchange nitrate removal are sometimes contradictory. In some French papers biological procedures are preferred [41] since the use of ion exchangers is not allowed in France for drinking water treatment. However, the proceedings of a symposium on nitrate in France in 1987 includes ion exchange procedures [42, 43]. This may be attributed to the fact that the IMAC HP 555 resin was allowed to be used for treating drinking water by French hygienic authorities.

In contrast with this, Sorg, research scientist of the US Environmental Protection Agency considered biological methods as non-allowable due to the following facts:

- usually organic material should be added to waters originally free from organic matter (this can be avoided by using H_2 and CO_2),
- a high bacterium population develops in waters generally free from bacteria,
- the system loses its efficiency if the biomass is deteriorated.

According to the paper by Sorg [44] the only procedure that can be widely accepted for nitrate removal from drinking waters is ion exchange.

In the following sections experiments made by using IMAC HP 555 type ion exchanger (Rohm and Haas) are described. The results are in some cases compared with those obtained strongly basic ion exchangers.

3. Nitrate removal experiments using hydrocarbonate cycle

3.1. *Experimental ion-exchanger, experimental conditions*

The ion-exchange column was a glass tube with a diameter of 21.6 mm. The length of the ion exchanger bed was 600 mm (220 cm³). Regeneration was carried out in the same direction as the nitrate removal, i.e. in direct flow. Model waters with different compositions were prepared from drinking water in Budapest by addition of potassium nitrate and sodium sulphate to tap water. The model waters were treated by an ion exchange procedure. The flow rates of water and regenerating solutions were chosen in accordance with manufacturer recommendations: generally 15 m/h, 25 BV/h for the raw water and 2–4 m/h, 3–5 BV/h for the regenerant (BV = bed volume). The ion exchanger was considered exhausted at a nitrate concentration of 0.3 meq/l (18.6 mg/l) in the effluent.

3.2. Methods of measurements

In the exhaustion phase the pH, alkalinity, chloride, nitrate and sulphate concentrations of the treated water were controlled according to Hungarian standard prescriptions (Hung. Stand. No 448, Pages 12, 13, 15, 21 and 22). From the data measured exhaustion curves were constructed by plotting the ionic concentrations (meq/l) of the effluent as function of the amount of water passed through.

3.3. Results

As mentioned earlier, traditional strongly basic ion exchangers can be regenerated in two steps, using chloride solution (e.g. 10% sodium chloride) in the first, and hydrogen carbonate solution (e.g. 5% sodium hydrogencarbonate) in the second step. This method was efficient for all the strongly basic anion exchangers used (Varion AD, Lewatit M 600, Wofatit SBW), but also for a weakly basic anion exchanger (Varion ADA). The strongly basic resins examined were found to behave very similarly.

With the resins mentioned practically complete nitrate and sulphate removal could be achieved (average nitrate concentration of the treated water 5 mg/l) using 170 g NaCl and 227 g NaHCO₃ for 1 l of resin. With these regenerant amounts resin capacities of 0.77–0.8 eq/l for Varion AD and Wofatit SBW and 1.02 eq/l for Lewatit M600 could be achieved. These capacities are

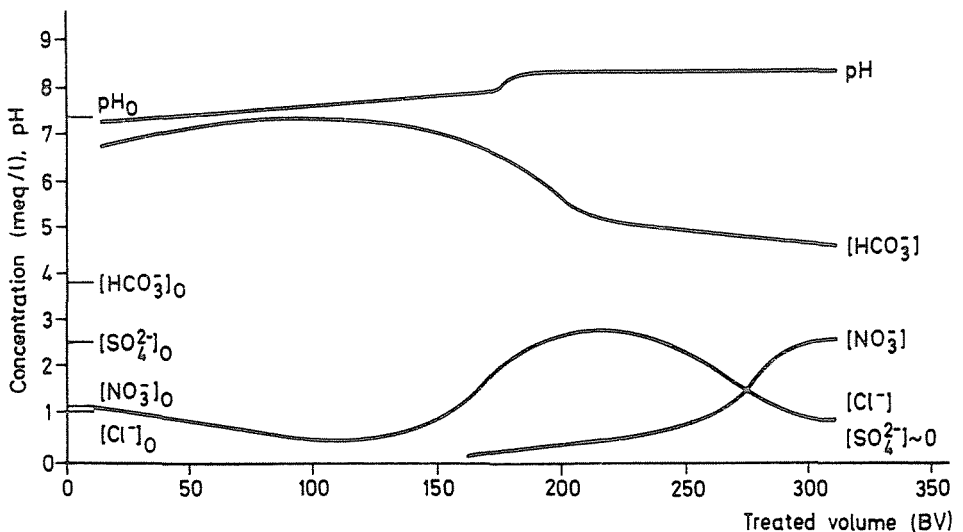


Fig. 1. Exhaustion of Varion AD ion exchanger (after treatment with a 170 g NaCl + 227 g NaHCO₃/l resin)

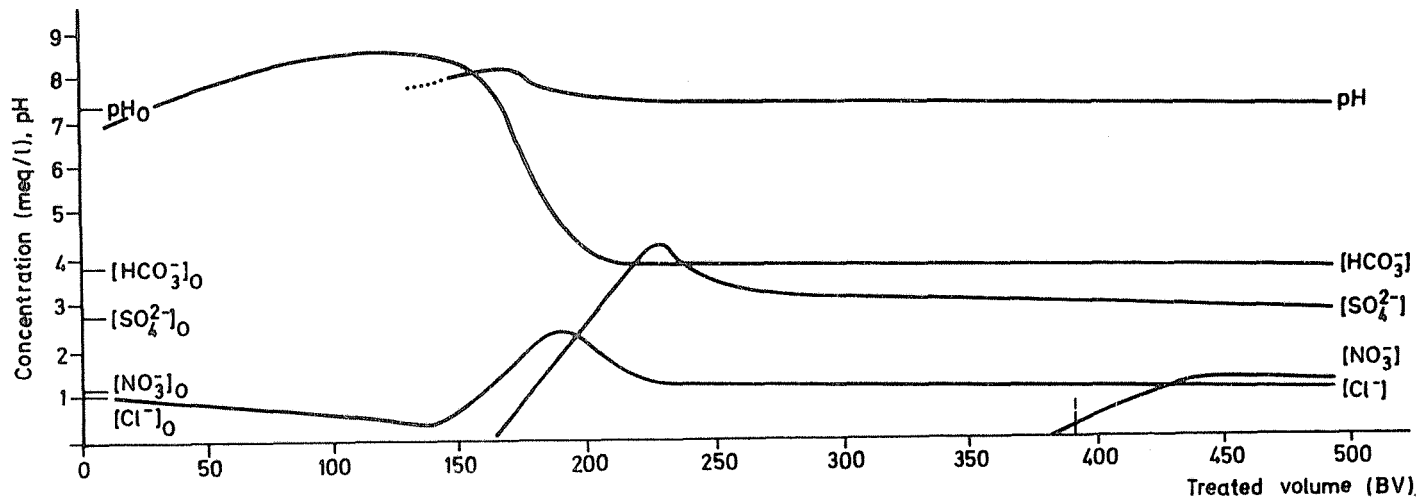


Fig. 2. Exhaustion of IMAC HP 555 ion exchanger (after treatment of the chloride form exchanger with 227 g NaHCO₃/l resin)

valid for nitrate and sulphate together. The capacities for the particular ions depend on the water composition, and they become less favourable for nitrate as the sulphate concentration increases.

E.g. for a raw water with 200 mg/l nitrate and 48 mg/l sulphate concentration the total capacity was 0.84 eq/l and the nitrate capacity 0.58 eq/l, whereas for a raw water with 70 mg/l nitrate and 115 mg/l sulphate the total capacity was 0.78 eq/l, and the nitrate capacity only 0.29 eq/l.

The exhaustion curve for the latter case with use of Varion AD ion exchanger is shown in Fig. 1.

The curve obtained for the same water sample on an IMAC HP 555 resin is shown in Fig. 2. The ion exchanger was used even after nitrate break-through. These experiments proved the great advantage of the nitrate-selective ion exchanger, namely that the nitrate concentration may increase only up to that of the raw water after break-through, but does not exceed it, as is the case with traditional strongly basic anion exchangers. Fig. 1 shows that for the latter the nitrate concentration of the treated water reaches twofold of the nitrate concentration of the raw water. The total capacity of the IMAC HP 555 was 0.81 eq/l, the nitrate capacity 0.49 eq/l in this case, i.e. nearly twofold that of the traditional strongly basic anion exchanger (See Table 1 including also data for Varion AD).

However, this cycle is not really comparable since the IMAC HP 555 resin in the chloride form was first transformed into the HCO_3^- form, using 227 g sodium hydrogencarbonate (in 5% solution) per 1 l of resin.

Starting from data given by P. Ambrus [38], 1.5-fold the amount used by him in counter-flow was applied in the present work for regenerating the exhausted resin in direct flow. In the next exhaustion experiment the concentration of the raw water was raised to twofold, at unchanged nitrate-to sulphate ratio. The results of exhaustion experiments carried out after resin

Table 1

Regenerating and exhaustion characteristics of IMAC HP 555 ion exchanger
(data with * refer to the exchanger Varion AD)

Regenerating chemical		Useful capacity		Average nitrate concentration of treated water mg/l
NaCl (10%)	NaHCO_3 (5%)	NO_3 cap.	total cap.	
g/l resin		eq/l resin		
90	120	0.25	0.67	40—50
160	180	0.31	0.71	40—50
350	227	0.37	0.75	15
500	227	0.47	0.79	8
170*	227*	0.29*	0.78*	5*

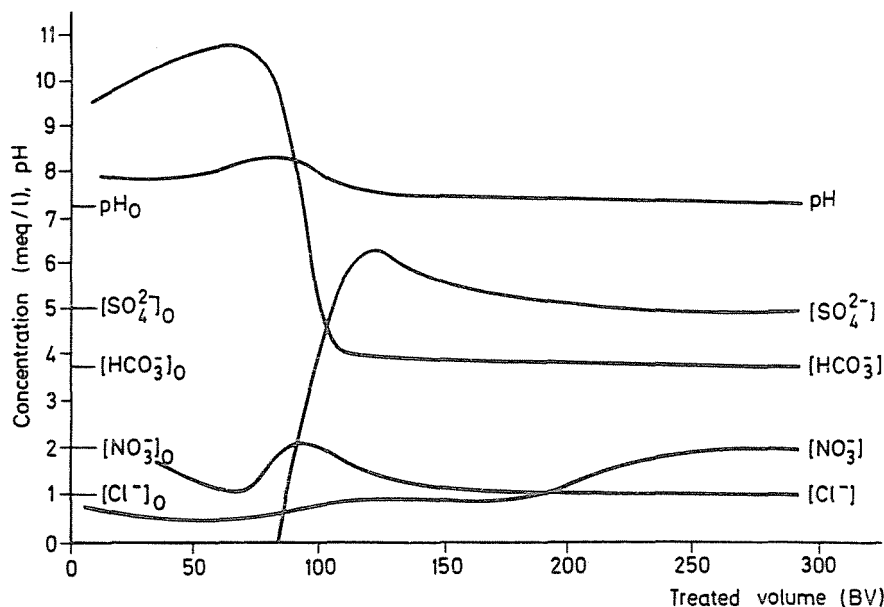


Fig. 3. Exhaustion of IMAC HP 555 ion exchanger (after treatment with a 90 g NaCl + 120 g NaHCO₃/l resin)

regeneration have shown that the regeneration was not sufficient to ensure a nitrate concentration of the treated water below 20 mg/l (See Fig. 3). If the limit value is 50 mg/l (0.8 meq/l), the efficiency of regeneration can be accepted, and the nitrate capacity of 0.25 eq/l as well. This is a remarkable achievement, since with a traditional strongly basic anion exchanger using nearly twofold amount of sodium chloride and sodium hydrogencarbonate a nitrate capacity of 0.29 eq/l could be attained.

Later on the amount of the regenerating chemical was increased at unchanged nitrate (120 mg/l) and sulphate (250 mg/l) concentrations. The purpose of the experiments was to determine the amount of regenerant necessary to keep the nitrate concentration in the treated water below 20 mg/l. The results are summarised in Table 1. On increasing the amount of regenerant the nitrate capacity and total capacity of the IMAC HP 555 resin increased, but a remarkable reduction in the nitrate content of the water was observed only when 350 g NaCl and 227 g sodium hydrogencarbonate was used for 1 l of resin. These amounts are acceptable even if the nitrate concentration should be kept below 20 mg/l.

Using 210 g of NaCl followed by 227 g of sodium hydrogencarbonate, or 227 g of sodium chloride (in 5% solution) and 227 g of sodium hydrogencarbonate in the regeneration step did not result any appreciable improvement in the resin capacity or the nitrate concentration of the treated

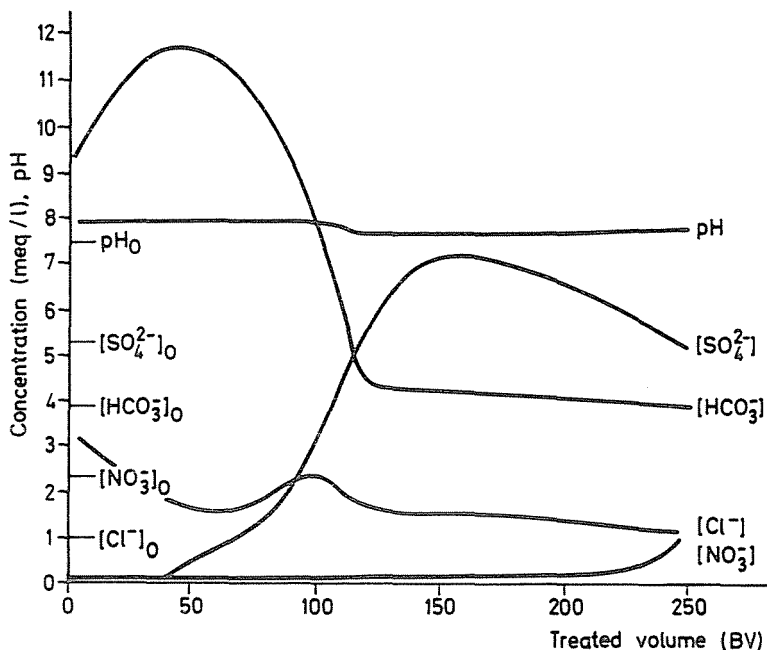


Fig. 4. Exhaustion of IMAC HP 555 ion exchanger (after treatment with a 500 g NaCl + 227 g $NaHCO_3/l$ resin)

water. The results of these experiments are not included in the table. Neither are given data for the regeneration experiments with use of sodium hydrogen-carbonate alone, which, similarly to the case of strongly basic anion exchangers, did not ensure a sufficiently good regeneration of the nitrate — selective resin.

If the treated water should contain nitrate below 5 mg/l, 500 g sodium chloride and 227 g sodium hydrogencarbonate should be used in direct-flow regeneration. An exhaustion experiment following a regeneration step made with the above quantities is demonstrated in Fig. 4. In this experiment more sodium chloride is needed than with strongly basic anion exchangers to keep the nitrate concentration low, which is in agreement with the result reported by P. Ambrus, namely that in the regeneration of the nitrate-selective resin with sodium chloride, the nitrate elution is tailing, the curve is flat, whereas the sulphate elution curve is sharply increasing and reaches a maximum. With traditional strongly basic anion exchangers the nitrate elution curve is also steep and has a maximum.

An evaluation of the data in Table 1 shows that for a raw water with a nitrate to sulphate concentration ratio of 1:2–2.6, threefold the amount of sodium hydrogencarbonate is needed with the IMAC HP 555 resin than with

the Varion AD resin to ensure a nitrate concentration of the treated water between 5 and 8 mg/l.

However, the amount of treated water is 1.6 times higher with the IMAC HP 555 resin, which means that for an equal amount of water with the IMAC resin the sodium chloride is 1.8-fold, the sodium hydrogencarbonate is only 0.62-fold the amount needed with the Varion resin.

In Hungary the price of sodium hydrogencarbonate is threefold that of sodium chloride, so the nitrate-selective resin is preferable in the case of waters with a relatively high sulphate content.

The situation is much better if a nitrate concentration of 15 mg/l is allowable in the treated water. At a limit of 50 mg/l, the specific regenerant use is reduced to the minimum value shown in Table 1. With counter-flow regeneration the regenerant consumption is even smaller.

Summing up it can be stated that the IMAC HP 555 nitrate selective ion exchange resin can be used advantageously for nitrate removal from waters with high sulphate concentration in the hydrogencarbonate cycle, with a favourable regenerant, requirement as compared to traditional strongly basic anion exchangers. In addition to a reduction in costs, the amount of the salt water by-product is reduced, thus reducing the environmental dangers of the procedure.

The continuation of the experiments by studies with waters with a different composition, and with use of nitrate-selective resins produced by other manufacturers seems to be necessary and desirable.

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