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DEIONIZATION OF WATER WITH A RECOVERABLE REGENERANT

A process, consisting of a mixed-bed ion exchange column operated in an organic phase, was followed by an ultrafiltration process, for deionization of water with a recoverable regenerant. The proposed process would have three advantages compared with conventional mixed-bed deionization. First, all the cations and anions retained in the exhausted mixed-bed resin column would be replaced by one organic regenerant. Second, the process would not require separation of the resins for regeneration. Third, the organic regenerant discharged from the column, during the service cycle, could be recovered for reuse through use of a UF membrane separation.

During the service cycle, for an influent feed solution containing 420 g Ca^{++}/m^3, 98 g Mg^{++}/m^3, 390 g $SO_4^{=}/m^3$, and 760 g Cl^-/m^3, the column utilization ratios were approximately 47% and 80% for the cation and resins, respectively. Approximately, 99% of the cations (Ca^{++} and Mg^{++}) and anions ($SO_4^{=}$, Cl^- and HCO_3^-) retained in the exhausted mixed-bed column, during the service cycle, were removed by introducing an 8% sodium gluconate regeneration solution to the column in a downflow made at 28.0×10^{-4} m^3/m^2s rate. A UF/RO (Sepa-97) CA membrane was successful for recovery of sodium gluconate with rejection efficiency of 97.5% to 98.2% and a water flux of 4.13 gpd/ft^2.

1. INTRODUCTION

Ionic pollutants produced from industrial plants, refineries and municipal sewage have a detrimental effect on the ecological balance of lakes, rivers streams and even the oceans. In addition, ionic pollution is known not only to destroy the food chain of marine life but also to cause hazards to swimmers and fishermen. In view of these facts, it is necessary to demineralize industrial water or waste streams prior to use or discharge into receiving bodies of water.

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Water can be demineralized by many processes such as distillation, reverse osmosis, chemical precipitation or ion exchange. Among them, the ion exchange processes have been preferred because of the high purity water produced, i.e., low TDS. However, the costs of chemicals required for these systems have been quite high per unit of various salts removed and the resulting spent regenerants are a worse problem in many cases than the wastes themselves. Therefore, the objective of this research was to investigate a new regeneration technique for the mixed-bed ion exchangers process which would be less complicated than the presently used method and which would not produce any spent regenerant chemicals other than the ionic species in the feed water to the units.

2. CHEMICAL PRINCIPLE

The basic scheme of the proposed process (shown in fig. 1) consists of operating a mixed-bed ion exchange (IE) column in an organic phase (sodium gluconate) followed by an ultrafiltration (UF) regenerant recovery process. During the service cycle, it was assumed that al lthe cations (or anions) would be replaced by Na^+ (or gluconate ion) when a test water was fed to the mixed-bed resin.

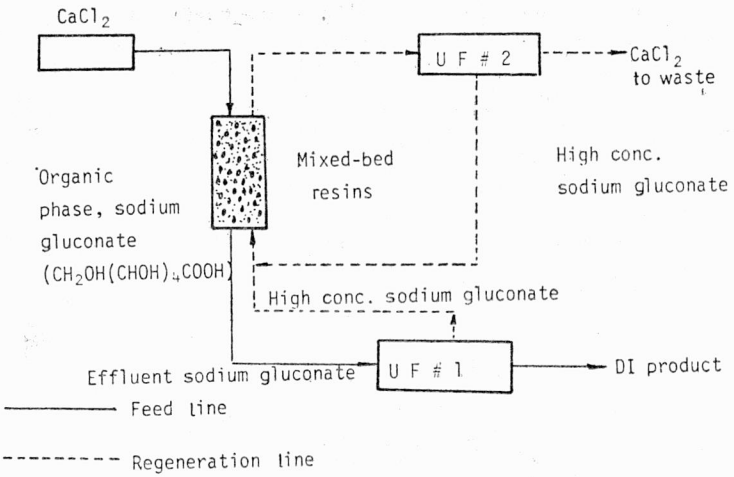

Fig. 1 Proposed process for regeneration of mixed-bed ion exchangers column

1 – service cycle: $CaCl_2 + 2Na^+ Z_C^- + 2Z_A^+ R^- \rightarrow Ca^{++} Z_{C2}^- + 2Z_A^+ Cl + 2Na^+ R^-$

2 – regeneration cycle: $Ca^{++} Z_{C2}^- + 2Z_A^+ Cl + 2Na^+ R^- \rightarrow 2Na^+ Z_C^- + 2Z_A^+ R^- + CaCl_2$

Z_C – cation exchanger, Z_A – anion exchanger, R^- – gluconate ion

Rys. 1. Proponowany proces regeneracji kolumny ze złożem mieszanym

1 – cykl pracy: $CaCl_2 + 2Na^+ Z_C^- + 2Z_A^+ R^- \rightarrow Ca^{++} Z_{C2}^- + 2Z_A^+ Cl + 2Na^+ R^-$

2 – cykl regeneracji: $Ca^{++} Z_{C2}^- + 2Z_A^+ Cl + 2Na^+ R^- \rightarrow 2Na^+ Z_C^- + 2Z_A^+ R^- + CaCl_2$

Z_C – kationit, Z_A – anionit, R^- jon glukonianowy

The IE effluent containing sodium gluconate is then applied to the UF process (UF #1), where the UF membrane can concentrate the organic regenerant for the next regeneration of the mixed-bed resins. In addition, the spent organic regenerant has to be separated from the smaller inorganic ions (Ca^{++}, Mg^{++}, $SO_4^{=}$, Cl^{-}), through the UF membrane process (UF #2).

3. MATERIALS AND METHODS

3.1. MIXED-BED RESINS COLUMN TESTS

The commercially available macroporus cation (Amb-200) and anion (IRA-900) exchangers were employed in these investigations. These resins having large discrete pores and high internal surface area, are capable of rapid removal of high molecular weight ions from solutions. The ions can then be more rapidly eluted from the resin upon regeneration than would ordinarily be observed with other exchangers. Although the macroreticular resins, on the whole, have lower capacities and higher regeneration costs compared to the gel type resins, this is often offset by the longer operating life of the macroreticular resins [6].

An ordinary pyrex 50 cm^3 burette (73.5 cm long and 1.2 cm in diameter) was used as an ion exchange column in these studies. The bed was supported by a 3 cm layer of pyrex glass beads and a small layer of glass wool. A 1000 cm^3 separatory funnel supplied the influent, and flow rate was adjusted by regulating the burette stopcock.

In general, the cyclic operation of the ion exchange column consisted of the following steps: backwash, regeneration, rinse and exhaustion (service). However, in these particular investigations, an additional initial cycle, i.e. resin conversion, was needed to convert the introduced anion exchanger from the Cl^- phase, as it was received, into the desired organic phase (gluconate). The schedule of the mixed-bed column test is listed in tab. 1.

3.2. UF MEMBRANE TESTS

The ultrafiltration studies were conducted using the apparatus shown in fig. 2. The membranes used were Amicon UMO 5 and Osmonics Sepa-97 CA. The documented molecular weight cut-off for these membranes was 500 and 200, respectively. The schedule of the UF membrane tests and their corresponding feed solutions are shown in tab. 2. Basically, these solutions simulated the treated effluent and the regenerant effluent that would normally be obtained from the mixed-bed resin column during service and regeneration cycles.

Table 1

Schedule of service cyle and regeneration cycle for IRA-900/Amb-200 mixed-bed resin column tests
Schemat badań cyklu pracy i cyklu regeneracji kolumny ze złożem mieszanym IRA-900/Amb-200

Run #1	Cycle name	Mixed-bed resins	Organic regenerant	Inogranic ions
MX-1	Resin conversion	IRA-900/Amb-200	1% sodium gluconate	–
MX-2	Service	IRA-900/Amb-200	–	$CaCl_2$ and $MgSO_4$
MX-3	Service	IRA-900/Amb-200	–	Tap water
MX-4	Regeneration	IRA-900/Amb-200	2% sodium gluconate	–
MX-5	Regeneration	IRA-900/Amb-200	5% sodium gluconate	–
MX-6	Regeneration	IRA-900/Amb-200	8% sodium gluconate	–
MX-7	Regeneration	IRA-900/Amb-200	8% sodium gluconate	–
MX-8	Regeneration	IRA-900/Amb-200	2% sodium gluconate	–
MX-9	Regeneration	IRA-900/Amb-200	8% sodium gluconate	–
MX-10	Service	IRA-900/Amb-200	–	$CaCl_2$ and $MgSO_4$

Table 2

Schedule of UF membrane tests and their corresponding feed solution
Schemat badań membran ultrafiltracyjnych i skład roztworów zasilających

Run #	Membrane	Feed solution	Pressure (MPa)
UF-1	Sepa-97 CA	5000 g sodium gluconate/m^3	0.86–1.03
UF-2	UMO 5	5000 g sodium gluconate/m^3	0.41–0.69
UF-3	Sepa-97 CA	40,080 g sodium gluconate/m^3 370 g Ca^{++}/m^3 and 390 g $SO_4^{=}/m^3$	0.86–1.03
UF-4	UMO 5	20,020 g sodium gluconate/m^3 370 g Ca^{++}/m^3 and 390 g/$SO_4^{=}/m^3$	0.41–0.69

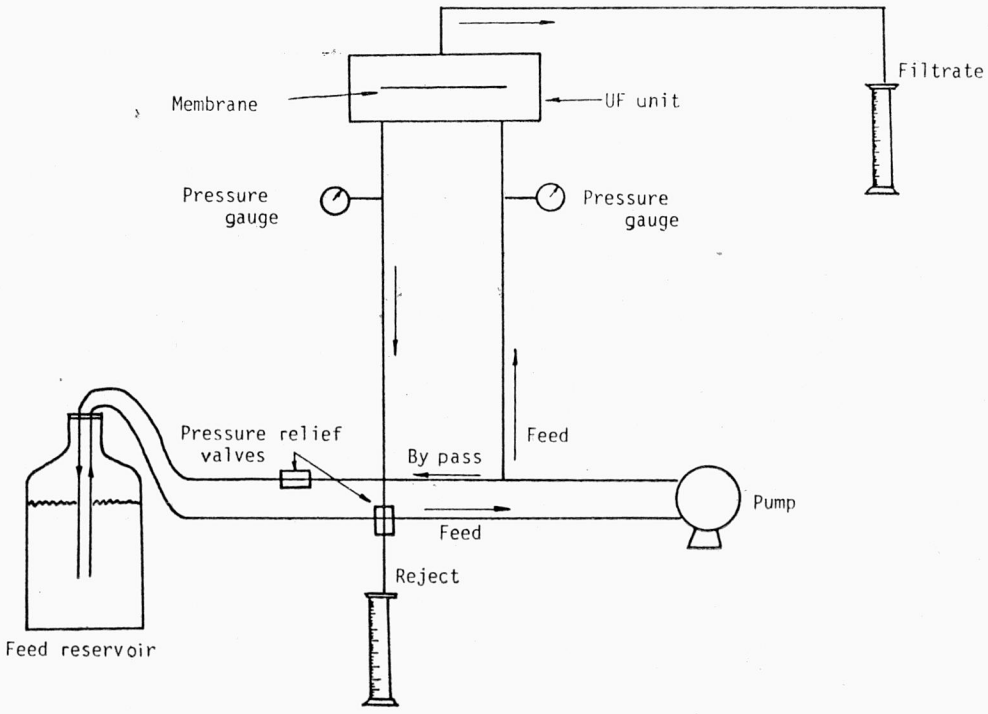

Fig. 2. Laboratory set-up for UF process operation
Rys. 2. Zestaw laboratoryjny do procesu ultrafiltracji

The Sepa-97 CA membrane was operated at a pressure of approximately 1.0 MPa, whereas, according to the manufacturer, the UMO 5 membrane was operated below 0.8 MPa. The resultant filtrate regenerate samples collected with time were analyzed, via hydroxamic acid formation [3] for their gluconate concentration.

4. RESULTS AND DISCUSSIONS

4.1. MIXED-BED RESIN COLUMNS

4.1.2. RESIN CONVERSIONS

As mentioned previously, the Amb-200 and IRA-900 resins were selected as the representative cation and anion exchangers, respectively, because of their high resistance to organic fouling, excellent physical stability, suitability for deionization and to their potential abilities of capturing high molecular weight organics.

A feed solution of approximately one percent sodium gluconate was added to the mixed-bed resin (Amb-200/IRA-900) column in a down-flow mode at

4.0×10^{-4}m/s, until the IRA-900 resin was exhausted. Figure 3 depicts the results of resin conversion by feeding one percent sodium gluconate solution to the column.

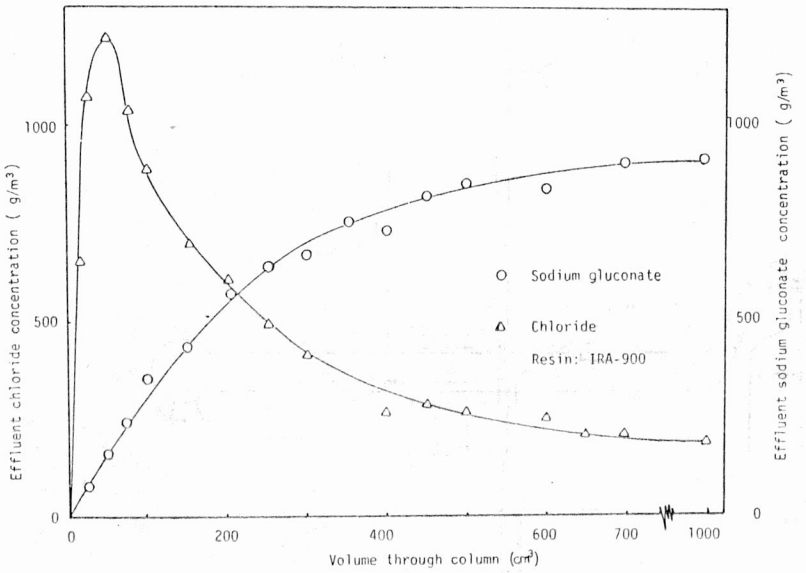

Fig. 3. Run # MX-1; initial sodium gluconate elution of the IRA-900 resin
Rys. 3. Próba MX-1; zawartość glukonianu sodu w wycieku ze złoża IRA-900

The higher column utilization (98.5 %) of the IRA-900 resin presented in fig. 3 indicates that the active sites of these macroporus resins were almost completely converted to the organic phase, i.e. to gluconate form, during the exchange process.

4.1.3. SERVICE CYCLE

The IRA-900 resin was assumed to be converted to the gluconate phase, when the effluent sodium gluconate concentration approximated that of the influent. The column was then thoroughly rinsed with distilled (DI) water. Subsequently, a test feed water was prepared as follows:

cations — 420 g Ca^{++}/m^3 and 98 g Mg^{++}/m^3,

anions — 390 g $SO_4^{=}/m^3$ and 760 g Cl^-/m^3.

This test water was introduced to the column for the initial service cycle (run #MX-2).

The resultig breakthrough curve for run #MX-2 is shown in fig. 3 illustrating that the breakthrough volumes of Cl^- and $SO_4^{=}$ were 300 cm^3 (6.42 meq) and 500 cm^3 (4.06 meq), respectively. Upon application of $SO_4^{=}$ and Cl^- to the mixed-bed resin column, the gluconate began to appear in the effluent, indi-

cating an exchange between the anions and gluconate. The effluent gluconate concentration reached a nearly constant concentration until Cl^- breakthrough. Prior to the occurrence of Cl^- in the effluent (fig. 4) it was observed that the amount of gluconate eluted (8.61 meq) was approximately equal to that of $SO_4^=$ (2.44 meq) and Cl^- (6.42 meq) retained in the column. In other words, for the mixed-bed DI system, the stoichiometric relationship between the gluconate and $SO_4^=$ (or Cl^-) was not changed even in the presence of the cations, i.e. Ca^{++} and Mg^{++}. The 88.6 % elution of sodium gluconate shown in tab. 3 implies that the same degree of column utilization for IRA-900 resin was also achievable in the system. This amount of sodium gluconate was expected to be separated and recovered through the use of a UF/RO Sepa-97 CA membrane.

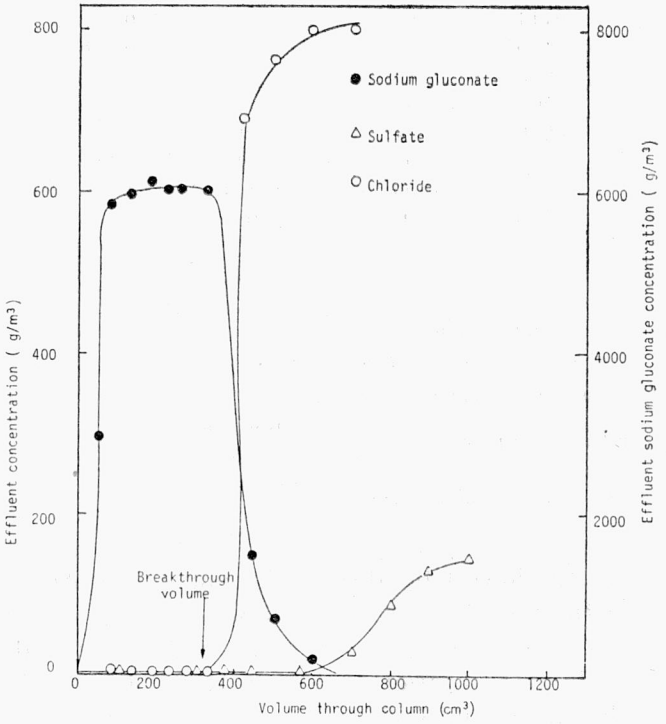

Fig. 4. Run # MX-2; service cycle — results of calcium chloride and magnesium sulphate application

Rys. 4. Próba MX-2; cykl pracy — wyniki zastosowania chlorku wapnia i siarczanu magnezu

On the other hand, the breakthrough volumes of Ca^{++} and Mg^{++} presented in fig. 4 were 650 cm^3 (13.7 meq) and 600 cm^3 (4.84 meq), respectively. The occurrence of the higher breakthrough volumes of Ca^{++} and $SO_4^=$ was ascribed to a stronger affinity for Amb- 200 and IRA-900 resins, respectively. In practice, the breakthrough volume in a mixed-bed DI system is established by the

Table 3

Run #MX-2 service cycle – results of test water (Ca^{++}, Mg^{++}, $SO_4^{=}$, and Cl^-) application

Przebieg cyklu pracy MX-2 w próbach z wodami modelowymi (Ca^{++}, Mg^{++}, $SO_4^{=}$ i Cl^-)

Vol. through column (cm^3)	Effluent gluconate (g/m^3)	Effluent Ca^{++} (g/m^3)	Effluent Mg^{++} (g/m^3)	Effluent $SO_4^{=}$ (g/m^3)	Effluent Cl^- (g/m^3)
50	2962	0	0	0	0
85	5854	0	0	0	0
135	5967	0	0	0	0
185	6114	0	0	0	0
235	6010	0	0	0	0
260	6028	0	0	0	0
300	6000	0	0	0	0
335	5980	0.04	0.02	0	2.0
445	1487	0	0.02	0.01	770
555	0	0.006	0.018	4.0	–
600	0	0	5.0	–	–
650	0	5.0	–	–	–

Resins: Amb-200/IRA-900 (10cm^3-wet each).

Feed solution: Ca^{++} – 420 g/m^3 (21.0 eq/m^3), Mg^{++} – 98 g/m^3 (8.07 eq/m^3), $SO_4^{=}$ – 390 g/m^3 (8.12 eq/m^3), Cl^- – 760 g/m^3 (21.4 eq/m^3).

Column utilization ratio for Amb-200: $\frac{0.300(21.0+8.07)}{(1.7)(10)} = 51.3\,\%$.

Column utilzation ratio for IRA-900: $\frac{0.30(8.12+21.4)}{(1.0)(10)} = 88.6\,\%$.

ion which possesses the lowest breakthrough volume. Accordingly, the breakthrough volume for the mixed-bed DI system was 300 cm^3 when a feed solution of 760 g $CaCl_2/m^3$ (as Cl^-) and 390 g $MgSO_4/m^3$ (as $SO_4^{=}$) was added to the column. As a result, the column utilization ratio for Amb-200 resin was determined to be 51.3 %, as shown in tab. 3.

Another part of the study dealt with the use of a naturally occurring hard water (Purdue University "Cold Tap" water), as opposed to the previous studies in which a laboratory prepared hard water was employed. This unsoftened, well-water supply was added directly to the column. Thus, influent feed characteristics were:

cations – 90 g Ca^{++}/m^3, 30 g Mg^{++}/m^3, and 15 g Na^+/m^3,

anions – 80 g $SO_4^{=}/m^3$, 19.5 g Cl^-/m^3, and 284 g HCO_3^- (as $CaCO_3$)/m^3.

In addition to the typical effluent analysis performed in previous runs, HCO_3^- (bicarbonate) concentration in the column effluent was measured with

time. However, in the presence of $SO_4^{=}$ and organic acid (gluconate) the common analysis for HCO_3^- presented in *Standard Methods* could not be utilized. Instead, the differential titration method proposed by *ASTM Standards* [1] was used for HCO_3^- analysis. Table 4 illustrates the characteristic effluent results for the service cycle of run #MX-3.

Table 4

Run #MX-3 service cycle – results of Purdue cold tap water (Ca^{++}, Mg^{++}, $SO_4^{=}$, Cl^-, and HCO_3^-) application to the mixed-bed (Amb-200/IRA-900) resins column

Przebieg cyklu pracy MX-3 w kolumnie ze złożem mieszanym (Amb 200/IRA-900) zasilanej zimną wodą wodociągową miasta Purdue

Vol. through column (cm^3)	Effluent gluconate (g/m^3)	Effluent Ca^{++} (g/m^3)	Effluent Mg^{++} (g/m^3)	Effluent $SO_4^{=}$ (g/m^3)	Effluent Cl^- (g/m^3)	Effluent HCO_3^- (g/m^3)
40	1436	0	0	0	0	0
95	1541	0	0	0	0	0
150	1592	0	0	0	0	0
215	1696	0	0	0	0	0
275	—	0	0	0	0	0
335	1696	0	0	0	0	0
385	1522	0	0	0	0	0
515	1592	0	0	0	0	0
685	1349	0	0	0	0	0
Breakthrough volume						
750	1522	0	0	0	0	4.0
835	1522	0	0	0	0	
1255	240	0.07	0.005	0	0	
1455	0	0.10	2.5		12.0	
2035	0	2.2			29.9	

Resins: Amb-200/IRA-900 (10 cm^3-wet each).

Feed solution: Na^+ – 15 g/m^3 (0.65. eq/m^3), Ca^{++} – 90 g/m^3 (4.5 eq/m^3), Mg^{++} – 30 g/m^3 (2.47 eq/m^3) $SO_4^{=}$ – 80 g/m^3 (1.67 eq/m^3), Cl^- – 19.5 g/m^3 (0.55 eq/m^3), HCO_3^- – 280 g/m^3 as $CaCO_3$ (5.6 eq/m^3).

Column utilization ratio for the Amb-200 resin: $\frac{(4.5+2.41)(0.724)}{(10)(1.7)} = 30\,\%$.

Column utilization ratio for the IRA-900 resin: $\frac{(1.67+0.55+5.6)(0.725)}{(10)(1.0)} = 56.7\,\%$.

It was noted that the Purdue "Cold Tap" water contained low concentrations of Cl^- and $SO_4^{=}$ and a high concentration of HCO_3^- which was not similar to the chemical composition of the prepared hardness water cited previously. As a result, the lesser column utilization ratio (56.7 %) for the IRA-900 resin was observed and ascribed to the fact that the HCO_3^- ion possessed a lower

affinity for the IRA-900 resin. Even with the anions (Cl^-, $SO_4^=$, and HCO_3^-) in the feed water, the amount of gluconate (5.58 meq) exchanged, during the service cycle, was approximately equal to the amounts of Cl^- (0.40 meq), HCO_3^- (4.06 meq), and $SO_4^=$ (1.21 meq) retained on the column. Thus, the stoichiometric relationship between the gluconate and $SO_4^=$ (Cl^- or HCO_3^-) held constant even in the presence of the HCO_3^- ion.

4.1.4. REGENERATION CYCLE

Figures 5 through 7 present the results of regeneration cycles for runs #MX-4, MX-5, and MX-6, in which 2%, 5%, and 8% sodium gluconate solution, respectively, was fed to the exhausted Amb-200/IRA-900 mixed-bed resin columns, at a 3.3×10^{-4} m/s downflow rate.

The higher peak in a short time on the elution curve presented in fig. 7 ndicated that the highest regenerant utilization of sodium gluconate was achieved while feeding 8% sodium gluconate solution to the mixed-bed resin column.

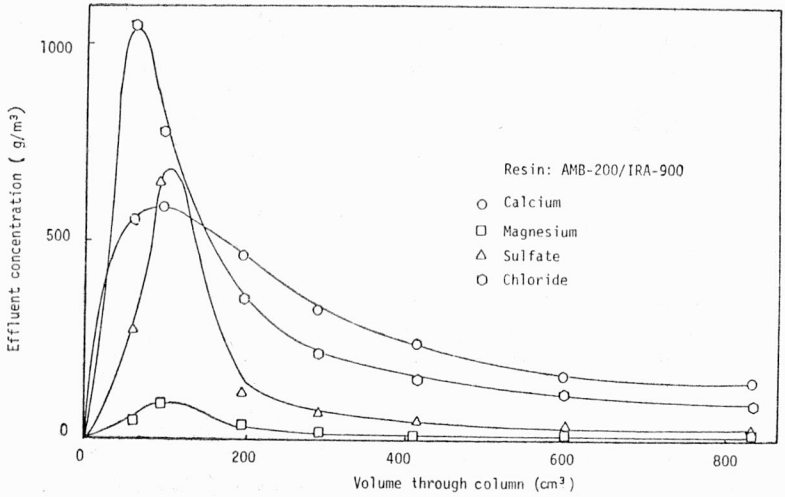

Fig. 5. Run #MX-4; regeneration cycle with feed of 2% sodium gluconate application
Rys. 5. Próba MX-4; cykl regeneracji zasilany 2-procentowym glukonianem sodu

Figures 8 through 11 depict the integral elution curves for each cation (or anion) at varying regenerant concentrations. In these experiments, the most effective curve was obtained when 8% sodium gluconate solution was added to the column. The results shown in tab. 5 yeld the same conclusion. Also, the regeneration effectiveness of Ca^{++} (Mg^{++}, $SO_4^=$ or Cl^-) presented in tab. 6 did not show a significant change when the HCO_3^- ion was present in the exhausted mixed-bed resin column (run #MX-7).

It was noted that an increased regenerant concentration increased the elution rate because of a displacement of the ion exchange equilibrium. On the other hand, the resin shrank at higher organic regenerant concentration causing a diminished diffusion velocity of the organic ions in the net structure of the resin; consequently, a lowered rate was not observed while feeding an 8% sodium gluconate solution to the column. This was ascribed to the advantage of utilizing the macroporus resins, i.e. Amb-200 and IRA-900.

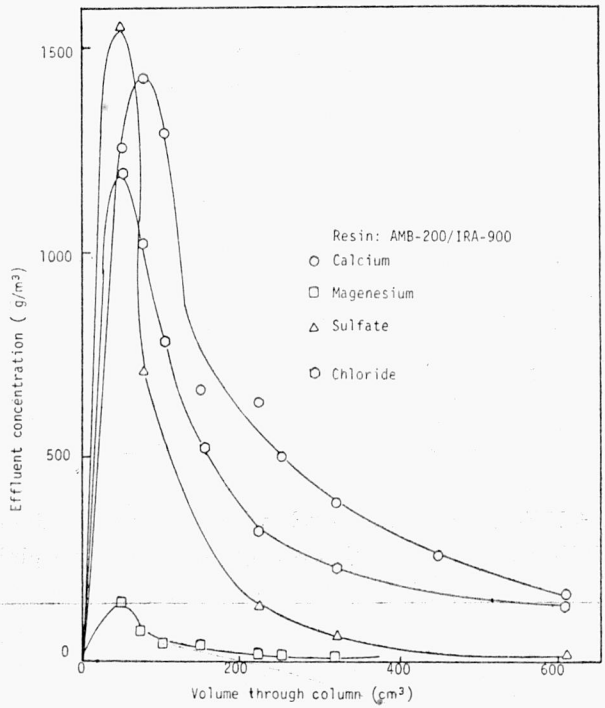

Fig. 6. Run # MX-5; regeneration cycle with feed of 5% sodium gluconate
Rys. 6. Próba MX-5; cykl regeneracji zasilany 5-procentowym glukonianem sodu

According to SAMUELSON [7], the flow rate has only a small influence upon the breakthrough or elution curves for an ion exchanger with an open network structure utilizing macroporus resins such as IRA-900 and Amb-200 resins. In addition, MILLAR and KRESSMAN [5] reported that the rate-determining step in the ion exchange process was normally controlled by the particle diffusion for the case of large organic ions. Consequently, the flow rate was not considered to be an important factor affecting the regeneration results in these particular investigations, provided that the flow rate was held in the range of 1.7×10^{-4}–5.1×10^{-4}m/s, during the regeneration cycle.

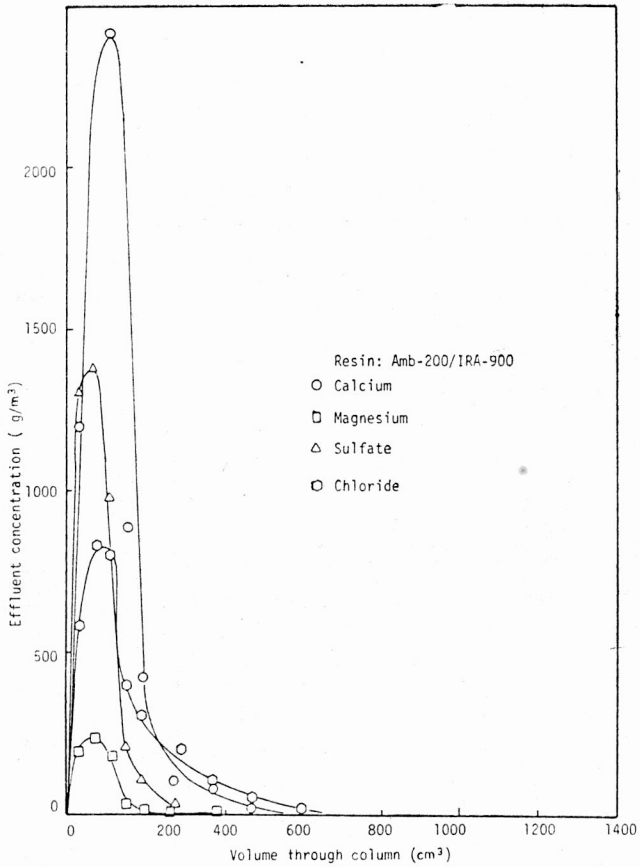

Fig. 7. Run #MX-6; regeneration cycle with feed of 8% sodium gluconate

Rys. 7. Próba MX-6; cykl regeneracji zasilany 8-procentowym glukonianem sodu

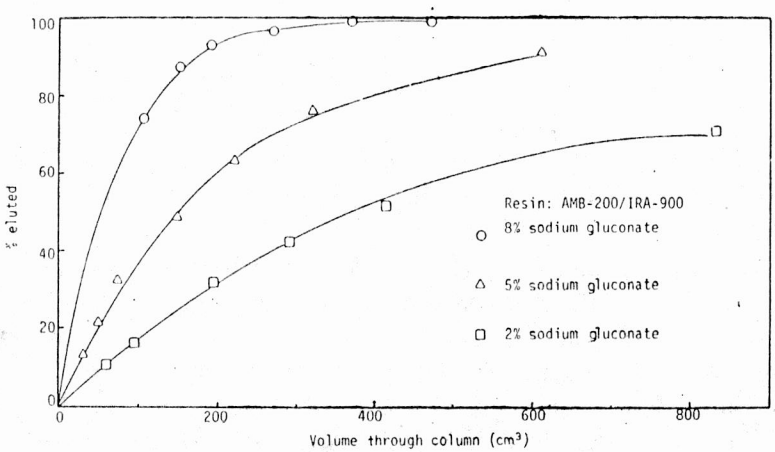

Fig. 8. Regeneration (elution) of Ca^{++} by application of 2% (5% or 8%) sodium gluconate to the Amb-200/IRA-900 mixed-bed resin column

Rys. 8. Regeneracja (wymywanie) jonów Ca^{++} przez zastosowanie 2% (5% i 8%) glukonianu sodu w kolumnie ze złożem mieszanym Amb-200/IRA-900

Table 5

Comparison of regeneration studies for IRA-900/Amb-200 mixed-bed resins column tests at 2% (5% or 8%) sodium gluconate concentration level

Badania porównawcze regeneracji kolumny ze złożem mieszanym IRA-900/Amb-200 przy stężeniu glukonianu sodowego 2% (5% i 8%)

Run #	Organic regenerant		Inorganics retained on resins (meq)				Inorganics removed (meq)			
	Composition and volume	Flow rate (10^{-4} m/s)	Ca^{++}	Mg^{++}	$SO_4^{=}$	Cl^-	Ca^{++}	Mg^{++}	$SO_4^{=}$	Cl^-
MX-4	2% GA 600 cm³	3.4	15.14	1.25	5.16	5.0	10.96 (72.4)	1.06 (84.8)	1.46 (28.3)	5.2 (100)
MX-5	5% GA 600 cm³	3.4	15.20	1.20	5.12	5.0	13.9 (91.4)	1.18 (98.3)	3.39 (66.0)	4.6 (92.0)
MX-6	8% GA 600 cm³	3.4	15.00	1.74	3.80	5.0	14.9 (99.3)	1.73 (99.4)	3.70 (97.3)	5.0 (99.8)

The numerical value in the parenthesis denotes the percent of regeneration efficiency.

Table 6

Summary of regeneration results for IRA-900/Amb-200 mixed-bed resins column test

Wyniki badań regeneracji kolumny ze złożem mieszanym IRA-900/Amb-200

Run #	Organic regenerant		Inorganics retained on resins (meq)					Inorganics removed from resin (meq)				
	Composition and volume	Flow rate (10^{-4} m/s)	Ca^{++}	Mg^{++}	$SO_4^{=}$	Cl^-	$HCO_3^{=}$	Ca^{++}	Mg^{++}	$SO_4^{=}$	Cl^-	$HCO_3^{=}$
MX-7	8% GA 600 cm³	3.4	3.76	2.06	1.39	0.46	4.17	3.70 (98.4)	2.0 (97.1)	1.38 (98.5)	0.45 (97.8)	4.02 (96.4)

The numerical value in the parenthesis denotes the percent of regeneration efficiency.

As noted previously, the objective of these investigations was to regenerate the exhausted resin in a mixed form. In other words, the proposed process would not require separation of the resins in or out of the mixed-bed exchanger before regeneration. However, a separatedlayer of resin in the mixed-bed column was produced, while the backwashing (or rinsing) flow took place in an

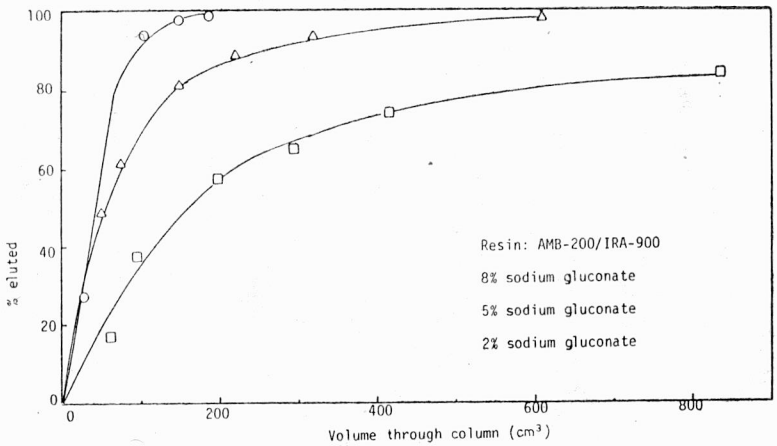

Fig. 9. Regeneration (elution) of Mg^{++} by application of 2% (5% or 8%) sodium gluconate to the Amb-200/IRA-900 mixed-bed resin column

Rys. 9. Regeneracja (wymywanie) jonów Mg^{++} przez zastosowanie 2% (5% i 8%) glukonianu sodu w kolumnie ze złożem mieszanym Amb-200/IRA-900

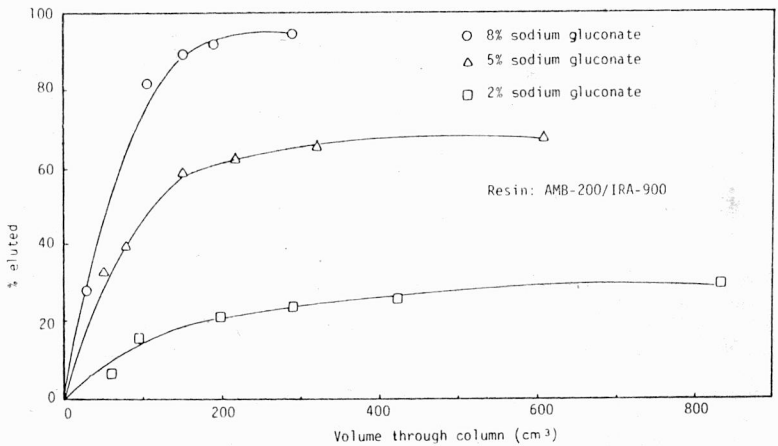

Fig. 10. Regeneration (elution) of $SO_4^{=}$ by application of 2% (5% or 8%) sodium gluconate to the Amb-200/IRA-900 mixed-bed resin column

Rys. 10. Regeneracja (wymywanie) jonów $SO_4^{=}$ przez zastosowanie 2% (5% i 8%) glukonianu sodu w kolumnie ze złożem mieszanym Amb-200/IRA-900

upflow mode. Using the previously cited regeneration studies (mixed-resin form) as a basis for comparison, runs #MX-8 and MX-9 regeneration cycle were undertaken by feeding 2% (or 8%) sodium gluconate solution to the separated-layer resin in a down-flow mode.

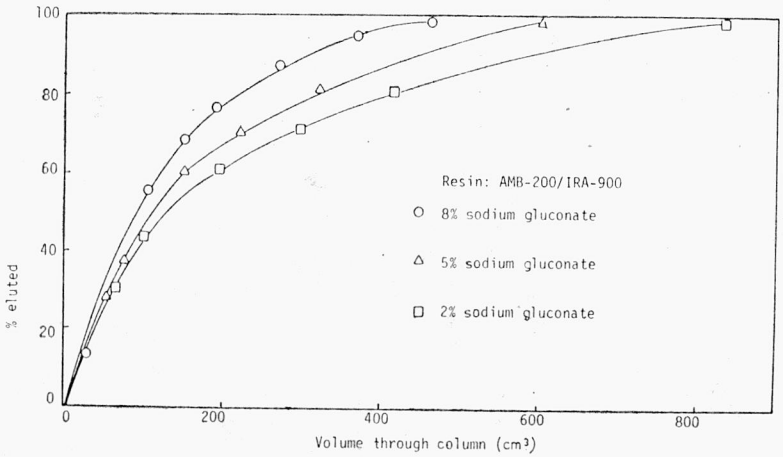

Fig. 11. Regeneration (elution) of Cl^- by application of 2% (5% or 8%) sodium gluconate to the Amb-200/IRA-900 mixed-bed resin column

Rys. 11. Regeneracja (wymywanie) jonów Cl^- przez zastosowanie 2% (5% i 8%) glukonianu sodu w kolumnie ze złożem mieszanym Amb-200/IRA-900

Table 7

Regeneration results for separated-resin column tests at 2% and 8% sodium gluconate concentration level, respectively

Wyniki badania rozseparowanych jonitów przy stężeniu glukonianu sodowego odpowiednio 2% i 8%

Run #	Cycle name	Inorganics retained (meq)				Inorganics removed (meq)			
		Ca^{++}	Mg^{++}	$SO_4^=$	Cl^-	Ca^{++}	Mg^{++}	$SO_4^=$	Cl^-
MX-8	Regeneration (2% Na^+GA^-)	15.2	1.68	5.16	5.0	7.31 (48.1)	1.63 (97.0)	1.37 (27.5)	5.0 (100)
MX-9	Regeneration (8% Na^+GA^-)	15.2	2.38	5.69	4.78	15.0 (98.7)	2.38 (99.9)	4.58 (80.5)	4.42 (92.5)

The numerical value in the parenthesis denotes the percent of regeneration efficiency.

The regeneration results of runs #MX-8 and MX-9 cycle were summarized in tab. 7. Comparison of tab. 5 and tab. 7 showed that the regeneration effectiveness of Ca^{++} (Mg^{++}, $SO_4^=$, or Cl^-) in the mixed-resin form was similar

to that obtained in the separated-bed resin form. Thus, the regeneration of the exhausted mixed-bed, in these investigations, was found to be just as acceptable in the mixed-resin form as in the separated-bed resin form and thus would be the regeneration method of choice due to the simplicity of operation.

In order to confirm the exchange capacity of the mixed-bed resins (Amb-200/IRA-900) after regeneration, run #MX-10 was essentially the same operationally as run #MX-2. Figure 12 and tab. 8 illustrate the results of the service cycle in which the exchange capacity and column utilization ratio for each resin was found to be very similar to that obtained in run #MX-2. It

Table 8

Run # MX-10 service cycle – results of synthetic hardness water (Ca^{++}, Mg^{++}, $SO_4^{=}$, and Cl^-) application

Przebieg cyklu pracy MX-10 w próbach z wodą o modelowej twardości (Ca^{++}, Mg^{++}, $SO_4^{=}$ i Cl^-)

Vol. through column (cm^3)	Effluent sodium gluconate (g/m^3)	Effluent Ca^{++} (g/m^3)	Effluent Mg^{++} (g/m^3)	Effluent $SO_4^{=}$ (g/m^3)	Effluent Cl^- $g(/m^3)$
50	4850	0	0	0	0
100	5008	0	0	0	0
150	7500	0	0	0	0
180	7275	0	0	0	0
200	5814	0	0	0	0
250	4230	0	0	0	0
270	—	0	0	2.0	10
350	3145	0.08	0.01	40	457
415	875	0.2	0.2	120	985

Resins: Amb-200/IRA-900 (10 cm^3-wet each).

Feed solution: Ca^{++} – 420 g/m^3 (21.0 eq/m^3), Mg^{++} – 98 g/m^3 (8.06 eq/m^3), $SO_4^{=}$ – 390 g/m^3 (8.12 eq/m^3) Cl^- – 760 g/m^3 (21.4 eq/m^3).

Column utilization ratio for Amb-200 $\frac{0.270(21.0+8.06)}{(1.7)(10)} = 46.2\,\%$.

Column utilization ratio for IRA-900 $\frac{0.27(8.12+21.4)}{(1.0)(10)} = 79.7\,\%$.

was thus concluded that the regeneration of the exhausted mixed-bed resin, by introducing one organic regenerant, i.e. sodium gluconate at an 8% concentration level, was successful.

4.2. UF MEMBRANE TESTS

Tables 9 and 10 illustrate the results obtained from UF studies for a single solute. It was observed that the rejection efficiency of gluconate for the Sepa-97 CA membrane (97.5 to 98.1 %) was slightly higher than that for the UMO 5 mem-

brane (96.8 to 97.3 %). The water flux rate (m/s) for the UMO 5 and Sepa-97 CA membranes were 15.2×10^{-4} and 28.0×10^{-4}, respectively. In general, the hydrophilic cellulose acetate membrane (Sepa-97 CA) yielded better results in these investigations than did the polyelectrolyte complex (UMO 5) membranes.

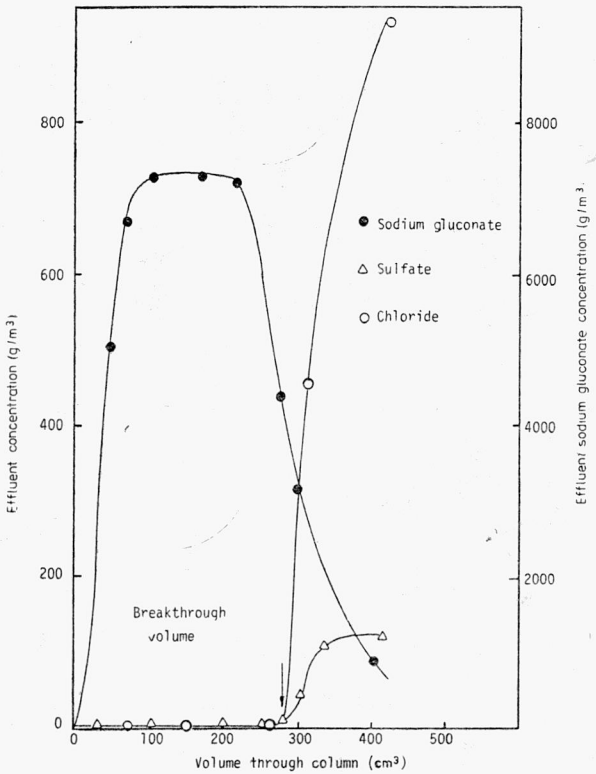

Fig. 12. Run # MX-10; service cycle — results of calcium chloride and magnesium sulfate application

Rys. 12. Próba MX-10; cykl pracy — wyniki zastosowania chlorku wapnia i siarczanu magnezu

The results of tab. 9 indicate a gradual build-up, over the entire study period, in the concentration of the resulting regenerate. An ultimate concentration, i.e. 13,000–15,000 g/m³, of sodium gluconate was observed in the reject pipe network of the UF unit (Sepa-97 CA membrane). This concentration of regenerant, 2.6–3.0 times the concentration of the influent, was less than ideal since optimum mixed-bed resin regeneration was at a concentration of 80.0 kg sodium gluconate/m³. However, the reject concentration may continue to increase with longer operation time as was found by JOHNSON [4].

UF-3 and UF-4 tests were performed to separate the gluconate from the spent organic regenerant containing Ca^{++}, $SO_4^{=}$, Na^{+}, and gluconate. The

Table 9

Results of UF (Sepa-97 CA membrane) study on sodium gluconate (Na^+GA^-)
Badania ultrafiltracji glukonianu sodu (Na^+GA^-) przez membrany Sepa-97 CA

Time of operation (h)	Gluconate filtrate concentration (g/m^3 as Na^+GA^-)	Gluconate reject concentration (g/m^3 as Na^+GA^-)	Rejection efficiency (%)
2	125	5320	9.57
4	100	5405	98.0
6	102	7860	98.0
8	102	10800	98.0
10	98	12080	98.1
12	110	12100	97.8
14	120	14200	97.6

a) Feed concentration: 5000 g/m^3 as sodium gluconate.
b) Average flux rate: 28.0×10^{-4} m/s.
c) Rejection efficiency: 97.5 % to 98.1 %.
d) Membrane: Sepa-97 CA.
e) Pressure: 125–150 PSI.
f) Filtrate concentration: 100–125 g/m^3 as sodium gluconate.

Table 10

Results of UF (UMO 5 membrane) study on sodium gluconate (Na^+GA^-)
Badania ultrafiltracji glukonianu sodu (Na^+GA^-) przez membrany UMO 5

Time of operation (h)	Gluconate filtrate concentration (g/m^3 as Na^+Ga^-)	Gluconate reject concentration (g/m^3 as Na^+Ga^-)	Rejection efficiency (%)
2	158	5060	96.8
4	148	5060	7.1
6	140	5640	97.0
8	142	5810	97.2
10	140	5050	97.2
12	138	5200	97.3
14	140	6400	97.2

a) Feed solution: 5000 g/m^3 as sodium gluconate.
b) Average flux rate: 15.2×10^{-4} m/s.
c) Rejection efficiency: 96.8 % to 97.3 %.
d) Membrane: UMO 5.
e) Pressure: 60–100 PSI.
f) Filtrate concentration: 138–158 g/m^3 as sodium gluconate.

Table 11

Results of UF (Sepa-97 CA membrane) study on sodium gluconate and calcium sulfate mixture

Badania ultrafiltracji mieszaniny glukonianu sodu i siarczanu wapnia przez membrany Sepa-97 CA

Time of operation (h)	Rejection line			Permeation line		
	Gluconate (g/m^3 as sodium gluconate)	Ca^{++} (g/m^3)	$SO_4^{=}$ (g/m^3)	Gluconate (g/m^3 as sodium gluconate)	Ca^{++} (g/m^3)	$SO_4^{=}$ (g/m^3)
2	43,280	654	784	4,505	61	86
2	44,000	660	786	3,900	45	84
6	44,200	662	790	3,940	44	84
8	44,300	670	798	3,800	44	82
10	44,320	680	800	3,780	42	80

a) Feed concentration: gluconate – 40 kg/m^3 as sodium gluconate, Ca^{++} – 370 g/m^3, $SO_4^{=}$ – 390 g/m^3.

b) Average flux rate: 10.2×10^{-4} m/s.

c) Rejection efficiency: gluconate – 88.7 % to 90.5 %, Ca^{++} – 83.5 % to 89.2 %, $SO_4^{=}$ – 77.9 % to 79.5 %.

d) Membrane: Sepa-97 CA membrane.

e) Pressure: 125–150 PSI.

f) Filtrate concentration: gluconate – 3.78–4.505 kg/m^3 as sodium gluconate, Ca^{++} – 42–61 g/m^3, $SO_4^{=}$ – 80–86 g/m^3.

Table 12

Results of UF (UMO 5 membrane) study on sodium gluconate and calcium sulfate mixture

Badania ultrafiltracji mieszaniny glukonianu sodu i siarczanu wapnia przez membrany UMO 5

Time of operation (h)	Rejection line			Permeation line		
	Gluconate (g/m^3 as sodium gluconate)	Ca^{++} (g/m^3)	$SO_4^{=}$ (g/m^3)	Gluconate (g/m^3 as sodium gluconate)	Ca^{++} (g/m^3)	$SO_4^{=}$ (g/m^3)
4	23,440	490	513	16,890	158	208
6	24,450	511	551	14,070	160	210
8	24,500	520	560	12,460	164	220
10	24,520	522	562	12,760	166	217

a) Feed concentration: gluconate – 20.20 kg/m^3 as sodium gluconate, Ca^{++} – 370 g/m^3, $SO_4^{=}$ – 290 g/m^3.

b) Average flux rate: 12.2×10^{-4} m/s.

c) Rejection efficiency: gluconate – 15.5 % to 37.7 %, Ca^{++} – 55.1 % to 57.3 %, $SO_4^{=}$ – 43.6 to 46.7 %.

d) Membrane: UMO 5 membrane.

e) Pressure: 0.41–0.69 MPa.

f) Filtrate concentration: gluconate – 12.46–6.89 kg/m^3, Ca^{++} – 158–166 g/m^3, $SO_4^{=}$ – 208–220 g/m^3.

results presented in tabs. 11 and 12 suggested that the UF membranes utilized in these investigations could not achieve the anticipated objective due to the limitation of current membrane technology. Another approach, recently shown by DIETRICH [2], demonstrated the separation of a EDTA–calcium and magnesium complex in a continuous ion-exchange electromembrane process to be technically feasible. Thus, it might be possible to use the same technique, i.e. ion-exchange electromembrane process, to separate a gluconate–calcium and magnesium complex in the spent organic regenerant for these investigations.

5. CONCLUSIONS

Based on the results of these laboratory investigations, the proposed process for deionization of water with a recoverable regenerant was shown to be technically feasible. Specifically, the following conclusions could be drawn:

1. By introducing only one organic regenerant (sodium gluconate) in the mixed-bed resin (Amb-200/IRA-900) column, during the regeneration cycle, it was observed that all the cations (Ca^{++} and Mg^{++}) and anions ($SO_4^{=}$, Cl^- and HCO_3^-) retained in the column.

2. The proposed process in these investigations would not require separation of the resins in a mixed-bed resin column before regeneration.

3. In these investigations, the most effective regeneration results (97.3 % to 99.8 %) were achieved while feeding 8 % sodium gluconate solution to the mixed-bed resin column at 3.4×10^{-4} m/s down-flow rate.

4. During the service cycle, for an influent feed containing 420 g Ca^{++}/m^3, 98 g Mg^{++}/m^3, 390 g $SO_4^{=}/m^3$, and 760 g Cl^-/m^3, the column utilization ratio for Amb-200 and IRA-900 resins was obtained approximately 89 % and 51 %, respectively.

5. The UF/RO Sepa-97 CA membrane was successfully to be utilized for recovery of organic regenerant, i.e. sodium gluconate, resulting in the sodium gluconate rejection efficiency of 97.5 % to 98.2 % and the water flux of 28.0×10^{-4} m/s.

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DEJONIZACJA WODY Z ODZYSKIWALNYM REGENERANTEM

Przedstawiono proces kolumnowej wymiany jonowej na złożu mieszanym, zachodzący w fazie organicznej, po którym następuje ultrafiltracja. Celem ultrafiltracji jest dejonizacja wody i zatężenie organicznego regeneranta. Proponowany proces, w porównaniu z konwencjonalną dejonizacją na złożu mieszanym, ma trzy zalety. Po pierwsze, wszystkie kationy i aniony pozostające w kolumnie z wyczerpanym złożem mieszanym można zastąpić jednym organicznym regenerantem. Po drugie, w proponowanej dejonizacji nie jest konieczne rozdzielenie wymieniaczy jonowych w celu regeneracji złoża. Po trzecie, organiczny regenerant usunięty z kolumny w cyklu pracy może być odzyskany i ponownie użyty po zastosowaniu separacji membranowej (ultrafiltracji).

Podczas cyklu pracy, w którym zastosowano roztwór zasilający o składzie: 420g Ca^{++}/m^3, 98g Mg^{++}/m^3, 390g $SO_4^{=}$ $/m^3$ i 760g Cl^-/m^3, stopień wykorzystania kolumny wynosił około 47% dla żywic kationowymiennych i około 80% dla żywic anionowymiennych. Około 99% kationów (Ca^{++} i Mg^{++}) oraz anionów ($SO_4^{=}$, Cl^- i HCO_3^-) pozostałych w wyczerpanym złożu mieszanym jest usuwanych po wprowadzeniu do kolumny 8% roztworu zregenerowanego glukonianu sodowego. Membrana UF/RO (Sepa-97) CA okazała się przydatna do odzyskiwania glukonianu sodowego. Sprawność membrany wynosiła 97, 5%–98,2% przy szybkości strumienia wody $28{,}0 \times 10^{-4} m^3/m^2 s$.

WASSERENTIONISIERUNG MIT RÜCKGEWINNENDEN REGENERANT

Es wurde ein Ionenaustauschersäuleprozeß, der in der organischen Phase verläuft und nach welchem Ultrafiltration auftritt, dargestellt. Das Ziel der Ultrafiltration ist die Wasserentionisierung und das Eindicken des organischen Regenerants. Der vorgeschlagene Prozeß, weist gegenüber der Konventionellmischbettentionisierung drei Vorteile auf. Erstens: alle Kationem und Anionen, die in der Säule mit verbrauchtem Mischbett vorhanden sind, kann man mit einem organischen Regenerant ersetzen. Zweitens: im Falle der vorgeschlagenen Entionisierung ist eine Trennung der Ionenaustauscher zwecks der Bettregeneration nicht nötig. Drittens: der organische Regenerat, der während des Arbeitszyklus beseitigt wird, kann nach Anwendung der Membranseparation (Ultrafiltration) rückgewonnen und wiederverwendet werden.

Während des Arbeitszyklus, in dem eine Speiselösung aus folgender Zusammensetzung: 420g Ca^{++}/m^3, 98g Mg^{++}/m^3, 390g $SO_4^{=}/m^3$ und 760g Cl^-/m^3 verwendet wurde, betraf der Säulenausnutzungsgrad für die Kationenaustauschharze ca 47% und ca 80% für die Anionenaustauschharze. Ca 99% der im verbrauchten Mischbett zurückgebliebeben Kationen (Ca^{++} und $Mg)^{++}$ und Anionen ($SO_4^{=}$, Cl^- und HCO_3^-) werden nach dem Einführen in die Säule einer 8% regenerierten Nariumgluconatlösung beseitigt. Die Membrane UF/RO (Sepa-97) CA hat sich bei der Rückgewinnung des Naturiumgluconats verwendbar erwiesen. Der Wirkungsgrad der Membrane bei der Wasserströmungsgeschwindigkeit $28{,}0 \times 10^{-}{}_4 m^3/m^2$ s betrug 97,5-98,2%.

ДЕИОНИЗАЦИЯ ВОДЫ С РЕГЕНЕРИРОВАННЫМ РЕГЕНЕРАТОМ

Представлен процесс колонного ионного обмена на смешанном слое, происходящий в органической фазе, после которого наступает ультрафильтрация. Целью ультрафильтрации является деионизация воды и концентрирование органического регенерата. По сравнению с конвенциональной деионизацией на смешанном слое, предложенный процесс характеризуется тремя достоинствами. Во-первых, любые катионы и анионы, остающиеся в колонне с истощенным смешанным слоем, могут быть заменены одним органическим регенератом. Во-вторых, в предложенной деионизации нет необходимости распределения ионообменников с целью регенерирования слоя. Во-третих, органический регенерат, удаленный из колонны в рабочем цикле, можно регенерировать и опять использовать после применения мембранной сепарации (ультрафильтрации).

Во время рабочего цикла, в котором применялся питательный раствор с составом: 420 г $Ca^{++}/м^3$, 98 г $Mg^{++}/м^3$, 390 г $SO_4^{=}/м^3$ и 760 г $Cl^{-}/м^3$, степень использования колонны равна около 47% для катионообменных смол и около 80% для анионообменных смол. После введения в колонну 8% раствора регенерированного глюкониана натрия удаляются около 99% катионов (Ca^{++} и Mg^{++}), а также анионов ($SO_4^{=}$, Cl^{-} и HCO_3^{-}), остающихся в истощенном смешанном слое. Мембрана UF/RO (Sepa-97) CA оказалась пригодной для регенерирования глюкониана натрия. Кпд мембраны равен 97,5–98,2% при скорости водяной струи $28{,}0 \times 10^{-4}$ $м^3/м^2с$.