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## COMPOSITION OF EFFLUENT AFTER REGENERATION OF CATION AND ANION RESINS WITH AMMONIUM CARBONATE DURING DESALINATION OF SUGAR THIN JUICE \*)

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**Key words:** sugar thin juice, desalting and regeneration of resins with ammonium carbonate, regeneration in ammonium and carbonate cycles.

Purified and preliminarily delimed sugar juice was desalted with polystyren ion exchange resins: strongly acidic cation and strong base anion exchange resins. The resin beds were regenerated cyclically with 3 N (5%) solution of ammonium carbonate with the efficiency above 95%. Total nitrogen, alpha-aminoacids, betain, and ion compounds (potassium, sodium, calcium, magnesium, chlorides, sulphates) were determined in the concentrated solution after regeneration.

In the course of desalting of sugar solutions nearly all soluble inorganic non-sugars and also ionic organic non-sugars are removed [10, 20]. Removal of the ionic non-sugars is most often carried out with cation and anion exchange resins in hydrogen and hydroxide forms. The non-sugars are eluted during regeneration of ion exchange resins and removed with the waste waters. The regeneration waste waters contains a percentage of organic and inorganic non-sugars as well as excess hydrochloric acid and sodium hydroxide used for regeneration of ion exchange resins. The treatment of the regenerant effluents and rinse waters is difficult. Before it is disposed into inland waters it must be properly treated because of the high contents of organic and inorganic compounds, high oxygen demand (BOD) and high TDS. In order to protect saccharose against hydrolysis, methods for desalting sugar juices in alkaline medium by the use of cation and anion exchange resins regenerated with ammonium carbonate were developed [6, 11, 25]. Optimum conditions for regeneration of resin

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beds by the use of ammonium carbonate were also given [26]. In the process ammonium carbonate is returned into the cycle thus eliminating the formation of waste. Regeneration of cation and anion exchange resins continues simultaneously. Cations absorbed by cation exchange resins are exchanged for ammonium ions deriving of the solution of ammonium carbonate while anions adsorbed by anion exchange resins are exchanged for carbonate ions originating from the same batch of ammonium carbonate. Components of the regeneration waste waters include cation and anion nonsugars, which were exchanged during regeneration, and come from unused ammonium carbonate solution. Ammonium carbonate is removed from the regeneration waste waters through distillation and then returned to the process [26]. In the exhausted liquid remain concentrated non-sugars, which can be used directly in upgrading nutritional value of beet pulp, after they are condensed and thickened to 40% of dry substance. In such a case the regeneration of ion exchange resins gives no waste.

In sugar technology all substances appearing along saccharose in beets and sugar juices are called non-sugars. Beet juice contains about 10% non-sugars (as dry substance). Only 4% is removed during traditional purification of juice while 6% passes into molasses [21].

The aim of the present study was to determine the chemical composition of the solution obtained after regeneration of cation and anion exchange resins with ammonium carbonate solutions in carbonate and ammonium cycles.

## EXPERIMENTAL PROCEDURE

There were used the following polystyrene resins made by VEB Chemiekombinat Bitterfeld, GDR: strongly acidic cation exchange resin — Wofatit KPS and strong base anion exchange resin — Wofatit SBW. Total exchange capacity of the resin beds were as follow: 59.8 eq. for cation exchanger and 72.8 eq. for anion exchanger.

Desalting involved thick juice diluted to 16% dry substance. The thick juice was delivered from a sugar factory in December and stored at the temperature of 5°C. Prior to desalting the juice was preliminarily delimed [23]. It was necessary since only small amounts of calcium ions are removed during regeneration of cation and anion exchange resins with ammonium carbonate solutions. Anion exchangers adsorb all the anions from sugar juice and colour bodies as well. Owing to forces of adsorption they are held by resins more strongly than their low degree of dissociation would suggest. Complete removal of colour bodies during the regeneration of anion exchange resin is impossible. Colour bodies poison anion exchange resins what reduces their working capacity. Colour bodies were removed from delimed juice by the use of grained active carbon Car-

bopol Z-Extra, which is not so expensive like the decolourizing resins [19, 27]. The preliminary decolourizing of sugar juice removed more than 70% colour bodies.

Desalting was carried out in ion exchange columns linked in series. The juice was first directed into the bed of cation exchanger in the ammonium form and then through the bed of anion exchanger in the carbonate form. The temperature of the process was 40°C. The amount of sugar juice desalted in the one operating cycle was calculated on the basis of the carbonate ash content of juice and the total capacity of the resin. Flow rate enabled the following average contact time: for cation exchangers — 5 minutes, for anion exchangers — 10 minutes. After the treatment of the whole amount of juice the sweetening — off was carried out.

The regeneration effluents and rinsing waters were divided into four fractions.

— Fraction A, which was the initial one and consisted of water pressed out by juice from the voids and the piping.

— Fraction B, with low contents of dry substance, that was collected from 0°Bx to 10°Bx. Average contents of dry substance in the fraction was 3°Bx.

— Fraction C, the proper one, had the contents of dry substance from 10°Bx to maximum and from maximum to 10°Bx. The fraction consisted of the desalted juice of the concentration ca 16°Bx.

— Fraction D, the final one, has 10°Bx to 0°Bx contents of dry substance. It consisted of the effluent collected during the final step of the cycle ca 4°Bx.

The sweetening — of [5] was carried out with the use of fraction B and fraction A. First of all was used fraction A and than fraction B. Final washing of the bed was done with distilled water. Utilization of fractions A and B reduces the consumption of fresh rinsing water by 40%.

Analysis of the juice before and after desalting (Fraction C) is given in Table 1. It contains: apparent contents of dry substance, purity, colour, alkalinity, pH, reducing sugars, calcium salts and sulphate ash. All of them were the standard methods used in sugar technology. Carbonate ash was determined by incinerate a sample of juice at 450°C without acid addition [15]. Concentration of free ammonia was determined by distilling under vacuum with addition of the borate buffer solution [8]. Ion exchange method was used to determine the total cations [22]. The total contents of nitrogen-free acids was also determined by ion exchange with the exception of aminoacids [2, 4, 9].

Following the appropriate sweetening-off the bed was regenerated in a circular way. Ammonium carbonate 3 eq/dm<sup>3</sup> initial concentration was used. The amount of the ammonium carbonate solution was kept within a range permitting the concentration of ammonium and carbonate ions in the voids between 2.4 eq/dm<sup>3</sup> and 2.8 eq/dm<sup>3</sup>. This corresponded to the

volume of ammonium carbonate staying within 0.55 BV to 1.1. BV. The temperature of regeneration was 23°-25°C.

The instalation for regeneration of ion exchange resins is showed on Fig. The regeneration was performed in the following way: ammonium carbonate from the receiver of distillate (N) was top-loaded into a column with anion exchange resins (An), and then again it was toploaded into a cation exchange resins column (Kt). The regeneration waste waters received at the bottom of the cation column was fractionated into three. Volumes of the fractions were calculated by measuring conductivity and by preliminary experimentation. The conductivity of the solution was measured with a glass pipe (R) with platinum electrodes ( $E_1$ ,  $E_2$ ) imbedded in the glass within 100 mm.

Table 1. Juice analysis

		Before desalination	After desalination and concentration, fraction C, cycle 15th
Apparent content of dry substance	%	16.0	49.3
Purity		93.4	96.4
Colour, specific absorbance $\lambda = 560$ nm		0.029	0.00
Alkalinity	g CaO/100 ccm	0.017	—
pH		8.9	8.2
Reducing sugars	g/100 g dry s.	0.025	0.020
Calcium salts	mg/CaO/100 g dry s.	31.9	0.0
Sulphate ash	g/100 g dry s.	3.26	0.259
Carbonate ash	g/100 g dry s.	2.53	0.159
Ammonia concentration as $NH_4^+$	meq/100 g dry s.	7.4	19.9
Total content of non-nitrogen acids	meq/100 g dry s.	36.1	13.4

Fraction I, collected in the receiver of fractions (P) consisted of water pushed out by ammonium carbonate from the voids and the piping. The fraction was fed into a tank (Z) and returned for a preliminary rinsing of exchangers after regeneration with concentrated ammonium carbonate. Fraction II consisted of a effluent containing the highest amount of non-sugars and most of ammonium and carbonate ions. Fraction II was fed directly into a distillation flask (K) and ammonium carbonate was separated here. The ammonium carbonate distillate was cooled in Liebig condenser (C) and then it passed into a receiver of distillate (N). 75% ammonium carbonate was recovered in the distillate. The concentration of non-sugars in the distillation residue was 5%. Fraction III, obtained from

the rinsing of ion exchangers with distilled water toward the end of the regeneration, was collected in the fraction receiver (P), measured, and rejected.

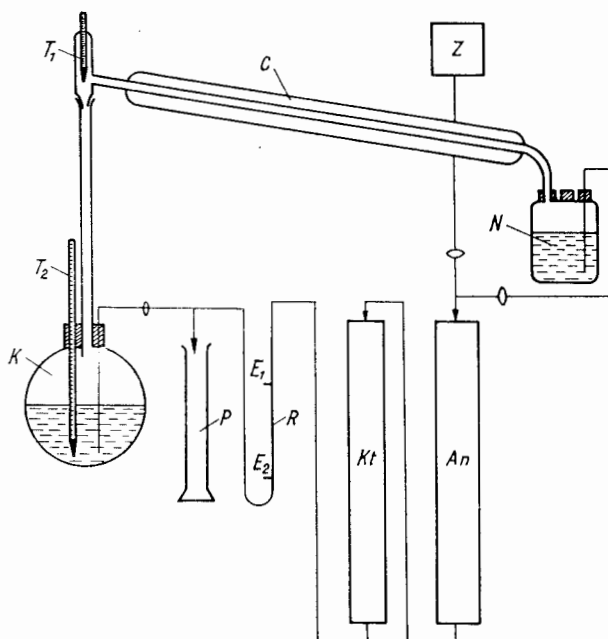


Fig. Instalation for regeneration of ion exchange resins; K—distillation flask, C—Liebig condenser, N—distillate receiver,  $K_t$ —cation exchange resins column,  $A_n$ —anion exchange resins column, R—glass pipe for measuring conductivity,  $E_1$ ,  $E_2$ —platinum electrodes, P—receiver, Z—distilled water tank,  $T_1$ ,  $T_2$ —thermometers

On the basis of previous tests it was known that the water demand for the rinsing of the bed amounted to 1.8 BV. Application of fraction I in the rinsing of ion exchangers after the ammonium carbonate regeneration made it possible to reduce the volume of fresh rinsing water from 1.8 to 1.3 BV.

## DISCUSSION OF RESULTS

The composition of non-sugars removed from cation and anion exchangers was determined in the regeneration waste water (fraction II), additionally concentrated in a vacuum evaporator to ca 13% dry substance. In the concentrated effluent the following were determined: total nitrogen [14], alpha-aminoacid nitrogen [3], amide and ammonia nitrogen [13], protein nitrogen [13], betain [13], non-nitrogen organic acids [2, 4, 9], chlorides [14, 16], phosphate [9, 17], sulphates [9, 17], sodium, potassium [24], calcium, magnesium [13].

Table 2 provides a balance of inorganic non-sugars removed from the

Table 2. Inorganic non-sugars removed by ion exchange — the 15th cycle of desalination and regeneration

	Juice before desalination meq./100 g dry s.	Juice after desalination meq./100 g dry s. of juice	Removed from juice 1-2 meq./100 g dry s.	Eluted non-sugars meq./100 g dry s. of juice	Quantity of non-sugars remained in ion exchange resins 3-4 meq./100 g dry s. of juice	Level of exchange 3 : 1 %	Level of regeneration 4 : 3 %
	1	2	3	4	5	6	7
Potassium	21.1	0.4	20.7	20.0	0.7	98.1	96.6
Natrium	19.1	2.4	16.7	16.4	0.3	87.4	98.2
Calcium, magnesium	1.4	0.0	1.4	1.0	0.4	100.0	71.4
<b>Total</b>	<b>41.6</b>	<b>2.8</b>	<b>38.8</b>	<b>37.4</b>	<b>1.4</b>	<b>93.3</b>	<b>96.4</b>
Chlorides	4.8	traces	4.8	4.86	0.06	100.0	101.3
Phosphates	0.1	0.0	0.1	0.08	0.02	100.0	80.0
Sulphates	2.2	0.0	2.2	2.07	0.13	100.0	94.1
<b>Total</b>	<b>7.1</b>	<b>0.0</b>	<b>7.1</b>	<b>7.01</b>	<b>0.09</b>	<b>100.0</b>	<b>98.6</b>

juice by ion exchange and then eluted from the ion exchangers during regeneration with ammonium carbonate (the 15th cycle of desalting and regeneration). The contents of particular inorganic non-sugars is given in meq./100 g of dry substance of untreated juice. There is a relatively high content of sodium — 19.1 meq./100 g dry substance — in the juice before desalting. This was due to strong treatment with sodium before the juice entered the evaporation station since its natural alkalinity of the juice processed at sugar factory is low.

Table 2 shows that cation exchanger in ammonium form removed the best from juice calcium ions and than potassium and sodium ions. Anion exchanger in carbonate form removed from juice nearly all inorganic anions. The recovery of the inorganic non-sugars in the regenerant effluents were as follow: 96.4% potassium, sodium, calcium and magnesium; 98.6% anions of chlorides, phosphates and sulphates. The ratio of the non-sugars adsorbed by the ion exchange resins (column 3) to non-sugars introduced with the juice (column 1) was regarded as the degree of regeneration.

Table 3 presents a balance of inorganic [8, 16] and organic [2, 4, 9] nitrogen-free acids, and alfa-aminoacids [3] removed by the ion exchange and then collected with the regeneration waste waters (the 15th cycle of desalting and regeneration). The contents of particular acids is given in meq./100 g of dry substance of untreated juice.

When looking at the degree of exchange of the nitrogenfree acids (Table 3) it can be noticed that inorganic nitrogenfree acids were adsorbed in 100% while organic acids in 55%. The latter was due to application of an insufficient quantity of anion exchange resins in the experiment, therefore the anion exchange resins did not exchange all anions.

The degree of exchange of alfa-aminoacids indicates that in the ammonium and carbonate cycles they are removed only below 50%. Such a high level of aminoacids remaining in the juice was probably due to formation of aminoacid carbamates, which develop easily since carbon dioxide reacts with amino groups ( $\text{NH}_2$ ). Chemistry of this process is rather complex, even if the reactions occur in pure water solution [7].

The apparently high level of alfa-aminoacid regeneration (180%) should be accounted for by formation of glutamic acid from pyrrolidone-carboxylic acid in the alkaline regeneration waste waters [12].

Table 4 gives the composition of organic nitrogen nonsugars in the juice before desalting, in desalted and concentrated juice, and in concentrated the regeneration waste waters. Particular contents are in gramms of nitrogen in 100 g dry substance of the juice being desalted. Total nitrogen, which is the sum total of organic nitrogen, was determined with a modified Kjeldahl method [14]. Amide ammonia and protein nitrogens were determined in accordance with the standard procedures used in sugar technology [13]: Ammonia nitrogen — distillation under vacuum with addi-

Table 3. Non-nitrogen acids and  $\alpha$ -aminoacids removed from juice by ion exchange — the 15th cycle of desalination and regeneration

	Juice before desalination meq./100 g dry s.	Juice after desalination meq./100 g dry s. of juice	Removed from juice 1-2 meq./100 g dry s. of juice	Eluted non-sugars meq./100 g dry s. of juice	Level of exchange 3:1 %	Level of regeneration 4:3 %
	1	2	3	4	5	6
Non-nitrogen acids:						
inorganic	7.1	0.0	7.1	7.0	100.0	98.6
organic	29.0	13.0	16.0	15.1	55.0	94.4
Total	36.1	13.0	23.1	22.1	64.0	95.7
$\alpha$ -aminoacids	5.6	3.0	2.6	4.7	46.4	180.8



tion of the borate buffer solution [8]; Amide nitrogen — by subtracting ammonia nitrogen [8] from the sum of amide and ammonia nitrogens [13]. Betaine nitrogen content was determined from the quantity of betaine, established by the colorimetric method with Reinecke salt [1]. Alfa-amino-acid nitrogen — according to the Stašek and Pavlas method, modified by Carolan [3].

Table 4. Organic nitrogen non-sugars removed by ion exchange — the 15th cycle of desalination and regeneration

Nitrogen	Juice before desalination 16.0% dry s. nitrogen g/100 g dry s.	Desalinated juice; concentrate 49.3% dry s. of juice before desalination	Concentrated regeneration waste waters 12.8% dry s.
Total	0.420	0.496	0.105
Amid and ammonia:	0.183	0.308	0.049
amid	0.079	0.038	—
ammonia	0.104	0.270	—
$\alpha$ -aminoacid	0.039	0.021	0.033
Betaine	0.139	0.128	0.007
Protein	0.028	0.000	0.007

Comparison of the contents of betaine nitrogen in predesalted and in desalted juices (Table 4) indicates that there is no removal of betaine by ion exchange with cation and anion exchange resins regenerated with ammonium carbonate solution.

Table 5. Composition of dry substance of concentrated regeneration waste waters 12.8% dry s. — the 15th cycle of desalination and regeneration

	Non-sugars g/100 g dry s.	Non-sugars meq./100 g dry s.
1. Inorganic cations, total:	33.80	1072.5
K <sup>+</sup>	22.40	572.9
Na <sup>+</sup>	10.80	469.6
Ca <sup>2+</sup> and Mg <sup>2+</sup>	0.60	30.0
2. Inorganic anions, total:	7.85	200.6
Cl <sup>-</sup>	4.93	139.0
SO <sub>4</sub> <sup>2-</sup>	2.85	59.4
PO <sub>4</sub> <sup>3-</sup>	0.07	2.2
3. Inorganic non-nitrogen acids as lactic acid, gram-equivalent = 90.0	38.90	432.2
4. -aminoacids as glutamic acid, gram-equivalent = 73.5	9.90	134.3
5. Betaine	1.70	14.3
6. Protein	1.20	—

Table 5 shows the composition of dry substance of the concentrated the regeneration waste waters (12.8 as dry substance) containing inorganic and organic non-sugars that occur in sugar juices. The following inorganic cations were determined: sodium, potassium, calcium, magnesium. The cations account for 33.8% total dry substance of the regeneration waste waters. In the case of inorganic anions, the following were determined: chlorides, phosphates, sulphates. They account for 7.85% dry substance of the regeneration waste waters. Nitrogen-free organic acids recovered from the ion exchange resins regenerated with ammonium carbonate — 38.9%. Their contents (%) are given in Table 3 in terms of lactic acid because of its highest proportion in relation to other acids in juices and molasses [18].

Alfa-aminoacids were determined as a separate group of nitrogen compounds. The most convenient method here was that of Staňek and Pavlas, modified by Carolan [3], which enables determination of alfa-aminoacids in the presence of ammonium salts. The contents of the alfa-aminoacid nitrogen in terms of glutaminic acid was 9.9% dry substance of the regeneration waste waters.

Betaine [1] and protein were also determined. The content of betaine in concentrated the regeneration waste waters is only 1.7% as dry substance. The presence of this compound in the effluent is probably due to adsorption forces and not to the ion exchange. Protein content 1.2% as dry substance.

On the basis of the results (Tables 1 through 5) it can be said that following a long series of tests the proper conditions for juice desalting and regeneration of the resin beds were finally given. More than 95% non-sugars separated from juice is next recovered from the bed.

Analyzing the composition of the dry substance of the regeneration waste waters (Table 5), it should be acknowledged that the solution may be added directly to beet pulp to increase its nutritional value as fodder, but first it must be concentrated to ca 40% dry substance. Owing to this fact the bed regeneration process does not lead to formation of waste.

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#### SKŁAD REGENERATÓW PO ODSOLENIU CUKROWNICZEGO SOKU RZADKIEGO W CYKLU AMONOWYM I WĘGLANOWYM

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#### STRESZCZENIE

Badano skład chemiczny roztworu otrzymanego podczas regeneracji kationitu i anionitu w cyklu amonowym i węglowym. Odsalano cukrowniczy sok o zawartości 16% suchej substancji. Do regeneracji jonitów stosowano 3 n roztwór węglanu amonowego sposobem kołowym, uzyskując stopień regeneracji powyżej 95%. Wyciek poregeneracyjny, zawierający nadmiar węglanu amonowego oraz niecukry jonowe poddawano ciągłemu zateżnieniu. Oddestylowany węglan amonowy zawracano do regeneracji jonitów, a pozostały roztwór niecukrów odbierano z aparatu destylacyj-

nego i dodatkowo zateżano do zawartości ok. 13% suchej substancji. W zateżonym regeneracie oznaczano: azot ogólny, betainę, azot  $\alpha$ -aminokwasowy, azot amoniakalny, ogólną zawartość kwasów bezazotowych, chlorki, fosforany, siarczany, a także potas, sód, wapń i magnez.

Roztwór niecukrów zateżony do 40% s.s. może być bezpośrednio wykorzystany do wzbogacania wartości paszowej wysłdków. Dzięki temu proces regeneracji jonitów nie będzie powodował powstawania żadnych ścieków.