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DECALCIFICATION OF SUGAR THIN JUICE AND REGENERATION OF CATION EXCHANGER BY SODIUM HYDROXIDE

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Key words: sugar technology, decalcification, thin juice, regeneration by NaOH

Decalcification of thin juice in the sodium cycle and regeneration of the cation bed by means of a 4% sodium hydroxide, prepared in the previously decalcified thin juice was examined. The eluate, containing NaOH, $\text{Ca}(\text{OH})_2$ and KOH can be recycled before the second carbonatation, which makes it possible to reduce the pollution of the environment.

During the processing of sugar beet of a deteriorated technological value, thin juice with a high content of calcium salts, (200-400 mg CaO/100 RDS) is obtained. This causes the heating surface of the evaporators to become scaled, and thus leads to a deterioration of heat transfer. It is then necessary to use additional decalcification methods, which make it possible to remove calcium salts from the juice, to an optimum degree [8, 12, 14, 15], eg. decalcification by means of the cation exchanger in the sodium cycle [2, 10, 13]. The advantage of this method is the introduction into the juice of sodium cations in an amount stoichiometrically equivalent to the removed calcium cations. To regenerate the cation exchanger, a 10% sodium chloride solution in an amount of about 220 g NaCl/dm³ of, the cation exchanger is mostly used [2]. The regeneration effluent contains calcium chloride which, together with a necessary excess of sodium chloride, causes formation of strongly saline waste-water. To eliminate the waste-water it is possible to use e.g. sodium hydroxide or the salts contained in the sugar thick juice, instead of sodium chloride [1, 3-7, 9]. Sweetening-off the cation exchanger bed before regeneration, and washing it after regeneration causes a considerable dilution of the juice.

The aim of the investigations was a decalcification of sugar thin juice in the sodium cycle and then regeneration of the cation exchanger bed by means of sodium hydroxide, prepared in the previously decalcified thin juice.

INVESTIGATION METHODS

The process of decalcification was carried out on a laboratory scale in the glass column (Fig. 1), in the sodium cycle by means of the polystyrene cation exchanger Wofatit KPS, produced in the GDR. The volume of the wet cation

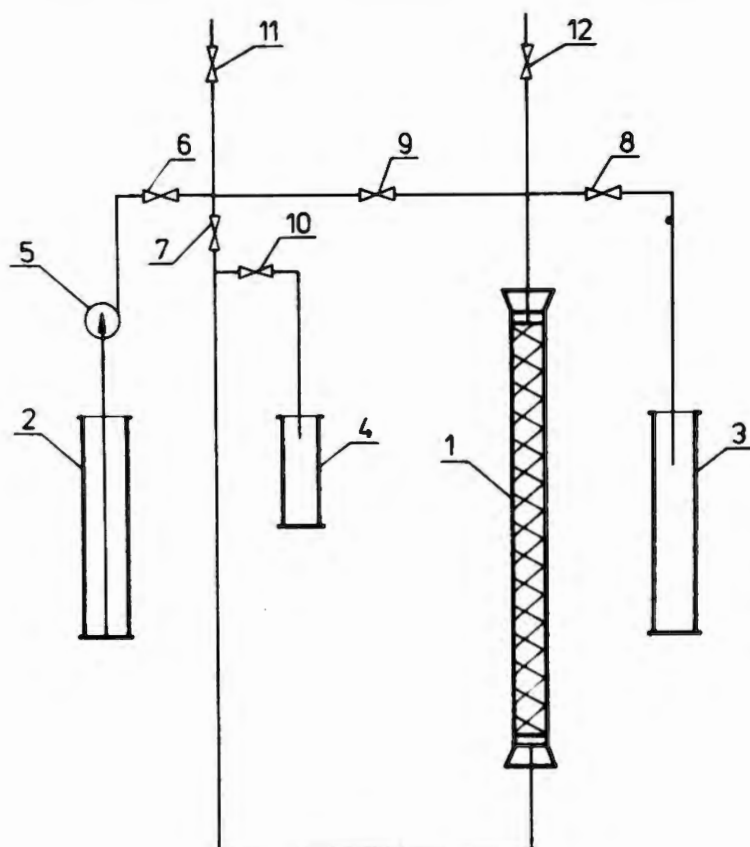


Fig. 1. Decalcification of thin juice and regeneration of the cation exchanger; 1 — column with the Wofatit KPS (210 mm, diameter 16.3 mm), 2 — feed vessel, 3 — recipient for decalcified thin juice, 4 — recipient for regeneration effluent (eluate), 5 — metering pump, 6-12 — valves. Valves open during decalcification: 6, 7 and 8; Valves open during regeneration: 6, 9 and 10

exchanger in sodium form was 42 cm^3 , which corresponded to 20.4 g of the ion exchanger dry substance. The exchange capacity of the resin bed in the column ($\text{Na}^+/\text{Ca}^{2+}$) was 88.2 meq. After preliminary trials, the following pattern of investigations was accepted. Thin juice passed through the exchanger upwards. The contact time of juice with the cation exchanger bed was 8 minutes. The process was carried out at a temperature 20°C .

After passing a definite volume of juice, the bed was regenerated in counter-current to the direction of juice, without previous sweetening-off (Fig. 1). The regenerating eluant was prepared as a 4% solution of sodium hydroxide, in the fully decalcified thin juice. The contact time with the resin bed was 30 minutes. The effluent was accumulated in fractions of a volume of 50 cm^3 . On completion of regeneration, the next cycle of juice decalcification was performed without previous washing of the resin bed with distilled water.

The post-regeneration eluate containing NaOH , $\text{Ca}(\text{OH})_2$ and KOH was used, in a separate experiment, for the purification of raw juice as an additional decalcifying agent for juice before the second carbonatation.

INVESTIGATION RESULTS

Several cycles of juice decalcification and of the cation exchanger bed regeneration were carried out. The course of the decalcification and regeneration processes was given as an example for two cycles (4th and 5th).

All the determinations were made according to routine methods used in the sugar industry [11]. The calcium salts in the eluate were determined by the versenate method after the sample had been neutralized with hydrochloric acid. The sulphated ash was determined by the gravimetric method, the amount of sodium and potassium by flame photometry. The flame photometric determination was made in the sulphated ash after dissolving it in a hydrochloric acid solution of a concentration of about 3 mol/dm³.

The results of the analysis of thin juice, after and before decalcification, were shown in Table 1, 2 and 3. In each cycle, 5 dm³ of thin juice containing 218 mg CaO/100 RDS of calcium and magnesium salts was decalcified. As a result of decalcification, the calcium and magnesium salts content decreased in the 4th cycle to 12.7 mg CaO/100 RDS, and in the 5th cycle to 10.6 mg CaO/100 RDS. The decalcification effect was 94.2% and 95.1%, respectively. The content of dry substance and the purity of juice did not change. The colour of the juice decreased slightly (Table 1).

The sum of calcium, sodium and potassium cations amounted to 33.4 meq/100 S before decalcification, and did not change as a result of decalcification (Table 2). The amount of sodium cations increased from 2.94 meq/100 S to 17.15 meq/100 S in the 4th cycle, and to 17.83 meq/100 S in the 5th cycle. Sodium cations in the juice before decalcification amounted to 8.3% of the total sum of cations, while after decalcification they amounted to about 50% of the total sum. The process of decalcification is accompanied by an exchange of potassium ions for sodium ions. The content of potassium ions decreased from 23.11 meq/100 S to 17.65 meq/100 S in the 4th cycle, and to 17.15 meq/100 S in the 5th cycle (Table 2). The decalcification of thin juice proceeded without disturbances. The cation

Table 1. Analyses of thin juice before and after decalcification by means of cation exchanger Wofatit KPS

	Unit	Before decalcification	After decalcification	
			cycle IV	cycle V
Volume	dm ³	5	5	5
RDS	%	11.35	11.28	11.30
Polarisation	%	9.45	9.40	9.40
Purity	%	83.3	83.3	83.2
Colour	IU ₅₆₀	215	203	202
pH	—	8.0	8.0	8.3
Sulphated ash grav.	g/100 S	3.40	3.46	3.51
Calcium and magnesium salts	mg CaO/100 g RDS	217.9	12.7	10.6
Effect of decalcification	%	—	94.2	95.1
Calcium and magnesium	meq/dm ³	9.28	0.54	0.45
Sodium	meq/dm ³	2.91	16.83	17.56
Potassium	meq/dm ³	22.80	17.35	16.83

Table 2. Cation content of thin juice before and after decalcification by means of cation exchanger

Cation	Thin juice before decalcification		Thin juice after decalcification			
			cycle IV		cycle V	
	meq/100 S	%	meq/100 S	%	meq/100 S	%
Calcium and magnesium	9.39	26.5	0.55	1.6	0.46	1.3
Sodium	2.94	8.3	17.15	48.4	17.83	50.3
Potassium	23.11	65.2	17.65	49.8	17.15	48.4
Total	35.44	100.0	35.35	99.8	35.44	100.0

Table 3. Balance of calcium and potassium cations after decalcification

Cation	Cycle	Introduced in thin juice, 5 dm ³	In the effluent (decalcified juice) 5 dm ³	Absorbed by cation exchanger bed	Loading of the resin bed
		meq	meq	meq	%
Calcium and magnesium	IV	46.4	2.7	43.7	49.5
	V	46.4	2.3	44.1	50.0
Potassium	IV	114.0	86.8	27.2	30.8
	V	114.0	84.2	29.8	33.8

exchanger bed was loaded with calcium ions to 50% and with potassium ions to over 30% (Table 3).

After each decalcification cycle the resin bed was regenerated. For the regeneration 0.4 dm³ of 4% solution of NaOH, prepared in decalcified thin juice, was used (Table 4). The regenerating eluant had a high alkalinity (pH = 13.6) and contained 1006 meq of sodium ions and 0.68 meq of potassium ions in 1 dm³.

The course of the regeneration process has been presented in Table and Figs. 2 and 3. It has been found that the maximum concentration of calcium and magnesium ions, amounting to over 500 meq/dm³, was reached in the second fraction, i.e. after passing 100 cm³ of the regenerating eluant. After passing 200 cm³ of the eluant, about 90% of calcium ions were removed from the resin bed. The use of another 200 cm³ of the eluant causes an approx. 6% increase in the degree of removal of calcium ions. It should be added that 200 cm³ of the eluant contains 8 g of pure NaOH, which constitutes about 200 g of NaOH per 1 dm³ of the cation exchanger.

The post-regeneration eluate contained in 1 dm³ about 700 meq of sodium cations, about 80 meq of potassium cations (on the average from two cycles) and over 100 meq of calcium and magnesium cations (Table 4).

In order to investigate the possibility of recycling the eluate after regeneration to the juice before the second carbonatation, the results of purification of raw juice by the eluate were compared (Table 6). The dose of the eluate used was 0.5

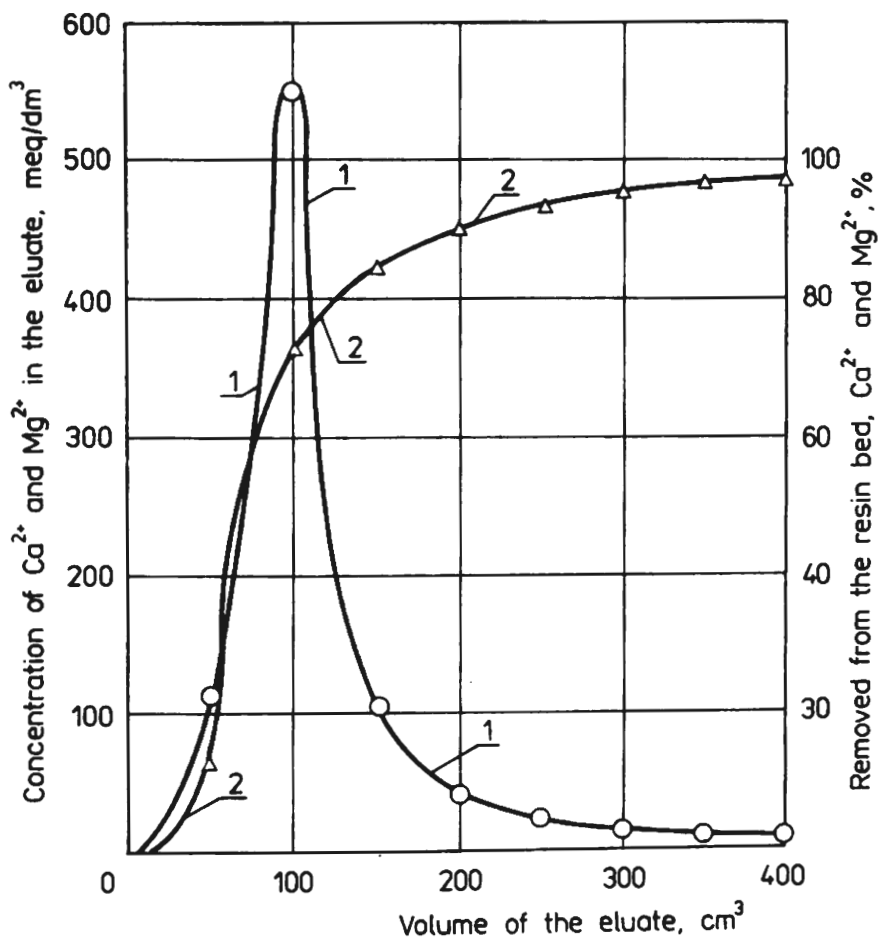


Fig. 2. Regeneration of cation exchanger bed by means of 4% NaOH in the decalcified thin juice — cycle IV; 1 — concentration of Ca²⁺ and Mg²⁺ in the eluate, 2 — removed from the resin bed, Ca²⁺ and Mg²⁺

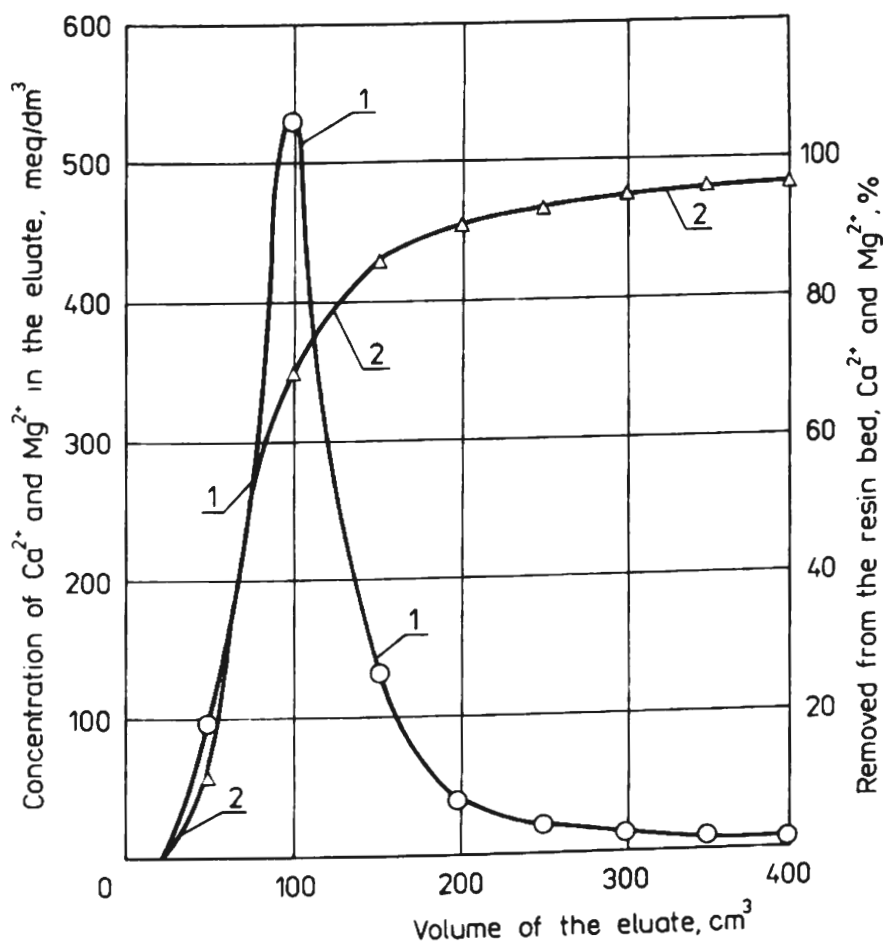


Fig. 3. Regeneration of cation exchanger bed by means of 4% NaOH in the decalcified thin juice — cycle V; 1 — concentration of Ca²⁺ and Mg²⁺ in the eluate, 2 — removed from the resin bed, Ca²⁺ and Mg²⁺

Table 4. Analyses of the regenerating eluant and the eluate

	Unit	Eluant	Eluate	
			cycle IV	cycle V
Volume	dm ³	0.400	0.400	0.400
RDS	%	17.5	16.4	16.5
pH	—	13.6	12.9	13.1
Sulphated ash grav.	%	7.01	6.34	6.41
Sodium	meq/dm ³	997.8	688.8	719.8
Potassium	meq/dm ³	0.68	91.4	65.6
Calcium and magnesium	meq/dm ³	0	105.1	106.5

Table 5. Regeneration of cation exchanger bed by means of 4% NaOH in the decalcified thin juice (Figs. 2 and 3)

Fraction	Volume of fraction	Cycle IV			Cycle V		
		Concentration of Ca ²⁺ + Mg ²⁺ in the fraction	Amount of Ca ²⁺ + Mg ²⁺ in the fraction	Removed from the resin bed, Ca ²⁺ + Mg ²⁺	Concentration of Ca ²⁺ + Mg ²⁺ in the fraction	Amount of Ca ²⁺ + Mg ²⁺ in the fraction	Removed from the resin bed, Ca ²⁺ + Mg ²⁺
		cm ³	meq/dm ³	meq	%	meq/dm ³	meq
1	50	96.5	4.82	11.0	112.6	5.63	12.8
2	50	527.9	26.39	71.4	541.1	27.06	74.1
3	50	128.7	6.43	86.1	104.1	5.20	85.9
4	50	39.6	1.98	90.7	40.0	2.00	90.4
5	50	20.7	1.04	93.0	23.6	1.18	93.1
6	50	12.1	0.61	94.4	13.6	0.68	94.7
7	50	8.6	0.43	95.4	10.0	0.50	95.8
8	50	6.4	0.32	96.2	7.1	0.36	96.6
Total	400	—	42.02	—	—	42.61	—

Table 6. Purification of raw juice in the laboratory

A — without an addition of the eluate after regeneration

B — with addition of the eluate to thin juice before the II carbonatation (0.5 meq Na⁺ + K⁺ per 1 meq Ca²⁺ + Mg²⁺ in thin juice)

	Unit	Raw juice	Thin juice	
			A	B
RDS	%	13.00	13.20	13.10
Polarisation	%	11.65	12.34	12.19
Purity	%	89.6	93.5	93.1
Colour	IU ₅₆₀	—	290	175
pH	—	—	9.2	9.3
Calcium and magnesium salts	mg CaO/100 RDS	—	240.3	57.8
Effect of decalcification	%	—	—	75.9

meq of sodium and potassium ions per 1 meq of calcium and magnesium ions contained in the thin juice, purified by the classical method, i.e. without an addition of the eluate. It has been found that the amount of calcium and magnesium salts decreased from 240 mg CaO/100 RDS to 58 mg CaO/100 RDS, which amounted to about 76% of decalcification. No deterioration of the quality of thin juice purified with an addition of the eluate has been found. The use of the eluate as an additive to juice before the second carbonatation causes an additional decalcification of the juice and a reduction in the amount of troublesome waste.

CONCLUSIONS

On the basis of the experiments carried out the following conclusions have been drawn.

1. The decalcification of thin juice with the help of the cation exchanger Wofatit KPS in the sodium cycle proceeded without any disturbances. The effect of decalcification of juice was over 90%.

2. The regeneration of the cation exchanger bed by means of a 4% solution of NaOH prepared in the decalcified thin juice proceeded correctly. Over 200 g of NaOH per 1 dm³ of the ion exchanger is needed to regenerate the resin bed in over 90%.

The post-regeneration eluate containing NaOH, Ca(OH)₂ and KOH can be recycled for decalcification of the juice before the second carbonatation, which makes it possible to reduce the pollution of the environment, too.

4. After the process of decalcification and regeneration the cation exchanger bed does not require sweetening-off or washing with water. Owing to this there is no dilution of the juice.

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ODWAPNIANIE CUKROWNICZEGO SOKU RZADKIEGO I REGENERACJA KATIONITU ZA POMOCĄ WODOROTLENKU SODOWEGO

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Streszczenie

Celem badań było jonitacyjne odwapnianie cukrowniczego soku rzadkiego i regeneracja kationitu za pomocą wodorotlenku sodowego przygotowanego w uprzednio odwapnionym soku rzadkim.

Proces odwapniania prowadzono w skali laboratoryjnej, za pomocą polistyrenowego kationu Wofatit KPS produkcji NRD, w cyklu sodowym, w tem. 20°C. Po zakończeniu odwapnienia złożę regenerowano, bez uprzedniego wysładzania wodą. Regenerację prowadzono za pomocą 4% roztworu wodorotlenku sodowego, przygotowanego w soku rzadkim całkowicie odwapnionym. Po zakończeniu regeneracji prowadzono kolejny cykl odwapniania soku, bez przemywania złoża wodą destylowaną. Wyciek poregeneracyjny zawierający NaOH, Ca(OH)₂ i KOH, wykorzystywano w procesie oczyszczania soku surowego, jego dodatkowy czynnik odwapniający sok przed II karbonatacją.

Osiągnięto efekt odwapnienia soku ponad 90%. Regeneracja kationitu za pomocą 4% roztworu NaOH rozpuszczonego w odwapnionym soku rzadkim przebiegała prawidłowo. Do zregenerowania złoża powyżej 90% potrzeba ponad 200 g NaOH na 1 dm³ jonitu.

Wyciek poregeneracyjny zawierający NaOH, Ca(OH)₂ oraz KOH może być zawrócony do soku przed II karbonatacją, co pozwala na zmniejszenie ilości uciążliwych ścieków. Złożę kationitu po procesie odwapniania i regeneracji nie wymaga wysładzania ani przemywania wodą, dzięki czemu nie następuje rozcieńczenie soku.