

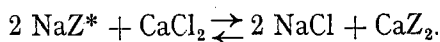
ION EXCHANGE

REPORT BY SUB-COMMITTEE ON EXPERIMENTS CARRIED OUT AT DARNALL WITH A LABORATORY ION EXCHANGE PLANT

The ion exchange process, or the process in which certain ions of salts in solution are exchangeable for ions in a solid matrix, has been practised industrially for the past forty years and more, in the form of water-softening with inorganic zeolites. The development of synthetic exchange resins, capable of almost complete de-ionization of solutions is, however, of much more recent date. But it is this latter development that has found application in a wide field and has been of particular interest to the sugar industries of the world, as it offers a means of eliminating nearly all the ash and a large portion of other non-sugar constituents, which together so adversely affect the quantity and quality of the sugars to be recovered.

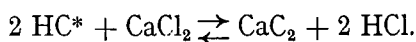
GENERAL PRINCIPLES.

The inorganic ion exchangers which are known as zeolites and consist of complex alumina silicates, are used to remove the hardness of water. Thus the sodium in the solid sodium aluminium silicate is exchanged for the calcium or magnesium ions in solution, and the objectionable calcium and magnesium are removed and now form part of the insoluble silicate complex, while the sodium is in solution.



The reaction is reversible and with an excess of sodium chloride the original sodium aluminium silicate is formed again. The zeolite can therefore be regenerated. Although hardness is eliminated in the process, other salts are formed in its place. The reaction is restricted to a narrow pH range close to neutrality.

The development of synthetic cation exchange resins which are stable over a wide pH range and in the acid region, meant that the soluble calcium could now be exchanged not only for a sodium ion in the solid resin, but also for a hydrogen ion in the insoluble matrix, and instead of another soluble salt being formed, an acid is now generated.

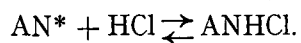


Again the reaction is reversible and by using excess acid the cation exchanger can be regenerated. For regeneration, a dilute strong acid such as hydrochloric or sulphuric acid will be used.

Where the natural zeolites take out only the heavy metals such as calcium, magnesium and iron, the synthetic cation exchange resins can, under favour-

able conditions, very nearly completely eliminate all positively charged ions. The amount of positive ions that can be eliminated depends, of course, on the rated capacity of the cation resins; but also on other factors. The reaction, as stated, is reversible and will depend on the hydrogen ion concentration, and if, therefore, a strong acid is liberated from a certain positive ion, the equilibrium of the reaction will be reached sooner than if a weak acid is set free. Thus, for example, less sodium will be absorbed by the resin if the salt in the influent is sodium chloride, than would be the case if sodium carbonate were the salt. In the first case free hydrochloric acid will be formed and the high hydrogen ion concentration will shift the equilibrium to the left; but where a weak acid such as carbonic acid is formed, more sodium will be eliminated. The anions have therefore a profound effect on the capacity of the cation exchange resins. The cations themselves are important. According to Tiger and Sussman,⁴ higher capacities are obtained with divalent than with monovalent cations. It can further be stated that if calcium and sodium chloride are both present in the influent, both will at first be absorbed in the ratio present, but as the exchanger becomes exhausted calcium in the influent will replace sodium in the exchanger and the concentration of the sodium in the effluent will increase.⁵ It is hardly necessary to mention that the life-cycle of the resin before regeneration will depend on the total concentration of the salts in solution.

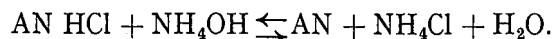
The use of the cation exchange process was very limited until such time that a resin was developed capable of removing the acid formed. This second resin is called the anion exchange resin. Although the reaction taking place is not fully established, an exchange of ions, as explained for the cation resin, may not necessarily take place and the acids may quite likely be eliminated by forming addition compounds similar to the formation of ammonium chloride from ammonia and hydrochloric acid. This explanation seems the more feasible as nearly all anion exchangers have amino or imino groups as their active components³ and these may form large insoluble molecules with the acids present.



The anion exchanger, like the cation exchanger, can be regenerated repeatedly. In this case, however,

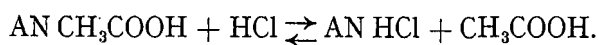
* Note.—For convenience of representation: Z is used for the natural zeolites, C is used for the synthetic cation exchange resin, AN is used for the synthetic anion exchange resin.

an alkali, such as sodium or ammonium hydroxide or sodium carbonate is used.



The laws of mass action which hold for cation exchange reactions are also applicable here, and to ensure good regeneration an excess of alkali is required.

The strongest acids, i.e. the most highly ionized acids, will be preferentially absorbed by the anion exchanger. Although, for example, both hydrochloric acid and acetic acid will be absorbed by the anion exchanger to start with, once the active groups in the exchanger have been satisfied hydrochloric acid will replace acetic acid and there will be leakage of the weaker acid.



In practice the liquid to be treated is first passed through the cation exchange resin and the positive ions are absorbed, but a small leakage will take place and this leakage will be greater if the concentration of salts in the influent is higher or if the cation exchanger approaches exhaustion. It also follows that there will be sodium leakage in preference to, say, calcium leakage, and that the concentration of sodium salts in the cation exchange effluent will increase as the resin gets more exhausted. The anion bed will remove the free acids and, as the salts present hydrolyse, the acid part will also be absorbed and the free alkali will be formed which will limit the capacity of the anion exchanger⁵. Cation leakage must therefore be reduced to a minimum. The free alkali will further combine with free acids, and as the stronger acids replace the weaker ones from the insoluble resins, it follows that, say, sodium of salts of the weak acids such as sodium carbonate and acetate will be found in the anion effluent rather than the divalent mineral salts of strong acids such as calcium chloride or magnesium sulphate.

The ion exchange process depends on the ionization of the salts or the hydrolysis of the salts and subsequent ionization of the bases and acids formed. A practically non-ionizable substance such as silica is hardly affected by the process and will be found in the final effluent, unless, of course, a fluoride is added and hydrofluoric acid is formed.⁶ Nevertheless, it is found in practice that, for example, in a sugar juice solution, the major portion of the total non-sugars is removed and a certain amount of the colloidal matter eliminated. The colloids, etc., are of course subjected to a very wide pH range in passing through the exchange beds. Waxes, gums and colloids thus eliminated may, however, have a very undesirable effect, in that a coating of these materials on the exchange granules may seriously

limit the capacity of the resins and may make regeneration very difficult.¹

PLANT AND OPERATION.

The laboratory plant used for carrying out the ion exchange experiments was obtained from the Dorr Company and was type L-4 D-1 unit consisting of a single pair of cells, i.e. one cation and one anion cell, each charged with 0.2 cubic feet of resins. The plant was complete with a solu-bridge and pressure indicator.

The cation resin was always regenerated with sodium chloride and sulphuric acid. The sodium chloride (200 grams in 4 litres) was first passed through the cell, the resin was then washed and the sulphuric acid (generally 500 ml. 98 per cent. in 6 litres) then passed through at the rate of 400 ml. per minute, before the final rinsing with water.

The anion resin was generally regenerated with 1,200 ml. 25 per cent. ammonia in 6 litres, but caustic soda and sodium carbonate were also used as regenerants. After all the alkali has passed through, the anion resin is rinsed with water which is first passed through the cation cell. Rate of regeneration was 400 ml. per minute.

The clarified juice was passed through the cells from a tank 9 feet 6 inches above the cation inlet at the rate of 1,000 ml. per minute and under a pressure of 3 lbs. per square inch. When the juice flow is started the exchange beds are full of water which is pushed out, but a certain amount remains and dilutes the treated juice.

The juice is passed through until the beds are exhausted or the break-through occurs, which is indicated by a sudden rise in micromhos on the solu-bridge.

Before regenerating again the cells are separately backwashed to clean the beds of foreign material and to loosen the resins.

EXPERIMENTAL.

The clarified juice from the Darnall factory still contains a fair amount of colloids. This juice, on being treated in the two-bed ion exchange system, emerged as a white, green or yellowish liquor, but was still rather cloudy. The colour became darker as the exchangers were being exhausted, and was also affected by the pH. Where soda ash was used as a regenerant the pH of the anion effluent was decidedly acid and this apparently was not due to carbon dioxide alone, as little if any rise in pH occurred on boiling. Results obtained from ammonium and sodium hydroxide were better and gave a decidedly alkaline effluent. The following results were obtained on factory clarified juice, using the sulphitation process of clarification.

TABLE I.—Test Runs, Clarified Juice ex Factory.

CLARIFIED JUICE.							TREATED JUICE.						
Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	pH.	Anion regenerant used.	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	pH.	Per cent. non-sugar removed.
12.9	11.21	86.9	0.32	2.85	7.4	Soda ash ...	11.9	10.95	92.0	0.38	3.47	5.5	57.6
12.6	10.86	86.2	0.32	2.95	—	Caustic soda	11.6	10.82	93.3	0.36	3.33	—	70.4
13.3	11.36	85.4	0.32	2.82	—	" "	11.7	10.80	92.3	0.45	4.17	—	71.2
13.2	11.39	86.3	0.34	2.98	7.4	Soda ash ...	12.0	10.91	90.9	0.45	4.12	—	55.1
13.8	11.98	86.2	0.39	3.25	7.3	Ammonia ...	11.6	10.51	90.6	0.48	4.56	7.6	52.0
14.1	12.27	87.0	0.32	2.60	—	" "	12.2	11.09	90.9	0.52	4.69	8.1	57.6
14.2	12.25	86.3	0.47	3.83	7.4	" "	12.0	10.98	91.5	0.61	5.55	8.2	69.6
13.9	11.95	86.0	0.43	3.60	—	" "	12.3	10.95	89.0	0.65	5.94	—	50.9
14.1	12.18	86.4	0.44	3.61	—	Soda ash ...	12.4	11.34	91.4	0.60	5.29	5.4	67.2
13.57	11.72	86.4	0.37	3.16	7.4	Average...	11.97	10.93	91.3	0.50	4.57	—	61.4

It was found that mixed juice samples limed without the use of sulphur dioxide and phosphoric acid gave high purities and generally good non-sugar removal, but the effluents were decidedly more

cloudy as a result of colloids passing through the exchangers. Juice treated with lime and phosphoric acid only, or lime and sulphur dioxide only, was also put through the ion exchange process.

TABLE II.—Test Runs, Clarified Juices Prepared in Pilot Plant.

CLARIFIED JUICE.							TREATED JUICE.							
Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	pH.	Anion regenerant used.	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	pH.	Per cent. non-sugars removed.	
Lime + phos....	11.6	9.00	85.3	0.38	3.84	7.8	Soda ash ...	10.1	9.34	92.5	0.42	4.50	5.5	72.9
" " ...	13.0	11.15	85.8	0.30	2.69	7.8	" " ...	11.1	10.15	91.4	0.38	3.74	5.9	60.0
" " ...	11.4	9.89	86.8	0.30	3.03	6.3	Caustic soda...	10.7	9.36	92.9	0.32	3.43	8.2	63.4
Phos. + lime ...	12.6	11.11	88.2	0.24	2.16	7.6	Soda ash ...	11.1	10.42	93.9	0.32	3.07	4.5	69.6
Lime + phos....	13.6	12.21	89.8	0.24	1.96	7.7	Caustic soda...	11.7	10.96	93.7	0.35	3.19	5.2	62.7
Lime only ...	12.6	11.04	87.6	0.29	2.63	7.7	Ammonia ...	10.6	9.92	93.6	0.40	4.03	7.8	75.8
" " ...	13.5	12.05	89.2	0.22	1.82	7.2	" "	11.6	10.97	94.6	0.30	2.73	8.2	70.8
Lime + sulph. ...	13.5	11.91	88.2	0.24	2.02	6.9	" "	11.7	10.92	93.3	0.34	3.11	8.0	64.8
Lime + phos....	16.0	14.24	89.0	0.32	2.25	7.9	Soda ash ...	14.2	13.32	93.8	0.42	3.15	5.2	66.1
Lime only ...	14.5	12.99	89.6	0.24	1.85	8.0	" " ...	12.8	12.00	93.8	0.43	3.58	5.0	69.0
" " ...	13.3	11.63	87.4	0.33	2.84	7.3	Ammonia ...	11.9	10.87	91.3	0.51	4.69	7.9	59.2
" " ...	13.9	12.44	89.5	0.29	2.53	8.4	" "	11.9	11.19	94.0	0.40	3.57	7.0	70.9
" " ...	13.7	11.98	87.4	0.30	2.50	7.4	" "	11.4	10.67	93.6	0.41	3.84	7.9	75.0
" " ...	13.3	11.80	88.7	0.29	2.46	8.1	" "	11.4	10.42	91.4	0.55	5.28	6.6	60.9
" " ...	14.9	12.53	84.1	0.54	4.31	8.3	" "	12.0	10.68	89.0	0.73	6.84	8.1	63.1
" " ...	14.3	12.74	89.1	0.29	2.28	8.0	Soda ash ...	12.9	11.95	92.6	0.32	2.68	4.6	47.3
Average ...	13.48	11.85	87.9	0.30	2.53	7.65	Average...	11.69	10.82	92.6	0.41	3.79	—	62.6

The throughput in Tables I and II was 9 to 10 gallons per run. Good pre-clarification gave the best results. Thus a Natal Estates syrup on being diluted yielded a brilliant product with a high non-sugar removal and a high throughput.

	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	Ash per cent.	pH.
Diluted Syrup	18.77	17.57	94.0	0.18	1.02	0.43	7.2

The anion resin was regenerated with caustic soda and the following results obtained for the treated juice :

Micromhos.	Quantity treated.	Colour.	Brix.	Sucrose.	Purity.	Reducing sugar.	Reducing sugar ratio.	pH.
70	First fraction	Water-white	16.0	15.74	98.4	—	—	8.7
65	Second fraction		17.2	16.84	97.9	—	—	8.2
55	Third fraction		17.6	17.05	96.9	0.21	1.23	8.2
150	Further 2 gallons	Opalescent	17.6	16.97	96.4	0.25	1.47	4.7
400	Further 2 gallons	Greenish	—	—	—	—	—	4.7

The break-through occurred at about the twelfth gallon of juice put through and the average analysis of this juice was such that the percentage of non-sugar removal was 83.2 per cent. and about 97 per cent. ash was eliminated.

To get a brighter juice at Darnall for the ion exchange process, the mixed juice was treated as

follows in a pilot plant: the juice was heated to 50°C., limed to 9.6 pH, sulphur dioxide passed through to pH 8.6 and phosphoric acid was added to pH 7.4. The juice was brought to boiling point and the clarified juice decanted by gravity. The following results were obtained on passing the juice through the exchangers:—

TABLE III.

CLARIFIED JUICE.						TREATED JUICE.									
Brix.	Sucrose	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	pH.	Regenerant used.	Quantity in gallons treated.	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	pH.	Per cent non-sugars removed.	
14.7	12.65	86.0	0.36	2.84	7.1	Soda ash ...	8	12.9	12.07	93.6	0.41	3.40	5.4/4.9	74.0	
15.1	13.27	87.9	0.46	3.47	6.8	Ammonia ...	9½	13.7	12.66	92.4	0.48	3.79	8.5/8.0	57.3	
16.1	14.16	88.0	0.36	2.54	7.5	„ ...	6	13.8	13.08	94.8	0.40	3.06	8.6	78.2	
13.9	11.26	81.0	0.96	8.52	7.2	„ ...	10	12.3	10.60	86.2	0.97	9.15	9.2	54.1	

The treated juices were all clear and the colour varied from water-white to faint yellow. Before treating the last sample the anion resin was changed and the first 6 gallons were water-white, the next 3 gallons slightly yellow and the last gallon yellow. The solu-bridge readings varied from 50 to 700 micromhos for the first two gallons to 525—700 for the tenth gallon of treated juice.

The de-ionized juice was, however, not as good as that obtained from the Natal Estates' syrup, neither could the same quantity be treated. The non-sugar removed varied from 54 to 78 per cent. on treating 10 and 6 gallons of juice respectively, whereas 83 per cent. non-sugars were removed from 12 gallons of Natal Estates diluted syrup.

It was realized that although a juice of good clarity was very desirable for the ion exchange process, the clarification should be such that a minimum of soluble salts are added in the process. Experiments were then carried out on an acid clarification. The mixed juice was acidified with sulphuric acid or sulphur dioxide to pH 3.2 and clay added to improve settling. After filtration the juice was put through the ion exchange process.

Juice clarified with sulphuric acid:—

	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.
Mixed juice	13.9	11.73	84.4	0.37	3.15
Clarified juice ..	13.4	11.47	85.6	0.43	3.75
Ion exchange juice 12½ gallons ..	11.8	10.96	92.9	0.44	4.01

	Brix.	Sucrose.	Purity.	Reducing sugar.	Ash per cent.	pH.	Reducing sugar ratio.
Diluted molasses ...	18.9	8.3	44.0	3.0	2.0	5.8	36.1
Treated molasses—							
Micromhos 300	10.6	7.4	69.8	2.1	0.05	6.7	28.4
1,000	11.9	8.0	67.2	2.3	—	6.6	28.7
to 4,000	13.8	7.8	56.5	2.6	—	—	33.3

The non-sugar removal was 72.1 per cent. on clarified and 76.4 per cent. on mixed juice. Juice clarified with sulphur dioxide:—

	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	Ash per cent.
Mixed juice	14.8	12.36	83.5	0.61	4.94	0.52
Ion exchange juice	12.4	11.49	92.7	0.67	5.83	0.03

Non-sugar removal 86.0 per cent. on mixed juice. Ash removal 93.8 per cent.

Juice clarified with sulphur dioxide to pH 3.2, limed to 7.6 pH, heated and settled:—

	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	Ash per cent.
Clarified juice ..	13.7	11.37	83.0	0.69	6.07	0.49
Ion exchange juice	11.9	10.78	90.6	0.77	7.14	0.02

Non-sugar removal 77.7 per cent. on clarified and 78.3 on mixed juice. Ash removal 95.7 per cent. on clarified juice.

A sample of final molasses was diluted to about 20° brix and after settling was passed through the exchange beds using the same resins. Only two gallons could be treated before the break-through occurred, but the increase in purity was very high, as the following results show:—

Even the first two gallons were cloudy, and on concentrating the colloidal matter could be skimmed off. The non-sugar removal on the first two gallons was 82.8 per cent.

An attempt was made to pass through the exchangers unclarified mixed juice, but it was found quite impossible as the beds were blocked almost immediately.

During the off-season Duolite anion resin A3 from the Dorr Company, described as being particularly suited for the treatment of material high in aldehyde groups, was tried on molasses samples instead of the A2 resin used up to now.

Sample No. 1 Darnall molasses:—

	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	Ash per cent.	pH.
Molasses	19.9	8.4	42.2	2.30	27.38	2.96	5.5

Analyses of each one-gallon passed through the ion exchange process.

Micromhos.	Quantity in gallons.	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	Ash per cent.	pH.	Non-sugars removed.
185—1,400	1	7.0	5.2	74.3	1.04	20.00	0.19	9.3	85.8
1,400—2,500	1	12.5	8.1	64.8	2.08	25.67	0.26	8.3	73.5
2,500—6,500	1	15.3	8.2	53.6	2.15	26.22	0.77	5.8	44.1
6,500—12,000	1	17.8	8.0	44.9	2.22	27.75	1.84	5.1	13.7

Sample No. 2, Darnall molasses:—

	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	Ash per cent.	pH.
Molasses	19.1	8.1	42.4	2.26	27.90	3.34	5.6

Analyses of each one-gallon passed through the ion exchange process:—

Micromhos.	Quantity in gallons.	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	Ash per cent.	pH.	Non-sugars removed.
200—1,400	1	7.2	5.3	73.6	1.21	22.83	0.16	9.2	87.4
1,400—3,500	1	12.4	8.0	64.5	2.04	25.50	0.35	8.1	72.1
3,500—8,000	1	15.3	8.0	52.3	2.20	27.50	1.16	5.9	40.7
8,000—15,000	1	17.3	7.9	45.7	2.22	28.10	2.21	5.1	15.9

The break-through occurred at the third gallon in both cases. If we include the third gallon and average the analyses of these two samples we get a non-sugar removal of 64.8 per cent. A third sample of Darnall molasses was then treated, and also single samples from the Natal Estates and the Refinery.

On the Natal Estates molasses the break-through occurred at the same point, but in the case of the Refinery molasses it happened in the fourth gallon. The results of the treatment, all based on the first three gallons, are given below:—

MOLASSES.								TREATED MOLASSES.							
Sample.	Brix.	Sucrose.	Purity	Reducing sugar per cent.	Reducing sugar ratio.	pH.	Ash per cent.	Brix.	Sucrose.	Purity.	Reducing sugar per cent.	Reducing sugar ratio.	pH.	Ash per cent.	Non-sugars removed
Average of first 2 samples, Darnall	19.5	8.25	42.3	2.28	27.64	5.55	3.15	11.6	7.13	61.5	1.79	24.62	7.6	0.48	64.9
No. 3 Darnall...	19.4	8.3	42.8	2.32	27.95	5.5	—	12.2	7.4	60.6	1.96	26.48	6.2	—	63.6
No. 4 Natal Estates	19.3	8.4	43.52	1.70	20.24	5.2	3.56	12.1	7.5	65.2	1.50	19.86	7.5	0.62	62.2
No. 5 Refinery ...	18.1	8.1	46.4	3.56	42.38	5.5	2.44	11.5	7.3	64.47	2.94	39.76	8.9	0.31	77.7

The best non-sugar elimination and also ash removal was obtained from the Refinery molasses, in which, as pointed out, the break-through occurred later. It will be noticed that there appear to be no sucrose losses due to inversion when treating molasses.

DISCUSSION.

Colloids. Claims have been made³ that the ion exchange process can be applied to cane and beet juices before defecation, and the small amount of

gums, colloids, etc., which have not been removed by the ion exchange process can be eliminated afterwards by filtration or an inexpensive chemical clarification. It is not known what mechanical clarification was applied prior to the de-ionization of the juice, but our experience has been, with the plant and resins at our disposal, that the better the clarification the better the results. Even moderately good clarified juice is inclined to be cloudy after treatment, and a simple filtration may be necessary. In many cases the milkiness seemed to disappear on concen-

tration; in others it came up in a scum, but a sediment was often seen on leaving the syrup standing. In one particular case the syrup, after being boiled up in an open pan, was clear, but on diluting a distinct precipitate formed, which was found to be silica. Silica, as was explained, will not be eliminated to any extent in the process and is probably the cause of the milky or cloudy appearance of many of our treated samples. It is, however, not the only cause. In one sample, on being boiled to a syrup in an open pan, a very heavy precipitate formed, probably due to imperfect regeneration and rinsing, which gave the following analysis:—

Pentosans	1.7 per cent.
Nitrogen...	1.33 per cent.
Ether extract	6.5 per cent.
Ash	59.1 per cent.

Ninety-two per cent. of the ash was found to be silica.

Even if some colloids and gums are eliminated in the ion exchange process, they may, as pointed out by Bloch and Ritchie¹, form a coating round the resin granules which prevents proper contact with the incoming liquid, and thus decreases the effectiveness of the resins. They are also very difficult to remove, and regeneration of the resins is therefore complicated.

Non-sugar Removal. Non-sugar removal depends, of course, on the quantity of juice put through, the completeness of the regeneration of the resins, etc., but with our two-bed system and passing through about 10 gallons of juice, a non-sugar removal of 60 to 70 per cent. should be obtained, with an increase in purity of about 5 to 6 degrees. Better results have, of course, been obtained. Some of the low non-sugar removal results, 50-60 per cent., were due to initial inexperience and imperfect regeneration.

The ash elimination was good, about 90 to 95 per cent. and even better, as the following results will indicate:—

Ash per cent. Clarified juice.	Ash per cent. Treated juice.
0.52	0.08
0.46	0.02
0.42	0.02
0.49	0.03
0.54	0.04

The treated juice is somewhat more dilute than the clarified juice, but the difference is so small as not to affect the results appreciably. In the last two treated juices the silica content of the ash was 67 and 50 per cent. respectively.

Inversion. There were no facilities to cool down the juice to be treated and most of the runs were

done at temperatures ranging from 20° to 30°C. The increase in reducing sugar per cent. juice was about 0.1 per cent., or from about 0.3 to 0.4 per cent., while the reducing sugar ratio increased approximately 1 or 1½ per cent. The reducing sugar ratio is low in South Africa, and will not be high even after the above increase, but a loss of more than one per cent. of the total sucrose present will have to be avoided in a commercial plant. It has been pointed out by Haagensen² and Ripley and Sanborn³ that, provided the temperature is kept down to about 20°C., inversion losses resulting from the acidity of the ion exchange process are small. Bigger losses are often due to bacterial action. Our results were, of course, obtained with one pair of cells and the pH of the cation effluent was about 2.5 pH. If more than one pair of cells is used for better elimination of non-sugars, inversion losses will be greater under similar conditions due to a longer period of high acidity and the longer contact with the cation exchange resins which will cause catalytic inversion.

Where molasses have been treated there is apparently no increase in reducing sugars.

Regenerants. In most of the experiments ammonium hydroxide was used to regenerate the anion resins. Sodium hydroxide was used for a few runs and for quite a number of runs the resin was regenerated with sodium carbonate, but, as stated, the anion effluent was on the acid side where the latter regenerant was used, and there were indications of incomplete regeneration.

According to the Dorr Company⁷ about 200 per cent. of theoretical sodium carbonate is required for regenerating the anion resin as compared with 125 per cent. of sodium hydroxide and 120 per cent. ammonium hydroxide. It is also pointed out that ammonia and caustic soda keep the resins cleaner than sodium carbonate and free from organic matter.

Ammonium hydroxide has the further advantage over sodium carbonate in that it has a lower equivalent weight.

It was also thought that by using ammonia there might be the possibility of economically recovering the ammonium sulphate as a by-product of the process.

The amounts of chemical regenerants used per unit elimination of non-sugar is, of course, of the greatest importance, as the cost of these chemicals will very largely determine whether the process will be economical or not. Haagensen² calculates that to remove 1 lb. non-sugars from beet juice by a single stage regeneration approximately 1 lb. 66 Be sulphuric acid and 0.6 lb. sodium carbonate will be required. Ripley and Sanborn,³ operating three pairs of exchangers in series, found that 18 lbs. of sodium

hydroxide and the same amount of sulphuric acid were required per ton of beet or to remove 43 lbs. of non-sugars. So that for 1 lb. non-sugars eliminated 0.42 lb. sulphuric acid and 0.42 lb. caustic soda will be required. Another estimate⁶ is that generally 15 to 25 lbs. of 66 Be sulphuric acid and 5 lbs. of anhydrous ammonia are necessary for regenerating purposes for 1 ton beet. If we assume here that 43 lbs. non-sugars are again removed, then the chemical requirements for 1 lb. of non-sugars eliminated are 0.35 lb. to 0.58 lb. sulphuric acid and 0.12 lb. anhydrous ammonia.

The amount of chemicals actually used at Darnall was calculated by estimating the quantity of free acid and alkali after regenerating and subtracting these from the quantities used. Thus a mixed juice clarified by heating to 50°C., limed to pH 9.6, sulphited to pH 8.6 and phosphoric acid added to pH 7.3, then boiled and subsided and treated by the ion exchange process, gave the following results:—

	Brix.	Sucrose.	Purity.	Reducing Sugar.	Reducing Sugar Ratio.	pH.
Mixed juice ..	14.1	12.21	86.6	0.30	2.46	—
Clarified juice ..	13.9	12.16	87.5	0.33	2.71	6.5
Processed juice 10 gallons ..	12.4	11.61	93.6	—	—	—
Processed juice 12½ gallons ..	12.6	11.79	93.6	0.38	3.22	7.7

	Clarified juice.	Ion exchange juice.
Sucrose ...	12.16	11.79
Reducing sugars ...	0.33	0.38
Total sugars ...	12.49	12.17
Non-sugars ...	1.41	0.43
Non-sugars per 100 total sugar ...	11.29	.53
Non-sugars removed ...	68.7 per cent.	
Total non-sugars present in 12.5 gallons =	821 grams.	
Sulphuric acid used for regeneration 500 ml. 98 per cent. =	901.6 grams.	

Free sulphuric acid present in 21,400 ml. effluent = 723.5 grams.

Therefore sulphuric acid used per 1 non-sugar removed = **0.32.**

Ammonia used for regeneration 1,200 ml. 25 per cent. = 270 grams.

Free ammonia present in 21,400 ml. effluent = 211 grams.

Therefore ammonia used per 1 non-sugar removed = **0.10.**

Similarly, in a case where 12½ gallons of juice pre-clarified with sulphuric acid and clay were used a 72.1 per cent. non-sugar removal was obtained, and it was found that for unit non-sugar removal 0.42 sulphuric acid and 0.15 ammonia were used.

According to the Dorr Company⁷ 120 per cent. of theoretical ammonia is required for regeneration. In the case of the cation resin 300 per cent. sulphuric acid is necessary, but Haagensen² has pointed out how a saving of 28.4 per cent. acid can be made for the same overall efficiency of regeneration, by using

two pairs of cells in series. The Dorr Company⁷ estimates that 200 per cent. of theoretical sulphuric acid is required when using a two-stage regeneration.

According to this information our ammonia requirements in the two samples will therefore be 0.12 and 0.18 lb. pure ammonia, or 0.48 and 0.72 lb. of commercial 25 per cent. ammonia per 1 lb. non-sugars removed. In the case of sulphuric acid 0.98 and 1.29 lbs. 98 per cent. sulphuric acid are indicated for a one-stage regeneration, and 0.65 and 0.86 lb. of the same acid seems probable for a two-stage regeneration.

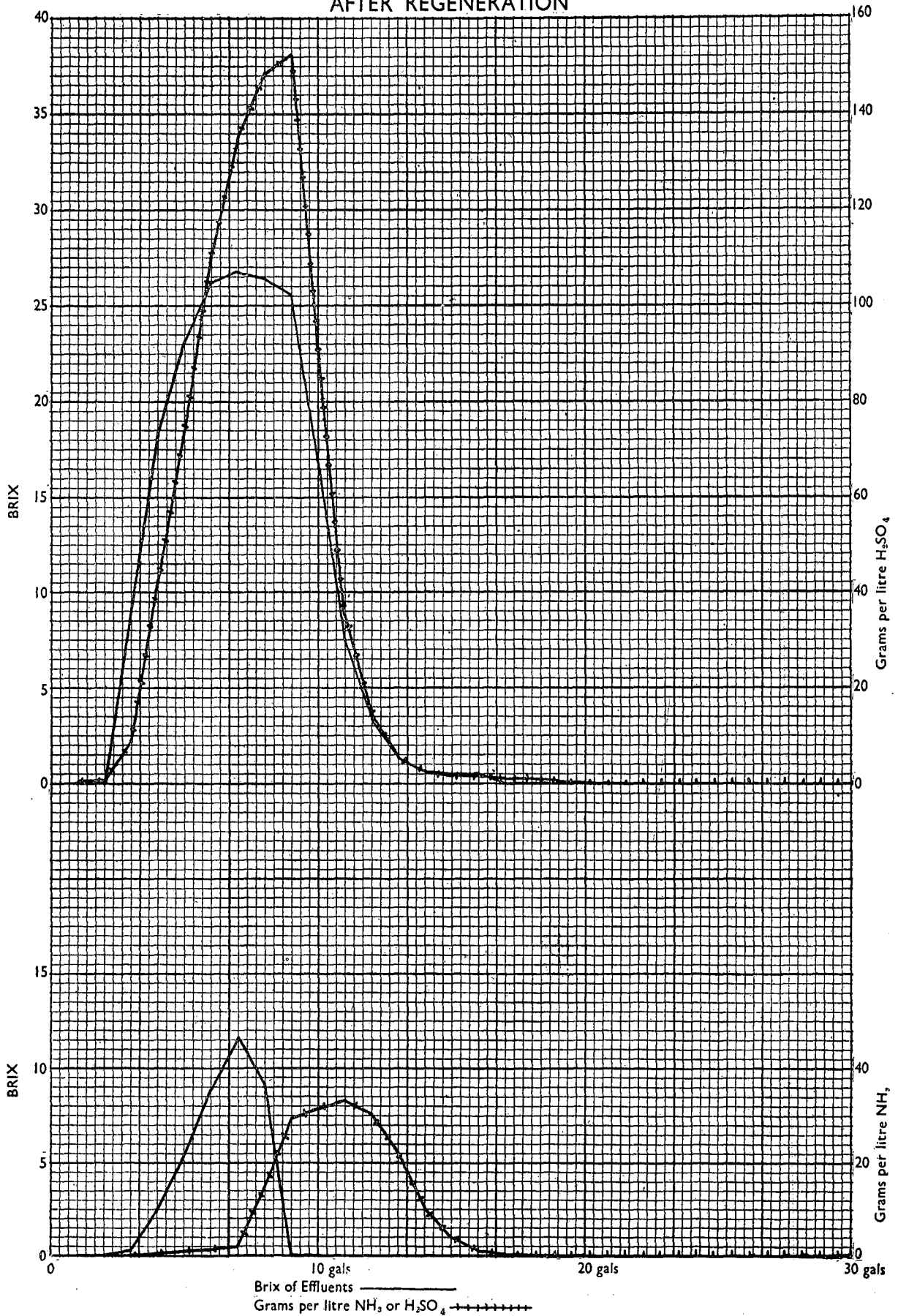
Bloch and Ritchie¹ found that 0.59 lb. sodium hydroxide and 0.79 sulphuric acid were used for 1 lb. non-sugars removal where a mixture of 3 parts cane syrup to 1 part molasses was treated. Here, however, only 35 per cent. of the cation exchanger beds were exhausted, whereas the anion exchanger was completely exhausted. After making the necessary alterations to the equipment it was found that 0.12 lb. sodium hydroxide and 0.32 lb. sulphuric acid per 1 lb. non-sugars were required to treat molasses.

It will be noticed that the amounts of regenerants vary appreciably and some of the causes have been indicated. Haagensen² also points out that the organic material to ash ratio in the non-sugars plays a part. The organic non-sugars have in general higher equivalent weights than the inorganic materials, and although the ash constituents are eliminated more completely they take more regenerants to remove per unit of elimination.

Water requirements. The total water requirements for the ion exchange process is also a very important consideration. According to the Dorr Company⁷ the maximum water requirements for exchange purposes will be about 1,000 U.S. gallons per ton of cane, but as backwash and rinse water would be used for other purposes, the total overall water requirements are likely to be about 675 U.S. gallons per ton of cane, which means, if we convert to imperial gallons and assume a ton of cane to be 190 gallons mixed juice, that about 3.0 gallons of water will be used for every gallon of juice processed. The amount of water used for sweetening off is 0.25 gallon per gallon of juice treated. Dilution of the juice, which is of course unavoidable, does not necessarily mean extra fuel requirements, because evaporation will be more efficient as a result of far less scale formation; but the total water consumption does indeed appear to be a formidable obstacle at many factories. Then, too, the water must be of a high degree of purity, and especially the water used in the anion exchange beds must be soft. This will probably necessitate pre-treating the water in a softening plant.

Effluents. The possibility of recovering some of the more valuable impurities in cane juice or molasses,

CONCENTRATION OF ANION AND CATION EFFLUENTS AFTER REGENERATION



such as potash from the cation effluents, or aconitic acid from the anion effluent after regeneration, has been mentioned by other workers; but where sulphuric acid and ammonia are used as regenerants, the most obvious recovery is ammonium sulphate, which will, of course, include impurities, some of which, such as potash, may also be valuable as a fertilizer. The analyses of the salt obtained by concentrating an anion effluent neutralized with the cation effluent were as follows:—

Total ash	7.44 per cent.
Ammoniacal nitrogen	15.63 per cent. as N
Sulphate	37.25 per cent. as SO_3
Chloride	2.16 per cent. as Cl
Silica	0.02 per cent. as SiO_2
Iron and aluminium	trace as Fe_2O_3 and Al_2O_3
Calcium	0.43 per cent. as CaO
Magnesium	0.25 per cent. as MgO
Potassium	0.79 per cent. as K_2O
Phosphoric	0.09 per cent. as P_2O_5

The following analyses of cation and anion effluents after regeneration, and the precipitates obtained after partial concentration, were made by Messrs. African Explosives.

Sample of cation effluent after regeneration:—

Specific gravity	1.066 at 20°C.
Total sulphates	6.44 per cent. as SO_3
Total chlorides	0.79 per cent. as Cl
Free acid	5.64 per cent. as SO_3
Potassium	0.32 per cent. as K_2O
Sodium	0.51 per cent. as Na_2O
Calcium	0.11 per cent. as CaO
Magnesium	0.13 per cent. as MgO
Iron	less than 10 parts Fe per million
Silica	less than 25 parts SiO_2 per million

Total solids 2.97 per cent.

After partial concentration of another cation effluent a solid of the following composition was obtained:—

Moisture on sample as received	1.7 per cent.
Total sulphate	61.3 per cent. as SO_3
Free acid	26.3 per cent. as SO_3
Iron	0.64 per cent. as Fe_2O_3
Silica	0.01 per cent. as SiO_2
Potassium	2.54 per cent. as K_2O
Sodium	5.22 per cent. as Na_2O
Calcium	17.50 per cent. as CaO
Magnesium	1.45 per cent. as MgO
Chloride	0.14 per cent. as Cl

Sample of anion effluent after regeneration:—

Specific gravity	1.004 at 22°C.
Free ammonia	0.62 per cent. as NH_3
Combined ammonia	0.30 per cent. as NH_3
Total solids (on evaporation)...	1.47 per cent.
Total solids (on ignition) ...	0.015 per cent.
Chlorides	0.23 per cent. as Cl
Sulphate	0.30 per cent. as SO_3

It will be noted that the concentration of the valuable ingredients in the effluents is low, and that fuel demands for possible recovery of the salts will consequently be high. The graph illustrates the concentration of ammonia and sulphuric acid in the effluents during regeneration from the laboratory plant at Darnall.

It would appear that if recovery of ammonium sulphate were considered, only the richer ammonical fractions of the anion effluent should be treated with the requisite amount of cation effluent highest in sulphuric acid.

Another method that suggests itself is to run the anion effluent, after neutralization, into irrigation dams, and save the cost of crystallizing the salts. There will, however, always be an excess of sulphuric acid to be disposed of (because the excess sulphuric acid required for regenerating the cation bed is far greater than the excess ammonia necessary for regenerating the anion bed), and this constitutes another problem.

Molasses. With the small experimental ion exchange plant at Darnall it was not possible to work up the treated juice to a final molasses, and to measure the extra recovery obtainable. There can be no doubt that the increased purity of the juice will considerably enhance the recovery, but it is impossible to foretell the amount and degree of exhaustion of the final molasses. It has repeatedly been claimed that the molasses resulting from the ion exchange process is edible and will therefore find a ready market. Here further experimentation under South African conditions seems advisable. The unpalatable potash salts are largely eliminated in the process and some other tastes and odours characteristic of molasses are also removed, but then, of course, further concentration and sucrose crystallization becomes possible, the net result being again difficult to forecast. It would appear, however, that the inorganic salt content will be much lower in a molasses obtained from ion exchanged juice because more ash is eliminated than organic non-sugars and the invert sugar is increased. So that for the same purity of final molasses, the ion exchange molasses will be higher in reducing sugars and lower in ash/organic non-sugar ratio, which will, of course, make for a more valuable end product.

CONCLUDING REMARKS.

It is generally considered that if the ion exchange process is to become firmly established in sugar it will find application in the beet industry before being used in the cane industry. The obvious reason for this is the fact that an equal quantity of non-sugar carries away far more sucrose in a beet molasses than in a cane molasses and consequently, for the equal cost of eliminating a unit of non-sugars, a

greater additional recovery of sucrose will be obtained in beet.

The process is still in its infancy as far as its application to sugar is concerned, but it is capable of revolutionising the industry, and experiments are being carried out on a vast scale to prove that it is economical. In fact, commercial plants are in operation and the results should be followed closely. Our experiments may be of technical interest for the cane industry, but the economic aspect has not been attempted. Certain deductions can be made from the results obtained, but there are too many unknowns to try and arrive at a possible profit-and-loss account. It is most desirable that experimentation should be continued in this country, so as to be able to learn as much as possible about the possibilities of the process as applied to our own industry, and to study the many problems peculiar to us.

Acknowledgments.

The committee is indebted to the South African Sugar Association for purchasing the laboratory plant; to Sir J. L. Hulett & Sons for providing the necessary facilities at Darnall and allowing Mr. Dymond and other members of their staff to undertake the investigation. Thanks are also due to African Explosives & Industries, and Mr. W. O. Christianson of the S.A. Sugar Experiment Station for carrying out certain analytical work. The whole-hearted co-operation of the Durban representatives of the Dorr and American Cyanamid Companies is appreciated, and the assistance rendered by these American companies in answering many queries is acknowledged. We acknowledge with special thanks the untiring efforts of Mr. G. C. Dymond, who was in charge of the plant at Darnall, and of Messrs. Odendaal and other laboratory staff who did most of the analytical work at Darnall.

SUMMARY.

A brief outline of some theoretical aspects of the ion exchange process is given and the plant and operation at Darnall described.

Cane juice, clarified by the sulphitation and carbonation factory processes, was treated by the ion exchange process. Special tests were also done by treating juice clarified with lime only, with lime, sulphur dioxide and phosphoric acid, and with either sulphuric acid or sulphur dioxide only. Diluted molasses were also put through the ion exchange process.

Regeneration of the cation resin was always done by sulphuric acid and sodium chloride, but the anion resin was regenerated by either ammonium hydroxide, sodium hydroxide or sodium carbonate. The last named regenerant was not entirely satisfactory.

The amounts of regenerants required per unit of non-sugar elimination are calculated and analyses given of the effluents after regeneration. The possibility of recovering ammonium sulphate, where sulphuric acid and ammonia are used as regenerants, is discussed.

About 60 to 70 per cent. non-sugars were eliminated from cane juice in the process. The removal of ash constituents was about 90 to 95 per cent. The treated juice varied from colourless and clear to yellow and cloudy. A large proportion of colloidal silica in the juice passes through the exchangers and is partly responsible for the milky appearance of most of the treated juices. Analyses of some colloids are given.

Inversion losses were high, more than 1 per cent. on sucrose, as there were no facilities for cooling down the juices before treatment.

The process, although in its infancy as far as sugar is concerned, is potentially capable of revolutionising the industry, and further experimentation under South African conditions is advisable, while developments in other countries should be closely studied.

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Report prepared by J. L. du Toit (Hon. Technical Secretary) on behalf of the Ion Exchange Committee:

G. BOOTH (*Convener*).
G. C. DYMOND.
J. L. DU TOIT.
J. RAULT.

The PRESIDENT, opening the discussion, said that in this paper Mr. du Toit had gathered together all the information available to the Committee.

Dr. DODDS wished to know if any information had been gained confirming the use of the ion exchange process in other industries in South Africa. He had a letter from a baking powder manufacturing company which stated that they had found the process

exceedingly valuable for the purification of cream of tartar.

He was also very interested in the cloudy condition of cane juices after passing through the ion exchange unit and would like to know if any factory had experimented with Bentonite.

Mr. BOOTH said that as Mr. du Toit had pointed out in his excellent paper there were many unknowns and a knowledge of physical chemistry was necessary so that this demineralisation process could be understood.

The process was revolutionary and in his opinion its demands on clarification methods and its effects on the factory process, especially boiling and curing, put it in a category comparable with the development of the use of the centrifugal for molasses separation.

The PRESIDENT drew attention to the sudden change shown in the experiments from about 14° Brix to 20° Brix. He pointed out that the analyses of the effluents showed a change from calcium being lower than sodium or potassium to being higher than these elements in another analysis. He asked for further information on the absorption of hydrochloric acid rather than the hydrogen ion by the anion exchanger.

Mr. DU TOIT in reply, explained that the juices treated had a low Brix of about 13° and that the higher Brix figures of about 20° referred to molasses. Nothing would have been gained by diluting the molasses still further, to make the Brix comparable with that of the juices treated. The difference in purities meant that in the case of juices, the Brix would be made up to a larger extent of sucrose than in the case of the purified molasses, and therefore there was no real comparison.

As far as the use of ion exchange purification of cream of tartar was concerned, the process was rather different. In that case the cream of tartar would be absorbed by the resins and be recovered from the effluents after regeneration.

With regard to the query about the absorption of acids by the anion resin, he was unable to give definite information as to whether the ions were absorbed or the whole acid was absorbed to form an additive compound with the resin. The authorities seemed to be at variance on that particular point.

He understood some other industries, including the gold mining industry, had imported plant for water purification.

Mr. DYMOND pointed out that in the analyses of the effluents it should be noted that calcium was low in the effluent itself but high in the concentrated product, as more calcium salts than sodium salts were thrown out on concentration.

Mr. VAN WYK said that other industries had purchased water softening plants for boiler feed water and other products. He had seen an apparatus used in connection with a big boiler in Johannesburg. In this case water was allowed to flow over some arrangement which apparently removed the salts. This apparatus was, of course, patented.

The PRESIDENT thought the water purifying plant mentioned was probably of the type discussed in the paper by Mr. Hill on boiler water treatment. The resins used in the Ion Exchange process were patented, the cation resins many years ago, but the anion resin fairly recently. The Dorr Company and another company in America were working on these resins.

Mr. DYMOND asked for further information on Bentonite.

Dr. DODDS said Bentonite was a kind of Fullers' Earth which had gained quite a vogue on the American continent for many purposes.

Mr. DU TOIT found the behaviour of refinery molasses in the Ion Exchange process very interesting. It was only slightly purer than other molasses, but the break-through occurred much later and the non-sugar elimination was more complete. He thought that this was due to the higher reducing sugar ratio. In ordinary molasses this ratio was from 20 to 27 whereas in refinery molasses it was 42. This meant that there was a lower proportion of objectionable salts and consequently the ion exchange unit could deal with a larger quantity of product. One part of non-sugars carried away 0.92 to 0.95 parts of sucrose in a raw sugar factory but as much as 1.26 parts of sucrose in the refinery molasses. The elimination of one part of non-sugars in refinery molasses made 1.8 parts of total sugars available, which for syrup manufacture seemed an effective proposition.