

The Role of Nitrites in Promoting High Ash Values in White Sugar

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Introduction

During the 1958 campaign, a beet sugar factory very suddenly had abnormally high ash values in its white sugar on two occasions. These two incidents, each lasting for several days, were about three weeks apart. Values of up to 0.166% conductivity ash were experienced. At times, an ash content of 0.017% was followed with a 0.111% value one hour later. Although this example was the extreme, there was no consistency in the conductivity ash readings. Extra-careful spinning and additional washing did not remedy the situation. An investigation was initiated to trace the cause of the high ash and to find suitable methods to avoid the reoccurrence of abnormally high ash.

At about this time the research staff of the British Sugar Corporation published a series of *Studies in the Chemistry of Sulphitation* (1)². In their attempt to establish a sulfur balance, Carruthers and co-workers reported an intriguing reaction mechanism that involved sulphites and nitrites which together form an end-product that was the real cause of some of their high-ash sugar. This end-product was proven to be a potassium salt of imidodisulphonate. Other researchers had found this compound in factory products on previous occasions (2).

In other publications Carruthers and co-workers reported on the *Nitrate Reduction by Thermophilic Bacteria in Sugar Beet Diffusion Systems* and *Activity of Thermophilic Bacteria in Sugar Beet Diffusion Systems* (3, 4). They definitely established bacterial activity as being the cause of nitrites in factory juices.

Results and Conclusions

In reviewing the findings of Carruthers and co-workers, together with the findings of this laboratory, the following results of this investigation are outlined to clarify the general relationship of nitrites in factory juices and high ash values in white sugar.

1. Nitrites are not native to the sugar beet.
2. Nitrites can be produced through reduction of nitrates by thermophilic bacteria.

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² Numbers in parentheses refer to literature cited.

3. These thermophilic bacteria are soil borne and may flourish at relatively high temperatures at any place prior to sulphitation.
4. Nitrites so produced may react with bisulphites to form imidodisulphonate and sulfate.
5. Bisulphite is formed in significant quantities if the pH in the evaporation is below 8.0.
6. The dipotassium salt of the imidodisulphonate may co-crystallize with the sugar in the white pan if conditions favor its crystallization.
7. These conditions include:
 - a. When the pH of the white pans is relatively low, i.e., less than 8.0, the less soluble dipotassium salt $\text{HN}(\text{SO}_3\text{K})_2$ predominates. If the pH is well above 8.0, then the more soluble tripotassium salt $\text{KN}(\text{SO}_3\text{K})_2$ prevails, causing the larger part of the imidodisulphonate to stay in solution and pass out into the molasses.
 - b. The concentration of the imidodisulphonate has to be sufficiently high for co-crystallization.

The presence of imidodisulphonate was proven after this compound was isolated from high-ash sugar and identified according to the procedures of Carruthers and co-workers.

Table I shows the actual composition of an ash constituent isolated from high-ash sugar. The calculated value of theoretically pure di-potassium-imidodisulphonate and values obtained from di-potassium-imidodisulphonate prepared by synthesis are added for comparison.

Table I.—Analysis of Ash Constituent from High-Ash Sugar.

	$\text{HN}(\text{SO}_3\text{K})_2$ Calc.	Isolated from Sugar	Synthetic Salt
% Sulfated Ash	68.79	71.09	67.77
% Potassium	30.87	31.60	30.27
% Sulphur	25.32	25.25	25.33
% Nitrogen	5.53	5.72	6.00

Dividing the percent element in Table I by their respective atomic weights will yield the factor expressing the atomic ratio for this compound, in this case—1 Nitrogen, 2 Potassium, and 2 Sulphur, which corresponds with di-potassium-imidodisulphonate. Although the molecular weight of the isolated ash constituent was not determined, the typical appearance of the $\text{HN}(\text{SO}_3\text{K})_2$ crystal could not be disputed. The isolated ash constituent was purified by 3 times recrystallization in isopropanol.

Table 2.—Typical Daily Composites of High Ash Sugar.

	1-12	1-13	1-14	1-15	1-16	1-17	1-18
% Conductivity Ash	.008	.033	.027	.035	.021	.011	.007
% Sulfated Ash		.052	.036	.057			
% K in Sugar	.0028	.0122	.0102	.0136	.008	.0043	.0023
% S in Sugar		.0099	.0074	.0112	.0056		
% N in Sugar		.0061	.0056	.0082	.0028		

In Table 2 the actual presence of various elements in daily composites of high-ash sugar is shown.

A superficial examination of the values in Table 2 does not reveal exact stoichiometric ratios that one might expect if $\text{HN}(\text{SO}_3\text{K})_2$ is the only ash constituent. However, the potassium sulfur ratio corresponds very closely to the ratio of pure $\text{HN}(\text{SO}_3\text{K})_2$. The ratio of these two elements to the conductivity ash is slightly increased in favor of the conductivity ash. This shift must be expected. The nitrogen values are too high to account for the imidodisulphonate only. Apparently the ash contains proportionally more nitrogen with increasing ash content. Two possible explanations for the high ratios between the gravimetric ash value and the conductivity ash value are suggested:

1. The C-Ratio for conductivity ash calculation is not specific for these particular ash constituents.
2. An abnormal increase of non-ionized ash constituents which are not subject to conductometric determinations are evidently present.

By this time there was a high degree of certainty that the reaction mechanism as outlined by Carruthers and co-workers (1) was the principal cause of the high-ash sugar. Factory liquors were also analyzed for the compounds involved in this reaction.

Table 3 shows the amount of nitrite nitrogen in parts per million on dry substance in factory liquors when analyzed at the time of sampling.

The low nitrite values for station 1, 2 and 3 of Factory 1 indicate low levels of bacterial infection. The contamination begins at station 4 and spreads through station 5 for Factory 1. The reduction in nitrite content between stations 5 and 6 was rather large while the pH was low. This nitrite loss is an indication of the magnitude of the imidodisulphonate formation. The nitrite level remained about the same for the 2 p.m. and 4 p.m. readings for stations 1 through 5 of Factory 1. However,

Table 3.—P.P.M. Nitrite Nitrogen in Factory Juices.

Station		1	2	3	4	5	6	7	8	
Day	Time	Diff. Juice	1st Carb.	1st Press	2nd Press	Thin Juice	Thick Juice	Std. Liquor	High Green	
Factory 1 ¹										
1	4 p.m.	3.3	4			91	19	5	
1	5 p.m.	3.6	4		96	29	5		
2	8 a.m.									Low
2	9 a.m.	3.2	5.3	50	105	24	8	3	pH
2	10 a.m.	3.5	5.5	75	116	28	3	4	
2	2 p.m.	2.2	5.3	42	108	61	17	28	
2	4 p.m.	3.6	3.9	60	121	70	25	33	Higher
3	8 a.m.							5	pH
3	9 a.m.	1.7	1.1	9	38	7	4	4	
Factory 2 ²										
1	2-3 p.m.	54.9		38.2	38	28	10	3	13	

¹ Factory 1 produced sugar with high ash.

² Factory 2 produced normal ash.

the decrease in nitrite between stations 5 and 6 was somewhat inhibited at higher pH's of the factory juices. The effect was not immediately seen in a low-ash sugar since large amounts of the imidodisulphonate were continually re-introduced from the raw side. In addition to that, there was still enough nitrite reacting to form excessive amounts of imidodisulphonate, but the ash in sugar was on the decline. The 9 a.m. reading on the third day reflects the measures to clean up the bacterial infection between the stations 4 and 5.

Factory 2 shows extensive activity of thermophilic bacteria at station 1. The nitrite level at station 5 is however within safe limits and the formation of imidodisulphonate is furthermore inhibited by relatively high pH of the factory juices.

The samples were taken from all stations at about the same time. Exact stoichiometric changes from station to station can not be expected for obvious reasons, but the general trend is definitely established.

Examination of the data requires a factory flow sheet to discover the head of bacterial infection. The sequence of the various stations at the beet end for this particular factory is in the following order:

- | | |
|------------------------------------|----------------------------------|
| A. Continuous Diffuser | F. Second Carbonation |
| B. Raw Juice Heater | G. Juice Boiler |
| C. Continuous First
Carbonation | H. Second Press |
| D. Dorr Thickener | I. Sulphitation of Thin
Juice |
| E. First Press | |

During the period of January 11 to January 18, 75 gallons of formaldehyde was added to the juice boiler to stop the bacterial infection there. The head of bacterial infection for the first high-ash period was not established. For the second period, when on the spot tests were conducted, the bacteria did survive all treatments through second carbonation to be reactivated in the juice boiler.

The unfortunate circumstance of using the juice boiler as a holding tank to adjust the flow without sufficient heating made this condition possible. As soon as proper corrections were made on the beet end, the quality of the sugar returned to normal.

Usually most of the bacterial activity is localized in the diffuser according to Carruthers and co-workers. These researchers report a close relationship between nitrate reduction, lactic acid production, and inversion in the diffuser. In fact, it is suggested that these processes are inter-related and caused by the same thermophilic bacteria (3, 4).

Temperature conditions in the beet end were investigated, but no deviation from normal could be observed.

In order to further follow the nitrite-sulfite reaction mechanism, composite samples of diffusion juice, first and second carbonation filtrates, thin juice, thick juice, standard liquor, and high green were collected at two factories. Three collections were made at one factory when the ash in white sugar was high, although not consistently high. Two collections were made at about the same time at another factory with low or normal ash values in white sugar. It is realized that these few samplings can not reveal the full complexity of the relationship between the interacting chemicals, factory conditions such as temperature, pH, bacterial infection, disinfection, etc. However, it is believed that a certain trend is indicated. The analysis consisted of the determination of nitrate nitrogen, nitrite nitrogen, and sulfate sulfur on diffusion juice, first and second carbonation filtrates. These analyses, plus surfite sulfur and imidodisulphonate sulfur, were made on all other factory products.

Table 4 is a typical comparison between Factory 1 which experienced high ash and Factory 2 producing sugar of normal ash content.

Table 4.—Analytical Comparison of Juices from Two Factories

	Diff. Juice	1st Press	2nd Press	Thin Juice	Thick Juice	Std. Liquor	High Green	
Nitrate—N	339	329	309	192	242	181	220	Factory 1
Nitrate—N	284		328	243	254	198	306	Factory 2
Nitrite—N	4	5	103	121	54	19	20	Factory 1
Nitrite—N	62		36	73	20	13	11	Factory 2
Sulfite—S	220	183	261	251	Factory 1
Sulfite—S	474	438	252	299	Factory 2
Sulfate—S	268	260	404	467	302	535	Factory 1
Sulfate—S	413		236	314	313	249	361	Factory 2
Imido-	167	561	2064	2418	Factory 1
disulf—S	121	189	127	213	Factory 2

Units: ppm on D.S.

In Table 4, the twenty-four hour composite of sugar at Factory 1 had a conductivity ash of 0.035%, with highs of 0.111% at 12 a.m. and 0.113% at 4 p.m. and a low 0.010% at 7 p.m.

It is surprising to find a significant amount of imidodisulphonate in thin juice. The conditions in the thin juice beaters are apparently sufficient to cause the formation of imidodisulphonate. The decrease in nitrite and sulfite and increase in sulfate and imidodisulphonate between thin and thick juice underlines the reaction mechanism as outlined previously. The enormous amount of imidodisulphonate amounting to about 1% on D.S. in Standard Liquor and High Green supports the reaction mechanism. Again, as in Table 3, the locality of nitrite formation is concentrated for Factory 1 somewhere between 1st presses and sulfur tower. Factory 2, although producing sugar with normal ash, shows again significant bacterial activity in the diffuser.

Relatively high levels of nitrite are not solely responsible for high ash sugar. The alkalinity in the evaporators has undoubtedly an effect on the kinetics of the nitrite-sulphite reaction. The average pH of thick juice for the high-ash period did not deviate from normal. However, during the first days of each high-ash period, the pH was lower than the average. Figure 1 shows the daily average pH trends of factory juices for one high-ash period.

These figures bear out the fact that the pH of thick juice was low enough to promote the formation of imidodisulphonate especially during the first days of each high-ash period. The relatively high pH level during the last part of this period undoubtedly help in overcoming the ash problem.

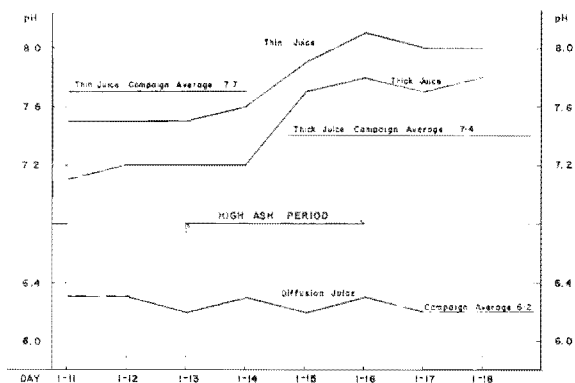


Figure 1.—Daily pH averages of factory juices.

In comparing the values of Figure 1, it is clearly shown that the pH of diffusion juice showed a very healthy level and makes a good showing when compared against the campaign average. The level is steady and not subject to fluctuation. Even the hourly readings did not deviate excessively from the average. The pH of thin and thick juice is shown to vary to a marked degree. Both curves run nearly parallel and start below campaign average at the beginning of the high-ash period. The rise of the pH during the high-ash period reflects the results of measures taken by operators to retard the sulphite-nitrite-imidodisulphonate reaction.

Both bisulphite and sulphite are present in factory juices after sulphitation. A pH of about 8 favors the sulphite but as the pH drops to 7 or less, the equilibrium is shifted in favor of bisulphite. Carruthers has shown that in the presence of nitrite the rate of imidodisulphonate formation is in the order of 1 to 72 as the pH drops from 7.7 to 6.3. It is obvious that unless a reasonably high pH is maintained through the white pans, the disulphonate formation can be serious if nitrites are present in the juice. Furthermore, each equivalent of nitrite nitrogen ties up three equivalents of sulfur, which means a loss of sulfur to the process.

However, the daily pH average may be grossly misleading in the face of highly fluctuating pH. Figure 2 shows the scope of the not-at-all-rare pH fluctuation in thick juice. Even though the average daily pH in thick juice may be as high as 7.8 or 8, there may be times when the pH will be less than 7.0. Fluctuations such as this should not be normal. Uniform operation and control of variables will do much toward the prevention of conditions conducive to high ash in sugar. What effect the bacterial

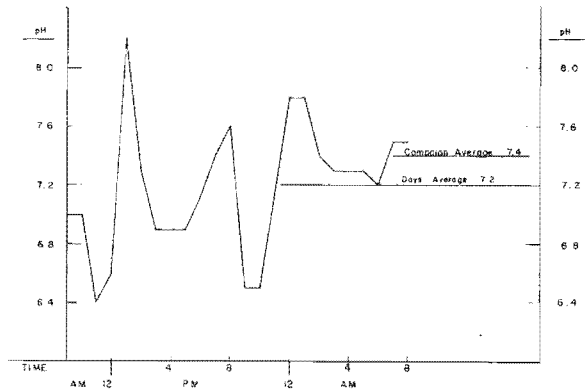


Figure 2.—Fluctuation of thick juice pH.

activity after second carbonation had on the fluctuating pH is subject to speculation. The extreme pH fluctuations may have been induced by the activity of thermophilic bacteria.

Figure 3 shows the typical relationship of white pan pH and white-sugar ash. The true picture is obscured by at least the following variables:

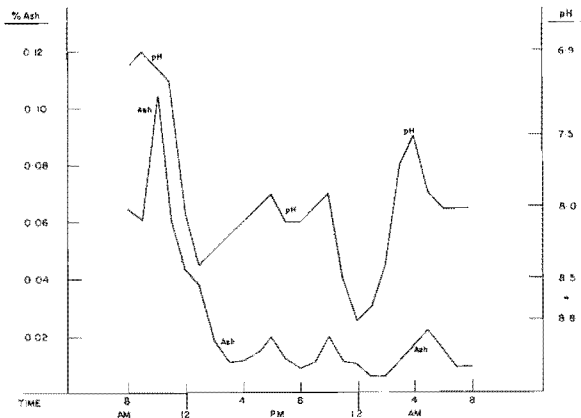


Figure 3.—Relationship between white fillmass pH and white-sugar ash.

1. The pH is taken directly from the fillmass prior to dropping the pan while the ash in the sugar is taken on an hourly basis on material in the mixture causing a carry-over from previous pans.
2. BaCl_2 was added to relieve the high-ash problem. This may indeed lower the conductivity ash, but may result in a higher gravimetric ash value.

3. Concentration of the imidodisulphonate in standard liquor will dictate the degree of its co-crystallization in the white pan.

Even though these variables may cause a slight shift in the true relationship of fillmass pH and sugar ash, Figure 3, nevertheless, represents some interesting relationships.

1. The negative correlation between fillmass pH and ash control of white sugar is very apparent.
2. The probability of producing unacceptable high-ash sugar is at least quite high if pH of the fillmass is kept below 8 in the presence of large amounts of imidodisulphonate.
3. White fillmass pH above 8 may greatly suppress ash in sugar but may not completely eliminate this problem in the presence of large amounts of imidodisulphonates.
4. A surprising point of Figure 3 is the human element. All the statistical material investigated established the fact that the second shift produced sugar with the lowest ash. They accomplished this by keeping the pH higher throughout the entire system.

Fortunately, it is only on rare occasions that a problem such as has been discussed develops. In any event, the margin of safety is increased by carrying the pH of juices and liquors at levels over 7.5 after sulfitation. By doing this, even if nitrites are present, the disulfonate formation is retarded because of a lesser amount of bisulfite, and if it is formed, the higher pH favors the formation of more soluble tri-potassium salt.

Summary

In summarizing the findings of this investigation, the following points are outstanding:

1. Sufficient bacterial control must be exercised on the beet end to keep the nitrite level low. This can be achieved by:
 - a. Adequate high temperature. Not below 75° C. in the diffuser and not below 80° C. beyond the raw juice heaters to sulphitation.
 - b. Extended storage of beet end juice prior to sulphitation at temperatures below 75° C. must be avoided.
 - c. Proper usage of formaldehyde or other disinfectant.
2. If nitrites do occur at excessive levels, the pH of the evaporators should be kept above 7.7 to suppress the formation of imidodisulphonate. In addition to that, the pH of the white pan must be kept above 8 to curtail the co-crystallization of the dipotassium imidodisulphonate which might have formed in the evaporators. The pH of

intermediate and raw pans must likewise be kept high to discard the imidodisulphonate into the molasses.

To what extent other methods of bacterial and factory operations are involved remain to be investigated. Among these could be listed:

1. Chlorination of the beet wash water (Partially investigated by Carruthers) (4).
2. Degree of beet deterioration.
3. Locality of beet growing area and storage conditions are reported by Schneider and Hoffman-Walbeck (5) to be factors influencing bacterial activity in beets.

In any case, the most effective control of problems like this is in its prevention, not in its cure.

The objective of any factory operation should be the complete elimination of nitrite formation. One ounce of prevention is surely worth ten pounds of cure in this case.

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