

Round-Table Discussion of "Lime Salts"

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Summary of Preliminary Remarks

A. Introduction

The purification of sugar-beet juices by the use of lime dates back to the early part of the nineteenth century, and the corollary use of carbon dioxide to only slightly later. In spite of repeated challenges—many hundreds of substances have been proposed for this use—this is still the standard method: the consequence of its strong advantages of effectiveness, cheapness and convenience. Its most important disadvantage is "lime salts."

This is an attempt to summarize the classical view of lime salts, and to point out problems and anomalies. In its preparation we have leaned heavily on the published works of Prof. J. Dedek, whose paper given before this Society in 1948 is the great classic in this field (1)².

B. Definition

Lime salts are soluble calcium salts which carry through to the sugar end of the factory. The plurality of the term must be kept in mind, to avoid the seemingly inexplicable.

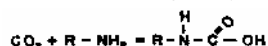
C. Harmful Effects of Lime Salts

1. Scale formation in heaters and evaporators.
2. Retarded juice boiling in evaporators and vacuum pans.
3. Increase in molasses produced.
4. Lowering of white sugar quality through:
 - a. hygroscopicity of ash
 - b. turbidity of sugar solutions.

D. Nature and Source of Lime Salts

1. From Healthy Beets.

These lime salts are not susceptible to control by the factory operator. Most of the substances listed are probably present in the beets as potassium or sodium salts. Among (a) aliphatic acids is found chiefly malic acid. (b) Amino acids are represented chiefly by glutamic, aspartic, and pyrroli-done carboxylic acids. These acids form calcium complexes, of the type CaAn^+ , and will compound with carbon dioxide as carbaminates, which, in turn, may slowly change to carbonates. (c) Betainates may be created, as well as (d) proteinates. The latter are surface active and generally unionized.



2. From Fermentations.

A considerable degree of control can be had over lime salts from this source. These lime salts represent double damage, since their formation

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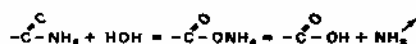
² Numbers in parentheses refer to literature cited.

usually involves destruction of sugar. The fermentations may occur in
 (a) stored beets, as a result of enzymatic or micro-biological action, and
 (b) in dilute factory juices such as raw juice. The products of fermentation are generally acidic in the earlier stages, and are represented chiefly by lactic and acetic acids.

3. From "Unavoidable" Destruction Reactions.

These occur as a result of the conditions in liming-carbonation, such as alkalinities and lime concentrations, high temperatures, and prolonged time intervals. (a) There is always some slight inversion of sucrose, and under certain conditions this may be appreciable. Chemical destruction of invert occurs to some extent in raw juice, and is virtually completed during first carbonation. The actual course of this degradation is very complex, due to the complex chemical environment. It is important to observe that lactic acid is one of the chief products. Most of the products are acids with soluble lime salts, and many are colored.

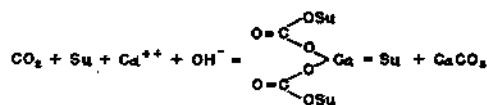
(c) The saponification of amides has traditionally been considered the most important source of lime salts. The amides in beet juices are mainly glutamine and asparagine. The saponification yields acids, plus ammonium ion or ammonia, depending upon the ambient pH. The reason for the importance of this type of reaction is that it has been attributed the chief responsibility for:



1. The differences in lime salts content from different types of beets.
 2. Thermolabile and thermostable juices.
 3. Differences in juices which make "vigorous" or "mild" de-fecation processes appropriate.
 4. Decrease in pH in the sugar end. The belief has been current that the amide content of beets is subject to some control through fertilization and irrigation practices.
- (d) A fourth source is the occasional degradation of pectin. Some of the smaller galacturonic acid units have soluble lime salts.

4. From Process Reagents, other than Lime.

Carbon dioxide in alkaline solution can combine with sucrose and lime to form alkyl carbonates, which may in time release the sucrose with formation of calcium carbonate. In addition, carbon dioxide takes a part in the formation of carbaminates, as already described.



Sulfur dioxide, when added in large enough quantities, may form appreciable quantities of calcium sulfate, which is somewhat less soluble than the sulfite, and may take an unpleasant part in evaporator scale.

D. Problems and Anomalies

1. Variation with Geographical Region

Mr. Weitz of the American Crystal Sugar Co. submitted data illustrating this effect. At the Oxnard factory, lime salts must be kept under 0.060 per-cent CaO on dry substance, otherwise the evaporators scale so rapidly that operations cannot continue. In spite of many efforts at reduction, it is here found necessary to use soda ash, sometimes up to 5 lbs./ton of beets. At their Clarksburg factory, lime salts are normally in the region 0.060-0.080 percent, but this figure has gone as high as 1.000 percent while working deteriorated piled beets, without shutting down the factory. At Missoula, lime salts above 0.030 percent make the juices so slow boiling that operation is restricted; heavy scaling is absent. At Mason City, 0.100-0.125 percent is normal for lime salts, with no particular difficulty.

Mr. Rorabaugh of the Holly Sugar Corporation contributed data on their Californi and Rocky Mountain plants, summarized below.

Table 1.—Lime Salts, Holly Sugar Corp. Factories.

	1952	1951	1950	1949
Rocky Mountain Plants	.046	.045	.037	.041
California Plants	.159	.110	.107	.116

Data obtained through interchange between sugar manufacturers in 1949 was classified, and a summary follows.

Table 2.—Summary.

Region	pH Change				Soda Ash
	L. S.	Evaps.	Evaps. to raw fl.	Beet apt	
Midwest	.087	+1	—7	86.5	.31
Rocky Mt.	.043	+5	0	87.1	.34
West Slope	.047	0	0	86.5	.48
Pacific	.107	—4	—8	84.8	.65

Differences such as are shown by the data described cannot be understood unless the plural number of "lime salts" is kept in mind.

2. Use of Soda Ash.

The normal method of reducing lime salts in thin juices is by addition of soda ash. There are a number of apparent anomalies in connection with its use, which can be explained by application of simple physical chemistry. By reference to a phase diagram (Figure 1 of reference (1)), it was shown why:

- (a) Soda ash can never precipitate equivalent quantities of lime salts.
- (b) Different degrees of deliming may be obtained in juices having the same lime salts contents.

(c) Two similar juices, differing only in amounts of lime salts, will show different degrees of deliming with the same soda ash addition.

Through reference to Figure 2 of the same work, it was shown why:

(d) The addition of soda ash sometimes increases instead of decreases scaling.

By the use of Figure 3 it was shown why:

(e) Either an increase or decrease of pH on concentration may be produced, depending whether there is an excess of calcium ion or carbonate ion in the juices. This effect does not involve amides.

MR. ALLAN WOODS, Union Sugar Co.

At Betteravia we have not been particularly successful in the addition of soda ash to our juices. Our lime salts are not reduced—in fact, we even notice an increase at times. We are wondering if this could come from the fact that we carbonate at higher alkalinity than most factories, thereby re-duc-ing the solubility products of the lime salts.

DR. MCGINNIS

General considerations might lead one to believe that if fewer non sugars of a type are present, the solubility products might more closely resemble those in pure water, but any such conclusions would certainly be tenuous.

MR. BLANKENBACH

We like to use soda ash sometimes when we have high lime salts, but frankly speaking, we never have good results. Lime salts always increase when we add soda ash. We are wondering what we are doing that is dif-ferent from other factories.

MR. WOODS

Our average alkalinity is about .090. We frequently run our alkalinity at 0.100, and with some beets we will go as high as 0.110 and 0.120.

DR. MCGINNIS

If we were able to operate at such alkalinities, we would not complain of lime salts.

MR. FRANK RAWLINGS, Amalgamated Sugar Co.

Hugh Rounds has never found any exceptions to the effective alkalinity concept. This concept offers, first, a rational concept for adding soda ash to a given control outlet. Secondly, it shows the proper second car-bonation alkalinity control point for minimum lime salts, which is very sharply defined. Tf soda ash is not added without this full concept in mind, the effect of its addition can be nullified. Even one or two hundredths deviation in second carbonation alkalinity can increase the lime salts 50 to 100 percent.

DR. MCGINNIS

May I ask Dr. Lucille Hac, of Internationals Minerals and Chemical Corp., to say a few words about organic nitrogen?

DR. HAC

As you know, we produce Ac'cent (monosodium glutamate) from the glutamic acid (GA) present in Steffen's filtrate. I do not believe our material can be responsible for the aforementioned pH drop across the evaporators. Our studies over a period of several years indicate that the potential source of GA in the beet root, itself, is glutamine. In diffusion juice there is roughly 10 percent free GA, 1 to 2 percent pyrrolidone carboxylic acid (PCA) and the remainder (88 percent) glutamine. Glutamine is a very unstable substance. Acid, alkali, or heat readily convert it, by the elimination of ammonia, into the stable ring compound, PCA.

Essentially all of the glutamine in diffusion juice is usually converted to PCA during carbonation and it continues as PCA throughout the sugar process to the Steffen's heaters. At this point, some hydrolysis of PCA to GA does occur; here roughly 30 percent is present as GA and 70 percent as PCA.

Obviously, if the ratios of both PCA and GA to sugar remain constant in thin juice, thick juice, and molasses, it is unlikely that our material can be blamed for the pH drop across the evaporators.

DR. MCGINNIS

Do these materials go through to the sugar end as lime salts?

DR. HAC

Yes, very probably both GA and PCA are a part of the constituents making up lime salts, but there certainly must be several other substances also. Do you always get all four of the deleterious effects of high lime salts which you pointed out, or do you sometimes have only one or two of the effects?

Could removal of calcium ions from solution; i.e., further precipitation during the evaporation (in the scale or elsewhere) account for the pH drop? Do you find calcium phosphate in the scale? If evaporation causes the precipitation of calcium salts or organic phosphates or other weakly acidic substances, a drop in pH would occur due to the removal of the calcium ions from solution. We have observed such increases in acidity accompanying slow precipitation in the barium hydrolysates of beets and factory juices used for GA determinations.

DR. MCGINNIS

Pacific Coast factories show the greatest pH drop across the evaporators. How do Pacific Coast beets compare with those from other regions in GA content?

DR. HAC

There are wide differences in the GA content of beets grown on the Pacific Coast as well as in other parts of the country. The beets in the Clarksburg, California, area are much higher in GA content than those in the Woodland area, and the high GA content of beets in the Mason City, Iowa, region is well known. You have pointed out that lime salts are a

greater problem at the Woodland factory than at either of the factories with higher GA. On that basis, also, I should assume that GA is not the cause of your troubles.

DR. MCGINNIS

You are correct, of course, in stating that all the adverse effects of lime salts do not occur together. If your thesis is correct, that amides are not responsible for the pH drop, a careful study of the situation is justified. There may be something that can be done to eliminate it.

I would like to make the statement, supplementing Mr. Rawlings' re-marks, that we do not use the effective alkalinity concept at the Spreckels factories; in the first place, because our effective alkalinity is too low, and too much soda ash would be required to raise the alkalinity to the optimum point. Secondly, we frequently cannot operate at the optimum second carbonation alkalinity because the pH drop across the sugar end would result in acid crystallizers.

DR. STARK, Western Regional Research Laboratory

I do not recall that there was much pH drop in the Washington factories. But our analyses of their molasses showed an extremely high amount of PCA as compared to the other coast factories, and so I think this should support Dr. Hac's contention.

DR. HARRY S. OWENS, Western Research Laboratory (by correspondence)

According to solubility product calculations there is as much as 1500 times as much Ca ion in thin juice as there should be. There must be a good physical reason or reasons for this. Because solubility of crystals increases with decreasing particle size, particularly near colloidal dimensions, sufficient time must be allowed to permit calcium carbonate crystals to grow to finite size. This source of excess lime salts would lead to scale formation in the evaporators. A second reason depends upon decreased activity of calcium ion because of amino acids, hydroxy acids, and perhaps sucrose. These compounds readily form complexes with calcium at alkaline pH values. If the pH drops during evaporation, this source of calcium could also cause scaling, depending upon the carbonate ion concentration. This second cause of lime salts might be eliminated by use of oxalic acid or sodium oxalate, rather than soda. This is something we may be able to try later on.

Literature Cited

- (1) DEDEK, J.
1948. Proc. Am. Soc. Sugar Beet Technol., 595.