Fundamentals of Beet Juice Carbonatation

Juice Purification in the beet sugar industry has been since 1970 mainly concentrated on two systems, the Classical Process and the Dorr Process and the use of chemical settling and flocculating aids has become general, as has the return of carbonation sludge to the prelimer or raw juice. Also is to observe a tendency to shut down small factories and increase the capacity of others (average factory capacity in Germany over 8.000 tons/day), to save in overhead costs.

Fundamental Operations
It is clear that there can be no reaction between lime and the nonsugars or between lime and carbonic acid unless the lime is first dissolved in the juice. When dissolved, the lime immediately start to react with the nonsugars present. Such reactions are of two types: 1) leading to the formation of precipitates, and 2) giving soluble products.

Thus, the first fundamental partial operation is the formation of insoluble products from nonsugars and lime. With normal juices from healthy beets, these reactions require only very small amounts of lime, of the order of 0.2-0.3% CaO on juice and this partial operation is thus called preliming or predefecation. Its aim is to precipitate as fully as possible all nonsugars able to form insoluble products with CaO.

The second partial operation includes those reactions between lime and nonsugars, which do not result in insoluble products. A reaction of this type is the destruction of invert sugar or the saponification of amides. These are all molecular, organic reactions, requiring appreciable time for their completion. Their velocity, completeness, and even the direction in which they proceed, are functions of the concentration of the lime in solution, and the temperature. They thus take place most fully in the completely limed hot juice.

This partial operation is called liming or defecation, and its chief function is in the destruction reactions. After the liming, when all the possible reactions between lime and nonsugar have taken place, the third fundamental operation is introduced, and it aims to precipitate with carbonic acid the excess of lime added to the juice. It has been found advisable to carry out this precipitation in at least two steps: first and second carbonation.

We therefore call this third operation the first carbonation. Its main purpose is to precipitate the excess of lime and to bring the alkalinity of the juice to a certain low value, of about 0.1% CaO.

The juice, which is normally separated from the precipitate first by thickening and later by filtration, is now further carbonated, not only to eliminate the balance of the lime left after first carbonation, but also to precipitate the Ca\(^+\) of the soluble lime salts in the form of calcium carbonate. This fourth operation is called second carbonation, and its primary aim is the final deliming of the juices.

These four fundamental operations are not always found distinct and clearly separated in the actual factory process. They very often take place simultaneously, or are partly suppressed, or even apparently do not take place at all. But in reality they are bound to occur.

Preliming
The precipitates produced in preliming can be divided into ionic and colloidal types. The first ionic reaction of lime is the neutralization of acidity. The other ionic reactions have been dealt with in the chemistry of acids giving insoluble lime salts.

Certain other reactions take place in preliming which do not start until there is a certain amount of lime in the juice. This second type of precipitation the so called colloidal reactions and involve the precipitation of protein substances, with the increasing alkalinization of juices.

There is a very distinct maximum for protein precipitation, (a), corresponding to a certain "optimum" alkalinity or pH (b) (see Figure).

When lime is added very slowly, a certain stabilization of the precipitates, when formed takes place, which makes it possible to add even a fair excess of lime without losing any of the coagulation already accomplished.

The fundamental condition is the slow and progressive increase of alkalinity or the so-called progressive liming of Dedek-Vasatko. The importance of this particular condition of progressive preliming was discovered by Brieghel-Muller and called stabilisation.

It now seems generally acknowledged that the effects of progressive preliming are very desirable. The colloids, such as proteins and pectins, are removed as a compact precipitate which settles rapidly and filters well.

In more recent methods progressive preliming has been further developed, not only by the stabilization of Brieghel-Muller, but also in the Wiklund process by the return of unfiltered first carbonation juice or thickened sluge to the prelimer. Here, the colloidal floc of the preliming is formed in the presence of a mineral skeleton of relatively high specific weight, which act in the capacity of seed, but also makes the precipitate heavier and less hydrated and so increases the velocity of sedimentation, besides enhancing agglomeration into large secondary particles.

**Liming**

The more important destruction reactions which may take place during liming are:

- saponification of amides such as glutamine and asparagine into the corresponding ammonium salts
- decomposition of glucose and fructose (invert sugar) into colored and acid products and
- formation of oxalic acid from the oxalogenic substances.

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Precipitation of protein beet juices. (Vasatko, 1933.)
A negative effect during liming is the general tendency, however, in the direction of a repertization of the precipitate (colloids such as **proteins** and **pectins**) already formed, and an increase in the degree of dispersion of long-chained molecules probably being split into shorter ones.

These destructions result in the formation of some acid products, which in the presence of lime must inevitably form lime salts. On the other hand, the use of large total amounts of lime will remove many of these lime salts by adsorption on the large calcium carbonate precipitate in first carbonation.

If it is desired to achieve the fullest effect of liming and to complete all the destruction reactions, as much as possible of the CaO must be put into solution in the juice, and it must act as fully as possible. In such a case, large quantities of lime must be added, such as 1.4 to 2.0% CaO.

Such a strongly alkaline juice must then be heated to a high temperature, such as 85 ° to 95 °C, and kept for 10 to 20 minutes before carbonation. This is what is termed an **energetic liming**.

The effect on color is, on the whole, very favorable. The resulting juices are "**thermostable**". They will stand further heating in the evaporators without alteration.

In contrast, a **mild liming** is one in which the destruction reactions are limited as far as possible. In this case, the slightly acid diffusion juice is heated and one of the methods of liming and first carbonation used in which the alkalinity is always maintained at a rather low value, such as when **liming and gassing are simultaneous, as in the Dorr system**. Specific local conditions determine which of these alternative methods is preferable.

### First Carbonation

The main purpose of this operation is to precipitate the excess of lime added during liming, or during the gassing itself, in the form of **calcium carbonate**.

The precipitated calcium carbonate is used in two different ways: namely, as a **reagent** for the further chemical purification of the juice, and as a **filter aid**.

These two uses make opposing demands on the physical quality of the precipitate formed. The chemical purification, which seems to be mostly due to adsorption, is favored by a **high surface area of the precipitated calcium carbonate**. On the other hand, small crystals are not compatible with sufficient velocities of sedimentation and easy filtration.

Any increase in the size of the calcium carbonate grains formed, which is equivalent to a smaller total precipitate surface, lowers the effect of chemical purification, but is, of course, favorable both for sedimentation and filtration.

The physical form of the calcium carbonate precipitate depends first on the initial alkalinity before gassing, or better, on the drop in alkalinity during gassing.

The greater this drop, and the more suddenly it takes place, the more rapidly is the precipitate formed, and the finer, its grain and thus the greater its total surface.

To obtain **coarse grained precipitates**, the first precaution is to avoid, as far as possible, high supersaturations of calcium carbonate. This means first of all a **low initial alkalinity**, for the incoming juices.

This low initial alkalinity can be best secured by using continuous carbonation with recycling several hundred percent of unfiltered first carbonation juices, which means diluting the limed juice with several volumes of a juice of much lower alkalinity or, finally, by liming and gassing simultaneously.

The recycling of unfiltered first carbonation juice involves also a "seeding" with preformed **CaCO3** particles, bringing into the limed juice a previously formed surface of CaCO3 on which it can easily crystallize, instead of forming small, new nuclei.
The second most important condition of first carbonation is its final alkalinity or pH.

Since the first carbonation sludges still contain particles of the colloidal matter precipitated during preliming, the final alkalinity of first carbonation should not be lower than the optimum value for preliming, to avoid redissolving again these particles, with resultant juice degradation.

It seems certain, that adsorption of nonsugars, in particular coloring matter, on the first carbonation sludge is favored by alkalinites slightly higher than the normal alkalinites of first carbonation (0.12 to 0.15% CaO).

Any lower alkalinity value due to overgassing, while the sludge is still in contact with the juice, involves freeing coloring matter passing back to the juice.

There are, of course, some beneficial effects from overgassing. Velocities of sedimentation and filtration are accelerated and sludge volume reduced. Such sludges do not normally contain any bound sugar, and are therefore easily sweetened off. Their greater porosity and lower resistance can, however, lead to a less efficient washing.

The finished first carbonation juice enters a tray clarifier or a filter thickener (reduced retention time) for sludge separation. Part of the thickened sludge is returned to the prelimer, but the greater part is filtered in rotary filters or nowadays processed with modern membrane filter presses.

The greatest change in the equilibrium between sludges and juice takes place at the moment of sweetening off. In the filters, juice is replaced by hot condensed waters, very often containing ammonia and carbonic acid. This is one of the reasons that the purity of the sweetwater is often so low, since quite appreciable amounts of nonsugars especially lime salts—are reptized. A further consequence of the softening of the cake particles is the loss of porosity, difficulting desweetening and therefore increasing cake sugar losses.

**Second Carbonation**

The chief aim of the **second carbonation** is the elimination by carbonic acid of all the lime which can be precipitated as calcium carbonate (elimination of calcium salts).

Each CaO molecule dissolving during liming in the form of Ca(OH)2 in the juice, yields not only its Ca= but also the corresponding number of OH- ions necessary for its precipitation by carbonic acid. Some of the Ca(OH)2, however, gives rise to the formation of soluble lime salts. The very important excess of OH- which is needed for the deliming of the Ca= of the soluble lime salts, having no corresponding OH-, is the "natural alkalinity" of KOH and NaOH formed through reactions giving insoluble lime salts. The greater this alkalinity, the more efficient is the deliming in second carbonation.

Actual conditions in second carbonation juices are, however, more complicated. Buffer substances present in the juice diminish the pH due to the natural alkalinity, and thus shift the HCO3-/CO3= equilibrium to give lower concentrations of CO3= and consequently a less efficient deliming.

It was therefore proposed to use the so-called **effective alkalinity** instead of the natural alkalinity as a measure of the possible deliming capacity of a given juice. Natural alkalinity if determined by titration to 8 pH, while effective alkalinity is determined by titration to pH 9.25, which is close to the usual optimum for second carbonation.

The very great influence of natural alkalinity is also the reason why it is so important to avoid unnecessary acid formation in the juices before second carbonation. Thus, acid-forming fermentations, such as those in the diffusion and the use of sulfur dioxide before second carbonation, should be carefully avoided.

The **minimum of lime salts in the finished juice**. This differs from the natural alkalinity, which ignores the
presence of bicarbonates and of buffering materials. The *optimum alkalinity*, depends on the particular chemical composition of juices and must be especially determinated.

If the natural alkalinity is not sufficient, an artificial one must be added if it is desired to delime the juices. The most popular agent is *soda ash* or recently *magnesium oxide* (MgO), which should be added latest at the beginning of second carbonation. The actual deliming is not completed, however, until all the CaCO3 formed has crystallized out.

**Sulfur Dioxide, Sulfurous Acid.**  
The use of sulfurous acid for juice purification in the beet-sugar industry is very old. It is a far stronger acid than H2CO3 and can consequently be employed for the neutralization of excess alkalinity in juices and syrups.  
Further, it is a well-known reducing agent, and can thus serve to decolorize juices, by reducing coloring substances to their leuco-bases.  
Still more important seems the preventive effect of even traces of SO2 or SO3= on many oxidations. This may explain the undisputably favorable effect of SO2 on evaporator thin juices. Calcium sulfate is definitely less soluble than calcium sulfite in sugar solutions and this transformation may, as a result, lead to deposits of calcium sulfate in the evaporators.

**Important Aims of Juice Purification**  
The chief aims of juice purification, from the mechanical point of view, are the formation of muds which are readily sedimented and filtered. They are relatively easily measured with the aid of laboratory sedimentation tests and measurements of filterability with a microfilter (Fk instrument).  
The chemical purification is aimed chiefly at forming juices which permit the production of a high quality white sugar, with a minimum loss of sugar in the molasses. It is not easy to determine this by chemical analysis.  
Due to low precision and doubtful interpretation of the analytical methods for the determination of purities and the calculation of the percent of nonsugars eliminated, lime salts and colors have become the most widely adopted criteria of the chemical effect of juice purification. They can be determined relatively easily, and with a high degree of precision. They are furthermore extremely sensitive to even small changes in the details of the juice purification procedure, and to differences in the chemical composition of the initial juices used.  
The perfected system is said to produce very thermostable juices, with good sludge settling (5 - 7 cm/min), mud volume ca. 18 % (25 min) and filtration properties (Fk< 2). The thin juices have low colors and lime salts, so the process is said to be relative insensitive to changing beet quality.

**General criteria for evaluation of a particular Juice Purification System**
- Elimination of nonsugars between raw juice and thick juice. Ø 35\%  
- Destruction invert sugar between raw juice and thick juice. > 90\% (Invert raw juice 0,60 g/100g ds)  
- Lime consumption. Ø 1,4 o.b.  
- Sugar losses in molasses. Ø 1,8 o.b.  
- Lime salts content in thin and thick juice. Ø 0,100 – 0,06 g/100g ds  
- Colour formation in thin and thick juice. Ø 350 – 450 Icumsa at 560 nm  
- Installed filter area (1.carbo juice, mud, 2.carbo juice and security). Ø 135 m²/1.000 tons beet  
- Energy consumption. Ø 5 kg heating steam/ 100 kg beets. (Evaporation heat 2.257 kJ/kg)
Sedimentation and Filtration. Sludges are required which are not easily mechanically deformed or compressible, and as little hydrated as possible. Such muds can be produced if the following conditions are observed:

1) The initial diffusion juice must not contain an unnecessarily large amount of colloids, especially pectins, which are introduced mostly through excessive heat or high pH in the diffuser, which dissolves the marc of the beet.

2) All useless high degrees of supersaturation of all substances which are precipitated during the liming and carbonation should carefully be avoided. This means a very slow increase of the alkalinity of the diffusion juice, as in Dedek-Vasatko preliming; low alkalinites during the whole juice purification, involving liming at high temperatures, recycling as in continuous carbonation, and liming and gassing simultaneously as in the Dorr process and high temperatures.

3) Graining during preliming, by recycling the thickened juice from clarifiers.

4) Over-carbonating and recycling to favor formation of agglomerated particles as by Wiklund's method.

5) Provide for ionic exchange of pectins and proteins into calcium-forms, using the stabilization principle of Brieghel-Müller.

Colors and Lime Salts. Low color and lime salts can be obtained frequently at the price of slower velocities of sedimentation and filtration. They are generally favored by:

1) A thorough progressive preliming

2) An energetic final liming, in which large quantities of lime are added to cold juice, heating to high temperature over relatively long periods.

3) A first carbonation precipitate of great adsorbing power, thus composed of small particles, and created through a high initial alkalinity in first carbonation and rapid carbonation.

4) High final alkalinity in first carbonation.

It should be emphasized that there are no generally valid rules which guarantee the best effects with every kind of juice. The details of the juice purification to be used must be adapted to the character of the juice to be treated. This is the most important duty of a good chemist in a sugar factory.

(Summary of references from R.A. McGinnis)

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