COMPARISON OF CARBONATATION AND PHOSPHATATION PROCESS FOR CLARIFICATION OF SUGAR SOLUTIONS.

A technical review to assist decision making over the appropriate Clarification Process for new Sugar Refineries.
Extracts from several specialized publications and edited by Leo Briones, Putsch Co., Feb. 2007.

Refining Processes

In recent years, it has been necessary for sugar factories to produce higher quality raw sugar for export and good quality refined or semi-refined white sugar for direct consumption. Consequently, clarification and decolorization processes used in sugar factories have had to be improved.

It is now almost universal for sugar refineries to use either Carbonatation or Phosphatation Process to clarify the melt liquor. These chemical processes, as well as removing the finely divided particles of insoluble and semi-colloidal matter, also eliminate significant amounts of color and other non-sucrose impurities which would otherwise have to be removed at greater expense in the subsequent decolorization or crystallization processes. Recent improvements to the traditional refining processes using new chemicals, techniques and equipment are described and discussed below.

Phosphatation/Flotation Process

Basically, the process consist of precipitating insoluble calcium phosphates of variable composition in hot melt liquor by first adding phosphoric acid, or an acid phosphate, followed by calcium hydroxide, either as slurry with water (milk of lime) or dissolved in sugar syrup as lime sucrate, to give a final pH of 7.2 – 7.4.

This treatment produces a calcium phosphate floc that is filtered with difficulty. Consequently, air flotation is commonly used to separate the precipitated solids from the liquor; such systems are called frothing clarifiers. During the flocculation and in the course of rising through the liquor, the floccules collect most of the fine suspended impurities in the solution. Impurities such as gums, waxes, fine are swept from the liquor and appear at the surface as scums. In this manner a rather complete separation of the precipitate and impurities is obtained without resorting to settling or filtration. The scums are then removed from the liquor surface by a skimming device.

One important modification to the Phosflotation process is the application of color precipitants, like Talofloc® or Colorgone® to refinery remelt liquors whereby anionic high molecular weight colour and other impurities are precipitated and subsequently removed as a flotation scum. Also the replacement of the conventional clarifiers type Jacobs or Williamson with modern, new circular design, high yield clarifiers has greatly improved the performance of the Phosflotation process.

Another advance is the extensive application of highly efficient polyacrylamide flocculants e.g. Taloflote®, which not only speeds up clarification, but also strengthens the floc against shearing forces mainly during the desweetening stage.

Color Removal

While phosphatation generally achieves a decoloration in the range of 25-30%, the addition of these color precipitant or cationic surfactants, increases the efficiency of color removal to a high level of about 70%.

Removal of insoluble solids

While particles of size under 200 micron are, as a rule, successfully enmeshed in the floccules and are removed in the process, insoluble solids such as bagacillo and fluff of over 200 micron have poor floatability characteristics. Consequently, if not separated by prescreening of the melter liquor, they are carried over with the clarified liquor, imparting to it a cloudy appearance. Furthermore, if present in sufficient quantity they seriously impede
liquor flow over the char, by forming a mat on the surface layer. Removal of 50-70% of solids present in the original melt is normally obtainable by the process.

**Secondary precipitation**
Formation of floc in phosphate-clarified liquor is usually referred to as the secondary precipitation. The occurrence of this floc has been reported by a number of observers. It, of course, creates problems in the processes subsequent to clarification. In a reasonably well-conducted flocculation process the residual P2O5 is well under 70 ppm and occurrence of secondary precipitation is not likely. But if something can happens, early or later will it happens.

**Removal of ash**
Removal of soluble inorganic constituent from melter liquor is one of the objectives of clarification. However, the level of removal obtained by any one of the three conventional methods of clarification is only marginal. Phosflotation, it has been reported by various writers, removes from nil to 20% of ash in the original liquor.

**Sucrose inversion**
Exposure of liquor to temperatures ranging from 85 to 99 °C, depending on the type of clarifier used, during the flotation period leads to inevitable inversion of sucrose. Most observers reported inversion of the order of 0.01%.

**Scums from phosphatation systems are generally sent to secondary clarifiers to reduce their sugar content. Two or three stage flotation separators, using polyacrylamide flocculating agents as mentioned, permit countercurrent desweetening, more or less without filtration equipment.**

Nevertheless refineries using modern Phosphatation/Flotation process still have to deal occasionally with some immanent drawbacks of the system, including high sugar losses, cloudy clarifier liquors and wet scums muds of difficult disposal. Most operators of the process admit having witnessed production of both excellent and poor liquors from a given installation.

With the notable exception of one or two refineries, conventional phosphatation-flotation is found in practice to be a sensitive process. Relatively minor changes can have a catastrophic effect on flotation characteristics, leading to the appearance of heavy carry-over in the clarified liquor. If flotation is incomplete, the liquor not only looks bad but is poor in quality and needs to be filtered before it becomes acceptable for the char or ion exchanger treatment.

The history of phosphatation for clarification of refinery liquors may be summarized as follows.

The advantages of phosphatation were recognized in the very early days of sugar refining, but it was slow to receive acceptance because of the difficulties of floc separation

The reasons for the interminable evaluatory debate may lie in the fundamental and inherent difference that exists between phosflotation and the two other processes carbonatation and diatomite filtration.

This difference is that flotation, unlike diatomite filtration or carbonation filtration, has no element of positive separation of the insoluble solids. In filtration of the liquor, if the liquor passes through filter cake, it is free of solids of a certain size or it does not pass through.

In flotation the liquor passes through a clarifier irrespective of whether complete or nil separation of coagulum is obtained.

**Carbonatation Process**
Refinery carbonatation has been used for over 100 years for the refining of raw sugar. It is a cheap and robust process. The process consists of adding a slurry of calcium hydroxide in water to the raw melt solution. Then carbon dioxide gas is bubbled into the sugar solution in saturators, under controlled conditions of pH and temperature. Generally the carbon dioxide is added to the saturators in two stages, with the major part of the gassing carried out in the first saturator. The impurities are both absorbed by, and enmeshed in, the conglomerated
particles of the calcium carbonate precipitated by the reaction of the carbon dioxide and calcium hydroxide.

New significant developments for the carbonanatation process, patented by Putsch Co. in the last years, has brought the carbonation, as the process of choice for updating existing installation or for new refineries. Namely the introduction of Richter Tubes as efficient gas distributors for carbonation vessels and the utilization of modern Membrane Filterpresses for single stage filtration of carbonated syrup has given the conventional carbonatation process an impulse to higher performance level.

The ease of separation of impurity from carbonated liquor in refinery practice is determined by the filtrability of the precipitated CaCO3. Provided the design and operating conditions of the saturators follow well-known principles of crystallization processes, the carbonatation system is relatively insensitive to minor variations.

It is considerably more dependent on the quantity of lime precipitated in the liquor. For every liquor there is a particular lime dose at which the filtrability will be greatest. The optimum lime dose varies from below 0.4 % CaO on solids in some liquors to over 1.2 % CaO in others. Approximately 30 times more lime is precipitated as carbonate during carbonatation than as phosphate during phosphatation.

Separation of the clear liquor and the calcium carbonate is done by pressure filtration. This filtration required expensive two-stage filtration plant for the separation and desweetening of the calcium carbonate precipitate. Nowadays single stage filtration is state-of-the-art.

A significant portion of the calcium carbonate cake is required to act as a filter aid and growth of a suitable filtering carbonate cake is as important as colour removal. One of the main objectives of carbonatation is the removal of the impurities present in the raw sugar entering the refinery. These impurities will have negative effects on some of the unit operations in the refinery.

Firstly certain impurities will have a profound effect upon the nucleation and growth process involved in the formation of the calcium carbonate conglomerate. As a consequence such impurities will impact upon the filtration processes in the refinery.

Secondly the presence of another impurities will adversely affect the sugar crystallisation process and lastly refined sugar quality will be influenced by this impurities.

Praxis have shown that carbonatation is very effective in the in the removal of the following impurities:

| Results of impurity removal from melt during carbonatation (1,10 % CaO addition on Brix) |
|---------------------------------|------------------|
| Colour                          | 55%              |
| Turbidity                       | 90%              |
| Starch                          | 93%              |
| Gums                            | 29%              |
| Sulphates                       | 86%              |
| Phosphates                      | 100%             |
| Magnesium                       | 67%              |

The following comments can be made regarding the results in the above Table:

- About 55% of the colour is removed
- Most of the turbidity (90%), starch (93%), sulphates (86%) and phosphates (100%) are removed.
- A small amount of the gums is removed.
- A high proportion of magnesium is also removed.
In addition, it has been shown that during carbonatation glucose, fructose and aconitic acid, if not precautions are taken, can be easily destroyed with increase in lactic acid and higher molasse losses. Basically reducing the contact time of raw melt with lime at high temperature, noticeably reduces the invert sugar destruction.

It has also been shown that carbonatation removed floc-forming impurities and it has generally been accepted that carbonatation refineries produce floc-free refined sugar. The two main components responsible for formation of floc are proteins and polysaccharides, known as floc precursors, which are removed by carbonatation. In addition it is confirmed that colour removal during carbonatation is a function of the melt colour, amount of lime added and the final pH.

**Comparative quality**

Being concerned with the problems of attaining maximum clarification at optimum costs, technologists inevitably ask which one of three processes of melt clarification - diatomite filtration, phosflotation or carbonatation - provides the best answer. This question arises in planning a new refinery or when the existing process becomes unacceptable either for technological or economic considerations.

A complete answer to this question can only be obtained by going thorough a close economic analysis of the alternatives involving such factors as cost of capital, labour, materials used in the alternative processes, level of education of the available labour, size of the plant etc. In the present context we can consider only the technical effectiveness of the respective processes. *Even though this appears to be a simple question it is not easily answered.*

There have been changes from one process to another since the 1950’s. Changes took place from diatomite filtration either to phosflotation or carbonatation. There were also changes from phosflotation to carbonatation. Of the newly built refineries the smaller sizes adopted, as a rule, phosflotation, while the larger ones preferred carbonatation.