Ultrasonic and Magneto Kinetics of Crystallization of Sucrose

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Department of Applied Chemistry

I, **dedicate** the present Thesis to the **almighty** the master of everything in our cosmos. My very esteemed obeisance goes to the nearest living symbols as God replicas in form of my beloved **Parents** and **Teachers**

DECLARATION

I hereby declare that the thesis entitled **"Ultrasonic and Magneto Kinetics of Crystallization of Sucrose"** has been prepared by me under the supervision of Prof. Kaman Singh, Head/Dean, Department of Applied Chemistry, School for Physical Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow. No part of the thesis has formed the basis for the award of any degree, diploma or fellowship previously. Further, I declare that the material embodied in the present work is based on original research work and the indebtedness to others has been duly acknowledged at relevant places.

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Place: Lucknow

CERTIFICATE

This is to certify that the thesis titled **"Ultrasonic and Magneto Kinetics of Crystallization of Sucrose"** submitted by Mr. Satya Prakash Gupta is an original research work and has not been previously submitted in part or full for the award of any other degree or diploma to this or any other university.

The thesis submitted to Babasaheb Bhimrao Ambedkar University Lucknow satisfies all the requirements as stipulated in the Doctor of Philosophy (Ph.D.) regulations-1999 as amended in 2008/2010/2013 and it is fit for submission and evaluation for the award of the degree of Doctor of Philosophy of the University.

Date: 23.02.2018

Supervisor

Head of the Department

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The present treatise would not have been possible without the blessings of 'God'.

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"Straight from the heart"'

Satya Prakash

Satya Prakash Gupta

CONTENTS

ABBREVIATIONS

Bx	Brix (Total dissolved solids (% m/m))
ICUMSA	International Commission for Uniform Methods of Sugar Analysis
FT-IR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
UV-VIS	Ultraviolet-Visible Absorption
ΔG	Gibbs Free Energy Change (mg L^{-1})
ΔH	Enthalpy Change (kJ mol^{-1})
ΔS	Entropy Change (kJ $mol^{-1}K^{-1}$)
PUS	Pulse Ultrasound
PMF	Pulsed Magnetic Field
XRD	X-Rays Diffraction
STAI	Sugar Technologiests' Association of India
HIFU	High Intensity Focused Ultrasound
Ea	Activation Enegry
UST	Ultrasonic Treatment
HTC	Heat Transfer Coefficient
IU	ICUMSA Unit
QA	Quality Assurance
QC	Quality Control

PREFECE

There are many problems during sugar processing particularly in crystallization step such as occurrence of latent period, excessive viscosity of the processing fluids and scale formation. These problems have received much attention several years ago unfortunately till date there is no effective solution.

Induction period exist in the initial interval time of sugar processing during crystallization. The induction period referred to decrease rate of sugar crystallization process in the initial interval of time leading to incomplete exhaustion of sucrose from the mother liquor. The occurrence of induction period in the crystallization processes presents a serious draw back and it hampers the economy of the industry.

High viscosity reduces the effective extraction of sucrose crystal from the mother liquor (industrial terms: massecuite and molasses). The viscosity of the mother liquor increases abruptly when low purity massecuite is cooled, and at the minimum temperature sucrose crystals cannot be separated effectively from molasses in the centrifuge. The option to reduce the viscosity of the massecuite is either by dilution or by heating the massecuite sufficiently to lower its super-saturation. However, dilution of the molasses leads to the loss of sucrose crystals due to its high solubility, whereas, heating of the massecuite may lead to sucrose loss due to inversion.

Scale is defined the precipitation of undesired solid material such as calcium phosphate, calcium carbonate, calcium oxalate, calcium sulphate and other minerals at phase interface. In sugar industry this occur on the heat exchanger surface of the heater evaporator and pans. Scale formation inside the pipe/tube during evaporation process is the inevitable problem which is difficult to manage and control under the operational condition. As a result of progressive accumulation of scale on heated surface, the heat transfer coefficient considerable declines with time causing significant economic loses.

The work embodied in this thesis refers to data collected during consultancy by our research group from different sugar factories of U.P., Maharashtra and Gujarat. This project was taken under R&D initiative of the Sugar Technologists' Association of India (STAI) under the supervision of Prof. Kaman Singh.

Non-chemical devices such as ultrasonic and pulse magnetic field were employed to handle above problems. The laboratory experiments coupled with commercial trials were confirmed to be beneficial for process and control of crystallization.

Chapter-1

General Introduction and Review of Literature

CHAPTER - 1

GENERAL INTRODUCTION AND REVIEW OF LITERATURE

1. History of sugar and sugar industries

Sugarcane is one of the most abundant crops on earth, forming raw material of crystal sugar and other sweetening agents for human consumption. Sugarcane i.e. 'Saccharum officinarum' is firstly domesticated by the people of New Guinea around 8000 BC. After that its cultivation is spread rapidly over south-east Asia and India. The earliest record of sugar cane is found in 'Atharvaved', one of the sacred Hindu Scriptures, considered supposed to have been composed 1000-5000 years before the Christian era. However, the first reference to Sugar is recorded in an ancient Indian Treatise 'Pratimoksha' dealing with Buddhist's code of conduct 2600 years back. The ancient Sanskrit literature produced is also replate with references to sugarcane and production of therefrom. In the legendry paradise created by sage Vishvamitra for the king Trishanku, Sugarcane was one of the plants grown, which was later thrown down on the earth as gift to mortals. Charak and Shushrut samhitas the standard works on the Hindu science of medicine 'Ayurved' dating back to 2nd or 3rd century B.C. mention besides sugarcane and its product the medicinal usage of sugar. References to sugar in Arthashastra of 'Kautilaya', the mentor and minister of Emperor Chandragupta, the founder of Maurya Dynasty (300 B.C) show the importance of sugar as commodity of general consumption liable for taxation. Thus, in India the cultivation of sugarcane of and the science of manufacturing sugar were developed in ancient times and from where it spread to different parts of the world [N. Deer, 1950].

India is known as original home of both sugarcane cultivation and sugar manufacturing. Sugar manufacturing was started in India between the 4th and 6th centuries. It was initially carried out through the simple process of crushing out into pieces of cane by a heavy weight and boiling the force so obtained until solid formed. These solids burning of uneven shape and size were called sarkara the sankrit term for gravel.The word sugar is derivative of the word sarkara. The larger solids were called khnad from which the word candy has descended.

Modern sugar processing industry by direct vacuum pan method in India is due to first enterprises of Englishmen who at the beginning of the 20th century set up half a dozen sugar factories in Uttar Pradesh in India. Another important landmark in the historical development of the Indian sugar industry was the release of new varieties of sugarcane as a result of the pioneering breeding research work at the Sugarcane Breeding Institute established in 1912. The Government of India acting on the report of the Tariff Board imposed high protective tariff to encourage indigenous industries. Consequently, the industry received a fillip and the number of factories rose to 132 before of the Second World War, especially in the subtropical belt of the country. During the British period in India, huge quantities of sugar were imported from other countries, which had reached peak in 1930 but dwindled thereafter to insignificant level by 1937 since by that time India had attained self sufficiency in sugar production. The decade before Second World War thus saw the renaissance of this vital industrial activity. However, real spurt of the activities in the various areas of development of this industry had to wait the dawn of Independence.

1.2. Present status of the world cane sugar industry

Now day's cane sugar industry is widely dispersed in different regions of the world like India, Australia, South America, Africa, U.S.A., and many parts of Asia, in tropical warm climate.

2. Sugar

Sugars in general are known as carbohydrates being formed of carbon, hydrogen and oxygen. Simple sugars like glucose, fructose, etc. are monosaccharides which cannot be further decomposed into simple carbohydrates by either acids or enzymes. When composed of five carbon atoms these carbohydrates like arabinose are termed as pentoses. Likewise sugars like glucose, fructose containing six carbon atoms are known as hexoses. Monosaccharides condense together to form disaccharides or even trisachharides containing two or three monosaccharides . Sucrose, maltose and lactose belong to the category of disaccharide which under influence of acid or enzyme forms simple monosacharides. Sucrose is the condensation product of glucose and levulose or fructose, the first being an aldehyde whiles the latter contains ketone group. Several polysacchhrides produced by condensation of monosaccharides, are present in sugarcane like gums ‘dextran’ starch, cellulose, which when reacted by acids or enzymes are converted to monosaccharides. The major components of sugarcane, besides water are as:

2.1. Sucrose

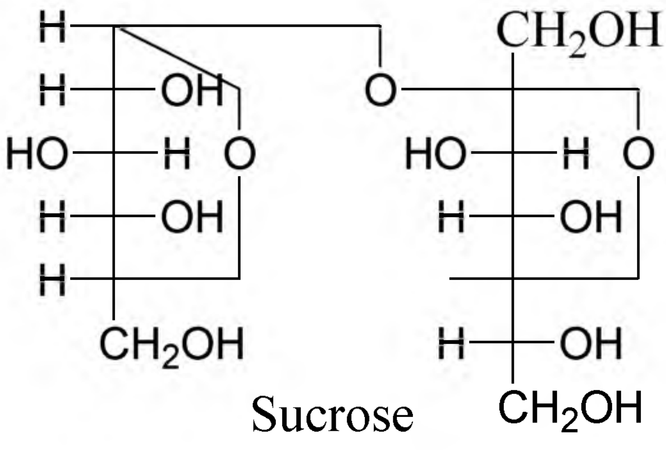
(i) Commonly known as sugar is the major constituent of sugarcane and belongs to the family of carbohydrates. Chemically sucrose is $C_{12} H_{22} O_{11}$ structurally it is represented as α-D glucopyronosyl β-D fructofuranoside. Following are some physical and chemical properties of sucrose which is basically a disaccharide:

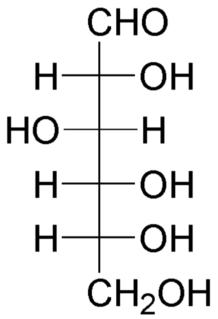
(ii) Molecular weight 342.3.

(iii) The melting point of sucrose is 188^0C but it decomposes on melting.

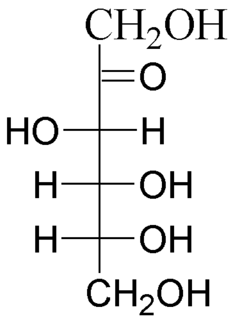
(iv) Sucrose is optically active and specific rotation of normal solution (26 g in 100 ml) is +66.53 at 20^0C but on inversion the solution has optical rotation of -39.7 at 20^0C.

The configuration of sucrose and its two main monosaccharides is as under-





D-Glucose



D-Fructose

In its pure form this sugar is crystalline in nature. Sucrose content in fully mature cane ranges from 12-15%. Under conditions of low pH or under influence of certain enzymes like invertase sucrose is hydrolysed into two monosacchrides viz. glucose and levulose in equimolecular proportions according to equation:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Above reaction is commonly known as inversion and the resulting solution as invert sugar. The term sugar usually refers to sucrose, which is also called "table sugar'' or ''saccharose''. Sucrose (Fig.1) is a disaccharide of glucose (left) and fructose (right), important molecules in the body.

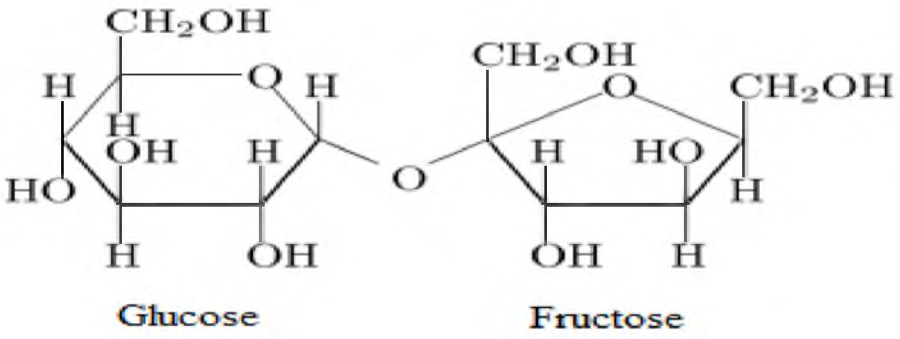


Fig.1 Structure of sucrose (Sugar).

2.2. Solid state properties of sucrose

The sucrose crystal (Fig-2) is monoclinic (a = 10.65 A, b = 8.70 A, c = 8.0A, β = $105^0 44'$).

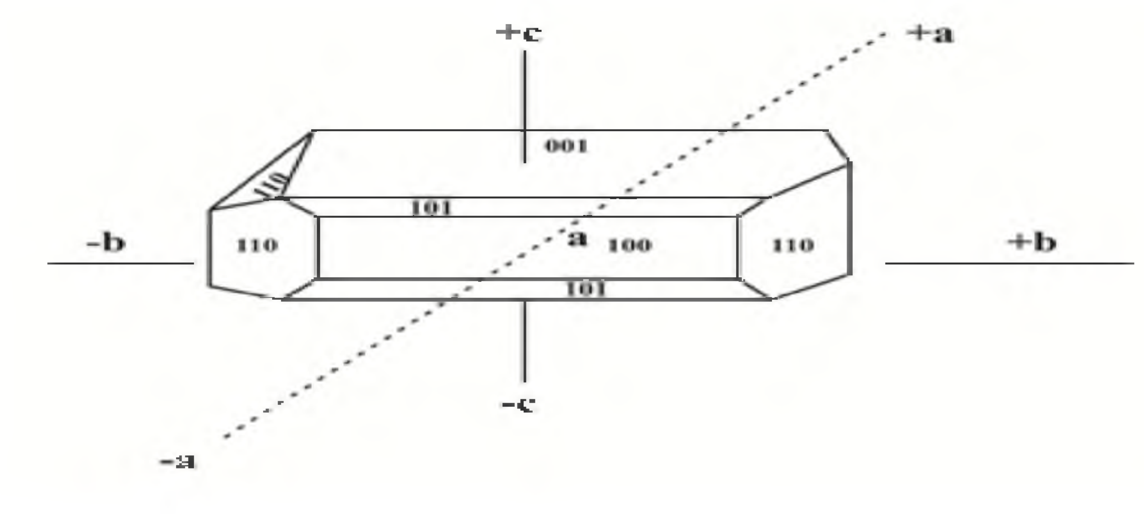


Fig. 2 Structure of sucrose in crystal form

The form, in which the sucrose molecule exists in its crystal network, is indicated in Fig. 3 and 4 (Prasad, Ramaiah and Gupta, 1965). Structure of sucrose in crystal form diagram Bond length in the sucrose molecule diagram Hydrogen bonding and valence angles in sucrose molecule.

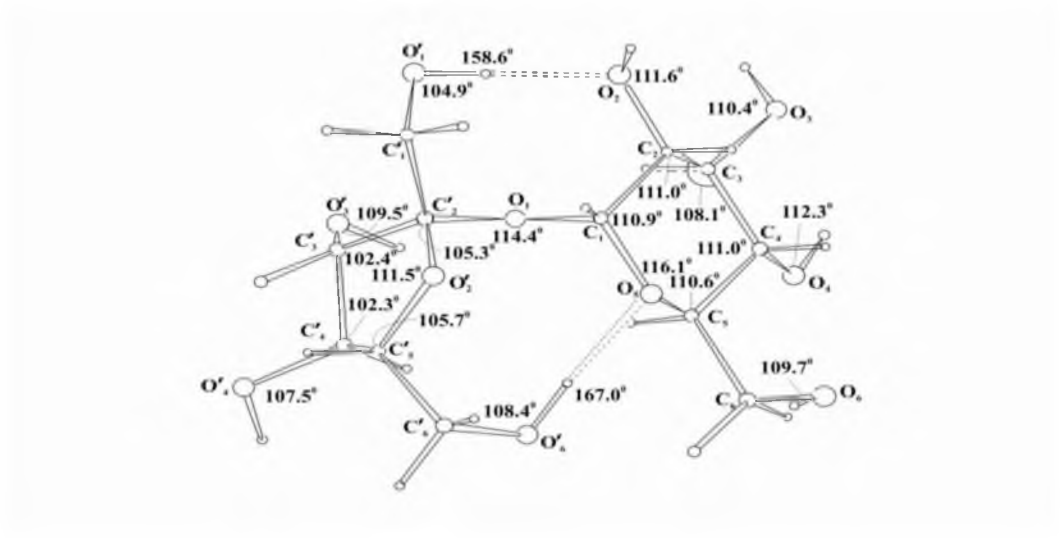


Fig. 3 Bond length and hydrogen bond in sucrose molecule

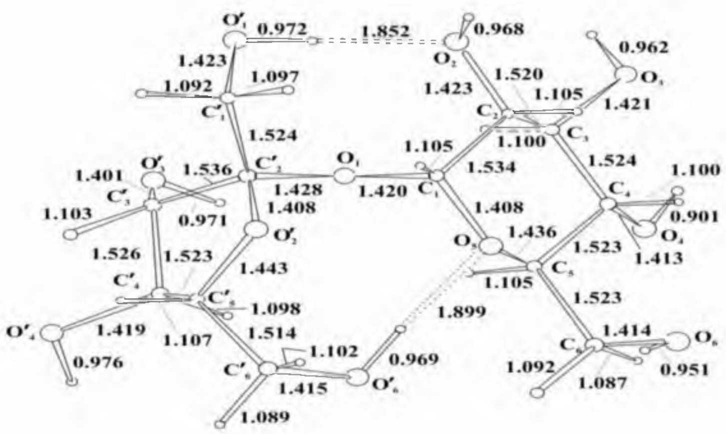


Fig. 4 Hydrogen bonding and valance angle in sucrose molecule

2.3. Solid phase conductance of sucrose

The sugar crystals have measurable electronic conductivities, with temperature dependence similar to that of conventional semiconductors [Singh and Prasad, 1999, 2005, M.M. Szostk, *et al.*, 2014]. The absolute value of the conductivity is several orders of magnitude lower than in most semiconductors, and is greater for the larger molecular species. As a group, it may be classified as poor insulator or semiconductor, according to preference. The observed electrical conductivity, very likely, has its origin the inclusion or absorption of impurities (ash and non sugars) in the $C_{12}H_{22}O_{11}$ crystal. Characteristics activation energies ranging from 0.27 to 0.35 eV suggest that there is a protonic conduction mechanism in the sucrose which is attributed to the protons of hydrogen bond (Fig. 4) network present in the sucrose crystal. A comparative study with the conductivity of octamethyl sucrose where there is no hydrogen bond brings considerable added assurance to both technique employed as well as enduring the validity of the results in the scene that octamethyl sucrose crystals have no electrical conductivity which confirms the participation of hydrogen bond as charge carrier which is thought to be responsible for the observed conductivity.

3. Crystallization

Crystallization refers to the formation of solid crystals from a homogeneous solution. Crystallization is the process by which a solid form, where the atoms or molecule are highly organized into a structures known as a crystal. In order to crystallization take place a solution must be supersaturated. Supersaturation refers to a state in which the liquid contain more dissolved solid that can be accommodated at that temperature

3.1. Crystallization of sucrose

Crystallization of sucrose is an important process on which the efficient performance and economics of sugar industry is primarily depends. Fundamental and applied work on various aspects of sucrose crystallization has therefore been the subject of major research work. The International Commission for Uniform Method of Sugar Analysis (ICUMSA) frequently considers the progress of research on this subject and communicates the significant results to the industry for the betterment of its performance. Sugar is perhaps the only chemical produced in large quantities in the purest form. India produces annually 4-5 million tonnes of plantation white sugar which is about 99.8% pure. This is possible primarily because of the application of the significant unit operation namely the crystallization. In our research work we give some of the important findings which will be useful for the improvement of the economy of the Indian Sugar Industry.

Crystallization of sucrose is a simple physical process which involves the transfer of sucrose molecule from the solution phase onto the solid seed surface. Kinetic of crystallization of sucrose attracted the attention of many research workers for obtaining data for design of pans, [De Coudry, 1946, Holven, 1942, Behne, 1939] crystallizers, etc for use in sugar industry, they also concentrate for finding out the phenomenon occurring during crystallization. The rate of crystallization of sucrose from pure super saturated solution was studied by A. Van Hook [A. Van Hook, 1944] and other workers [B. N Das *et al* 1960]. The rate of crystallization of sucrose plays an important role in economic functioning of a sugar factory [Jenkins, 1941]. It becomes the dominating factor in controlling the time required for the strike in a pan boiling process [A. Van Hook *et al,* 1959]. The data on the rate of crystallization under varied experimental conditions and especially their theoretical interpretation formed the basis for the recent improvements in forced circulation in pans [Webre, 1945], modified and controlled boiling systems, [Webre, 1945, de Coudray, 1946, Holven, 1942], crystallizer designs, etc the various phenomenon occurring during crystallization, have attracted the attention of several research workers. The kinetic studies initiated by Kuckarenko, [Kucharenko, 1928, Gloassco, 1922, Nees *at el*, 1936, Orth, 1938, Kucharenco, 1928)], have been deeply investigated by A. Van Hook [A. Van Hook, 1935, A. Van Hook, 1940], Kelly [Kelly, 1960], and others [Ingelman, 1947, Amagasa, 1931, Harris *et al*, 1952].

4. Importance of kinetics studies

Kinetic studies of a process refer simply the finding out the amount of substance undergone change at different intervals time. Thus if a substance 'A' alters itself through the process or a reaction into 'B', we can represented the system as-

$$A \rightarrow B \ \ldots\ldots \ (i)$$

In the case of crystallization of sucrose, A refers to the sucrose molecules in solution and B, sucrose molecule to that on the crystal surface. The reaction (i) refers to the deposition of sucrose molecules, from the solution phase, on the crystal surface. The system is obviously a heterogeneous one involving two phases: (i) sucrose solution and (2) solid crystal. In the process of crystallization, sucrose molecule does not undergo any chemical change. It is however, to be mentioned that the sucrose molecule in solution differ of certain physical and thermodynamics properties. The process seems to be a purely physical reaction. The studies on the kinetics of the reaction (i) enable one to understand the following:

(a) Order of the reaction
(b) Occurrence of latent period if any an its elimination
(c) Thermodynamic properties associated with the process.
(d) Viscosity of molasses and massecuite
(e) Scale formation during crystallization

4.1. Order of the reaction

The order of the reaction gives us knowledge of the number of molecules taking part in the elementary process of a reaction that are responsible for the progress of the reaction. In this respect we examine the validity of different order of reaction on crystallization.

There are two methods which are employed in investigating the kinetics of crystallization of sucrose in pure and impure sugar solutions, [A. Van Hook, 1944, 1959].

(I) In first method sucrose solutions of known concentration or supersaturation are suspended with crystal of definite size and weight, which act as the seed; the system is maintained at constant temperature and solution may be either stirred at desired number of revolution per min. or kept stationary. The loss in sucrose content in the solution on account of the deposition of sucrose molecules on the seed crystal due to crystallization process at different intervals of time t, is noted by a refractometer. Refractive index is a liner function of sucrose concentration [Browne *et al* 1941]. If the initial concentration of sucrose is represented by a, refractometer reading recorded at varied t, give the concentration of sucrose exiting in the solution phase at t, viz (a-x), where x is the concentration of sucrose underwent change at t, from the law of mass action, [Huishelwood, 1940, Glastone, 1956] we get .

$$dx/dt = k\,(a-x)^n \;\ldots\ldots\; \text{(ii)}$$

where n and k are the order velocity constant of the reaction respectively.

The second method involves the measurement of the dimensions of individual growing crystals at different interval of time. The increase in crystal width (d) say between 100 or pinacoid faces of the crystal at different time t, were taken to correspond to the values of x, and the difference between the values of d at the start and at the end of the process to a. From these, kinetic considerations are examined.

The measurement of the refractive index at different intervals of time as in first method indicates definitely the mode of loss of the initial reacting substance viz. sucrose, the variation in the dimension of a crystal face does not give any knowledge on the above aspect, since the growth is not confined to one face only [Hungerford, 1935]. Hence we use refractive index measurement for sugar concentration.

4.2. Occurrence of latent period (Induction period)

The occurrence of the latent period has long been detected during the progress of a number of chemical reactions. Probably the presence of latent period was first recorded in gaseous reactions which are generally catalyzed with the help of light of various wavelengths. In the photochemical combination of hydrogen and chlorine and latent period was first discovered by Burgess and Chapman [C.H. Burgess *et al,* 1906] during this period practically no combination takes place. This was due to the presence of nitrogenous impurities which give rise to nitrogen chloride and inhibit reaction. The inhibitors are gradually destroyed by the light and the combination starts. In the absence of nitrogenous impurities the latent period disappears.

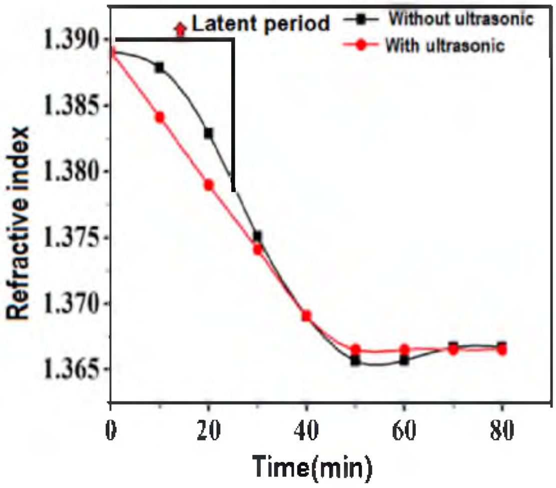


Fig.5 Graph showing latent period

The most important study of the latent period on the kinetics of crystallization of sucrose was studied by Van Hook [Van Hook, 1944] and other [Ramaiah *et al,* 1961]. The kinetics of the process was followed in a relative way by means of the change in concentration of supersaturated syrup in which crystal seeds are uniformly suspended. Although any property dependent on concentration may be used for this purpose. The refractive index is most direct and convenient. Theoretically we can expect that if deposition of sucrose molecules on crystal seed occurs from the beginning of the process the refractometer reading would follow according to curve 2 in Fig.1 but it has been noticed that the refractometer did not indicate any decrease in the initial intervals of time which is referred to as the latent period in the crystallization process. In other words, the latent period refer to decreased rate of crystallization process in the initial intervals of time leading to incomplete exhaustion of sucrose from the mother liquor. The latent period in the crystallization process presents a serious drawback especially in sugar processing where the rate of crystallization is undoubtedly hampered due to its presence which may ultimately affect the economy of the industry.

The studies on the occurrence of latent period and mechanism for the latent period during the crystallization of sucrose have attracted the attention of a number of workers. Walker et al [Walker *et al,* 1959] studied the crystallization process dialatometrically and found that when change in supersaturation is plotted against time a straight line is obtained for the portion of a run from about 25% to 75% completion but the pronounced upward curvature to the slope during the early part of the run indicate that rate law are not followed during this period. Van Hook et al [Van Hook *et al,* 1953] investigated the influence of seed/sucrose ratio the occurrence of latent period and found that at very low seed/sucrose ratios, their latent period becomes more pronounced and extended. He also observed that at very low supersaturation the latent period never occurred during the crystallization process. It was studied by Ramaiah *et al,* [1962] the effect of grain size on the latent period and found that for the same seed/sucrose ratio, the crystal with dimension less than 0.3 nm gave no latent period when used as seed. The occurrence of latent period during crystallization of sucrose in static and stirring methods is also studied by Ramaiah *et al,* [1962]. In the static method the system is kept stationary and the stirrer was not rotated whereas in the stirring method the stirrer was rotated by a particular number of rotations per minute. In our research work we eliminate latent period by treatment of ultrasonic.

4.3. Thermodynamic properties associated with the crystallization process

The study of thermodynamic data enables one to get deep insight into the phenomenon operative during crystallization. The recommendation of the international commission for uniform method of sugar analysis (13th session held at Hamburg, 1962) rightly emphasizes the need for work on the determination of thermodynamic properties of crystallization of sucrose. The detail investigations have been carried out in the past. During our research work the change in free energy (ΔG), heat content (ΔH) and entropy change (ΔS) is calculated. The significance these thermo dynamical quantities in an apparently physical process of transfer of sucrose molecules from the solution phase onto the seed crystal is discussed in detail in our research work.

4.4. Viscosity of molasses and massecuite

High viscosity reduces the effective [J.C.P. Chen, 1985] extraction of sucrose crystal from the mother liquor (industrial terms: massecuite and molasses). The viscosity of the mother liquor increases abruptly when low purity massecuite is cooled, and at the minimum temperature sucrose crystals cannot be separated effectively from molasses in the centrifuge. The option to reduce the viscosity of the massecuite is either by dilution or by heating the massecuite sufficiently to lower its supersaturation. However, dilution of the molasses leads to the loss of sucrose crystals due to its high solubility whereas, heating of the massecuite may lead to sucrose loss due to inversion. In our research work we use ultrasonic and pulsed magnetic field, non chemical devices to reduce viscosity.

4.5. Scale formation during crystallization

Scale formation/scaling is defined as the precipitation of undesired solid materials such as $CaSO_4$ $CaSiO_3$, $Ca_3(PO_4)_2$, $CaCO_3$, CaC_2O_4, and other minerals at phase- interface [W.O.S. Doherty, 2008]. In sugar industry, this occurs on the heat exchanger surfaces of the heaters, evaporators and pans. As a results of the progressive accumulation of scale on heating surfaces, the heat transfer coefficient (HTC) considerably declines with time causing significant economic losses [P.Honig, 1963]. The magnitude of this problem may be realized by considering that scale can cause degradation or complete failure which increases initial and operation cost. Poor conductivity of a 25 mm thick $CaCO_3$ scale layer can decrease heat transfer [J. Glater *et al,* 1980] by 95% whereas SiO_2 scale layer 0.5 mm thick result in a 90% decrease in heat transfer [J.F. Grutsch *et al,* 1984]. It has been well established [Fedral Technology, 1998] that 1 mm scale thickness is equivalent to 8-10 % more energy loss and furthermore, a huge amount of chemicals used for cleaning and their subsequent effect on the environment are major issues in today's context. In 1997, British National economic losses were estimated at 0.5 billion pounds [A. Hu *et al,* 2006] due to increase of energy and decrease of production capacity resulting from scale in sugar industry.

The above literature clearly illustrates that while the aforesaid problems have received much attention for several years, unfortunately, to date there is no effective solution yet. To reduce or control scale formation, various options [N. O. Shmidt *et al,* 1954, N.O. Shmidt *et al,* 1958, C. Frank *et al,* 1996, S. K. Gupta e*t al* 2006, K. Singh *et al,* 2009] have been tried, however, reliable solution is not achieved till date. The use of ultrasound has been reported [A.Hu. 2006, Hai-Qin *et al,* 2005, Tai-Qiu-Qiu, 1999, G.J. Peric, 2011] as beneficial for scale control and improvement in HTC and evaporation efficiency. The factory management informed us that the HTC of the evaporators were low and scale problem was very serious and lots of chemicals had to be used to clean the bodies and hence, the shut-down frequency had increased. Therefore we decided to employ ultrasonic device in the industrial scale to evaluate the application and potential of ultrasound to reduce or control viscosity and scale formation during sugar manufacture.

4.5.1. Mechanism of scale occurrence

The calcium in solution is derived either from dissolution from natural resources, or from chemical deliberately added during clarification of juice. $CaCO_3$ become less soluble at higher temperatures and on heating, CO_2 escapes favoring the bicarbonate decomposition reaction which causes $CaCO_3$ to precipitate.

The reaction in the formation [J. Peric, *et al,* 1996] of $CaCO_3$ can be straight forwardly represented as:

$$2HCO^-_3 \longrightarrow CO_3^{2-}+CO_2+H_2O \qquad (1)$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3 \qquad (2)$$

Although this is a simplification and initial precipitation via an intermediate precursor solid When CO_2 is bubbled through the solution reaction I will retard and so the precipitation will be slower as observed.

Scale formation on evaporating surfaces

4.5.1.1. Mechanism of scaling

The Deposition of unwanted material on heating surface is known as scaling, The amount of scaling component vary considerably from mill to mill and from period to period in evaporator bodies, operating conditions influencing the rate of scaling: (1) presence of suspended matter, and (2) concentration of incrustating components present in thin juice. Therefore amount of scaling is less, the greater the rate of evaporation.

It was found that with the edition of the fifth body, the rate of scaling increased considerably. As a representative example, statistical analysis of the amount of scale formed collected gave the result shown in Table1 [P.Hoing, 1963].

Table 1. Intensity of scaling in mg/kg cane processed in relation to average rate of evaporation

Incrustating components	Rate of evaporation > 30 $kg/m^2/h$	Rate of evaporation < 24 $kg/m^2/h$
SiO_2	4.0	6.8
P_2O_5	< 0.5	1.9
SO_4	0.6	0.5
CaO	3.6	9.0

The intensity of scaling is also increased, when a factory has frequent stops of short duration, and also the capacity of a mill is reduced when the intensity of scaling increases usually with a reduction in grinding rate

Another operational factor in scaling is the juice level in the vessels. When the juice level or flow rate is maintained at a constant value between 10 and 20% of the tube length and with high rate of evaporation, scaling is at minimum. Modern evaporators with guided circulation and film evaporators of the Kestner and semi-Kestner type usually show less scaling in relation to the amount of evaporated water than evaporators where the juice levels are controlled manually, i.e. when they are maintained at a too high level and are not constant.

When an evaporator is functioning at full capacity and with a constant flow rate, the effect of turbid matter on the rate of scaling is negligible. It has been observed in factories where the juices were sent to the evaporators with an extremely high percentage of suspended matter, and in cases where unsettled limed juices were going straight to the first body of an evaporator and the settling of the juices was done between the first and second body, that there was a small scaling intensity in the first bodies.

Above observations have led to the application of practices to reduce scaling by deliberated adding suspended solids to the clarified juice. Additions of decolorizing carbon have been applied on factory scale, with the observation of reduse scaling, but the corban increased the electrolitic corrosion of the tube sheets in contact with the tubes. The addition of kieselguhr to the thin juice resulted in reduction of scaling in first bodies; however, it gave an increased scaling of silica in the last bodies. This could be attributed to the solubility of silica in kieselguhr in hot cane juices. Kieselguhr is not completely inert material towards sugar solutions; some commercial grades of kieselguhr dissolve to a certain extent in sugar juices, low brix liquors and sweet waters to 40 parts of SiO_2 per liter of sugar juice or liquor.

Generally suspended matter in juices under good operational conditions is not the cause of scaling, however, the quantitative aspects of scaling; collected at different sugar mills the general picture shown in Table 2 [P. Honig, 1963] is obtained.

Table 2. Intensity scale formation per liter of evaporated water in cane sugar mills

	Vessel 1	**Vessel 2**	**Vessel 3**	**Vessel 4**
Distribution of scale in quadruple effect (%)	35	20	10	35
Amount of scale per liter evaporated water (mg)	3.5 – 7	2 – 4	1 – 2	3.5 – 7
Average composition of scale (%):				
Organic	40	30	20	5
P_2O_5	25	15	10	9
SiO_2	5	10	15	10 – 35
Organic acids	-	-	-	5 – 20
Carbonates	0 – 10	0 – 5	-	-
SO_4	-	-	-	0 – 20
CaO and MgO	20	25 – 30	20 – 40	20 – 40
Fe_2O_3	10	6	4	5 – 8
Average amount of scaling components per liter of evaporated water (mg):				
Organic	1.2 – 2.4	0.6 – 1.2	0.2 – 0.4	0.17 – 0.35
P_2O_5	0.9 – 1.8	0.3 – 0.6	0.1 – 0.4	0.3 – 0.6
SiO_2	0.2 – 0.4	0.2 – 0.4	0.15 – 0.30	0.35 – 1.4
Organic acids	-	-	-	0.17 – 1.4
Carbonates	0 – 0.7	0 – 0.2	-	-
SO_4	-		-	0 – 1.4
CaO and MgO	0.7 – 1.4	0.5 – 1.2	0.2 – 0.4	0.7 – 2.8
Fe_2O_3	0.3 – 0.7	0.1 – 1.2	0.04–0.008	0.17 – 0.56

Comparing this scale formation with the concentration of scaling components present in the clarified juices, the relation is presented in Table 3 [P. Honig, 1963]. These data show that a very small percentage of the scaling components present in the juices are actually deposited on the heat transfer surfaces.

Table 3. Relation between the amounts of scaling components in incrustations and the concentration of the components in thin juices

Component	**Total amount of scaling components in mg deposited on heating surface per liter of evaporated water**	**Average concentration of scaling components in juice (mg/l)**	**Concentration of scaling components in juice per liter of evaporated water**	**Percent of scaling components in incrustation (% juice)**
Organic	2.2 – 4.4	-	-	-
P_2O_5	1.4 – 3.4	40 – 70	50 – 90	3 – 5
SiO_2	0.8 – 2.5	250 – 250	200 – 300	0.5 – 2
Organic acids	0.2 – 1.4	-	-	-
Carbonates	0 – 0.9	-	-	-
SO_4	0 – 1.4	400 – 600	400 – 800	0 – 1.5
$CaO + MgO$	2.1 – 5.8	500 – 800	600 – 1000	0.3 – 0.6
Fe_2O_3	0.6 – 1.6	30 – 40	40 – 50	1.2 – 2.5

* Calculated from the concentration of scaling components in thin juice and evaporated water in concentrated syrup.

These are all indications that actual scaling takes place when:

a) The scaling components become supersaturated in the concentration process; this is, for instance, the case with $CaSO_4$ and with calcium aconitate.

b) Calcium magnesium phosphate, and probably also iron phosphate, are precipitated: (1) in the first bodies, as an effect of the high temperature of the tubes; (2) in the last bodies, as a result of precipitation caused by the concentration effect; and (3) most important is the precipitation of scaling non-sugars resulting from the mixing of clarified juices of different clarifier compartments, having different pH values. It is a fact that pH of clarified juices from multi-tray clarifiers is different from that of the juices from the upper trays and from the bottom compartment. When these juices, after carefull filtration, are mixed and boiled after precipitation occuress. These precipitates consist of Ca-Mg phosphates, Fe – phosphates, Fe silicate, SiO_2

and proteinic non-sugars. The solubility and coagulation of these non-sugars in thin juices have a high pH coefficient. In sugar factories using sugar batch settling tanks, it was observed that the introduction of pH control in the liming process made a substantial contribution to the reduction in scaling. The introduction of multi-tray continuous subsides resulted in many factories in increased scaling when the pH of clarified juices from the different compartments differed. The addition of filtered mud juices to the decanted clarified juice had the same effect.

c) The scaling of organic substances such as protein, gums, proteinic matter and lipids are partly the result of coagulation effect caused by the high temperature. This is an after coagulation, which has not been achieved in the clarification system.

d) The scaling by SiO_2 is only partly coagulation on the heating surfaces, resulting from higher temperatures. SiO_2 dissolved in clarified juice becomes super saturated during the concentration effect. The solubility of SiO_2 is less in high brix sugar solutions than in low brix juice. The solubility of SiO_2 in pure water at 20° C at pH 7.0 – 7.2 is 100 p.p.m.; in a 60 brix solution the solubility is 70 p.p.m. The solubility of SiO_2 is much higher at 95° – 100° C (clarified juice temperature), namely 380 p.p.m. SiO_2; at 60° C (temperature of syrup in last vessel) the solubility is 300 p.p.m.

e) The scaling by iron oxide is different in the first body of an evaporator from that in the last body. In the first body of an evaporator the iron contained in the scales is soluble in 1/100 N acid and is possibly iron phosphate. In the last bodies the iron can only be dissolved by the use of higher acid concentrations and is combined in some way with the SiO_2 as iron silicate.

The medium of scaling is so complex and it is not exclusively the effect of the concentration of the scaling components in the processed juices but is also affected by the operational condition that is temperature of the heating surfaces and the flow rate of the juices in the evaporation process.

There have been many ways to control the rate of scaling during sugar processing. Most successful alternative has been the replacement of calcium in thin juice by sodium by means of ion exchangers. This practice can be applied in beet sugar factories where the thin juice has low calcium content and is perfectly filtered in the carbonation filter station. The same practice can be applied in cane sugar factories using the carbonation process but it is not practical system in raw cane sugar mills where the calcium content is high and where the filtration of settled juices through a cation exchanger without proper pre-filtration is impossible from a practical point of view. This process is however not economical.

A number of systems using an electrical current to change the charge of impurities present in the colloidal state have been purpose and tried in the sugar industry. The disadvantage of these are that firstly, these systems have never been based on sound theoretical principles and secondly, what is most important for sugar industry, the practical result on scaling rates, based on experience during a number of years, have been disappointing.

Others systems were based on the addition of colloidal solutions or protective colloids such as alginates, methyl - carboxy - cellulose and mucilages in plant extracts. Systematic investigations with replications have shown that these additives had no practical effect on reducing the rate of scaling in the cane sugar factories.

There are in the sugar industry as a whole grate differences in scaling rates, which are determined primarily by the composition of the inorganic non-sugars in clarified juice. It has been found to be advantageous for some ortho - phosphate to be present in the clarified juice in solution. This results in the formation of a phosphate containing scale. This kind of scale is easily removal with acid and is therefore not considered to be one of the difficult scale to eliminate in cleaning.

The quantity of phosphate to be added to clarified juice is determined primarily by the amount of phosphate remaining in the juice after clarification. The amounts added were of a magnitude of 5 – 20 mg P_2O_5 per liter of juice.

In Fig. 6 and 7 the effect of the phosphate concentration, expressed as total phosphate (ortho and organic phosphate), on scaling is represented.

The effect of phosphate addition to clarified juice on the composition of the scale can be observed primarily in juices which are originally low in phosphate. This addition is of practical significance for factories where there is a periodic weekly cleaning of the evaporators and which wish to change the cleaning system from mechanical to chemical cleaning. It does not mean that there is a total reduction in scaling, but it introduces a change in the character of the scaling. This can be an attractive advantage

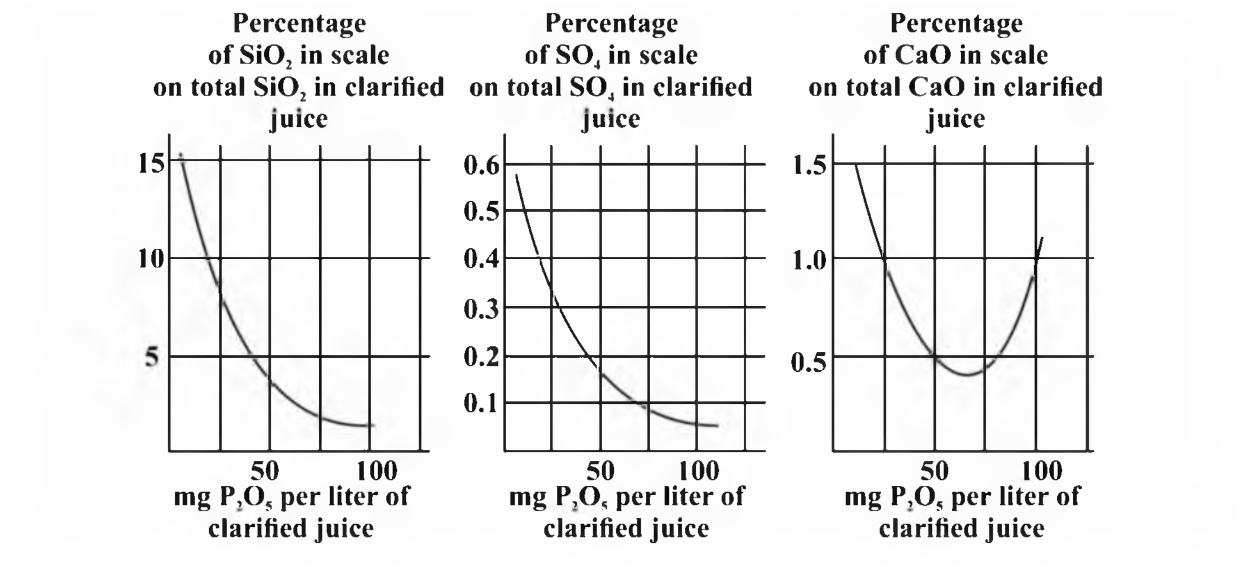


Fig.6. Scale forming nonsugars in evaporators scales % nonsugars present in clarified juice in relation to the total P_2O_5 content in clarified juice

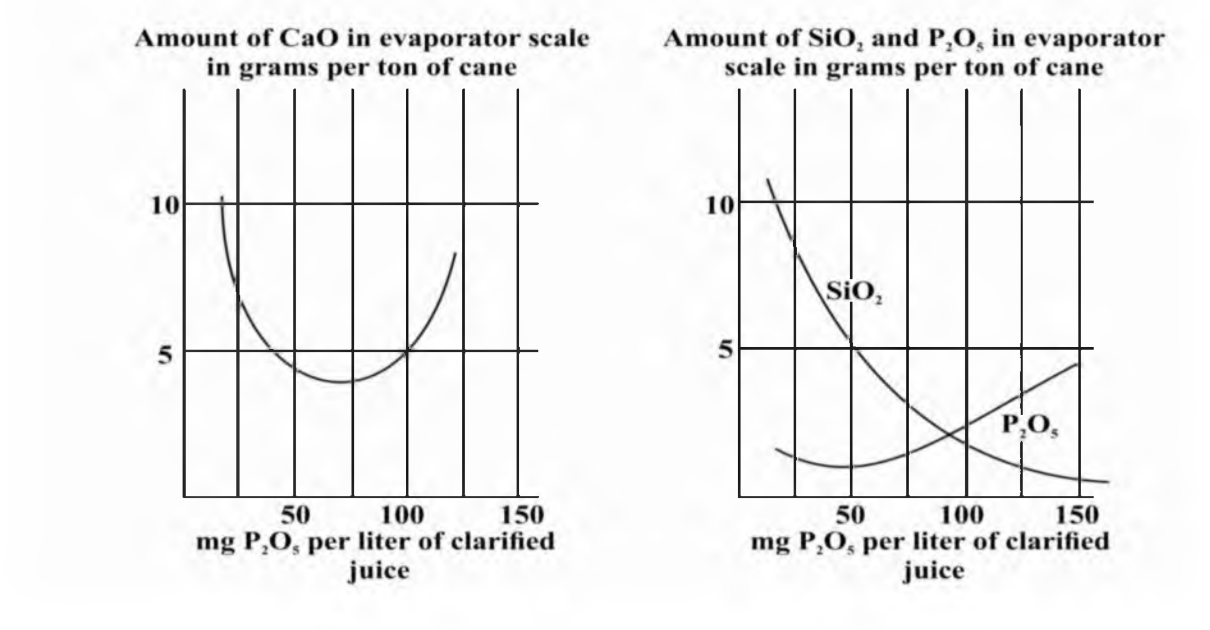


Fig.7. The amount of scale form per ton of milled cane in evaporator in relation to the P_2O_5 in clarified juice

On the basis of the experience and published work it can be summarized as follows:

i. For minimum scaling the capacity of the evaporating surface is important. Maximum capacity results in minimum scaling.
ii. In general maintenance of a flow rate and uniform operational conditions are essential for a minimum rate of scaling.
iii. The use of electrical systems and the addition of anti-scaling components have shown to be of no substantial benefit in practice.
iv. The maintenance of a certain phosphate content in the clarified juice by the addition of a small amount of soluble ortho-phosphate to the clarified juice, assists in the formation a phosphate-containing scale, which can easily be removed by acid cleaning.
v. Suspended matter in clarified juice has no significant effect on scaling under good conditions of operation.
vi. The use of cation exchangers on carbonated juices has contributed substantially to the reduction of the rate of scaling.

4.5.1.2. Rate of scaling in relation to the time an evaporator is in operation

Whether the rate of scaling is proportional to the time of operation or whether it is affected by the amount of scale already formed can be a certain with help of an equation. Practical experience has shown that when an evaporator has not been properly cleaned and put into operation, the scaling rate, which is detected by the decrease in heat transfer coefficient with the time of operation, is greater than when an evaporator has been freed perfectly from all incrustations.

The heat transfer in a scaled evaporator can be expressed by the formula:

$$\text{Overall heat transfer} = \frac{1}{\frac{1}{\lambda\text{clean}} + \frac{\text{dscale}}{\lambda\text{scale}}} \qquad \text{(A)}$$

In this formula λclean is the overall heat transfer in the clean evaporator, i.e. the specific heat conductivity; dscale is the thickness of the scale formed in meters; λscale is the specific heat transfer of the scale, normally varying between 0.2 and 1 for the types of scale found in sugar mills. clean is, in a scale free evaporator and for the first two evaporator bodies, approximately 2,000 cal/m^2/h/°C and between 800 and 1,200 for the last body of an evaporator. If we know the rate of scaling, that is, the thickness of the scale formed per day, under normal working conditions, it is possible to use this formula to calculate the change in overall heat transfer of an evaporator. For practical purposes it is advisable to use the weight of scale in g per m^2 formed, per unit of time, instead of the scale thickness, and to express the specific heat conductivity of th scale as specific heat transfer 100 g scale/m^2 evaporating surface by the symbol λ.

It is possible to use this formula to calculate the change in the heat transfer, or the specific effect of scale, if we know the amount of scale in g per m^2 evaporating surface, and to calculate with this formula the resulting specific heat transfer. In this analysis of the rate of scaling, it is possible of the heat transfer to determine the change in the heat transfer resulting from the scale formation Table 4 [P. Honig, 1963].

Table 4. Relation between chemical composition of scaling components and specific heat conductivity

Scale Component	Specific heat conductivity*	Porosity	Scale thickness in mm for 100g of scale per m^2 evaporating surface**
$CaSO_4$.2 aq., Ca-oranates***	0.50 – 1.50	25 – 50	0.04 – 0.08
Ca – Mg phosphate	0.25 – 0.80	40 – 65	0.04 – 0.12
SiO_2, R_2O_3	0.10 – 0.25	55 – 85	0.06 – 0.25

* The specific heat transfer is expressed in kcal/m^2/h/°C for a length of 1m. For a thickness of scale of 1mm the value has to be multiplied by 1000.

** 100g per m^2 is a light scale. To calculate the thickness of a scale of this weight in mm, we have to apply the formula:

$$\frac{1}{\text{specific gravity}\ \frac{(100-\text{porosity})}{100}}$$

** The true specific gravities for different scaling components are: $CaSO_4$. 2 aq., 2.3; Ca – organates, 2.0 – 2.4; Ca – Mg phosphate, 3.0 – 3.2; SiO_2 (amorphous), 2.2; Fe_2O_3,

It is customary to use a formula other than above to express the continuous change in the heat transfer during scaling,

$$\frac{1}{(\text{heat transfer})^2} = a + bT \qquad (B)$$

[P. Honig, 1963]

where a and b are constant; T = time of operation of a scaling evaporator in days.

In a large number of determinations, covering daily observations during 6 consecutive grinding seasons with two evaporator sets, with an average operational period between cleanings of 11 days, it was found that the reduction in the heat transfer as expressed in the formula (A), dsacle/λscale is proportional to the time of operation, respectively that b in formula (B) may be considered for the same evaporator and uniform grinding rate to be constant.

We may therefore assume that in an operating evaporator the scale formation is proportional to the time of operation. There are, however, restrictions to be made to the following effect:

i. The rate of scaling may be constant during a short period of operation, but it is not constant for a specific evaporator for different grinding seasons and for different periods of the same grinding season (beginning, middle and end of crop). When in an operating period between cleanings the grinding rate fluctuates strongly or the number of mill stoppages is large, the calculated values of dsacle/λscale and b increase substantially.
ii. The scale formation is substantially greater When an evaporator body has not been cleaned properly, Than when an evaporator starts with thoroughly cleaned evaporating surface.
iii. It is found that most of the scale is deposited at the lower tube end, where the tube is much less scale at the upper part of the tubes, where most of the

heat transfer and evaporation takes place. It is possible, when this upper part of the tube contains traces of scale that it acts as nuclei for the scaling components in the juices when the evaporator is restarted.

4.5.1.3. Composition of evaporator scales

Experience has shown that composition of evaporator scales vary from factory to factory and from season to season in the same mill and in different bodies of the evaporators in the same factory at the same time. The composition of the scale is dependent firstly on the concentration of the scaling components in the evaporator juices and, secondly, on the concentration and temperature of the juices in the successive evaporating vessels. Juices high in sulfate cause the formation of sulfate scales in the last bodies of multiple evaporators.

There are a number of general observations in connection with the composition of scales in cane sugar factories:

a. It has been found that the incrustation in an evaporator consists of various components. It consists of a mixture of inorganic and organic non-sugars.
b. The scales in evaporator are mainly inorganic in nature (more than 50% of the dry matter).
c. The scales in the first bodies of evaporators are usually higher in phosphate and organic components than those in the last bodies. Sulfate is practically never found in the scales of the first bodies.
d. Magnesia is, compared with calcium, relatively in higher concentration in scales in the first effect; the scales in last effects contain always smaller amounts of magnesium than calcium.

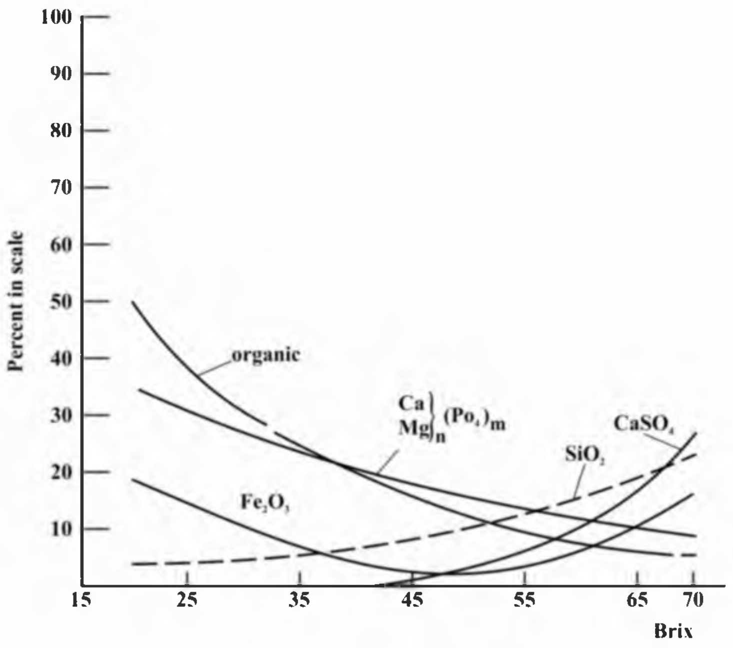
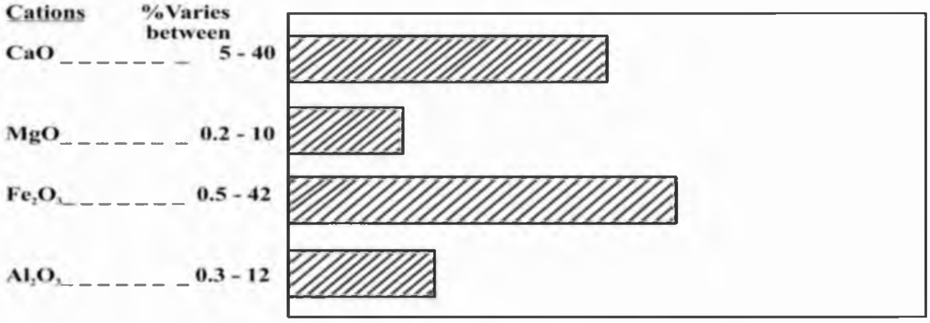


Fig.8. Relation between composition of scale and concentration (brix) in evaporator

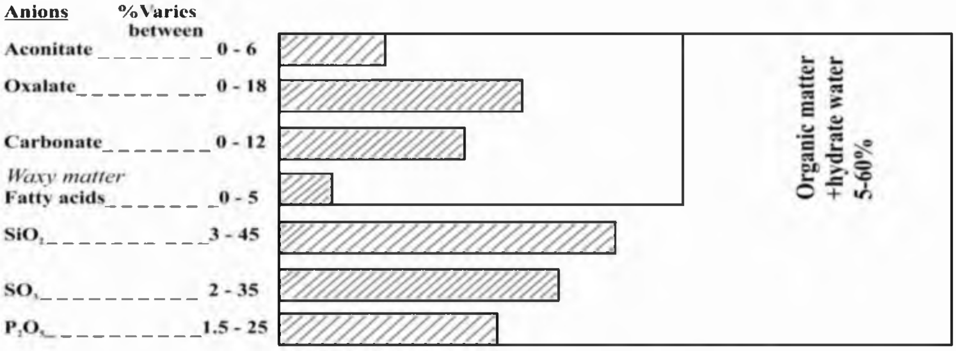
In a schematic form the change in the composition of scales is given in Fig. 8. [P. Honig, 1963]. Following table 5 [P. Honig, 1963] illustrate the representative comparison of evaporator scale found in raw sugar mill.

Table 5. Composition of scales in evaporators of raw sugar mills

Component	Low	Medium	High
CaO	< 10	10 – 30	> 30
MgO	< 3	3 – 8	> 8
Fe_2O_3	< 3	3 – 10	> 10
Al_2O_3	< 1	1 – 2	> 3
SO_4	<5	5 – 25	> 25
P_2O_5	< 5	5 – 25	> 25
SiO_2	< 5	5 – 30	> 30
Organic acids(oxalic and aconitic acid)	< 2	2 – 15	> 15
Percentage of analyzed samples	< 10	80	10



Cations : Percent of total washed scale varies betweem 20 and 60



ANIONS: Percent of total washed dry scale varies between 40 and 80

Fig.9. Variation in composition of evaporators scale in cane sugar mill

In Fig. 9 the variations in the amounts of cations and anions for 120 scales, originating from the 3rd and 4th evaporator bodies of Cuban mills (Oriente province), are given.

In investigations on scaling a technical difficulty is the collecting of representative scale samples. This can only be done by handscraping of tubes, after the body has been emptied and washed with water, and collecting the removed scales in a dish. Scale sample collected in this way are a mixture of large flakes of incrustation and soft mud, always contain a certain amount of sugar. For the analysis of the 'scale' the collected sample has to be washed with water, but not excessively as this would dissolve some of the scaling components, till it is free of sugar. To do this, the collected scale is mixed with about 10 times its volume of hot water (80°C – 90°C), the mixture of water and scale is stirred for approximately one hour, and the residue filtered and washed on the filter with water till the filtrate is free of sugar. It can be observed that the filtrate of washed scale has a dark color, resulting from caramelized organic material.The filter and residue after washing are dried and the residue collected from the filter and powdered in a mortar to obtain a homogeneous mixture on which a quantitative analysis can be made.

Cane sugar mills scale always contain same organic matter, Which can be extracted with chloroform. It consists of fatty acids, waxy matter and phosphatides. The percentage of these components is highest in the scales of the first bodies. Normally the chloroform is of a magnitude of 0.5 – 1%, but there are observations that the chloroform extract of scales of first and second bodies is as high as 5%. The chloroform extract after incineration shows practically always the presence of organic phosphates.

A term of the meaning is vague but which is of practical significance is 'organic matter' in scales. Organic matter is defined as the percentage difference between the dried scale (105°C) and the residue after incineration. This difference consists of: (1) organic acids such as, for instance, aconitates; (2) decomposed organic non-sugars; (3) non-sugars which are not water-soluble such as, for instance, proteins, lipids, Ca-proteinates, finely disintegrated bagacillo; (4) absorbed water combined with SiO_2; (5) hydrate water combined, for instance, with calcium sulfate. This loss of dried sales on ignition can be high.

The results reported in the literature on organic matter in scales are not always comparable as the procedure in preparing the scale samples before analysis, specifically the prewashing of the scales, is seldom known.

In Table 6 [P. Honig, 1963] comparison has been made with data of scale analyses from Cuban mills with other countries.

Table 6. Percentage organic matter in scales of evaporators

Source	Vessel 1	Vessel 2	Vessel 3	Vessel 4
PRINSEN GEERLIGS, Java	20 – 30	13 – 25	11 – 30	5 – 40
SPENCER-MEADE, U.S.A.	20	13	11	5
G. C. DYMOND, Natal, 1951	10 – 22	11 – 22	15 – 18	9 – 11
P. HONG, Cuba data	10 – 45	5 – 15	3 – 8	5 – 20

It was observed that the scales of first bodies contain more complex poly-molecular organic matter, in the form fine bagacillo (high pentosan value), chloroform-soluble components (lipids) proteins and caramelized sugars and non-sugars, than the scales from the following bodies. The scale of last bodies contain more organic anions such as aconitates and oxalic acid and more hydrate water which is not removed by drying at 105°C. The nature of the organic components in the scales of first and last bodies is fundamentally different.

For a better understanding of the nature of the incrustations in sugar mills, it is possible to clarify the scales by the main components. A classification can be used as given in Table7 [P. Honig, 1963].

Table 7. Specification classes of scale in raw sugar mills

Type of scale	**Chief constituent**	**Composition**
Phosphate	Phosphate of lime and magnesium	>25% P_2O_5
Sulfate	Sulfate of calcium	>25% SO_4
Silicic acid	Silicic acid usually combined with sesquioxides	>30% SiO_2
Sesquioxide	Fe_2O_3 and Al_2O_3 usually combined with SiO_2 and phosphates	>15% $Fe_2O_3 + Al_2O_3$
Organic acid	The only organic acids actually determined and analyzed in scales are oxalic acid and aconitic acid	>10% oxalic acid and aconitic acid
Organic	Organic matter minus oxalic and aconitic acid	>40% organic matter (weight loss on incineration of dried scale + original weight of scale dried at 105°C)

The above classification has practical significance for the cleaning procedures and for a better understanding of the effect of different types of scale on the reduction of heat transfer, i.e., the capacity of the evaporator system.

General rule on the composition of scale as affected by the concentration of the certain type of non-sugars and in relation to the system of processing as:

i. If the sulfate content of clarified juice exceeds 800mg SO_4 per liter, a typical sulfate scale in the fourth body of the evaporator is formed.
ii. If the phosphate content of the raw juice is high (over 450mg P_2O_5 per liter) and the pH of the clarified juice is over 8, or below 6.5, a typical phosphate scale is formed in the first two bodies of the evaporators.
iii. The lime and magnesium content of clarified juice are of great significance in relation to the rate of deposition and the composition of scale formed. If the total hardness (CaO and MgO) of the clarified juice exceeds 800mg CaO per liter it is found that the scales are high in calcium in the last three bodies of the evaporator and that a substantial percentage of magnesia is found in the first body of the evaporator.
iv. If the evaporator supply juice consists of a mixture of clarified juice from the clarifiers and filtrate combined with sweet juices from the press station, there is great risk of formation of scales high in silicic acid in the last bodies of the evaporator and high in sesquioxides in the first bodies of the evaporator.

Data available in the literature indicate that it is specifically the different in the pH values of clarified juice and filtered juice which causes precipitation of certain non-sugars in the evaporators, where this precipitation in statu nascendi is the cause of this typical scaling.

Further it has been found that the sweet waters from filter press stations are undesirable in mixed clarified juice, causing a high degree of scaling, especially scales high in sesquioxides and silicic acid. This degree of scaling cannot be correlated with the concentrations of these non-sugars; it is caused more by the physical-chemical nature of the juices during concentrations. Clarified juices have been made deliberates either acid by the use of sulfur dioxide, or slightly alkaline by the addition of milk of lime to settling before filtration, as a corrective method to prevent either discoloration in the evaporators process or to prevent the formation of acid condensates, which can occasionally be observed in factories where acid juices are concentrated, or to improve the rate of filtration. These practices are responsible for an increase in the rate of scaling. A precipitation reaction occurs on concentration and heating after mixing and the precipitated non-sugars are partly deposited on the heating surfaces.

In the standard system of processing of juices in cane sugar mills, it is inevitable that the different types of scaling components remain in the clarified juice and that on concentration a part of these non-sugars are precipitated as incrustation on the evaporating surfaces. It is also certain when some of the components are present in high concentration that they will have a substantial effect on the rate of scaling and the composition of the scales.

The concentration of scaling components in cane sugar mills in well clarified juice depends primarily on the quality of raw material for the purification, i.e., the raw mill juice Table 8 [P. Honig, 1963].

Table 8. Nonsugar concentration clarified juice in mg per liter

Component	**Low**	**Medium**	**High**
CaO	< 300	400 – 500	> 600
MgO	< 100	100 – 200	> 200
Fe_2O_3	< 20	30 – 40	> 45
Al_2O_3	< 5	5 – 20	> 25
SiO_2	< 150	200 – 250	> 300
P_2O_5	< 30	40 – 70	> 100
SO_4	< 300	300 – 400	> 600

In the analyses of scales it is possible to determine the amount of cations and anions; for certain types of anions it is known that they can only be present in scales in combinations with specific cations. Sulfate can only be present in the scales of such evaporators as calcium sulfate, aconitates as Calcium-Magnesium aconitates, oxalate as calcium oxalate and phosphates are only present as calcium-magnesium phosphates.

When an analysis of the scale has been made and the composition is expressed in mol. eq. percentages, it is possible to describe the scale by its component compositions.

In Table 9 an example of the complete analysis of the scale of the fourth body of a quadruple effect is presented. The difference between the crystalline, micro-crystalline and amorphous components will be discussed in later.

A study of the composition of scales is a complicated analytical investigation for the staff of an operating mill. In addition, the collecting of representative samples is time-consuming, as each stop for evaporator cleaning has to be as short as possible for economic reasons, and studies to enable a better understanding of scaling phenomena are not within the normal program of the chemical control laboratory of operating sugar mills. However, these studies can be made. When it is well organized, the collecting of a sample should not take more than 20 – 25 min per vessel. The scales can be kept for analysis and study till the crop is finished; the activities of most sugar laboratories are limited between the grinding seasons, so there is ample time and opportunity for this kind of investigation.

A better understanding of scaling, of which the detailed knowledge of scale composition is a part, is useful for the staff of all sugar factories, as anything which can contribute to a reduction of the rate of of scaling or to an improvement in the efficiency of the removal of scales, as a part of the cleaning operations, is a direct contribution to the economy of the sugar mills.

Table 9. Detailed analysis of the composition of evaporator scal and the ratio of the different component classified as crystalline, microcrystalline and amorphous

					Mol. amounts scaling components per 100g				**Calculated percentages incrustation components in scales**		
Component	**Content (%)**	**Mol. Weight**	**Number of mol. eq. per 100g scale**	**Incrustation component**	**Cryst.**	**Micro. Cryst.**	**Amorp-hous**	**Mol. weight incr. comp.**	**Cryst.**	**Micro. Cryst.**	**Amorp-hous**
CaO	28.3	56	0.505	Ca-oraganates of unknown composition	0.330	-	-	90*	29.7	-	-
MgO	0.28	40.3	0.007	$(MgO)_3(P_2O_5)_2$	-	0.002	-	373	-	0.75	-
Fe_2O_3	1.80	159.7	0.011	Fe_2O_3	-	-	0.011	159.7	-	-	1.8
Al_2O_3	Trace	101.9	-	Al_2O_3	-	-	-	101.9	-	-	-
SiO_2	25.7	60	0.428	SiO_2	-	-	0.428	60	-	-	25.7
P_2O_5	9.2	126	0.073	$(CaO)_3(P_2O_5)_2$	-	0.034	-	420	-	14.3	-
SO_4	0.01	96	0.001	$CaSO_4$ 2aq.	0.001	-	-	154	0.01	-	-
Heat loss + water	34.5	-	-	-	-	-	-	-	-	-	-
oxalate $(COO)_2$	2.0	124	0.016	Ca-Oxalate (Ca) $(COO)_2 + H_2O$	0.016	-	-	182	2.5	-	-
Aconitate $C_3H_3(CO_2)_3$	6.4	171	0.037	Ca-aconitate $Ca_3(C_3H_3(CO_2)_3)_2$ 3aq.	0.019	-	-	526	10.0	-	-
Unknown org. acid residue	16.6	50*	-	-	-	-	-	-	-	-	-
Water (160°C)	9.5	-	-	-	-	-	-	-	-	-	-
									42.2%	15.1%	27.5%
Unknown (water, crystal water) 15.2% calculated specific heat conductance: 0.15 found: 0.18											

* Calculated as two-basic acid.

The system of analysis of scales can be the standard procedure for inorganic mixtures. These analyses have been described in many manuals on analytical chemistry. But even if the analysis is limited to the determination of calcium and magnesium, silicic acid, phosphate, sulfate, organates and sesquioxides, a valuable contribution is made to the knowledge of scale composition.

The components in scales of evaporators in raw cane sugar factories are always the following:

SiO_2
Fe_2O_3
Al_2O_3

Cations	Anions	organic components
CaO	P_2O_5	N x 6.25 = proteins
MgO	Sulfate	soluble in chloroform (lipids)
	Oxalate	dist. with HCl → furfurol
	Aconitate	to be determined with
	Carbonate	phloroglucine = pentosans
	Unknown acid residues	gums and pectinates

Water is held by SiO_2 and Al_2O_3. Crystallization water occurs, coupled with Ca-Mg phosphates and as $CaSO_4$ 2 aq., Ca-oxalate 1 aq., Ca-aconitate, 3aq and with unknown organic Ca salt.

4.5.1.4. Physical characteristics of scales

The classification of scales can for practical purposes be carried out to three different characteristics:

A. Physical hardness; the scale structure can be classified as:

  i. soft, easily descalable by brushing; these are primarily the scales in the first bodies of evaporators, consisting of complex organics and phosphates;
  ii. compact cohering scale with no crystalline structure, easily descaled from the heating surface and are found in the first bodies of evaporators, where

they consists of carbonates and sesquioxides mixed with relatively small amounts of complex organics, but descaleable using scraping without difficulties;

iii. compact, strongly adhering to the heating surface, difficult to remove by scrapping, non-crystalline, found in the last bodies of evaporators and consisting of a high percentage of silicic acid;

iv. crystalline, consisting of calcium sulfate (and in white sugar factories of calcium sulfate) is common and calcium aconitates; these scales can be extremely hard and are difficult to remove with manual scrapers; if these scale have to be removed mechanically completely fitting rotary scrapers are preferable to remove these scales.

B. reactivity, respectively disintegration of scales by chemical means; this classification is given in Table 10 [P. Honig, 1963] as a representative example.

Table 10. Type of scale and its removal by chemicals

Type of scale	**No. of vessel in which chiefly found**	**Method of removal by chemical agents**
Phosphate	First	Acid
Sulfate	Last	Soda and soda ash, followed by acid
Carbonate	First	Acid
Silicic acid	Last	Conc. NaOH or acid + fluoride
Sesquioxides	First and Last	Acid
Organic acids	Last	Acid
Complex organics	First	NaOH

C. Effect on the heat transfer; the aforesaid difficult scaling components have very great influence in heat conductivity. According to porosity and heat conductivity classification is given in Table 11 [P. Honig, 1963].

Table 11. Type of scale and its effect on the heat transfer

Type of scale	Category of scale	Heat transfer
Phosphate scale $\left\{\begin{matrix}Ca\\Mg\end{matrix}\right\}_m(PO_4)_n$	Microcrystalline	0.30 – 0.70
Sulfate ($CaSO_4$)	Crystalline	0.60 – 1.00
Carbonate ($CaCO_3$)	Microcrystalline	0.35 – 0.70
Silicic acid (SiO_2)	Amorphous	0.15 – 0.35
Sesquioxides (Fe_2O_3 + Al_2O_3)	Amorphous	0.30 – 0.55
Organic acids (Calcium-magnesium aconitate and oxalate)	Crystalline	0.60 – 1.00
Complex organics (pentosans, gums, proteinic substances, lipids, etc.)	Amorphous	0.20 – 0.40

Generally speaking the scales are amorphous, microcrystalline and crystalline in nature. This classification corresponds to the porosity from high to low. The distinction between crystalline, microcrystalline and amorphous scales can be made using microscopic observation $CaSO_4$ and calcium-magnesium aconites are present in scales as distinguishable crystals; microcrystals can be observed in polarized light, however amorphous fine materials have no specific optical properties. The general classification is given in Table 11.

From practical point of view the effect of the heat transfer of the amorphous scale is high. Measurements of heat transfer in scaled evaporators have demonstrated that 10 g per m^2 of silicic acid has the same effect on the heat transfer as 70 – 80g of calcium sulfate or calcium organates per m^2.

A detailed study has been made on the heat transfer of different types of scales. The specific heat transfer of a scale can be calculated

$$\lambda = \frac{(\%\ \text{mol. cryst. comp.})0.8 + (\%\text{mol. microcryst. comp.})0.4 + (\%\text{mol. amorph. comp.})0.1}{100}$$

A study with boiler scales gave a similar relationship between porosity and heat transfer of the scales as for the evaporator scales (Fig. 10)

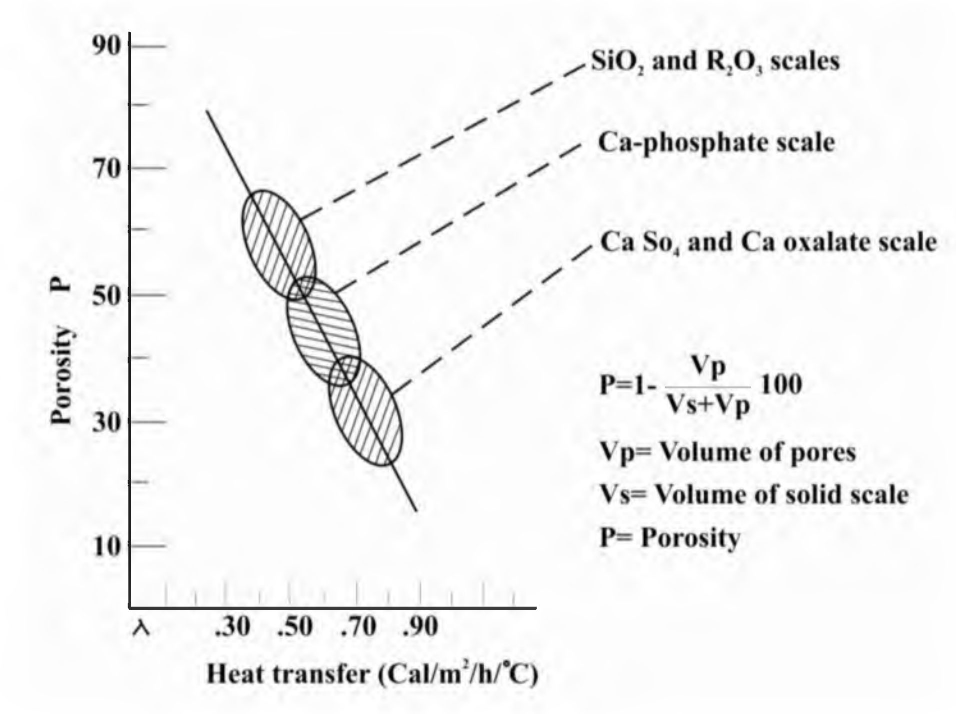


Fig.10. Relation between scale porosity and heat transfer

The above problems can be resolved with the help of:

1. Ultrasonic treatment 2. Pulse magnetic field treatment

5. Ultrasonic treatment

5.1. Ultrasound

Sound is our experience of the propagation of pressure waves through some physical elastic medium, such as air, or liquid. The pressure waves are generated as a consequences mechanical disturbance. Generally, human hearing cannot go beyond about 18 kHz, sound beyond this limit is inaudible and is defined as ultrasound [K. S. Suslick, 1988]. Ultrasound as sound above 20 kHz and up to 100 kHz can generate greater acoustic energy, and affect chemical reactivity [T. J. Mason-1988]. Up to now, the ultrasound range applied. in sonochemistry has been extended to 2 MHz. Fig.10 illustrate the frequency ranges of sound and the applied frequencies in sonochemistry.

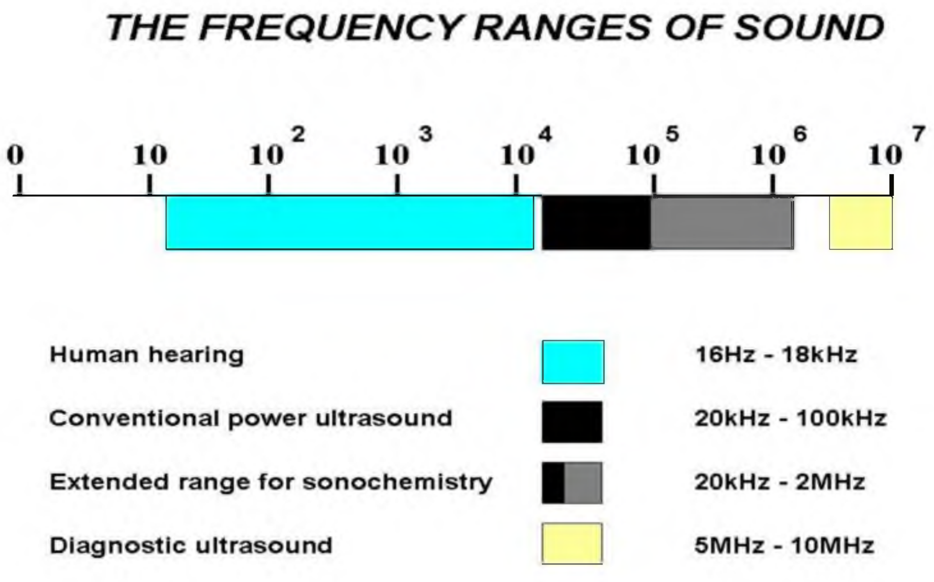


Fig.11. Frequency range of sound and its application

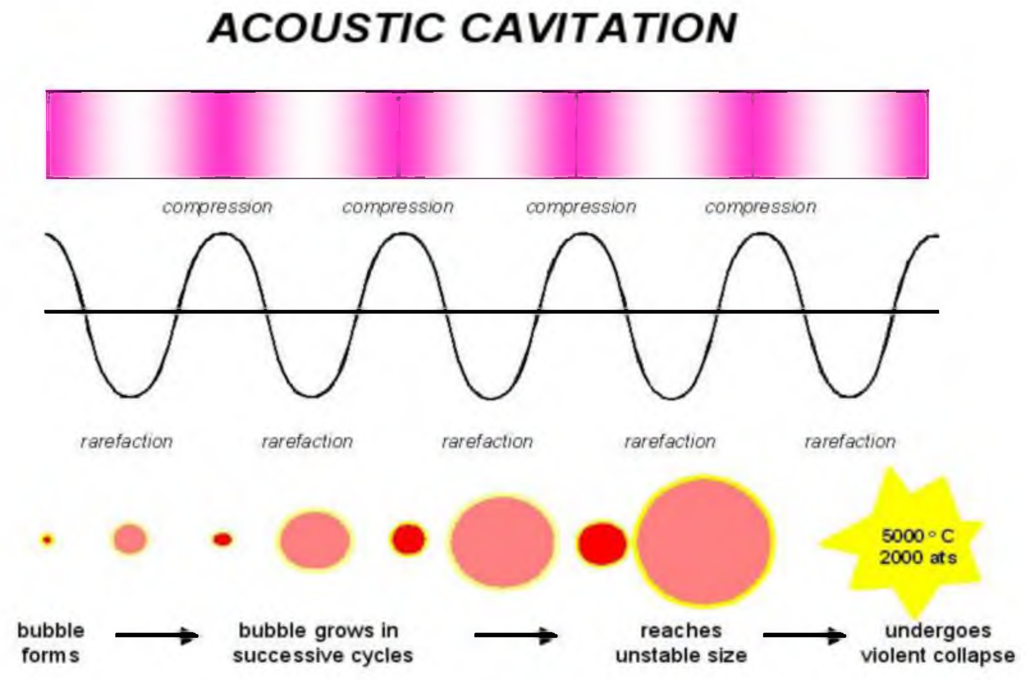
The ultrasound is used to promote or modify chemical reaction [P. W. Cains *et al,* 1998, J. L. Luche, 1998, S. V. Ley, 1989]. The first application of ultrasound on crystallization that is sonocrystallization was studied by Richards *et al,* [W. T. Richards *et al,* 1927]. Concept of application of ultrasound was extended to industrial scale. Recent advances in equipment have made its implementation on industrial scale [L. J. McCausland *et al,* 2004]. In recent year the sonocrystallization is used in the pharmaceutical and fine chemical sectors of industries where it has received further impacts with the increased focus on specificity of effect, and the corresponding requirement to prepare and purify complex chemical entities to very exacting standards.

The sonocrystallization improved the crystal of number of organic compounds such as aspartame [L. J. McCausland, 2003], adipic acid [H.W. Anderson, 1996], amino acid [Li. Hong *et al,* 2006, O. Narducci *et al,* 2012, S. Devarakanda *et al,* 2003, S. Kim, 2003] fenoteral HBr, larger molecule . Such as proteins and peptides and highly water solar or polar compounds.

Ultrasound may influence crystallization through the process of cavitations and acoustic streaming[K. S. Suslick *et al,* 1990]. Cavitation induces nucleation which provides a well defined starting point for the crystallization process.

5.2. Acoustic cavitation

Acoustical energy is mechanical energy, and it is not absorbed by molecules. When liquids are irradiated with ultrasound, it can produce bubbles, when the pressure within the liquid drops sufficiently, and lower than the vapor pressure of the liquid. This process is called "cavitation". There are various ways of producing bubbles such as turbulent flow, laser heating, electrical discharge, boiling, and radiolysis, etc These bubbles oscillate, growing a little more during the expansion phase of the sound wave than they shrink during the compression phase. Under the proper conditions, these bubbles can undergo a violent collapse, which generates very high pressures and temperatures. Fig.12 illustrates three discrete stages of acoustic cavitation: nucleation, bubble growth, and collapse in a liquid. In principle, sonochernictry derives from acoustic, cavitation [K.S. Suslick, 1988].



1

Transient cavitation: The origin of sonochemistry

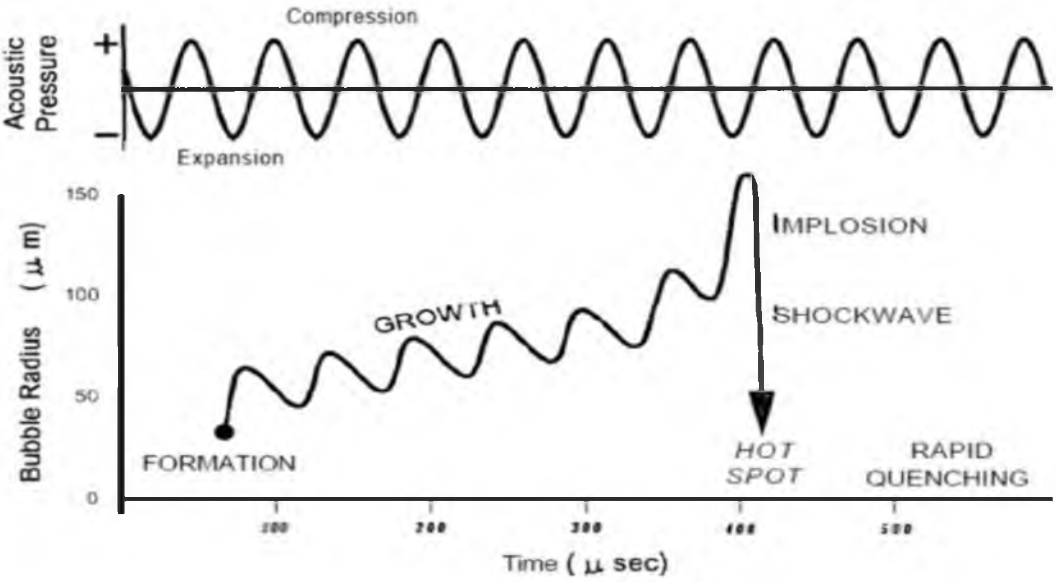


Fig.12. Germination and life of an acoustic bubble

Stable and transient are two known form of cavitation [K.S. Kaushik, 1988] stable and transient. Stable cavitation means that a bubble oscillates many times with limited change about its equilibrium radius. Whereas in transient cavitation, a short-lived bubble undergoes large excursions of size in a few acoustic cycles and may terminate in a violent collapse. Both stable and transient cavitation may occur simultaneously in a solution and a bubble undergoing stable cavitation may change to transient cavitation.

The sizes of the cavities before collapse were calculated to be about 170 µm at 20 kHz, 4.6 µm at 500 kHz, and about 3.3 µm at 1 MHz. Literature survey reveals that the bubbles are short lived, with maximum lifetimes near 0.4 µs and 10 µs at 500 and 20 kHz, respectively [K.S. Suslick, 1988, 1990, T.J. Mason-1988, A. Henglien-1987].

5.2.3. Milestones of sonochemistry

1867	Early observations of cavitation (TOMLINSON, GERNEZ)
1880	Discovery of the piezoelectric effect
1883	Earliest ultrasonic transducer by GALTON
1894	Cavitation as phenomenon recognized and investigated on propeller blades of HMS 1894 Daring (THORNYCROFT and BARVABY, Minutes of

	Proceedings of the Institution of Civil Engineers 122 (1895) 51)
1915-17	Pioneering work on ultrasonic acoustics by LANGEVIN
1917	First mathematical model for cavitational collapse predicting enormous local 1917 temperatures and pressures (RAYLEIGH)
1927	First paper on chemical effects of ultrasound published (RICHARDS and LOOMIS, J. Am. Chem. Soc. 49 (1927) 3086)
1933-35	Observation of sonoiuminescence effects
1933	Reports on the reduction in the viscosity of polymer solutions by ultrasound
1943	First patent on cleaning by ultrasound (German Pat. 733-470)
1944	First patent on emulsification by ultrasound (Swiss Pat. 394.390)
1950s	intensification of cavitation and ultrasound research, increasing number of applications using ultrasound
1950	Effect of ultrasound on chemical reactions involving metals (RENAUD, Bull. Soc. Chim. Fr. (1950) 1044)
1950	Hot spot model (NOLTINGK and NEPPIRAS)
1953	First review on the effects of ultrasound (BARNARTT, Quart. Rev. 7 (1953) 84)
1963	Introduction of plastic ultrasonic welding
1964	First monograph on physical, chemical and biological effects of ultrasound (ELPINER)
1970s	Renaissance of sonochemistry research
1980s	Growing research on sonochemical effects
1986	First ever international meeting on sonochemistry
1990	Foundation of the European Society of Sonochemistry and ESS 1 Meeting

6. Pulse magnetic field treatment

Application of suitable pulse magnetic field can significantly reduce the viscosity of sugar (molasses and massecuite) the viscosity reduction method does not change the temperature of molasses and massecuite, instead, it temporary aggregates the particle. The particle aggregation changes the rheological property of the molasses and massecuite and leads to the viscosity reduction.

The effective viscosity depends on how much freedom the suspended particles have in the suspension. The less freedom for the particle, the faster the energy dissipates and the higher the effective viscosity.

The number of experiments shows that in flow through capillary tubes the viscosity is further reduced for large suspended particles because of a tendency for large particle to migrate towards the comets of the tube. That is aggregating small particle into large one in a liquid suspension will reduce the effective viscosity. This aggregation can be realized with the help of pulsed magnetic field.

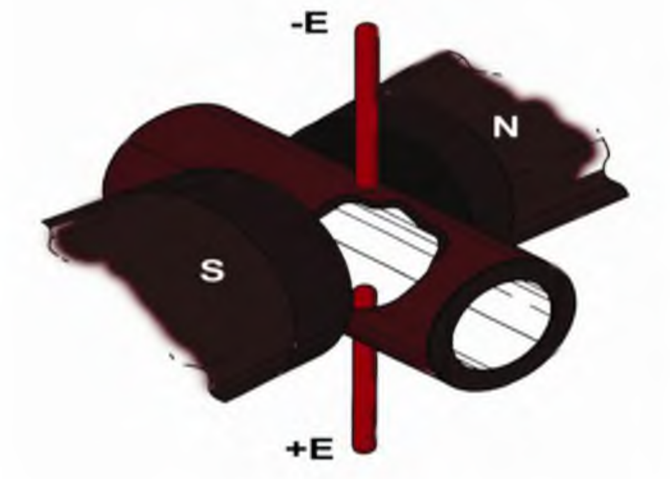


Fig.13. Pulsed magnetic field generator and cell in industrial tests

In a magnetic field, the particle are polarized along the field direction. If the particle are of uniform spheres, the dipole moment will be act on the sphere. The interaction between two induces magnetic dipoles takes place. If this interaction is strong enough to overcome the Brownian motion, the particle aggregates and align in the field direction. If this interaction is very strong, the particle quickly aggregate into macroscopic chains or columns to jam the liquid, which results in increase in viscosity.

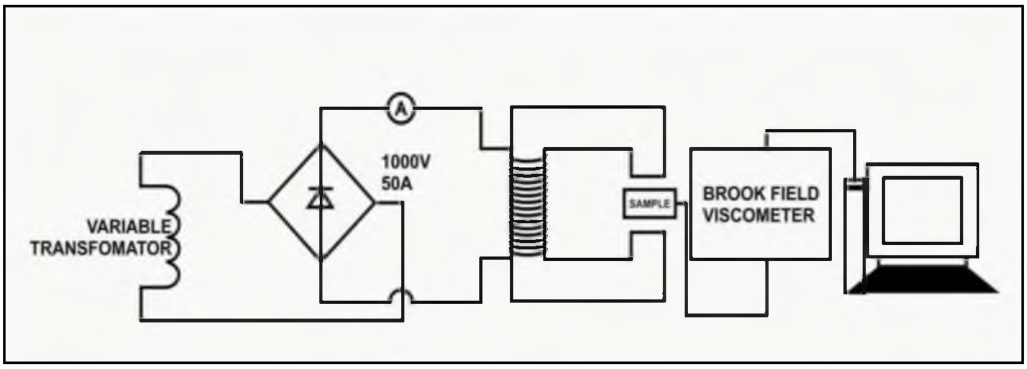


Fig.14. Magnetic circuit arrangement in the laboratory PMF tests

On the other hand, if the applied magnetic field is in such a short pulses that the dipalars interaction does not have enough time to assemble particle seprated by macroscopic distance but has enough time to assemble nearby ones together, the assembles clusters are of limited size. The aggregated particles have their size increased. During the application of the field, the viscosity changes rapidly. However, after the magnetic field is turned of, the resulting suspension has reduced viscosity.

7. Objectives and plan of work

Relevant literature survey on purposed topic has revealed that there is a need of an investigation on the effect of ultrasonics during crystallization of sucrose. The aim of proposed study is to determine the effect of ultrasonics on the sucrose crystallization from its aqueous solution. Therefore, keeping in view the aforesaid problems of the sugar industry during crystallization, we propose the following :-

I. To study the kinetics of crystallization of sucrose from aqueous solution with/without the use of ultrasonics/PMF.

II. The effect of ultrasonic on induction (latent) peried occuring on crystalization of sucrose.

III. A comparative study on kinetics of crystallization of sucrose will be studied in absence and presence of ultrasonics.

IV. The proposed work will be extended on industrial scale for improved crystallization (sonocrystalizatoin) during sugar processing.

V. The viscosity, purity, conductivity, pH and other relevant parameters will be determined before and after ultrasonics irradiation/PMF application.

VI. Thermodynamics parameters related with sonocrystallization of sucrose employing ultrasoics and PMF will be investigated.

8. Importance of the work

The proposed work has academic as well as industrial importance. Kinetic and thermodynamic data are considered to be very important in physical chemistry. Eyring equation and Arrhenius equations were not found applicable as long as induction period persists during crystallization, however, employing ultrasonics, induction period can be eliminated and in such a situation Eyring or Arrhenius equations can be applied to crystallization process. Thermodynamic parameters provide valuable information regarding any process. Hence, low values of ΔG^o and ΔS^o during crystallization can be explained, on this basis of solution and solid state structure and properties of sucrose. Additionally, the proposed work has industrial importance as to where industrial crystallization, scale formation on heating surface and control or minimization of excessive viscosity of fluids can be managed by the proposed techniques in this thesis such as ultrasonic and pulse magnetic field.

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Chapter-2

Methodology

CHAPTER - 2

METHODOLOGY

2.1 Introduction

Sonocrystallization and pulse magnetic field is carried out to overcome occurrence of induction period during crystallization of sucrose, scale formation in evaporator and reduction in viscosity of syrups such as molasses and massecuite. X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infra Red (FTIR) techniques were used to characterize the scales. Brookfield Digital Viscometer was used to measure the viscosity of the processing fluids such as syrup, molasses and massecuite.

2.2. Experimental

2.2.1. Chemicals and reagents

Sucrose B.D.H AnalaR sample was used which was dried at 60^0C in vacuum oven for 6 hrs. The sucrose content of the sample was 99.97%.

2.2.2. Preparation of solutions

AnalaR sample of sucrose was dried at 60°C in a vacuum oven for about five hours. The sucrose content of the samples was 99.97% with undetectable ash. The syrup was prepared by usual method with water of pH 7.0. Calculated quantity of sucrose to give desired supersaturation at the experimental temperature T was weighed and dissolved in water at a higher temperature (80^0C) and cooled slowly to the experimental temperature T. The supersaturation (S) was calculated according to the following formula.

$$S = \frac{\text{Weight of sucrose/Weight of solution at temprature T}}{\text{Weight of sucrose/Weight of saturated solution at temprature T}}$$

Syrup of known supersaturation was prepared and transferred carefully into the crystallizer where it was allowed to attain the constant temperature for about half an hour. The crystallizer employed in these studies was similar to the one used usually in commercial sugar factories with all the required conditions for the kinetic studies.

2.3. Various techniques for characterization

2.3.1. UV-visible spectroscopy

UV-Vis spectrophotometer uses visible light and ultraviolet to analyze the chemical structure of substance. A spectrophotometer is a special type of spectrometer, which is used to measure the intensity of light. When ultraviolet light project to various substance, they will absorb it. So, we can use UV-Vis spectrophotometer to measure the absorption of light by compound and with result, we have its molecular structure, as well as the related information.

2.3.1.2. Principle of UV-visible spectroscopy

The spectrophotometer is a much more refined version of a colorimeter. In a colorimeter, filters are used which allow a broad range of wavelengths to pass through, whereas in the spectrophotometer a prism (or) grating is used to split the incident beam into different wavelengths. By suitable mechanisms, waves of specific wavelengths can be manipulated to fall on the test solution. The range of the wavelengths of the incident light can be as low as 1 to 2 nm. The spectrophotometer is useful for measuring the absorption spectrum of a compound, that is, the absorption of light by a solution at each wavelength.

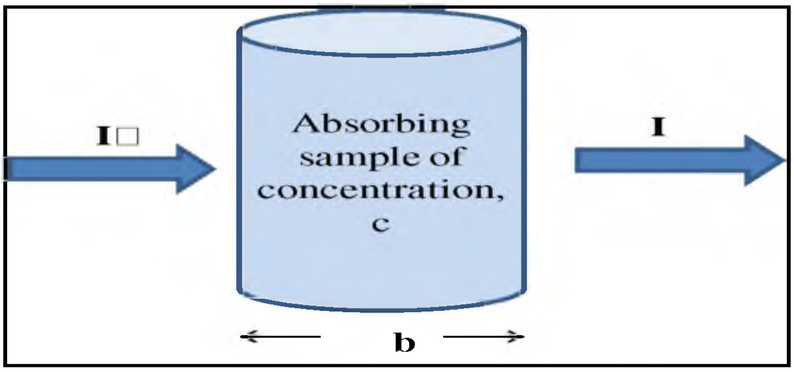

Fig.1. Absorption of light by a sample in UV-Visible Spectrophotometer

2.3.1.3. Quantitative relationships for optical spectroscopy

Beer and Lambert laws

$$A = \varepsilon bc$$

$$A = -log\,T = log\frac{I_0}{I} = \varepsilon bc$$

$$T = \frac{I}{I_0}$$

(Where A= Absorbance, I_0= intensity of incident light, I= Intensity of emitted light, = molar absorptivity coefficient , T= Transmittance, b= path length of sample,

c =molar concentration of solute)

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption.

2.3.1.4. Instrumentation and working of UV-visible spectroscopy

Instrumentation and working of the UV spectrometers can be studied simultaneously. Most of the modern UV spectrometers consist of the following parts-

Light Source

Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

Monochromator

Monochromators generally composed of prisms and slits. The most of the spectrophotometers are double beam spectrophotometers. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

Sample and reference cells

One of the two divided beams is passed through the sample solution and second beam is passé through the reference solution. Both sample and reference solution are contained in the cells. These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.

Detector

Generally two photocells serve the purpose of detector in UV spectroscopy. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

Amplifier

The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servometer. Generally current generated in the photocells is of very low intensity, the main purpose of amplifier is to amplify the signals many times so we can get clear and recordable signals.

Recording devices

Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound (Aman Thakur, 2011)

Fig.2. UV-visible spectrophotometer at DAC, BBA University, Lucknow, U.P.

2.3.2. Fourier transform infrared (FT-IR) spectroscopy

Fourier transform Infrared Spectroscopy (FT-IR) is a extremely useful technique particularly for identifying to different types of chemical bonds in a molecule of unidentified materials [P. Pandey *et al.* 2011]. FT-IR spectroscopy is a very powerful method for the identification of functional groups. In general, the goal of FT-IR Spectroscopy is to measure how well a sample absorbs or transmits light at each different wavelength. To use the FT-IR, a continuum source of light is used to produce light over a broad range of infrared wavelengths. The principal experimental method in this work is FT-IR, which allows us to detect infrared (IR) absorption and reflection properties over a broad spectral region. IR spectroscopy also known as vibrational spectroscopy, which concerned with the study of absorption of IR radiation by a molecule, causes the molecular bonds to vibrate including vibrational transition in a molecule.

FT-IR is used with the basic goal of determining changes in the intensity of infrared light as it interacts with a material as a function of wavelength. Therefore, infrared spectroscopy can applied as a very powerful tool for qualitative identification of different functional group and chemical bonds in different environment [B. C. Smith, 1996].

In FT-IR analysis there are three commonly examined pieces of data known as peak position, the peak width and the peak intensity. The peak position is probably the most commonly used for the identification of materials. These peaks are unique since, at characteristic frequencies, certain functional groups will display their own set of peaks. This is because infrared techniques measure the vibrational energies of the molecules. In order for a molecule or functional group to be IR active, the dipole moment of the molecule must change. When the desired sample for testing is opaque, transmission experiments are not practical. To overcome this problem, reflection experiments in the FT-IR become more appropriate.

When the infra-red beams enter in the sample as shown in Fig. 3. it can be reflected, transmitted or absorbed. The infra-red energy reflecting off the surface is typically lost. The infra-red beam that passes through a particle can either reflect off the next particle or to be transmitted through the next particle. Scattered infra-red energy is collected by a spherical mirror that is focused onto a detector. These are the basics of how the diffuse reflectance mode of the FT-IR works [Ronald A. Holser, 2012].

Fig.3. FT-IR at USIC, BBA University, Lucknow, U.P., India

With the help of FTIR spectra, the study of different compound formed as scale during characterization of sucrose is carried out.

2.3.3. Scanning electron microscopy (SEM)

A scanning electron microscope (SEM) is a special type of electron microscope which produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and give information about the sample's surface topology and composition. The electrons beam is generally scanned in a raster scan pattern and the beam's position is pooled with the detected signal to produce an image. SEM can achieve resolution better than 1 nm. The most common SEM mode for the detection of secondary electrons is emitted by atoms excited by the electron beam. The numbering of secondary electrons depends on the angle at which beam meets the surface of specimen, i.e. on specimen topography. By scanning the sample and collection the secondary electrons with the special detector, an image displaying the topography of the surface is created [Antonio da Costa, 2014].

2.3.3.1. Principle and working of scanning electron microscopy

Different types of signals produce by a SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, cathode luminescence (light), specimen current and transmitted electrons. In all SEM, secondary electron detectors are standard equipment but it is rare that a single machine would have detectors for all possible signals, result from exchanges of the electron beam with atoms at or near the outer part (surface) of the sample. In the standard detection mode, SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. SEM microscopes have a large depth of field yielding a characteristics three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnification is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 5, 00,000 times, about 250 times the magnification limit of the best light microscopes [C. W. Oatley et al. 1965].

BSE are the beam electrons that are reflected from the sample by elastic scattering. It is often used in analytical SEM along with the spectra made from the characteristics X-rays because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen. BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immune-labels of 5 or 10 nm diameters, which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens [K.C.A. Smith and C.W. Oatley, 1955]. Characteristics X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher-energy electron to fill the shell and release energy and used to identify the composition and quantify the abundance of elements in the sample. The ray diagram of a typical SEM with photograph has been represented by Fig. 2.4.

Fig. 4. Photograph of SEM at USIC, Lucknow, U.P., India

2.3.4. Digital viscometer (Brookfield DV-II + pro programmable viscometer)

The viscosity of a fluid is its resistance to flow [Puri, *et.al.*, 1997]. During sugar processing viscosity of molasses and massecuite play an impotant role . Viscosity of the high density intermediate process materials were recorded using Brookfield DV-II + pro Programmable Viscometer (Brookfield Engineering Laboratories, Inc. USA) which measures fluid viscosity at a given shear rates. The accuracy of Brookfield Viscometer is ± 1.0 % of full scale range with repeatability of ±0.2 %, and temperature accuracy of ±1^0C (-100^0C to +149^0C) and ±2^0C (+150^0C to + 350^0C)

Prior to measurement the viscometer was calibrated using viscosity standard fluids (Silicone oil with viscosity 1000, 30000, 50000 and 100000 cps at 25^0C). A test sample containing molasses/massecuite was taken in Griffin beaker (600 ml) and was kept in circulating water bath (TC-202) and viscosity was measured by following the catalogue directions.

Fig.5. Photograph of viscometer at L.U., Lucknow, U.P., India

2.3.5. Refractometer

The operation of the refractometer is based on the physical principle of light refraction (Snell's law). Light slows down as it passes into more optically dense media, and speeds up as it passes into less optically dense media. The change in speed is accompanied by a change in direction, and at a certain angle of incidence, the light does not refract in the second medium at all, but is entirely reflected. The angle at which this occurs is known as the critical angle, and it is this angle that the refractometer measures.

Fig.6. Photograph of refractometer at L.U., Lucknow, U.P., India

Since concentration of sucrose is linear function of refractive index hence to know sucrose concentration refractive index is noted at different time interval. Refractive index with an accuracy of ± 0.0005 was noted using digital refractometer (Anton Paar Model 300).

2.3.6. Ultrasonication

Crystallization control, one of the key operations in the food industry (sugar, juice), pharmaceutical industry (agents, vitamins) and in the chemical industry (fertilizers, salts). The solid phase will be achieved by evaporation or cooling crystallization from a solvent or a melt. Measurement and calculation of the degree of supersaturation from the sound velocity to determine the optimal point to add the seeding substances. The sucrose solution was irradiated with ultrasonic waves (20 kHz, 750 W) for 5min with help of ultrasonicater (Sonics, vibra-cell 20 kHz±50Hz, 750 W).

Fig.7. Photograph of Ultrasonicator at DAC, BBAU, Lucknow, U.P., India

2.3.7. X-ray Diffraction (XRD)

X-ray diffraction (XRD) is one of the powerful characterization tools used in solid state chemistry and material science. The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction. It is a material characterization technique that can be useful for analyzing the lattice structure of a material. The sample is irradiated with non-chromatic X-ray light and the stray radiation recorded. An important field of application is the identification of crystalline fractions in powders [B. D. Cullity *et al.* 2001]. The X-ray radiation most commonly used is emitted by copper having characteristic wavelength of the K radiation is 1.5418 Å. When the incident beam strikes sample diffraction occurs in every possible orientation of 2θ. The diffracted beam may be detected by using a moveable detector such as Geiger counter, which is connected to a chart recorder. In normal use, the counter is set to scan over a range of 2θ values at a constant angular velocity. Routinely a 2θ range of 10° to 80° is sufficient to cover the most useful part of the powder pattern. The scanning speed of the counter is usually 2θ of 2 °/min and therefore about 30 minutes are needed to obtain a trace

2.3.7.1. Basic principle of XRD

XRD analysis uses the property of crystal lattices to diffract monochromatic X-ray light. This involves the occurrence of interference of the waves scattered at the successive planes which are described by Braggs Eqn. 2.3.

$$n\lambda = 2d \sin\theta \ (n = 1, 2, 3, \ldots\ldots) \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where λ is the wavelength, n is the order of diffraction, d is the lattice plane distance and θ is the half the diffraction angle. This relation is used for the structure analysis of crystals. The basic process of XRD is shown in Fig. 2.1. From XRD pattern, we can find crystallite size of crystals by Scherrer's formula shown in Eqn. 2.3 [H.G. Jiang *et al.* 1999].

2.3.7.2. Crystallite Size Calculation

The crystallite size of particles can be calculated by suitable analysis of X-ray line broadening. Generally, in XRD pattern, diffracted lines are not always sharp and may be broadened due to instrumental factors/ or nature of the specimen (mainly crystallite size). If the particles are varied small, the lines are broader than usual. The broadening increases with decreasing crystallite size. The crystallite size of a sample could be determined using Scherrer's formula given in Eqn. 2.4 [M.T. Weller, 2001].

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \quad \text{……………………………………………………………………(2)}$$

The typical XRD pattern of scale samples was analyzed using XRD facility from Ita Lab Mumbai.

2.3.8. Pulse magnetic field treatment

Application of suitable pulse magnetic field can significantly reduce the viscosity of sugar (molasses and massecuite) the viscosity reduction method does not change the temperature of molasses and massecuite, instead, it temporary aggregates the particle. The particle aggregation changes the rheological property of the molasses and massecuite and leads to the viscosity reduction.

The effective viscosity depends on how much freedom the suspended particles have in the suspension. The less freedom for the particle, the faster the energy dissipates and the higher the effective viscosity.

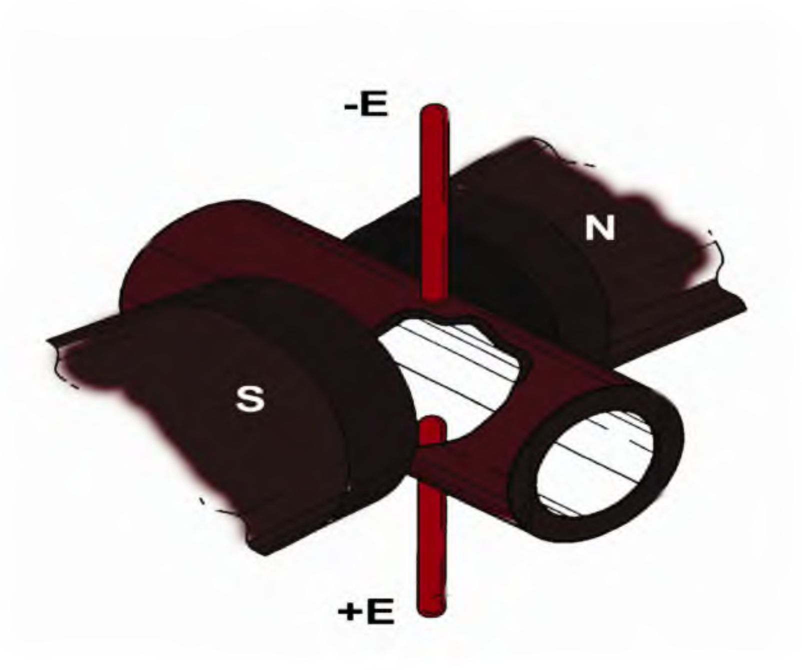

Fig.8. Pulsed magnetic field generator and cell in industrial tests

The number of experiments shows that in flow through capillary tubes the viscosity is further reduced for large suspended particles because of a tendency for large particle to migrate towards the comets of the tube. That is aggregating small particle into large one in a liquid suspension will reduce the effective viscosity. This aggregation can be realized with the help of pulsed magnetic field.

In a magnetic field, the particle are polarized along the field direction. If the particle are of uniform spheres, the dipole moment will be act on the sphere. The interaction between two induces magnetic dipoles takes place. If this interaction is strong enough to overcome the Brownian motion, the particle aggregates and align in the field direction. If this interaction is very strong, the particle quickly aggregate into macroscopic chains or columns to jam the liquid, which results in increase in viscosity.

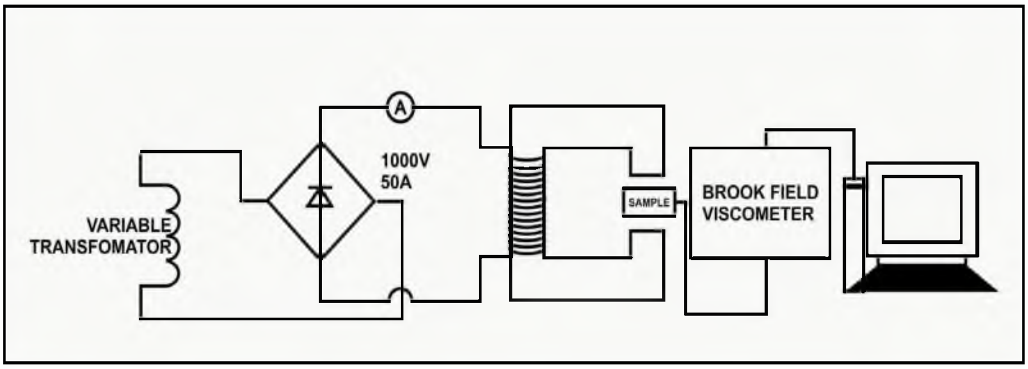

Fig.9. Magnetic circuit arrangement in the laboratory PMF tests

On the other hand, if the applied magnetic field is in such a short pulses that the dipalars interaction does not have enough time to assemble particle seprated by macroscopic distance but has enough time to assemble nearby ones together, the assembles clusters are of limited size. The aggregated particles have their size increased. During the application of the field, the viscosity changes rapidly. However, after the magnetic field is turned of, the resulting suspension has reduced viscosity.

The crystallite size of particles can be calculated by suitable analysis of X-ray line broadening. Generally

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Chapter-3

The effect of High Intensity Focused Ultrasound (HIFU) on the Kinetics of Crystallization of Sucrose: Elimination of Latent Period

CHAPTER - 3

THE EFFECT OF HIGH INTENSITY FOCUSED ULTRASOUND (HIFU) ON THE KINETICS OF CRYSTALLIZATION OF SUCROSE: ELIMINATION OF LATENT PERIOD

Abstract

The application of a technique to eliminate the latent period during crystallization of sucrose by high intensity focused ultrasound (HIFU) was investigated in this chapter. Employing HIFU (20 kHz, 750W) to crystallization of sucrose, latent period was eliminated and it was found to obey first order kinetics (K ~10^{-5} sec^{-1}) in the temperature range of 30-50°C. Employing Arrhenius equation, the average energy of activation (E_a) estimated as 5.0 kcal/mole. Traditional knowledge indicates that that crystallization is sufficiently spontaneous; however, the magnitude of "K" and other thermodynamic quantities of the process indicate that crystallization is actually a slow process. Generally, chemical reactions which posses low rate constants, need high energy of activation. On the contrary, the energy of activation is appreciably less. The energy of activation with rate constant of the order of 10^{-5} sec^{-1} could be predicted of the order of 20 kcal/mole at 27 °C. The low energy of activation for crystallization of sucrose is of interest. A very interesting elucidation can be had from neutron diffraction data and transport property of the sucrose which is discussed in details in this chapter.

1. Introduction

Crystallization of sucrose is a vital step during sugar processing on which the economy of sugar industry depends significantly. Therefore, fundamental and applied works on various aspects of crystallization of sucrose have been the subject of many research projects in the past. A review of literature reveals that the kinetic data were complex and Arrhenius or Eyring's equations were not applicable as such as long as the latent period resists. The occurrence of the latent period has long been detected during the progress of a number of chemical reactions. The presence of latent period was first observed in gaseous reactions which are generally catalyzed by different web length of light. In the photochemical combination of hydrogen and chlorine a latent period was first observed by Burgess and Chapman [C.H. Burgess *et al* 1906]. During latent period practically no change takes place. It was found that this was due to the presence of nitrogenous impurities which give rise to nitrogen chloride and inhibit the reaction. The latent period refers to decrease of rate of crystallization in the initial intervals of time leading to incomplete exhaustion of sucrose from the mother liquor. The latent period in the crystallization process presents a serious drawback especially in sugar industry where the rate of crystallization is undoubtedly hampered due to its presence which may ultimately affect the economy of the industry.

The studies on the occurrence of the latent period and mechanism during the crystallization of the sucrose have attracted the attention of a number of workers. VanHook *et al* [Van Hook, 1935] investigated the influence of seed/source ratio on the occurrence of latent period and found that, the crystal with dimension less than 0.3mm gave no latent period when used as seed. The kinetic studies initiated by VanHook [Van Hook, 1944, Van Hook, 1946, Van Hook, 1959] have been thoroughly investigated [N.A. Ramaiah *et al,* 1965 and K. Singh *et al,* 2003]. Ramaih and his co-workers reported that latent period or induction period can be eliminated by a deliberate adition of seed crystal with dimension less than 0.28 mm. However, the process of deliberate seeding seems to be cumbersome from practical point of you as it is not always easy to evaluate the correct adition point, Moreover, deliberate seeding required opera national requirement. Power ultrasound has been used in crystallization to induce nucleation [G. Ruecroft *et al,* 2005, H.W. Andersion *et al, 1995*] in many organic reactions[Li. Hong *et al,* 2006, O. Narducci *et al,* 2012, S. Devarakanda *et al,* 2003, S. Kim *et al,* 2003] however, there is a dearth of such application in crystallization of sucrose. Hence, in the present work a non chemical device; HIFU is used for its application in industrial scale for removal of latent period. In present work, we have used ultra sonic technique as it leads to reduction in latent period and process intensification in many chemical reactions.

In this chapter studied the kinetics of sonocrystallization of sucrose has been studied. This study enables us to understand the following:

(i) The extent of elimination of latent period and mechanism thereon
(ii) Order of the reaction

(iii) Specific reaction rate
(iv) Energy of activation and
(v) Thermodynamic properties

2. Significance of entropy change during crystallization of sucrose

Here we present a brief discussion on the theoretical consideration could be obtained from the data on the entropy change occurring during crystallization.

2.1. General significance

Entropy of system depends on temperature and is change with change in temperature. Entropy measures the total movement or randomness of the system. The absolute value of entropy cannot be determined practically, however; change in entropy (ΔS) due to the physical or chemical reaction in the system can be obtained from simple physical, chemical consideration. The determination of ΔS gives knowledge about the formation of new molecular species, loss or gain of various degree of freedom of motion in one molecular system. For example of any substance into or more fragments result in increased in entropy because of increased in molecular motion in the system. The movement around single and double bond also effect the entropy for example if ethylene is hydrogenated to ethane the entropy system increased.

2.2. Sucrose molecule in solution phase

Sucrose molecule shows high solubility in a queues solution. A general hypothesis is that, solute, the molecules of which can adjust themselves into the network of polar water molecules will go into the solution phase. The sucrose molecule posses a number of hydroxyl groups and the molecule can be easily solvated through hydrogen bonding with water molecules. The sucrose molecule remains surrounded by water molecules and enters into the solution phase. The number of water molecules entering into this combination through hydrogen bonding depends upon space configurational availability of hydroxyl groups. This shows that sucrose molecule, in its solution phase exist in a complex form, linked with water molecule through hydrogen bounding.

2.3. Sucrose molecule in solid phase

With the help of X-ray and neutron diffraction studies the crystalline state structure of sucrose is find out the sucrose crystal is monoclinic ($a = 10.65^0$A, $b = 8.70^0$A, $C=8.00^0$A, $\beta = 105^0 44'$). The effect of entropy on solid phase of sucrose if discussed in detail in this chapter later on.

3. Experimental

AnalaR sample of sucrose was dried at 60°C in a vacuum oven for about five hours. The sucrose content of the samples was 99.97% with undetectable ash. The syrup was prepared by usual method with water of pH 7.0. Calculated quantity of sucrose to give desired supersaturation at the experimental temperature T was weighed and dissolved in water at a higher temperature (80^0C) and cooled slowly to the experimental temperature T. The supersaturation (S) was calculated according to the following formula.

$$S = \frac{\text{Weight of sucrose/Weight of solution at temprature T}}{\text{Weight of sucrose/Weight of saturated solution at temprature T}}$$

Syrup of known supersaturation was prepared and transferred carefully into the crystallizer where it was allowed to attain the constant temperature for about half an hour. The crystallizer employed in these studies was similar to the one used usually in commercial sugar factories with all the required conditions for the kinetic studies,

The refractometric brix of this solution was initially noted. The mother liquor was withdrawn after different intervals of time and analyzed for its sucrose content. The sucrose solution was irradiated with ultrasonic waves (20 kHz, 750 W) for 5min with help of ultrasonicater (Sonics, vibra-cell 20 kHz±50Hz, 750 W). Refractive index with an accuracy of ± 0.0005 was noted using digital refractometer (Anton Paar Model 300). In all these experiments the temperature was maintained at 35 ±0.05°C.

4. Results

4.1. Effect of ultrasonic and supersaturation on latent period

Syrup of two different coefficient of supersaturation (1.08 and 1.13) were prepared during these studies. Typical set of kinetic data obtained are given in Figure 1. It is observed from the curve that the latent period invariably present at the initial interval of time (approx. 20 min). The duration of latent period can be calculated by extrapolation of the curve. This is also obtained by finding out the time up to which the first order of kinetic was not applicable.

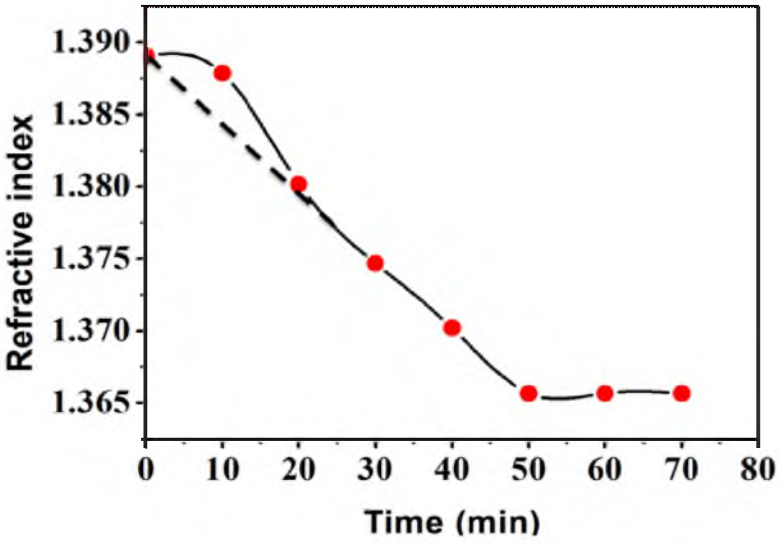

Fig. 1. Graph showing latent period during crystallization of sucrose (S = 1.08)

In another experiment, two sets of sucrose solutions with supersaturation index (S = 1.13) were taken. A solution was irradiated with ultrasonic waves (20 kHz, 750 W) for 5min with help of ultrasonicater and another was followed without treatment. The curves shown in Figure 2 clearly illustrated the occurrence of latent period (approx. 30 min) in the absence of ultrasound whereas latent period completely eliminated employing HIFU.

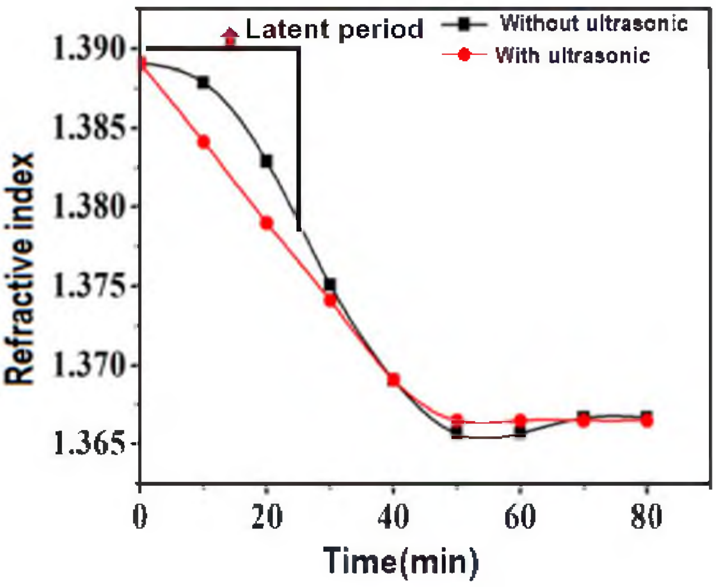

Fig. 2. Graph illustrating elimination of latent period by HIFU (20 kHz, 750 W) during crystallization of sucrose (S= 1.13)

4.2. Kinetic studies on the slow crystallization of sucrose

During crystallization, sucrose molecule does not undergo any chemical change. The sucrose molecule in solution differs from that on the crystal in respect of certain physical and thermodynamical properties. The studies on the kinetics of the reaction enable one to understand order of the reaction, specific reaction rate, energy of activation and thermodynamic properties associated with process. Kinetic studies of a process refer simply the investigation on the amount of substance undergone change at different intervals of time. Thus, crystallization of sucrose can be represented as

Sucrose (in solution) $\longrightarrow$ Sucrose (in solid phase) ……………..…. (i)

The reaction (i) refers to the deposition of sucrose molecules from the solution phase on the crystal surface. The system is obviously a heterogeneous one involving two phases; sucrose solution and solid crystal.

A sucrose solution of known concentration or supersaturation is maintained at constant temperature either stirred at desired number of revolution per min. or kept stationary. The loss in sucrose content in the solution on account of the deposition of sucrose molecules due to crystallization process at different intervals of time ‘t’ is noted by a refractometer (Anton Paar Model 300). Refractive index is a liner function of sucrose concentration if the initial concentration of sucrose is represented by ‘a’, refractometer reading recorded at varied time ‘t’, give the concentration of sucrose existing in the solution phase at time ‘t’, *viz* (a-x) where x is the concentration of sucrose underwent change at ‘t’, from law of mass action, we get.

$$dx/dt = K\,(a-x)^n \qquad \ldots\ldots\ldots\ldots\ldots\ldots(ii)$$

where n and K are the order and rate constant of the reaction, respectively.

Following the kinetics of sucrose solutions by this method, the loss of sucrose molecules from the solution phase occurs according to the following equation.

$$K = \frac{2.303}{t} log_{10} \frac{a}{(a-x)} \qquad \ldots\ldots\ldots\ldots\ldots (iii)$$

From obtained data at different sonication time the rate constant were computed and such representative data are shown in Table I.

Table 1. Data showing the values of refractive indices and rate constant of sonocrystalization of sucrose

a=1.38907

S.No.	Sonication time (min.)	(a-x)	K ($min.^{-1}$) $x10^{-3}$
1	0	1.38907	-
2	10	1.38412	**0.357**
3	20	1.37899	**0.364**
4	30	1.37408	**0.361**
5	40	1.36906	**0.362**
6	50	1.36786	0.307
7	60	1.36665	0.271
8	70	1.3665	0.232
9	80	1.3665	0.203
10	90	1.3665	0.180

Data shown in Table I clearly illustrate that during sonocrystallizaton, the validity of the application of first order kinetics was observed in the initial phase of the reaction. Such characteristics are of diffusion controlled reactions. In such reactions, experimentally measured rate is not the rate of interaction between the molecules but is, instead, the rate of diffusion.

4.3. Calculation of thermodynamic parameters

Studies on the kinetics of crystallization of sucrose in the temperature range of 30-60^{0}C enabled us to obtain thermodynamic data (Table II). Applying Arrhenius equation to these data activation energy was found as 5.0 kcal/mole (Fig.3).

The following equation due to Eyring representing the velocity constant (K) in terms of fundamental thermodynamic quantities is of interest for the consideration of its application to data of sonocrystallization of sucrose.

$$K = kT\Delta/h.\exp. \quad (\Delta S\text{-}\Delta H/T)/R$$

Where k is the Boltzman's constant; T is the absolute temperature; h, the Planck's constant; R, the gas constants, TΔS the change in entropy and ΔH is the change in the heat content of the system.

Table- II gives the values of thermodynamics quantities of crystallization of sucrose evaluated from the Eyring's equation. It is of interest to see that of these quantities, the entropy change is negative in nature and suggests the loss of degree of freedom during the sonocrystallization process.

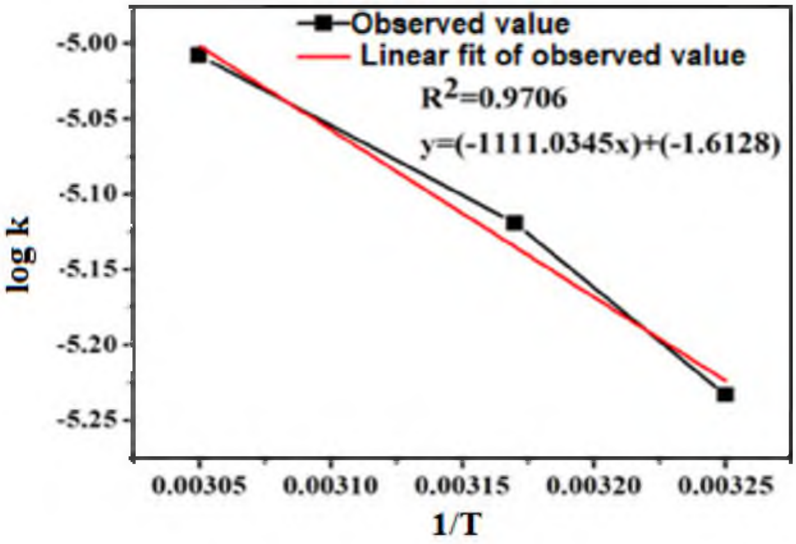

Fig. 3 Arrhenius plot for sonocrystallization of sucrose

Table 2. Thermodynamic parameters of sonocrystallization of sucrose

Temp. (K)	K (x10^{-5} sec^{-1})	ΔG (kcal/mole)	ΔH (kcal/mole)	ΔS (cal/K/mole)
308	0.5846	7.375	4.472	-9.427
318	0.7599	7.449	4.452	-9.424
328	0.9821	7.516	4.432	-9.402

5. Discussion

The magnitude of the velocity constant K ≃ 10^{-5}sec^{-1} is surprisingly of a low order as the crystallization process is thought to be very fast. For reactions with K ≃ 10^{-5} sec^{-1}, the energy of activation could be predicated to be of the order of 20.0 k cal/mole. The low value of energy of activation (5.0 kcal/mole) recorded for sonocrystallization of sucrose is of significance and throws light on the mechanism of this process. In the process of sonocrystallization, sucrose molecules do not undergo any change. The process is purely a physical reaction. The data, however, suggest that some energy, in the form of activation energy is required by sugar molecule in the solution phase before it is deposited on the crystal surface. This energy seems to be involved for the following two processes.

(i) As in adsorption process, the sugar molecule has to acquire certain amount of energy to overcome the surface barrier before it is deposited into the crystal lattice.

(ii) The sucrose molecule in solution phase remains solvated with water molecules attached by loose bonds to its many polar OH groups, A part of activation energy may, therefore be taken as the energy required to pull the loosely bound solvent molecules apart, to give isolated, unsolvated sucrose molecules as only such molecules can only be crystallized.

The process I or/ and II involve low energies and hence the low order of activation energy (5.0 k cal/mole) for crystallization of sucrose. The positive values of ΔG and ΔH further indicate the slow nature of the sonocrystallization process in accordance with low magnitude of velocity constant $K \simeq 10^{-5}$ sec^{-1}.

The low energy of activation for sonocrystallization of sucrose is of interest. A very interesting elucidation can be had from well established [G.M. Brown *et al,* 1963, 1973, C. A. Beevers, 1947] neutron diffraction data and transport property of the sucrose. The sucrose crystal is monoclinic (a = 10.65Å, b = 8.70Å, c = 8.0 Å, $\beta = 105^0$ 44'). The form in which the sucrose molecule exists in its crystal network is indicated in Fig. 4. It is of interest to note that two bonds indicated in Fig. 4 by dotted lines between H'_6 and O_5 and H'_1 and O_2 in glucose and fructose units, are due to intermolecular hydrogen bonding. The formation of these two hydrogen bonds in addition to the ether linkage (through O_1 see Fig. 4) between glucose and fructose units renders it to simulate the formation of a triple bond.

The presence of hydrogen bond network further supports the fact that solid phase conductance in sucrose [K. Singh *et al,* 2005, M.M. Szostk *et al,* 2014] and its allied crystalline products attributes to the protons of the hydrogen bond network in sucrose.

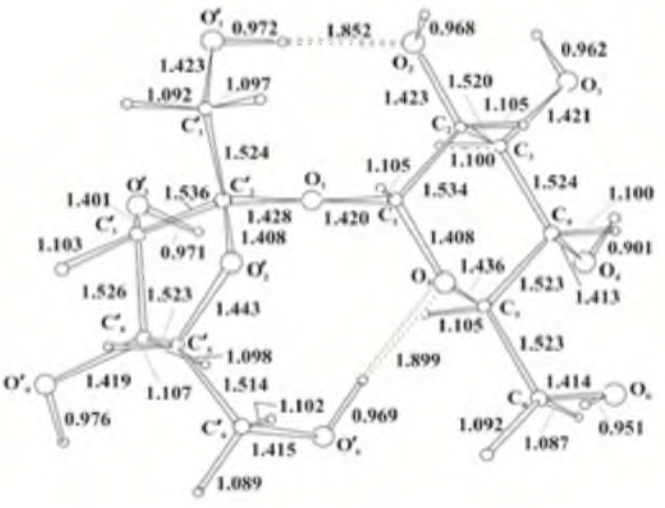

Fig. 4 Sucrose molecules in solid phase

The solvated sucrose molecules cannot be set into the crystal lattices. For this purpose these are de-solvated by breaking the hydrogen bonds with which the water molecules are attached to it and it is done at the expense of some energy by molecular collisions (activation energy, etc.) All the pure, simple and de-solvated molecules are not suited for crystallization. Only those molecules in which the rotation of glucose and fructose units around the ether linkage hydrogen atoms H'_1 and H'_6 of fructose unit near to O_2 and O_5 of glucose unit such that the hydrogen bonds referred to above can be formed. In solution state, the glucose and fructose units rotate independently around O_1 whereas in the crystalline state, the formation of the above hydrogen bonds restricts the rotational movements, consequently; reduces entropy, as actually observed in the present work.

6. Conclusion

The present study concludes that occurrence of latent period (20-25 min) during crystallization of sucrose can be eliminated by high intensity focused ultrasound (20 kHz, 750W). This aspect of the HIFU is very important from practical point of view and it can be applied to initiate and control crystallization on industrial scale and moreover, intentional seeding which is common in industrial crystallization processes could be avoided if operation is carried out under the influence of ultrasound. Furthermore, it is a non-chemical device and easy to operate as well. As long as latent period persists, observed data are not amenable to follow first order kinetics. However, crystallization of sucrose under the influence of power ultrasound was found to obey first order kinetics in the temperature range of 30-50°C. The magnitude of the velocity constant $K \simeq 10^{-5}sec^{-1}$ is surprisingly of a low order as the crystallization process is thought to be very fast. For reactions with $K \simeq 10^{-5}$ sec^{-1}, the energy of activation could be predicated to be of the order of 20.0 k cal/mole. The low value of energy of activation (5.0 kcal/mole) recorded for sonocrystallization of sucrose is of significance and throws light on the mechanism of the process. In solution state, the glucose and fructose units rotate independently around ether linkage whereas in the crystalline state, the formation of the hydrogen bonds restricts the rotational movements, consequently; it reduces entropy.

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Chapter-4

Application of Ultrasonics on Viscosity and Scale Control: An Eco-Friendly Technique for Saving Energy in the Sugar Industry

CHAPTER - 4

APPLICATION OF ULTRASONICS ON VISCOSITY AND SCALE CONTROL: AN ECO-FRIENDLY TECHNIQUE FOR SAVING ENERGY IN THE SUGAR INDUSTRY

Abstract

Excessive viscosity of the processing fluids and scale formation in evaporators are two major problems faced by the sugar technologists. High viscosity reduces the effective extraction of sucrose crystal from the mother liquor. The deposition of $CaCO_3$ which is commonly known as scale costs billions of rupees to the world wide economy. This problem has received much attention from several years; unfortunately, to date there is no effective solution yet. The first experimental evidence with proposed theory of ultrasound (US) on scale reduction or control is presented here. The SEM analysis of the scale implied that the ultrasonic treatment suppresses the formation of calcite crystals (hard) and prefers vaterite; a thermodynamically least stable (soft) polymorph. The results are consistent with the literature model of $CaCO_3$ crystallization. The laboratory experiment coupled with commercial trials is confirmed to be beneficial for process control and significant energy saving during sugar manufacturing. A complete mechanism and explanations are offered to explain the experimental results. A technique to reduce or control scale formation employing an eco-friendly technique employing ultrasonics during sugar processing is developed.

1. Introduction

1.1. Background

India is one of the leading sugar producers in the world. It is undeniably true that sugar manufacture is a mature technology. There are over 600 Sugar Mills across the country, however, in such a mature industry there is still no cost effective means [J. K. Gehlawat, 1998 and S. K. Thampy, 1999] where the undesired products can be reduced / monitored throughout the manufacturing process.

There is, therefore, an urgent need for improvement / “add on technology” in the sugar process manufacture. Any improvement in the sugar industry will result in significant benefits for a large section of rural society. The industry should be equipped to produce sugar as per domestic and global requirements with high quality through cost-effective technologies.

1.1. Problems

The two major problems [J.C.P. Chen, 1985] faced by the sugar technologist are (a) excessive viscosity of the processing fluids and (b) scale formation in evaporators

High viscosity reduces the effective extraction [J.C.P. Chen, 1985] of sucrose crystal from the mother liquor (industrial terms: massecuite and molasses). The viscosity of the mother liquor increases abruptly when low purity massecuite is cooled, and at the minimum temperature sucrose crystals cannot be separated effectively from molasses in the centrifuge. The option to reduce the viscosity of the massecuite is either by dilution or by heating the massecuite sufficiently to lower its super-saturation. However, dilution of the molasses leads to the loss of sucrose crystals due to its high solubility, whereas, heating of the massecuite may lead to sucrose loss due to inversion.

Scale formation / scaling is defined as the precipitation of undesired solid materials such as $CaSO_4$, $CaSiO_3$, $Ca_3(PO_4)_2$, $CaCO_3$, CaC_2O_4, and other minerals at phase interface [W.O.S. Doherty, *et al*, 2008]. In sugar industry, this occurs on the heat exchanger surfaces of the heaters, evaporators and pans. As a results of the progressive accumulation of scale on heating surfaces, the heat transfer coefficient (HTC) considerably declines with time causing significant economic losses [P. Honig, 1963]. The magnitude of this problem may be realized by considering that scale can cause degradation or complete failure which increases initial and operating cost. Poor conductivity of a 25 mm thick $CaCO_3$ scale layer can decrease heat transfer [J. Glater, *et al.* 1980] by 95% whereas a SiO_2 scale layer 0.5 mm thick result in a 90% decrease in heat transfer [J.F. Grutsch, *et al.* 1984]. It has been well established [Federal Technology Alert, 1998] that 1 mm scale thickness is equivalent to 8-10 % more energy loss and furthermore, a huge amount of chemicals used for cleaning and their subsequent effect on the environment are major issues in today's context. In 1997, British National economic losses were estimated at 1.0 billion pounds [A. Hu, *et al.* 2006] due to increase of energy and decrease of production capacity resulting from scale in sugar industry.

The above literature clearly illustrates that while the aforesaid problems have received much attention for several years, unfortunately, to date there is no effective solution yet. To reduce or control scale formation, various options [N.O. Schmidt, 1954, N.O. Schmidt, 1958, C. Frank, *et al,* 1996, S. K. Gupta, *et al,* 2006, K. Singh, *et al,*. 2009] have been tried, however, reliable solution is not achieved till date. The use of ultra sound has been reported [A. Hu, *et al,* 2006, Hai-Qin Lu, *et al,* 2005, Tai-qiu Qiu, *et al,* 1999, G. J. Peric, *et al,* 2011] as beneficial for scale control and improvement in HTC and evaporation efficiency. The factory management informed us that the HTC on the evaporators were low and scale problem was very serious and lots of chemical had to be used to clean the bodies and hence, the shut-down frequency had increased. Therefore, we decided to employ ultrasonic device in the industry scale to evaluate the application and potential of ultrasound to reduce or control viscosity and scale formation during sugar manufacture.

1.1. Mechanism of scale occurrence

The calcium in solution is derived either from dissolution from natural resources, or from chemical deliberately added during clarification of juice. $CaCO_3$ becomes less soluble at higher temperatures and on heating, CO_2 escapes favoring the bicarbonate decomposition reaction which causes $CaCO_3$ to precipitate.

The reactions in the formation [J. Peric, *et al,* 1996] of $CaCO_3$ can be straightforwardly represented as:

$$2HCO_3^- \longrightarrow CO_3^{2-} + CO_2 + H_2O \qquad (1)$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3 \qquad (2)$$

Although, this is a simplification and initial precipitation proceeds via an intermediate precursor solid. When CO_2 is bubbled through the solutions, reaction 1 will be retarded and so the precipitation will be slower, as observed.

2. Working principles

The equipment consists of three components: ultrasonic generator, ultrasonic transducers and reaction vessels. Transducers can endure a high temperature (110–115^{0}C) and protect themselves automatically. Due to its special design, the equipment system can run for a long time. Under the influence of ultrasonic cavitation, the induction period of nucleation of a various materials that form scale is shortened, thus crystal scale nuclei are produced in a short time. A large proportion of the non-sugars, especially inorganic or organic impurities, can be deposited onto the nuclei, instead of on the surface of the heating tubes. These deposits remain suspended in the sugar solution, and flow out of the evaporators with the syrup. They can then be separated from it. Thus the amount of precipitate deposited onto the surface of evaporator tubes can be greatly reduced.

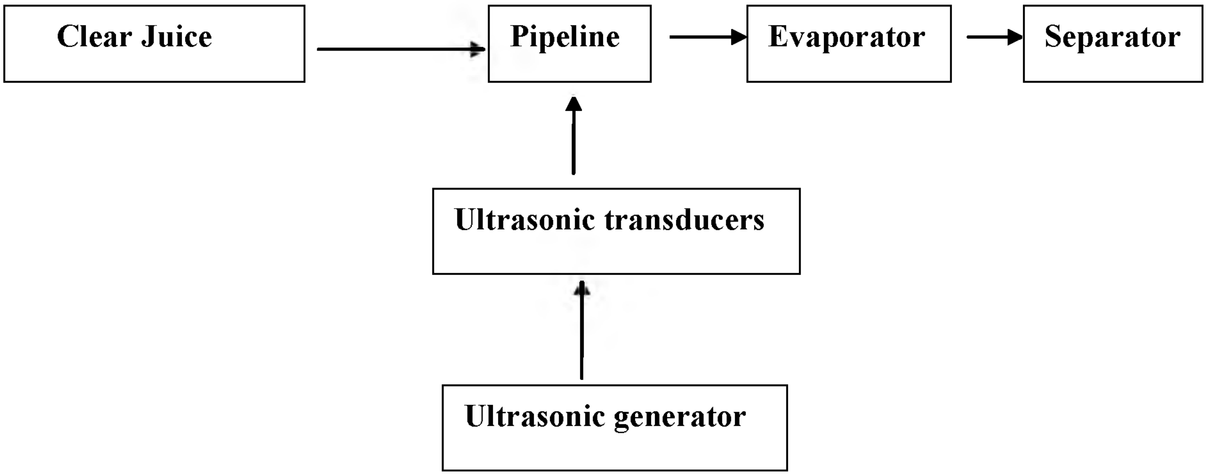

Fig. 1. Flow chart showing installation position of ultrasonic equipment at a sugar factory

Since, H.T.C. and viscosity is related [A. Hu, et al 2006] as $K \alpha a\mu^{-x}$ (K is H.T.C., "a" is heat conductivity coefficient and μ is solution viscosity, x varies from 0.25 to 0.60). Therefore, H.T.C. and evaporation rate (ER) increases as the viscosity of the syrup declines. As a result of the E.R. and H.T.C. being improved by ultrasonic treatment, the residence time of the syrup in the evaporators is reduced, and the sucrose losses due to inversion decreases. Similar mechanism has been suggested by [A. Hu, et al 2006].

3. Experimental

3.1. Viscosity measurement

Viscosity of the high density intermediate process materials were recorded using Brookfield DV-II + pro Programmable Viscometer (Brookfield Engineering Laboratories, Inc. USA) which measures fluid viscosity at a given shear rates. The accuracy of Brookfield Viscometer is ± 1.0 % of full scale range with repeatability of ±0.2 %, and temperature accuracy of $\pm 1^0C$ (-100^0C to $+149^0C$) and $\pm 2^0C$ ($+150^0C$ to $+ 350^0C$)

Prior to measurement the viscometer was calibrated using viscosity standard fluids (Silicone oil with viscosity 1000, 30000, 50000 and 100000 cps at 25^0C). A test sample containing molasses/massecuite was taken in Griffin beaker (600 ml) and was kept in circulating water bath (TC-202) and viscosity was measured by following the catalogue directions.

3.2. Laboratory scale experiment

$CaCO_3$ synthesis: All the materials used were of A. R. grade. Calculated amounts of $CaCl_2.2H_2O$ and $NaHCO_3$ were dissolved in 250 ml distilled water to obtain 0.01 M $CaCl_2$ and 0.02 M. The CO_2 gas was bubbled through the solution for 10 min. Hence, this solution was irradiated with ultrasound employing 20 kHz. During sonication, the temperature of the bulk solution was maintained at 75^0 C. The precipitates was recovered by vacuum filtration through a 0.45μm milli pore filtration assembly, washed twice with distilled water, once with acetone, and dried in air at 80^0C. The same procedure was repeated for $CaCO_3$ precipitation without ultrasound treatment. The crystals were examined by scanning electron microscopy (SEM) technique.

3.3. Investigation on scale formation

Investigations on scale control by ultrasonic sonication were monitored in the evaporator bodies.

3.4. Chemical analysis of the scale samples

The chemical analysis of the representative samples of scale deposited onto different evaporator bodies were done from Ita lab Private Limited (Industrial Testing and Analytical laboratories, Mumbai, India).

3.5. Scanning electron microscopy (SEM) of scale samples

Particle morphologies were studied using a LEO 430 scanning electron microscope (Cambridge U.K.). Sample was mounted on aluminum stub with the help of double sided tape. Mounted stubs were coated with gold palladium for analysis using a Polaron sputter coater. This faculty we availed from Birbal Sahni Institute of Palaeobotany, BSIP, Lucknow, India.

4. Results and discussions

4.1. Influence of ultrasonics on viscosity of molasses and massecuite

The ultrasound seems to have tremendous effect on viscosity of the fluids. Mother liquor is a mixture of many different constituents with high viscosities which is mainly due to suspended particles. Tables1and 2 illustrate that the mother liquors were considerably less viscous when ultrasound was applied than when it was not. The viscosity of ‘C’ massecuite (Table 1) and final molasses (Table 2) was reduced by 30-40% by application of the ultrasound.

Table 1. Comparative data (average of the analysis of 15 days)

Parameters	**Mixed juice**		**Clear juice**		**Unsulphured. Syrup**		**C-Massecuite**		**Final molasses**	
	WITH US	WOT US	WITH HUS	WOT US	WITH US	WOT US	WITH US	WOT US	WITH US	WOT US
pH	5.15	5.05	7.11	6.95	6.46	6.29				
Brix*	16.04	16.09	15.85	15.96	59.42	52.22	101.57	101.71	90.50	90.22
Pol%	13.80	13.98	13.68	13.90	53.49	45.43	48.46	50.33	28.65	30.40
Purity	86.04	86.88	86.33	87.13	90.03	87.00	47.71	49.49	31.66	33.70
R.S.%100Bx	3.69	3.82	3.78	4.08	3.96	4.39				
CaO	823	869	1213	1386						
Apparent viscosity (cp)							67154	98756	1476	2256
Temp. ^{0}C							48.5	48.5	50.2	50.2
% exhaustion molasses									62.66	59.90

SK= Semi-kistner

The other important finding of the present investigation recorded was the reduction in final molasses purity which is an indication of sugar recovery. Reduction of viscosity (massecuite and final molasses) to the aforesaid magnitude indicates that the evaporator efficiency (EE) of the centrifuge and HTC would also increase.

Average of 5 determinations

*Brix of A-M/c-94-96, B-M/c-96-98 and C-m/c-100-101. The brix spindle is calibrated on the basis of sucrose content in the standard sugar solution. In the C-massecuite non sugar are more than the A and B Massecuite. Hence C-m/c is having higher brix in the range of 101. This is due to non sugars having different property than the sucrose.

4.1. Characterization of scale

(i) Physical examination: Examining the physical characteristics of scale revealed that the scale after US treatment was found to be loose, soft sludge type and white in color after being dried. It could be easily removed without brush. However, the scale without treatment was dense, hard and yellowish in color after drying. It could not be removed completely even by a cutter. Therefore, not only could the scale be reduced significantly, but its physical character was changed by US treatment. Thus, US treatment enhances the operational time of the processing units by reducing labor cost, chemicals consumption and time used to clean up the evaporators.

(ii) Chemical analysis: The factory management informed us that the HTC of the evaporators were low and scale problem was very serious and lots of chemicals had to be used to clean the bodies and hence, the shut- down frequency had increased. Therefore, we decided to analyze the scale samples and such representative data without US treatment are shown in Table 1 which clearly indicates high percentage of the main contributors towards scale formation. Due to high percentage of these contents, the probability of precipitation of salts in the insoluble form has increased. One interesting observations recorded was that of the occurrence of silica in scale deposits. Silica exists naturally in cane sugar and enters into the juice and through absorption of water. The chemical analysis of the scale showed that the silica was found to be as much as 18.78, 30.6 and 43.54, respectively, at E-2, E3 and E-4 body, respectively. It is suspected that the source of this abnormal silica could be its route from impure lime used in clarification process. The physical examination of lime revealed that it contained much sand with un-burnt stone. Further chemical analysis of the lime shown in Table 2 showed that presence of silica was 2.45%. It is, therefore, recommended that the lime used in clarification should be free from silica. The nature of silica is that it is soluble in higher temperature (at the temperature of clarified juice or at the temperature of SK). Therefore, it remains in the soluble form at SK and E-1 body temperature (high temperature range), however, in the E-2 and E-4 body ($\approx 60^0$C in the last vessel), silica starts to coagulate and deposits as hard scale

Table 2. Analysis of scale from different evaporators (analysis of dry basis) (without US treatment)

Sr. No.	Parameters	Result (% by wt.)					
		Scale sample					
		Vapor cell	SK	E-1	E-2	E-3	E-4
1	Physical appearance	Gray colour material	Dark brown colour material	Faint brown colour material	Off white colour material	Off white colour material	Off white colour material
2	Moisture	36.82	32.65	36.89	54.16	41.05	37.64
3	Loss on ignition	19.85	17.80	20.88	15.06	18.30	13.86
4	Calcium (as CaO)	42.06	43.74	36.45	37.01	33.64	23.55
5	Magnesium (as MgO)	2.0	1.6	Not detectable	0.1	4.0	1.3
6	Sulphate (as SO_4)	2.4	4.0	2.0	9.6	10.2	9.6
7	Phosphate (as PO_4)	20.74	27.99	18.84	4.86	1.25	1.36
8	Iron (as Fe_2O_3)	0.3010	0.4808	0.399	0.0817	0.156	0.255
9	Silica (as SiO_2)	1.14	1.13	2.74	18.78	30.6	43.54
10	Sodium (as Na_2O)	0.483	0.805	0.866	0.15	1.87	0.6
11	Potassium (as K_2O)	0.044	0.024	0.072	0.050	0.1008	0.0072
12	Chloride (as Cl)	0.04	0.04	0.06	0.08	0.1	0.12

Table 3. Analysis of lime

Sr. No.	Parameters	Results (% by wt.)
1	Total calcium (as CaO)	88.47
2	Magnesium (as MgO)	1.85
3	Ash	96.98
4	Iron (as Fe_2O_3)	0.179
5	Silica (as SiO_2)	2.45

4.3. SEM analysis

4.3.1. Laboratory scale study

The SEM images shown in Fig. 2-4 clearly demonstrated that the application of a PUS reduced calcite crystal growth, changes in the nature, the morphology or the size of calcium caronate. It is clear that a large amount of calcite and aragonite were present in the absence of ultrasonics and there seems to be a transformation of calcium carbonate. If we compare SEM images of PCC it was clear that a large amount of thermodynamically least stable vaterite is formed after treatment. The SEM images reveal that in the absence of treatment, the scale sizes were various and much larger compared with PUS treatment. Thus, application of PUS plays a crucial role in changing the nature of PCC from hard (calcite) to soft (vaterite) which is easily de-scalable.

4.3.2. Industrial scale study

All samples of scale show different particle sizes and pore sizes as samples were characterized by the SEM analysis which revealed the presence of silica that may introduced into juices through lime as evidenced in our analysis of a representative sample of lime. Scale deposits were found soft and loose after ultrasonic treatment. For comparison, SEM picture of standard $CaCO_3$ was taken which indicated that the crystal structure transforms from a compact stick-shape to a loose shape so that the scale can be washed away easily instead of being deposited on the heat transfer surface. Scale layer of deposited $CaCO_3$ obtained in the experiment without sonic treatment is denser and thicker than that with treatment. The SEM analysis of the scale implied that the ultrasonic treatment suppresses the formation of calcite crystals (hard) and prefers vaterite; a thermodynamically least stable (soft) polymorph [W. Z. Ostwald, 1897, T. Threlfall, 2003, E. Dalas, 2000, G.T. Zhou, *et* *al.* 2010]. Thus by US, precipitates predominating vaterite were recorded. The results are consistent with the literature model [G. J. Peric, *et al.* 1996, 2001, E. Dalas, 2000, G.T. Zhou, 2010] of $CaCO_3$ crystallization Pure $CaCO_3$ is found in three general forms, i.e. vaterite, calcite, and aragonite with calcite being the major constituent in $CaCO_3$ scale. Solid calcite is less soluble than vaterite as mentioned in following table.

Scale form	**K_{sp} at 25^0C**	**Stability**
Calcite	3.3×10^{-9}	Highest
Aragonite	4.6×10^{-9}	Intermediate
Vaterite	1.2×10^{-8}	Lowest

In accordance with Ostwald's Law of Stages [W.Z. Ostwald, 1897, T. Threlfall, 2003] the initial phase formed on precipitation is least stable that is vaterite. The vaterite then transforms into calcite by a dissolution-recrystallization process. The activation energy for the solid state transition of vaterite to calcite is 252.8 +48.7 kJ mol^{-1}. Therefore, it does not seem that the vaterite-calcite transition would occur by a different mechanism.

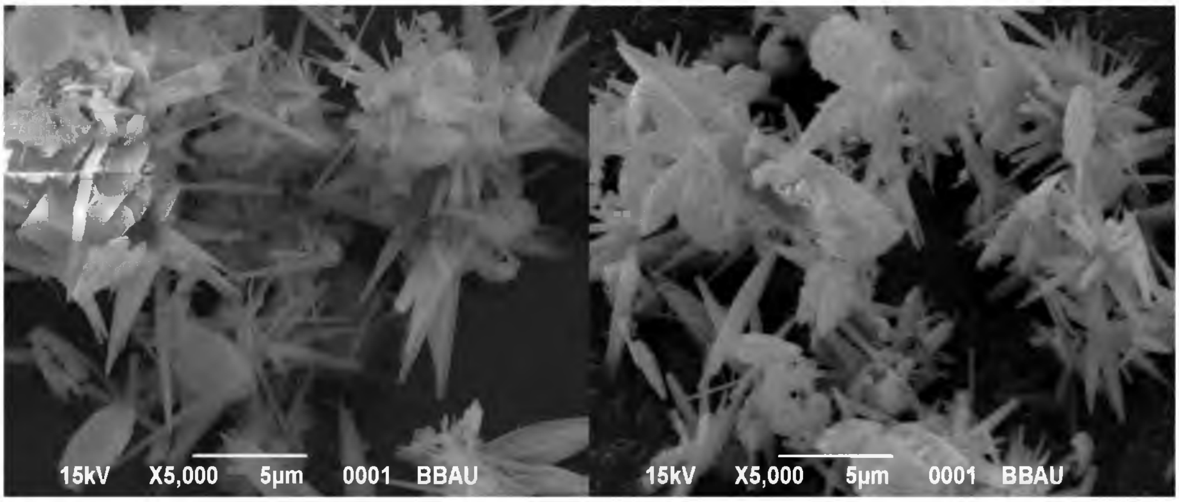

Fig.2. Typical SEM images of untreated and treated (PUS) calcium carbonate at pH 5.5

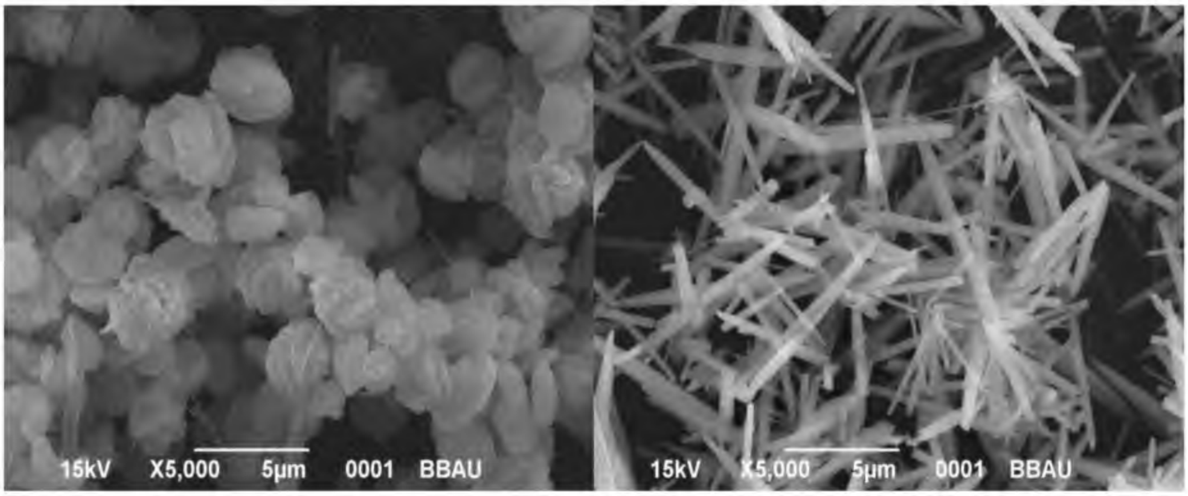

Fig.3. Typical SEM images of untreated and treated (PUS) calcium carbonate at pH 6.5

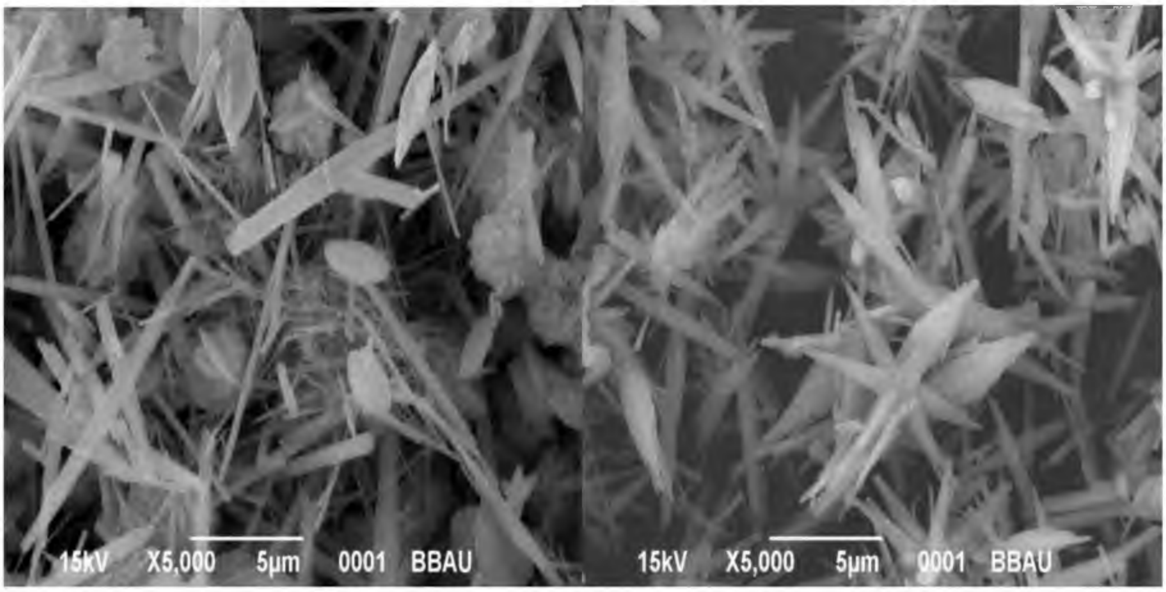

Fig.4. Typical SEM images of untreated and treated (PUS) calcium carbonate at pH 7.5

4.4. FT-IR spectra

FT-IR is incredibly simple spectral finger print for the identification of carbonate polymorphs (Wang *et al.* 1999, Lote *et al.* 2003). The FT-IR spectra of the PCC are shown in Fig. 5-6. There are significant differences in the IR spectra. The FTIR spectrum of the precipitated calcium carbonate (PCC) samples after PUS treatment presents the characteristic absorption peaks of vaterite at 1112 and 1134 cm^{-1} . (White, 1974; Zhou *et al.*, 2004). No characteristic peaks belonging to calcite at 713 and 876 cm^{-1} were detected after PUS treatment. However, partial characteristic peaks belonging to aragonite were appeared after treatment at 649 cm^{-1}.

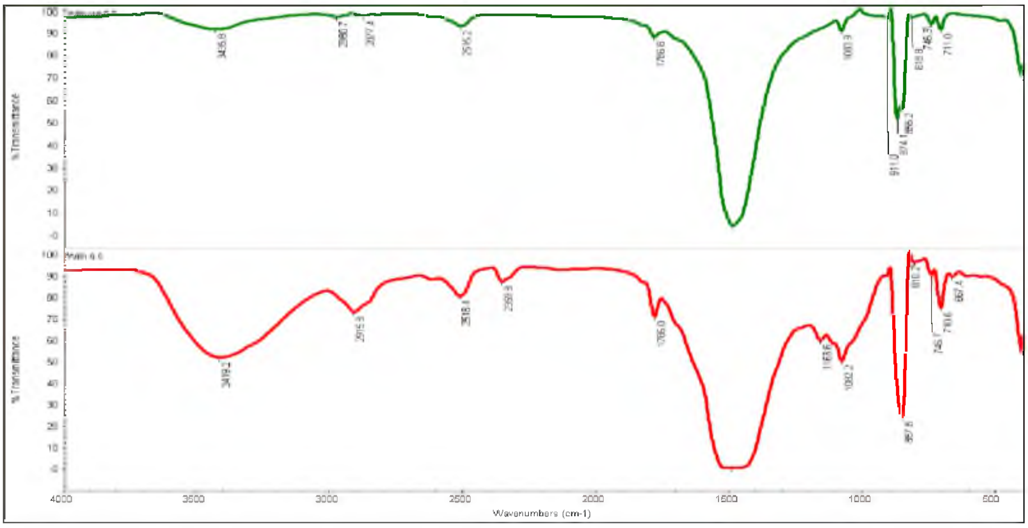

Fig.5. Typical FTIR spectra of untreated and treated (PUS) calcium carbonate at pH 5.5

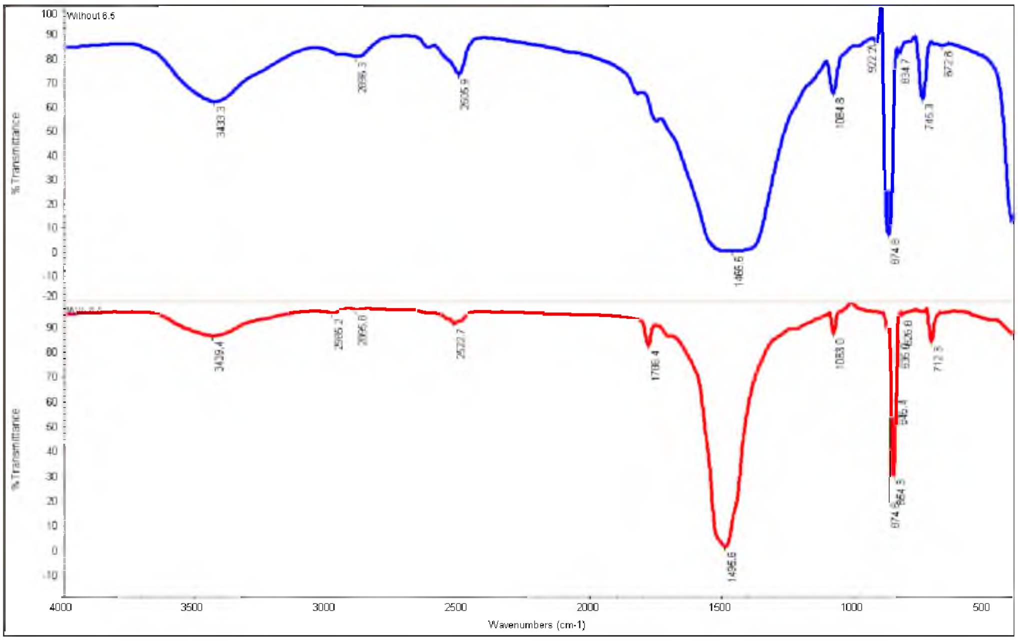

Fig.6. Typical spectra of treated and untreated (PUS) calcium carbonate at pH 6.5

4.5. Influence of ultrasound on the efficiency of scale removal

In order to examine the efficiency of scale removal, heating tubes (two numbers) were used for sampling before the evaporators were cleaned. The scale deposited on the heating surfaces were collected, examined, dried and weighed. The efficiency of scale removal in percentage was calculated as follows:

$$\frac{Scale\ weight(g.\ without\ UST) - Scale\ wieght(g.\ with\ UST)}{Scale\ weight\ without\ UST} X100$$

To compare time of cleaning of scale with and without treatment, time spent on cleaning the two sampling tubes and evaporators were chosen. It was observed that the scale deposition in evaporator E-2 and E-4 were highest. It was found that time spent in removing scale on tubes of evaporator was significantly less with ultrasound to that of without treatment. Such representative data are shown in Table 4.Thus, it requires less labour and time to clean up the evaporator when ultrasound was in operation.

Table 4. Comparison of time spent on de-scaling evaporator scale

Evaporator No. (E.N.)	Evaporator Heating Area (EHA) in m2	Evaporation Time (ET) in days	No. of people in time	
			Without ultrasound (person x time h)	With ultrasound (person x time h)
Vapor cell	2500	14	5X2.5	5X1.4
SK	2300	12	5X1.8	5X1.0
E-1	1670	8	5X2.5	5X2.0
E-2	1500	8	7X2.2	7X1.5
E-3	1100	7	7X2.3	7X1.9
E-4	750	7	6X2.4	6X1.6

Remarks: Person x time = 5x2.0 means 5 person spent 2 h on removing scale deposit on all heating tubes of the evaporator, the cabers were expressed in the same manner.

4.6. Influence of ultrasonic (US) on the use of chemicals on cleaning

One of the most important advantages of Ultrasound found was the significant reduction in chemical consumption for cleaning. The time between evaporator cleaning increased to 21-24 days (with treatment) from 10-12 days (without treatment). The use of sodium hydroxide and hydrochloric acid and disposal costs were found to be reduced by 55-60%.

4.7. Quality Assurance and Quality Control (QA & QC)

The quality of the end product was found improved by the sonic treatment. Since, quality of sugar is determined as per ICUMSA protocol [ICUMSA Methods

Book, et al 2009] and quality parameters of sugar produced after treatment were all within white sugar specifications. Such representative data have been shown in Table 5. The colour and sulfur contents were found to reduce by employing ultrasound.

Table 5. Effect of UST on quality assurance and quality control (QA & QC)

S. No.	Test parameters	S-30		M-30		Test method
		WOT Ultrasound	With Ultrasound	WOT Ultrasound	With Ultrasound	
1	Colour, IU	94	80	102	84	GS 2/3-10 (2007)
2	Moisture, %	0.038	0.030	0.040	0.033	GS 2/1/3/9-15 92007)
3	Cond. Ash, %	0.051	0.034	0.054	0.036	GS 2/3-17 (2002)
4	SO_2, ppm	15.85	9.15	16.45	10.79	GS 2/1/7-33 (2005)
5	R.S, %	0.019	0.014	0.022	0.013	GS 2/9-6 (2007)

5. Conclusion

Industrial application of ultrasound in sugar processing leads to the following important conclusions:

(a) Viscosity of massecuite and final molasses was reduced by 30-35%.

(b) Changes the physical configuration of the scaling from hard, dense to soft, porous sludge type.

(c) The SEM analysis of the scale implied that the US treatment suppresses the formation of calcite crystals (hard) and prefers vaterite; a thermodynamically least stable (soft) polymorph. The results are consistent with the literature model of $CaCO_3$ crystallization.

(d) Chemical consumption to clean and descale the evaporators was reduced significantly.

(e) Time to clean up the evaporators and labour cost is reduced significantly

(f) Colour and sulphur contents were found to reduce.

(g) The laboratory experiment coupled with commercial trials is confirmed to be beneficial for process control and significant energy saving during sugar manufacturing.

(h) The theory proposed here is consistent with the experimental results.

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Chapter-5

Application and Potential of Pulsed Magnetic Field (PMF) in Controlling Scale Formation in Cane Sugar Processing

CHAPTER - 5

APPLICATION AND POTENTIAL OF PULSED MAGNETIC FIELD (PMF) IN CONTROLLING SCALE FORMATION IN CANE SUGAR PROCESSING

Abstract

The deposition of calcium carbonate commonly known as scale costs billions of dollars to the world wide economy. This is also a customary problem for cane sugar processing across the world. The present work is essentially an extension of our earlier work on the effect of pulsed magnetic field on cane molasses and massecuite. A suitable magnetic field pulse can effectively reduce scale formation and also changes the nature of the scale formed. Examining the physical characteristics of scale samples revealed that the scale after PMF treatment was found to be loose, soft sludge type and easily de-scalable. The FTIR spectrum of the scale samples after PMF treatment presents the characteristic absorption peaks of vaterite at 1112 and 1134 $cm^{-1.}$ No characteristic peaks belonging to calcite at 713 and 876 cm^{-1} were detected after PMF treatment. However, partial characteristic peaks belonging to aragonite were appeared after treatment at 649.4 cm^{-1}. The Scanning Electron Micicrograph (SEM) image clearly demonstrates the vaterite image after PMF treatment. Thus, application of PMF plays a crucial role to sugar evaporators changing the nature of scale from hard (calcite) to soft (vaterite) which is easily de-scalable.

1. Introduction

During manufacturing of sugar, unwanted materials are deposited as scale on the heating surface of evaporator tubes in sugar factories. Scaling in the tube during operation of factories is mainly due to.

(i) When water evaporates the concentration impurities in sugar solution increases is the concentration of impurities exceeds their solubility, they have tendency to be deposited an evaporating surface, thus forming scale.

(ii) Colloids in sugar solution are also responsible for scale. Colloids such as silica dioxide, pectin, iron oxide etc. can agglutinated and forming scale.

(iii) Non sugar in sugar solution such as bicarbonate and bisulphite decomposes and forming in soluble carbonated or sulphite.

(iv) Various non-sugars may interact forming scale for example dissolved calcium and carbonate interacts to from precipitate of calcium carbonate.

The main cause of scaling is deposition of calcium carbonate on evaporator body. In our research work we concentrate only on this.

Calcium carbonate is one of the most common minerals in nature. Calcium carbonate occurs in three main crystal polymorphs, calcite, aragonite and vaterite. Among these, calcite, have rhombohedra shape and is most thermodynamically stable. Aragonite have needle- like orthorhombic crystal and is favored at high temperatures and pressure. It is metastable slowly converts into calcite. Vaterite have pregnable crystal and is thermodynamically least stable polymorph. Vaterite is rarely seen in the naturally occurring minerals [C.Y. Tai *et al* 1998]. Different polymorphs impart different properties [M. Kitamura, 2001] hence, control over the crystal from is important. Therefore, aragonite and vaterite usually transform into the stable calcite phase. Crystallization and precipitation of calcium carbonate minerals has been the topic of intensive investigation owing to its polymorphic and morphologic varieties in geological and biological system and to its important industrial applications [Sims *et al*. 1995, Walsh and Mann, 1995, Jung *et al*. 2000, Qi and Ma, 2002, Zhou *et al*.2010]. However, the unwanted precipitation of calcium carbonate has been a customary problem in heat exchangers and it is one of the most important scale-forming minerals in oil and gas production [Andreassen, 2005]. This is also a routine problem for cane sugar processing and it costs billions of dollars to the world wide economy. Scale sticks to the tube strongly hence it removal requires the use of several synergistic methods. However, whatever method is used, the evaporation process must be stopped and the evaporator required to worm and corroded.

It has been well established that 1 mm scale thickness is equivalent to 8-10 % more energy loss and furthermore, a huge amount of chemicals used for cleaning and their subsequent effect on the environment are major issues. In 1977, due to increase of energy and decrease of production capacity resulting from scale British National economic losses were estimated at 0.5 billion pounds [Qui, 1999]. Hence, there is a considerable interest to find methods that effectively prevent/control the formation of this deposit. As a results of the progressive accumulation of scale on heated surfaces, Scale formed, is a poor conductor of heat. The influence of scale on heat transfer coefficients (HTC) is large and hence scale should be removed regularly. The heat transfer coefficient (HTC) considerably declines with time causing significant economic losses [Aijun *et al.* 2006].

The present work is essentially an extension of our earlier work on [K. Singh, *et al.* 2016] the effect of pulsed magnetic field on cane molasses and massecuite. Model studies at laboratory and on industrial scale established that application of suitable magnetic field leads to 40-45% viscosity reduction of cane molasses and massecuite. In this communication we will show that application of a suitable magnetic field pulse can significantly reduce scaling tendency and changes the nature of the scale in sugar evaporators.

2. Working principles

The general operating principle for the proposed PMF is a result of physics of interaction between a pulsed magnetic field and moving electric charge (in the form of ions). When ions pass through the magnetic field pulse, a force is exerted in each ion. The forces on ions of opposite charges are in opposite directions. The redirection of the particle tends to increase the frequency with which ions of opposite charge colloid and combine to form a mineral precipitate or insoluble compound. Since this reaction takes place in a low temperature region of a heat exchanger system, the scale formed is non-adherent. At the prevailing temperature conditions, this form is preferred over adherent form, which attaches to heat exchange surfaces.

A surface charge is imposed on the ions so that they repel instead of attracts each other. Thus, the two ions (positive and negative, or cation and anion respectively) of a kind needed to form scale are never able to come close enough together to initiate the scale forming reaction.

2.1. PMF Treatment

For application of a pulsed magnetic field on an industrial scale, the cell design of the PMF generator presented in Fig. 1 was employed. All experiments were performed employing PMF intensity in the range of 0.15 T to 1.5 T and pulse duration between 5 to 720 seconds.

2.2. The present study is organized as follows:

The PMF generator is installed in sugar evaporator bodies as shown in Fig. 2 (a) and 2 (b) for a definite period (15 days) and scale collected at 5th body was examined/characterized to assess the effect of PMF on calcium carbonate precipitation. Similarly, scale formed after 15 days without PMF treatment was procured for comparison. All other process parameters were kept almost constant in both the cases.

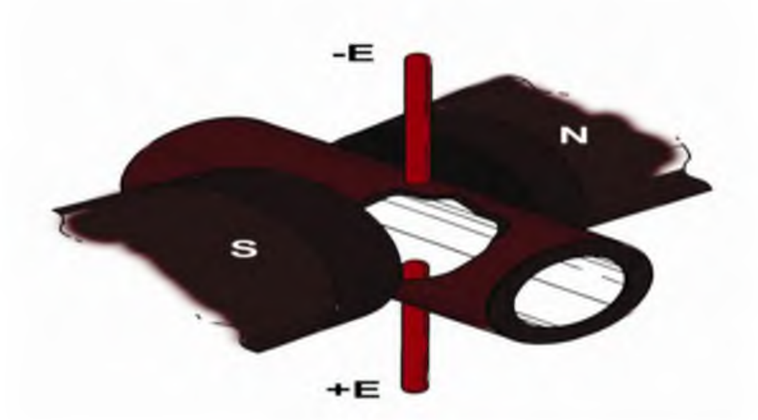

Fig. 1. Pulsed magnetic field generator and cell in industrial tests

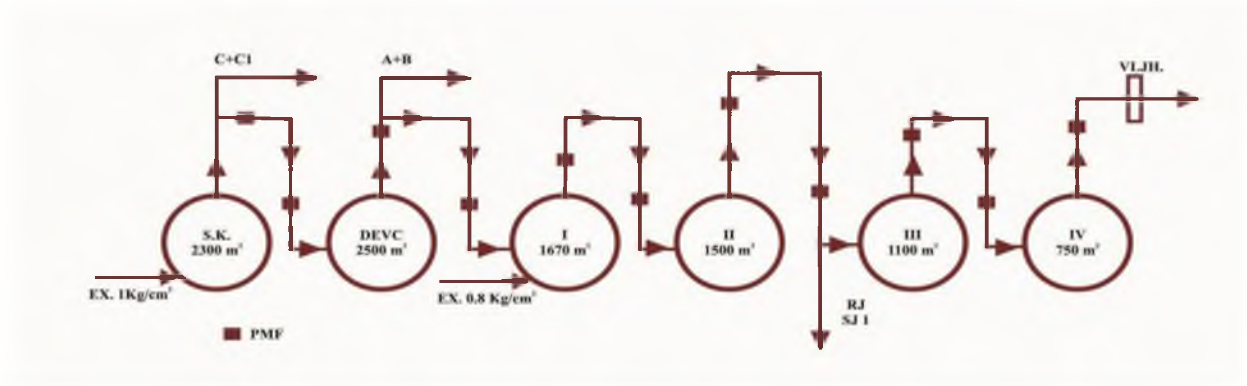

Fig. 2 (a). Installation of PMF generator on juice piping evaporation station

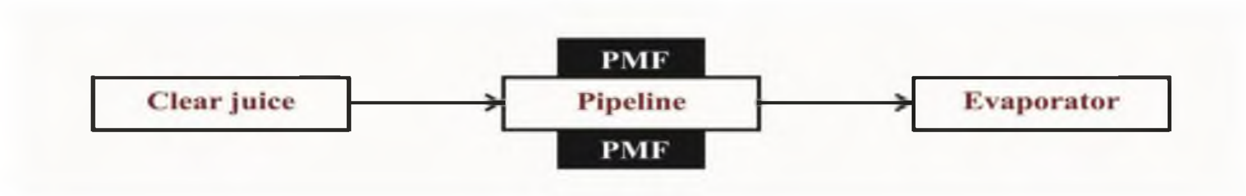

Fig.2 (b).Flow chart showing position of PMF generator equipment at a sugar factory

3. Results and discussion

Examining the physical characteristics of scale sample revealed that the scale after PMF treatment was found to be loose, soft sludge type and easily de-scalable. The comparative chemical composition of evaporator scale (5th body) with and without treatment is shown in Table 1. Data shown in Table 1 illustrates that the amount of calcium and sulphate were 35.5% and 58.6%, respectively in the absence of PMF while application of PMF reduces it to 30.66 % and 51.21%, respectively. An important observation found was that of the presence of silica (2.89%) with PMF treatment. Since silica naturally occurs in cane juice and inters into the juice through absorption of water. It is suspected that the source of silica could be its route from impure lime employed in clarification. However, the lime used was of same batch in both conditions. Since silica is soluble at higher temperature (at the temperature of clarified juice or at the temperature range of Semikistner). Therefore, it remains in the soluble form at Semikistner and first body temperature (high temperature range), however, in the last body (60°C), silica starts to coagulate and deposit as scale

Table 1. Evaporator scale sample (5th body) without and with PMF

Parameter	Without PMF treatment (%)	With PMF treatment
Moisture content	29.39	16.55
Loss on ignition	41.89	34.51
Silica as SiO_2	0.22	2.89
Iron as Fe_2O_3	0.07	0.13
Alumina as Al_2O_3	3.72	12.51
Calcium as CaO	35.50	30.66
Magnesium as MgO	1.50	1.93
Sodium	0.08	0.06
Potassium	0.07	0.19
Chloride as Cl	0.20	0.13
Sulphate as SO_4	58.60	51.21
Phosporous as P_2O_5	0.04	0.28

Table 2. Chemical composition of material separated by separator

Parameter	%
Moisture content	14.95
Loss on ignition	48.19
Silica as SiO_2	-
Iron as Fe_2O_3	7.96
Alumina as Al_2O_3	2.68
Calcium as CaO	36.40
Magnesium as MgO	4.45
Sodium	0.12
Potassium	0.36
Chloride as Cl	0.04
Sulphate as SO_4	46.46
Phosporous as P_2O_5	1.52
Particle greater than 45 μ	69.33
Particle between 45 to 20 μ	25.31
Particle between 20 to 10 μ	0.64
Particle between 10 to 5 μ	0.55
Particle between 5 to 2 μ	0.24
Particle less than 2μ	3.92

The Scanning Electron Micicrograph (SEM) images (Fig. 3-7) clearly demonstrated that the application of a suitable magnetic pulse reduced calcite crystal growth, changes in the nature, the morphology or the size of scale. It is clear that a large amount of calcite and aragonite were present in the absence of PMF and there seems to be a transformation of calcium carbonate. The SEM images of the scale after chemical treatment (soda boiling) at different magnification are shown in Fig. 3. If we compare SEM images of scale after PMF treatment (Fig. 5) with standard materials (aragonite and calcite, Fig. 6 and 7 respectively) demonstrate that a large amount of thermodynamically least stable vaterite is formed after PMF treatment. Thus, application of PMF plays a crucial role to sugar evaporators changing the nature of scale from hard (calcite) to soft (vaterite) which is easily de-scalable.

The SEM images reveal that in the absence of treatment, the scale sizes were various and much larger compared with PMF treatment. There are two possible reasons for these. Firstly, because the crystal growth rate slowed down, the crystal size became smaller, so the fouling became soft and loose, which was easy to remove. Secondly, application of a suitable magnetic field pulse, the suspended particles in syrup existing as colloid were broken and dissolved, so the rates of absorption were reduced, and the scale forming tendency decreased. It is therefore apparent from the SEM images that without PMF treatment the scaling and inevitable scaling is greater, more problematic and requires more time to clean.

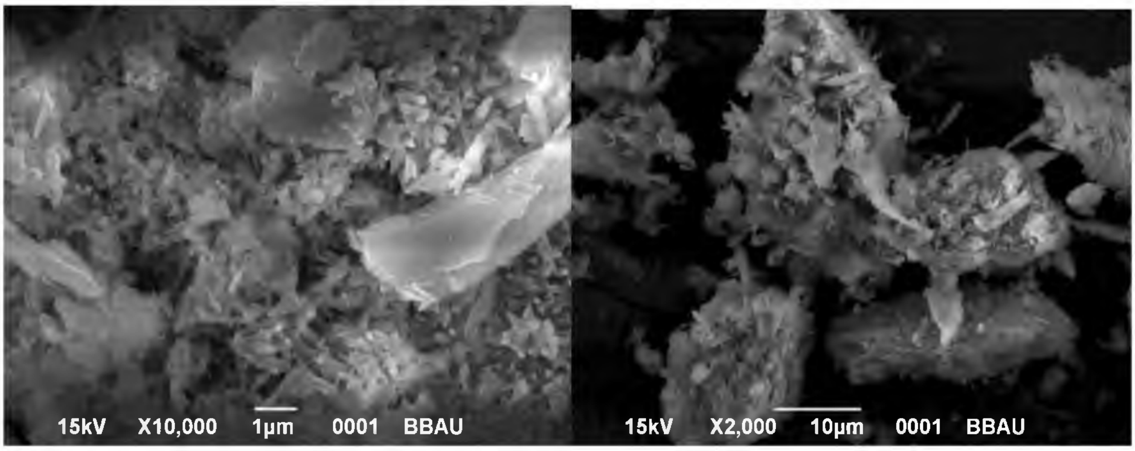

Fig. 3. SEM images of Scale after chemical treatment (soda boiling)

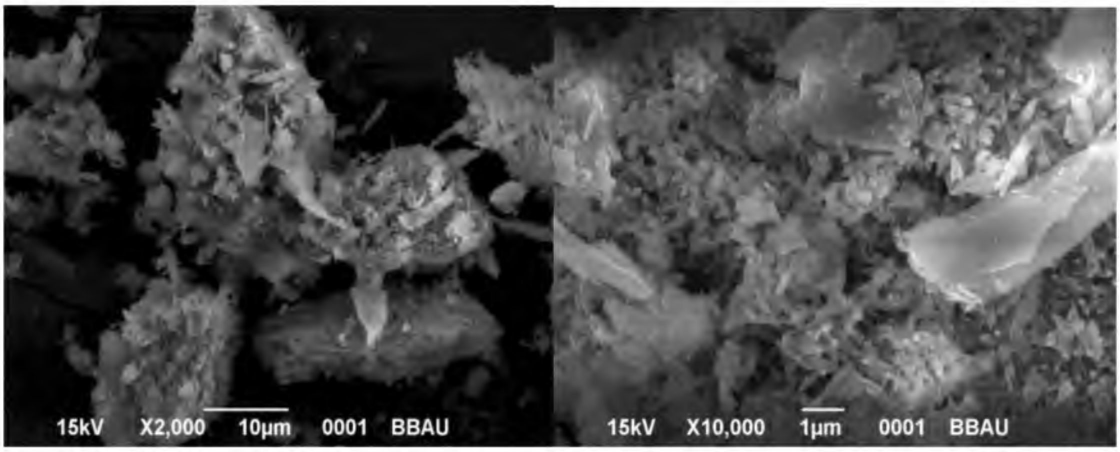

Fig. 4. SEM images of Scale without chemical treatment/without PMF treatment

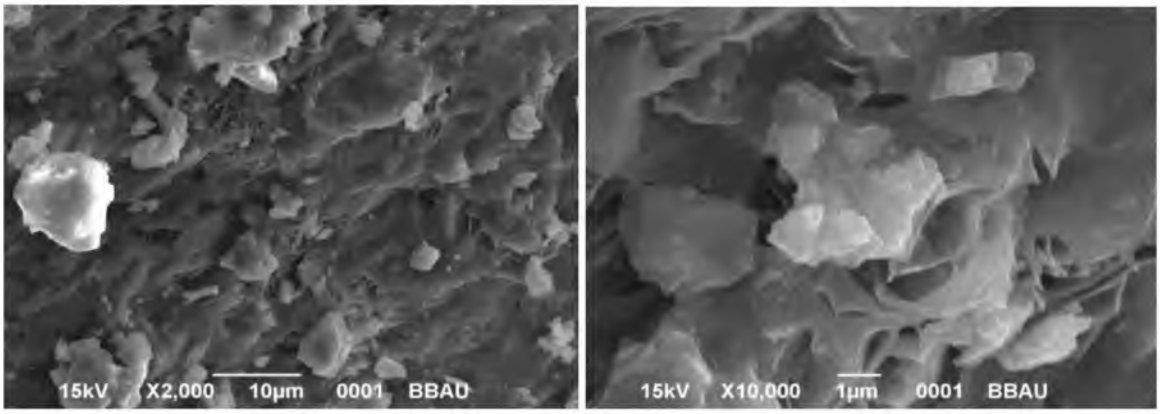

Fig. 5. SEM images of Scale with PMF treatment

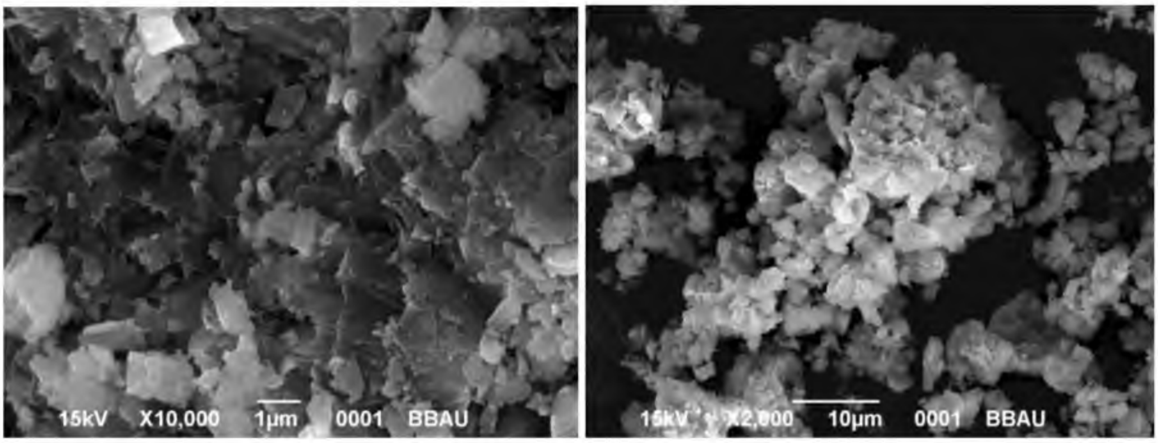

Fig. 6. SEM images of Aragonite

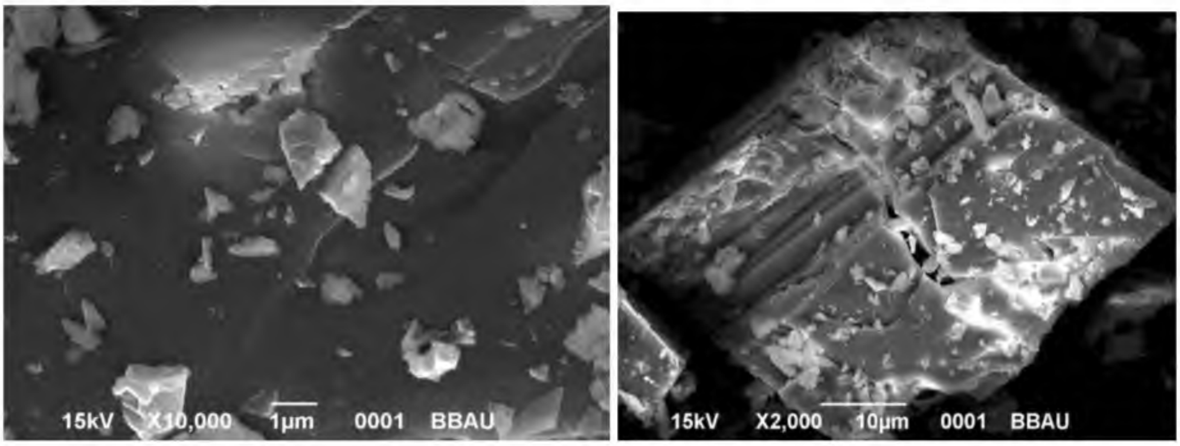

Fig. 7. SEM images of calcite

FT-IR is incredibly simple spectral finger print for the identification of carbonate polymorphs [Wang *et al.* 1999, Lote *et al.* 2003]. The FT-IR spectra of the scale samples are shown in Fig.8. There are significant differences in the IR spectra. The FTIR spectrum of the scale samples after PMF treatment presents the characteristic absorption peaks of vaterite at 1112 and 1134 cm^{-1}. [White, 1974; Zhou *et al.*, 2004]. No characteristic peaks belonging to calcite at 713 and 876 cm^{-1} were detected after PMF treatment. However, partial characteristic peaks belonging to aragonite were appeared after treatment at 649 cm^{-1}.

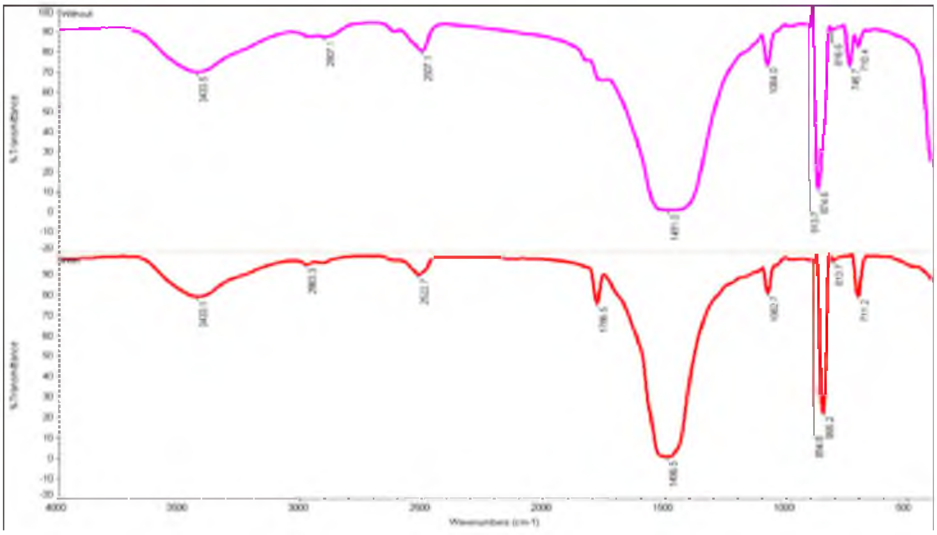

Fig. 8. FT-IR spectra of standard carbonate scale with and without PMF treatment.

The typical XRD pattern of scale samples shown in Figure 9 provides definitive proof of CaCO3 in the scale of evaporators in the sulphitation process of sugar processing.

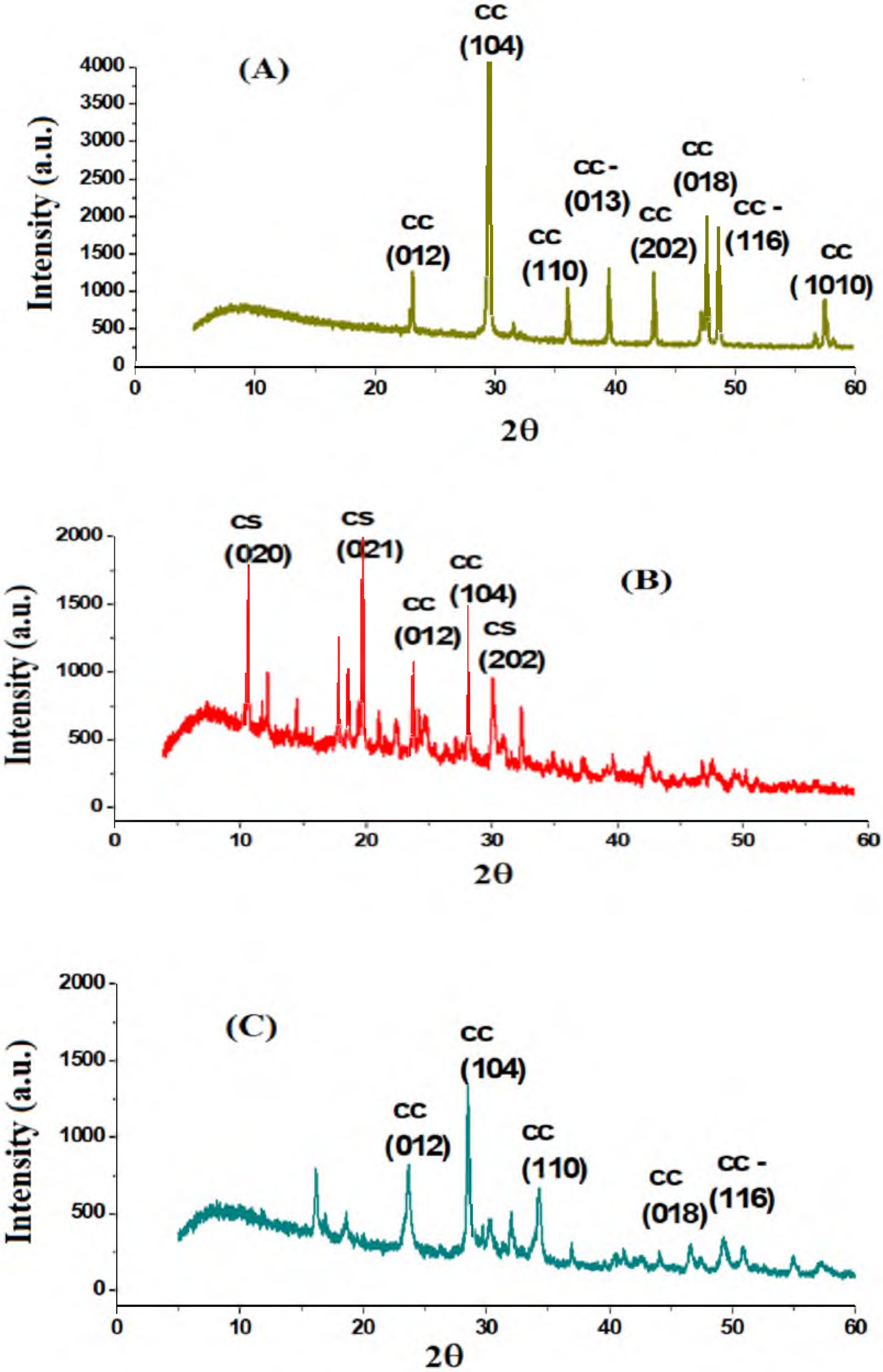

Fig. 9. Typical XRD pattern of scale samples collected before and after PMF treatment. A - standard calcite: B - sample after PMF treatment: C - sample without PMF treatment; CC = $CaCO_3$, CS = $CaSO_4$.

4. Conclusion

The application of a suitable magnetic field pulse in cane sugar evaporators leads to following important conclusions:-

(a) The physical configuration of the scale changes from hard and dense to soft, porous sludge type which is easily de-scalable.

(b) The SEM images demonstrate that a large amount of thermodynamically least stable vaterite is formed after PMF treatment.

(c) The FT-IR spectral finger print for the identification of carbonate polymorphs after PMF treatment demonstrate the characteristic absorption peaks of vaterite at 1112 and 1134 cm-1; a thermodynamically least stable polymorph of calcium carbonate.

(d) Thus applications of a suitable PMF suggest that the PMF application could lead to an energy saving process for cane sugar manufacturing.

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Chapter-6

Reducing Viscosity of Molasses and Massecuite with Pulsed Magnetic Field (PMF)

CHAPTER - 6

REDUCING VISCOSITY OF MOLASSES AND MASSECUITE WITH PULSED MAGNETIC FIELD (PMF)

Abstract

Laboratory and industrial tests were conducted on reducing viscosity of cane molasses and massecuite with pulsed magnetic field (PMF). Employing PMF treatment, viscosity was reduced by 40-45% in comparison with untreated materials. It is hypothesized that in response to PMF treatment, non-sugar components (molecules) in the molasses and massecuite aggregate leading to changes in the rheological property of the fluids. The 5 minute PMF at 0.15 tesla (T) produced maximum viscosity reduction (40-45%). After about 3 hours viscosity begins to rise and after 10 to 12 hours after the PMF treatment returns to the original value. These laboratory studies coupled with some commercial trials suggest that the PMF application could lead to an energy saving process for cane sugar manufacturing.

1. Introduction

Viscosity is a measure of a fluids resistance to flow. High viscosity reduces the effective extraction of sucrose from the mother liquor. The viscosity of the mother liquor increases abruptly when low purity masscuite is cooled, and at the minimum temperature it has been found that the crystal of sucrose cannot be separated effectively from molasses in the centrifuge. The option to reduce the viscosity of massecuite is either by dilution or by heating the massecuite sufficiently to lower its supersaturation. However, dilution of the molasses leads to the sucrose loss due to its high solubility whereas, heating of the massecuite may lead to sucrose loss due to inversion.

Viscosity of processing fluids such as syrup molasses and mesquite is a vital factor in several stage of sugar processing, any practical way that would reduce process viscosity, particularly in the low-grade part of the process is therefore important. Viscosity depends mainly on the water content and the temperature, and less on the proportion of various impurities. The organic non-sugars probably have a strong effect; compounds with high molecular weight tend to increase the viscosity significantly. On the other hand, inorganic salts usually reduce viscosity of sugar solutions. Generally sodium and potassium salts are known to reduce viscosity of sugar solutions and complex-forming calcium ions increase it. At the same total solids concentration, invert sugar solutions have lower viscosity than pure sucrose.

Clarke and Cole in Louisiana [Clarke *et al,* 1996] reported benefits from using permanent magnets in sugar factory evaporators. Bacri and Perzynski [J.C. Bacri *et al,* 1995], Tao and Xu [R. Tao *et al,* 2006] and Homayuni *et al* [F. Homayuni *et al,* 2011] reported that viscosity of crude oil was decreased by pulsed electric and magnetic field confidence.

Magnetic field applied to suspensions of magnetic particles induces interactions between the particles. If the interactions are strong enough to overcome the thermal energy of the molecules and the Brownian motion, the particles may aggregate and align in the direction of the magnetic field. If this interaction is very strong or the magnetic field is applied for long time interval, the particle aggregate into macroscopic chains or columns, impede the fluid flow and increase the viscosity. On the other hand, if the magnetic field is applied as a short pulse, then the interaction does not have enough time to affect particles (molecules) separated by macroscopic distance, but it has enough time to assemble some into clusters. These clusters are of limited size, perhaps in the (sub) micrometer range. Although, some particles may not join the aggregates if the magnetic field is exposed only for a short time, viscosity of the juice may be reduced. The volume fraction (of non-water molecules) remains the same but the particle (cluster) size distribution has changed. By this theory, viscosity of the sugar process fluids increases after being exposed to a strong magnetic field for a long time, but decreases if a short magnetic field pulse is applied.

2. Experimental procedures

2.1. Sampling

Samples of molasses and massecuites in each batch were taken once every hour. Temperature of the samples was noted at the source as well as in the laboratory. Triplicate samples over a period of 2 hours were mixed as collected samples for analysis of Brix, apparent purity and apparent viscosity.

The purity of the C-massecuite was in the range of 46-48 and purity of final molasses was in the range of 31-32. Massecuite Brix was in the range of 80-90 whereas molasses Brix was in the range of 70-80.

2.2. PMF Treatment

For application of a pulsed magnetic field on an industrial scale, the cell design of the PMF generator presented in Fig. 1 was employed. In Fig. 2 is the experimental set up used in the laboratory tests. All experiments were performed at the temperature of the source materials, at PMF intensity in the range of 0.15 T to 1.5 T and pulse duration between 5 to 720 seconds.

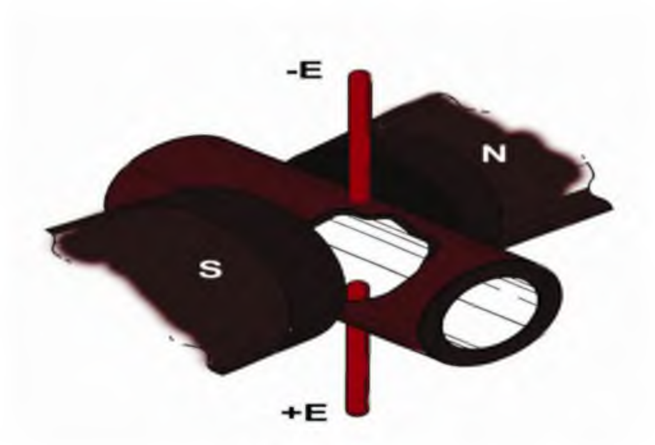

Fig. 1. Pulsed magnetic field generator and cell in industrial tests

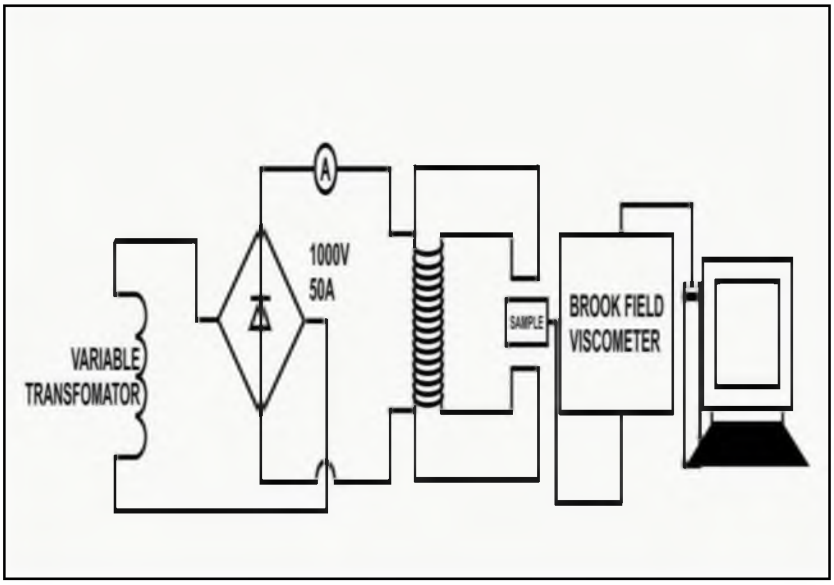

Fig. 2. Magnetic circuit arrangement in the laboratory PMF tests

2.3. Viscosity measurement

Viscosity of the high density intermediate process materials was measured using a Brookfield DV-II + pro programmable viscometer (Brookfield Engineering Laboratories, Inc. USA) which measures fluid viscosity at a given shear rate. The accuracy of the viscometer was ± 1.0 % of full scale range with repeatability of ±0.2 %, and temperature accuracy of $\pm 1^0$C.

3. Results and discussion

3.1. Laboratory scale tests

In the laboratory experiments, molasses and massecuite samples were diluted to 40 % solids and treated with PMF. For comparison, a high quality refined sugar solution was tested in an exactly same manner. At 28 ^{0}C, before PMF treatment, the refined sugar solution had a viscosity of 2.655 cP, whereas molasses had viscosity 900 cP (measured at 10 rpm). Some representative data are shown in Fig. 3 and 4. Employing a pulse of 0.25 T for 5 minutes, the viscosity of the refined sugar solution and molasses decreased to 1.062 cP and 500 cP, respectively. Viscosity then gradually increased and after 4 hours the values were 2.556 cP for the sugar solution and 800 cP for molasses, but were still lower than their original viscosities. After 12 hours, in each case the viscosity was back to the original value. At the rotational speeds from 10 to 100 rpm, the 5 minute treatment seemed to produce the maximum viscosity reduction of the materials under study.

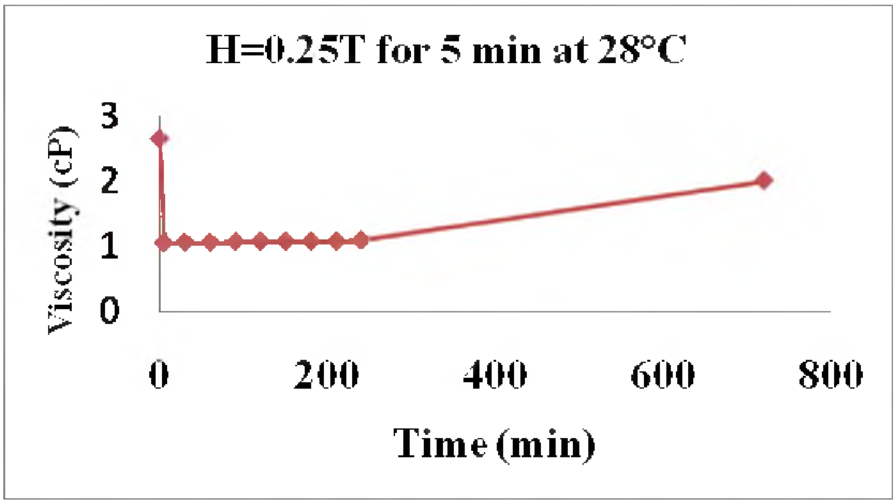

Fig. 3 PMF effects on viscosity of refined sugar solution at 40% dilution in the laboratory scale PMF experiment.

Table-1

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(with PMF System)

Parameters	M.J.				CI.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	4.95	5.05	5.12	5.08	6.92	6.97	7.02	6.88	6.48	6.56	6.45	6.38								
Brix	16.17	15.7	15.2	16.12	16.79	15.74	15.30	16.12	59.00	56.60	55.60	59.40	101.10	101.30	100.80	103.10	90.40	89.50	91.10	92.10
Pol%	13.71	13.44	13.14	13.84	14.29	13.5	13.25	13.86	50.20	48.60	48.24	50.90	47.70	48.70	47.50	49.20	28.60	28.20	28.90	29.40
Purity	84.79	85.61	86.45	85.86	85.11	85.77	86.6	55.98	85.08	85.87	86.76	85.69	47.18	48.08	47.12	47.72	31.64	31.51	31.72	31.91
R.S.%100 Brix	4.01	4.2	4.08	3.91	3.79	4.00	4.23	4.12	3.85	4.11	4.31	4.28								
CaO	840	807	820	780	1240	1310	1210	1220			….	…								
Viscosity(c.P)													228000	310700	218000	304400	870	1020	1050	980
Temp ^{0}C													51.0	49.5	49.0	50.6	49.0	50.0	50.0	50.6

Table-2

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(with PMF System)

Parameters	M.J.				Cl.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	5.10	5.06	5.20	5.32	6.94	7.04	7.05	6.98	6.51	6.56	6.45	6.35								
Brix	16.1	16.2	15.9	16.8	15.78	14.46	15.80	16.42	53.92	54.20	67.20	64.08	101.60	100.40	100.30	101.30	90.30	87.30	90.30	90.80
Pol%	13.8	13.7	13.4	14.6	13.55	12.28	13.35	14.22	46.36	46.08	56.84	55.44	48.30	48.70	49.40	48.30	28.00	27.40	28.90	28.70
Purity	85.8	84.8	84.2	86.6	85.87	84.92	84.49	86.6	85.98	85.02	84.58	86.52	47.54	48.51	49.25	47.68	31.01	31.39	32.00	31.61
R.S.%100 Brix	3.55	3.59	3.91	3.15	3.61	3.87	3.73	3.41	4.15	4.06	3.93	3.99								
CaO	820	780	740	790	1220	1240	1230	1150			….	…								
Viscosity(c.P)													263000	256000	229000	285000	850	920	970	760
Temp ^{0}C													48.20	50.00	49.60	49.50	49.50	51.00	51.00	51.50

Table-3

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(with PMF System)

Parameters	M.J.				Cl.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	5.09	4.95	5.25	5.04	6.88	7.05	6.95	7.1	6.53	6.61	6.40	6.61								
Brix	15.6	16.2	16	16.5	15.9	15.8	16.08	16.3	64.96	61.12	62.00	64.88	101.90	100.90	101.50	101.80	90.40	91.00	89.70	90.40
Pol%	13.5	14	13.8	14.5	13.7	13.8	13.9	14.3	56.00	53.12	53.40	56.96	47.90	48.20	48.00	47.80	28.30	28.40	28.80	28.70
Purity	86.2	86.8	86.1	87.6	86.1	87.1	86.3	87.8	86.21	86.91	86.13	87.78	47.01	47.77	47.29	46.95	31.31	31.21	32.11	31.75
R.S.%100 Brix	3.65	3.59	3.69	3.45	3.84	3.87	3.84	3.62	4.01	3.80	3.98	3.70								
CaO	820	810	790	810	1150	1170	1230	1190			....	...								
Viscosity(c.P)													349800	334500	435000	428000	750	910	970	990
Temp ^{0}C													44.00	46.00	44.10	46.50	46.00	50.00	50.00	50.9

Table-4

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(with PMF System)

Parameters	M.J.				Cl.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	5.28	5.2	5.22	5.25	6.95	7.12	7.07	7.05	6.31	6.30	6.38	6.32								
Brix	16.05	16.74	16.31	15.96	15.8	15.2	15.66	15.6	62.16	65.92	63.76	64.80	100.40	101.00	101.50	101.10	90.70	88.60	89.60	91.20
Pol%	13.78	14.11	14.24	13.94	13.6	12.9	13.7	13.7	53.48	55.80	55.84	56.68	46.90	47.70	46.90	47.50	28.40	28.40	28.40	28.60
Purity	85.86	84.29	87.31	87.34	85.9	84.6	87.5	87.5	86.04	84.65	87.58	87.47	46.71	47.23	46.21	46.98	31.31	32.05	31.70	31.36
R.S.%100 Brix	4.11	3.52	3.65	3.82	3.73	3.81	3.7	3.77	3.91	4.13	3.58	4.02								
CaO	920	840	850	840	1260	1210	1180	1210			….	…								
Viscosity(c.P)													3E+05	3E+05	3E+05	4E+05	910	880	840	940
Temp ^{0}C													48.40	45.30	50.10	45.50	49.60	50.80	50.0	49.0

Table-5

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(with PMF System)

Parameters	M.J.				Cl.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	5.10	5.16	5.25	5.2	6.96	7.02	6.91	6.91	6.61	6.62	6.42	6.52								
Brix	16.3	51.5	16.5	15.6	16.2	16	15.84	16.1	62.24	65.52	62.04	62.44	102.30	101.80	101.80	103.30	92.10	90.60	89.10	92.40
Pol%	14.1	13.3	14.4	13.3	14.1	13.9	13.8	14.00	54.28	56.64	53.96	53.16	49.63	48.90	48.70	49.80	29.50	28.40	28.60	29.20
Purity	86.8	86	87	85.1	87	86.5	87.2	87.2	87.21	86.45	86.98	85.14	48.51	48.04	47.84	48.21	32.03	31.35	32.10	31.60
R.S.%100 Brix	3.44	3.82	3.39	3.66	3.64	3.93	3.60	3.74	3.86	4.15	3.68	3.91								
CaO	810	780	860	840	1220	1210	1220	1210			….	…								
Viscosity(c.P)													3E+05	2E+05	3E+05	3E+05	1120	970	840	1080
Temp ^{0}C													49.0	50.1	50.0	49.2	50.3	51.0	50.0	50.8

Table-6

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(with PMF System)

Parameters	M.J.				Cl.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	5.23	5.19	5.25	5.12	7.06	7.02	6.91	9.95	6.52	6.42	6.38	6.42								
Brix	15.89	16.06	15.90	15.72	15.74	15.87	16.01	15.78	60.16	67.04	63.44	62.88	103.40	101.40	101.90	101.80	91.40	92.80	89.90	90.40
Pol%	13.63	13.78	13.74	13.58	13.56	13.69	13.89	13.67	51.88	57.76	55.08	54.44	50.10	49.20	49.10	48.90	29.10	29.80	28.70	28.30
Purity	85.78	85.80	86.42	86.39	86.15	86.26	86.76	86.63	86.24	86.16	86.82	86.58	48.45	48.52	48.18	48.04	31.84	32.11	31.92	31.31
R.S.%100 Brix	3.52	3.67	3.58	3.63	3.62	3.78	3.69	3.74	3.99	4.06	3.79	3.88								
CaO	850	860	830	810	1200	1250	1200	1180				…								
Viscosity(c.P)													316500	312000	288000	276000	1010	1030	950	630
Temp ^{0}C													48.60	47.9	50.0	49.5	50.5	49.5	48.8	50.1

Table-7

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(without PMF System)

Parameters	M.J.				Cl.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Ph	5.07	5.4	4.78	5.08	6.95	6.92	7.02	6.9	6.28	6.02	6.21	6.18								
Brix	16.26	16.54	17.02	16.84	16.04	16.36	16.06	16.66	57.12	60.24	57.12	61.76	101.20	102.30	102.20	100.30	91.10	90.60	91.30	89.60
Pol%	14.23	14.34	14.41	14.58	14.08	14.21	13.66	14.47	49.96	52.36	48.36	53.76	49.40	50.60	51.20	49.30	30.10	30.50	31.10	30.00
Purity	87.52	86.70	84.67	86.58	87.78	86.86	85.06	86.85	87.46	86.92	84.66	87.05	48.81	49.46	50.10	49.15	33.04	33.66	34.06	33.48
R.S.%100 Brix	3.75	4.05	3.64	3.86	3.92	4.28	3.92	4.14	4.27	4.58	4.55	4.53								
CaO	840	870	920	910	1290	1310	1340	1340				…								
Viscosity(c.P)													94400	1E+06	1E+06	9E+05	1840	1840	1980	1720
Temp ^{0}C													49.20	49.2	50.0	49.8	50.2	48.9	51.5	50.5

Table-8

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(without PMF System)

Parameters	M.J.				Cl.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	4.91	4.72	4.50	5.03	6.90	7.03	6.91	6.88	5.85	6.44	6.02	6.08								
Brix	16.39	16.54	16.58	15.84	16.3	16.16	16.05	15.8	47.92	57.36	51.20	54.28	100.80	101.30	101.80	100.30	90.10	88.30	92.10	89.50
Pol%	13.68	14.42	14.66	13.88	13.59	14.13	14.24	13.83	40.00	50.24	45.16	47.44	50.50	49.90	49.80	49.70	30.40	29.80	30.60	30.50
Purity	83.47	87.18	88.42	87.63	83.37	87.44	88.72	87.53	83.47	87.59	88.20	87.40	50.10	49.26	48.92	49.55	33.74	33.75	33.22	34.08
R.S.%100 Brix	3.72	3.75	4.04	3.66	4.05	4.21	4.24	4.05	4.26	4.46	4.61	4.35								
CaO	900	820	860	880	1310	1270	1280	1310				…								
Viscosity(c.P)													986000	1E+06	984000	109000	2120	1840	2110	1760
Temp ^{0}C													48.90	49.0	50.0	49.2	51.2	48.9	51.4	50.6

Table-9

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(without PMF System)

Parameters	M.J.				Cl.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	5.04	5.16	5.25	4.96	6.91	6.89	6.91	7.11	6.66	6.42	6.53	6.35								
Brix	15.46	16.04	14.14	15.38	15.77	15.38	15.95	15.88	52.72	58.16	55.20	57.88	102.10	102.80	100.60	101.50	89.80	88.30	90.40	89.10
Pol%	13.37	14.13	12.33	13.31	13.69	13.54	13.96	13.83	45.48	51.04	48.36	50.16	49.70	50.30	50.10	50.80	30.00	30.10	30.50	30.50
Purity	86.48	88.09	87.2	86.54	3.93	88.04	87.52	87.09	86.27	87.76	87.61	86.66	48.68	48.93	49.80	50.60	33.41	34.09	33.74	34.23
R.S.%100 Brix	3.75	3.74	3.89	4.03	3.93	4.03	4.14	4.35	4.40	4.20	4.35	4.65								
CaO	870	880	820	840	1310	1290	1270	1270				…								
Viscosity(c.P)													9E+05	1E+06	9E+05	1E+06	1830	1690	1910	1730
Temp ^{0}C													50.40	49.4	49.6	50.6	50.0	52.2	50.4	52.3

Table-10

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(without PMF System)

Parameters	**M.J.**				**CI.J.**				**Unsul.Syp.**				**C-Massecuite**				**Final Molasses**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
pH	4.85	5.22	5.02	5.28	6.77	7.05	6.92	6.91	6.35	5.98	6.14	6.32								
Brix	15.72	16.06	16.24	15.94	15.42	15.25	15.98	16.06	51.12	55.84	54.56	57.36	101.80	102.40	100.80	101.40	90.30	90.50	87.90	92.60
Pol%	13.69	14.18	14.22	13.93	13.50	13.52	14.03	14.14	44.76	49.56	47.84	50.40	50.40	51.30	49.20	49.80	30.60	30.50	30.00	30.90
Purity	87.09	88.29	87.56	87.39	87.55	88.66	87.80	88.04	87.56	88.75	87.68	87.87	49.51	50.10	48.81	49.11	33.89	33.70	34.13	33.37
R.S.%100 Brix	3.94	3.86	3.76	4.08	4.15	4.07	3.94	4.30	4.46	4.37	4.18	4.67								
CaO	870	890	900	880	1410	1420	1420	1330				…								
Viscosity(c.P)													1002000	866000	832000	946000	1950	1720	1640	2040
Temp ^{0}C													47.30	50.8	48.0	49.4	48.5	50.0	50.0	50.9

Table-11

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(without PMF System)

Parameters	M.J.				Cl.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	5.00	5.24	4.97	5.05	6.95	6.88	7.02	6.93	6.42	6.45	6.35	6.37								
Brix	16.16	15.84	16.10	16.34	15.5	15.66	15.94	15.94	55.84	56.80	55.84	57.04	103.10	101.70	102.30	101.90	91.20	90.80	90.60	89.80
Pol%	14.00	13.89	14.07	14.38	13.47	13.67	13.96	14.04	48.24	49.48	48.72	50.16	50.80	49.80	51.30	50.80	30.50	31.20	30.60	30.00
Purity	86.63	87.69	87.39	88	86.9	87.29	87.58	88.08	86.39	87.11	87.25	87.94	49.27	48.97	50.15	49.85	33.44	34.36	33.77	33.41
R.S.%100 Brix	3.71	3.72	3.97	3.49	3.87	4.09	4.27	3.83	4.15	4.30	4.58	4.21								
CaO	820	830	880	870	1340	1330	1390	1400				…								
Viscosity(c.P)													963000	905000	812000	808000	1840	1590	1680	1960
Temp ^{0}C													48.90	49.2	50.0	50.4	48.8	51.5	50.0	49.4

Table-12

Analysis work done at Sahkari Khand Udyog Mandal Ltd.,Gandevi (Gujrat)

(without PMF System)

Parameters	M.J.				Cl.J.				Unsul.Syp.				C-Massecuite				Final Molasses			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	5.21	5.15	5.25	5.05	6.96	7.05	6.91	7.07	6.40	6.36	6.4	6.34								
Brix	16.84	15.91	16.10	15.8	16.54	16.01	16.28	15.95	55.52	53.92	14.58	13.92	102.80	101.80	102.20	101.60	90.30	91.20	89.80	90.10
Pol%	14.44	13.67	13.87	13.76	14.23	13.82	14.11	13.94	47.68	46.40	12.66	12.14	51.30	51.10	50.80	50.10	30.50	30.60	30.20	30.00
Purity	85.75	85.92	86.15	87.09	86.03	86.32	86.67	87.4	55.88	86.05	86.83	87.21	49.90	50.20	49.71	49.31	33.78	33.55	33.63	33.30
R.S.%100 Brix	3.8	3.96	3.66	3.86	4.05	4.18	3.87	4.08	4.39	4.38	4.25	4.20								
CaO	890	850	910	860	1370	1330	1390	1350												
Viscosity(c.P)													980000	886000	1004000	842000	1940	1780	1820	1780
Temp ^{0}C													50.10	50.0	49.1	50.4	50.3	51.0	49.8	50.8

Table-13

Viscosity Test Report(When PMF in line)

Dalmia Chini Mills,Nigohi, Shahjanpur(U.P.)

With System

S.No.	Particulars	Spindle	RPM	%Torque	Viscosity (cP.)	Temp.C
1	C-Massecuite	64	0.3	33.60%	814000	53.3
2	C-Massecuite	64	0.3	35.00%	840000	58.0
3	Final Molasses	63	20	43.20%	3110	54.1
4	Final Molasses	63	20	46.90%	3140	53.2
5	C-Massecuite	64	0.3	44.60%	850000	51.1
6	C-Massecuite	64	0.3	45.10%	880000	52.0
7	Final Molasses	63	20	37.00%	3440	53.8
8	Final Molasses	63	20	38.00%	3480	55.3
9	C-Massecuite	64	0.3	87.00%	820000	54.0
10	C-Massecuite	64	0.3	89.00%	856000	54.6
11	Final Molasses	63	20	37.00%	3100	54.1
12	Final Molasses	63	20	42.00%	3230	52.6
13	C-Massecuite	64	0.3	90.10%	898000	52.1
14	C-Massecuite	64	0.3	50.00%	920000	52.4
15	Final Molasses	63	20	49.80%	3230	50.2
16	Final Molasses	63	20	48.30%	3410	54.0
17	C-Massecuite	64	0.3	81.00%	78000	54.6
18	C-Massecuite	64	0.3	84.00%	910000	51.1
19	Final Molasses	63	20	50.00%	3190	54.0
20	Final Molasses	63	20	48.20%	3370	51.0
Average	C-Massecuite				856800	53.3
	Final Molasses				3270	53.2

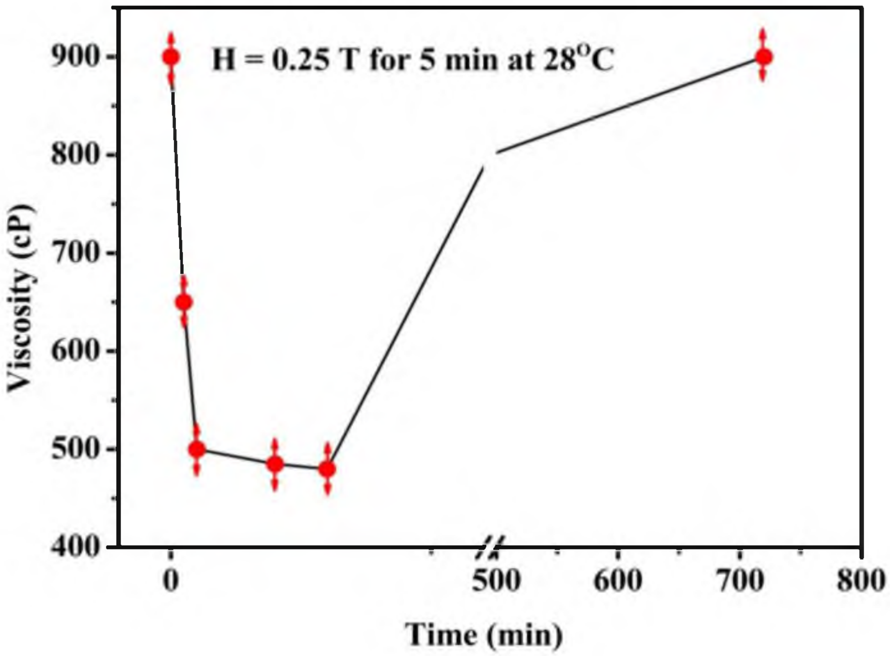

Fig. 4 PMF effects on viscosity of diluted final molasses (40%) in the laboratory scale experiment

3.2. Industrial scale tests

In these tests, PMF was applied on process fluids without dilution. Samples of the treated materials were collected in a 500 ml beaker, and the original temperature was maintained with a thermostat during viscosity measurement. Prior to viscosity determination, temperatures of the fluid in the process were noted, as well as its Brix and purity.

Data shown in Fig. 5 and 6 shows that the average treated molasses and massecuite viscosity decreased by 40 to 45% compared with untreated samples

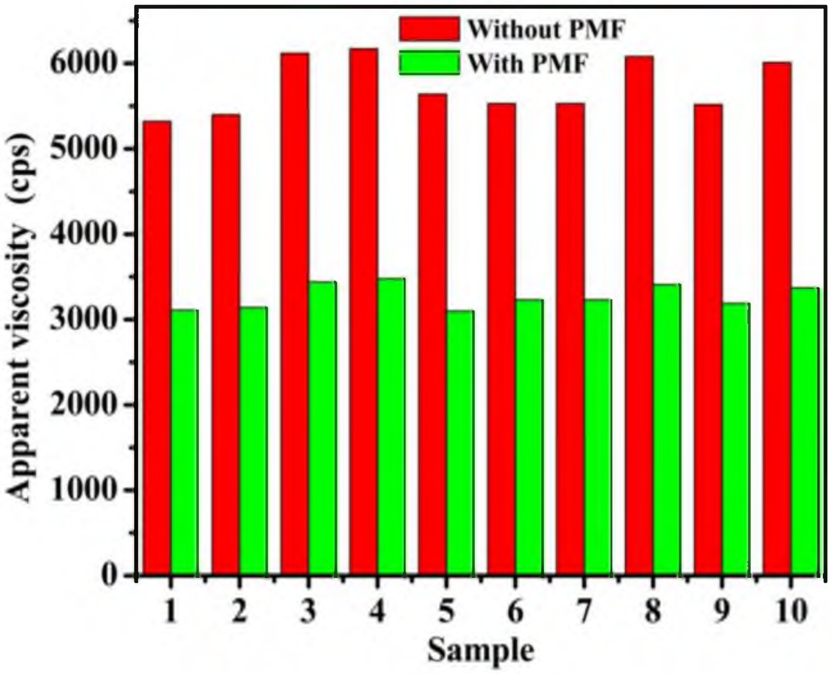

Fig. 5. Plot illustrating apparent viscosity of molasses with and without PMF treatment at 53^{0}C.

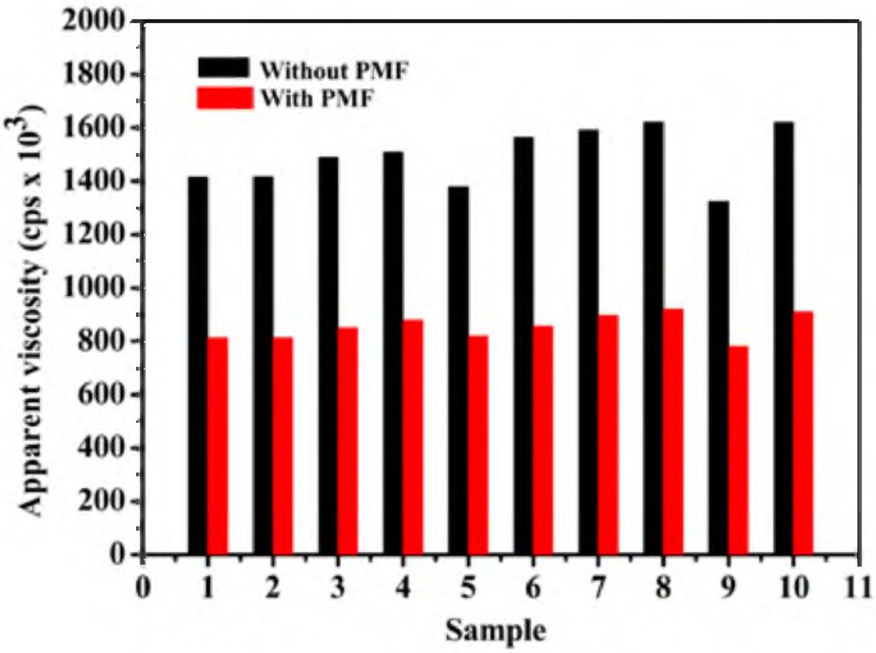

Fig. 6. Plot illustrating apparent viscosity of massecuite with and without PMF treatment at 53^{0}C

A pulsed magnetic field (PMF) was found effective to reduce viscosity of sugar processing fluids. It is hypothesized that by employing PMF, non-sucrose molecules in molasses and massecuite aggregate temporarily to (sub-)micron-sized clusters; consequently changing rheological properties of the fluids, and reduction their viscosity. Furthermore, the magnetic energy may be partially converted into the linear momentum of the molecules which in turn is converted into hydrodynamic motion and decreased viscosity of molasses and massecuite. This viscosity reduction is not permanent, but it lasts for several hours and is repeatable. The viscosity effect on refined sugar solution raises some doubt whether the effect is due to clustering of non-sugar components. However, in concentrated solutions of molasses and massecuite the magnitude of the effect is several orders higher than in refined sugar solution. Other or additional possible mechanism can be a temporary disruption by PMF of the solvent-solute arrangement in concentrated sugar solutions. However, regardless of the mechanism of PMF action, the results suggest that the technology may have potential for use in cane sugar processing.

4. Conclusions

(a) With the PMF treatment, viscosity of massecuite and final molasses was reduced significantly, by 40 to 45%.

(b) Application and re-application of PMF may help in effectively transporting the concentrated fluids (molasses and massecuite) in the sugar process.

(c) The laboratory experiments support commercial trials, confirmed the expected benefits for process control and energy savings during sugar manufacturing**.**

(d) The present study clarifies the existing controversy regarding the suitability of magnetic fluid conditioners or even permanent magnets in the sugar manufacturing process. The use PMF provides reproducible data on viscosity of the molasses and massecuite.

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Annexure-I

List of Publications

LIST OF PUBLICATIONS

RESEARCH PAPERS

1. Application and potential of power ultrasound (pus) in sugar manufacturing a non-chemical green technology, Vimalesh Kumar Singh, Sudhir Kumar Verma, Bhuwan Chandra, S**atya Prakash Gupta** and Kaman singh, *J. Pure Appl. Ultrason.* 35 **(2013**) 137-140

2. Studies on the occurrence of latent period in crystallistation of sucrose: effect of pulsed ultrasonics, Kaman Singh and **Satya Prakash Gupta**, *Proc. Sug. Tech. Asso. India,* 72 **(2013)** 595-598

3. Application and potential of a pulsed magnetic field in controlling scale formation in cane-sugar processing, K Singh, B Chandra, **SP Gupta** and A Kumar , *Proc. Int. Soc. Sug. Cane Tech.* 29 **(2016)** 566-571

4. Reducing viscosity of molasses and massecuite with puled magnetic field (PMF), Int. Sug. J. Kaman Singh, Bhuwan Chandra and **Satya Prakash Gupta**, 118 **(2016)** 269-271

5. Effect of ultrasonics on morphology of precipitated calcium carbonate (PCC) for controlling scale formation in cane sugar processing: Laboratory scale experiment, Kaman Singh, Ajay Kumar and **Satya Prakash Gupta**, *Proc. Sug. Tech. Asso. India,* 74 **(2016)** 579-587

PAPERS AND POSTERS PRESENTED IN DIFFERENT CONFERENCES

1. **International Conference on Chemistry and Materials : Prospects and Perspectives (ICCMPP-2012)** held during December 14-16, 2012 at Department of Applied Chemistry, School for Physical Sciences (A Central University) Lucknow, India.

2. National Conference on **Current Trends in Computational Methods in Science and Engineering (CTCM-2013)** held during April 22-23, 2013 at Govt. Model Science College Jiwaji University, Gwalior (M.P.).

3. **International Conference on Emerging Trends in Chemical Sciences (ICETCS 2013)** held during March 14-15, 2013 at School of Chemical Sciences, Central University of Gujarat, Gandhinagar.
4. **72nd Annual Convention of the Sugar Technologists Association' of India (2013)** held during September 26-28, 2013 at Lucknow.

5. Participated in the **100th Indian Science Congress Association** held during January 3-7, 2013, at Caclutta University, Kolkata.

6. National Conference on **Sustainability Issues in Food Processing Sector (SIFPROS-2015)** held during June 18-19, 2015 at National Institute of Food Technology Entrepreneurship and Managemant, Haryana, India.

7. National Conference of the **Frontiers of Chemical Sciences and Potential Interfaces (FCSPI-2015)** held during April 10-11, 2015 at School of Chemical Sciences, Central University of Gujarat, Gandhinagar.

8. National Conference on **Food Safety and Consumer Awareness** held during February 21-22, 2016 at Innovation Center on Food Processing and Food Technology, University of Lucknow.

9. Presented a Poster in the **Asia-Oceania Sonochemical Society (AOSS-3) International Conference** held during September 14-16, 2017 at SRM Research Institute, SRM University, Chennai, Tamil Nadu, India.

10. National Conference on **Recent Advances and Innovations in Chemical and Materials Science (RAICMS-2017)** held during February 23-24, 2017 at J. N. PG College Lucknow.

STUDIES ON THE OCCURRENCE OF LATENT PERIOD IN CRYSTALLISATION OF SUCROSE: EFFECT OF PULSED ULTRASONICS

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ABSTRACT

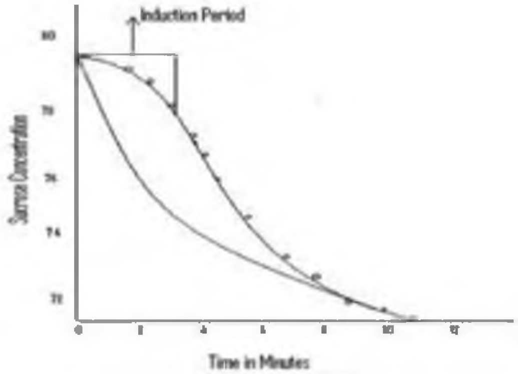
The present invention introduces a specific technology based on pulsed sonication principle to develop a process for anticipated commercial application in sugar industry. The induction period in the crystallization process presents a serious drawback where the rate of crystallization is undoubtedly hampered due to its presence which may ultimately affect the economy of the industry. To get rid of this problem, the application pulsed sonication to sugar manufacturing is studied It includes both the results from the research and development programs carried out in laboratory scale and industrial scale as well. Thus, application of pulsed sonication reduces occurrence of induction period and thus have multiple benefits during sugar manufacturing.

INTRODUCTION

Rate of crystallization of sucrose plays an important role in economics of the industry. Fundamental studies on the kinetics of crystallization of sucrose have, therefore, been attracted the attention of Kuckarenk, Van Hook, Kelly, Ramaiah and others.

The data in Fig. 1 show that deposition of sucrose molecules onto the crystal, took place from the beginning, leading to a continuous decrease in the refractometer reading. A few workers (Kelly *et al.*,), however, noticed that the refractometer did not indicate any decrease in the initial interval of time (Fig. curve 1), which is referred to as the induction period in the crystallization process.

FIGURE 1 – PLOT SHOWING INDUCTION PERIOD DURING SUGAR CRYSTALLIZATION



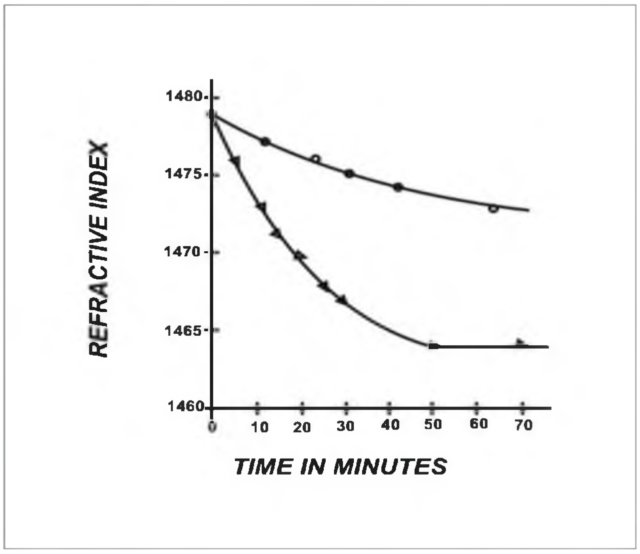
Source: Ramaiah, N.A. and Sanyal, S.K., Proc. Sugar Tech. Assoc of India, 1961, 29, 65.

Induction period refers to low rate of crystallization process, leading to decreased exhaustion of molasses in the massecuites. In the present paper we have studied the effect of pulsed sonication on the occurrence of induction period during crystallization of sucrose.

Experimental

Sucrose (250 g) and deionized water (25 mL) were transferred into each crystallization vessel. The thick slurry in each vessel then cooled from 95^0 C for 1 h. The solutions were then cooled from 95^0 C to the equilibrium solubility temperature of 85^0 C followed by linear cooling at 0.2^0 C/min to 60^0 C. The solution in vessel A, fitted with the P100 probe, was treated with ultrasound using a 7 μm displacement for 30 s at every 1^0 C drop in temperature until turbidity was observed. Turbidity typically became noticeable from 75^0 C in vessel A, whilst the control vessel B still remained a clear solution at 60^0 C. This solution **exhibited a broad MZW with solution clarity being observed as low as 22^0C.**

FIGURE 2



Results: Fig. 1 clearly illustrates that the induction period is invariably present at the initial period of time. The duration of induction period can be estimated by extrapolation the curve as shown in Figure 2. The duration can also be estimated by evaluating the time upto which the first order kinetics was not applicable.

CONCLUSION

The results observed in this study showed that the induction period observed in the crystallization of sucrose could be eliminated, employing pulsed ultrasonics. The elimination of induction period would increase exhaustion of molasses. Thus, the application of pulsed sonication reduces occurrence of induction period and thus have multiple benefits during sugar manufacturing.

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J. Pure Appl. Ultrason. 35 (2013) pp. 137-140

Application and potential of power ultrasound (pus) in sugar manufacturing: a non-chemical green technology

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The application of power ultrasound (PUS) to sugar processing is accompanied by reduction in viscosity of molasses and masscuites and control in scale formation. The FT-IR and SEM analysis of the scale implied that the PUS treatment suppresses the formation of calcite crystals (hard) and prefers vaterite; a thermodynamically least stable (soft) polymorph. The results are consistent with the Ostwald's repining principle. The laboratory experiments coupled with commercial trials were confirmed to be beneficial for process control and significant energy saving.

Keywords: Ultrasonic, viscosity reduction, scale control, induction period, sonocrystallization, energy saving, analysis of scale, FT-IR, SEM.

Introduction

Viscosity of the processing fluids and scale formation in evaporators are the two major problems faced by the sugar technologists' all over the world. The high viscosity reduces the effective extraction of sucrose from the mother liquor (industrial terms: massecuite and molasses). The viscosity of the mother liquor increases abruptly when low purity massecuite is cooled, and at the minimum temperature it has been found that the crystal of sucrose cannot be separated effectively from molasses in the centrifuge. The option to reduce the viscosity of the massecuite is either by dilution or by heating the massecuite sufficiently to lower its super-saturation. However, dilution of the molasses leads to the sucrose loss due to its high solubility, whereas, heating of the massecuite may lead to sucrose loss due to inversion.

The deposition of $CaCO_3$ which is often termed as 'Scale' contributes billions of dollars to the world wide economy[1-6].The aforesaid problems have received much attention for several years, unfortunately, to date there is no effective solution yet. To reduce viscosity and scale formation, various methods[1-6] such as chemical, ion-exchange, electric, magnetic and ultrasonic techniques were reported. However, these techniques are not used widely in the sugar processing due to technical/operational constraints. Recently, use of magnetic fluid conditioning (MFC) technique was reported[5-8] to be effective in the reduction of viscosity and scale formation, but use of MFC for the aforesaid purpose is a controversial subject with results raging from total success to total failure. The reason for this is low reproducibility of results and lack of plausible mechanism to explain the working of this device. Recently we surveyed comprehensive literature on this subject and concluded that many contradictions exist and that even when performance is reported to be effective, the results are typically characterized by low reproducibility.

The application of PUS to chemical processes is one of the intensification technologies[10] that have undergone serious and wide-ranging development over the past two decades. The driving force for these developments has many facets; however, the increasing concern for environmentally clean technology that minimizes the production of waste at source is an important factor. Energy input via ultrasound offers new possibilities and potentialities for cleaner reactions through improved product yields/ recovery and quality through application to various steps such as clarification, evaporation, crystallization, etc.

Ultrasound above 20 KHz up to 100 kHz can be generated with high acoustic intensity which can affect chemical reactivity[10,11] through acoustic cavitation in liquids. When the pressure within the liquid during the expansion phase of a cycle of high intensity ultrasonic wave decreases lower than the vapor pressure of the liquid, bubbles are formed within the liquid. These bubbles grow further during the expansion and undergo a violent collapse during compression, which generates shock waves. This phenomenon, called acoustic cavitation[10,11], has three discrete stages; nucleation, bubbles growth, and collapse in a liquid generating shock waves, which bring about various effects in liquids including affecting the chemical reactions.

Working Principle of PUS to Sugar Evaporators

This equipment consists of three components: ultrasonic generator, ultrasonic transducers and reaction vessels. Transducers can endure a high temperature (100–105 °C) and protect themselves automatically. Due to its special design, the equipment system can run for a long time without any special care and its operation is also easy. Under the effects of ultrasonic cavitation, the induction period of nucleation of materials that form scale is shortened, thus crystal nuclei are produced in a short time. A large proportion of the non-sugars, especially inorganic or organic impurities, can be deposited onto the nuclei, instead of on the surface of the heating tubes. These deposits remain suspended in the sugar solution, and flow out of the evaporators with the syrup. They can then be separated from it. Thus, the amount of precipitate deposited onto the surface of evaporator tubes can greatly be reduced.

Experimental

Viscosity measurement

The viscosity was measured by Brookfield DV-II + pro viscometer with accuracy of ± 1.0 % of full scale range with repeatability of ±0.2 %, and temperature accuracy of ±1 °C (-100 °C to +149 °C) and ±2°C (+150 °C to + 350 °C).

Calibration of the Brookfield viscometer

The viscometer was calibrated using viscosity standard fluids (Silicone oil with viscosity 1000, 30000, 50000 and 100000 cps at 25 °C).

Sampling

Composite samples of massecuite and final molasses were analyzed at half hour intervals with temperature recorded at the source. The pressure and temperature of each evaporator as well as the flow rate of clear juice was recorded at the same time. Samples of clear juice and syrup were collected at half hour intervals. Every four samples collected over a period of two hours were mixed for analysis.

Scale analysis

Investigations on scale control by PUS were monitored in five evaporator bodies. To assess the performance of the PUS, viscosity of massecuite and final molasses with brix and purity of the same reference were probed.

Scanning electron microscopy (SEM) of scale samples

Particle morphologies were studied using a LEO 430 scanning electron microscope. Sample was mounted on aluminum stub with the help of double sided tape. Mounted stubs were coated with gold palladium for analysis using a Polaron sputter coater.

Results and Discussions

Influence of PUS on viscosity of process fluids

The use of PUS seems to have tremendous effect on viscosity of the fluids. Tables1 and 2 illustrate that the mother liquors were considerably less viscous when the PUS was applied than when it was not. Employing PUS, viscosity of 'C' massecuite (Table 1) and final molasses (Table 2) was reduced by 40-50%. Hence, these results also support the fact that

Table 1—Apparent viscosity-purity (gravity) of molasses 63 °C and 30 RPM

	Aerometric Dry Substance Content (%)	Sugar Content (%)	Purity	Apparent Viscosity (1000CP)
With PUS range	87.3-92.8	27.4-29.8	29.8-31.3	0.63-1.12
Average	90.5	28.7	30.5	0.927
Without PUS range	87.9-92.6	29.8-31.2	32.05-33.36	1.59-2.12
Average	90.2	30.4	32.7	1.84

Table 2—Apparent viscosity-purity (gravity) of massecuite 65 °C and 0.3 RPM

	Aerometric Dry Substance Content(%)	Sugar Content (%)	Purity	Apparent Viscosity (1000CP)
With PUS Range	100.3-100.4	46.9-50.1	46.21-49.25	265-715
Average	101.6	48.2	47.5	450
Without PUS	100.3-103.1	46.9-50.1	48.7-50.6	856-1120
Average	1.1.7	50.3	49.5	946

the viscosity of solution would be reduced by applying PUS[7-9]. The massecuite and molasses are non-Newtonian fluids and viscosity of such fluids therefore changes as the shear rate is varied. The experimental parameters such as spindle, RPM, shear rate and speed have an effect on the measured viscosity and this measured viscosity is called the "apparent viscosity" of the fluid. The reduction in final molasses purity is an indication of sugar recovery. Reduction of viscosity (massecuite and final molasses) to the aforesaid magnitude indicates that the evaporator efficiency (EE) of the centrifuge and HTC would also increase.

Characterization of scale

***Physical examination*:** The physical characteristics of scale revealed that the scale after PUS treatment was found to be loose, soft sludge type and white in colour after being dried. It could be easily removed without brushing. However, the scale without PUS treatment was dense, hard and yellowish in colour after drying. It could not be removed complete even by a cutter. Therefore, not only could the scale be reduced significantly, but its physical character was changed by PUS treatment. In addition, during cleaning, scale was found to be removed easily after the treatment, compared to without PUS treatment. It could be inferred that some scale previously formed had already been prevented by PUS. Thus, PUS treatment enhances the operational time of the processing units by reducing labour, chemicals and time used to clean up the evaporators.

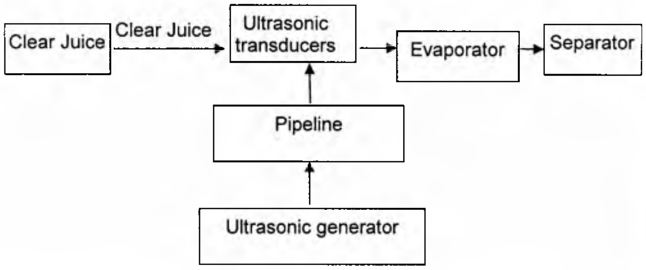

Fig 1—Flow chart showing installation position of ultrasonic equipment at a sugar factory.

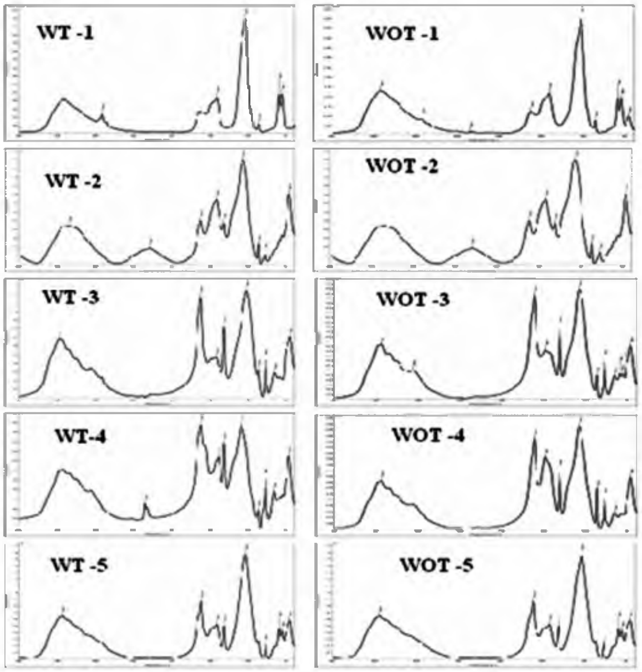

Fig. 2—SEM images

The representative FT-IR spectra present the characteristic absorption peaks of vaterite at 1090, 876 and 743 cm^{-1}. No chatrcteristic peaks belonging to aragonite at 713 and 700 cm^{-1}, as well calcite at 713 and 876 cm^{-1} were detected, further demonstrating that the cauliflower-shaped architecture (SEM images) are vaterite[12].

***SEM Morphologies*:** The impact of treatment with PUS on the microstructures of the scale are shown in Figure 3. The SEM images reveal that the PUS

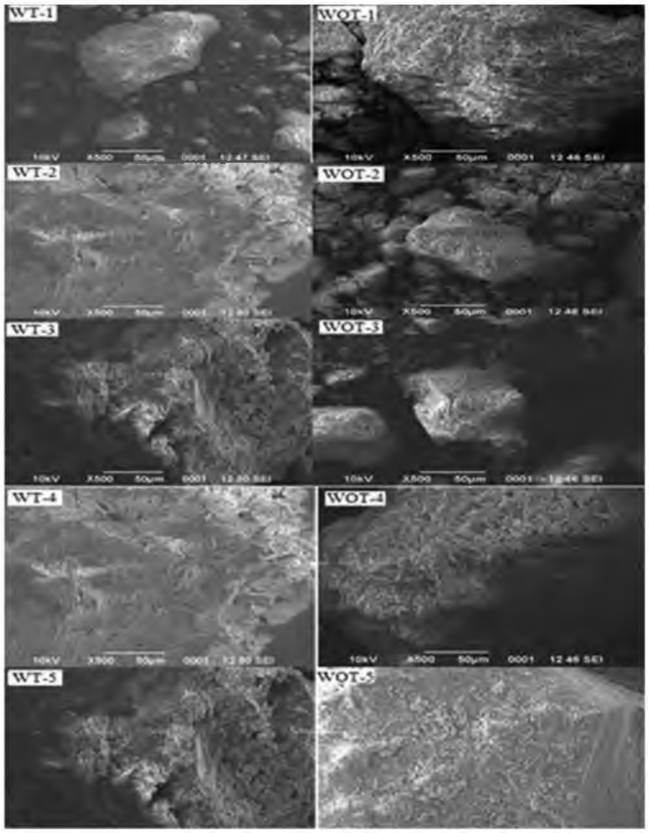

Fig. 3—SEM images

treatment suppresses the formation of calcite crystals and prefers vaterite and aragonite, which are less stable and more soluble polymorphs of calcium carbonate which is evidenced from the cauliflower-like structure[12].

Conclusions

The use of PUS to sugar processing leads to following important conclusions:-

(a) Viscosity of massecuite and final molasses was reduced by 40-50 %.
(b) The physical characteristic of the scale was fond to chance and favours the formation of vaterite which is thermodynamically least stable polymorphs of scale (calcium carbonate).
(c) Sodium hydroxide usages and disposal costs were reduced 65%
(d) Hydrochloric acid usages and disposal were reduced 60 %.
(e) Time to clean up the evaporators and labour cost is reduced significantly.
(f) The time between evaporator cleaning increased to 22-24 days (with treatment) from 10-12 days (without treatment).
(g) Powder consumption was reduced.

Acknowledgment

We are thankful to the Sugar factory and their management team for their support, cooperation and facilities provided to us during our stay. Authors acknowledge the help provided by Coordinator, USIC, Babasaheb Bhimrao Ambedkar Central University, Lucknow for the SEM facilities.

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Reducing viscosity of molasses and massecuite with pulsed magnetic field (PMF)

Abstract

Laboratory and industrial tests were conducted on reducing viscosity of cane molasses and massecuite with pulsed magnetic field (PMF). By the PMF treatment, viscosity was reduced by 40-45% in comparison with untreated materials. It is hypothesized that in response to PMF treatment, non-sugar components (molecules) in the molasses and massecuite aggregate leading to changes in the rheological property of the fluids. The 5 minute PMF at 0.15 tesla (T) produced maximum viscosity reduction (45%). After about 3 hours viscosity begins to rise and after 10 to 12 hours after the PMF treatment returns to the original value. These laboratory studies coupled with some commercial trials suggest that the PMF application could lead to an energy saving process for cane sugar manufacturing.

Keywords: reducing viscosity of molasses and massecuite with pulsed magnetic field (PMF)

Introduction

Viscosity of processing fluids during sugar manufacturing is a limiting factor in several stages of the sugar process; any practical way that would reduce process viscosity, particularly in the low-grade part of the process is therefore important. Viscosity depends principally on the water content and the temperature, and less on the proportion of various impurities. The organic non-sugars probably have a strong effect; compounds with high molecular weight tend to increase the viscosity considerably. Inorganic salts on the other hand usually reduce viscosity of sugar solutions. In general sodium and potassium salts are known to reduce viscosity of sugar solutions and complex-forming calcium ions to increase it. At the same total solids concentration, invert sugar solutions have lower viscosity than pure sucrose.

The use of magnets to control scale in the sugar industry has been controversial since its inception at least two decades ago. Several mills in UP, Gujrat and Maharastra (India) installed magnets. While the sugar mills in UP soon discarded them as worthless, in Maharastra and Gujrat in several mills they are still in use today. There is very little published and authenticated literature on the topic and much information is merely by word of mouth or through commercial literature. Apparently low reproducibility of the results and lack of proven mechanisms to explain the effects led to skepticism regarding the technology. In 1986 Busch *et al* (1) surveyed approximately 60 papers on this subject and concluded that many contradictions exist and that even when positive performance is reported, the results are typically characterized by low reproducibility. However, in 1996 Clarke and Cole in Louisiana (2) reported benefits from using permanent magnets in sugar factory evaporators.

Our group has been engaged since 2008 in such studies, and we have also faced similar skepticism regarding the effect of magnetic field on the viscosity. However, contribution by Bacri and Perzynski (3), Tao and Xu (4) and Homayuni *et al* (5) on reducing viscosity of crude oil by pulsed electric and magnetic

RESEARCH NOTE

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field gave us confidence to continue studies of this topic.

Magnetic field applied to suspensions of magnetic particles induces interactions between the particles. If the interactions are strong enough to overcome the thermal energy of the molecules and the Brownian motion, the particles may aggregate and align in the direction of the magnetic field. If this interaction is very strong or the magnetic field is applied for long time interval, the particle aggregate into macroscopic chains or columns, impede the fluid flow and increase the viscosity. On the other hand, if the magnetic field is applied as a short pulse, then the interaction does not have enough time to affect particles (molecules) separated by macroscopic distance, but it has enough time to assemble some into clusters. These clusters are of limited size, perhaps in the (sub) micrometer range. Although, some particles may not join the aggregates if the magnetic field is exposed only for a short time, viscosity of the juice may be reduced. The volume fraction (of non-water molecules) remains the same but the particle (cluster) size distribution has changed. By this theory, viscosity of the sugar process fluids increases after being exposed to a strong magnetic field for a long time, but decreases if a short magnetic field pulse is applied.

Experimental procedures

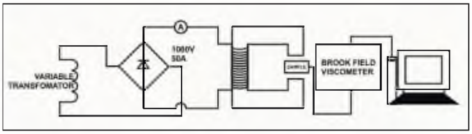
Sampling

Samples of molasses and massecuites in each batch were taken once every hour. Temperature of the samples was noted at the source as well as in the laboratory. Triplicate samples over a period of 2 hours were mixed as collected samples for analysis of Brix, apparent purity and apparent viscosity.

The purity of the C massecuite was in the range of 46 48 and purity of final molasses was in the range of 31-32. Massecuite Brix was in the range of 80-90 whereas molasses Brix was in the range of 70-80.

Figure 1 (a): Pulsed magnetic field generator and cell in industrial tests

Figure 1 (b): Magnetic circuit arrangement in the laboratory PMF tests



PMF Treatment

For application of a pulsed magnetic field on an industrial scale, the cell design of the PMF generator presented in Figure 1(a) was employed. In Figure 1(b) is the experimental set up used in the laboratory tests. All experiments were performed at the temperature of the source materials, at PMF intensity in the range of 0.15 T to 1.5 T and pulse duration between 5 to 720 seconds.

Viscosity measurement

Viscosity of the high density intermediate process materials was measured using a Brookfield DV-II + pro programmable viscometer (Brookfield Engineering Laboratories, Inc. USA) which measures fluid viscosity at a given shear rate. The accuracy of the viscometer was ± 1.0 % of full scale range with repeatability of ±0.2 %, and temperature accuracy of ±10C.

Results and discussion

Laboratory scale tests

In the laboratory experiments, molasses and massecuite samples were diluted to 40 % solids and treated with PMF. For comparison, a high quality refined sugar solution was tested in an exactly same manner. At 28 0C, before PMF treatment, the refined sugar solution had a viscosity of 2.655 cP, whereas molasses had viscosity 900 cP (measured at 10 rpm). Some representative data are shown in Figures 2 and 3. Employing a pulse of 0.25 T for 5 minutes, the viscosity of the refined sugar solution and molasses decreased to 1.062 cP and 500 cP, respectively. Viscosity then gradually increased and after 4 hours the values were 1.087 cP for the sugar solution and 800 cP for molasses, but were still lower than their original viscosities. After 12 hours, in each case the viscosity was back to the original value. At the rotational speeds from 10 to 100 rpm, the 5 minute treatment seemed to produce the maximum viscosity reduction of the materials under study.

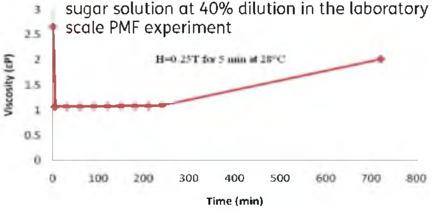


Figure 2: PMF effects on viscosity of refined sugar solution at 40% dilution in the laboratory scale PMF experiment

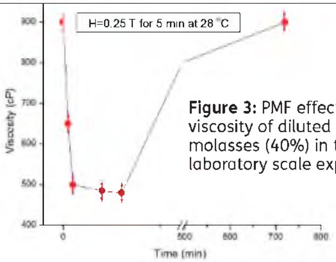


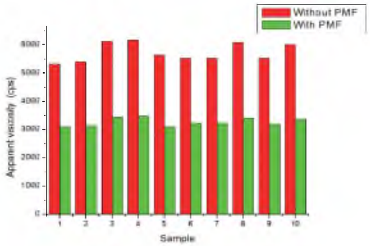
Figure 3: PMF effects on viscosity of diluted final molasses (40%) in the laboratory scale experiment

Industrial scale tests

In these tests, PMF was applied on process fluids without dilution. Samples of the treated materials were collected in a 500 mL beaker, and the original temperature was maintained with a thermostat during viscosity measurement. Prior to viscosity determination, temperature of the fluid in the process were noted, as well as its Brix and purity.

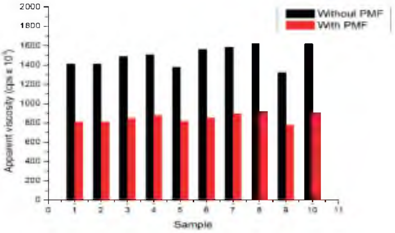
Data shown in Figures 4 and 5 show that the average treated molasses and massecuite viscosity decreased by 40 to 45% compared with untreated samples

Figure 4: PMF effects on viscosity of refined sugar solution at 40% dilution in the laboratory scale PMF experiment



A pulsed magnetic field (PMF) was found effective to reduce viscosity of sugar processing fluids. It is hypothesized that by employing PMF, non-sucrose molecules in molasses and massecuite aggregate temporarily to (sub-)micron-sized clusters; consequently changing rheological properties of the fluids, and reduction their viscosity. Furthermore, the magnetic energy may be partially converted into the linear momentum of the molecules which in turn is converted into hydrodynamic motion and decreased viscosity of molasses and massecuite. This viscosity reduction is not permanent, but it lasts for several hours and is repeatable. The viscosity effect on refined sugar solution raises some doubt whether the effect is due to clustering of non-sugar components. However, in concentrated solutions of molasses and massecuite the magnitude of the effect is several orders higher than in refined sugar solution. Other or additional possible mechanism can be a temporary disruption by PMF of the solvent-solute arrangement in concentrated sugar solutions. However, regardless of the mechanism of PMF action, the results suggest that the technology may have potential for use in cane sugar processing.

Figure 5: Plot illustrating apparent viscosity of massecuite with and without PMF treatment at 53°C



Conclusions

(a) With the PMF treatment, viscosity of massecuite and final molasses was reduced significantly, by 40 to 45%.

(b) Application and re-application of PMF may help in effectively transporting the concentrated fluids (molasses and massecuite) in the sugar process.

(c) The laboratory experiments support commercial trials, confirmed the expected benefits for process control and energy savings during sugar manufacturing.

(d) The present study clarifies the existing controversy regarding the suitability of magnetic fluid conditioners or even permanent magnets in the sugar manufacturing process. The use PMF provides reproducible data on viscosity of the molasses and massecuite.

Acknowledgements:

The authors thank M/s Indian Sugar Tech, Surat, Gujrat (India) for installation of PMF generator under the trade name of EFFC. The authors acknowledge sincere thank to Prof. M. Saska for his valuable comments and suggestions for shaping the paper which improved the quality of the paper.

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Application and potential of a pulsed magnetic field in controlling scale formation in cane-sugar processing

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Abstract The deposition of calcium carbonate ($CaCO_3$), commonly known as scale, costs billions of dollars to the world-wide economy. This is also a common problem for sugar refineries that use the carbonation process. However, carbonate scale is unusual in plants using the sulphitation process; hence, it would be useful to know the composition of the scale formed. A suitable magnetic field pulse can effectively reduce scale formation and also change the nature of the scale formed. Examining the physical characteristics of scale samples showed that the scale after a PMF treatment was of a loose, soft sludge type and easily removed. Scanning electron micrograph (SEM) images, FT-IR spectrum and X-ray diffraction pattern (XRD) provides definitive proof of the existence of $CaCO_3$ scale in the sulphitation process of sugar manufacture.

Key words $CaCO_3$ scale, sugar evaporator, pulsed magnetic field, energy saving

INTRODUCTION

Calcium carbonate is one of the most ubiquitous minerals in nature. Among the three anhydrous crystal polymorphs, rhombohedral calcite, orthorhombic aragonite and hexagonal vaterite, calcite is the most stable phase at ambient temperature, aragonite is metasable polymorph, while vaterite is thermodynamically unstable at all external conditions. The unwanted precipitation of $CaCO_3$ has been a common problem in heat exchangers and it is one of the most important scale forming minerals in oil and gas production (Andreassen 2005). This is also a likely problem for sugar refineries using the carbonation process. As a result of the progressive accumulation of scale on heated surfaces, the heat transfer coefficient (HTC) considerably declines over time causing significant economic losses (Hu *et al.* 2006). Hence, there is considerable interest in finding methods that effectively control the formation of this deposit.

This work is essentially an extension of our earlier work (Singh *et al.* 2016) on the effect of a pulsed magnetic field (PMF) on the viscosity of cane molasses and massecuite. In this paper we show that application of a suitable magnetic field pulse can significantly reduce scaling tendency and changes the nature of the scale in sugar evaporators.

PMF TREATMENT

The general operating principle for a proposed PMF has been described elsewhere (Singh *et al.* 2016). For the application of a PMF on evaporators, the cell design of the PMF generator given in Figure 1 was used. All experiments were performed using a PMF intensity in the range of 0.15 T to 1.5 T and pulse duration between 5 and 720 s. The chemical composition of the scale samples was tested in the Ita Lab, Mumbai.

Our study was undertaken in a sugar mill (5000 t of cane per day) in western India that produces plantation-white sugar using the sulphitation process. The PMF generator was installed in the evaporators as shown in Figure 2 for 15 days and scale collected at the fifth body was examined to assess the effect of the PMF on the scale deposits. Scale formed after 15 days without PMF treatment was collected for comparison. All other process parameters remained unchanged in both the cases. The cane throughput was the same (juice analyses were similar). To assess the reproducibility, tests were done consecutively with and without the technology in a season or even at different times in the season.

Fig. 1. Pulsed magnetic field generator and cell used in industrial tests.

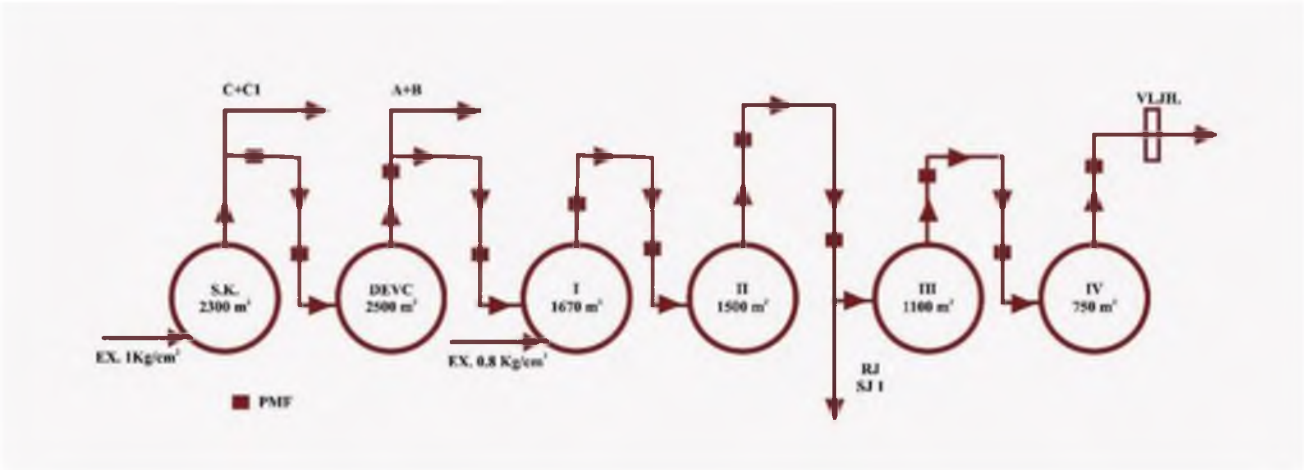

Fig. 2. Installation of pulsed magnetic field generators on juice piping at evaporators.

RESULTS AND DISCUSSION

Examination of the physical characteristics of the scale samples showed that the scale after PMF treatment was of a loose, soft sludge type and easily de-scalable. The comparative chemical composition of dried samples (fifth body) with and without treatment (Table 1) shows that the amount of calcium and sulphate were 35.5% and 58.6%, respectively in the absence of PMF, while application of PMF reduced it to 30.7% and 51.2%, respectively. However, we observed that in the presence of carbonate (28.1%), CaO can react with atmospheric CO_2 leading to the formation of $CaCO_3$. In cane sugar factories with large changes of the pH value of the juice during evaporation, some $CaCO_3$ may be found in scales of later effects but not in large quantities. In beet sugar factories and refineries with carbonation, $CaCO_3$ is found in the heat exchangers for limed/carbonated juice.

Another important observation was that of the presence of silica (2.9%) with PMF treatment. Silica occurs naturally in cane juice and also in the impure lime employed in clarification. However, the lime used during the trials was from the same batch. Silica is soluble at higher temperatures, such as the temperature of clarified juice and at the temperature range of semi Kestners. Therefore, it remains in the soluble form in the semi Kestner evaporator at typical first-body temperatures (high temperature range). However, in the last effect body (typically about 60°C), silica starts to coagulate and deposit as scale.

Table 1. Evaporator scale sample (fifth body, dried samples) without and with PMF.

Parameter	Without PMF (%)	With PMF (%)
Moisture content	29.39	16.55
Loss on ignition (850°C)	41.89	34.51
Silica as SiO_2	0.22	2.89
Iron as Fe_2O_3	0.07	0.13
Alumina as Al_2O_3	3.72	12.51
Calcium as CaO	35.50	30.66
Magnesium as MgO	1.50	1.93
Sodium	0.08	0.06
Potassium	0.07	0.19
Chloride as Cl^-	0.20	0.13
Sulphate as SO_4^{2-}	58.60	51.21
Phosphorous as P_2O_5	0.04	0.28
Carbonate as CO_3^{2-}	28.13	21.7

The SEM images (Figures 3-6) clearly demonstrate the change in nature, morphology or the size of scale. Comparing the SEM images of scale after PMF treatment (Figure 4) with standard materials (aragonite and calcite in Figures 5 and 6 respectively), it is clear that a large amount of thermodynamically least stable vaterite is formed after PMF treatment. There are two possible reasons for this. Firstly, because the crystal growth rate slowed down, the crystal size was smaller, so the fouling became soft and loose, which was easy to remove. Secondly, application of a suitable magnetic field pulse, the suspended particles in syrup existing as colloid were broken and dissolved, so the rates of absorption were reduced, and the scale forming tendency decreased. It is, therefore, apparent from the SEM images that without PMF treatment the scaling is greater, more problematic and requires more time to clean.

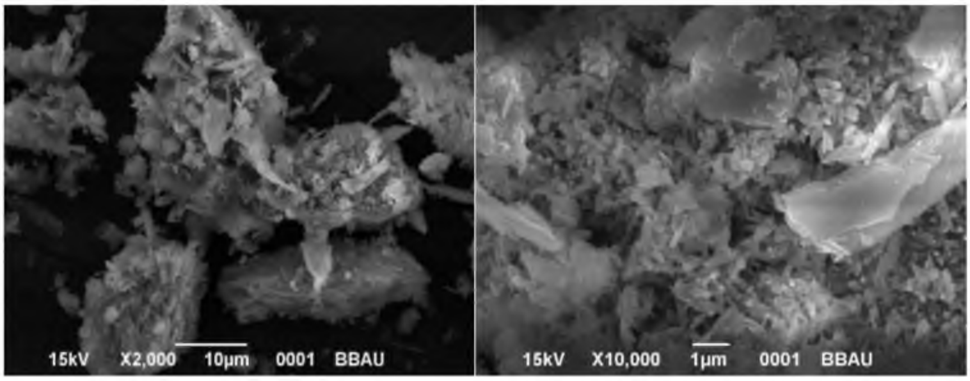

Fig. 3. SEM images of scale without PMF treatment.

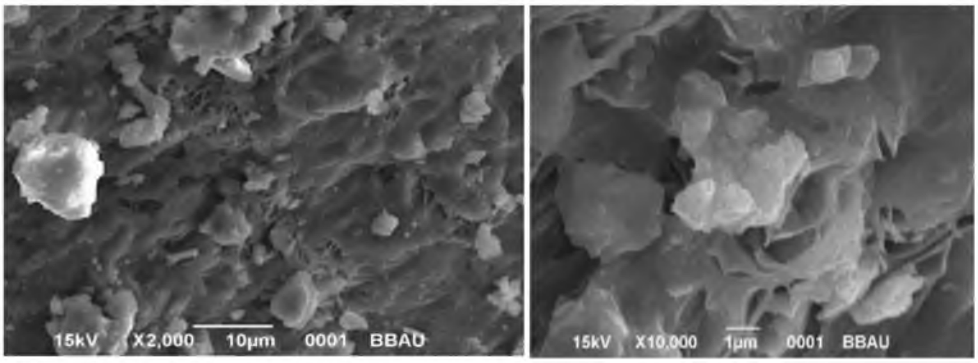

Fig. 4. SEM images of scale with PMF treatment.

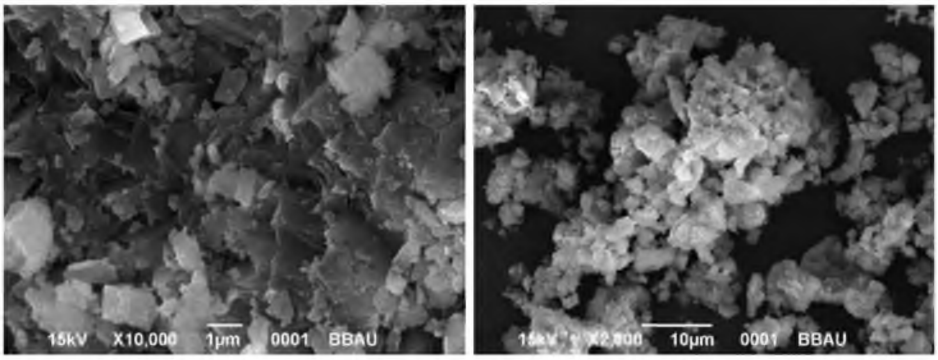

Fig. 5. SEM images of aragonite.

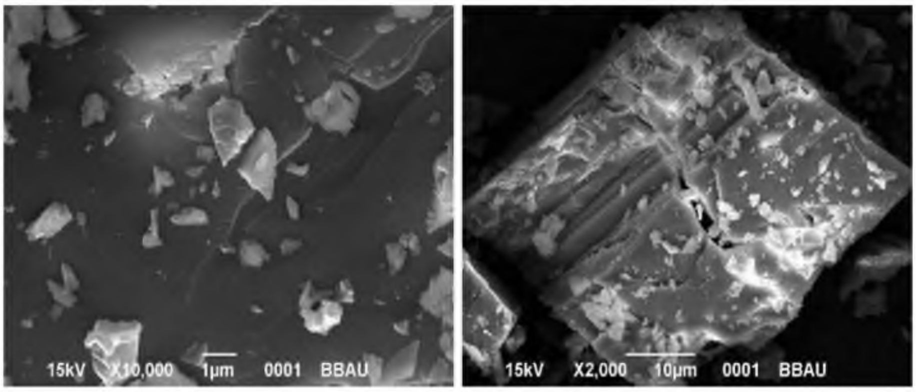

Fig. 6. SEM images of calcite.

The FT-IR spectra of the scale samples shown in Figure 7 demonstrate the characteristic absorption peaks of calcium carbonate at 1112 and 1134 cm^{-1} (White 1974; Zhou *et al.* 2004). No characteristic peaks belonging to calcite at 713 and 876 cm^{-1} were detected after PMF treatment. However, partial characteristic peaks belonging to aragonite appeared after treatment at 649 cm^{-1}.

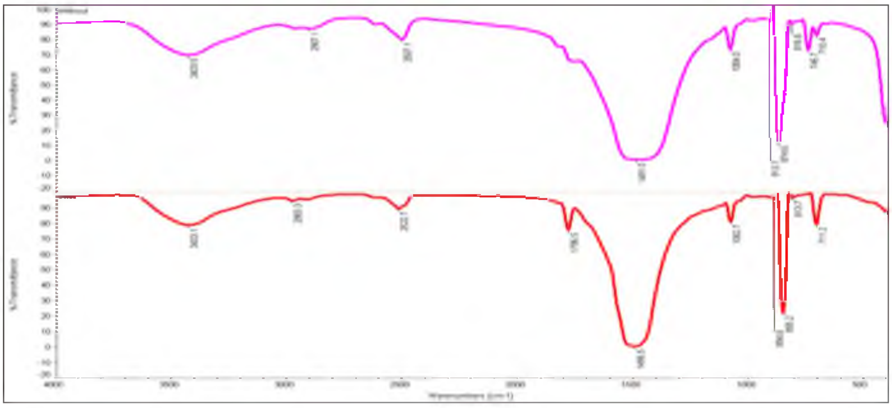

Fig. 7. FT-IR spectra of standard carbonate scale with and without PMF treatment.

The typical XRD pattern of scale samples shown in Figure 8 provides definitive proof of $CaCO_3$ in the scale of evaporators in the sulphitation process of sugar processing.

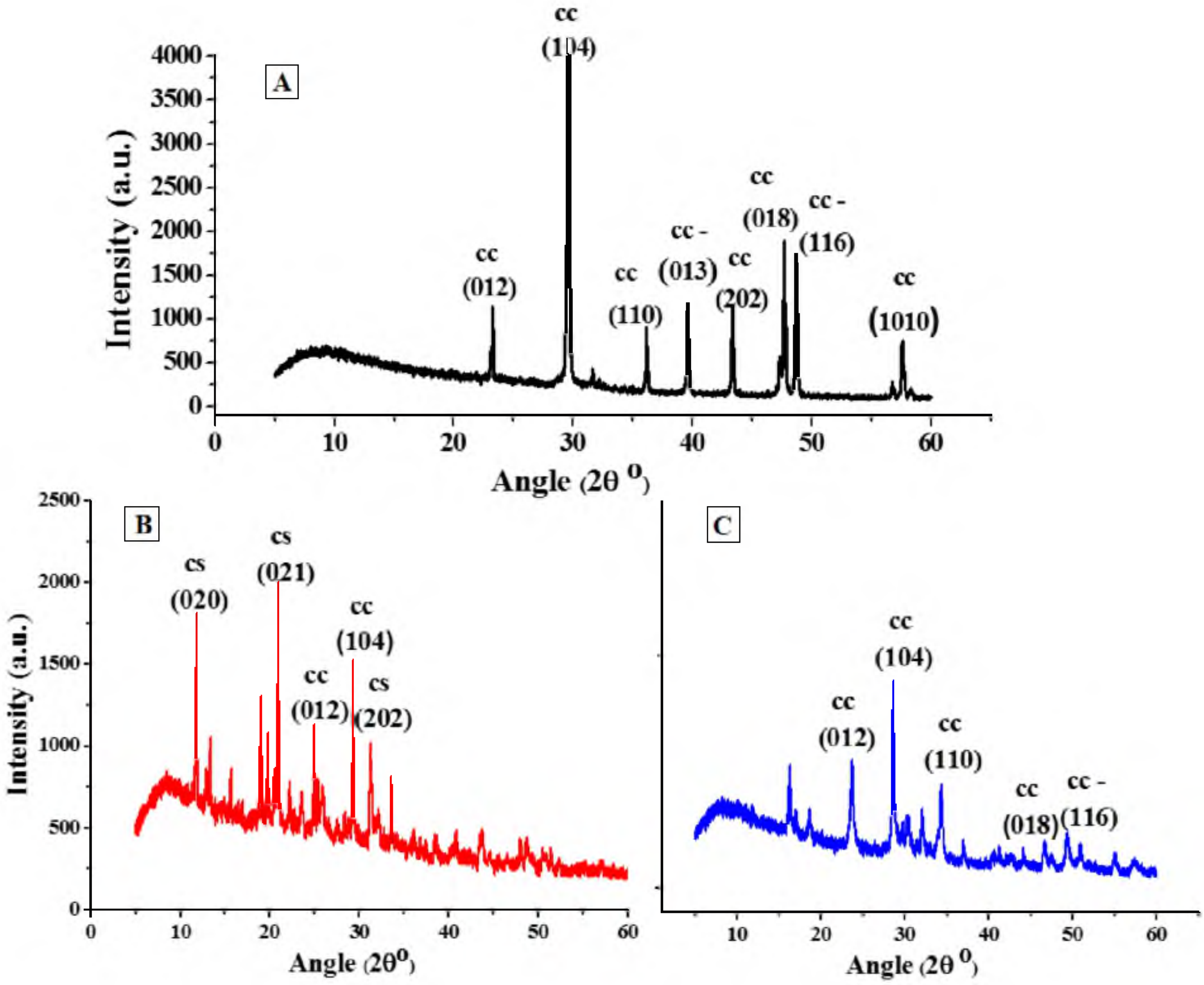

Fig. 8. Typical XRD pattern of scale samples collected before and after PMF treatment. A - standard calcite: B - sample after PMF treatment: C - sample without PMF treatment; CC = $CaCO_3$, CS = $CaSO_4$.

CONCLUSIONS

The SEM images, FT-IR spectrum and typical XRD pattern of the scale provides definitive proof of $CaCO_3$ scale with $CaSO_4$ in the sulphitation process of sugar processing.

The application of PMF changes the physical configuration of the scale in that it changes from hard and dense to soft, porous sludge type which is easily de-scalable.

Applications of a suitable PMF suggest that they could lead to an energy-saving process for cane sugar manufacturing.

ACKNOWLEDGEMENTS

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Application et potentiel d’un champ magnétique pulsé pour le contrôle de la formation de tartre pendant la fabrication du sucre de canne

Résumé. Les dépôts de carbonate de calcium ($CaCO_3$), communément appelé tartre, coûte des milliards de dollars à l’économie dans le monde entier. C’est également un problème courant pour les raffineries de sucre qui utilisent le procédé de carbonatation. Cependant, l’incrustation de carbonate est rare dans les sucreries ou le soufre est utilisé; par conséquent, il serait utile de connaître la composition des tartres formés. Une impulsion magnétique appropriée peut réduire la formation de tartre et également modifier la nature des incrustations formées. L’examen des caractéristiques physiques des échantillons de tartre ont montré que les incrustations après un traitement de PMF étaient un genre de boues fluides, moles et faciles à enlever. L’utilisation des images obtenues par une microscopie électronique (SEM), des spectres FT-IR et la diffraction des rayons X (DRX) fournissent la preuve irréfutable de l’existence d’incrustations de $CaCO_3$ dans le processus de fabrication du sucre en sulphatation.

Mots-clés: Incrustations de $CaCO_3$, évaporateur de sucre, champ magnétique pulsé, économie d’énergie

Aplicacion y potencial de un campo magnetico pulsado para controlar la formacion de incrustaciones en el proceso de cana de azúcar

Resumen. El depósito de carbonato de calcio($CaCO_3$), comúnmente conocido como incrustaciones, cuesta billones de dólares a la economía mundial. Esto es también un problema común de las refinerias de azúcar que usan el proceso de carbonatación. Sin embargo, las incrustaciones de carbonato son inusuales en las plantas que usan el proceso de sulfitación, por lo tanto sería útil conocer la composición de las incrustaciones formadas. Un campo magnético pulsado apropiado puede reducer la formación de incrustaciones efectivamente y también cambiar la naturaleza de las mismas. Examinando las características físicas de las muestras de incrustaciones, éstas mostraron que luego de un tratamiento PMF eran de tipo de lodo suelto, suave y fácilmente eliminable. Imágenes de micrografías electrónica de barrido (SEM), espectro FT – IR y patrón de difracción de rayos X (XRD) se provee de pruebas definitivas de la existencia de incrustaciones de $CaCO_3$ en el proceso de fabricación de azúcar por sulfitación.

Palabras clave: Incrustaciones de $CaCO_3$, evaporador de azúcar, campo magnético pulsado, ahorro de energía.

EFFECT OF ULTRASONICS ON MORPHOLOGY OF PRECIPITATED CALCIUM CARBONATE (PCC) FOR CONTROLLING SCALE FORMATION IN CANE SUGAR PROCESSING : LABORATORY SCALE EXPERIMENT

Kaman Singh[1]*, Ajay Kumar[2] & Satya Prakash Gupta[2]

ABSTRACT

The deposition of calcium carbonate commonly known as scale costs billions of dollars to the world wide economy. This is also a customary global problem for cane sugar processing. The present work is essentially an extension of our earlier work on the effect of power ultrasound on cane sugar processing. Application of ultrasonics can effectively reduce scale formation and also changes the nature of the precipitated calcium carbonate (PCC). The FTIR spectrum of the CaCO3 after PUS treatment presents the characteristic absorption peaks of vaterite at 1112 and 1134 cm^{-1}*. No characteristic peaks belonging to calcite at 713 and 876 cm*$^{-1}$ *were detected after treatment. However, partial characteristic peaks belonging to aragonite were appeared after treatment at 649.4 cm*$^{-1}$*. The Scanning electron micicrograph (SEM) images clearly demonstrates the vaterite (thermodynamically least stable polymorph of* $CaCO_3$*) image after PUS treatment. Thus, extension of these laboratory scale model experiments to industrial scale could lead to an energy saving process for cane sugar manufacturing.*

Keywords: Precipitated calcium carbonate (PCC), power ultrasound (PUS), characterization, sugar evaporator, energy saving.

INTRODUCTION

Calcium carbonate is one of the most ubiquitous minerals in nature. Among

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the three anhydrous crystal polymorphs, rhombohedral calcite, orthorhombic aragonite and hexagonal vaterite, calcite is the most stable phase at ambient temperature; aragonite is metasable polymorph, while vaterite is believed to be thermodynamically unstable at all external conditions. Therefore, aragonite and vaterite usually transform into the stable calcite phase. Crystallization and precipitation of calcium carbonate minerals has been the topic of intensive investigation owing to its polymorphic and morphologic varieties in geological and biological system and to its important industrial (Sims *et al.* 1995, Walsh and Mann, 1995., Jung *et al.* 2000, Qi and Ma, 2002, Zhou *et al.* 2010). However, the unwanted precipitation of calcium carbonate has been a customary problem in heat exchangers and it is one of the most important scale- forming minerals in oil and gas production (Andreassen, 2005). This is also a routine problem for cane sugar processing and it costs billions of dollars to the world wide economy. In 1977, due to increase of energy and decrease of production capacity resulting from scale British National economic losses were estimated at 0.5 billion pounds (Qui, 1999). Hence, there is a considerable interest to find methods that effectively prevent/control the formation of this deposit. As a results of the progressive accumulation of scale on heated surfaces, the heat transfer coefficient (HTC) considerably declines with time causing significant economic losses (Aijun *et al.* 2006).

Ultrasound has been used in many diverse fields such as medical imaging and diagnostics, biological cell-disruption, non-destructive testing of materials, under-water ranging (SONAR) and thermoplastic welding. Large-scale equipment is available for the application of power ultrasound to wastewater treatment (in particular, anaerobic digestion) and to a range of activities in the food processing industry (*e.g.,* emulsification, microbial fermentation, cell disintegration, homogenizing). Many of the devices available use high power ultrasonic probes and sonotrodes. The application of power ultrasound (20-100 kHz, but can be as high as 2MHz) to chemical processing. The first application of ultrasound to crystallization (sonocrystallization) in 1927 predates by decades any serious application to chemistry **(Richards and Loomis, 1927, ACS)**. In addition, there is considerable literature from the former Soviet Union in the 1950s to the 1970s, albeit dealing with small-scale applications **(Kapustin 1963, Martynovskaya 1970)**. However, whilst the concept of ultrasonic processing is not new, ability to use it on an industrial scale is. Indeed, recent advances in equipment have made its implementation at industrial scale feasible **(McCausland and Cains, 2002)**. Interest in the application of ultrasound to crystallization in the pharmaceutical and fine chemicals sectors of industry has received further impetus in recent years with the increased focus on specificity of effect, and the corresponding requirement to prepare and purify complex chemical entities to very exacting standards. Ultrasound may influence crystallization through the mechanisms of cavitation and acoustic streaming **(Young, 1989)**. Cavitation appears to be particularly effective as a means of inducing nucleation, and there is evidence of dramatic improvements in reproducibility obtained through such sononucleation. Furthermore, using ultrasound to generate nuclei in a controlled and reproducible way provides a well-defined starting point for the crystallization process. This allows focus on controlling the crystal growth via the residence time in the crystallizer. This combined approach to influence crystal size distribution, assists morphological control and elimination of impurities in the crystal, and improve solid-liquid separation behaviour. Sononucleation can also eliminate the requirement to add seed crystals, and this can be particularly advantageous in contained crystallizations.

Medical diagnostic applications **(Clarke 2004)** using UST is *fait accompli*, but its use in analytical systems and in process control is in nascent stage. Bubnik et al reported on the optimization of cooling crystallization by an ultrasonic technique. Both pure and technical sucrose solutions were used and it is possible to monitor the metastable zone for sucrose and determine the nucleation parameters.

The present work is essentially an extension of our earlier work on (Singh *et al.* 2013, 2016) the effect of PUS on viscosity of cane molasses and massecuite. Model studies at laboratory and on industrial scale established that application of suitable magnetic field leads to significant viscosity reduction of cane molasses and massecuite. In this communication, we will show that effect of PUS on precipitated calcium carbonate (PCC) which can be extended to industrial scale in sugar evaporators for controlling scale formation.

EXPERIMENTAL PROCEDURE

All chemicals used were of analytic reagent grade. Anhydrous calcium chloride ($CaCl_2$) and sodium bi-carbonate ($NaHCO_3$) were purchased from Fisher. All chemicals were directly used without further treatment. The calcium carbonate crystallization experiments were carried out by using a method developed by Zhou *et al.* (2009). In a typical synthetic process, 0.01 mole (0.14702 g) of $CaCl_2$ and 100 ml of distilled water were added to a three necked flask of 100 ml volume to obtain a homogeneous solution. This $CaC1_2$ solution was adjusted to pH 5.5 to 7.5 with a 5 M HC1 solution. Fresh solution of $NaHCO_3$ was prepared by dissolving 0.02 mole (0.168 g) of $NaHCO_3$ in 100 ml of distilled water. The CaCl2 solution was thermostated in a 75 ^{0}C oil bath for 45 min using a set of reflux condensing system, and then 100 ml of NaHCO3 solution at 75 ^{0}C was quickly injected into the $CaCl_2$, The solution were sonicated at 70 ^{0}C for 45 min employing ultrasonicator (200 W model UP200ht, Hielscher, Germany Ultrasonic Processor, Ti horn, 26kHz) by employing a direct immersion titanium horn to form a white precipitate. The final pH of the reaction solution was 7.5 After continuously being stirred for 45 min in the thermostated oil bath, the white precipitate was retrieved by filtration and washed with distilled water and absolute ethanol for several times, and finally dried overnight at room temperature in a vacuum oven. Precipitation conditions except the pH of $CaCl_2$ solution were the same for all other experiments.

FT-IR spectra were recorded on a Nicolet Magna IR-750 spectrophotometer, the KBr pellet method was employed. The morphology of the resulting samples was observed on a JEOL JSM-6700F filed emission scan¬ning electron microscope.

RESULTS AND DISCUSSION

The SEM images shown in Fig. 1-3 clearly demonstrated that the application of a PUS reduced calcite crystal growth, changes in the nature, the morphology or the size of calcium caronate. It is clear that a large amount of calcite and aragonite were present in the absence of ultrasonics and there seems to be a transformation of calcium carbonate. If we compare SEM images of PCC it was clear that a large amount of thermodynamically least stable vaterite is formed after treatment. The SEM images reveal that in the absence of treatment, the scale sizes were various and much larger compared with PUS treatment. Thus, application of PUS plays a crucial role in changing the nature of PCC from hard (calcite) to soft (vaterite) which is easily de-scalable.

FT-IR is incredibly simple spectral finger print for the identification of carbonate polymorphs (Wang *et al.* 1999, Lote *et al.* 2003). The FT-IR spectra of the PCC are shown in Figs 4-6. There are significant differences in the IR spectra. The FTIR spectrum of the precipitated calcium carbonate (PCC) samples after PUS treatment presents the characteristic absorption peaks of vaterite at 1112 and 1134 cm-1 . **(White, 1974; Zhou *et al.*, 2004).** No characteristic peaks belonging to calcite at 713 and 876 cm-1 were detected after PUS treatment. However, partial characteristic peaks belonging to aragonite were appeared after treatment at 649 cm^{-1}.

CONCLUSION

The effect of a power ultrasonic pulse on precipitated calcium carbonate (PCC) leads to following important conclusions:-

(a) The physical configuration of the calcium carbonate changes from hard and dense to soft, porous sludge type.

(b) The SEM images of PCC demonstrate that a large amount of thermodynamically least stable vaterite is formed after ultrasonic treatment.

(c) The FT-IR spectral finger print for the identification of carbonate polymorphs after ultrasonic treatment demonstrate the characteristic absorption peaks of vaterite at 1112 and 1134 cm^{-1}; a thermodynamically least stable polymorph of calcium carbonate.

(d) Thus, extension of these laboratory scale model experiments to industrial scale could lead to an energy saving process for cane sugar manufacturing.

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FIGURE 1 – TYPICAL SEM IMAGES OF UNTREATED AND TREATED (PUS) CALCIUM CARBONATE AT pH 5.5

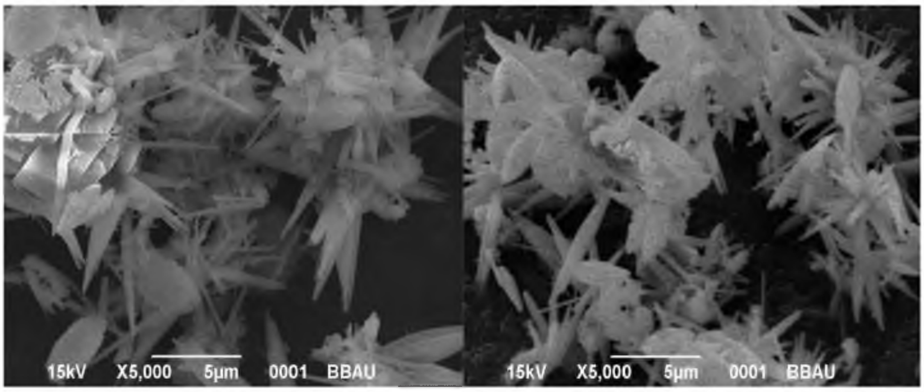


FIGURE 2 – TYPICAL SEM IMAGES OF UNTREATED AND TREATED (PUS) CALCIUM CARBONATE AT pH 6.5

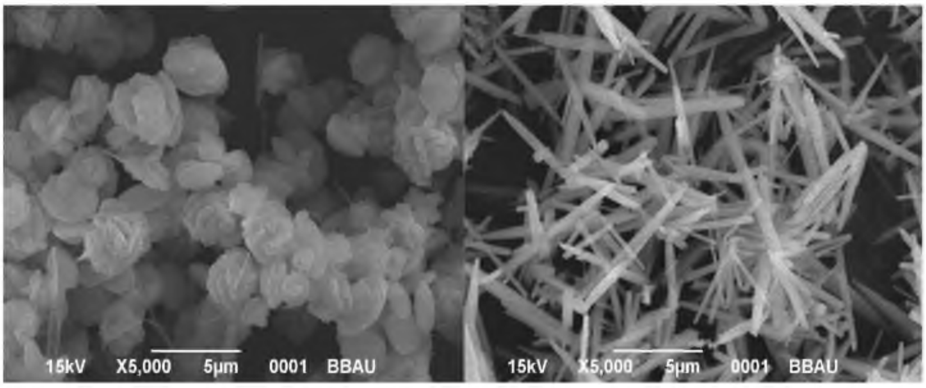


FIGURE 3 – TYPICAL SEM IMAGES OF UNTREATED AND TREATED (PUS) CALCIUM CARBONATE AT pH 7.5

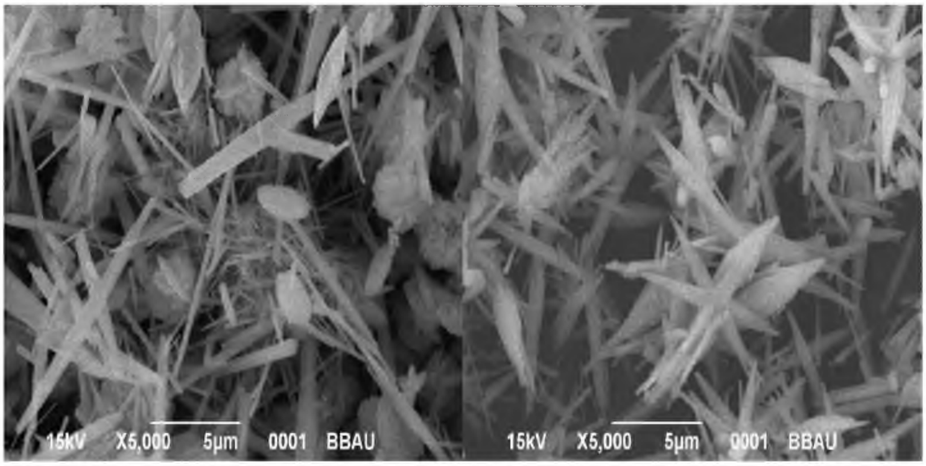


FIGURE 4 – TYPICAL FTIR SPECTRA OF UNTREATED AND TREATED (PUS) CALCIUM CARBONATE AT pH 5.5

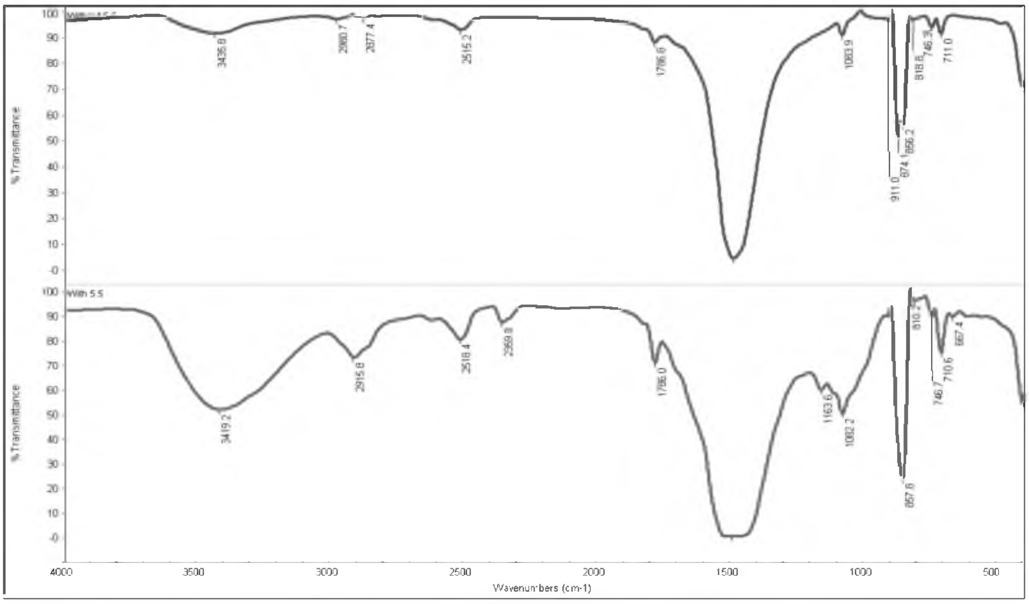
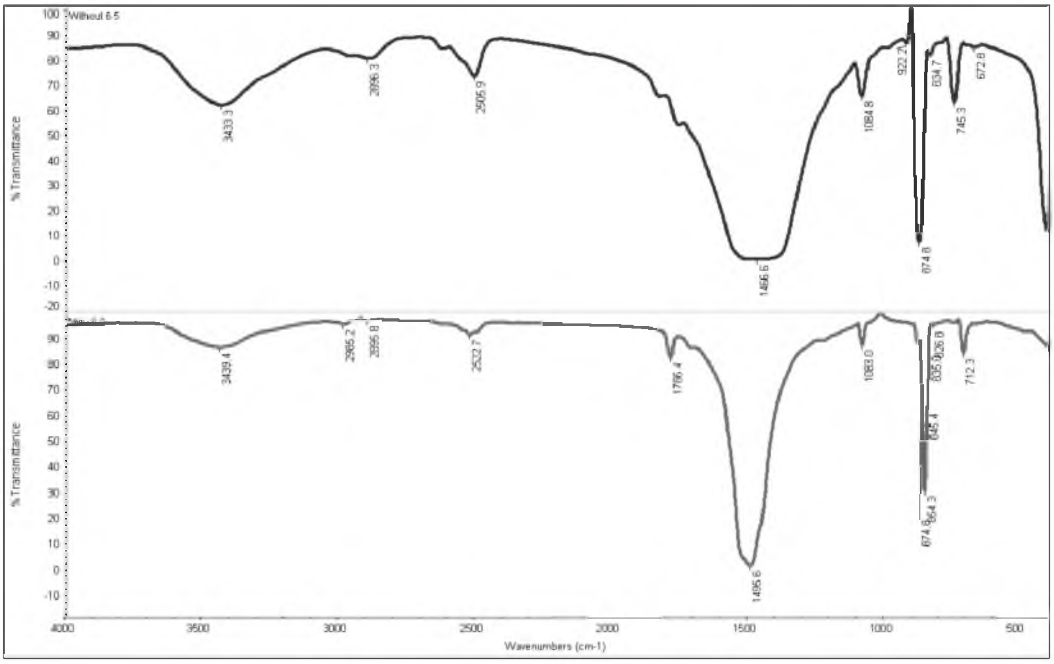


FIGURE 5 – TYPICAL SPECTRA OF TREATED AND UNTREATED (PUS) CALCIUM CARBONATE AT pH 6.5



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