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SIMULATION STUDIES

ON A COLUMN CRYSTALLIZER

BY

Neshat Muhammad Akhtar

A thesis submitted for the degree
of Doctor of Philosophy
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Industrial Chemistry Department
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ABSTRACT

Mathematical modelling and simulation of a continuous column crystallizer is carried out under dynamic conditions compared to the usual steady state modelling. The column used is of the Schildknecht type using an Archimedean transportation screw within a polished stainless steel jacket.

The process of column crystallization is considered as a multi-stage separation process similar to a distillation column. In this investigation the column is considered as a single piece of equipment, containing freezing and melting sections at either end of the column and a long purification section in between. Crystals formed in the freezing section are transported along a screw, through the purification section towards the melting section, where they are melted and some of the melt is allowed to flow countercurrently thus washing adhered impurities by reflux. Most of the melt is removed as pure product while impure product is removed from the opposite end.

The processes involved are those of mass transfer, heat transfer, mixing, transfer of impurities due to countercurrent contacting of pure and impure liquids and diffusion due to concentration gradient of the impurity. The purification section is considered to be theoretically divided into a number of stages involving temperature and purity gradients, similar to the theoretical plates of a distillation column. The column was tested for desalination purposes.

Mathematical models were developed into simulation models for each of the three sections. The freezing section was developed first, and on successful operation the other two simulation models were joined to form the entire column. The programme was written in FORTRAN IV and was simulated on a CDC 7600 computer. It is possible that a fuller understanding of the mechanism of the column could lead to large scale desalination plants of the column crystallizer type.

LIST OF SYMBOLS:-

A	Empirical constant in nucleation rate equation	(SI units)
AA	Cross sectional area of the column available for mass transfer	m^2
AAA(N)	Total surface area available for mass transfer in any stage (N)	m^2
AM	Available crystal surface area for heat transfer	m^2
AW	Area of freezing section wall	m^2
AWM	Area of melting section wall	m^2
C	Crystal mass rate to purification section	KgS^{-1}
C(1)	Crystal mass rate to purification section	KgS^{-1}
C(11)	Crystal mass rate going to melting section	KgS^{-1}
CF	Specific heat of refrigerant	$JKg^{-1}K^{-1}$
CM	Mass of a single crystal	Kg
CMM	Mass of a single crystal in melting section	Kg
C(N)	Crystal mass rate going out of any stage(N)	KgS^{-1}
CP	Specific heat of liquid	$JKg^{-1}K^{-1}$
CWM	Specific heat of heating liquid	$JKg^{-1}K^{-1}$
D	Diffusion co-efficient	m^2S^{-1}
DP	Diameter of ice crystal	m
E	Empirical constant of adhering liquid	SI Units
ETA(N)	Mass fraction of free liquid in stage(N)	mass/total liquid
EX	Ratio of actual thermal driving force to apparent driving force	
F	Mass transfer from liquid to solid in freezing section	KgS^{-1}

F(1)	Mass transfer from liquid to solid in freezing section	KgS^{-1}
FF	Mass transfer from solid to liquid in melting section	KgS^{-1}
F(N)	Mass transfer from liquid to solid in any stage (N)	KgS^{-1}
FR	Function of crystal radius (R)	
G	Crystal growth rate constant	SI Unite
GA	A constant Omega in driving force ratio	SI Units
GB	Liquid entrained within solids	Mass/unit mass ice
HF	Height of freezing section	m
HP	Planck's constant	SI Units
HZ	Height of a stage in purification section	m
J	Rate of nucleation in freezing section	Particles S^{-1}
J(1)	Rate of nucleation in freezing section	Particles S^{-1}
JM	Number of crystals in the melting section	Particles
J(N)	Nucleation rate in any stage (N)	Particles S^{-1}
K	Over all liquid phase mass transfer coefficient	mS^{-1}
L	Feed liquid flowing in	KgS^{-1}
λ	Latent heat of solids	$JKg^{-1}K^{-1}$
LD(1)	Adhering liquid going out of freezing section	KgS^{-1}
LD(11)	Adhering liquid going out of last stage of purification section	KgS^{-1}
LD(N)	Adhering liquid going out of stage (N) of purification section	KgS^{-1}

LE	Liquid take off as bottom product	KgS^{-1}
LF	Flow rate of refrigerant	KgS^{-1}
LP(1)	Feed liquid going out of freezing section	KgS^{-1}
LP(11)	Feed liquid going out of last stage of purification	KgS^{-1}
LP(N)	Feed liquid going out of any stage (N)	KgS^{-1}
LTP	Liquid take off as top product	KgS^{-1}
LWM	Rate of heating liquid coming in	KgS^{-1}
MD(N)	Diffusion within free liquid stage (N)	Kg^{-1}
MF	Mass of refrigerant around freezing section	Kg
MK(N)	Mass transfer of impurity from adhered to reflux stage (N)	KgS^{-1}
ML	Liquid mass hold up in freezing section	Kg
ML(N)	Liquid mass hold up in stage (N)	Kg
MLD(N)	Adhered liquid mass hold up in stage (N)	Kg
MLM	Liquid mass hold up in melting section	Kg
MS	Solid mass hold up in freezing section	Kg
MS(1)	Solid mass hold up in freezing section	Kg
MS(N)	Solid mass hold up in stage (N)	Kg
MSM	Solid mass hold up in melting section	Kg
MWM	Mass of heating liquid around melting section at all times	Kg
N	No. of stages in Purification section (2 to 11)	
NJ(N)	Number of crystals in Stage (N)	Particles

P(N)	Density of liquid in stage (N)	Kgm^{-3}
PS	Density of ice	Kgm^{-3}
Q(1)	Reflux coming down to freezing section	KgS^{-1}
Q(2)	Reflux going out of stage (2) of purification section	KgS^{-1}
Q(N)	Reflux going out of stage (N) of purification section	KgS^{-1}
Q(12)	Reflux coming in from melting section	KgS^{-1}
QQ	Total heat transfer in melting section	JS^{-1}
R	Average radius of crystal	m
RG	Ideal gas constant	$JK^{-1}mole^{-1}$
RM	Average radius of crystal in melting section	m
TB	Temperature of bulk liquid in freezing section	K
TB(1)	Temperature of bulk liquid in freezing section	K
TB(N)	Temperature of bulk liquid in stage (N)	K
TBM	Temperature of bulk liquid in melting section	K
TF	Freezing temperature	K
TI	Ice/Liquid interface temperature	K
TIF	Temperature of refrigerant	K
TIN	Temperature of feed coming in	K
TIW	Temperature of heating liquid	K
TW	Temperature of freezing section wall	K

TWM	Temperature of melting section wall	K
U	Overall heat transfer co-efficient	$Jm^{-2}S^{-1}$
V	Vertical velocity of screw	ms^{-1}
VS	Vertical velocity of screw	ms^{-1}
WD(11)	Salt fraction mass in adhered liquid going out of stage (11)	mass of salt/ mass of liquid
WD(N)	Salt fraction mass in adhered liquid in stage (N)	mass of salt/ mass of liquid
WL	Mass fraction of salt in freezing section	mass of salt/ mass of liquid
WL(1)	Mass fraction of salt in freezing section	mass of salt/ mass of liquid
WL(N)	Mass fraction of salt in stage (N)	mass of salt/ mass of liquid
WLI	Mass fraction of salt in feed	mass of salt/ mass of liquid
WLM	Salt mass balance in melting section	mass of salt/ mass of liquid
WQ	Salt mass fraction in reflux	mass of salt/ mass of liquid
Σ	Salt mass in solids	mass of salt/ mass of liquid

Original variables in the Melting Section re-assigned

CNP = C(11)

LDP = LD(11)

LPP = LP(11)

Q = Q(12)

TBP = TB(11)

WDP = WD(11)

WLP = WL(11)

CHAPTER 1

INTRODUCTION

Chapter 1 INTRODUCTION

There are three main areas of study involved in the analysis of the subject matter "Mathematical Modelling and Simulation of a Column Crystallizer". The first is the Column crystallizer itself, second is the Mathematical Model representing the column and process and the third is the Simulation with the use of a computer.

The process of analysis starts with the definition of a problem in the field of separation of mixtures. Man during his evolution has heavily relied upon the separation and purification of mixtures. Crystallization is probably the earth's oldest fractionation process; the oldest example being the solidification of the earth's molten layer, the magma. Distillation has also been in evidence since the formation of the oceans due to the evaporation of water and subsequent precipitation as rain. Thus mother nature has been extremely kind by providing rain (potable water) for agriculture and an important source for drinking when accumulated in reservoirs. Medicine has also greatly depended upon separation and purification processes.

Sailors have always been aware that sea ice contains less salt than the surrounding water, though the credit is taken by

Thomas Barthelemous (97) for the report. The first results on the desalination of sea water by freezing were published by Maria Lorgna (7) in Venice (1786). By repeated freezing she was able to obtain almost pure water from brine.

The crystalline state belongs to the solid phase of matter; the purification which occurs upon freezing of a solution or melt is due to the inability of the rigid crystal lattice to tolerate the presence of other species.

Man's ability to survive is limited by the availability of potable water. Potable water is considered to be that containing no more than 500 ppm of dissolved salts, although in some parts of the world people are able to survive on water containing greater than 1000 ppm of salts.

Rain is the natural source of fresh water. Traditionally water supply has been by means of storage in reservoirs and subsequent transportation by aquaducts as necessary. Thus as the population increases, the supply of fresh water by means of traditional methods may not be possible. Because of this, a desalination process is required to augment the traditional methods. Several large desalination plants are operating in the U.S.A. In the Middle East where salty sea water is the main source of water, populations depend heavily on desalination.

Desalination by means of distillation or other high energy requiring processes are quite expensive. Thus it was conceived that a column similar to distillation but using liquid/solid phases instead of those of liquid/vapour and very low energy requirements would be valuable. Desalination of sea water by the vacuum-freeze-vapour-compression method operated successfully in Israel (129).

Fractional crystallization is the separation of the components of a mixture by the dissolution and formation of crystals. In the case of liquid/solid phases there are two mechanisms which govern the process. In the first case purification takes place by addition of solvent and subsequently crystallizing out pure product (known as Fractional crystallization). The second technique known as fractional solidification, utilises the solid/liquid phase transition without the addition of solvent (e.g. desalination).

Fractional solidification has many analogies with fractional distillation; in the former case purification being due to liquid/solid phase transition similar to liquid/vapour transition of distillation. Both processes depend upon a concentration difference between two phases at equilibrium and separation of these phases from each other. There is a great resemblance between the column crystallizer and a packed distillation column and both processes can be operated batchwise or continuously using counter current flow techniques. There are few differences as well between the two processes. When liquid to solid phase change occurs - solid solubility is usually low, whereas warm liquid mixtures are often completely miscible. The effect of pressure - there being little change for the liquid/solid phases, whereas liquid/vapour is solely dependant on it. There is a loss of convective mixing once the solid phase is formed causing large concentration differences within the crystals.

Distillation, at present, mainly because of the petroleum industry, is a well practiced technology, but suffers several disadvantages compared to crystallization column:-

(1) Increased fire hazards

(2) High energy required to overcome latent heat of vaporization

(3) High capital outlay to construct plant because of vapour phase, involving large volumes contained at equivalent pressures

(4) Heat sensitive compounds decompose at high temperatures

(5) Close boiling points component are expensive to separate

(6) Corrosion and scaling are very high at high temperatures for desalination.

A comparative analysis of various desalination processes has shown that freezing could become the most competitive process. Thus crystallization is becoming an economically viable and efficient separation process.

Column crystallizer is a piece of cylinder containing three sections as presented in Fig (1). At either end of the column, smaller pieces are known as freezing and melting sections. The long piece of middle section is known as the purification section. Brine is fed in near to the freezing end of the column. A refrigerant circulating around the freezing section, freezes the water into ice causing primary separation and excess salt expelled into solution is taken out as low melting product. The ice crystals with some salt impurities, adhered and occluded, are transported by means of an Archimedean spiral conveyor to the melting section. Here it is melted and taken out as pure water, while a small portion is used to act as reflux to wash impurities in the purification section. Eddy diffusion and mass transfer of impurities from adhered to reflux, are considered to be the main mechanisms of purification in the purification section.

Modelling deals with construction of models of the real world systems. A model is an imitation or an approximate representation of a real system, object, concept or process. Models are used to study, plan, design or control the real substance. In most

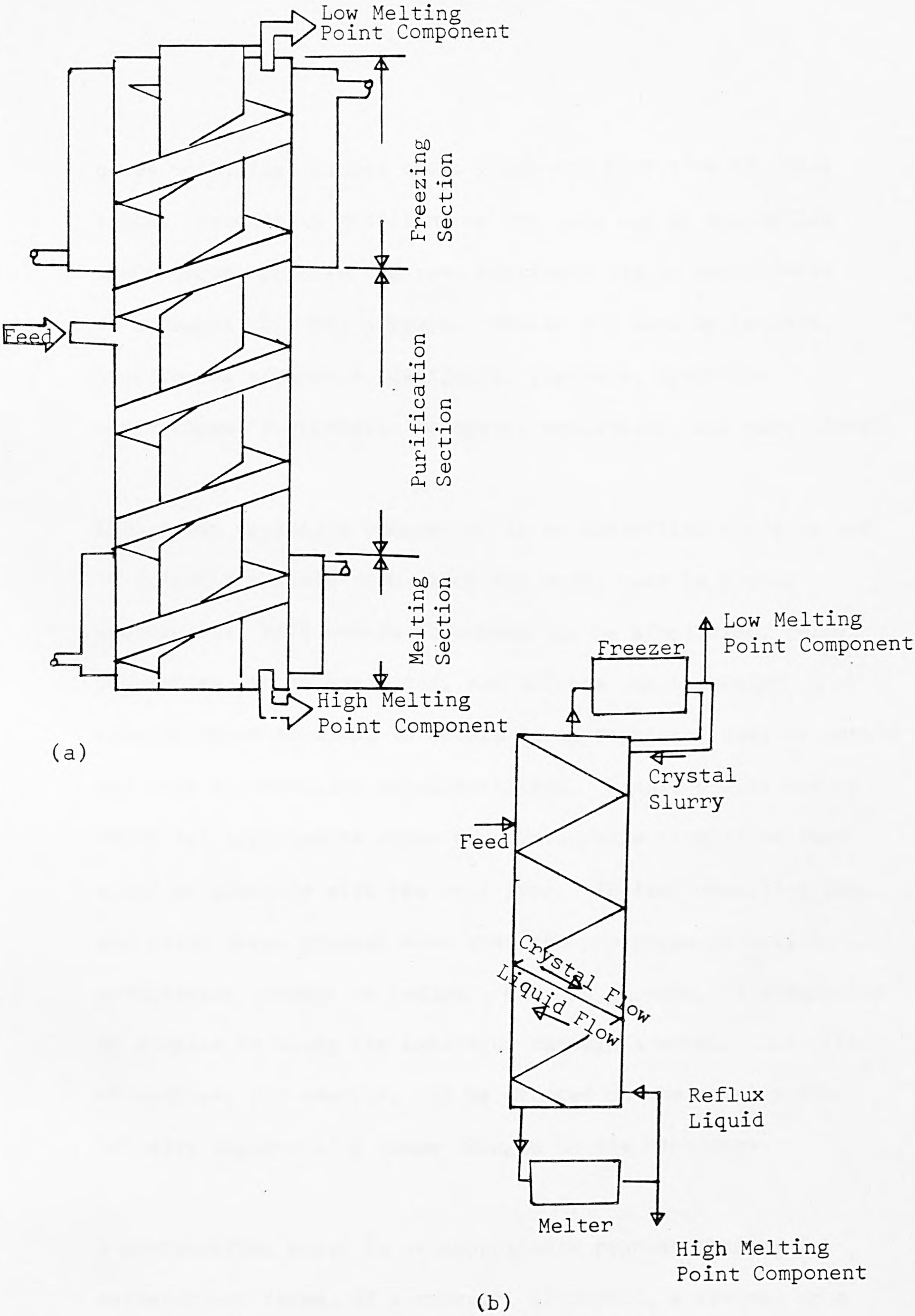


Fig 1 (a) Column Crystallizer Configuration

(b) Column Flow Diagram

cases modelling reduces cost, risks and flow time of these tasks. Frequently modelling is the only way to accomplish these tasks, because the real substance may be unavailable or unusable for this purpose. Models are used by artists, architects, engineers, designers, planners, operation researchers, economists, managers, scientists, and many others.

Models may replace a phenomenon in an unfamiliar field by one in a familiar field with which the model user is better acquainted. With models phenomena can be simplified, relevant properties can be extracted, and effects can be scaled up or down in space or time, to obtain an appropriate level of detail and ease of modelling experimentation. Models enable one to carry out experiments under more favourable conditions than would be possible with the real type. In fact modelling can, and often does, proceed even when the prototype is only a preliminary concept or design. And, in general, it frequently is simpler to study its behaviour through a model. The effect of changes, for example, can be studied on the model without actually implementing these changes in the real type.

A mathematical model is an approximate representation, in mathematical terms, of a concept, an object, a system, or a process. The model behaves something like the real system and is basically a set of instructions for generating behavioural data usually in the form of X, Y plots etc.

In a mathematical model the representation of the real substance is symbolic, in mathematical terms including variables, parameters, and relationships such as equations and inequalities. Mathematical models frequently have to be implemented on analog, digital, or hybrid computers to make possible the data handling and calculations involved in modelling studies. Generally then, mathematical model building or adaptation and computer implementation precedes mathematical modelling studies or experiments.

Simulation with the use of a computer generally entails writing the mathematical symbols in terms of a programming language. The most common programming language for scientific purposes is FORTRAN, though some special purpose languages such as DYNAMO, SIMULA etc. are also available.

Because of the increased viability of the crystallization process, column crystallization has been studied mathematically by various workers (97,103,110,111). Each one has tried to analyse the column under steady state conditions and has presented discussion regarding the purification mechanisms. Steady state modelling can lead to plant size calculations and physical data calculations. But for proper control and operation of the continuous column crystallizer it is necessary to study it under dynamic conditions hence Dynamic Mathematical Modelling and Simulation of the continuous column crystallizer was carried out.

CHAPTER 2

LITERATURE SURVEY

Chapter 2 LITERATURE SURVEY

2.1 Crystallization Processes

Crystallization, until recently, was generally understood to be batch operated. One of the common sites of this type of crystallization is in the sugar industry (1) where, boiling under low temperature takes place and supersaturation is reached for crystallization (2). Thus in batch crystallization a mass of crystals in mother liquor exist which have to be separated out. This separation is most commonly and easily achieved by centrifugation and washing (3), as an important process in the sugar industry (4,5). A few other crystallization processes used for purifying materials as part of fractional solidification techniques is discussed below.

2.1.1 Progressive Freezing

Progressive freezing is the slow solidification of a melt, with a well-defined solid/liquid interphase progressing through the liquid. The first of these techniques was put forward by Jessup, 1940 (6) and Schwab and Wickers (7) involved the slow lowering of a tube containing stirred molten benzoic acid out of a heater. Redistribution during progressive freezing of an impurity soluble in the solid phase was made by McFee in 1947 (8).

A continuous progressive freezing for the purification of aluminium on an industrial scale was developed by Dewey in 1965 (9,10). Partial freezing as reported by Glasgow and Ross (11) is included as part of progressive freezing process.

2.1.2 Zone Melting

In 1952 Pfann (12,13) invented a crystallization technique called zone melting. This was mainly to overcome the necessity to discard a portion of the ingot after each solidification to carry out repeated purifications by batch progressive freezing (since remelting the solid stores homogeniety). In zone melting only a thin zone of solid is melted. This zone is caused to move slowly through the solid from one end to the other, either by means of moving the solid or by moving the heater. Many subsequent zones may easily be caused to follow the first, with each contributing to the separation of components.

Pfann and Olsen (14), working on purification of germanium reported dramatic success by the zone refining method. There are two types of zone melting reported in the literature, one known as batch zone melting and the other as continuous zone melting. In batch zone melting no flow of material in or out of the system occurs and following treatment, the solid is separated into fractions according to the desired application (15,16,17).

Continuous zone melting is discussed broadly by Moates and Kennedy (18,173). According to Ball et al (19) an essential requirement for separation or purification by zone melting is that the compound exists in a crystalline form or that it be crystallizable by cooling.

2.1.3 Zone Precipitation

Zone precipitation as a technique was described by Eldib in 1962 (20,21) for fractionating petroleum microwax. It is a modified form of the zone melting process. Zone precipitation is particularly applicable to fractionation of materials which do not form crystals on solidification, but form amorphous, gel-like or solid solutions. Solvent is added to the material to be fractionated and a heater is applied to a zone of the gel. The solid in the vicinity of the heater will liquefy and as the heater moves on, the liquid behind the heater solidifies rejecting the most soluble components. These will be depleted behind the moving heater and concentrated in the direction of its movement; the last soluble component will be concentrated behind the heater. By repeated passes greater separation can be obtained.

2.1.4 Rotary Drum Crystallizers

The concept of rotary drum crystallizers can be traced back to early 1940. The design was studied and discussed by

Chaty (22) and patented by Graham (23) in 1953. It basically consists of a horizontally mounted hollow cylinder which is partially immersed in the melt with cooling medium entering and leaving the inside of the cylinder through hollow trunnions. As the cylinder rotates, crystals that have formed on the immersed portion of the cylinder, emerge from the melt as a crystalline cake, are air cooled to some degree, and then the cake is removed by a suitable device such as a doctor knife.

2.1.5 Counter-current Flow Processes

Among the fractional solidification processes, those processes which involve counter-current flow techniques are of primary importance to us. Parallel to zone melting, in 1951 Arnold (24) reported an operation using a pulsed countercurrent flow of melt and small crystals in a column. Though it was patented in 1951, its conception goes back to 1947. His crystallizer had no transportation mechanism for the crystals, but he however, proposed that some form of transportation may be necessary if crystals did not move freely along the column and scraping of the adhered crystals from the cooling walls.

In continuation at the Phillips Petroleum Co. (25,26,27) exploitation of countercurrent flow crystallization techniques for separation and purification progressed. Contributions were made by Schmidt (28,29) in 1952 and 1954, by Weedman (30) and Hackmuth, (31) in 1956, by Thomas (32) in 1958, by Hackmuth, (33) in 1959 where he combined pulsed flow and crystal transportation. Crystals are introduced to the column, compressed by a porous hydraulic piston on to a grid into a melting section where pure product is withdrawn.

A significant contribution was made by McKay (34) in 1960 by constructing a bench scale model. The equipment consisted of a scraped surface chiller, a 4 in. diameter dolumn, a reciprocating piston faced with a filter screen (to permit passage of liquid as the piston pushes crystals down the column), and a heat-exchange coil (to provide energy to melt the crystals). This type of plant has been known to produce high purity products. Later McKay et al (35) reported in 1963 that beer and other products could be concentrated by removal of high purity water without loss of aroma or taste. McKay (36) in 1965 reported that column performance varies with column size and explained various sized columns for purifying p-xylene and other organic and aqueous systems.

2.1.6 Column Crystallization

Although a substantial amount of work has been reported concerning separation by column crystallization, some researchers are still quite sceptical about the process and nurture great doubts towards its use in industrial scale.

A related technique to Arnold's process was developed by Schildknecht (37) and, Schildknecht and Vetter (44), which they called Column Crystallization. The difference between the Schildknecht type and others is that in this case the crystals are formed internally, thus avoiding a slurry movement problem.

The freezing section can be at the top (40) or base of the purification section as long as the melting section is at the opposite end. Helices (37,40) are proposed as satisfactory scraping and conveying devices.

The purification section is normally insulated, and glass wool, styrofoam and vacuum jackets are typical means of insulation. The length and diameter of the purification section are dictated by the desired separation and through put (37,38, 39,40).

In the melting section a heat source is recommended to melt the crystals and heating elements as electrical resistance heaters (40), and heat exchangers have proved satisfactory.

Many types of conveyors are employed for transportation of crystals. Suitable conveyors proposed by Schildknecht are spiral (37,39) or multiple intermeshing screws (41). Spirals of many cross sections have been used, however, the best performance being obtained with a spiral having a thin lenticular cross section (42). The thin edges of the spiral are effective in scraping the crystals from the column walls. The relatively flat surfaces exert a force on the crystals substantially parallel to the walls of the column. This reduces the possibility of column plugging. Spirals of this type are commercially available (43). The drive mechanisms for the spiral conveyors frequently impart an oscillatory as well as rotary motion to the spiral (45). Schildknecht (46) also demonstrated the suitability of continuous column crystallizers in the production of ultrapure solvents.

Improvements and scale up of operations have resulted in many applications. A wide variety of mixtures have been separated, both binary (48,49) and multicomponent systems (49,50,51). These mixtures include aromatic (52), Paraffinic (53) hydrocarbons, aqueous systems (54), systems forming entectics (49,53) as well as those forming solid solutions (47,53).

Column crystallizer has been extensively studied by Powers et al (103) and McGrath et al (96,97,98,99). Scale up of operations using Schildknecht type column crystallizer was undertaken by McGrath and Hobson (95). They built a column of 100 mm diameter and 150 cm in length and used an Archimedean screw conveyor.

2.2 Desalination

Man's most common source of potent water is rain which relies on the process of evaporation from sea and precipitation as rain. The freezing processes occurring at the North and South poles are also a major source of water.

The first case of evaporation/precipitation falls under the distillation process and has been generally used by man for artificially purifying salt water, into drinkable or usable water. There are various methods of desalination by distillation and variations to each method.

Other methods of desalination are OSMOSIS, ELECTRODIALYSIS, ION-EXCHANGE RESINS or a mixture of more than one single process. Distillation plants are also being operated in conjunction with power stations, either conventional or nuclear and recently solar distillation has taken some root.

2.2.1 Submerged Coil Evaporator (55)

Multiple-effect pool boiling distillation is represented below by the figure (2). It consists of a series of shells, each attached with a steam heating coil, a boiler to initially give steam for its first effect and condensor cooled by cold sea water, part of which is bled off for the evaporator feed. Provision is made for distillate removal and brine blowdown to ensure that the evaporation brine concentration does not rise unduly.

In operation, the heating steam causes evaporation to take place from the brine surface. The vapour which is pure from the first effect is lead to the heating of the second effect and so on till the last effect. Also the pressure in each succeeding effect must be less than the previous for effective transfer of latent heat of vaporisation from each effect.

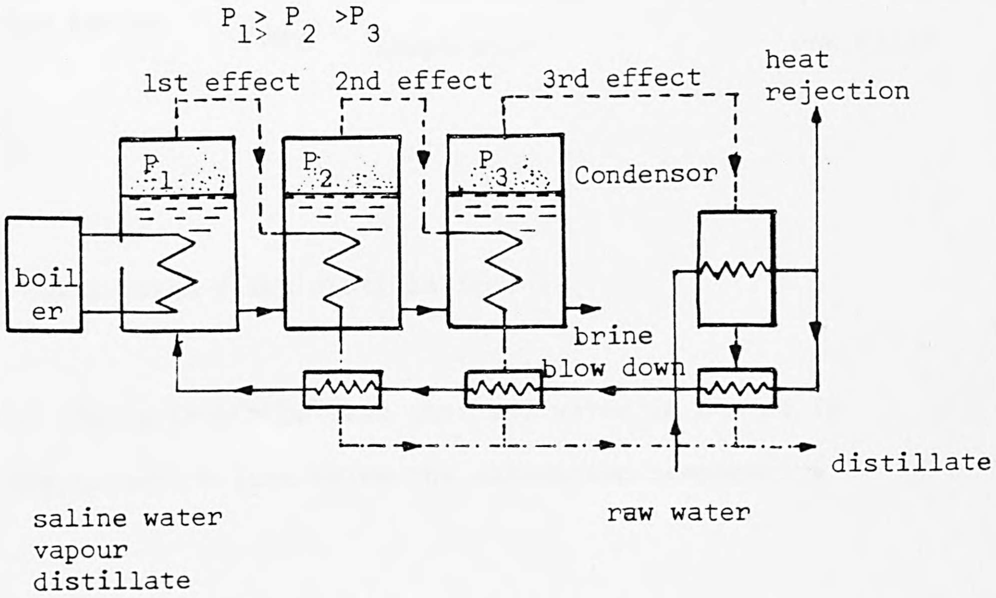


Fig. 2. Multiple-effect pool boiling distillation.

2.2.2 Multi-stage Flash Distillation MSF

The submerged tube boiling distillation has almost entirely been superseded by multi-stage flash distillation, generally referred to as MSF. The large scale application of MSF techniques to sea water distillation is mainly due to two men A. Frankel (56) and R.S. Silver (57) and is thoroughly described by them in the above mentioned reports. A diagram is presented below for a visualisation of MSF plant. Fig (3).

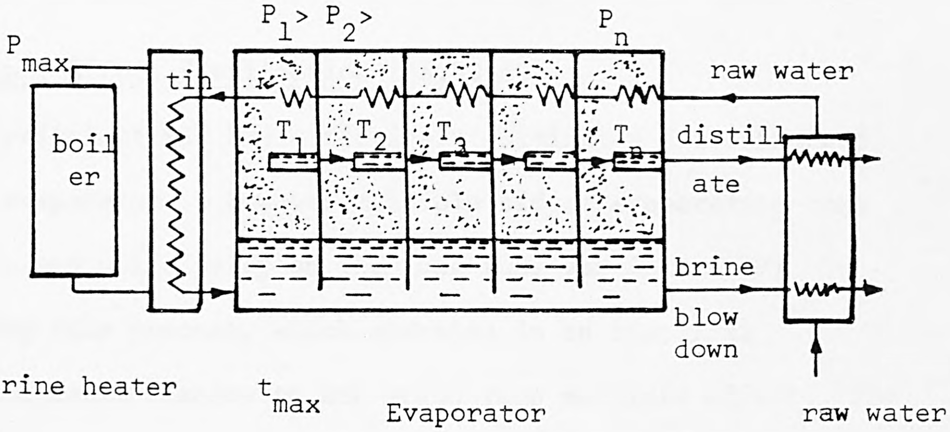


Fig. 3 Multi-stage flash distillation.

From the figure it can be seen that sea water is heated in the brine heater to just below the saturation temperature

t_{max} at P_{max}. It then enters the stage at reduced pressure P_1. The reduction in pressure causes the heated feed to 'flash' or commence evaporation to obtain thermal equilibrium with stage saturation condition dictated by P_1. A series of chambers separated by walls, and each successive chamber is at a lower pressure than the previous one, comprises the plant. The vapour formed in flashing condenses on the tubes cooled by feed sea water. This raises the temperature of the brine flowing in opposite direction to flashing thus aiding heat recovery and a reduced temperature difference for heat transfer.

2.2.3 Multiple Effect Distillation (58,59,60)

The arrival of MSF had effectively eliminated the submerged coil evaporators. However multiple effect evaporators came back based principally on the long-tube verticle (LTV) falling film process, which operates in an identical thermodynamic fashion to submerged tube multiple effect. The principle is that steam generated in the first effect is condensed in the second, thus producing more steam which is cascaded to the third and so on. There are claimed to be certain advantages of the VTE over MSF and Hawes (61) claimed a substantial reduction in product cost of VTE to MSF. Some of the advantages are as follows:

1. Energy economy as, unlike MSF the brine is not heated above its boiling point and vapour is used at the temperature,

at which it is generated.

2. The feed is at its lowest concentration at highest temperature hence scale formation is minimised (62).
3. The feed flows in series and as maximum concentration occurs in last effect, worst boiling point elevation losses are confined to it.
4. The MSF has a high electrical demand because of re-circulation pumping.
5. Multi-stage flash is prone to equilibration problem.
6. Plant simplicity is achieved by VTE as for the same performance ratio a lesser number of effects are needed by VTE and MSF stages.

A diagram of LTV using the VTE process is presented in Fig (4)

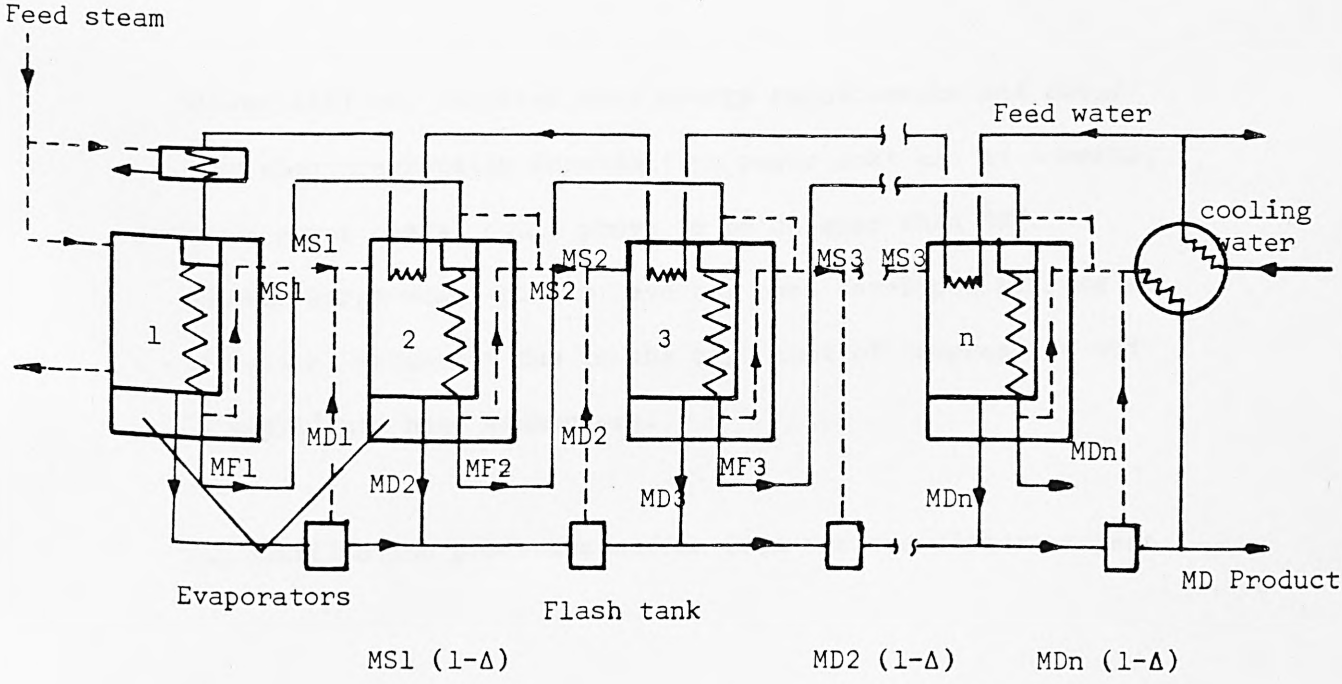


Fig. 4. VTE Multiple effect distillation flow sheet

2.2.4 Vapour Compression Distillation

Most of the vapour compression evaporation process centres around the use of vapour compressor multi-stage flash systems as proposed by Stormer and Lowes (63) and Wood and Herbert (64). In the vapour compression distillation the inlet feed is heated in liquid/liquid heat exchangers by the blowdown and product streams respectively, then passes to a brine heater where it is heated by vapour which has been discharged by the evaporator compressor at a temperature greater than the evaporator vapour temperature. The heated feed passes into the evaporator where flashing takes place. The vapour released is compressed and used as the steam supply for the brine heater and the condensate discharged as the product stream. The compressor may be linked to a flash chamber or a distillation effect.

Silver (65) has compared some energy requirements and found that they are totally dependant on power cost and at somewhat lower power costs, could prove to be cheaper than MSF. However large scale plants have not been developed because it is capital intensive due to the high cost of compressors and liquid/liquid heat exchangers.

All distillation processes suffer from various disadvantages:

1. High energy requirement
2. Corrosion problems are high at high temperature
3. Prone to scale formation
4. Need of extensive insulation.

2.2.5 Solar Distillation

To solve some of the above problems alternative sources of energy and processes have been investigated. The only free source of energy is the sun, therefore solar distillation has been suggested. Though it may not always be available at all places, there certainly is abundance of it in arid areas and it gets rid of problems of expensive energy, scaling, corrosion, etc.

Solar distillation utilises the incident short-wave solar radiation transmitted through a transparent material (e.g. glass) to vaporise water in flat tanks. The vapour condensing inside the roof drains off as fresh water.

Solar heat gains from incident radiation and solar radiation intensities have been calculated by Pilkington (66) and Lof (67). Many solar still designs have been mooted - Bloemer et al, (68), Howe and Tleimat (69), Morse (70), most with emphasis on cheap construction and use of plastics. However glass is still considered best by Porteous (71) as utilised when he built a glass-roof basin still for the Royal Society Research Station on the island of Aldabra in the Indian Ocean. However the major disadvantage of solar distillation is in requiring a large area per unit production and availability of sunshine.

2.2.6 Low Temperature Difference Distillation LTD

Low temperature difference distillation is a means of utilising the low-grade thermal energy content of reject cooling streams from processing plants, diesel engine water jackets etc.

The LTD plant is a chamber or a series of chambers with provision for heated effluent feed entry and cooling by a simple tube bundle arrangement with circulation of sea water as coolant. Such a plant has been designed and constructed by A. Ahlstrom Osakeyhitio Co (72). Howe et al (73) also published details of an LTD pilot plant successfully run at the University of California. Similarly geothermal energy may be employed in LTD installation.

Some other concepts which have been taking ground are controlled flash evaporators described by Roe and Othmer (74) and use of non-metallic heat transfer through surfaces (75) for cutting down distillation plant costs.

Combined power and water production units are also becoming increasingly common. In a combined plant, utilisation of turbine exhaust steams can result in greater energy utilisation. There has been a considerable interest in the use of nuclear reactors (81) for combined power and water supplies. This is mainly because of lower marginal operating costs than fossil fuel boilers. Chambers and Wood (76) have presented a cost analysis of AGR source and Chambers and Hitchcock (77) have discussed the optimisation of water and power plants based on Nuclear Reactor.

2.2.7 Electrodialysis

Electrodialysis (78,79) involves the passage of electric current through brackish or low salinity water in a chamber in which many closed spaced ion selective membranes are placed, thus dividing the chambers into compartments. The electric current causes the salts to be concentrated in alternate compartments with reduced salt content in the remainder. In electrodialysis the power consumption is proportional to the total dissolved solids and hence the cost performance effectiveness is with low salinity waters.

2.2.8 Reverse Osmosis

This is another process which is power consuming proportional to dissolved solids and is thus applied to brackish water only.

Reverse osmosis (79,80) uses the reverse application of osmotic pressure. When salt water and fresh water are separated by a semi-permeable membrane, osmotic pressure causes the fresh water to flow through the membrane to dilute the saline water until osmotic equilibrium is established. Applying this in reverse, if a greater pressure is applied to the salt water then pure water will pass through the membrane leaving a concentrated brine to be disposed of.

On a very limited scale, salt water has also been desalinated by use of solvent extraction (82), depending on solubility characteristics of certain secondary and tertiary amines with water and salt. Ion-Exchange resins (83,84) processes have been employed for desalination using low salinity feed of about 3000 ppm.

2.2.9 Freeze Desalination

The other big general group of principles opposite to distillation, under which desalination occurs is freezing. This also has many methods and variations to each method.

The first successful working method of freeze desalination is reported back to 1786, when Lorgna, as mentioned earlier, was successful in producing almost pure water from brine, by repeated freezing of melt from previous crystallization in five stages. An account of early experiments in purifying sea water by freezing is presented by Nebbia (85). The simplest method of desalination by natural freezing is described by Wankat (86). The equipment consists of shallow, levelled, well insulated container with a shallow layer of water, fully exposed to the night sky. During the night heat is lost by radiation to the sky cooling the water layer, possibly sufficient enough to crystallize. This process however, is applicable in relatively warm climates with a clear sky and has been found that water from ice was up to six times less salty than feed.

Another early and rather simple method was patented by Whitney (87) in 1944. A jet of impure water at low temperature is forcibly projected against a surface maintained at a sufficiently low temperature for formation and progressive accumulation of ice on the surface. Because of the velocity of water, the impurities rejected by ice formation are washed away as fast as they appear.

Since then freeze desalination has slowly progressed and various methods have been reported. All freezing processes employ virtually the same process steps: a) freezing, b) separation, washing, c) condensing melting, and d) heat exchange. Each process differs mainly in the detailed scheme for carrying out the steps.

2.2.9.1 Secondary Refrigerant Freezing Process

Also known as butane freezing process (88,89,90,91) it has been studied quite extensively but has been found unsuitable for drinking purposes, because of a lingering of the butane taste even after effective separation and washing. The process in fig (5) consists of precooled sea water entering a freezer where liquid butane is bubbled through it. The butane vaporises and lowers the temperature, resulting in formation of salt-free ice crystals and brine slurry. The ice-brine slurry is pumped to a washer melter. The slurry rises within the washer and the ice crystals are compacted into a porous bed of ice. The bed of ice is removed upward by a slight positive pressure caused by the brine flowing through the bed and outward through screens positioned near the middle of the column. The bed is washed and ice is removed to the melter. The product and the butane flow to a decanting unit where the two liquids are separated. Because of the taste and smell, most works on secondary refrigerant freezing were curtailed.

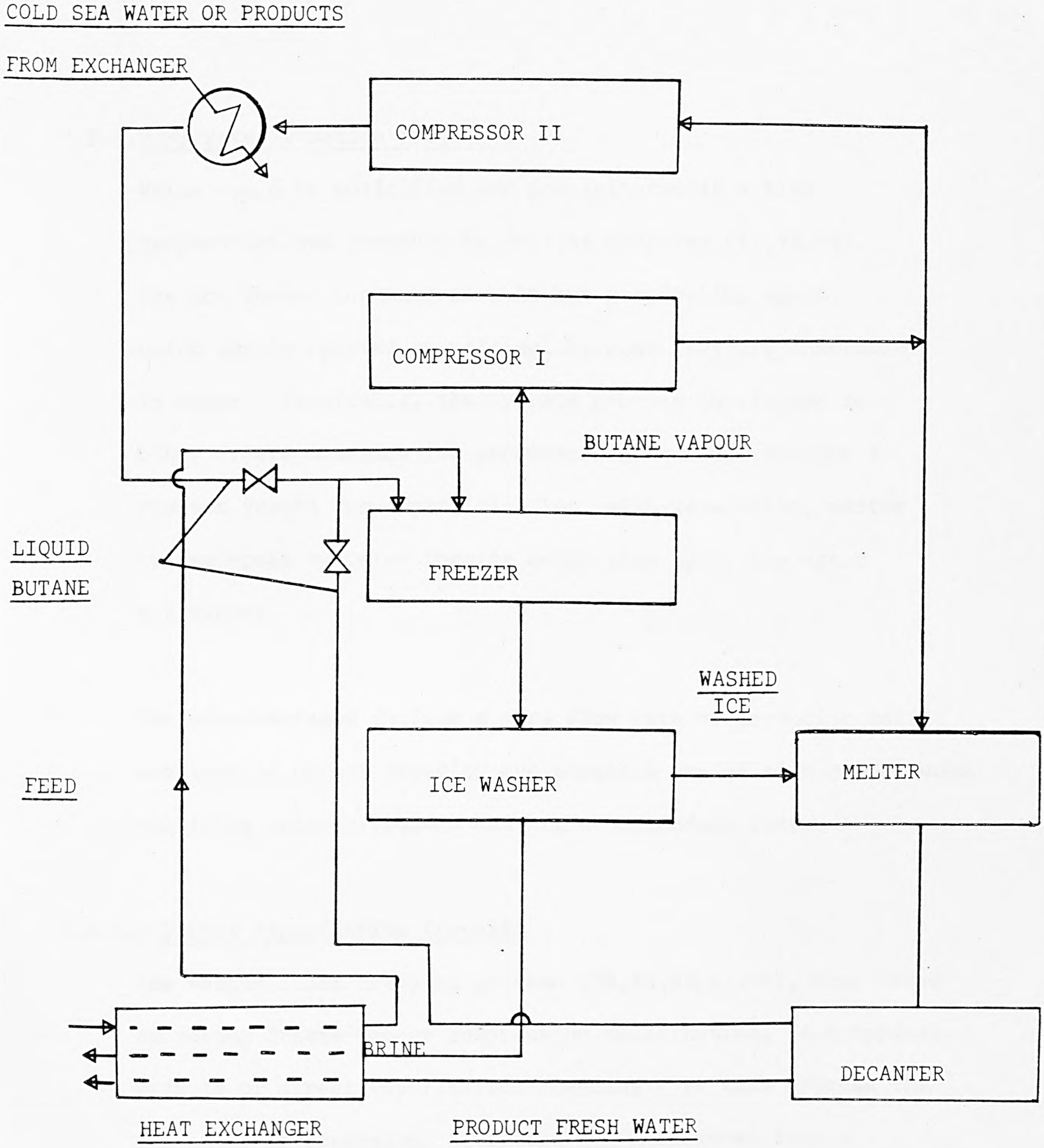


Figure 5 Block diagram of indirect freezing process.

2.2.9.2 Hydrate Formation Processes:

Water could be solidified and precipitated at a high temperature and pressure by forming hydrates (79,88,89). The ice formed contains no salt but a hydrating agent, which can be removed on melting, because they are insoluble in water. Physically, the hydrate process is similar to other freeze desalination processes in that it contains a reactor vessel for crystallization, wash-separation, melter to decompose hydrates forming water plus hydrating agent and washer.

The disadvantages include a very slow rate of producing solid compared to direct freezing and possible use of higher pressures requiring thicker vessels and higher attendant costs.

2.2.9.3 Direct Vaporization Freezing

The vacuum flash freezing process (79,89,92,93,94), also known as vacuum freeze-vapour compression desalination, is a typical example of direct-vaporization freezing. In this process the sea-water is precooled, deaerated and introduced into a freezing chamber at reduced pressure. Some of the water flashes and latent heat is removed from the water due to vaporization. This cools the rest of the water and ice is formed.

The slurry of crystals and brine is pumped to a separation column, where crystals rise to the surface and form a compact bed, while brine is sucked out through the perforated sides. Wash water from the product stream is caused to flow downward from top to remove residual salt solution. The washed ice is continuously harvested by a cutting blade as it emerges from the top of the column.

The large amount of water vapour formed must also be continually removed and condensed, and there are various methods of doing it.

2.2.9.4 Column Crystallizer Desalination

All the above desalination plants discussed so far consist of various stages and equipment. Not only distillation processes, but even freezing processes contain separate pieces of equipment for crystallization, washing, melting, separation etc.

To augment all this, freeze desalination by continuous column crystallizer was put forward by Hobson and McGrath (95). A column crystallizer as proposed by Schildknecht and using a spiral conveyor has many advantages over other freezing processes. The three separate processes of crystallization, washing and melting takes place in one piece of equipment.

Feed goes in at a point near freezing section and purified water comes out of the melting section. The speed of conveyor and inputs/outputs can be easily controlled, thus avoiding any blocking, and giving effective control of the washing mechanism.

Suitability of the column apparatus for desalination was further investigated by Gladwin (96) and continued on a much larger scale by Bates, Gladwin and McGrath (97). It has been found that with proper control of the screw speed, feed and outputs, it can prove a viable desalination process (98,99).

So, ever since the early days of Buchanan in 1874, the analysis of water from freezing had started and has been studied extensively by researchers from time to time (100,101,102). Some have concentrated on nucleation, growth, shape, size of crystals, while others on factors such as stirring, equipment and performance of a certain type of crystalliser.

2.3 Modelling of Column Crystallizers

Only few workers had concentrated on analysis of the crystallizers till recently. Orcutt (104,105) modelled the operation of a well mixed crystallization vessel and the nucleation and growth of ice crystals in secondary refrigerant freezing. From his report it is possible to calculate mean particle size, growth and nucleation. He has also studied scale-up of crystallization processes.

Detailed analysis to some extent has been presented by Powers et al, Bolsatis and Gladwin. All of these models and analyses are for steady state operations. The only dynamic state simulation has been presented by McGrath and Akhtar for the freezing section of the crystallizer.

One of the earliest attempts on modelling was done by Anikin (106) in 1963, when he attempted to model column concentration profiles due to recrystallization, without any washing effects being taken into account.

Devyatekh (109) developed a model based upon diffusion in the solid phase being the rate-determining stage in mass exchange between liquid and crystals. Arkenbout (107,108) recognized the column equation for exchange processes for the interfacial mass transfer by extractive washing and recrystallization. Powers (103) developed a model dependent upon mass transfer between the adhering and free liquids and diffusion along the column. He presented separate solutions to eutectic systems and those forming solid solutions.

Bolsatis (110) modelled a Schildknecht type column by splitting the column into a Stripping and Enriching section similar to distillation columns. Stripping efficiency (defined as fraction of crystallizable material which is removed from the solution entering that section) determines the performance of a stripping section. Once the crystals form they are acted upon by gravitational, bouyant and viscous drag forces which lead to a minimum size of crystal above which transportation is allowed, the smaller crystals leaving with the stripped stream. The enriching section equations only apply to cases where the volumes of desired product and impurity are approximately equal.

Powers with Albertins (111) developed a model for batch operation considering three distinct cases.

a) crystals were pure

b) crystal impurity was constant along the length of the column but diffusion has negligible influence on the concentration profile.

c) the resistance to mass transfer between the reflux liquid and the adhering liquid has negligible influence on concentration profile.

Since the crystals were known to be impure the first case was rejected outright. The experimental results proved diffusion to be the major factor in determining the concentration profile in the column. This was evident from the fact that an increase in crystal rate resulted in an increase in separation.

A year later in 1970, Gates (112) working with Powers, presented similar models to Albertins. But in his case, he treated eutectic systems separately to those forming solid solutions. The use of mass transfer and diffusion coefficients with the assumption of constant impurity along the column gave better values for coefficients. The results strengthened the belief that diffusion is the main factor in considering concentration profiles.

Henry (113) and Power presented models for continuous column crystallizer, in a manner similar to those as presented by Bolsatis. Henry divided the whole column into two sections, the Enriching and the Stripping sections. Thus there are no separate freezing, purification and melting sections for analytical purposes.

In his opinion the important factors in determining the column crystal profile are the crystal rate, diffusion of impurity along the column and mass transfer between the free and adhering liquids. The model behaves reasonably well till the enriched product rate approaches the crystal. Then the model breaks down due to the flat composition profile obtained.

Bates, Gladwin and McGrath (97) presented mathematical models similar to Henry and Powers based on the analogy with packed extraction columns. They extended the equations of Henry for calculations of maximum theoretical crystal rate above which separation decreased.

They found that for low values of C (crystal rate), the diffusion factor was dominant and H (separation factor for enriching section) decreased, whereas, when C became large, the mass transfer assumed greater importance. The value of H was raised as D (diffusion factor) increased and fell as Ka (mass transfer factor) increased. Thus for good separation, they recommended that diffusion should be minimised whilst mass transfer was increased.

Akhtar, McGrath and Roberts (114,115) for the first time attempted to put together a dynamic mathematical simulation model for the column crystallizer. The three sections of the column were treated separately as freezing, purification and melting. Relative heat and mass balances and purification mechanisms indigenous to each section were considered. The freezing section was simulated first to give an idea of the possibilities and difficulties which we would be facing when starting a simulation model.

Initially there had been various difficulties with the choice of equations and a few simulation models had to be discarded. The programming of the nucleation rate equation faced great problems because of its exponential nature and thus raising overflow conditions very often. However when it was finally decided to proceed with the other two sections, which would be joined together to give the total column, the freezing section simulation model was behaving like a continuous crystallizer with no break downs of models suggesting either overflow or blockage.

Ellier, Guryamov and Devyatekh 1978 (116) based on a diffusion model derived an equation to calculate the degree of purification and the separation efficiency attainable in a crystallization column under steady state conditions. They found that the separation efficiency depends on its operating conditions, i.e. rate of removal of product,dispersion, flow rates etc.

The Institute of Atomic Energy, Tokyo (1979) claimed the design and operation of a multi-stage continuous crystallizer (117). The process was useful in the crystallization and purification of Al_2O_3.

Dozonov and Makarov 1980 (118) presented an analysis of Ion-exchange and crystallization columns. Mathematical relations for describing the steady state distribution of concentration are compared. An integral description of boundary conditions enables presentation of analytical calculations without preliminary analysis.

Melikhov and Berhner 1981 (119) presented a simulation model of batch crystallizer. A closed mathematical model of a mixed batch crystallizer is presented, which takes into consideration crystal growth rate fluctuations producing an increasing spread of crystal sizes. Numerical methods are proposed for cases when growth rates can be expressed as a product of supersaturation and size functions.

CHAPTER 3

THEORY

Chapter 3 THEORY

3.1 Crystallization (120,121,122)

The nucleation and growth of crystals comprise a very complicated mechanism depending on the solvent and number of solids dissolved. However we shall take the simplest case and define them in their barest terms.

By crystallization we mean the formation of crystals from a solution which generally involves the three basic steps of

a) attainment of supersaturation or cooling

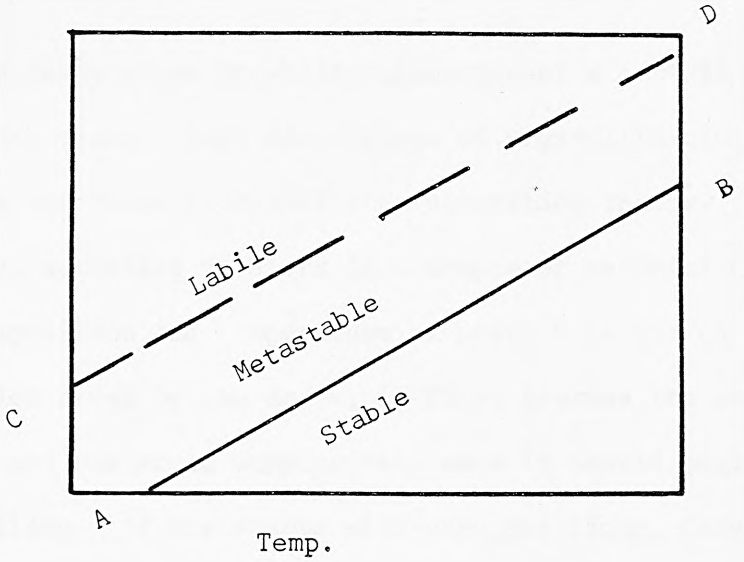
b) nucleation

c) and growth of nucleus into stable crystals.

3.1.1 Saturation

When a solid is in equilibrium with the liquid in solution then it is said to be in a state of saturation. If extra solids are dissolved in the solution then the equilibrium condition is disturbed and a supersaturated state exists which is very essential for any crystallization operation. This state of supersaturation may be achieved by various methods such as cooling, evaporation, addition of precipient or by a chemical reaction.

From a saturation point of view there are three states in which solids exist in a solvent. They were defined by Ostwald as labile, metastable and stable as presented in the fig (6).



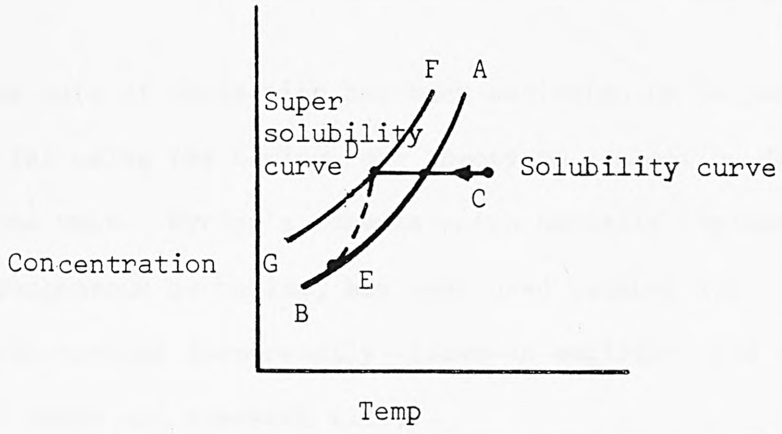
AB = Solubility curve
CD = Supersolubility curve

Fig (6) Saturation curvesfor solids in solvents

In the case of the labile state, supersaturation exists and spontaneous nucleation is possible. In the metastable state, spontaneous crystallization is not possible but growth of crystals may take place as it is in a saturated state. In the case of the stable state it is unsaturated therefore no spontaneous nucleation can take place and neither is growth of crystals possible.

Solubility is a factor concerning agitation and temperature and greatly depends on them. In the case of column crystallization the state of saturation is achieved by supercooling or preferential cooling of the solution to the desired temperature at which nucleation of a certain substance will take place. Most discussions of crystallization involve the Miers (123,124) supersaturation theory. In fig (7), according to Miers if a sample of material having the composition and temperature of point C is cooled in the direction shown by the arrow, it first crosses the solubility curve, and one would suppose that here it should begin to crystallize. If one starts with pure solutions, carefully freed from all solid particles, not only of the substance itself but of any foreign solid matter, the solution will not begin to crystallize until it has supercooled considerably past the curve AB. Somewhere in the neighbourhood of the point D, according to the Miers theory, crystallization begins, and the concentration of the substance then follows roughly according to the curve DE.

In the absence of any solid particles the curve FG (called the super-solubility curve) represents the limit at which nucleation formation begins spontaneously and, consequently, the point where crystallization can start. According to the Miers theory, short of this point (i.e. at any position along the line CD), nuclei cannot form and therefore crystallization does not occur. The general tendency at the present time is to consider this critical supersolubility range not as a definite line FG but as an area. For instance it is known that with sufficiently great length of time nuclei can form even well below the supersolubility curve (125).



AB = Normal solubility curve
FG = Supersolubility curve
CDE = path of solution on cooling

Fig (7) Miers Supersaturation theory

3.1.2 Nucleation

Supersaturation is a function of temperature and thus a solution saturated at room temperature will become supersaturated at lower temperatures. For the case of column crystallization, cooling and supercooling are the main methods of crystal formation. As soon as the required temperature of crystallization of a particular component in solution is achieved, that particular substance has the capacity to crystallize. At this state the formation of solid sites at which crystallization can commence is essential. Nucleation may occur spontaneously or by inducement. In the case of column crystallization it is artificially induced by stirring.

The rate of nucleation has been estimated by Vanhook (126) using the Eyring rate theory to nucleation data from melt. Eyring's formula which normally implies a homogeneous mechanism, has been used because its mathematical form readily allows an empirical fit to data of Umano and Kawasaki (127).

Umano carried out freezing experiments by batch-cooling sea water in a temperature controlled vessel and recorded temperature versus time.

His work gave graphs similar to fig (8).

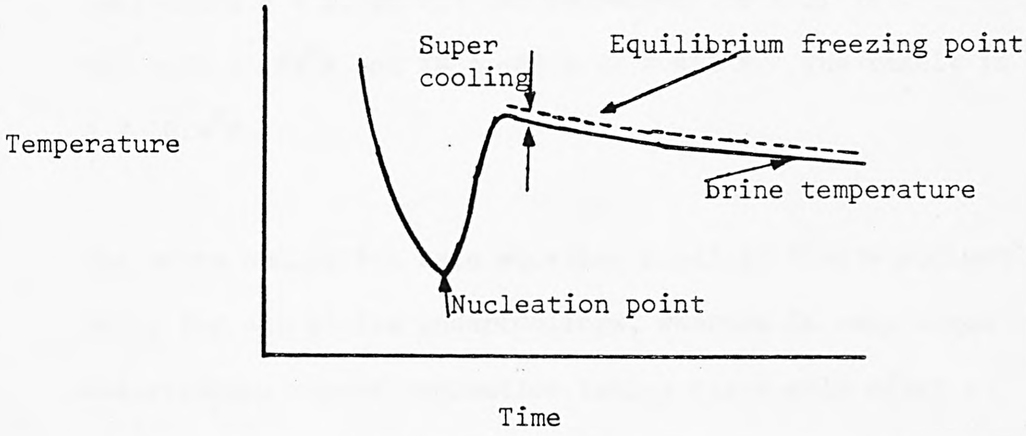


Fig (8) Freezing curve.

The nucleation rate equation may be stated as

$$J = \frac{RG.TB}{H} \exp \frac{A.TF^2}{TB\ (TF - TB)^2} \cdot \text{particles (time Mole)}^{-1} \qquad (1\ )$$

where A is an empirical constant, TB the salt solution temperature, TF the equilibrium transition temperature (freezing point), and H = Planck's constant.

The value of A can be calculated from Umano's freezing point data or from the initial temperature at which nucleation occurs, as reported by Farrar and Hamilton (104). This point presumably occurs at the sharp temperature reversal in the freezing versus time diagram and was noted at about 22°F for unseeded stirred sea water. Assuming that at nucleation J = 1, eq (1) can be solved for A if TF = 460 + 29 = 489°R and TB = 460 + 22 = 482°R. The result is A = 16.4°R.

The above nucleation rate equation predicts finite nucleation rates for all finite undercoolings, whereas in many cases observations report nucleation taking place only after a minimum undercooling has been achieved. Due to the form of equation (1) the nucleation rate can change by several orders of magnitude within a small range of TB. Because of this sensitivity, the temperature driving force $\Delta T = (TF-TB)$ must be restricted to within some practical limits to avoid computing disproportionate values of vessel size or particle diameters for a given total production rate.

3.1.3 Crystal Growth

Once the nucleus has formed then the crystal starts to grow. It might be supposed that the controlling factor in growth rate would be the rate of diffusion of the solute from the mass of solution to the interface. But this hardly seems to hold true. Removal of heat from the surface of the crystal seems to play a dominant role in crystal growth rate, as proposed by Harriott (104). Harriott assumed that for a well mixed crystallizer, growth rate is limited by the rate at which heat of fusion can be transferred from the face of the crystal. Because salt is being excluded by the water at the surface, it must be transferred into the bulk liquid and is therefore most highly concentrated at the crystal surface. The equilibrium freezing temperature at the crystal surface is therefore lower than the equilibrium freezing temperature in the bulk solution. The actual thermal driving force which governs the growth rate is therefore less than the apparent driving force.

Assuming that crystals are spherical (104), and if internal temperature gradients and heat capacity effects are neglected, the rate of increase in the mass of the crystal can be equated to the heat transferred from the crystal surface divided by the latent heat of fusion:

$$\frac{d}{dt}\left(\frac{4}{3}\ \pi P_s\ r^3\right) = \frac{4\pi r^2 HL\ (TI - TBL)}{\Delta HF} \qquad (2)$$

where r is the crystal radius, P_s the ice density, TBL the temperature in bulk liquid, TI the temperature at the ice/liquid interface, ΔHF the latent heat of fusion, and HL the effective heat transfer co-efficient.

According to continuity of mass flow, the crystal growth rate must also equal the rate of transfer of salt away from the interface times the ratio of the mass fraction of water to salt in the bulk liquid; hence

$$\frac{d}{dt}\left(\frac{4}{3}\ \pi P_s\ r^3\right) = 4\ r^2 KL\ \hat{P}\ (WI - WL)\ \left(\frac{1 - WL}{WL}\right) \qquad (3)$$

where WI is the mass fraction of salt at the interface, WL the mass fraction of salt in the bulk liquid, $\hat{P}$ the average density of liquid between interface and bulk, and KL the effective mass-transfer coefficient.

Equating equations 2 and 3 gives the relationship

$$\frac{WI - WL}{TI - TBL} = \frac{HL}{\hat{P}KL \ \Delta HF} \cdot \frac{WL}{1 - WL} \qquad (4)$$

The equilibrium freezing curve for brine can be approximated quite well by a linear relationship

$$TF = 492 - MWL \qquad (5)$$

for an NaCl composition of 7 or 8 wt %. The constant M has the value 104°F for sea water. This value will vary depending upon the freezing curve determined for a particular brine, because it is the shape of the initial part of the freezing curve.

Using equations 4 and 5 and rearranging, one can derive a formula for X (the ratio of the actual thermal driving force to the apparent driving force) in terms of WL and Ω where Ω is a dimensionless quantity as defined by Ranz and Marshall (104). The ratio X in terms of the thermal driving force is

$$X = \frac{TI - TBL}{TF - TBL} \qquad (6)$$

For crystals of diameter greater than 0.002 in. the crystal growth rate, in terms of the thermal driving force may now be expressed as

$$\text{growth rate} = \frac{dDP}{dt} = \frac{G}{DP}(TI - TBL) = \frac{G\,\Delta TI}{DP} \qquad (7)$$

where DP is the crystal diameter ($DP = 2r$), ΔTI is $TI - TBL$, and G is $2KL\ \{2+0.6\ (RE)^{\frac{1}{2}}\ (Pr)^{\frac{3}{2}}\}/$ $P_s(\Delta HF\{1 + \Omega WL/(1 - WL)\}$ or, assuming mean values for the physical properties,

$$G = 0.0342/\ \{1 + 77WL/(\ 1 - WL)\} \qquad (8)$$

3.2 Fractional Solidification

Fractional solidification is crystallization from a melt where the solid/liquid phase transition is utilised without the addition of any agent. If one has a binary solution and crystallizes out one component the process is fractional solidification. As presented in Fig (9), if a solution of $NaNO_3$ in water (128) is allowed to cool ice will separate to the left of the Eutectic and $NaNO_3$ to the right.

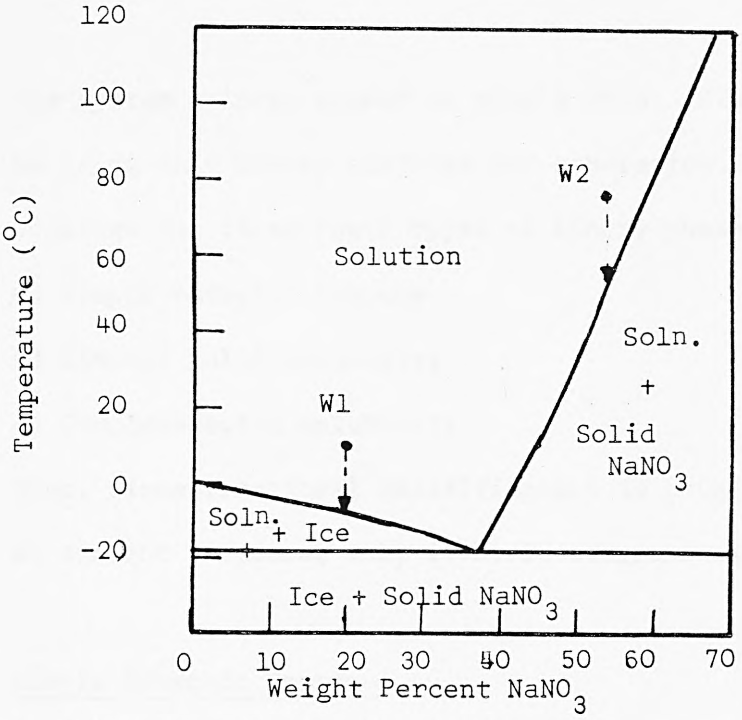


Fig (9) Phase diagram for $NaNO_3$ - H_2O

The extent of separation that can be achieved in any fractional solidification depends upon the most basic parameters of thermodynamics which are expressed clearly in phase diagrams of the system components under consideration. The phase diagram indicates the maximum change of concentration or degree of segregation that is theoretically realizable by the freezing of a liquid.

A phase diagram describes the various equilibrium between the components involved as functions of the relevant variables, e.g. composition, temperature and pressure. The number of different types of phase diagrame is small and, more complex diagrams may be considered as combining in one system a large number of simple ones. Since we shall be using only binary mixtures for separation, we shall consider the three basic types of binary phase diagram (129).

a) Simple eutectic systems

b) Limited solid solubility

c) Complete solid solubility

Also, since fractional solidification is usually practiced at ambient pressure, only isobaric diagrams will be discussed.

3.2.1 Simple Eutectic Systems

The values of the variables (temperature and pressure) at which solid and liquid phases are in equilibrium are known as melting and freezing points. The melting and freezing points of a pure crystalline solid are identical if no supercooling occurs. If an impurity is added which is less soluble in the solid than in the liquid, the freezing point is lowered. Freezing points of hypothetical component A, as impurity B is added, is represented by curve T_A-e in Fig (10), while T_B-e is obtained when A is added to pure B. The intersections of the two curves e is the eutectic point, whose coordinates are eutectic temperature and etuectic composition T_e and W_e respectively. This type of binary-phase diagram is known as the "simple-eutectic' type.

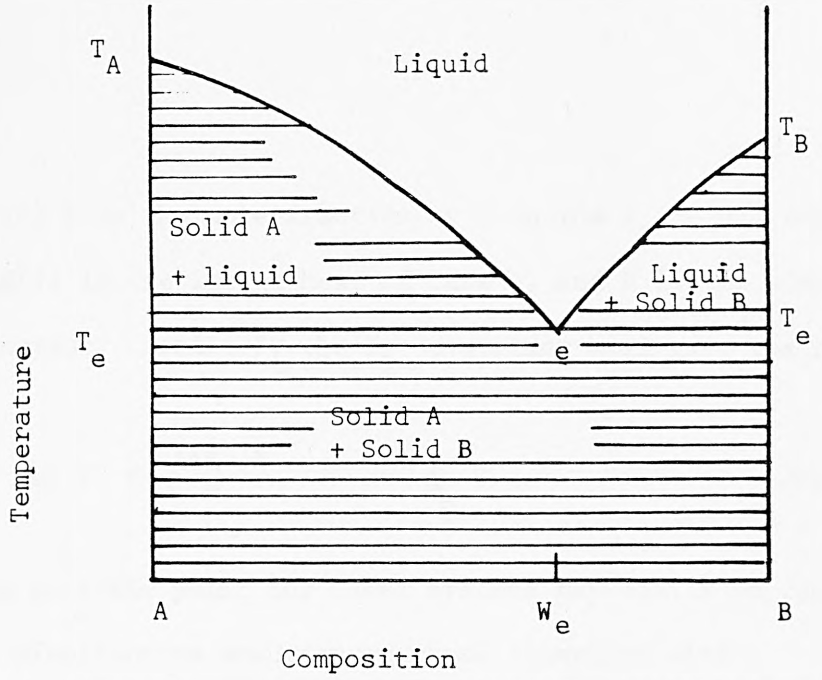


Fig (10) Simple eutectic phase diagram at constant pressure.

It shows that above the freezing point curve called collectively the liquidus, there is just one liquid phase which is a homogeneous molten mixture of A and B. The areas between the liquidus and eutectic temperature are two-phase regions, where pure solids A or B are in equilibrium with the liquid, whose compositions are specified by a horizontal line called the tie line. The eutectic tie line, connects three phases, both pure solids and a liquid of composition, W_e while below T_e a mechanical mixture of solids A and B.

Schroeder-van Laar (129) has presented the following equation for calculating the liquidus

$$- \ln (1-X) = \frac{(\Delta HF)\ A}{R} \left(\frac{1}{T} - \frac{1}{T_A}\right) \qquad (9)$$

where X is the mole fraction of B on the T_A -e portion, $(\Delta HF)A$ is the latent heat of pure A, and R is the ideal gas constant. Similarly the T_B -e portion will give the result

$$-\ln X = \frac{(\Delta HF)B}{R} \left(\frac{1}{T} - \frac{1}{T_B}\right) \qquad (10)$$

The eutectic point for ideal systems may easily be found by simultaneous solution of these equations with

$X = X_e$ and $T = T_e$

From these equations the general rules that can be drawn are for ideal systems, but have also proved applicable to non-ideal systems are

a) the solubility of a solid increases with temperature

b) if the latent heat is held constant, the solubility increases as the melting point of the solid decreases

c) if the melting point is held constant, the solubility increases as the latent heat of fusion decreases and

d) if the solution is ideal, the solubility does not depend on the solvent.

3.2.2 Limited Solid Solubility

Sometimes it so happens that the impurity is slightly soluble in the solid phase of the component being purified. This leads to a phase diagram of the type presented in fig (11).

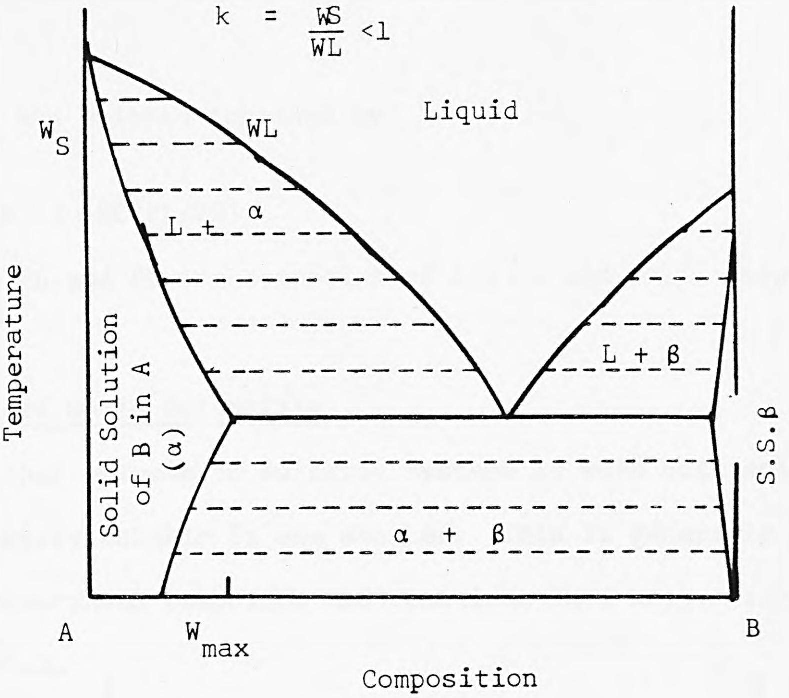


Fig 11 Phase diagram for components exhibiting limited solid solubility. Phases α and β are homogeneous solid solutions.

The horizontal dotted lines are the isothermal isobaric tie lines, connecting phases that co-exist in equilibrium with one another when the mean system composition lies on them.

The tie line (conodes) serve to define the equilibrium distribution co-efficient K, which in terms of weight fractions is

$$KW = \frac{WS}{WL} \qquad (11)$$

and in terms of concentration $KC = CS/CL$, which are related together by

$$KW = KC(PL/PS) \qquad (12)$$

where PL and PS are densities of liquid and solid respectively.

3.2.3 Complete Solid Solubility

The other extreme to eutectic systems is when both solids are completely soluble in one another. This is generally common in isomorphous compounds and sometimes in a krypto-isomorphous compound.

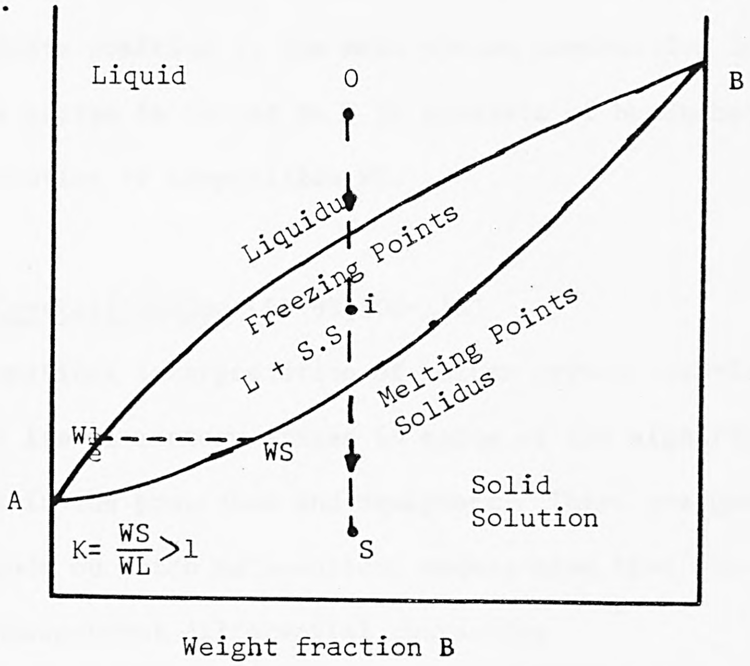


Fig 12 Phase diagram for components exhibiting complete solid solutions.

Vapour/liquid phase diagrams are analogous to the above diagram fig (12).

If B is considered an impurity in A, then distribution coefficient K>1 and if A is considered an impurity in B then K<1. While the freezing operation of an etuectic system is simple, the operation of complete solid solubility is much more complicated (129).

Starting at O if the melt is cooled, the liquid composition moves down the liquidus towards WL while the solid composition moves down the solidus towards WS. At an intermediate position i, the mean system composition is WO. When the system is cooled to S it consists of homogeneous solid solution of composition WO.

3.3 Column Crystallization (96-99,106-115)

The theoretical interpretation of column crystallization is still in its elementary stages in spite of the significant advances in the processes and equipment. There are generally two methods on which mathematical models have been based:

1) Countercurrent differential contacting
2) Countercurrent stagewise contacting

3.3.1 Countercurrent Differential Contacting

The person who has been to a great extent responsible for development based on this principle is Powers. He originally presented it in a paper in 1963. The approach of Powers is based on packed bed distillation column.

Powers presented two separate analyses for different ranges of solid solubility. In the first case, an eutectic system (little or no solid solubility) in which washing is the dominant mechanism of purification was assumed. In the second case solid solubility was considered with recrystallization as the dominant mechanism.

3.3.1.1 Eutectic System

For a simple case of etuectic system where no solid of eutectic composition is allowed it was assumed that

$$MT = AK^{1'}PL(C_{L'} - C_L) \qquad (13)$$

where MT is the rate of mass transfer of impurity from adhering to free liquid, K mass-transfer coefficient, A interfacial area for mass transfer, P density and composition is C (expressed as mass fraction). The subscripts L' and L refer to adhering and free liquid.

For a column operating at total reflux and steady state, to relate the composition of the free liquid to position Z, the above equation was applied in conjunction with standard techniques for differential countercurrent contacting analysis to yield (103)

$$C_L(Z)\ C_L(0) = \exp\ \{-Z/HTU'\} \qquad (14)$$

where Z is positive in direction of crystal flow from freezing section. Height of a transfer unit (HTU') is assumed independent of position and is defined as

$$HTU' = \frac{\{1 + (ML'/MC)\}\, ML'}{K'\, \alpha APL} + \frac{P_C D_L A\, \eta_L}{ML} \qquad (15)$$

where M is mass flow rates, α interfacial area per unit column volume, A the cross sectional area of the empty column, D_L an effective diffusion co-efficient and η_L is the volume fraction of liquid, and L' and C refer to the adhering liquid and crystal part of the solid phase.

The above analysis predicts that the distribution of impurity at steady state is an exponential function of position, which was confirmed by data of Powers.

For columns with continuous flow of feed and product, an expression relating to the degree of purification can be obtained in terms of product flow rates(103)

$$\frac{CE}{CS} = \frac{RE - 1}{RS + 1} \quad \frac{RS + \exp\{-(1+RS)LS/HTU'S\}}{RE - \exp\{(1-RE)LE/HTU'E\}} \qquad (16)$$

where

$$\begin{aligned} RE &\equiv ME/MC \\ RS &\equiv MS/MC \end{aligned} \qquad (17)$$

where ME is rate of purified product, MS rate of impurities, and MC is internal flow rate of crystals; LE and LS are lengths of enriching and stripping sections respectively, and C_E and CS refer to the composition of products leaving the enriching and stripping sections.

3.3.1.2 Systems Forming Solid Solutions

Recrystallization has been considered as the dominant mechanism of purification in solid solution systems. It involves simultaneous transfer of heat and mass, but only mass transfer is considered for simplicity. The rate of mass transfer from re-crystallization is assumed to be related to the concentrations in the solid phase and the free liquid, which are in contact by an overall mass transfer co-efficient

$$MT = KS.PS(CS - CS^{*}) \qquad (18)$$

where M_T is the rate of transfer of one component from the solid phase to the free liquid, K, is the mass transfer co-efficient, CS^{*} is the composition of a hypothetical solid phase in thermodynamic equilibrium with the existing liquid phase, and the use of S is to designate solid phase.

Application of the rate expression in conjunction with standard techniques, to analyse the differential countercurrent contacting of the liquid and the solid phases of a binary mixture with solid solubility, in a column crystallizer operated at total reflux after attainment of steady state gives the following result

$$\frac{Z}{HTU} = \int_{CL(O)}^{CL(Z)} \frac{d\ CL}{Cs^{*} - CL} \qquad (19)$$

where

$$HTU \equiv \left(\frac{MS}{PS\ KS \cdot aA} + \frac{PL\ DL\ A\ NL}{MS} \right) \qquad (20)$$

and mass flow rate and HTU are independent of Z. Based on the above interpretations of theoretical aspects of column crystallization, Albertins and Powers presented general solutions in 1969 for the three cases where (a) crystals are pure; (b) crystals are not pure and mass transfer between adhered and free liquid is the major mechanism of purification; (c) crystals are not pure and eddy diffusion is the major cause for purification.

Considering mass transfer, eddy diffusion, impurity content of adhering liquid and impurity content in crystals, Albertins obtained ordinary differential equations whose solutions for the case in which $X \neq f(Z)$ are:

$$Yr\ (Z) = C_1 \exp\ (S_1 Z) + C_2 \exp\ (S_2\ Z) + X \qquad (21)$$

where Yr is impurity in reflux, C_1 and C_2 are constants to be evaluated from boundary conditions, and X is weight fraction of impurity in crystals

$$S_1 S_2 = \frac{-\beta \pm \sqrt{\beta^2 - 4\alpha}}{2\alpha} \qquad (22)$$

$$\beta = \frac{R(R+1)L}{Ka\ PA\ E} + \frac{DPA\ E}{L} \qquad (23)$$

$$\alpha = RD/Ka \qquad (24)$$

D is the diffusion co-efficient, Ka the mass transfer co-efficient, L crystal rate, A cross sectional area of the column, a, area of mass transfer from adhering to reflux liquid E volume fraction of liquid and

$$R = \frac{Va}{L} \qquad (25)$$

where Va is the adhered liquid rate.

For X ≠ 0 and eddy diffusion as the dominant mechanism, a simpler expression is

$$Yr(Z) = C_6 \exp\ (-\phi Z) + X \qquad (26)$$

where $$\phi = \frac{L}{DP\ A\ E} \qquad (27)$$

Albertins concluded that the third case of $X \neq 0$ and eddy diffusion play the cominant role in determining the composition profile for batch steady state conditions. The following year in 1970 Gates and Powers presented separate analyses of etuectic and solid solution systems. In the same year, Henry and Powers presented models based on the analogy with packed extraction column.

Bates, Gladwin and McGrath in 1976 (97) presented an extension of Henry's works and confirmation of their validity. They described the columns in terms of the stripping and enriching sections and developed differential equations around the enriching section whose solution was presented as

$$\frac{Y - YP}{YQ - YP} = \exp - \frac{Z - ZF}{H} \qquad (28)$$

where $$YP = \frac{CE - LE.YE}{C - LE} \qquad (29)$$

and $$H = \frac{1}{C - LE} \qquad \frac{D\zeta AP + \alpha(1+\alpha)C^2 - \alpha LE.C}{Ka.AP} \qquad (30)$$

These equations allow prediction of concentration or impurity in the column for any value of Z, C or LE once the constants ζ, A, P and α have been determined and YP, YQ, D and Ka are estimated.

If H in equation (30) is differentiated with respect to C, it is possible to evaluate the maximum theoretical crystal rate above which separation decreases.

i.e.

$$\frac{dH}{dc} = \frac{1}{(C-LE)^2} \quad -D\zeta AP + \frac{\alpha(1+\alpha)}{Ka \cdot AP} \quad (C^2 - 2CLE) + \frac{\alpha LE^2}{Ka\ AP} \qquad (31)$$

For a maximum or minimum value $\frac{dH}{dC} = 0$ (32)

and

$$D\zeta AP = \frac{\alpha(1+\alpha)\ (C^2 - 2CLE)}{Ka\ AP} + \frac{\alpha LE^2}{Ka\ AP} \qquad (33)$$

which may be solved for C provided $C \neq LE$.

Where C is crystal rate production, LE enriched stream, ζ volume fraction of free liquid, α is ratio of adhering liquid stream to crystal rate, H is separation factor, Y is impurity content of reflux and YQ impurity content of reflux liquid at feed point.

They found that an optimum value of crystal rate will be obtained above which the separation factor H decreases. The value of H is raised as D increases and falls as K_a increases. For a good separation, diffusion should be minimised while mass transfer is increased.

3.3.2 Counter-current Stagewise Contacting

Anikin (106) has presented discussions based on the above principles. He presented expressions based on the analysis of rectifying columns because he assumed the column crystallizers embrace similar physiochemical processes to rectifying columns. He also presented equations for the calculation of the number of theoretical stages.

However, his assumptions have not been tested experimentally and thus lack strict validity.

3.4 Modelling and Simulation

The phrase Modelling and Simulation (130) consists of two independent activities. However they are both linked together in such a way that it is almost impossible to separate them and are therefore treated under one heading.

Many books have been published on modelling and simulation and many of them represent special problems in biological, social, economic and behavioural science problems. Others are more general, physical science problems such as those of Alexander and Bailey 1962, Naylor, Balintfy, Burdick and Chu 1966 (131), Yaohan Chu 1969 (132), Stephenson 1971 (133), Wolberg 1971, Furman 1972, Ord-Smith and Stephenson 1975 (134), Bender 1978, Zeigler, Elzas, Klir and Oren 1978 (135). Modelling and simulation in chemical engineering has been specially discussed by Roger Frank 1967 (136) and 1972 (137).

Most models (141) fall in one of the two broad categories of physical and symbolic models. Physical models are classified such as iconic models, scale models, analog computer models etc. Drawings, verbal, and mathematical models are symbolic models. Mathematical models are the most versatile, flexible and effective types of symbolic models. Such models are represented in the abstract mathematical form of variables, parameters, equations and inequalities, and do not resemble in any form the real system. This requires elaborate computation and usually requires the aid of a computer. From now on mathematical models shall be generally referred to as model.

Modelling deals primarily with the relationship between real systems and models (138,139) and Simulation (140) refers to the relationship between computers and models. This constitutes the three basic elements:

a) the real system

b) the model

c) the computer.

A model is basically a set of instructions for generating behavioural data of the form in fig (13)

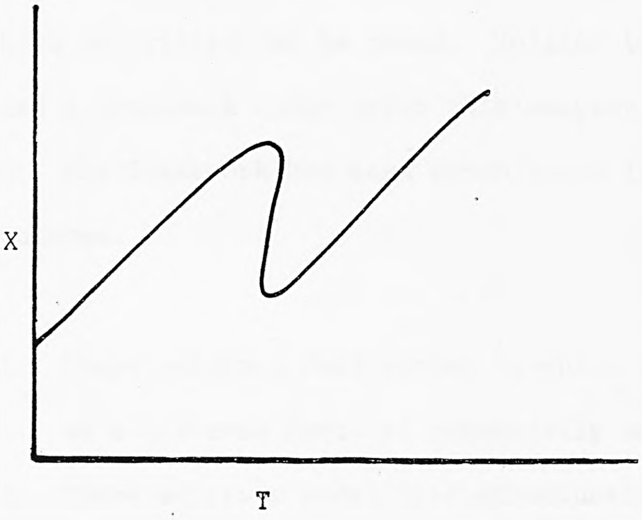


Fig 13 General Behavioural data generated by a mathematical model

Models are often expressed in certain common ways by differential equations, in automata theoretic notation, or in discrete event formalism. Simulation is the construction of a computer programme that will faithfully generate the behaviour of the model. Hence the modelling relation concerns the validity of the model and simulation relation concerns the faithfulness with which the computer carries out the instructions intended by the model.

3.4.1 Postulates

Like every other activity in science, the activity of modelling and simulation requires the presentation of some formal theory (143) on which activities can be based. Zeigler (130,144,145) has presented a framework under which this complex activity can proceed. His framework has been established in terms of twelve postulates.

Postulate 1. There exists a real system R, which is identified as a universe (set) of potentially acquirable data.

Postulate 2. There exists a model that structurally characterizes the universe of potentially acquirable data R. We call such a model a base model and denote it by B.

The base model is a time invariant transition system (a system without output).

$$B = \langle TB, XB, (XB, TB), QB, \delta B \rangle \qquad (34)$$

Postulate 3. There exists a set of experimental frames restricting experimental access to the real system. We denote this set by ξ and a typical member frame by E.

Postulate 4. An experimental frame is a structure

$E = \langle \Omega E, YE, \lambda E, VE \rangle$ (35)

where ΩE is a set (the input segments applicable in E)

YE is a set (the output value set observable in E)

λE is a function (the observation function in E)

VE is a set (the range of validity of E)

Postulate 5. The real system observed within the experimental frame E is structurally characterized by a model denoted by B/E and called the base model in E.

Postulate 6. The base model in E is a structure.

$B/E = \langle T, X, \Omega, \mathcal{Q}, \gamma, \delta, \lambda \rangle$ (36)

where $T = TB$ (time base of base model

$X = \{W(t)/W \varepsilon \Omega E,\ t\ \varepsilon\ \mathrm{dom}\ (W)\}$ (union of generator ranges)

$\Omega = \Omega E$ (input segments specified by the frame)

$\mathcal{Q} = \lambda\varepsilon^{-1}(V_E)$ U $\{\phi\}$ (the set of base model states yielding readings that lie within the valid input set together with a distinct special symbol (ϕ).

$\gamma = V_E$ U$\{\phi\}$ (the nonvalid output region is collapsed into ϕ)

$\delta: \mathcal{Q} \times \Omega \rightarrow \mathcal{Q}$ is defined by

$$\delta(q,\omega) = \begin{cases} \delta_B(q,\omega) & \text{if } \delta_B(q,\omega_{t>}) \varepsilon \lambda^{-1}(V_E) \text{ for all } t \varepsilon \text{ dom } (\omega) \\ \phi & \text{otherwise} \end{cases}$$

for $q \neq \phi$, and $\delta(\phi,\omega) = \phi$

$\lambda: \mathcal{Q} \rightarrow Y$ is defined by

$$\lambda(q) = \begin{cases} \lambda_E(q) & \text{if } q \neq \phi \\ \phi & \text{if } q = \phi \end{cases}$$

Postulate 7. The data potentially acquirable by observation of the real system within experimental frame E are identified with the I/O relation of the base model in E, $R_{B/E}$

Postulate 8. The real system R is the set of data potentially acquirable by observations within any of the experimental frames in the set ε , that is,

$$\mathcal{R} = \bigcup_{E \,\varepsilon\, \xi} R_{B/E}$$

Postulate 9. A lumped model is an iterative system specification M. Let S(M) be the system specified by M.

Postulate 10. A lumped model M is valid for the real system in experimental frame E if its I/O relation $R_{S(M)} = R_{B/E}$.

Postulate 11. A computer is an iterative system specification C.

Postulate 12. A computer C is a valid simulator of a lumped model M if there is a specification morphism from C to M.

Thus it has become necessary now to define in brief our original three basic elements that constitute the complex activity of modelling and simulation.

The real system is a source from which data can be observed. A model is a representation of this real system in abstract terms. To observe date from the real system it has to be subjected to certain experiments or may be subjected to many such sets of experiments. A model which would provide a complete explanation of the behaviour of a real system will naturally comprise many, many components and interactions. Thus this model will be valid for all sets of experiments on the real system. Such a model is called a base model and its complexity is likely to be very great.

However, simpler models could be developed which may be valid for a particular experimental set. This is called a lumped model which is often constructed from the base model by lumping together components and simplifying interactions accordingly. A lumped model which is valid under one experimental set may not be valid for another set. Thus the validity of the model developed must be considered before it is simulated.

3.4.2 Communication

Communication (142) is a very important aspect of modelling and simulation but unfortunately it is very little appreciated. Though the construction and testing phases are more exciting and challenging, it is equally important that these activities be reported precisely and clearly for others to use, implement or further develop. Communication aspects are important in influencing the use and impact, a simulation study may enjoy. The most fundamental aspect of communication is that of generating an informal model description which would then lead to a formal model description.

The informal description of a model consists of the specifications of components, descriptive variables including parameters. component interaction, and presentation of the assumptions implied by the specifications of interest.

Formal model description helps to detect omissions and inconsistencies, and to resolve ambiguities inherent in the informal description. A formalised model can be considered to be a shorthand means of specifying a system.

3.4.3 Difficulties of Mathematical Modelling

There are many difficulties of mathematical modelling:

1. Because of lack of understanding of the real system it may not be possible to define the mathematical relationship.
2. Even if the relationship is defined, it may not constitute a solvable problem.
3. Even if they are solvable, sufficient data for modelling may not be available.
4. Errors due to the chain of approximations and computations involved in modelling may be excessive.
5. Cost of the computations may be prohibitive.
6. It may be difficult to validate mathematical models.

The role of models in scientific research is discussed in an article by Wiener 1945 (139) in a general way. The importance of modelling in engineering and in planning has increased enormously since this article was published. According to Rosenblueth and Wiener the following conditions are both necessary and sufficient for a physical model to be useful:

1. A phenomenon in an unfamiliar or less familiar field (prototype "space") must be replaced by a phenomenon in a (more) familiar field (model "space").
2. Modelling experiments must be carried out under more favourable conditions (including cost, flow, time etc.) than experiments with the prototype.

The same holds true for mathematical models with additional conditions imposed of

1a. Computational (numerical) results must be validated and interpreted in real "space" (not "numerical garbage"). Otherwise the phenomenon in model "space" is not interpretable and hence unfamiliar to the model user.

2a. The mathematical modelling problems must be solvable, otherwise experiments cannot be carried out at all.

3.4.4 Computer Programming

The development of a computer programme (146) or computer implementation of a mathematical model is one of the major steps in the mathematical model - building process. Without a computer programme, the modelling computations may be difficult or impossible to carry out. The following conditions are necessary for successful completion of the programme development step:

1. Complete, precise and non-ambiguous specification of all processes which will be carried out by the programme (computational, data transfer, etc.).
2. Proven and tested correctness of the programme with respect to these specifications.
3. Proper programme structure and format.
4. Programme coding in a suitable language.
5. Full programme documentation.

Computer programme development is expensive and time consuming and thus has to be properly managed. The development of computer programmes is an exacting and difficult task, requiring much ingenuity and proper organisation.

Solution of a problem with the aid of a computer has a sequence starting from recognition of a problem, definition, specification, design, adaptation, construction and testing, certification, installation and then maintenance of the programme for future use.

Once the mathematical model has been formulated and executed in terms of a computer programme then its validity has got to be considered. Initially this is mathematical verification and computer programme verification. Finally, model validation is done by analysis of mathematical formulation and comparison of results with experimental results.

3.4.5 Model Validations

Two main positions on validations have developed through history of science: rationalism and empiricism. Rationalists (147) hold that a model is a system of logical deduction from a set of assumed premises which are not open to empirical verification. Consequently validation can be reduced to the problem of identifying a set of fundamental premises which control the behaviour of the prototype: If such premises are found and accepted, then the model is valid and no empirical manipulation and comparisons are necessary.

3.4.6 Categories of Models

There are many categories of mathematical models, and various methods of classifying them. Models can be classified according to several different criteria, including:

1. Time-related behaviour of the model (Dynamic or steady state)
2. Type of model data, parameters and mathematical expressions (Deterministic or steady state)
3. Degree of model refinement and model structure (Distributed or lumped)
4. Mathematical modelling problem type (Algebraic, Differential equation etc.)

Mathematical models can also be categorized according to purpose (148) especially when considering huge continuous plants such as distillation units:

I Models to assist plant design and operation:

a. Detailed, physically based, often non-dynamic models to assist in fixing plant dimensions and other basic parameters.
b. Economic models allowing the size and product mix of a projected plant to be selected.
c. Economic models to assist decisions on plant modernization

II Models to assist control systems design and operation:

a. Fairly complete dynamic models, valid over a wide range of process operations to assist detailed quantitative design of a control system.
b. Single models based on crude approximations to the plant, but including some economically quantifiable variables, to allow the scope and type of control system to be decided.
c. Reduced dynamic models for use on-line as part of a control system.

The information on which the model is based includes material-flow diagrams, block diagrams, circuit diagrams, algebraic and differential equations, curves, tables and experimental results.

In simple terms the different steps involved in developing a mathematical model are:

1. Scope and accuracy of desired model
2. Writing equations that cover all aspects
3. Supplement it with empirical equations if necessary
4. Manipulate these equations to form a typical programme solution by a computer.
5. To obtain experimental data and unknown parameters
6. To use linearization and other mathematical techniques for solving.
7. To acquire enough data to validate the model.

3.4.7 Reasons for Model Failure

A model may fail due to:

1. Lack of sufficient relevant data with which to develop the model.
2. Failure to obtain a well structured foundation to support the later stages of model refinement - this is due to lack of expertise or lack of process knowledge.
3. Numerical or computational problems of model implementation including
   - failure of convergence of iterative loops
   - excessive time requirements of computation so that the model is virtually useless.

3.4.8 Chemical Plant Modelling

In any chemical plant operations the basic physical and chemical phenomena involved are:

1. mass transfer
2. heat transfer
3. chemical change.

The process equations are formulated from fairly elementary concepts of physical and chemical dynamic balance and equilibrium.

A very common chemical plant is one having distillation units. There are a few types of distillation columns, but, because of the resemblance of a column crystallizer to a packed type binary distillation column (149,150,151,152), it is presented in fig (14) and a few equations are developed. For developing the equations a conceptual cell of a rectifying section is shown fig (15).

From the figures it can be seen that vapour and liquid streams flow past one another at rates denoted by V and L moles per unit time, the streams being composed of mixtures of two components to be separated. X denotes the mole fraction of the more volatile component in the liquid mixture and Y that in the vapour stream. Primes are asociated with the variables in the stripping section and suffixes s and r associated with the flow rates denote stripping section and rectifier quantities. The boiling mixture is fed into the column between stages, the liquid at F_L composition Z and vapour F_V composition z. Products are withdrawn at top $V_r - L_r$ composition X(N+1) and bottom $L_s - V_s$ composition $Y'(-M-1)$.

Within each cell, under adiabatic conditions, if only latent heats are considered; the heat balance merely constrains the flow rates, V_r, V_s, L_r and L_s to be spatially invariant.

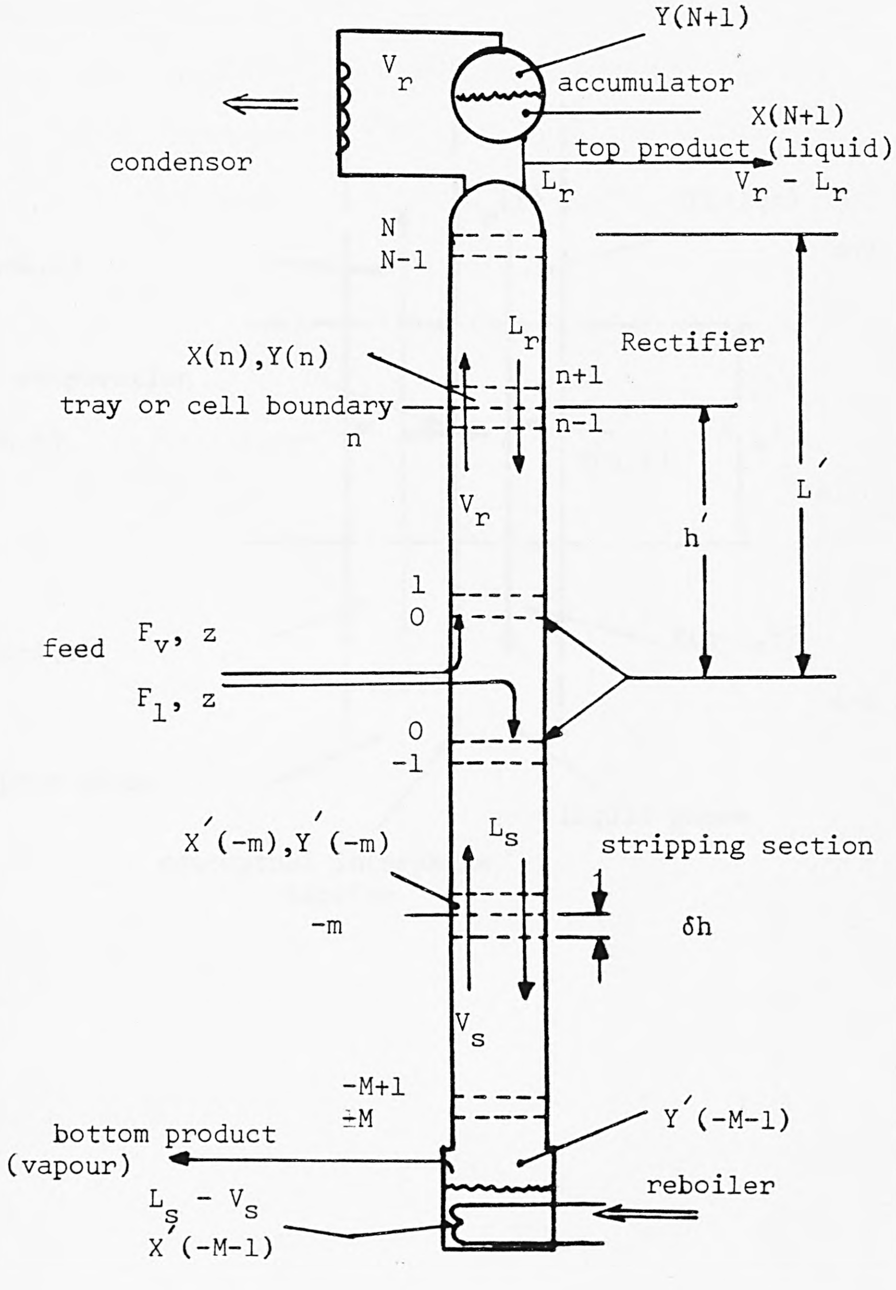


Fig 14 General arrangement of column for binary distillation Column

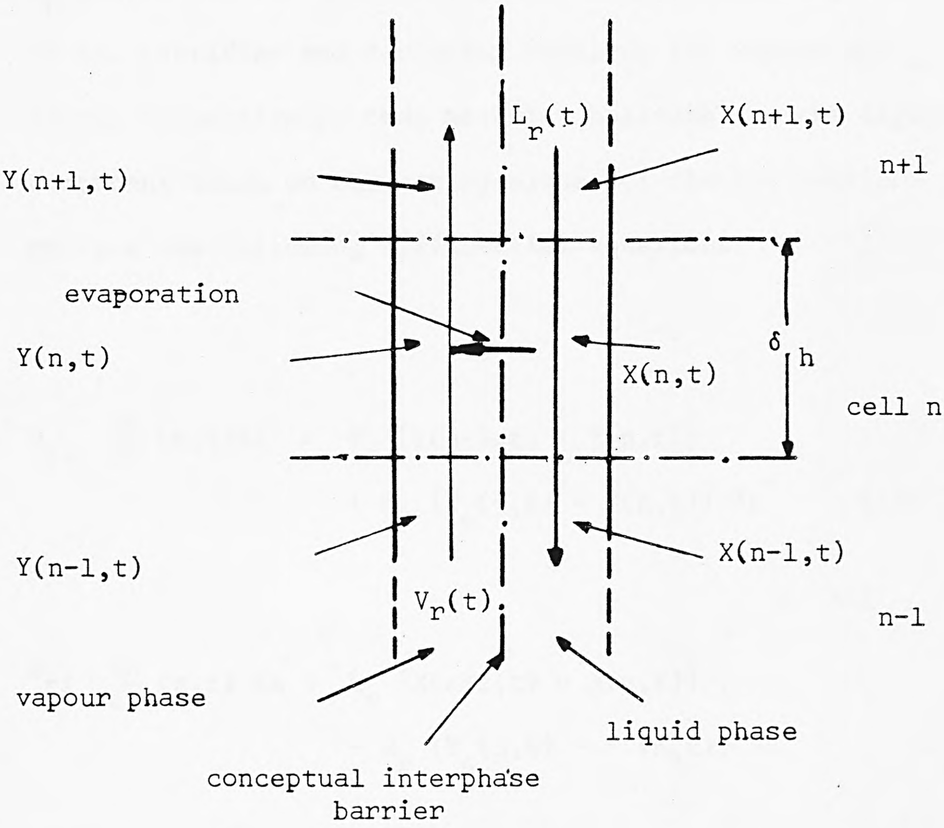


Fig 15 Variables associated with nth cell of rectifying column

The dynamic effects are produced by the material balance and are considered in more depth. If H_{rv}, H_{rc}, H_{sv}, and H_{Ω} denote the fixed molar capacitance per unit length of the rectifier and stripping sections for vapour and liquid respectively, then material balances for the lighter component taken on elementary slices of the two sections produce the following differential equations.

$$\begin{aligned} H_{rv} \frac{dY}{dt}(n,t)\delta h' &= V_r \{Y(n-1,t) - Y(n,t)\} \\ &\quad + K_r \{Y_e(n,t) - Y(n,t)\} \delta h' \qquad (38) \\ & \qquad\qquad\qquad\qquad n > 1 \\ H_{rl} \frac{dX}{dt}(n,t)\delta h' &= L_r \{X(n+1,t) - X(n,t)\} \\ &\quad - K_r \{Y_e(n,t) - Y(n,t)\} \delta h' \end{aligned}$$

$$\begin{aligned} H_{sv} \frac{dY}{dt}(n,t)\delta h' &= V_s \{Y'(n-1,t) - Y'(n,t)\} \\ &\quad + K_s \{X'(n,t) - X'_e(n,t)\} \delta h' \\ & \qquad\qquad\qquad\qquad n < -1 \qquad (39) \\ H_{sl} \frac{dX}{dt}(n,t)\delta h' &= L_s \{X'(n+1,t) - X'(n,t)\} \\ &\quad - K_s \{X'(n,t) - X'_e(n,t)\} \delta h' \end{aligned}$$

where K_r and K_s are constant coefficients of evaporation and suffix e indicates equilibrium quantities.

The above quantities represent net rate of evaporation of the lighter component which ceases when neighbouring liquid and vapour mixtures are in so called "thermodynamic equilibrium" with one another. For ideal mixtures equilibrium relationships are discussed by Judson and King (153) to be

$$\beta = Y_e \, (1-X) / \{X(1-Y_e)\} \qquad (40)$$

where Y_e is the composition of a vapour in equilibrium with a liquid of composition X and in terms of stripping section quantities

$$\beta = Y' (1-X'_e) / \{X'_e \, (1-Y')\} \qquad (41)$$

where X'_e is the composition of a liquid mixture with which vapour of composition Y' would produce equilibrium. Approximations to equilibrium curves (154), represented by linear relationships for rectifying and stripping leads to elimination of X and Y and build up of partial differential equations which can be later solved by computers.

3.4.9 Special Simulation Languages

Sometimes in real life we are confronted with a modelling problem which cannot be cast in mathematical form amenable to analytical or numerical solution techniques. Despite this, we may hypothesize the real world problem by the use of special language to construct a procedural model that behaves like the real thing. Under this process fall two kinds of simulation models, the discrete and continuous models. Although almost every general-purpose computer language such as FORTRAN, ALGOL, PL/I, can be used for this purpose, the use of special languages may greatly increase use of a simulation model.

3.4.9.1 Discrete System Simulation Languages

Discrete system simulation languages may be represented by SIMSCRIPT 11.5 (155), GASP (156), CSL (157), MILITRAN (158), SIMULA (159), SOL(160), GPSS (161) etc. Of the above the commonly used ones are Simscript 11.5 which is event oriented, GPSS which is transaction flow oriented and SIMULA which is process oriented.

3.4.9.2 Continuous System Simulation Languages

Continuous system simulation languages are designed to facilitate modelling and solution of dynamic problems, formulated in terms of ordinary or partial differential equations.

Emulators for analog and hybrid computers are MIDAS (162), MADBLOCK (163), CSMP 1130 (164).
Expression based languages are MIMIC (165), DAREP (166), CSMP/360 (167), CSSL-111 (168), PROSE (169), ACSL (170), EASY (171) and of course the commonly known DYNAMO (172) of the MIT group.

The languages vary in approaches and are not all implemented on any single computer. Different computers have facilities for different languages; thus the choice will depend not only on what is required, but also on what is available on any particular machine and system.

CHAPTER 4

MODELLING AND SIMULATION OF THE COLUMN

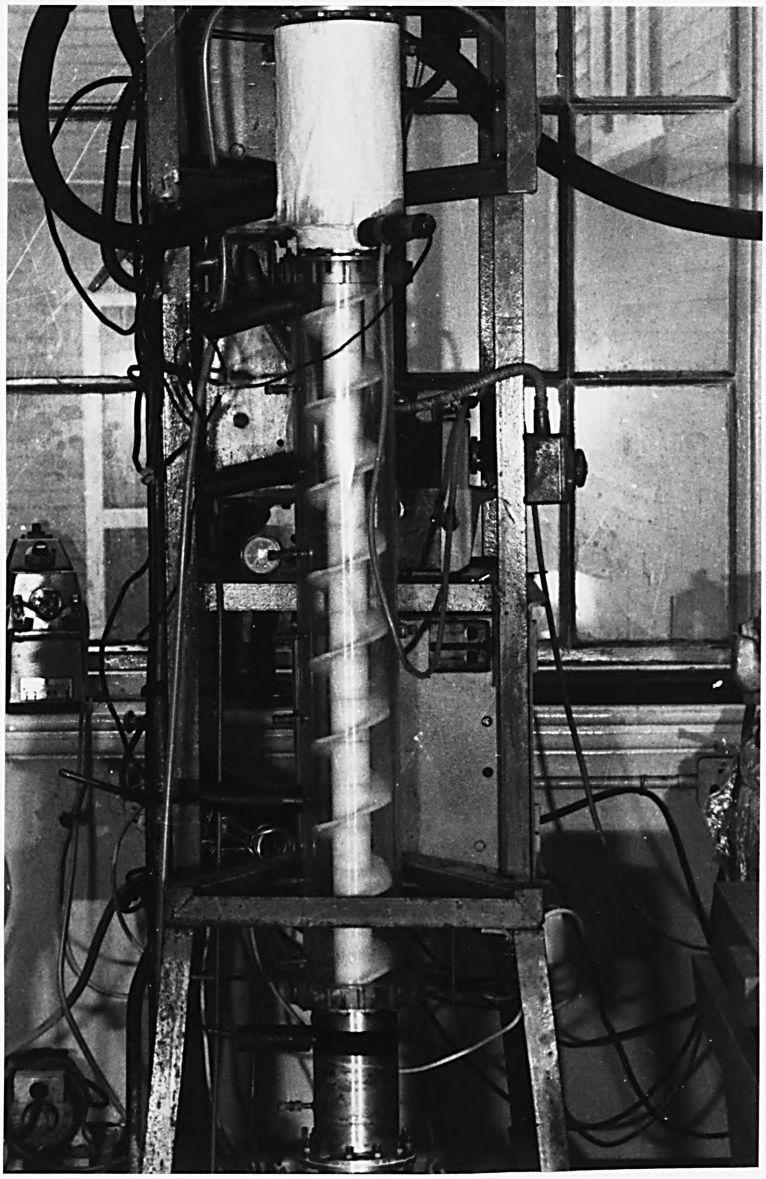


Plate 1 - Arrangement of the entire Column for continuous operation

Chapter 4 MODELLING AND SIMULATION OF THE COLUMN

Dynamic mathematical models simulated in a manner which can be solved with the use of digital computers are developed here. We must consider the different mechanisms which are prevailing in the entire column to build up its mathematical models. The process of purification in the column is discussed earlier, where it is shown that crystals are formed in a stage, either at the bottom or the top of the column depending upon the position of the freezing section of the column. In either case a spiral conveyor is used to transport the crystals to the opposite end of the column.

The opposite end as we know is the melting section where the crystals are melted with either application of heat or due to a pressure build up. The in-between is the purification section where impurities, both adhered and occluded, are washed and removed from the body of the crystals to leave them relatively pure.

As we can see, the column could easily be divided into three distinct sections, called the Freezing, the Purification and the Melting section, each involving certain sets of purification mechanisms indigenous to the section. Some of the models are similar to all the sections of the crystallizer but others which have got only very minor or no effects for a particular section, are neglected, for that section. These effects can better be discussed separately under each section.

Also, since it would be a very cumbersome and complicated job to build just one simulation for the entire column, it is better to break up the column in parts. This gives us an opportunity to test our simulation models in parts and it is much easier to develop them. For this reason the freezing section was attempted first and work proceeded to the other sections only after satisfactory results were obtained. The purification and the melting sections were then added to it to build the entire column. Therefore let us consider the freezing section first.

4.1 Modelling and Simulation of Freezing Section

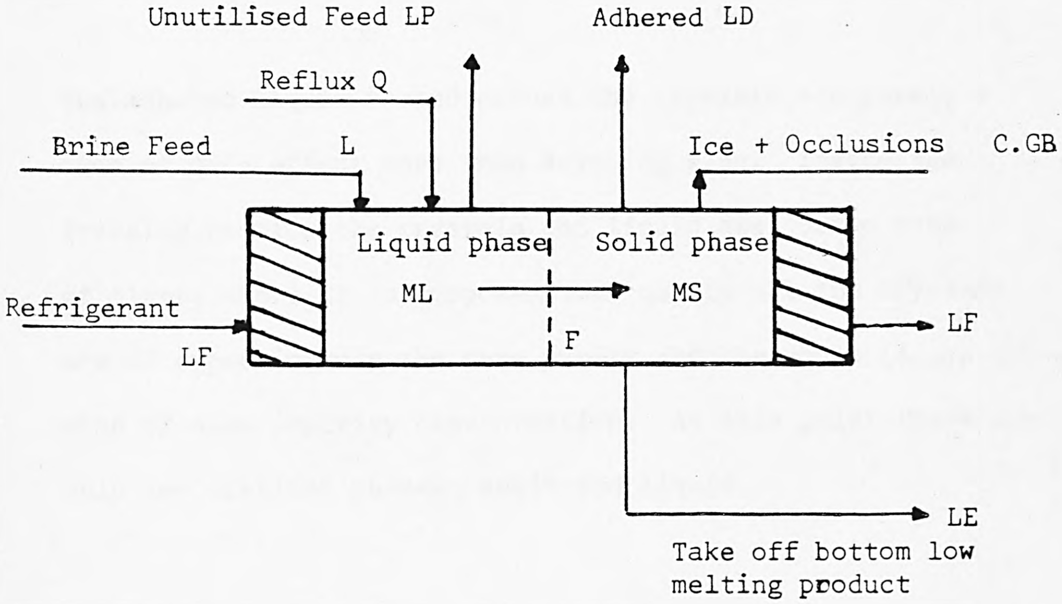


Fig 16 Schematic of the Freezing Section.

The process under study is that of formation of ice crystals from brine (salt water or sea water). The diagram above fig (16) is presented for the visualisation of the physical phenomena that are supposed to be taking place in the freezing section. It also presents the mechanisms which are governing the flow of certain materials in and out of the freezing section. What is then actually happening can simply be presented as liquid brine which flows in from an external source at a constant controlled rate and is cooled down until ice crystals appear. These crystals grow, the size depending upon the holding time of the freezing section and move upward or downward with the help of the spiral. Thus the spiral is the major factor in transporting the crystals. If the freezing section is at the top of the column as presented by R. Gladwin the flow of liquid might be affected by gravity. But the effect of gravity on crystals seems to be very small.

The adhered liquid formed around the crystals are purely a case of drag effect more than anything else. Inside the freezing section the crystals and liquid are just a mass of slurry where it is supposed that nearly all the crystals are of approximately the same purity and the whole liquor mass of same impurity concentration. At this point there are only two distinct phases, solid and liquid.

As the solids move up, due to a great difference in the density and purity of the liquor, in the freezing section and the purification section, the solids tend to associate with a much denser (adhered) liquid around themselves from the freezing section. The difference in the liquids is due to the fact that the freezing section is surrounded by a mass of refrigerant which readily cools it down and plus the fact that freezing expels salt from ice crystals. So there is a large increase in salt or impurity concentration in the liquid in freezing section while the reflux or the free liquid present in the bottom of the purification section is still of a much lower impurity concentration. This is very important to understanding the mechanism of formation of adhered liquid.

One might argue that adhered liquid might still be present in the freezing section as the crystals are moving up within the freezing section. Though there might be a slight gradient in the impurity content of the liquor, between the bottom and top of the freezing section, it seems very unlikely that this would give rise to building of adhered liquid due to drag effect within the freezing section. Therefore the adhered liquid as a separate phase has been presented in the purification section only. Amounts of adhered liquid formed leaving the freezing section is calculated from the data of freezing section but any transfer of this adhered impurity to free liquid does not take place until the crystals and adhered reach the purification section.

The main mechanism in the freezing section is of course that of formation of crystals, that is crystallization. There are a lot of data available on crystallization of different materials in batch or even continuous crystallizers of the conventional types. But so little is available on crystallization in columns that it has been of great difficulty to simulate a model for the freezing section. In fact very little is known even about the forms of crystals of ice in column crystallization. Since at room temperature it melts to form water it has been extremely difficult to observe microscopically. Though disc and needle shaped ice crystals have been reported in open trough and cylinders respectively, Orcutt is of the opinion that ice crystals formed in the column crystallizer are spherical.

In case of nucleation the general nucleation rate equation as presented in Desalination by Orcutt (105) is used. It is hoped that this equation would still hold true as it is a general equation for formation of ice crystals under certain temperature ranges. The shape of the column and internal rotation should not have much effect on this basic equation.

The only thing probably that has been affected by the screw conveyor is the shape which gives rise to spherical crystals, instead of disc or needle shaped crystals.

Now that these aspects of the freezing section are considered we are ready for modelling. It would involve the balancing of the different constituents going in and out such as liquid mass balance, solid mass balance, temperature etc. The column considered is one which has the freezing section at the bottom and the feed point is just above the freezing section, in which case the feed almost directly enters the freezing section.

The present simulation model that we have,has been developed gradually. A couple of simulation models were developed, each one an improvement on the past. The earlier simulation models are not presented as they did not yield appreciable results but did show us the way to develop new ones.

4.1.1 Modelling of the Freezing Section

The models are developed on the principle factors as shown in Fig.16, and we shall start with the mass balance first. During development of the models which solve for a particular factor we shall meet other unknown quantities on which the model is dependent and those unknown in turn would have to be solved as well until there are no unknowns left.

(a) Liquid Mass Balance (ML)

The mass balance on the liquid in the freezing section is

$$\frac{dML}{dt} = L - LE - LD - F - C.GB + Q \qquad (42)$$

where ML is the liquid mass hold up

L is the liquid feed (brine) coming in

LE is the liquid take-off as bottom product

LD is the adhered liquid going up with crystals

F is the mass transfer from liquid to solid

C is the crystal mass rate to purification section

GB is the liquid entrained within solids lost with crystals taken as constant and

Q is the reflux coming down.

In the above equation L, LE GB and Q are supplied as data but LD, F and C will have to be calculated. Although Q will eventually come from purification section data when the whole column is constructed at this stage we shall consider it as a fixed quantity.

(b) Adhering Liquid (LD)

The amount of liquid going out of freezing section with the crystals to purification section as adhered liquid will naturally be a function of the crystal size $F(\bar{R})$ and proportional to the amount of crystals going out represented as

$$LD = CE\ F(R) \tag{43}$$

where R is the average radius of the crystal and E is a constant of proportionality supplied as data.

(c) Mass Transfer (F)

The rate of mass transfer from liquid to solid; in this case from water to ice; that is the weight of ice being formed per unit time may be simply represented as

$$F = J \times CM \tag{44}$$

where J is the rate of nucleation and CM is the mass of a single crystal. Under steady state conditions the rate of mass transfer should naturally be approximately equal to the total mass of ice leaving the freezing section per unit time.

(d) Crystal Rate to Purification Section (C)

The crystal mass rate to purification section is defined in terms of screw speed which is used to transport the crystals and is expressed as

$$C = \frac{MS.V}{HF} \qquad (45)$$

where V is the vertical velocity of the screw, MS is the solid mass hold up and HF is the height of the freezer. Now we satisfy all the conditions of solving differential equation (1) so we can proceed to the next equation.

(e) Radius of Crystal (R)

The average crystal size is dependent on the growth rate as defined earlier and is represented as

$$R = \frac{DP}{2.0} \qquad (46)$$

where DP is the particle diameter.

(f) Heat Balance on Solid Phase (DP)

The particle diameter is calculated by considering the thermal driving force of growth rate as discussed earlier under crystal growth, which is in effect a sort of heat balance on solid phase and is represented as

$$\frac{dDP}{dt} = \frac{G}{DP}\ (TI - TB) \qquad (47)$$

where G is the growth rate constant, TI is the temperature at ice/liquid interface and TB is the bulk temperature.

(g) Growth Rate Constant (G)

The crystal growth rate constant is defined earlier as

$$G = 0.6129 \times 10^{-8} / \{1.0 + 77.0\ WL/(1.0 - WL)\} \qquad (48)$$

where WL is the salt concentration of the bulk liquid.

(h) Ice/Liquid Interface Temperature (TI)

The ice liquid interface temperature may be calculated from the ratios of the actual thermal driving force to the apparent driving force

$$\text{i.e. from} \quad EX = \frac{TI - TB}{TF - TB} \qquad (49)$$

Re-arranging the terms we get

$$TI = (TF - TB)\ EX + TB \qquad (50)$$

where TF is the freezing temperature supplied as data.

(i) The Driving Force Ratio (EX)

To calculate for TI we have to find out the ratio (EX) first. By looking at the growth rate from a different angle than the thermal driving force, we had been able to deduce earlier that the growth rate also equals the rate at which salt is being transferred away from the interface, i.e. time the ratio of the mass fraction of water to salt in the bulk liquid. This would eventually lead to an equation

$$EX = 1.0/ \{1 + GA(\frac{WI}{1.0 - WL})\} \qquad (51)$$

where GA is estimated to have a value of 77.0 a dimensionless quantity for a stable nuclei.

(j) Nucleation Rate (J)

The basic concept involved in solidification is that of formation of stable crystals to be transported which is naturally dependent on nucleation and growth. We have presented above the equations for calculation of growth. To determine the nucleation rate, the formula as discussed earlier based on the Eyring (126) rate theory of nucleation from melt, shall be used and may be stated as

$$J = \frac{RG.TB}{HP} \quad \exp \frac{A(TF)^2}{TB(TF-TB)^2} \qquad (52)$$

where RG is the ideal gas constant, HP is Planck's constant and A is an empirical constant. The value of A may be calculated by equating J = 1 at the initial nucleation temperature. This nucleation rate equation was chosen because of Umano and Kawasaki's work on desalination of sea water (127).

(k) Mass of Single Crystal (CM)

To solve equation (44) we must know the mass of a crystal of ice which can be calculated from the shape and radius of the crystal. The radius is calculated in equation (5) and assuming an almost spherical shape of the crystals the mass will be

$$CM = \frac{4}{3}\pi R^3 . PS \qquad (53)$$

where PS is the density of the ice.

(l) Solid Mass Balance (MS)

To solve equation (45) the mass balance on the solids in the freezing section will have to be carried out and is represented as

$$\frac{d\ MS}{dt} = F - C \qquad (54)$$

where MS is the solid mass hold up in the freezing section, F is the mass transfer from liquid to solid and C is the crystal mass rate to purification section from freezing section.

(m) Heat Balance on Liquid Phase (TB)

To find out the temperature of the bulk a heat balance on the liquid phase in the freezing section will have to be carried out. In the calculations, heat effects due to entrained liquid (C.GB.CP) is neglected because the effect is minute. Heat effects due to reflux (Q) are also neglected because the temperature of the reflux is almost equal to the bulk temperature when it enters the freezing chamber. Performing a balance on the other factors will give us

$$\frac{d}{dt}(ML.CP.TB) = L.CP.TIN-LE.CP.TB-LD.CP.TB-U.AW(TB-TW) -F(CP.TB+\lambda) \quad (55)$$

Assuming CP (Specific heat) is constant

$$CP.ML\frac{dTB}{dt} + CP.TB(L-LE-LD-F) = L.CP.TIN-LE.CP.TB-LD.CP.TB -U.AW(TB-TW)-F(CP.TB+\lambda) \quad (56)$$

Expanding, we get

$$CP.ML\frac{dTB}{dt} + L.CP.TB-LE.CP.TB-LD.CP.TB-F.CP.TB = L.CP.TIN -LE.CP.TB-LD.CP.TB-U.AW(TB-TW)-F.CP.TB-F.\lambda \quad (57)$$

Cancelling terms we get

$$CP.ML.\frac{dTB}{dt} = L.CP.TIN-L.CP.TB-U.AW(TB-TW)-F.\lambda \quad (58)$$

Rearranging terms

$$CP.ML\frac{dTB}{dt} = L.CP(TIN-TB)-U.AW(TB-TW)-F.\lambda \quad (59)$$

which will give us our TB as a differential equation

$$\frac{dTB}{dt} = \frac{L.CP(TIN-TB)-U.AW(TB-TW)-F.\lambda}{CP.ML} \qquad (60)$$

where CP is the specific heat of the liquid, U is an overall heat transfer co-efficient, AW is the area of the wall, λ is the latent heat of solids, TW is the wall temperature and TIN is the temperature of the feed flowing in.

(n) The Wall Temperature (TW)

The wall temperature will vary with the refrigerant flow and the liquid bulk flow. A heat balance on the wall with respect to refrigerant and bulk in a manner similar to calculations of bulk temperature will result in an equation stated as

$$\frac{dTW}{dt} = \frac{LF.CF(TIF-TW) + U.AW(TB-TW)}{CF.MF} \qquad (61)$$

where LF is the rate of the refrigerant entering, CF is the specific heat of the refrigerant, TIF is the temperature of the refrigerant coming and MF is the mass of the refrigerant around the freezing section at all times.

(o) Salt Mass Balance in Liquid (WL)

The mass balance of salt or impurity in liquid is necessary to determine in order to find the driving force ratio depended upon the amount of salt being transported away from the surface of the crystals. Assuming perfect mixing a differential equation will result as

$$\frac{d}{dt}(ML.WL) = L.WLI-LE.WL-LD.WL-C.GB.WL+Q.WQ \qquad (62)$$

Differentiating by parts

$$ML\,\frac{dW^{L}}{dt} + WL(L-LE-LD-F-C.GB+Q) = L.WLI-LE.WL-LD.WL$$
$$-C.GB.WL+Q.WQ \qquad (63)$$

Expanding the equation we get

$$ML\,\frac{dWL}{dt} + L.WL-LE.WL-LD.WL-F.WL-C.GB.WL+Q.WL =$$
$$L.WLI-LE.WL-LD.WL - C.GB.WL+Q.WL \qquad (64)$$

Cancelling like terms

$$ML\,\frac{dWL}{dt} +L.WL+Q.WL+F.WL = L.WLI+Q.WQ \qquad (65)$$

Rearranging

$$\frac{dWL}{dt} = \frac{1}{ML}\{L(WLI-WL)+Q(WQ-WL)+F.WL\} \qquad (66)$$

where WL is mass fraction of salt in freezing section, WLI is mass fraction of salt in feed L and WQ is the mass fraction of salt in reflux Q.

(p) Mass Balance of Salt in Solids (Σ)

The mass balance of salt in solids due to occlusions is

$$\frac{d}{dt}(\Sigma MS) = \Sigma F - \Sigma C \tag{67}$$

Differentiating by parts

$$\Sigma \frac{dMS}{dt} + MS \frac{d\Sigma}{dt} = \Sigma(F-C) \tag{68}$$

$$MS \frac{d\Sigma}{dt} + \Sigma(F-C) = \Sigma(F-C) \tag{69}$$

Rearranging

$$\frac{d\Sigma}{dt} = 0 \tag{70}$$

where Σ is the occluded salt in solid and in this case it is a constant as its derivative is zero. From previous experimental results of Albertins and others it has also been shown that the occluded impurity is a constant of about 77 ppm, throughout the operation and the length of the column.

All the above equations can now be solved as each equation has got only one unknown quantity while the rest are supplied either as data or through another preceding equation. This would then obviously result in a convergent model. Now that all the factors and mechanisms involved have been considered and each one can be solved, a simulation model can be set up for a solution by the computer. The simulation model may be represented as in fig (17).

4.1.2 Simulation model for Freezing section Page 127

4.1.3 Subroutine Model of Freezing Section Page 128

4.1.4 Analysis and Programming

A set of data is presented under the headings Data, Boundary inputs, and Initial conditions for solving differential equations.

The simulation was programmed by using FORTRAN IV and was run on the CDC 7600 computer of the University of London Computer Centre. To solve the differential equations, the HPCG (Integration subroutine) as described in the IBM Scientific Subrouting Programmes Manual was valuable. The integration step size IHLF = 10 was used and an error was recorded if the IHLF value was more than 10. Thus the programme had to be adjusted such that the IHLF value was never greater than 10.

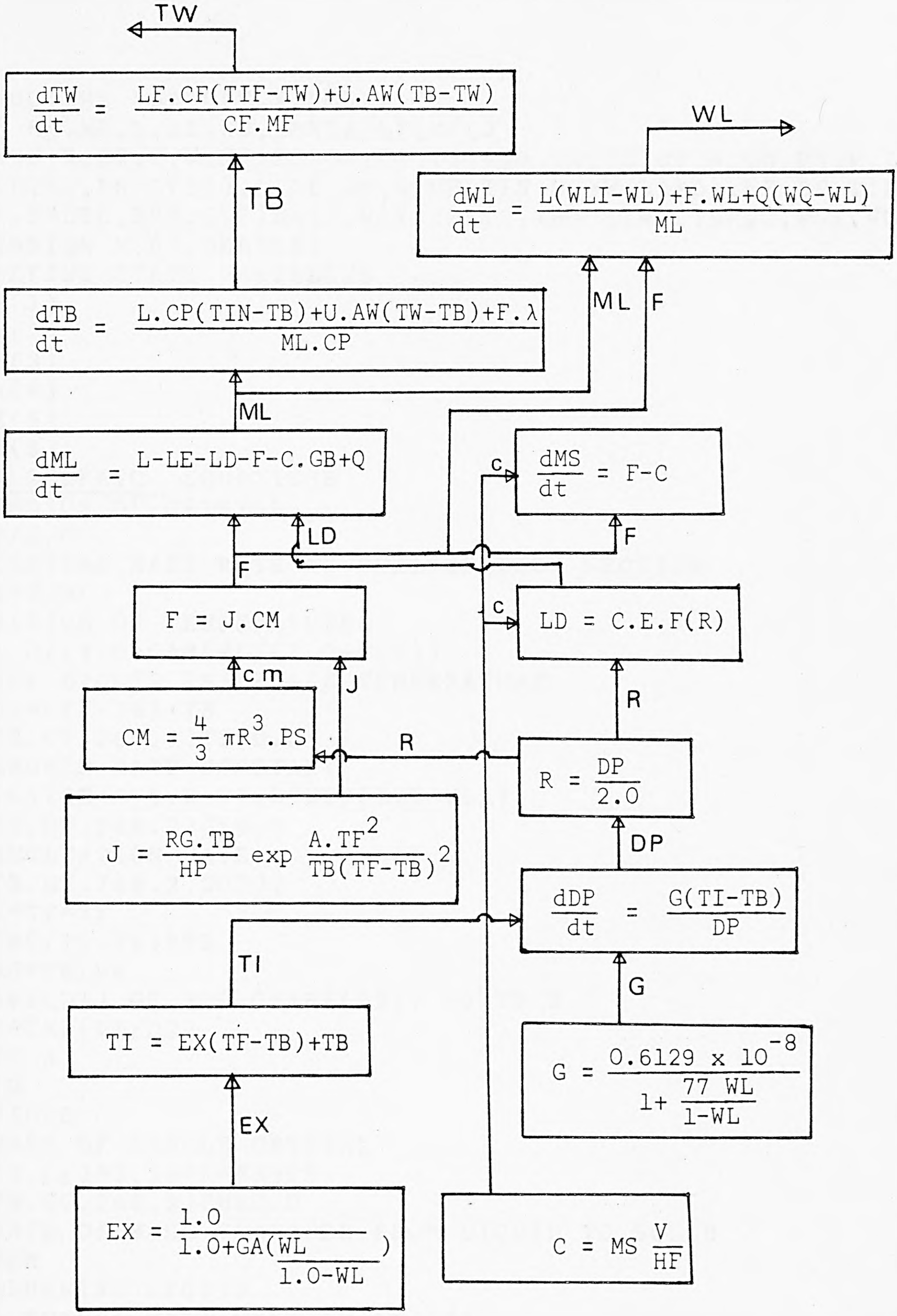


Fig 17 Simulation Model for the Freezing Section

The value of Delt = 0.001, 0.005 and 0.01 were used and it was found that there was no difference between 0.001 and 0.01 so Delt = 0.01 was adopted. To cut down computer time Delt = 0.1 was also tried but it resulted in overflow.

The main programme of the Simulation model was called SUBROUTINE MODEL and is presented here for a ready reference. Other subroutines were also used in the main programme for different purposes. The main programme is called <u>Programme Frez</u>. Simulation of the crystallizer freezing section. A subroutine output was used for control of information out of the programme. A subroutine Func. was used to calculate F(R) and a Subroutine Debug to send out information on all calculated values at any time the programme did not work due to fault or satisfying any control parameters.

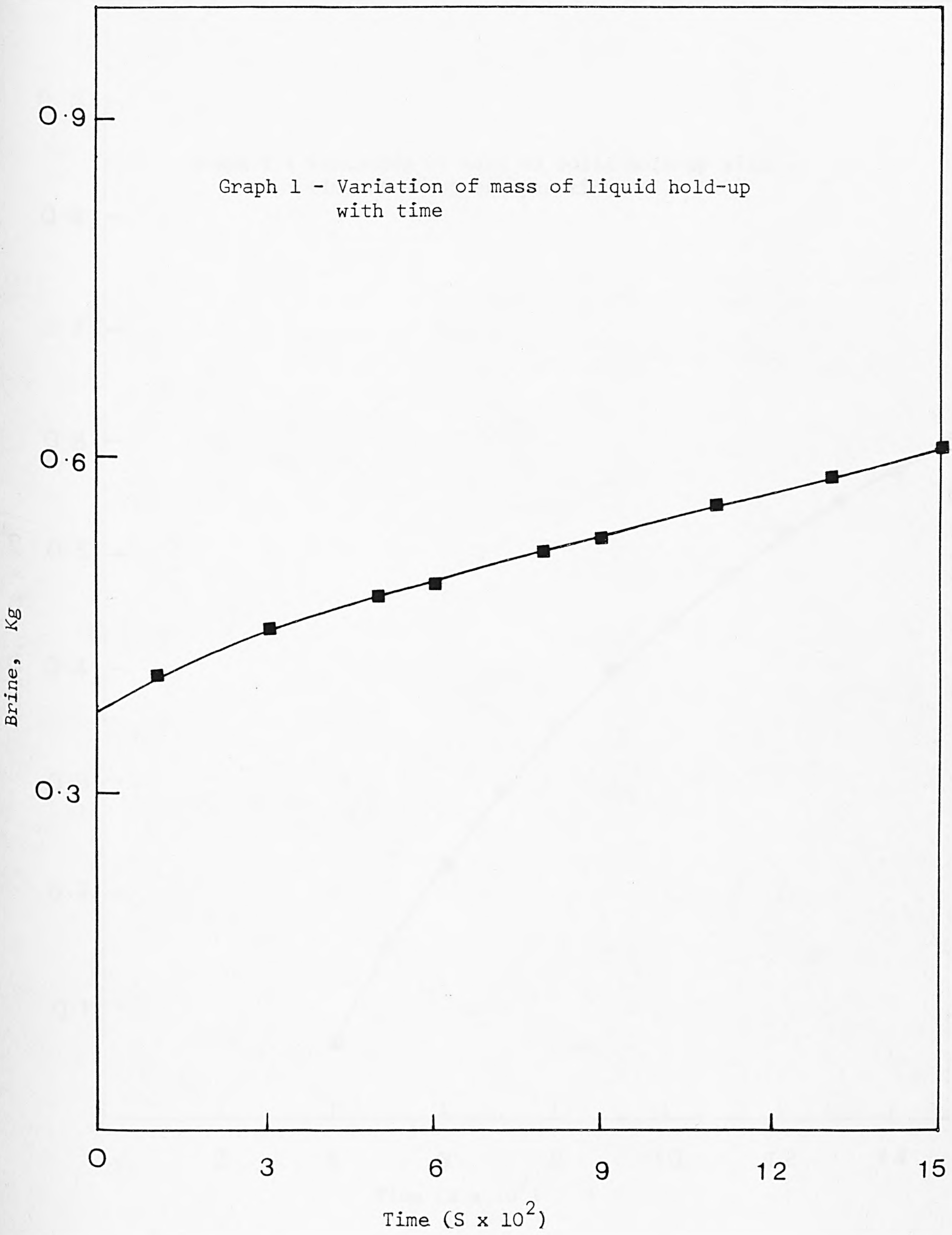
4.1.5 Results and Discussion

It was found that the model worked quite well for a reasonable length of time. There was some initial difficulty in programming because of the exponential nature of the nucleation rate equation. Careful manipulations had to be done in avoiding the denominator of the exponential to get to a very low number which would lead to heavy overflow conditions.

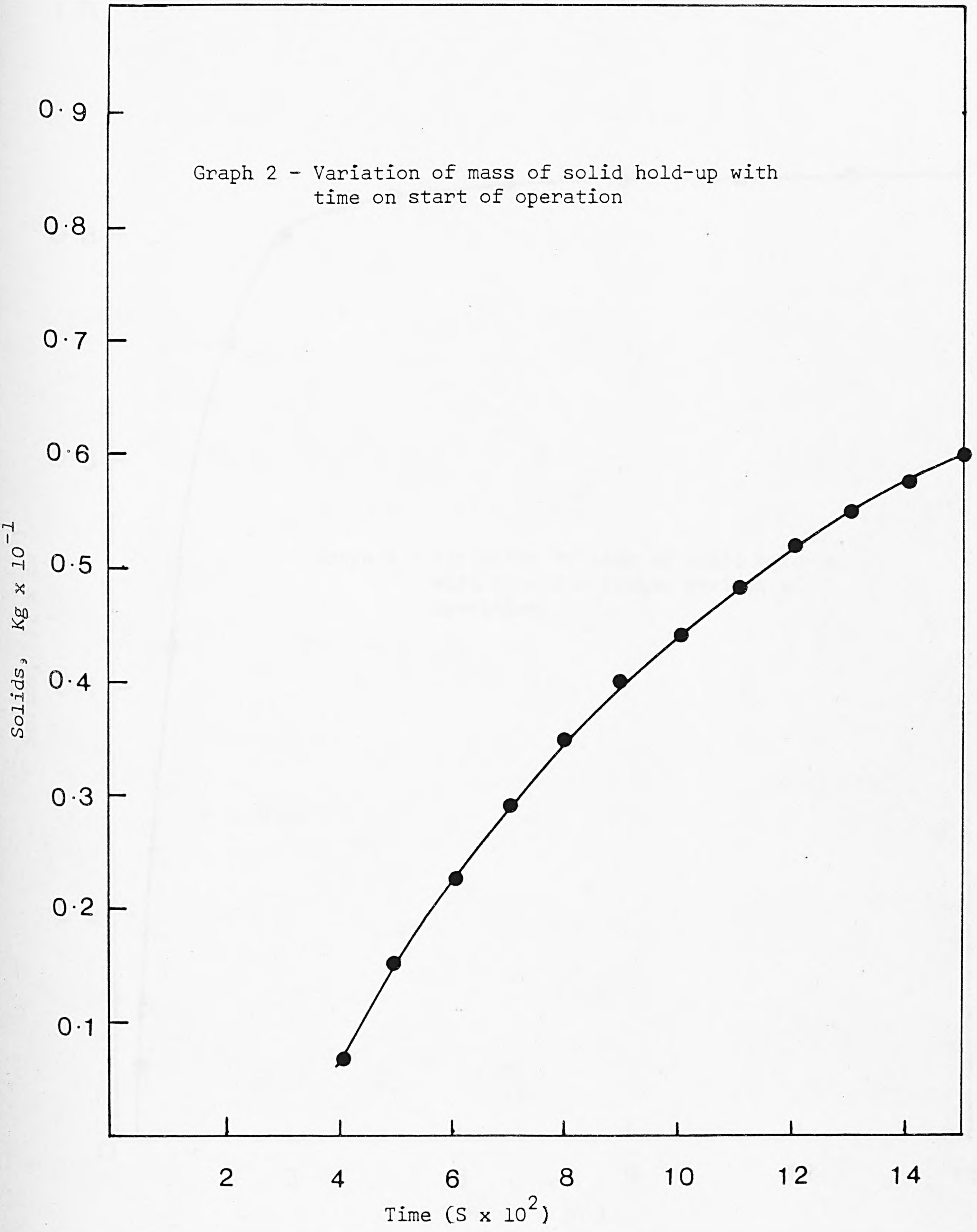
Results were run out for every second of the column run initially and later for longer intervals of the column time. Even then, because of the massive amount of output as rows of figures, it is very inconvenient to present it as such. For this reason we have tried to present all relevant results in the form of graphs which give us a good view of the operation of the column and its stability.

The column was found to reach steady state conditions in about three hours after start-up. This is evident from the graphs and in the beginning a very good example is presented in Graph (3), where the graph completely flattens from about 8000 seconds onwards; showing that it is steady, or in other words, a constant amount of ice is being produced and held up. From Graph (1) we can see that there is a sharp rise in ML, but soon the graph is levelling off. Its tendency to steady off is very evident from the beginning compared to Graph (2) which keeps rising at a fast rate, but in Graph (3) we can see that after a couple of hours it has started to steady out.

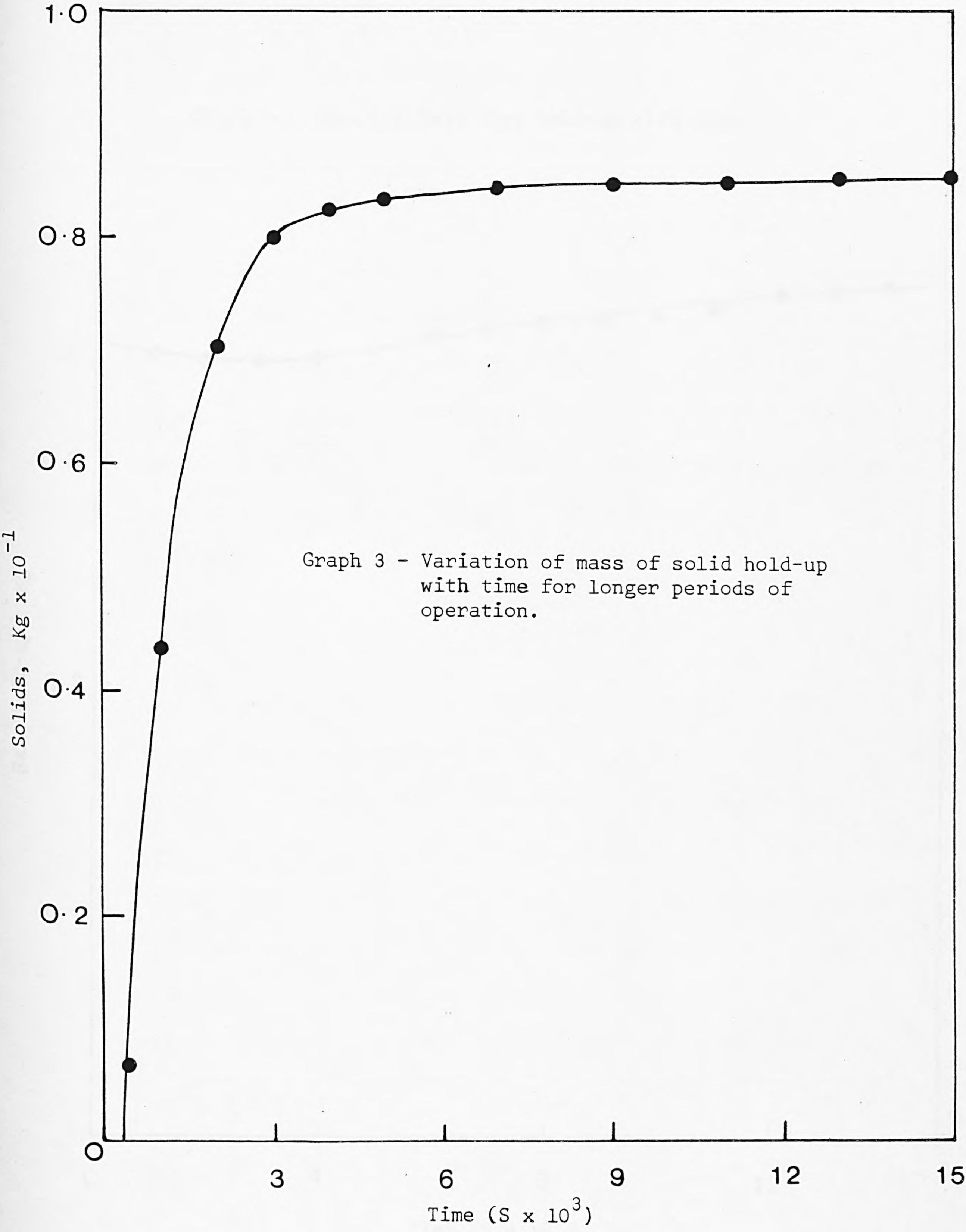
Taking a look at the salt balance graph (Graph 4) we can also see that the graph is showing a tendency to flatten out with the passage of time. There is a slight drop in the salt concentration of the bulk liquid at the point of nucleation. But as nucleation reaches a steady state so does the salt concentration and is greater than the original concentration



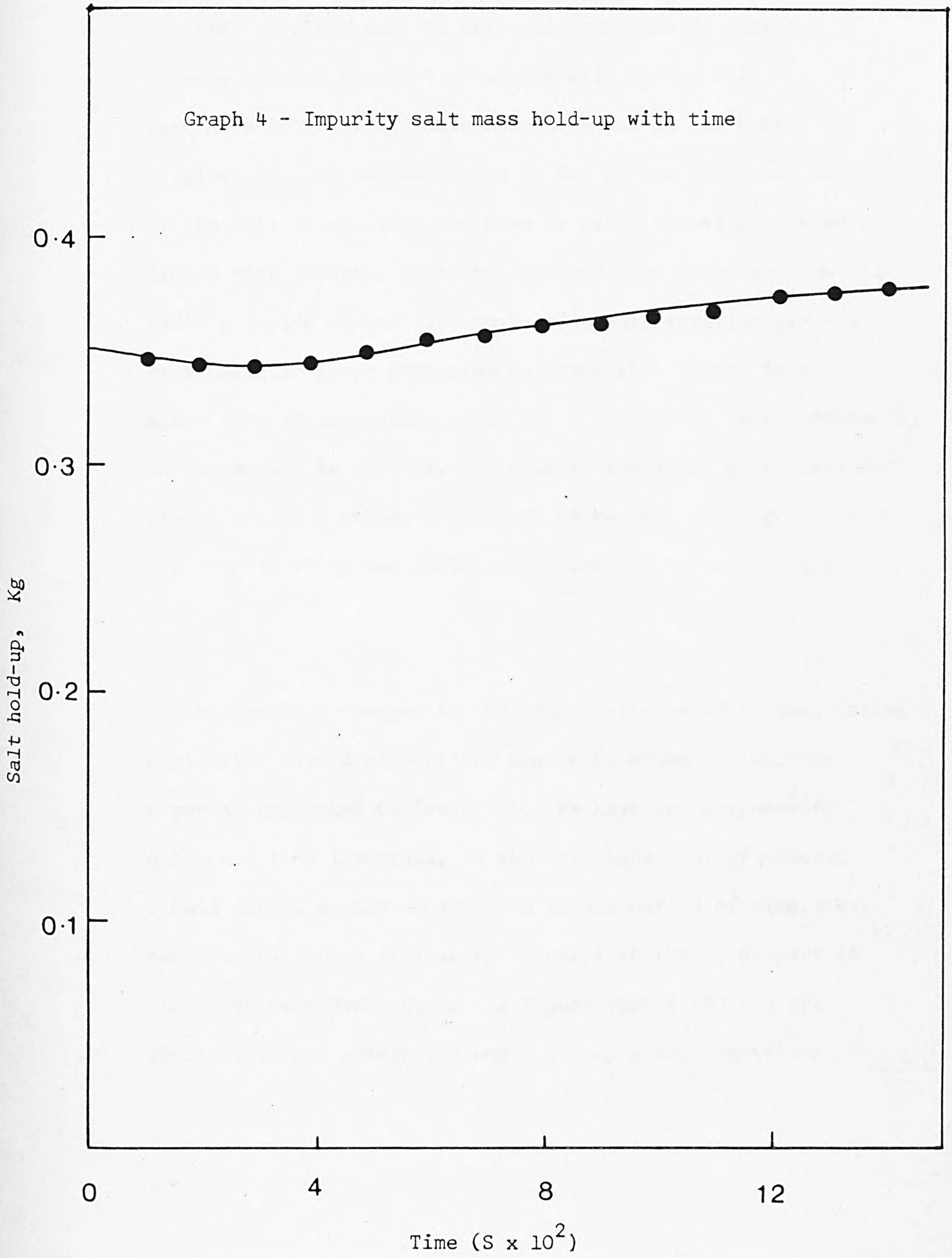
Graph 1 - Variation of mass of liquid hold-up with time



Graph 2 - Variation of mass of solid hold-up with time on start of operation



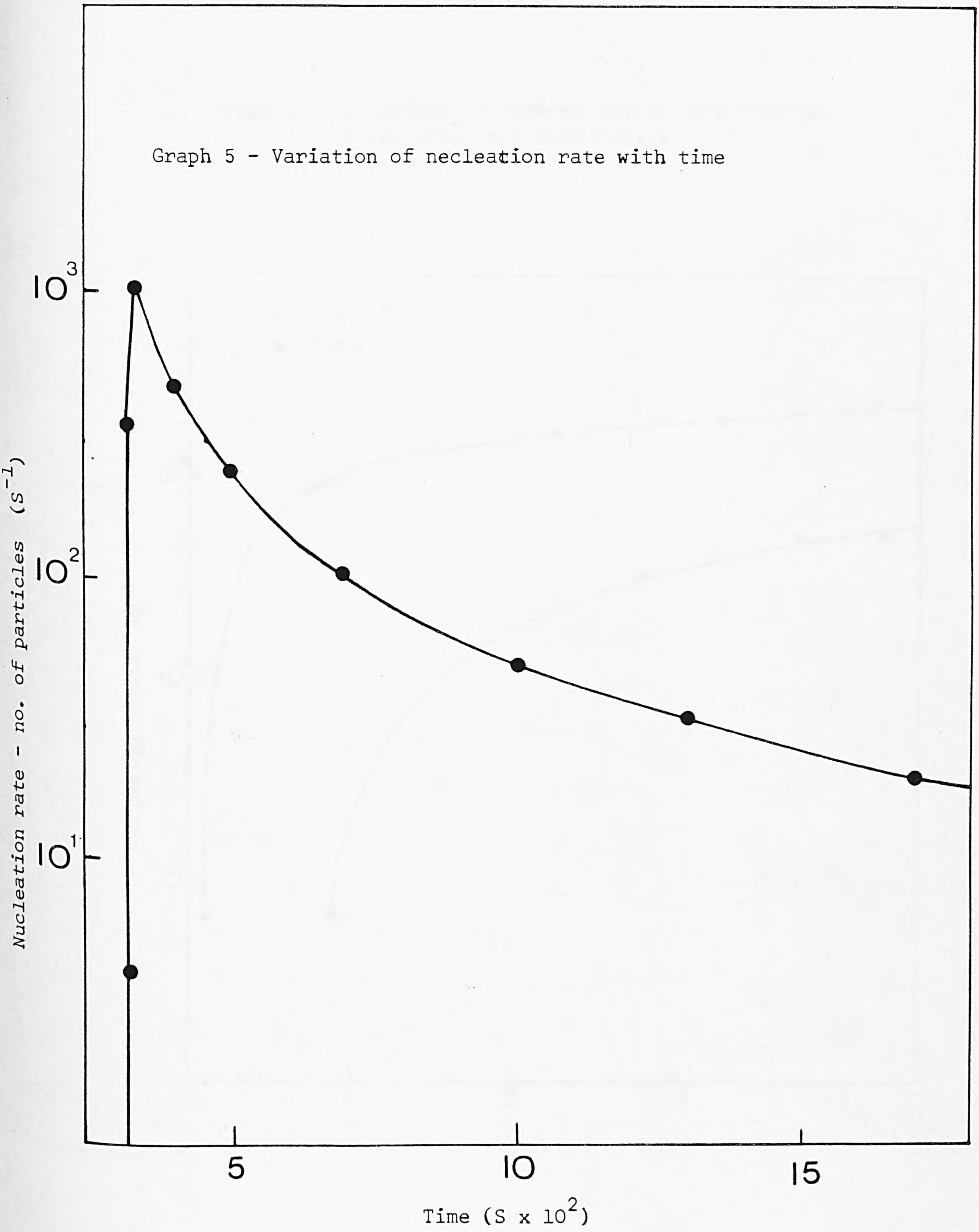
Graph 3 - Variation of mass of solid hold-up with time for longer periods of operation.



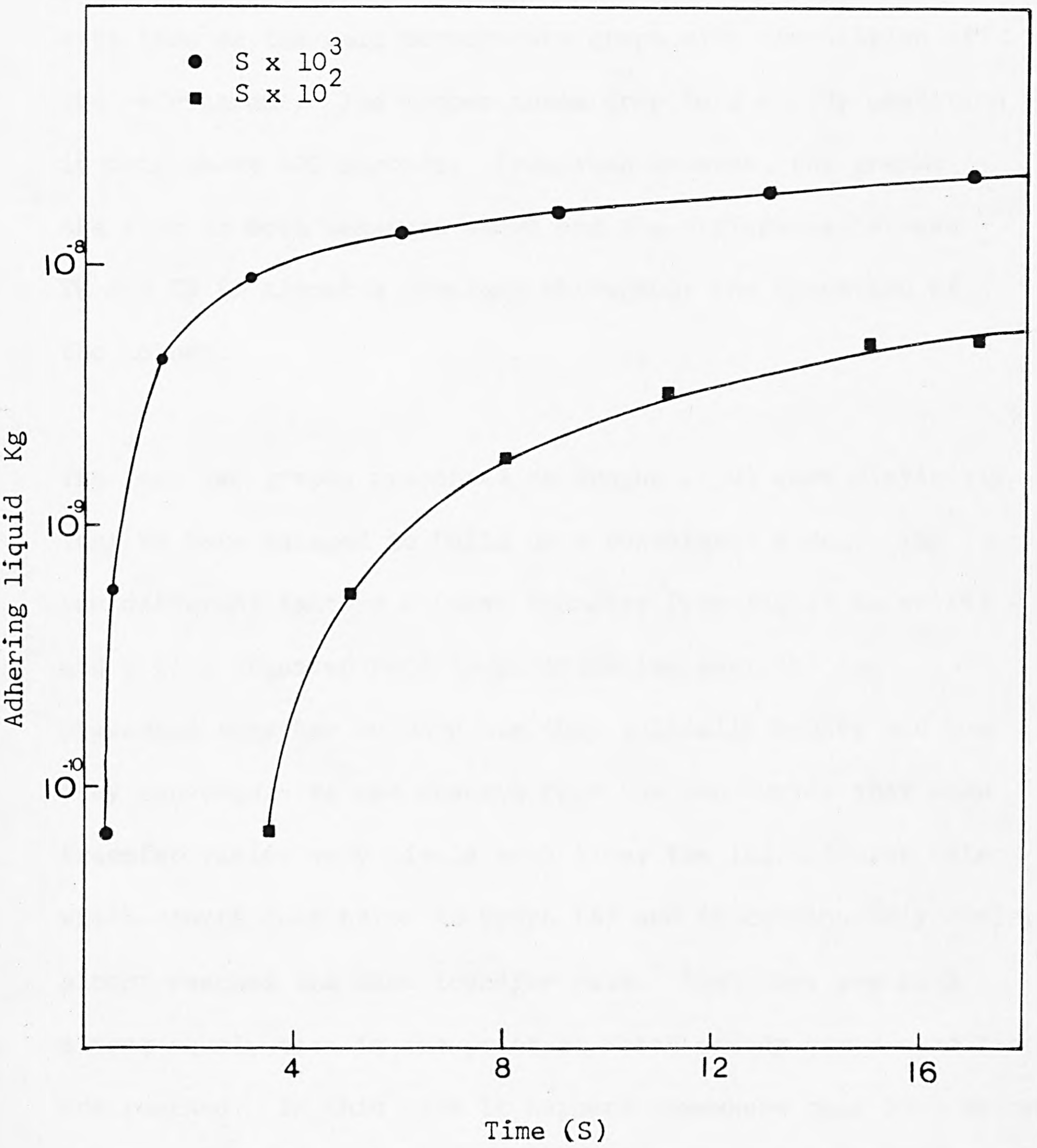
Graph 4 - Impurity salt mass hold-up with time of feed. The increase in salt concentration is expected because some of the salt returning with reflux will naturally increase the salt concentration in the bulk. The original drop in concentration is due to the fact that some of the salt is occluded and some is going out with adhered liquid when crystals start to form and then these factors all reach a steady state. The nucleation rate equation gives a very peculiar graph presented in Graph (5). There is a great jump in nucleation rate, for a very short time difference, as nucleation is started, but then it drops off quite fast and levels out to a steady production of nuclei; which grow and are carried along the purification section to the melting section.

Due to manifold changes in the amount of adhered liquid, (being nucleation rate dependent) it has to be drawn on semi-log paper as presented in Graph (6). We have two graphs with different time intervals, to show the behaviour of adhered liquid during a shorter and then longer period of time. We can see that there is a sharp increase in the first part of the curve very dominant in the figure marked (●) and then it flattens out eventually under steady state conditions.

Graph 5 - Variation of necleation rate with time

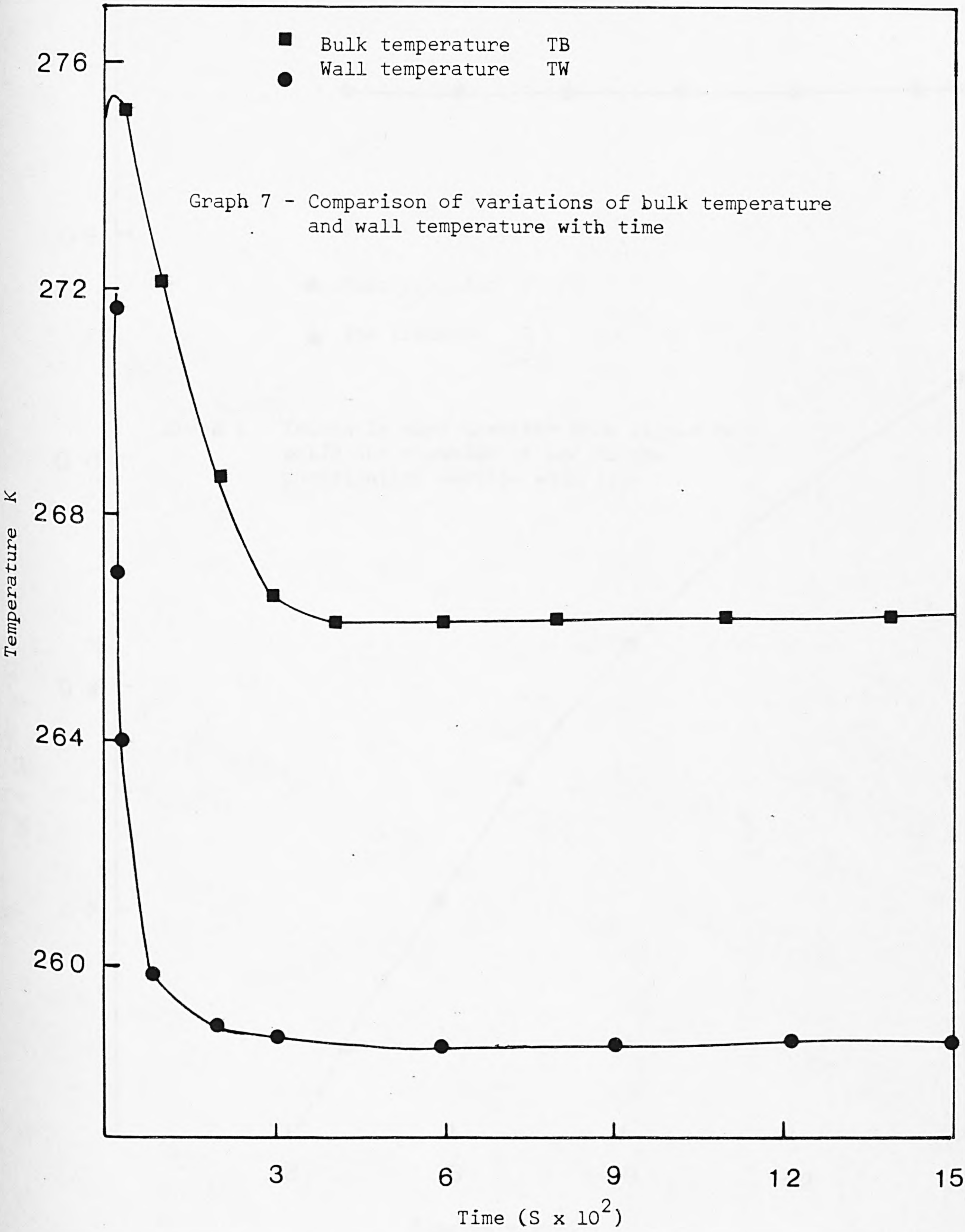


Graph 6 - Variations of adhered liquid mass hold-up at two different time scales

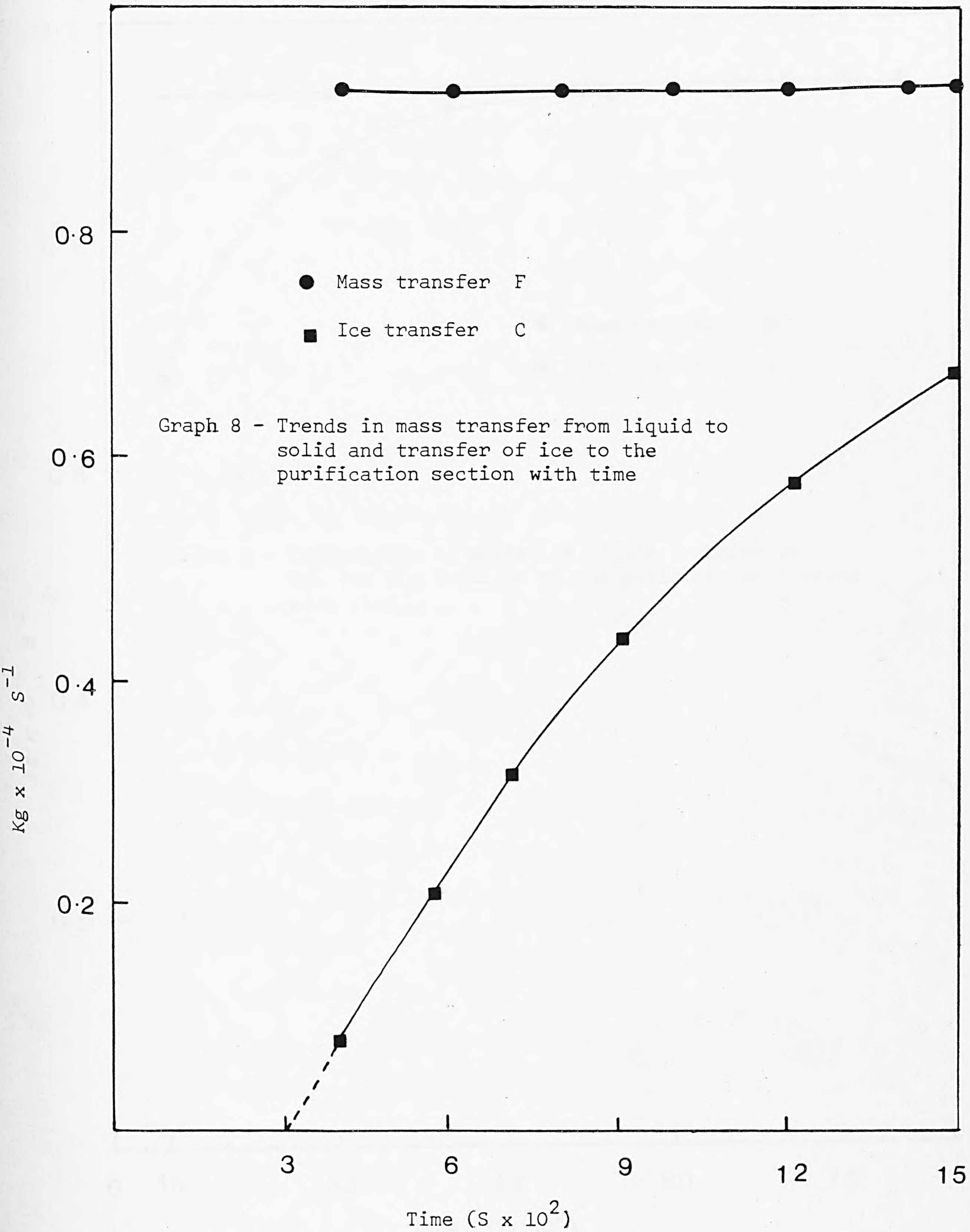


The graphs presented in Graph (7) show the behaviour of temperatures with time. The TB (bulk temperature) and TW (wall temperature) are drawn together so that it would give us a comparable behaviour with time. The TB curve initially shows an increase in temperature because of the high temperature of the freezer wall, and then it drops with time as the wall temperature drops with circulation of the refrigerant. The temperatures drop to a steady condition in only about 400 seconds. From then onwards, the graphs are flat in both cases as shown and the difference between TW and TB is almost a constant throughout the operation of the column.

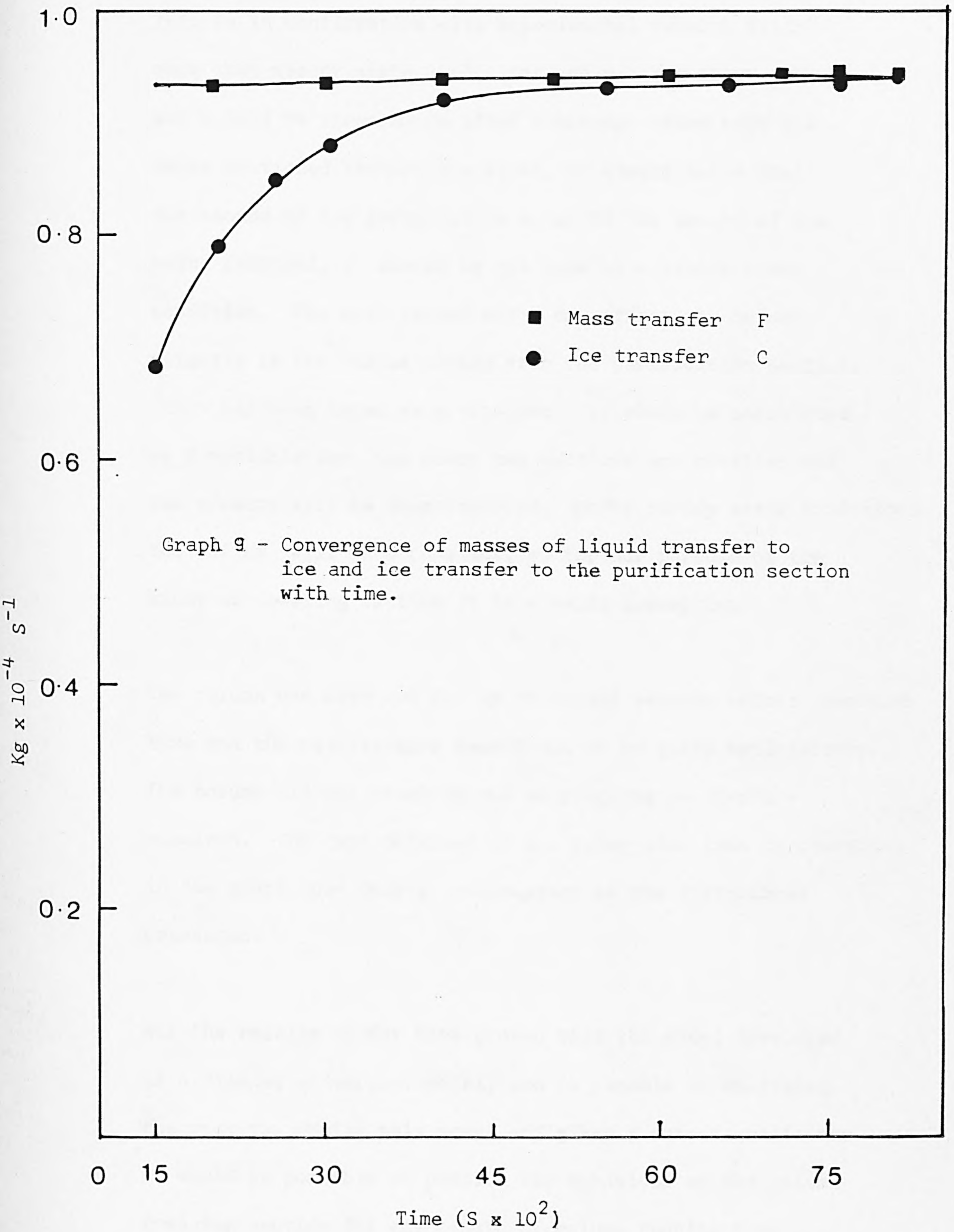
The last two graphs presented as Graphs (8,9) show distinctly that we have managed to build up a convergent model. The two different factors F (mass transfer from liquid to solid) and C (ice transfer rate to purification section) are presented together to show how they initially behave and how they converge. We can observe from the two curves that mass transfer varies very little with time; the ice transfer rate which starts down below in Graph (8) and is continuously rising, almost reaches the mass transfer rate. When they are both almost equal, then is the point at which steady state conditions are reached. In this case it happens somewhere near 9000 seconds.



Graph 7 - Comparison of variations of bulk temperature and wall temperature with time



Graph 8 - Trends in mass transfer from liquid to solid and transfer of ice to the purification section with time



Graph 9 - Convergence of masses of liquid transfer to ice and ice transfer to the purification section with time.

This is in confirmation with experimental results which show that steady state conditions are reached about two and a half to three hours after start-up. When both the above mentioned factors are equal, it simply means that the amount of ice going out is equal to the amount of ice being produced, as should be the case in a steady state condition. The only factor which may affect the column slightly is the reflux coming from the purification section, which has been taken as a constant. It shall be calculated as a variable when the other two sections are modelled and the effects will be then recorded. Under steady state conditions the reflux will be a constant, so for our purpose of the study of freezing section it is a valid assumption.

The column had been run for up to 60,000 seconds column operation time and the results have been found to be quite satisfactory. The column did not break up and no plugging or overflow resulted. The data obtained at any later time than is presented in the graph show only a continuation of the flat curves presented.

All the results so far have proved that the model developed is a viable, convergent model, and is capable of analysing the results. Using this model and given a set of conditions it would be possible to predict the behaviour of the column freezing section for any length of column running time.

With our freezing section model completely developed, we are in a position now to develop models for the other two sections viz. Purification and Melting sections. When these two sections are joined to the Freezing section then Simulation models for the entire column are presented. Everything leaving the Freezing section enters the purification Section except for heavy brine referred to as low melting product. From the purification section everything enters the melting section except reflux which is flowing in the opposite direction. Solids and liquids enter the melting section where the solid is melted and forms a mass of liquid. The melt from the top is taken out as pure high melting top product. A small amount of this melt is allowed to flow back as reflux. That is why at every stage in the purification section all substances flow in from previous stage denoted as (N-1) except reflux which comes in from above stage and is denoted as (N+1).

4.2 Modelling and Simulation of Purification Section

Similar equations to the freezing section are set up for the purification section. They basically involve the mass and heat balances as before. There are a few factors which did not play any role in the freezing section but are the prevailing mechanisms in the purification section.

Plate 2 - Column under continuous operation showing ice crystals in the purification section

These factors are mainly the mass transfer of impurity from adhered to reflux (denoted by MK) and mass transfer of impurity within the free liquid (denoted by MD). It has been considered by Powers and his co-workers and later by McGrath and Gladwin (96) that the above two factors are the main mechanisms by which purification takes place in the purification section. A diagram is presented below for visualisation of the purification section.

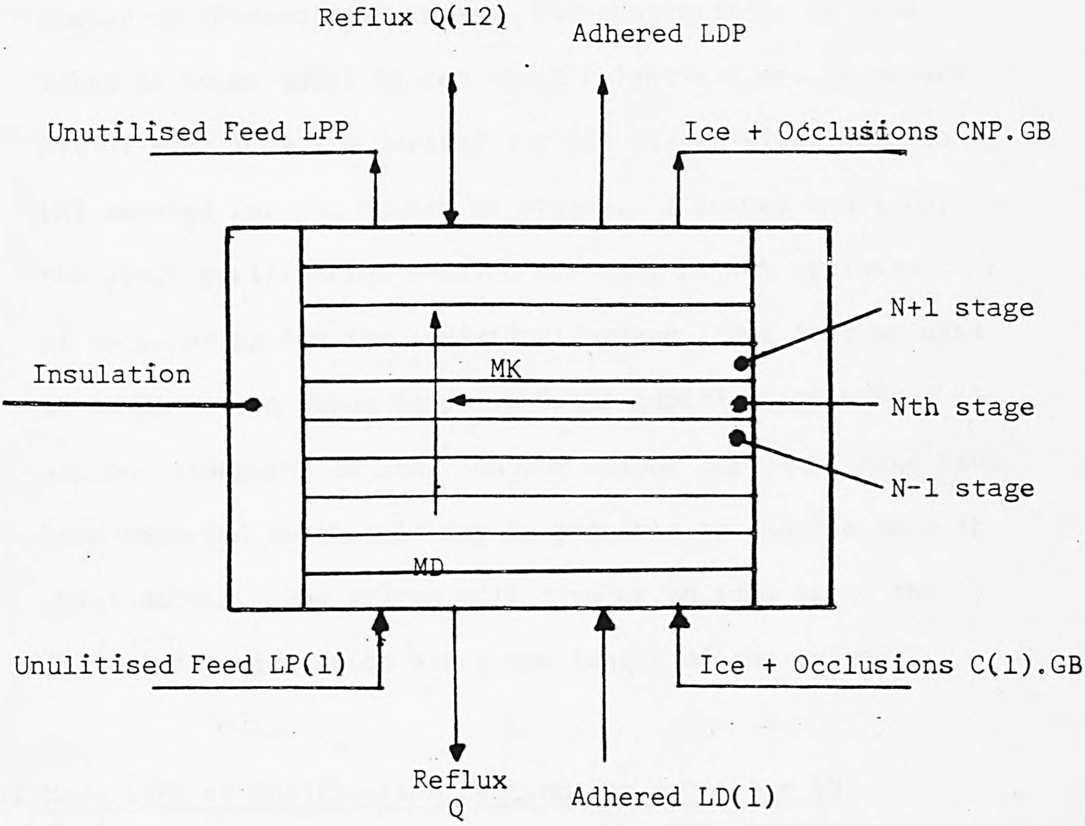


Fig 18 Schematic of the Purification Section

Similar to a distillation column, the purification section has been divided into a number of theoretical stages. Though the column appears as a whole it has been found that there is a gradient of temperature and purity from top to bottom. Since the two mechanisms of mass transfer (MK and MD) are different in their direction it is much more appropriate to divide the whole column into strips of smaller ΔZ so that exact calculations may be obtained. So far there is no existing method of calculating the number of theoretical stages. For convenience, we have taken it to be equal to ten equal height stages. A general set of equations are derived for all stages with variable (N) denoted for the number of stages. A lumped model for the whole purification section can also be set up instead of calculating for the individual stages. But in that case we shall have a value only for total purification effect and not along the column. Output values for each stage have been recorded so that it may be possible to examine them in great detail. The values will give us an idea as to the degree of purification along the length of the column.

4.2.1 Modelling of Purification Section for any Stage (N)

(a) Liquid Mass Balance ML (N)

The mass balance of liquid in any one stage at a particular time can be calculated from the equation

$$\frac{dML(N)}{dt} = LP(N-1)-LP(N)+LD(N-1)-LD(N)-F(N)+C(N-1) * GB - C(N) * GB + Q(N+1) - Q(N) \qquad (71)$$

where LP(N-1) is rate of liquid coming in from the (N-1) stage, LP(N) is rate of liquid going out of stage (N), LD(N-1) is rate of adhered liquid coming in from stage (N-1), LD(N) is rate of adhered liquid goint out of stage (N), F(N) is mass transfer from liquid to solid in stage (N), C(N-1) is crystal mass rate coming from stage (N-1) C(N) is crystal mass rate going out of stage (N), GB is mass fraction of embedded liquid, Q(N+1) is reflux coming in from stage (N+1) and Q(N) is reflux going out of stage (N).

All the variables coming in from stage below or above are calculated in that particular stage. As a result we shall be calculating for the variables which originate from this atage. Dealing with the different variables one by one, the first one to be calculated is LP(N)

(b) <u>Rate of Liquid Brine Going Out</u> LP(N)

The amount of liquid going from one stage to another at any particular time is given by the equation

$$LP(N) = LP(N-1) - F(N) \qquad (72)$$

where LP(N-1) is liquid brine coming up from stage (N-1) and F(N) is mass transfer from liquid to solid in the Nth stage. Liquid brine coming in from previous stage LP(N-1) will originally initiate in the freezing section which is not present in our original model. Therefore the model of the freezing section was modified and calculations for the modified model are shown later and the new freezing section model is also presented.

(c) Adhering Liquid Going Out LD(N)

The amount of adhered liquid going out from one stage to another will still be a function of the crystal size (R) minus whatever impurity is transferred from adhered to bulk liquid and is represented as

$$LD(N) = C(N)\,EF(R) - MK(N) \qquad (73)$$

where C(N) is the crystal mass rate going out of stage (N) and MK(N) is mass transfer of impurity from adhered to free liquid in stage (N).

(d) Mass Transfer From Liquid to Solid F(N)

The mass transfer from liquid to solid is entirely dependent on nucleation and will only take place when there is new nucleation in the purification section. This provision has been kept, so in case of temperature falling below freezing temperature any new formation of nucleus may be accounted for and is used in solving equation(72)

$$F(N) = J(N) \cdot CM \tag{74}$$

where J(N) is the nucleation rate in stage (N) and CM is the mass of a single crystal as defined in the freezing section.

(e) Crystal Mass Rate Going Out C(N)

Crystal mass rate is derived in terms of solid mass hold up, the screw speed and the length of the column and is used in solving equation (73):

$$C(N) = MS(N) * VS/HZ \tag{75}$$

where MS(N) is the solid mass hold up in stage (N), VS the velocity of the screw and HZ the height of column. The variable (GB) entrained liquid in solid is taken as a constant and has the same value as in the freezing section since it comes from the freezing section.

(f) Reflux Liquid Going Out Q(N)

The reflux which is generated in the melting section, as it passes countercurrently to free liquid and solids, it is effected by the mass transfer from adhered to bulk and diffusion within the bulk. Due to some technical programming difficulty the equation is presented as Q(12-N) and not as Q(N). However since it is generated at the other end of the column and (N) is made to vary independently in this case from 2 to 11, then for every increasing (N) we shall be calculating the reflux in the decreasing order of stages.

$$Q(12-N) = Q(13-N) + MK(12-N) - MD(12-N) + MD(11-N) \quad (76)$$

where Q(12-N) is the reflux going out of that particular stage, Q(13-N) is the reflux coming in from (stage N+1), MK(12-N) is the mass transfer within that stage, MD(12-N) is the diffusion out of the stage and MD(11-N) is the diffusion coming into the stage.

This completes all the calculations of variables involved in solving equation (71) and the equation will be solved. Proceeding further our equation (74) has an unknown J(N), (mass transfer from liquid to solid) which has to be solved.

(g) <u>Nucleation Rate</u> J(N)

This is not a common happening of the purification section but rather a phenomenon of the freezing section. However provision has been kept as explained earlier that in case of temperature going down enough for nucleation to take place, then we shall be able to account for the extra solids. The same nucleation rate equation based on Eyring's Rate Theory (126) was used.

$$J(N) = \frac{RG.\ TB(N)}{HP} \exp \frac{A(TF)^2}{TB(N)\cdot(TF-TB(N))^2} \qquad (77)$$

where TB(N) is the bulk temperature in stage (N) and the rest of the variables are as defined under the freezing section nucleation rate equation. Since we have already derived equations for adhering liquid rate and crystal mass rate, we can now derive equations for their mass balances

(h) Adhering Liquid Mass Balance MLD(N).

The adhering liquid mass balance in stage (N) is dependent on the adhering liquid rates, in and out of the stage and mass transfer within the stage between adhering and reflux, which may be represented as

$$\frac{d}{dt}\ MLD(N) = LD(N-1) - LD(N) - MK(N) \qquad (78)$$

where LD(N-1) rate of adhering liquid coming in, LD(N) is rate of adhering liquid going out and MK(N) is the mass transfer between adhering and reflux in stage (N).

(i) Solid Mass Balance MS(N)

The solid mass balance in stage (N) is dependent on the rate of solids coming in and going out stage (N) and any new formation of crystals in stage (N)

$$\frac{d}{dt} MS(N) = C(N-1) - C(N) + F(N) \qquad (79)$$

where C(N-1) is crystals coming in from stage (N-1), C(N) is crystals going out of stage (N) and F(N) mass transfer from liquid to solid in stage (N).

At this point it is best to define the impurity balances and factors which effect the impurity balances. Let us start with mass transfer between adhered and reflux.

(j) Mass Transfer of Impurity from Adhered to Reflux MK(N)

The mass transfer from adhered to reflux as discussed earlier and presented by Powers and his co-workers is represented as

$$MK(N) = P(N)K.AAA(N)(AA)(WD(N)-WL(N)) \qquad (80)$$

where PN is the density of the liquid phase, K is the overall liquid phase mass transfer co-efficient, AA is the cross sectional area of the column available for mass transfer, AAA is the total area available for mass transfer from adhering liquid to reflux liquid, WD(N) is salt concentration in adhered liquid stage (N) and WL(N) salt concentration in free liquid stage (N). Now we are ready to calculate the impurity balance in adhered liquid.

(k) Salt Concentration in Adhered Liquid WD(N)

A mass balance on the salt in adhered liquid will result in

$$\frac{d}{dt} \mathrm{MLD(N)\ WD(N)} = \mathrm{LD(N-1)\ WD(N-1) - LD(N)\ WD(N) - MK(N)\ WD(N)} \tag{81}$$

expanding the equation we get

$$\mathrm{MLD(N)} \frac{d\mathrm{WD(N)}}{dt} + \mathrm{WD(N)} \frac{d\ \mathrm{MLD(N)}}{dt} = \mathrm{LD(N-1)\ WD(N-1) - LD(N)\ WD(N) - MK(N)\ WD(N)} \tag{82}$$

Substituting equation (79) for $\frac{d\ \mathrm{MLD(N)}}{dt}$ and transferring,

$$\mathrm{MLD\ (N)} \frac{d\ \mathrm{WD(N)}}{dt} = \mathrm{LD(N-1)\ WD(N-1) - LD(N)\ WD(N) - MK(N)\ WD(N) - LD(N-1)\ WD(N) + LD(N)\ WD(N) + MK(N)\ WD(N)} \tag{83}$$

cancelling and regrouping,

$$\frac{d}{dt}\, WD(N) = \frac{LD(N-1)\,(WD(N-1) - WD(N)) - MK(N)\,(1+WD(N))}{MLD} \qquad (84)$$

where $LD(N-1)$ is the rate of adhered liquid coming, $WD(N-1)$ mass balance on salt coming with adhered, $MLD(N)$ is mass of adhered liquid in stage (N) and $MK(N)$ is mass transfer of impurity from adhered to reflux in stage (N).

(1) Salt Concentration in Bulk Liquid $WL(N)$

Salt concentration in the bulk liquid may be calculated by considering all the salt holding variables in the bulk at any given time in any stage as:

$$\begin{aligned}\frac{d}{dt}\, ML(N).WL(N) = {} & LP(N-1)\,WL(N-1) - LP(N)\,WL(N) + LD(N-1)\,WD(N-1) \\ & - LD(N)\,WD(N) - F(N)\,WL(N) + C(N-1).GB.WL(N-1) \\ & - C(N).GB.WL(N) + Q(N+1)\,WL(N+1) - Q(N)\,WL(N) \qquad (85)\end{aligned}$$

$$\begin{aligned}ML(N)\frac{dWL(N)}{dt} + WL(N)\frac{dML(N)}{dt} = {} & LP(N-1)\,WL(N-1) - LP(N)\,WL(N) \\ & + LD(N-1)\,WD(N-1) - LD(N)\,WD(N) \\ & - F(N)\,WL(N) + C(N-1).GB.WL(N-1) \\ & - C(N).GB.WL(N) + Q(N+1)\,WL(N+1) \\ & - Q(N)\,WL(N) \qquad (86)\end{aligned}$$

Substituting $\frac{dML(N)}{dt}$ from equation (71)and transposing

$$\begin{aligned}ML(N)\,\frac{d}{dt}\,WL(N) = {} & LP(N-1)\,WL(N-1) - LP(N)\,WL(N) + LD(N-1) \\ & WD(N-1) - LD(N)\,WD(N) - F(N)\,WL(N) \\ & + C(N-1).GB.WL(N-1) - C(N).GB.WL(N) \\ & + Q(N+1)\,WL(N+1) - Q(N)\,WL(N) \\ & - LP(N-1)\,WL(N) + LP(N)\,WL(N) - LD(N-1) \\ & WL(N) + LD(N)\,WL(N) + F(N)\,WL(N) - C(N-1). \\ & GB.WL(N) + C(N).GB.WL(N) - Q(N+1)\,WL(N) \\ & + Q(N)\,WL(N) \end{aligned} \tag{87}$$

cancelling like terms and regrouping we have

$$\frac{d}{dt}\,WL(N) = \frac{1}{ML(N)}\left\{\begin{aligned} & LP(N-1)\,(WL(N-1) - WL(N)) + LD(N-1) \\ & (WD(N-1) - WL(N)) + LD(N)(WL(N) - WD(N)) \\ & + C(N-1).GB.(WL(N-1) - WL(N)) + \\ & Q(N+1)\,(WL(N+1) - WL(N)) \end{aligned}\right. \tag{88}$$

where WL(N-1) is the bulk salt mass coming in from the stage (N-1) and the rest of the variables are as defined under previous equations. Proceeding further to solve equation (76) it is necessary to have values for the diffusion effects within the free liquid.

(m) <u>Diffusion Within Free Liquid</u> MD(N)

Diffusion within the free liquid as defined by Powers (103) and later by Albertins, Gates and Henry et al (111-113), is dependent upon the concentration of the impurity at different heights of the purification section and in terms of diffusion co-efficient may be defined as

$$MD(N) = \frac{P(N)\ D\ ETA(N)AA(WL(N)-WL(N+1)}{HZ} \qquad (89)$$

where D is the diffusion co-efficient, ETA(N) is the mass fraction of free liquid, HZ is the height of any stage and the rest of the variables are as defined under various equations.

(n) Mass Fraction of Free Liquid (ETA(N))

The mass fraction of free liquid in stage (N) may be represented by the ratio of the different masses occupying the volume as

$$ETA(N) = \frac{ML(N) - MLD(N)}{ML(N) + MS(N)} \times \frac{100}{P(N)} \qquad (90)$$

where the ML(N), MLD(N), MS(N) and P(N) are all variables as defined and calculated earlier.

(o) Total Surface Area Available for Mass Transfer AAA(N)

The total surface area available for mass transfer from adhered to reflux is dependant on the number of crystals and the assumption that the crystals are spherical in nature.

$$AAA(N) = 4NJ(N)\ \pi R^2 \qquad (91)$$

where NJ(N) is the total number of crystals in stage (N).

(p) <u>Number of Crystals</u> NJ(N)

The number of crystals present in stage (N) at any one time is entirely dependant on the total mass of solid, in this case ice

$$\mathrm{NJ(N)} = \frac{\mathrm{MS(N)}}{\mathrm{CM}} \tag{92}$$

where the variables have been defined earlier.

(q) <u>Heat Balance on Liquid Phase</u> TB(N)

And finally we have to consider the heat balances. It has been considered that the wall of the purification section is a constant because no external heat is either supplied or removed from the system. It is also insulated so that there is very little heat dissipation to the atmosphere. Thus a heat balance on the bulk inside the purification section will be the only factor to consider.

A heat balance on the different phases in Stage (N) will result in

$$\begin{aligned}\frac{d\ \mathrm{ML(N)\ CP\ TB(N)}}{dt} = {} & \mathrm{LP(N-1)\ CP\ TB(N-1) - LP(N)\ CP\ TB(N)} \\ & + \mathrm{LD(N-1)\ CP\ TB(N-1) - LD(N)\ CP\ TB(N)} \\ & + \mathrm{F\ (N(}\ \lambda + \mathrm{CP\ TB(N)\ ) + C(N-1).GB\ CP\ TB(N-1)} \\ & - \mathrm{C(N).GB\ CP\ TB(N) + Q(N+1)\ CP\ TB(N+1)} \\ & - \mathrm{Q(N)\ CP\ TB(N)}\end{aligned} \tag{93}$$

Differentiating by parts

$$ML(N)\ CP\ \frac{dTB(N)}{dt} + CP.TB(N)\frac{dML(N)}{dt} = LP(N-1)\ CP\ TB(N-1)\ldots.$$
$$\ldots..\ - Q(N)\ CP\ TB(N) \qquad (94)$$

Substituting $\frac{d\ ML(N)}{dt}$ from equation(71) and transposing

$$\begin{aligned} ML(N)\ CP\ \frac{dTB(N)}{dt} = {} & LP(N-1)\ CP\ TB(N-1) - LP(N)\ CP\ TB(N) + LD(N-1) \\ & CP\ TB(N-1) - LD(N)\ CP\ TB(N) + F(N)\cdot\lambda + F(N)\ CP \\ & TB(N) + C(N-1)\ GB\ CP\ TB(N-1) - C(N)\ GB\ CP\ TB(N) \\ & + Q(N+1)\ CP\ TB(N+1) - Q(N)\ CP\ TB(N) - LP(N-1) \\ & CP\ TB(N) + LP(N)\ CP\ TB(N) - LD(N-1)CP\ TB(N) \\ & + LD(N)\ CP\ TB(N) - F(N)\ CP\ TB(N) - C(N-1)\ GB \\ & CP\ TB(N) + C(N)\ GB\ CP\ TB(N) - Q(N+1)\ CP\ TB(N) \\ & + Q(N)\ CP\ TB(N) \qquad (95) \end{aligned}$$

cancelling like terms and re-arranging,

$$\frac{dTB(N)}{dt} = \frac{1}{ML(N)CP}\left\{\begin{aligned} & LP(N-1)\ CP\ (TB(N-1) - TB(N) + LD(N-1)\ CP\ (TB(N-1) - TB)(N) \\ & + F(N).\lambda \quad + C(N-1)\ GB\ CP\ (TB(N-1) - TB(N)) \\ & + Q(N+1)\ CP\ (TB(N+1) - TB(N)) \end{aligned}\right. \qquad (96)$$

where all the variables have been defined previously.

This completes all the mathematical equations for the purification section and needed to form a simulation model which can be solved by computer. Since all the equations can be solved

4.2.2 Simulation Model for the Purification Section

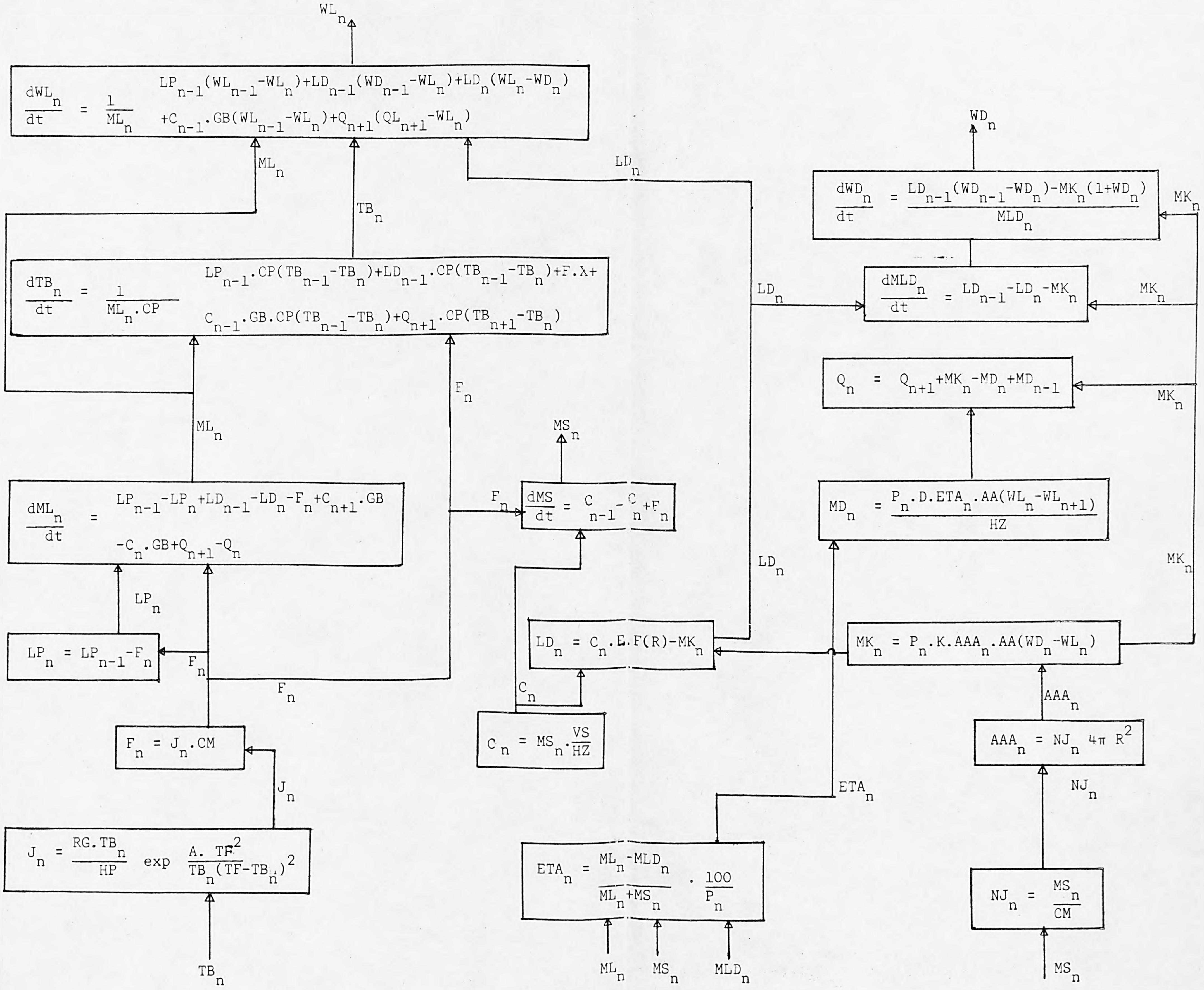


Fig. 19 Simulation Model for the Purification Section

now either by means of supplied data or an equation in the system previous to it, then a convergent model should result. A flowchart of the simulation model is presented in Fig (19). This model was not used as an independent model but rather as part of the whole column. The melting section model was developed simultaneously to this so that a complete model for the whole column in parts could emerge. The programme for this model was written separately as for freezing section, in FORTRAN, which is also presented. In actual analysis the model was broken down into two subroutines, one of algebraic equations and one of differential equations. This was done so that all the differential equations could be solved simultaneously, while the algebraic equations were grouped into one. The development of the melting section was undertaken at the same time and resulted in a similar model to freezing section with opposite phenomena.

4.3 Modelling and Simulation of Melting Section

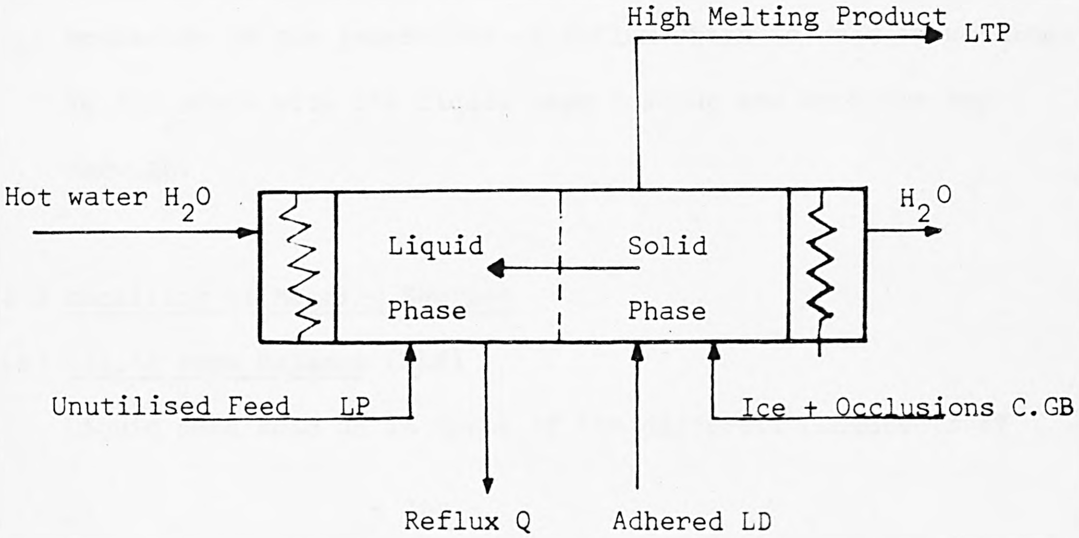


Fig 20 Schematic of the Melting Section

The process in the melting section is just the reverse of the freezing section. The diagram above is presented for the visualisation of the physical phenomena that are taking place. It also presents the mechanisms which are governing the flow of certain materials in and out of the melting section.

The solid which is formed in the freezing section is carried by means of a conveyor, through the purification section until it reaches the melting section. Here the crystals, which are relatively pure by now, are melted by the application of heat. Most of the melt is taken out as pure top high melting product, in this case water, and a small fraction is allowed to flow back as reflux. The reflux generated is used to wash away adhered liquid around the pure crystals in the purification section.

General heat and mass balances will be carried out in the manner as before on the different components. The important mechanism is the generation of reflux which is used in washing. We can start with the liquid mass hold up and work our way through.

4.3.1 Modelling of Melting Section

(a) Liquid Mass Balance (MLM)

Liquid mass hold up in terms of the different components of liquids entering and leaving the section may be defined as

$$\frac{dMLM}{dt} = LP^P + LD^P + FF - Q - LTP \qquad (97)$$

where LPP is the liquid brine coming in from the last stage of the purification section, LDP is the adhered liquid mass coming in from the last stage of the purification section. FF is the mass transfer from solid to liquid due to melting, Q is the reflux generated in the section and will be going down the last stage of the purification section and LTP is the mass of top product taken out as pure high melting product. The LPP and LDP are coming in from purification where they are calculated for, and LTP is supplied as data for controlling the column feed and products. That leaves us with FF mass transfer and reflux Q.

(b) Mass Transfer from Solid to Liquid (FF)

The mass transfer from solid to liquid may be calculated in terms of the total heat utilised for melting

$$FF = \frac{QQ}{\lambda + CP(TBM - TF)} \qquad (98)$$

where QQ is the total heat transfer, λ is the heat of fusion, TBM is the bulk temperature in the melting section and TF is the freezing temperature as defined earlier. To solve the equation we have to know QQ which is defined as below.

(c) Total Heat Transfer (QQ)

The total heat transferred is dependent on the heat transfer coefficient, temperature difference and surface area available for heat transfer.

$$QQ = U.AM(TBM - TF) \qquad (99)$$

where U is the heat transfer co-efficient and AM is the available crystal surface area for heat transfer, which may be calculated from the number of crystals in the melting section.

(d) Available Surface Area for Heat Transfer (AM)

Available area may be calculated from the number of crystals and average size of each crystal.

$$AM = JM\ 4\ \pi RM^2 \qquad (100)$$

where JM is the number of crystals in the melting section and RM is the average radius of a single crystal in the melting section and is taken to be equal to R.

(e) Number of Crystals (JM)

The number of crystals in the melting section depends upon the total mass of the solid divided by the mass of a single crystal

$$JM = \frac{MSM}{CMM} \qquad (101)$$

where MSM is the solid mass hold up and CMM is the mass of a single crystal.

(f) Mass of a Single Crystal (CMM)

The mass of a crystal depends upon the density of the solid and its size.

$$CMM = \frac{4}{3} \pi RM^{3} PS \qquad (102)$$

where PS is the density of the solid, in this case ice and RM is the radius of the crystal.

(g) Solid Mass Balance MSM

The solid mass hold up defined in terms of the crystals coming in and melting is:

$$\frac{d\ MSM}{dt} = CNP - FF \qquad (103)$$

where CNPis the rate of crystals coming in from the last stage of the purification section, which is calculated in that stage.

To solve equation(97) we have to calculate the reflux being generated and is represented as below.

(h) Reflux Generated(Q)

The reflux generated depends upon the mass of liquids flowing in, the mass of meltable pure solid and whatever liquid is removed as pure top product.

$$Q = CNP + LDP + LPP - LTP \qquad (104)$$

where all the variables are as defined earlier.

To solve equation (98) we need to have the temperature of the bulk so we must calculate the wall temperature and the bulk temperature.

(i) Heat Balance on Liquid Phase(TBM)

A heat balance on the different liquid components of the melting section will give us the temperature of the bulk. Since we are doing a balance on the liquid phase and FF is the original solid phase changing over to liquid phase, it is considered best to take the total heat transfer QQ instead of allowing it to be re-calculated as FF. Therefore, assuming constant heat capacity, our equation will result in

$$\frac{d\ MLM\ CP.TBM}{dt} = LPP.CP.TBP + LDP.CP.TBP - Q.CP.TBp - LTP.CP.TBM - QQ + UAWM\ (TWM-TBM) \qquad (105)$$

$$\mathrm{MLM.CP}\,\frac{d\,\mathrm{TBM}}{dt} + \mathrm{TBM.CP(LPP + LDP - Q - LTP)} =$$

$$\mathrm{LPP.CP.TBP + LDP.CP.TBP - Q.CP.TBM - LTP.TBM - QQ + UAWM(TWM-TBM)} \qquad (106)$$

transposing the terms we have

$$\begin{aligned}\mathrm{MLM.CP}\,\frac{d\,\mathrm{TBM}}{dt} &= \mathrm{LPP.CP.TBP + LDP.CP.TBP - Q.CP.TBM - LTP.CP.TBM} \\ &\quad \mathrm{- QQ + UAWM(TWM-TBM) - LPP.CP.TBM - LDP.CP.TBM} \\ &\quad \mathrm{+ Q\ .CP.TBM + LTP.CP.TBM}\end{aligned} \qquad (107)$$

Cancelling and rearranging

$$\frac{d\,\mathrm{TBM}}{dt} = \frac{1}{\mathrm{MLM.CP}} \begin{array}{l}\mathrm{LPP.CP(TBP - TBM) + LDP.CP(TBP - TBM)} \\ \mathrm{- QQ + UAWM(TWM - TBM)}\end{array} \qquad (108)$$

where all the variables have been discussed earlier except TWM which is the temperature of melting section wall and AWM is the area.

(j) Temperature of the Wall of Melting Section (TWM)

Assuming negligible thermal capacity of the wall and a heating liquid flowing in to heat the melting section, in this case hot water, we have an equation

$$\frac{d\,TWM}{dt} = \frac{LWM.CWM\,(TIW - TWM) - UAWM(TWM - TBM)}{CWM.MWM} \qquad (109)$$

where LWM is the rate of heating liquid coming in, CWM is the specific heat of the heating liquid, TIW is the temperature of the heating liquid, and MWM is the mass of the heating liquid around the melting section at all times.

(k) Total Salt Mass Balance (WLM)

Lastly, though we have not used salt mass fraction anywhere, we should calculate for the impurity in the melting section, because we are basically concerned with purification, i.e. removal of impurities and should know the impurity content at all times.

A salt mass balance on the different components of the melting section will yield the salt mass hold up. The salt embedded in the solid during the freezing in the freezing chamber will be given up with solution as the solid ice melts. Therefore the mass transfer will have to be multiplied by Sigma which was discussed in the Freezing section.

$$\frac{d\,MLM.WLM}{dt} = LPP.WLP + LDP.WDP + FF.\Sigma - QWLM - LTP.WLM \qquad (110)$$

Differentiating by parts

$$MLM\frac{d\,WLM}{dt} + WLM\frac{dMLM}{dt} = LPP.WLP + LDP.WDP + FF.\Sigma - QWLM - LTP.WLM \qquad (111)$$

Substituting MLM from equation one and transposing

$$\begin{aligned} MLM\,\frac{dWLM}{dt} = {} & LPP.WLP + LDP.WDP + FF.\Sigma - Q.WLM - LTP.WLM \\ & - LPP.WLM - LDP.WLM - FF.WLM + Q.WLM + LTP.WLM \qquad (112) \end{aligned}$$

Cancelling and rearranging

$$\frac{d\,WLM}{dt} = \frac{1}{MLM} \quad LPP(WLP - WLM) + LDP(WDP - WLM) + FF(\Sigma - WLM) \qquad (113)$$

where WLP is the mass fraction of bulk salt coming in from the last stage of purification section and WDP is the mass fraction of adhered liquid salt coming in from last stage of purification section and Σ is occluded salt coming in from the original freezing.

This sums up the equations for the melting sections. All the equations can now be solved as they have each only one unknown quantity while the rest of the variables in any equation is either supplied as data or from a previous equation or even from another section.

This should result in a convergent model. A simulation model can now be constructed as a flow diagram in fig (21).

The three flow diagrams combined together make the whole

4.3.2 Simulation Model for Melting Section

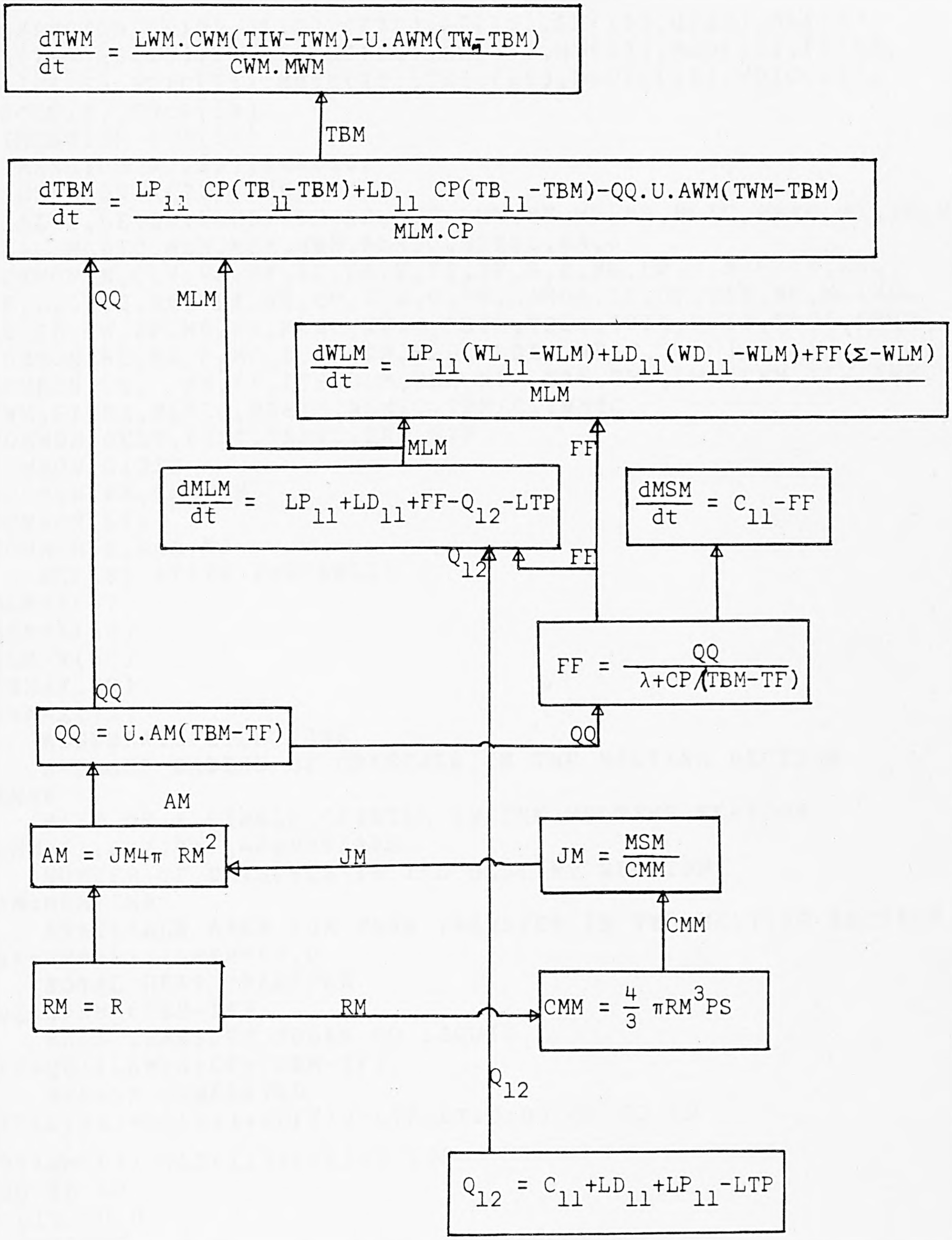


Fig 21 Simulation Model for the Melting Section

simulation model of the column crystallizer. However, in actual programming certain changes had to be made for a proper solution of the model.

4.4 Programming and Difficulties

Before the three parts could be connected together and run as a single programme, many changes had to be made in the original separate programmes.

The purification section was assumed to be divided into 10 equal stages. However, we did not start from one and finish at ten. The whole column was considered to have twelve stages, assigning stage one (1) to the freezing section and stage twelve (12) to the melting section. In between the two extremes, the purification section was comprised of two to eleven stages. Thus some of the variables going out from the freezing section into the purification section were assigned the subscript (1); and variables coming from the melting section into the purification section such as reflux were assigned the subscript (12).

As discussed earlier, because of the exponential nature of the nucleation rate equation it would overflow very easily. Therefore, the equation was put under certain limits so that the programme would not be thrown out of the computer whenever slight disturbances occurred, but would adjust and continue until favourable operating conditions were achieved after start-up. Similarly breakdowns of the whole equation into controllable constraints were put in both the freezing and purification sections. Since there was no question of nucleation in the melting section, the equation was excluded from the model.

Reflux was generated in the melting section and passed along the purification to the melting section. Just after start-up the whole column was filled only with liquid and we were not interested in any liquid coming back as reflux until formation of solids took place. For this reason proper constraints were also put so that liquid with the same composition as the feed, which would be the case at start-up would not be called as reflux. The values of reflux, generated only when proper crystals were formed and reached the melting section where they were melted to create reflux.

The adhering liquid was assumed to be a function of the crystal size and therefore dependent on R. Thus a function subroutine was used to solve for the adhering liquid.

Also all the reflux was generated at one time in the programme and distributed along the column. The difficulty arose because (N) varied from 2 to 11 and reflux was generated at the end of the column, as Q12. So while the calculations were being done for N = 2 the reflux was generating as N = 12. Thus it was thought proper that all the reflux in the programme should be generated at one time and distributed along the stages and a convergence subroutine used to determine the final value. Implicit loop function using Wegsteins (137) method was employed to do the convergence test.

Due to some technicalities in programming the whole of the subroutines, purification and melting could not be called one after another. All the algebraic equations had to be grouped into one while the differential equation into another. For this reason the purification section model was split into an algebraic model called PURN and a differential equation model called PURD, while the melting section was split into an algebraic model called MELT and differential equation model called MELD.

Use was made of a numerical integration subroutine called HPCG which is called by the main programme to solve the differential equation. Once you define the simulation parameters such as DELT, PRDEL, ERR, FINT, etc. the subroutine adjusts itself to calculate and print out results according to the parameters defined. The IHLF is fixed so as not to exceed ten (10) in this case. If IHLF should increase to more than 10 then an error message will be recorded. Initial conditions for solving differential equations were also supplied.

So in our subroutine MODEL which is the model for the freezing section we call all the other models. At the end of the algebraic equations in the subroutine MODEL we call subroutine PURN and at the end of the algebraic equations in PURN we call subroutine MELT. However, note that this is called just before the reflux equation, because we know that reflux is being generated in the melting section. Once we have a value for the reflux we can find the values for the rest of the reflux in different stages. Also note that the convergence subroutine is called just after subroutine PURN in the subroutine MODEL.

Then the programme in the subroutine MODEL naturally passes over to the differential equations arranged in successive orders. At the end of the differential equation in the subroutine MODEL, the subroutine PURD and after that the subroutine MELD is called.

The calculations once they are processed for each defined period of time, are conveyed out through the output subroutine.

Since the calculations take up massive amounts of computer core, it is a must that output should be adjusted to every second or a maximum of 10 secs. of actual column time. If outputs were arranged for longer periods of column time then overflow conditions occurred. Final time for the column is defined by the parameter FINT in seconds.

A complete programme is presented at the back in Appendix which was developed for the column. Initial developments were very slow because there was very little knowledge available on it. Some of the earlier programmes were discarded after much labour, because they were found to give no accurate information.

Because of the massive computer time required for calculations, it was not possible to run the programme on the ICL 1902T at the City University. The programme had to be simulated on the CDC 7600 at the University of London Computer Centre, which is linked by Courier Service, thus limiting the availability of the output to once a day. Thus the process of development was a slow task.

A subroutine was used to debug the whole programme at the point of fault or failure in the programme. That is, if due to any reason the programme failed to run at a certain point of time, then at exactly that time the debugging subroutine will point out the values of all the variables and derivatives.

The output was controlled by a subroutine called OUTPUT, so that we could call at any time interval the output subroutine to give us the appropriate values. The output subroutine was controlled through a parameter in the main programme which allows us to call the subroutine after certain time periods. Thus the results could be had every second or every 5 seconds, 10 seconds etc.

4.5 New Freezing Section MODEL

The freezing section model was slightly changed in the final analysis. Some of the variables were given subscript one (1). Besides minor adjustments due to programme technicalities, certain factors which were taken to be constants at the beginning were now needed to be calculated, for example, TF the freezing temperature and LP(1)the brine going up the column in case all the liquid feed is not completely frozen. The above factors and other which consequently result because of these are presented below as equations.

(a) The Freezing Temperature (TF)

The freezing temperature was originally considered to be constant as presented by Orcutt (104). But since we are dealing with formation of ice from brine and we know that salt affects the freezing temperature of ice significantly, it is considered to be sound judgement that we include an adjustment in the freezing temperature depending upon the salt concentration

$$TF = 273.0 - 40.0\,(WL) \qquad (114)$$

where WL is the salt concentration of the bulk in the freezing section and is defined as $WL(1)$

(b) Liquid Brine Going to Purification Section LP(1)

Under steady state conditions, since all the brine coming in would be instantly frozen, there would be no LP(1). This is what we had originally in mind and therefore did not include in our first analysis of the freezing section alone. However, since we shall be dealing from the moment of start-up of the column and the whole column has to fill up before freezing state, then it is best to include it and we have defined it as

$$LP(1) = L - LE - LD(1) - F(1) + Q(2) \qquad (115)$$

where all the variables are as defined earlier. This also affects the liquid hold up in the freezing section and we added the factor in the hold up equation to give

(c) Liquid Mass Balance (ML(1))

$$\frac{dML(1)}{dt} = L - LE - LD(1) - F(1) - C(1) * GB + Q(2) - LP(1) \tag{116}$$

where all the variables have been earlier defined. These will alter the freezing section MODEL and a new model is presented as was used in the final analysis.

4.6 New Simulation Model for Freezing Section

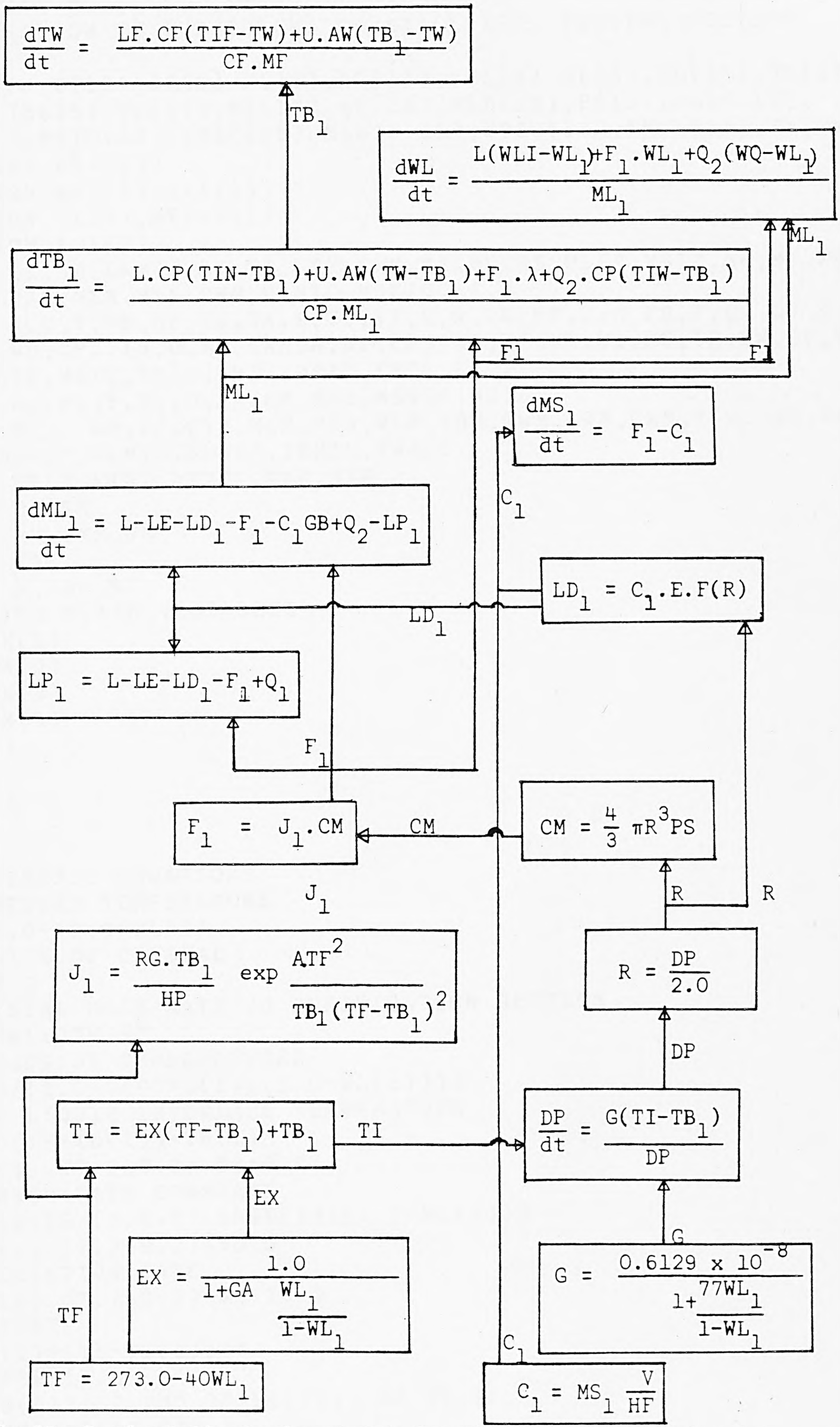


Fig 22. Revised Simulation Model for the Freezing Section

CHAPTER 5

DISCUSSIONS

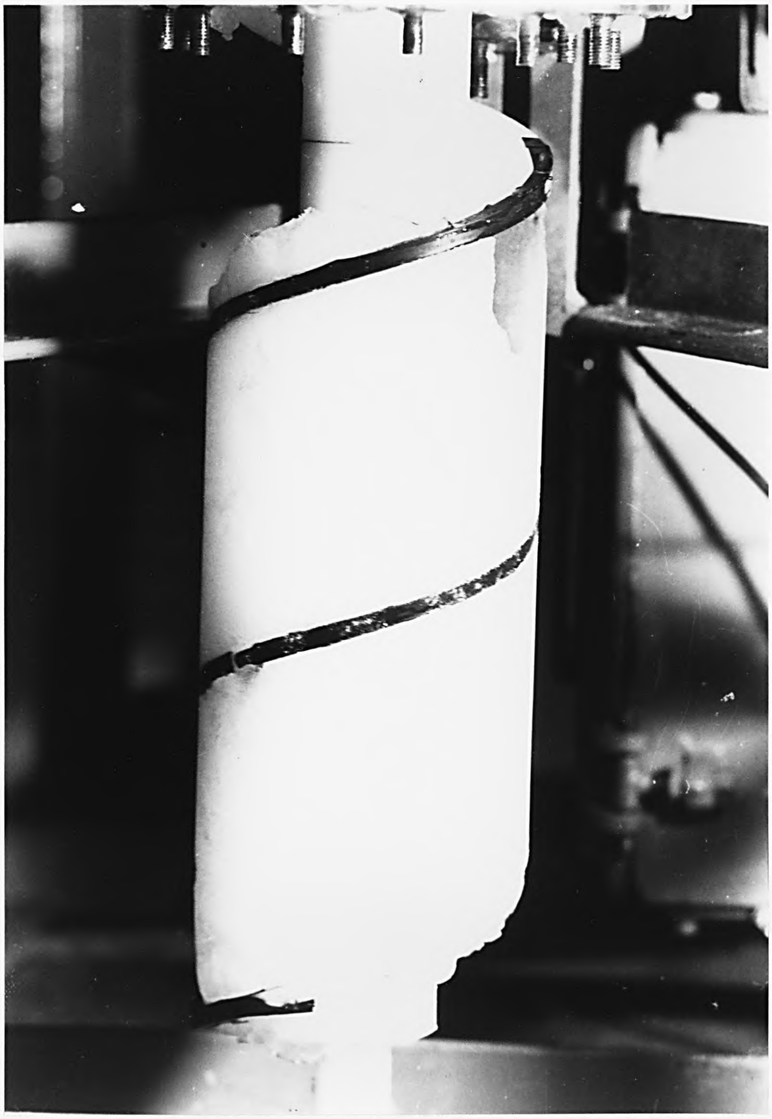


Plate 3 - Mass of ice crystals attached to the spiral after a period operation

Chapter 5 DISCUSSIONS

The freezing section has been discussed earlier extensively with graphs presenting an overall view of the effect of freezing of saline water in a jacketed cylinder. Graphs have been presented showing primary separation/purification by formation of pure crystals. Thus nucleation and growth have been discussed and problems associated with them. Also the formation of adhered liquid is presented, giving rise to impurity that is supposed to be washed away in the purification section, leaving rather pure crystals of ice, producing potable water fit for human consumption.

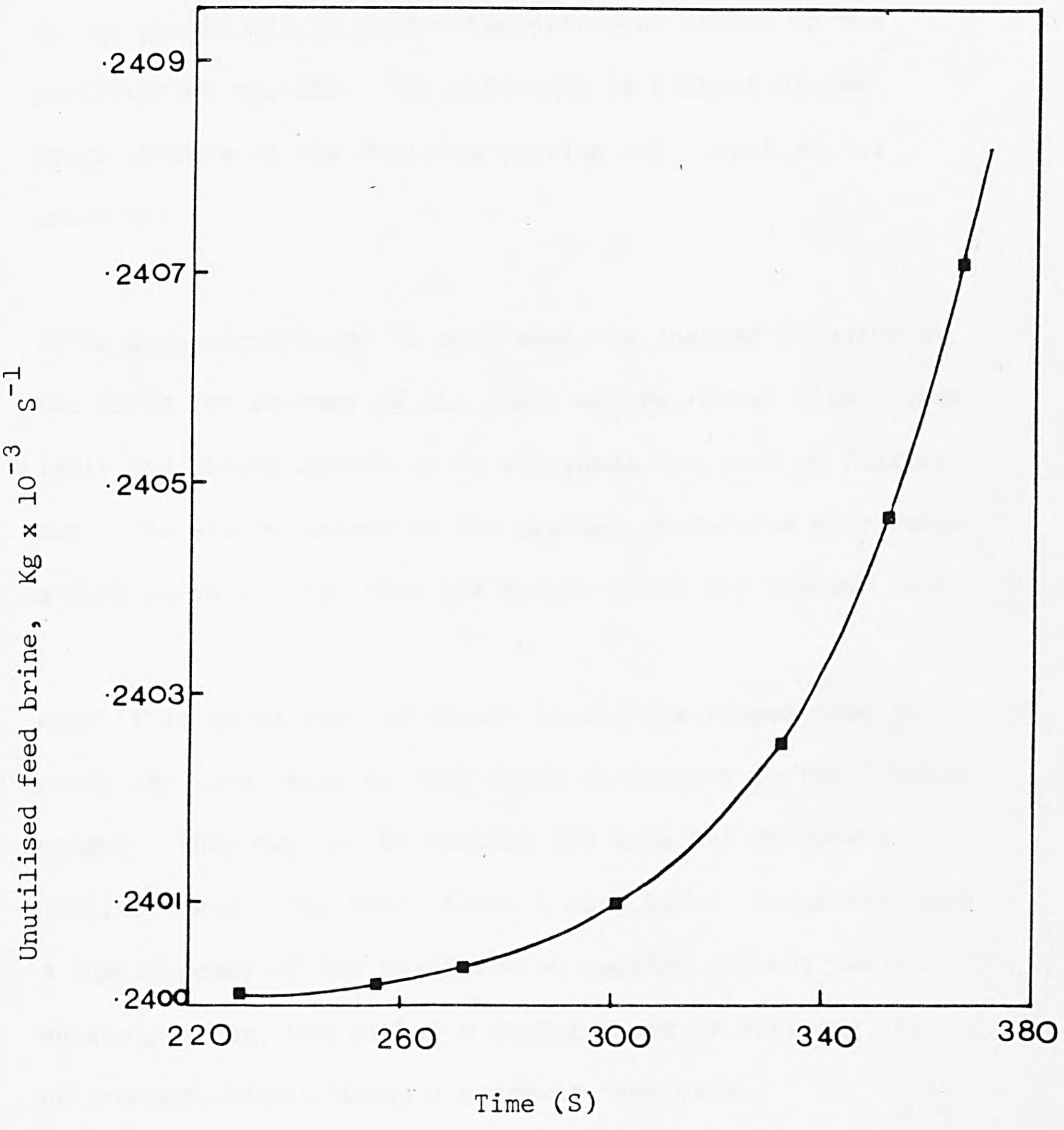
So the process of washing is indegenous to the purification section which we have represented in terms of two factors MK and MD.

My colleagues in the City University and other authors have studied these phenomena under steady state conditions with reasonable success. However, workers have so far not ventured to try to present start-up conditions of the column, which would be desirable for any continuous plant.

Data has been gathered and presented here graphically of the start-up operation conditions for the 1st 360 seconds of the column time, simulated on the computer. It is interesting and very revealing to study, some of the factors which are affected, as soon as the operation begins.

The two factors that are of primary interest are of course the washing mechanism and the factor that causes the washing, the reflux. Some data on the liquid LP(I) going out of the freezing section and progressing along the columns through the different stages, as liquid, is presented in graph (10). It is of interest to note that this could prove rather useful in predicting secondary nucleations. Should there be some variation in the value of LP(I) in any stage these would generally tend to mean that it has been caused by secondary nucleation. However we observed that there was no change in any stages, therefore only one graph is presented. The temperature of the liquid could be significantly low in the stages, just above the freezing section, and in the presence of other ice carried along the column, the ice could freeze. However under start up conditions there seems to be a general slow increase in the LP(1), most probably because of the reflux being created at the other end, flows down to add up the total volume. With nucleation and growth this would probably reach a steady state condition, as has been practically observed.

Graph 10 - Variation of mass of free liquid coming into the purification section with time



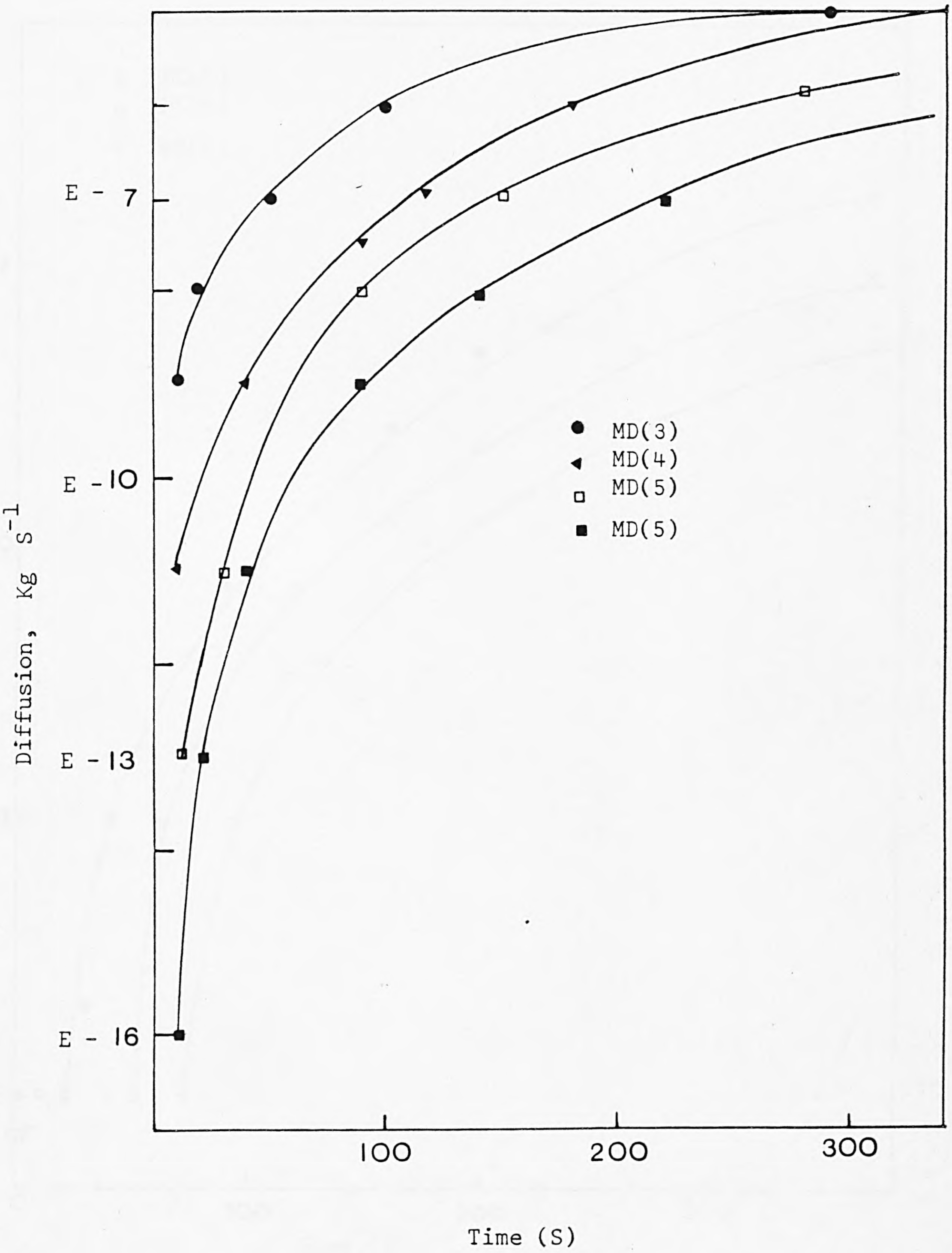
Among the horizontal mass transfer effects and the eddy-diffusion back mixing effects the latter is very prominently present from the very beginning. The output is presented in the graphs (11,12,13)for the different stages of the purification section. The diffusion is highest at the stage closest to the freezing section and lowest at the other end.

It is also significant to note that the changes in value at the first few seconds of the start up are rather high. Then slowly the graphs smooth up in all cases and tend to flatten out. The stages nearer to the crystal production side reach a flat curve earlier than the stages which are further away.

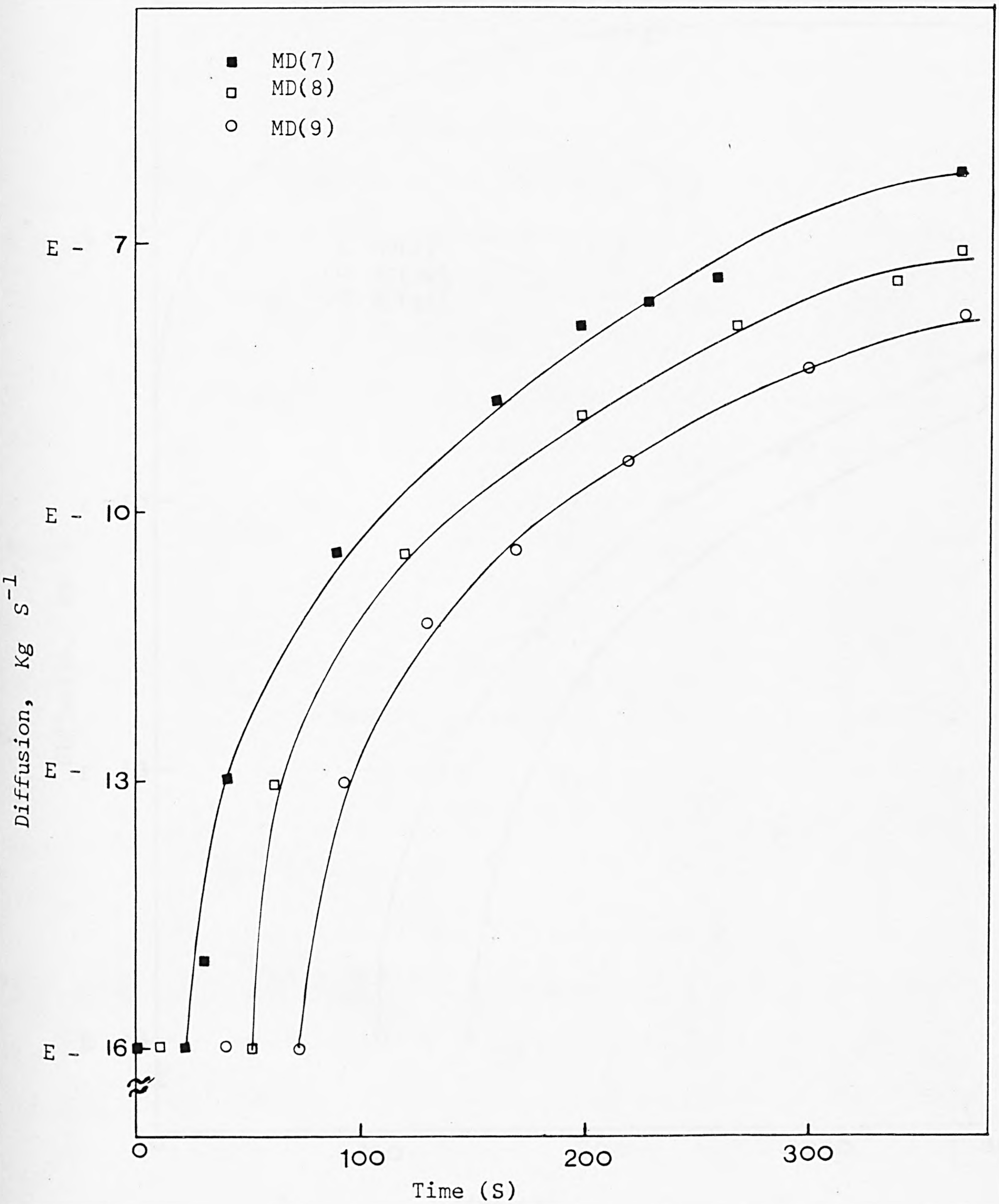
Also it is noted that diffusion in all the stages tend to reach the same value to that which is present in the initial stages. They may not be exactly the same but do show a similar trend. For this reason I have later suggested that a lumped model of the purification section may not prove entirely wrong, but rather a useful means of refining the programmes, before doing a stagewise analysis.

In the first 5-6 stages of the purification section there is a sharp rise in the diffusion effects after start-up. However after the 6th stage the diffusion effects remain constant at

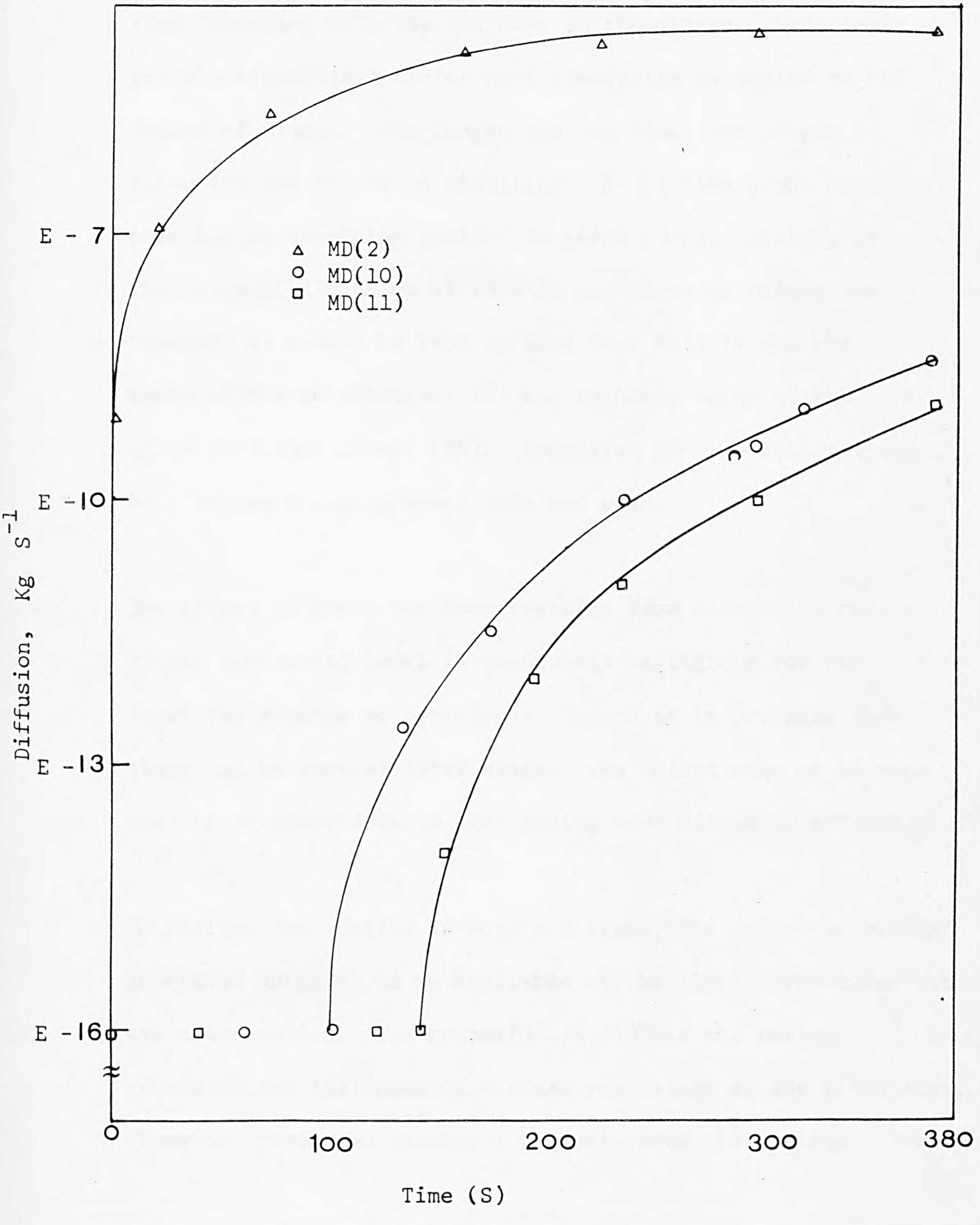
Graph 11 - Trends in the Diffusion effects in the 3rd, 4th, 5th and 6th stages of the purification section with time.



Graph 12 - Trends in the Diffusion effects in the 7th, 8th and 9th stages of the purification section with time



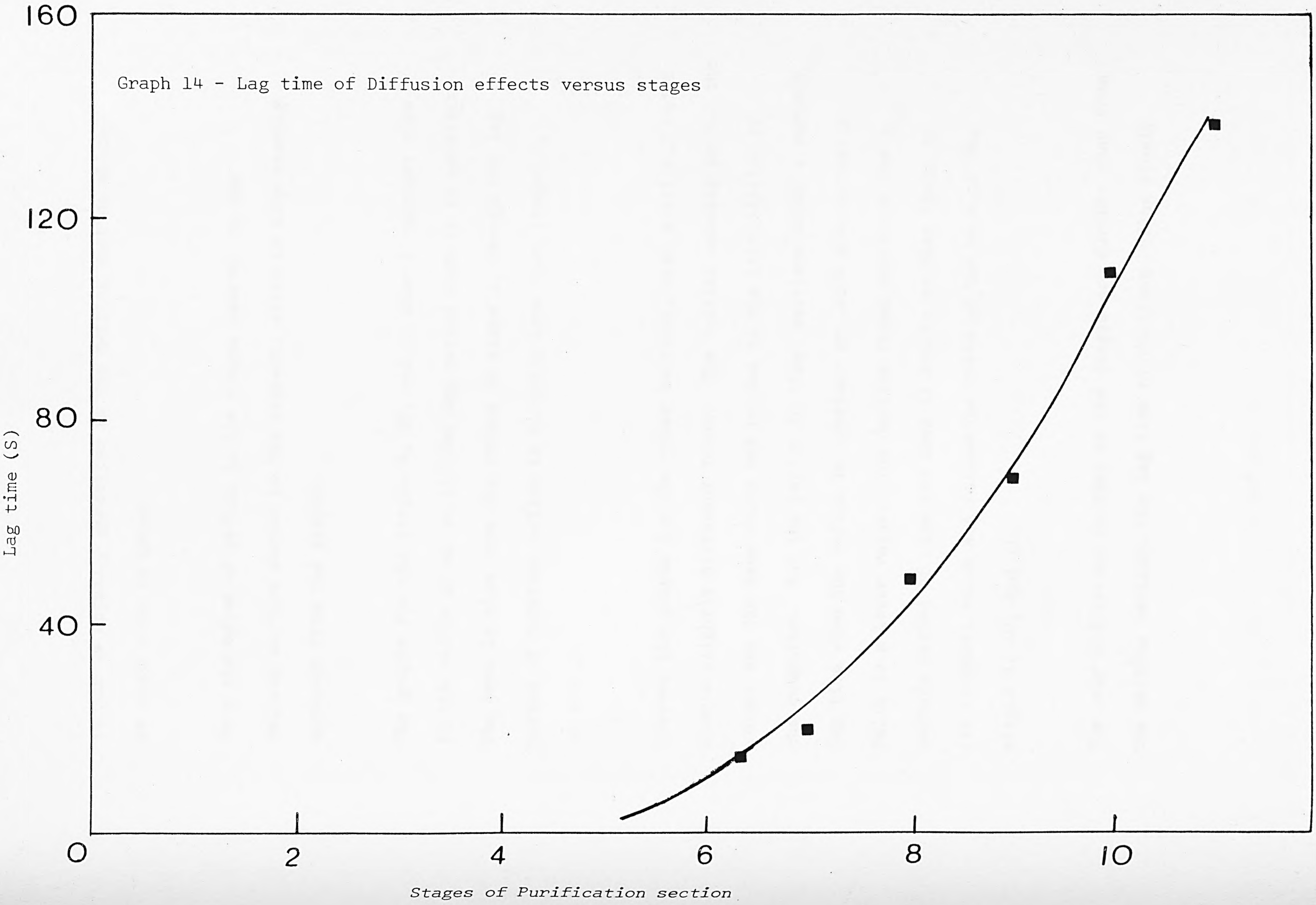
Graph 13 - Comparison of Diffusion effects of the initial and final stages of the purification section with time.



a very low value for a much longer period in time. Though there is a sharp rise instantly once the values start to change but it seems that there is a lag time. And the lag time increases with the increase in the stages. This could prove a significant factor when eventually we decide on the number of stages. The longer the lag time, the longer it takes for the column to stabilise. A lag time graph may possibly be something similar to graph (14). Looking at the value of diffusion effects it seemed to be rather low. However, it should be kept in mind that this is not the value of the co-efficient (D) but rather a value of the whole diffusion effect (MD). Provision for the calculations of D values though present were not used.

The effect of (MK), the mass transfer from adhered to reflux at the horizontal level is absolutely negligible for the first few minutes of operation. Though it is possible that there may be some at later stages, the values seem to be much smaller in comparison to back mixing eddy diffusion effects.

To realise the washing effects and steps, the amount of reflux generated which would be available at the first crystallization was also studied. The graphs(15,16,17)show the reflux generated and that passing through each stage at any given time. These are presented to show a general trend that exists. The


Graph 14 - Lag time of Diffusion effects versus stages
160
120
80
40
Lag time (S)
0
2
4
6
8
10
Stages of Purification section

reflux is actually generated in the melting section which we shall come to later.

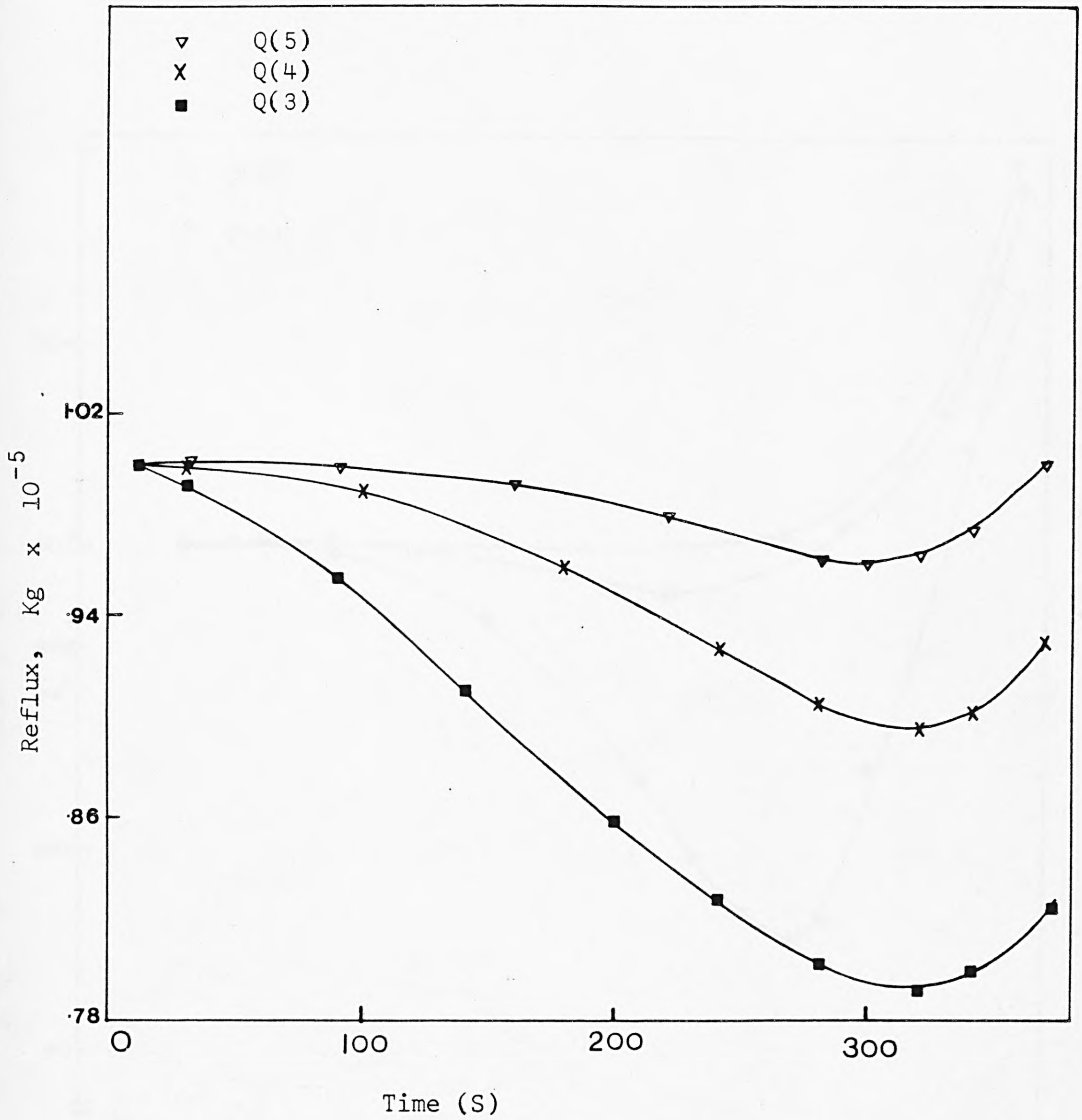
Thus the value of reflux in the stages nearest to the melting section should be the highest, which is also readily apparent from the graphs.

The graphs for the stages 9, 10, and 11 show a constant rise in the reflux after an initial lag period when it is constant. The same is also true for reflux in stage 2, though its lag period of constant reflux is slightly less than stages 9, 10 and 11.

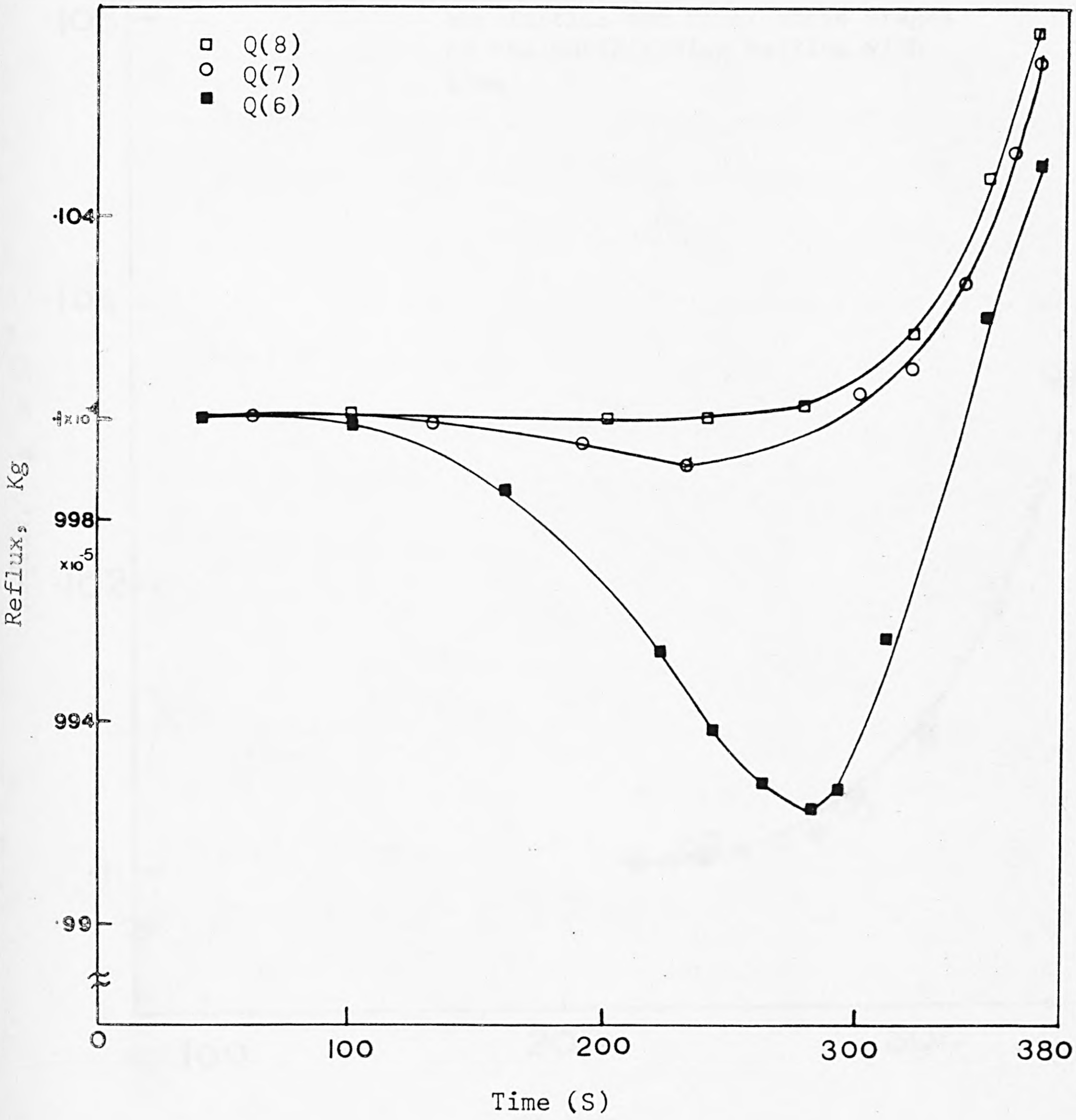
However the graphs for the other sections, viz: 3,4,5,6,7 and 8 show a slightly different trend. The initial reading in all the stages are the same which may be due to the initialising by the computer. But the reflux in these sections after a certain lag time when the reflux is constant at .1000 E-4, actually falls to a lower value. The decline trend continues for a certain period of time and then it starts to rise again to its original value and follows the trend of the rest of the stages 9, 10, and 11.

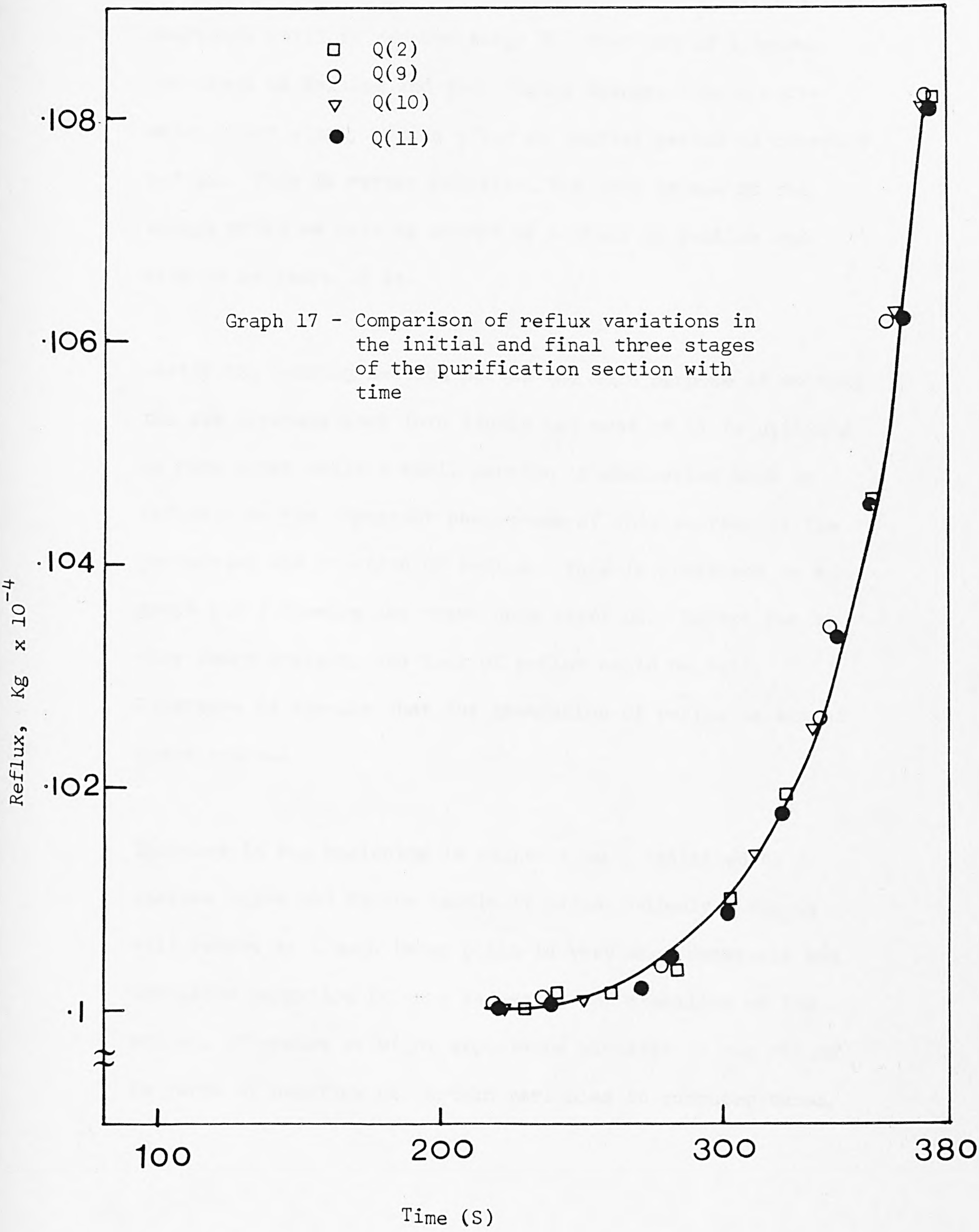
The only difference is that as the stages are further away from the melting section, the lag time of constant reflux slowly

Graph 15 - Trends in reflux variations in the 3rd, 4th and 5th stages of the purification section with time.



Graph 16 - Trends in reflux variations in the 6th, 7th and 8th stages of the purification section with time.

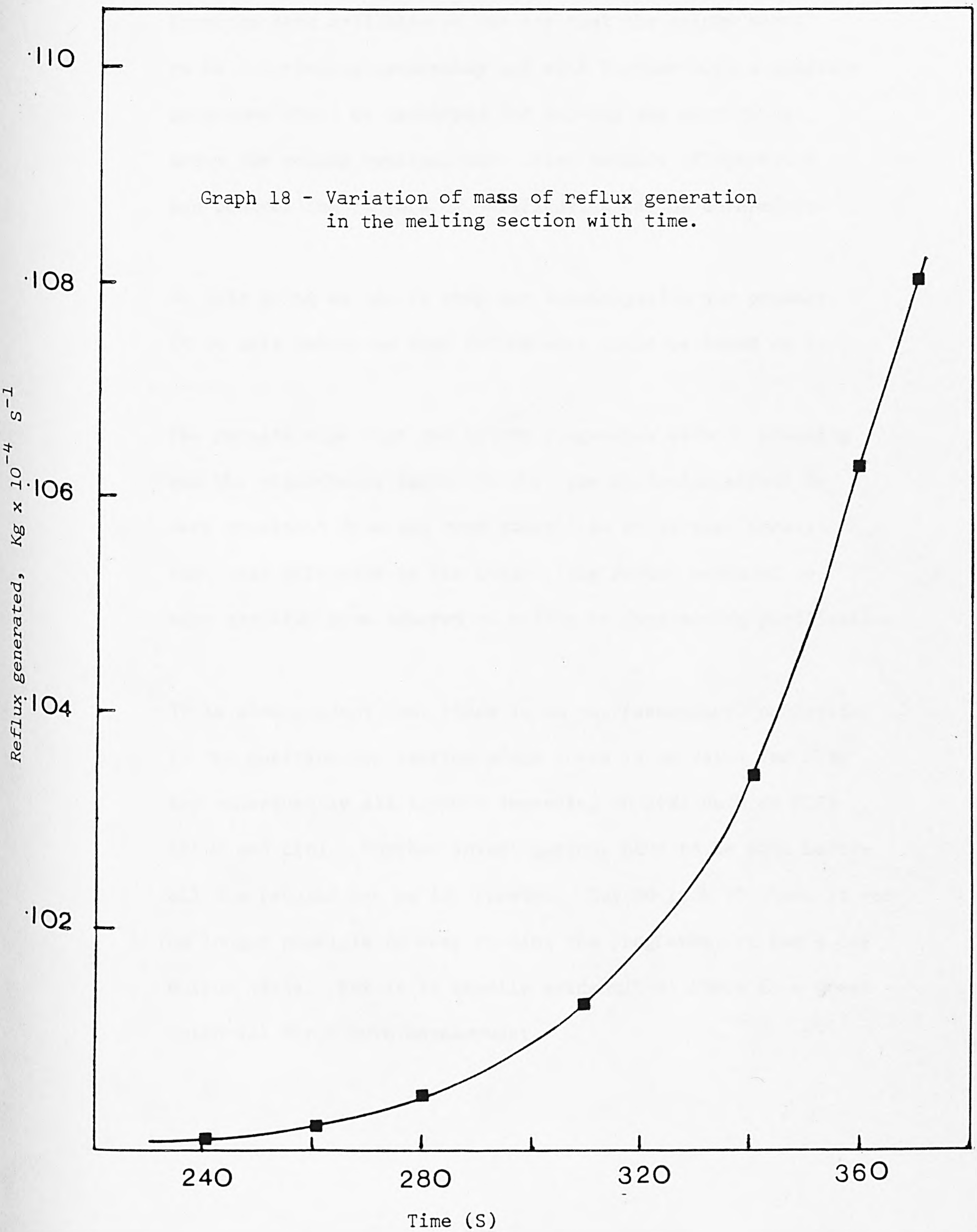




Graph 17 - Comparison of reflux variations in the initial and final three stages of the purification section with time decreases until it reaches stage 2. Then all of a sudden the trend of falling and then rising changes into a curve which shows simply rising after an initial period of constant reflux. This is rather peculiar, but that is one of the things which we have to accept as a start up problem and have to be aware of it.

Lastly the melting section serves the main purpose of melting the ice crystals back into liquid and most of it is utilised as pure water while a small portion is channelled back as reflux. So the important phenomenon of this section is the production and creation of reflux. This is presented as a graph (18) showing the trend upon start up. Except for a very short instant, the lack of reflux could be felt. Otherwise it appears that the generation of reflux is almost instantaneous.

Increase in the beginning is rather slow , explained by a shallow curve and in the middle it rises suddenly. How it will behave at a much later point is very much debatable but immediate formation is very necessary for stability of the column, otherwise we might experience blockage of the column in terms of overflow of certain variables in computer terms.



Graph 18 - Variation of mass of reflux generation in the melting section with time.

From the data available we can say that the column seems to be functioning reasonably and with further work a complete programme could be developed for solving any conditions about the column crystallizer. Also methods of operation and controlling factors of purification can be determined.

At this point we had to stop our investigation and present it in this manner so that future work could be based on it.

The results show that the column progresses without breaking and the significant factor is that the diffusion effect is very prominent from the very start. So it is most likely that eddy diffusion is the controlling factor compared to mass transfer from adhered to reflux in determining purification.

It is also evident that there is no new (secondary) nucleation in the purification section since there is no value for J(N) and consequently all factors depending on J(N) such as F(N) LD(N) and C(N). Further investigations have to be done before all the results can be interpreted. Due to lack of time, it was no longer possible to keep running the programme, at one a day output basis. But it is readily evident that there is a great potential for future development.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Chapter 6 CONCLUSIONS AND RECOMMENDATIONS

Now that the initial foundations for the programmes have been developed it will give a good basis for future work. It has all the potential of developing into such programmes similar to distillation programmes.

I used a lumped model for the freezing and melting sections with the assumption that there is complete mixing, which would be very valid for the two extreme sections. However, I have used a number of stages theory for the purification section, and have used a finite difference type method for analysis of certain variables. This seems to be the most logical form to follow as there is a temperature and impurity gradient along the length of the purification section. However, the differential equations becoming of enormous proportions are difficult to handle in the initial stages of a simulation development.

For this reason, I suggest a lumped model of the entire purification section might be easier to handle initially. Also it could cut down other equations thus reducing time. The lumped model will give us the total purification achieved, and it would enable us to calculate values of K and D and then we can utilise it to develop and calculate a stagewise model. The lumped model will give a better understanding of mass transfer from adhered to free liquid and eddy diffusion effects.

CHAPTER 7

APPENDIX

DATA:-

A = -8.88

AW = 4.05×10^{-2} m^2

CF = 3.138×10^{3} Joules/kg/ K

CP = 4.0167×10^{3} Joules/kg/ K

E = 0.06

GA = 77.0

GB = 0.5×10^{-5}

HF = 0.33 meters

HP = 6.6256×10^{-34} Joules/sec

λ = 3.3305×10^{5} Joules/kg

MF = 0.45 kg

PS = 9.2×10^{2} kg/m^3

Q = 3.45×10^{-5} kg/sec

RG = 8.31441 $J\ K^{-1} mole^{-1}$

TF = 271.7 K

U = 142.256 $Joules/m^2/sec/\ K$

WQ = 0.0035

BOUNDARY INPUTS:-

L = 3.45×10^{-4} kg/sec

LE = 1.5277×10^{-4} kg/sec

LF = 0.02 kg/sec

TIN = 275.0 K

TIF = 258.0 K

V = 3.704×10^{-4} m/sec

WLI = 0.035

SIMULATION PARAMETERS:-

DELT = 0.01
FINT = 30,000
PRDEL = 10.0
ERR = 0.00001
STP = 0.0

INITIAL CONDITIONS FOR SOLVING DIFFERENTIAL EQUATIONS:-

DPIC = 0.00005 m
MLIC = 0.3795 kg
MSIC = 0.0 kg
TBIC = 275.0 K
TWIC = 292.0 K
WLIC = 0.035

These pages (p. 212-223) of computer programs have been removed for possible copyright reasons

DATA:-

A = -8.88

AA = 0.1243

AW = 4.05 E-2

AWM = 2.45 E-2

CF = 3.138 E3

CP = 4.0167 E3

CWM = 4.0167 E3

D = 0.0124

E = 0.06

GA = 77.0

GB = 0.5 E-5

HF = 0.33

HP = 6.6256 E-34

HZ = 4.7 E-2

KA = 0.74 E-3

LAMDA = 3.3305 E5

LWM = 3.45 E-4

MF = 0.45

MWM = 0.27

PS = 9.2 E2

P = 1.03

RG = 8.31441

SIGMA = 7.7 E-5

TIW = 323.0

U = 142.256

WQ = 0.0035

BOUNDARY INPUTS :-

L = 3.45 E-4

LE = 1.1500 E-4

LF = 0.02

LTP = 2.2 E-5

TIF = 258.00

TIN = 275.00

VS = 3.704 E-4

WLI = 0.035

SIMULATION PARAMETERS:-

DELT = 0.10

FINT = 30,000

PRDEL = 100

ERR = 0.00001

STP = 0.0

INITIAL CONDITIONS FOR SOLVING DIFFERENTIAL EQUATIONS:-

MLIC = 0.3795

WLIC = 0.035

MSIC = 0.0

TBIC = 292.0

TWIC = 292.0

DPIC = 0.00005

MLIC(N) = 0.395

MLDIC(N) = 0.0

MSIC(N) = 0.0

WDIC(N) = 0.0

WLIC(N) = 0.035

TBIC(N) = 292.0

MLMIC = 0.23

MSMIC = 0.0

WLMIC = 0.035

TBMIC = 292.0

TWMIC = 292.0

CHAPTER 8

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