International
Fertilizer Industry
Association

IFA Technical Conference

Paris, France

5-8 November 1984

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

SIGNIFICANT ENERGY SAVINGS IN THE ODDA PROCESS

by M.H.G. Jennekens, Stamicarbon BV & G.H.M. Calis, DSM, Netherlands

CHAPTER I

SUMMARY

Where the Odda process is used for the production of highly water-soluble nitrophosphate fertilizer, it is possible to reduce energy consumption in a number of areas.
This paper discusses the energy savings which can be achieved in the calcium nitrate tetrahydrate crystallisation section.

Stamicarbon is now developing a new variant of the Odda process, based on discontinuous crystallisation, by which disadvantages of other processes are reduced or eliminated.$^{1)}$
A salient feature of the modified process is that the crystallizers are operated without excessive supersaturation at a maximum temperature difference between process liquor and cooling medium. Encrustations on the cooling surface are avoided completely and the crystals are very uniform, coarse and pure, so that crystal separation is almost perfect.
This enables the production of highly water soluble fertilizers at a higher final crystallisation temperature than usual.

The coolant temperature is continuously adjusted for each crystallizer with a microprocessor-based control system.
This is achieved in that each crystallizer consecutively uses coolant from a number of cooling systems, each of which operates within a different temperature range, rather than using one common cooling circuit.
In this way energy savings can be achieved, mainly by:

(1) operating at a final crystallisation temperature higher than that usually necessary to obtain fertilizer containing P_2O_5 with a rel. water solubility of 80-85 %;
(2) using closed-loop refrigeration units operating at as high a temperature as possible, resulting in a considerable increase in efficiency of these units;
(3) heat exchange between cold mother liquid and coolant;
(4) using cooling water for part of the cooling system, if the water temperature is low enough.

It is concluded that, though the new crystallisation process has more assets, it is the reduced energy consumption which makes this process attractive.

CHAPTER II

INTRODUCTION

As is well known, the main source for fertilizer P_2O_5 is rock phosphate. Most rock phosphate ore is of the so called apatite structure, the P_2O_5 of which is not readily available to the crop. In phosphatic fertilizer production, the structure of the apatite is broken down and the P_2O_5 is subsequently processed to a more or less water soluble salt, which improves the assimilation to the desired level.
The apatite structure is represented by the formula '$(Ca_3\ (PO_4)_2)_3 .\ Ca\ X_2$', X very often being fluorine, the fluorapatite. Owing to the presence of impurities, the CaO/P_2O_5 molar ratio is abt. 4.0 so that the phosphate ore can be represented as $(Ca_3(PO_4)_2)_3 .\ CaF_2 .\ 2\ CaX_2$. Depending on the composition of the ore X may be, for example, 0.5 CO_3, F or Cl. The rock is decomposed by dissolution in a strong, inorganic acid. Processes based on the use of sulphuric acid as well as nitric acid have been developed.
After completion of the acidulation, the dissolution liquor, containing P_2O_5 mainly as phosphoric acid, is processed to phosphatic fertilizer.
To prevent the formation of citrate-insoluble phosphates, this can only be done if the CaO/P_2O_5 molar ratio (originally being about 4.0) is decreased to a value below abt. 2.0. The final value is dependent on the desired water solubility (e.g. for 80 % rel. water solubility of the P_2O_5, the CaO/P_2O_5 molar ratio is to be abt. 0.75 to 0.80). Thus, the removal or inertisation of a substantial part of the CaO initially present in the rock is required in order to guarantee sufficient water solubility of the end product.

In processes based on acidulation of the rock with sulphuric acid, CaO is precipitated during decomposition of the rock, e.g. according to equation (1) of Annex I.
After separation of the gypsum precipitate, the resulting liquor may be neutralised with ammonia to ammonium phosphates.

It is quite obvious that processes based on the sulphuric acid route are dependent on the availability of sulphur since relatively large amounts of sulphuric acid are required, which are usually disposed of as the fatal byproduct gypsum.

On the other hand, processes using acidulation with nitric acid are virtually independent of sulphur when based on the original Odda process. In this process, developed by E. Johnson in 1928, the acidulate is obtained by reaction of rock phosphate and nitric acid, e.g. according to equation (2) of Annex I.
After completion of the dissolution reactions, the liquor is cooled to a temperature below 25 °C, as a result of which the maximum solubility of $Ca(NO_3)_2 \cdot 4H_2O$ is exceeded.
In older applications of the process, about 55 % of the $Ca(NO_3)_2$ was removed by crystallisation, resulting in a water solubility of the P_2O_5 in the end product of abt. 40 %, as can be represented by equation (3) of Annex I.

In modern variants of the Odda process a relative water solubility of 80 to 85 % can be achieved, e.g. according to equation (4) of Annex 1.
As can be seen from these equations, from every 12 moles of $Ca(NO_3)_2$ (see equation 2), only 2.40 moles remain in the liquor after CaO- removal, if a relative water solubility of 80 % is required, as can be represented by equation (4) of Annex I.

Hence, at least 80 % of the initial CaO has to be removed in the calcium nitrate separation section.
An example of a relationship between calcium nitrate solubility (expressed in moles CaO/moles P_2O_5) and temperature is presented in Figure 1.
The final water solubility of the end product at various values for the crystal slippage is also presented. It can be seen that a rather low final crystallisation temperature is required for producing fertilizer the P_2O_5 of which has a relative water solubility of 80 % or more. In this figure, the quite important role of efficient crystal removal in the separation section is obvious. When the crystal slippage is 10 % w/w, a final crystallisation temperature of -5 °C is required in the example given.

Although a substantial part of the cooling energy required in the modern Odda process is obtained by evaporation of ammonia which is necessary in the process, a considerable input of electrical cooling energy is still needed.
In a continuous crystallisation process, almost 50 % of the electricity consumption is required in the crystallisation and crystal separation sections. A substantial reduction of the electricity demand, in combination with its sulphur-independency, would make this process a very attractive alternative for producing NP(K) fertilizers.

CHAPTER III

THE STAMICARBON CONTINUOUS CRYSTALLISATION PROCESS

About thirty-five years ago, Stamicarbon adapted the original Odda process to a continuous crystallisation process. As was common practice at that time the crystallisation section was part of a fertilizer plant producing complex fertilizer with a relative water solubility of the P_2O_5 of up to 50 %. This process is performed in a single series of large tank crystallizers, equipped with vertical cooling surfaces. After reaching the final crystallisation temperature, the crystal slurry is transferred to the crystal separation section. Here, in a solid bowl decanter centrifuge, the mother liquor and crystals are separated. The crystals are washed with cold nitric acid and subsequently separated from the washing liquor.
Although the slippage of crystals in the mother liquor separation section is quite high, up to abt. 15 %, the final crystallisation temperature is only moderate (abt. 12 °C), as can be seen from Figure 1.
In this process encrustations formed on the heat-exchanging surface are removed by means of a thawing system. To this end, the cooling medium is briefly replaced by a heating medium, by which the scaling is dissolved.
The variation of the final crystallisation temperature as a function of crystal slippage at a relative water solubility of abt. 50 % is rather small (see Figure 1). Thus, control of water solubility by varying the final crystallisation temperature is very well possible.

The process has gradually been adapted to the demand for fertilizer containing P_2O_5 with a high relative water solubility (80 to 85 %), as is required in many countries. To achieve this, 80 % or more of the calcium nitrate has to be removed effectively.
With increasing water solubility, adaptation of the process becomes more and more difficult. From the solubility curve (Figure 1) it can be seen that below about 5 °C the decrease of calcium nitrate solubility with temperature is rather small.
For this reason, compensation of crystal slippage by lowering the temperature of the magma is impossible beyond a certain amount of slippage.

Furthermore, the flexibility of the process, necessary to digest various types of feedstock, is rather small.

Problems that may be encountered in the production of fertilizers with a high relative water solubility of the P_2O_5 are:

A. With excessive nucleation, rather small, non-uniform crystals are produced, causing crystal slippage in the separation section. This requires the use of sophisticated equipmentin this section. In Figure 2, typical size distribution curves are presented.

B. The use of a sophisticated crystal separation installation often requires the separation of inerts from the process liquor. In case the phosphate ore has a too high content of inert particles, these have to be removed before the liquor enters the crystallisation section.

C. The formation of encrustations on the heat-exchanging surface makes it necessary to install a so-called thawing system. The energy losses because of this de-frosting circuit will increase with the required relative water solubility of the P_2O_5 in the product (high temperature difference between process liquor and cooling medium). At abt. 80 % water solubility of the P_2O_5, the energy losses are abt. 80 kWh/tonne P_2O_5.

An example of a flow scheme of a nitrophosphate plant based on the continuous crystallisation route is presented in Figure 3.
Such a plant, having a capacity of 1000 tpd NP 1:1 (80 % relative water solubility of the P_2O_5) fertilizer (i.e. 230 tpd P_2O_5) incorporates:

- an inerts separation section based on solid bowl peel type centrifuges(see No 8);
- a crystallisation section with at least 4 series of crystallizers, each containing 8 to 10 crystallizers (see No 12);
- a 1st crystal separation section containing at least 4 two-stage pusher-type centrifuges(see No 14);
- a 2nd crystal separation section to minimize the overall crystal slippage. In this section hydrocyclones might be used (not indicated).
- a closed loop refrigeration unit, the required capacity being 3.2 MW
- an open evaporator for process ammonia.

The problems, mentioned for the production of NP(K) fertilizer with at least 80, preferably 85 % rel. water solubility of the P_2O_5, can be mastered if the following requirements are fulfilled:

1. The crystallisation process must be adjustable, resulting in coarse and very uniform crystals.

2. The crystallisation process must not only be controllable, it should also be possible to predict it on the basis of small-scale experiments, which implies that both the crystallisation process and the (hydro-)dynamics of the crystallizer are well defined. The use of all kinds of rock phosphate must be possible.

3. The crystals obtained in the process can be separated from the mother liquor by a one stage filtration section. Slippage of crystals should be less than 5 % by weight. The P_2O_5concentration of the crystals after washing should not exceed 0.25 % w/w.

4. Optimum energy management is to be achieved, leading to minimal energy requirements.

CHAPTER IV

COMPARISON OF POSSIBLE CRYSTALLISATION METHODS

In the previous part we have given our requirements to be fulfilled in an ideal crystallisation process. In the existing continuous and batch crystallisation processes, not all of these are fulfilled. In this part, the principles of existing and alternative crystallisation processes are discussed and compared in order to clarify our selection of the most appropriate method.

Four crystallisation mechanisms are schematically represented in Figure 4. In all four schemes, a solid line indicates the equilibrium solubility curve and a dashed line the nucleation curve. The area between these curves is the metastable region, where supersaturation is mainly reduced by crystal growth. At the nucleation curve, the increase in supersaturation is just balanced by nucleation.

Two other solid lines give the actual calcium nitrate concentration (expressed in terms of the CaO/P_2O_5 molar ratio) as a function of the temperature of the process liquid (Tp) and the temperature of the cooling medium corresponding with this concentration (Tc). These latter lines must be situated inside the metastable region in order to avoid excessive nucleation. Only in this case are coarse and uniform crystals obtained, which is necessary to fulfill all our requirements.

The four methods are:

1. Conventional continuous crystallisation (Figure 4A).
2. Continuous crystallisation without excessive nucleation (Figure 4B).
3. Conventional batch crystallisation (Figure 4C).
4. Batch crystallisation without excessive nucleation (Figure 4D).

1. Conventional continuous crystallisation

In a process as represented in Figure 4A, a slurry of process liquid with calcium nitrate crystals is passed through a number of crystallizers, connected in series, each operating at a constant average temperature of the process liquid, e.g. Tp_1 for the first crystallizer, Tp_2 for the second one, and so on.

The temperature differences between subsequent crystallizers are such that the slurry entering a crystallizer is immediately cooled down beyond the nucleation curve, resulting in excessive nucleation. Moreover, in all crystallizers Tc is at the same low level (about -12 ^0C), which causes permanent nucleation at the cooling surface. The result of a process based on this crystallisation method is a wide crystal size distribution and large quantities of fines (see Figure 2), as has been indicated before.

2. Continuous crystallisation without excessive nucleation

In a continuous process, excessive nucleation can only be avoided by operating subsequent crystallizers at temperatures which differ less than the width of the metastable region and by using in each crystallizer cooling medium of a temperature inside the metastable region. This is represented in Figure 4B. The vertical arrow (↑) indicates the seeding point, where a well-defined number of seeds is introduced.

Due to the continuous character of this process, the temperature of the cooling medium in each crystallizer must be constant and determined by the composition of the incoming liquid phase. As a consequence, the temperatures of the process liquid (Tp_1, Tp_2, Tp_3,...) and the cooling medium (Tc_1, Tc_2, Tc_3...) differ only slightly in each crystallizer, so that the cooling rate and the capacity of the crystallisation system are reduced to unacceptable levels. For this reason, this crystallisation method can never lead to a commercial process, although our requirements can be fulfilled in principle.

3. Conventional batch crystallisation

In a batch process the temperature of the cooling medium Tc is not necessarily constant, if excessive nucleation is to be avoided. A typical batch process is represented in Figure 4C. The process starts by filling a crystallizer with hot dissolution liquid, which is subsequently cooled. Crystallisation can be initiated by seeding. In the method described by Figure 4C, the seeding point is usually below the nucleation temperature, causing excessive nucleation. On cooling the dissolution liquid is quite easily supersaturated, even beyond the nucleation curve. Furthermore, Tc is not within the metastable region, causing continuous nucleation at the cooling surface. Crystal growth takes place on both the seeding crystals and the secondary nuclei.

Usually, a commercial set up is based on a number of crystallizers, operating in cycles, phase shifted with respect to each other. In this way the cold cooling liquid can be used to cool the coldest crystallizer, from which it is passed on to the next coldest one, and so on, countercurrently through the process.

On the basis of our experiments and of application of theory, we conclude that, although this cooling system results in moderate temperature difference between process liquor (Tp) and cooling medium (Tc), the temperature of the cooling medium is not within the metastable region. This crystallisation method can yield large crystals, with a rather wide size distribution, however, which is unfavourable in the separation step. Moreover, due to scaling and secondary nucleation the crystallisation behaviour in technical systems can neither be controlled nor predicted.

4. Batch crystallisation without excessive nucleation

In order to avoid excessive nucleation and scaling under all circumstances, T_c must be kept within the metastable region during the batch time, as is schematically indicated in Figure 4D. This crystallisation method, developed at the R and D department of DSM, will be applied in the new Stamicarbon batch crystallisation process[1].

T_c is continuously adjusted and kept just above the nucleation temperature to assure maximum cooling capacity. Crystallisation is initiated by seeding slightly below the temperature of the saturated dissolution liquid, with a defined number of uniform crystals. These crystals grow simultaneously

throughout the process, yielding very uniform crystals. The final size is determined by the number of seeding crystals. The resulting narrow size distribution is caused only by growth dispersion, since nucleation is negligible in the metastable region (Larson $^{2)}$ for example stated that axial mixing does not affect the size distribution).
When using this method, the crystallisation behaviour is predictable and controllable and uniform, coarse crystals can be obtained. The requirements for a crystallisation process, as mentioned in the previous chapter, can be fulfilled.

The crystallisation method described in Figure 4D has been tested in numerous laboratory experiments. An illustrative example is given in Figures 5 and 6. Figure 5 shows the solubility and nucleation curves of calcium nitrate in dissolution liquid of Jordan rock phosphate. These curves have been determined by a laser transmission method. The nucleation curve varies with the cooling rate. Also two curves (1 and 2) are given that represent the calcium nitrate concentration as a function of process temperature in two comparable experiments. Both curves demonstrate only a slight decrease in the original concentration (CaO/P_2O_5 m.r.= 2.75) in the first part of the process, due to the small crystal surface available for growth directly after seeding. The difference between the two curves is caused by a difference in cooling conditions. These conditions are such, that in the experiment described by curve 1 excessive nucleation occurs since the nucleation curve in exceeded. This is not the case in the experiment described by curve 2, carried out under milder cooling conditions (given in the comments on Figure 5, Annex III).
Figure 6 shows the corresponding crystal size distributions, obtained at the end of these batch experiments. This figure clearly demonstrates the importance of appropriate cooling conditions. The conditions resulting in curve 2 yield very uniform crystals with a narrow size distribution, whereas the more severe conditions of curve 1 yield crystals with a very wide size distribution due to excessive nucleation.

The appropriate cooling conditions can be derived from laboratory experiments. The initial temperature of the cooling medium and the cooling rates depend on the width of the metastable region. Directly after seeding, the cooling rate is limited by the crystal growth rate, G. In our experiments, G has been estimated from microscope photographs of crystals, separated from slurry samples (size distribution), and the concentration of the corresponding liquid phase.
Chen and Larson $^{3)}$ also describe measurements of G for $Ca(NO_3)_2.4H_2O$ under similar circumstances. Depending on the supersaturation, values between 0.05 and 0.15 micron/s have been found, regardless of crystal size.

If the nucleation curves as a function of cooling rate and the growth rate as a function of supersaturation are known, the optimum cooling programme (shortest batch time without excessive nucleation) can be derived. The minimum batch time to obtain 1 mm crystals appears to be about 2 hrs, if the process is not limited by heat transfer.

CHAPTER V

ENERGY SAVINGS ASPECTS OF THE IDEAL BATCH CRYSTALLISATION PROCESS

As mentioned in the previous chapter, a crystallisation process fulfills all our requirements if the metastable region is not exceeded and the right amount of seeding crystals is supplied at the right time.
Only in a batch process is it possible to adjust the temperature of the cooling medium continuously in such a way that on the one hand the metastable region is not exceeded, not even in the boundary layer on the heat transfer surface, while on the other hand the temperature difference between process liquor and cooling medium is, at any moment, as high as possible.

To this end, a single crystallizer preferably obtains its cooling medium from a specific cooling circuit only serving that specific crystallizer (see Figure 7). The temperature of the cooling medium flowing to the crystallizer is only governed by the temperature of the process liquor inside the crystallizer.
A typical example of a useful temperature profile is given in Figure 8, where the temperature of the cooling medium, initially being 26 ^{0}C, gradually decreases to -9 ^{0}C.

Integrating a crystallizer with its own specific cooling system means that the capacity of that cooling system has to be large enough to cover the period of maximum heat flux. This maximum heat flux occurs only during a relatively short period (see Figure 8). The cooling system is therefore underloaded during a substantial part of the cycle. Consequently, the use of evaporation systems of liquid process ammonia for cooling purposes would hardly be feasible.
It is therefore obvious that a set of crystallizers should be combined in one integrated cooling system in such a way that especially the evaporators for liquid process ammonia are operated at a constant load.

Heat-exchange between ammonia and the cooling medium in use in the crystallisation system takes place in the evaporator.

The refrigeration unit in principle is a heat pump. The overall efficiency ($N_{overall}$) of this pump is determined not only by the compressor efficiency (including efficiency of the drive), (N_{compr}), but also by the so-called 'Carnot-efficiency', (N_{Carnot}):

$$N_{overall} = N_{compr} * N_{Carnot}$$

$$N_{Carnot} = \frac{T_{c.w.}}{\Delta T}$$

$T_{c.w.}$ = average cooling water temperature, in K

ΔT = cooling water temperature - evaporator temperature

The overall efficiency and electricity requirements at $T_{c.w} = 33\ ^{o}C$ and $N_{compr} = 0.54$, are given in Table 1:

TABLE 1 PERFORMANCE OF A CLOSED-LOOP REFRIGERATION UNIT AT VARIOUS TEMPERATURES:

Cooling medium temp.	N_{Carnot}	$N_{overall}$	P_{spec}
- 20 ^{o}C	5.28	2.85	0.54
- 12 ^{o}C	6.12	3.31	0.43
+ 12 ^{o}C	11.77	6.34	0.19
+ 22 ^{o}C	19.13	10.33	0.11

P_{spec} is the amount of electricity (in kWh), required to transfer 1 kWh of energy from the cooling medium (low temperature) to the cooling water (high temperature).

$N_{overall}$ is defined as the ratio between units of the total heat transferred by the system and the amount of supplied energy (e.g. electricity)

From Table 1 it follows that the efficiency of the refrigeration units is strongly influenced by the temperature of the cooling medium (at the same cooling water temperature).

When the unit is operated at a cooling medium temperature of + 22 °C instead of - 12 °C, the electricity consumption per unit of heat transferred from low to high temperature drops to only 26 %. Operation at a cooling medium temperature of + 12 °C requires 44 % of the original input at -12 °C.

Thus, integration of a set of crystallizers in various cooling circuits rather than using only one circuit may lead to interesting energy savings, since some of these cooling circuits are operated at elevated temperatures.

Such an integrated system is presented in Figure 9.

It should be noted that the crystallizers in Figure 9 represent a specific status. This means that, for example, the status of crystallizer A in this figure is such that it is taking all its cooling energy from closed-loop refrigeration unit I. After a certain period, the status of crystallizer A will be such that it takes all its cooling energy from closed-loop unit II. At that time, another crystallizer may take cooling energy from closed-loop unit I. Depending on its status (i.e. the temperature), a specific crystallizer takes its energy from one of the cooling systems.

In an integrated system as described above, application of several interesting features is very well possible:

1. The temperature of the mother liquor after calcium nitrate separation is abt. 5 °C. Since use is also made of a cooling system having a temperature of 22 °C, heat exchange between this mother liquor and the cooling medium is very well possible. This direct regeneration of heat in the crystallisation process leads to energy savings.

2. In many countries, cooling water having a temperature below abt. 20 °C is available. The cooling energy required in the cooling system operating at abt. 22 °C can therefore quantitatively be obtained from cooling water rather than via an electrical cooling unit.
   Since the heat exchange between the cooling water and the crystallisation unit occurs via intermediate cooling medium circuits, no interference of cooling water and cooling medium takes place. Again, interesting energy savings may be achieved.

CHAPTER VI

THE STAMICARBON BATCH CRYSTALLISATION PROCESS

The combination of a set of crystallizers, each operating with a well defined and limited temperature difference between cooling medium and process liquor, in an integrated cooling system (as in Figure 9) raises some important problems which need to be solved. First of all there is the aspect of heat transfer.

Secondly, the maximum tip speed of the pump is limited in order to avoid damage to the crystals, which sets limits to the pressure drop in the heat exchanger.

These problems have been solved by designing a crystallizer with sufficient heat-exchanging surface and a special type of agitator.

For this crystallizer design, the heat flux can be calculated. The equations describing the heat balances of the crystallizer and the cooling medium as well as the overall heat balance are presented in Annex II. The enthalpy of the process liquor (Hp) can be calculated as a function of Tp, the temperature of the process liquor. From this relationship the derivate $\delta Hp/\delta Tp$ is obtained.

The other parameters in the equations of Annex II are design parameters which can be inserted.

Starting from an initial value for Tp (e.g. 35 °C), and using the optimum cooling programme, the derivation of which is indicated in chapter IV, Tp is subsequently evaluated as a function of time. From this curve, both the total batch time and the heat flux are derived (e.g. Figure 8).

An additional problem is caused by the discontinuous character of the process. Since the temperature difference between Tp and Tc varies considerably throughout the process (e.g. from 1 to 16 °C), the heat flux also varies enormously. As has been mentioned before, a set of crystallizers should be integrated in order to operate the cooling system (i.e. the ammonia evaporators) at a constant load. For this reason it is necessary to establish the optimum combination of the set of crystallizers

and the various parts of the cooling circuits (such as buffer volumes, pumping capacities and temperature levels).
In order to optimize the crystallisation section, a dynamic simulation of an industrial batch process, in which both the heat balances of Annex II and the regulation characteristics of the control system are combined, is set up.

With the aid of the dynamic process simulation, the following parameters can be optimized:

A. The required number of crystallizers and their capacity.

B. Temperature control of the crystallizers, influenced by:
- the regulation characteristics of the temperature control unit;
- the capacity of the cooling medium pumps;
- the volume of secondary coolant buffer tanks.

C. Capacity of the closed-loop refrigeration units, influenced by:
- the volume of primary buffer tanks;
- the regulation characteristics of the closed-loop refrigeration units with respect to capacity control.

D. The flow of coolant between primary and secondary cooling circuits.

An example of such a system, used in the dynamic simulation, can be seen in Figure 10. Each specific crystallizer unit consists of a crystallizer, a cooling medium buffer tank (the secondary buffer) and a cooling medium pump. The cooling medium supply from the primary cooling circuits to the crystallisation units is controlled by means of a control valve and a selector which selects the required cooling circuit. The temperature control of a crystallisation unit is in effect a flow control by which a controlled amount of cooling medium from a large storage (primary circuit) is supplied to the secondary buffer tank of the corresponding unit. In this way the temperature of the secondary buffer (Tc) is adapted, in dependence on the temperature of the crystallizer (Tp), according to the optimum cooling programme. The buffer volume of cooling medium in a crystallisation unit is rather small in order to ensure a quick response in temperature control. The volume of cooling medium in the primary circuits, on the other hand, needs to be large in order to obtain a steady process. To prevent coincidence of large flows from one primary circuit to the crystallisation units, the various crystallizers are in phase shifted operation, while a time control unit is mastering the total crystallisation section.

From the results of this simulation, we arrive at an integrated batch crystallisation system, consisting of a number of crystallizers and primary cooling circuits.

Solely for reasons of illustration, a typical example of a crystallisation batch, based on the operating parameters for ideal batch crystallisation, is presented. The various operating parameters given in this example depend on, amongst others, feedstock composition, product requirements and local conditions. Adaptation is necessary for every specific case.
Figure 10 represents a simplified process flow sheet of this example.

Before entering the crystallisation section, the process liquor (Tp is abt. 60 °C) is cooled with cooling water to a temperature of abt. 35 °C.
Subsequently, one of the crystallizers is filled and taken into operation while being controlled by the time control unit.
In the first part of the cooling process (e.g. down to a temperature of 25 °C), coolant from the primary cooling circuit, operated at a temperature of 22 °C, is used to control the temperature of the correponding secondary buffer.
After a process temperature (Tp) of 25 °C has been reached and control of the time control unit has been released, continuation of the cooling programme is effected by means of the second primary cooling circuit, which is operated at a temperature of 12 °C. Finally, at a process temperature of 18.5 °C, the third primary cooling circuit, maintained at a temperature of - 12 °C, supplies the cooling medium.
The temperature-time profile for a specific crystallizer, obtained from the simulation, is presented in Figure 11. In the indicated period of 1000 minutes (16.7 hrs), more than three cycles have been completed.

One of the most interesting results of such a dynamic simulation is the total 'peak to peak' load of each closed-loop refrigeration unit. These loads, presented in Figure 12, appear to be within the range from abt 60 to 100 % of the maximum load required.

Thus, dynamic process simulation shows, it is well possible to design an integrated crystallisation and cooling system on industrial scale that fulfills our basic requirements (yielding coarse and uniform crystals by avoiding excessive supersaturation).

According to this example the optimized design for a 1000 tpd NP 1:1 plant would comprise the following:

- Seven crystallizers.
- Seven secondary cooling medium buffer tanks.
- Seven secondary cooling medium pumps.
- A closed-loop refrigeration unit, the required capacity being 1.25 MW, operating at an average temperature of 22 °C. The average load of this unit is abt. 0.9 MW.
- A closed-loop refrigeration unit, the required capacity being 0.80 MW, operated at abt. 12 °C. The average load of this unit is abt. 0.6 MW.
- An open NH_3-evaporator to evaporate the liquid ammonia which is required in the neutralisation and conversion sections of the plant.
- Three primary cooling medium buffer tanks.
- Three primary coolant pumps.
- One shell and tube heat-exchanger for heat exchange between cold mother liquor and cooling medium. Capacity of this unit being abt. 0.22 MW.
- An intermediate buffer tank for crystal slurry.
- A small unit to generate seed crystals.
- Temperature control of the crystallizers needs to be very accurate and overall monitoring of the cooling circuits, especially with regard to the selection of the various cooling units, is required. Furthermore adaptation of the cooling programme to the actual composition of the process liquor is necessary. To this end, control of the whole crystallisation section is performed fully automatically by means of a microcomputer and automatically operated analytical equipment.
- The crystal separation section is provided with a filter.

The design is based on small-scale experiments and computer-aided simulation of the industrial process. The experiments have shown that our batch crystallisation process can be fully controlled by choosing the appropriate cooling programme, which can also be done on industrial scale, for which the composition of the process liquor is monitored. The computer simulation shows that a commercial crystallisation section based on our batch process can be realized by integrating a set of crystallizers with cooling units.

The performance of the new Stamicarbon crystallisation process can be compared with existing processes by means of Table 2:

TABLE 2 PERFORMANCE OF VARIOUS CRYSTALLISATION PROCESSES

	Continuous process	Conventional* batch process	New Stamicarbon batch process
P_2O_5 with min. 80 % water solubility	achievable	well achievable	easily achievable
flexibility with regards to rock phosphate characteristics	limited	improved	high
Adjustable crystallisation process	no	no	yes
Crystals separation by means of:	centrifuges	filters	filters
Crystal slippage	abt. 12 %	5 to 10 %	abt. 1 %
Scale up from lab. experiments	impossible	difficult	well possible
Scaling	heavily	yes	none at all
Thawing system	required	not required	not required
Estimated heat transfer - coefficient, $W/m^2.K$	abt. 120 average	abt. 300 initially abt. 50 finally**	300-400

* based on tests and application of theory.

** decreasing because of the formation of encrustations on the heat-exchanger surface.

Typical operating parameters and electricity consumption figures of the new Stamicarbon process are compared with those of existing processes by means of Table 3:

TABLE 3 COMPARISON OF VARIOUS PROCESSES:

	Continuous process	Conventional* batch process	New Stamicarbon batch process
final crystallisation temp, °C	-5	abt. 0	4
No. of cooling circuits	1	1	3
operating temp. of closed-loop units, °C	-12	-12	22 12
efficiency of closed-loop units	3.3	3.3	10.3 6.3
electricity ** consumption, excl. closed-loop units, MW	0.7	0.6	0.7
electr. consumption ** of closed-loop units, MW	1.4	0.8	0.2
total electricity ** consumption, MW	2.1	1.4	0.9
rel. electr. consumption **, kWh/t.P_2O_5	222	148	94

* based on tests and application of theory

** for 1000 tpd, NP = 1:1, with 80 % water soluble P_2O_5 in the fertilizer, for the crystallisation section only.

Stamicarbon is now constructing a nitrophosphate demonstration unit, to be completed before the end of 1984. This installation, also microcomputer-controlled, will be realized in the nitrophosphate unit of UKF in Geleen. It will be possible to operate the unit independently of plant operating parameters, in order to investigate the suitability of various phosphate ores. Furthermore, it will be possible to study long-term effects by using process liquor from the nitrophosphate plant.

CHAPTER VII

CONCLUSIONS

1. The Odda process can be adapted properly to the demands imposed by changing feedstock and process conditions provided that it is applied as a batch crystallisation process without excessive nucleation.

2. The fundamental know-how necessary to design an ideal batch crystallisation process, characterized by the controlled production of coarse and uniform crystals, has been developed.

3. With the aid of a dynamic process simulation, an optimum design for industrial application of the ideal batch process can be made for any type of phosphate ore.

4. By integrating a number of batch crystallizers and various cooling circuits, considerable energy savings can be realized.

5. Comparison of the characteristics of the various crystallisation processes clearly demonstrates the advantages of the new Stamicarbon batch crystallisation process.

6. A batch crystallisation demonstration unit will be available by the end of 1984.

REFERENCES

1) Patent applied for.

2) M.A. Larson, private communication.

3) Ming Rei Chen, M.A. Larson, accepted for publication in Chem. Engineering Science.

Annex I

(1), sulphuric acid dissolution

$(Ca_3(PO_4)_2)_3 \cdot CaF_2 \cdot 2\ CaX_2 + 12H_2SO_4 \xrightarrow{aq}$
$12\ CaSO_4 + 6\ H_3PO_4 + 2\ HF + 4\ HX$

(2), nitric acid dissolution

$(Ca_3(PO_4)_2)_3 \cdot CaF_2 \cdot 2\ CaX_2 + 24\ HNO_3 \xrightarrow{aq}$
$12\ Ca(NO_3)_2 + 6H_3PO_4 + 2HF + 4\ HX$

(3), the neutralisation resulting in P_2O_5 having a water solubility of 40%

$5.35\ Ca(NO_3)_2 + 6\ H_3PO_4 + 2\ HF + HX + 12.6\ NH_3 \xrightarrow{aq}$
$3.6\ CaHPO_4 + 1.9\ NH_4H_2PO_4 + CaF_2 + 10.7\ NH_4NO_3 + 0.25\ Ca(H_2PO_4)_2 +$
$0.5\ CaX_2$

(4), the neutralisation resulting in P_2O_5 having a water solubility of 80%

$2.40\ Ca(NO_3)_2 + 6\ H_3PO_4 + 1.6\ HF + 0.8\ HX + 9.6\ NH_3 \xrightarrow{aq}$
$1.2\ CaHPO_4 + 4.8\ NH_4H_2PO_4 + 0.8\ CaF_2 + 0.4\ CaX_2 + 4.8\ NH_4NO_3$

Annex II

A. The heat balance of the crystallizer:

$$dQ/dt = (G_p * dTp * \frac{\delta Hp}{\delta Tp} + P_A + P_p)$$

Where:

Q = amount of heat, in kJ

G_p = amount of process liquor, in kg

T_p = process temperature, in K

t = time, in s.

H_p = enthalpy of the process liquor, in kJ

P_A = power input of the agitator, in kW

P_p = power input of the pump, in kW

B. The heat absorption of the cooling medium:

$$dQ/dt = F_c * Cp_c * (T_{c1} - T_{c2})$$

Where:

F_c = flow of cooling medium, in kg/s

Cp_c = specific heat of the cooling medium, in kJ/kg K

T_{c1} = temperature of the cooling medium at crystallizer inlet, in K

T_{c2} = temperature of the cooling medium at crystallizer outlet, in K

C. Overall heat balance:

$$dQ/dt = U * A * (T_p - T_c)$$

Where:

U = overall heat-exchange coefficient, in kW/m^2K

A = Heat-exchanger area, in m^2

T_c = mean cooling medium temperature, in K.

Comments to the enclosed figures

Figure 1:

Calcium nitrate solubility curve for dissolution liquid from Jordan rock phosphate and 60 % nitric acid (solid line).
Also indicated is the calcium nitrate concentration of the mother liquid after separation of crystals at some values for the relative crystal slippage (dashed lines). The calcium nitrate concentration is expressed as the CaO/P_2O_5 molar ratio and is related directly to the relative water solubility of P_2O_5 in the end product.

Figure 2:

Typical size distributions of calcium nitrate crystals obtained in the continuous crystallisation process. Nine crystallizers are connected in series. Their operating temperatures vary from about 22 ^{0}C in the 2nd crystallizer to -5 ^{0}C in the final crystallizer.

Figure 3:

The Stamicarbon continuous crystallisation process.

Figure 4:

Four crystallisation methods are schematically represented:
A: Conventional continuous crystallisation
B: Continuous crystallisation without excessive nucleation
C: Conventional batch crystallisation
D: Batch crystallisation without excessive nucleation
In all four curves a solid line indicates the solubility curve, a dashed line the nucleation curve. Also indicated are the average process liquid temperature, T_p, and the average cooling medium temperature, T_c.
(↑) indicates the seeding point.

Figure 5:

Calcium nitrate concentration during two batch crystallisation experiments, starting from dissolution liquid from Jordan rock and 60 % nitric acid and an initial CaO/P_2O_5 molar ratio of 2.75. A solid line indicates the solubility curve, the two dashed lines are nucleation curves, determined at cooling rates of 0.10 and 0.25 ^{o}C/min., respectively. The measurements have been made under different cooling conditions:

curve 1: Initial cooling medium temperature 22 ^{o}C, initial cooling rate 0.25 ^{o}C/min.

curve 2: Initial cooling medium temperature 25 ^{o}C, initial cooling rate 0.10 ^{o}C/min.

Figure 6:

Crystal size distributions of crystals separated from the mother liquid at 5 ^{o}C, obtained in the batch experiments represented in Figure 5.

Figure 7:

A crystallisation system for the ideal batch process.
The temperature measurement, the valves and the control units have been indicated (TRC = capacity control).

Figure 8:

Temperature profile for an ideal batch crystallisation process.
Both the temperature of the process liquid and the temperature of the cooling medium are given as a function of time. Also indicated is the required cooling energy.

Figure 9:

An integrated system of crystallizers and three cooling circuits. The figure merely represents one status of the system: in this figure, crystallizer A is served by cooling circuit I, B by II and C by III.

Figure 10:

Simplified flow scheme for an integrated crystallisation system.

Figure 11:

Temperature-profile of one specific crystallizer. The temperatures of process liquid and cooling medium inside the crystallizer have been calculated via dynamic simulation of an industrial-scale process.

Figure 12:

The total load on the refrigeration unit and the mother liquor heat exchanger as a function of time, calculated via the dynamic process simulation.

Calcium nitrate crystallisation curve

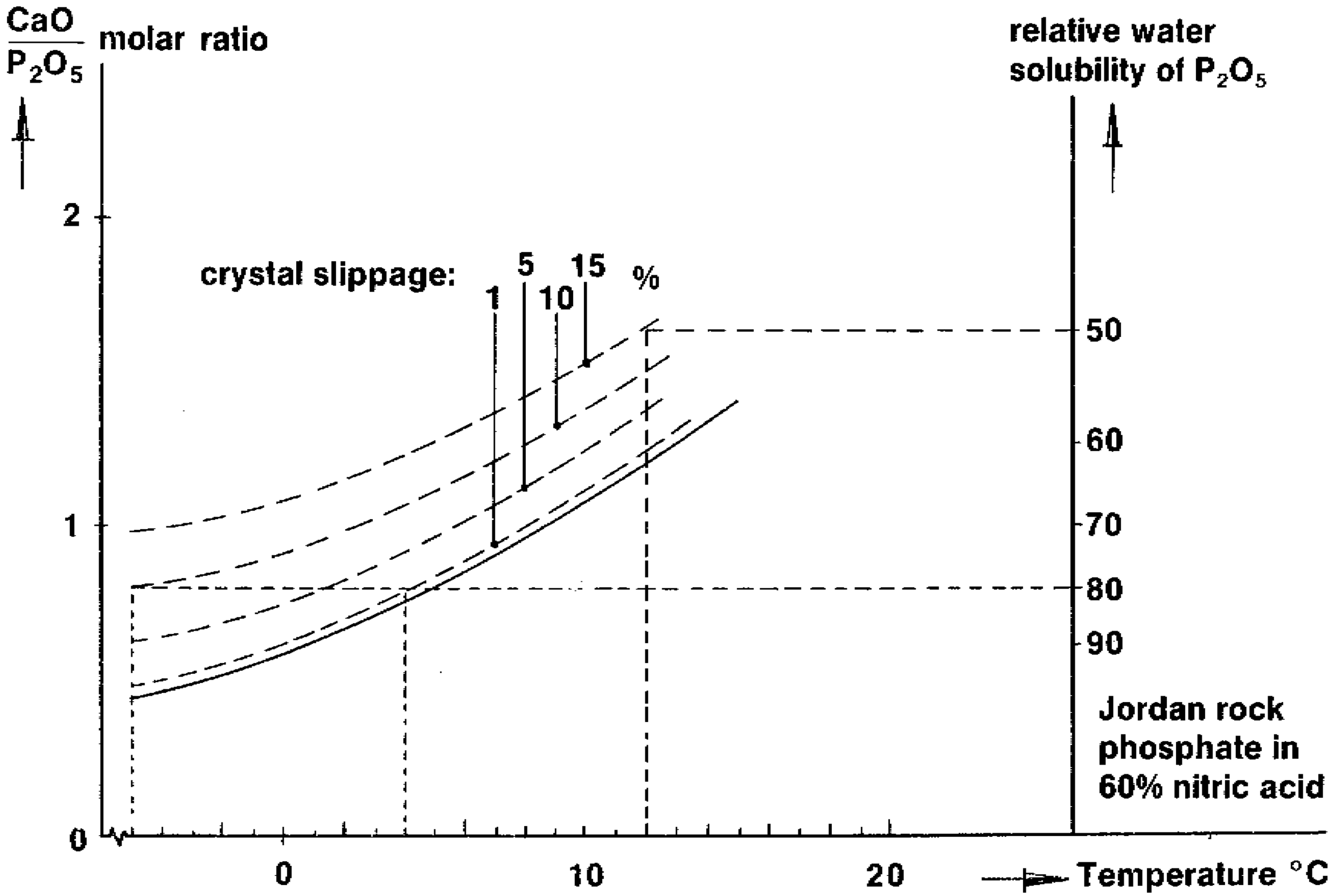


Figure 1

Crystal size distributions, for the continuous calcium nitrate crystallisation process

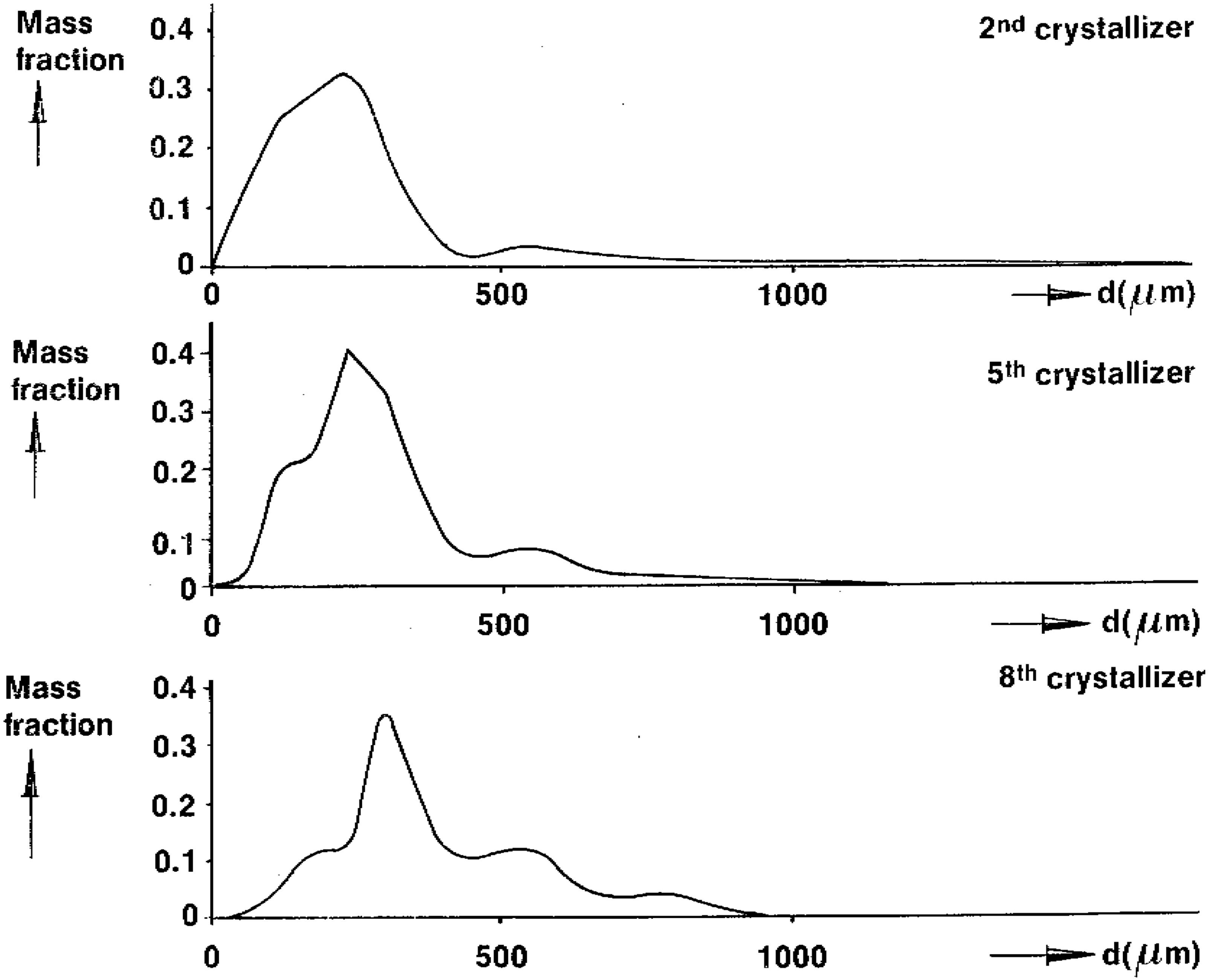
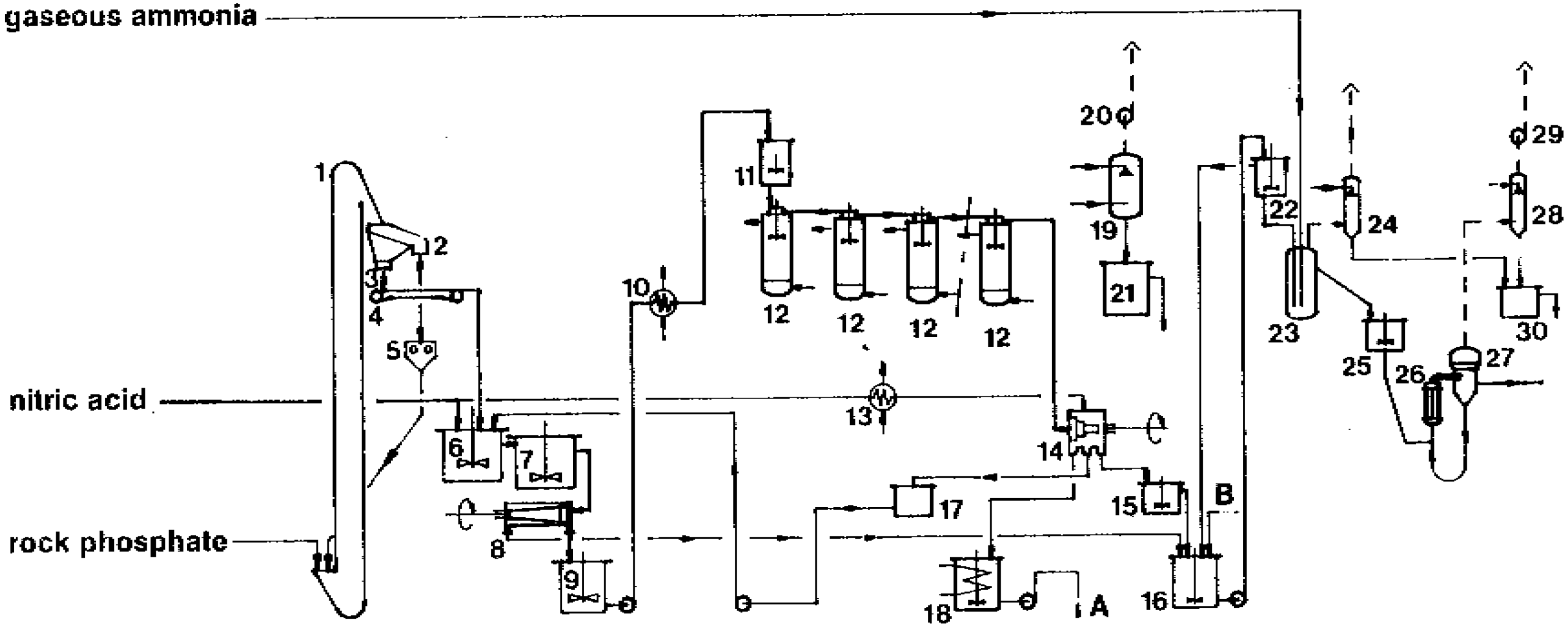


Figure 2

Stamicarbon continuous crystallisation process



1. bucket elevator
2. coarse screen
3. dosing device
4. weighing device
5. crusher
6. 1st dissolving tank
7. 2nd dissolving tank
8. inert centrifuge
9. buffer tank for dissolution liquor
10. cooler
11. head vessel
12. crystallizers
13. nitric acid cooler
14. centrifuge
15. intermediate vessel
16. mother liquor tank
17. washing acid tank
18. melt tank for CN crystals
19. scrubber for exhaust gas
20. suction fan
21. seal pot
22. head tank
23. neutralizer
24. mixing condensor for neutralizer
25. intermediate tank
26. evaporator
27. separator
28. direct condensor
29. vacuum pump
30. seal pot

A. CN solution
B. recycle AN solution

Figure 3

Typical temperature profiles for various crystallisation processes

Continuous crystallisation process A

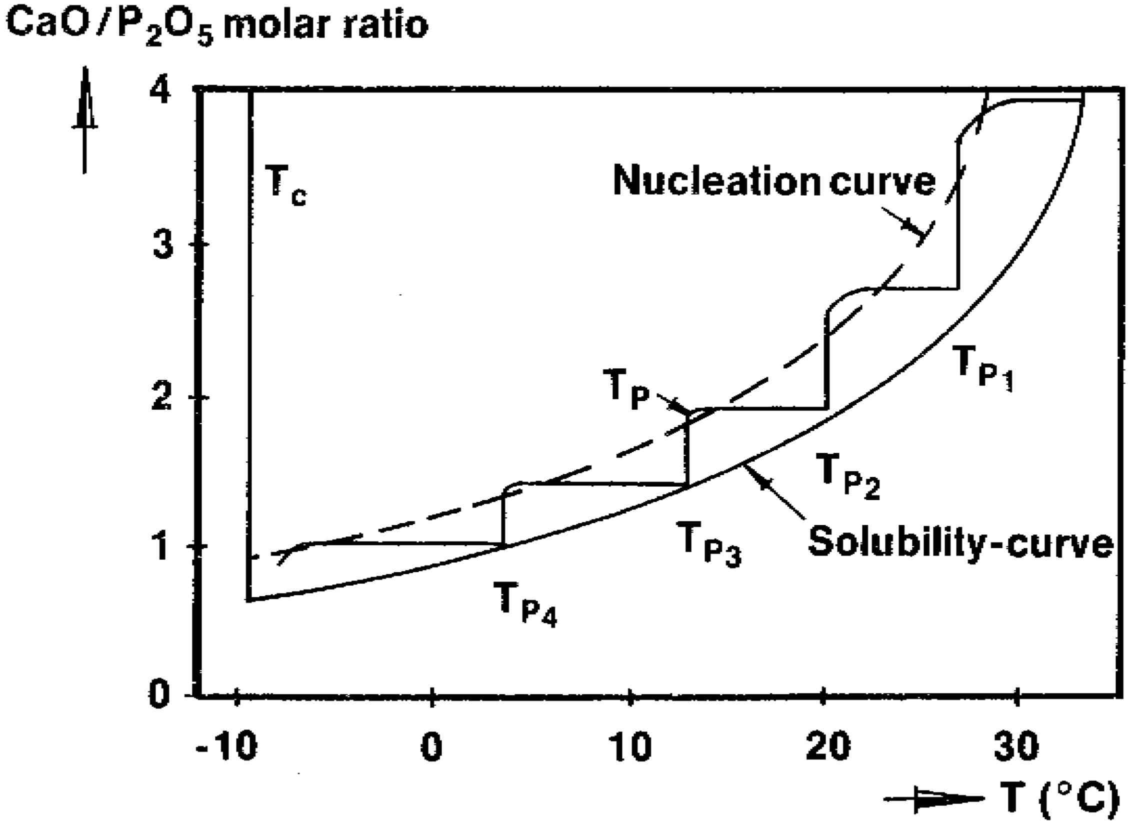


Figure 4a

Continuous crystallisation process without excessive nucleation

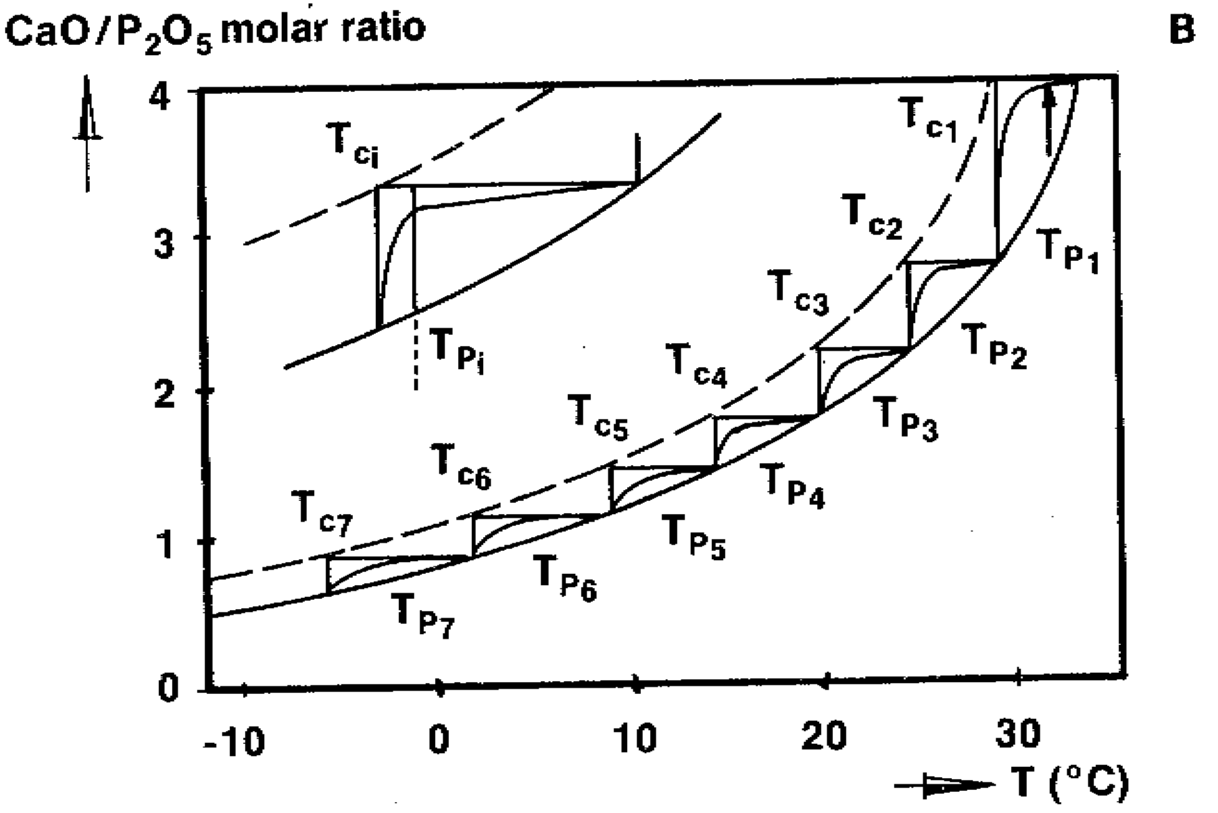
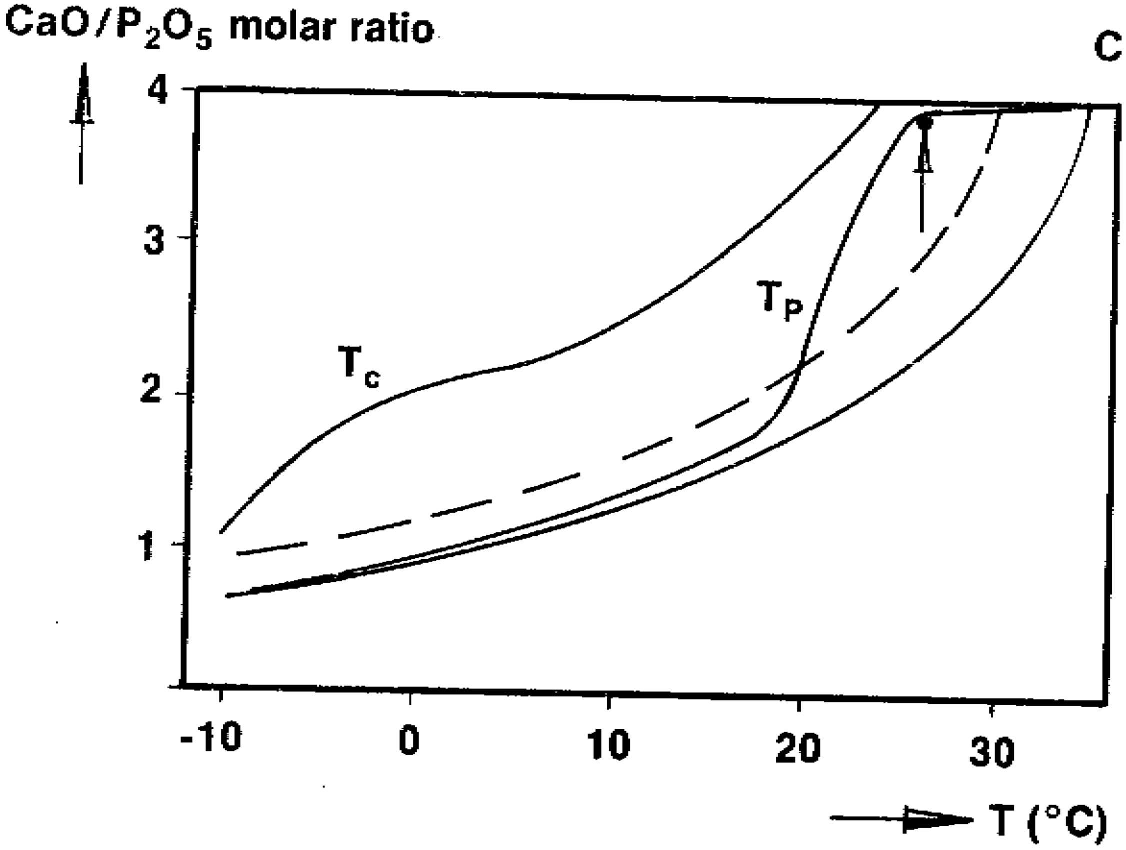


Figure 4b

Conventional batch crystallisation process



Batch crystallisation process without excessive nucleation

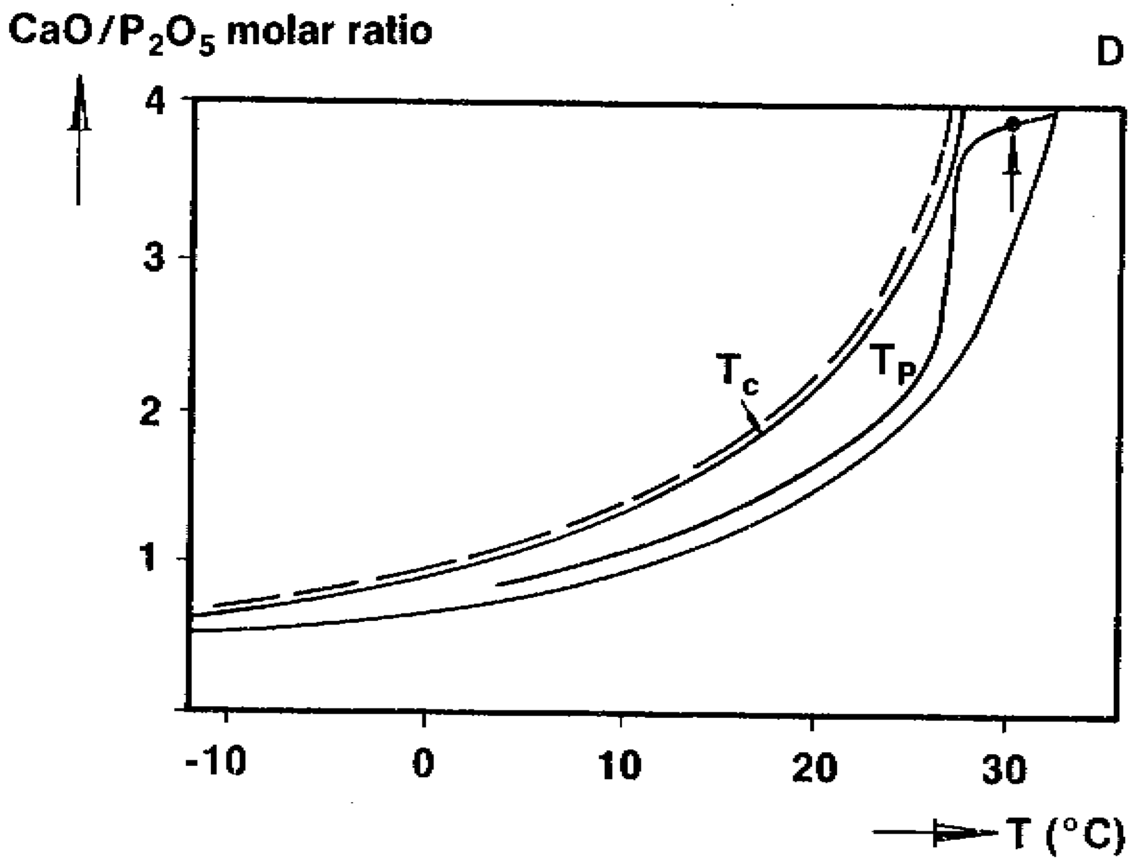


Figure 4d

Solubility and nucleation curves

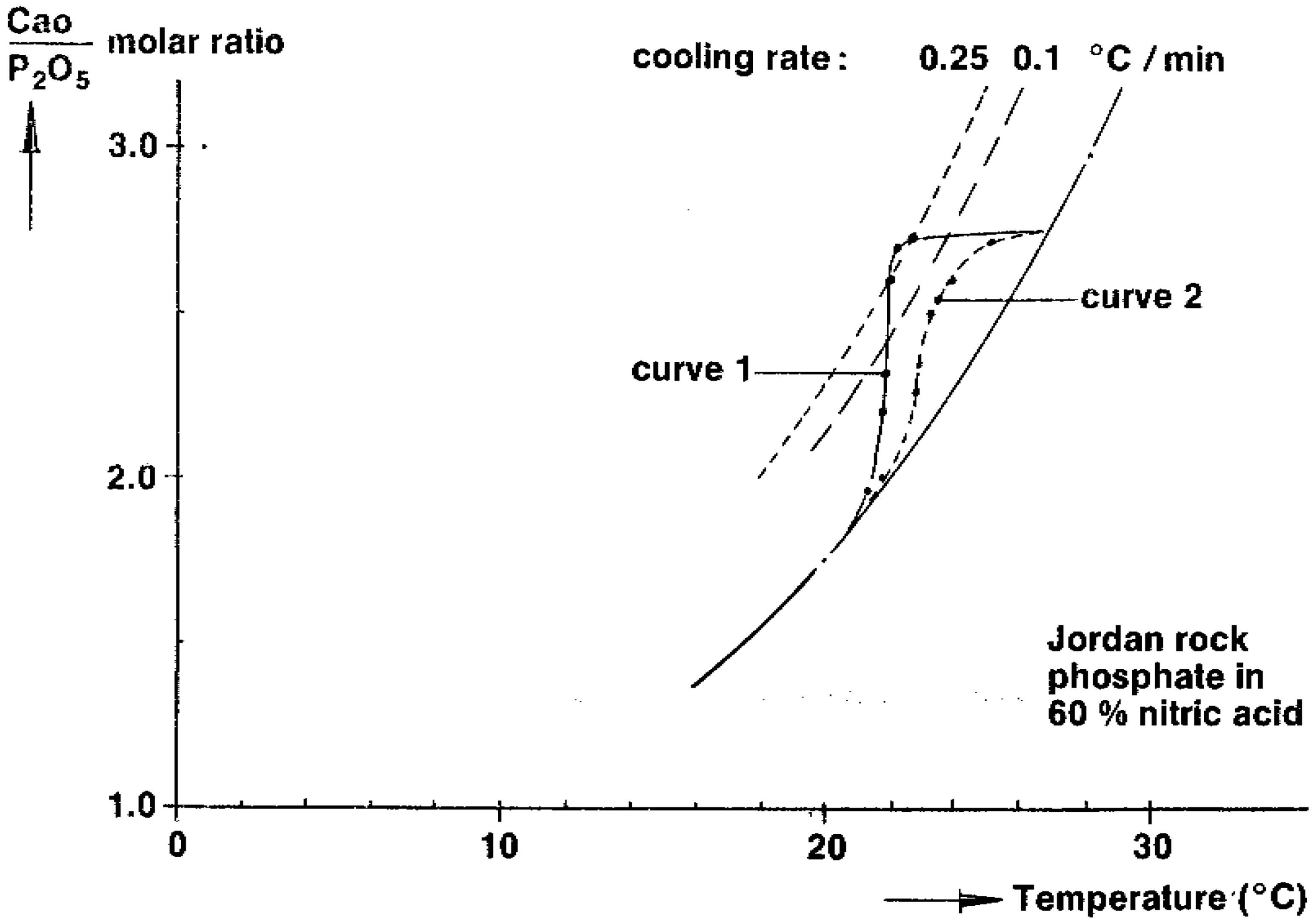


Figure 5

Crystal size distribution, for the batch calcium nitrate crystallisation process

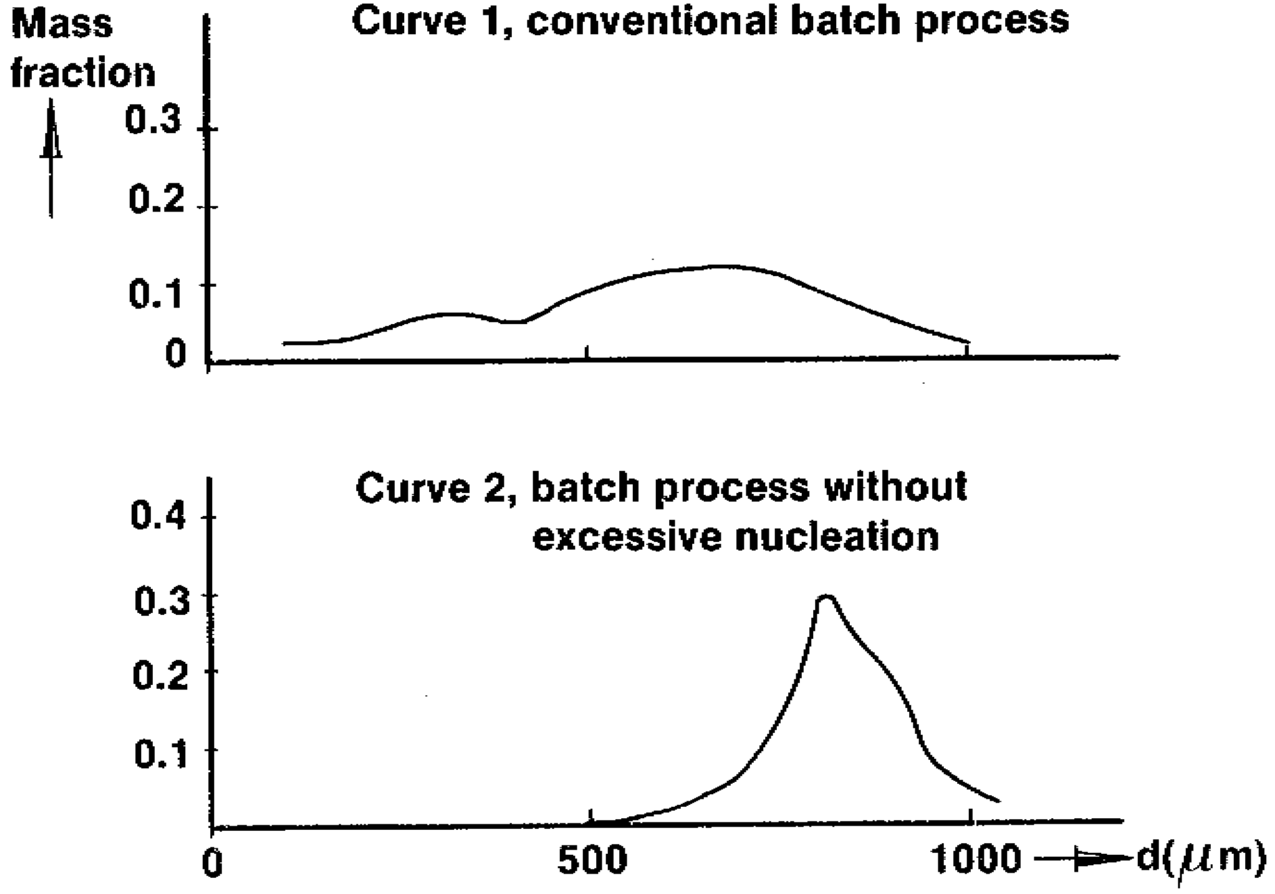
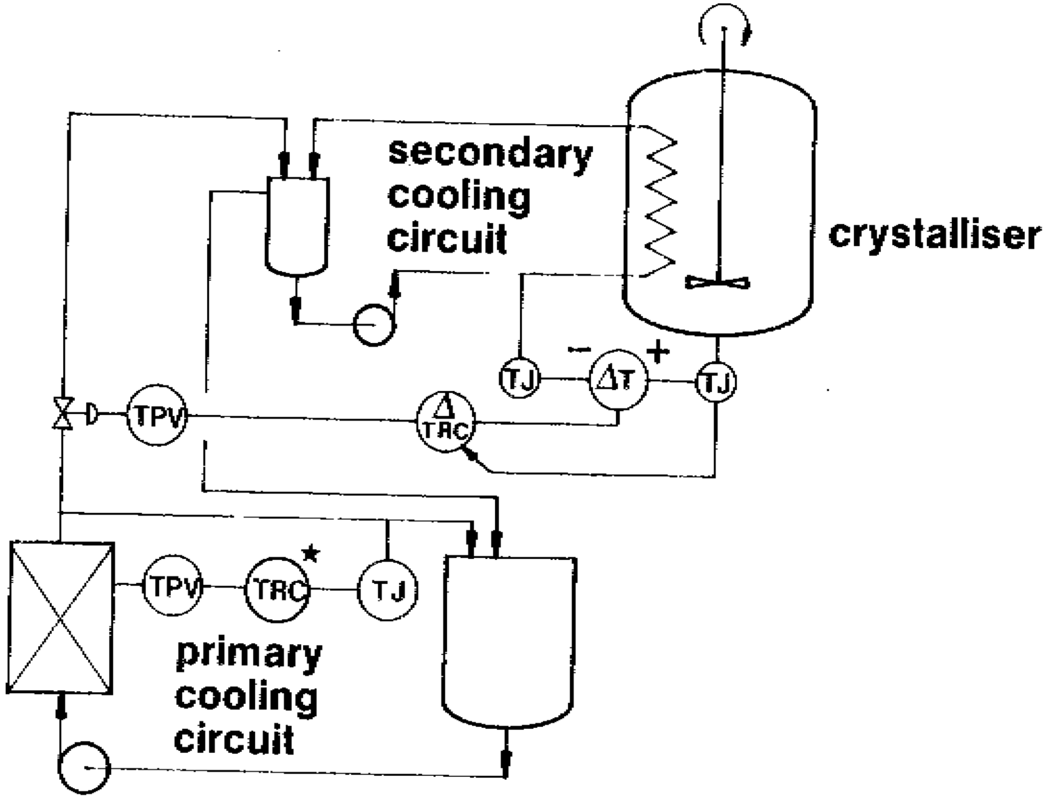


Figure 6

Flowscheme for an ideal batch crystalliser



★ capacity control

Figure 7

Typical temperature-profile for an ideal batch crystallisation process

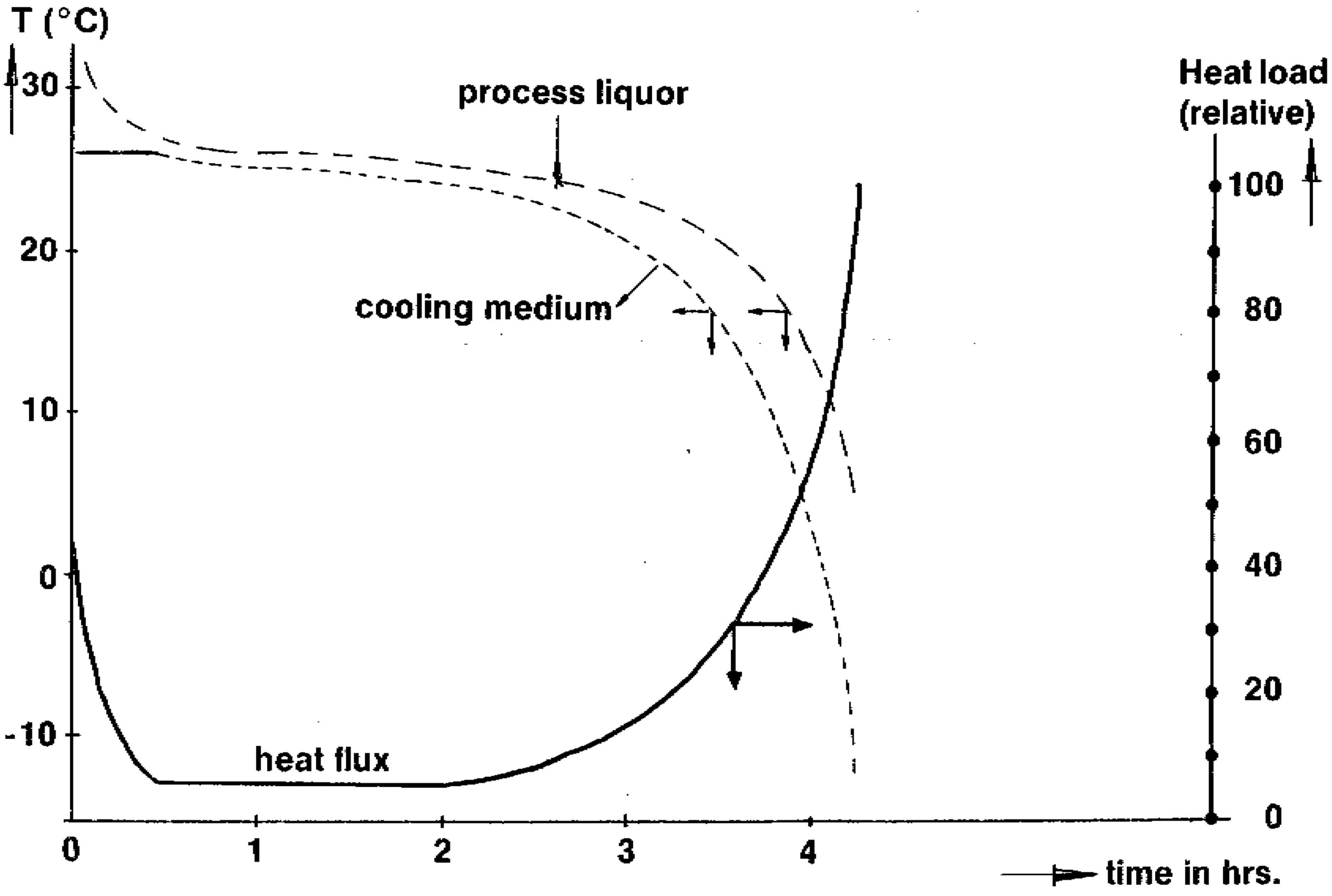
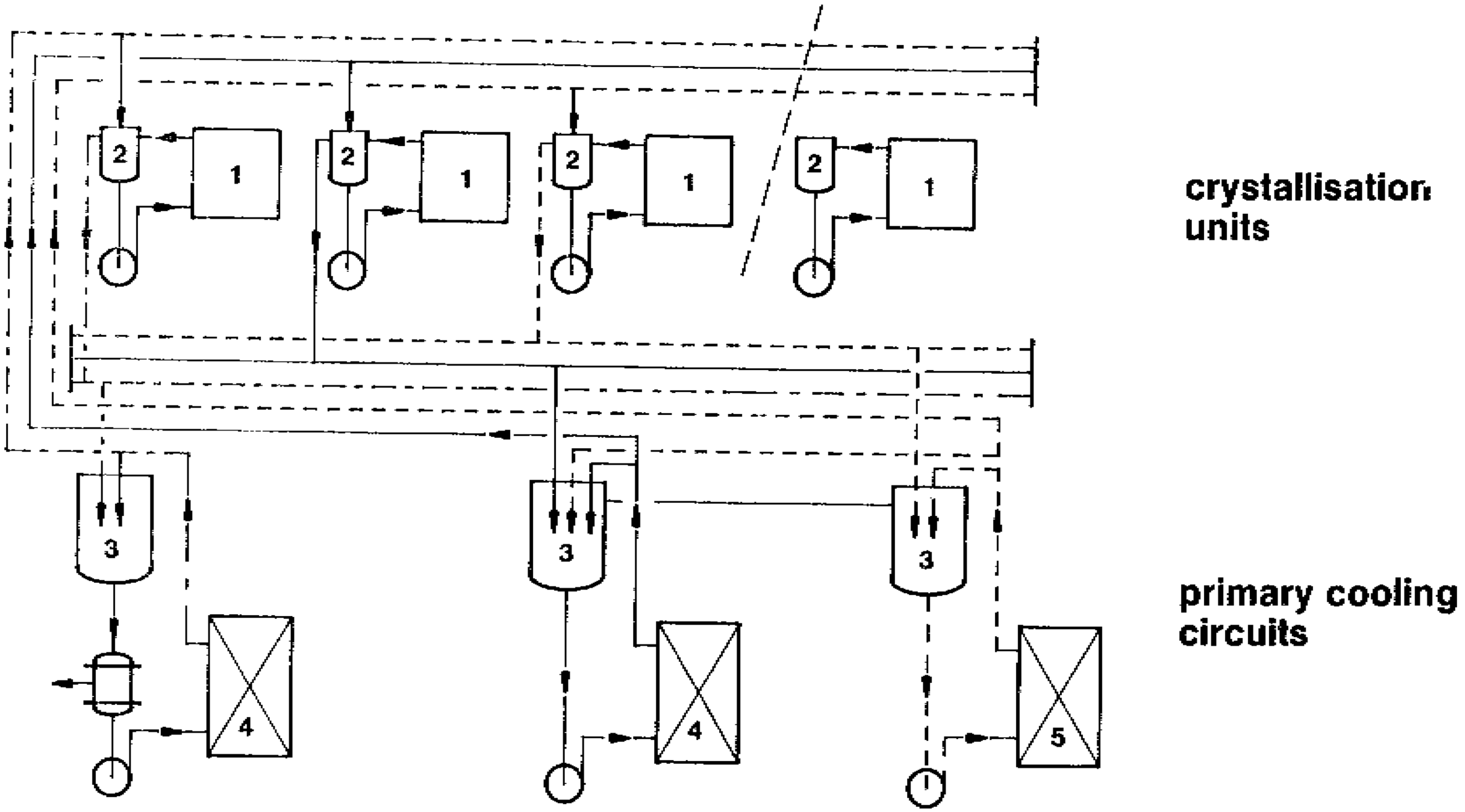


Figure 8

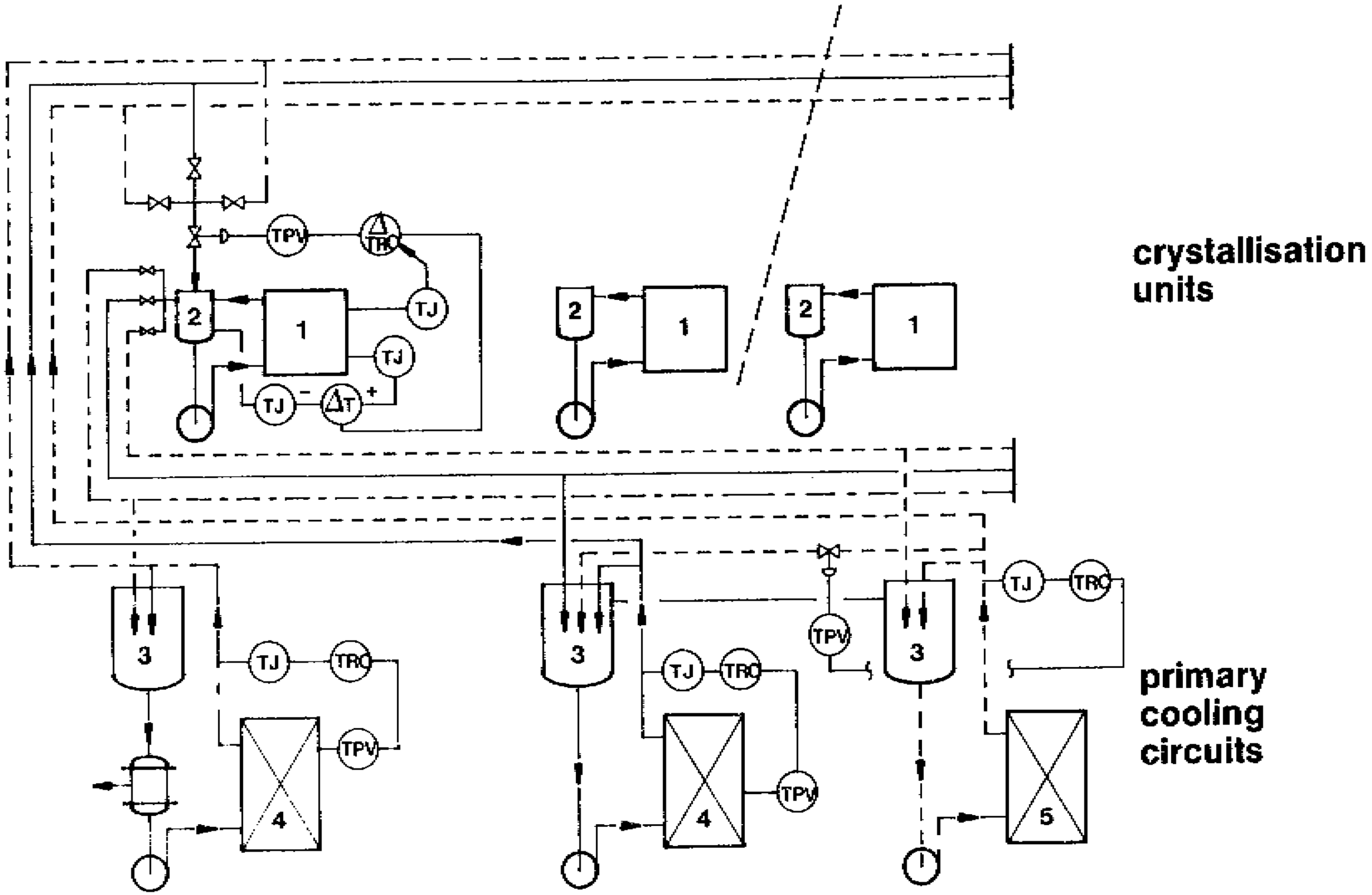
Representation of an integrated batch crystallisation process



1. crystalliser
2. secondary buffer
3. primary buffer
4. refrigeration unit
5. open NH_3-evaporator

Figure 9

Flowscheme for an integrated batch crystallisation process



1. crystalliser
2. secondary buffer
3. primary buffer
4. refrigeration unit
5. open NH_3-evaporator

Figure 10

Typical temperature-profile for an ideal batch crystallisation process

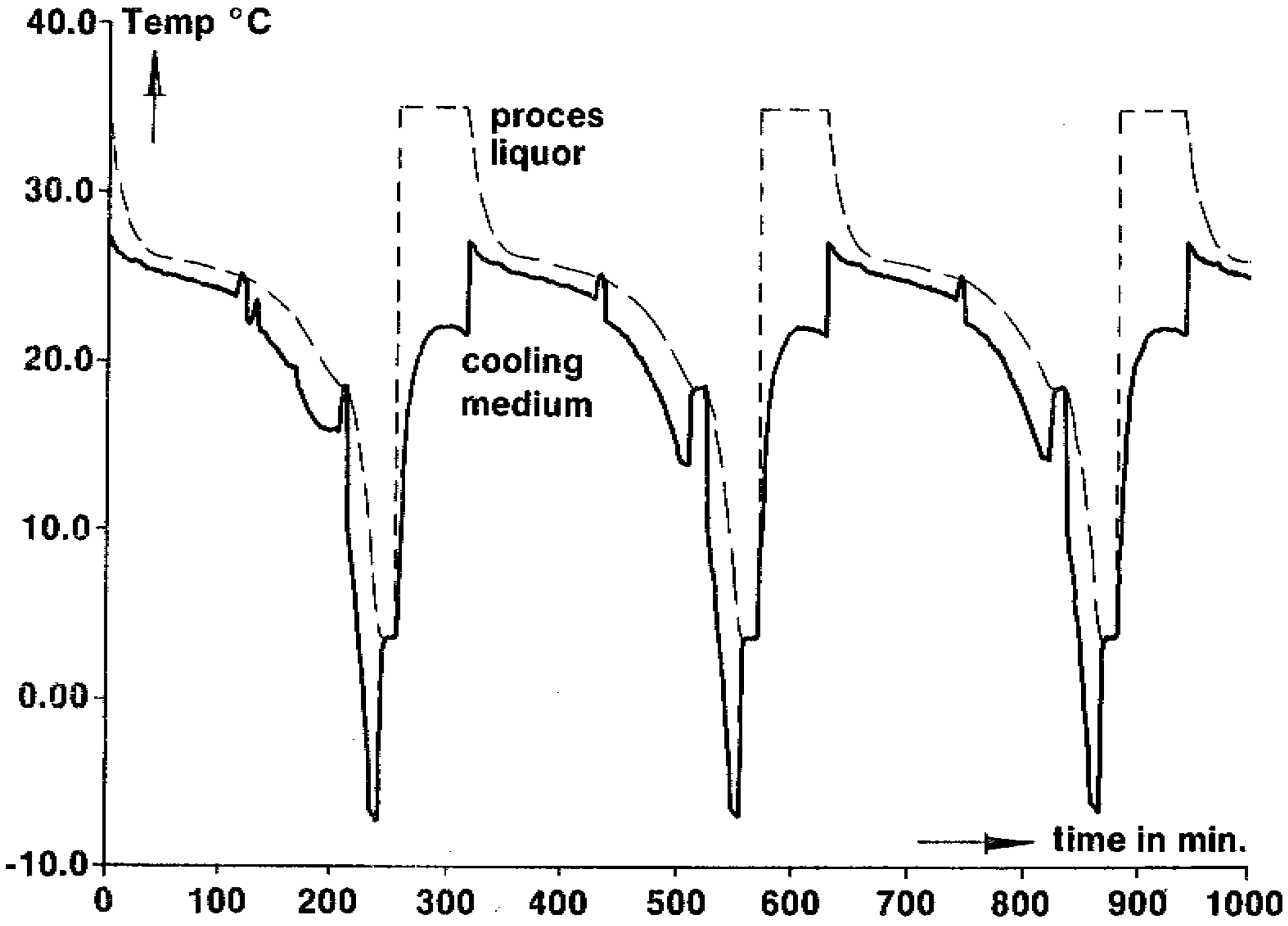


Figure 11

Heat load on various refrigeration units

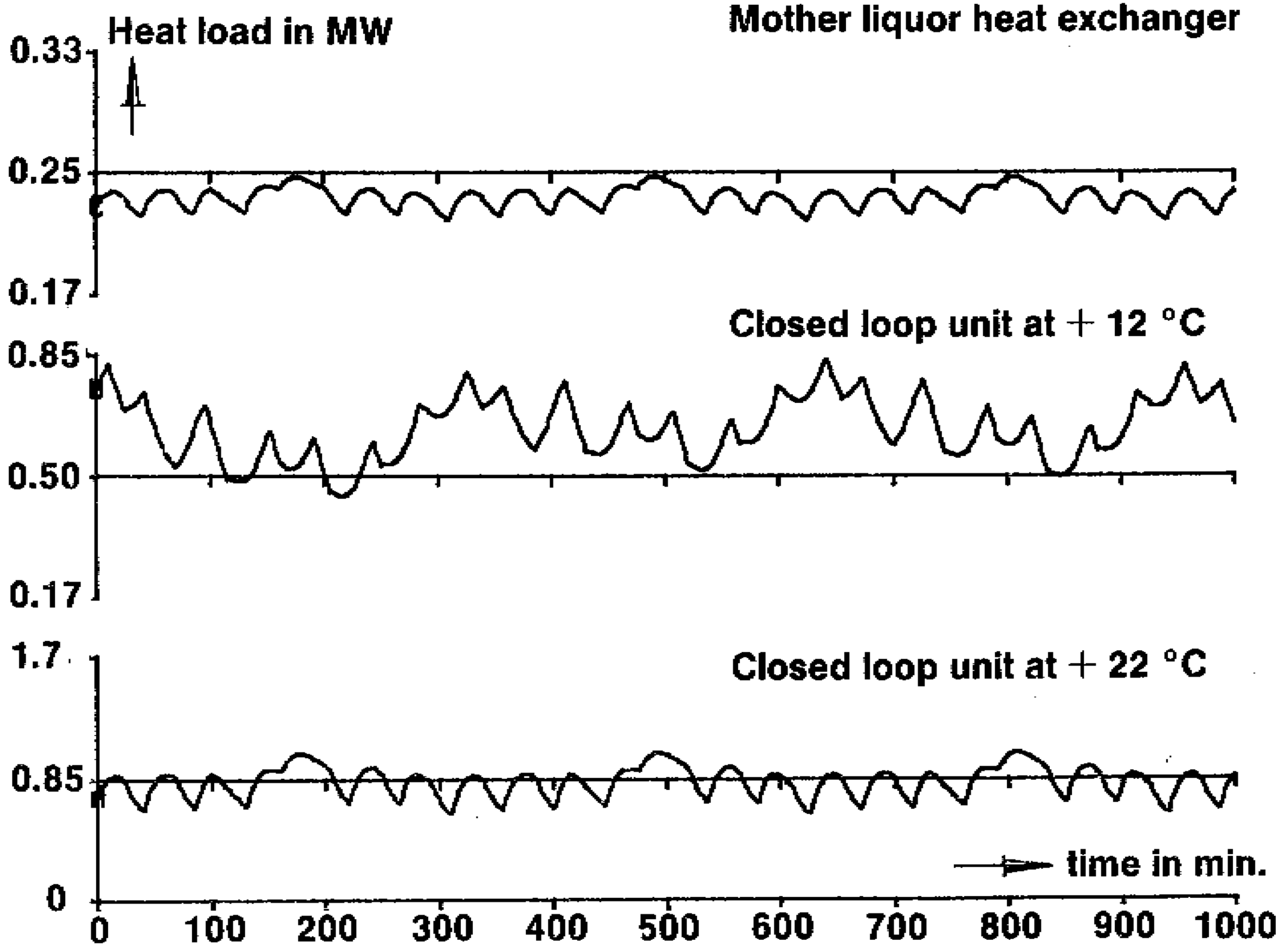


Figure 12

TA/84/19 Significant energy savings in the ODDA process by M.H.G. Jennekens, Stamicarbon BV & G.H.M. Calis, DSM, Netherlands

DISCUSSION: Rapporteurs L.K. RASMUSSEN, Superfos AS, Denmark and B. PERSSON, Supra AB, Sweden

Q - Mr. B.K. JAIN, FAI, India

In the New Stamicarbon batch crystallization process the number of cooling circuits required are more than for continuous process. While integration of the set of crystallizers in various cooling circuits leads to energy savings, the installed costs of equipment may be higher. Some idea of the relative cost of production per tonne P205 may be given for the continuous and the new batch process.

A - The Engineering Department of DSM made an investment estimate of the three variants of the process. It indicates that no significant differences in investment figures, and thus in fixed costs of the product, were noticed.

In my paper I have shown that considerable energy savings may be realized, which of course directly affect the variable costs of the end product. Comparison of the continuous crystallization process with the new batch crystallization process shows that the total price of the end product is 7 US$ per ton of P205 lower.

Q - Mr. G. KONGSHAUG, Norsk Hydro, Norway

Do you find it correct to compare the new crystallization process with existing conventional processes when this is only based on your own tests and your own understanding of the theory?

There are many differences in opinion as to numbers and assumptions in tables 2 and 3.

A - Well, it is not our understanding of the theory but fundamental crystallization theory which we are referring to. I think that, by the two experiments described in the paper, the validity of this theory is demonstrated clearly. Concerning the differences you note, I would like to invite Norsk Hydro to discuss comparable figures extensively on a later occasion.

Q - Mr. L.K. RASMUSSEN, Superfos AS, Denmark

How did you determine the crystal size distribution?

A - The crystal size distribution has been determined in two ways: The first method is to wash and dry the crystals, followed by sieving. The second method is used for a more accurate size distribution. We applied a microscopy technique in which a photograph of a number of crystals is made. The photograph is scanned with a light beam of very precise dimensions. This is done with 16 different beam sizes and results in a very accurate size distribution analysis of the crystals.

Q - Did you install some kind of automatic equipment for on-line analysis of crystal size distribution in your industrial plants?

A - No, we never did and we don't intend to. However, we do intend to install on-line analysis equipment to determine the CaO/P2O5 molar ratio of the process liquor before the crystallization section and, also, to install a microprocessor-based control system in the crystallization unit. This system calculates the temperature profile for a given dissolution liquor based on this CaO/P2O5 molar ratio. With the process as just described to you, we always have the same coarse and uniform crystals.

Q - Mr. A. DUROCHER, BASF, Germany

A question related to maintenance costs. Can you give some indication of the life of the sieves in your two-stage pusher-type centrifuges?

A - Well, the new process, which is based on batch crystallization, results in very coarse and uniform crystals, which can easily be separated by means of a conventional filter. This is what we are going to apply in our process, and certainly no pusher-type centrifuges. So I think the question is not relevant.

Q - Mr. E. AASUM, Norsk Hydro, Norway

On page 10 the theory of conventional batch crystallization is described where the cooling medium passes countercurrently through the crystallizer in the process.

On the basis of your experiments and of application of theory you conclude for several reasons that crystallization behaviour in technical systems can neither be controlled nor predicted.

In the Norsk Hydro nitrophosphate process the batch crystallization is operated with this countercurrent flow of cooling medium and our experience on crystallization behaviour in technical system does not follow your predictions.

There are now 10 commercial units with a total P2O5-capacity of 3000 MT P2O5 per day operating on this principle, the first one being in operation for 10 years.

A - Well, the most recent paper of Norsk Hydro, which was presented at the Fertilizer Round Table in Baltimore, USA, contains an important typing error. If 85% of the crystals is to be removed, the final crystallization temperature should be -5°C instead of the printed +5°C, which proves that our predictions are right. We have no intention at all of condemning the conventional batch crystallization process, we only wanted to demonstrate that considerable improvements of this process concerning energy savings as well as production flexibility can be realized.