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CHECK-UP FOR PHOSPHORIC ACID UNITS

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RESUME

Grâce à l'association de l'expérience de ses quarante années de développement avec l'usage de l'informatique, la technologie de l'usage des minerais de phosphate en vue de la production d'acide phosphorique dispose d'un outil de travail nouveau.

L'examen informatique du comportement des différents minerais au niveau du réacteur phosphorique, surtout au niveau cristallographique, a permis de mettre en évidence un certain nombre de paramètres caractéristiques.

Un examen simple de la bouillie réactionnelle, assisté par un logiciel spécifique, permet de diagnostiquer les anomalies éventuelles d'une unité phosphorique et d'optimiser sa rentabilité.



1. SUMMARY AND CONCLUSIONS

1.1. Check-up and Definition

Phosphoric acid production essentially depends on calcium sulfate crystals separation from acid by filtration. Crystals nucleate (baby crystal birth) and grow within reaction slurry that is continuously produced in the reactor. Nucleation rates, N° , vary widely from one production plant to another: from 2 to over 20 million nuclei per hour and cubic centimeter reaction slurry. Total number for crystals (nuclei and older crystal generations) currently yield between 20 to 70 million/cm³, depending on retention time in the reactor.

Nucleation rates N° , provided they are collected from faultless¹ operations, follow an exponential function of slurry mean retention time, t_m (**Figure 1**). They affect crystal sizing and consequently the filtration quality of the slurry. Thus, N° can be considered as the quality label for its related plant: definition of N° can be regarded as a quick and simple check-up procedure for a phosphoric acid unit.

1.2. The Survey

By initiating a comprehensive crystal size distribution survey including 17 phosphoric acid operations with 7 different process systems and rating from bench scale size up to 1200 t P₂O₅/day, a nucleation rate function $N^\circ = k f(t_m)$ could be established. It could be pointed out that the N° function applies to all types of process systems and equipment examined, in spite of widely differing systems and operating conditions, agitation energies and using unground or ground rock. To eliminate potential side effects related to feed rock qualities, the survey was limited to two consistent qualities².

1.3. Conclusions

1. Mean retention time t_m , via N° , initiates a chain effect:

$t_m \rightarrow N^\circ \rightarrow \text{Crystal size} \rightarrow \text{Filtration}$

¹ "faultless operation": within mechanical and chemical conditions proper to normal production standards.

² Togo and Senegal rock were selected because of their chemical and physical similarity, both mined from large homogeneous deposits such as the survey could rely on minimum side effects due to rock quality interferences.

2. N° can be recognized as a key factor for filtration quality and considered as the "health certificate" for a phosphoric acid processing system. Checking N° towards t_m will be a quality criteria for phosphoric acid plants. Higher nucleation rates than predicted from the N° function reveal the presence of crystallization nuisances and guide for their removal.
3. N° will be a helpful indicator for phosphoric acid reactor or filter sizing and their extrapolation.
4. Specific filtration rates for rock qualities should only be expressed with associated mean retention time t_m .

2. QUALITY CRITERIA FOR PHOSPHORIC ACID PLANTS

Taking rock quality into consideration, a dihydrate phosphoric acid plant using Togo or Senegal rock can be considered satisfactorily performing when the following three criteria are satisfied :

1. Name capacity is achieved or surpassed
2. Product acid concentration 29-32% P_2O_5
3. Recovery yields 95.5-97%

Top conditions for the three criteria essentially depend on filtration quality of the gypsum cake.

Filtration quality is affected by what we commonly call crystallization quality, the latter being related to crystal size and size distribution.

"Good" crystal quality is achieved when impregnating phosphoric acid liquor is easily and thoroughly removed from the gypsum cake during filtration operation, leaving few impregnation losses (0.5%, or at the least less than 1% average).

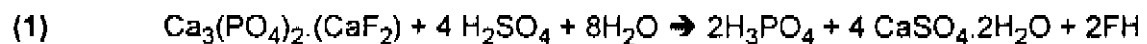
Such conditions usually occur :

1. When surface/volume ratios of the crystals are low (large sized crystals);
2. When crystal shapes (cluster type or thick rhombic type) permit wide capillary channels through-out the cake layer and offer easy liquid drainage.

In general, crystal shape is imposed by the raw material and the manufacturer has to cope with it. But for all qualities, the size of the crystals can be controlled and optimized to obtain the best of the filtration conditions compatible with the crystal shape.

3. FACTORS GOVERNING CRYSTAL GROWTH: G_n .

Phosphoric wet process acid plant operate with large agitated reaction tanks. The function of these tanks is to mix the reactants, to perform the chemical reaction and to achieve optimum crystal growth for best filtration conditions according to the simplified reaction :



As a general rule, phosphoric acid producers creates the best mixing conditions of the reactants with the reaction slurry to control supersaturation and as such nucleation should be maintained at lowest levels.

To limit supersaturation within mixing and reaction areas, large tanks with high flow agitation or interconnected multi-tank systems with high circulation flow in-between tanks have been designed. Supersaturation will be affected by the ratio: (slurry production / reaction volume).

Crystals, provided they remain in supersaturated slurry suspension, sustain their growth. It could be pointed out that their size essentially depend on their residence time in agitated slurry with controlled supersaturation. With smaller reaction volumes higher supersaturation will take place, higher nucleation rates N° will occur. This reduces crystal sizes and consequently filtration quality.

It could also be demonstrated that filtration quality of gypsum cakes essentially depend on the percentage of the smaller sized crystals (below 40 microns). A filter cake with only 20% of material sized minus 40 μ will show 50-60% improved filtration rates when compared with a cake (originating from the same ore) but containing 40% minus 40 μ sized material.

Increased feed ratios with associated supersaturation increase both crystal growth and nucleation rates. Nucleation rates however, being governed by an exponential function, will have the dominant effect.

4. NUCLEATION AND CRYSTAL GROWTH

A phosphoric acid reaction system consists of an agitated, steady outflowing slurry volume. The phosphate rock and sulfuric acid added to the system create supersaturation which becomes the driving force for both nucleation and crystal growth. Nucleation, the birth of baby crystals, requires higher energy levels (thus higher supersaturation levels) than crystal growth. Passing a certain supersaturation threshold, nucleation will increase exponentially.

To achieve large crystals, we have to control low nucleation rates. The more crystal babies we create, the more babies we have to feed, the smaller will be the individual crystal size.

At first sight crystal growth equation depends on three variables :

1. Mean Residence Time : t_m
2. Crystal Growth Rate : G_h
3. Nucleation Rate : N°

In fact as it will be seen, there is only one variable : both N° and G_h are effected by t_m .

4.1. Mean Residence time: t_m

Among the three listed variables affecting crystal growth, mean residence time t_m is the one that can be directly calculated from plant characteristics (reaction volume) and operating conditions (feed rate and solid contents) (Figure 2).

Since the reaction system operates continuously by overflow feeding the filter, mean residence time for the crystal population, t_m , is the result of the ratio :

$$(2) \quad t_m = \frac{\text{Reaction Volume}}{\text{Slurry Flow to Filter}}$$

As an example: for 500 t P_2O_5 per day reactor, with a reaction volume of 1000 m^3 , pumping every hour 180 m^3 of slurry to the filter, mean residence time t_m will be :

$$t_m = 1000/180 \approx 5.56 \text{ hours}$$

Similarly, every hour, 180 crystals out of 1000 leave the system.

After $t = 5.56$ hours or one residence time period, 62% of the original crystals born at time $t = 0$, have left the reactor. This 62% number related to one residence time remain constant whatever the feed ratio.

But residence time t_m of the crystals is not only a function of reactor size and rock feed, it is also a direct function of the solids content of slurry. There will be less slurry produced when the solids content is high, with higher solids content, there is higher residence of growth time and bigger crystal sizes result. Operating slurries with 32% crystals by volume instead of 20% means to increase residence time by 60% as demonstrated by the following table applied to a 1000 m³ reaction volume producing 500 t/day P₂O₅ from 80 BPL rock:

Table 1 - Mean Residence time t_m , Function of Solids Content
(Related to Case Study of Equation 2)

Vol % solids	t_m	Slurry m ³ /h	m ³ /t P ₂ O ₅ (reaction vol)	kg Gypsum pptd per m ³ slurry/h
20	5.5	182	2	84
22	5.1	165	2	84
24	6.6	152	2	84
26	7.1	140	2	84
28	7.7	130	2	84
30	8.3	121	2	84
32	8.8	113	2	84

From above table, it can be seen that mean retention time t_m and other currently used volumetric ratios like m³/t P₂O₅ per day ratio or precipitated calcium sulfate per reaction volume are not within stable ratios.

There is however an upper limitation for solids in slurry because of the rheological properties. The limitation is affected by crystal shape. For Togo and Senegal rocks, it is up to 32% by volume.

4.2. Crystal Growth G, Growth Rate: G_h :

From the time crystals have nucleated, they grow until they leave their supersaturated reaction slurry medium.

Crystal growth rates, (G_h) has a function of time, are almost a linear function. Crystals are supplied with growth material (Ca⁺⁺ and SO₄⁻ ions) via liquid/solid transfer. Suspended in the agitated slurry, crystals are subject to differential solid/liquid settling speed that promotes transfer rates for growth material from mother liquor towards the solid phase. Larger crystals having higher sedimentation speeds are subject to higher material transfer coefficients and collect more growth feed per time unit. However, this growth increment being relatively small within the range of the 0-60 μ sized crystals, we can use for the purpose of this study the more simple conception of a linear growth rate function. We then will write for crystal size as a function of time:

$$(3) \quad D = f(G_h t_h)$$

D: for crystal diameter; G_h : linear growth rate in μ/h; t_h : for crystal growth time in hours.

This direct function (3) is of great advantage when tracing crystal size distribution diagrams because the X axis can represent simultaneously the two parameters: time (t) and crystal size (D).

Crystal growth rates G_h will be calculated from crystal size distribution diagrams currently resulting from screening analyses. Such diagrams display crystal size distribution as weight percent, (from 0 to 100%), expressed as a function of crystal width in microns along the X axis of the diagram. They show shaped curves as depicted on Figure 3.1.

This diagram, which is the integrated presentation of the individual size fraction diagram **Figure 3.2.**, offers interesting characteristics:

The inflexion point of the S curve is always located on the intersection with the horizontal 35.5% co-ordinate. This intersection also locates the dominant size generation³. The vertical co-ordinate to this intersection hits the X-axis at a crystal size corresponding precisely to a growth time of 3 mean residence time (3 x t_m); see **Figure 4**. These numbers are constant characteristics for all diagrams.

This 35.5% crossing point at 3 t_m locates precisely the inflection points precise location and consequently permits to calculate growth rate G_h :

$$(4) \quad G_h = (\text{crystal size at 35.5\% crossing}) / (3 \times t_m)$$

Crystal growth rates, G_h , yield currently 2-4 μ /hour by width in systems operating within 3-6 hours mean residence time t_m .

4.3. Nucleation, Nucleation Number N° :

N° is the number of crystal nuclei created within the slurry. They are normally generated by supersaturation resulting from phosphate rock dissolution and sulfuric acid addition to the reaction slurry.

Nucleation N° are expressed in million of nuclei per cm^3 reaction slurry and per hour; currently N° represents between 2 and 15 million nuclei/ cm^3 -hour

High nucleation results with smaller crystal sizes. Large crystal sizes will be obtained by controlled low nucleation rates. As we are demonstrating, the dominant factor to control nucleation is mean retention time t_m .

Both nucleation rates (N°) and growth rates (G_h) are calculated from crystal size distribution diagrams. The basic crystal growth equation is:

$$(5) \quad N^\circ f_v \int_{t=0}^{t=15t_m} (E_h)^t (G_h t)^3 dt = (\text{Vol \% solids}) 10^{10}$$

where:

N° : expressed in nuclei per cm^3 -hour;

f_v : volumic shape factor of the crystals;

E_h : hour-based extinction factor;

G_h : growth rate (μ /hour);

t_h : time in hours;

Vol %: volume % of crystals in slurry.

With $t = 15 t_m$, integral is equivalent to 100% of a crystal population volume.

The volumic shape factor, f_v is empirically estimated from microscopic crystal shape metering, it represents:

$$(6) \quad f_v = (\text{Volume of crystal in } \mu^3) / D^3$$

where D: screening diameter of crystals. Volumetric shape factors are to compensate the different shapes of crystals occurring with phosphogypsum calcium phosphates (**See also Figure 5**).

³ Dominant crystal size generation: crystal generation where individual volume x number = maximum.

E_h , the hour based extinction factor of the reaction system is derived from reaction volume V (in m^3) and filter feed rate $v/60$ in m^3/minute : (minute flow integration is needed for sufficient accuracy).

$$(7) \quad E_h = (V - v/60/V)^{60} \quad (\text{See also Figure 2})$$

Equation (5) is the basic formula for the typical S shaped size distribution equation presented in Figure 3.

By using equation (5) we now can calculate N° :

$$(8) \quad N^\circ = \frac{10^{10} (\text{Vol \% solids})}{f_v \int_{t=0}^{t=15t_m} (E_h)^t (G_h t)^3 dt}$$

Equation could be confirmed within ranges: $t_m = 2$ and $t_m = 8$

5. PLANTS RESULTS - NUCLEATION DIAGRAM

By investigating crystal size diagrams (by screening) for the 17 different phosphoric acid operations, we calculated for each case nucleation number N° and crystal growth G_h .

We could then plot consistent diagrams for both nucleation numbers N° and crystal growth rates as function of mean retention time t_m .

The different plants were all processing Togo or Senegal rock but operated with differing parameters: ground or unground rock, dry or wet feed, return acid mixed or crude sulfuric acid feed, multi or single tank, high or low recirculation (within 7-40 filter feed ratios), reaction temperatures between 75 to 90°C, agitation energy input between 0.35 and 2 kW/ m^3 and product acid strength between 26 to 32% P_2O_5 .

Operating conditions and characteristics of the reference plants and bench-scale used for the purpose of this study are listed in Appendix 1.

Diagram (Figure 6) presents plotted nucleation numbers N° for each plant as a function of mean retention time t_m .

For the diagram, it can be seen:

1. Nucleation numbers N° , even so originating from differing process systems and operating conditions (Appendix 1), could be closely lined up along an exponential curve which is controlled by mean retention time t_m .
2. Nucleating function $N^\circ = f(t_m)$, increases at slow pace when retention time t_m moves from 9 to 6, it skyrockets when t_m reaches 5 and less.

The t_m 5-6 hours threshold area corresponds to a calcium sulfate dihydrate crystallization rate of 100/120 kg/ m^3 reaction slurry). From literature (Ref. 1, 2), we know that crystallization-rates above the 120 kg/ m^3 mark enhance strongly nucleation.

With increasing nucleation, filtration rates decrease, as can be seen from the related curves from the diagram (Figure 7).

Crystal growth rates G_h appears as an nearby linear function of t_m , that can be expressed within $t_m = 2$ and $t_m = 8$ as:

$$(9) \quad G_h = 4.2 - 0.47 (0.959^{t_m-2}) (t_m - 2)$$

G_h expressed in μ/hour (Figure 7)

6. COMMENTS ON NUCLEATION DIAGRAM

Nucleation diagram was plotted on the basis of faultless monitored phosphoric acid and bench scale units.

The 17 consistent nucleation and growth-rate assessments include widely different dihydrate systems: Prayon Mark 2, Mark 4, Rhône-Poulenc, Nissan Dihydrate, Bader Isothermal, Cofaz Multi-tank, Single tank bench scale units, with different agitation devices and energy inputs. Smallest recirculation rate for multi tank plant registered was 7 to 1 (recirculation-flow/filter feed).

In spite of the listed differences, all nucleation numbers N° follow very closely the exponential nucleation function $N^\circ = f(t_m)$.

Growth rate function G_h being a direct function of t_m (Equation 9) we can replace G_h from equation (8) by equation (9). But also, extinction factor E_h , being a function of t_m , can be replaced:

$$(10) \quad E_h = (1 - 1 / (60 t_m))^{60 t}$$

and eventually equation (8) becomes:

$$(11) \quad N^\circ = \frac{10^{10} (\text{Vol \% solids})}{f_v \int_{t=0}^{t=15 t_m} (1 - 1 / (60 t_m))^{60 t} (4.2 - 0.47 (0.959^{t_m-2}) (t_m - 2) t)^3 dt}$$

For $t=0$ to $t=15 t_m$ integration (100%) of the crystals) we can write:

$$(12) \quad N^\circ = \frac{\text{Vol \% } 10^{10}}{5.9 f_v (t_m)^4 (4.2 - (0.47 \times 0.959^{t_m-2}) (t_m - 2))^3}$$

By equation (12), it is clearly demonstrated that nucleation number N° is a function dominated by a single parameter: Retention time t_m .

This phenomenon can be explained by following arguments:

1. Nucleation, considered within the operating units of this study, is essentially effected by supersaturation, the latter being a function of retention time as demonstrated. Surprisingly, other factors like those to be related to the listed process systems, operating conditions and equipment or reactor types are of negligible effect.
2. With shorter retention time, higher supersaturation enhances both growth rate and nucleation. However, beyond $t_m = 5$, growth rates can no more balance the effect of increasing feed rates and nucleation N° is then forced into exponential increments.

3. Crystal growth rates G_n in suspended slurries are only moderately affected by supersaturation and settling speed. Agitation energy, once suspension energy is reached, no longer affects growth rates G_n .

REFERENCES

1. Sven Eric Dahlgren-Chemistry of Wet-Process Phosphoric Acid Manufacture. Slack, Phosphoric Acid, Part 1, page 96, Marcel Dekker NY.
2. P. Becker, Phosphates and Phosphoric Acid, page 93, Marcel Dekker NY.

Appendix 1

Reference Plants used to establish Nucleation Diagram.

Plant	t m	$\mu/3tm$	Eh	Gh	$N^{\circ} \times 10^6$	%solids
1	1.72	30	0.5570	4.50	115.0	28
2	3.0	33	0.7159	3.67	20.22	25
3	3.05	33	0.7198	3.61	19.11	25
4	3.60	36	0.7570	3.33	13.04	25
5	3.82	33	0.7696	3.14	12.17	25
6	3.85	37	0.7708	3.20	13.93	31
7	4.0	37	0.7784	3.16	9.90	25
8	4.12	39	0.7841	3.15	10.58	29.5
9	4.16	41	0.7862	3.28	7.60	29
10	4.3	41	0.7927	3.18	7.27	25
11	4.9	45	0.8170	3.06	4.85	26
12	5.0	44	0.8185	2.93	5.12	25
13	5.3	48	0.8278	3.02	4.16	28
14	6.15	48	0.8497	2.60	3.46	27
15	6.66	50	0.8627	2.50	2.44	25
16	6.83	46	0.8636	2.25	2.88	22
17	8.8	44	0.8925	1.67	2.89	25

Plant	Grind	t °	R-Vol.	Recy	kWh/m ³	%P205	t/day
1-T	yes	-	4.5 lit	SingT	2	-	BS
2-T	no	78	-	-	-	28	BS
3-S	yes	90	9.4lit	-	2	-	BS
4-S	no	90	231	1800	0.75	28	180
5-S	yes	-	420	SingT	0.41	28	300
6-T	no	80	1000	4240	0.51	30	1000
7-T	no	78	9.4 li	S	-	-	BS
8-S	no	85	1000	4240	0.51	29	800
9-T	no	80	-	SingT	2	29	BS
10-S	no	-	1800	SingT	0.35	28	1200
11-T	no	-	900	-	-	29	660
12-T	no	78	-	SingT	2	30	BS
13-T	yes	-	1320	8250	0.60	32	820
14-S	no	-	1320	8250	0.60	28	650
15-S	yes	82	1200	SingT	0.35	28	480
16-T	no	-	2000	12000	0.60	26	800
17-S	no	-	1700	3700	0.65	26	600

BS =Bench Scale Operation

Figure 1

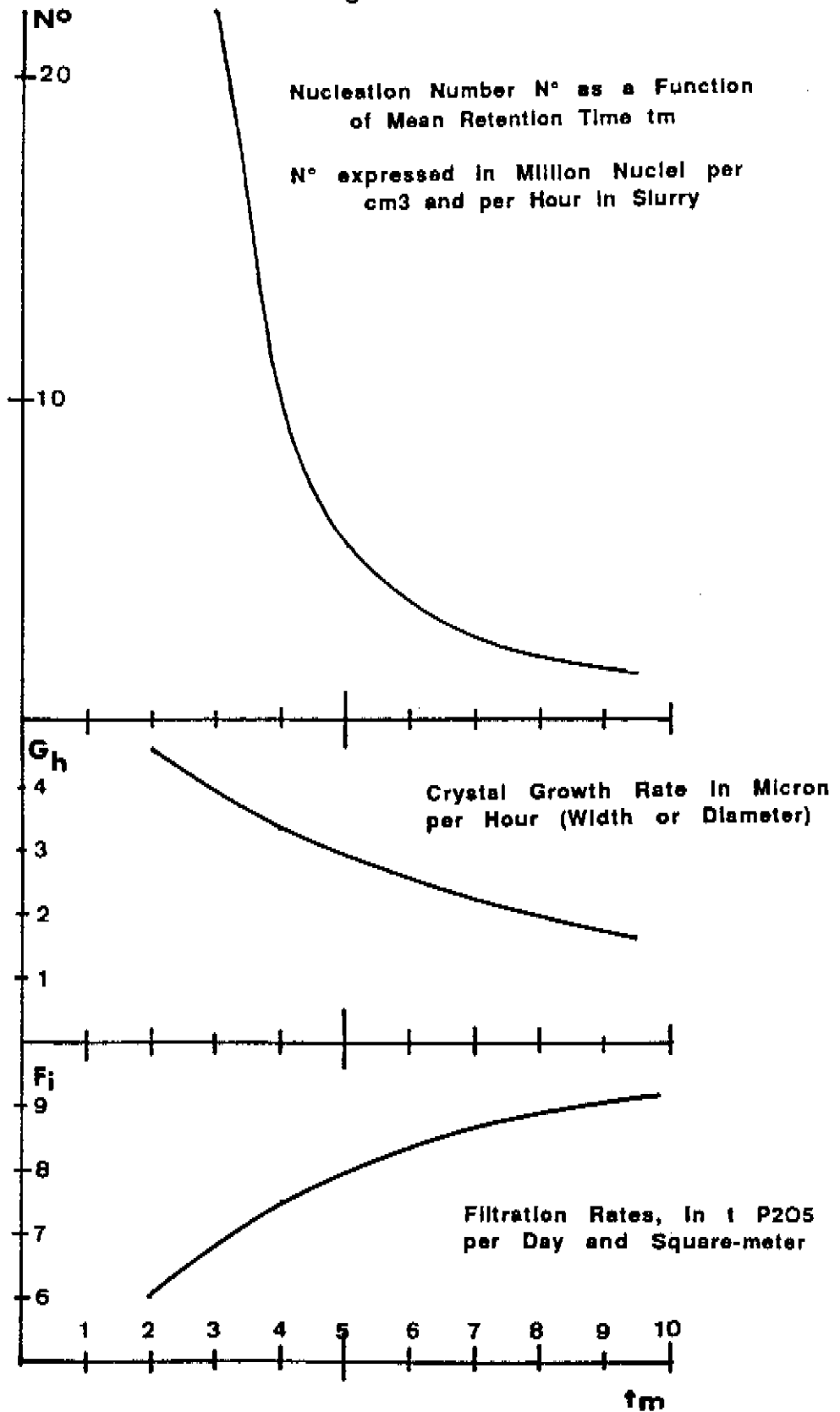
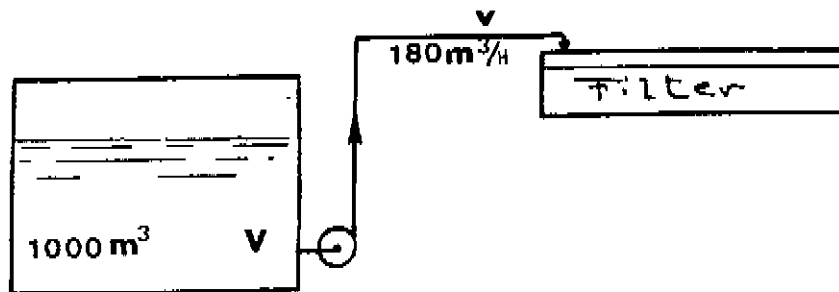


Figure 2: Mean Retention Time, t_m 

$$\frac{V}{v} = t_m \text{ expressed in hours}$$

for depicted case

$$\frac{1000}{180} = 5.56 \text{ hours}$$

Figure-1: Mean Retention Time. By continuous nucleation and simultaneous overflow elimination, a crystal population can be compared with human world population. The largest generation by number are the new borns. But very many are eliminated by various causes before they grow up. Same happens for crystals: because of the overflow rate to the filter, after one mean residence time t_m , only 37% of the original generation population are still in the reaction system.

After 3 t_m , there are only 5% left, and after 5 t_m there are less than 0.7%.

But due to the uninterrupted growth rate, the 0.7% by number represent 7% of the crystal weight or volume %.

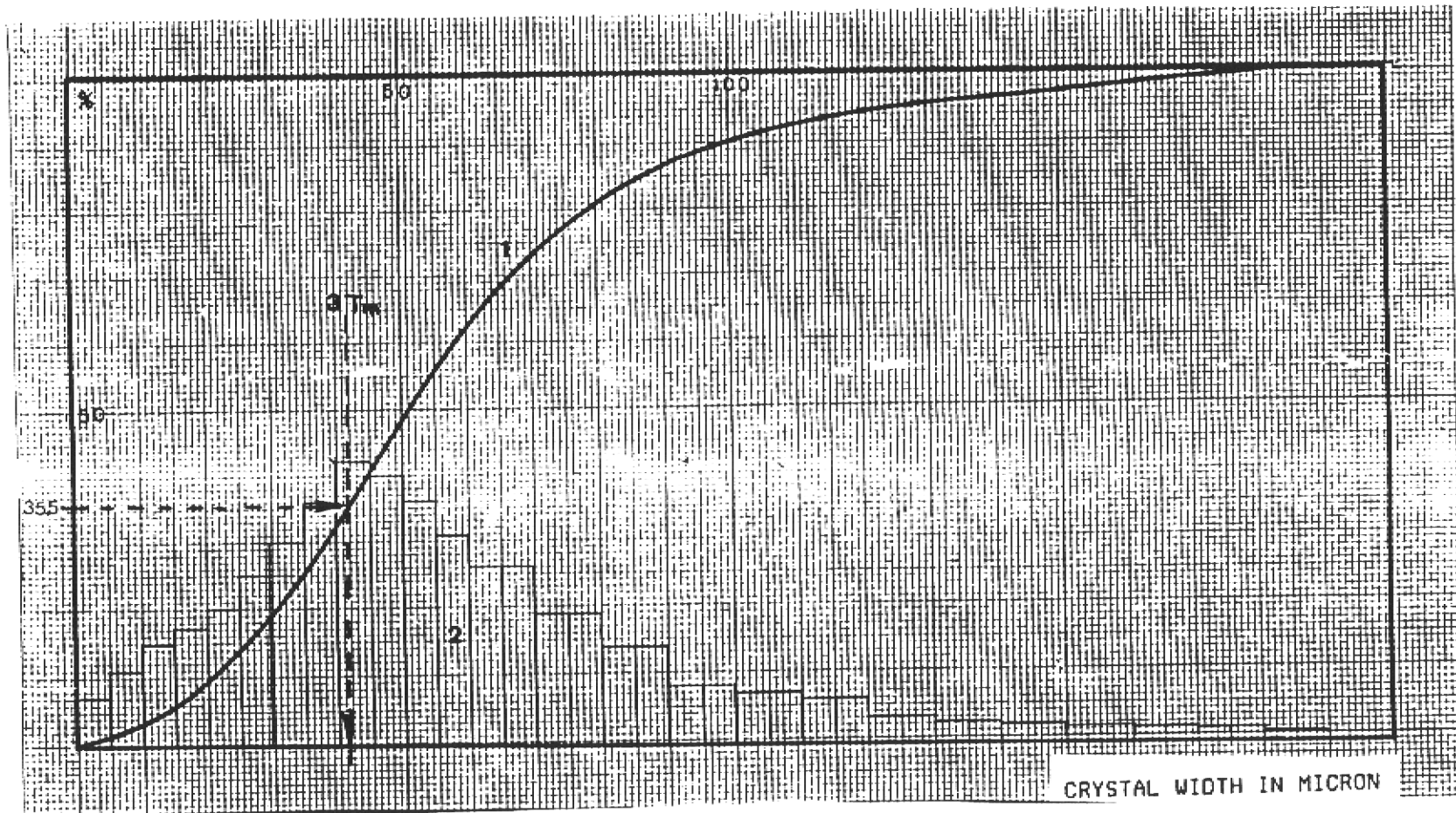


Figure 3: Typical Crystal Size Distribution Diagram

S-line 1: Such diagrams are resulting from washed and dried filter cake screening, weighing and cumulating oversize fractions. X axis indicates the width of rhombic crystals and tabular crystals, or diameter when they are cluster shaped. Y axis indicates the percentage from 0 to 100% (longish crystals go through mesh by width).

The surfaces, 2, represent the respective weight % of the crystal generation sized between the 5μ spaced vertical lines. Each 5μ square stands for 1 weight-% of the total solids.

The first 5μ generation counts for 0-5m sized crystals and there are 12 millions in one cubic centimeter for our presented case. At the inflexion point of the S curve, (35.5 weight %) the dominant crystal generation appears: it is the generation where the product: number \times size = max. In case of Fig 1 with a diameter between 40 and 45μ , there will be only about 600 000 units left because the time gap between 5 microns and 45 corresponds to 9 hours which reduce the number to some 5 % of the original. The unit crystal however has a volume 5000 times bigger than that of the 0- 5μ generation. Once the 100m size is reached, the number of units/cm³ is reduced to 6500, their unit volumic size is 33 000 times bigger than the smallest generation.

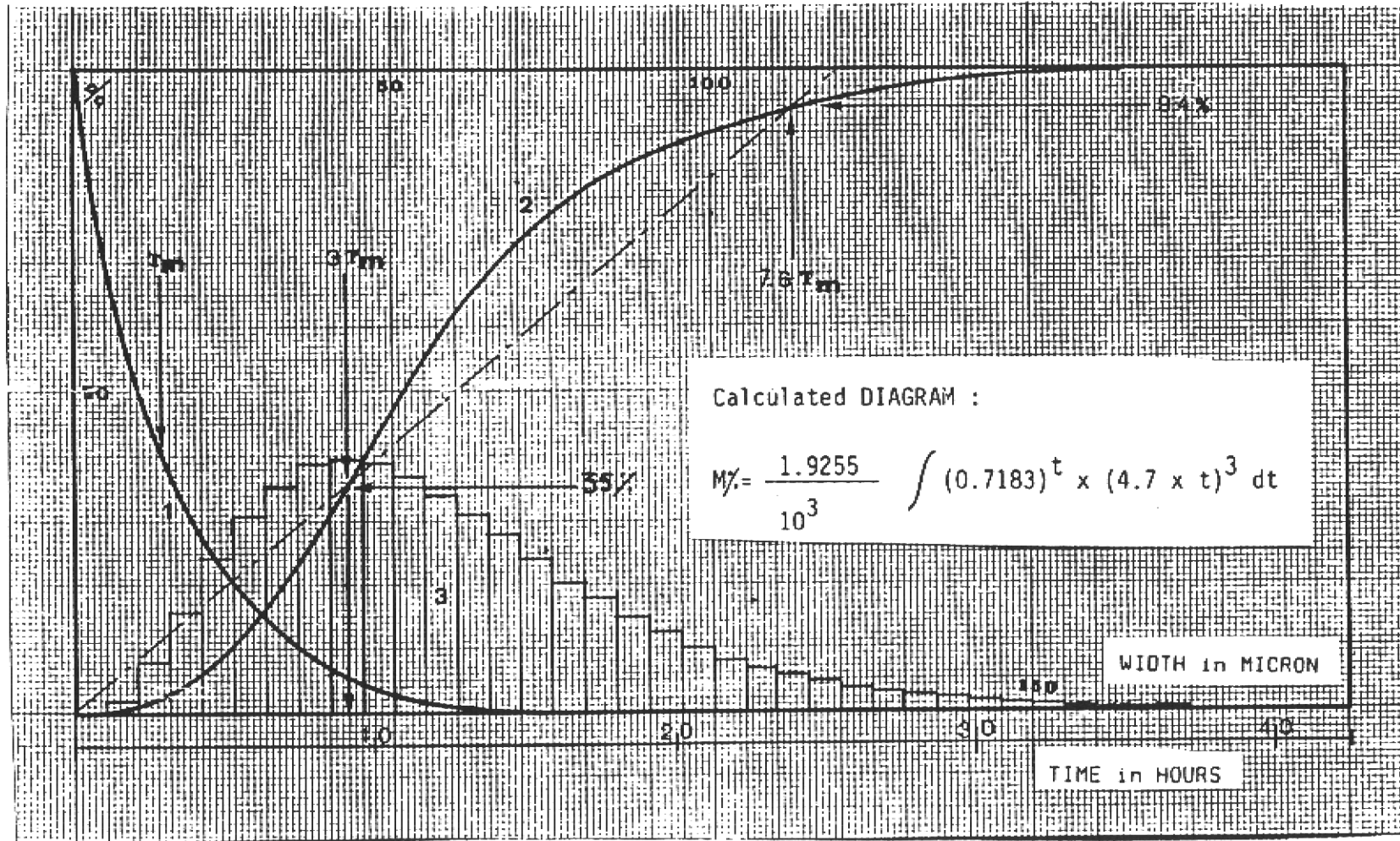


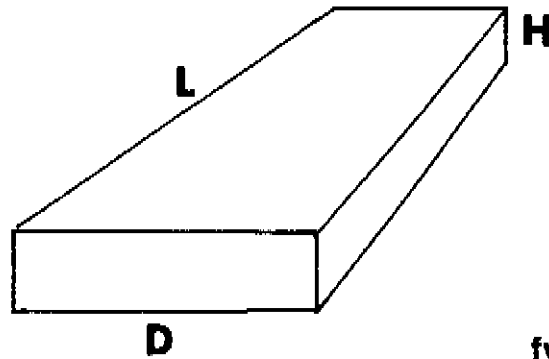
Figure 4: Specific Characteristics of Crystal Diagrams

Curve (1): Expresses the effect of Extinction factor E; after one mean residence time t_m , 61% of the originally born crystals have left the system by overflow. This number is constant for all diagrams. At time $3 \times t_m$, only 5% of the original generation remains in the reactor; but these 5% represent 64.5% of the total crystal volume or weight present in the slurry. Since $3 \times t_m$ locates

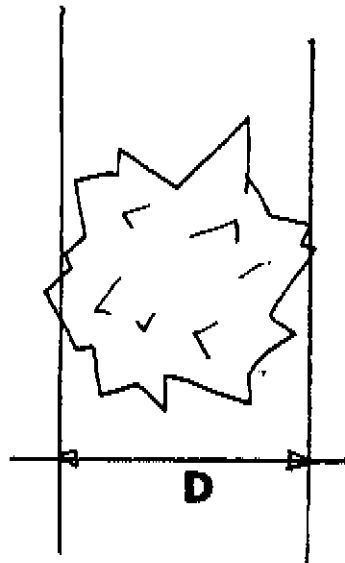
also the dimension of the dominant crystal generation, it is very convenient to point out the inflexion point of the S curve (2) by reading the crossing of the Sline with the 35.5% level (see Arrows at $3 t_m$ and 35%).

Since the equation is based on linear constant growth rate, the X axis stands for both time and size. In fact this is not entirely true because we could demonstrate that crystal growth is in fact a function related to crystal size: $G = (k + 0.01t)$, but for the purpose of this study and the minor reciprocal consequences we can neglect this effect.

Figure 5: Volumic Shape Factor



$$fv = \frac{D \cdot L \cdot H}{D^3} = \frac{L \cdot H}{D^2}$$



$$fv = \frac{(D/2)^3 \cdot \pi \cdot 4/3}{D^3} = 0.52$$

D, L, H to be measured by microscopic crystal examination.

Screen analyses should be realised repeatedly until constant diagrams obtained. Samples should be taken after continuous trouble free operation at the least 10 mean residence time, if possible 15.

**NUCLEATION NUMBER N° as a FUNCTION
of MEAN RETENTION TIME t_m .**

N° is expressed in Million Nuclei/cm³ Slurry
On X Axis t_m is expressed in Hours. Circled Numbers
correspond to refered Production Plants where the
measurements were operated (Appendix 1).

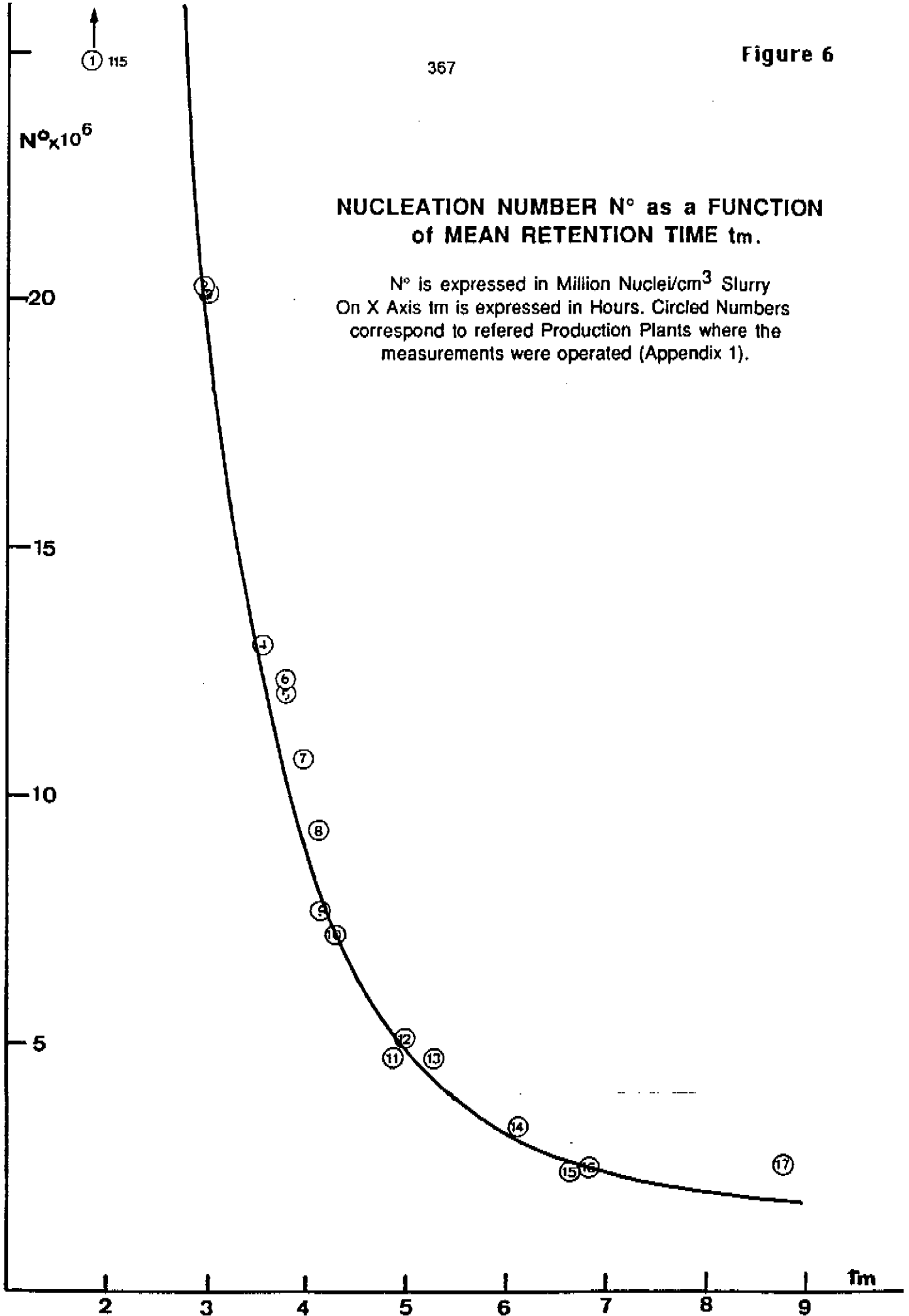
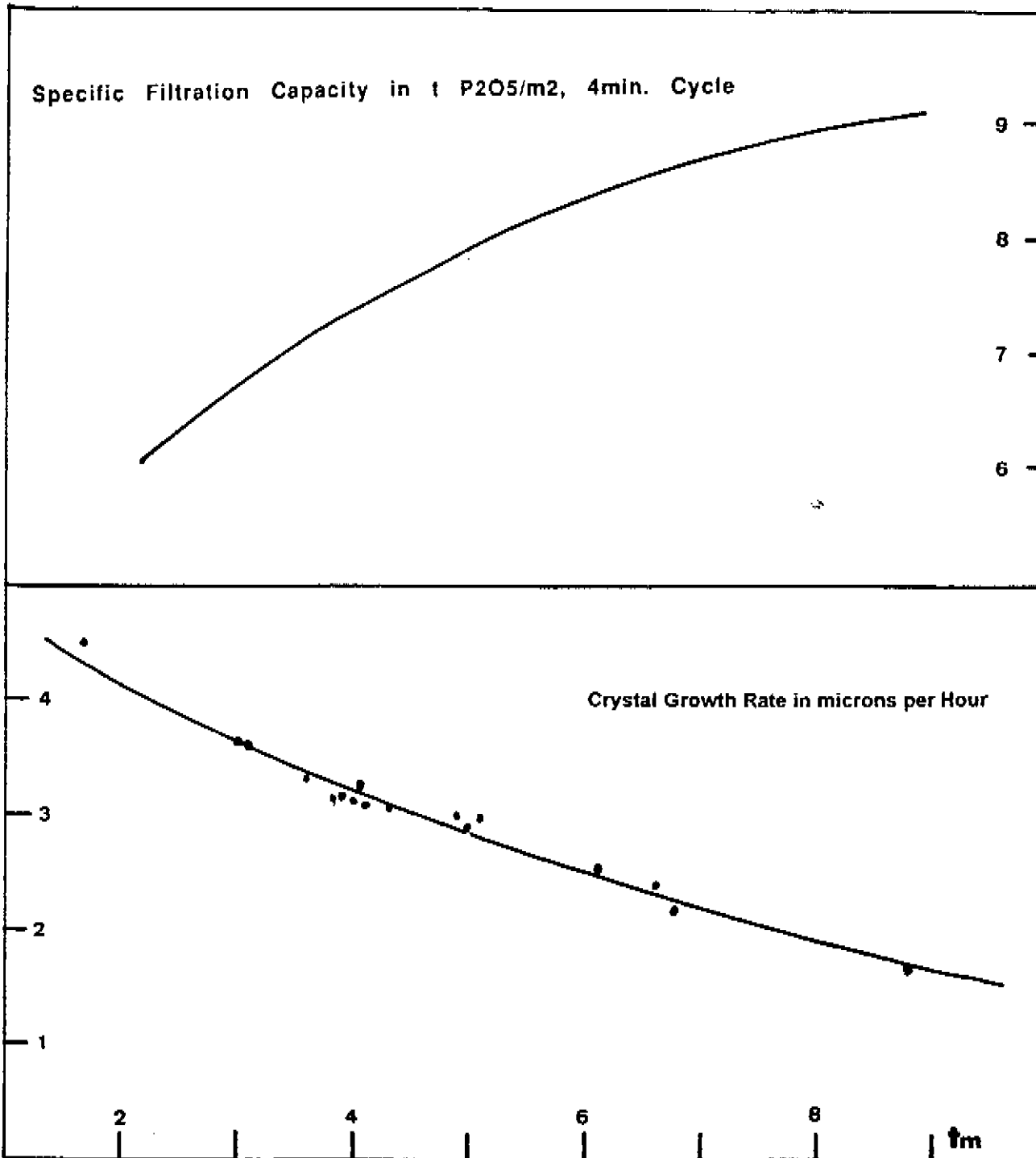


Figure 7



Specific Filtration Capacity and Crystal Growth Rate as a Function of mean Residence Time, t_m