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MATHEMATICAL MODEL OF FILTRATION AND WASHING IN
PHOSPHORIC ACID MANUFACTURE

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SUMMARY

Application of constant pressure filtration shows that the gypsum cake behaves as an incompressible sediment. The filtration time versus collected acid volume obeys a parabolic law.

Mathematical modeling of water washing of the gypsum cake shows that the stagnant zone model applies to a great part of the studied field and describes physical phenomena. However equations describing axial dispersion model may be applied also to a fraction of the studied field for the calculation of parameters which are only reached experimentally by the stagnant zone model.

INTRODUCTION

Until now phosphoric acid manufacture depended upon the experience gained in operating the plant and the knowledge of the phosphate ore used. Mathematical models are not yet widely used in the various stages of that manufacture : kinetics of phosphate dissolution, crystallization of calcium sulphate, filtration of phosphoric acid slurry and washing of the calcium sulphate cake.

In the present paper the equations expressing filtration and washing of incompressible sediments and the material balance for the product to be removed from the porous cake were used to introduce mathematical models in the last two stages of phosphoric acid manufacture. However single stage water washing was considered only.

I. FILTRATION OF PHOSPHORIC ACID SLURRY

1.1) Equations of filtration at constant pressure

The various equations concerning the filtration of an incompressible sediment are presented in table 1.

TABLE 1

EQUATIONS OF FILTRATION AT CONSTANT PRESSURE

General laws	$R = \Delta P/Q$	(I.1.)
	$Q = dv/dt$	(I.2.)
	$R = R_s + R_t$	(I.3.)
	$R_s = \beta e/S$	(I.4.)
	$\beta = k \mu$	(I.5.)
	$S = S_0 \epsilon$	(I.6.)
Definition relations	$R_t = \Delta P/SU'$	(I.7.)
	$\bar{c} = S \cdot e (1 - \epsilon)/V$	(I.8.)
	$F = \frac{k \mu}{\Delta P} \cdot \frac{\bar{c}}{1 - \epsilon}$	(I.9.)
Filtration equations	$dt = \frac{F}{S^2} V dV + \frac{1}{SU'} dV$	(I.10)
	$t = \frac{F}{2S^2} V^2 + \frac{1}{SU'} V + \frac{1}{S} \int_0^V \frac{V}{U'^2} dU$	(I.11.)
	$\frac{t}{V} = \frac{F}{2S^2} V + \frac{1}{SU'} (U' \text{ constant})$	(I.12.)

V indicates the volume of filtrate collected at moment t and under pressure ΔP . R , R_s and R_t mean the total resistance of the cloth and of the sediment, the resistance of the sediment and the resistance of the cloth respectively. Q is the output of the filtrate collected; β the resistance coefficient of the sediment; μ the viscosity of the liquid collected; e the thickness of the sediment during formation; S the area capable of letting the liquid flow through the sediment; S_0 the area of the filter or of the sediment; ϵ the porosity of the sediment deposited; \bar{c} the proportion of solids in the suspension; U' the flow rate of the liquid through the filter cloth and F the filtrability of the suspension concerned.

Equations (I.1), (I.2), (I.3) and (I.4) of table 1 were established by analogy with electrical equations. Equation (I.5) can be deduced from POISEUILLE, DARCY and CARMAN-KOZENY [1], [2], laws.

Equation (I.12) shows that the filtration curve at constant pressure is a straight line on diagram $(V, t/V)$, when the flow rate through the filter U' is constant. The slope of the straight line is inversely proportional to the filtrability coefficient F of the suspension.

I.2) Application to phosphoric acid filtration

Fig 1 shows that the curves obtained in the filtration of slurries produced with four phosphate rocks called A, B, C and D are straight lines. The gypsum of the phosphoric acid slurry behaves like an incompressible sediment. However the initial part of the curve is not always straight for two reasons :

- The instability of the calcium sulphate cake when its formation starts
- The progressive blinding of the filter cloth resulting in an increased rate which finally reaches a constant level corresponding to a constant rate U' .

The main advantage of the filtration straight line lies in the calculation of the filtrability coefficient of the phosphoric acid slurry and the rate U' .

The filtrability involves the following factors : proportion of solids in the slurry, viscosity of the acid produced, pressure applied, geometric properties of the cake such as porosity of the layer and specific crystal areas.

If the first three factors are kept constant, only the crystal shape would effect the filtration results.

The crystal shape is determined by the operating conditions during manufacture.

A decreased slope of the filtration straight line, $F/2S^2$, indicates an improved filtration of the phosphoric slurry for the same value of the rate U' calculated by starting from the ordinate at the origin of the filtration line. The value of U' depends on the rate of blinding of the cloth by impurities of the phosphate ore.

Fig 1 shows that the slurry obtained with phosphate A enjoys better filtration than those from phosphates C and D.

II. MATERIAL BALANCE OF PHOSPHORIC ANHYDRIDE DURING GYPSUM CAKE WASHING.

II.1) General equation of the material balance

The material balance in a layer of thickness dz for uniform incompressible filter cakes, undergoing a single direction flow can be expressed as follows [3]

$$\frac{\partial C}{\partial t} + \frac{\epsilon_s}{\epsilon} \frac{\partial C_s}{\partial t} + \frac{\epsilon_f}{\epsilon} \frac{\partial C_f}{\partial t} + U \frac{\partial C}{\partial z} = \frac{\partial}{\partial z} (D \frac{\partial C}{\partial z}) \quad (\text{II.1.1.})$$

C is the concentration of dissolved material in the flow channels of the washing liquid ; C_f its concentration in the stagnant parts and C_s its concentration in the liquid phase. D refers to the coefficient of axial dispersion ; t to the time, U to the flow rate of liquid through the porous layer, z to a coordinate on the cake axis ; ϵ to the porosity corresponding to the flow channel of the wash liquid, ϵ_f to the porosity corresponding to the stagnant parts and ϵ_s to the fraction of volume occupied by the solid phase.

In the case presented in the paper, P_2O_5 exists in the solid phase in the form of unreacted phosphate particles and of dicalcium phosphate cocrystallized with

gypsum. That P_2O_5 is thus not recovered during washing.

Assuming that the axial dispersion coefficient is constant, equation (II.1.1) takes the following simplified form :

$$\frac{\partial C}{\partial t} + \frac{\epsilon f}{\epsilon} \frac{\partial Cf}{\partial t} + U \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial z^2} \quad (\text{II.1.2})$$

II.2) Fields of application of the two mathematical models of washing

Physically filter cake washing can be divided into two consecutive processes [3] :

- Hydro-dynamic transport process
- Diffusion transfer process.

The hydrodynamic transport process is the first washing stage ; the washing liquid expels the impregnating liquid by flowing through the porous medium. The ideal flowing front is plane and corresponds to a typical plug flow. In practice this front is always disturbed by non-uniformity of cake porosity resulting in local variations of the flow rate of the washing fluid. The processes which contribute to the disturbance of the flowing front are put together and called axial dispersion.

When a washing volume equal to the porous volume of the cake has flowed through the cake, the initial "transport" stage is over. However some impregnating liquid remains in the inactive parts of the cake. The washing then continues by diffusion between the impregnating liquid remaining in the stagnant parts and the washing liquid flowing through the cake under load (difference of pressure between the two sides of the cake).

According to the relative importance of the first and second stages, washing will be achieved through axial dispersion or diffusion.

When washing occurs mainly during the first stage, it will follow the mathematical equations describing the model of axial dispersion. In practice it means that the stagnant parts are negligible and that the concentration C of dissolved material in the liquid at the outlet of the cake quickly tends to zero when the volume of washing liquid exceeds the porous volume of the cake.

On the other hand, if the diffusion stage removes an important part of the dissolved material, washing will follow the equations describing the diffusion model. In that case the stagnant parts of the cake are important and the concentration C of dissolved material in washing the liquid will tend to zero only when a liquid volume equal to several times the porous volume of the cake is reached.

As a result, the cake structure, the experimental determination of porosities and the shape of the concentration curve of dissolved material in the washing liquid as a function of time will enable an assumption on the anticipated type of washing to be established. The application of mathematical models would allow the initial assumption to be confirmed or refuted.

II.3) Model for the stagnant parts

To use that model it was assumed that :

- the axial dispersion was negligible
- the layer is thin as compared to the stagnant parts (C_f is independent from z)
- the transfer kinetics between the stagnant parts and the flow channels of the washing liquid is linear and governed by equation (II.3.2) in table 2 which gives the main indications concerning that model. In this table, K refers to the transfer constant between the stagnant parts and the flowing channels of the washing liquid.

TABLE 2

MODEL FOR STAGNANT PARTS

Method of resolution used	LAPLACE conversion	
Washing equation	$\frac{\partial C}{\partial t} + \frac{\epsilon_f}{\epsilon} \frac{\partial C_f}{\partial t} + U \frac{\partial C}{\partial z} = 0$	(II.3.1)
	$\frac{\partial C_f}{\partial t} = -K C_f$	(II.3.2)
Mathematical model	$C/C_0 = \frac{\epsilon_f}{\epsilon} e^{-Kt} (e^{kz/U} - 1)$	(II.3.3)
	$C_f/C_0 = e^{-Kt}$	(II.3.4)
Initial conditions	$0 < t < z/U \quad C = C_f = C_0$	(II.3.5)
Conditions at limits	$t > z/U \quad z = 0 \quad C = 0$	(II.3.6)

II.4) Model for axial dispersion $\overline{[4]}$, $\overline{[5]}$, $\overline{[6]}$, $\overline{[7]}$, $\overline{[8]}$.

This model does not take account of the stagnant parts. Table 3 gives the main indications of that model of which the solution was already established $\overline{[4]}$.

TABLE 3
MODEL FOR AXIAL DISPERSION

Method of resolution used	LAPLACE conversion	
Washing equation	$\frac{\delta C}{\delta t} + U \frac{\delta C}{\delta z} = D \frac{\delta^2 C}{\delta z^2}$	(II.4.1)
Mathematical model	$C/C_0 = \frac{1}{2} + \frac{1}{2} \operatorname{erf} \frac{(z-ut)}{\sqrt{4Dt}}$ $- \frac{1}{2} e^{Uz/D} \operatorname{erfc} \frac{(z+Ut)}{\sqrt{4Dt}}$	(II.4.2)
Initial conditions	$0 < t < z/U$ $C = C_0$	(II.4.3)
Conditions at limits	$t > 0$ $z = 0$ $c = 0$	(II.4.4)

III. WATER WASHING OF THE GYPSUM CAKE

III.1) Washing equations at constant pressure

All the equations are presented in table 4.

TABLE 4
WASHING EQUATIONS AT CONSTANT PRESSURE

$R = \Delta P/Q$	(III.1.1)
$Q = dV/dt = S.U$	(III.1.2)
$R = \beta e/S$	(III.1.3)
$e = Z$	(III.1.4)
$\beta = k\mu$	(III.1.5)
$dt/dV = \frac{KZ}{S \cdot \Delta P} \mu = P$	(III.1.6)
$S = S_0 \epsilon$	(III.1.7)

As soon as it is formed the cake has a constant thickness Z and a much more important resistance than that of the cloth.

If the viscosity of the wash liquid after the filter is constant, equation (III.1.6) of table 4 results in a straight line in diagram (V, t) .

III.2) Application to filter cake washing

Washing tests were conducted immediately after the formation of a dry surface after filtration to avoid cracks and separations on the BUCHNER walls.

The measurement of flow volumes as a function of time was done with movie recording. By plotting the results on diagram (V, t), as shown in figure 2, two straight lines were obtained : the slope p_1 of the straight line AE is proportional to the viscosity of the acid produced. The slope p of the straight line EX is proportional to the viscosity of the washing liquid at the filter outlet. The variations of viscosity are small. Curve EX can be considered as a straight line.

All the equations which enable the porosity to be calculated correspond to the flow channels of the wash liquid in the gypsum cake, porosity ϵ_f corresponds to the stagnant parts ; total porosity ϵ_t and the flow rate U of the wash liquid in the cake are given in table 5. In that table P_s means the weight of the dry cake and d_v the actual density of the gypsum.

TABLE 5
USE OF THE WASHING STRAIGHT LINE

: $\epsilon = V_E / S_0 Z$: (III.2.1) :
: $\epsilon_t = 1 - \frac{P_s / d_v}{S_0 Z}$: (III.2.2) :
: $\epsilon_f = \epsilon_t - \epsilon$: (III.2.3) :
: $1/p = \frac{d_v}{d\theta} = S_0 \epsilon . U$: (III.2.4) :

For phosphate D, the ϵ , ϵ_f , ϵ_t and U values calculated from figure 2 are given in table 6

TABLE 6
 ϵ , ϵ_f , ϵ_t AND U VALUES CALCULATED
FROM DIAGRAM IN FIGURE 2

: Designation	: Val.
: ϵ (%)	: 31
: ϵ_f (%)	: 36
: ϵ_t (%)	: 67
: U (cm/sec.)	: 0,4

IV. APPLICATION OF THE TWO MODELS TO FILTER CAKE WASHING.IV.1) Model for stagnant parts

Table 7 presents the model for stagnant parts which takes account of the first washing stage where the liquid with an equal concentration to that of the acid produced undergoes plug flow in the filter cake at a rate U_1 different from rate U .

An observer placed at the filter outlet watches the liquid concentration reduction only after time Z/U_1 , Z being the thickness of the gypsum cake. This remark leads to changing the variable defined by equation (IV.1.3) in table 7.

TABLE 7
MODEL FOR STAGNANT PARTS APPLIED TO FILTER CAKE WASHING

Method of resolution: used	LAPLACE conversion	
	$\frac{\partial C}{\partial \theta} + \frac{\epsilon_f}{\epsilon} \frac{\partial C_f}{\partial \theta} + U \frac{\partial C}{\partial z} = 0$	(IV.1.1)
Washing equation	$\frac{\partial C_f}{\partial \theta} = -K C_f$	(IV.1.2)
	$\theta = t - Z/U_1$	(IV.1.3)
	$U_1 = 1/P_1 S_0$	(IV.1.4)
Mathematical model	$C/C_E = \frac{\epsilon_f}{\epsilon} e^{-K\theta} (e^{KZ/U_1} - 1)$	(IV.1.5)
	$C_f/C_E = e^{-K\theta}$	(IV.1.6)
Initial conditions	$\theta < 0 \quad C = C_f = C_E$	(IV.1.7)
Limit conditions	$\theta > 0 \quad z = 0 \quad C = 0$	(IV.1.8)
Characteristic relation	$\epsilon/\epsilon_f = e^{KZ/U_1} - 1$	(IV.1.9)

$P_2 O_5$ concentration C of the washing liquid is measured at the filter outlet ($z=Z$). Concentration C_E is different from the concentration of the acid produced C_q (figure 3) owing to the diffusion taking place between the wash liquid and the phosphoric acid which impregnates the surface of the filter cake.

To take account of that diffusion, it is possible to look for a model which no longer depends on limit conditions in table 7 but on the following limit conditions [5] :

$$\theta > 0$$

$$z = 0$$

$$n = N$$

$$C = C_E \sum_{n=0}^N (\xi k_n \theta^n) e^{-\gamma \theta} \quad (\text{IV.1.10})$$

The characteristic washing relation (IV.1.9) in table 7 was established by making $C=C_E$ for $\theta=0$ in relation (IV.1.5) of the same table. The last relation shows that the conditions of application of the stagnant part model follow a straight line on diagram $(\theta, \text{Log } C_E/C)$ with a slope equal to the transfer constant K.

Figure 4 shows that the stagnant part model as described by equations (IV.1.1) and (IV.1.2) is applicable to the whole field but seems somewhat disturbed when washing is achieved. It is interesting to continue the study by replacing equation (IV.1.2) by equation (IV.1.11) which follows and maintains the assumption of linear transfer kinetics between the stagnant parts and the flow channels of the wash liquid, but which introduces the concentration difference between the two parts as transfer driving force.

$$\frac{\delta C_f}{\delta \theta} = -K (C_f - C) \quad (\text{IV.1.11})$$

IV.2) Axial dispersion model

Instead of using solution (11.3.2) of table 3 concerning a model which does not take account of the interference of stagnant parts, we preferred to look for a special solution more readily applicable using BOLTZMANN conversion. This solution makes it possible to calculate all the parameters of the washing equation by using two models simultaneously. Table 8 presents the various data concerning this model.

TABLE 8
MODEL OF AXIAL DISPERSION APPLIED TO GYPSUM
CAKE WASHING

: Method of resolution:	BOLTZMANN conversion	:	:
: used		:	:
: Washing equation	$\frac{\delta C}{\delta \theta} + u \frac{\delta C}{\delta z} = D \frac{\delta^2 C}{\delta z^2}$:	(IV.2.1)
:		:	:
: Mathematical model	$C/C_E = 1/2 + 1/2 \operatorname{erf} \left(\frac{z - u\theta}{\sqrt{4D\theta}} \right)$:	(IV.2.2)
:		:	:
: Initial conditions	$\theta = 0 \quad C = C_E$:	(IV.2.3)
:		:	:
: Limit conditions	$\theta = \infty \quad C = 0$:	(IV.2.4)

The application of BOLTZMANN conversion is a practical means of getting a special solution for the washing equation corresponding to the axial dispersion model, possibly the general solution of that equation. The description of the calculations involved in that conversion can be found in appendix 2.

The conditions of application of that model follow a straight line with slope p_2 on diagram $(\theta, 2W\sqrt{\theta})$, W being the argument of the error function.

Figure 5 shows that the model gives a mathematical formulation of the washing curve on diagram $(\theta, C/C_E)$ in figure 6 which follows the experimental curve over part of the washing stage except for the beginning and the end and which can be used to calculate parameters of the washing equation by the resolution of the system of equations given by the two models as shown in table 9.

TABLE 9
CALCULATION OF THE PARAMETERS OF THE WASHING EQUATION

: $W = (Z - U\theta) / \sqrt{4D\theta}$: (IV.2.1)	:
: $P_2 = U / \sqrt{4D\theta}$: (IV.2.2)	:
: $C/C_E = 0.5 \Rightarrow W = 0 \Rightarrow \theta/2 = Z/U$: (IV.2.3)	:
: $U = Z/\theta^{1/2}$: (IV.2.4)	:
: $\mathcal{E} = 1/pSo U$: (IV.2.5)	:
: $\mathcal{E}_f = \mathcal{E} / (e^{Kz/U} - 1)$: (IV.2.6)	:
: $\mathcal{E}_t = \mathcal{E} + \mathcal{E}_f$: (IV.2.7)	:
: $D = U^2 / 4P_2^2 \theta^{1/2}$: (IV.2.8)	:

One single model gives insufficient equations to calculate all the parameters of the washing equation.

Table 10 compares the values of the different parameters obtained by using the washing straight line and the two models simultaneously.

TABLE 10
CALCULATION OF PARAMETERS IN THE WASHING EQUATION

: Parameters	: Use of the washing straight line	: Combination of the two washing models:
: \mathcal{E} (%)	: 31	: 32
: \mathcal{E}_f (%)	: 36	: 33
: \mathcal{E}_t (%)	: 67	: 65
: U (cm/sec)	: 0.40	: 0.38

The following comments should be made about figure 6 on the relative location of the models for stagnant parts of axial dispersion and of the experimental model. At the beginning of the curve the stagnant part model coincides with the experimental model. In the middle the three models coincide. At the end the three models diverge.

IV.3) Geometrical construction of the point where concentration decreases by half on the washing straight line

TABLE 11

GEOMETRICAL CONSTRUCTION OF THE POINT WHERE CONCENTRATION DECREASES BY HALF ON THE WASHING STRAIGHT LINE

:	:	:
:	$\theta = Z/U$:(IV.3.1):
:	$\theta_{I}^{1/2} = 1/2$:(IV.3.2):
:	$\theta_{I} = P \cdot V_{I}$:(IV.3.3):
:	:	:
:	$1/P = S_o \cdot \xi \cdot U$:(IV.3.4):
:	$\xi = V_L / S_o Z$:(IV.3.5):
:	$V_I = V_E$:(IV.3.6):
:	:	:

This geometrical construction results from the axial dispersion model. It is then unnecessary to draw the curve of figure 6 to know the point for which C/C_E equals 0.5.

The knowledge of $\theta_{I}^{1/2}$ is important to judge the quality of gypsum crystals obtained.

Good crystallization with a phosphate low in mineral or organic impurities gives a time $\theta_{I}^{1/2}$ lower than three seconds under the prevailing experimental conditions: a 80 cm² filter area, a gypsum cake thickness varying from 3 to 5 cm, an average 30 % solid content of the phosphoric slurry and a 400 mm Hg vacuum. A phosphate rich in impurities with a medium crystallization gives a time $\theta_{I}^{1/2}$ sometimes exceeding 10 sec.

V) APPLICATION OF MATHEMATICAL MODELS TO FILTER CAKE WASHING OF FOUR PHOSPHATES

The results of the calculation of flow parameter (K, U) and of the gypsum cake structure (ξ , ξ_f , ξ_t , D) for four phosphates A, B, C and D are given in table 12. The experimental values of that table were taken from figures 2, 3, 4 and 5. The calculation procedure is illustrated by table 9. Results of several experiments with phosphates C and D were given in order to show the variations of the values of the different parameters with the operating conditions for manufacture of the phosphoric slurry.

TABLE 12

CALCULATION OF THE WASHING EQUATION PARAMETERS
FOR FOUR PHOSPHATES

Phosphate	Z (cm)	U (cm/sec)	D_2 (cm/sec)	K_{-1} (sec)	$\Theta 1/2$ (sec)	ϵ (%)	ϵ_f (%)	ϵ_t (%)	ϵ/ϵ_f
A	3.2	1.36	1.76	0.30	2.3	28	23	51	1.2
B	3.2	1.08	1.62	0.25	3.1	27	25	52	1.1
C ₁	4.1	0.58	1.61	0.10	7	30	31	61	0.98
C ₂	4.4	0.92	1.28	0.14	4.9	33	34	67	0.97
C ₃	4.4	0.85	1.50	0.14	5	34	35	69	0.96
D ₁	4.5	0.38	29.2	0.06	13.8	32	33	55	0.97
D ₂	4.5	0.41	31.6	0.06	10.9	36	37	72	0.97

The results in table 12 lead to the following comments :

- Parameters U, K and $\Theta 1/2$ which vary on average in the same direction make the classification of phosphates possible. As compared with phosphate A, with a good reputation, the following classification was obtained in a decreasing order : A, B, C, D.
- The ratio ϵ/ϵ_f is nearly equal to one. The stagnant parts have thus the same importance as the flow channels of the washing liquid in the gypsum cake.

A and B phosphates show a ϵ/ϵ_f ratio higher than one. This shows a good gypsum crystallization.

CONCLUSION

The filtration and washing time depend mostly on the shape of the gypsum crystals.

Mathematical models improve the understanding of the gypsum cake (ϵ , ϵ_f , ϵ_t , B') and of the flow mechanism which take place in it (U, K). It could result in the optimization of the wash cycle of an industrial plant.

The study we have undertaken could be continued by working out mathematical models for weak acid washing or be completed by the research of a mathematical model representing the entire washing with water taking account of the diffusion which occurs at the surface of the cake between the washing water and the acid present in the gypsum cake.

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APPENDIX 1 :

Filter cake washing with water is not necessarily represented by two straight lines on diagram (V, t). It can be represented by three straight lines as in the case of phosphate C (figure 7).

The conditions of application of the stagnant part model gives on diagram (t, Log $\frac{C_0}{C}$) a straight line intermingled with the time axis and corresponding to a zero value of the transfer constant for the first washing stage, a straight line with slope K_1 for the second stage and a curve which starts as a straight line and with slope K_2 for the third washing stage.

Transfer constant K_2 is higher than K_1 .

APPENDIX 2 :

Let us develop the calculations which resulted in the particular solution (IV.2.2) of equation (IV.2.1) in table 8 by BOLTZMANN conversion.

The equation concerned can be written :

$$\frac{\delta C}{\delta t} + U \frac{\delta C}{\delta z} = D \frac{\delta^2 C}{\delta z^2} \quad (\text{A.2.1})$$

Let us change the variable as follows :

$$y = z - U \theta \quad (\text{A.2.2})$$

Equation (A.2.1) becomes the heat equation and can be written :

$$\frac{\delta C}{\delta \theta} = D \frac{\delta^2 C}{\delta y^2} \quad (\text{A.2.3})$$

The application of BOLTZMANN conversion implies the choice of variable defined as follows :

$$\eta = y \alpha_1 \quad \theta \alpha_2 \quad (\text{A.2.4})$$

By developing the calculations and choosing $\alpha_1 = 1$ and $\alpha_2 = -1/2$, equation (A.2.3) is reduced to the following differential second order equation :

$$\frac{d^2 C}{d \eta^2} + \frac{1}{2D} \eta \frac{dC}{d \eta} = 0 \quad (\text{A.2.5})$$

The integral of this equation can be written :

$$C = K_1 + K_2 \operatorname{erf} \left(\frac{z - U \theta}{\sqrt{4D \theta}} \right) \quad (\text{A.2.6})$$

The calculation of constants K_1 and K_2 implies the knowledge of initial and final conditions.

The initial conditions can be written :

$$\theta = 0 \quad C = C_E \quad (\text{A.2.7})$$

The following final condition was chosen to facilitate the calculation of constants K_1 and K_2 :

$$\theta \rightarrow \infty \quad C = 0 \quad (\text{A.2.8})$$

This means that there is a volume of wash water beyond which additional washing does not improve the efficiency.

With these conditions, relation (A.2.6) becomes :

$$\frac{C}{C_E} = 1/2 + 1/2 \operatorname{erf} \left(\frac{z - U \theta}{\sqrt{4D \theta}} \right) \quad (\text{A.2.7})$$

It is possible to find the general solution of equation (A.2.1) through BOLTZMANN conversion by taking account of the two following remarks :

- the linear combination of the two particular solutions of that equation is also a particular solution
- if $f(U, z, \theta)$ is a particular solution of equation (A.2.1) ; $e^{Uz/D} f(-U, z, \theta)$ is also a particular solution of that equation.

If we choose solution (A.2.6) as a particular solution and if we calculate the four constants by the following conditions :

$$t = 0 \quad C = C_E \quad \text{irrespective of } z \quad (\text{A.2.8})$$

$$z = 0 \quad C = 0 \quad \text{irrespective of } t \quad (\text{A.2.9})$$

We then find the following solution already established by LAPLACE conversion on table 3.

$$\frac{C}{C_E} = \frac{1}{2} + \frac{1}{2} \operatorname{erf} \left(\frac{z - U\theta}{\sqrt{4D\theta}} \right)$$

(A.2.10)

$$\frac{1}{2} e^{-Uz/D} \operatorname{erf} \left(\frac{z + U\theta}{\sqrt{4D\theta}} \right)$$

ACKNOWLEDGEMENTS

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- la Compagnie des Phosphates et de Chemin de Fer de Gafsa (Tunisie)
- la Compagnie Togolaise des Mines du Bénin (TOGO)
- la Compagnie Sénégalaise des Phosphates de Taïba (SENEGAL)
- la Société du Djebel Onk (Algérie)

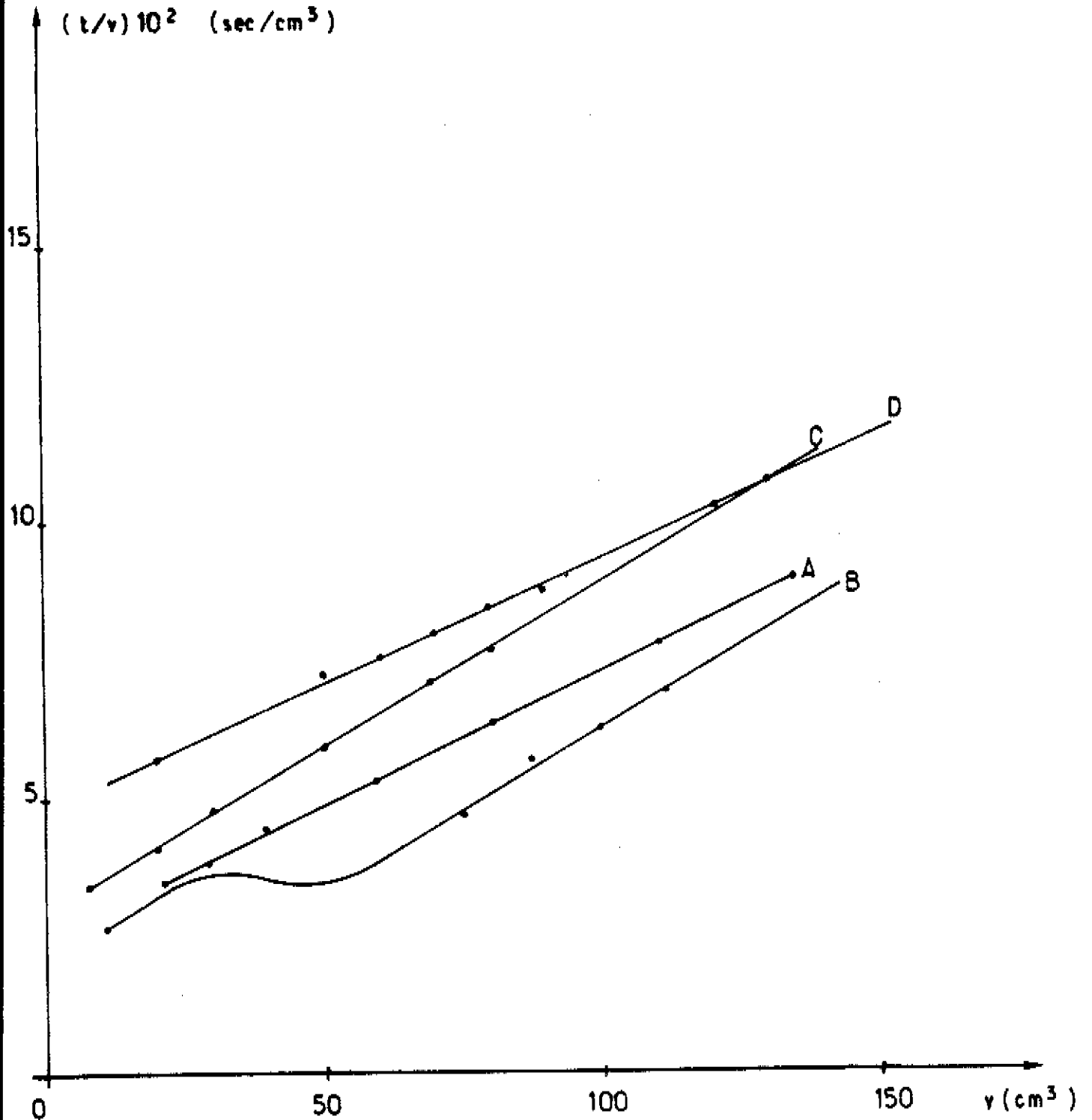


FIGURE 1

FILTRABILITY OF THE PHOSPHORIC SLURRY OF A FEW PHOSPHATES

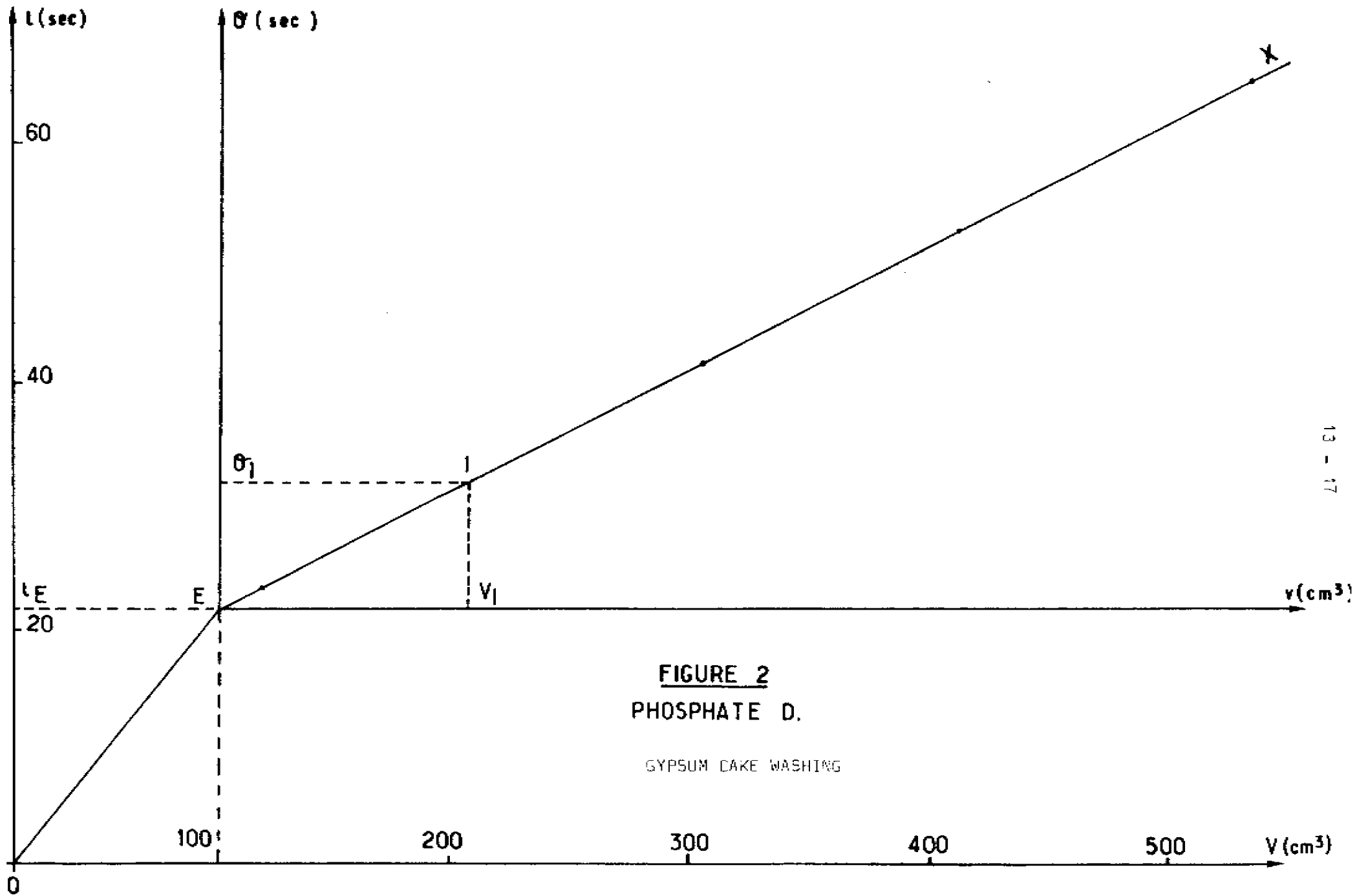


FIGURE 2
PHOSPHATE D.

GYPSUM DAKE WASHING

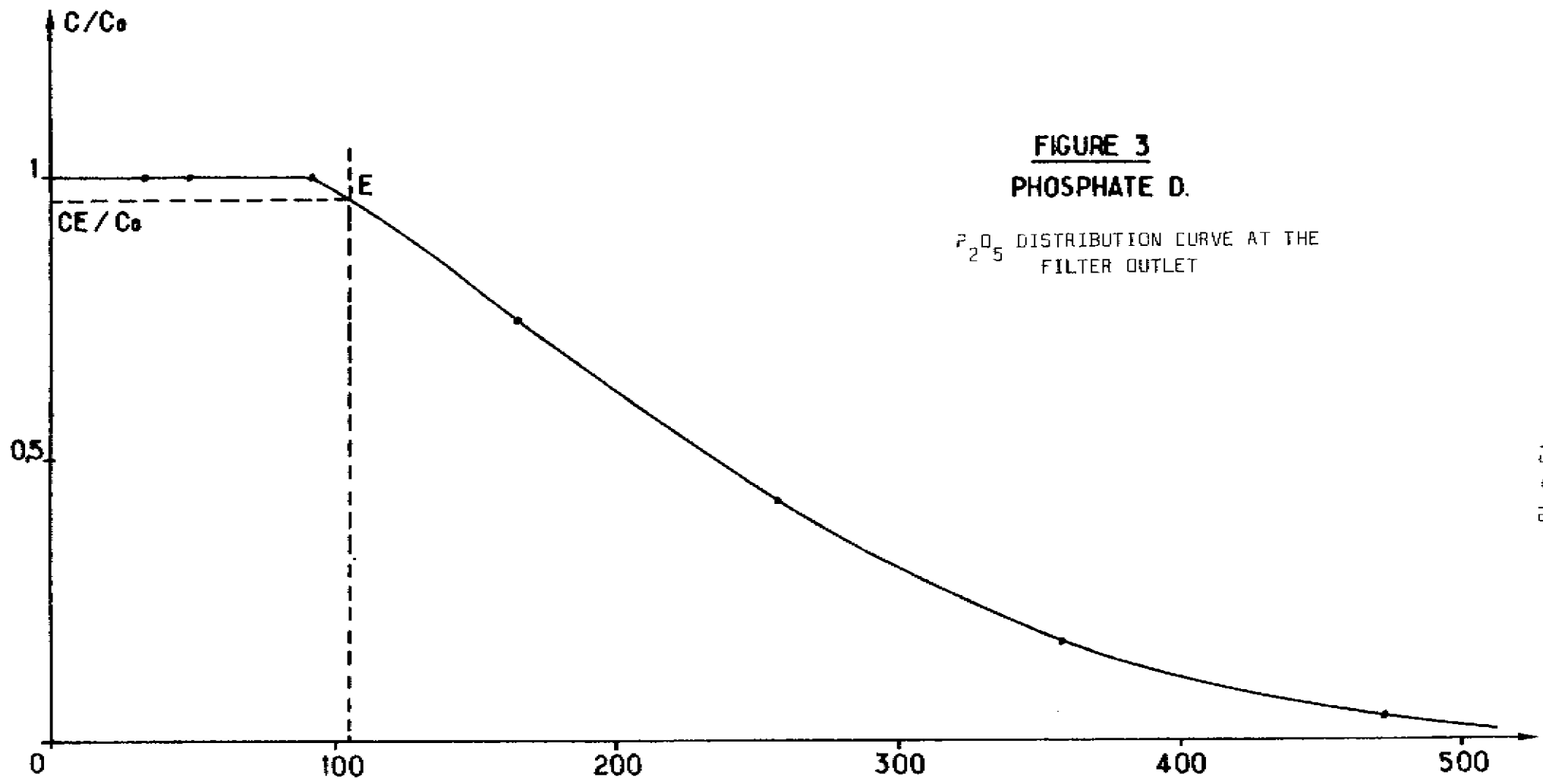
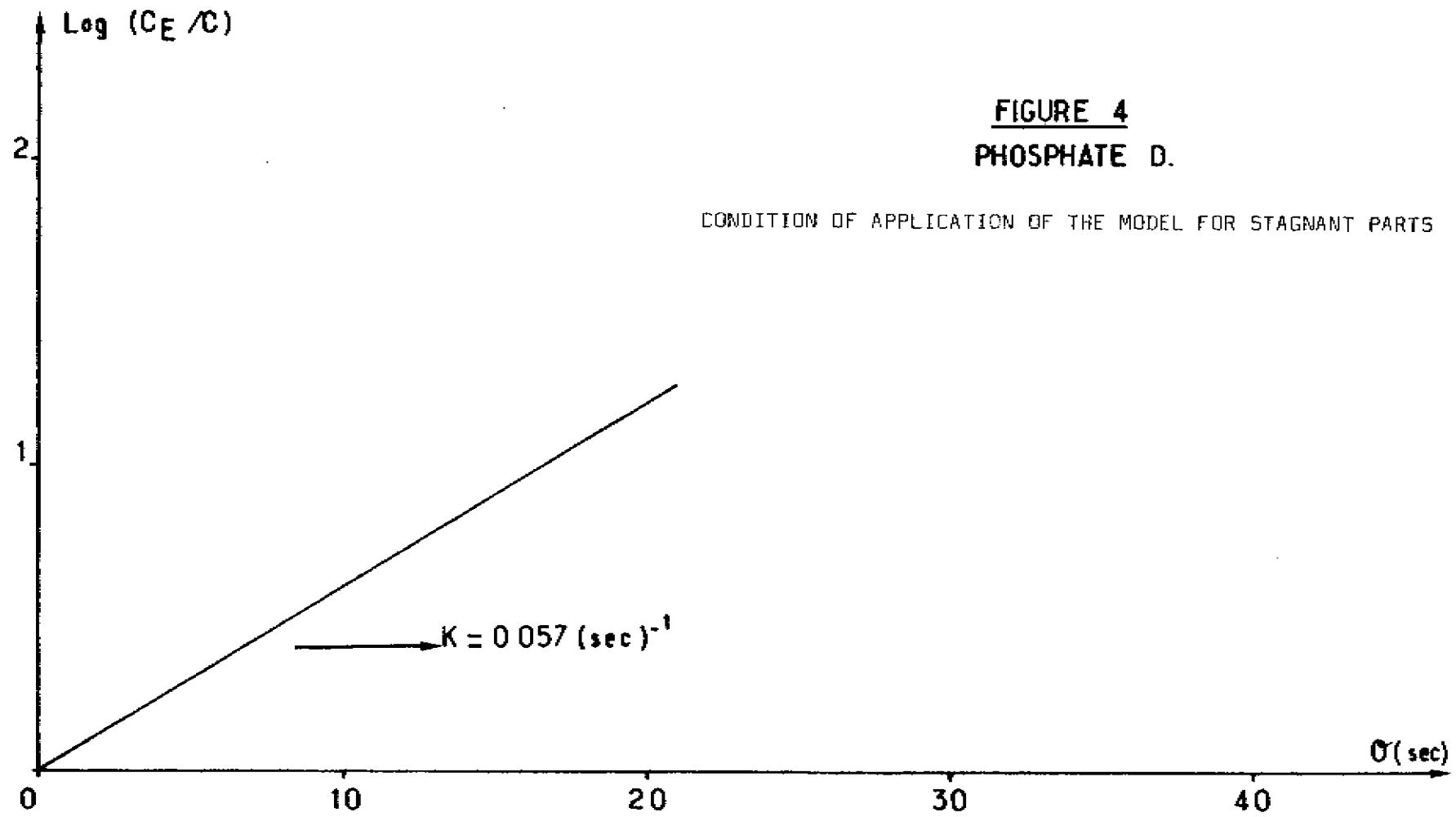


FIGURE 3
PHOSPHATE D.

P_2O_5 DISTRIBUTION CURVE AT THE
FILTER OUTLET

FIGURE 4
PHOSPHATE D.

CONDITION OF APPLICATION OF THE MODEL FOR STAGNANT PARTS



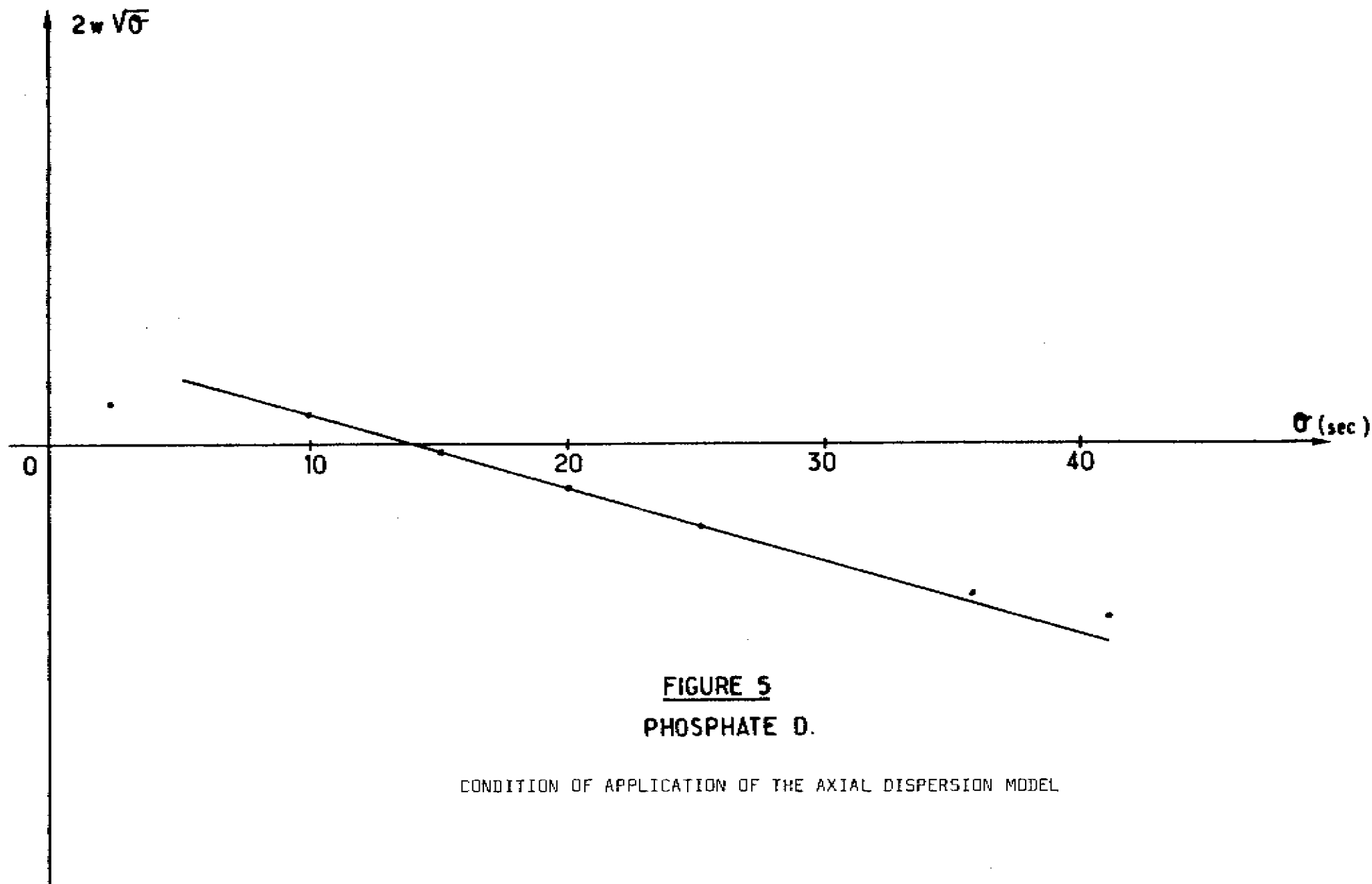


FIGURE 5
PHOSPHATE D.

CONDITION OF APPLICATION OF THE AXIAL DISPERSION MODEL

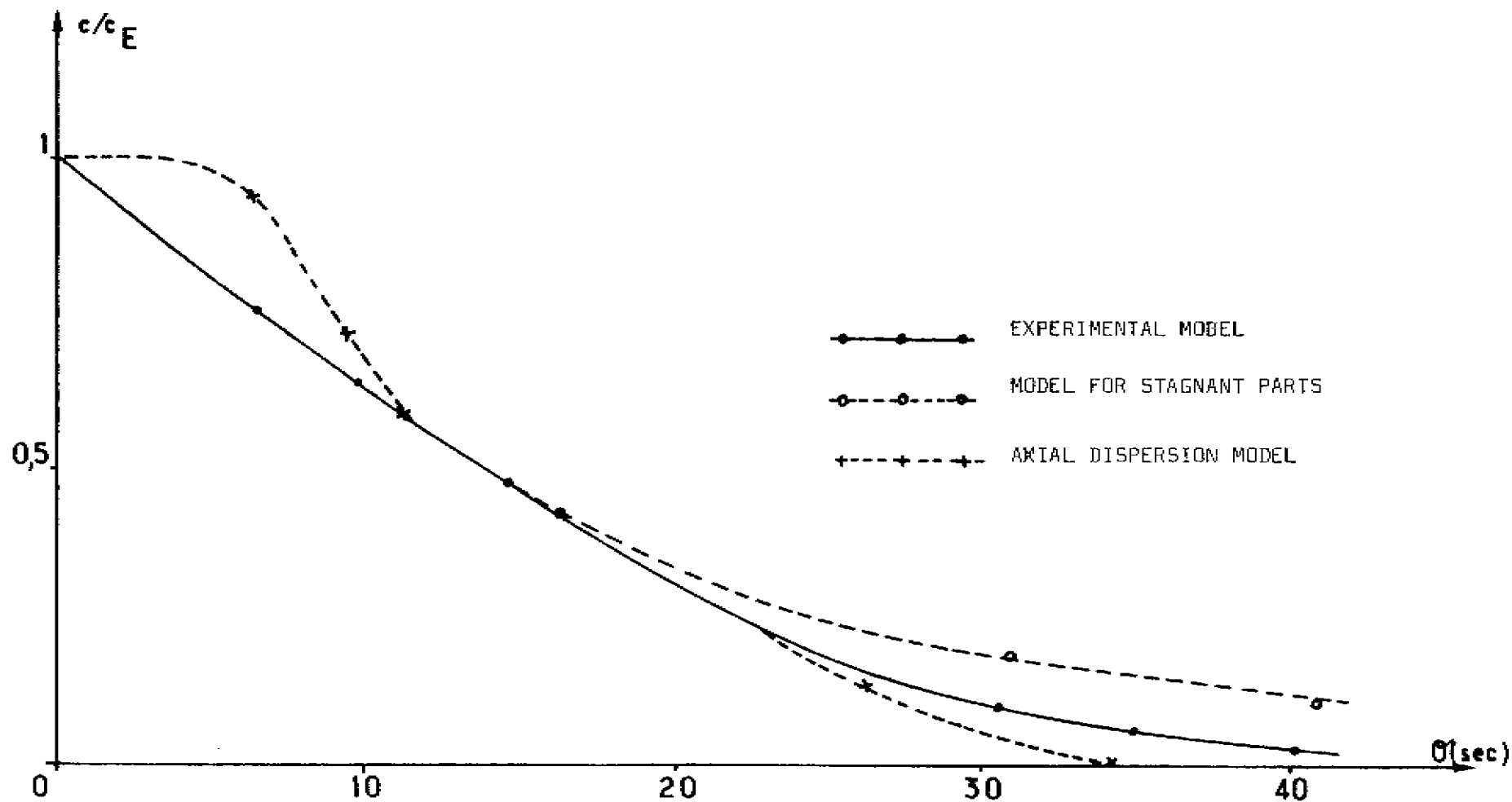


FIGURE 6.
PHOSPHATE D.

COMPARISON OF THE STAGNANT PARTS AND AXIAL DISPERSION MODELS WITH THE EXPERIMENTAL MODEL

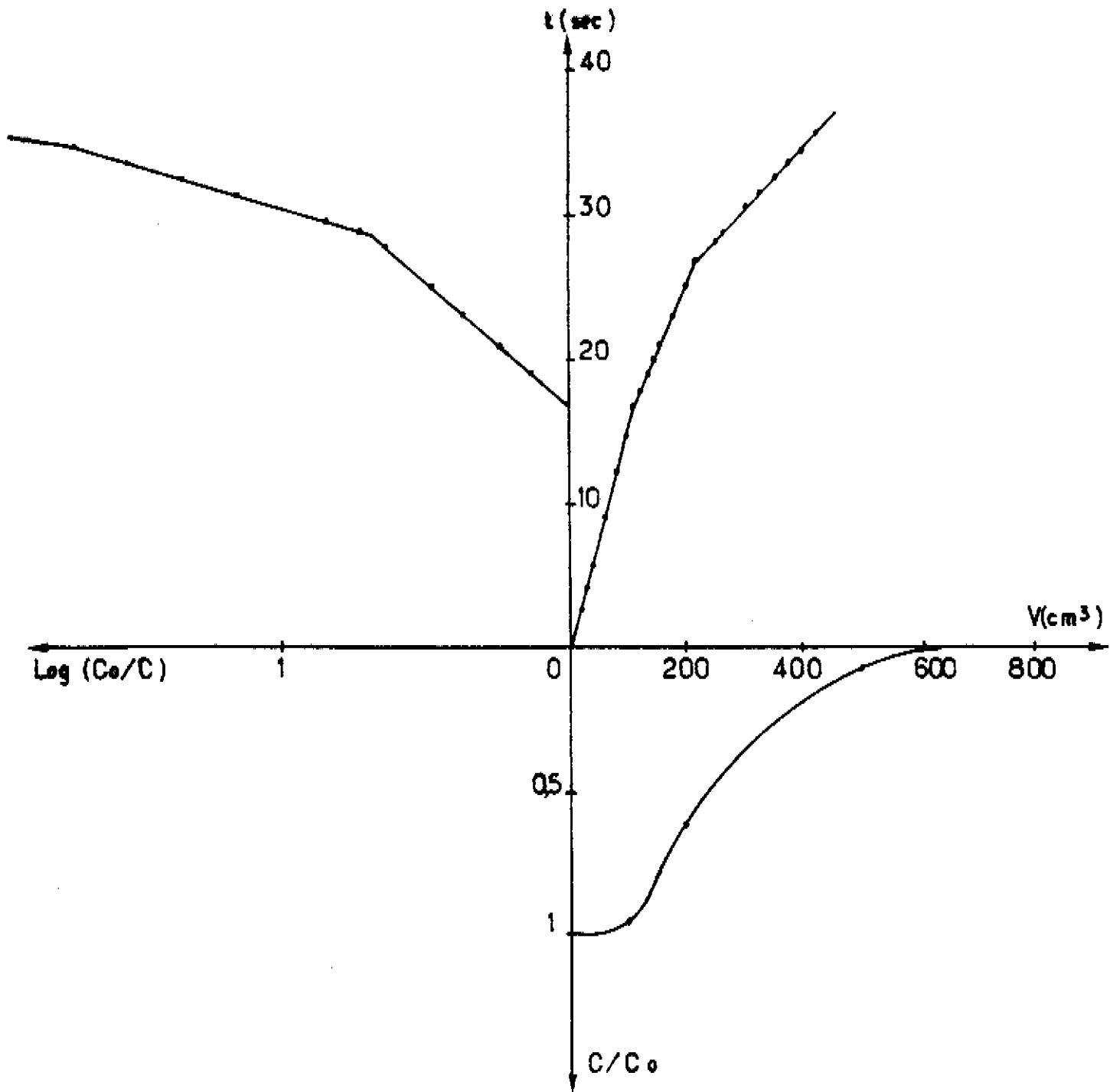


FIGURE 7.

GYPSUM CAKE WASHING OF PHOSPHATE C

DISCUSSIONMr JEMMA (S I A P E., Tunisia)

The manufacture of phosphoric acid has, up until now, been related to the knowledge of the phosphate rock used and the operating conditions related to it. The mathematical modelisation has not been introduced at the different stages of manufacture of this acid, for example reaction, crystallisation of the calcium sulphate or filtration and washing. In this publication, we have tried to introduce a mathematical model and to apply this to the case which interests us and see what results this gave and compare them with the experimental results.

Let us start with the filtration .

First Slide : we expose there the different filtration equations at constant pressure on the assumption that the gypsum cake formed during the filtration of the slurry is an incompressible cake and we therefore started from the equations analogical to the laws of electricity and we also applied those relative to flowing, in particular those of Carman, Kogeny, Darcy, and we therefore arrived at the following equation : T being the time, V the volume of filtrate collected. When we noted that experimentally, during gypsum cake formation, we have turbulence phenomena, phenomena of instability of the gypsum cake that lead to a non-constant flow of liquid through the filter cloth. When the cake is left to stabilize, we can assume that the rate of passage through the filter cloth is constant and we therefore obtain an equation of parabolical shape giving time as a function of volume; by setting on abscissae the volume and tB on ordinates we should obtain a straight line. Here are the straight lines obtained for some of the phosphates and we have called them in this case A, B, C and D. We quite easily manage to get a rectilinear portion. At the beginning of filtration, you get a progressive clogging of the filter cloth which becomes constant and also an unstable gypsum, gypsum cake and, after a certain time, we obtain a phenomenon which is more or less permanent.

We now go on to the second phase, which is the mathematical modelisation of the washing process. We have modelised the washing process in one single stage with water. Of course, these are only laboratory experiments on phosphoric slurry made on a pilot-plant. We used a sort of universal equation of the washing process, a partially derivative equation of the second degree. C stands for the concentration of P_2O_5 in the outflow channels of the washing liquid, Cf stands for this same concentration in the stagnant areas, which are the fine liquids which cover the gypsum crystals, Cs stands for the concentration of P_2O_5 in the solid phase; D the coefficient of axial dispersion; U the interstitial rate of the liquid flowing through the sediment, z being an axial distance within the gypsum cake; E the porosity corresponding to the outflow channels; Ef the fraction which is occupied by the solid phase. We have a number of simplifying theories : the P_2O_5 is not eliminated by the washing process in the solid phase, above all the unreacted syncrystallized material, therefore our equation is simplified.

If we suppose that the axial dispersion coefficient is constant, we find this equation. Once this equation was found, we therefore considered two cases : that of the stagnant area model, e.g. without any axial dispersion, which corresponds to a piston-like movement, and the case of axial dispersion. In the stagnant area model, the axial dispersion having been neglected we have two parameters C , C_f , we therefore had to introduce a second equation in order to solve this system using as a base the geometric figure on the transfer kinetics between the stagnant areas and the liquid outflow channels. The solution of this system is indicated here, it is an exponential product, in fact, quite a simple solution. The axial dispersion model is one that was solved in the literature and here is the solution, the mathematical model representing it. Experimentally, we therefore have time as a function of volume. We note that we have two linear portions : a first one which corresponds to the acid leaving the cake, this is a piston-like movement, and we have a second linear portion which corresponds to the washing process itself. We shall come back to this figure later and we shall then see that all the outflow parameters can be calculated from mathematical models and can also be simply calculated from the washing straight line in question. Here, we have the variation of the P_2O_5 concentration at the filter exit. It is a curve that looks like this, whereas here we have taken this origin in the mathematical model because there is a certain dilution which occurs after the addition of water on top of the gypsum cake. We therefore used our model because of this piston-like movement phase which corresponds to the coming out of the phosphoric acid by making the change from variable, which was imposed by this first washing phase, and the model exposed previously therefore becomes like this, θ standing for the time defined by this equation. Here, you have the application mechanism of this model by leading to θ in abscissae and in ordinates, the logarithm of the initial concentration relation and the concentration during the time θ . As a rule we obtain a straight line.

You can notice that, at the beginning of the washing phase, we get a straight line, the slope of which is equal to the transfer constant. Still adapting this model to experimental reality to take into consideration this first washing phase, which corresponds to the outcome of the phosphoric acid, you have here the model of axial dispersion by using a particular solution such as it was given to us by the Boltzmann transformation.

The application mechanism of this model in this diagramme ($\theta, 2 W \theta$) W standing for the error function, is also a straight line; we note that at certain points of the washing phase, this model can be applied.

In this case, we have equations that enable the exploitation of the washing straight line which enable the calculation of the parameters simply from the washing straight line. Therefore, here is the rest of the equations and here are the values which were calculated in an experimental way, the porosity corresponding to the outflow channels 31, porosity corresponding to the stagnant areas 36, outflow rate 0.4 cm/sec. By the exploitation of these two models, you get all equations leading to the same parameter. We have here the comparison of the calculations by the two methods, the combination of the two mathematical models and exploitation of the washing straight line. You can see that the results agree.

Here, we have a simple account of the equations that enable us to find the point on the washing line where the concentration of P_2O_5 falls by half at the filter exit. Just take a volume equal to the phosphoric acid volume taken from the cake during the filtration phase.

You have here the experimental model, the model of the stagnant areas, which coincides with the experimental model practically until the end, and you have the axial dispersion model on the concentration diagram according to the time that only coincides in the middle of the washing phase. Here is what these models gave for some of the phosphates named A, B, C and D. Speaking in terms of these parameters, we can, if you wish, judge of the state of the calcium sulphate crystals obtained and compare between each other the different phosphates. Just as in the statement on filtration, we find here the same classification in a decreasing order : the phosphate A, B, C and D.

Here, a last figure that shows that during the washing phase we can have one single straight line and we can also have two straight lines and sometimes even three, each linear part being characterised by a different transfer constant. Here, you have the concentration curve in terms of the volume, the time in terms of the volume, and also two linear parts. The criterion of the application of the stagnant areas, for each linear part, corresponds to two straight lines, the slope of which is equal to the transfer constant.

Mr VINCKE (Windmill, Netherlands)

It is certain that filtration is one of the oldest manipulations used by mankind. The earliest records indicate it : "accepted as an established practice in the efforts to prepare food and drink".

The name filtration is said to stem from the art of wine making. It seems safe to say that it is also certain that filtration today is still one of the least understood technical processes.

Development work reported to ISMA technical meetings is mostly based on empirical work in laboratory and pilot plants and full scale plant operations.

Very few papers have been presented on the fundamental of unit operations used in our industry, such as filtration of gypsum in phosphoric acid plants.

It is very difficult - if not impossible to design a model describing in full detail the complicated mechanism of filtration and subsequent cake washing of a gypsum filter. At present it seems to be wishful thinking to say that a filter can be calculated and designed purely based on mathematics.

One may argue that an empirical approach is more practical and yields direct results which may be applied in practice.

However, because of the many influences involved this approach will be very time consuming, if not supported by theoretical models which improve our understanding of the phenomena involved.

In their most interesting work the authors have again revealed some secrets of filtration which may help to improve the design of - and the control over filters. As suggested by the authors the study could be continued by working out mathematical models for weak acid washing or be completed by the research for a mathematical model representing the entire washing. However, I think that two important phenomena in filtration will be almost impossible.

to work into a useful mathematical model. The first is the two phase flow gas-liquid which occurs in the drying of the cake between different stages. It can be said that air can exert a considerable blinding effect. Secondly, preferential flows through the filter cake occur at points of lowest resistance. For instance there were cracks formed in the cake.

May I receive the comment from the authors on these two influences?

One more question :

Figure I shows that the filtration curve at constant pressure and constant flow-rate through the filter (U') is a straight line on diagram $(V, t/v)$ in the filtration of slurries produced with phosphate rock A, C and D. The slope of this straight line is equal to the resistance of the sediment per volume of filtrate collected.

If this slope decreases the resistance of the sediment per volume of filtrate decreases also; thus, you have an improved filtration of the phosphoric acid slurry, if the resistance of the cloth is equal in both cases. The slope of the filtration curve obtained in filtration of the slurry produced with phosphate D is less than the slope of curve A. Poor filtration of slurry D is caused by high resistance of the filter cloth (blinding etc.). Is this increase in resistance only caused by impurities from the rock or is blinding caused also by small gypsum crystals ?

Mr. JEMAA

As far as the turbulences that can occur in an industrial filter, such as the introduction of a gas pocket, in the gypsum cake or cracks appearing on the surface of the gypsum cake, are concerned, one must say that we have, in our model, assumed a perfect gypsum cake, one that we manufacture ourselves in the laboratory that did not cause many problems but I suppose that, effectively, in this particular case, the mathematical model becomes really complicated and one would have to try to introduce these turbulences in the mathematical model. We did not consider these two cases, mainly because we wanted essentially to find, in the best experimental conditions possible, a model that could describe not only the flow within the porous cake, but also the structure of this porous cake.

As far as figure one is concerned, we do have a slope that is different for the phosphate D. Is this bad filtration of phosphate D due to impurities contained in this phosphate or else to a bad crystallisation of the gypsum ? In the conditions we have adopted, the gypsum crystallisation was rather good. It's more the impurities, especially the deposit of a layer of organic material which probably comes from tar, which actually brought on this strong resistance and deteriorated the filtration qualities.