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THE PREDICTION OF ROCK DISSOLUTION RATES IN THE NORSK HYDRO HEMIHYDRATE PHOSPHORIC ACID PROCESSES

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SUMMARY

The Norsk Hydro Hemihydrate phosphoric acid processes are designed to allow a coarse grind of phosphate rock to be processed. In both the Hemihydrate and Hemi-Dihydrate processes the rock is dissolved in the first of two reaction stages. The residence time used for the first stage must take into account the size distribution and reactivity of the rock being processed.

A Design Method to predict rock dissolution rates has become important due to today's trend of using coarser rocks and reduced reactor residence times. Such a method has recently been developed which has been checked using experimental data obtained on the laboratory and pilot plant scales.

The Design Method allows the dissolution of a phosphate rock of known particle size distribution to be calculated. This allows any phosphate rock feedstock to be checked to see if it is suitable for use on an established plant. Alternatively, for a new plant the residence time and reactor design can be determined for the proposed rock feed.

INTRODUCTION

The Norsk Hydro Hemihydrate and Hemi-Dihydrate phosphoric acid processes are designed to produce a concentrated acid containing from 40% to 50% P_2O_5. The choice of acid concentration is usually influenced by the performance of the rock and the use to be made of the acid.

In both processes phosphate rock is dissolved in the first reaction zone where the sulphate concentration is maintained at a very low level. Complete precipitation of calcium sulphate hemihydrate is achieved in the second reaction zone by the addition of sulphuric acid. Slurry is recycled from the second reaction zone to the first at a controlled rate to achieve hemihydrate crystal growth and maximise filterability.

It is essential that complete dissolution of the rock occurs in the first reaction zone if P_2O_5 efficiency and hemihydrate filterability are to be maximised. The first reaction zone in both processes is shown as Reactor 1A and 1B in the simplified flow diagrams given.

The design procedures used for both processes normally provide sufficient residence time in the first reaction zone to completely dissolve the phosphate rock. However, in the cases of unreactive rocks, or rocks having very coarse size distributions, a method is needed which will predict dissolution rates with sufficient accuracy to allow size distribution and/or

residence time to be defined. Such a design method was first applied to the dihydrate process and the results published (1) in 1964. The technique involved the assumption that the rate of dissolution of a rock particle approximates to a first order reaction in a batch reaction system. The batch data were then translated to continuous stirred tank systems using residence time distribution functions. Although the technique gave a reasonable prediction of the degree of conversion, it had insufficient accuracy to be used to evaluate rocks, due mainly to the inhibiting effect of sulphate ions. As a result, the method was abandoned in favour of direct measurement for an individual case.

As the sulphate concentration in the first reaction zone is very low in the Hemihydrate processes the effect of inhibition on dissolution rate has little significance. Furthermore, any design method is only expected to provide guidelines for reaction volumes and/or size distributions. It is not expected to provide P_2O_5 efficiency losses due to unreacted rock in the absence of experimental verification.

This paper describes the application of the design technique to the Hemihydrate processes and considers the implications.

FACTORS AFFECTING RATES OF DISSOLUTION

For a given acid P_2O_5 concentration and reaction temperature, the most important factors which will influence the degree of dissolution of a rock in the hemihydrate process are:

(a) Reactivity of rock
(b) Particle size distribution of rock
(c) Residence time in reactor

From earlier work(1) it is known that reactivity is largely dependent on the specific surface area of the rock particles. The higher the specific surface area, the higher the reactivity. Sedimentary rocks, such as Khouribga, Florida, Jordan, etc., have a higher specific surface area and higher reactivity than igneous rocks, such as Kola or Phalaborwa, of the same particle diameter.

In the dihydrate process the influence on reactivity of the fine, internal pore structure is not very significant due to the presence of a large excess of SO_4 ion and the clogging of the pore structure with calcium sulphate.

In the hemihydrate process, where the SO_4 concentration at the point of rock dissolution is very low, the internal pore structure is of more importance, and the specific surface area based on gas absorption becomes more relevant to reactivity compared to areas based on air permeability.

(1) Janikowski S M, Robinson N, Sheldrick W F, Fertiliser Society Proceedings No.81, 18 February 1964.

Specific surface areas for some typical commercial rocks measured by gas absorption are as follows:

Phosphate Rock (63-76 micron fraction)	Absorption Value m^2/g
Khouribga	20.1
Togo	12.7
Florida	13.5
Nauru	11.2
Taiba	7.5
Phalaborwa	0.4
Kola	0.1

From these figures it becomes clear why igneous rocks such as Kola or Phalaborwa exhibit such low reactivities and require fine grinding to compensate.

The influence of particle size distribution on the rate of dissolution will depend on the proportion of large particle sizes present. For rocks of low reactivity the particle size required to achieve a given rate of dissolution will be lower than the size required for reactive rocks. To evaluate the effect of particle size distribution a technique is required which takes into account the rates of dissolution of individual particle sizes and integrates these dissolution rates according to the weight percentages of individual particle sizes present in the rock blend. Such a technique would allow the rate of dissolution of any blend of rock to be assessed for a given reaction system of known residence time.

The alternative to this experimental/mathematical approach would be to determine experimentally the dissolution rate of a given blend, reaction system and residence time. Using continuous tests this could be very time consuming before a satisfactory solution was found.

MATHEMATICAL MODEL (Reference 1)

If the conversion of a rock particle of given diameter in a batch reaction system can be expressed with sufficient accuracy by the expression

$$C = 1 - \left(\frac{Di - AT}{Di}\right)^3$$

where Di = Diameter of the rock particle at time T
C = 1 when $T = Di/A$

then the rate constant, A, can be evaluated from experimental data using rocks of known particle size distribution.

Batch conversion data can be converted to a continuous stirred tank reactor system (C.S.T.R.) using the following relationship:

$$C = 1 - \int_{T=0}^{Di/A} \left(\frac{Di - AT}{Di} \right)^3 d\,F(T)$$

where F(T) is the displacement function for the reactor sequence being used.

For a single, continuous reactor:

$F(T) = e^{-T/\theta}$ where θ is the mean residence time in the reactor

For two, equal sized reactors, operating in series:

$$F(T) = e^{-T/\theta} \left(1 + \frac{1}{\lfloor 1} \cdot {}^{T}/_{\theta}\right)$$

For three, equal sized reactors, operating in series:

$$F(T) = e^{-T/\theta} \; 1 + \frac{1}{\lfloor 1} \cdot {}^{T}/_{\theta} + \frac{1}{\lfloor 2} \cdot ({}^{T}/_{\theta})^2$$

If recycle from the end of the reaction train to the first reactor is involved then the displacement equations become very complicated. In the hemihydrate process, once the rock passes through the low SO_4 zone the rate of dissolution will be significantly reduced. This is due to the retarding effect of the high SO_4 concentration in the second zone. If significant quantities of unreacted rock pass through to the second zone then not only will be P_2O_5 efficiency be affected, but also hemihydrate filterability. It is important, therefore, that the mathematical model simulates the dissolution of rock particles on a once-through basis and considers only the first reaction zone.

To calculate the percentage dissolution of a given particle size it is necessary to integrate the product of the rate equation and the displacement function for the system being considered

For a single, continuous reactor:

$C = 3p^3 \; [2 - 2/p + 1/p^2 - 2e^{-1/p}]$

where $p = \Theta A/Di$

Θ = Mean Residence Time

For two, equal sized ractors, operating in series:

$C = 6p^3 \; [4 - 3/p + 1/p^2 - e^{-1/p}(4 + 1/p)]$

where $p = \Theta A/Di$

Θ = Mean Residence Time of First Reactor

For three, equal sized ractors, operating in series:

$C = 3p^3 \; [20 - 12/p + 3/p^2 - e^{-1/p}(20 + 8/p + {}^{1}/_{p^2})]$

where $p = \Theta A/Di$

Θ = Mean Residence Time of First Reactor

Once the continuous conversion for each size range has been calculated then the predicted conversion for any blend can be obtained using the following expression:

$$C_B = \sum \frac{C_D \times S_D}{S_D}$$

where C_D = Conversion of particle size D in a continuous reaction system of given residence time.

S_D = Percentage by weight of size range in blend.

C_B = Predicted conversion of a blend.

EVALUATION OF RATE CONSTANTS

To evaluate a blend of rock using the technique outlined in the previous section it is necessary to determine the rate constant for a specific rock. Approximate values were initially determined using batch experiments involving the dissolution of close sieve fractions. Continuous trials were then carried out using a single, stirred tank reactor and a rock blend of known size distribution to evaluate the rate constant more accurately. A computer program was developed to optimise the constants for different rocks. This program was then modified to provide a design procedure which evaluates the expected rate of dissolution of rock blends for different residence times and reactor arrangements.

PILOT PLANT EVALUATIONS

Florida Rock

Continuous pilot plant trials were carried out using two coarse size distributions when producing 42-43% P_2O_5 acids.

Samples of slurry were taken over the last three days of each trial and the amount of unreacted rock determined.

The percentage dissolution of the rocks for the blends and conditions used were as follows:

		Blend 1	Blend 2
Dissolution of Rock from First Zone	(%)	97.9	97.0
Mean Residence Time of First Zone	(mins)	18.5	38.4
Reactor Sequence Used for First Zone		1:1	1:1:1

Table 1 gives the size distributions of each blend used in the pilot plant trials. Table 2 gives the variation of the predicted conversion with the residence time of the first stage using the computer program.

TABLE 1 : SIZE DISTRIBUTIONS OF FLORIDA ROCK

Mean Particle Size (mm)	Percentage of Size in Blend	
	Blend 1	Blend 2
1.7	0.1	0.3
1.4	0.1	1.7
1.0	0.2	16.0
0.85	0.2	17.0
0.60	3.4	20.8
0.50	3.9	10.6
0.421	5.6	5.9
0.355	7.9	4.8
0.300	9.5	4.5
0.250	12.6	4.3
0.212	12.4	3.6
0.180	11.5	2.8
0.150	15.3	3.1
0.125	8.7	1.8
0.106	1.6	1.0
0.089	1.6	0.4
0.075	2.3	0.6
0.063	1.4	0.2
0.053	0.2	0.1
0.045	1.5	0.5
	100.0	100.0

TABLE 2 : PREDICTED RATE OF DISSOLUTION OF FLORIDA BLENDS (2 REACTOR SYSTEM)

Residence Time of First Zone	Blend	
	1	2
	Percentage Dissolution of Blend	
0	0	0
4	77.15	54.54
6	85.53	66.64
8	90.00	74.79
10	92.66	80.51
16	96.40	90.00
20	97.49	93.15
26	98.39	95.81
30	98.75	96.87
40	99.24	98.32

Phalaborwa Rock

A similar exercise was conducted using two blends of Phalaborwa rock producing 49% P_2O_5 acid.

In this case the experimental dissolution rates obtained for the blends were as follows:

	Blend 1	Blend 2
Dissolution of Rock in First Stage (%)	89.3	93.5
Mean Residence Time of First Zone (mins)	32	32
Reactor Sequence Used for First Zone	Single	Single
Acid P_2O_5 (%)	49	49

Table 3 gives the size distributions of each blend used in the pilot plant.

Table 4 gives the variation of the predicted dissolution of the blends with residence time.

TABLE 3 : SIZE DISTRIBUTIONS OF PHALABORWA BLENDS

Particle Size (mm)	Percentage of Size in Blend	
	Blend 1	Blend 2
1.4	0.6	
0.68	3.8	
0.327	3.7	
0.275	6.2	2.1
0.231	6.9	6.2
0.195	8.7	4.5
0.165	3.2	8.2
0.137	11.2	9.1
0.115	5.8	7.0
0.098	5.6	5.6
0.082	5.3	6.3
0.069	8.9	8.9
0.058	1.4	3.0
0.053	28.7	39.1

TABLE 4 : PREDICTED CONVERSION OF PHALABORWA BLENDS

Residence Time of First Zone (mins)	Blend 1	Blend 2
	Percentage Dissolution of Blend	
0	0	0
4	61.34	67.62
10	78.87	83.76
14	83.66	87.79
20	87.76	91.11
24	89.51	92.47
30	91.35	93.88
34	92.25	94.55
40	93.32	95.35

ASSUMPTIONS

The design method involves the following assumptions and approximations:

(a) The continuous stirred tank reactors are assumed to be perfectly mixed.

(b) The experimental sieve analyses used to calculate size distribution will give perfect separation.

(c) A stepwise rather than a continuous procedure is used to evaluate the conversions of rock diameters.

(d) Particles are assumed to be spherical of a given diameter and have a smooth surface.

AGREEMENT

The following shows the agreement between experimental and calculated data:

Rock	Florida 1	Florida 2	Phalaborwa 1	Phalaborwa 2
Blend				
Acid P_2O_5 (%)	42 - 44	42 - 44	49	49
Expt. Dissolution	97.9	97.0	89.3	93.5
Calcd. Dissolution	97.2	98.2	91.8	94.3

CRITICAL PARTICLE SIZES

The reactor sequence used in the first zone of the Norsk Hydro hemihydrate processes has a volumetric ratio of 1:1. These reaction vessels are used for rock dissolution and the total volume required depends on the reactivity of the rock, its size distribution and acid P_2O_5 concentration. The volume can range from less than 0.7 m^3/tonne P_2O_5 fed to 2.7 m^3/tonne P_2O_5 fed, although a range of 0.7-1.3 is most commonly employed.

The computer program has been used to calculate the dissolution of a range of particle sizes using the above reactor sequence operating at different residence times.

The maximum particle sizes which provide 95% dissolution using total reaction volumes of 1.0, 2.0, 3.0 and 4.0 m^3/tonne P_2O_5 fed are indicated as follows:

Total Reaction Volume m^3/tonne P_2O_5 Fed	Residence Time of First Zone (mins)	Maximum Particle Size which Provides 95% Conversion (mm)	
		Florida	Phalaborwa
1.0	24.22	0.421	0.15
2.0	48.44	0.7	0.3
3.0	72.66	1.0	0.5
4.0	96.88	1.4	0.7

For a given residence time the effect of the different sizes on dissolution of a rock will depend on the percentage of these sizes in the blend. It is clear from the above that Phalaborwa rock needs to be ground more finely than Florida rock.

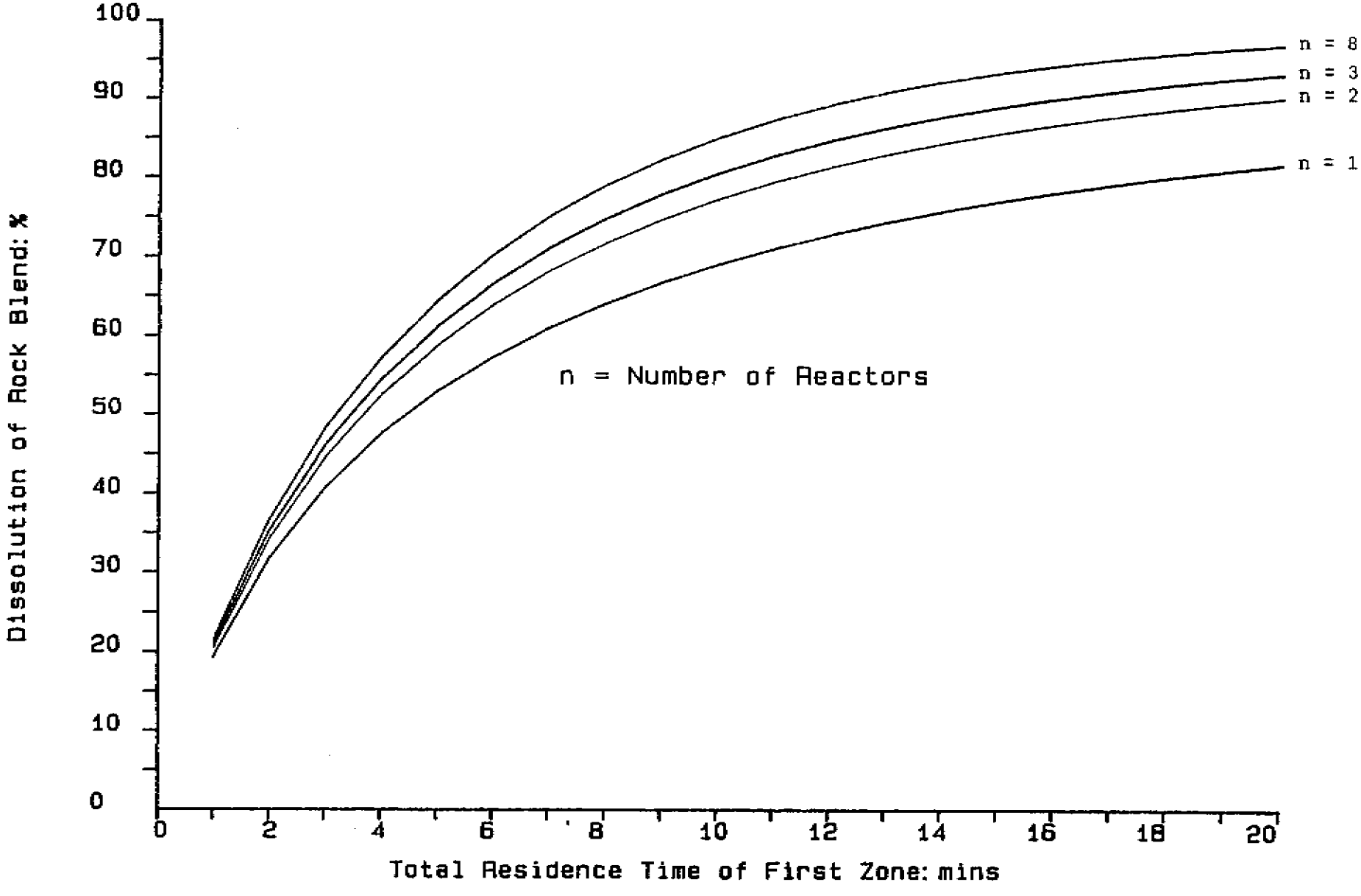
CONCLUSIONS

A design method has been developed to calculate the percentage dissolution of a rock blend in the first zone of the Norsk Hydro hemihydrate processes.

The accuracy of the method is considered sufficient to determine whether a given rock blend is suitable for an existing plant. Alternatively, it allows a reaction system for a new plant to be designed to meet the requirements of a proposed rock blend.

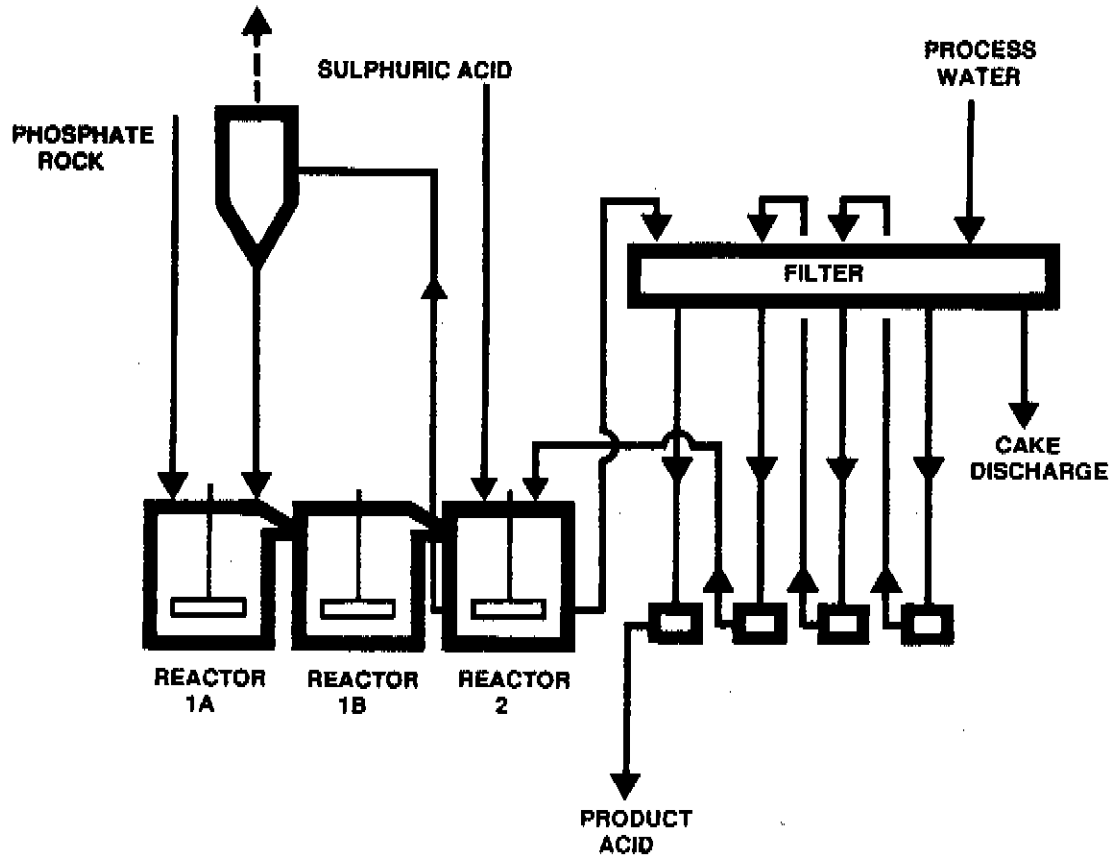
The first reaction zone may comprise any number of separate stirred tank reaction vessels. The given graph shows the relationship between the rate of dissolution and total residence time using different numbers of reaction vessels. In all cases the same blend of Florida rock was processed. From this it can be seen that higher rates of dissolution are obtained at a given total residence time as the number of reaction vessels increases. This conclusion is important with respect to hemihydrate plants which have been converted from Dihydrate processes. Very often these Dihydrate plants comprise a large number of reaction vessels which can be sub-divided in the most optimum manner to give the first and second zones of a hemihydrate process which maximise dissolution. For a new plant two reaction vessels are normally selected for the first zone. This usually gives the best compromise with respect to capital cost and rate of dissolution.

Finally, the computerisation of the design technique allows all the variants of a specific case to be explored quickly, allowing important decisions to be made early in the life of a given project.



THE INFLUENCE OF REACTOR STAGES ON DISSOLUTION

NORSK HYDRO LICENSING HEMIHYDRATE PROCESS



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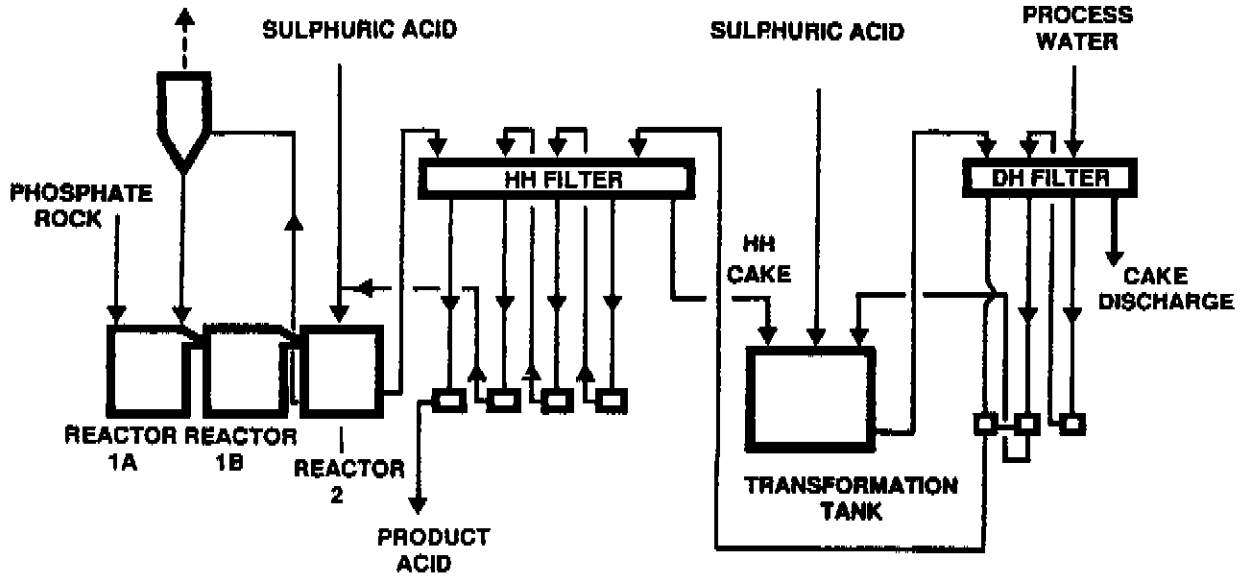

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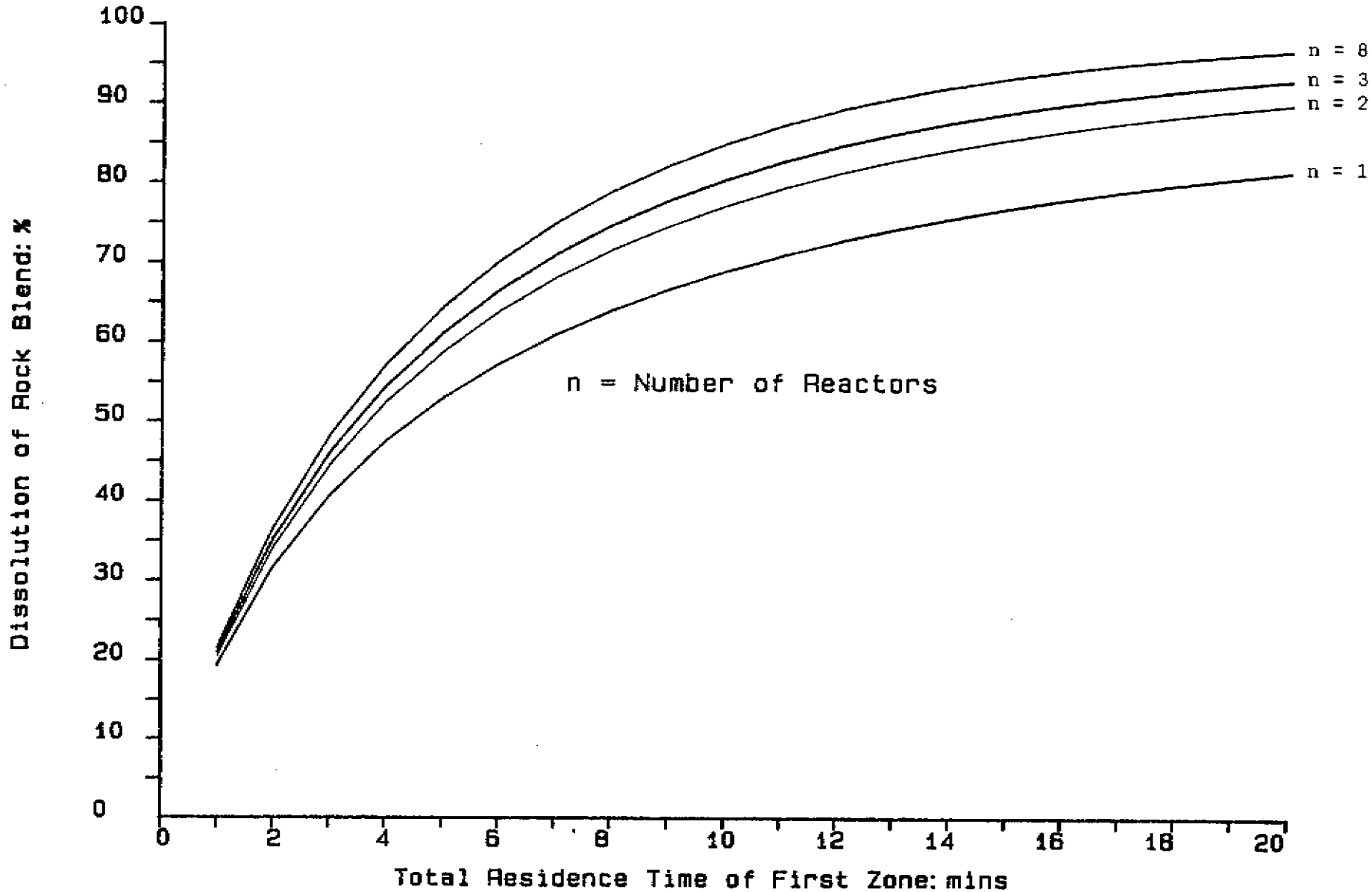

THE INFLUENCE OF REACTOR STAGES ON DISSOLUTION

TA/88/18 The prediction of rock dissolution rates in the Norsk Hydro hemihydrate phosphoric acid processes, by N. Robinson, Norsk Hydro Fertilizers, U.K.

DISCUSSION (Rapporteur Mr.C.M.H. Vincke, Windmill Holland, Netherlands)

Q - Mr. N. YAMANAKA (Nissan Chemical Industries Ltd., Japan)

There are other parameters than dissolution rate of rock in the first stage to design a phosphoric acid plant with a rock the nature of which is not known. Do you think that this design method is sufficient to completely eliminate a continuous small-scale test in designing a plant with new rock ?

A - I think the question relates to whether, in fact, this method of design is the complete story when designing a reaction system for the hemihydrate process. And the answer, of course, is that it is not. It is only one aspect of it, but it is an important aspect in that there is no point in designing a reactor for optimizing crystal growth or minimizing foaming or anything else if you do not dissolve the rock. You must dissolve the rock, and this is one of the parameters which must be satisfied, but it is not to say that this is the only parameter.

Q - Mr. P. SMITH (Prayon, Belgium)

Does the acid viscosity affect the dissolution rate ? If so, what is the relative magnitude of the viscosity and particle size effects ? Can the rates be compensated for ? Can you compensate for the effect of viscosity ? Similarly, does the slurry viscosity affect the dissolution rate ?

A - The question is: Is the slurry viscosity more important than particle size distribution, and will it affect dissolution ? The answer is yes. The viscosity of a slurry can affect the dissolution rate particularly if it affects the mixing efficiency. Really, it is a question of what design of agitator you have, what the residence time is, what the mixing time is, etc., but the higher the slurry viscosity the harder it is to achieve a good mixing.

I think, personally, that a particle size redistribution has a bigger effect, has a quicker effect. The slurry viscosity is taken into account by the determination of a dissolution constant which, as I have mentioned, must be determined practically. I am not recommending that you try to calculate a dissolution constant from theoretical principles. We did try to do this many, many years ago, and it really is just not accurate enough.