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NEW DEVELOPMENTS IN THE DUAL PIPE REACTOR PROCESS

by P. CHINAL & Y. COTONEA, CdF Chimie AZF, France -

This communication continues the presentation of the GESA DUAL PIPE REACTOR process, given at Kalithea in 1982.

Since that time, numerous pipe reactors have been started up both in our factories and elsewhere in the world.

Our present purpose is to take into account the experience of DAP obtained with this process and to present the extension of this process with co-neutralisation of phosphoric and nitric acids.

Since December 1983, when the GESA and APC companies merged within the CdF Chimie group, the GESA process has been marketed under the name of the new CdF Chimie company "Azote et Fertilisants" (Nitrogen and Fertilizers), namely "AZF Dual pipe reactor process".

The result of this merger has been to combine the assets of the two companies GESA and APC, both of long standing in the fertiliser world.

At the present time, the resulting group incorporates 15 factories, including 18 NP and NPK plants and 22 pipe reactors operating within the group. On a worldwide scale, 40 AZF pipe reactors are at present operating or being installed.

- o During the 60's, TVA's efforts have contributed to the development of the tubular reactor concept, but the technical problems - pumps, instrumentation, control - have limited the trials to pilot scale.

- o During the 70's, while TVA continued its work and extolled the merits of the "pipe reactor", the message was clearly received in Europe, and several European companies fitted pipe reactors for the production of NPK. Two of our plants (35 t/h) started up in 1975 and 1977, fitted with pipe reactors without a preneutralisation tank. . The American industry remained reticent.

  Finally, since 1980, the majority of the preneutralisers in Europe have been consigned to museums and today no operator would wish to return to the agitated tank epoch.

  In the USA and, as a result, in the countries which produce DAP, the doubt remained.

  There was no doubt about the success so far as the NPK were concerned, but the experience with DAP remained inadequate - problem of scaling and acid quality.

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- o A recent international demonstration in our "L'Oseraie" factory has helped to dispel the doubt and to demonstrate all the merits of the GESA-AZF process for the manufacture of 18.46.0.

1 DESCRIPTION OF THE PROCESS

Table 1 recalls the main characteristics of the AZF process.

- 1 reactor in the granulator.
- 1 reactor in the drier tube

producing monoammonium phosphate which crystallises in the drying air stream.

This MAP passes through the screening fines or through the discharge of the drier air circuit cyclones before being recycled to the granulator for more ammoniation.

Table 2 shows the various molar ratios measured at different points in the loop in the case of a DAP manufacture.

2 MANUFACTURE OF DAP USING 2 AZF P.R. AT L'OSERAIE

The l'Oseraie plant was started up in 1977 for the manufacture of NPK type fertilisers 3 x 17 at 35 t/h.

It was originally fitted with a pipe reactor in the granulator and in 1979 the installation of a second reactor in the drier tube has made it possible to attain 50 t/h.

In 1984, the required modifications have been carried out to make it possible to produce DAP at 50 t/h.

2.1 - EQUIPMENT - See Table NO. 3 -

(14)	Pipe reactors : AZF design		
(3)	Granulator: Ø 3 m	Length: 6 m (Ø 9'10" l 19'8")	
(4)	Drier: Ø 4 m	Length 32 m (Ø 13'1" l 105')	
(5)	Elevators 200 t/h		
(8)			
(6)	Screens 2 lines area 21 m2 (226 Sq. Ft)		
	1 finishing screen 5.1 m2 (55 Sq. Ft)		
(7)	Grinders 2 lines		
(10)	Cooler Area	Area = 18 m2 (194 Sq. Ft)	
(13)	Gas scrubbing	Granulator	40,000 m3/h (23.500 ACFM)
		Drier	100,000 m3/h (58.860 ACFM)
	Plant sweetening		50,000 m3/h (29.400 ACFM)

2.2 - GENERAL CONDITIONS -

The acid employed is Moroccan acid of 52% strength; ammonia is introduced into the loop in liquid form and sulphuric acid is introduced into the gas scrubbing before it enters the pipe reactor.

The entry pressures of the liquids introduced into the reactors - ammonia - phosphoric acid - scrubbing liquid - are a minimum of 5 bars (72,5 psi) at the flanges. The recommended steam pressure is 8 bars (116 psi) to permit injection during operation. All the liquid lines are fitted with non-return valves.

2.3 - MATERIAL BALANCE - Table No. 4 -

The distribution of raw materials is shown in Table No. 3 for a DAP production of 50 t/h, i.e.
50% of P2O5 in the Dryer Pipe Reactor
50% of P2O5 in the Granulator Pipe Reactor and gas scrubbing.

The ammoniation ratios are shown in Table No. 2.

2.4 - CONTENTS - YIELDS

Rate	50 t/h
N content	18.5 %
Total P2O5	46.80
AOAC P2O5	46.75
WS P2O5	43.76
Hardness	5 kg
N* yield	99.3%
P2O5* yield	99.9%

NOTE

The yields are computed from losses measured in the only chimney stack of the unit.

2.5 - UTILITIES

Fuel oil	0.5 kg/t	(0,147 g/t)
Steam	ε	
Electricity	25 kWh/t	
Water	0.250 m^3/t	(66 g/t)

3 IMPROVEMENT OF EXISTING UNITS

The experience gained in our plants and by our licencees enables us to offer three types of modification to existing units, intended to:

- increase the production
- reduce energy consumption
- improve the operating rate
- reduce maintenance costs
- improve personnel working conditions

a - Installation of 2 pipe reactors , one in the granulator, the other in the drier.
We have carried this out in 8 units. A ninth is being fitted out.

b - Installation of a pipe reactor in the drier with the preneutraliser being retained (4 units).

c - Installation of a pipe reactor in the granulator either with or without the use of the existing neutraliser (2 units).

The first case results in the granulator being fitted and, possibly, a modification of the gas scrubbing unit.

Case (b) is particularly suitable for the DAP units.
This is illustrated by the GABES example later.

- Easy installation
- Minor modifications
- Very short plant stoppage

Case (c) is envisaged for sulfo-phosphate formulations (16.20.0 - 20.10.0).

3.1 - DESIGN OF THE AZF REACTORS -

Our experience is today based on 25 pipe reactors installed in various factories since 1975.

The design of our reactors is very simple and good operating conditions are based on the reactor diameter, good spraying direction of the mixture, and control of the conditions under which the liquids enter the reactor - flows - monitoring and regulation.

The problems of blocking encountered in the early industrial plants were quickly overcome.

Phosphoric acids of diverse sources may be employed equally well (Tunisia - Morocco - Togo - Jordan - Florida).

3.2 - RECENT PLANTS -

3.2.1 - May 1982 - SICNG - THESSALONIKI - GREECE

Revamping of a unit with installation of a pipe reactor producing ammonium sulfo-phosphate (9 t/h NH_3). A detailed analysis of this plant was given at British Sulphur (London - November 1983).

3.2.2 - December 1982 - SPIC - MADRAS - INDIA

Revamping of a DAP unit.
Capacity will be increased from 500 to 1000 t/day after installation of the DUAL pipe reactor process.

3.2.3 - March 1983 - DONAU CHEMIE - PISCHELSDORFF - AUSTRIA

Revamping of an old super-phosphate and a PK unit intended to produce NPK at 25 t/h (6.12.24 - 9.15.15 - 12.10.15), being started up.

3.2.4 - <u>April 1983</u> - SAEPA - GABES - TUNISIA
Revamping of a 1200 t/day unit to produce 1700 t/day. Its description is given later.

3.2.5 - <u>September 1983</u> - AZOT SANAYI - SAMSUM - TURKEY
Revamping of a conventional 710 t/day DAP unit to produce 950 t/day of 18.46.0 after installation of a pipe reactor in the drier. In progress.

3.2.6 - <u>September 1983</u> - IHP PRAHOVO - YUGOSLAVIA
Revamping of an NPK unit to increase production from 20 to 31 t/h and also to produce 25 t/h of MAP - 11.52.0 and 20 t/h of DAP.

3.2.7 - <u>October - November 1983</u> - MELEOUS - KRASNODAR - USSR
Test run on two NPK lines at 130 t/h of 17.17.17 per line with a pipe reactor in the granulator.
These start-ups are the subject of another communication.

4 AN EXAMPLE - THE REVAMPING OF THE SAEPA DAP UNIT AT GABES - TABLE NO. 5 -

This plant designed for an output of 1000 t/day in a conventional loop, preneutraliser plus granulator drum, after two years' operation produced about 1200 t/day of DAP.

The mere installation of a pipe reactor at the entry of the dryer has made it possible to reach 1700 t/day.

During the 3-day trial, the following results were obtained:

4.1 - CAPACITY -

Date	Operating hours	Output in 24 h
23.4.83	24	1637
24.4.83	22	1640
25.4.83	24	1680

During the test run, the averaged increase was 492 t/day, i.e + 43%.

On 28.4.83, not included in the trials, the capacity increase was 576 t/day.

4.2 - GAS - CONSUMPTION

Without the pipe reactor, the consumption was 6 Nm3/t ; with the pipe reactor it fell to 3.12 Nm3/t, i.e. (-48 %).

4.3 - AMMONIA YIELD -

Because of a lack of total ammonia metering, indirect calculation was possible by taking into account the quantities of phosphoric acid introduced into the scrubbers and the molar ratios measured in the scrubbing liquids. Comparing these data to the results before modification, it appears that the ammonia yield is at least as good and probably better.

5 OTHER USES OF THE PIPE REACTOR

The comparison of the physical properties of the particles obtained by drum granulation and spherodiser granulation would result in preference being given to the "onion peel" structure - better sphericity and increased resistance to humid environments.

This finding led us first of all to envisage spraying nitrate solution in the drier, which resulted in coating the granules originating from the granulator.

The results have, in fact, been reflected in an appreciable improvement in the sphericity and in the granulation yield at the exit of the drier and improved product quality, provided that a well-controlled coating is applied.

The development of pipe reactors in the dryer has replaced this technique and the combination of both systems has led to an industrial-scale trial of <u>co-neutralisation of both nitric and phosphoric acids</u> in one and the same pipe reactor.

This trial was successfully carried out in our Rouen plant on the manufacture of 3 x 17.

- No ammonium nitrate aerosol formation.

- Appreciable improvement in grain sphericity at the exit of the drier.

- Particle size distribution clearly narrowed towards larger sizes.

- Identical density.

- Better resistance to accelerated ageing tests despite a greater moisture regain.

The table below shows the results obtained for the commercial product during the same campaign. Before introduction of nitric acid into the tubular reactor and during powdering of ammonium phosphonitrate in the drier.

	Before	During
Particle size mm 4 - 3.15 %	20	48
3.15 - 2 %	79	52
Sphericity %	40	78
Crushing resistance (g)	3815	3445

6 ECONOMIC ASPECTS

Apart from the attractive technical aspects, a quick calculation shows the major benefits made possible by a revamping of a plant by installing an AZF pipe reactor in the dryer tube.

Let RM the cost of raw materials
FC the fixed costs (manpower, maintenance, energy)
S the sale price

The gross operating margin is:

$$\boxed{N_1 = S - RM - FC}$$

The installation of a P.R. in the dryer drum results in the introduction of 40% of additional RM into the loop for the same fixed costs.

The new gross operating margin will be:

$$\boxed{N_2 = 1.4\ S - 1.4\ RM - FC}$$

giving a profit per tonne:

$$\boxed{\Delta N = 0.4\ (S - RM)}$$

In 1984: $S \simeq 195\ \$$
$RM \simeq 180\ \$$
$\Delta N \simeq 6\ \$/T$

i.e. for a unit producing 1000 t/day of DAP, the annual profit amounts to

$$\simeq 2\ M\ M\ \$$$

7 PATENT

The AZF 2-tubular-reactor process is the subject of a patent filed in many countries.

European Patent 18.11.1981 - No. E.P. 40,122
U.S. application 28.04.1981 - N°. 258.460

8 REFERENCES

- ISMA communications TF/78/19 Orlando USA. Pilot scale development and demonstration of fertiliser production using crossed tubular reactors. B.R. Parker, M.M. Norton, J.W. McCamy, D.G. Salladay, T.V.A.

- Proceedings of the Round Table 1977.
  . Conservation of Energy in Ammoniation - Granulation plants - F. P. Achorn - D.G. Salladay.
  Experience with the pipe-cross reactor in Making N.P.K. Fertilizer J.L. Medbery.
  MFA's Experience with the TVA Pipe-cross Reactor, D.J. Brunner - K.J. Baggett.

- IFA Technical Congress Kalithea - Greece - October 1982 - Ph. Moraillon - Y. Cotonéa. "Savings on energy by a new method of using pipe reactors"

- "Fertilizer 1983" British Sulphur, Nov 83 - London - P. Chinal - Y. Cotonéa - "Reducing energy consumption in the granulation of ammonium sulphophsphate by installation of a pipe reactor".

- GESA Patent No. 2,481,611 5/05/1980 - Ph. Moraillon US Application No. 258,460 28/04/1981

- P. Chinal - Y. Cotonea - C. Debayeux "Reduction of investments and production cost in DAP and NPK fertilizers plants" Aiche Clearwater - May 84

A.Z.F. _ PROCESS

DAP_ NPK PRODUCTION _ GRANULATION LOOP

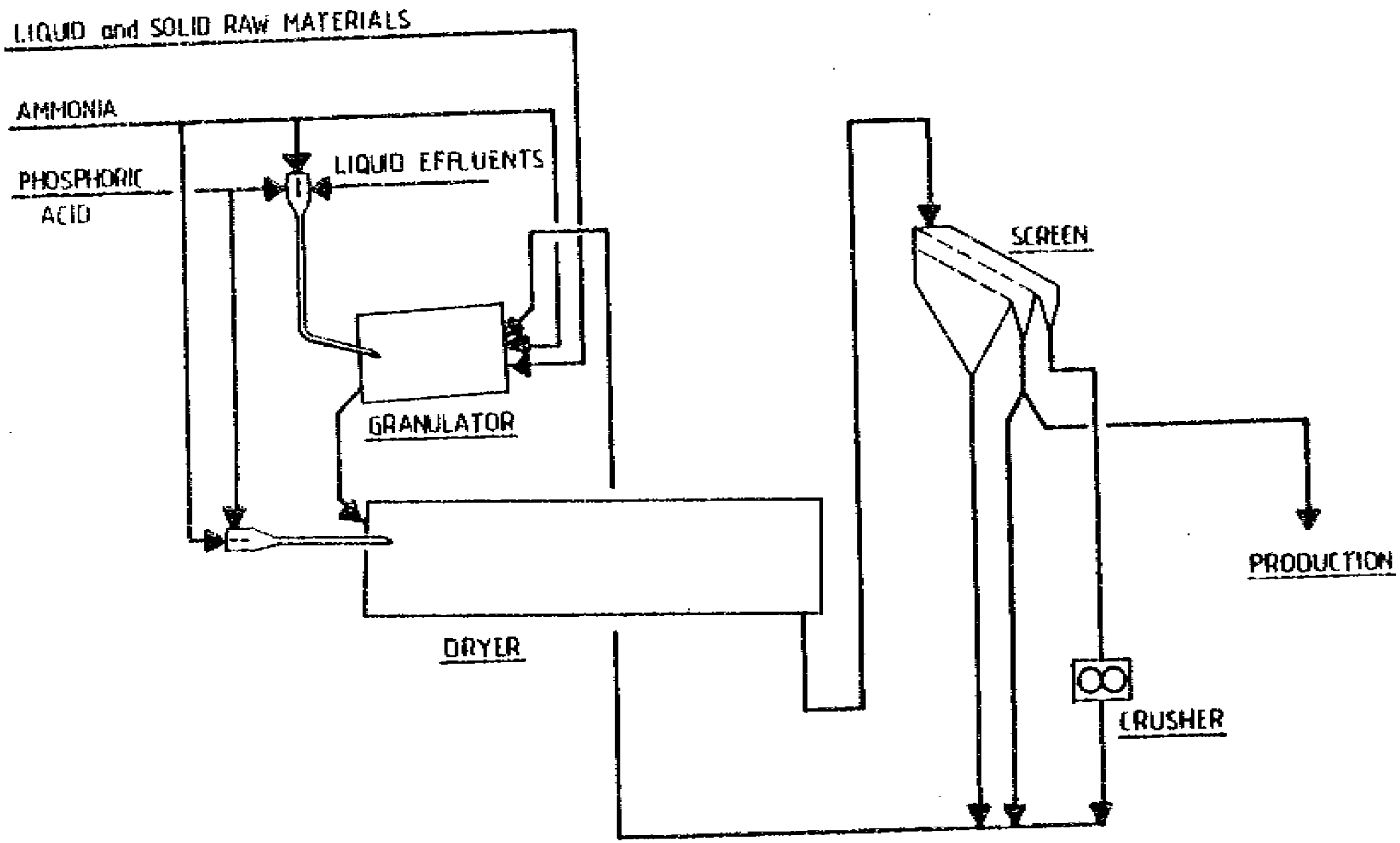
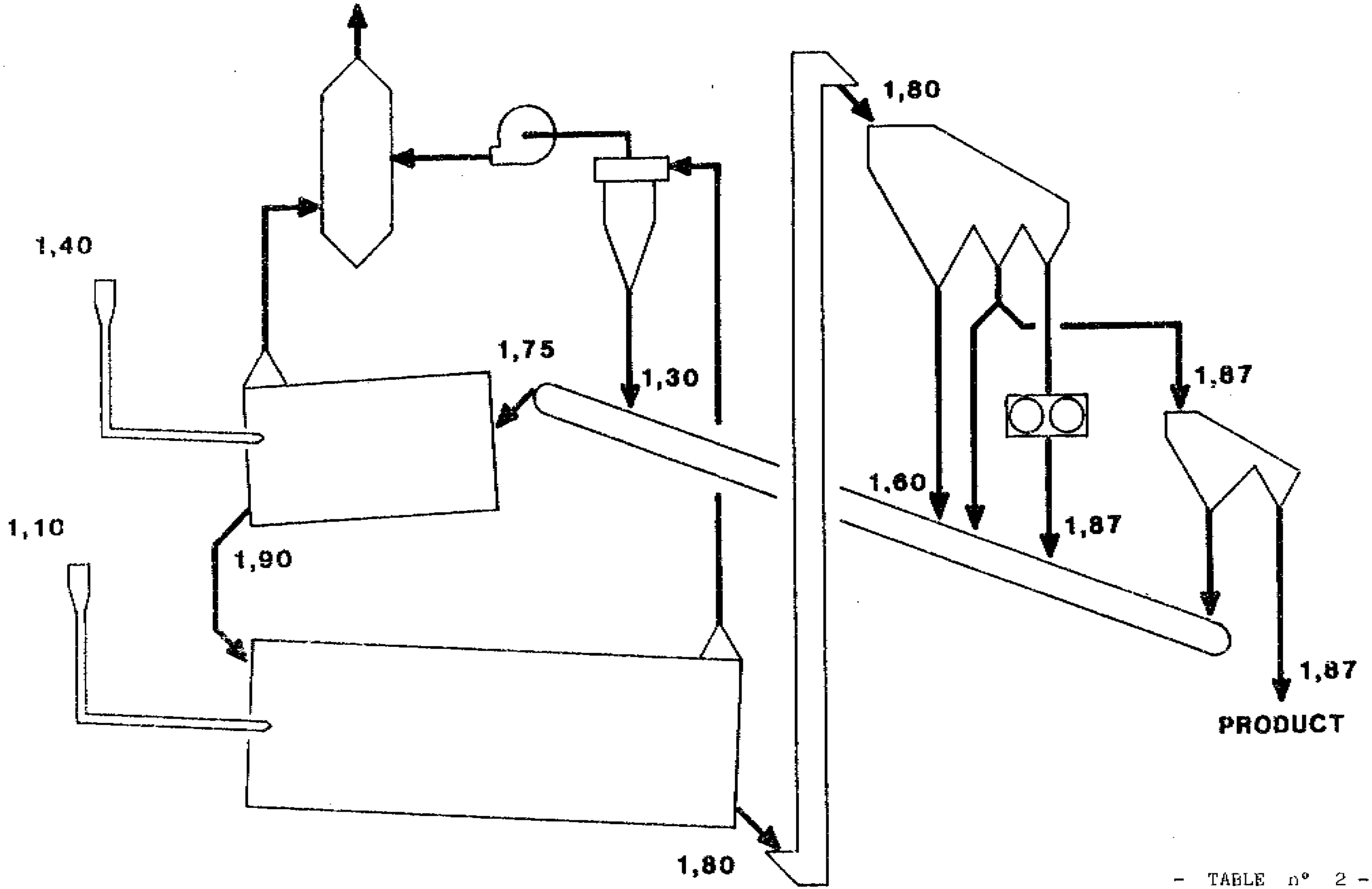


TABLE N° 1

N/P RATIO

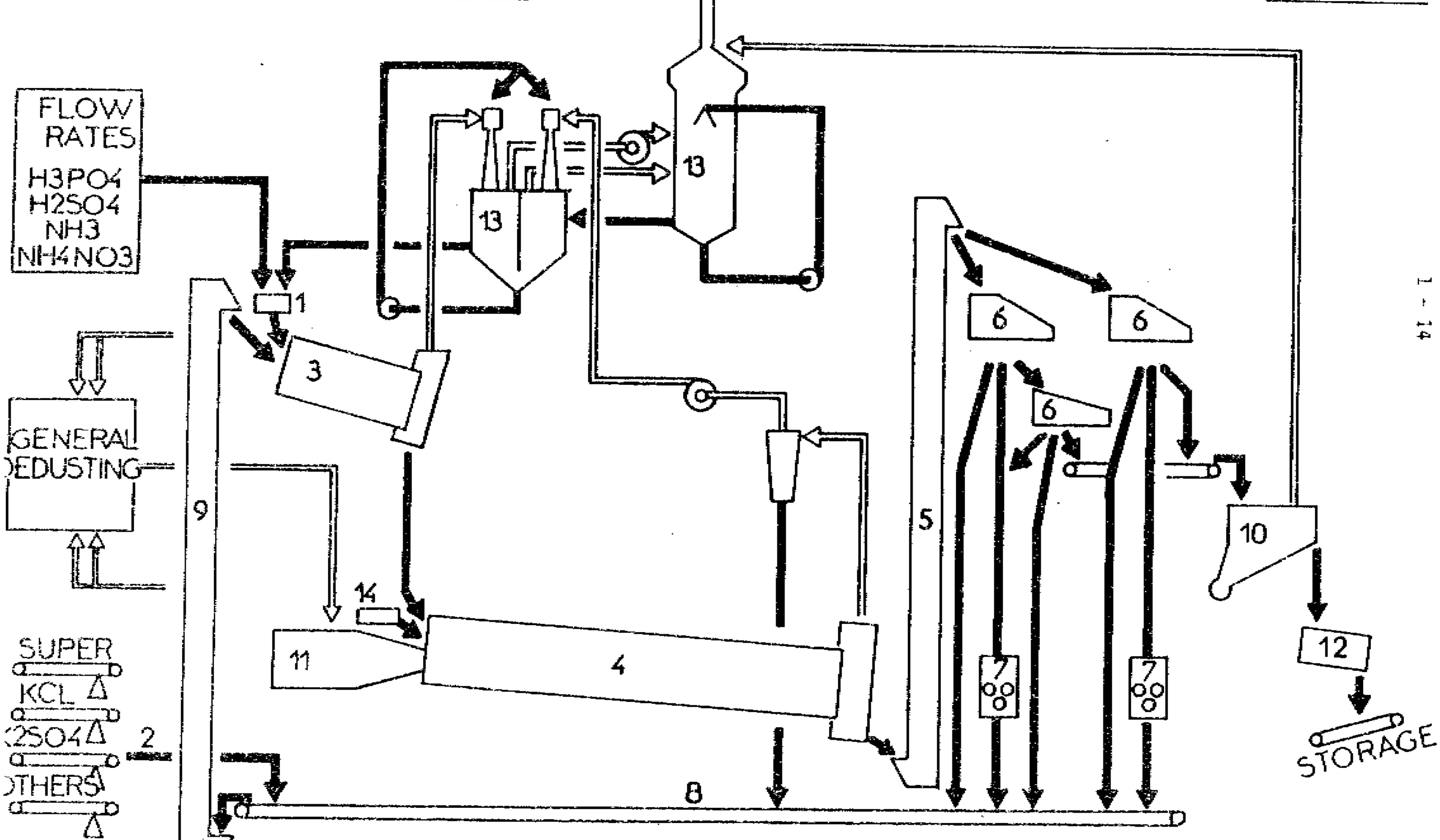


- TABLE n° 2 -

CDF CHIMIE AZF

EG III L'OSERAIE

table n° 3



CdF Chimie AZF CdF Chimie Azote & Fertilisants DÉVELOPPEMENT TECHNIQUE 76120 GRAND QUEVILLY B.P. 204	DAP L'OSERAIE 50 t/h	TABLE N° 4

kg/h 18.5 - 46.8 - 0

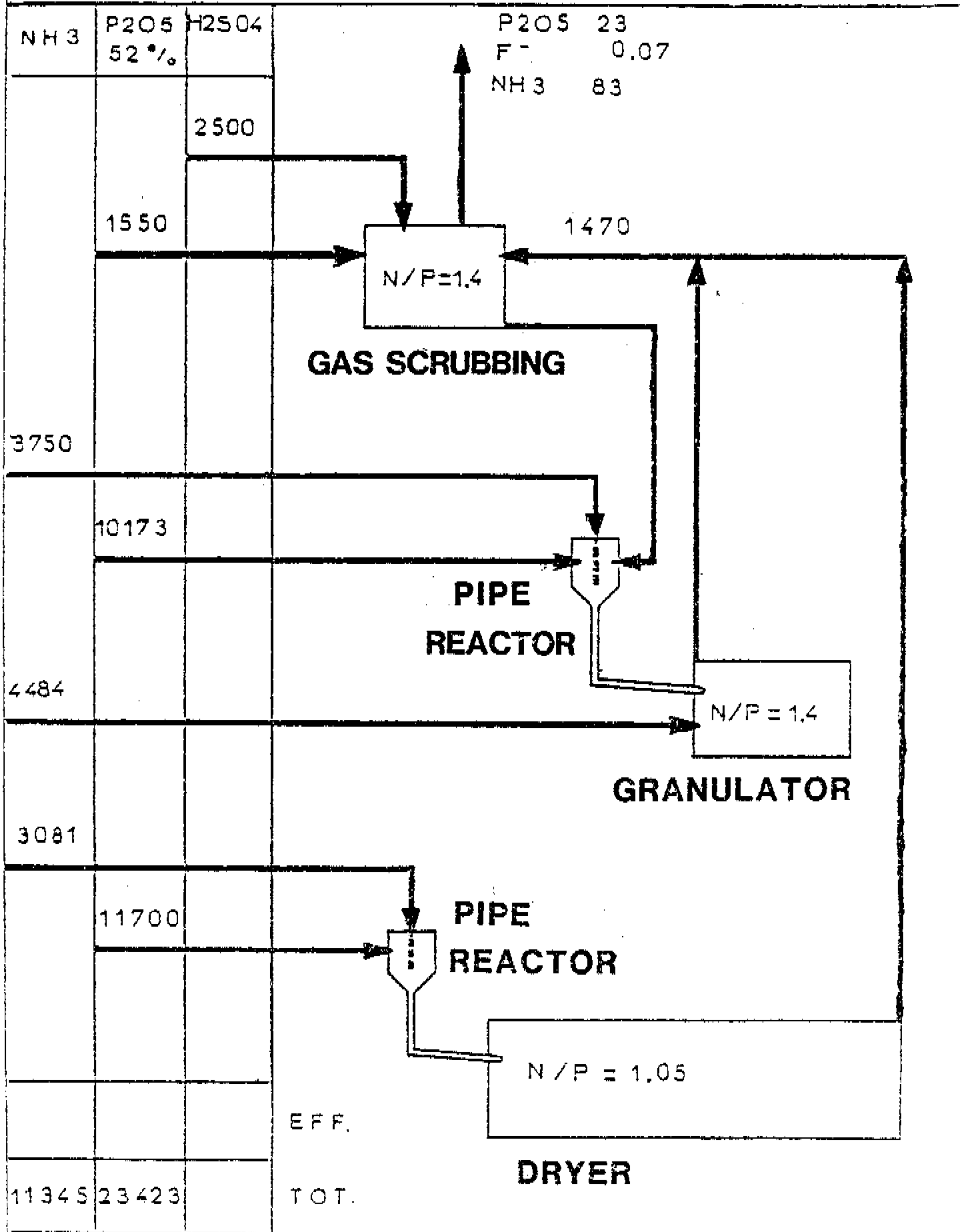


TABLE N° 5

REFERENCE LIST

August 1984

AZF PIPE REACTORS

FOR PRODUCTION OF FERTILIZERS

PLANT (COUNTRY)	PLANT OWNER	P.R. START UP: DATE	NUMBER & PLACE OF P.R.	PRODUCT & CAPACITY (met. t/hr)	REMARK
ROUEN B (FRANCE)	GESA - AZF	1975 1981	1/Granulator 1/Dryer	NPK - 45	D.P.R. Process
SAS VAN GENT (NETHERLANDS)	ZUID - CHEMIE	1976 1981	1/Granulator 1/Dryer	NPK - 50	D.P.R. Process
BORDEAUX (FRANCE)	GESA - AZF	1977	1/Rotary Tube	MAP (Powder) 13	
BORDEAUX (FRANCE)	GESA - AZF	1977 1983	1/Granulator 1/Dryer	NPK - 40	D.P.R. Process
L'OSERAIE (FRANCE)	GESA - AZF	1977 1979	1/Granulator 1/Dryer	NPK - 50	D.P.R. Process
RIEME (BELGIUM)	GESA - AZF	1978	1/Storage	MAP (Powder) 40	
ROUEN A-EG IV (FRANCE)	GESA - AZF	1978 1983	1/Granulator 1/Dryer	NPK - 55	D.P.R. Process
ROUEN A - EG V (FRANCE)	GESA - AZF	1978 1984	1/Dryer 1/Granulator	NPK - 100	D.P.R. Process Under construction
TOULOUSE (FRANCE)	GESA - AZF	1980 1981	1/Granulator 1/Dryer	NPK - 30 DAP - 20	D.P.R. Process

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TABLE N° 5 (suite 1)

REFERENCE LIST

August 1984

AZF PIPE REACTORS

FOR PRODUCTION OF FERTILIZERS

PLANT (COUNTRY)	PLANT OWNER	P.R. START UP DATE	NUMBER & PLACE OF P.R.	PRODUCT & CAPACITY (met. t/hr)	REMARK
MONTOIR DE BRETAGNE (FRANCE)	GARDILOIRE	1981	1/Dryer	NPK - 65	
TESSALONIKI (GREECE)	S.I.C.N.G.	1982	1/Granulator	NPK - 90	
BAYONNE (FRANCE)	SOCADOUR	1982	1/Dryer	NPK - 50	
GABES (TUNISIA)	S.A.E.P.A.	1982	1/Dryer	DAP - 70	
MAZINGARBE (FRANCE)	APC - AZF	1983 1983	1/Granulator 1/Dryer	NPK - 50	D.P.R. Process
MELEUS (U.S.S.R.)	TECHMASHIMPORT	1983	1/Granulator	NPK - 130	
BYELORECHENSK (U.S.S.R.)	TECHMASHIMPORT	1983	1/Granulator	NPK - 130	
ROUEN (FRANCE)	GESA - AZF	1984	1/Storage	MAP (powder) 40	

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TABLE N° 5 (suite 2)

REFERENCE LIST

August 1984

AZF PIPE REACTORS

FOR PRODUCTION OF FERTILIZERS

PLANT (COUNTRY)	PLANT OWNER	P.R. START UP DATE	NUMBER & PLACE OF P.R.	PRODUCT & CAPACITY (met. t/hr)	REMARK
PRAHOVO (YUGOSLAVIA)	RTB-BOR - IHP	1984 1984	1/ Granulator 1/Dryer	NPK-DAP 31	D.P.R. Process under construction
PISCHELSDORF (AUSTRIA)	DONAU-CHEMIE	1984	1/ Granulator	NPK - 30	
SAMSUN (TURKEY)	AZOT - SANAYII	1985	1/ Dryer	DAP - 42	Under construction
BALARUC (FRANCE)	AZF	1985	1/ Dryer 1/ Granulator	NPK - 30	D.P.R. under construction
ROZDOL (USSR)	TECHMASHIMPORT	1985	1/Granulator	NPK - 130	under construction
JORFLASFAR (MOROCCO)	MAROC PHOSPHORE III et IV	1986	4/Granulator 4/ Dryer	DAP ASP 4 x 60	D.P.R. under construction
TOTAL			40		

IMPROVEMENTS OF EXISTING UNITS

NPK PLANT ROUEN AZF CDF CHIMIE

3 X 17

	BEFORE	AFTER	
PRODUCTION	1600 T/D	2400 T/D	+ 50%
ENERGY	8 KG/T	1,5 KG/T	
YIELD	99%	99%	

DAP PLANT SAEPA - GABES TUNISIA

	BEFORE	AFTER	
PRODUCTION	1200 T/D	1700 T/D	+ 42%
ENERGY	6 Nm3/T	3,1 Nm3/T	
YIELD	=	UNCHANGED	
ACID CONCENT.	43%	43,5%	

TA/84/1 New developments in the dual pipe reactor process by P. Chinal & Y. Cotonea, CdF Chimie AZF, France

DISCUSSION: Rapporteur J. CARIOU, COFAZ SA, France

Q - Mr. H.G. JENNEKENS, UKF, Netherlands

Is it possible to by-pass the pre-neutraliser in DAP-production after plant modification as proposed by you?

A - Yes, we can revamp a DAP plant with the use of a pipe reactor without preneutraliser. We have adapted the internal equipment of the granulator.

Q - Mr. K.L. PARKS, Agrico, USA

Would you indicate the iron, aluminium and magnesium content of the 52% P_2O_5 acid used in DAP manufacture and forecast, if actual data not available, what DAP analysis you would expect for 52% P_2O_5 acid containing about 1.7% Fe_2O_3, 1.4% Al_2O_3 and 0.8% MgO.

A - Analysis of P_2O_5: (ex Togo) P_2O_5 : 49, Al_2O_3: 1.6, Fe_2O_3: 2.0, MgO: 0.36 ; Analysis of product: 17.8 - 46.25.

Q - What is the maximum capacity you would project for DAP in a single train?

A - Maximum capacity: 100 t/h without any problem.

Q - Mr. N. KOLMEIJER, Windmill Holland, Netherlands

Concerning application of a pipe reactor in the drier, I presume there is a potential danger of build-up by solidification of pipe reactor-slurry on the wall of the drier. Does it occur? Can you prevent it? Is there a certain minimum drier diameter?

A - We don't meet problems of build-up in our dryers. We avoid it by the use of classical hammers on the first part of the dryer. Minimum drum diameter is 2.5 m.

Q - Mr. K.L. PARKS, Agrico, USA

Can you expand on the statement, "The problems of blocking encountered in the early industrial plants were quickly overcome"? What are a) pipe cleaning methods, b) periods between cleaning, c) nature of scale, d) influence of acid composition on scaling rate, e) reasons for this improved operation?

A - Pipe cleaning method - by use of steam.

Q - Mr. R. MONALDI, Fertimont SpA, Italy

The installation of the pipe reactor in the dryer has provoked several questions during the IFA Conference held in Greece centred almost on the problems connected with the production and recycling of the MAP dust in the DAP production.

I should like to consider this under a different point of view. The circulation in the dryer practically consists in the blending of products that have a different grade of ammoniation.

I should like to know what is the variation, possibly in statistical terms, of the content of the N and of the P2O5 in the finished product.

A - The maximum content of MAP in the final product is 4% (several analysis).

Q - Have you ever used the pipe reactor in the ammoniation of the slurry which comes from nitric attack of the rock?

If so, what are the operating problems during ammoniation?

A - The pipe reactor is not used in a nitric reaction of phosphate, but can neutralize $HNO_3+H_3PO_4$ with NH_3.

Q - Mr. N. LOUIZOS, SAHPEC, Greece

What is the estimated life of a pipe reactor especially when sulphuric acid is used? What is the optimum material of construction?

A - The life time of the reactor, especially with H_2SO_4, is 2 years. Material of construction, stainless steel to produce MAP, and teflon with $H_2SO_4+H_3PO_4$.

Q - Mr. E. SEUNA, Kemira Oy, Finland

How do you measure the sphericity of the granules? How do you control the granulation when manufacturing different grades with different granulating properties? How does the capacity change when producing different grades?

A - The sphericity is measured by one test in which the granules are made to slide on an inclined plane and the number of granules are counted at the bottom.
Capacity range is of the same order as in conventional processes.

Q - Mr. I.K. WATSON, UKF Fertilizers Ltd, United Kingdom

We also operate pipe reactor but in conjunction with a blunger. We have also noticed that a much higher moisture content is possible for products made with the pipe reactor, and in particular 17-17-17 (see page 1-9). Do the authors have an opinion or knowledge to explain this phenomenon?

A - AZF experience is that it is necessary to maintain a low humidity to ensure good storage properties.

Additional questions put in writing

Q - Mr. K.J. BARNETT, Norsk Hydro Fertilizers Ltd, United Kingdom

Norsk Hydro Fertilizers experience is that MAP is difficult to ammoniate in the solid phase. The situation must be easier if the

MAP produced in the dryer is finely divided. This goes against efficient cyclone operation:

1. Would Mr. Cotonea care to comment.

2. Is there any control over MAP particle size produced by the dryer pipe reactor. What is the optimum mean particle size?

3. On the converted SAEPA plant, how does dryer dust loading and cyclone efficiency compare before and after the conversion?

A - The size of MAP crystals does not affect the efficiency of cyclones. When we revamp a DAP plant, we check the good running conditions of valves of the cyclones.

For example in SAEPA, the content of dust in the scrubbing system was not changed before and after the start-up of the pipe reactor in the dryer.

Q - Mr. R. SCHOEMAKER, UKF, Netherlands

In one of your schemes you show the pipe reactor at the outlet of the granulation-drum. If this is a correct image, what function has the granulator since the major part only serves for transportation of the bulk of the recycle plus the solid raw materials?

A - Yes the pipe reactor is at the outlet of the granulation drum. The slurry is sprayed down to the bottom of the drum. And the efficiency of the granulator is the same as with a slurry system.

Q - Mr. H. BOUCHENY, Sté J. Boucheny et Cie, France

Why do you use a Venturi type scrubber? Is it because of the problems associated with the pipe reactor or of the formation of ammonium nitrate mist in the dryer?

What is the loss of pressure in the Venturi scrubber and its efficiency?

A - The Venturi scrubber ensures a good contact between gas and liquid and a good dust collection.