

# IFA Technical Conference

Edmonton, Canada  
12-15 September 1988

EFFECT OF RAW MATERIALS, PROCESS OPERATION AND CONDITIONS ON  
PHYSICAL CHARACTERISTICS, CHEMICAL PROPERTIES AND BEHAVIOUR  
OF N.P.K FERTILIZERS.

A. Barbera, R. Monaldi, F. Cocquio, V. De Lucia

(Agrimont S.p.a., Italy)

Due to the constant improvement of agricultural technology, during the past recent years international market demand for high quality fertilizers has continually increased.

The fertilizer industry has responded by offering a wide range of grades and high quality products to its customers paying particular attention to the reduction of caking and dusting tendencies of the fertilizers.

Through long experience in fertilizer production, Agrimont has been able to face the fertilizer quality problem on a large scale, carrying out research on the basic influencing factors.

Agrimont has two types of production processes for N.P.K. fertilizers. Both are based on the phosphoric, sulphuric nitric attack of phosphate rock.

The slurries thus obtained can be granulated either with the traditional rotary drum (Fig. 1) or with the more recent spouted bed (Fig. 2) presented at the IFA Conference in 1986 (1). The processes are very flexible; in fact every grade of fertilizer, including MAP and DAP, can be obtained.

Agrimont takes a lot of care to optimize and control the parameters that can influence fertilizer quality. This activity works along the following lines:

- preliminary evaluation of the production feasibility and costs for new formulations;
- pilot plant experimentation to define the best process operating conditions, taking into consideration both the raw materials available and the fertilizers to be industrially produced;
- industrial optimization of process parameters defined in the pilot plant;
- accurate process control to maintain the optimum running parameters.
- research into efficient anti-caking and anti-dusting treatments and their application;

- fertilizer quality control during manufacture, storage in the factory, shipment and storage at customers' premises;
- production of fertilizers with a minimal self-sustaining decomposition (S.S.D.) tendency.

This paper refers to the different activities carried out by Agrimont to obtain high quality fertilizers.

### Raw materials

Agrimont's nitric attack process requires an accurate definition of slurry production and granulation steps with regard to the type and quality of the raw materials available.

The problems arising from phosphate rocks and phosphoric acid are usually connected with  $P_2O_5$  retrogradation which may occur in the ammoniation step due to impurities present in those raw materials such as Fe, Al, Mg, the amount of which depends on the supply source (2). The problem occurs when high ammoniation grades are used during slurry production.

Precipitation of water and/or ammonium citrate insoluble  $P_2O_5$  can be prevented by correctly ammoniating the phosphoric slurries in the neutralization reactors and by establishing their residence time there-in (Fig. 3).

The formulations for the various grades are designed to fix the calcium from phosphate rock only as calcium sulphate and calcium monophosphate (water soluble). If the rock attack and the ammoniation are not carefully operated calcium can precipitate water insoluble forms of phosphates. The positions in the process where to feed the raw materials are carefully arranged to avoid the said unwanted reactions.

Generally, fertilizers with a high w.s.  $P_2O_5$  content are produced, not only to satisfy market demand but also to optimize the granulation step whose performance improves together with an increasing amount of granulating liquid phase.

The ammonium sulphate used in fertilizer production is a by-product of petrochemical and other industries. Generally, this salt is available in large crystals, which cause bad granulation if fed directly into the granulation drum.

The fertilizer granules thus obtained would be of low hardness and have a high tendency to cake especially because

of reactions occurring during storage between free ammonium sulphate and ammonium nitrate to give ammonium sulphate nitrate salts (3).

To prevent such problems the ammonium sulphate is fed into slurry coming from the attack reactors before ammoniation in order to dissolve it and make it react with the calcium in the solution to precipitate calcium sulphate.

Potassium sulphate is used as a source of potassium in chlorine free products. Like ammonium sulphate, potassium sulphate if fed directly into the granulation drum, causes fertilizers to have a minimal chemical stability and to cake because of reactions occurring during storage between  $K_2SO_4$  and  $NH_4NO_3$  (3). Also in this case the salt is added to the process slurries where it behaves like ammonium sulphate.

In order to obtain stable solid phases in the manufactured fertilizers (3) potassium chloride is dissolved in the slurry before the granulation drum.

The "equilibrium state" of fertilizers is tested by an improved x Ray quantitative analysis method (Appendice 1).

#### Process Parameters

To test new raw materials and new formulations, Agrimont uses a pilot plant with granulation both in a rotary drum and a spouted bed.

The main process parameters developed in the pilot plant are:

- phosphate rock attack: temperature, residence time, H/CaO ratio,  $SO_4/CaO$  ratio, solid/liquid ratio, phosphate rock/phosphoric acid ratio;
- ammoniation: grade of neutralization in the different steps, temperature, residence time, yield of ammonia absorption;
- dissolution of potassium salts: temperature, residence time, yield of dissolution;
- granulation: temperature, slurry/recycle ratio, granulation pH, granulation efficiency;
- drying: temperature, residence time.

The products obtained in the pilot plant are tested to evaluate their quality and optimum amount of anti-caking and anti-dusting agents.

The process parameters thus developed in the pilot plant are transferred to and optimized for the industrial plant.

Particular attention is paid to the definition of parameters necessary for obtaining slurries with the required rheological characteristics to allow high ammoniation and granulation efficiency at a high capacity of the plants.

### Process Slurry Rheology

The process slurry rheology is studied in particular detail since the quality of final products depend greatly on this.

Slurries consist of solid crystalline phases suspended in a liquid phase which is virtually saturated with salts.

The suspension viscosity value, at given temperatures, is directly influenced by the following parameters :

- viscosity of the suspending liquid phase;
- weight ratio between the solid and the liquid phase;
- shape, size and nature of the solid particles;
- external specific surface of the particles;
- electrostatic interactions between the solid particles and the liquid phase.

From the point of view of rheological behaviour, the slurries can be either newtonian, or pseudoplastic or plastic type.

The newtonian slurries are characterized by a constant viscosity, independent from the shear stress they are subjected to. The viscosity of pseudoplastic slurries depends on the shear stress they are subjected to. The rheological behaviour of the plastic slurries is similar to that of plastic ones except that a minimal shear stress value must be exceeded in order for them to flow.

Newtonian slurries make the process work at steady state in each section of the plant including the points where the flow speed is low. Often, when pseudoplastic slurries are present, manufacture is difficult and anomalous.

It is obvious from the above that the newtonian slurries must be of the lowest possible viscosity with a minimum water content to avoid reductions of production capacity.

The best situation occurs when the suspended solids are highly crystalline and therefore do not absorb water. This can seldom occur because of the impurities (Fe, Al, Mg, organic matters) forming colloidal complexes.

To optimize the quality of the slurries the following is essential :

- to choose the type of phosphate rock attack (nitric, phosphonitric or sulphonitric) at given temperature and solid/liquid, H/CaO, SO<sub>4</sub>/CaO ratios;
- to define the number of ammoniation steps, grade of neutralization and temperature of each one;
- to choose the best solid/liquid ration and temperature in the potassium salt dissolution phase.

It must be kept in mind that in slurries when increasing:

- the solid/liquid ratio, the viscosity increases exponentially;
- the temperature, the viscosity decreases proportionately
- the water content, the viscosity decreases exponentially.

The viscosity value and rheological behaviour of the slurries influence the basic steps of the fertilizer production process: ammoniation and granulation:

The newtonian slurries at low viscosity allow the maximum efficiency of neutralization with ammonia. They induce, during the granulation step, salt deposition in subsequent layers that is the optimum for fertilizer quality.

In conclusion for each grade relationships similar to those showed in Figure 4 are derived at different operating conditions.

The importance of the rheological behaviour of slurries becomes clearer from the table given below:

15.15.15 from pilot plant

		Newtonian slurry	Plastic slurry
Hardness	Kg	2,5	1,7
Dustiness	ppm	200	600
Sphericity Index		0.90	0.75
Average Granule Size	mm	3.10	2.6
Anticaking Efficiency	%	92	73

Physical Storage Parameters

Storage times of fertilizers vary considerably, from less than a month to several months. It is essential that, during this storage, either the fertilizer remain completely free flowing or that "caking" be so minimal that the normal handling will restore the original free flowing conditions.

The caking phenomenon can be caused by chemical reactions occurring between the granule surfaces, by physical factors related to the quality of granules (particle size distribution, hardness, sphericity etc.) or by storage factors (time, temperature, heap height etc.).

Air humidity can cause moisture absorption/desorption on/from granules, leading to degradation of products, that depending on critical relative humidity of fertilizers. But it's our experience that the behaviour of bulk quantities of fertilizers in a heap is quite different from that of individual particles. That is, air humidity is not so critical for the caking tendency of the whole heap and it only affects surface layers of granules in the heap.

By laboratory storage simulations and by observing the real behaviour of bulk heaps, it was possible to derive the following general relationships for our fertilizers treated with a standard content of conditioners :

$$I_t = A (t)^{0,21}$$

$$I_T = B (T)^{1,86}$$

$$I_H = C (H)^{1,70}$$

where

I is a measurement of the caking tendency of fertilizers

- t is the time of storage in days  
 T is the fertilizer temperature during storage  
 H is the height of bulk heaps.

Coefficients A, B, C depend on the type of product, that is, chemical and physical characteristics of the granules.

From the above relationships it becomes evident that the temperature and the height of heaps considerably influence fertilizer caking tendency, much more than time.

Following the above observations our products are normally stored in bulk heaps not higher than 10 meters, after having been cooled at 30-40 °C before being stored.

Empiric relationships have been derived for all our fertilizers in order to optimize the anticaking treatment, taking into account physical storage conditions and moisture of products. In the case of the 13.13.21 fertilizer, for example, the following relationship has been deduced at constant heap height:

$$I = - 42.8 + 0.008 (T)^{1.86} + 11.0024 (t)^{0.21} + 4.22 (\% H_2O)^{1.78} + 7.65 / (\% \text{ Anticaking} + 0.1)$$

Figures 5 - 9 show simple correlations between caking index I and the variables used to derive the above relationship.

According to our experience and our products, the caking tendency of fertilizers can be interpreted as follows:

Index I	Caking Tendency
0 - 5	free flowing
5 - 9	low
9 - 15	medium
> 15	high

### Anti-caking and Anti-dusting Conditioners

An anti-caking conditioner is a chemical substance which is applied to the surface of the granules to maintain them free flowing during storage and handling.



Most of the anti-caking conditioners are composed of very fine inert powders, whose purpose is to form a physical barrier between the granules.

The anti-dusting conditioners (oils and waxes) are used to lower the "natural" dustiness of granules and also of that caused by the anticaking powders. The antidusting conditioners are applied after the anti-caking treatment.

Using the above treatments, the most diffused nowadays and defined as double step type, it is not always easy to get the maximum anti-caking and the minimum anti-dusting effect simultaneously.

Consequently, the fertilizer industry has tried to solve the anti-caking and anti-dusting treatment problem by using one step conditioners of a liquid type, generally consisting of amminated waxes containing polymeric substances.

Agrimont uses both double step treatments and recently introduced one step liquid treatments. Both treatments give final products with high anticaking and anti-dusting efficiency.

However, an increased use of the liquid treatment is foreseen, since this lowers environmental dustiness a lot during fertilizer production and handling.

To optimize the double step treatment a rotating drum has been developed which allows the liquid to be sprayed on to a "falling curtain" of granules and so coat them homogeneously with the correct quantity of anti-caking conditioner.

The liquid substance is fluorescent, and the coating efficiency can therefore be checked by an ultra-violet lamp.

#### Consideration on self-sustaining decomposition and how to limit it

Fertilizers containing ammonium nitrate and potassium chloride may show self sustaining decomposition, a phenomenon in which a decomposition front, initiated locally, will spread gradually throughout all the fertilizer. This decomposition is accompanied by the evolution of gases containing toxic components and a considerable loss in weight of the fertilizer.

The tendency for a fertilizer to undergo this type of decomposition can be determined at ambient temperature and at elevated temperature by means of the "Through test" (4). The sensitivity of the test at ambient temperature does

not permit measurement of propagation rates of the decomposition front (PRDF) of less than 5 cm/h. The method at elevated temperature has been developed further to assess those fertilizers which only exhibited a borderline tendency for self-sustaining decomposition when tested at ambient temperature.

The above equipment is generally suitable for looking for self heating properties of fertilizers in terms of propagation of decomposition. Quantitative estimates of fertilizers' behaviour during the decomposition phenomenon may be made via calorimetric techniques.

A calorimeter working under confined, adiabatic conditions is available in Agrimont's Research Centre. The equipment allows a search for exothermic reactions, to measure absolute rates of decomposition, to determine the amount of heat involved in occurring reactions.

Tests for PRDF measurements and calorimetric estimates of SSD can be accompanied by quantitative X Ray determination of salts constituting fertilizers, by chemical analysis and by physical measurements.

Gases evolved during fertilizer decomposition can also be analyzed by gas-chromatography and/or via conventional analysis. Resulting solids after decomposition can be examined via X Ray and chemical analysis.

From a general point of view fertilizer calorimetric data have showed an initial endothermic phenomenon, due to evaporation of free and crystalline water in addition to decomposition of ammonium phosphates. This first step is followed by an accelerated rate of exothermic reactions of a different type.

Fertilizer granules show a critical temperature below which no decomposition occurs even if they have been maintained around that temperature for days in adiabatic conditions.

The total reaction enthalpy was found in the range 100 - 170 cal/gr., depending on the different types of formulations. The relationship between the reactivity of fertilizers (amount of heat developed per weight unit) and the PRDF (cm/h) has shown to be poor.

In fact the PRDF is strongly influenced by the particle size distribution and porosity of granules, while calorimetric measurements are hardly influenced by these physical parameters.

An increase of the free water content of fertilizers induces a decrease of PRDF but, generally this parameter is

not taken into account for lowering PRDF of fertilizers because generally an increase of the water content of granules also increases their caking tendency.

An increasing content of organic matter also increases PRDF of fertilizers. Calcinated rocks with low content of organic matter can limit their effect on PRDF but the production costs may rise. For the same reason it is advisable to coat fertilizer granules with low rates of oils and/or waxes.

The rate of decomposition of fertilizers decreases with an increasing content of ammonium sulphate, diammonium phosphate and urea.

Urea can be used in those fertilizers where ammonium nitrate has totally reacted with potassium chloride or potassium sulphate. In fact the mixture of urea with ammonium nitrate gives high hygroscopic compounds: the result would be a low quality fertilizer.

Simultaneous presence of  $N - NO_3$  and  $Cl -$  at low pH enhances fertilizer decomposition rate. Therefore fertilizer pH should not be below 5.5,

Cu, Cr, and Co can increase the rate of decomposition of fertilizers. But, generally, at the concentration level they are found in phosphate rocks, there is no practical influence on S.S.D. In this respect problems might arise from plant corrosion phenomena, which generally are well controlled.

Physical properties of fertilizers (like hardness, porosity, granule size, dustiness etc.), in addition to chemical properties, have an influence on S.S.D. The best control in this respect is to produce quality fertilizers, paying a lot of attention to the granulation step.

A practical way to produce fertilizers with low tendency for self sustaining decomposition is to increase water soluble  $P_2O_5$ . This could be a problem (but it is not) in NPK processes, like Agrimont's based on the sulphuric nitric attack of phosphate rock without calcium removal, because of the competition in the formation of  $NH_4H_2PO_4$  /  $(NH_4)_2 HPO_4$  and  $CaHPO_4$ .

On the other hand the presence of calcium sulphate dihydrate in fertilizers manufactured with our process is a further guarantee against S.S.D. because of the presence of crystallization water.

The precipitation of calcium using either sulphuric acid and/or ammonium sulphate does not sometimes solve the problem in getting high w.s.  $P_2O_5$ , unless some specific operating process conditions are maintained.

Table 1 shows main chemical data of three different types of 15.15.15 manufactured without/with using  $H_2SO_4$  and improving ammoniation. It clearly shows that only an increase of w.s.  $P_2O_5$  gives a fertilizer free from S.S.D.

The possibility to reduce S.S.D. by increasing w.s.  $P_2O_5$  content of fertilizers is easier for high grade formulations than for low grade formulations. A typical example is given by N.P.K. 12.9.27. Table 2 shows that the fertilizer could be produced free from S.S.D. only by adding DAP in the formulation.

On the other hand, when necessary, crystalline ammonium sulphate and simultaneously DAP are used as raw materials to further limit S.S.D.

### Quality assurance

Agrimont's Quality Assurance represents an advanced conception of the traditional Quality Control and tends to guarantee the conformity of fertilizers with customer's requirements.

It deals with the following main fields of activities:

- technical assistance to production plants;
- examination of fertilizers stored in the factories;
- examination of fertilizers stored by dealers and farmers;
- study of causes which have eventually given rise to fertilizer quality problems;

Electronic Data System (E.D.S.) managed by the Quality Assurance Department (Q.A.D.) allows Agrimont's factories and Agrimont's sale divisions a daily storage of all requested information inside a main computer situated in Porto Marghera - Venice (Figure 10).

Thus Q.A.D. personnel can immediately initiate in time the above activities, when necessary. Furthermore E.D.S., in addition to allowing standard process and quality data processing, makes available easily and quickly all information about the whole story of fertilizers which have caused customers' complaints.

Thus an interaction of personnel in different positions of responsibility is made possible; problems are pointed out and solved in the right way and quickly.

It must be pointed out (1) that plants' performances are monitored by automatic instruments to control:

- concentration of liquid feeds
- $N-NH_3$ ,  $N-NO_3$ ,  $K_2O$  and  $P_2O_5$  content of slurries;
- viscosity of slurries;
- water content of products leaving granulators;
- water content of products leaving driers.

Furthermore plant personnel perform once every shift the following measurements on the manufactured fertilizers:

- anti-caking and anti-dusting content;
- particle size distribution;
- hardness;
- dustiness;
- caking tendency by an accelerated test method.

Plant personnel thus receives necessary information in time and can control production processes efficiently.

### Conclusions

Most of the problems encountered with fertilizers are those resulting from deficiencies in physical properties; frequent problems include caking, dustiness poor flowability, segregation and excessive hygroscopicity.

Customer acceptance or preference for a particular fertilizer to another of equal plant food content is always based on physical properties of the product.

Furthermore, during the past recent years international demand for high quality fertilizers has continually increased.

All the main fertilizer industries have responded by improving their products.

Agrimont has faced and is facing quality problems carrying out extensive research on the basic influencing factors.

The purpose of this paper was not to show particular specific results. We simply wanted to stress that the

improvement of the "Old Fertilizer" need a lot of investigation, a lot of research in different fields, safety and ecology included.

The "Old Fertilizer" needs further improvement; the main international industries are thus competing for that and Agrimont is ready for the competition.

APPENDICE 1AN IMPROVED X RAY QUANTITATIVE ANALYSIS OF FERTILIZERS

As outlined in MONTEDISON's report TF/80/12, a lot of theories regarding caking of fertilizers have been developed over the years but none of them was completely satisfactory.

The paper stressed the important role of the "equilibrium state of granules" on caking tendency of fertilizers. A powerful technique to evaluate this "state" is given by X Ray Quantitative Analysis of Fertilizers.

Theory and results, are discussed below with reference to an improved method of analysis developed by us.

Introduction

Klug and Alexander (5) first examined thoroughly the problem of quantitative X - Ray analysis, pointing out the relevant difficulties. The intensity of diffracted beam by a polycrystalline mixture is affected by several factors, apart from concentration.

The most important ones are : absorption effects of the specimen, diffraction angle (which determines the value of polarization Lorentz factor), particle size of the specimen, preferential orientation of crystalline powder occurring during sample preparation before analysis. These disadvantages can be kept within certain limits using a suitable technique in sample preparation (that is in the specimen must be ground, sieved and accurately mixed before the pattern recording).

X - ray diffraction is generally used for quantitative analysis of compounds showing at least a non-superimposed diffraction line. A suitable technique is the indirect analysis by means of an internal standard: this method is precise but too time consuming.

Another method uses the relation hereunder (n°3): by this it is possible to calculate directly the concentration of a phase by measuring the intensity of a pure component diffraction line, the same line intensity in the mixture under analysis and calculating the mass absorption coefficients of the mixture and pure component.

In the analysis of certain rock samples the use of uncorrected X-ray diffraction data have supplied good results (6).

If the pattern lines of the component to be analyzed are all superposed, it is necessary to carry out line

deconvolution by computer (7) or with multilinear regression program (8): both methods require the recording and the measurement of mixture and pure compounds X-ray diffraction patterns.

### Theory

Klug and Alexander (5) demonstrated that for a uniform powder mixture of a crystalline component it holds the following relationship:

$$1) \quad I_i = \frac{K_i \cdot c_i}{d_i \cdot /u_s}$$

Where :

$I_i$  = intensity of X-ray diffracted by the i-th component of the mixture by some selected plane h.K.l.

$c_i$  = weight fraction of the i-th component.

$d_i$  = density of the i-th component.

$/u_i$  = mass absorption coefficient of i-th component.

$/u_s$  = mass absorption coefficient of the mixture.

$k_i$  = constant depending upon the nature of the component and the geometry of the apparatus.

For a pure component it becomes :

$$2) \quad I_{i_0} = \frac{K_i}{d_i \cdot /u_i}$$

Dividing 1) by 2) the following equation is derived :

$$3) \quad I_i = \frac{I_i \cdot /u_i}{/u_s} c_i$$

Weight fraction of the i-th component can be obtained if the mixture pattern gives a non-superimposed line of the phase to be analyzed. This is a rather infrequent case in the fertilizer patterns; therefore relationship 3) (if a peak is present on which n compounds reflect) becomes:

$$4) \quad I_n \cdot /u_s = I_{i_0} \cdot /u_i c_i$$



Where  $I_n$  gives peak intensity of  $n$  reflecting components. The above relationship can be written for each diffraction line by the following :

$$5) \quad I_n \cdot \frac{u}{s} = Y \quad \text{and} \quad I_{i_0} \cdot \frac{u}{i} = X$$

Relationship 4) becomes :

$$6) \quad Y = \quad X_i \cdot c_i$$

According to the least square theory, (9) if each variable  $X_i$  is independent, coefficients  $c_i$  can be obtained solving the following relationship :

$$7) \quad c = S \cdot R^{-1} \cdot s$$

Where  $S$  and  $R$  are two matrices ( $R^{-1}$  is the inverse matrix),  $\sigma$  is the standard deviation of the variables,  $r$  is the correlation coefficient among the independent variables,  $c$  is the coefficient vector (the unknown quantity),  $s$  is the correlation vector among the independent and dependent variables.

The following relationships are thus defined :

$$8) \quad S = \begin{vmatrix} d_1/d_{x_1} & 0 & \dots & 0 \\ 0 & d_2/d_{x_2} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & d_n/d_{x_n} \end{vmatrix}$$

$$9) \quad R = \begin{vmatrix} 1 & r_{x_1 x_2} & \dots & r_{x_1 x_n} \\ r_{x_2 x_1} & 1 & \dots & r_{x_2 x_n} \\ \dots & \dots & \dots & \dots \\ r_{x_n x_1} & r_{x_n x_2} & \dots & 1 \end{vmatrix}$$

$$10) \quad c = \begin{vmatrix} c_1 \\ c_2 \\ \cdot \\ \cdot \\ \cdot \\ c_n \end{vmatrix}$$

$$11) \quad S = \begin{vmatrix} r_{x_1 y} \\ r_{x_2 y} \\ \cdot \\ \cdot \\ \cdot \\ r_{x_n y} \end{vmatrix}$$

### EXPERIMENTAL PROCEDURE

All the patterns have been recorded using a Philips diffractometer mod. PW 1140 with automatic chart-recorder (scan speed = 1°/min, the radiation employed was Cu K $\alpha$  ( $i = 25$  mA,  $V = 40$  kV)).

The computation of data has been performed with the aid of a program stored in the START-PACK library of a computer UNIVAC 1100.

The analysis of a fertilizer sample is performed operating by the following scheme :

- sample pattern is recorded
- the different compounds constituting the sample are qualitatively determined and peak intensities are measured
- the mass absorption coefficient of the fertilizer sample is calculated by the internal standard method : a suitable standard should be inert and should have one of the strongest lines not superposed by the mixture pattern. The value  $\mu_s$  is calculated using relationship 3).
- using the above experimental data and the theoretical data on pure compounds necessary to define relationship 4) a multilinear regression program is run in order to obtain the coefficient values  $c_i$  and their standard errors.

### Results and Discussion

To test reproducibility and accuracy for the developed method, several multicomponent crystalline mixtures have been prepared and analyzed. Observed data, listed in Table 3 and 4, show a deviation from true values of 2 per cent maximum, according to the values given by Klug and Alexander (5) for the quantitative analysis of single component using the internal standard technique. With regard to the reproducibility, the percentage variation coefficient results less than 10 per cent in 2/3 of the determination this deviation is certainly about the normal one for this kind of analysis and can be considered quite satisfactory.

The error arises from the following factors :

- instrument stability and reproducibility
- particle size: mixture of samples and standards are ground in a ball mill and sieved under 32  $\mu$ m; it was

demonstrated (5) that an effective crystallite size of less than 10  $\mu\text{m}$  is necessary for good reproducibility (2-3 per cent). This result can be obtained with a prolonged grinding or with the use of sedimentation techniques to eliminate the coarser size fractions; this however would notably lengthen analysis time.

- density : a difference of specimen density leads to a variation of layers stricken by the X-ray beam and, consequently, of diffracted beam intensity.

Samples of compound fertilizers have been analyzed using the procedure explained above after having been accurately prepared in the laboratory double salts and solid solutions.

Analytical results are listed in Table n° 5. The data have been obtained from double analysis and an averaging. The sum of the phases concentration results less than the theoretical value: that derives both from the presence of amorphous compounds and from impurities in the raw materials that cannot be noticed.

Percentages of elements N/  $\text{P}_2\text{O}_5/\text{K}_2\text{O}$  have been calculated from diffraction data and the values have been compared with the chemical analysis results, as listed in table n° 6. Differences are less than 2 per cent (in absolute terms), as in the pure salt analysis.

### Conclusions

A method for the quantitative analysis of crystalline phases in the fertilizers has been explained in the present paper.

Compound pattern is recorded and peak areas are measured.

Diffraction line intensities of mixtures are compared with pure phase peaks using a multilinear regression program.

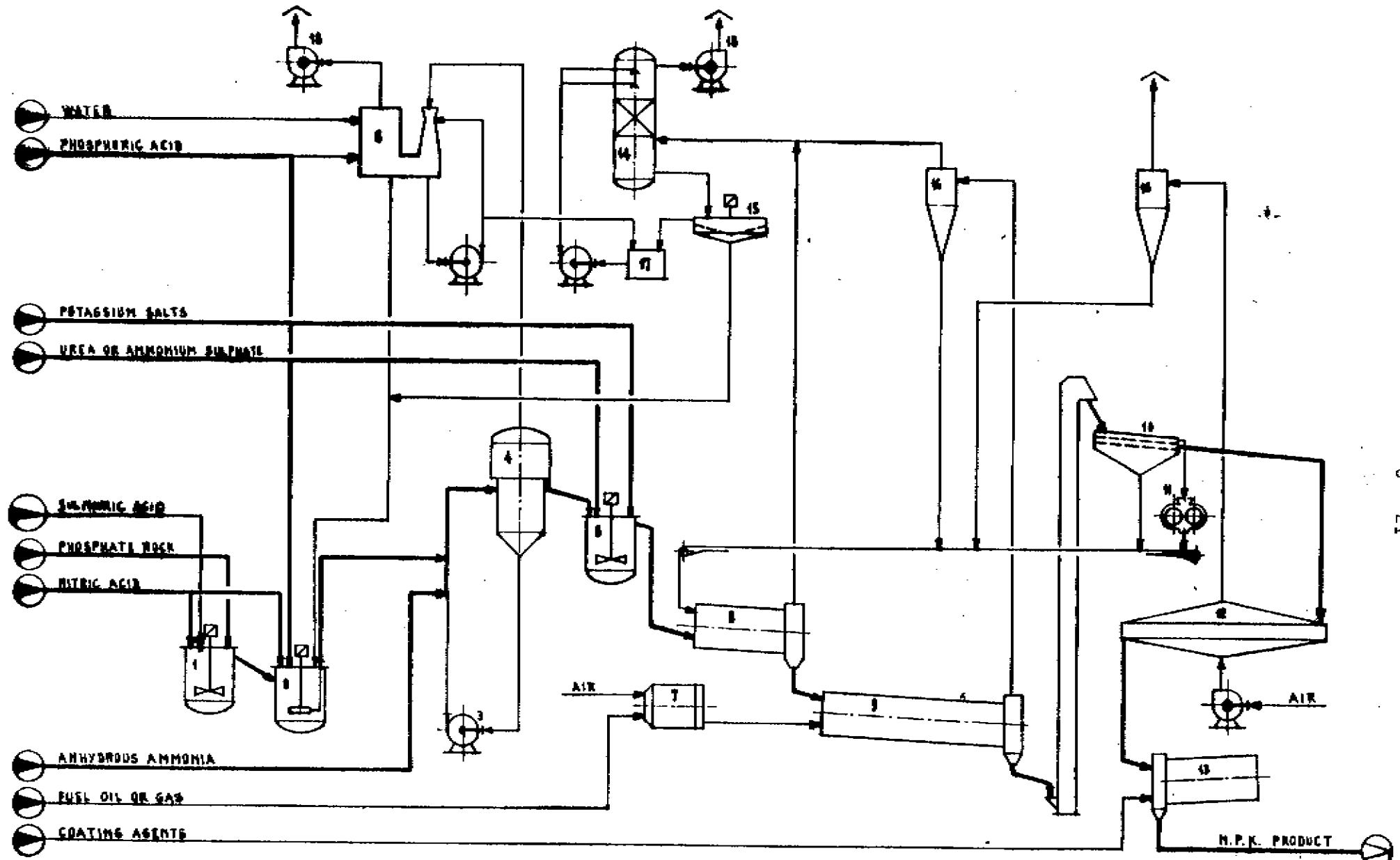
Both pure salts mixtures and compound fertilizers have been analyzed.

The results obtained in the present work show a percentage variation coefficient within 10 per cent and absolute errors within 2 per cent.

**REFERENCE**

- 1) G. Brusasco, R. Monaldi, V. De Lucia, A. Barbera  
Production of NPK fertilizers with a spouted bed  
granulator dryer  
IFA Technical Conference - October 1986
- 2) A.I.Ch.E. Meeting 1987
- 3) ISMA - APEA - Technical Conference - November 1980  
A. Barbera R. Monaldi  
Utilisation des attachements chimiques et physiques  
pour analyser la production d'engrais granules
- 4) ISMA - APEA - Epreuves pour la stabilité thermique des  
engrais 1973
- 5) Klug H.P. and Alexander I.E., X ray diffraction  
procedures, John Wiley New York 1967
- 6) Renton J.J., Use of uncorrected X-ray diffraction data  
in quantitative analytical determinations, West  
Virginia Geological and Economic Survey, Morgantown WV  
26505, July 1977
- 7) Slaughter M., Deconvolution of overlapped X-ray powder  
diffraction spectra for quantitative analysis,  
Electron. Microsc. X-ray Appl. Environ. Occup. Health  
Anal. 1981, 2, 77-114
- 8) Vonk C.G., Heck H.G. and Pijpers A.P., Analyses quan-  
titative des constituants cristallins des engrais par  
diffraction des rayons X, ISMA technical Meeting, 1976
- 9) Barba D., Calcolo elettronico nell'ingegneria chimica,  
Ed. Siderea, Roma

FIGURE 1- NITRIC ATTACK FERTILIZERS PRODUCTION WITH DRUM GRANULATION. PROCESS FLOW SHEET.

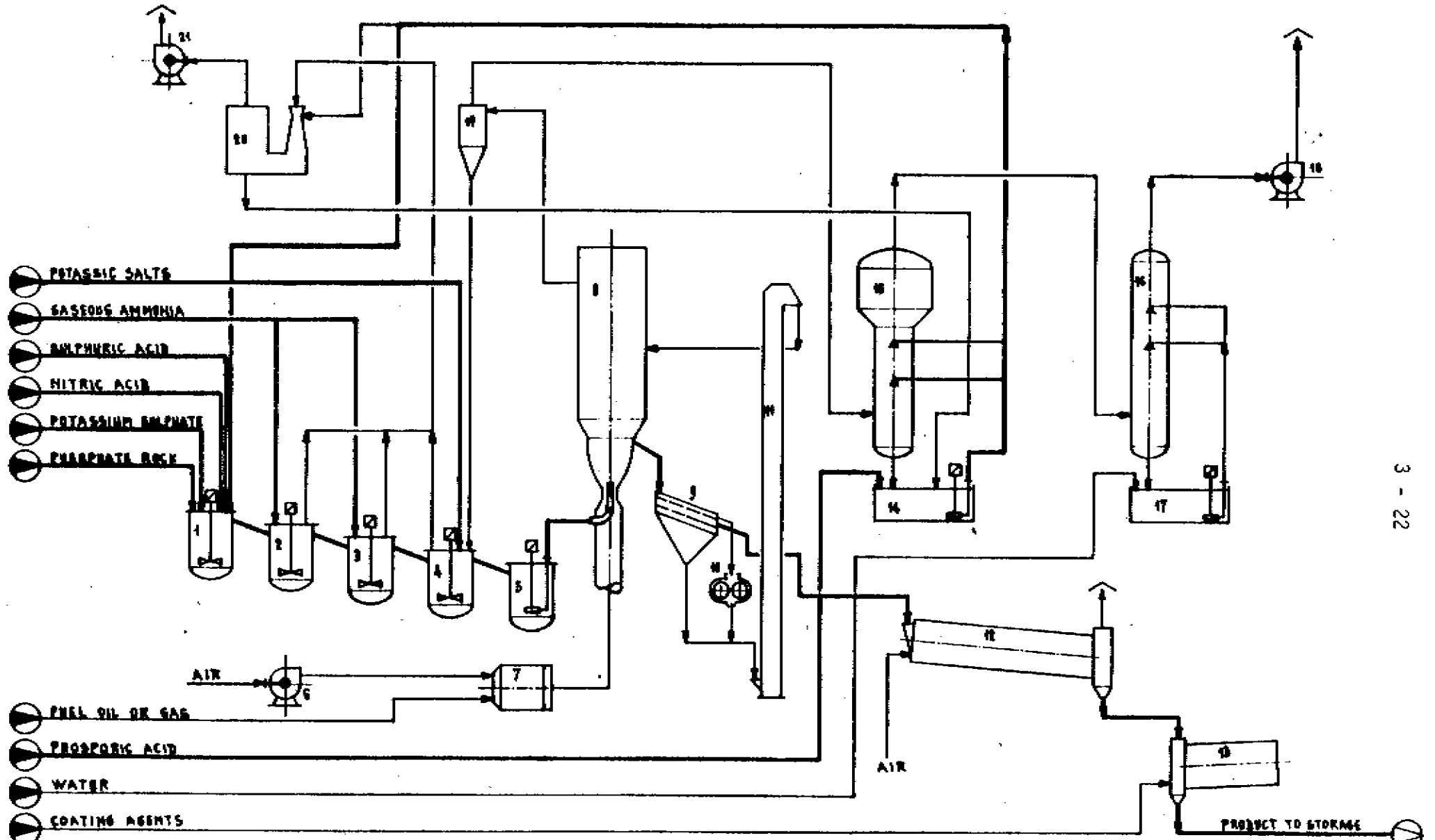


- 1- REACTOR
- 2- REACTOR
- 3- RECIRCULATING PUMPS
- 4- HIGH EFFICIENCY AMMONIATOR (HEA)
- 5- MIXER
- 6- SCRUBBER

- 7- AIR HEATER
- 8- DRUM GRANULATOR
- 9- DRYER
- 10- SCREEN
- 11- CRUSHER
- 12- FLUIDIZED BED COOLER

- 13- COATING DRUM
- 14- GAS CLEANER
- 15- THICKENER
- 16- DUST CYCLONES
- 17- TANK
- 18- FANS

FIGURE 2- NITRIC ATTACK FERTILIZERS PRODUCTION WITH SPUTED BED GRANULATION. PROCESS FLOW SHEET OF PRIGLO PLANT.



- POTASSIC SALTS
- GASEOUS AMMONIA
- SULPHURIC ACID
- NITRIC ACID
- POTASSIUM SULPHATE
- PHOSPHATE ROCK

- FUEL OIL OR GAS
- PROPIONIC ACID
- WATER
- COATING AGENTS

- |               |                     |                        |                  |
|---------------|---------------------|------------------------|------------------|
| 1- REACTOR    | 7- AIR HEATER       | 13- COATING DRUM       | 18- DUST CYCLONE |
| 2- AMMUNIATOR | 8- SPUTED BED       | 14- TANK               | 19- SCRUBBER     |
| 3- AMMUNIATOR | 9- SCREEN           | 15- GAS WASHING COLUMN | 20- FAN          |
| 4- DISSOLVER  | 10- CRUSHER         | 16- GAS WASHING COLUMN |                  |
| 5- SURGE TANK | 11- BUCKET ELEVATOR | 17- TANK               |                  |
| 6- FAN        | 12- COOLING DRUM    | 18- FAN                |                  |

Figure 3 : Insoluble P<sub>2</sub>O<sub>5</sub> vs. mole ratio at different times in liquid

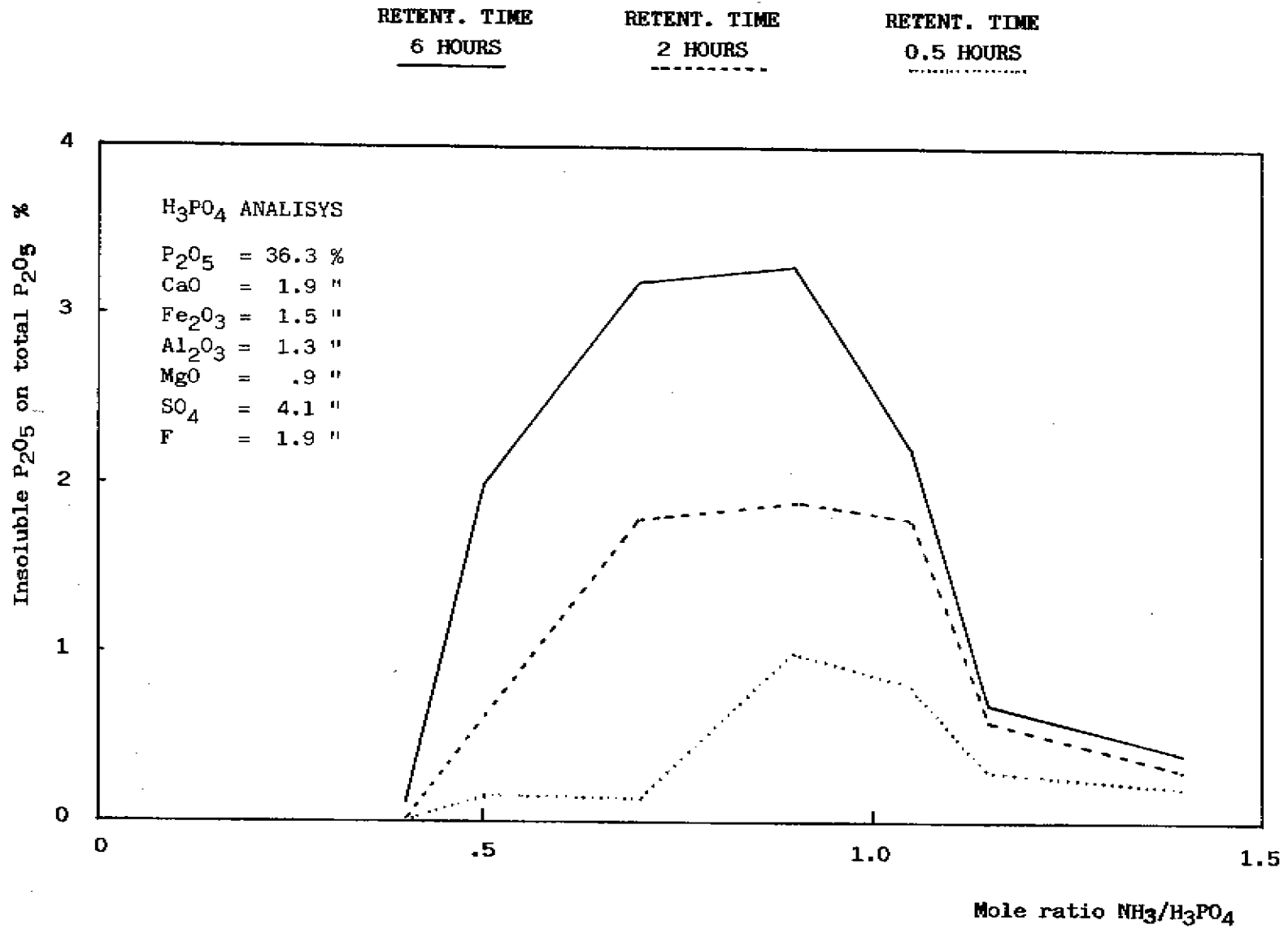




Figure 4 : Rheological properties of a fertilizer's slurry

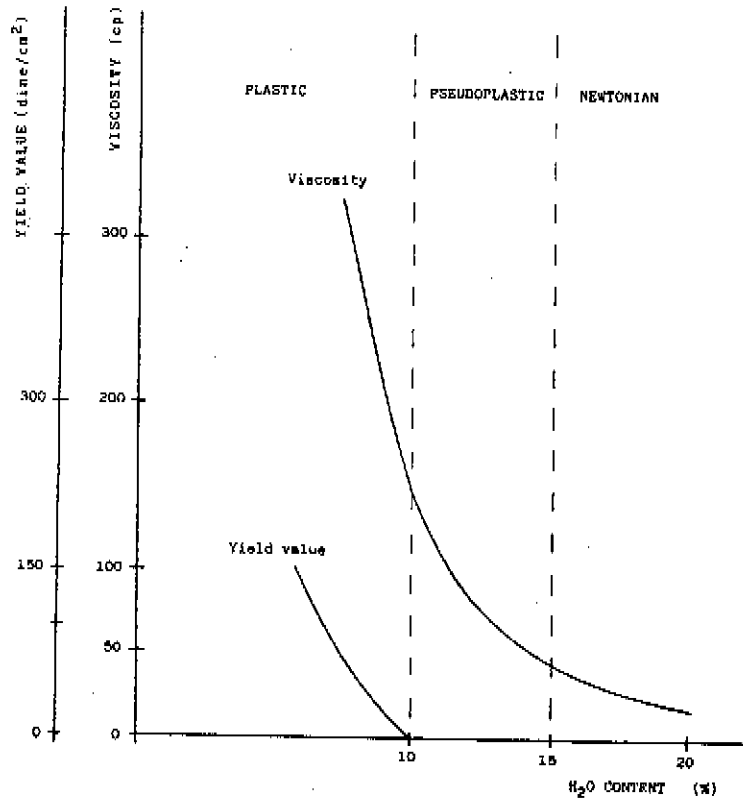


Figure 5 : Caking Index of N.P.K. 13.13.21 vs. water content of the fertilizer

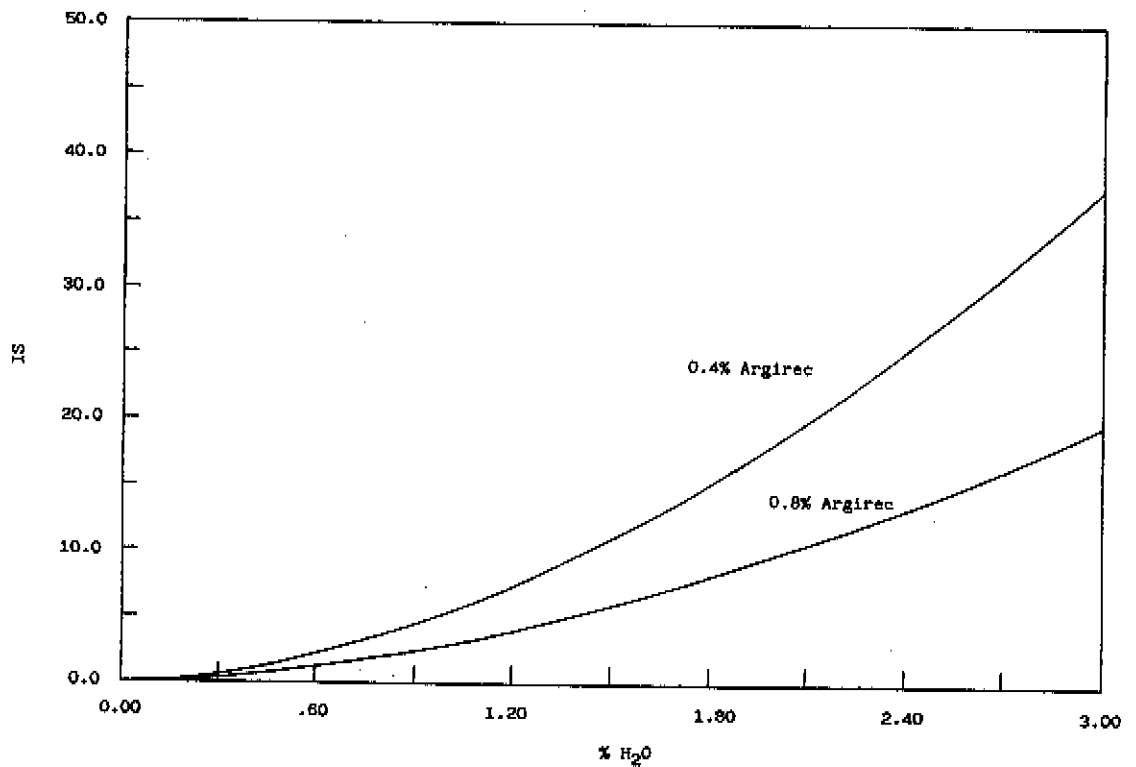


Figure 6 : Caking Index of N.P.K. 13.13.21 vs. anticaking content of fertilizer

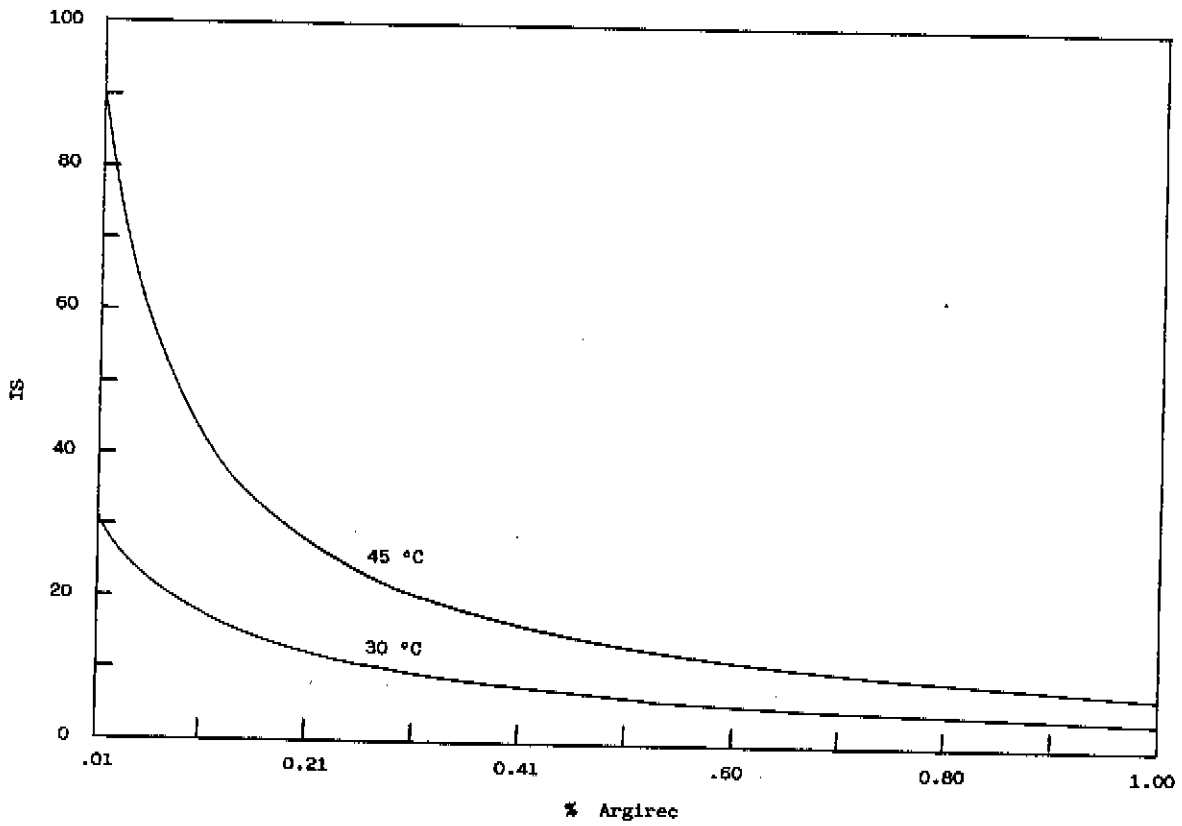


Figure 7 : Caking Index of N.P.K. 13.13.21 vs. storage time of the fertilizer

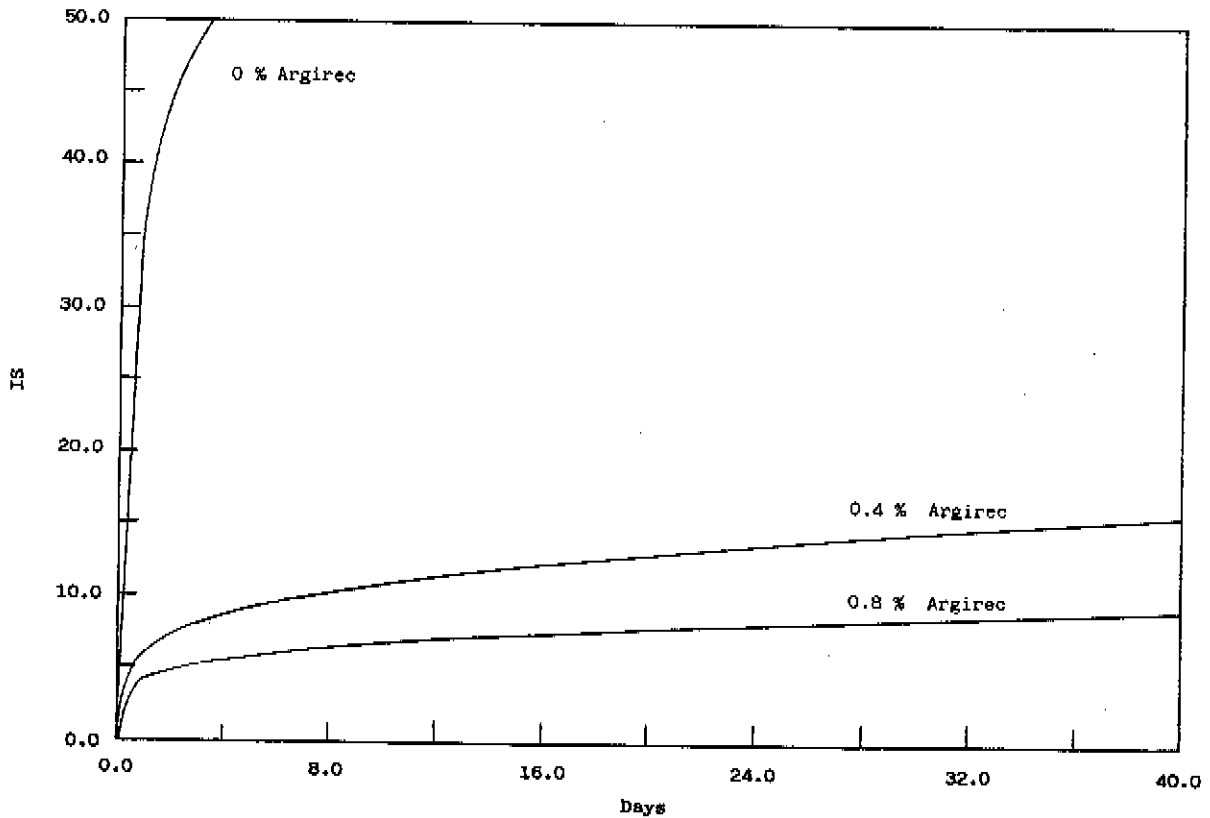


Figure 8 : Caking Index of N.P.K. 13.13.21 vs. bulk heap hight of the fertilizer

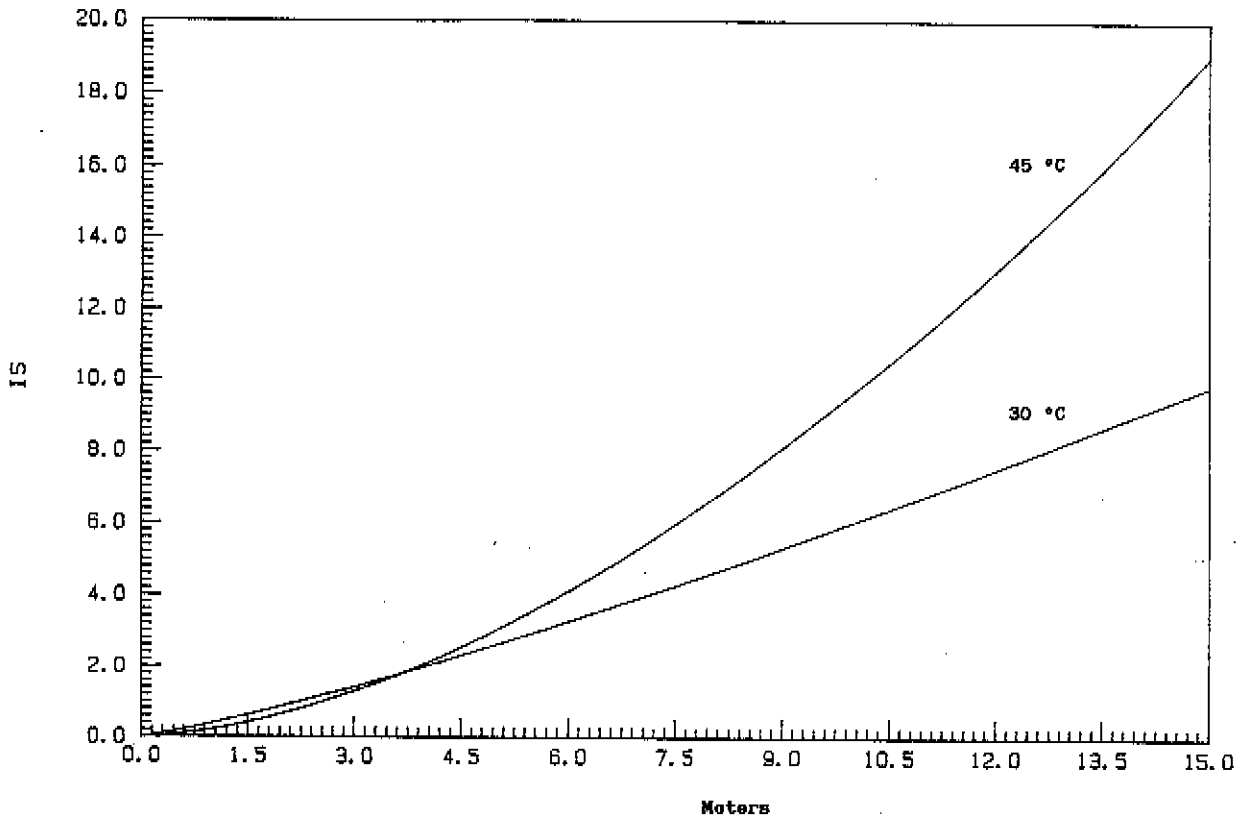


Figure 9 : Caking Index of N.P.K. 13.13.21 vs. storage temperature of the fertilizer

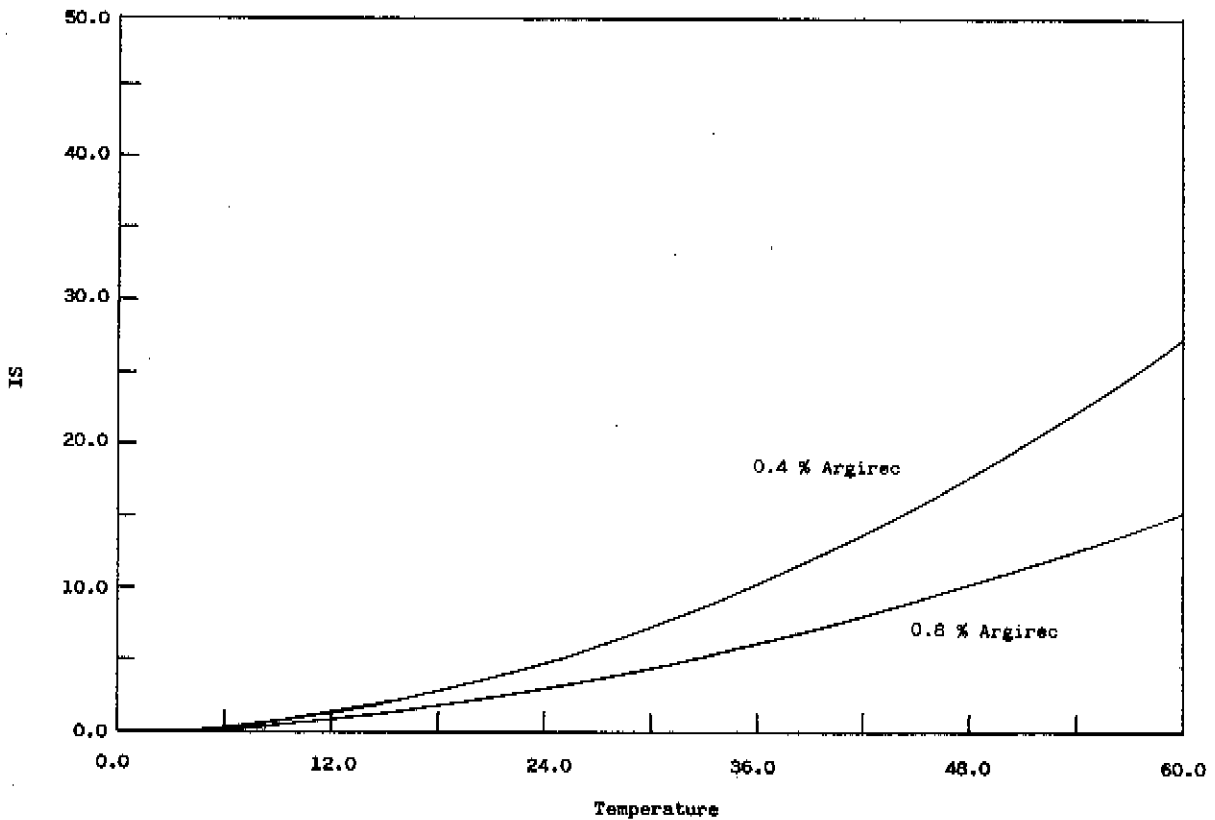


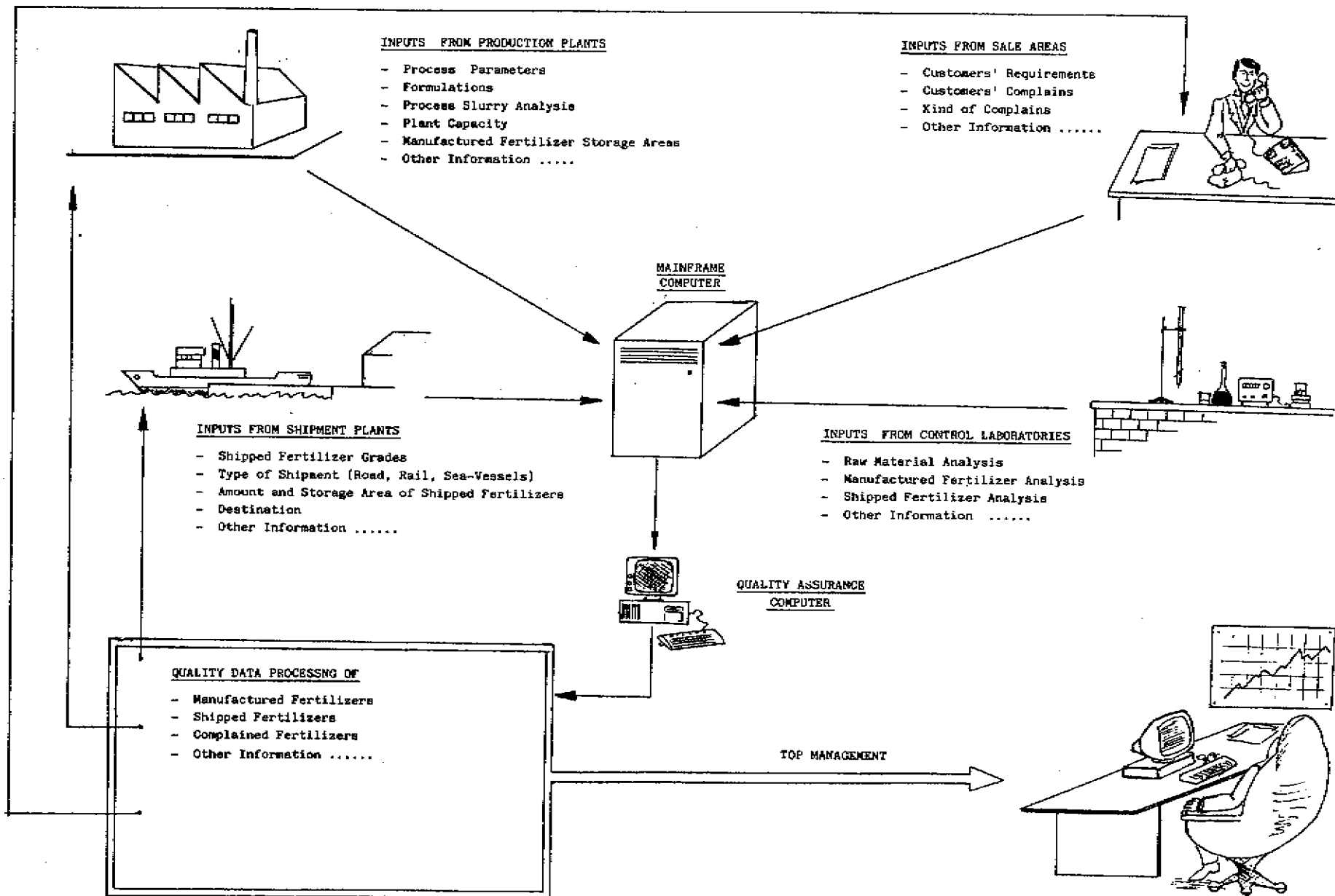
TABLE 1 N.P.K. 15.15.15 RESULTS

		Chemical Analysis and PRDF		
		Without $H_2SO_4$ 1 Ann. Step	With $H_2SO_4$ 1 Ann. Steps	With $H_2SO_4$ 2 Ann. Steps
N - $NO_3$	%	6.9	5.5	6.0
N - $NH_3$	%	8.2	9.5	9.0
w.s. $P_2O_5$	%	6.8	9.0	12.2
w.c.s. $P_2O_5$	%	15.0	15.1	14.8
Insoluble $P_2O_5$	%	0.1	0.1	0.1
w.s./w.c.s. $P_2O_5$	%	45.3	59.6	82.2
Total $P_2O_5$	%	15.1	15.2	15.0
$K_2O$	%	14.9	15.0	15.1
Moisture	%	1.7	1.3	1.3
pH	/	5.7	5.8	5.8
PRDF	cm/h	20	8	0

TABLE 2 N.P.K. 12.9.27 RESULTS

		Chemical Analysis and PRDF		
		Without $(NH_4)_2SO_4$ and DAP	With $(NH_4)_2SO_4$	With $(NH_4)_2SO_4$ and DAP
N - $NO_3$	%	5.5	4.7	4.6
N - $NH_3$	%	6.6	7.3	7.3
w.s. $P_2O_5$	%	4.5	8.1	7.0
w.c.s. $P_2O_5$	%	9.1	9.2	9.0
Insoluble $P_2O_5$	%	0.1	0.1	0.1
w.s./w.c.s. $P_2O_5$	%	49.5	88	77.8
Total $P_2O_5$	%	9.2	9.3	9.1
$K_2O$	%	27.1	26.9	27.4
Moisture	%	1.5	1.5	1.2
PRDF	cm/h	28	15	0

**Figure 10 : Quality assurance management**



FOUR - COMPONENT MIXTURE ANALYSIS

Components	Theoretical Value (%)	Experimental Value (%) *	St. Dev.	Percentage Variation Coefficient
$K_2SO_4$	13.3	14.5	2.0	13.8
$KH_2PO_4$	25.2	25.3	1.6	6.3
KCl	9.5	10.2	0.4	3.9
$KNO_3$	52.0	49.7	1.8	3.6

Components	Theoretical Value (%)	Experimental Value (%) *	St. Dev.	Percentage Variation Coefficient
$KNO_3$	12.0	11.3	1.5	13.3
KCl	17.1	17.4	0.3	1.7
$KH_2PO_4$	23.3	25.1	1.6	6.4
$K_2SO_4$	47.6	46.9	1.6	3.4

Components	Theoretical Value (%)	Experimental Value (%) *	St. Dev.	Percentage Variation Coefficient
KCl	23.3	22.0	1.8	8.2
$KNO_3$	25.2	23.4	3.0	13.1
$KH_2PO_4$	39.8	37.9	1.2	3.2
$K_2SO_4$	11.7	9.5	1.3	13.7

\* : calculated from the average of five determinations.

TABLE 4

SIX - COMPONENT MIXTURE ANALYSIS

Components	Theoretical Value (%)	Experimental Value (%) *	St. Dev.	Percentage Variation Coefficient
$K_2SO_4$	27.7	25.5	2.3	9.0
KCl	5.6	4.8	0.9	18.7
$KNO_3$	18.1	17.7	1.3	7.3
$KH_2PO_4$	9.4	10.4	1.1	10.6
$NaNO_3$	23.4	23.0	1.2	5.2
$Na_2SO_4$	15.9	17.6	1.3	7.4

Components	Theoretical Value (%)	Experimental Value (%) *	St. Dev.	Percentage Variation Coefficient
KCl	10.6	9.7	0.3	3.1
$KNO_3$	19.9	18.9	1.0	5.3
$KH_2PO_4$	10.2	10.4	1.5	14.4
$K_2SO_4$	16.6	14.5	1.1	7.6
$NaNO_3$	20.7	21.3	0.7	3.3
$Na_2SO_4$	22.0	23.7	3.4	14.3

\* : calculated from the average of five determinations.

TABLE 5

## ANALYSIS OF A 15.15.15 N.P.K. FERTILIZER

Components	Observed Concentration in % w/w
$\text{CaSO}_4$	1.0
$\text{NH}_4\text{Cl}$	17.8
$\text{K}_2\text{SO}_4 \cdot 2\text{NH}_4\text{NO}_3$	13.9
$(\text{K}, \text{NH}_4)_2\text{H}_2\text{PO}_4$	21.6
$\text{KNO}_3 \cdot \text{NH}_4\text{NO}_3$	34.9
$\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	3.8

## ANALYSIS OF A 15.15.21 N.P.K. FERTILIZER

Components	Observed Concentration in % w/w
$(\text{NH}_4, \text{K})\text{Cl}$	2.7
$\text{NH}_4\text{Cl}$	26.2
$\text{KNO}_3$	36.2
$(\text{NH}_4)_2\text{HPO}_4$	9.0
$(\text{K}, \text{NH}_4)_2\text{H}_2\text{PO}_4$	13.7

## ANALYSIS OF A 12.12.12 N.P.K. FERTILIZER

Components	Observed Concentration in % w/w
$(\text{NH}_4, \text{K})\text{NO}_3$	22.8
$\text{CaHPO}_4$	21.7
$\text{NH}_4\text{Cl}$	10.4
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	12.2
$3\text{KNO}_3 \cdot \text{NH}_4\text{NO}_3$	21.6

TABLE 6

## ANALYSIS OF 15.15.15 N.P.K. FERTILIZER

	Concentration calcu lated in % w/w	Concentration ana lyzed in % w/w	Difference
N	16.8	15.6	+ 1.2
P <sub>2</sub> O <sub>5</sub>	12.7	14.4	- 1.7
K <sub>2</sub> O	16.2	14.2	- 2.0

## ANALYSIS OF 15.15.21 N.P.K. FERTILIZER

	Concentration calcu lated in % w/w	Concentration ana lyzed in % w.w.	Difference
N	15.2	15.1	- 0.1
P <sub>2</sub> O <sub>5</sub>	12.9	14.6	- 1.7
K <sub>2</sub> O	20.6	21.3	- 0.7

## ANALYSIS OF 12.12.12 N.P.K. FERTILIZER

	Concentration calcu lated in % w/w	Concentration ana lyzed in % w/w.	Difference
N	13.2	11.9	+ 1.3
P <sub>2</sub> O <sub>5</sub>	11.3	12.9	- 1.6
K <sub>2</sub> O	11.2	11.0	+ 0.2



TA/88/3 Effect of raw materials, process operation and conditioners on physical characteristics, chemical properties and behaviour of NPK fertilizers by A. Barbera and R. Monaldi, Agrimont, Italy.

DISCUSSION (Rapporteur J.M. BIRKEBAEK, Superfos Fertilizers, Denmark).

Q - Mr. J.D. CRERAR (Hydro Fertilizers Ltd., UK)

Please give information about the granulation pilot plant.

a/ What size/capacity ?

b/ Continuous or discontinuous operation ?

c/ Costs and manpower needed.

d/ How are heat losses compensated for in calculating the heat balance ?

A - a/ When the plant runs, the capacity is 200 kg/day (i.e. approx. 13 kg/hour).

b/ The pilot plant is running continuously 16 hours per day.

c/ The cost of the pilot plant was about 500 mio Lire. Manpower in the plant is 3 persons/shift.

d/ The plant is very well insulated. We have measured the heat loss and we compensate all data obtained by this figure.

We have found excellent correspondence to data obtained in the full scale plant.

(Q.d was answered by Mr. G. BRUSASCO).

Q - Mr. H. HERO (Kemira Oy, Finland).

1/ How do you measure the real viscosity in situ (in reactor ?)

2/ Have you a method to measure the crystal size in the (oversaturated) slurry ?

3/ How do you see the relationship between crushing strength of granules and caking tendency ?

4. Do you see any dilemma between capacity and physical quality, especially concerning slurry viscosities ?

A - 1/ The measurement of the slurry viscosity is of special importance in the spouted-bed granulation process.

The apparatus we have installed is a rotary type viscosimeter, i.e. a rotor situated in a coaxial cylinder. We measure the "strength" (i.e. torque) to maintain a constant speed of the rotor.

2/ We do measure the crystal size in the slurry. It can be measured by optical microscopy, electronic microscopy, Coulter counter, etc.

.../.../...

In particular, we measure the nucleation rate and the growth rate of the gypsum crystals coming from the wet-process phosphoric acid. We do this by screen analysis and optical microscopy.

3/ Caking is reduced by producing large granules whereby the number of contact points between granules is reduced.

Mechanical weakness of granules usually promotes excessive caking as these granules tend to deform in the storage and form relatively large contact areas. In this case, Thompson mechanisms and capillary adhesion has a most important role in fertilizer caking. Also fracturing granules can form fines that promote caking.

4/ Yes, since it is difficult to have high plant capacities and good quality of the fertilizer.

To reduce problems, lots of experiments must be done in pilot and industrial plants to control all parameters in the right way.

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

Your coating system contains a fluorescent substance giving the possibility of measuring the coating efficiency.

Can you tell us more about the fluorescent substance - the chemical composition and the amount ?

A - A fluorescent substance can be added, but, if the coating substance contains aromatic compounds, then generally there is enough fluorescence.

Q - Mr. B. CHRISTENSEN (Superfos Fertilizer, Denmark).

1/ By what equipment or method are the viscosity and plasticity measured ?

2/ Can you explain the reason for decreasing the cigar-burning effect (S.S.D.) by adding DAP to NPK 12-9-27 ?

A - 1/ We measure the viscosity in a rotary viscosimeter with continuous flow of slurry. What we measure is the strength necessary to rotate the rotor at a constant speed in the drum.

2/ Addition of DAP reduces the cigar-burning effect because it absorbs heat. DAP can also be used in forest fire fighting.

Q - Mr. ORPHANIDIS (Duetag, France).

1/ What is the explanation for the high insoluble P2O5 increase with time for N/P mole ratio between 0.6 and 1 as shown in Fig. 3 ?

2/ What happens with solubility retrogradation beyond 6 hours (24,48,...) ?

3/ Can you please give more details about the Argirec applications shown in Fig. 9 (temperature of granules, temperature of Argirec, cooling of granules after spraying, size/RPM of coating drum).

.../.../...

A - 1/ In this pH-range are precipitated a lot of different insoluble phosphates, for ex/ Al, Mg, Fe and others.

2/ In the equilibrium state a lot of insoluble phosphates are present. The equilibrium is reached in days not in hours, so the solubility loss is higher in equilibrium than shown after 6 hours.

3/ The data presented in Fig. 9 are based on laboratory test.

We heat 10 kg of fertilizer in a rotary drum for 30 min., and have the possibility of varying many different parameters as shown.

The temperature during treatment in the plant is 70-80° C, and the product is cooled to below 40° C.

We use at present "Argirec" powder, but are going to change to liquid and only liquid coating materials.

Q - Mr. R. HUTCHINS (Texasgulf Inc, USA).

What is the anticaking agent "Argirec", and how would one go about getting samples for evaluation ?

A - The anticaking agent "Argirec" is an inert powder, clay type. Samples for evaluation can be got from:

Blancs Minéraux de Paris, 40 rue de Vignobles, 78400 Chatou, France.