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In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).

NEW WAYS OF OBTAINING POTASSIUM AND
AMMONIUM-POTASSIUM POLYPHOSPHATES

By

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and A. Gamero

1.   INTRODUCTION

Fertilizers based upon oxygen, potassium polyphosphates
and their ammoniated derivatives, have obvious
advantages as compared with traditional NPK fertilizers,
viz:

1)   High content of fertilizer units, which means a
      reduction in transport costs

2)   High solubility in water, making it possible to
      obtain liquid formulations with a high content of
      nutrients

3)   In the case of polyphosphates, their chelating
      capacity makes it possible to add minor elements
      to the formulations of clear liquids as well as
      permitting a higher concentration of nutrients.

4)   Their minimal chloride content renders them
      particularly suitable for crops or soils which
      will not tolerate excessive salinity. (1,2,3)

The methods of obtaining potassium phosphates known
from the literature on the subject are not attractive
from the economic point of view because of their use
of potassium hydroxide or carbonate, or because the
reaction conditions are such as to produce metaphos-
phates which are insoluble in water. (4,5,6,7)

Recently, a more economical method has been investigated,
based upon natural phosphate and using acid in the
presence of potassium sulphate.   This process, combined
with precipitation with methanol produces monopotassium
phosphate suitable for use as a fertilizer.   Goulding
introduced the process at the previous ISMA conference
(8).

The object of the present paper is to describe new ways
of obtaining ortho- and polyphosphate compounds directly
from the liquids resulting from the reaction or "attack"
of the phosphate, avoiding precipitation with methanol
and the equipment necessary for its subsequent recovery.

In our particular case, when there are various potassium

sulphate plants in operation where the HCl acid is recovered, a wet-process phosphoric acid plant and another for the polymerisation of phosphates, the economy of the process is sufficiently attractive to merit a thorough investigation.

The first part of the process (attack of natural phosphate in the presence of SO_4K_2) was carried out on an industrial scale, working continuously in one of our phosphoric acid plants.

The second part of the different methods was investigated at Laboratory and pilot-plant level.

2.   DESCRIPTION OF THE PROCESS

2.a Production of monopotassium-phosphoric liquid

The first stage of the process is to obtain a mixture of phosphoric acid and monopotassium phosphate in equimolecular proportion. In the tests carried out in our industrial plant we arrived at the following conclusions:

1)   It is necessary to work with a concentration of P_2O_5 not exceeding 20% -22%

2)   The reaction must take place in two stages. In the first stage a slight excess of free SO_4H_2 must be left so that the gypsum formed may be easily filtered. In the second stage sufficient phosphate is added to complete the reaction:
      $PO_4H_3 + (PO_4)_2 Ca_3 + SO_4K_2 -- PO_4H_2K + SO_4Ca$

3)   In our case, we worked with an attack efficiency of 98% and extraction yield of 95-96%, maintaining the following reaction constants:

        Unitary capacity   = $3m^3$/tonne P_2O_5

        Filtration surface   = $0.3m_2$/tonne   "

      In this way a solution is continuously obtained of the following average composition:

        Total P_2O_5 =   20-22%

        Free P_2O_5 =   10-11%

        SO_4 =   1-2%

        Ca   =   0.3%

        F   =   0.1%

4) The presence of K_2SO_4 in the reaction causes the precipitation of the fluorine as K_2F_6Si, which is lost with the gypsum during filtration. This may be a disadvantage in those plants designed for reclamation of residual fluorine.

**2.b Treatment of liquid obtained in the first stage:**

In this second stage, all the phosphoric acid present in the liquid of the first stage is neutralised, producing solutions which are polymerised directly. The methods investigated in the pilot plant were as follows:

2.b.1 Treatment with phosphate:

The hot liquid from stage 1 is treated in a reactor provided with mixing and heating facilities, a fresh supply of natural phosphate and potassium sulphate being added in sufficient amounts to produce the reactions:

$$4\ H_3PO_4 + Ca_3\ (PO_4)2 \quad -- \quad 3\ Ca\ (H_2PO_4)2$$

$$Ca\ (H_2PO_4)_2 + K_2SO_4 \quad -- \quad 2\ KH_2PO_4 + CaSO_4$$
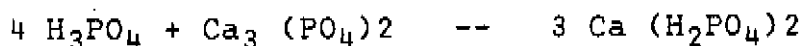
In some cases some $(OH)_2Ca$ or $Ca\ CO_3$ is added at the end in order to transform part of the phosphate into dipotassium phosphate according to the reaction:

$$2\ KH_2PO_4 + Ca\ (OH)_2 \quad -- \quad CaHPO_4 + K_2HPO_4 + H_2O$$
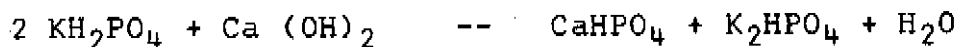
The gypsum formed is filtered and solutions of the following composition are obtained:

Total P_2O_5	=	24 -26%
$PO_4H_2K/\ PO_4HK_2$	=	>12
SO_4	=	1 - 1.5%
Ca++	=	0.3%

.with a yield of P_2O_5 of the order of 90%.

Optionally, it is possible to improve this output by passing the remaining gypsum to the attack plant of stage 1, where the dicalcium phosphate which has been precipitated is recovered.

The liquid obtained is concentrated up to about 45% of P_2O_5 and conveyed to a rotary polymeriser where the final product is obtained in the form of granules.

Table 1 gives the characteristics of the polymers produced with different initial P/K ratios.

2.b.2 Simultaneous production of pure dicalcium
       phosphate

The liquid obtained in the (2-b-1) process can be
converted into dicalcium phosphate and dipotassium
phosphate or tetrapotassium pyrophosphate of very
high purity, suitable for technical and food
purposes, in accordance with the reaction:

$$2 \ KH_2PO_4 + (OH)_2 \ Ca \quad -- \quad Ca \ HPO_4 + K_2 \ HPO_4$$

The lime is added in two stages: the first up to a
pH of 3.0 - 3.2, so that most of the metallic
impurities are precipitated in the form of mixed
phosphates.

This precipitate can be used by itself as source of
minor elements for fertilizer formulations, or may be
passed to the attack tank of the first stage in order
to recover the P_2O_5.

In the second stage the addition of lime up to pH =
3.5 - 4.0 is completed, the precipitated dicalcium
phosphate being filtered.

The liquid is concentrated or polymerised in order to
obtain $K_4P_2O_7$.

The products obtained have the following type
analyses:

	Phosphates 1st precip.	Ca HPO$_4$	K$_4$ P$_2$O$_7$
Total P_2O_5	49%	47%	42-43%
Soluble P_2O_5 citrate	46%	46.5%(K$_2$O)	55-56%
F	1-2%	0.1%	-
Heavy metals	2-3%	100p.p.m	10p.p.m
Solubility H$_2$O (20°C)	-	-	15gr/100

2.b.3 Production of NPK fertilizers with ammonia -
       Polymerisation drum

The liquid from stage 2a is neutralised with ammonia
gas and then subjected to polymerisation in a rotary
cylinder. Graph I indicates some of the results
obtained

With an initial liquid composition varying between

$$Total\ P_2O_5\ =\ 20\text{-}40\%$$

$$K_2O\ =\ 7\text{-}15\%$$

neutralised with NH_3 gas at pH = 4 and polymerised at different temperatures, stable, non-hygroscopic products are obtained of average composition (NPK) (5-50-20) with a percentage of polymerised P_2O_5 varying between 20 and 70%.

Polymerisation in continuous reactor

The reaction can be produced in a single stage by means of a T-reactor similar to that described in the paper "Preparation of ammonium polyphosphate solutions for liquid fertilizers" presented to this Congress by CROS.

Recently, since this paper was written, Hodge of Iowa State University published a paper on the polymerisation in T-reactor of monopotassium-phosphoric liquids with NH_3 (9).

The conclusions reached agree with those obtained in our apparatus

2.b.4   Production of NPK fertilizers by polymerisation with urea

By adding urea to the concentrated liquid produced in stage 2.a and heating the resultant slurry in a special continuous reactor (see Spanish Patent No. 395, 830) designed by CROS, NPK compounds with a high degree of polymerisation are obtained.

Starting with liquid of the following composition:

$$\overset{(*)}{P_2O_5\ T} = 38\%;\ \overset{(*)}{P_2O_5\ 1} = 18\%;\ K_2O = 14\%$$

and adding 15 parts of urea to 100 parts of liquid and polymerising at different temperatures, water-soluble products are obtained of a composition ranging between:

$$N\ =\ 6\text{-}8\%$$

$$P_2O_5\ =\ 45\text{-}50\%$$

$$K_2O\ =\ 18\text{-}22\%$$

with a % of poly-P_2O_5 of up to 50%.

Graphs II and III show the loss of NH_3 and the degree of polymerisation as a function of the residence time and the temperature.

(*) P_2O_5T = Total P_2O_5 in all its forms

(*) P_2O_51 = % P_2O_5 in the form of H_3PO_4

The products obtained are totally water-soluble up to about 30%, giving stable solutions suitable for formulations of clear liquid fertilizers.

It is necessary to have a system of recovery of NH_3 with phosphoric acid, or else to convey to stage 2.b.3 for utilisation the ammonia released.

The saving achieved by the process depends on the availability and cost of urea

3. USES OF THE PRODUCTS OBTAINED

3.a Granulated fertilizers

These have the advantage of a high content of fertilizing units, which reduces transport costs.

The absence of Cl^- is an advantage in those cases where they are to be used in very saline soils or with intolerant crops.

The highly-polymerised PKs exhibit slow water-solubility, so that they can be regarded as "low-release" fertilizers for humid climates.

3.b Liquid fertilizers

Their absence of Cl^-, increased water-solubility and high polyphosphate content make it possible to obtain stable formulations of high concentration to which minor elements and fungicidal products may be added. All this reduces the cost of use.

For example, with a base solution (3-20-10) prepared according to stage 2.b.4, it is possible to prepare stable solutions at 0°C of the following compositions:

(9-9-9) (8-16-8) (5-15-10) etc. by adding suitable quantities of urea, ammonium nitrate and potassium nitrate.

4. FINANCIAL CONSIDERATIONS

Table II shows the production cost of the monopotassium-phosphoric solution, compared with the cost of a 50% phosphoric acid obtained in the same plant and with the same tonnage, and the cost of the Super triple 45% P_2O_5 obtained with this acid in an associated plant.

As regards the production of the monopotassium-phosphoric solution, the amortisation of the additional new equipment needed to modify the plant was taken into account.

Table III is a comparison of the cost of a typical product obtained by ammonisation and polymerisation in the new plant, i.e. a (5-50-20), with the cost of an equivalent mixture of Super triple 45% and potassium sulphate, and another of Super 18% and potassium chloride.

It is considered that the costs of granulation are similar in the three cases, and the only difference is the additional fuel for polymerisation in the first case.

This cost does not include the costs of bagging, loading and transport.   Table IV shows the incidence of these expenses on the cost price in the three cases. The "break point" is 630 pesetas per metric ton in the second case, and 800 pesetas per metric ton in the third case.

No evaluation has been made in this calculation of the presence of P_2O_5 polymer in the case of the 5-50-20 which, depending on the purpose for which the product is intended, may carry some weight when making a decision.

TABLE I - PK POLYMERS AS A FUNCTION OF THE P/K RATIO

	-1-	-2-	-3-	-4-
Molar P/K ratio	0.76	0.88	1.11	1.13
Temperature	350°C	350°C	350°C	350°C
Residence time	1 h.	1 h.	1 h.	1 h.
Product obtained				
Total % P_2O_5	47.0	50.6	55.29	57.75
% K_2O	40.8	37.8	34.25	32.23
% CaO	0.2	0.2	2.40	2.70
% Poly-P_2O_5	99.0	99.0	97.00	96.00
Hygroscopicity (1)	4.61%	4.66%	3.68%	2.48%

(1) Hygroscopicity is determined by the increase
    in weight of a 10 gramme sample in a controlled
    atmosphere with 67% relative humidity and
    temperature of 25°C for 120 hours.

TABLE II — COMPARATIVE COSTS OF (20% SOL) and SP - 45%					
MONOPOTASSIUM PHOSPHOR LIQUID (20% P_2O_5)			**50% PHOSPHORIC ACID**		
Raw materials	Kg/Tonne	Price/Tonne	Pesetas/Tonne	Kg/Tonne	Price	Pesetas/Tonne

Raw materials	Kg/Tonne	Price/Tonne	Pesetas/Tonne	Kg/Tonne	Price	Pesetas/Tonne
Ground phosphate	642	1,180	757.5	1,685	1,180	1,988.3
98% Sulphuric	480	1,300	624	1,575	1,300	2,047.5
Potassium sulphate	148	3,200	473.6	-		-
Costs of process						
STAFF) POWER) AMORTISATION)			243.9			610
Amortisation new installation			19.5			
Production Cost			2,118.5			4,645.8

SP - 45%			
Raw materials	Kg/Tonne	Price	Pesetas/Tonne
Ground phosphate	394	1,180	464.9
50% Phosphoric acid	685	4,645.8	3,182.4
Process Costs			
STAFF) POWER) AMORTISATION)			300
Production Cost			3,947.3

TABLE III - COMPARATIVE COSTS FOR A 5-50-20

1 metric ton of 5-50-20

	Kg/Tonne	Price/Tonne	Pesetas/Tonne
20% Phosphoric liquid	2,500	2,118.5	5,296.25
Anhydrous ammonia	65	5,000	325
Polymerisation fuel			700
COST			6,321,25

Equivalent mixture of SP-45 and potassium sulphate

Total quantity = 1,530 Kg

	Kg/Tonne	Price Tonne	Pesetas/Tonne
SP-45%	1,115	3,947.3	4,401.25
Anhydrous ammonia	65	5,000	325
Potassium sulphate	400	3,200	1,280
COST			6,006.25

Equivalent mixture of SP-18% and potassium chloride

Total quantity = 3,028 Kg

	Kg/Tonne	Price/Tonne	Pesetas/Tonne
SP-18%	2,780	1,273	3,538.9
Anhydrous ammonia	65	5,000	325
Potassium chloride	333	2,574	857.1
COST			4,721.0

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DISCUSSION

MR. A. GAMERO (Sociedad Anonima Cros, Spain).
If a natural phosphate is attacked by sulphuric acid in
the presence of potassium sulphate, mixtures of phosphoric
acid and monopotassium phosphate are obtained.

Various methods of carrying out this process economically
are known, using conventional wet process phosphoric acid
plants. These processes involve precipitation with organic
solvents (methanol is most frequently used) to give
monopotassium phosphate.

The purpose of this paper is to describe new ways of
obtaining ortho- and polyphosphate compounds directly from
the liquid resulting from the attack of the natural phosphate,
avoiding precipitation with methanol and the equipment
needed for its subsequent recovery.

In our case, the fact that we have various potassium
sulphate plants in operation in which hydrogen chloride is
recovered, as well as a wet process phosphoric acid plant
and another for polymerisation of phosphate makes the
economy of the process sufficiently attractive for thorough
investigation. We carried out the first part of the
process (attack of the natural phosphate in the presence of
potassium sulphate) on an industrial scale, on the basis of
continuous operation, in one of our phosphoric acid plants.

The second part, i.e. testing of the different ways of
obtaining ortho- and polyphosphate compounds, was investigated
on a laboratory and pilot-plant scale. The first part of
the process thus consists in obtaining a mixture of phosphoric
acid and monopotassium phosphate in equi-molecular proportion.
The tests carried out in our industrial plant showed that it
was necessary to work at a P_2O_5 concentration not exceeding
20-22%. In order to resolve the basic problem of efficient
filtration of the gypsum formed, we were forced to conduct
the reaction in two stages: in the first, a small excess
of free sulphuric acid must be left in order to ensure
that the gypsum formed is easily filterable. In the second
stage, sufficient phosphate is added to complete the
formation of monopotassium phosphate at the expense of the
phosphoric acid obtained in the first phase.

The presence of potassium sulphate in the reaction causes
precipitation of the fluorine as potassium fluosilicate,
which is lost with the gypsum during filtration. This may
be a drawback in plant fitted with equipment to make use
of the residual fluorine. On the other hand, we feel that
with plants which have as yet no recovery system it may be
an advantage, since it gets round the problem of contamination.

The equimolecular mixture of phosphoric acid and mono-potassium phosphate is then capable of various forms of treatment. It can be treated with more natural phosphate and potassium sulphate, with lime, with ammonia or with urea.

The treatment with natural phosphate and potassium sulphate converts the phosphoric acid into monopotassium phosphate and filterable gypsum. Some dipotassium phosphate may be obtained if some lime is added at the end. We have obtained solutions with the following composition:

Total P_2O_5 in the region of 24-26% and a monopotassium phosphate/dipotassium phosphate ratio in excess of 12: i.e. we have not made much progress in obtaining dipotassium phosphate in this phase. The liquid obtained is concentrated up to about 45% P_2O_5 and conveyed to a rotary polymeriser where the final product is obtained in the form of granules. Table I of our paper shows the characteristics of the polymers obtained for various starting P/K ratios.

Alternatively, if instead of concentrating and polymerising the monopotassic liquid we continue to add lime up to a pH of 4 or more, it can be converted into dicalcium and dipotassium phosphate. The potassium salts may possibly be polymerised to potassic polymers. All these products are of high purity and suitable for technical and food purposes.

As stated, the liquid of the equimolecular mixture of phosphoric acid and monopotassium phosphate may be neutralised with ammonia gas and subjected to polymerisation in a rotary cylinder.

The products obtained are stable, non-hygroscopic, with an average composition of 5-50-20, and a degree of poly-merisation of between 20 and 70%. Similar results should be obtained in a single stage by ammoniating in a T reactor according to the now standard process.

By adding urea to the concentrated monopotassium-phosphate liquid and heating the resulting slurry in a specially designed continuous reactor, NPK compounds with a high degree of polymerisation are likewise obtained, as described in our article. The graphs we have included show the loss of ammonia and the degree of polymerisation in terms of residence time and temperature. The products obtained are totally water-soluble up to about 30% giving stable solutions suitable for formulations of clear liquid fertilisers.

A system must be provided for the recovery of ammonia with phosphoric acid or, alternatively, the ammonia given off must be conveyed to one of the ammoniation phases previously described for utilisation. The economy of the process is dependent on the availability and price of urea.

Finally, a brief economic study is included, which
compares the industrial costs of the various products
which can be obtained with the new technology with the
industrial costs of similar products obtained using
conventional raw materials and technology.

It must be borne in mind that the new products have
physical, chemical and agricultural characteristics, and
characteristics of purity and concentration etc., which
must be duly weighed when comparing them with equivalent
conventional products.

The general conclusion to be drawn from such considerations
is that the products have commercial application in certain
defined markets and areas of use.

MR.F.J.HARRIS, (Scottish Agriculatural Industries Ltd.,
United Kingdom.) I would first like to congratulate the
authors on the ingenuity they have shown in the work
described in this paper. They have certainly covered a
considerable number of aspects of the calcium, potassium,
phosphate and sulphate system.

Some years ago, we in Scottish Agricultural Industries
worked with this system, though we made as an end product
water insoluble potassium metaphosphate. I might add that
radio tracer studies using water soluble materials showed
rapid hydrolisis in the soil. The metaphosphate was a
very good fertiliser though, I fear, when applied to the
soil it showed no advantages over a traditional mixture
of superphosphate and potassium chloride. Indeed, in
spite of considerable effort, to the best of my knowledge
there are still no more efficient fertilisers in terms of
P_2O_5 and K_2O uptake by most agricultural crops. Nevertheless,
one willingly accepts the advantages put forward by the
authors provided they can be achieved economically, although
I believe it would be fair to say that the advantages of
high concentration and low extraneous salt content would be
equally applicable to the insoluble metaphosphate which
generally I would expect to be cheaper to make although it
is unsuitable for use in solution fertilisers without
further treatment. On the other hand I believe that in
moving from a K_2O: P_2O_5 ratio of from 1:1 to around 1.5:1
the authors have made a major step forward. Indeed I
suppose that the further this ratio can be moved toward a
2:1 ratio as in K_2HPO_4 or $K_4P_2O_7$, then the more attractive
the material will become, particularly in those countries
where fertilisers, particularly phosphates, have been used
for a great number of years. And further to introduce
nitrogen into the molecule of the new fertiliser material
as the authors have done on a production scale is a very
noteworthy achievement. May I then turn to the technicalities
of the process. The first point I would like to make
concerns the addition of potassium sulphate to the phosphoric
acid process. We have done this on a number of occasions

and our experience has been, as the authors state, that potassium silico fluoride is precipitated; the solution however remains saturated with respect to the silico fluoride and, when this passes through the filter cloth used in separating the gypsum, some flash evaporation due to the reduced pressure and consequently cooling occurs and potassium silico fluoride crystallises in the pores of the filter cloth so that it becomes blocked and no more liquid will pass. In our case, this was most noticeable after about 3 to 5 days of operation, depending upon the rock source being used. I wonder if the authors have encountered this difficulty and, if so, how they have overcome it? Perhaps this is one reason for working with fairly dilute acid. I also wonder what the fluorine content of the fertiliser is?

In section 2.b.1 the authors mention that calcium hydrocide or calcium carbonate may be added to transform part of the phosphate to the dipotassium form. I believe that the best example quoted shows the equivalent of about half of the KH_2PO_4 converted to the dipotassium salt.

I would like to know if this ratio is about the maximum the authors might expect to achieve, and how far the reaction can be pushed when using calcium carbonate. In section 2.b.2 the authors finally add lime to bring the liquor to a pH of 4 and then, on concentrating and polymerising this liquor, obtain $K_4P_2O_7$ as product. This must suggest that K_2HPO_4 is present at pH4 which is surprising since one would normally expect the mono salt at this pH. Having since spoken to the authors I believe the $K_4P_2O_7$ to be a mistake.

The polymerisation in the presence of urea is certainly most interesting. Since the liquor taken with the urea has a pH of around 3, it is interesting to speculate whether urea phosphate is formed although I would think it unlikely that it would be precipitated in the concentrations being used. It is even more interesting to speculate on the compounds that are found when this urea/phosphate liquor is heated; does the urea play any part in the condensation? Does it just decompose and its ammonia combine with the KH_2PO_4 to give eventually a mixed ammonium potassium polyphosphate. I should certainly be interested to hear whether the authors have done any work on the composition of the product. It definitely cannot be a mixture of potassium metaphosphate and condensed urea products because it is water soluble. Finally, I would like to ask the authors their opinion on the maximum ammonia loss they consider to be tolerable during the polymerisation stage.

MR. GAMERO. Before replying to your questions, I should say that in our country we have so far endeavoured to avoid producing metaphosphate which, owing to its insolubility, is not as yet well-received by our farmers. As to the rest, I am entirely in agreement on what you say about its characteristics and properties. I am not sure whether I shall be answering your questions in the order in which you put them.

The first point to be clarified is of course the possible error in the article where it states that, with a pH of 4, dipotassium phosphate can be obtained by the addition of lime which can be polymerised to polyphosphate.

In fact, as shown by the data given in the article, for a given production of dicalcium phosphate we give the corresponding production of polymer and, as you noted, the K_2O/P_2O_5 ratio is of the order of 1.5 to 1. Obviously this ratio depends on the starting pH of the solution of mono-potassium phosphate, dipotassium phosphate which we obtain by adding lime. Thus the polymer finally obtained depends on the pH achieved. I feel that this point is thus clarified.

As regards the use of calcium carbonate to obtain a little dipotassium phosphate in conjunction with the monopotassium phosphate in the second treatment with natural phosphate and potassium sulphate conducted with the original mother liquor, we must admit that we ourselves have worked only with lime; we have never used calcium carbonate. The fact that we added calcium carbonate in our article is because we have read of the possibility of using it in this way in the literature on the subject - although I doubt whether results similar to those achieved with lime can be obtained. In any case, the choice is utilitarian; it is a question of economics. In polymerisation with urea, we have not conducted any practical research to ascertain what intermediate compounds are formed in the special reactor we have designed for this polymerisation.

The only thing we can say is that, as has already been stated in the article, we add to the equimolecular mixture of mother liquor containing phosphoric acid and monopotassium phosphate the correct quantity of urea required to form (and we think it does in fact form) the adduct of phosphate of urea. We do not note any precipitation; i.e. we consider that this adduct remains in solution and it is on heating that all the urea then disappears; we do not, when using the stoichiometric quantity of urea, note its presence in the final product. We therefore consider that the urea has broken down into ammonia and, reacting with the phosphoric acid, has produced ammonium polyphosphate. It would be risky to claim that part of the acidity of the monopotassium phosphate is also neutralised by the ammonia deriving from the decomposition of the urea, producing compounds we refer to as potassium ammonium compounds. In the ammonia recovery process with urea treatments ammonia is lost; in the article, thinking in terms of the need to specify clearly the amount of ammonia which can tolerably be lost or given off, and which we then recover or send to other ammoniation stages, as described, we have included some graphs which show the loss of ammonia in terms of temperature and residence time. The reactor we designed is particularly devised to give a minimum residence time, so as to reduce the ammonia loss as far as possible. We have been able to operate with residence times which ensure, we feel, that not more than 10 or 15% of the ammonia is lost

outside the system and has to be recovered. This ammonia recovery is effected in a tower with a normal scrubber which was already at the plant. It works in the conventional way with phosphoric acid in a nitrogen/phosphorous ratio of the order of 0.7.

Finally, an important point(and it is interesting that Mr Harris should have brought it into the discussion) is the question of the effect of the potassium fluosilicate which may precipitate during the filtration of the gypsum. In the first part, obtaining an equimolecular mixture of phosphoric acid and monopotassium phosphate with filtration of the residual gypsum, we did not encounter any difficulty. And the reason we have not encountered problems is, we feel, because this phase of the process is one which we have investigated most thoroughly both in the industrial phase and from the physical/chemical aspect of precipitation of the gypsum in the laboratory. Operating under the conditions set out in our paper, i.e. with a very dilute or dilute solution of the order of 20 to 22%, and dividing the reaction into 2 phases, i.e. with 2 reactors in succession, in the first of which we maintain an excess of sulphuric acid, we have shown that if the residence time, temperature, acidity are properly adjusted in this first phase it is possible to obtain gypsum crystals which are relatively long, thick needles; on passing to the second phase the precipitation of gypsum which occurs there takes place on these crystals. We therefore think that these crystals grow at the expense of the former, and give rise to the formation of a filter cake which offers no difficulties of any kind. We have brought microscope photographs with us which we can show to anyone interested. They will be able to see the extraordinary difference in the crystalline texture of the gypsum precipitated under these conditions in comparison with the texture, behaviour and shape of the crystals obtained when we depart from these operating conditions. We think it unlikely, therefore, that the existence of a small quantity of fluosilicate which under vacuum filtration conditions may flash and become deposited on cooling on the filter cake would block the pores of the filter cake and cause problems. Moreover, our experience in industrial testing shows that after 5 days of continuous operation of an industrial plant under these conditions not the slightest blockage of the filter cake was noted.

GRAPH I - Polymerisation of monopotassium liquid
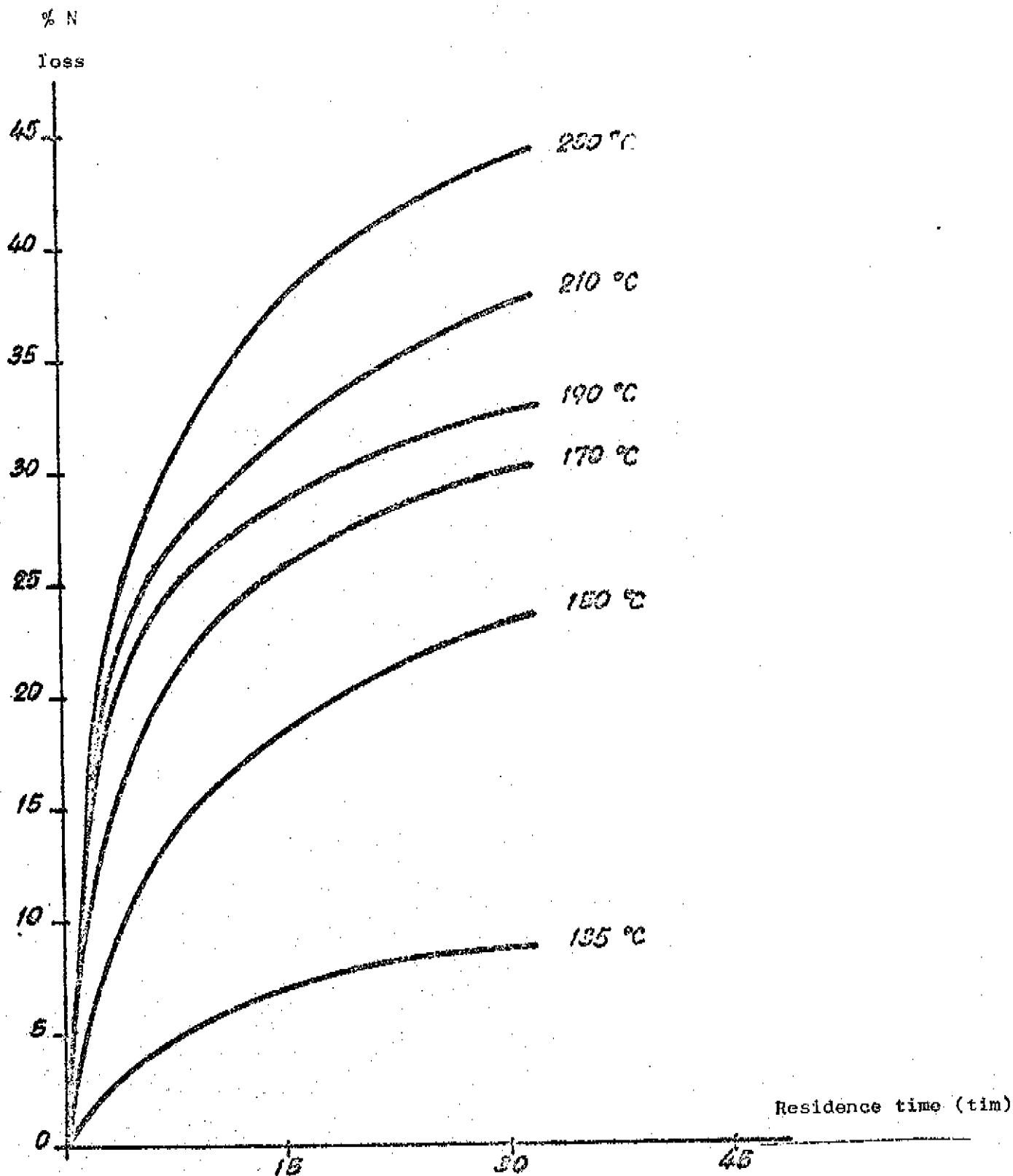treated with NH_3 at PH = 4

Residence time = 5 minutes
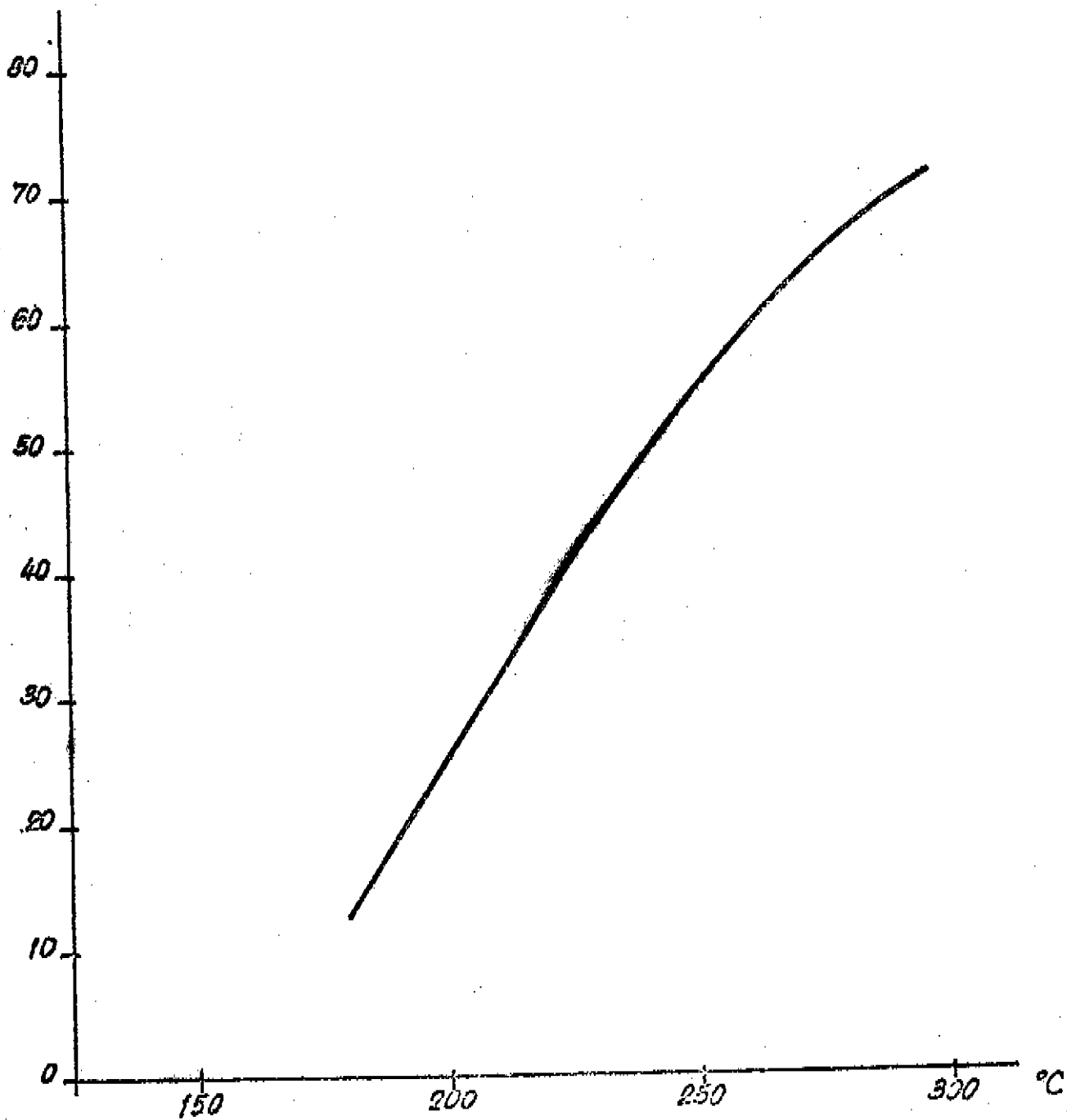
GRAPH II - Polymerisation of monopotassium phosphoric liquid
with urea. Degree of polymerisation as a function
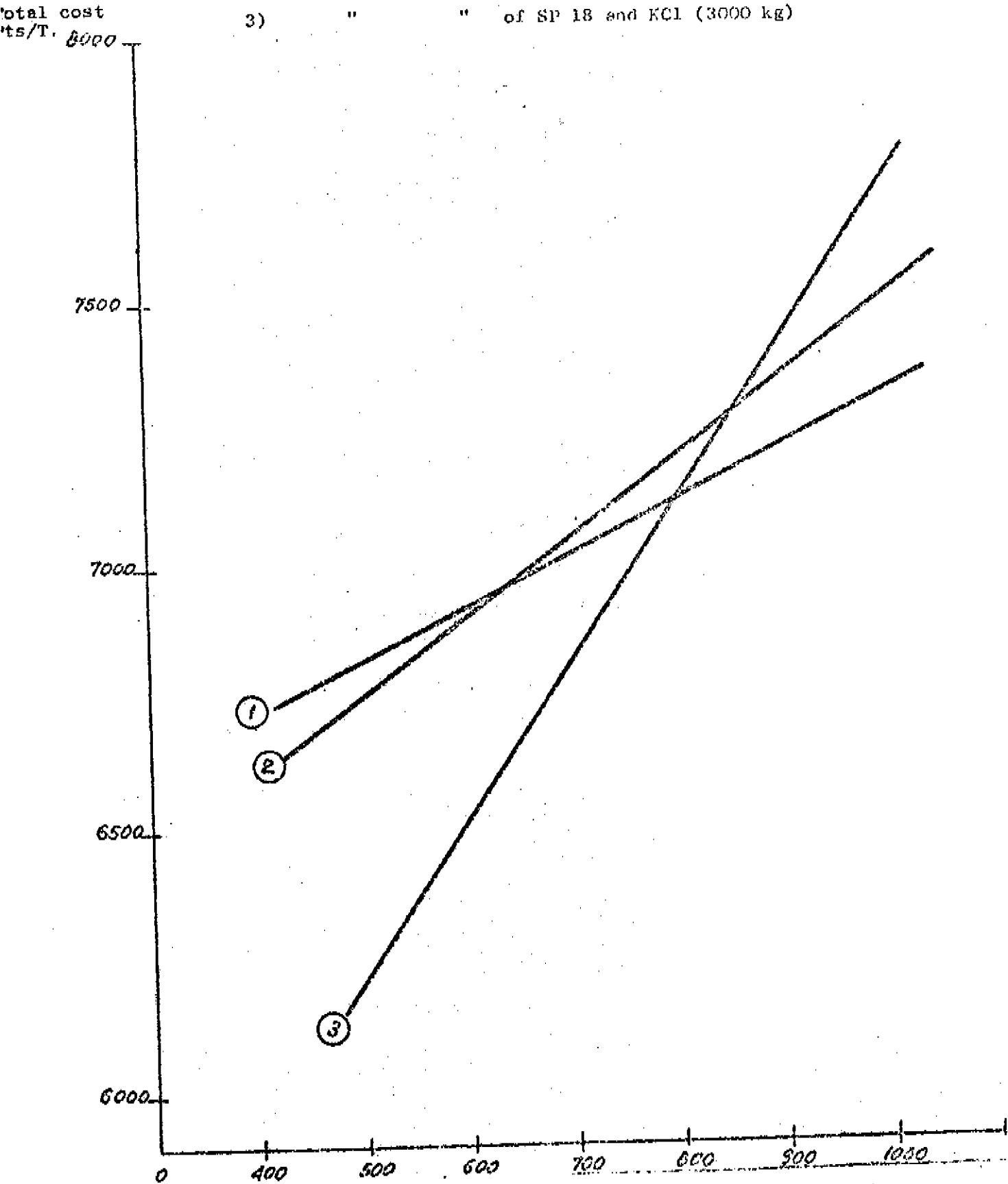of temperature and residence time.
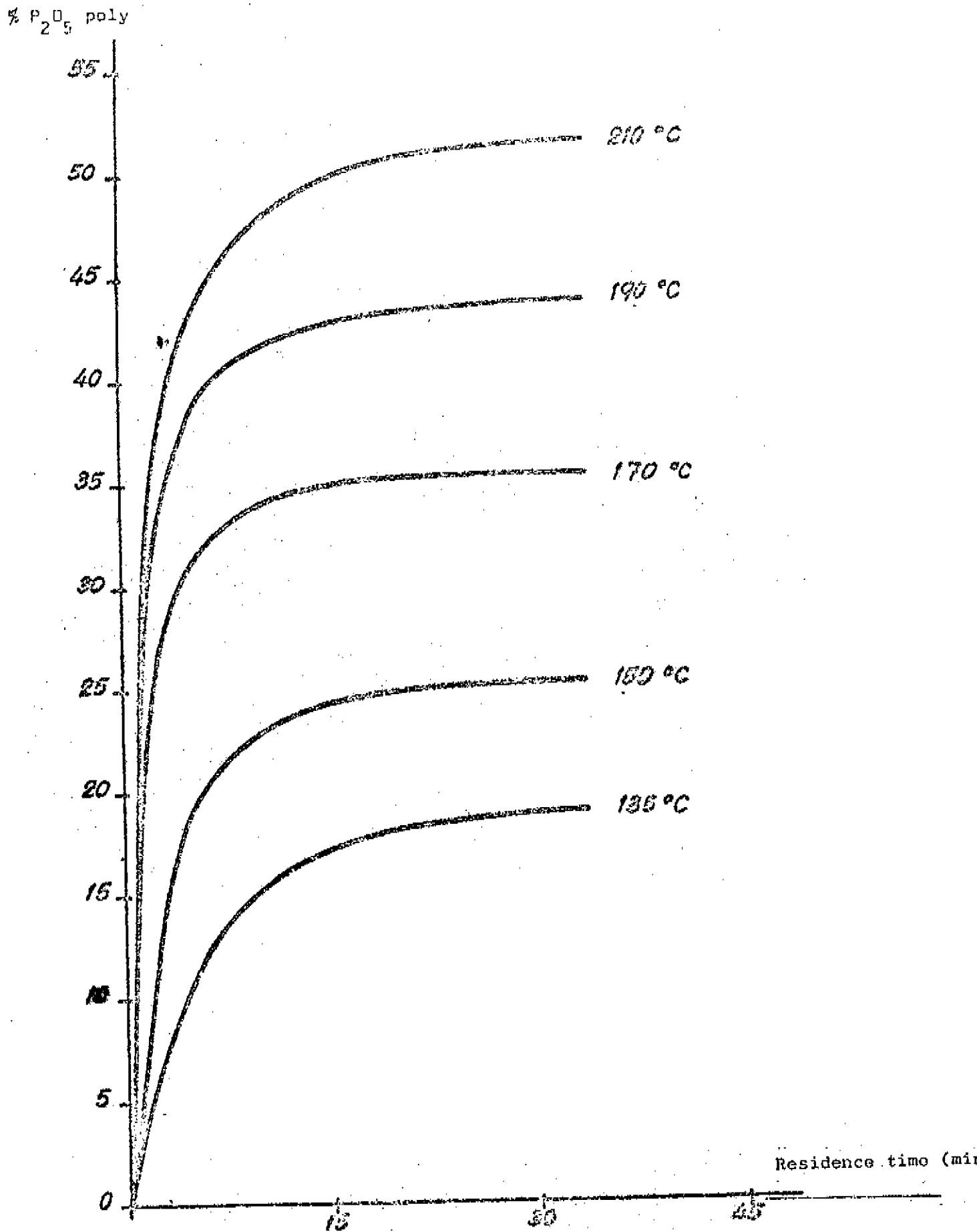
GRAPH III - Polymerisation of monopotassium phosphoric liquid
with urea. Loss of N as a function of the temperature
and residence time.

GRAPH IV - COMPARISON OF COSTS

1) (5-50-20) poly (1000 kg)

2) Equivalent mixture of SP 45 and K_2SO_4 (1500 kg)

3) " " of SP 18 and KCl (3000 kg)

Total cost
Pst/T.

8000

7500

7000

6500

6000

0   400   500   600   700   800   900   1000

Cost of bagging & transport Pst/Tonne

Phosphate

H_2O

Residual Gypsum

Reactor

Reactor

Filter Solution

SO_4

PO_4

Liquid H_3PO_4 KH_2PO_4

Phosphate

Filter → Gypsum

SO_4

CaO

Reactor

NH_3 → Reactor

NH_3 → T Reactor

Urea → Reactor

Liquid KH_2PO_4

CaO

Concentrator

Concentrator

Polymeriser

Polymeriser

Reactor

Concentrator

Crystalliser

Filter

Polymeriser

Crystalliser

Filter

Filter

Dryer

Filter

KH_2PO_4

Poly PK

$Ca HPO_4$

$K_4P_2O_7$

K_2HPO_4

Poly-NPK

Poly-NPK

Poly-NPK