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

POTASSIUM DIHYDROGEN PHOSPHATE MANUFACTURE

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1. INTRODUCTION

Potassium dihydrogen orthophosphate has obvious advantages as a fertiliser material. It is a highly concentrated source of P_2O_5 and K_2O , and it can be ammoniated to yield a ternary compound containing all the three plant foods, N, P_2O_5 and K_2O .

Many methods have been proposed for the manufacture of potassium phosphate, including a number based on the reaction of phosphoric acid with potassium hydroxide or potassium carbonate. These processes in general are economically impractical. The most obvious route is by the reaction of phosphoric acid with muriate of potash. This reaction, however, requires excess acid and high temperatures to remove chloride as hydrochloric acid. The residual acid must be finally neutralised with relatively expensive caustic potash or potassium carbonate, adversely affecting the economics. All the chlorine cannot be driven off by this means without at the same time heating the phosphate to such a point that substantially all of it is converted to the water insoluble potassium metaphosphate.

In this paper a process is described for the manufacture of potassium dihydrogen phosphate, the economics of which are comparable with those of other fertiliser materials. The first stage of the process production of potassium phosphate in solution, has been carried out on an industrial plant scale. The other stages, the recovery of the solid product and the use and recovery of methanol, have been carried out only in the laboratory.

The name Marina Salt has been used for the material initially for reasons of secrecy, and later for reasons of convenience. The material is so referred to in the text.

2. PROCESS

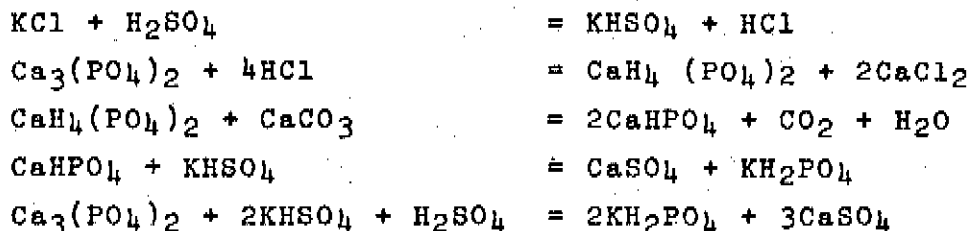
a) Chloride Conversion

Muriate of Potash is reacted with excess sulphuric acid in the Chloride Converter. Hydrogen chloride is released quantitatively at relatively low temperatures (less than 200° C). It is recovered by absorption in water, for sale as a marketable product, for chlorine manufacture or for use in the process to replace some of the sulphuric acid.

b) Sulphate Reaction

The chloride free acid slurry of potassium bisulphate in sulphuric acid is reacted with phosphate rock in a phosphoric acid type reactor where potassium phosphate is formed. Co-produced calcium sulphate is separated on a gypsum filter.

The basic reactions are :



In order to obtain filterable gypsum and facilitate complete solution of the rock, high acid levels are maintained in the reaction slurry. The first filtrate from the gypsum filter, which is a solution of potassium phosphate and phosphoric acid is concentrated and sent to a precipitation vessel.

c) Potassium Phosphate Separation

The separation of potassium phosphate from the acid solution by crystallisation is not straightforward. Methanol is therefore added in the precipitation vessel to precipitate the potassium phosphate which is separated by centrifuge.

d) Methanol and Pure Acid Recovery

The centrifuge liquor is stripped of methanol in a simple distillation column. The recovered methanol from the top of the column is sent to storage for re-use in the process. The column bottoms which contain phosphoric acid of high purity and some residual potassium phosphate are returned to the process to maintain the reactor acidity or drawn off for the

manufacture of pure phosphates. In the latter case the reactor acidity is maintained either by the addition of wet process acid from an outside source or by feeding additional rock and sulphuric acid to the reactor.

3. CO-PRODUCT HYDROGEN CHLORIDE

The hydrochloric acid released by the action of the sulphuric acid on the muriate can be used in the process with a consequent economy in sulphuric acid usage. To this end, part of the phosphate required in the reaction is reacted with the hydrochloric acid evolved in the Chloride Converter to produce mono-calcium phosphate and calcium chloride in solution.

The phosphate is precipitated as dicalcium phosphate by the addition of ground phosphate and limestone. The precipitated solids are filtered, washed free of chloride and sent to the main reactor and reacted with the acid sulphate solution.

Alternatively, the hydrochloric acid can be absorbed in water and sold as a marketable product or used for the production of chlorine by electrolysis.

4. CO-PRODUCT PHOSPHORIC ACID

The acid from the methanol recovery still bottoms has an analysis of approx. 50% P₂O₅, 0.8% K₂O. It can be concentrated and the K₂O level reduced by addition of further quantities of methanol, to yield a product, the analysis of which is compared with wet-process acid below :

	<u>Co-product Acid</u> %	<u>Wet-process Acid</u> %
P ₂ O ₅	54.0	54.0
SO ₄	0.018	3.4
Fe	0.002	0.2
K	0.45	0.04
F	0.003	0.5

The acid so produced can be used for liquid fertiliser production or for the manufacture of detergent or other phosphates. Sodium phosphates derived from the acid have a high degree of whiteness.

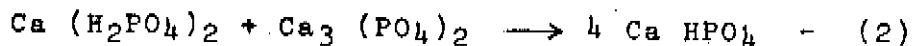
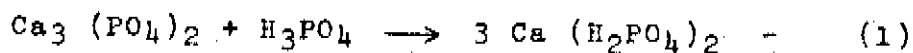
5. CRYSTALLISATION OF MARINA SALT LIQUORS

The crystallisation of potassium phosphate from the acid Marina Salt liquors is complicated by the presence of impurities and the formation of an addition compound with phosphoric acid $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$. The solubility of monopotassium phosphate increases greatly with increasing acidity, up to a maximum at a $\text{P}_2\text{O}_5/\text{K}_2\text{O}$ level approx. 3.0. Above this level of acidity the double salt $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$ is deposited from solution. The solubility data for the system $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ is shown in Figures I, II and III.

Difficulty in separation only obtains so long as the liquors are acid. If the pregnant liquor is neutralised with lime to pH 4.5 and the precipitated dicalcium phosphate separated, the crystallisation of the potassium phosphate is straightforward and simple. In practice, however, this procedure is uneconomic, for although neutralisation with lime is inexpensive, sulphuric acid must be subsequently added to remove the calcium.

Neutralisation with soda or ammonia adversely affects the K_2O analysis. Solids with analysis 6 N, 46 P_2O_5 , 12 K_2O have been obtained from the liquor by neutralisation with ammonia and evaporation to dryness.

Attempts made to neutralise the liquor by addition of part of the phosphate required in the reaction, showed that Morocco rock (both ground and unground) was attacked by the acid in the filtrate, only insofar as the carbonate present was attacked. When, however, the filtrate was concentrated from s.g. 1.3 to s.g. 1.7 attack took place, but only according to equation 1 and precipitation of dicalcium phosphate was not achieved according to equation 2.



Precipitation was achieved by the addition of lime to pH 4.5.

After separation of the dicalcium phosphate potassium phosphate crystals in filterable form were easily obtained. The economics of the process were adverse however, because of the sulphuric acid subsequently required to remove the added calcium.

Efforts to salt out the potassium phosphate by the addition of muriate of potash were unsuccessful. The recovered solids were, in general, mixtures of potassium chloride and potassium phosphate.

Use of a Water Miscible Solvent

Potassium phosphate of good analysis and low free acid could be obtained from the acid liquors by the use of a water miscible liquid in which the potassium salt was insoluble. A number of organic liquids were investigated comprising mainly lower molecular weight alcohols and ketones. All the liquids investigated precipitated the phosphate as a solid or as a liquid, phase rich in potassium phosphate which solidified on standing.

Use of Methanol

Methanol was chosen for the process on the grounds of cost, availability and ease of recovery.

The removal of methanol from methanol and water mixtures is a simple, cheap and well known distillation process. Using a 120 cm continuous packed distillation column it was found that the separation of methanol from Marina Salt liquors was uncomplicated and proceeded substantially the same as from methanol water solutions, containing comparable percentages of water. A methanol water vapour liquid equilibrium diagram is shown in Figure 4.

Mono potassium phosphate has a low solubility in methanol, Figure 5. The yield of this salt by addition of methanol to the acid liquors is high, Figure 6. The yield of solids increases as the initial concentration increases.

The solids are precipitated by methanol as very small microcrystals. By control of the crystallising conditions a great improvement in average particle size was achieved, see Figure 7.

The solids precipitated had a high free acid of the order 10% P_2O_5 . This could be reduced by washing with methanol. When the crystals were washed with an equal volume of methanol to that used for precipitation, the acid value was reduced to 4.0 - 5.0% P_2O_5 .

6. CAPITAL COST

The capital cost of a plant to produce 58,000 short tons/year P_2O_5 equivalent (126,000 short tons Marina Salt) has been estimated at £ 1.9 m. (\$ 4.36 m.).

The capital cost of a plant to produce 58,000 short tons/year P_2O_5 equivalent as Marina Salt and 58,000 short tons/year P_2O_5 as pure acid concurrently is estimated at £ 2.4 m. (\$ 5.8 m.).

7. COSTS OF PRODUCTION

The costs of production on a plant built in Ireland are given in the attached nomographs (Appendices I and II). The fixed charges in Appendix I are based on an annual output of 58,000 short tons P_2O_5 equivalent as Marina Salt and in Appendix II are based on an annual production of 58,000 short tons P_2O_5 equivalent as Marina Salt and also 58,000 short tons P_2O_5 as phosphoric acid. In both cases interest and depreciation are each charged at 10% and maintenance at 8% of capital.

a) Marina Salt Alone

A cost comparison of the production of Marina Salt and triple superphosphate under Irish conditions is given in Appendix III. A comparison of the cost of Marina Salt and its equivalent weight of triple superphosphate and sulphate of potash and triple superphosphate and muriate of potash is given in Appendix IV, and a graphical representation showing the comparison of costs of handling, bagging, storage and freight of Marina Salt and its equivalent weight as triple superphosphate and sulphate of potash and triple superphosphate and muriate of potash, is given in Appendix V.

It can be seen, within the limits of accuracy of the estimates, that Marina Salt is competitive with the mixture of sulphate of potash and triple on the factory floor. When the costs of handling, bagging, storage, freight and distribution are considered, the advantages of the Marina Salt high concentration levels rapidly become of economic significance. In the case of muriate of potash and triple superphosphate, Marina Salt becomes competitive when the total costs of distribution including bagging, storage, handling and freight amount to \$ 20.5 per short ton.

b) Concurrent Acid Production

If the plant is designed so that there is a concurrent production of phosphoric acid with the primary Marina Salt product, a considerable overall economy is achieved. The nomograph (Appendix IV) gives the production costs of soluble P_2O_5 as acid and Marina Salt for a plant built in Ireland, producing 58,000 short tons P_2O_5 as Marina Salt and 58,000 short tons P_2O_5 concurrently as pure acid. Under these conditions the cost of production of soluble P_2O_5 overall including the acid and salt is only \$ 10/short ton dearer than the cost of P_2O_5 as acid produced on a plant producing 116,000 tons P_2O_5 .

The graphical representation showing the costs of distribution of Marina Salt and triple superphosphate based equivalent mixtures has been redrawn in Appendix VII and the

Marina Salt costs have been adjusted for concurrent production of acid. The acid is credited as wet process cost A, and for purity, at a premium cost of \$ 5/short ton, B - \$ 10/short ton, C - \$ 20/short ton, D. It can be seen that Marina Salt becomes competitive with triple superphosphate and muriate on the factory floor, when a premium of \$ 25/short ton over the cost of wet process acid is allowed to the pure acid.

8. MARINA SALT PROPERTIES

The Marina Salt is a fine greenish-white, non-hygroscopic, free flowing powder.

Analysis	20% P, 25% K (46% P ₂ O ₅ , 30% K ₂ O)
Free Acid	5% P ₂ O ₅
Moisture	0.5%
Melting Point	200° C

Minor Constituents

	%		%
Al	0.59	Fe	0.5
Ca	0.22	Mg	0.04
Cr	0.05	Pb	0.0002
F	1.50	V	0.002
		SO ₄	3.1

ADVANTAGES

The main advantages of the material are :

a) The absence of chloride

There are a number of sensitive crops where chloride is undesirable even at low dressing levels, such as tobacco, potato and citrus. Marina Salt has obvious advantages for use on these crops.

Its use in irrigation water would avoid the build up of chloride in the soil to damaging levels, with the consequent necessity for wasteful flushing out.

b) High Solubility

The water solubility of the material, particularly of the ammoniated compound leads to much higher analysis in liquid fertilisers than conventional materials.

c) Low Melting Point

The melting point is approx. 200° C. This is of considerable advantage in the formulation of NPK fertilisers for manufacture by prilling or melt granulation.

d) Safety in Handling

The compound, unlike potassium nitrate is free from explosion and combustion hazards and is, therefore, not subject to restrictions for transport or storage. Unlike the chloride it will not give rise to "cigar burning" in stored bulk fertilisers containing ammonium nitrate.

e) High Concentrations

It is a highly concentrated plant food, 46% P₂O₅, 30% K₂O, both elements of which are water soluble. It contains no burden of extraneous ions such as chloride, sulphate or carbonate.

The process is outlined in the attached schematic flow diagram (Appendix VIII).

9. USES FOR MARINA SALTa) Use in Liquids

Marina Salt can be ammoniated to give a solid product of analysis 5% N, 18% P, 23% K. The ammoniated product shows a maximum solubility at N:P molar ratio of 0.7. Figure 8 shows the solubility data for a KH₂PO₄.KCl system in which the K P level is 1.0 at various levels of ammoniation. Use of Marina Salt in ammoniated solution leads to considerable increases in analysis of liquid fertilisers compared with materials in current use as shown in the following table.

Liquid Fertiliser Analyses

<u>Marina Salt</u>			<u>Normal Materials</u>		
N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O
13	13	13	9	9	9
5	15	15	3	9	9
16	8	8	16	8	8
7	14	14	5	10	10
9	27	9	6	18	6
11	22	11	8	16	8

The above solutions are all stable at 0° C. Marina Salt has high potential in liquid fertilisers. It is also expected to find use in glasshouse culture, horticulture and in foliar spraying applications.

b) Use in Prilling and Melt Granulation

There is a considerable development in the manufacture of prilled NPK fertilisers. Muriate of Potash causes difficulty in the prilling process because of its high melting point and insolubility in the melt. Marina Salt has a unique advantage as a source of potassium in prilling mixtures, because of its low melting point, and compatibility with other melt components.

c) Use in Fertilisers containing Ammonium Nitrate

Certain mixtures containing ammonium nitrate are liable to deflagrate in storage. For such deflagration to occur the simultaneous presence of NO_3 , NH_4 and Cl is essential (1). Use of Marina Salt will reduce this hazard.

d) Use on Chloride Sensitive Crops

Marina Salt has obvious an application for use on chloride sensitive crops, and has apparent economic advantages over Sulphate and Nitrate for this use. This is of importance in the production of tobacco, in potato production for crisps manufacture and on citrus plantations. The deleterious effect of the presence of chloride over a wide range of other crops is only now beginning to become apparent (2) and the availability of a chloride free fertiliser source will become of increasing significance in the future.

e) Use in Irrigation Systems

Marina Salt will be of importance in areas of low rainfall and under irrigation conditions where salinity due to chloride build up presents a problem. The continued use of muriate as a source of K_2O can lead to build up of chloride in the soil, which has to be flushed out by flooding, with consequent loss of plant nutrients and usage of large quantities of water. Use of Marina Salt allows large amounts of potassium to be used, without adding damaging quantities of chloride.

f) Use in Granulation

Marina Salt has a high solubility coefficient (i.e. the

solubility increases rapidly with increasing temperature). This will increase soluble salt content of the liquid phase at granulation temperatures and provide rapid decrease in the liquid phase in the latter stages of processing. It will therefore act as a useful granulation aid in the processing of mixed fertilisers. The solution of Marina Salt in phosphoric acid from the gypsum filter can be ammoniated and used directly in slurry granulation plants.

g) Use in Food and Other Phosphates

Marina Salt can be purified by crystallisation and provides a possible starting material for the manufacture of food and detergent phosphates.

10. CONVERSION OF EXISTING PHOSPHORIC ACID PLANTS

A feature of the Marina Salt Process is that a major portion of the plant is identical to that of a wet process phosphoric acid plant. Existing wet process plants can, therefore, be readily converted to manufacture Marina Salt by the addition of Chloride Conversion, Potassium Phosphate Separation, and Methanol Recovery sections. The cost of such conversion is of the order of 50% of the capital cost of a new phosphoric acid plant of equivalent P_2O_5 output.

11. REFERENCES

- (1) The Prilling of Compound Fertilisers.
F.E. Steenwinkel and J.W. Hoogendonk. Proceedings
Fert. Soc. No. 109, p. 5, 1969.
- (2) Phosphorus and Potassium Fertilisers : Their Forms
and Their Places in Agriculture.
G.W. Cooke. Proceedings Fert. Soc. No. 92, p. 21, 1966.

DISCUSSION

Mr. W.H. THOMPSON (Goulding Fertilisers Ltd., Ireland) :
In our paper we describe a process for the manufacture of fertiliser grade potassium phosphate which we believe is commercially viable.

The process involves the reaction of acid potassium sulphate slurry with phosphate rock in an agitated reactor similar to that in phosphoric acid manufacture. Calcium sulphate is precipitated. In order to obtain filterable gypsum, high acid levels are maintained in the reaction slurry. This acid later manifests itself in the filtrate liquor and causes considerable difficulty in the separation of the potassium phosphate by crystallisation.

Figure 1. In the first figure we show the solubility of KH_2PO_4 in H_3PO_4 solution. A rapid increase in solubility with increasing acid level is apparent up to a maximum which corresponds to a $\text{P}_2\text{O}_5:\text{K}_2\text{O}$ ratio of approximately 3:1. At acid concentrations less than this ratio KH_2PO_4 crystallises from solution, at acid concentrations higher than this a compound $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$ or $\text{KH}_5(\text{PO}_4)_2$ crystallises. The solubility data is shown in the more conventional triangular diagram in slide 2. The red graphs are for pure materials and the blue for impure materials as obtained in the process. Here can be noted the higher solubility for the impure materials possibly due to the presence of sulphuric acid and fluorine acids and the peak solubility is apparent particularly at the lower temperatures.

Figure 2. The filtrate liquors when evaporated approach the peak solubility and low yields of crystals by evaporation of the liquors are obtained. Because of high viscosity of the liquors and the presence of impurities, the product is of very small crystal size and is difficult to separate. In order to overcome the difficulty of separation we have used an organic water soluble liquid as a precipitant. A number of organic liquids can be used for this purpose. We have chosen methanol on the grounds of cost, availability and physical suitability. Potassium phosphate has a low solubility in methanol. This solubility data is shown for water methanol mixtures in slide 3.

Figure 3. It is virtually nil at high methanol concentrations and high yields are obtained by precipitation of solids from Marina Salt acid liquors as shown in slide 4.

Figure 4. If say, 150% of methanol on a volume basis is added to the filtrate liquor yields in the region

of 80/90% depending on the liquor s.g. can be obtained. The method of methanol addition and the control of the precipitation conditions is important in the recovery of filterable solids.

Figure 5. This shows how the particle size and distribution is affected by the precipitation conditions used. Controlled conditions were maintained in the upper graph, precipitation under uncontrolled conditions are shown in the lower graph, and a considerable difference in particle size and distribution is evident. Another point in favour of methanol as a precipitant is the ease of recovery from acid liquors.

Figure 6. This shows the well-known methanol water vapour liquid equilibrium diagram. We have found the system containing also phosphoric acid not to depart substantially from this diagram and only trace quantities of methanol remain in the bottoms liquor using a simple column.

One of the most promising outlets for this material is in liquid fertilisers. We have found it possible using Marina Salt to produce liquid fertiliser solutions in the laboratory of much higher analyses than those using conventional materials, particularly if the solutions are ammoniated.

Figure 7. A flow diagram of the process is shown in slide 7. Muriate of potash and sulphuric acid are reacted in a chloride converter with the evolution of hydrochloric acid which can be absorbed in water and sold as a marketable product or used in the process with a consequent economy in sulphuric acid. The acid sulphate slurry is reacted with the dicalcium phosphate-phosphate rock mixture from the filter or the phosphate rock can be fed directly to the sulphate reactor. The calcium sulphate is separated on the filter and the liquors are concentrated in the evaporator and sent to the precipitation vessel where the solids are precipitated by the addition of methanol. The solids are dried and sent to storage. The acid methanol solution is sent to a column for recovery of the methanol and the residual bottoms acid, which is free of methanol, is drawn off for manufacture of pure phosphates or returned to the process.

Figure 8. This shows the solubility of KH_2PO_4 in ammonia solutions. This is slightly different from that in the text, in which the $\text{P}_2\text{O}_5:\text{K}_2\text{O}$ is maintained at a level 1/1 on weight basis by addition of KCl. The slide shows the data for the pure compound in which the P:K ratio on a mole basis is 1/1. In both cases however, maximum solubility is shown for an N:P mole level of approximately 0.6.

Under Irish conditions the cost of production of one ton of Marina Salt is approximately equal to that of the equivalent tonnage of triple superphosphate and sulphate of potash on the factory floor. When freight, handling, bagging and storage are considered, the advantages of the high analysis in Marina Salt rapidly becomes of economic significance.

Appendix IV. This shows the factory floor costs of equivalent mixtures of Marina Salt and triple and sulphate of potash and Marina Salt and triple and muriate of potash.

The latter mixture is naturally considerably cheaper.

Appendix V. This shows a graphical representation of the costs of handling, bagging, storage and freight of Marina Salt and the equivalent systems. It becomes competitive with the equivalent mixture of sulphate of potash when total distribution costs are approximately \$ 2.5/short ton and with the equivalent muriate mixtures when the total distribution costs are \$ 20.5/short ton.

Mr. Y. BERQUIN (Azote et Produits Chimiques, France) : This paper considers a very topical problem for the fertiliser industry : how to obtain a better cost for concentrated fertilisers. Furthermore the process put to us allows a chlorine-free potash fertiliser to be obtained economically. These aims have been the subject of research for a long time and numerous solutions have already been proposed.

For example, I should like to quote what was done from 1929 by P.E.C., now A.P.C. after the merger with ONIA. As here, the potassium sulphate was, and still is, obtained by reaction of the sulphuric acid on potassium chloride. The hydrochloric acid by-product was used in the natural phosphate attack to obtain finally dicalcium phosphate. This was then mixed with potassium sulphate to obtain an NPK fertiliser without chlorine.

But the results are not as notable as those which have been put to us today, since the fertiliser obtained was both much less concentrated and its P_2O_5 citrate soluble, but water insoluble, and these factors have become indispensable due to market pressures.

P.E.C. has in fact studied a variant which might interest the authors. We carried out the transformations of potassium chloride into sulphate at ordinary temperatures by counter-current treatment of chloride with 50 to 60%

sulphuric acid. The apparatus used was an inclined worm of vulcanised steel. On the one hand there was obtained a drained salt with about 2% chlorine, and on the other hydrochloric acid of about 19°. At the time P.E.C. filed a patent on this process.

We never proceeded further. Although we had in mind the attack of raw phosphate with bisulphate we were stopped by different problems. These have also been resolved by the Goulding research people, who thus open up a new route which appears fruitful.

I should now like to ask for some complementary information :

1. Does the mixed sulphuric acid-potassium sulphate attack give gypsum with a filterability comparable to the best wet-process acid processes at present available ? What for example, is the productivity per m^2 of filter ? Do temperature influences play a role ? The potassium sulphate comes out very hot and its immediate use would allow a significant contribution of calories.
2. What are the yields from the P_2O_5 attack as a function of the acid consumption ?
3. Does the concentration of calcium sulphate, normally present in wet-process acid and coming from the filter in significant quantities, increase or decrease in the acid due to the presence of K ions ?
Also, how is its separation between solid and mother liquor effected after the addition of methanol ? Does it not obstruct the potassium sulphate/mother liquor separation ?
4. The phosphoric acid co-product contains practically no more fluorine after concentration and addition of methanol. What became of this ? In what form is it emitted ? Does it cause problems, and, if so, how are these remedied ?
5. What part of the P_2O_5 comes from the direct attack of the phosphate by $K_2SO_4 + H_2SO_4$ and what part comes from the re-attack of the dicalcium phosphate ? Does not this result in an increased consumption of sulphuric acid ? Perhaps this extra cost could be avoided by attacking the dicalcium in a second vessel with liquor coming from the natural phosphate attack, this still being strongly acid.

6. There is evidently a certain consumption of methanol, it being 9 kg per tonne of product for the Marina Salt according to the table in Appendix III. Is the consumption of methanol used for the preparation of phosphoric acid during reprecipitation, after concentration of the mother liquor, included in this figure ?

Is it necessary to correct Appendix VII ? And by how much ?

Mr. THOMPSON : The first question referred to the attack of the sulphuric acid-potassium sulphate slurry and does it give a good quality gypsum ? As in phosphoric acid technology, if you have a good process, the conditions are right in the reactor, the acidity is right and the temperature is right, then you get good gypsum. In our experience if these conditions are right we get as good gypsum as we get in our phosphoric acid plant.

We have not operated our plant at full load but we have been up to 4 tons P_2O_5 /day/m² i.e. about 20 tons gypsum/m²/day.

2. As far as P_2O_5 is concerned, the efficiency we work on for budget purposes is 92% recovery.

3. The next question referred to the amount of calcium sulphate in the filtrate liquor. We do not really know what effect the potassium phosphate has on the amount of calcium sulphate in the liquor. It seems from the figures we have available, that the calcium sulphate content, compared with wet-process phosphoric acid, is reduced by about 30%. The amount of calcium in the liquor after precipitation with methanol only amounts to a trace. All the calcium is precipitated and manifests itself in the Marina Salt, in quantities of between 0.2-0.3%. We have found no interference by calcium sulphate in separation when precipitating with methanol.

Mr. SOMERS :

4. In reply to Mr. BERQUIN's question on fluorine, Mr. THOMPSON has already corrected the fluorine content of the Marina Salt on page 7, section 8, to 1.5%, from 0.4%, and so you can see that some 55-65% of fluorine finds its way into Marina Salt. Approximately 25-35% goes out with the gypsum. The co-product phosphoric acid contains some 30 p.p.m fluorine. In reply to the last part of his question, fluorine has caused us no particular problems to date.

Mr. THOMPSON :

5. Concerning the fraction of the P_2O_5 which comes from the dicalcium phosphate and the fraction coming from the raw rock feed. The only reason we make dicalcium phosphate in this process is to get rid of the HCl and by reacting half the phosphate rock required in the process with diaqueous HCl, you get a solution of monocalcium phosphate and calcium chloride. In order to obtain that phosphate back as a solid, we have to revert it with calcium carbonate. The answer, in short, is half, if it is necessary to use HCl, i.e. if you cannot sell it.

6. Concerning the consumption of methanol and Appendix III where it says that there is a 9 kg loss of methanol/ton. This is an estimated figure on our part. We feel it is too high and it can be easily improved. Then he asks if this is a total loss. It is a total loss. Its omission from Appendix VII is because labour, salaries, process materials and overheads are all lumped together in those two columns. Methanol was looked upon as a process material. It is not necessary to correct the table.

Mr. DRECHSEL (Duval, U.S.A.) : The Duval Corp. is a wholly owned subsidiary of Pennzoil United Inc., Houston, Texas. On September 2nd 1970, last week, my firm announced a somewhat related process directed primarily toward the manufacture of potassium polyphosphates with controlled water solubility characteristics. I have two questions which perhaps are already, in view of the earlier questions, answered.

1. Is the exercise to produce monocalcium phosphate, TSP, thence to dicalcium phosphate with limestone, really necessary or is this merely to accommodate HCl utilisation ?
2. Since the Marina Salt specifications on page 16-17 section 8 shows no sulphate ion content, may we assume that the calcium to sulphate ratio is stoichiometrically in balance and that excess hydrogen ion is supplied by phosphoric acid ?

Mr. SOMERS :

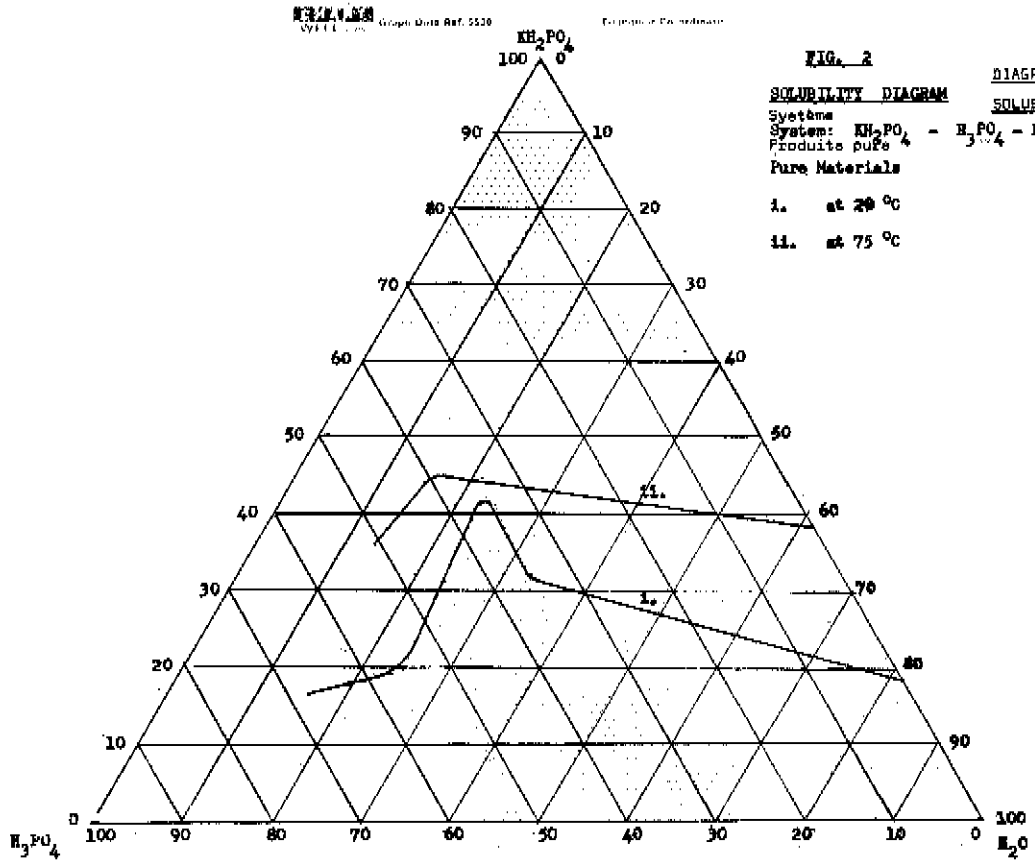
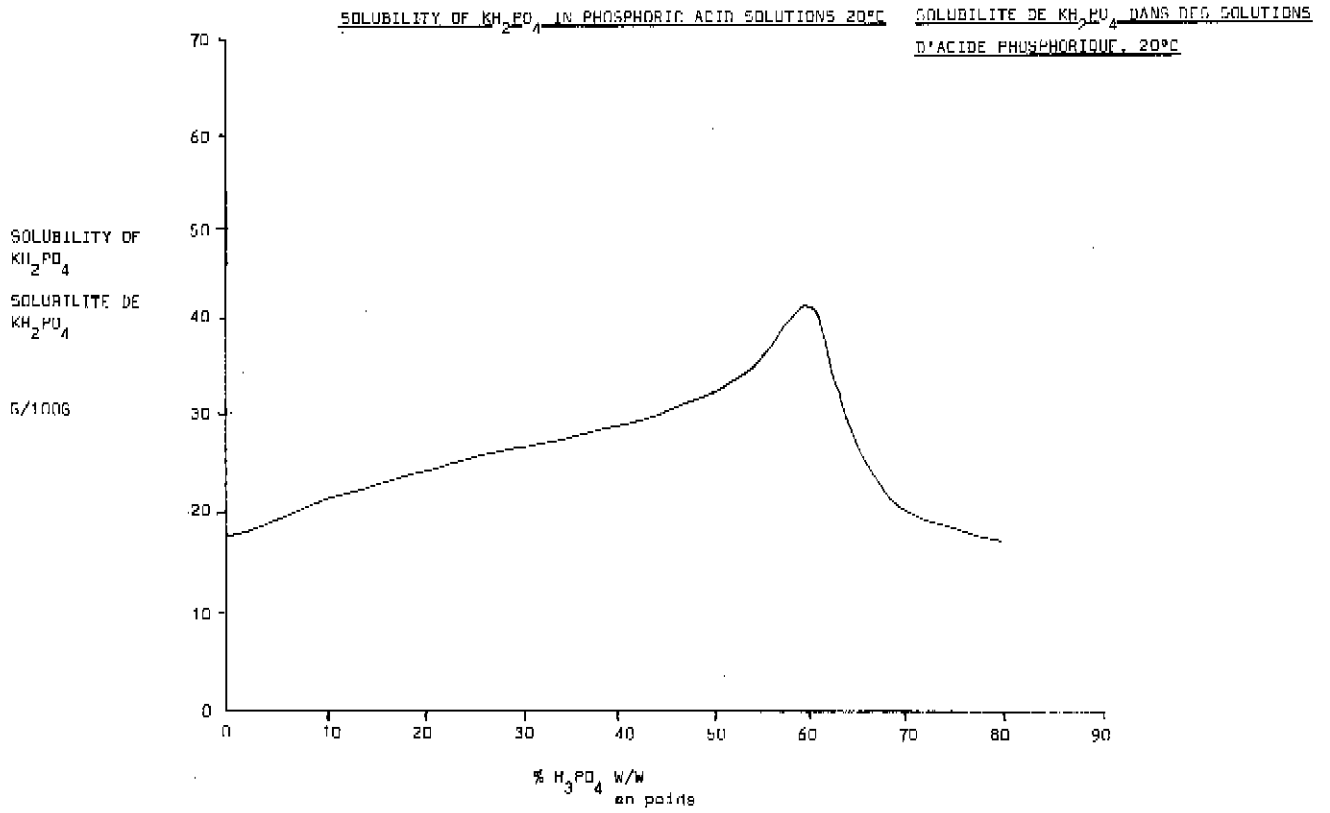
1. We merely use the HCl when we cannot sell it. It is more desirable to be able to sell the HCl and not to bother with this part of the process.
2. Mr. THOMPSON has already stated that there is, in fact, an SO_4 content in Marina Salt of the order of 3.1%.

Mr. BELPAIRE (Asybel, Belgium) : Can you give more detail of the losses of K_2O and citrate soluble, citrate insoluble and water soluble P_2O_5 in the gypsum in the case where raw phosphate only is used in the reaction ? How do you explain the total solubility in water of P_2O_5 and K_2O when the Marina Salt included more than 1% iron and aluminium ?

Mr. THOMPSON : Concerning the aluminium and iron in Marina Salt and P_2O_5 solubility, you must remember that there is a free acid content of 5% P_2O_5 . We are not talking in terms of neutral or alkaline solution.

Fig. 1

PTF/70/16



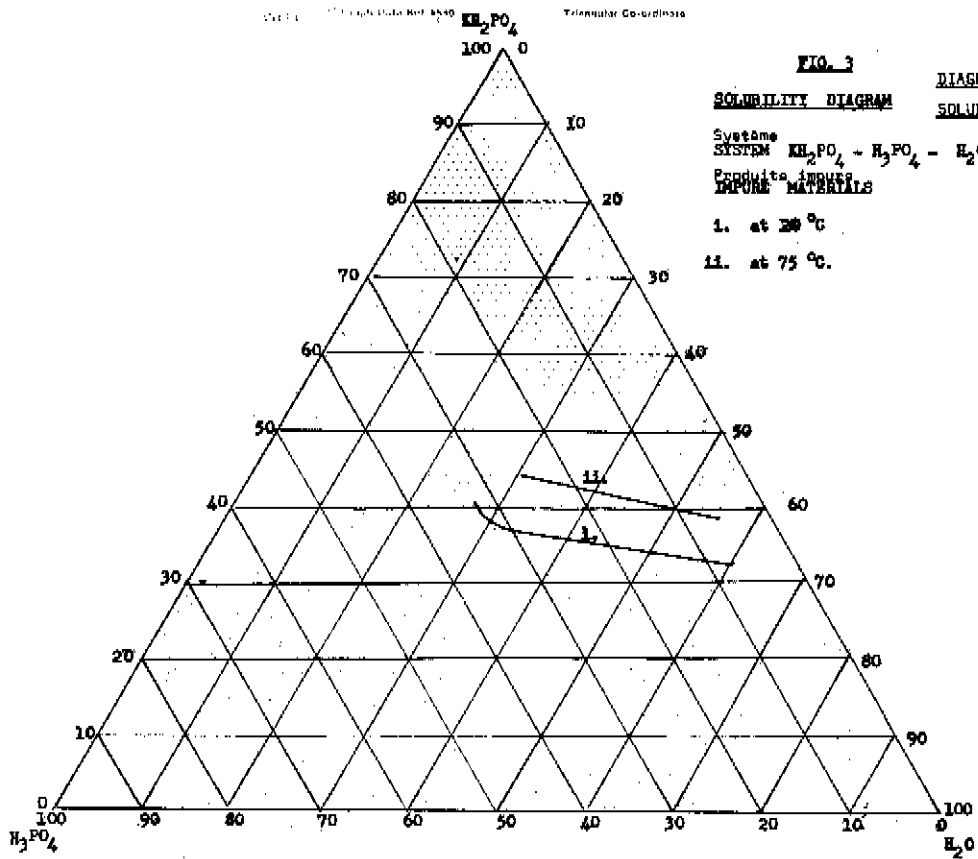
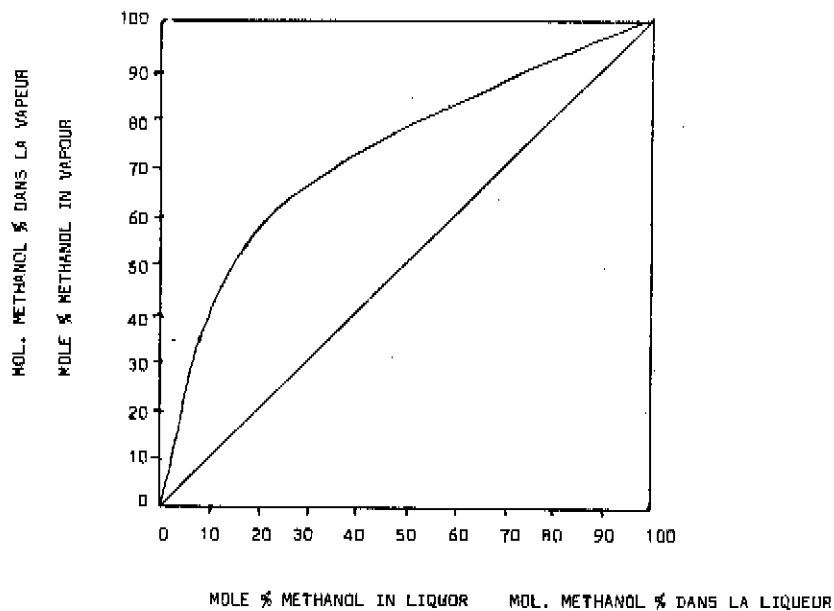


Fig. 4

PTF/70/16

METHANOL - WATER - VAPEUR - LIQUID EQUILIBRIUM

EQUILIBRE METHANOL - EAU, VAPEUR - LIQUIDE



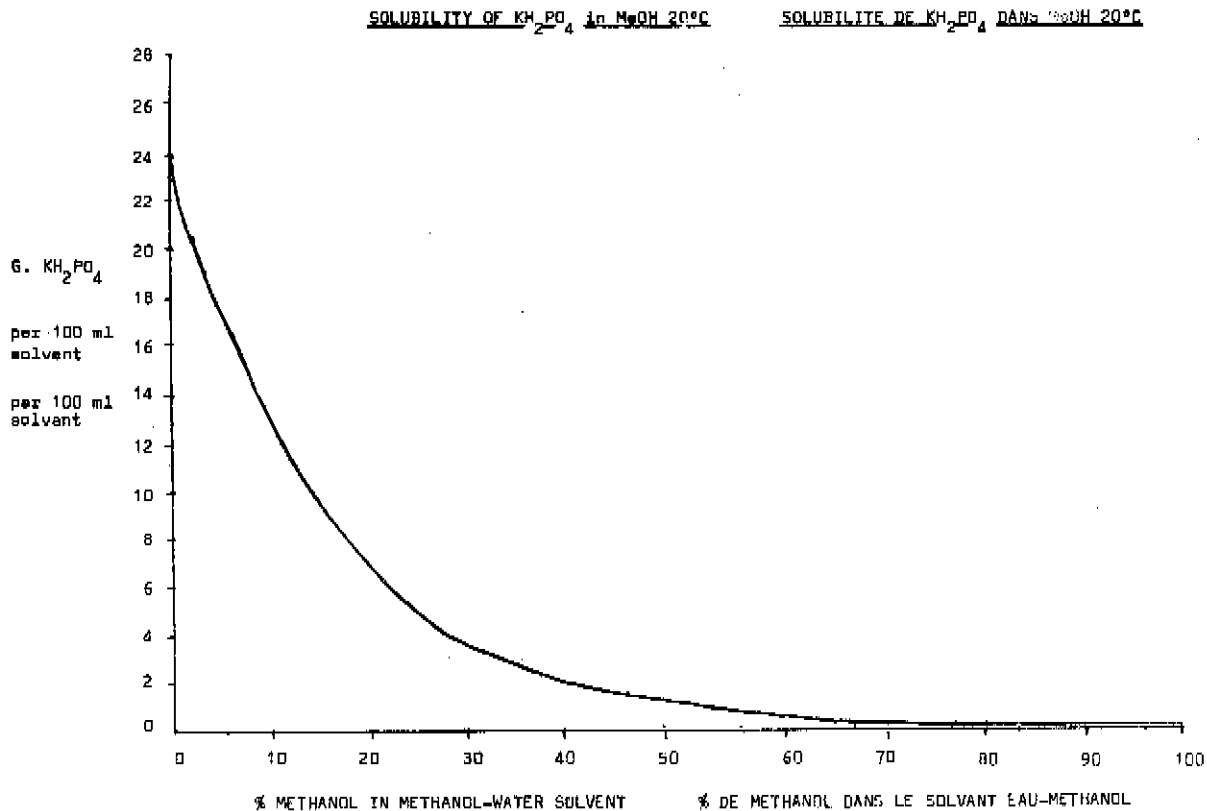


Fig. 6

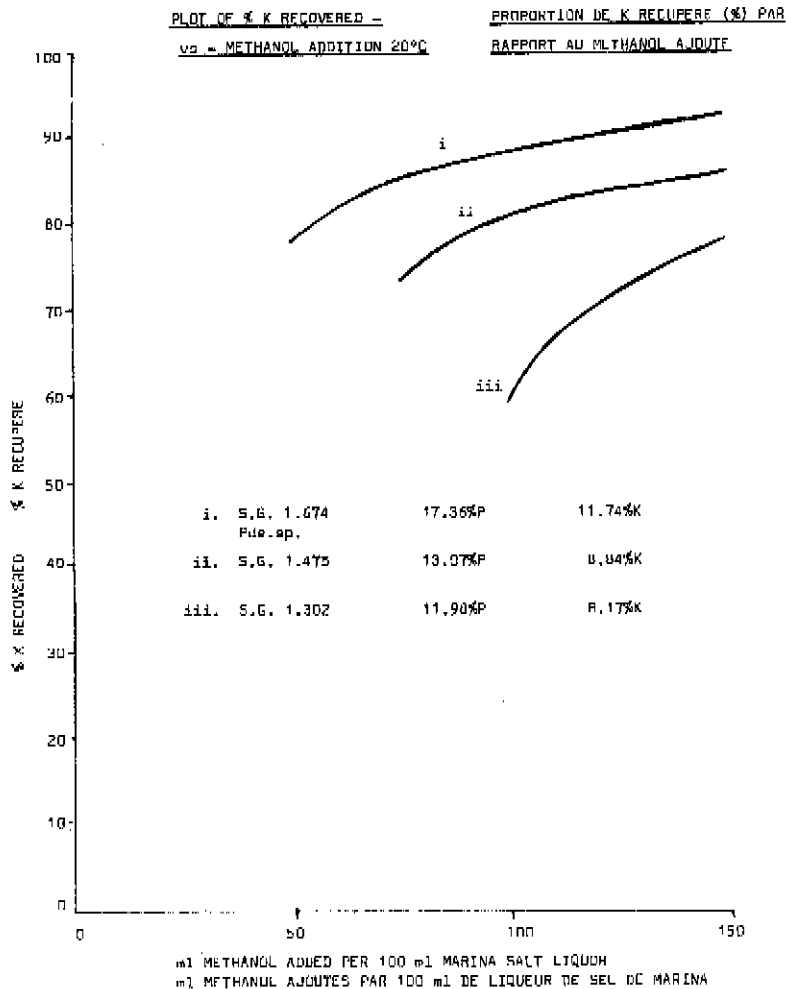


Fig. 7. DISTRIBUTION DES DIMENSIONS DE PARTICULES PARTICLE SIZE DISTRIBUTION OF
DE SEL DE MARINA D'APRES DES TESTS DE MARINA SALT FROM LABORATORY
LABORATOIRE TESTS

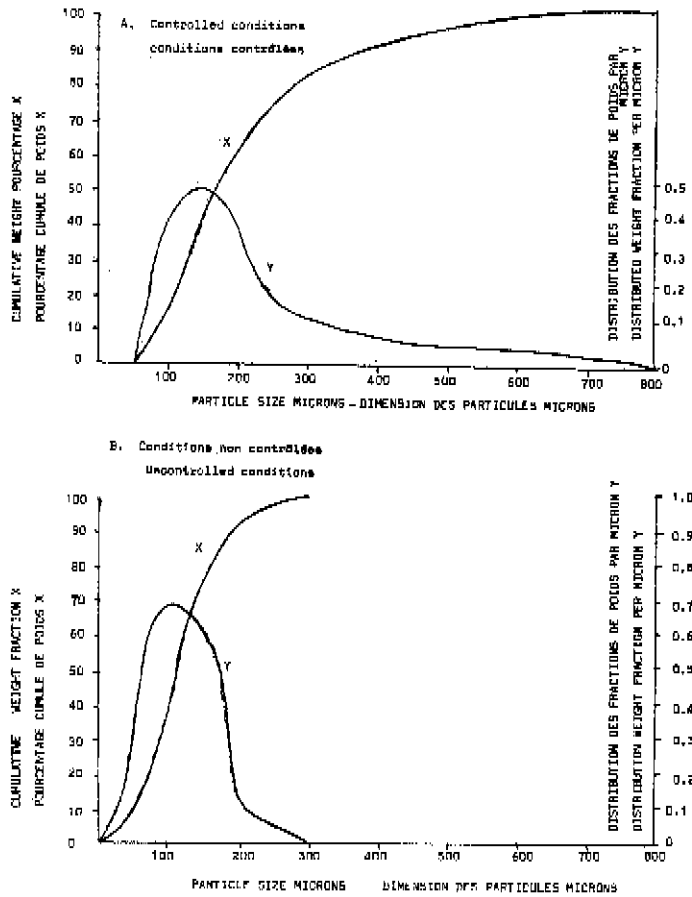
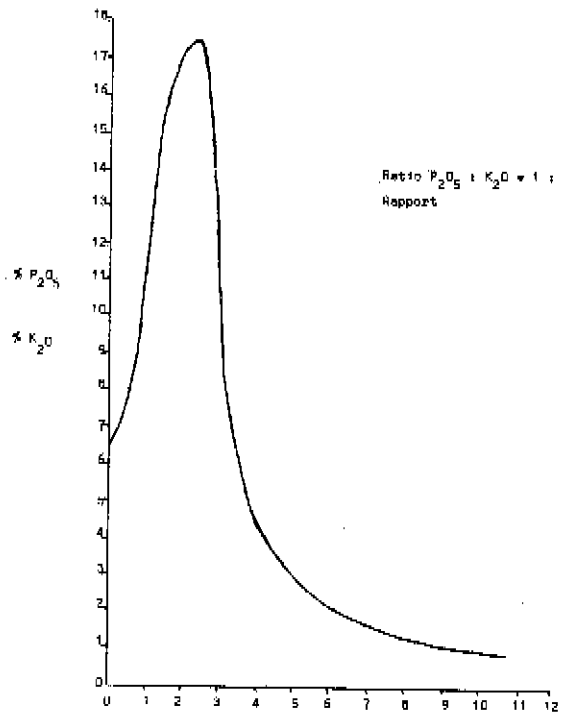
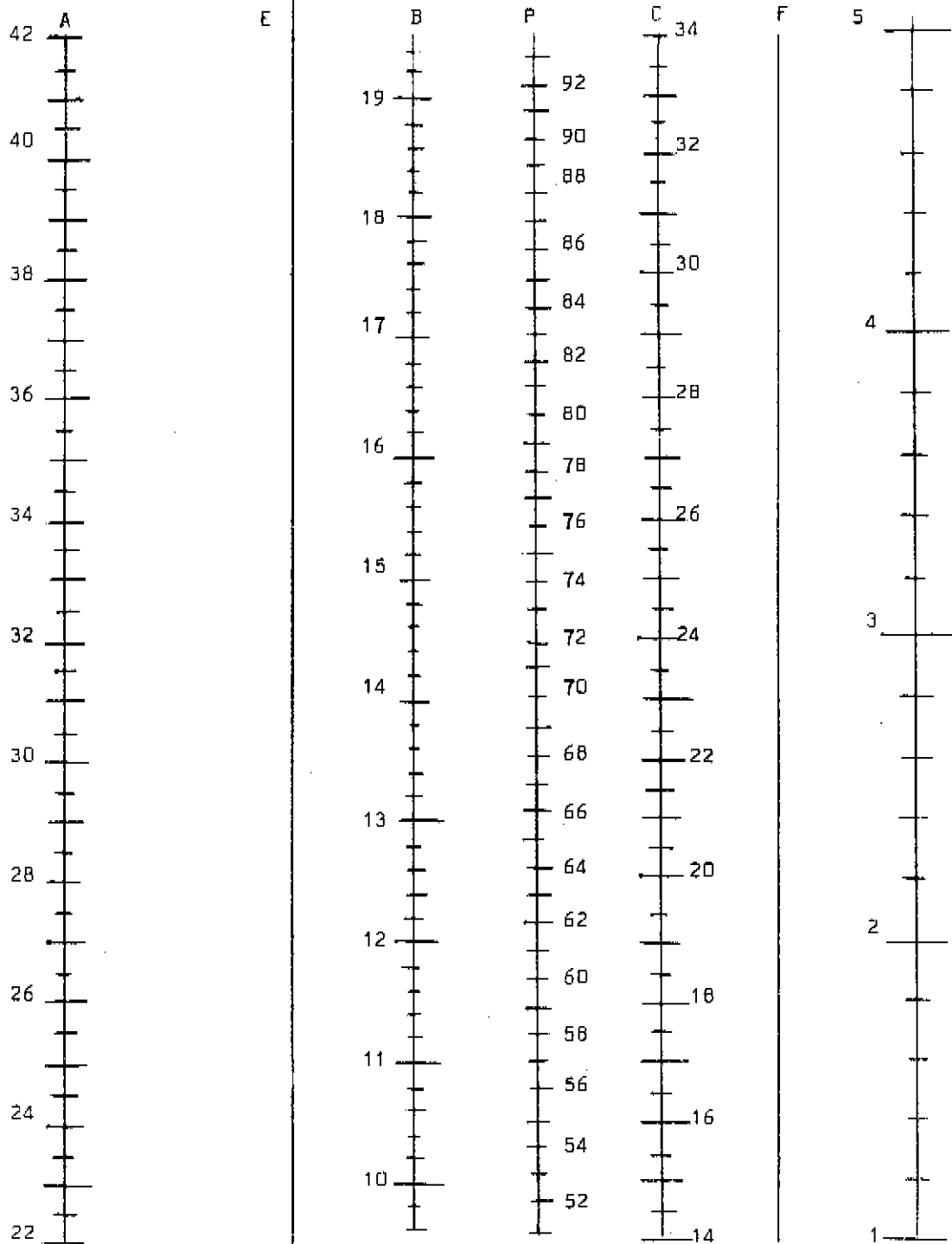


Fig. 8. SOLUBILITY OF AMMONIATED MARINA SALT IN WATER 20°C
SOLUBILITE DANS L'EAU DU SEL DE MARINA AMMONIÉ 20°C



ANNEXE I - COUT DU SEL DE MARINA PAR TONNE

APPENDIX 1- MARINA SALT COST PER TON



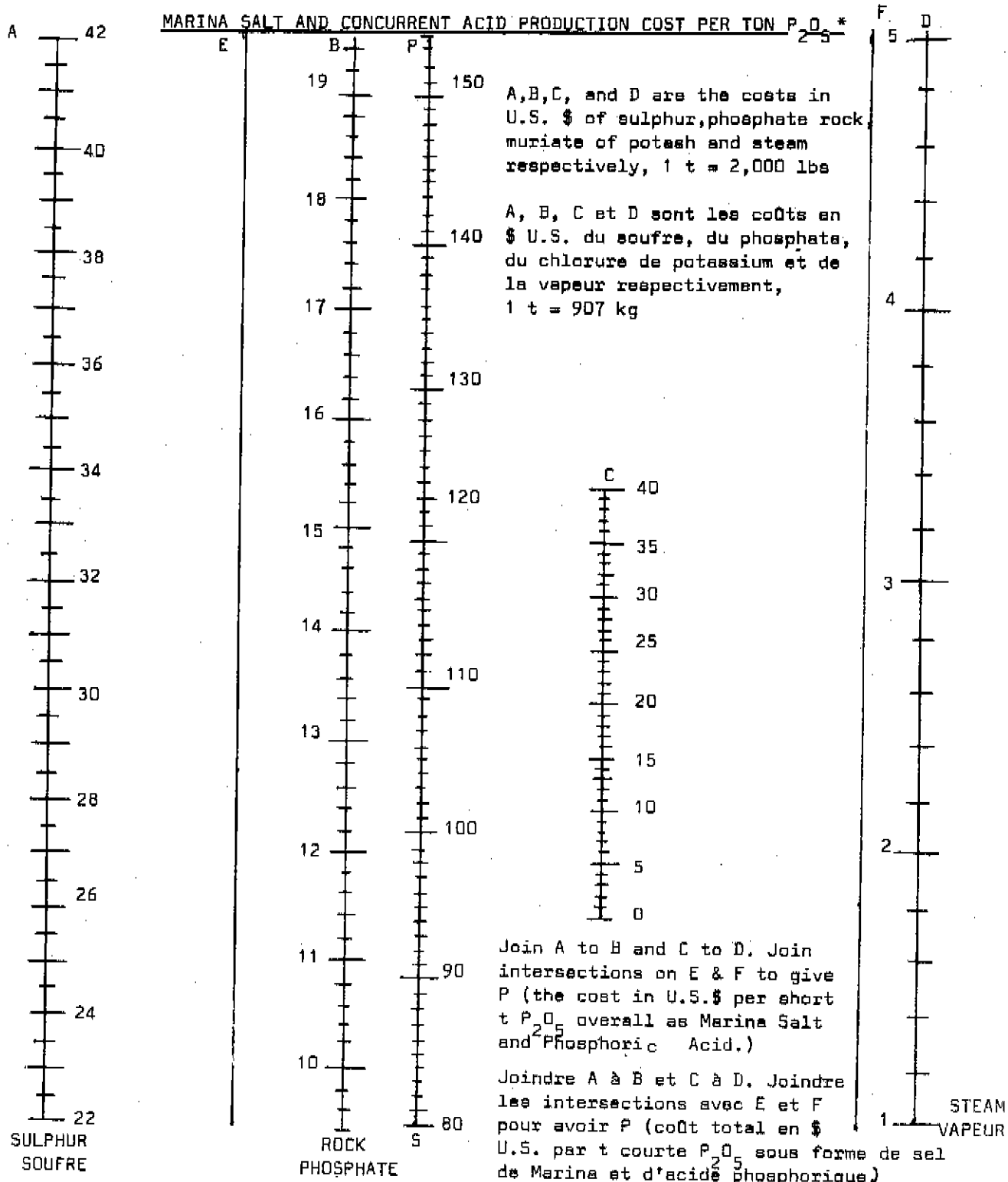
Cost of (\$/short t) - coût de (\$/t courte)

- A = Sulphur - soufre
- B = Phosphate Rock - phosphate
- C = Potash (50%K) - Potasse (50% K)
- D = Steam (30 p.s.i.g.) - Vapeur (2kg/cm²)
- P = 1 t of Marina salt - 1 t de sel Marina

Join A to B and C to D and join intersections on E and F to give P.

Joindre A à B et C à D, et joindre les intersections avec E et F pour avoir P.

1 ton = 2,000 lbs. = 907 kg



* For a plant producing 50,000 t P_2O_5 as phosphoric acid (50% P_2O_5) and 50,000 t P_2O_5 as Marina Salt, the K in Marina Salt is allowed for at the price of K in muriate of potash
The costs refer to the overall production of P_2O_5 present in the Marina Salt and in the acid concurrently produced.

Pour une usine produisant 50,000 t P_2O_5 d'acide phosphorique, (50% P_2O_5) et 50,000 t P_2O_5 sel de Marina, le prix de K dans le sel de Marina est le même que celui de K du chlorure de potassium
Les coûts appartiennent à la production globale de P_2O_5 sous forme de sel de Marina et d'acide phosphorique produits simultanément.

Appendix III

MANUFACTURING COST COMPARISON for MARINA SALT AND TRIPLE SUPER

	126,000 tons/yr MARINA SALT (58,000 tons P ₂ O ₅)			132,000 tons/yr TRIPLE S/P (58,000 tons P ₂ O ₅)	
	Unit Cost \$/ton	Tons/ ton product	Cost/ ton product \$	Tons/ ton product	Cost/ ton product \$
Phos. rock (unground)	15.0	1.488	22.320	1.051	15.765
Phos. rock (ground)	16.07	-	-	0.440	7.071
Sulphuric Acid	17.14	1.158	19.851	0.904	15.497
Muriate of Potash	30.0	0.529	15.870	-	-
Limestone	2.14	0.200	0.429	-	-
			<u>58.470</u>		<u>38.333</u>
Steam	2.14	2.455	5.261	0.804	1.723
Methanol	96.43	0.009	0.868	-	-
Oil	0.075	-	0.482	-	-
	(/U.S. gal)				
Electricity	0.015	-	0.844	-	0.482
	(/kWh)				
			<u>65.925</u>		<u>40.538</u>
Labour			0.549		0.613
Salaries			0.285		0.272
Overheads (200% Labour)			1.095		1.224
Licence Fee			0.536		-
Process Material			0.285		0.454
Maintenance, Ins. etc. at 8% of capital			2.897		1.817
Depreciation at 10% of capital			3.619		2.271
Interest at 10% of capital			3.619		2.271
			<u>78.810</u>		<u>49.46</u>
			=====		=====

1 Ton = 2,000 lbs.

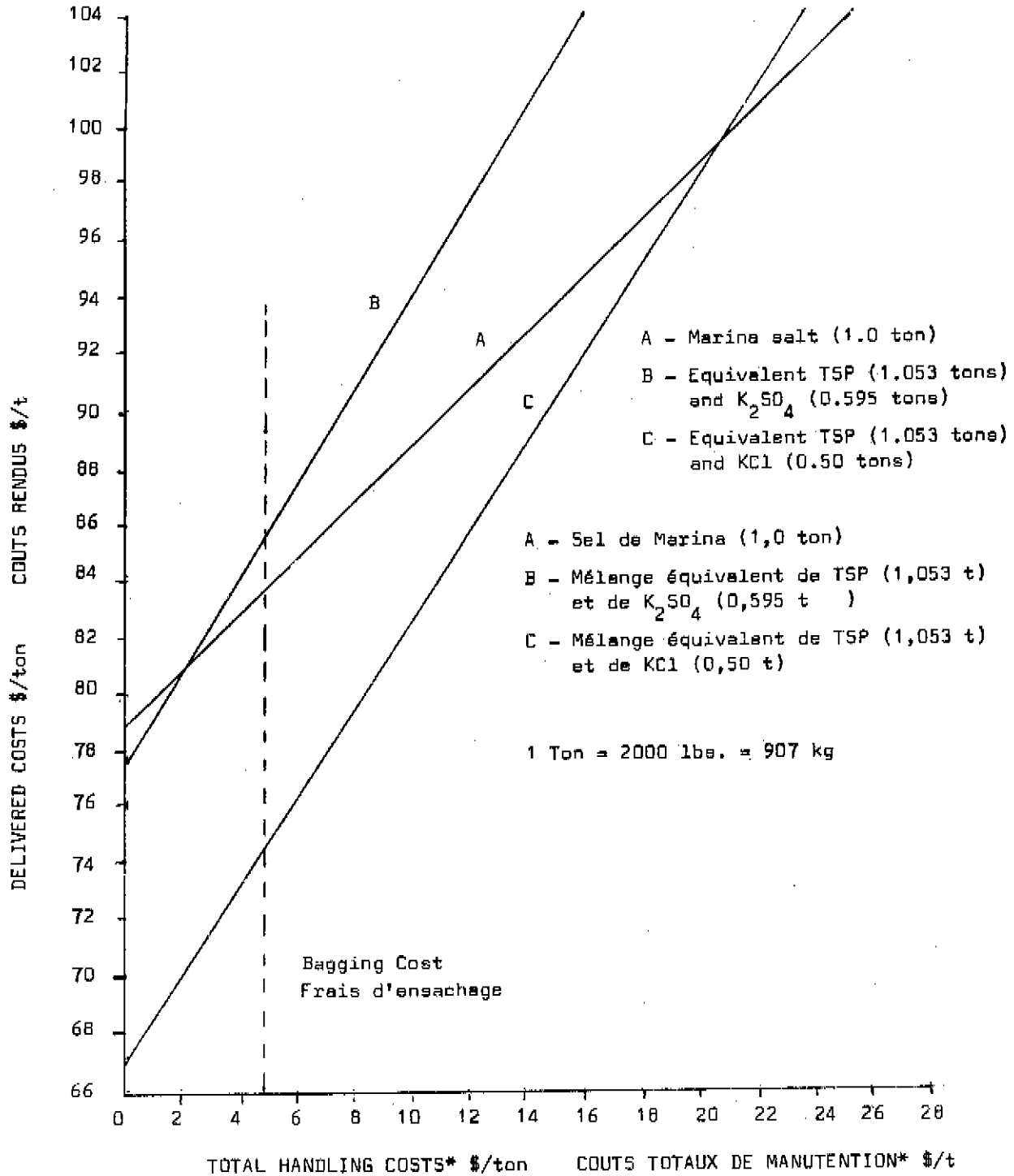
Appendix IV

COMPARATIVE FACTORY FLOOR COSTS

1 Ton Marina Salt 20% w.s.P, 25% K (46% w.s. P ₂ O ₅ , 30% K ₂ O)	\$ 78.8
Equivalent mix with potassium sulphate and Triple Super.	
1.052 tons T.S.P. 19% w.s.P (43.5% w.s. P ₂ O ₅) at \$ 49.5/ton	\$ 52.07
<u>0.593 tons K₂SO₄ 42% K, (50% K₂O)</u> at \$ 42.86/ton	<u>\$ 25.50</u>
1.648 tons mixture 12.1% P, 15.2% K (27.7% P ₂ O ₅ , 18.3% K ₂ O)	\$ 77.57
Equivalent mix with muriate of potash and Triple Super.	
1.052 tons T.S.P. 19% P at \$ 49.5/ton	\$ 52.07
<u>0.500 tons KCl 50% K (60% K₂O) at \$ 30.0</u>	<u>\$ 15.00</u>
1.553 tons mixture 12.9% P, 16.1% K (29.5% P ₂ O ₅ , 19.4% K ₂ O)	\$ 67.07

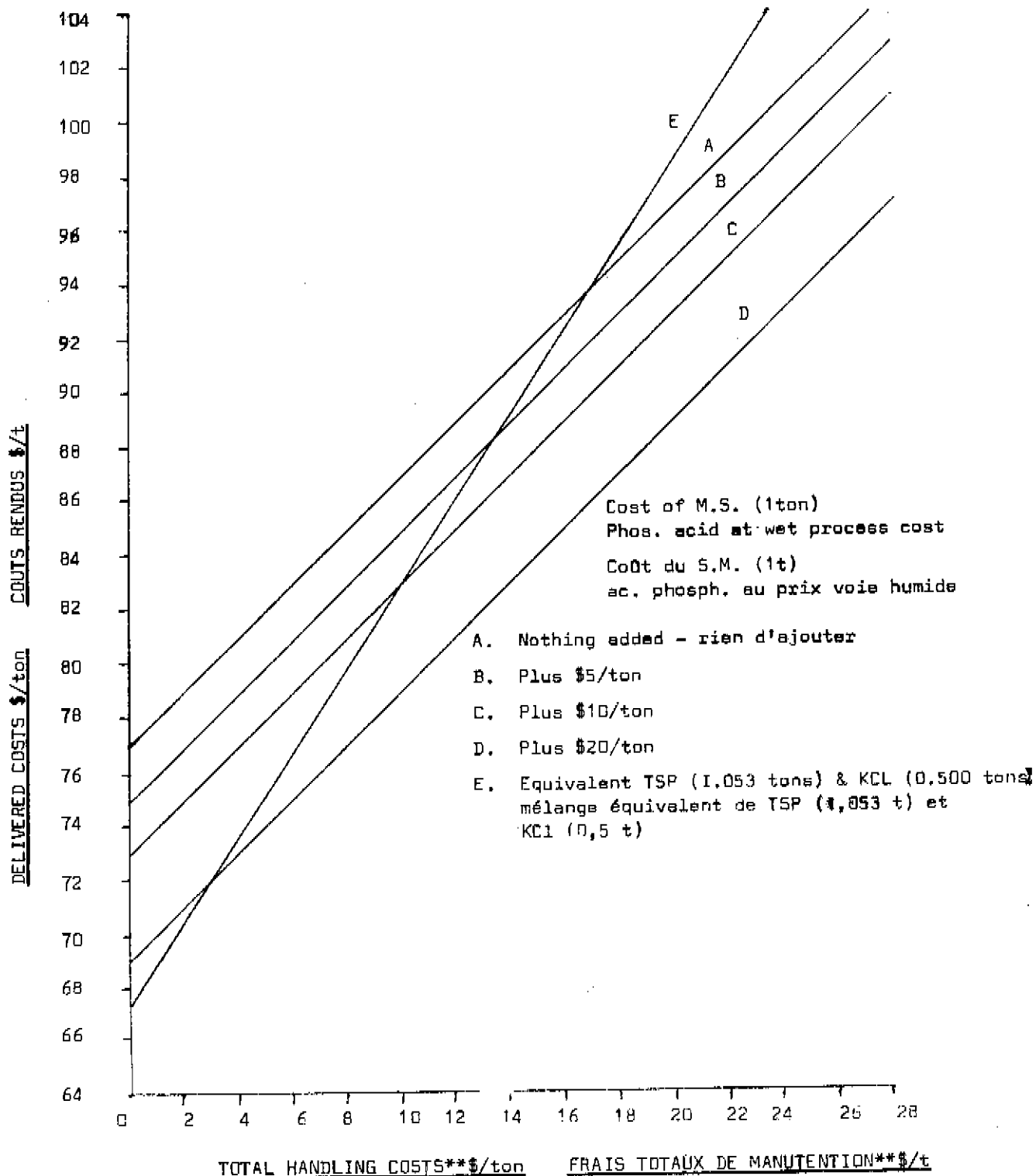
Reference to Appendix V shows the total delivered cost of the sulphate mixture will equal that of Marina Salt if total handling costs, including freight, storage, and bagging are \$ 2.0 per ton handled. Bagging costs alone will generally be greater than this.

The total delivered cost of the muriate mixture will be equal to that of Marina Salt when total distribution costs including bagging total \$ 20.50 per ton.



* Handling costs include bagging, handling, storage and freight.

* Les frais de manutention comprennent l'ensachage, les manipulations et les frets.

DELIVERED COSTS* COÛTS RENDUS*

* For a plant producing 58,000 tons P_2O_5 as Marine salt & 58,000 tons P_2O_5 as purified phosphoric acid concurrently

** Handling costs include bagging, handling storage and freight

FRAIS TOTAUX DE MANUTENTION**\$/t

* Pour un atelier produisant 58 000 t courtes P_2O_5 sous forme de sel de Marine et 58 000 t.C. sous forme d'acide phosphorique simultanément.

** Y compris ensachage, manipulation, stockage et fret.

Appendix VII

Manufacturing cost comparison for soluble P₂O₅ on a phosphoric acid plant and on a Marina Salt/Phosphoric Acid Plant.

	<u>Phosphoric Acid</u> (tons P ₂ O ₅)	<u>Marina Salt/Phosphoric Acid</u> (tons P ₂ O ₅)
Annual Plant Capacity	116,000	58,000 as Marina Salt 58,000 as Acid
Capital cost of plant	\$ 4.21 m.	\$ 5.50 m.

Manufacturing Cost

	<u>Phosphoric Acid</u>			<u>Marina Salt/Phosphoric Acid</u>	
	Unit Cost \$ ton	Tons/ton	Cost/ton \$	Tons/ton	Cost/ton
Phosphate	15	3.284	49.260	3.281	49.215
Sulphuric Acid	17.14	2.825	48.429	2.779	47.640
Muriate	30.0			0.580	17.400
			97.689		114.255
Steam	2.14		4.286		9.665
Electricity	0.015/kWh		1.350		1.690
Oil	20.00				.480
Labour, Salaries, Process Materials					
Overheads			4.121		5.143
Maintenance, Ins. etc. (8% Capital)			2.891		3.793
Depreciation (10% Capital)			3.614		4.741
Interest (10% Capital)			3.614		4.741
					144.508
Credit for K at cost					16.530
Cost/ton P ₂ O ₅			\$ 117.575 =====		\$ 127.978 =====

1 ton = 2,000 lbs.

SCHEMATIC FLOW SHEET

