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A REMEDY FOR THE WORLD SHORTAGE OF SULPHUR

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S u m m a r y

This paper discusses the French experience during and since World War II in the field of economising Sulphuric Acid for Fertiliser Production.

I. EVOLUTION OF WORLD MARKET FOR SULPHUR.

The average consumption of sulphur throughout the world for the period 1935 - 1939 was about 8 million long tons, of which 4,350,000 tons from pyrites, 2,175,000 from American crude sulphur and the balance from other sources. In 1950 the world consumed about 11,500,000 tons of sulphur, i.e., an increase of some 40% in ten years.

It can be assumed that some 75% of the world consumption of sulphur in all forms is for the production of sulphuric acid and that some 35 to 40% of the world sulphur consumption is in fact used to manufacture superphosphate and sulphate of ammonia. Fertiliser production continues to expand and the following estimate for the U.S.A. is given:

(in thousand tons)

	: Average : consumption : 1935 - 39 :	: Estimated : consumption : 1949-50 :	: Estimated : require- : ments : 1950-51 :	: Anticipated : requirements : 1959-60 :
Nitrogen (N):	371	: 1,030	: 1,350	: 2,200
Soluble Phos- phoric acid (P ₂ O ₅)	719	: 2,060	: 2,300	: 3,600
	:	:	:	:

In France the "Plan" authorities stated in 1947 that it was expected that the consumption of soluble phosphoric acid from raw phosphates would rise from 191,800 tons in 1946 - 47 to 560,000 tons at the end of the "Plan".

It would seem that for the O.E.C.E. countries and the U.S.A. alone sulphur requirements are increasing at the rate of a million tons a year.

CONSUMPTION OF SULPHUR IN ALL FORMS
(in thousand metric tons of sulphur contained)

Period	Grade Sulphur	Pyrites	Blancs	By-pro-duct & various	Anhydrite and gypsum	Total	Average over 3 years
17 O.E.C.E. countries.	1948-49 : 916 1949-50 : 1,025 1950-51 : 1,160	1,882 2,015 2,358	272 313 349	142 148 166	221 229 236	3,433 3,730 4,259	3,810
U.S.A.	1949 : 3,477 1950 : 4,030 1951 : 4,310	442 512 510	- - -	266 306 438	- - -	4,185 4,898 5,258	4,780

World consumption increased, in round figures, from 7,500,000 to 9,500,000 tons in three years, i.e., by 1,000,000 tons in the space of one year, divided approximately in the proportion of 11 to 8 between the U.S.A. and the 17 O.E.C.E. countries.

The sulphur shortage is already acute, and it does not seem possible that the increasing needs can be met at the current price level, and it is imperative to study means of economising sulphuric acid in the production of fertilisers.

French experience in 1940-45 can be studied with advantage since, during that period, her shortage was even more acute than the present world shortage.

II. THE FRENCH SHORTAGE OF SULPHUR DURING THE 1939-45 WAR.

Sulphur imports fell to practically nothing during the war years and sulphuric acid was produced solely from French pyrites and existing stocks. The production figures were as follows:

1938	1941	1942	1943	1944
424,000	152,000	122,000	114,000	51,000

The entire chemical industry was affected and, especially so, the production of superphosphate and sulphate of ammonia; expressed in tons of N, production of sulphate of ammonia was:

1938-39	1939-40	1940-41	1941-42	1942-43	1943-44	1944-45
83,149	65,564	37,120	25,597	22,032	22,566	11,144

and, expressed in tons of P_2O_5 , production of superphosphate was:

1938	1939	1940	1941	1942	1943	1944
175,000	177,000	69,000	40,500	7,800	3,500	nothing

It can be said that in 1944, the fifth war year, these industries were dead.

III. FRENCH EFFORT SINCE THE START OF THE 1939-45 WAR.

Every effort was made to economise acid and to develop the relatively poor national resources of sulphur and pyrites and to use other raw materials, and what were the results?

A) EFFORTS TO INCREASE THE PRODUCTION OF SULPHUR.

It did not prove practicable substantially to increase the 1939 figure of pyrites extraction (86,000 tons) and indeed the average for the war years was only about 87,000 tons (tons of sulphur).

Blonde deposits are limited and extraction could only be increased from 40 tons of sulphur in 1938 to 3,500 tons in 1947, and finally, 7,500 tons in 1950.

Native sulphur is almost non-existent, but the Narbonne deposit was exploited, and production from this source is only expected to reach a level of some 20,000 tons of sulphur for the year 1951-52.

Recovery of gases only brings in some 2,500 tons per annum for 1949 and 1950.

Gypsum only produced some 5,000 tons of sulphur in 1949 and 10,000 tons in 1950. However, gypsum can also be used for the direct production of sulphate of ammonia and replaced some 17,000 tons of sulphur per annum in 1938 and as much as 26,000 tons in 1949.

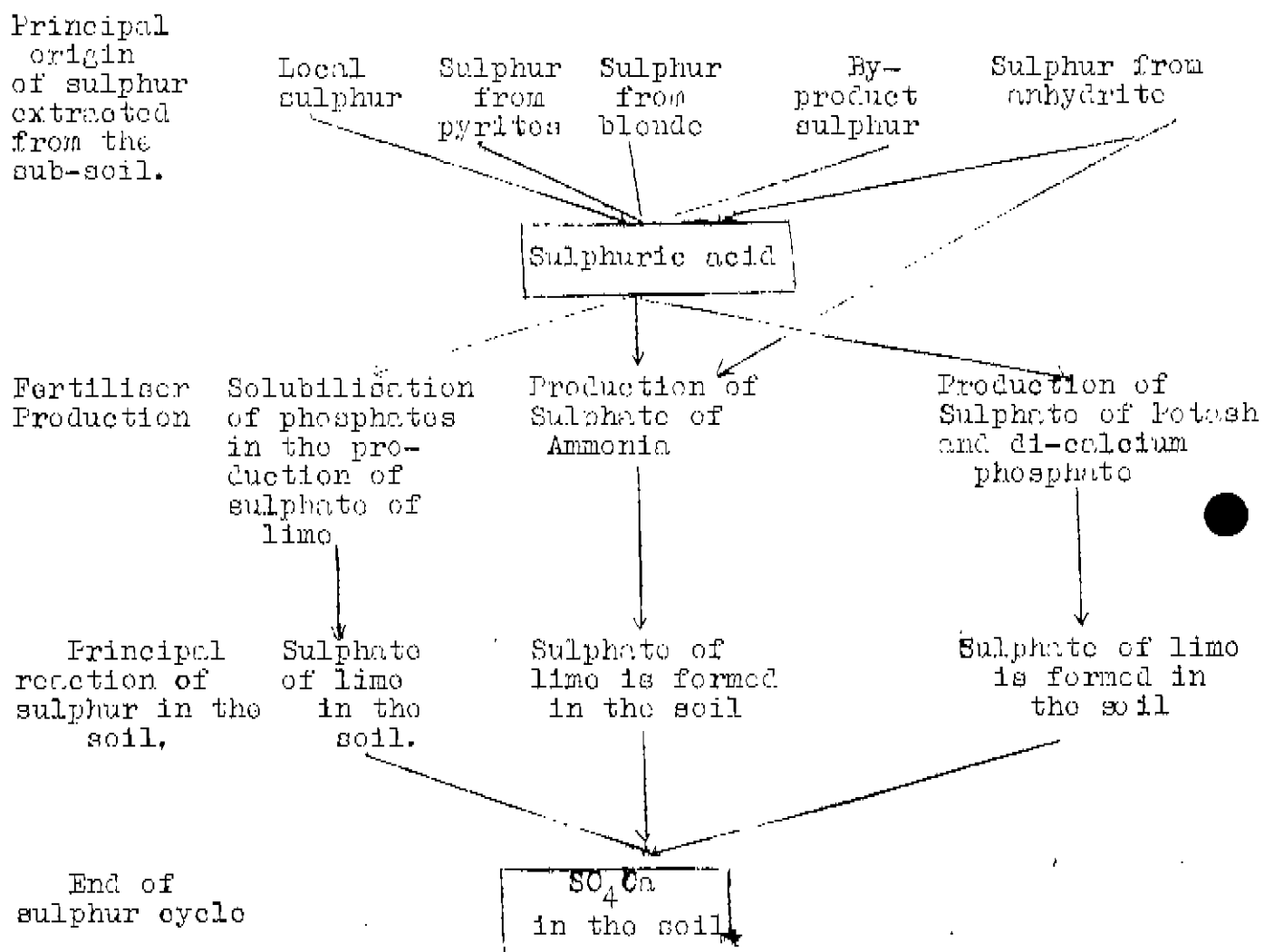
French requirements of sulphur in all forms amount to some 750,000 tons per annum to-day.

B) ECONOMIES OF SULPHUR IN FERTILISER PRODUCTION.

In 1938, out of a total French consumption of 572,000 tons, 308,000 tons of sulphur were used to produce fertilisers, of which 190,000 tons for phosphatic fertilisers, 90,000 tons for sulphate

of ammonia, 7,000 tons for sulphate of potash and 21,000 tons for sulphate of ammonia direct from gypsum.

The following plan shows what happens to sulphur in fertilisers:



If applied to Germany, the direct treatment of magnesium sulphate with muriate of potash for the production of sulphate of potash must be added to this plan.

C) THE PART PLAYED BY SULPHUR IN THIS CIRCUIT.

When producing superphosphate or triple super, the sulphuric acid has the effect of fixing as sulphate of lime that portion of lime, contained in the raw phosphate, which exceeds one molecule per molecule of P_2O_5 .

Thus the carbonate of lime contained in the rock and $2/3$ of the lime, which is in the form of tri-calcium phosphate, are fixed as sulphate and there remains the monocalcium phosphate, the P_2O_5 content of which is soluble in water. This involves in France the consumption of 2.3 tons of 100% sulphuric acid per ton of solubilised P_2O_5 , i.e., approximately 0.85 tons of sulphur.

In the production of sulphate of ammonia the technical role of the sulphuric acid is simply to support the nitrogen. This involves 3.5 tons of 100% sulphuric acid to 1 ton of N., i.e., 1.35 tons of sulphur.

D) DICALCIUM PHOSPHATE.

Finally, in producing sulphate of potash, the sulphuric acid frees hydrochloric acid, which can be used to produce di-calcium phosphate. Thus, in this case, the sulphuric acid has in fact a double use. This product has been manufactured in France and Belgium for some 20 years and gives rise to some 30,000 tons per annum of P_2O_5 in the form of precipitated di-calcium phosphate, soluble in basic citrate of ammonia. This must be considered an efficient fertiliser and this fact is a fundamental basis for considering the problem of sulphur economy.

E) RECENT EVOLUTION IN THE USE OF FERTILISERS.

The theoretical objects of producing a soluble P_2O_5 fertiliser and of producing nitrogen in a form requiring less sulphuric acid than sulphate of ammonia could not be attained without a natural evolution in the technique of using fertilisers and of the requirements of agriculture. The following figures show the evolution of nitrogen consumption in France.

FRENCH CONSUMPTION OF NITROGEN (in thousand tons)

	Sulphate of ammonia	Ammonium nitrates	Sodium nitrate, nitrate of lime & others	Complex fertilisers	Total
1938-39:	83	32	103	-	218
1939-40:	66	35	76	-	177
.....					
1948-49:	57	100	68	23	248
1949-50:	61	92	68	24	245

It will be seen that a reduction in the use of sulphuric acid has been obtained, whilst the use of nitrogenous fertilisers has increased. As regards soluble P_2O_5 , the tendency towards compound fertilisers helps to make it possible to produce additional quantities of fertilisers, requiring less sulphuric acid.

Expressed in terms of $N-P_2O_5-K_2O$ and in thousands of tons, the production of compound fertilisers developed before the war as follows:

Yearly average from 1928-29 to 1935-36	1936-37	1937-38	1938-39
72	198	242	292
10 %	26 %	28 %	31 %

The plan, drawn up in 1947 and 1948, by the Compound Fertiliser Sub-Commission of the "Plan" foresees that 56% of French fertilisers will ultimately be in the form of compounds. In France compounds, produced by combination rather than by mixing of fertilisers, are also called "Complex Fertilisers".

Since 1938/39 the proportion of N used in "Complex Fertilisers" has steadily increased and in 1948/49 accounts for about 12.2% of the total N, consumed in France. The quantities of P₂O₅ and K₂O, consumed in the form of "Complex Fertilisers", have followed the same progression. This progress is however just the start of a new industry, now being set up, the equipping of which was delayed by the war until 1948.

DEVELOPMENTS PROVIDED FOR IN THE PLAN:

The development of the production of compounds has been mentioned above. The following table shows the transformation which is to take place in the type of nitrogenous fertilisers to be used.

PRODUCTION CAPACITY OF NITROGENOUS FERTILISER WORKS

	Sulphate of ammonia	Ammonium nitrates	Complex Fertilisers	Sodium nitrate & nitrate of lime	Various	Total
Capacity 1947	28 %	32.5 %	11.5 %	24.5 %	3.5 %	100 %
Anticipated capacity for achievement of "Plan"	21.5%	32.5 %	28.5 %	13.8 %	3.7 %	100.0%
Variation of percentages	-23 %	0 %	+150 %	-43.5 %	0 %	

The phosphatic fertiliser industry is expected to be transformed in accordance with the following table:

PHOSPHATIC FERTILISERS (in percentage, not including Basic Slag and ground phosphates)

	Superphosphate and Triple Super	Precipitated Di-calcium Phosphate	Complex Fertilisers	Total
Consumption 1946/47	91 %	4.5 %	4.5 %	100 %
Anticipated manufacture for achievement of "Plan"	48 %	2 %	(Capacity) 50 %	100 %

It can be seen that, in spite of the stagnant period of the war years, there is a continual progress towards the use of compound fertilisers, and that the proportion of complex fertilisers is rapidly increasing since the end of the war.

IV. HOW TECHNICAL EVOLUTION TOWARDS COMPLEX FERTILISERS TENDS TO SOLVE THE SULPHUR PROBLEM.

A) PRACTICAL DEFINITION OF COMPLEX FERTILISERS:

In France a "complex fertiliser" means any fertiliser containing the three elements, obtained directly by chemical reaction from the basic raw materials, such as rock phosphate, gaseous ammonia, nitric acid, also sulphuric acid and sylvinitic chloride or sulphate of potash.

Since 1920, the technique of manufacture has been the object of considerable research, particularly in Germany, but it was really only a few years before the last war that certain types of process, relatively simple and of practical application, were chosen.

B) THE TWO PRINCIPAL CYCLES.

Without endeavouring to cover all the processes developed, it can be stated that most of these belong to two principal classes, namely:- the treatment of rock phosphate by nitric acid without the use of sulphuric acid.

The excess lime from the rock phosphate is separated in the form of nitrate of lime and one obtains, after saturation by ammonia and the addition of potash salt, two products 1.) Complex Fertiliser and 2.) Nitrate of Lime, as a by-product. We will call this type of process the nitric cycle.

The second class of process fixes the excess lime in the phosphate in the form of sulphate of lime with the use of a limited quantity of sulphuric acid. One then obtains, after addition of a potash salt, the complex fertiliser without any by-product. The sulphuric acid can play its part in this reaction either as such or in the form of a salt, such as sulphate of ammonia or sulphate of potash.

We will call this second type of process the "sulpho-nitric cycle".

The first cycle avoids the use of sulphuric acid and the fertilisers obtained contain approximately equal quantities of nitrogen and phosphoric acid, so that the quantity of soluble phosphoric acid obtained is in proportion to the quantity of nitrogen available to the manufacturer.

Practically speaking, in the sulpho-nitric cycle one obtains about 1 kg of soluble phosphoric acid for 1 kg of nitrogen and 1 kg of sulphuric acid. The phosphoric acid is obtained in the form of di-calcium phosphate and gives an economy of more than 50% in the sulphuric acid, which would be required to solubilise the P_2O_5 in making superphosphate. (Exact economy: $\frac{1.3}{2.3} = 56.50\%$)

In the nitric cycle one frequently finds 2/3 of the nitrogen in the complex fertiliser and 1/3 in the by-product nitrate of lime.

In both cycles the fixation of the nitrogen does not require sulphuric acid.

From the point of view of economy it is interesting to consider whether the reduction in consumption of sulphuric acid of more than 50%, obtained in the sulpho-nitric cycle for the solubilisation of the P_2O_5 is sufficient, in view of the sulphur shortage, and to compare it in this connection with the application of the nitric cycle.

The nitrogen production in France is 200,000 tons N, and the production of soluble phosphoric acid is 250,000 tons, which consumes 212,500 tons of sulphur ($250,000 \times 0.85 = 212,500$). Of the nitrogen produced, 60,000 tons are fixed in the form of sulphate of ammonia, consuming 80,000 tons of sulphur. ($60,000 \times 1.33 = 79,800$). The total consumption of sulphur for these two fertilisers is therefore 292,500 tons.

The general application of the sulpho-nitric cycle would produce 200,000 tons of soluble phosphoric acid, consuming 74,000 tons of sulphur, so that there would remain to be produced 50,000 tons of soluble phosphoric acid in the form of superphosphate, consuming 42,500 tons of sulphur. The production of sulphate of ammonia would have disappeared since the whole of the nitrogen production was in the form of complex fertilisers. The total sulphur consumption would be $74,000 + 42,500 = 116,500$ tons, instead of with the old method, 292,500 tons. The total economy would be 176,000 tons of sulphur or about 60% of the former consumption. It would, furthermore, be necessary to produce 100,000 tons of nitrogen in the form of nitric acid, which would appear to be within the present production capacity.

If the nitric cycle was applied fully, it would lead to the following results:

Of the 200,000 tons of nitrogen about $\frac{2}{3}$ i.e. 132,000 tons would be found in the form of complex fertilisers and the rest, about 68,000 tons in the form of nitrate of lime. To the 132,000 tons of N in complex fertilisers would correspond 132,000 tons of soluble phosphoric acid, produced without the use of sulphuric acid. It would, therefore, be necessary to continue to manufacture in the form of superphosphate: $250 - 132 = 118,000$ tons of soluble phosphoric acid, consuming 100,300 tons of sulphur. The saving in sulphur would then be 192,200 tons out of 292,500 tons or 65% of the former consumption. Compared with the sulpho-nitric cycle, the additional economy for the nitric cycle would correspond to only 16,200 tons, i.e., about 5% of the quantity of sulphur used in the old way.

It can be seen that by applying either of these cycles to the full, considerable, and an approximately equal economy, in sulphur would be made.

This theoretical note shows clearly the importance of the effort to be made and the resulting economy in sulphur, which could be made by the development in France of the manufacture of complex fertilisers.

As regards the choice to be made between the two cycles, this depends upon the wishes of the farmer and particularly upon the desirability of producing a considerable quantity of nitrate of lime, and also upon the present equipment of the fertiliser works.

Furthermore, this choice must be influenced by the simplicity of the apparatus and working conditions, the quality and final stability of the products obtained and the need for elasticity in manufacture to enable the formulas of the fertilisers to be varied at will.

V. CAN FRENCH EXPERIENCE CONTRIBUTE TO REDUCING THE DANGER FOR THE WORLD IN THE SHORTAGE OF SULPHUR?

In order to reduce this danger in the world, it must be reduced in the United States, which alone represents more than 50% of the world fertiliser market and where technical skill is so developed as to allow the setting of an example.

It has been noted that the consumption of compound

fertilisers is rapidly growing in France, both as regards actual value and expressed as percentage of fertiliser consumption (34.5% to date).

It has, however, been noted that in the production of compound fertilisers, complex fertilisers are developing very rapidly and are resulting in a considerable saving in the use of sulphur. Generally, these complex fertilisers contain an easily soluble P_2O_5 in the form of a di-calcium phosphate, which has excellent fertilising properties.

In the United States the situation is very different; practically 20% of fertilisers are now consumed in the form of compounds, but little or no complex fertiliser is made in this country.

A further important difference between French and American products is that the ratio of soluble P_2O_5 and nitrogen is about 2 in the United States to 1 in France.

If therefore, with the object of economising sulphuric acid and sulphur, the United States decided to tend towards the manufacture of complex fertilisers, it would be necessary that a means of producing fertilisers, containing on the average two units of P_2O_5 or more to one unit of nitrogen, should be found.

The work done in France shows that this object can easily be attained by adding, as a fourth element into the manufacturing cycle, ammoniated superphosphate or di-calcium phosphate.

The future development of complex fertilisers in the world appears to be only possible as a result of industrial liaison, similar to that which assisted the French development in this field.

The six principal French producers of complex fertilisers are either among the largest manufacturers of superphosphate or di-calcium phosphate, or else, among the principal producers of ammonia.

The works for the production of complex fertilisers have been set up either in old phosphatic fertiliser works, which already possessed sulphuric acid plants, or else in former nitrogen works, which possessed nitric acid plants. The flow-sheets of the raw materials handled depend upon this initial choice of the location of the works.

In the first case, it has been necessary to construct alongside of the superphosphate or di-calcium phosphate works, a nitric acid plant. Raw materials brought to the works are pyrites, rock phosphate, chloride or sulphate of potash and ammonia in tank cars.

In the second case, raw materials brought to the works are rock phosphate, chloride or sulphate of potash and, if necessary, sulphuric acid and, if it is desired to increase the phosphoric acid content of the complex fertilisers, either ammoniated superphosphate or di-calcium phosphate.

It has been shown above how the theoretical full application of the sulphur-nitric cycle to the production of complex fertilisers can, in the case of France, lead to considerable economy in the use of sulphur.

Assuming now a country, which consumes a million tons of nitrogen, of which 200,000 tons in the form of by-product sulphate of ammonia and 200,000 tons in the form of sulphate of ammonia, produced by synthesis, and which consumes $1\frac{1}{2}$ million

tons of soluble P_2O_5 as ordinary superphosphate, assuming furthermore that its nitric acid works are capable of producing 400,000 tons of nitrogen in the form of nitric acid, the present consumption of sulphur for fertilisers is:

$$\begin{aligned} 400,000 \times 1.33 &= 532,000 \\ 1,500,000 \times 0.85 &= 1,275,000 \end{aligned}$$

i. e. 1,807,000 tons of sulphur.

With the application of the sulpho-nitric cycle it would be necessary to retain the by-product sulphate of ammonia which is essential. There would then remain 800,000 tons of nitrogen which would solubilise 800,000 tons of P_2O_5 of the $1\frac{1}{3}$ million tons to be produced. The consumption of sulphur would then become:

Sulphur for by-product sul. of amm.	200,000	x 1.33 =	266,000
Sulphur for solubilising phosphate	800,000	x 0.37 =	296,000
		+	700,000 x 0.85 =
			595,000
Total			1,157,000

The total saving would therefore be:

$$1,807,000 - 1,157,000 = 650,000 \text{ tons or } 37\%.$$

A similar calculation would show that the general application of the nitric cycle would lead to a saving of 719,000 tons of sulphur or 39%, but with at least 266,000 tons of nitrogen in the form of nitrate of lime.

It is not necessary to make this theoretical study to show that each time an industrial development permits of replacing a tonnage of compound fertilisers by a tonnage of complex fertilisers, containing the same quantity of fertilising elements, an important saving of sulphuric acid is achieved.

The high proportion in any given country of compound fertilisers, as compared with a total tonnage sold, would appear to be a factor facilitating the development of complex fertilisers, and consequently a considerable saving in the sulphur consumption.

This is a fundamental fact which will probably enable the principal obstacles to be overcome more easily in certain countries like the U.S.A. than in France, these obstacles being in general more due to human nature than to technical or economical factors.

A considerable part of the necessary evolution has already been started, since agriculture is used to consuming compound fertilisers and industry knows how to produce such fertilisers by modern methods, involving an economy in the use of sulphur.

Closer cooperation between superphosphate manufacturers who produce compound and nitrogen fertilisers will facilitate this process.

In conclusion, if the acute shortage of sulphur from which France suffered in the period 1939 to 1945 was one of the main causes of technical progress in this field, there appears to be no obstacle to the application of this progress elsewhere in the world.

The author believes that superphosphate and ammonia producers are primarily interested in the development of these new methods and that it is up to them to take advantage of them, and that producers as well as farmers will benefit by obtaining the quantities of fertiliser required in the desired form.

The author believes furthermore that the adoption of pro-

coses already in being on full industrial scale will save a number of years by avoiding the necessity of long preliminary work.

Faced with the seriousness of the present supply position should one not to-day complete the time-honoured phrase by saying "time is money and sulphur".

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