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POLI: A Phosphate Fertilizer from Phosphate Rock and Sulphur Trioxide

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A new, dry process for producing a phosphate fertilizer by direct action of gaseous sulphur trioxide on solid powdered phosphate rock has been developed in the Institute of Chemical Engineering of Warsaw Technical University, Poland. The process can be arranged to work on a sidestream of sulphur trioxide-containing gas from a conventional sulphuric acid plant. Because it obviates the need for certain of the processing stages associated with wet phosphate processes, including separation of waste sulphur values, the new process has certain practical and economic advantages, including high phosphate efficiency, reduced sulphur and utilities consumption, no unwanted by-product and low investment cost, in addition to which it is capable of operation on phosphate rocks which are unsuitable for use in wet processes.

The solubility characteristics of the product (known as POLI fertilizer) are such that it combines the advantages of superphosphate with those of ground phosphate rock. POLI has been tested with favourable results under both temperate (Poland) and tropical (Thailand) conditions, and has been found to be particularly effective in lateritic phosphate-fixing soils common in tropical zones, where high-solubility fertilizers are not particularly satisfactory.

A plant is now in operation in Bangkok, Thailand, and the product has been tested and approved by the Thai Ministry of Agriculture.

NEED FOR SIMPLER ALTERNATIVES TO WET PHOSPHATE PROCESSES

Apart from ground phosphate rock, the majority of phosphate fertilizer produced in the world today comes from wet processes (acidulation of phosphate rock), which yield products containing over 95% of the total P_2O_5 in water-soluble forms. But it is the economy of the process itself, rather than the economy of action of the phosphate fertilizers in agriculture, that has been responsible for the predominance of this type of phosphate fertilizer over all others. It is known, for example, that the effect on crop yields of phosphate fertilizer obtained by thermal processes, such as Rhenania-phosphate or meta-phosphate, is equivalent to that of superphosphates, even though they contain no water-soluble P_2O_5 . It is also known that fertilizers containing water-soluble phosphorus compounds are not universally effective; they do not act with the same efficiency in soils of differing quality and in different climatic zones. From the agricultural point of view, therefore, the choice of available fertilizers is unduly limited.

Wet phosphate fertilizer processes are subject to an increasing number of problems associated with the declining quality of the raw material (phosphate rock) and the increasing cost of both the raw material and energy. Their high energy demand, as well as the high investment cost of plants based on phosphoric acid as an intermediate product, are increasingly burdensome, and for this and other reasons, such as operating problems (difficult running of the plant) and the unfavourable trade balance arising out of the need to import raw material and equipment, that developing countries seldom invest in phosphate fertilizer production, even though demand for this type of fertilizer is tremendous.

Perhaps the problem which most severely threatens the future prospects of the wet processes is the availability of raw materials with a suitable chemical composition. A greater degree, and new techniques, of beneficiation or preliminary treatment (including flotation, calcination or leaching) are necessary to compensate for the lower grade and purity of phosphate rock and – especially considering energy costs – this is bound to involve greater expense.

There are thus a number of pointers to indicate the possibility of a future change in the development of the phosphate fertilizer industry away from the difficult intensive processes, giving phosphate fertilizers as chemical compounds of technical grade, in favour of simpler production methods with more modest investment costs and energy consumption, but still turning out phosphate fertilizers which are as efficient in their agricultural performance as fertilizers obtained by wet processes.

It was with this prospect in mind that work was carried out, in co-operation with Polimex-Cekop Ltd., at the Institute of Chemical Engineering of Warsaw Technical University in the years 1974-1980 on a

new alternative to wet phosphate fertilizer processes, which will now be described.

DEVELOPMENT OF THE "POLI" PROCESS

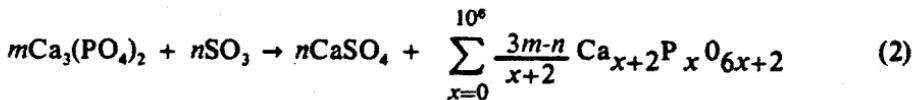
As a result of extensive laboratory research and pilot-scale experiments, a new process to produce a new type of phosphate fertilizer has been investigated and developed. This process, unlike wet processes, is based on the direct reaction of sulphur trioxide and ground rock phosphate in a two-phase (gas-solid) system.

Chemistry

Reactions between acid anhydrides and inorganic salts are, of course, well known to inorganic chemists. It was found in the preliminary studies that when ground rock phosphates are treated with gaseous sulphur trioxide at temperatures below 500°C, the apatite structure of tricalcium phosphate is broken down and calcium sulphate and monocalcium phosphate are formed according to reaction 1.



At the same time, calcium poly- and metaphosphates of varying degrees of condensation are formed according to reaction 2.



The occurrence of calcium poly- and metaphosphates in the products of the reaction between sulphur trioxide and rock phosphates has been confirmed by chemical, chromatographic and X-ray analysis. It was found that the higher the reaction temperature, the higher is the degree of condensation of the phosphates.

Sulphur trioxide also reacts with carbonates and fluorides present in rock phosphate to give solid calcium sulphate, carbon dioxide and fluorine-containing vapours, thus partly defluorinating the phosphate. The reaction between gaseous sulphur trioxide and rock phosphate is exothermic, evolving 250-400 kJ/kg of rock phosphate according to the reactivity and chemical composition of the rock.

Industrial realization

On the basis of the results of laboratory studies, process operating conditions were determined and a pilot plant was designed and built for testing the process. It performed as predicted, and as a result the first commercial plant in the world to produce phosphate fertilizer by dry treatment of rock phosphate with gaseous sulphur trioxide was constructed and put on stream by Polimex-Cekop Ltd. in Bangkok, Thailand. This plant is owned by The Siam Chemicals Co. Ltd., Bangkok. Some information is presented below on the process, showing its simplicity and future potential, particularly in view of the growing economic problems in the world market.

Raw materials

Rock phosphate used in the process is ground to at least 60% minus 200 mesh, which corresponds to the grinding degree typical for wet processes. Soft rock phosphates of sedimentary or metamorphic origin, for example from North Africa, Jordan or South-East Asia, are the best feed rocks for the POLI fertilizer production process. The feed rock can be of practically any composition, containing any amount of organic matter, silica, chlorides, carbonates, iron and aluminium compounds, but it should not contain more than 5% water.

Sulphur trioxide for the gas-solid reaction can be a component of a gas mixture or pure gas, as when derived through oleum desorption. The SO_3 concentration in the gas mixtures used in the process is not limited. Gases leaving the converter from any sulphuric acid plant or any off-gases containing free sulphur trioxide can be utilized in the process. Sulphur dioxide, carbon dioxide and other components of the gas mixture have no influence on the process.

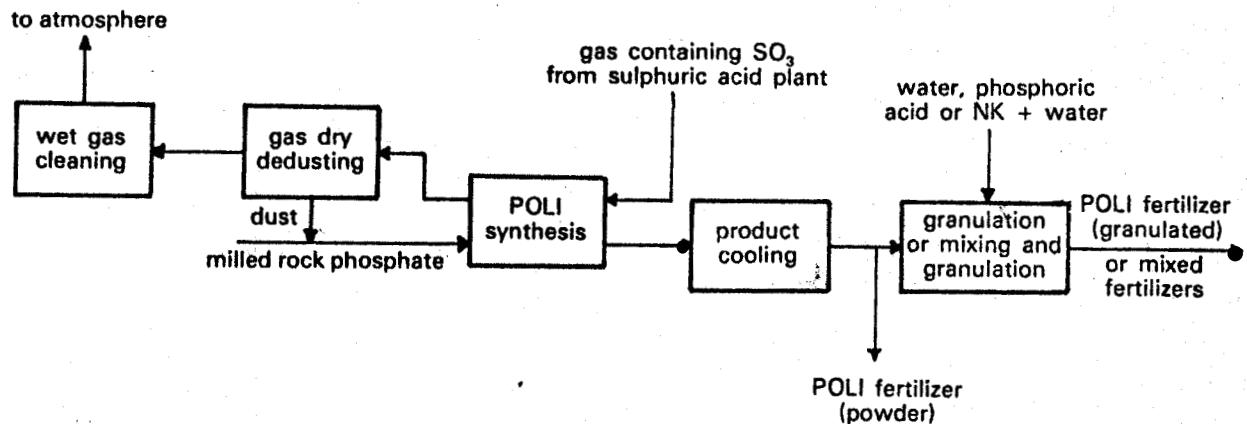
Process outline

A flow diagram of the process is shown in Fig. 1. The gas-solid reaction runs autothermally in counter-current arrangement in one reactor of suitable but simple design, starting with drying of the rock phosphate feedstock followed by reaction with gaseous sulphur trioxide.

Ground rock phosphate and gas containing SO_3 are fed into the reactor, their respective flow ratio being automatically kept at the level of stoichiometric consumption of the reaction substrates. Powder product leaving the reactor is cooled in a diaphragm cooler and bagged or, alternatively, granulated or mixed with other fertilizers and then bagged.

Gases leaving the reactor pass through a dry filter; dust removed then is

Fig. 1 : Block Flow Diagram of the POLI Fertilizer Process



returned to the reactor. Off-gases contain no sulphur trioxide; they are easy to clean by wet methods.

In Fig. 2 possible ways of connecting the POLI plant with a sulphuric acid installation are shown. In layout A, gas containing sulphur trioxide is withdrawn from the acid plant between the economizer and the absorber. Layout B, is an arrangement for an installation producing over 20% oleum. In this case, essentially pure sulphur trioxide, desorbed from oleum, containing over 99% SO₃, is used, and this significantly influences the dimensions of the reactor and off-gas cleaning system.

Product characteristics

The product of the reaction between sulphur trioxide and rock phosphate is a mixture containing anhydrous calcium phosphate (CaSO₄), monocalcium phosphate (Ca (H₂PO₄)₂), calcium pyrophosphate (Ca₂P₂O₇), calcium meta- and polyphosphates (hence the process name) and unreacted rock phosphate. Its chemical composition depends on the composition of the rock phosphate reacting with gaseous SO₃, and the reaction temperature and is within the range:

	%
P ₂ O ₅ , total	23-30
SO ₃	12-28
CaO	30-43
CO ₂	1-4
H ₂ O, maximum	5
Free acids (as H ₂ SO ₄), maximum	2

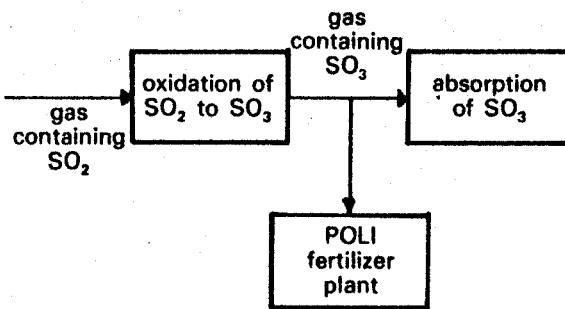
Fertilizer leaving the reactor is a dry, non-caking, flowing powder with an apparent density of 1 kg/dm³ and grain size close to that of the rock phosphate used. No maturing is necessary; powdered POLI fertilizer leaves the installation in a form ready for application in agriculture or for further processing to a granulated fertilizer or as a component for powdered or granulated mixed fertilizer.

According to the presently used classification standards of the phosphorus compounds contained in phosphate fertilizers, POLI fertilizer contains:

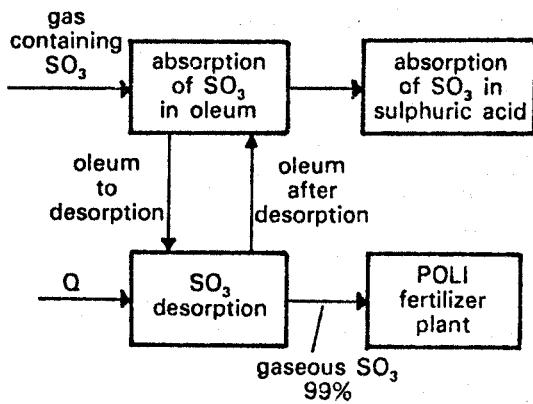
- phosphorus compounds soluble in water (20% to 40% of the total P₂O₅);
- phosphorus compounds soluble in Peterman reagent at 60°C (40-60% of the total P₂O₅) and at 100°C (60-85% of the total P₂O₅);
- phosphorus compounds soluble in weak organic acids (2% citric acid) (60-85% of the total P₂O₅); and
- phosphorus compounds insoluble even in weak organic acids (15-40% of the total P₂O₅).

Fig. 2 : Alternative Ways of Connecting POLI Fertilizer Process to a Sulphuric Acid Plant

A: Using Sidestream of Converted Gas



B: Using High-Concentration SO₃ Desorbed from Oleum



From the point of view of the solubility of its phosphorus compounds, POLI fertilizer is thus a new and hitherto unknown type of phosphate fertilizer.

Of the types of phosphate fertilizer familiar hitherto, chemically produced ones such as superphosphate and ammonium phosphate contain over 95% of their total phosphorus in the form of water-soluble compounds, while the thermophosphates (exemplified by Rhenania phosphate, and Thomas phosphate) contain a similar percentage of compounds which are soluble in weak organic acids but no water-soluble phosphates; and, finally, ground rock phosphate contains practically no water-soluble compounds, but up to 20% of its total P_2O_5 is soluble in weak organic acids.

The three forms of phosphorus compounds mentioned above, different in their ability to pass into the soil condition, are all present in POLI fertilizer at the same time. From this point of view, POLI thus combines the features of superphosphates, thermophosphates and ground rock phosphate. The water-soluble compounds in POLI, being available to plants immediately after application of the fertilizer, are considered as a phosphorus starter, but they are not present in sufficient amount to undergo immobilization in the soil to any serious degree. In contrast to the water-soluble compounds, the compounds soluble in weak inorganic acids (mainly meta- and polyphosphates) become available to plants only after slow hydrolysis in the soil. These compounds make up for depletion of the level of water-soluble phosphates resulting from absorption by the crop and from immobilization in the soil. Finally, the phosphate components which are insoluble in weak organic acids constitute a reserve of phosphorus which is eventually made available to plants as a result of slow soil transformations by the same mechanisms as take place with ground rock phosphate.

POLI is easy to granulate when mixed with water or aqueous solutions of other mineral fertilizer components such as nitrogen, potassium or other phosphatic compounds. POLI granules are very resistant to crushing (the crushing strength of a 2-mm granule is 1.5-2 kg), do not cake and do not change their properties when moist.

A very important feature of POLI is its ability to granulate with phosphoric acid, in which case it is not necessary to dry the granules obtained (so-called "cold granulation"). The ratio of P_2O_5 in the POLI to P_2O_5 added in the phosphoric acid can be varied within the range 1 : 0.15 to 1 : 0.6. Granulation in this manner with phosphoric acid enables the total P_2O_5 content to be raised to 35% and the water-soluble P_2O_5 content to be increased to 80% of the total P_2O_5 .

Comparison with wet processes

Table I compares material and utility consumptions and cost elements for POLI production with those for triple superphosphate.

Table I
Comparison of Consumptions and Costs of Phosphate Fertilizer
Production by POLI and Triple Superphosphate Routes

	POLI fertilizer installation (as Fig. 2A)	Sulphuric acid + TSP installation
Phosphorus efficiency, %	100	90-98
Consumptions, per tonne P_2O_5 :		
Sulphur, tonne	0.26-0.35	0.8-0.95
Water, m^3	1.2-6.8	9-20
Electric power, kWh	35-55	150-300
Steam (6 ata), tonnes	0	4-6
By-product (phosphogypsum), tonne/tonne P_2O_5	none	4.5-6.5
Relative overall production cost	0.7-0.9	1
Relative investment outlay/unit P_2O_5 *	0.4	1

* including rock milling and sulphuric acid installation.

The POLI process saves on energy and raw materials; less than half as much sulphur is required to obtain a given amount of P_2O_5 in the form of POLI fertilizer as is needed to produce it as triple superphosphate; in other words, from a given amount of sulphur, around 2.5 times as much P_2O_5 can be obtained as POLI than as fertilizers based on phosphoric acid (SSP, TSP, MAP, DAP). As there is no separation stage in the POLI process, all of the P_2O_5 in the raw material passes into the product in the same way as in normal superphosphate manufacture — there are no P_2O_5 losses. It is therefore obvious that this process is attractive for importers of both sulphur and rock phosphates.

The electricity requirement of the POLI process (in which it is used for driving machines) is considerably smaller than in any wet process).

The low investment cost of a POLI plant combined with a plant generating gases containing SO_3 , is due to the simplicity and small sulphur requirement of the process: the dimensions of a plant to produce SO_3 are small in comparison with those of a sulphuric acid plant processing 2.5 times as much sulphur. Apart from that, no storage tanks, acid diluting or cooling units are necessary.

Thus, the low overall production cost of POLI, calculated per unit of the total P_2O_5 present in the product fertilizer, results from low sulphur and rock phosphate consumption figures, low energy consumption and small investment costs.

A POLI plant is very simple to construct — its equipment can be manufactured of standard materials, available in every market. It is very easy

to operate, too, particularly if provided with automatic regulation of the raw materials feeds. The POLI process is not sensitive to impurities present in rock phosphates which can make them useless as a raw material for wet methods. Silicate, iron, aluminium, chlorides and organic matter do not have any negative influence on the solid-gas system; and neither do they degrade the properties of the fertilizer nor (because it is a dry process) do they accelerate corrosion of the equipment. The POLI process thus provides an excellent opportunity for processing so-called "difficult" rock phosphates, very troublesome to treat by wet methods on account of their impurity content. It is not so important to beneficiate the rock feed as it is for the wet processes. No by-product is obtained in the POLI process; all of the calcium sulphate remains in the product, admittedly decreasing its total P_2O_5 concentration, but at the same time enriching it with sulphur, which is deficient in the soil of many areas of the less industrialized world.

AGRICULTURAL PROPERTIES OF "POLI" FERTILIZER

From the foregoing, it is clear that the POLI production process possesses some marked practical and economic advantages over phosphate fertilizer manufacturing methods based on wet processes. The obvious question remaining is: how well does the product perform in comparison with other types of phosphate fertilizer? To determine this, agricultural tests on POLI were run at the same time as the process itself was developed.

Performance in temperate climate

Studies on the fertilizing action of POLI in a temperate climate started in Poland in 1976 in pots and experimental fields. They were conducted by the Institute of Chemistry and Agricultural Chemistry of the Academy of Agriculture, Warsaw, and the value of POLI as a source of phosphorus for several basic crops such as rye, spring barley, oats, potatoes, maize and field peas was judged in comparison with other fertilizers such as triple superphosphate and ground phosphate rock.

The field tests were conducted over a period of three years (1977-1979) in a blanched soil of $pH_{KCl} = 5.9$ and $pH_{H_2O} = 6.4$ with available phosphorus (determined by the Egner-Riem method) 6.8 mg/100 g soil. The results are shown in Table II.

To ascertain the transformations undergone by the phosphorus introduced into the soil in the POLI fertilizer, extensive chemical investigations of the soil were performed at the same time.

The results obtained in each case were compared with those obtained when

Table II
Comparison of the Influence of POLI Fertilizer, Triple Superphosphate and Ground
Phosphate Rock on the Crop Yield (in quintals/ha) of Representative Crops
in Field Trials in Poland

Dose*	(No phosphorus)	POLI		TSP	Ground rock phosphate
		NK	NKP ₁		NKP ₃
Potatoes	1977	192	219	215	214
	1978	207	247	231	242
	1979	237	370	340	348
	Average	212	279	262	268
Maize	1977	659	710	714	716
	1978	575	633	620	616
	1979	393	511	483	469
	Average	541	618	606	600
Field peas	1977	152	195	182	162
	1978	160	178	190	189
	Average	156	186	186	175
Spring barley	1977	24.2	27.2	32.1	27.8
	1978	21.1	23.6	24.1	23.8
	1979	18.2	30.5	29.7	31.2
	Average	21.0	27.1	28.6	27.6

*Fertilizer dosages:

N (potatoes and barley): 90 kg/ha N
 (maize and field peas): 120 kg/ha N
 K (potatoes and maize): 120 kg/ha K₂O
 (barley): 110 kg/ha K₂O
 (field peas): 100 kg/ha K₂O

P₁ (all crops): 70 kg/ha P₂O₅,
 P₃ (all crops): 210 kg/ha P₂O₅

N and K applied annually before sowing;
 P applied before sowing, once in 3 years.

using ground rock phosphate (the same rock as was used in producing t POLI) and with those obtained from tests with triple superphosphate used as standard. In the pot trials Rhenania phosphate was also used as an addition standard. This was because, although Rhenania phosphate has fallen out of use in recent years owing to its high cost, it was assumed on the basis of laboratory tests that POLI would have similar agricultural properties. This was confirmed by the growth trials.

Studies of the phosphorus transformations in soil reveal that POLI is an intermediate fertilizer between the ground rock phosphate and triple superphosphate: in an acidic soil the phosphate transformations were similar to those of triple superphosphate, in basic soil to those of ground rock phosphate.

The results of the vegetative and field tests indicate that POLI is particularly suitable for light, acidic or slightly acidic soils. Under such conditions it is closer in its fertilizing action to superphosphates, and sometimes, in acidic soils, it is even better on account of its resistance to immobilization. Its action is inferior to that of superphosphates only in neutral and freshly limed soils.

It can be concluded from the results of the POLI agricultural tests in Poland that under European conditions this new fertilizer can successfully fill the gap in the range of phosphate fertilizers left after thermophosphates were withdrawn from the market.

Performance under tropical conditions

Agricultural studies in a tropical climate started in 1978 in Thailand, where the fertilizer is known as "Polyphosphate". The crops tested were soya bean, maize, peas and rice. On the basis of the results of the agricultural tests carried out up to now, the Ministry of Agriculture of Thailand has endorsed the fertilizer produced by Siam Chemicals Co. Ltd. and has certified "Polyphosphate" for distribution in Thailand.

Table III shows examples of the results of the field tests in Thailand. Of particular interest is the very good action of POLI on rice, confirmed many times. It was found that POLI gives yields equal to those of TSP and DSP, while in soils of pH < 6, deficient in sulphur and phosphorus, the crops are even better than those obtained when fertilizers produced in wet processes are applied. It was also confirmed that when a phosphate fertilizer containing phosphorus compounds of varying solubility in the soil medium is used, the uptake of phosphorus by the crop is better than when this fertilizer contains only water-soluble phosphorus compounds.

The favourable results obtained in the tropical climate with POLI in comparison with TSP and DSP can be explained by the different climatic conditions. The large rainfall in the tropics washes bases out of the soil, so, in these areas, soils are predominantly acidic. At the same time, these soils are rich in

aluminium and iron (lateritic), and this kind of soil tends to fix or immobilize the water-soluble phosphate values of superphosphate-type phosphate fertilizers as insoluble aluminium and iron phosphates. It is because of these changes that the soils of the tropics (laterites, red humuses, yellow humuses, etc.) are characterized by their very low contents of plant-available phosphorus — perhaps only one-tenth or less of the general levels of European soils. But because a large proportion of the total phosphate content of POLI is not water-soluble and is only gradually transformed to plant-available forms by soil processes, POLI hardly undergoes any phosphate fixation and is therefore often a better fertilizer in the tropics than superphosphate.

Table III
Results of POLI Field Tests in Thailand

Plant	Soil pH	Fertilizer	Grain yield, quintal/ha	Plant crop dry mass, quintal/ha	Plant height, cm	
Soya bean	5.5	None	8.7	14.5	71	
		NK + TSP	13.3	24.4	95	
		NK + POLI	19.5	27.0	97	
Maize	6.0	None	13.2	87.0	165	
		NK + DSP	19.5	103.0	190	
		NK + POLI	22.7	100.0	197	
Rice	5.0	None	6.2			
		N + TSP	12.4			
		N + POLI	28.0			
Fertilizer dosages:		N and K ₂ O in optimal doses for crop.				
		P ₂ O ₅ (soya bean): 110 kg/ha				
		(maize): 125 kg/ha				
		(rice): 75 kg/ha				

Results of the laboratory and crop growth experiments give rise to the conclusion that POLI is a particularly suitable fertilizer for soils in tropical areas. It can be assumed that favourable conditions for its application can be found in many areas of Asia, Africa and South America.