



TOGETHER
for a sustainable future

OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org



05665

Distr.
LIMITED

ID/WG.175/18
19 August 1974

ORIGINAL: ENGLISH

United Nations Industrial Development Organization

Expert Group Meeting on Minimizing Pollution
from Fertilizer Plants

Helsinki, Finland, 26 - 31 August 1974

FERTILIZER INDUSTRY - ENVIRONMENT POLLUTION SOURCE^{1/}

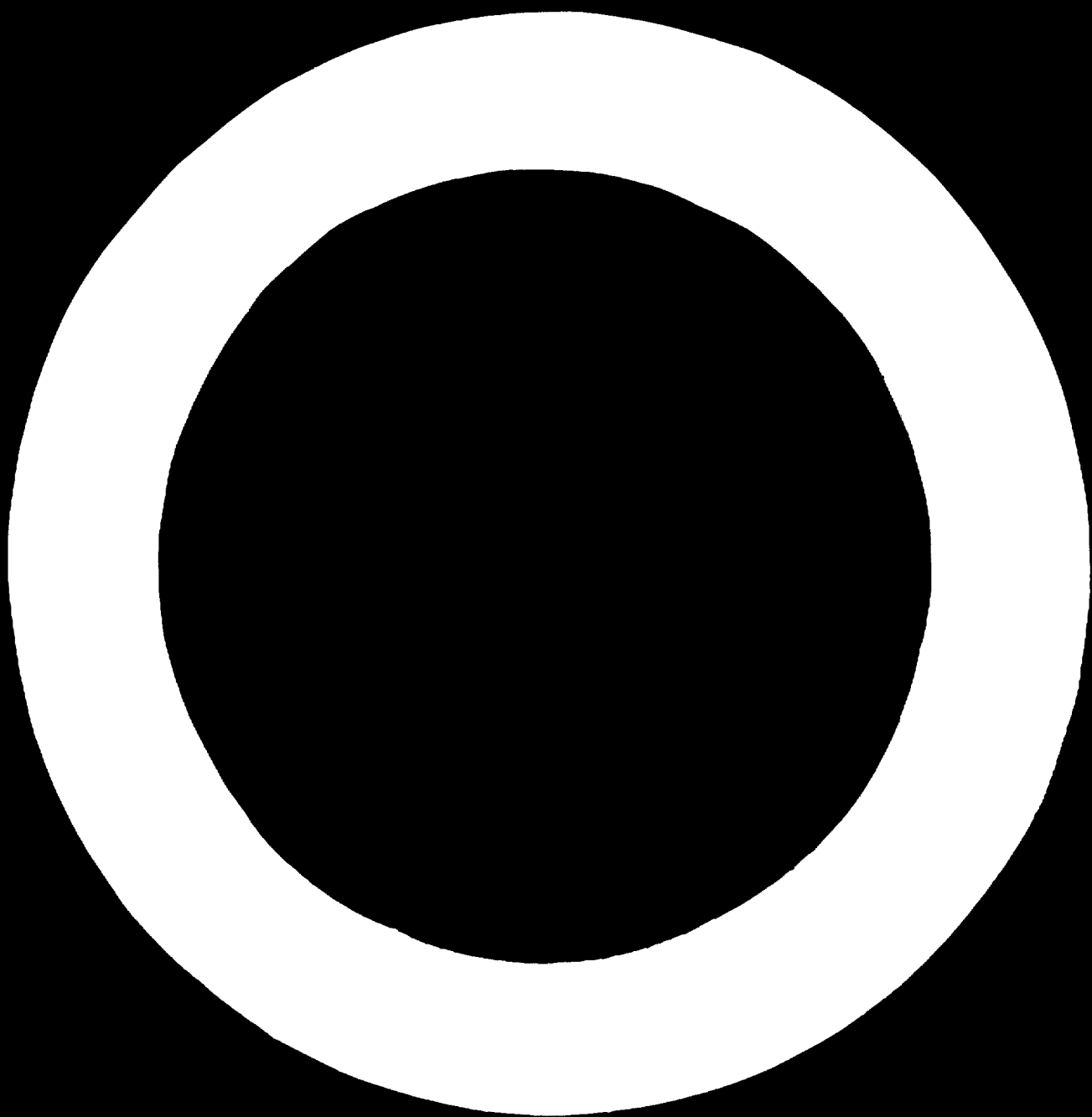
Technical Solutions and Technological Advances
Made in Romania to Control Environmental Pollution
Effects Arisen from Fertilizer Plants

N. Popovici*

* IPROCHIM, Bucharest, Romania.

^{1/} The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.



The technical progress made in the fertilizer industry is part of the technological revolution of our era which in this field is reflected in a few major features, namely:

- concentration of high capacity industrial units in huge size complexes.
- establishment of technological plants on ever larger manufacturing trains, which has been possible by the progress made in the machine-building industry.
- integration of fertilizer plants, including intermediate product units, or location of the latter in neighbouring areas, and pipe transport of these intermediates (NH_3 ; H_3PO_4)

- Location of fertilizer plants, on account of big amounts of imported or exported products, in the neighbourhood of seashores or along large river banks, to enable river transport.
- Development of complex fertilizer production.

The designation of the fertilizer production places it - as compared to other branches - at a low profit level which has imposed a steady research work to seek after new solutions for as low as possible investment and operation costs.

In the light of the recent struggle for environment protection, the fertilizer industry appears to be a main factor of pollution; moreover, technology studies are insufficient to meet the requirements newly imposed by norms and regulations for pollution control.

The elements that have caused this situation are given below:

- concentration of production capacities in great complexes, which leads to proportional increase in emissions of noxious substances.
- insufficient preoccupation in carrying out the research activity to reduce pollution effect.
- tendency to apply simple solutions requiring low costs in the construction of plants, taking into account the low profit level.

- operational accidents, infraction of operating discipline and rules, determined in some cases by the lack of professional skill of the personnel; over running of plants all through the peak fertilizer seasons, when higher prices are get-at-able.
- setting up of fertilizer plants on sea-shores or along large river banks has permitted the infringement of the limitations regarding the amounts of noxious substances to be disposed in the environmental zone.
- a low technical level of some plants or an advanced wear of others that will bring about increasing amounts of noxious substances in the environmental zone.
- lack of severe protection rules and restrictive norms (that have come up but recently being adopted throughout the world) have permitted disposal of big amounts of noxious substances from fertilizer plants in the zone.

Strict measures taken of late by national authorities or international bodies for the environment protection have entailed the acceleration of the research activity and the industrial scale application of the results obtained to diminish the detrimental effect of the pollution on the environment by the fertilizer industry, in this respect being obtained rather important achievements.

The Romanian fertilizer industry with a rather short existence, practically covering two decades (1955-1975) and including the units under construction, has known a boom from 10,7 thousand tons/yr to 2,700 thousand tons/yr nutrients expectable at the end of this period (see Table 1).

Development of Romania Fertilizer Industry
('000 t/y nutrient)

	<u>Table 1</u>				
	1955	1960	1965	1970	1975
Nitrogen fertilizer					
100% total	3,4	18,9	166,3	647	1920
out of which:					
Ammonium nitrate	1,9	14,2	155,1	397,5	660
Nitrochalk	1,5	2,2	3,0	19,9	10
Urea	-	-	1,8	172,1	810
Ammonium sulphate	-	2,5	6,3	10,6	10
Nitrogen in complex fertilizer	-	-	0,1	46,9	430
Phosphatics fertilizer					
100% P ₂ O ₅ total	7,3	52,1	121,5	244,2	720
out of which:					
as complex fertilizers	-	-	0,3	91,5	410
Potassium fertilizers					
100% K ₂ O total (in complex fertilizer)	-	-	-	4,2	78,0

Literature quoted: Florescu M "Romanian Chemical and Petrochemical Industry, Bucharest, 1972, page 550.

As concerns the technical level the Romanian industry bears the mark of the technological progress of the period being based on up-to-date processes in most of the cases.

Considering the Romanian fertilizer industry from the "environment protection standpoint" it is necessary to point out some characteristic features, namely:

1. It has been developed in high capacity industrial complexes, reaching outputs of 500,000 t/yr NH_3 ; 500,000 t/yr of 100% HNO_3 ; 300,000 - 500,000 t/yr urea; 400,000 t/yr H_2SO_4 ; 120,000 - 150,000 t/yr P_2O_5 , figures that are representative for most of our complexes.

2. As to location, the fertilizer plants are placed near the rivers, the majority with rather small flows, and in the neighbourhood of densely inhabited areas; These plants are spread throughout the country in agricultural zones, which causes a decrease in the transportation costs of the fertilizers to the consumers.

Regarding the hydro-geological structure of these zones, many plants are located in hydrographic basins feeding underground water layers or underground water deposits of high socio-economic importance.

The climate in our country is characterized by rather few winds with a moderate intensity and most zones have almost no winds, which reduces dispersion effect.

3. Considering the production profile, the manufacture of sulphuric acid is based - to a great extent - on pyrites, phosphoric acid-on wet process, ammonia-on methane, practically free of sulphur. We are producing fertilizer grades so to meet the local consumers' requirements, with nutrients showing a high solubility in water, prevalent in the nitrogen production being the ammonium nitrate and urea, while in the complex fertilizer industry, nitrophosphates are prevailing (about 3,500,000 t/yr).

4. In the above mentioned conditions, the Romanian recently developed fertilizer industry observes the environment protection rules that are at present enforced by a strict state law.

When defining the industrial complex policy, one has to take into account the problem of "environment protection" and the best way to solve it.

Depending on the factory profile, the above considerations should be born in mind, at: 1). Designing stage

2). Operating life

Designing stage:

- 1.1.- Choice of the location
- 1.2.- Choice of manufacturing processes and their completion with auxiliary pollution control units.
- 1.3.- selection of appropriate constructive solutions for general/auxiliary services on

the platform (water loop cooling system for process purposes, sewage, etc).

- 1.4.- Endowment with control/alarm facilities to detect the pollution degree.

Operating life

- 2.1.- Training of the operating/maintenance personnel with a special regard to the environment protection rules observance.
- 2.2.- Operation of plants in accordance with the conditions and the process parameters provided in the project.
- 2.3.- No process improvement or increase in the plant operating capacity should be carried out without taking on adequate environment protection step.
- 2.4.- Maintenance of pollution control units on the platform under adequate operation conditions.
- 2.5.- Permanent and severe observance of allowable limits of noxious element emissions.
- 2.6.- All measures taken during operation to reduce as much as possible the risk of technical accidents.

1. Designing stage

1.1. Selection of location

The modern fertilizer industry, on account of its high technical level, from social and ecological reasons must be located in the vicinity of towns or give birth to others.

This neighbourhood should not of course be too close, since a certain protection area ought to be considered. This distance would then imply facilitating of a transport system rather convenient for the personnel to travel between the plant complex and the town.

Likewise, there ought to be taken into account any industrial objects in the neighbourhood that could increase the pollution effects as for instance adsorbing or catalytic dusts likely to heighten the aggressiveness of fertilizer plant emissions (E.g: carbon black or coal dust, increases 3-4 times the noxious effect of SO_2 on flora).

The pollution effects of fertilizer complexes can appear very severe especially in industrial zootechnical units bringing about serious economic disturbances.

The nature of crops do matter as far as the plant sensitivity to noxious emissions is concerned and so does their designation.

For example fluorine emissions effects on pasture lands and forage crops are most important because this element is directly introduced into the animal body even if the actual concentration of the emission to the atmosphere is rather low and does not cause a visible effect on the plant growth.

Such reasons ought to be considered in preliminary studies of the intended fertilizer complex location especially in atmosphere and hydrological/geological surveys. Thus:

- the survey on the atmosphere should provide the elements for the determination of the area likely to be affected by the gaseous noxious compounds as well as the dispersion possibilities.

- the hydrological and geological survey should make evident the elements referring to underground water deposits or underground water layer of socio-economic importance, their connection to the neighbouring areas, since the environmental protection also depends on the impermeability degree of the surface geological layers where the plant and the used water manifolds are located and on the emissary dilution capacity, etc.

As an example to the point, we can mention the complex we intend to build in Moldavia; the hydrological and geotechnical survey was developed in parallel with the location study; yet the conclusions of the former came up with a certain delay to the general location study. Other data led us to select seemingly optimum location for the fertilizer complex, in the southern part of Moldavia. The hydrological survey revealed the existence in the selected area of an important underground potable water layer liable to be turned to account as a supplying source for a densely inhabited urban centre. Although the project was in an advanced stage, the location was shifted to another area, running the least risk of contamination of the potable water basin, regardless of the fact that the project had provided most efficient measures for contaminated water pipelines and trenches built of resistant material and of tight construction.

These considerations are based on the fact that the fertilizer industry despite the present technological level still continues to be a source of environment pollution.

The problem is to control pollution to low limits and diminish it as much as possible.

Although the new technologies have enabled a perceptible control of pollution, the creation of huge complexes has - as a counterpart - led to absolute noxiousness values exceeding the preceding ones. For instance in the production of contact sulphuric acid, after a long stagnant period in the catalysis process of SO_2 to SO_3 , with an efficiency of 98% an important leap was made by the "double absorption" technique and the oxidation yield reached 99,5%. Owing to this performance, SO_2 from off-gases was reduced to 1/4. At the same time, from economic reasons and due to the technological progress in the equipment construction, the erection of giant plants became possible, bringing about a concentration of production in fertilizer complexes, yielding 3-5000 t/day sulphuric acid, which represents an increase of 10-15 times as compared to the preceding period when only the conventional single catalysis was applied. Under the said circumstances in spite of the technological progress in the sulphuric acid production, an ultramodern fertilizer complex producing its own sulphuric acid has turned into a pollution centre several times larger than in the past. Incidents of the kind occur with other industries too.

1.2. Selection of processes to be used in manufacturing plants and plant completion with auxiliary facilities for pollution control purposes

At the present stage, the criterion of maximum profit cannot be accepted without considering the imperative corrective of ensuring as low a pollution degree as possible, a universal consideration, all the more valid in the fertilizer industry.

In choice of processes, if this principle is admitted -and it must be- and considering all the factors affecting the environment protection degree, processes and designs with lower economic disadvantages may be selected. It is known that the measures taken for environment protection require additional expenses. With the fertilizer industry, where prices - from widely known reasons - are much lower than those of other industries, particular solutions requiring minimum costs should be applied.

From our experience, we know that the environment protection expenses can be cut down in most cases, if the technology is directed to diminishing the noxious emissions from the plants to a large extent.

Of equal importance is the choice of the most efficient constructive solutions for equipment and piping to prevent poisoning leakages, as for instance dry seal pumps, adequate fittings flanges and gaskets, etc.

Another factor to avoid the risk and frequency of pollution is the use of adequate materials resistant to corrosive media. A way to cut down these additional expenses is to turn the noxious agents into valuable products, so that by their turning to account, a partial decrease in the additional costs is achieved. Here are some examples of solutions of technologies applied in our country:

- fluorine recovery from off-gases from phosphate processing;
- partial use of phosphogypsum from phosphoric acid;
- use of CaCO_3 from the calcium nitrate conversion in the nitrophosphate plants;
- turning to account of the ammonium nitrate and the demineralized water from the treatment of waste waters with NH_3^+ contents, in using ion exchangers and regeneration with concentrated nitric acid.

The choice of pollution removing methods through control units, when needed, should be made judiciously; the mere shifting of the noxious matters from the air into the water or vice-versa can by no means solve the problem.

This will do as a first step followed by neutralization-elimination of the noxiousness itself.

1.3. Application of adequate constructive solutions for general/auxiliary facilities on the industrial platform

This refers - first of all - to auxiliary discharging

storing and grinding units of phosphates necessary in phosphorus and complex fertilizers, and of calcium carbonate in case of nitrochalk manufacture, which can be a dust polluting source of the atmosphere. It is recommended that an adequate sealed conveying system should be adopted in close dependence on the handled material. The pneumatic transport is an efficient system that was applied in one of our plants; the system is disadvantageous because of high investment and operation costs incurred.

An important aspect of the problem under discussion is the danger of water being contaminated with possible noxious matter, leakages in the draining system, permeating the soil and the underground water layer. It is also worth mentioning the cooling loops for industrial waters contaminated as a rule - with deleterious components, especially those from sulphuric acid, phosphoric acid and complex fertilizer plants (nitrophosphates included).

From our experience we can state that it is imperative to provide efficient insulations in the building and on manufacturing platforms, wash leakage or spilling to be carefully drained and collected and then directed to sealed sumps. As regards sewers themselves, it is appreciated that the conventional solutions recommending ceramic tubes joined together by union couplings cannot provide a perfect tightness. These tubes have to be replaced by plastic (F.R.P) tubes with possibilities to check their tightness, or in certain cases

by overhead piping mounted on scaffold bridges, more expensive and more difficult to operate.

As for the water cooling systems used for technological plants that may incidentally be contaminated by noxious agents, the stress should be laid on applying closed systems even if there are temporarily sufficient amounts of fresh water to allow an open circulation.

With certain plants, where cooling is achieved by indirect heat transfer, as for instance ammonia, urea, nitric acid plants, the air cooling heat exchangers belittle as much as possible the danger of water contamination. On the other hand, there should be taken into account the possibility to use water cooling towers in which case the resulting purges must be subjected to treatment, if their discharge into the emissary is not allowed.

With the plants provided with direct cooling or where there is a frequent danger of water being contaminated with the cooled medium (sulphuric acid, phosphoric acid, complex fertilizers, nitrophosphates included); the specific cooling systems with overhead piping and corrosion-resistant cooling towers is the safest solution, anyway preferable to that with cooling ponds where the danger of contamination for the soil and freatic water is much greater and harder to control. This aspect shall further be dealt with, illustrated by an example of a nitrophosphate plant.

The disposal of solid wastes from the fertilizer industry is a virtual pollution source. The most important polluting wastes from the fertilizer industry are:

- pyrite ashes and arsenic sludges from sulphuric acid plants (based on pyrites)
- phosphogypsum from phosphoric acid plants.
- calcium carbonate from nitrophosphate plants in case of processes based on the conversion of calcium nitrate into ammonium nitrate.

1.4. Pollution control/signalling systems in plants and factories.

As early as the design stage, or in case of existing plants - later on, control/alarm devices should be installed to signalize the noxious emissions going beyond admissible limits, in plants, manifolds, sewage or discharge points. The maintenance and revision of the systems should be under direct control of the factory head managing staff or higher Bodies. No doubt, such a measure is not sufficient and in any case an Inspection Authority ruling on territorial criteria should be assigned.

Such a control system implemented in Rijiumond (Holland) besides offering the pollution control advantage made also possible cost savings in the involved industries, since, these being warned of the deficiencies occurred, due arrangements for controlling the plant operation at the optimum parameters may be made.

2. Operation

Some experts in environment protection matter are of the opinion that the factor that plays an important part in minimizing the pollution effects is one off educational, psychological order.

The care for a correct operation of the plants, a severe observance of process norms and regulations and a steady run of the equipment and plants designed to trap or treat the noxious emissions from plants or factories is the most outstanding factor for the control of environment pollution.

It stands to reason that the training of the operating personnel with a view to strictly observing the process parameters and maintaining the pollution control systems should be paid special attention.

Any penalty for non-observing the environment protection regulations, can be realistic enough, but to it other factors should be added too: the educational plus the stimulating elements, all these forming a long string of means designed to one and the same effect. The training program in schools, organization of lectures for the renewal of knowledge in plants, and efficient public propaganda are bound to generate a sound public attitude towards environment protection.

Main aspects of environment pollution
caused by Romanian fertilizer industry

Here are below the most important Romanian fertilizer plants, virtual noxious emissions, solutions/processes applied or under research, with the view of further pollution control:

There are considered:

- A = atmosphere pollution (air)
- B = water contamination
- C = soil contamination
- P = possible/incidental pollution

1. Sulphuric acid

out of sulphur			out of pyrites		
A	B	C	A	B	C
SO ₂ , SO ₃ sulphur dust (P)	H ₂ SO ₄ ; SO ₄ ⁻²	-	SO ₂ , SO ₃ pyrite dust, py- rite ashes dusts	H ₂ SO ₄ ; SO ₄ ⁻² As, Se, non- ferrous and iron metal salts (sulphates)	Pyrite ashes containing soluble me- tallic salts, sludge with As, Se and other salts

2. Wet phosphoric acid

A	B	C
F ⁻ ; phosphate/SiO ₂ dusts	CaSO ₄ ; H ₃ PO ₄ ; H ₂ SiF ₆ HF ortophosphates	CaSO ₄ (pneophogypsum) containing H ₃ PO ₄ and F ⁻

3. Single superphosphate

A	B	C
F^- ; SiO_2 , phosphate dust	SO_4^{-2} ; H_3PO_4 ; PO_4^{-3} H_2SiF_6 ; HF	-

4. Ammonia out of methane

A	B	C
NH_3 ; CO (P)	process condensate with: NH_3 ; organic matters; metals (under 1 ppm) K_2CO_3 (P) or $As_2O_3 + As_2O_5$ (P)	-

5. Urea

A	B	C
NH_3 ; urea dust	NH_4 urea	-

6. Ammonium nitrate and nitrochalk

A	B	C
NH_3 ; NH_4NO_3 and $CaCO_3$ (P) dust, NO_x (P)	NO_3 ; NH_4	-

7. Nitric acid

A	B	C
NO_x ; NH_3	HNO_3 ; NH_4^+	-

8. Ammonium phosphates and complex fertilizers with additional nitrate, sulphate urea

A	B	C
F^- ; NH_3 ; NO_x (P), fertilizer dusts	NH_4 ; PO_4^{-3} ; SO_4^{-2} (P) F^- ; NO_3^- (P), urea (p) K^+ ; Cl^- (p)	-

9. Nitrophosphates

(Odda process, with conversion of $\text{Ca}(\text{NO}_3)_2$ to NH_4NO_3)

A	B	C
$\text{NO}_x; \text{F}^-; \text{NH}_3$, phosphate dusts; NPK dusts	$\text{NO}_3; \text{NH}_4; \text{PO}_4^{-3}$ $\text{Cl}(\text{P})\text{K}^+; \text{F}^-$	CaCO_3 , with NH_4NO_3 F and P_2O_5 .

1. Sulphuric acid

In the Romanian sulphuric acid industry the preoccupations and applications have been turned towards air pollution control, by improving the retaining systems of SO_2 and SO_3 gases, as well as towards the arsenic sludge treatment, and the utilization of pyrite ashes.

To decrease the SO_2 amounts in flue gases, the technique of "double absorption" or "double catalysis" has been widely applied these years. By this, conversion efficiency of SO_2 to SO_3 goes up from 98% (in single conversion) to 99.5%.

The decrease of SO_2 amounts in tail gases in case of double absorption as compared to single one becomes even more obvious, as the catalyst activity lowers. Here are below a few comparative data:

Table 2

% final single catalysis	% after layer 3 (average figures from practice)	% final Double absorption
98	95.0	99.6
97	93.5	99.5
96	92.0	99.4
95	90.5	99.3
94	89.0	99.2
93	87.5	99.1
92	85.0	99.0

It results from the above that while the decrease of the final conversion efficiency in case of single catalysis is by 1%; by applying the double absorption it is only by 0.1%.

It goes without saying that by using this procedure, higher investment costs are incurred, and the output obtained as a result of an output improved efficiency, can but partly compensate for the additional expenses. In Mr. I.M. Connor's opinion ("Chemico"), under the economic conditions of 1969 the application of "double absorption" in a plant of 400 t/day H_2SO_4 adds 1 \$/t H_2SO_4 .

We have developed numerous flowsheets based on "double absorption" known ever since 1924, all concerns being focussed on the assurance of an optimum thermal balance of the contact unit, with heat transfer surfaces used most economically.

The results of our studies have led to the following conclusions: for a sulphuric acid line of 600 t/day (on pyrites) the application of "double absorption" will require an additional equipment volume of 430t, out of which 180 t metal, which correspondingly increases the investment costs.

In case of a plant based on sulphur the investment cost increment is 12-18%.

The operating costs for contact plants based on

sulphur are within the following limits:

electric power, by 20-30% greater

cooling water " 10-20% "

maintenance " 10-16% "

indirect expenses:

Pay-off " 12-18% "

Overhead " 2-4% "

Considering the economic disadvantages of the "double absorption" methods, we have developed a procedure of our own that perfectly fits to a fertilizer complex based on ammonia and sulphuric acid.

The procedure consists in absorption of $\text{SO}_2 + \text{SO}_3$ contained in the flue gases in the presence of ammonia and desorption of ammonium sulphite/bisulphite solution with phosphoric acid. The 15-18% SO_2 gases so obtained are sent back to the sulphuric acid plant and the acid ammonium phosphate solution is further processed in the fertilizer plant.

The procedure, ensuring a retaining efficiency similar to that of "double absorption" offers the advantage of retaining SO_3 too, thus taking over the bad effects of possible troubles at the SO_3 final absorption in sulphuric acid plants.

From the point of view of construction, the plant is less sophisticated requiring a lower volume of equipment. So, for processing $45,000 \text{ Nm}^3/\text{hr}$ flue gases containing SO_2 ,

the plant is 75 t in weight, out of which 25 t is acidproof protection material, most of it of ceramics.

The utilities consumption is also reduced, as seen below:

- electric power	60 Kwhr/t ⁺)
	recovered SO ₂
- steam (4 Kgf/cm ²)	3.5 t/t SO ₂
- industrial water	5 m ³ /t SO ₂

+) if flue gases have not an available pressure of 80-100mm WG a fan should be inserted, thus increasing the electric power consumption.

The attached diagram (Fig.1) shows the absorption section within a fertilizer complex.

In one of our plants there operates a unit of the kind, consisting of three absorption trains each processing 45,000 Nm³/hr of 0.2 - 0.4% SO₂ flue gases.

At present, we are developing a new project for a capacity of 65,000 Nm³/hr gases (1.2 %) from a pyrite ashes processing plant.

Fig.2 is an illustration of a plant model consisting of three absorption trains of 45,000 Nm³/hr each.

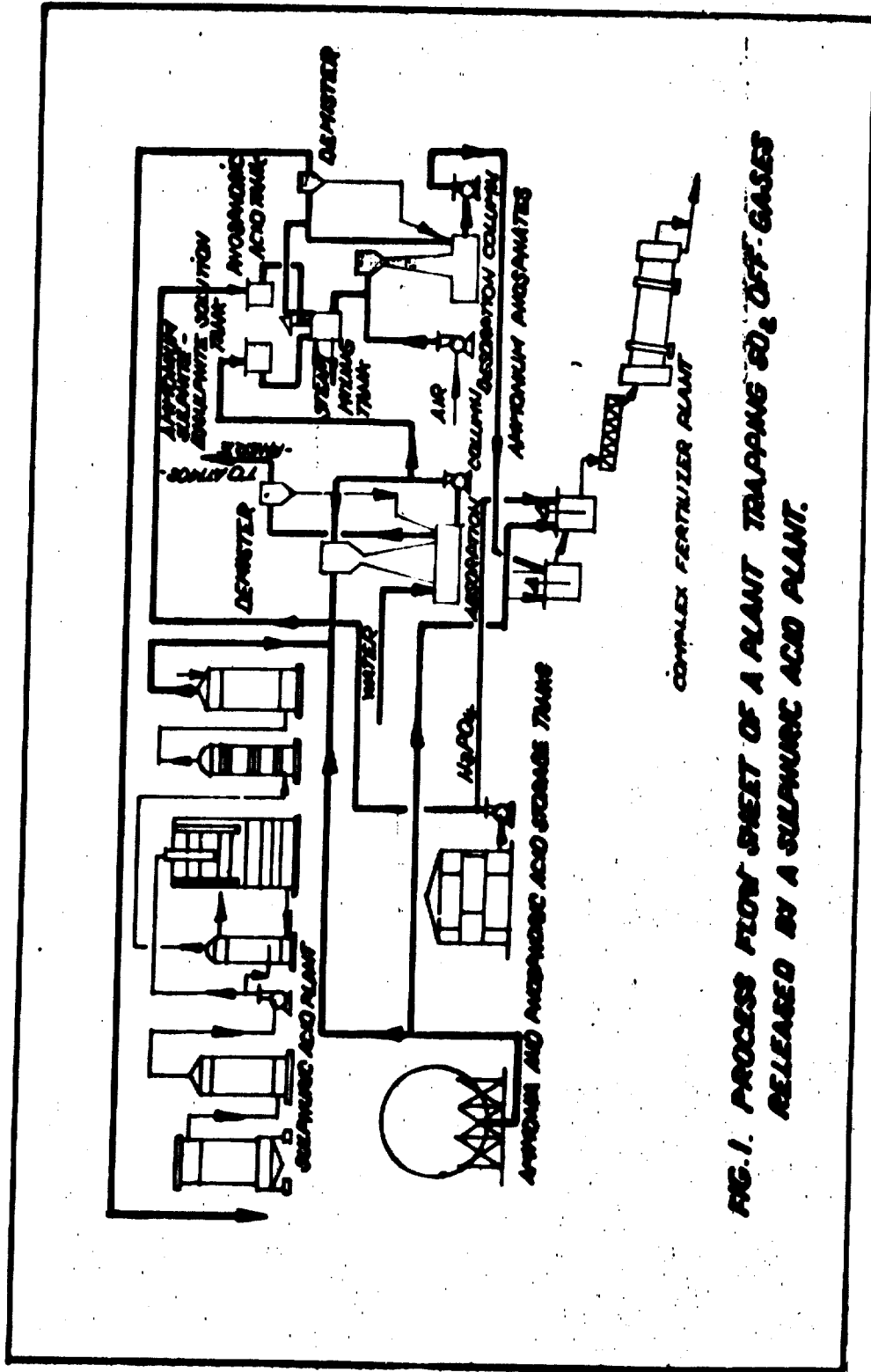


FIG. 1. PROCESS FLOW SHEET OF A PLANT TRAPPING SO₂ OFF-GASES RELEASED BY A SULPHURIC ACID PLANT.

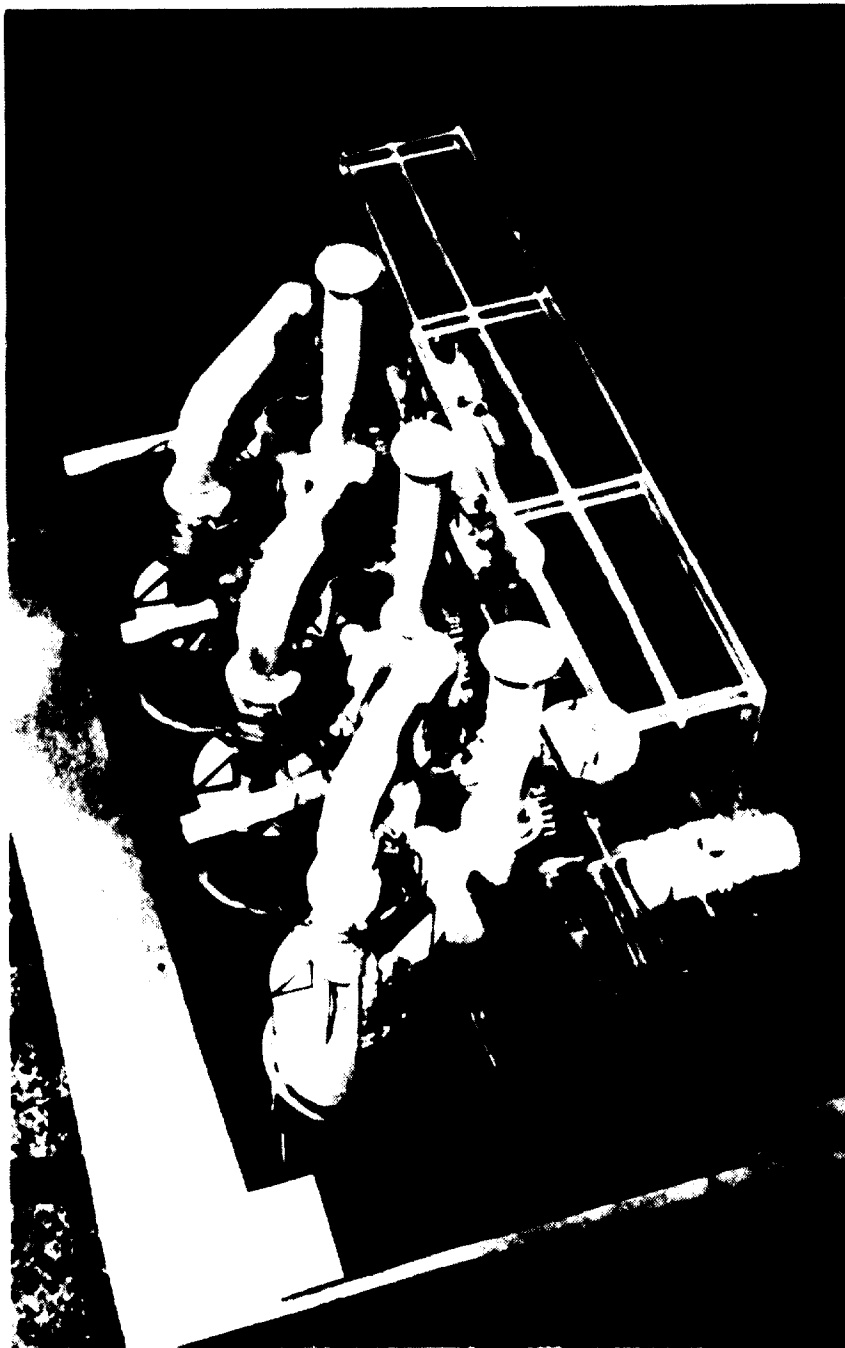


Fig.2. Model of a plant for trapping flue gases from a sulphuric acid plant with a treatment capacity of $3 \times 45,000 \text{ Nm}^3/\text{hr}$.

The sulphuric acid manufacture based on pyrites as raw material also amplify the environmental pollution problems, on account of :

- sludges from gas washing, containing a great number of metallic salts as well as extremely harmful As compounds.
- big amounts of pyrite ashes (0.7-0.75t/t H_2SO_4) the disposal of which is a source of air pollution with dusts, of soil contamination by degradation of neighbouring zones, and of waters got impurified by rain washing the soluble components, mainly non-ferrous/heavy metal salts.

Of course, the analysis of both washing sludges and noxious elements in pyrite ashes is affected by the nature and composition of used pyrites.

To eliminate As from gas wash waters, and sludges we have developed a technology that provides an advanced removal degree of soluble arsenic compounds contained in these sludges by transforming them into insoluble salts. Thus, by treating arsenic waste waters (330 m³/day containing about 3 grAs/l) from a large chemical plant producing over 1,300 t/day sulphuric acid on pyrites, a reduction in the arsenic content down to 1 mgrAs/l is achieved by arsenic retaining procedure.

The problem to control the pollution effects caused

by the pyrite ashes storages from the sulphuric acid manufacture has been studied for years, with a view to turn them to account in metallurgy.

During 1954-1972 a grain pyrite ashes treatment plant of 80,000 t/yr was in operation in Romania. The shutdown of the plant was due to the fact that at present the amounts of ashes come out entirely from flotation pyrites that do not fit to the early applied method.

At present, there is under construction near one of the biggest pyrite-based sulphuric acid plants a unit processing 450,000 t/yr pyrite ashes on the TEC licence (Toyo Engineering Corporation). Here, pyrite ashes, after being treated for the removal of S, As and non-ferrous metals that are rendered profitable, is transformed into a ferrous mineral of high quality to be used in metallurgy. We have chosen the location of pyrite ashes processing plants in the vicinity of the ashes discarding plants to prevent the conveyance of this fine material across long distances which, in addition to extra cost, would increase pollution danger, if common cheap conveying means were used.

After proving the process in the first plant -, we have in mind the expansion of the pyrite ashes processing to ensure the use of the whole stock of ashes likely to be produced in the future by the sulphuric acid plants.

As already mentioned at the beginning of this report,

this is an example of our preoccupations to minimize pollution control expenses, and of our steady endeavour to turn to account the products that are now polluting factors.

2. Wet phosphoric acid

The production of phosphoric acid, widely developed in the last period, is an important factor of environmental pollution.

If we refer to air pollution, the most harmful agent are the fluorine products that are evolved during the digestion and concentration stages, their repartition being greatly determined by the process used and by the nature of the processed phosphate.

One of the first measures we have taken to control air pollution was the exclusive use - at digestion - of vacuum cooling, instead of air cooling of the reaction vats, even in the case of processes based on "single reactor". Thereby, the air amount loaded with fluorine compounds after scrubbing is 3-4 times smaller, which proportionally reduces the fluorine amount vented to the atmosphere.

Likewise, during concentration (with steam, under vacuum) in all plants were provided systems to retain fluorine which is further used for the fluorine salt production, reducing thus the fluorine content in cooling waters.

We consider that the cheapest procedure to prevent contamination is to use a closed loop for the cooling water, the

system being thus designed to provide perfect tightness, and to direct the purges to lime milk treatment stations, where - by precipitation - the most dangerous noxious agents, as F^- , PO_4^{-3} and SO_4^{-2} compounds are retained.

Phosphogypsum, a waste product obtained in large amounts from the wet phosphoric acid processing in a proportion of 4.5-5 to related to 1 ton of P_2O_5 output is by far the most severe problem related to soil/water contamination caused by wet phosphoric acid plants.

The rather alluring idea of "closed sulphur cycle" in the production of wet phosphoric acid - practically demonstrated on full scale by the recent construction of a plant (350 t/day H_2SO_4) at Phalaborwa in South Africa (whose economic operating conditions are unknown to us) does not seem to be a thoroughgoing way to solve the phosphogypsum problem.

Under the present conditions of energy prices, if considered the technology progress in the manufacture of Portland cement, where the fuel consumption is intended to go below 100 Kcal/Kg Klinker, the consumption required by the phosphogypsum processing to klinker (about 2,800 Kcal/Kg) appears altogether uncompetitive.

We have developed a number of comparative economic studies in which data from Romanian industrial plants as well as from literature were considered and were adapted to the conditions in this country. These comparative data are summed up

in the following tables:

Tables 3 and 4 comparatively present certain specific indices for the cases various raw materials are used in the manufacture of sulphuric acid:

Table 3

Sulphuric acid plant: 200,000 t/yr

Index	Raw material				Remarks
	1	2	3	4	
	2	3	4	5	6
1. Investment					
- index	1 ^{x)}	2.1 ^{x)}	6.1 ^{x)}	7.1 ^{xx)}	sulphur investment = 1
2. Produced/consumed thermal energy.					
- steam production t/t H ₂ SO ₄	1.1	1.0-1.1	-	-	
- coke consumption t/t	-	-	0.137	0.137	
- fuel oil consumption	-	-	0.42	0.65	
3. Electric power					
Kwhr/t consumption	25	100	150	250	

x) According to IPRAN/IPROCHIM designs

xx) According to literature.

Table 4

Economic evaluation of sulphuric acid production
(capacity, 200000 t/yr)

Comparative indices

Indices	M/U	Procedures based on:			
		1 sulphur	2 40% pyrite	3 anhy- drite	4 dry phospho- gypsum

1. Raw/energy materials (annual consumption)

		1	2	3	4	5	6
a. Sulphur material	tons	68,000	186,000	340,000	380,000		
ruling price	\$/t	25	10	1.3	-		
b. Electric power	MW	17,000	20,000	30,000	50,000		
Fuel oil equivalence	tons	5,400	6,400	9,600	16,000		
ruling price	\$/t	25	25	25	25		
c. Fuel oil	tons	-	-	84,000	130,000		
Total fuel oil	tons	5,400	6,400	93,600	146,000		
d. Metallurgic coke	tons	-	-	26,400	26,400		
ruling price	\$/t	-	-	20	20		
Total value	mil.\$	1.8	2.0	3.3	4.2		

2. Product evaluation (annual)

a. Sulphuric acid	tons	200,000	200,000	200,000	200,000		
ruling price	\$/t	20	20	20	20		
b. Steam	tons	220,000	200,000	-	-		
Fuel oil equivalence	tons	17,600	16,000	-	-		
c. Pyrite ashes	tons	-	140,000	-	-		
ruling price	\$/t	-	3.0	-	-		
d. Cement	tons	-	-	185,000	185,000		
ruling price	\$/t	-	-	11.0	11.0		
Total value	mil.\$	4.4	5.0	6.0	6.0		

1	2	3	4	5	6
3. Currency savings					
(2 minus 1)	mil.\$	2.6	3.0	2.7	1.8
4. International					
market costs	\$/t	10.0	13.0	16.0	22.0
index		100	133	160	220
5. Personnel					
requirement	No.off	80	100	400	500

The YOWA University experts who studied the process of calcium sulphate decomposition to SO_2 and CaO , claim that this procedure is by far more economical than that of Portland cement manufacture.

Another way to use phosphogypsum would be its application as building material in plaster boards and blocks.

The plaster boards selling possibilities are limited and the phosphoric acid manufacturers - importers of phosphates - have to face certain technological difficulties in obtaining the right phosphogypsum quality due to the necessity of changing rather frequently the phosphate supply sources.

In Romania, on the basis of studies undertaken, the problem of phosphogypsum disposal is partially solved by using it for the following purposes:

1. Sodium sulphate manufacture by the reaction with Na_2CO_3 on a procedure of our own, is used in a plant for many years.

2. The use of partly dried phosphogypsum as an amendment of soils with a higher sodium chloride content was experienced and is to be commercially extended.
3. There was under research - and it is to be extended on an industrial scale - the possibility to use phosphogypsum as setting time controller at the manufacture of certain Portland cement grades

All these utilizations permit but the use of low quantities of waste phosphogypsum from phosphoric acid plants. That is why, considering the present level of knowledge and technological possibilities, the efficiency of this waste disposal should be judiciously approached, in close dependence on location, economic value of neighbouring lands, soil geological features underground water layers of socio-economic importance.

Considering the factors above, the following suggestions are thought most appropriate for the waste disposal:

a) Hydraulic conveyance of phosphogypsum into ponds, whose surface could be after filling reclaimed by covering it with a vegetable layer in view of further use as agricultural production area.

b. Dry disposal in heaps of this waste products by using mechanical means and taking previous measures to make the land surface waterproof and to collect the rain waters flowing down this piled material.

The solution is imperative in those zones where small available ground areas exist or where they have an important economic value.

3. Single/concentrated superphosphate

In the manufacture of the above fertilizers fluorine gas emissions represent - at almost the same way as in the case of wet phosphoric acid production - the most noxious atmospheric agent.

The most important fluorine emissions occur in two stages of the process: reaction and storage/aging.

In Romania, all the superphosphate plants are equipped with 2-step water washing systems of the fluorine gases from the reaction to recover them as H_2SiF_6 intended to be used in fluorine salts manufacture.

Since the fluorine retaining efficiency (with water washing) could not ensure the removal within admissible limits in the gases released to the atmosphere, there was carried on research and it is now experimentally applied in one of our superphosphate plants - an additional washing with some alkaline solution: it does provide a satisfactory washing of fluorine in reaction gases.

The fluorine gaseous emissions in the curing halls, is a more complex problem implying much higher expenses, since the storages are very large and the zone of dispersion to the atmosphere spreads across large areas.

To control fluorine emissions from these curing halls there should be provided suction units with gas washing facilities, thus ensuring 2-3 air changes per hour.

An experimental project providing the installation in the curing hall of several gas scrubbers with a capacity of 100,000 m³/hr. using a Na₂CO₃ diluted solutions, requiring a total installed power of 60 Kw is in course in Romania. Thus, a fluorine retaining efficiency of 90% is achieved.

Progress in turning to account the
fluorine recovered from fertilizer
plants.

In order to control the pollution degree in the phosphatic fertilizer industry, our phosphoric acid/superphosphate plants are furnished up with washing systems of fluorine gases on which bases the entire fluorine salts industry has been developed.

Thus, a double effect was attempted and proved successful: pollution control on one side and turning to account of a valuable compound - fluorine - by its transformation into useful products.

In this sense, we are producing Na₂SiF₆, NaF, AlF₃, cryolite (AlF₃.3NaF).

There are in operation, based on the OSW Linz licence, three aluminium fluoride plants totalling up an output of 7,000 t/yr.

The fluorine recovery from H₂SiF₆ into AlF₃ was but partial, as an important amount of fluorine was still remaining in the mother liquors that was passed to treatment in a station

where fluorine was retained as insoluble waste, before being discharged into the river.

ICECHIM's research work in co-operation with the Năvodari Plant, has led to the development of a procedure enabling the turning to account of most fluorine from these mother liquors (from the production of AlF_3) as cryolite, thus obtaining an output of 0.3t cryolite/lt AlF_3 , so that at present all mother liquors from AlF_3 plants are processed to cryolite. In this way the fluorine emissions likely to contaminate the waters and the pollution control costs were reduced.

In Romania, on the line of fertilizer plant fluorine trapping and processing, a great number of research works have been undertaken, having in view the atmosphere/air pollution control and a most efficient processing of retained fluorine into products of high economic importance, which contributes to the cutting down of pollution control costs.

All research, studies, and their application in practice on an industrial scale were aiming at many important directions, from among there can be mentioned:

- increase in retaining efficiency of fluorine from gas, emissions from fertilizer plants.
- reduction of P_2O_5 content in H_2SiF_6 from the phosphoric acid production, for its use in AlF_3 manufacture.
- release of ever larger amounts of fluorine from the phosphoric acid manufacture.

- cryolite processing from AlF_3 production mother liquors.
- production of high quality cryolite out of H_2SiF_6
- efficient treatment of fluorine containing waste waters, to reduce their content under the admissible sanitary limits.
- designing of treatment stations for fluorine containing cooling waters (from nitrophosphate plants) to lower the contamination degree of freatic water where such plants are located.

4. Ammonia

In the ammonia production, the modern plants are based on the Kellogg licence; for process condensates with a critical content of NH_3 are provided stripping columns to reduce NH_3 down to 20 ppm.

5. Urea

An up-to-date urea plant of 1,300 t/day, discharges about $40 \text{ m}^3/\text{hr}$ process waters with about 100 ppm NH_3 and 300 ppm urea.

Periodically - at intervals of 3-4 days - there are collected from washings and purges about $40 \text{ m}^3/\text{hr}$ water with a variable content of noxious matters, consisting of NH_3 , urea, CO_2 and oil; for these are provided retaining sumps and treatment stations. The emissions therefrom to the atmosphere consist of $1,600 \text{ m}^3/\text{hr}$ gases with 1.6% NH_3 (by volume) and of cooling air from the prilling towers, which means $500,000 \text{ Nm}^3/\text{hr}$, with 40 mgr NH_3/Nm^3 and 50 mgr urea dust $/\text{Nm}^3$.

These emissions have been so far considered sanitarly allowable; however, we have very much in mind some possibility to subject the cooling air from the prilling towers to washing too.

6. Ammonium nitrate and nitrochalk.

An ammonium nitrate plant of 1,000 t/day provided with prilling towers and prilling devices would discard condensates ($7.5 - 8\text{m}^3/\text{hr}$) with $1.5-3\text{gr NH}_4\text{NO}_3/\text{l}$ and $2\text{ gr. NH}_3/\text{l}$.

As for the atmosphere, it is affected by high air volumes released from prilling towers (about $500,000\text{ Nm}^3/\text{hr}$. with a content of 100 mgf/m^3 dusts) and by the prills conditioning (with cooling air) ($200,000\text{ Nm}^3/\text{hr}$ with 150 mg/Nm^3).

Considering the environment protection limitations imposed by neighbourhoods, NO_3^- noxiousness for human being and animals, and the expenses incurred by the rapid plant corrosion, it is imperative to study the necessity gas scrubbing with the involved charges needed by the treatment of wash waters, a rather difficult matter.

Atmospheric pollution is less severe if different granulation units, such as tray granulator (in a small plant) or spherodiser are used instead of prilling towers.

Seeing the danger by waters being contaminated with NH_4^+ and NO_3^- common to all plants in a nitrogen fertilizer complex, we have paid great attention to this problem by developing ample comparative studies, designs and research work.

As a result of this activity, we have developed our own procedure to treat NH_4^+ and NO_3^- containing waters by DUOLITE type ion exchangers produced by the French firm - DIAPROSIM. The practice has demonstrated that this is the most economical and efficient treatment for waste waters with rather low noxiousness, as resulting from nitrogen fertilizer units.

A comprehensive report on our research work was delivered at the "Seminaire sur l'Industrie Chimique et l'Environnement" - Varsovie (Pologne), 3-8 décembre 1973, under the control of the "Comission Economique pour l'Europe - Comité de l'Industrie Chimique". The paper bears the title "LA PURIFICATION DES EAUX RESIDUAIRES DEVERSES DES USINES D'ENGRAIS AZOTES" by eng. A. Arion (IRPOCHIM).

Here is a summary of the work:

The IPOCHIM procedure consists in the treatment of ammonium (NH_4^+) and nitrate (NO_3^-) waste waters in a complex plant with moving bed ion exchangers where the waste waters are completely demineralized and are recycled to supply steam boilers.

The ammonium/nitrate ions retained on cation/anion exchanging resins are eluted with 56% HNO_3 , 18% NH_3 respectively;

the 20-28% ammonium nitrate solutions are concentrated down to 74% and turned to account in ammonium nitrate plants.

Ion exchanges are carried out in moving-bed ion exchange columns, (complete automatic), where the ion resin in closed circuit goes across loading, exhaustion, conditioning, regeneration and washing sections according to a program.

To obtain highly concentrated ammonium nitrate solutions, ion resins are regenerated with concentrated agents: 47-60% HNO_3 and 17-20% NH_3 .

With this aim in view, IPROCHIM in cooperation with DIA-PROSIM, as the manufacturer of DUOLITE ion resins, have developed a regeneration technique and a procedure to obtain specific resins strongly resistant to highly concentrated regenerants.

The process was experimented in a pilot plant and will be applied on industrial scale in the fourth quarter of 1974 in a plant with $80 \text{ m}^3/\text{hr}$.

The procedure offers the following main advantages:

- Through treatment of waste waters with NH_4 and NO_3^- ions.
- Complete recovery of NH_3 and NH_4NO_3 as a 20-28% ammonium solution.

- Production of highly pure demineralized water
(0.3 - 0.5 μ S/cm)
- Possibility to treat waste waters containing NH_4^+
and NO_3^- ions, variable with time, respectively:
0.5 - 10 gr/l NH_4
0.5 - 15 gr/l NO_3
- Use of highly concentrated regenerating agents:
47-60% HNO_3 ; 17-20% NH_3 .
- Advanced automation
- Safe Operation



Fig. 3

Partial view of the pilot treatment plant for waste waters from nitrogen fertilizer plants.

7. Nitric acid

In nitric acid plants, nitrogen oxides emissions (NO_x) from absorption flue gases are the most harmful polluting agent.

The nitrogen oxides content of flue gases may vary from 2000 to 200 ppm NO_x , in dependence on the plant type and operating conditions.

We have used two ways to control NOx flue gases.

- for early plants releasing large amounts ^{of} NOx flue gases a catalytic combustion method studied at Timișoara Chemical Research Institute, is being now experimented on pilot scale.
- in the more recent plants (based on absorption at 9 ata pressure) with 400 ppm NOx gas emissions, constructional improvements were operated on the absorption column, thus reducing NOx content down to 200 ppm.

A comprehensive report on these achievements was delivered at the seminary in Warsaw (3rd-8th of December, 1973) bearing the title "Reduction de la quantité des oxydes d'azote des gaz résiduares résultés à la fabrication de l'acide azotique" par E.Cristescu, I.Horescu, V.Medeleanu.

8. Ammonium phosphates and complex fertilizers with addition of nitrogen and potassium in various forms

The manufacture of these fertilizer grades causes air pollution by NH₃ emissions, fluorine gases and dusts.

The amounts of noxious emissions to the atmosphere, the harm they may cause (this being related to their analysis) are in close dependence on the adopted process, the product grades, the gas washing/dust trapping efficiency as well as on the adopted granulation equipment.

By adopting and improving technologies developed abroad, we have reached the conclusion that the spherodizer granulating-drying unit is most convenient because it enables the control of noxious emissions. Yet in addition to that, the flue gases should be purified by the wet process.

As to ammonia emissions from the neutralization, they should be washed with phosphoric acid, which is at the same time a pre-ammoniation operation. Wash waters and incidental leakages ought to be collected and sent to a concentration station then sent back to the process. Since concentration is expensive enough, it requires a maximum reduction of these amounts, attempts being made to obtain as highly concentrated solutions as possible.

9. Nitrophosphates

The control of environment pollution caused by nitrophosphates plants, - especially by those on the Odda process, to which $\text{Ca}(\text{NO}_3)_2$ conversion to NH_4NO_3 is added, - appears as an extremely complex problem if viewed in relation to the environment protection limitations, quite severe now.

In this case, we have to face the accumulation of multiple noxious agents generated at a time by phosphoric acid, nitric acid, ammonium nitrate and ammonium phosphates likely to cause the air, water and soil poisoning.

From the reasons presented at the beginning of this

paper, the problem had not yet been satisfactorily solved in practice because, on the whole, the said processes had been developed long ago, when pollution control aspects were not seriously considered; moreover, some recent plants, where the pollution control was neglected were shut down by Authorities.

In the adoption of the process for the nitrophosphates production in four large complex fertilizer plants, being aware of the harm they may do to the environment, we developed studies and research works, followed by amendment and changes in the initial project solutions and giving due consideration to pollution control problems.

Our concerns were mainly focussed on the following aspects and operations:

- Separation of the acid water loop from that of alkaline water, that were originally circulated together.
- Acid gases from the digestion, mainly containing F and NO_x (representing 15% of the gas total volume) are washed in a closed loop with a substance able to decompose most of NO_x, thus substantially decreasing the nitrite/nitrate contents in the wash water. The absorbed fluorine precipitates and separates by settling.
- Alkaline gases - main heat carriers - from neutralization and concentration, mainly containing

NH_3 are washed with an acid solution, so adding salts (especially NH_4NO_3) to the wash water. This water also used as coolant must be cooled in order to be recycled to the plant. The cooling with ponds was initially considered as a possible way for this. It must be kept in mind that this water after some time gets into a dilute salt solution (5-6%) in which NH_4NO_3 content prevails.

In Romania's climatic conditions, a cooling area of about 15 ha would be necessary for a plant with a capacity of 150 t/day P_2O_5 .

Since the operations to make this area impervious to infiltration and to prevent the ground water contamination turned out expensive, three of our four nitrophosphate plants were provided with corrosion-proof cooling towers and with above-ground pipes, which eliminates any risk of uncontrolled leakage.

The solution has proved safer and more economical.

The purge from the cooling system plus incidental leakages and contaminated waters from the periodical washing of units, collected in special sumps, are partly sent back to the plant for washing CaCO_3 precipitate on the filter, while for the remaining water a concentration station was provided where the valuable components are recovered.

- A series of constructive measures, such as floor/

channels insulating, use of dry-sealed pumps, of tight safe pipe lines through which noxious matters are running, were considered in the detail designs in order to minimize leakages, or, if unavoidable, to collect and drain them out of the plant.

The liquid effluent collecting system is thus designed to prevent any possible interference with the general sewage system of the industrial complex; the amount of purge, wash, leakage water is entirely collected and returned to the process with or without a pretreatment.

From the $\text{Ca}(\text{NO}_3)_2$ conversion unit there results a big quantity of CaCO_3 precipitate with about 20% moisture, 2-3% NH_4NO_3 and 1% P_2O_5 . If stored with no regard to protection rules, this material containing soluble polluting components could become a polluting agent while penetrating into the soil, or contaminate the ground waters if washed down by the rain.

The CaCO_3 precipitate being a reactive product that cannot be used as such in the nitrochalk manufacture in using know processes. One of our fertilizer plants in cooperation with IPROCHIM has developed a new process that makes use of this product in the high quality nitrochalk manufacture.

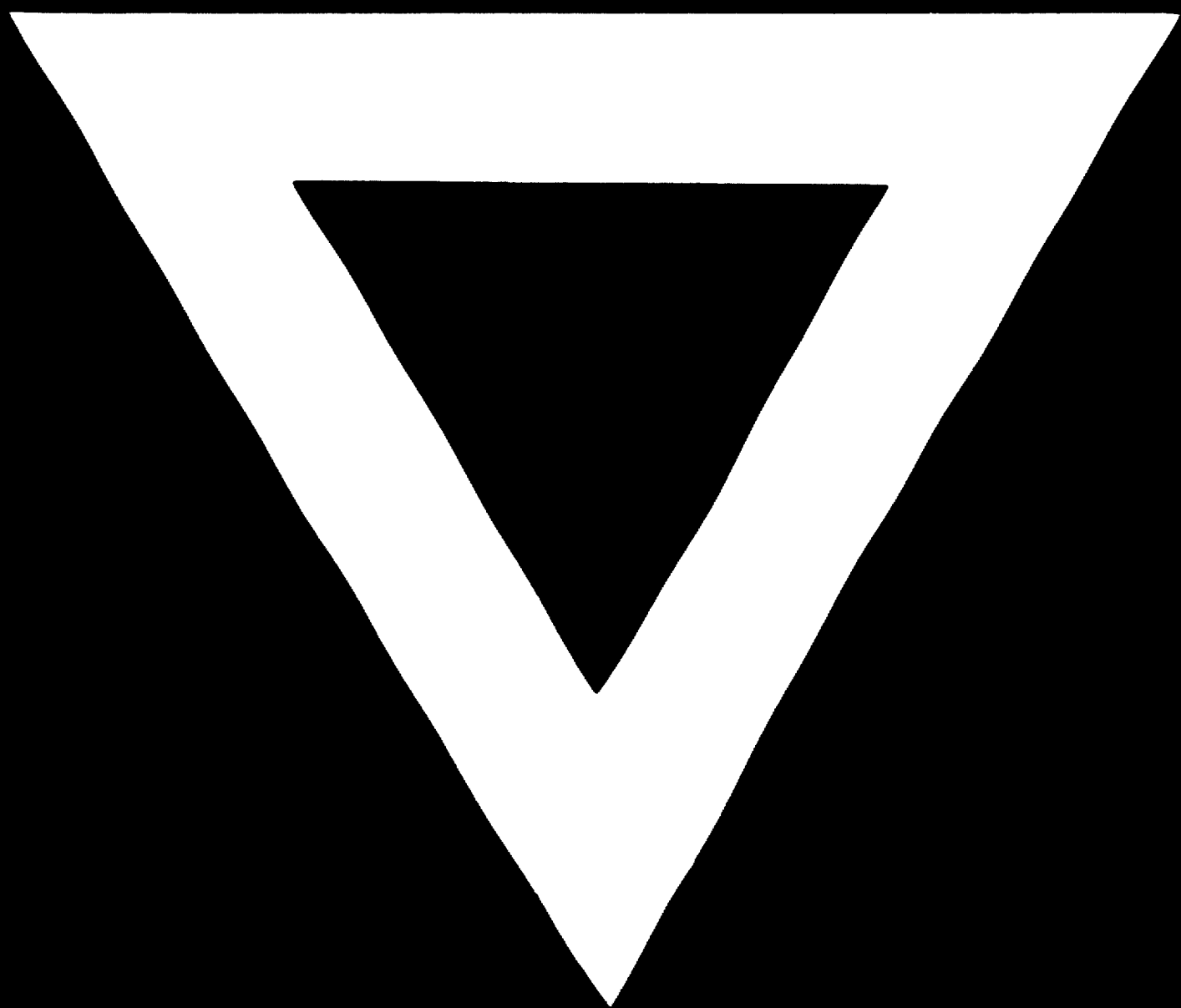
This utilization of CaCO_3 and the application in agriculture of CaCO_3 from nitrophosphate plants has imposed the

achievement of CaCO_3 drying units for all nitrophosphate plants, thus solving the pollution problem caused by this waste.

Another concern of ours is now separation and turning to account of fluorine from the nitrophosphate production, and we have carried on a lot of research with this problem.

We have endeavoured in this report to make known our attempts, interest and achievements in the Romanian fertilizer industry, aiming at minimizing the environment pollution caused by a vital industry, our keen desire being to do away with its bad effects and emphasize only its contribution to making life better on our planet.





74. 10. 9