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## WINDMILL HOLLAND AND ITS ENVIRONMENT

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## INTRODUCTION

In practically every country nowadays, environmental matters no longer belong to the side-issues of the fertilizer business, but have become topics of primary importance. For Windmill Holland this has been the case for a long time and has been brought about to a great extent by the special geographic situation of the site. When the company was founded in 1920, the works was situated some distance from the town of Vlaardingen, but since then the town has grown to such an extent that nowadays the Windmill site lies within the built-up area.

This has not been the only factor : the town of Vlaardingen lies in the "Rijnmond" area, one of the largest industrial areas in the world with a particularly strong concentration of chemical and petrochemical production. With the rapid expansion of this industry, particularly during the sixties, the pollution level also went up and this led to growing resistance by the population of the area who wanted to keep their living-climate healthy and pleasant.

In this context Windmill Holland has been in a rather difficult situation, particularly since our works is one of the few potentially polluting companies at the northbank of the river - the majority of the large chemical and petrochemical companies being located at the southbank, just opposite Windmill. In the eyes of many Vlaardingen citizens, Windmill was a major offender and we became one of the main targets of action-groups, although on many occasions this was

unjustified. However, as a result of this situation, interference by the authorities also became relatively intense. Of course, all this has influenced our own activities and we believe that Windmill has taken more measures than the average company, notably on air pollution, to improve the situation, both with regard to the abatement of emissions as well as to the monitoring of such emissions.

We thought that it would be of interest to many of you to tell you what we do in the field of anti-pollution activities and what practical experiences we have.

#### AIR POLLUTION, EMISSION POINTS AND ABATEMENT

As already mentioned in the introduction, the main emphasis on environmental activities at Windmill Holland during the last decade or so has been in the area of air pollution.

Windmill Holland is a producer of sulphuric acid, phosphoric acid, single and triple superphosphate, mono-ammonium-phosphate, ammonium nitrate solution, compound fertilizers, feedgrade phosphates and silicofluorides. This range of products implies the following potentially emissible materials :

- dust,
- $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ ,
- $\text{HF}$ ,  $\text{SiF}_4$ ,
- $\text{NH}_3$ ,
- water vapour,
- mists, notably mixtures of  $\text{NH}_3$  with acid gases already present in the atmosphere.

The approach at Windmill Holland has always been to try if possible to attack the pollution problem at the source. If not possible, abatement with filters, scrubbers, etc. has been applied. In the following paragraph a number of examples are given.

#### Dust

##### (a) Unloading of bulk materials from ships

Still one of the most important potential emissions at Windmill Holland is dust which can escape when ships or barges

with powdery materials are unloaded with cranes. Largest in quantity by far is phosphate rock ; others being potassium chloride, potassium sulphate and some other materials in lower quantities.

The measures that we have taken are :

- ensuring that not too fine powdery materials are purchased,
- if this cannot be avoided, transport the powder by closed lorries rather than by ship,
- the strict adherence to internal instructions, in connection with wind direction and velocity (in this connection we have installed a windmeter instrument which records in the office of the mechanical handling supervisors),
- the use of special completely-closed grabs which give relatively little spillage (see figure 1),

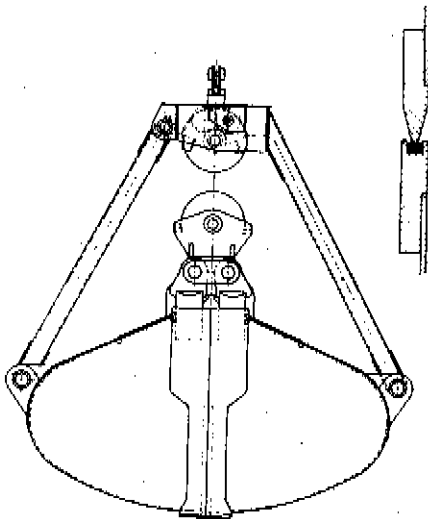


Figure 1

Fully-closed grab

- the use of hoppers which are designed so that when the grab discharges and the air wants to escape from the hopper, it is trapped by rubber flaps (see figure 2)...

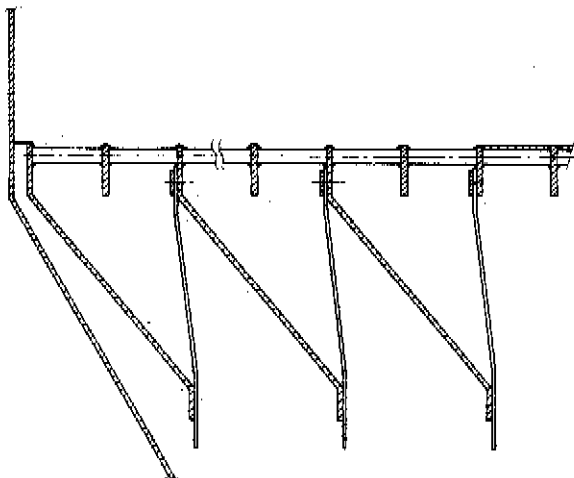


Figure 2

Hopper with  
air-lock using  
rubber flaps

(b) Bulk loading of ships

A considerable amount of granular fertilizer is dispatched in bulk by ship and also some powdery material has to be loaded into barges. To minimize dust levels, we use a telescopic device which brings the material as near as possible to the bottom of the ship or the surface of the already discharged material (see figure 3).

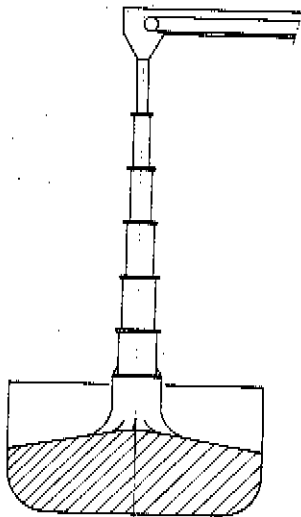


Figure 3

Bulk-loading of  
ships

This device suppresses the dust to a great extent, but it is not sufficiently effective to avoid the emission of some coating dust which comes off the granules. We still have not found a coating agent applicable in our plant which gives complete binding onto the granules. If somebody in the audience knows an effective coating agent which does not come off at all, we kindly invite him to pass on his suggestion to us.

(c) "Process" dust

In this category is dust which is generated through mechanical handling of solids in elevators and at discharge points of conveyor belts, but also dust which is formed in pulverizers, screens and what is entrained e.g. from granulation, drying and cooling equipment.

The way in which the gas is treated depends on the specific case - we use cyclones, bag-houses and wet scrubbers or combinations of these.

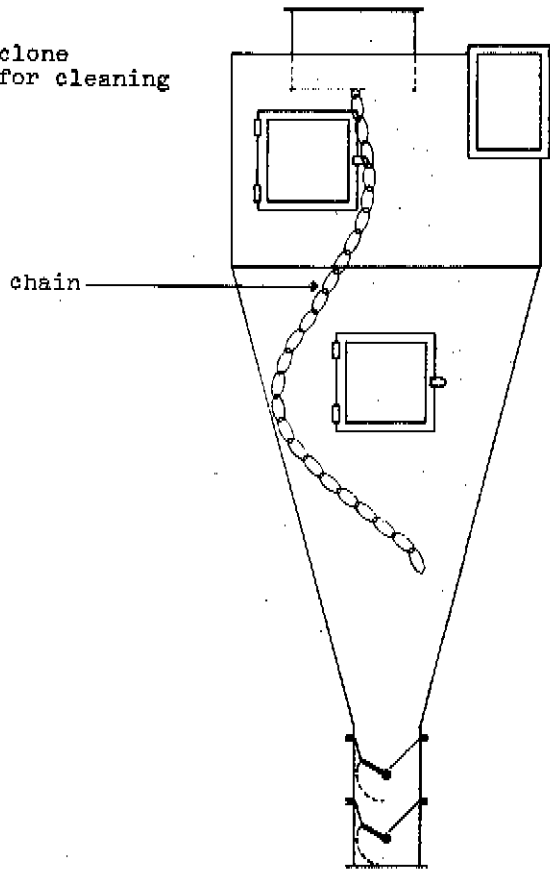
On cyclones we would like to remark that it is our experience that in phosphatic fertilizer plants the so-called "high-efficiency" cyclones are not always effective, because often the security of service is not good. In more difficult cases (materials which tend to give build-up), we prefer larger-diameter cyclones which are easy to clean. For the powder discharge we used to apply "partly-collapsed" plastic bags, but these have been replaced now by double-reciprocating valves (see figure 4).

Of the 30 or so bag-filters which we have on our site, we may remark that most of these are of the conventional "nose"-type in which the dust sets on the inside of the tubes and is knocked off by shutting one compartment and vibrating the tubes under backflow (see figure 5a).

For the more difficult cases we have tended over the last few years to switch to a type of filter in which the dust is trapped on the outside and cleaning takes place during normal operation by intermittent pulses with compressed air (see figure 5b).

Figure 4

Large-diameter cyclone  
with easy access for cleaning



On our site we have approximately 15 wet scrubbers for dust control. Almost every type of scrubber described in literature is in use at Windmill Holland. Our principal type is the conventional wash tower ; in many cases it is an old once-through spray tower, which we have optimized to get a more efficient and less water consuming system : i.e. by increasing the number of sprays, extending the unit with a circulation system, introduction of internals such as moving-ball beds, demisters and addition of more instrumentation (see figures 6a and 6b).

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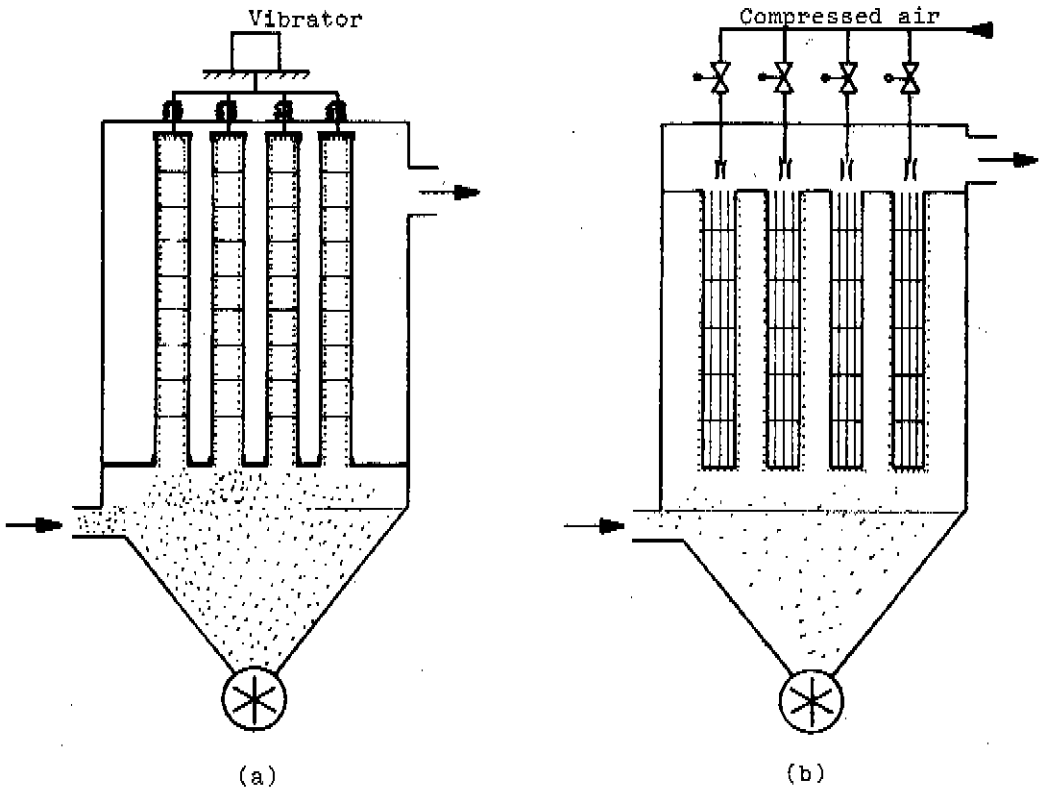
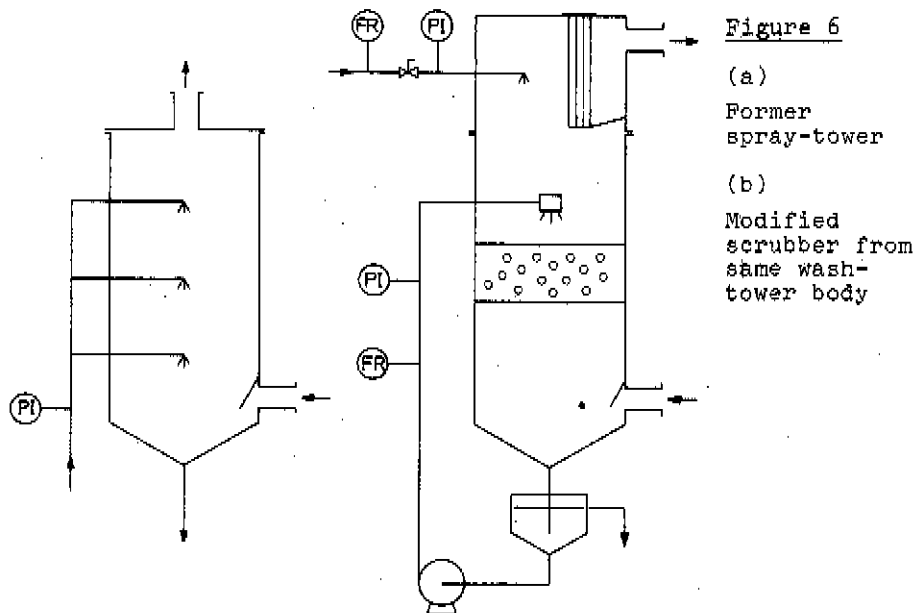


Figure 5

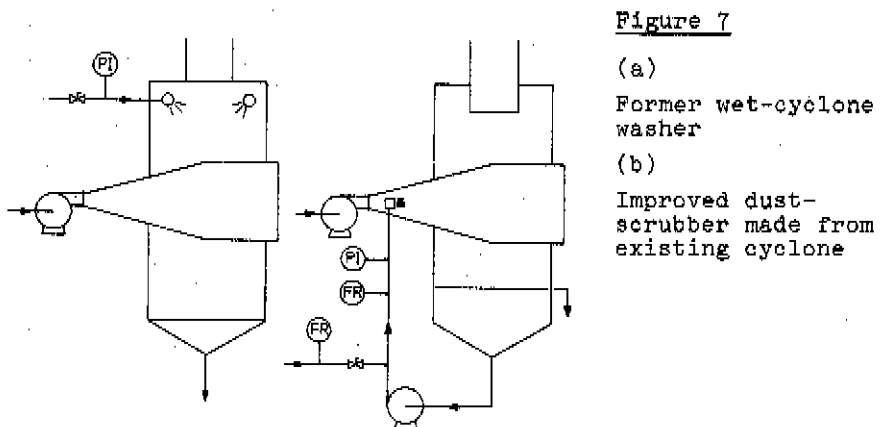
Two types of bag-filter

When working with circulation systems, we avoid as much as possible the use of fine sprays with narrow passages, because these tend to get blocked.



Another example of the successful improvement of an existing scrubber is shown in figures 7a and 7b.

The modified system is a gas-motivated venturi-scrubber, in which the circulating suspension is distributed very roughly in the high-velocity gas stream.





With regard to somewhat more advanced systems, we may say that we have good operating experience with scrubbers of the self-induced spray type. These are able to handle high dust loadings with low water consumption and no sprays or outside recirculation systems are required. The scrubbing efficiency is very good with a moderate pressure drop.

An important item is the demister. We have operating experience with cyclones, lamella eliminators (horizontal and vertical types) and axial flow entrainment separators.

We prefer the vertical lamella-demister as indicated in figure 6b, because of good separation efficiency at low pressure drop, compact construction and because the construction allows easy access for cleaning. Good scrubbing is of course essential for security of operation.

#### SO<sub>2</sub>-, SO<sub>3</sub>- and H<sub>2</sub>SO<sub>4</sub>-mist

Windmill Holland operates two relatively small sulphuric acid plants of the single absorption type (sulphur burners) which were built in 1956 and 1962 respectively. The plants were built by an English contractor and at that time emissions complied with the standards set by the British Alkali Inspectorate. In the late sixties the authorities no longer accepted the emissions which were released at relatively low stack level and something had to be done. In 1968 we extended the no. 1 plant with a Lurgi Sulfacid unit, a system in which the off-gas is after-treated in a water-irrigated bed of active carbon and where part of the SO<sub>2</sub> is converted to SO<sub>3</sub>, which is absorbed. Our experience with the system is not very positive. While 90% "scrubbing"-efficiency was anticipated, only 50-70% was achieved in practice and this only after a long period of experimentation and at the unforeseen extra cost of a considerable amount of steam (0.25 t/t H<sub>2</sub>SO<sub>4</sub>).

The results were anyway not sufficiently positive to consider extending the no. 2 plant with such a unit and therefore it was later decided to provide this plant with a wire-mesh demister and a 100 m high stack.

Any new plant to be built on our site would have to be of the double absorption type and to be provided with efficient

demisting devices. In 1969 the considerable  $\text{SO}_2$ -emissions from steamboiler and drier-stacks were brought down to nil by converting the systems for the use of natural gas.

### HF and $\text{SiF}_4$

#### (a) Dihydrate phosphoric acid plant

Scrubbing of the reactor off-gases takes place in a simple once-through water-spray system and this is perfectly adequate. The scrubbing liquid is drained as it contains only a small quantity of fluorine. Up to 1966 all concentrated phosphoric acid was made in submerged combustion units which were provided with fluosilicic acid recovery units of the well-known Doyle-type followed by once-through water-fed scrubbers of the same design for condensation and further reduction of the F-content of the combustion gases.

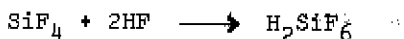
The off-gases from evaporators and the reactor battery were released through two 80 m high stacks in parallel. It proved to be necessary to install demisters at the top of these stacks, because droplets with fairly high F-concentrations formed by condensation, were entrained with the gas stream.

Later, when the authorities demanded still lower emission levels, we started to use the stacks themselves as extra scrubbing units by injecting water at about half-height. This system provided sufficient transfer units to attain the desired emission standard.

Since 1966 we have gradually replaced the submerged combustion units by steam-heated vacuum evaporators with total condensation. There were two reasons :

- to suppress the heavy plumes on the 80 m high stack (being a "pollution-symbol" of the town of Vlaardingen),
- to avoid the considerable  $\text{P}_2\text{O}_5$ -losses which were inherent in the submerged combustion system as it was practised in our case.

All vacuum evaporators are provided with fluorine recovery units. When we concentrate the filter acid from 28 to 52%  $\text{P}_2\text{O}_5$ , there is no problem with  $\text{SiO}_2$ -formation in these scrubbers due to the composition of the gas. In rough terms the following reaction takes place :



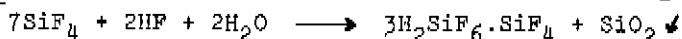
(Silica-number S =  $\frac{\text{gramatoms Si} \times 6}{\text{gramatoms F}} = \text{approximately } 1.0$ )

(b) Hemihydrate Phosacid plant

In this plant which operates on a process developed by Fisons Ltd., we directly manufacture a 50%  $\text{P}_2\text{O}_5$ -acid under conditions of high concentration and temperature in the reactor battery. Under these circumstances, the fluorine is released :

- at the slurry-surface in the reactors, from where it is sucked away by the ventilation system,
- in the vacuum cooler,
- at the surface of the filter, from where it is sucked away by the ventilation system,
- in the filter vacuum system.

Scrubbing is not a simple operation due to the fact that  $\text{SiO}_2$  is formed, roughly according to the following equation :



(S = approximately 1.4)

The gas ventilated from the reactor battery and filter is scrubbed as shown in figure 8.

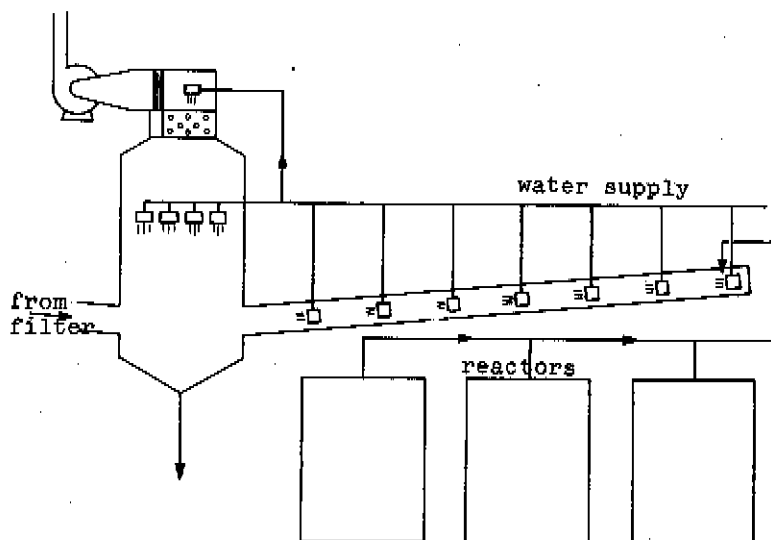
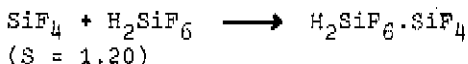


Figure 8 - Ventilation/scrubbing system of hemi-plant

This is a once-through system designed carefully in such a way that at any spot where  $\text{SiO}_2$  could form, it would be directly flushed away.

It should be mentioned that the bed of moving balls at the top of the spray-tower was added later. Before it was installed, the scrubbing efficiency of the system was not sufficient to keep the demister free from  $\text{SiO}_2$ -deposits. The ball-bed proved to give surprisingly good efficiency with no fouling whatsoever, enabling the demister to operate satisfactorily. Emission from the stack is now very low.

The gas from the vacuum cooler passes through a fluorine-recovery system before it goes to the condenser. Being a circulation system it was very difficult in the beginning to keep it going, again because of the  $\text{SiO}_2$ -precipitation. At present the system operates successfully since we pass the fluosilicic acid which is prepared in the dihydrate plant through the scrubber. As long as  $S \leq 1.20$ , no  $\text{SiO}_2$  is formed :



The original design of the vacuum system of the filter was no different from that of a conventional dihydrate plant : the gases were sucked from the filtrate air-separators through a condenser to a water-ring vacuum pump. It soon became clear that the condenser did not wash out the fluorine satisfactorily and the vacuum-pump had to do the final scrubbing. As a result the system often had to be cleaned of  $\text{SiO}_2$  and the pump eroded/corroded rather quickly.

The problem was solved by replacing the conventional direct-contact condenser by a specially-designed scrubbing tower, providing sufficient transfer units for F-gas absorption, again making use of moving balls.

#### (c) Other units with F-emission

In some other manufacturing units where we lose fluorine in the form of  $\text{SiF}_4$ , HF and/or fluosilicate salt-dust, we successfully apply scrubbers of the floating-ball and venturi-type.

### NH<sub>3</sub> and nitrous gases

Up to 1968 we operated our complex fertilizer plant with a wet section consisting of a series of ventilated reactors in which a mixture of nitric and phosphoric acid was ammoniated. The slurry was subsequently concentrated in a submerged combustion evaporator. Scrubbing of the off-gases was difficult and not very effective and as a consequence the unit was a notorious polluter. Emitted gases were NH<sub>3</sub>, nitrous gases, NH<sub>4</sub>NO<sub>3</sub>-mist and water vapour. The system was replaced by a separate ammonium nitrate solution plant and a powdered MAP unit, both with total condensation of the process steam, so the emission was brought down to nil. At the same time the capacity of the complex plant was almost doubled due to the lower recycle requirement.

A little NH<sub>3</sub> is still injected in the granulator in order to attain the desired pH. Some of this NH<sub>3</sub> escapes and up to now this is not entirely scrubbed out. Shortly a more effective scrubbing system will be installed.

No further volatile NH<sub>3</sub>-losses occur in the granulation plant as we base our compounds essentially on ammonium phosphate with an N/P-ratio not much higher than 1.0.

### WATER POLLUTION

In the introduction it was mentioned that in the past Windmill Holland has concentrated on abatement in the area of air pollution. Partly we have made use of recovery or recycle-systems, but still a major part of the material is passed to the sewer. This created a new problem because in November 1970 a decree on water pollution was introduced in The Netherlands. In this decree two elements are used to effect decrease of water pollution :

- restriction of dumping of pollutants,
- levying charges, when permission is given.

The system of charges for drainage of polluting substances has been in effect since 1971. The amount of pollutant charged is expressed as a "per capita population equivalent" (PCPE).

This represents the average daily discharge of pollution of an inhabitant. The annual rates per PCPE are :

<u>year</u>	<u>charge</u>	f 1.-- = \$ 0.38
1971	f 2.--	
1972	f 5.--	
1973	f 8.--	
1974	f 11.--	
1975	f 13.--	
1976	f 15.--	
1977	f 17.--	

The PCPE is based on the amount of :

- organic carbon compounds,
- organic and inorganic ammonia compounds,

basically the compounds which use oxygen while they are decomposed. When discharging a pollutant into surface water, part of the pollutant will be decomposed by the oxygen present in the water. Healthy water (with live fish and fast elimination of germs) has to contain not less than 5 mg/l O<sub>2</sub>.

One of the methods for the determination of O<sub>2</sub>-consuming compounds is the Biochemical Oxygen Demand (BOD) test. However, this test has some drawbacks and therefore, for determination of the PCPE, the Chemical Oxygen Demand (COD) is used instead of the BOD. Ammonium compounds which use oxygen are determined by the Kjeldahl-method.

In our case pollution with organic compounds is very low, but losses of ammoniacal nitrogen are appreciable : the 1976-budget for charges is about f 800,000 !

Much attention is therefore paid at present to improvement of the efficiency of ammonia-consuming plants (ammonium nitrate, MAP and complex fertilizer). One of the approaches is to provide effective monitoring.

#### MONITORING

To get optimum effect from all previously-described abatement activities etc., it is of course essential to provide good monitoring of the performance of all systems. Monitoring is effected by means of the following methods :

- instrumentation ; we have now reached the stage that in new plants we install a special panel in the control room for "environmental control" as a matter of normality,
- recording and checking of operating data,
- sampling and measurements.

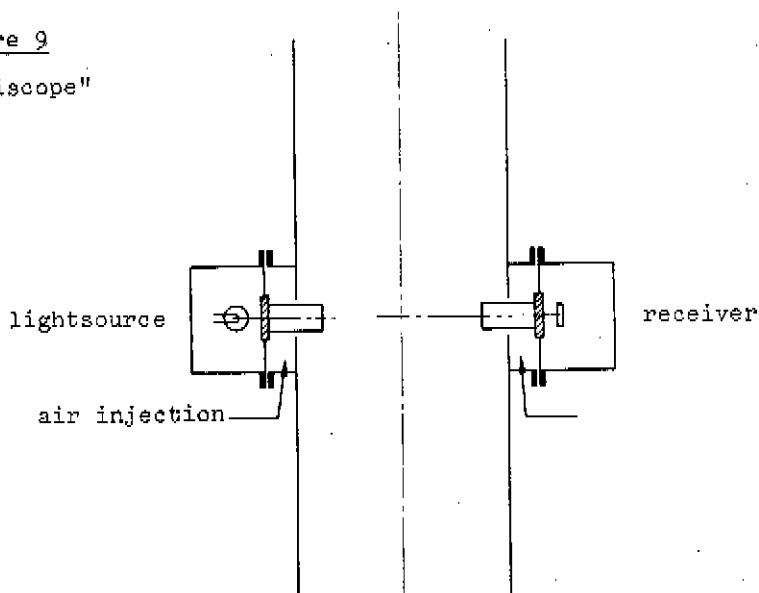
### Instrumentation

#### (a) Direct measurement of emissions : dust

To get a direct indication on dust emissions from bag-filter systems, we have installed so-called "Rodiscopes" (see figure 9) in many places, which have been developed from the classic flue-gas density-meter.

Figure 9

"Rodiscopes"



These instruments give a direct warning when a bag has got loose or gone to pieces. Its operation is based on throwing a beam of light through the dust-laden air which falls on a photo-electric resistance at the opposite side of the duct. The output from the cell is amplified and sent to an indicating/recording instrument in the control room.

The original flue-gas meter had to be adapted mechanically to permit cleaning of the optical parts during operation, without drift of its calibration. The standard design was such that it took a lot of effort and time before lamp and receiver could be brought into line. Therefore we made a heavy hinge-construction on which the device can be turned away for maintenance and cleaning. The entire handling of cleaning takes only about 10 minutes now (see figure 10).

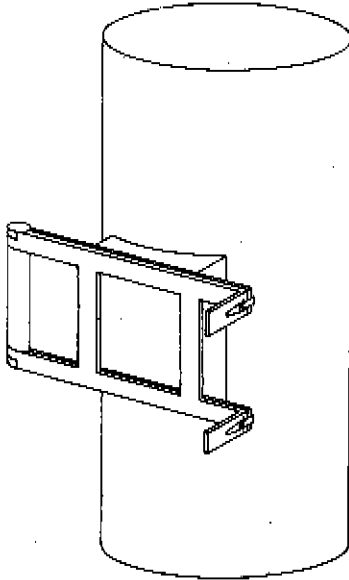


Figure 10

Fastening of Rodiscope on gas-duct

Another modification is that we have provided special facilities for electrical connections at the light source and receiver, in order to make it possible to test the system during operation.

To prevent build-up of dust at the light source and receiver, it has proved to be essential to purge instrument-air at both points.

(b) Direct measurement of emissions : SO<sub>2</sub>

Direct measurement of SO<sub>2</sub> in stacks of the sulphuric acid plants takes place with infra-red analyzers. A few adaptations had to be made, such as installation of equipment to clean the off-gas from oleum-droplets before it is allowed to enter the measuring cells.



### (c) Instrumentation on wet scrubbers

Standard instrumentation on wet scrubbing units at Windmill Holland comprises : flow-recording of fresh water supply, flow-recording on circulation liquid, pressure indicators on spray supply, indicator for pressure difference across scrubber.

Circulation flow-meters are normally of the magnetic type, because the liquid practically always contains solids.

To check whether too much dust from cyclones is entrained to wet scrubbers, we have installed "Rodiscopes" at some critical points (e.g. drier and cooler in the large granulation plant).

### Recording and checking of operating data

The primary responsibility for compliance with the emission levels of course lies with the production operators and supervisors, who periodically read off the instruments, write the data on logsheets and check these. The observations are compared with the standards and if there is no compliance, the operators have to take action.

The logsheets are checked daily by the production supervisors. A copy of these logsheets is verified by the process group who also look at the chemical analysis of the scrubber effluents. In this way we have a second check by the people who have the daily task of looking at the efficiency of the manufacturing units.

When a new modified gas-treatment unit is commissioned, members of this group determine by measurements the emission- and effluent data at varying process parameters. From these the standards which are used on the logsheets are derived.

In our opinion this method is better than the system demanded by the authorities in their new air pollution act conditions, namely spot-measurements once every three months.

### Effluent monitoring

As mentioned earlier, we have two good reasons for providing effluent-monitoring :

- the high effluent-charge levied by the government for which we have to carry out the measurements ourselves (verified by the authorities),
- to check plant efficiency.

As far as  $\text{NH}_3$ -measurements are concerned, until now a periodic composite sample is collected and analyzed over a working day, which is acceptable as the flow is not very variable. We are studying the installation of a continuous monitor for ammoniacal N. We have found that an ion-selective electrode must be replaced every 40 days (cost about f 1,000.-). A monitoring system which measures a related parameter, e.g. a conductivity probe, which is used very frequently to monitor ionic wastes, is not suitable. So the only possibility left is colorimetric determination. A study on this topic will be made.

In the same study we will look at the possibilities of using the monitor for the continuous determination of  $\text{P}_2\text{O}_5$  in the gypsum discharge of the phosphoric acid plants. We feel that, in this case, sampling can become a serious problem.

As already stated, related parameters are frequently used for monitoring. Many conductivity and pH probes are installed in waste-water discharge lines.

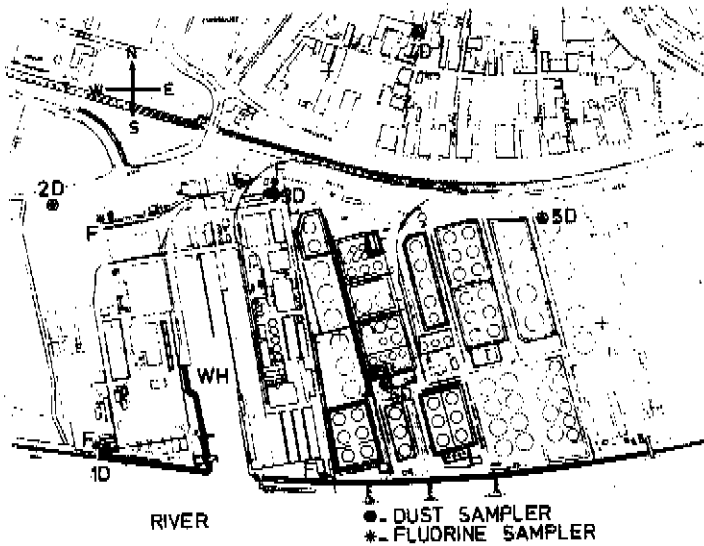
Other examples are cooling water circuits where we use conductivity systems. There it is necessary to measure both at the inlet and the outlet of the cooler, the inlet figure giving the reference point (the quality of river water can vary a lot, e.g. at very low water levels).

### Immission measurements

#### (a) Dust

Because dust is one of the major air-pollutants, we collect dust samples on and near to our site in order to verify our contribution to the dust loading of the Vlaardingen area. For this we use a number of so-called "Hibernia-funnels", a type of collector also used by the authorities. The samples are located as indicated on the map (see figure 11) with the mark "D".

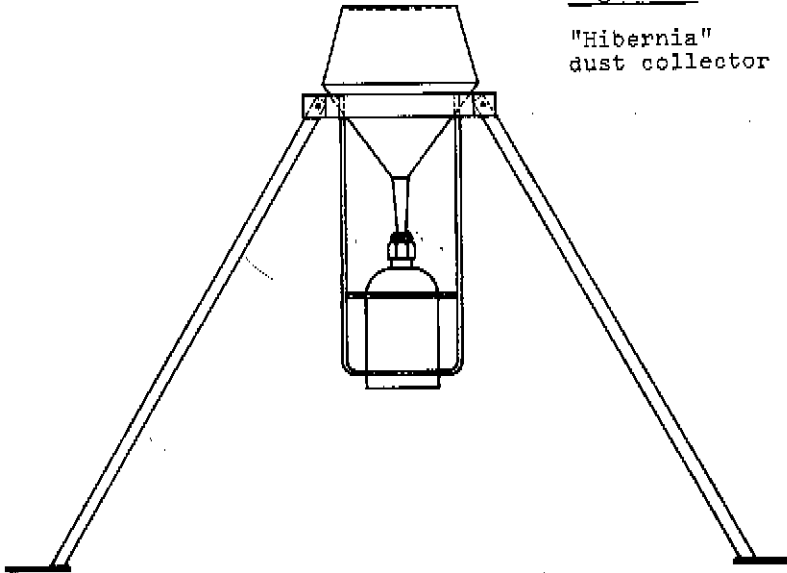
Figure 11



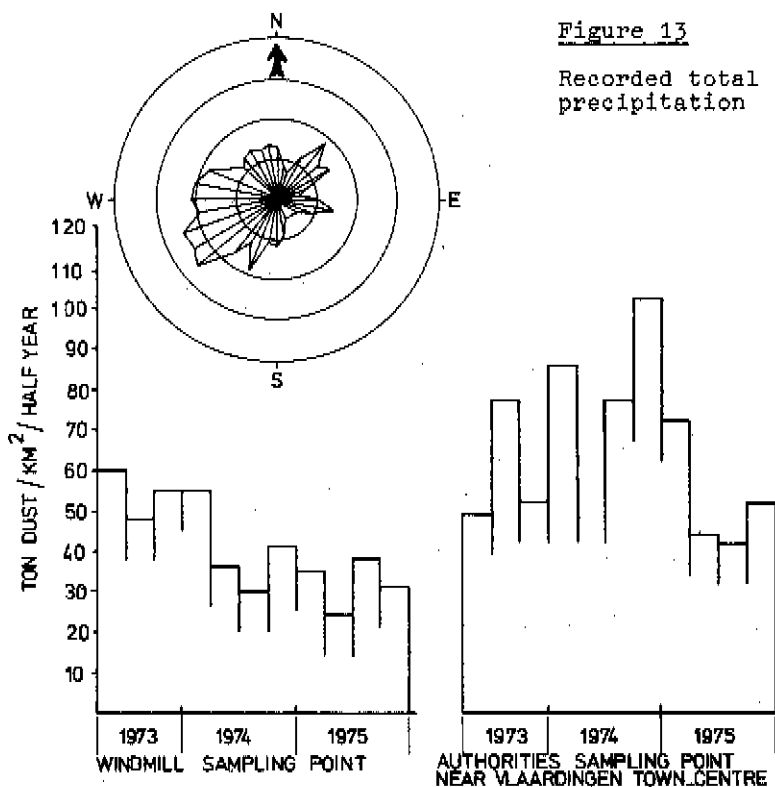
This funnel has been designed in such a way that it is effective under both dry and humid conditions (see figure 12). It should be located at such a place that the trapped dust is representative for the area.

Figure 12

"Hibernia"  
dust collector



The contents of the funnels are analyzed at the end of each month, and we look for water-soluble and insoluble dust. For a non-industrial area an insoluble dust loading up to  $10 \text{ t/km}^2/\text{half-year}$  is considered normal. In this area with heavy industry, harbour activities, etc., a dust-load of  $30\text{-}40 \text{ t/km}^2/\text{half-year}$  is not unusual. Figure 13 shows the dust-load as determined at sampling point 4 over the past few years. As is shown on the wind-frequency distribution graph, this sampling-point is located downward of the most common wind-direction. For comparison, "official" dust-load data from a point closer to the centre of Vlaardingen are given. The data show that the dust-load at point 4 is not significantly higher.



#### (b) Fluorine

Recently Windmill Holland has carried out a series of tests with a Technicon air monitor. It was our intention to measure directly air samples with F-concentrations of the order of

1-10  $\mu\text{g}/\text{m}^3$ , but the instrument proved to be not sufficiently sensitive. We have now decided to install four automatic air-samplers at locations which are shown on figure 11, marked F.

The air is sucked through two different impregnated filters so that gaseous and solid F-containing substances can be distinguished.

The filters are leached in the lab and then the resulting liquid is analyzed using an ion-selective electrode.

## DECOMPOSITION GASES FROM AMMONIUM NITRATE CONTAINING COMPLEX FERTILIZERS

### Introduction

Although it would have been possible to deal with this subject under the section on Air Pollution, we have decided to write a separate chapter because of the special nature of this case. This is because the decomposition gases do not belong to the regular emissions and if these highly poisonous gases are formed in an appreciable quantity, we are immediately in a disaster situation, because a large number of citizens are in danger.

In the past we have had two decomposition accidents at Windmill Holland : in 1963 with 12+12+12 in a large heap in a bulk storage shed and in 1970 with 12+10+18 in a 1000 tons storage box.

Of course we have learnt a lot from these incidents. Besides that, much information about the hazardous properties of compounds containing ammonium nitrate has become available in publications from the industry, international organisations and governments.

Windmill Holland has also done work in this field and because we have not written about our experiences in literature which is available to everybody, we are reporting here relatively comprehensively about our warning-systems etc. This may provide useful information for some of you.

### Description of bulk storage facilities

Windmill Holland's main compounds bulk storage consists of a building, which is divided into 20 compartments of 1,000 tons each, which are separated by thick concrete walls. The quantity in each box varies from 700 to 1,000 tons, depending on the danger-class of the products.

The boxes have been built according to the rules provided by the authorities for the construction of storage buildings for ammonium nitrate containing compounds. Furthermore two chimneys have been placed on each box (1 dm<sup>2</sup>) to detect any evolution of gases, and openings (0.5 x 1 m) have been made in the roof for efficient ventilation and fire-fighting in case of a decomposition. The front of the boxes in the storage building is made of steel profiles, which can be removed easily to empty the box either as a matter of routine or in case of local decomposition. In case of fire-fighting with water, the sludge is then allowed to flow out of the storage box. The humidity of the building is controlled by the use of warm dry air.

### Discussion of potential hazards

As stated earlier, we now have a fairly good understanding of the very complicated hazardous character of the materials. Three categories of compounds are distinguished :

#### (a) A-grades

These are products which can detonate (violent explosion which occurs at supersonic speed and has a strong destructive effect). The formulas in the production program of Windmill Holland all contain less than 65% ammonium nitrate and there is no danger of detonation.

#### (b) B-grades

Compounds which can deflagrate, but not detonate (characterized by a slowly-occurring reaction zone of 500°C max. and the development of large quantities of fumes, but no destructive effect provided the process does not take place in a confined space). These grades are only produced by Windmill

Holland when there is a strong demand from agriculture and if there is no alternative.

### (c) C-grades

Compounds which do not have the above properties (some of these may sustain or promote a normal fire in other materials, but decomposition does not propagate itself and the temperature remains at about 120°C, with only fair formation of fumes). This is the main category of product we produce at Windmill Holland.

There are two ways in which a B-grade can begin to decompose. The most frequent is ignition by an outside source (lamp, fire, hot object), when the material starts decomposing locally if the supplied heat exceeds the quantity of heat which flows away. Subsequently the decomposition will propagate itself through the rest of the material. The second but seldom-occurring cause is by so-called "self-heating". As a result of deviations in the composition (raw materials) chemical reactions may occur which produce more heat than can flow away to the surroundings.

A bulk heap (or part thereof) of compound fertilizer will be heated up, at first slowly, but more quickly as the temperature goes up, until the symptoms of deflagration occur. To get an idea of the time involved : 2-3 weeks will elapse between filling the storage and the moment of deflagration.

When the material is decomposed, as much as 20-50% of the material is lost in the form of gases. The composition of the fumes depends on the formulation, but normally the following toxic gases will be present :  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{NO}_x$ , as well as  $\text{N}_2\text{O}$ . For 12+10+18 the amount of toxic gases is e.g. about 10 m<sup>3</sup>/ton.

### Preventive measures

If we look at the potential causes of decomposition, it is clear what has to be done :

- formulate grades that are as safe as possible,
- prevention of ignition by an external source,
- prevention of self-heating,

- detection of self-heating,
- limitation of the quantity of bulk fertilizer storage,
- early warning in case of decomposition.

#### (a) Formulation

Normally there are several ways to compose a compound fertilizer of a certain formula, depending on the raw materials and intermediates used. The cost of raw materials and production capacity are important criteria used in the choice, but the deflagration danger aspect is also of primary importance. Frequently we are able to judge the formulations from past experience, but sometimes we decide to carry out special deflagration tests in the laboratory.

When a client asks for a potentially dangerous grade, we often succeed in persuading him to buy a different safe grade. There is a daily check on the danger-class of the material produced and if relevant the decomposition rate is determined.

#### (b) Prevention of ignition by an external source

Contact of the compound with heat sources must be prevented and in this respect :

- we use only conveyor belts made from flame retarding material,
- lighting of the storage has been changed in such a way that contact with the material is impossible,
- welding etc. may take place only after written consent from the production supervisor,
- prohibition of smoking in certain areas.

#### (c) Prevention of self-heating

Serious self-heating which leads to an accident is not an intrinsic property of ammonium nitrate containing fertilizers. It will only occur when a product is produced in a faulty way. The following guidelines have been given for the safe production of compounds :

- Limit concentrations of organic substances. Single superphosphate used for compounds is therefore no longer produced from waste sulphuric acid. The percentage of coating material is kept as low as possible and does not



5 - 25

contain any substances (e.g. unsaturated aromatics) which may react with ammonium nitrate.

- Limit acidity : pH in a 1:100 solution should be higher than 4.5. Every 20 minutes the pH's of the end-product and the granulate are determined and recorded on the panel. We have developed a special system for that reason. When the pH is too low, the product is stored separately and as soon as possible worked up.
- Limit temperature : maximum temperature of the product to storage 40-45°C (winter-summer). Temperature of the product sent to storage is continuously measured and recorded.
- Use of trace elements, e.g. copper, is forbidden.

(d) Detection of self-heating by temperature measurements

Direct measurement of the temperature in the heap is the best method of checking whether self-heating is occurring. The temperature is measured by thermo-couples of copper-constantan, coated with polyethylene (Siemens). Polyethylene has been chosen because of corrosion resistance and insulation against the catalytic influence of copper on self-heating. The cable has a length of 10 m, and the lowest point is 3.5 m above the ground to prevent damage by motor-shovels. This problem has not yet occurred and does not seem to be of any great significance, particularly since the cable can withstand pulls of up to 2,000 kg.

Each successive thermo-couple is 2 m higher than the preceding one, so the temperature can be measured at 3.5, 5.5, 7.5 and 9.5 m from the floor.

The thermo-couples are connected with a millivolt to a current converter (Foxboro, 10-50 mA) with automatic cold junction compensation. A linear deflection is obtained from 0-100°C. By means of 2 switches it is possible to select each of 4 points in the 20 storage boxes :

- switch 1 = height of the measuring point,
- switch 2 = box-selection.

At present an operator reads the temperatures every shift on his round through the NPK-storage. We are working on the design of a system to get an automatic alarm at a preset value.

An automatic scanner for the 80 measuring points will be required and presumably a computer may be used for this purpose.

There is one drawback and that is that compounds are such good insulators, comparable with asbestos. So the measured temperature only gives a reading for one small part of the heap.

When the temperature rises to 60°C or higher, the storage box is emptied and the material is spread to cool.

(e) Limitation of the stored quantity of bulk fertilizer

At Windmill Holland we make sure that B-grades are not stored in quantities larger than 700 mtons, which is much less than the maximum allowed according to the official rules set by the authorities.

(f) Early warning in case of decomposition

A lot of work has been done to develop an alarm system. Several investigations on gas detection have been published on chlorine. In Germany the Cerberus fire detector has found application. The Cerberus responds only to large particles, so, in the case of decomposition fumes, only to  $\text{NH}_4\text{Cl}$ -particles and to a smaller extent to  $\text{Cl}_2^-$  and  $\text{NO}_2^-$ -molecules (necessary concentrations 30  $\text{g/m}^3$   $\text{NO}_2$  and 20  $\text{g/m}^3$   $\text{Cl}_2$ ). Decomposition fumes with a low  $\text{NH}_4\text{Cl}$ -content have a relatively long response time, and problems of dust build-up are also arising.

In the introduction, the "chimneys" on the boxes were mentioned, but later Windmill Holland developed a warning system which responded to  $\text{N}_2\text{O}$ -molecules, because  $\text{N}_2\text{O}$ -gas is assumed not to be absorbed by the undecomposed fertilizer, it is easy to detect by IR-absorption in very low concentrations, and last but not least,  $\text{N}_2\text{O}$  is always evolved in high concentrations at decompositions.

Before starting to design the system, some preliminary investigations were made to get an idea of the effectiveness :

- Emission of  $\text{N}_2\text{O}$  below decomposition point

Three formulas (mixtures of ammonium nitrate, phosphate and potassium chloride) were tested at 80°C for 10 days and at 100°C for 7 days. No detectable amounts of  $\text{N}_2\text{O}$

were given off. At 130-140°C varying amounts were emitted :

15+12+24	after 3½ h	at 140°C	5x10 <sup>-2</sup>	mg N <sub>2</sub> O/kg.min
17+17+17	after 1 h	at 130°C	5x10 <sup>-2</sup>	mg N <sub>2</sub> O/kg.min
17+17+17	after 3½ h	at 140°C	10x10 <sup>-2</sup>	mg N <sub>2</sub> O/kg.min
23+23+0	after 1 h	at 130°C	2x10 <sup>-2</sup>	mg N <sub>2</sub> O/kg.min
23+23+0	after 3½ h	at 140°C	4x10 <sup>-2</sup>	mg N <sub>2</sub> O/kg.min

So in principle, below the point where a homogeneous or zonal decomposition of the compounds starts, detectable amounts of N<sub>2</sub>O are already emitted, which if detected give us timely warning.

- Absorption of N<sub>2</sub>O by compounds

Pure N<sub>2</sub>O was brought into contact with several compounds. None of them absorbed any N<sub>2</sub>O. But although N<sub>2</sub>O is not absorbed by the compounds the question of when the gas will be released from a heap remains a problem. However, it is likely that there are convection-streams in the heap, so that we think it will not be necessary to fill the whole void volume with gas first, before it is released from the heap.

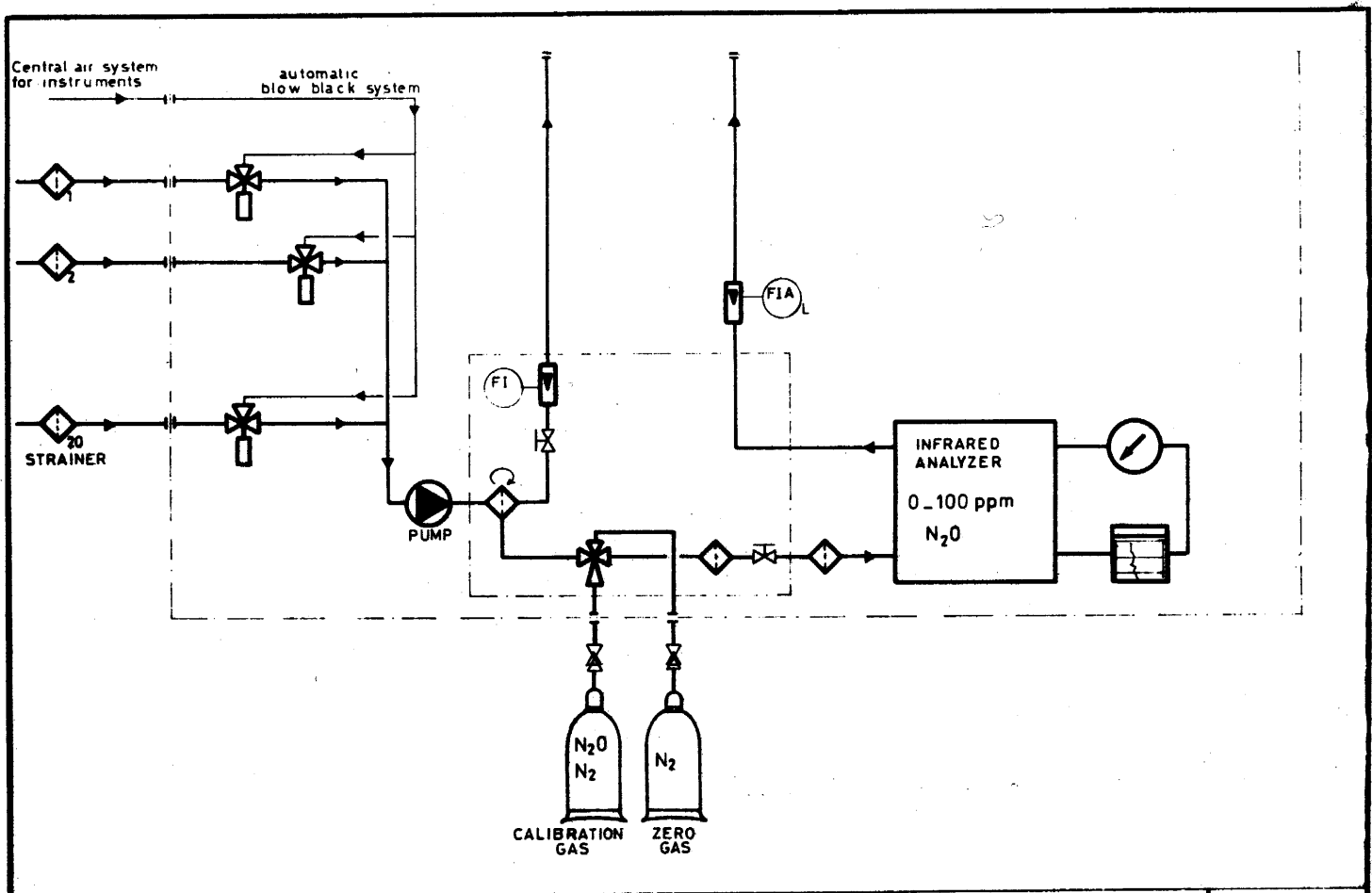
- Detection method

Many methods are suitable for the analysis of traces of N<sub>2</sub>O in a gas mixture. We have chosen an industrial infra-red analysis, which has proved its value in practice : the Non-Dispersive Infra-Red system with a selective gas filter which enables us to detect N<sub>2</sub>O-gas very specifically in a multi-component stream.

- The "hardware"

The system (scheme shown in figure 14) was developed in cooperation with MSA-Nederland B.V. The sampling system consists of 20 suction points in the different boxes. There is a possibility to extend to 24 points. Suction points are opened or closed by magnetic valves ; by means of three-way magnetic valves all sampling points except one are blown off. This is to prevent standstill of air in the lines, and thus to shorten the response time of the entire system.

One measuring point is sucked off by a pump, and via a



**WINDMILL HOLLAND B.V.**  
**Vlaardingen**  
**24 POINTS**  
**N<sub>2</sub>O DETECTION SYSTEM**  
 Get.: a.i.      date 17.5.76

Figure 14

flow-failure alarm and a selection switch "calibration/zero gas" the sample is led to the measuring instrument. An extra three-way magnetic valve can be placed in the system for suction of fresh air. This valve can be excited by the flow-failure alarm, which works when the sampling line is blocked. The system is provided with a fully automatic sequence stream selector with the possibility of manual operation. For this purpose, 24 Bowater electronic control units working fully transistorized and contact-less are used in the system. Each one has an adjustable cycle time between 0 and 30 seconds. When this time is elapsed, the next unit is started by a pulse. The total cycle time is about 10 minutes.

By means of switches the following adjustments can be made :

Push-button switch with a built-in green signal lamp to indicate which measuring points are considered to belong to the system. Measuring points which are switched off are not considered in the total cycle time.

A push-button switch with a yellow signal lamp to indicate which point is analyzed. When a switch is pushed, that point will be measured for an indefinite time. A red signal lamp indicates "manual operation".

As stated before, the concentration of the  $N_2O$  is measured in a NDIR absorption meter. The range is 0-500 vol. ppm  $N_2O$ , but equipped with a special unit, the range is 5-100 ppm. At the same time there is a possibility to connect a recorder.

The alarm unit can be adjusted to 10% of the measuring range. The timer will then be stopped until the reset knob is pushed manually. When the alarm is confirmed, a recorder starts to run in order to record the  $N_2O$ -concentration. The recorder can also be started manually.

A second alarm unit is built in to protect the IR-meter. The cycle, however, is not stopped when the high alarm is confirmed (see figure 15).

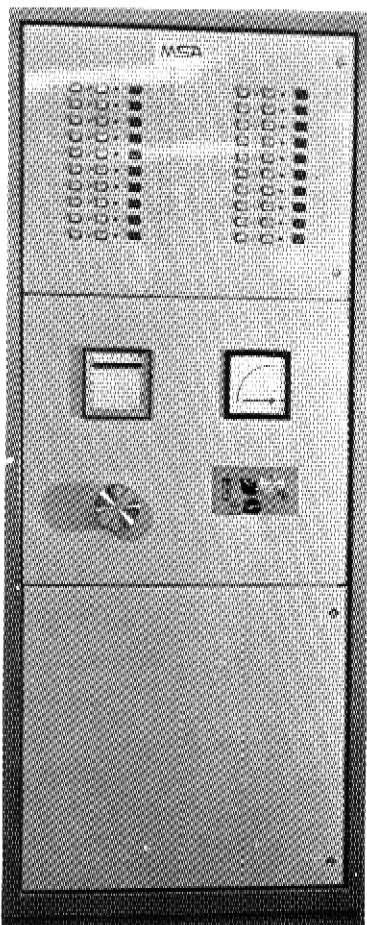


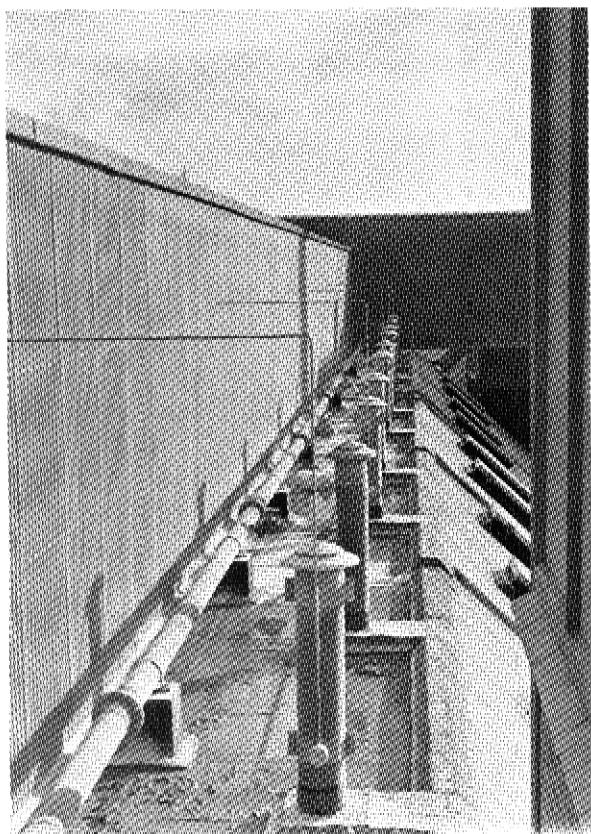
Figure 15

Random stream selector

Some further investigations with the system

Before installing the final set-up of the system, two parts of the system were investigated. In the first place the sampling unit (see figure 16). Even under severe conditions, the volume taken by the sampling unit was constant and no condensation was observed. Secondly the detection. The first test done in an empty storage box was the decomposition of 1 kg of NPK in a trough, which was first heated to 500°C. Irrespective

Figure 16



Sampling for  $N_2O$   
in chimneys of  
the boxes

of where the trough was placed, the detection system indicated an  $N_2O$ -concentration of more than 10 ppm within 2 minutes. The second test performed was in a box containing an NPK which has a very good thermal stability. On the surface of this heap a decomposition, as described earlier, was performed. Now the IR-meter recorded a concentration of  $N_2O$ -gas in 11 min of 15 ppm, with a maximum of 45 ppm after 6 minutes. The question remained of how fast  $N_2O$  will be released from a heap in which only a part decomposes. To check up on this, a pipe-line was put on the bottom of a box and NPK was dumped in it. Through this pipe-line  $1 \text{ m}^3$  of an air/ $N_2O$ -mixture (90+10) was injected to a total of  $6 \text{ m}^3$  in

30 minutes. The first  $N_2O$  was detected (15 ppm) only  $3\frac{1}{2}$  h after the last injection, going up in the next  $1\frac{1}{2}$  h to 25 ppm and then decreasing in the next 20 h to 10 ppm. From these investigations it may be concluded that  $N_2O$  is detected in a few minutes when the decomposition is on the surface. The experiment with the gas mixture in the heap has not given us the answer to the question of whether decomposition on the bottom of a filled box can be detected very early.

However, the evolution of decomposition gases and injection of air/ $N_2O$ -mixture cannot really be compared (mainly because of the temperature effect). The final answer cannot be given by testing as it is impossible to start a decomposition of NPK deliberately in a filled storage box.

For a period of 6 months the system was working continuously and was watched carefully. The experience was very positive : no condensation, no blocking of lines due to dust, resulting in a constant volume of air and very small drift of the IR-meter.

In May 1974, Windmill Holland decided to order the full system, based on the satisfactory experience we had. Some modifications were made on basis of our experiences, and now the system has been installed. The alarm can be triggered at 5 ppm, for background concentrations are much smaller than 5 ppm, and the drift is also at the most 5 ppm in 3 days.

We have become experienced with this system and in the near future we expect to be able to report favourably on this kind of early warning system for the decomposition of ammonium nitrate containing compounds. However, we hope that the system will never have to prove its usefulness.

It should be remarked that the system works because of storage in boxes and the favourable air movements in these boxes. In big warehouses there will be more difficulties to overcome.



Fire extinguishing

When, in spite of all preventive actions, a zonal decomposition occurs, it is still possible to extinguish the fire.

One of the methods is to spread out the reacting material, but this is feasible only with small quantities. The method is to bring the material into contact with a lot of water. For this we have the openings in the roofs of the boxes and permanent fire-fighting piping which in case of emergency can be connected to water-supply hoses.

To penetrate into the heaps we use the special water-lances, which have been developed by Gewerkschaft Viktor.

Our fire-brigade has been trained specially for this kind of fire with the help of the fire-brigade of the town of Vlaardingen, and they possess the most effective equipment available.