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INFLUENCE OF ENVIRONMENTAL PROTECTION OF THE FERTILIZER PRODUCTION TECHNOLOGIES[1]

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The manufacturing process in a technology consists of the transformation of the raw materials into the final products and into byproducts respectively, this is the case also in fertilizer production. The degree of the transformation is never complete, partly because the raw materials contain ballast materials, partly because the transformation and recovery of the last portions of the products would be difficult and expensive.

This fact can be illustrated in general on a typical Shenky diagram of the material flow of a plant /Fig.1/.

The formation of wastes begins already in the moving and preparation of the raw materials /dust and vapor, No.1/, and continues during the manufacturing technology simplified on the diagram as a single step /No.2/. The main sources of waste materials are the tail gases /No.3/, the waste water /No.4/ and the solid waste at the end of the technology. Finally some waste will be derived also through the manipulations of the final

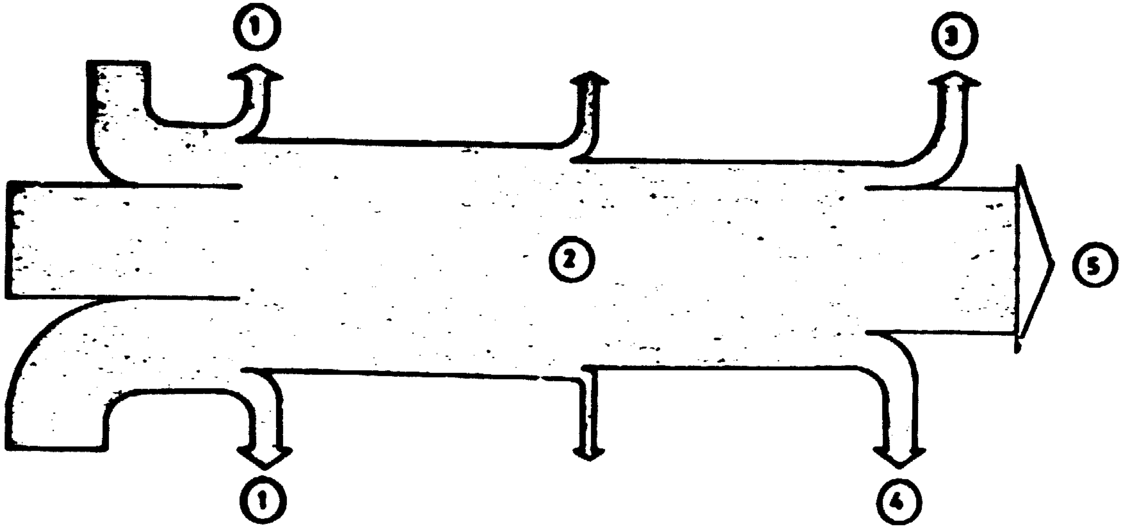

Fig.1. The Shenky diagram of a plant. Input of raw materials at the left side. Output of products and wastes at the right side.

Symbols: 1. Emissions through the moving and preparation of raw materials.
2. The technology is simplified to one step, possible recirculation etc. being omitted. A few intermediate effluents are indicated.
3. Tail gas.
4. Liquid wastes including waste water.
5. Possible emission by the handling of the final product.

products /No.5/. Plants using air and/or water in a large quantity constitute a special situation from the point of view of the emission of waste materials. In these cases the emission of wastes will increase in a considerable degree. The diagram is simplified, it does not contain any complications originating from the interaction of the different wastes, e.g. dust end carbon separation from the tail gases, solid waste precipitation from the liquid waste etc. Nevertheless the diagram represents the fact that the quantity of the waste will decrease with improved yield.

However, an improvement of the yield is limited by economical considerations. Fig.2. represents the specific investment costs and Fig.3. the specific manufacturing costs as a function of the recovery of a solid product from a gaseous stream /1/. The curves are caracteristic. The initial linear section turns in an exponential curve over 90 per cent of recovery. If the specific costs are referred to the recovered substance and not to the volumetric gas flow /as on Figs. 2. and 3./, the resulting curves have minima at about 90 per cent recovery. This region of the yield would be the optimum from point of view of the economic production in this example. But a factory designed for a recovery of 90 per cent would emit 10 per cent of its production in form of different wastes.

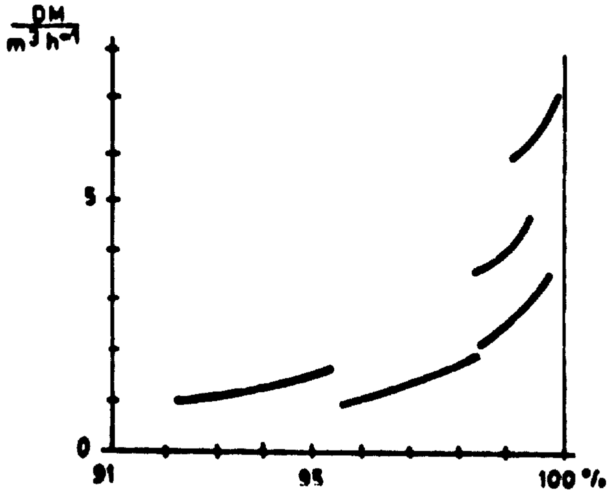

Fig.2. Specific investment costs /1970/ of the recovery of solid materials [1]

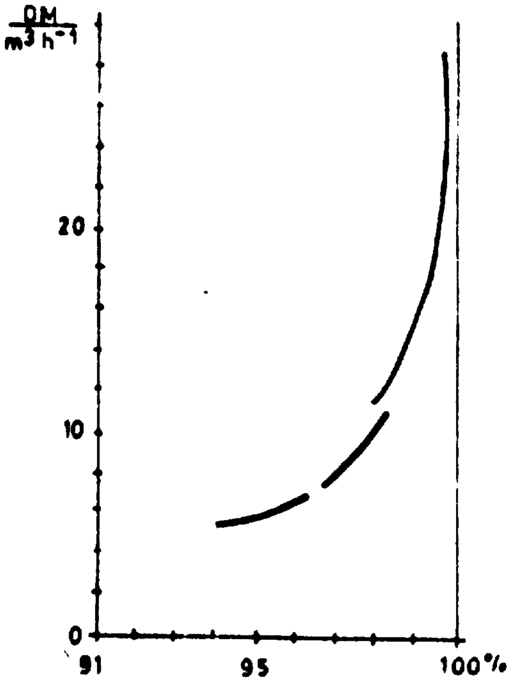

Fig.3. Specific operating costs /1970/ of the recovery of solid materials [1]

Nominal output 100000 m^3h^{-1}

Symbols: 1. cyclone
2. multicyclone
3. filter
4. electrofilter
5. wet electrofilter

The situation is similar in all fields of the fertilizer production, e.g. the absorption technologies of the nitrous gases and of sulfur trioxide have their own optimal recovery. Indeed, factories working at a calculated optimal recovery, were built with planned losses, according to our present nomenclature, with planned waste emission.

After the worldwide introduction of environmental protection regulations, the situation has thoroughly changed. In many cases, waste emission calculated by economical optimation of the technology is higher then permitted by environmental regulations. Operating plants have two possibilities to fulfil the new environmental requirements: to built additional purification equipment, or to increase the percentage product recovery of the plant. Planning a new plant the planning offices and institutes are faced with a similar situation. They are in a more advantageous situation only in so far that they can make decisions without restrictions, existing in an operating factory.

Of course, the decisions in designing should consider also further on economic aspects, but the observance of the environmental protection regulations represent a cost factor which must be taken into account.

As mentioned already, there are two main ways to reduce emission, i.e. to improve the yield or to build in addicional waste eliminating equipments. Since there are more methods for both solutions, which have different effects and exact different costs, the simple function of specific cost calculation mentioned above will be converted to a polifunctional relation. The methods increasing the recovery percent are competitive with the waste elimination methods.

In the light of the present energy crisis and the shortage of raw materials, the methods improving the yield seem more reasonable. Therefore, the later method of waste reduction will be preferentially chosen under otherwise equal conditions. Indubitably, the increase in production costs, on the one hand, and the increase of the cost of disposition of wastes on the other hand, will make in the long run methods improving production more desirable.

Eliminating processes producing byproducts are purposeful also from the point of view of the industrial production. However, unfortunately, the waste eliminating methods are usually improductive, transforming the given waste into another less harmful or inactive form, thus the problem remains although the situation seems to be better. Such methods are for example, where waste water is produced by the washing of tail gases or less harmful gases are produced by the aeration of effluents. The methods forming precipitation from the impurities of waste water are not much better, due to the difficult disposition of the precipitate formed.

Owing to the problems mentioned above, caused by the introduction of environmental rules, the technologies working at higher production efficiency have their Renaissance now. The higher investment and production costs of these more expensive technologies working at higher yield are equalized by the additional costs of the waste eliminating equipments of the cheeper technologies. Of course this condition will be fulfilled only in the case, when the emission of the improved technology sufficiently low, so that the plant does not need eliminating equipment.

This fact will be illustrated by two examples from the fertilizer technology.

In the first step of superphosphate manufacture, sulfuric acid manufacture by the classical contact sulfuric acid technology, a gaseous emission of sulfur dioxide and of sulfuric acid fog is produced, which usually exceedes both in quantity and in concentration all environmental rules. The problems originate in the conversion and the absorption steps.

The sulfur dioxide produced by the roasting of pirite or by the burning of elementar sulfur are further oxidized with air in a multistage contact furnace.

The oxidation reaction of the sulfur dioxide/1/

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3 \qquad /1/$$

leads to an equilibrium. Practically the reaction will be stopped at 0.2 volume per cent of sulfur dioxide, and this residual sulfur dioxide forms the largest part of the emission. As the starting concentration of the sulfur dioxide is about 10 volume per cent, the yield of the conversion is near 98-98.5 per cent. The absorption of sulfur trioxide, performed by washing with sulfuric acid of 93 per cent, has a 99.5 per cent yield. If the sulfur dioxide gas contained organic substances, or if the cooling of the absorption tower was too intensive, in the course of the washing process sulfuric acid fog will also be produced. This fog will not be absorbed and the emission increases.

With respect to the above mentioned objective conditions given by the technology, the losses met in the contact sulfuric acid plants are as follows:

conversion	1.5 per cent
absorption	0.5 per cent
others	1.0 per cent.

It should be mentioned finally that these data are valid only for new plants or plants in good maintenance with regenerated catalyst bed etc.

Methods are known in the literature for the adsorption of the residual sulfuric compounds of the tail gas, but these did not find general applications in practice.

Actually the solution of the problem was given already earlier by the use a two step contact process, but in practice the conditions raised by the environmental requirements lead only to their realisation. The new method based on the mass effect law is able to diminish the theoretical conversion loss to 0.02 per cent.

It follows from reaction scheme /1/ that the equilibrium conditions of the conversion will be shifted to the right side by diminishing the concentration of sulfur trioxide. This concept can be realised by an intermediate absorption step between two conversion steps. Another possibility to improve the yield is to diminish the reaction temperature in the catalyst bed. Reaction /1/ is exothermic, therefore the equilibrium conditions will be more favourable at lower temperatures.

The realisation of the double contact sulfuric acid technology involves a four-stage catalytic tower with the usual intermediate heat exchangers between the stages. The primary gas mixture (air + 10 per cent of sulfur dioxid is flowing through the first three stages and undergoes a 90 per cent conversion to sulfur trioxide. This gas is passed through a heat exchanger into an absorber and washed with 93 per cent sulfuric acid. Thereafter the washed gas containing one per cent of sulfur dioxide is recirculated into the fourth stage of the catalytic tower and is subjected to catalytic oxidation again. At equilibrium composition attained at the end of the reaction, the gases contain 0.02 per cent of sulfur dioxide.

The losses of a double conversion sulfuric acid plant are as follows:

conversion	0.05 per cent
absorption	1 per cent
others	0.5 per cent

The practical results measured in operating plants [2] are:

	Gaseous emission of a		
	/normal/ contact	double contact	
	sulfuric acid plant		
SO_2	0.3 - 0.4	0.11	vol. per cent
$SO_3/+H_2SO_4$	0.1 - 0.3	0.1	vol. per cent

It can be seen that the emission values in actual plant operation are far from the /calculated/ optimal concentrations, nevertheless the values of the double contact plant are satisfactory from the point of view of the emission standards /generally 0.2 vol. per cent of SO_2/. The reason for this is that the efficiency of catalysis and of absorption is depending on many parameters /temperature, flow rate, concentration data etc./, and the optimum conditions will be realized only within a narrow range of each parameter mentioned. The problem can be solved by the automation of the process. The plants examined were not automated.

The double contact technology has the advantage that it is applicable not only to new plants, but older plants can also be reconstructed. The reconstruction costs of a plant of a yearly capacity of 100000 metric tons are about one million US $ /1972/. The automation of the plant would cost additionally about 200 thousand US $.

Similar expectations were made in connection with nitric acid production at elevated pressure with regard to environmental protection requirements.

One of the most important nitrogen fertiliser, ammonium nitrate, is produced in three steps:

1. synthesis of ammonia
2. manufacturing of /diluted/ nitric acid by the

oxidation of ammonia

3. manufacturing of ammonium nitrate by the neutralization of nitric acid with ammonia.

At present the manufacturing of diluted nitric acid is the critical part of the production from the point of view of both economy and environmental protection.

Ammonia is oxidized with air on catalyst sieves to nitrogen dioxide, which is then absorbed in water or in diluted nitric acid, according to the general reaction formula /2/ as follows:

$$3\ NO_2 + H_2O \rightleftharpoons 2\ HNO_3 + NO \qquad /2/$$

One third of the nitrogen dioxide is obtained as nitrogen monoxide gas, and must be re-oxidized to dioxide again.

Nitrogen monoxide is insoluble in diluted acid, it leaves the liquid phase and must be oxidized again with air-oxigen in the gaseous phase to nitrogen dioxide. This reaction is time consuming and requires sufficient residence time, i.e. large free reactor volume in the flow system, whereas absorption needs a large liquid surface. Taking into account the conflicting alternative solutions, the planning of the absorption towers of the nitric acid production is always a compromise and the improvement of the yield is limited by the high costs of the absorption towers.

It can be seen from Eq. /2/ that the gaseous volume ratio is 3 : 1, therefore, higher pressure furthers nitric acid production. For this reason the novel type nitric acid plants will be planned to work under pressure.

This type of nitric acid plant is favorable from the point of view of the specific reaction volume capacity and of some other parameters. It was expected that the yield will also improve.

The later hopes were not realised in the practice. This fact was demonstrated also by our emission measurements [3].

The yield of nitric acid, and therefore the emission of nitrous gases depends on many parameters, out of which two were established as the most essential [3]: the load of the plant and the temperature of the diluted acid in the absorption towers. The temperature changes from point to point in the towers, so that caracteristic differences can be found only between the conditions in summer and in winter.

In Figure 4. the emission concentration of nitrous gases /i.e. the loss/ of two old nitric acid plants working at atmospheric condition is plotted as a function of the load per cent of the plants. Points and the trends are different for the values measured in summer and in winter.

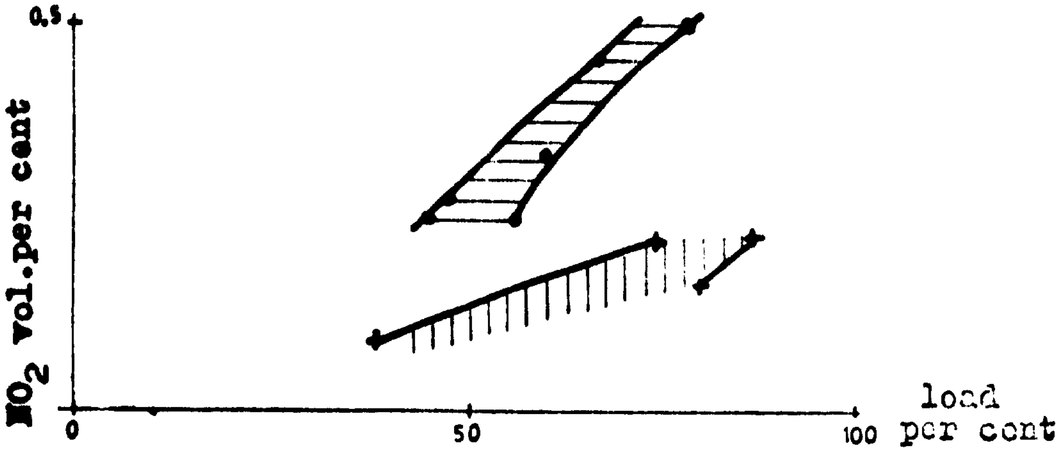

Fig. 4. Nitrogen dioxide emission concentrations of nitric acid plants working at atmospheric conditions as a function of the load of the plant in summer and in winter [3].

Symbols: ● mean data of measured series in summer
▤ random data in summer
✦ mean data of measured series in winter
▥ random data in winter

The points plotted represent mean values of individual measuring series, in total 541 data in summer and of 505 data in winter.

We have also studied the statistical distribution of the data measured for emission. It should be mentioned that 79 per cent of the data measured in summer are lower than the provisional permissible emission of 0.35 volume per cent, and all the data measured in winter are lower than the permissible value of 0.30 volume per cent for winter.

Fig. 5 represents data of nitrogen dioxide emission measured at four nitrogen fertilizer plants, involving nitric acid plants working at medium pressure /3.5 ata/ absorption.

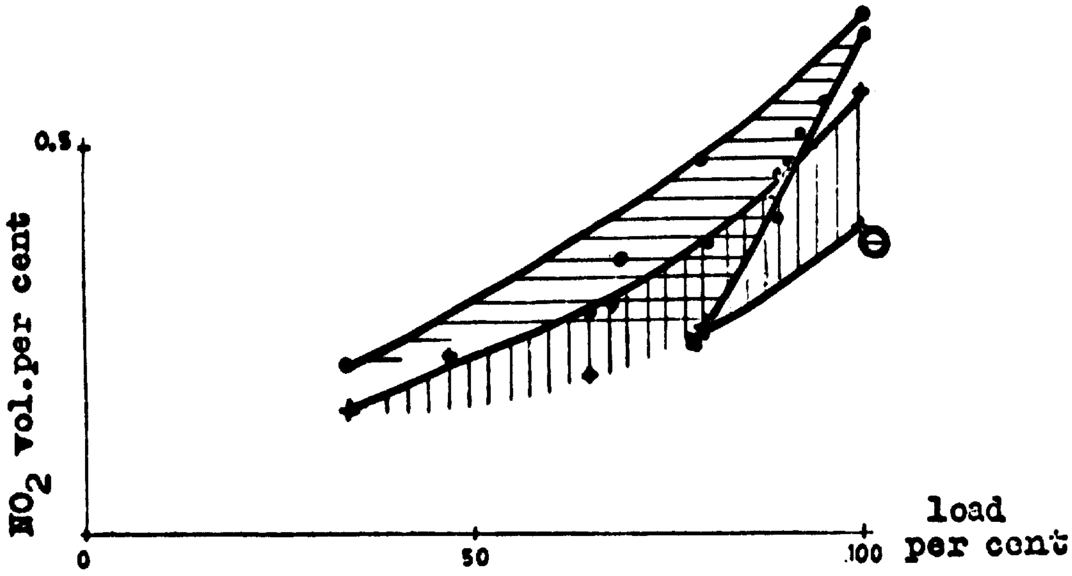

Fig.5. Nitrogen dioxide emission concentrations of nitric acid plants, operating at medium pressure absorption, as a function of the load of the plant in summer and in winter [3].

Symbols: • mean data of measured series in summer

▱ and ⊖ random data in summer

♦ mean data of measured series in winter

▥ random data in winter.

The mode of representation is the same as in Fig.4. The points represent mean values of measured series, in total 993 data in summer and 841 data in winter. The areas representing the individual trends in summer and in winter are partly overlapping. The emission values compared to those of Fig.4. are better in summer, whereas they are more unfavorable in winter.

The statistical distribution of the emission data measured were studied also for plants with absorption at medium pressure.

The situation represented by the data measured is more unfavorable from point of view of environmental protection and also from that of output, than for plants working under atmospheric conditions. The reason for this situation is on the one hand that the provisional permissible emission is smaller for this type of plant than those discussed earlier , i.e. in summer: 0.25 per cent and in winter: 0.20 per cent of nitrogen dioxide, and on the other hand that the plants examined are operated under much higher load than those mentioned before.

Fig.5. shows also that the emission concentrations can be very different depending on the given conditions in the plants. For example, the value in the vicinity of the point with the parameters 101 per cent of load and 0.39 per cent of nitrogen dioxide belongs to the emission of a novel plant in summer and can not be connected with the data of the other three plants.

Only 6 per cent of the data measured in summer were lower than 0.25 per cent of nitrogen dioxide and 23 per cent of the data measured in winter were lower than 0.20 per cent.

Finally, it can be establish that the nitric acid technology using medium pressure in the absorption step did not meet the expectations regarding environmental control, and that the low temperature of the diluted nitric acid used for the absorption of nitrogen dioxide is more important then any of other parameter.

Taking into consideration that the requirements of the environmental rules are not yet met in nitric acid production by additional eliminating equipment alone, it can be understood that urea will be a competitor of the ammonium nitrate fertilizer on the world market.

In the case of the production of solid final products e.g. urea, ammonium nitrate, superphosphate, etc. the improvement of the yield and the reduction of the emission are the same process, i.e. recovery of the product from the tail gase stream. The costs of these processes have been discussed in connection with Fig. 2 and 3. It is probable that the limits of the recovery of the products are different for production and elimination purposes, but the result is always an additional recovery of the product. From this point of view the dry methods are more reasonable than the wet methods.

The recovery of pulverised products is a transition to the additional processes producing utilisable byproducts in the course of the elimination of wastes.

From the field of fertilizer technologies, the absorption methods of nitrous gases and of the fluorine containing gases will be discussed.

It was mentioned earlier that a satisfactory elimination of the nitrous oxides from the tail gases of a nitric acid plant is not yet solved. A further possibility to improve the absorption is to use a basic absorbent solution instead of diluted nitric acid. The absorption efficiency and costs are different depending on the solution used.

Absorption in sodium carbonate has the advantage to use a clear solution. The disadvantage is that the solution absorbs only an equimolar quantity of NO_2 and NO, and the molar ratio is 1:2 to 1:3, while a part of nitrogen oxide remains in the gaseous phase, so that the effectivity is only 60-70 per cent. The investment costs of an additional equipment of medium capacity are about 1 million US $. The product is a mixed solution of sodium nitrate nitrite.

Absorption in calcium hydroxide suspension is cheeper and has an absorption efficiency of 90-95 per cent. The problem of this method is that the product, a mixture of calcium nitrate and nitrite salt, is not easy to dispose on the fertilizer market. The investment costs of an additional equipment of medium capacity is about 1,5-2 million US $.

The superphosphate production is another caracteristic technology utilising a part of wastes as byproduct.

The phosphates used for production are mainly fluorine apatite from primary source, as e.g. Kola apatite or from secondary source, as e.g. phosphorite, containing about 1 per cent of fluorine. The fluorine content is liberated during the reaction with sulfuric acid, and forms a gaseous waste of hydrogen fluoride or silicon tetrafluoride.

On account of the aggressiveness and the hazards connected with the fluorine compounds, all plants feature eliminating equipment, involving the washing of the gases with water with more or less efficiency. Here, the gaseous impurity is transformed into waste water, which is purified by the addition of calcium hydroxide suspension.

While the fluorine compounds are wanted at present by the aluminium and plastic industry, some production plants are sited on the basis of the waste water containing fluorine compounds of the superphosphate plants. This water containes about 100-200 kg/m^3 of hydrofluorosilicilic acid or H_2SiF_6 .

Such products are

sodium silicofluoride
sodium fluoride
aluminium fluoride and
cryolite

produced as byproducts of the superphosphate plants in a quantity of some thousand metric tons per year.

These all are crystalline products and more or less soluble in water, therefore the mother liquor forms again a waste, although its quantity is much less than originally.

Almost all of the known equipments producing fluorine compounds have been additionally installed to working plants.

Other waste eliminating methods do not produce valuable products are not interesting from the point of view of the development of fertilizer technologies. For example, the catalytic reduction of nitrous gases to nitrogen practiced now as method of elimination is unreasonable from point of view of the industrial production, however it seems more economical than the additional absorption methods reviewed previously.

It is to be mentioned that there are some results for the working factories originated immediately from measuring of the emission of wastes.

This measuring method makes possible e.g. to estimate the correlation between the load and the emission of the plant. In many cases there is a minimal specific rate of waste emission, probably meeting the rules for environmental protection and only the overload of the plant gives inadmissible contamination.

Moreover, some plants have used the results of the emission measurement to control their own production.

From the point of view of the metrology, it is clear also that you can measure a few per cent of losses with higher accurancy than the whole production. Therefore, a new method is given by the systematic analytical control of the emission concentration, which can be used also to control the yield.

Summary

The manufacturing process in a technology consists of the transformation of the raw materials into the final products and into byproducts respectively. The degree of the transformation, the yield is never complete, factories were built with planned losses, according to our present nomenclature, with planned waste emission.

After the worldwide introduction of environmental protection, the situation is thoroughly changed. There are two possibilities to fulfil the environmental requirements:to build additional purification equipment or to increase the yield. The simple function of specific cost calculation will be converted to a polyfunctional relation. The methods increasing the recovery per cent are competitive with the waste elimination methods.

In the light of the present energy crisis and the shortage of raw materials, the methods increasing the production are more reasonable. Eliminating processes producing byproducts are purposeful also from the point of view of the production. However, unfortunately the waste will usually be transformed by the eliminating method into another less harmful form.

Owning to the problems mentioned above the technologies working at higher production efficiency have a Renaissance now. The more expensive technologies are equalised by the additional costs of the waste eliminating equipments of the cheeper technologies. This fact will be illustrated by two examples from the fertilizer production, e.g. the higher efficient sulfuric acid production and the nitric acid production using pressure by absorption are preferred.

The additional equipments applied for production of new or more byproducts from waste, e.g. nitrite-nitrate salt producing with an alcalic absorbent, (e.g. soda or line) and the fluorine compounds formation by washing the gaseous substances of the superphosphate manufacturing are also reasonable.

Examples for the unreasonable conversions of a contaminating compound into an other one are: washing the fluorine containing gases forming waste water, and the catalytic conversion of the nitrous gases to nitrogen.

There are also some further results for the working factories originated immediately from measuring of the emission of wastes. The most successful is the estimation of the correlation between the load /production rate/ and the waste emission of the plant. In many cases there is a minimal specific rate of waste emission meeting the requirements for environmental protection and only the overload of the plant gives inadmissible contamination.

Moreover, some plants have used the results of the emission measurement to control their own production. From the point of view of the metrology it is clear also that you can measure a few per cent of losses with higher accurancy than the whole production.

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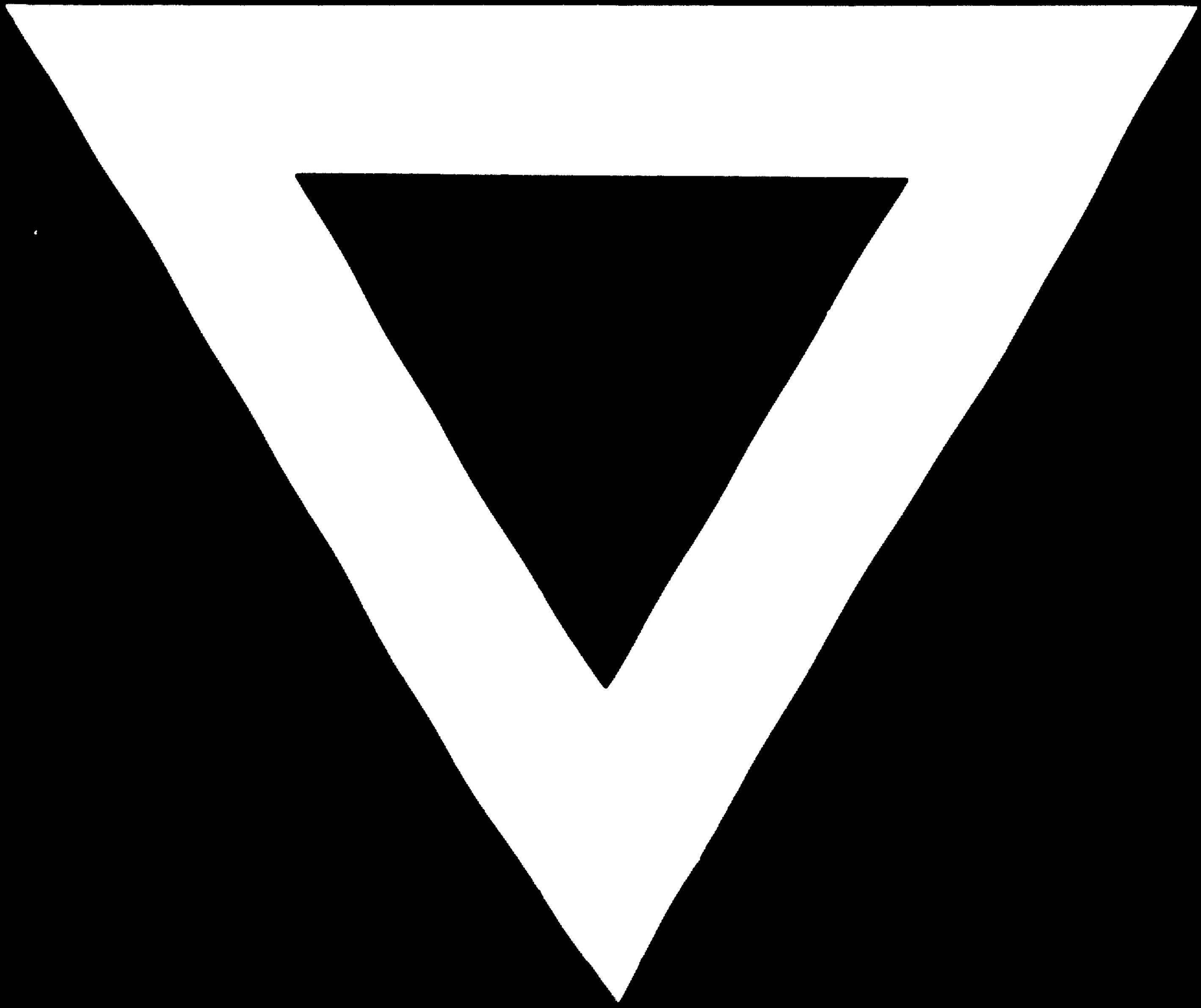

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