



**TOGETHER**  
*for a sustainable future*

## OCCASION

This publication has been made available to the public on the occasion of the 50<sup>th</sup> 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](mailto:publications@unido.org) for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at [www.unido.org](http://www.unido.org)



D03552



United Nations Industrial Development Organization

Distr.  
LIMITED

ID/MG.127/5  
27 June 1972

ORIGINAL: ENGLISH

Meeting for Identification and Development  
of Fertiliser and Pesticide Industries in  
the Developing Countries served by ECE

Bucharest, Romania, 10-14 July 1972

SULPHURIC ACID PRODUCTION TECHNOLOGY AND PLANT CONSTRUCTION  
IN THE PEOPLE'S REPUBLIC OF POLAND <sup>1/</sup>

by

Jan Wosniakowski  
Study, Design and Execution Office for Inorganic Industry  
Gliwice, Poland

<sup>1/</sup> 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 paper has been reproduced without formal editing.

id.72-4122

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.

## CONTENTS

	<u>Page</u>
1. Introduction	3
2. Raw-materials for sulphuric acid production	3
3. Sulphuric acid technology	5
4. Sulphuric acid production on base of anhydrite and phospogypsum	15
5. Sulphuric acid production on oake base	17
6. Sulphuric acid production SO <sub>2</sub> - containing gases base	17
7. Sulphuric acid production on pyrite base	18
8. Export of sulphuric acid and its transportation means	18
9. Sulphuric acid production economics	19
10. Polish sulphuric acid industry research, design and executing possibilities	22

## 1. Introduction

Sulphuric acid is a very important intermediate for manufacturing a series of chemical products, its total country production being constantly the measure of national economy and industrial development. Sulphuric acid is used mainly for production of fertilizers, dyes, inorganic compounds, synthetic fibres and many others. There is practically no chemical product made without sulphuric acid being involved.

As formerly stated, sulphuric acid is used mainly in fertilizer production. The world development trends show that the most justified way in phosphate production is its production on phosphoric acid base, this being produced by the wet method by treatment of phosphate rock with sulphuric acid.

Considering today's low sulphur prices and further increases in mining or extracting, the method of phosphate production on a phosphoric acid base seems to have good reasons for further development, as by this way, the high analysis fertilizers NP-18-46 and even higher, on superphosphoric acid base, can be obtained. Independently of this, the NP-granulated phosphates can be mechanically mixed with other monocomponent granules, or macro grain phosphates, leading thus to the production of a series of tricomponent fertilizers, with microelements included, according to the agricultural demands. This is also the direction in which the Polish phosphate production is developing; thus sulphuric acid production gains in importance and the proper technology and the kind of raw material become very significant.

## 2. Raw-materials for sulphuric acid production

Poland is in a lucky position to have at its disposal a number of sulphur containing raw materials, and first of all - sulphur of a very high purity. Besides sulphur itself, the following raw-materials are used in sulphuric acid production in Poland:

- anhydrite and gypsum
- sulphur refining wastes / cake /
- sulphurdioxide /  $SO_2$  / containing gases, being the wastes of non-ferrous ores calcination / zinc, lead, copper /
- hydrogen sulphide and off-gases

The installations working on pyrites up to 1970, have been renewed and reinstalled on sulphur base. The unprofitableness and relatively high pyrites mining costs taken into account, resulted in the close down of the pyrites mines.

Polish sulphur, supplied mostly in a liquid state, is characterized by a high purity, containing 99,9 % of pure elemental sulphur. Thus, no additional preparation before use in production is needed. The installation itself is relatively simple and investment costs are the lowest ones.

Anhydrite and natural gypsum, being still used in one of our plants is to be replaced by phospho-gypsum being the waste in phosphoric acid production. Semi-technical pilot-plant tests followed by tests on industrial scale revealed the possibility of sulphuric acid production on this base according to the standards for this product.

Sulphur refining wastes rich in elementary sulphur composed of:

sulphur / S /	- 35-40 %
gypsum /CaSO <sub>4</sub> /	- 1,2-1,8 %
calcium carbonate /CaCO <sub>3</sub> /	- 52-58 %
water /H <sub>2</sub> O/	- 4-6 %

are very suitable for sulphuric acid production, giving waste-calcoines used as calcium fertilizers.

Waste-calcoines consist of:

calcium carbonate /CaCO <sub>3</sub> /	- 84-90 %
gypsum /CaSO <sub>4</sub> /	- 9-16 %
calcium sulphide /CaS/	- 0,1-0,5 %
elementary sulphur /S/	- 0,1-0,5 %

Gases containing SO<sub>2</sub> - being the wastes of non-ferrous metallurgy, contain 4-12 % of /SO<sub>2</sub>/ sulphurdioxide, and because of pollution standards being steadily sharpened, must be utilized or used in sulphuric acid production.

Hydrogen sulphide /H<sub>2</sub>S/ extracted from postgaseous masses finds its small application in some plants working in Poland, and sulphuric acid produced from it is used in ammonium sulphate production, thus making the whole unit economic.

3. Sulphuric acid technology

3.1. Methods used in Poland

Over 90 per cent of the sulphuric acid plants in Poland operate on the contact principle. The remaining 10 % of sulphuric acid plants work on the chamber methods and are destined to be closed down, as the need arises, up to complete liquidation in 1980-85.

The sulphuric acid production in Poland increases relatively quickly. After the World War II in 1946 it was as low as 190 thousands t/y, in 1965 it stepped over 1 million t/y, and in 1970 it reached 2 millions t/y or monohydrate. In the same time the national raw material base has been changed. The table below shows this distinctly.

	<u>1965 %</u>	<u>1970 %</u>
sulphur	40	68
pyrites	18	-
metallurgy waste gases	17	10
sulphur refinery wastes	14	15
anhydrite -gypsum	9	6
others	2	1
<b>Total</b>	<b>100</b>	<b>100</b>

Shortly after the World War II the plants of comparatively low capacities of 30-50 thousands t/y were mostly built. Nowadays much larger units are erected, the capacity of 50 th. t/y being the lowest. The largest units now in operation in Poland reach the capacity of 250 th. t/y. On designers desks there are units of 500 th. t/y, to be built in the coming years either in the country or for export and the present largest unit ever built by Polish designers and contractors in the 300 th. t/y unit in Federal Republic of Germany.

The majority of plants are based on single conversion and absorption principle. Since 1968 there are sulphuric acid units producing on double conversion and absorption principle - the double contact has been in our country the initiation of Polish designers. It is expected that early built units working on single principle and on base of sulphur refining wastes or natural sulphur - will be constantly redesigned and reconstructed on double contact principle.

Sulphuric acid plants based on sulphur dioxide /SO<sub>2</sub>/ gases from calcination in non-ferrous metallurgy, work on single contact principle. SO<sub>2</sub>-content in flue-gases are diminished by ammonia absorption, the ammonium sulphate being the by-product.

With connection to the increase in Polish and world sulphuric acid production on sulphur base, as evident in the coming years, I would put greater attention in this paper to this very method. The other methods, being less attractive and more rarely applied, will be described superficially only. In order to probe this, the table below is cited; the shift of world raw material base in sulphur direction is clearly shown

Raw materials consumption by sulphuric acid production

Raw material	World %		Europe/West/%		USA %	
	1952	1969	1952	1969	1946	1970
sulphur	43,8	58,2	18,0	35,7	79,1	77,9
metallic sulphates	51,4	26,6	78,8	47,0	13,3	8,4
others	4,8	15,2	3,2	17,3	7,6	13,7

### 3.2. Sulphuric acid production on sulphur base

/The suitable flow-sheet is annexed to this paper/

#### 3.2.1. Raw material /sulphur/

Poland is one of the few countries in the world disposing of rich sulphur deposits, so the sulphuric acid production on this base develops in this direction. The share of sulphur in sulphuric acid production increased so much that the production of sulphuric acid in Poland on this base amounted to:

- in 1965 - 40 %
- in 1970 - 64 % and nowadays
- in overcomes - 70 % of the total country capacity.

Polish sulphur is of high purity.



Polish Standard states the following composition of sulphur:

	<u>liquid s. %</u>	<u>solid s. %</u>
elementary sulphur, over	99,95	99,85
impurities /total/, below	0,05	0,15
arsenium            "-	0,000	0,0000
selenium            "-	0,000	0,000
acids /reduced to s. a.monohydrate/ below	0,007	0,01
organic compounds   below	0,015	0,02
ashes                "-	0,04	0,1

### 3.2.2. Sulphur transport and storage.

Sulphur is transported in solid or liquid state, while the participation of the latter increases up to 90 %. As transportation means for solid sulphur mostly open railway freight cars are used. To protect them against atmospheric influence and spilling they are covered with canvas. Unloading of the cars is simplified by means of holder gentry or self-propelled shovel. Storage takes place in covered warehouses with 3 m high retaining walls around.

Size of granules range between 0 and 50 mm. The solid sulphur may also be stored on open stacking yards. The liquid sulphur is transported in special 30 t railway tanks, equipped with heating steam coils for melting of solidified sulphur. The heating during the time of transportation remains inactive.

On plant territory, tanks before clearing are heated by means of 5-6 ata saturated steam coils. Melting period varies from 5 to 10 hours, according to weather conditions, distance and period of transportation. Clearing of tanks is carried out through bottom tank pipe connections, by means of piping, heated by 5-6 ata saturated steam. In another way- the clearing of tanks is carried out by pumping out through upper hatch, by means of special movable pipe-arm with elastic joint, direct into main storage tank or into an intermediate tank, where from, it is pumped out, by means of submerged pumps into the main storage tank. Clearing period lasts 0,5 - 2,0 hours, in accordance to unloading method.

Liquid sulphur is stored in steel containers, equipped with steam heating coils, thus the liquid state of sulphur is secured. In order to diminish the heating steam consumption, all tanks and pipings for liquid sulphur are insulated and covered with aluminium sheet, which provides protection against damage or weather influence.

The capacity of industrial sulphur storage tanks in use varies in accordance to demand and delivery conditions. In most cases the capacity ranges from 500 to 3000 m<sup>3</sup>. The design of the main storage tanks enables the periodic clearing of residues consisting mostly of impurities. Subsequent filtration prevents the solidification of the dirty sulphur in the tank bottom, and permits the eliminating of the bottom steam coils. The total heating steam consumption including railway tanks, storage tanks, filtering equipment, pumps and piping, up to sulphur furnace - amounts to 80 - 100 kg/t of produced sulphuric acid, depending on distance and period of transportation. By use of solid sulphur, the total consumption number reaches 100-120 kg/t of sulphuric acid.

### 3.2.3. Sulphur preparation

In case of solid sulphur, being in use in some older plants only, it is taken from storage into the melting tanks directly by means of grab, or indirectly by belt conveyor and belt scales registering the quantities of sulphur being transported to the intensive melting tank, to be melted.

The melting tank is equipped with steel pipe roast, serving as melting elements; the tank itself equipped with heating coils to keep sulphur in liquid state. The melted liquid sulphur reaches the primary network filter before being fed into dirty sulphur underground storage tank. The intensive melting tank, besides steam coils, is equipped with a special mixer to speed up the melting process. The melted sulphur feeds the dirty sulphur storage tank, after being filtered in primary network filter.

The underground storage tank for dirty sulphur is made of concrete, lined with acid-proof bricks, equipped with heating steam coil and compartments for diatomaceous earth precoat feeding of candle filters. One or more pumps are installed in this tank. The first operates the filtration process, the others serve the unloading of railway-tanks, eventually pumping into the storage tanks.

Filtration of sulphur, being the pumping process through the filter cake, follows the formation of a diatomaceous earth precoat.

In case of liquid sulphur, the underground storage tank serves as railway-cars clearing tank; to speed up the clearing activities additional pumps of greater capacity must be installed.

The capacity and pressure of unloading and filtration pumps depend on solid sulphur size, distance to storage tanks and of the kind of the filter. Normally graphite candle-filters are used, whereas for 100 thousands t/y of sulphuric acid unit only two of them are needed, each of ca  $2,6 \text{ m}^2$  filtering surface.

For larger units, larger candle filters or pressure filters with special stainless steel network are used. In normal filtration conditions, pure sulphur containing 99,999 % of elementary sulphur is possible to be obtained. The filtration process is controlled by the sulphur pressure indications on the manometer. In case of graphite candles, the pressure reaching 3,5 ata, the pumps are stopped and filtration process finished. By introducing a reverse flow of steam, the filter cake with all impurities is stripped off, being immediately solidified in cold water. The cake received by this manner containing ca 50 % elementary sulphur, serves in another plant as raw material. The similar material obtained by sulphur refining process is also in use. The quantity of these impurities depends on raw sulphur purity.

According to our experience, 0,16 kg of a special kind of diatomaceous earth is used per 1 t. of e.a. monohydrate.

Filtered sulphur is fed into the pure sulphur tank, wherefrom it is pumped out by means of gear pumps, through the flow-meter into the burner in the furnace.

The pure sulphur tank is designed either as the underground tank, its construction being similar to the dirty sulphur tank, or in form of the steel ground tank. The sulphur furnace feed pumps have different capacities according to the productivity of the unit, the pressure ranges between 12-16 ata to permit fine sulphur atomizing in the furnace. Output regulation of the pumps occurs by means either of speed of rotation, or needle valve control. In all cases the sulphur pumps output control is automatically guided by sulphur dioxide  $\text{SO}_2$  concentration in boiler gas gases.

### 3.2.4. Sulphur combustion and heat utilization.

The sulphur combustion process releases a large amount of heat. The combustion reaction to  $\text{SO}_2$  is a highly exothermic process, one kg of burned sulphur emits 2211 kcal. Theoretically, the sulphur combustion in air enables the concentration of  $\text{SO}_2$  in gases up to 21 %, in the same time the concentration of sulphur vapour is considerable. Practically by sulphur combustion, sulphur vapour free gases are to be obtained up to the  $\text{SO}_2$  concentration of 18 %. This requires a large extended combustion surface, by means of additional ceramic grate after-burner. Specific heat loading of this assembly is obviously lower. This kind of combustion is used in case of by-production of liquefied  $\text{SO}_2$ , by partial  $\text{SO}_2$  condensation out of cooled gases, where the remaining  $\text{SO}_2$  containing gases are processed into sulphuric acid.

In conventional s.a. plants, sulphur combustion process is operated so as to get the 8-14 %  $\text{SO}_2$  concentration.

There are in Poland two kinds of sulphur burning installations. In lower capacity units, ca 150 thousand t/y of sulphuric acid, the sulphur combustion up to 12-13 %  $\text{SO}_2$  content is preferable.

Gases of such concentration are further processed by cooling down, beginning from the second converter shelf, by direct air blending, and in this way the proper conversion of  $\text{SO}_2$  into  $\text{SO}_3$  is obtained.

In large capacity units of 200-500 th. t/y the sulphur burning process up to 9-10 %  $\text{SO}_2$  content is preferable. The  $\text{SO}_2$  concentration of 10 % is mostly in use.

Filtered sulphur is burned with dry air being warmed up to 250-260°C by post contact gases in contact department. The temperature of 1140°C in furnace exhaust side is then reached.

The gases passing through the boiler are cooled down to 430-440°C and then may be fed over the first contact shelf.

In smaller units, the horizontal furnace working at the same time as the boiler is used, its construction being of such a kind, that in the axial part of it the combustion takes place, and the emitted heat is radially given to the boiler elements forming the external walls as well. In large units the furnace and boiler are separated, the latter following the former one.

In sulphur combustion furnaces the specific heat load of 180,000 - 200,000 kcal/m<sup>3</sup>.h - is obtained.

In newer ones, of specially designed combustion chambers, the specific heat load of 600,000 kcal/m<sup>3</sup>.h - is reached. The combustion process and its intensivity depend on the sulphur atomising degree and air feeding; the main furnace elements are the burner and the air inlet nozzle arrangement. Burning is started by means of fuel gas or oil.

There are in Poland horizontal and vertical sulphur furnaces, the former ones are preferable because of construction reasons.

Boilers, utilizers of heat of sulphuric gases are of both designs, with natural and forced circulation. Working conditions of the boiler are: steam pressure - 20-40 ata, steam temperature - 350-450°C, according to steam utilisation conditions. Steam generation output varies between 1,1-1,0 t of steam p.ton of monohydrate depending on whether it is a single or double contact unit. Boilers are fed with warm water, this passing first through the economiser in which it is degassed by warming up to 250°C, by means of hot contact exhaust and tower incoming gases. Circulating and water feed pumps are driven either by electrical motors, fed by two independent sources, or by both, electrical and steam drives. Boiler flue gases having the temperature of 430-440°C, in new installations are not filtered, as the sulphur filtration is sufficient to keep the gases clean.

### 3.2.5. Contact

In sulphuric acid single contact unit with capacity of 150 th t/y, the five-shelf contact apparatus is used, reaction heat of the gases after the first shelf being taken away in an exchanger by the combustion air, while the gases after having passed three shelves are cooled by cold air intake.

In this case the intake gases on the first shelf have the SO<sub>2</sub> - concentration of - 12 %, whereas in the exhaust the SO<sub>3</sub> - concentration of - 8,5 % is kept. Conversion ratio amounts in this case to 98-98,5 %. Catalyst requirement amounts 200-220 l/t. day of monohydrate.

In sulphuric acid single contact units of larger capacities, reaction gases after each shelf are cooled with sulphur combustion air in heat exchangers. In this case the four shelf contact apparatus is used together with three pipe exchangers. Conversion ratio and catalyst requirement remain on the previously cited levels. After the first shelf the conversion ratio reaches 60-70 %, whereas after the second one - 30-32 %.

In sulphuric acid double contact units, one four-shelf contact and a number of heat exchangers are used. The first conversion stage consists of three contact shelves, the fourth one forming the second conversion stage. The gases leaving the first shelf attain a conversion of 60 %, then they pass through the first exchanger warming up the gases destined for the second stage. Gases after the second shelf reach a total conversion ratio of 85 %, and after the third shelf, 92-92,5 %. Gases leaving each shelf are cooled with fresh gases passing to the second stage, those leaving the third shelf being additionally cooled with air for sulphur burning, in order to keep the temperature of gases being guided to the first absorption tower at the 200°C level. Gases leaving the first absorption tower pass through heat exchangers, being there warmed up to the temperature of 430°C and guided into the second conversion stage. After this stage the total conversion ratio amounts 99,8 %.

In our new designs the total conversion ratio of 99,9 % is expected.

Gases leaving the second stage pass through the economizer there they are cooled down to the temperature of 220°C, whereas the boiler water is being warmed up to 260°C. Gases leaving the second stage enter the second absorption tower. In accordance with the kind of catalyst, the intake gases over the respective shelves have the following temperatures:

number of the shelf	temperature °C	conversion ratio
I	430-440	60-70 %
II	440-450	85-88 %
III	430-440	92-94 %
IV	430-440	99,8-99,9 %

Catalyst requirement by double contact unit amounts to 180-200 l/t.day - according to the kind of catalyst. The satisfactory working period lasts over 10 years, under condition that the layer on the first shelf is screened or eventually reactivated every 2-5 years, according to the sulphur filtration assembly condition.

In our designs, the insulating brick lined contact apparatus is used. The elements in contact with  $\text{SO}_2$  or  $\text{SO}_3$  gases are made or covered with aluminium. Shelf supports and plates are made of heat resistant cast iron and screens are made of heat resistant steel being  $\text{SO}_2$  and  $\text{SO}_3$  proof. Special designs of gas distribution over the shelves enable uniform flow through the total contact mass surface, thus the high conversion ratios are reached. So now the most principal problem is to keep the  $\text{SO}_2$  concentration of effluent gases as low as  $0,8 \text{ g SO}_2/\text{Nm}^3$  of gas at the highest possible conversion ratios. Heat exchangers are aluminium sprayed and the working period of the unit lasts as long as 350 days in a year. The economiser of a single conversion unit is steel and brick lined, and the pipes are ripped and cast iron coated.

In double conversion units the economiser may be steel as well, the  $\text{SO}_3$  concentration in second conversion stage being very small, the ripped pipes must be used to keep its dimensions in proper limits.

All the equipment, ducts and pipings in contact units are externally insulated.

The start up of the unit / warming up / is done with the help of furnace heat whereby the air warming the catalyst and exchangers is heated up. The forming of the catalyst may be secured, either by burning of small quantities of sulphur in the furnace, or by feeding 100 %  $\text{SO}_2$  to the hot air pumped into the contact apparatus.

### 3.2.6. Drying and absorption

In sulphuric acid units on sulphur base the drying tower serves for drying, the air being pumped by the blower through the tower and the heat exchanger into the sulphur furnace.

In our designs, blowers are installed before the drying tower. By this means steel blowers can be used, this being not without importance. The special oil filter for air filtering and damper for noise silencing below 85 dB, are installed on the blower. The air from the tower exhaust contains less than  $0,1 \text{ g}/\text{Nm}^3$  of moisture. For

air drying 94-96 % sulphuric acid is used. The towers are packed with ceramic rings diam. 50 x 50 or diam. 80 x 80. On the top of them demisters are used to catch mist or droplets and carried away; thus the life-period of the exchanger is lengthened. Special designs assure the proper distribution of the sprayed acid. The bottom part serves as a pump sump, while the submerged pumps are used for circulating acid, spraying and cooling. Acid is pumped through the exchangers and the cast-iron drip coolers, which have been recently replaced by acid proof steel spiral coolers. We also use air coolers for regions where water supply is low.

The tower cycle is fully automated enabling the production of a given acid concentration.

The temperature on the tower inlet is kept at the 40-45°C level. The absorption assembly of single contact units consists, either of one absorption tower or one oleum-tower and one absorption tower. For double contact the said assembly is enlarged by a second tower with its circulation equipment. The circulation cycle of the absorption towers is similar to the drying tower with the exception that the former ones have a more intensive spray system, the acid concentration being 98,5-99,0 % and the temperature 60-70°C. The absorption tower inlet gas temperature is kept at the 200-220°C level and the quenching intensity of 20-36 m<sup>3</sup>/m<sup>2</sup>.h is kept, according to the tower type.

In case of oleum production, the capacity equal to the total is possible, provided that the low air humidity and concentration below 25 % of free SO<sub>3</sub> is maintained. In our designs the production of 37 % free SO<sub>3</sub> oleum is possible. The oleum tower cycle is identical with the absorption and drying towers, the first tower being made of steel. To keep the proper working conditions of the oleum tower, on the gas side it is by-passed together with the first absorption tower, thus the absorption inlet gases temperature is high and the absorption itself is very complete, and the 99,98 % ratio is by this way guaranteed.

The installed demisters diminish the dust content in the flue gases. The SO<sub>3</sub> concentration in the tower exhausting gases is as low as 0,1 g/Nm<sup>3</sup>. The acid and oleum being produced are directed into the storage tanks, and according to the given concentration they are drained out, either from the drying or the second absorption tower -



in the double contact case. The absorption and drying tower cycles /eventually oleum tower/ are automatically coupled together, thus giving the required concentrations of the product.

### 3.2.7. Acid and oleum storage

Products are stored in steel tanks, the oleum tank is additionally heated by means of water coils installed on the outside wall, the whole being insulated. The acid and oleum storage tanks draining operation is done from the bottom, by the help of small submerged pumps close by. There are double valves on the draining flanges installed. The total acid and oleum production is cooled down to the temperature of 40°C and is metered with the help of the flow-meters.

### 3.2.8. The sulphuric acid double contact unit - representative data:

Sulphur consumption /recalc. on 1t of NH /	- 332 kg/t NH
electrical energy                    "-	- 40 kWh/t NH
cooling water	- 30-40 m <sup>3</sup> /t
conversion ratio	- 99,8-99,9 %
absorption	- 99,98 %
steam generation	- 1,0 t/t NH
steam consumption	- 80-120 kg/t NH
crew	- 3/shift

The sulphuric acid units on sulphur base are built in the open air without housing or roofing.

The blowers and control desk only are situated inside of the housing. The whole unit is automated to a large degree which secures automatically the main working parameters.

## 4. Sulphuric acid production on base of anhydrite and phosphogypsum

Existing in Poland are sulphuric acid plants working on anhydrite base with the capacity of 70 thousands t/y in one unit. The erection of new plants based on this raw material in future is not taken into consideration because of high capital costs. The reinstalling on phosphogypsum base may be the only considered reasonable solution instead. The industrial tests in Poland revealed that cement of "350" quality and sulphuric acid may be produced. The production process consists of four phases:

- raw material preparation
- calcinating of process mixture
- sulphuric acid production / of  $SO_2$  - containing gases/
- clinker fabrication for cement

The raw materials are dried, ground and finally made into a mixture of phosphogypsum, coke, lime, sand and calcines. The most difficult problem in this process is drying with simultaneous degasification and removal of considerable quantities of fluorine in a special absorber. The calcination is carried on in rotary kilns 70-100 m long, being the standard in cement industry. Gas, oil or coal-dust are the source of heat to produce an inside temperature of  $1250^{\circ}C$ . The exhaust  $SO_2$  containing gases after having been dedusted in dry electroprecipitators, cooled and washed in quench towers and wet precipitators, dried in drying tower - constitute together with air,  $SO_2$  concentration of 5,5-6,0 %, the base of sulphuric acid production. The specific problem of the gas working system is the strict washing discipline to remove fluorine, the last being, besides  $SO_2$ , the main component of phosphogypsum and the contact mass poison. The clinker is fabricated in the normal way for cement.

The raw materials consumption data:

- phosphogypsum /recalculated on 100 % calcium sulphate/ $CaSO_4$	- 1700 kg
- coke /80 % of element. carbon/	- 110 kg
- lime, sand, pyrite calcines /recalc. on dry mass/	- 250-300 kg
- electr. energy	- 240 kWh
- cooling water / $20^{\circ}C$ /	- $50 m^3$
- fuel oil /heating volume $9000 \frac{kcal}{kg}$ /	- 360 kg

The installation is able to produce, besides sulphuric acid, also small quantities of 25 % oleum.

The described process, in times of low sulphur prices, is unprofitable, but the necessity of utilisation of wastes from the future phosphoric acid production makes the process interesting in that respect.

The cement of "350" quality is characterized by:

	<u>after 3 days</u>	<u>after 7 days</u>	<u>after 28 days</u>
Bending strength	25	40	60
Compressive strength	130	225	350

5. Sulphuric acid production on cake base

Poland, having large quantities of sulphur refining wastes /cake/, uses them as raw material for sulphuric acid production. The calcinating process is carried out in fluidised bed calciner with a bed surface loading of 10 t/m<sup>2</sup> day. The fluidised bed is artificial, made of 2-4 mm grain sand. Inside the bed, boiler pipe elements protected against abrasion are installed. The calciner exhaust gases of SO<sub>2</sub> - concentration of 13 % and of temperatures of 550°C pass through the boiler, there they are cooled down to the temperature of 400-450°C and further processed in normal sulphuric acid units, which are additionally furnished with cooling and washing system, wet electrostatic precipitators, drying tower, blowers, contact and absorption assemblies. By single contact the conversion ratio of 98 %, and by double conversion the 99,5 % ratio is achieved. The wash waters of the scrubbing system, after SO<sub>2</sub> is desorbed and neutralised, are fed into the sewage system.

The calcines, being the wastes of the method, are used in agriculture as lime fertilisers.

The very important element of this method is the proper dust collection, thus special large dry precipitators are installed to clean the gases before they are washed to the maximum possible degree.

Dry electrostatic precipitators, working on high 60 kV voltage must have the efficiency of 99 %, if not, large SO<sub>2</sub> losses occur and the calcines represented in large amount by the calcium carbonates are contaminated with SO<sub>2</sub> and SO<sub>3</sub> gases.

6. Sulphuric acid production SO<sub>2</sub> - containing gases base

In non-ferrous metallurgy, particularly in copper gases containing 4-12 % SO<sub>2</sub> are received. The composition of the gases changes in the course of the time depending on copper converter operation. In Poland there are two large copper metallurgy plants;

each of them has installed several converters working discontinuously. Their working time must be settled in a manner securing the most uniform gas concentration. Practically it is difficult to achieve, therefore, in order to prevent the contact cooling or low conversion ratio, additional sulphur burning furnaces have been built, the role of which is to stabilize  $\text{SO}_2$  content and keep high  $\text{SO}_2$  conversion ratios.

The gas temperature during converter working period swings between  $1200-350^\circ\text{C}$ , which is the cause of sulphuric acid condensation in coolers and in the electrostatic precipitator. By means of sulphur afterburning the gas temperature is elevated, the corrosion possibility is diminished, the conversion ratio reaches 96 % which is satisfactory in that sort of installations. The resulting  $\text{SO}_2$  gas is captured by ammonia absorption,  $\text{SO}_2$  conversion ratio of 80-90 % and  $\text{SO}_3$  ratio of 50 % are obtained. The cooling and washing system waters contain large amounts of dissolved  $\text{SO}_2$  and therefore, before sewage discharging, must be desorbed in a tower by an air stream and neutralized. The further equipment, from washing tower assembly to the storage, is similar to the cako base unit.

#### 7. Sulphuric acid production on pyrite base

Poland, having nowadays no s. acid pyrite base working unit, supplies and supplies abroad new complete plants of that type. The base of a 360 th. t/y of monohydrate unit is the Dorr Oliver license.

Independently, the Polish experience on similar working units on zinc blende and cako base made possible the further improving and modernizing of the licensed units. At present, to the primary licensed unit working on single contact principle, the double contact principle is being introduced in consequence of which a considerable  $\text{SO}_2$  content drop in flue gases is possible. The considerable number of changes and improvements on several equipment assemblies, thus diminishing the investment costs, are to be done.

#### 8. Export of sulphuric acid and its transportation means

In summer time in Poland sulphuric acid concentrated up to 98 %, and in winter up to 93-95 %, because of low temperatures and freezing possibilities - is produced. At the same time oleum 25-35 % or 65 % of free  $\text{SO}_3$  is produced. Besides the technical acid and oleum of great purity, also reagent of special purity for analysis - is steadily produced.

In Poland deliveries are made by producers, as sulphuric acid plants own all kinds of railway transportation equipment and cars, which is also the case in export activities. In case of larger quantities, the receivers may get the product in trains, or much more frequently now, by means of se tankers.

Poland has a large surplus of sulphuric acid, and in case of urgency, 250-300 thousands of tons per year may be exported. In our sea-harbours the bases for loading of tankers up to 10 000 DWT have been extended, the storage parks and necessary equipment enable the short period of loading or discharging functions.

Sulphur acid transportation is difficult because of its corrosive character.

Much more economical and reasonable is the transportation of raw material i.e. sulphur, the sulphuric acid being produced by the receiver, because only 1 ton of sulphur is sufficient to produce 3 tons of the acid. Acid transportation is reasonable only in case the receiver wants to avoid troubles connected with the flue gases, although the  $SO_2$  quantities in these cases are very small, or in want of avoiding sewage poisoning by acids, possible only in the case of breakdowns.

Oleum export significance is negligible because of small demand for oleum, nevertheless the necessary quantities may be delivered in railway cars or steel containers. During the year 1971 only, Poland exported abroad over 150 th. tons of sulphuric acid, by railway or by sea in tankers. At present Poland is already in possession of the first special sea tanker.

#### 9. Sulphuric acid production economics

The erection of a sulphuric acid plant requires considerable capital. Capital absorptiveness of the installation is very differentiated and depends mainly on the kind of the raw material.

Erection costs of the sulphuric acid unit, comprised within "battery limits" on base of sulphur, calcinated pyrite or calcium sulphates /anhydrite, gypsum/ being the world main raw materials - are in approximate proportion of: 1 : 3 : 9. It must be pointed out that with anhydrite or gypsum, besides sulphuric acid, clinker /cement/ is produced, the compounded production exerting its influence on capital and operating cost.

Erection costs of sulphuric acid unit on  $\text{SO}_2$ -containing gas base, are not taken into account, as the enterprise of that type is generally necessitated only by air pollution counteraction, and their cost is higher than that on pyrite base.

The most economic therefore is the sulphur base unit. The actual cost of the unit of that kind, of capacity about 300 th.t/y, double conversion and absorption principle, within "battery limits" - amounts \$4,0 mln. whereas the proportional capacity unit on pyrite base and adequate "battery limits" - amounts to \$12-13 mln. The total cost of the plant is, as a matter of fact, much greater, the additional and connected cost of energy, transportation, administration and others, being taken into account. Capital and scope depend in any case on local needs, the more that the sulphuric acid units are as a rule comprised in larger plants or integrated factories, where the acid serves as a semiproduct to final product fabrication.

Operating costs are very differentiated, those of sulphur base unit are the lowest. In large units it is the rule that direct operating costs are covered approximatively by steam generation income, as the sulphur combustion heat is utilised. In consequence in these units the operating costs are defined by sulphur preparation and indirect costs as amortisation, capital lock up, and overall unit, plant or factory costs. The fabrication costs on all basis except sulphur base being much higher, with comparison to the said raw materials prices, recalculated on sulphur, must be much lower than the price of elementary sulphur ones, hence the tendency of pyrite sulphuric acid producers to reduce pyrite prices. For example, in 1971 the prices of pyrites /f.o.b. export harbours/, composed of 48 % of elementary sulphur - amounted 9-10 \$/t, recalculated on pure elementary sulphur-reached 19-21 \$/t, whereas the imported sulphur prices in Europe ranged between 23-26 \$/t depending on location. In this respect the pyrite competitive prices should be as low as 7-8 \$/t, which is rather impossible to be obtained in view of mining and separation costs that are much higher, with the sulphur prices falling steadily at the same time.

It is therefore obvious that several pyrite sulphuric acid plants are destined to be reinstalled on sulphur base, which is already the fact in many cases.

Newly built sulphuric acid plants shall be therefore based on sulphur, and only the countries disposing of very cheap pyrite may be interested in pyrite plants development. Sulphuric acid prices, by train deliveries, range 20-30 \$/t with tendency to drop, because of low and steady dropping of sulphur prices and utilization of larger transport means like tankers, the ultimate prices being as low as 18-25 \$/t. Raw material transportation costs play its considerable role in sulphuric acid economics, depending mainly on specific quantity of the raw material used to produce 1 t of acid. By sulphur base production only 332-340 kg of this material is sufficient to produce 1 t of acid. In consequence the location of sulphur base plants is unrestricted, and is not bound with sulphur sources, as the weight of the transported raw material is three times lower than that of the product itself. In pyrite case, the total weight of raw material increases up to 75-80 % of weight of the produced acid, remaining, however still lower. In case of smaller sulphur content pyrites, the total weight of raw material may equalise the product. It is reasonable that plants of both sulphur or pyrite base are generally located near the consumption centers, mainly being the components of large phosphates plants. Another situation exists in anhydrite or gypsum fabrication, in this case its consumption amounts to 1,8 - 2,0 t per ton of produced acid and additional large quantities of such materials like sand, lime, pyrite calcines and others amounting 0,25 t/t, and together with fuel 0,4 t/t make the total materials weight 2,5 - 2,6 times greater than the weight of the produced acid.

Although comparatively great masses of cement are obtained the location of these plants does not depend on the demand of cement but on the nearness of sources of anhydrite or phosphogypsum.

Another factor in s. acid economics is the capacity of the unit; the larger the producing unit the lower are operating costs, consequently the lower are the prime costs. The optimal unit capacity is expected to be among higher capacities. It is obvious that the largest units may be erected only on sulphur base, where the highest  $SO_2$  concentrations are available in combustion process, and the necessary oxygen concentration of such degree that the conversion ratio reaches the height of 99,9 %. There are nowadays acid plants of capacity as high as 600-700 thousands t/y.

thus the prime cost falls below 10 \$/t. Foreign trade, being the important factor in sulphuric acid production development, shows the increasing tendencies and its role in total world consumption data is represented by 1,2 - 1,6 % only. In the coming years the foreign trade increase is to be foreseen, the main reasons of it are the following:

- a/ the fabricating costs are largely differentiated; in cases of non-ferrous metallurgy the acid is the by-product only and its price can be fixed very low indeed; other producers may be competitive in case of disposing very cheap raw materials or large production units
- b/ the transportation costs are inversely proportional to the trade increase, the long distance supplies being profitable and the receivers being thus not necessitated to start their own production at low cost.

Under specific conditions, all this may induce the trade increase, instead of production development.

#### 10. Polish sulphuric acid industry research, design and executing possibilities

Poland is among the countries of Council for Mutual Economic Aid the leader in sulphuric acid technology progress, and her export of this kind of industry to several countries is considerable. Over 30 sulphuric acid complete plants or installations both on sulphur and pyrite base, single or double contact principle were exported. The capacities of the majority of the units exported to COMECON countries, varied from 100 thousands to 360 th. t/y of NH<sub>3</sub>. Independently, in the country itself over 30 plants were built, on different raw material bases, all the unusual equipment and the majority of machines and typical equipment having been produced in the country by specialised industrial firms.

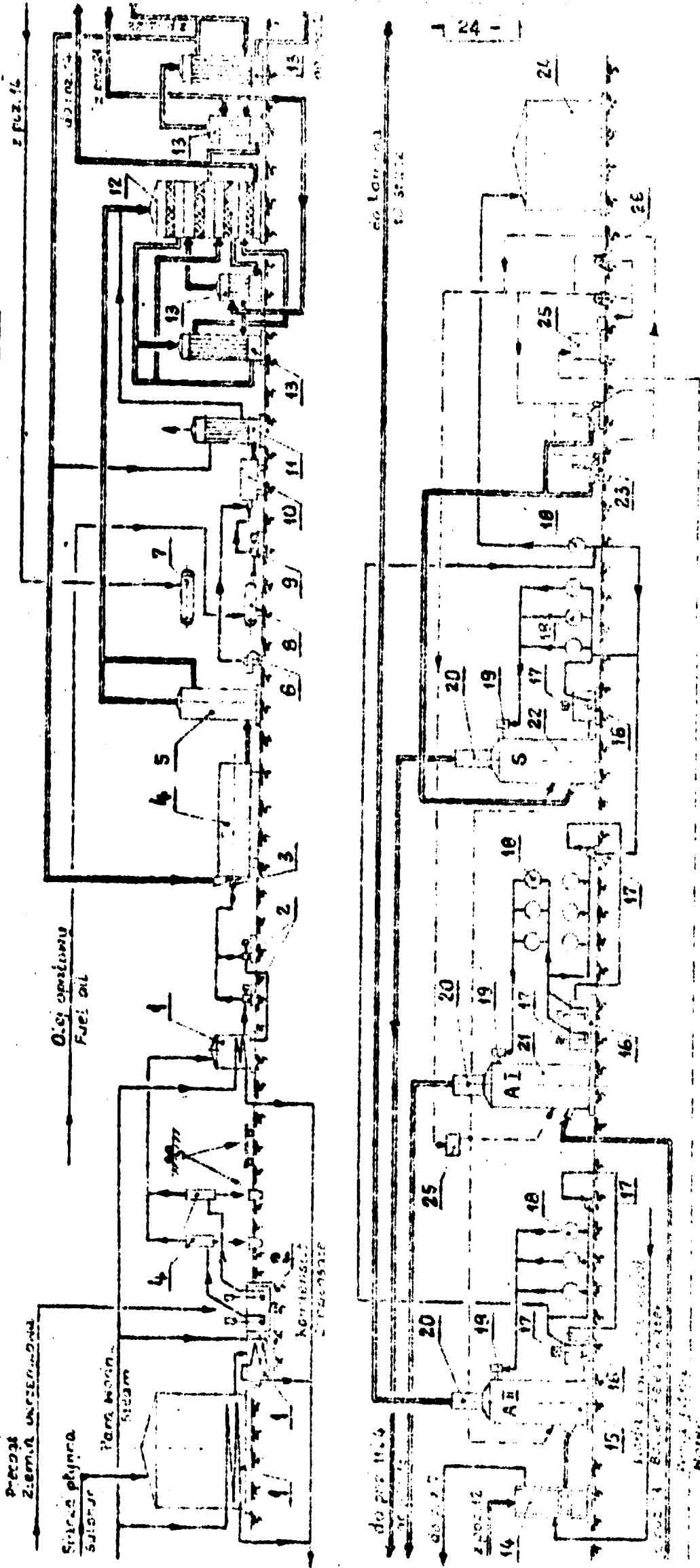
At the moment, the import of the equipment from Western Countries is confined to several types of control instruments and fittings. Of course, in case of Client's wish and limited delivery periods, special equipment may be imported. Polish catalyst production being insufficient in the face of newly erected units, in many cases is imported from German Democratic Republic or Western Countries.



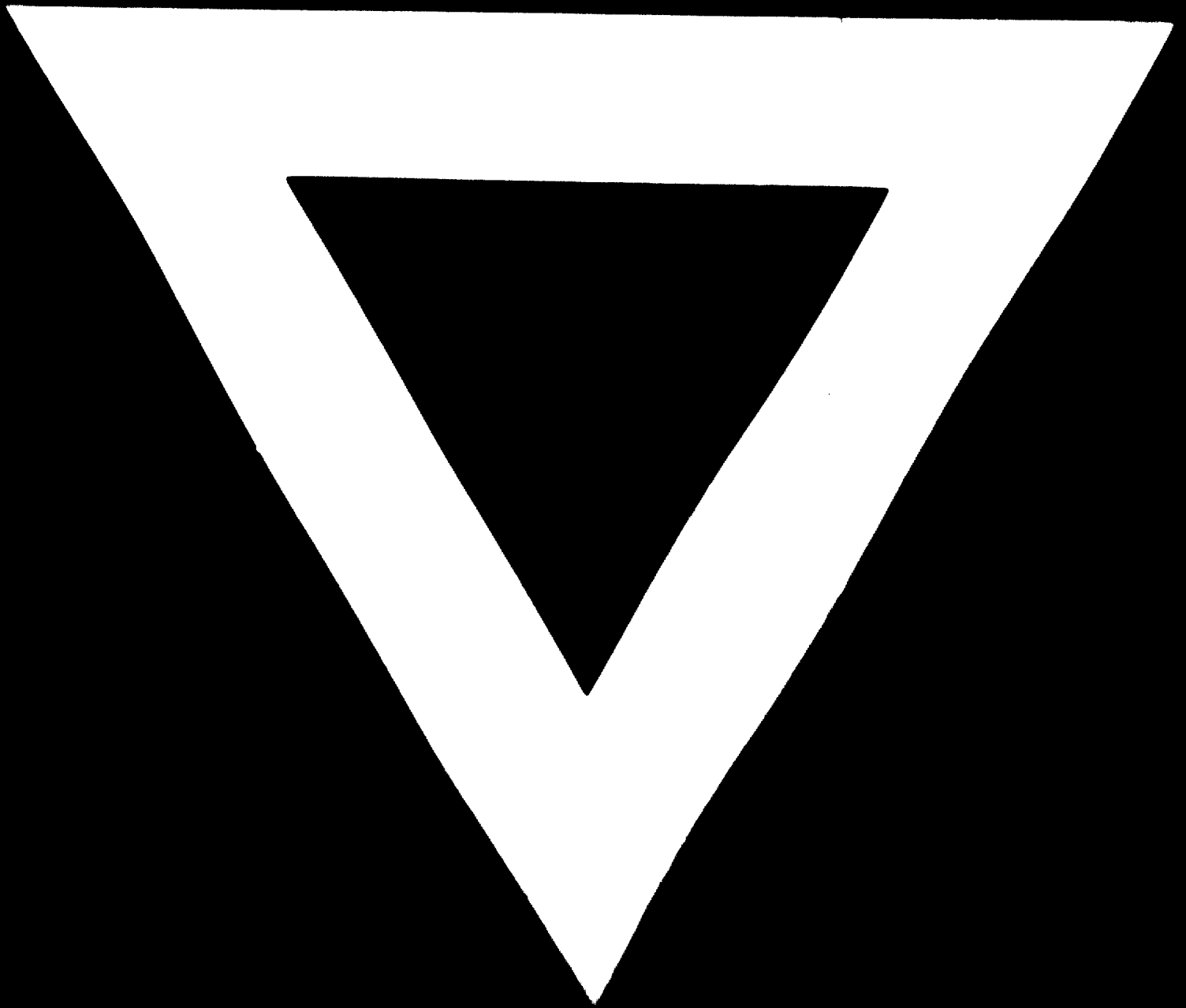
In order to keep the leadership in sulphuric acid technology the research institute, design office, experimental base and executing forces have been developed, and licences for special equipment production were bought. Under the leadership of Study, Design and Executing Office "Biprokwas" - in Gliwice with newly submitted Experimental Works, by the aid of Inorganic Chemistry Institute and on the base of experience of about 30 industrial works - overall progress of the said technology has been secured to develop.

By the aid of our own industrial potential and eventual cooperation with specialised firms from abroad, Polish commercial institutions are able to export sulphuric acid ordered in "battery limits" or under "turnkey" - conditions, up to 500 thousands t/y of monohydrate on sulphur base or 360 th. t/y on pyrite base, in short delivery periods, in whatever direction, according to specific Client's wishes, and by the help of our own or Client's executing forces. The first step in Western direction has been made already - in Duisburg - Federal Republic of Germany.

# INSTALACJA DO PRODUKCJI KWASU SIARKOWEGO Z SIARKI MET. PODWOJNEJ KONWERSJI SULPHUR - BURNING DOUBLE CONTACT PROCESS SULPHURIC ACID PLANT



- |   |   |  |   |  |  |
|---|---|--|---|--|--|
| 1. Zbiornik magazynowy siarki<br>Sulphur storage tank | 5. Kotłociepłota<br>Boiler                          | 9. Pompa do oleju<br>Oil pump              | 13. Wymiennik ciepła<br>Heat exchanger      | 17. Pompa do kwasu<br>Acid pump        | 21. Kłoda absorpcyjna<br>Absorption tower I  |
| 2. Pompa do siarki<br>Sulphur pump                    | 6. Wentylator<br>Air fan                            | 10. Palenisko startowe<br>Start-up furnace | 14. Podgrzewacz wody<br>Economizer          | 18. Chłodnica spirali<br>Spiral cooler | 22. Kłoda absorpcyjna<br>Absorption tower II |
| 3. Palenik siarki płynnej<br>Sulphur burner           | 7. Zbiornik wody kłottowej<br>Boiler feedwater tank | 11. Wymiennik ciepła<br>Heat exchanger     | 15. Kłoda absorpcyjna<br>Absorption tower I | 19. Filtr kwasu<br>Acid filter         | 23. Zbiornik<br>Tank                         |
| 4. Pies do spalania siarki<br>Sulphur furnace         | 8. Zbiornik oleju<br>Oil tank                       | 12. Aparat kontaktowy<br>Converter         | 16. Zbiornik cyklu<br>Pump tank             | 20. Zbiornik<br>Demister               | 24. Zbiornik mag. kwasu<br>Acid storage tank |
|   | 25. Zbiornik wody<br>Water tank                     |  | 26. Pompa do wody<br>Water pump             |  |  |



**30. 11. 73**