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PROCEEDINGS OF : THE REGIONAL SEMINAR ON FOLLUTION PROBLEMS IN FERTILIZER PLANTS IN ARAB STATES BAHRAIN, NOVEMBER, 16-18, 1981

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<u>KUWAIT</u> January, 1982

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INTRODUCTION

The seminar is one of the 1981 activities of the regional cooperation programme for the development and promotion of fertilizer production and utilization in Arab Countries.

The seminar was organized by Arab Industrial Development Organization (AIDO-in Baghdad) and Arab Federation of Chemical Fertilizer Producers(AFCFP-in Kuwait) in cooperation with Bahrain Society of Engineers and Ministry of Health in Bahrain under the sponsorship of United Nations Industrial Development Organization(UNIDO, Vienna) acting as executing agency on behalf of the United Nations Fevelopment Programme(UNDP, New York).

H.E. Dr. Ali Fakhro, Minister of Health, president of the High Committee for the protection of the Environment in Bahrain opened the Seminar. His Highness made a welcome address to the participants and stressed in the inaugural speech on the need of clean environment and urged that more effort should be taken to protect against pol lution through cooperation and coordination between industry and research institutions.

Earlier, Mr. Hassan Fakhro, the Chairman of BANDCO and President of Bahrain Society of Engineers, welcomed the participants and ex pressed his happiness for choosing Bahrain to hold this important Seminar. He demonstrated the importance of protection of environment particularly the air we breath and the water we use in different purposes of life.

Mr. Farouk al-Ma'ayouf, Secretary General of Arab Federation of Chemical Fertilizer Producers made a statement expressing his appreciation for the contribution that has been made by other's.He pointed out that the Arab Region is witnessing rapid development in fertilizer industry which might cause adverse effects on the quality of the en vironment. He expressed his hope that the discussions at the seminar would help to understand pollution problems in fertilizer industry and share experiences gained by participants in tackling the pollution effectively.

Dr. Ghanim representative of Arab Industrial Development Organization expressed his gratitude to the government of Bahrain. He re fered to the cooperation between AFCFP, AIDO and UNIDO in implementing the Regional Cooperation Programme for Development and Promotion of Fertilizers in the Arab Region.

Over (50) participants from both fertilizer companies and concerned organizations in the Arab Region and abroad participated in the Seminar (Bahrain, Jordan, Algeria, Saudi-Arabia, Syria, Iraq,Qatar, Kuwait, Lebanon, Norway, Belgium, Italy, Germany and Denmark).

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WORKING SESSIONS

• FIRST DAY: Sunday, November 15th.

Chairman: Mr. Farouk Al-Ma'ayouf, Secretary General,

AFCFP, Kuwait.

Rapporteurs: Dr. Ghanim Jasim, AIDO, Baghdad.

Mr. M. Ezzat, AFCFP, Kuwait.

* <u>Morning Session</u> :

1-Pollution Control in Fertilizer Industry in Arab States.

2- Recent Developments in Environmental Aspects in Indian Fertilizer Industry.

3-Effluents and Measures of Pollution Control in JFI's Fertilizer Complex in Aqaba, Jordan.

* Afternoon Session:

4-Stepping Forward to Environmentally Balanced Fertilizer Complex by Integral Planning, Effective Operation and Preventive Maintenance.

5-Lower Nitrogen Effluent from Urea Plants.

6-Process Condensate Pretreatment, A New System Designed for Ammonia Plants in Kuwait.

* Discussions

1- Pollution Control In Fertilizer * Industry In Arab States

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- 1- Introduction
- 2- Fertilizer Industry Situation in Arab Region
- 3- Sources of Polution in Fertilizer Industry
- 4- Pollution regulations and legislations in fertilizer industry
- 5- Pollution Control Techniques and cost
- 6- Conculsions and recommendations
- References

1- Introduction:

In the line with efforts in the Arab Region to boost food production and exploite the available sources of raw materials, the fertilizer industry expanded very fast during the last docade and high capacities are expected to come on stream during this decade. Consequently, pollution control of gaseous emissions and effective treatment of liquid effluents and solid wastes are becoming important issues. The gaseous emissions from fertilizer manufacturing plants contain various pollutants like SO_2 , SO_3 , NO_2 , NH_3 , F, vapours, mists, and dusts, while liquid effluents contain a variety of substances such as oils, alkalies, acids, urea, ammonia, phosphates, fluorides ..etc. The main solid waste is the phosphogypsum resulting as by-product from phosphoric acid manufacure. It is one of the major pollution problems worldwide.

By: Eng. Mahmoud Ezzat Arab Federation of Chemical Fertilizer Producers.

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The major causes of pollution by the fertilizer industry have been intensively studied in recent years, leading to the introduction of effective control techniques and treatment methods.

The protection of environment against pollution from fertilizer industry particularly of the air we breath and the water we utilize in diffirent purposes, is of increasing and universal concern. Stringent regulations and Legislations are adopted by many developed countries. Similar legislations and guidelines dealing with air and water pollution by fertilizer industry have been formulated recently in some of developing countries like india. In the Arab Region the fertilizer producers also have taken various steps for prevention and control of air and water pollution. Certain countries have already laid down the limits of allowable concentrations of pollutants in the effluents and emissions from their fertilizer plants as guidelines for pollution control.

The pollution control by applying modern techniques available will certainly increase the cost of production but in many cases the increase in the cost of production can be offset by the recovered values. Available data on cost of pollution control are usually estimates depending on: techniques, pollution regulations, location, ..etc..

The total expenditures on a world-wide basis, by all countries for air and water pollution control in the fertilizer industry was estimated for 1980 at about 5 billion U.S. Dollars.

The second follow-up meeting of the UNDP Regional Cooperation Programme held in Baghdad last August decided to carry out a technical field study on fluorine. uranium, and phosphogypsum recovery in a phosphatic fertilizer complex by a team of experts. Morocco, Tunisia, Algeria, Iraq. Jordan and Syria will be included in this study which is expected to start in the first half of 1982.

2- Fertilizer Industry Situation in the Arab Region:

At present, most of the types of nitrogenous, phosphatic and compound fertilizers are produced in the Arab Region and high capacities will come on stream in the eighties, while potassic fertilizers will be produced from the Arab Potash Project in Jordan.

Therefore huge quantities of raw materials such as sulphur and phosphate rock will be produced to meet the requirements of the fertilizer industry.

Tables (1), (2), (3) and (4) give the existing installed capacities and actual production of fertilizer raw materials, intermediat.s, and finished nitrogeneus and phosphatic products, and the expected increase in the installed capacities by 1985 in the Arab Region.

It may be seen from these tables that there exists a wide gap between the installed capacity and the actual production, and efforts are being done to improve the performance of fertilizer plants in the Arab Region. One of these efforts is directed to control pollution along with the recovery of valuable products, thus increase the effective production capacity of the fertilizer plants.

Table (1) Sulphur & Phosphate Rock Production in the Arab Region

Million Tonnes Product

Year Raw Material	1979	1980	<u>1982</u>	1985
SULPHER	1.3	1.7	3,1	4.4
PHOSPHATE ROCK	30,3	30.4	46.8	61.9

	Table	(2)	The	Production	of	Fertiliza	er	Intermediates
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1000 Tonnes

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in the Arab Region

Year	19:	79	19	80	1982	1985
Туре	Cap.	Prod.	Cap.	Prod.	Cap.	Cap.
Ammonia as N	3504	1723	3504	1911	4893	7 32 8
Nitric Acid as (100 %)	1366	805	1366	796	2124	2504
Sulphuric Acid as (% 100)	6394	4700	9234	4489	12501	19219
Phosphoric Acid as P2 05	1795	1035	2620	1323	3760	5874

Table (3) Nitrogeneous Fertilizers Production

<u>1000 To</u>	<u>nnes N</u>
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In The Arab Region

Year	1 9	79	1 9	8 0	1982	1985
Туре	Cap.	Prod.	Cap.	Prod.	Cap.	Cap.
UREA	1792	1069.7	2209	1331.0	2778	3 902
Ammonium Sulphate	• 104	32,9	104	28.5	104	171.01
Ammonium Nitrate	350	247.9	350	249.2	715	842
Calcium Ammonium Nitrate	38,5	19.8	38.5	12.7	38.5	38.5
Calcium Nitrate	39	31.0	39.0	31,0	39.0	39.0
МАР	32	7,1	32.0	6.7	57.0	80.0
DAP	77.4	2.5	77.4	40.3	210.4	291.0
ASP	28	9.9	28 .0	20.6	28.0	28.0
NPK	56,3	28.7	56.3	26.1	105.3	105.3
1 O T A L	2517.3	1445	293 4 .2	1746.1	4075.2	5496. 8

Table (4) Phosphatic Fertilizers Production In The Arab Region 1000 Topnes P2 05

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Year	19	79	19	8 0	1982	1985
Туре	Cap.	Prod.	Can.	Prod.	Cap.	Cap.
SSP	184.6	138.6	184.6	132.0	240.6	240.6
TSP	752.8	487.1	964.8	352.9	1312.8	1444.5
G.P.R	55	50	55.0	27.0	65.0	65.0
МАР	176	39.1	176.0	36.9	313.5	440.0
DAP	206,4	6.7	206.4	107.5	561.4	775.4
ASP	56	20.3	56.0	41.1	56.0	56.0
NPK	97.6	43.7	97.6	54.4	146.6	146.6
Total 1	528.4	785.5	1740.4	751 .8	2695.9	3168.1

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The following is a brief summary of the fertilizer situation in the Arab Countries:

- Jordan: Jordan is one of the major producers of phosphate rock in the Arab Region. Aqaba phosphatic ertilizer complex is expected to come on stream by the end of this year. Sources of pollution in fertilizer industry in Jordan can be summarized as follows:
 - Dust from phosphate rock beneficiation plants and loading and unloading facilities of phosphate rock and imported sulphur.
 - Gaseous effluents include SO₂, SO₃, HF and fluorides from sulphuric acid plants, phosphoric acid plant and granulation unit.
 - Liquid effluents from the sulphuric acid plant, phosphoric acid plant, granulation unit, utilities and sanitary sewage.
 - Phesphogypsum from phosphoric acid plant. Aqaba complex is designed according to very stringent emission and effluent criteria and therefore no pollution problems are expected except the stock-piling of phosphogypsum (2 km to east of phosphoric acid plant.

U. A. E. The Ruwais fertilizer plant will include:

- One NH₃ unit 1000 MT/D (Halder Topsoe)
- One Urea unit 1500 MT/D (Stami Carbon)
- Utilities

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- Offsites storage of NH₃ and bulk urea and NH₃ loading facilities

The plant is expected to come on stream by the end of 1983. The environmental aspects have been taken into consideration during the design stage. There will be a pollution control system with the necessary monitoring instruments.

<u>Bahrain</u>: The new plant for the Gulf Petrochemical Industries Company will be built on the north east coast of Bahrain near Bahrain refinery and Sitra Island. It will consist of two seperate process plants, one for the production of (1000) MT/D of ammonia and the other will produce (1000) MT/D of methanol. Both

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plants will employ the most-up to date technology and have common utilities and offsite facilities, including a desalination plant, emergency power generator, a nitrogen unit and a boiler feed water treatment plant. Storage tanks for the finished products will be installed, with pumping and ship loading facilities.

The complex will have its own pollution control equipment in addition to pollution monitoring system. Pollution control emphasised in the design of the complex will be according to international standards in order to mininize the discharge of pollutants to the environment.

<u>Tunisia</u>: The current production of phosphate rock in Tunisia is more than (4.5) million tonnes. Most of phosphate rock production is directed now to home fertilizer industry.

The two biggest fertilizer complexes are located at Gabes and Sfax near the sea and produce all types of phosphatic fertilizers in addition to phosphoric and sulphuric acids.

Phosphogypsum is now temporary dumped in the Gulf of Gabes while fluoride gases are washed and scrubbed by sea water. They have studied fitting up of a gypsum pond near the tertilizer complex of Gabes and the recovery of fluorosilicic acid. This is an efficient action for limiting the pollution of the Gulf.

The recovery of ammonium sulphate by scrubbing SO_2 and SO_3 from sulphuric acid plants was done successfully in Sfax and may be applied in near future in Gabes.

Nitric acid and ammonium nitrate units for S.A.E.P.A. are expected to come on stream by the begining of 1982. CO_2 will be the main by-product from ammonia plant.

On the other hand the liquid effluents of this plant will be considered in the overall plant in controlling pollution in Gabes area.

<u>Algeria</u>: Fertilizer production in Algeria is currently concentrated at two major complexes- the nitrogen complex at Arnew and the phosphate fertilizer complex at Annaba. Another two major nitrogen fertilizer projects started production this year one at Arzew (Arzew - 11) and the other at Annaba (Annaba - 11). Each includes ammonia and ammonium nitrate plants.

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The phosphate fertilizer project at Tebessa and the ammonia/ urea project at Skikda are expected to come on stream by 1984. Recently a great attention have been paid to control pollution in fertilizer industry which expanded fast during the last ten years. Phosphogypsum and the liquid effluents from the above mentioned fertilizer complexes are the major pollutants.

Saudi Arabia: A fertilizer complex for (Safco), including ammonia/urea, sulphuric acid and utilities plants, is located in Dammam area and started production since 1969. Another fertilizer complex for Al-Gubail Fertilizer Co. is now under construction at the industrial area of Al-Gubail and expected to come on stream by 1982.

> Safco lately made great progress in all areas including production and all other support functions and systems and put solutions for most of the serious technical problems which were facing the ammonia/urea plants in the early years. Many improvement projects were implemented to increase production and control pollution:-

- Minimising pollution from the effluent blowndown from the cooling tower to the sea. This was achieved by new chemical treatment system which reduces the chromate contents in the effluent.
- The urea revamp project implemented in1979 at an expense of SR 15.5 million improved the performance of prilling tower and minimized the urea fallout.
- Installation of high capacity refrigiration system to recover ammonia vapour from storage tank instead of flaring it

Pollution and its control at Safco attracts considerable attention. The new sulphuric acid for Safco which started production two years ago have been designed according to sophisticated technology (DCDA) and provided by very high stack to ensure against any pollution problems that may affect the population centres or governmental installations.

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Standards of evolution of toxic and noxious gases derived and enforced by the British Government for domestic plants have been followed in the design of this plant.

<u>Sudan</u>: A small ammonia/urea complex based on Naphta and located (10) kilcmeters to the south of Khartoum have been completed. It is expected to start production this year. Another simillar ammonia/urea project is now under planning.

The treatment of effluents and emissions to control pollution is of great importance due the nature and climatic conditions of Sudan.

Syria: At present Syria produces more than (1.3) million tonnes of phosphate rock from two phosphate deposits at Kneifis and Eastern (A & B). The phosphate beneficiation plants located near the mines are facing dust pollution problems. Syria also possesses nitrogen and phosphate fertilizer complexes located at Homs. The old and new nitrogencomplexes are based on naphta. Fluorides from phosphate complex will be recovered to produce aluminium flouride, while phosphogypsum is now temporarily stockpiled near the plant.

<u>Iraq</u>: At present Iraq possesses two nitrogen fertilizer complexes: one at Abu El-Flus and the second at Khor -Zubair, with a total capacity more than (1.5) million tonnes urea.

The phosphate project located at Al-Qaimis expected to come on stream by 1982. It is planned to include two small emmonia units for compound fertilizer manufacture.

The liquid effluents from nitrogen fertilizer plants at Abu-El Flus are neutralized before discharge.

The fluorides from phosphate complex will be recovered to produce aluminium fluorides, while sulphur oxides emissions from sulphuric acid plants included in the complex will be within the standard limits. The liquid effluents will be treated before discharging. Phosphogypsum will be stockpiled near the plant.

<u>Kuwait</u>: The fertilizer division of the Petrochemical Industries Company includes three ammonia plants, with a rated capacity of (2000 MT/D), three urea plants with a rated capacity of (2500

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MT/D), one ammonium sulphate plant, (500 MT/D), sulphuric acid (400 MT/D) and utilities. The fourth ammonia line with a capacity of (1000 MT/D) is expected to come on stream by the end of 1983. These plants are part of the big industrial complexes located at the Shuaiba Industrial Area.

P I C implemented some years ago remedial projects to control gaseous, dust and liquid effluents from ammonia and usea plants. For example, the recovery of ammonia from purge gases and using new elevated stack resulted in decreasing of ammonia concentration to the required limi (2.5) ppm.

The dust emiss 1 is now meeting the current guidelines for the Shuaiba area, after the modification of the prilling system and controlling of dust emission from cyclones and convayor.

Process condensate from ammonia plant is recycled and reused while the liquid effluent from urea plants is treated in hydrolizer to drop both urea and ammonia and then pumped (16) $K_{\rm M}$ far from the plant to be used for irrigation after dilution with sweet water.

The treatment and utilization of such effluents reflect significance to keep a good quality of sea water since the sea water is utilized to produce drinking water in North and South Power Stations.

- <u>Qatar</u>: Qatar Fertilizer Company (Qafco) forms an important part of the industrial development based on the natural resources of Qatar. The company includes two ammonia plants with a design capacity of (1800) MT/D, two urea plants with a design capacity of (2000) MT/D and utilities. These plants are located at Umm-Said, near the sea. Qafco pays great attention to control pollution, especially the urea dust, to protect neighbouring stores of grains from contamination.
 - Libya: At present there is a nitrogen fertilizer complex at Mersa Brege consisting of ammonia plant with capacity of (1000) MT/D; urea plant with (1500) MT/D and utilities. A simillar ammonia/ urea complex is now under construction in the same area and is expected to come on stream by the end of 1982.

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Libya also has other projects for phosphate and nitrogen fertilizers production in the planning stage and are expected to come on stream during the second half of this decade.

The country pays a great attention to pollution and its control and started to study some remedial projects to control gaseous and dust emissions from ammonia/urea plants.

Morocco:

Morocco is one of three major producers of phosphate rock in the world, these producers are U.S.A. U.S.S.R. and Morocco.

At present Morocco produces about (20) million MT/Y phosphate rock from mines at Khouribga, Youssoufia and Ben Guerir. (15%) of this production is converted into downstream products in phosphate rertilizer complex at Safi.

In the Safi phosphate fertilizer complex located on the Atlantic coast, there are four separate plant sites Maroc Chimie I, Maroc Chimie II, Maroc Phosphore I, and Maroc Phosphore II.

It is planned to build another big phosphate complex at Jorf Lasfar and Nador on Atlantic Coast, midway between Safi and Casablanca. The complex will include (12) phosphoric acid plants, the contract of them was awarded to Rhone Poulenc in Sept., 1980.

The huge quantity of sulphur required for these complexes will be imported in Solid form, then melted and stored as liquid at the port.

Stringent control on gaseous and dust emissions, liquid effluents and the huge quantity of the solid waste of phosphogypsum from these fertilizer complexes have to be imposed to avoid any adverse effect on atmosphere and the ecology cf sea water,

2- Sources of Pollution in the Sertilizer Industry

We have seen from the previous chapter that a nitrogen or phosphate fertilizer complex is composed of different production units which produce a number of products at the same plant site. There are three major effluents discharged from fertilizer industry: gaseous, liquid and solid wastes.

The following is a brief summary of emissions and effluents discharged from different fertilizer plants.

Ammonia Production:

Most of ammonia plants in the Arab Region are based on steam reforming of natural gas. Jaseous emissions and liquid effluents from such plants are:

- Gaseous emissions:
 - Flue gas from primary reformer contains sulphur and nitrogen oxides. The sulphur oxides emissions (mainly NO2) depend on the type of fuel used for firing in the primary reformer. Incase of using natural gas, emission of sulphur dioxide may reach (0.3)kg/MT ammonia, and increases to (3) kg/MT ammonia when using fuel oil.

Nitrogen oxides measured as NO_2 may reach in some cases (0.5) kg NO_2 per MT of ammonia produced.

- 2- Ammonia emissions occur sometimes as result of leaks in equipment and from pressure releive valves. If ammonia is not recovered from purge gas, this will be another source of ammonia emissions.
- 3- Carbon doixide released to the atmosphere during the CO_p removal step.

Liquid effluents:

Most of liquid effluents in ammonia plants are obtained as condensates from the process gas after Co shift conversion and methenation. This condensate contains NH_3 , CO_2 , methanol and others in concentrations ranging from $(0, 8 - 1) \text{ kg NH}_3/\text{m}^3$, $(1 - 2) \text{ kg of } CO_2/\text{m}^3$ and $(1.5 - 3) \text{ kg of methanol } / \text{m}^3$. The quantity of condensate from ammonia plants will vary according to the design of the plant. It may reach 2 m³ per MT ammonia.

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Nitric Acid production:

Residual concentrations of nitrogen oxides in nitric acid tail gases from the absorption tower due to incomplete absorption give rise to air pollution problems. A typical nitric acid plant of (350) MT/D capacity would emit about (35) $Nm^3/$ hr of tail gas with nitrogen oxides content ranging from (0.1 - 0.3%). In other words, the total nitrogen oxides emissions would be over (15) kg/MT of acid (100% basis)

Regarding liquid effluents other than cooling tower blowndown, there is small amounts of ammonia and nitrate in the effluents arising from leaks, spills, and process upsets. Generally there is no discharge of process waste water from nitric acid plant.

Ammonium, Nitrate Production:

Major sources of air emissions in ammonium nitrate plants are neutralizer, evaporator, prilling tower, dryer, and cooler.

Emissions consist of ammonia, ammonium nitrate dust, fumes, liquid particulates and nitric acid mist.

Ammonia, ammonium nitrate and nitric acid mist are emitted from nuetralizer. Losses from neutralizer due to this emission reach in normal cases (2)Kg Ammonia, (2)Kg Ammonium nitrate and (0.2)Kg nitric acid per MT Ammonium nitrate product

Losses of ammonium nitrate as fames and liquid particulates due to emission from evaporator may reach(0,2)Kg per MT ammonium nitrate product

Emissions from prilling tower contain ammonia, ammonium nitrate dust and ammonium nitrate fumes. Losses in well operated plants may be expected to reach (2) kg ammonium nitrate perMT product.

The major source of liquid effluent in ammonium nitrate plant is process condensate from neutralizer. The liquid effluent containSammonia and ammonium nitrate in quantities of (1)Kg and (7) Kg of ammonium nitrate per MT of product. This liquid effluent can be treated to remove ammonia and ammonium Aitrateions to the extent of (0,1)Kg per MT product and (0,13)Kg per Mt product respectively. The treated effluent can be zeused as make-up for boiler feed water or cooling tower.

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Urea Production

Urea dust which is the major source of air pollution is emitted with the air coming from the top of the prilling tower. Ammonia also is emitted in considerable quantity from the prilling tower. The flow rate of air through a natural draft tower of (1000) MT per day wrea plant is (400 000) N m³ /hr. The actual dust concentration may reach $(400) \text{ mg/N m}^3$ or even more. Losses of ammonia and wrea due to this emission may reach (0.5)Kg per MT product and (1.2)Kg per MT product respectively.

The process condensate from vacuum concentration /crystallization section and the prilling tower effluent are the major sources of the process waste water. The quantity of this effluent will range from (0.5) to (1)m³ per MT of Urea produced. Ammonia and urea concenvary according to the design of the plant. In some tration will cases these concentrations range from (2- 6 %) for ammonia and (0.2 - 0.5%) for area by weight. Ammonium Sulphate Production

Air pollution sources include crystallizer and dryer. The vapours at crystallizer contain ammonia, Which is usually condensed and recycled . While the off-gas of dryer contain ammonium sulphate dust in quantity of (0.15) Kg of ammonium sulphate per MT product.

Liquid effluents in ammonium sulphate plant originate from spills, leaks and contaminated waters from condensers

The liquid effluents are returned to the process and a discharge is not necessary.

The volume of liquid effluents from direct contact condenser may reach (35)m3/MT product while that spills, leaks and clean-up

water may reach (0 4)m3/MT product.

Sulphuric acid production

 $S02 + \frac{1}{2} 02 \implies S03 + HEAT$

Sulphur oxides " SO2, SO3 ", acid mist, acidvapours and nitrogen oxides are pollutants evolved from the manufacture of sulphuric acid. The most important pollutants are sulphurdicxide and acid mist. The concentration of these pollutants in vent gases will vary depending on the conversion efficiency of (SO2 to SO3) and the process conditions. Vent gases from a conventional sulphuric acid plant " single contact plant"contain about (4000 ppm) of $302 \text{ and } (2000 \text{ mg/m}^2)$ of acid mist.

In a double contact sulphuric acid plant equiped with mist eliminator, the concentration of (SO2) and mist can be reduced to less than (500 ppm of SO2 and 50 mg/m3) of acid mist.

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(Table	5)	Concentration	01	poilitants in	sulphuric
				acid plant	tail	gases	

Pollutants	Concentration range	🕉 Equivalent H2SO4
	p p m	Loss
S02	200 - 4000	0.2 - 4%
s03	0 – 100	0.1%
H2SO4 Vapour	250 - 1000	U . 1 %
H2SO4 Mist	10 - 500	1,0 %
Nitrugen oxides	0 - 200	0.5 %

Phosphoric acid Production " wet process ":

Fluorides, phosphate dust, some liquid effluents and by product gypsum are the main pollutants in wet process phosphoric acid plants.

The fluorine in the Phosphate rock when reacted with sulphuric acid is distributed in the by-product gypsum, phosphoric acid and exhaust gases. About (30 /) or more of fluorine in the rock is released during the concentration of phosphoric acid from (30 /) to (54 /).

A considerable amount of fluorine is contained in the gas emitted from the reactor , filter and storage tanks,

The fluorine compounds contained in the gas consist mainly of HF and SiF 4. The concentration of these compounds in the gas vary widely depending on the type of rock used and the process conditions. fluorine content in the reactor gases ranges from (200 - 1000) mg F/m3 while that in went gases from the filter and storage tanks is less than (100) mg F/m3.

Usually fluorine compounds from reactor, filter , tanks, vent gases and concentration section are removed by absorption in scrubbers to recover fluorine as (17% - 23%) H2SiF6 solution which can be used for Aluminium fluoride and cryolite manufacture .

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Whate water from direct contact condensers contains flucride

and P205 in low concentration mbout (0,02%) H2SiF6 and(0,002%) P205, has to be neutralized with lime prior to disposal. The recovered H2 SiF6 solutions if not utilized is also to be taken for neutralization.

The major sources of dust evolution in Phosphoric acid plant are handling and grinding of Phosphate rock.

Phosphogupsum is the main solid waste from phosphoric acid plants. Depending on the technology applied it can be used in manufacturing several products such us cement and Sulphuric acid, ammonium sulphate, plaster boards and others.

Single Superphosphate production

Depending on the acidulation conditions and the quality of phosphate rock about (40-70%) of the fluorine in the phosphate rock is evolved during the processing, while (30-60%) remain in the product. The main sources of fluorideemistions are mixer, den, conveyors and storage pile(curing). The concentration of fluorides in guseous effluent from mixer, den and conveyors ranges from (1000 to 8000) mgF/m3.

Singlesuperphosphate plant liquid effluents contain pollutants fluorides, phosphates and suspended solids in concentration reach in some cases to (600 ppm) of fluorides and (1000 ppm of P205). The source of this effluent is the scrubber used for the removal of fluorides from gaseous effluent. The quantity of water used for scrubbing may reach 1m3 per MT of (P205) produced. This scrubber effluent is usually recycled and only bleed is drained after neutralization. It is possible to produce (15 - 20 // H2 SiF6) solution and containing (50 ppm P205) only.

Triple Superphosphate production

Fluorides are evolved during the acidulation of rock phosphate with phosphoric acid.

Ca10 (PO4)6 F2 + 14H3 PO4 ----- 10Ca(H2PO4)2+ 2HF

In the process of production of powder TSP the main sources of these fluorides are the effluent gases coming out from the reaction section which include, mixer, den, cutter, conveyor, and curing house. In granular TSP the sources are reaction section and granulation section, the later includes granulator, drier, screen and storage.

About (8 KgF/MT of P205 produced) is evolved during the processing of powder TSP, while about (16 KgF/MT P205 produced) remains with the product.

Water is used to scrub the effluent gases in appropriate scrubbing equipment. The quantity of this water is about the same as for singlesuperphosphate. A suitable system of cyclones should be installed before the gas scrubbers, thus it is possible to produce (15 -20%) H2SiF6 containing (P2O5) contamination not exceeding (50 ppm).

The collected dust and washing liquid recoveries are consumed in granulation section thus minimize waste water to be treated.

Nitrophosphate production

The basic reaction in the nitrophosphate production is the acidulation of rock phosphate with nitric acid instead of sulphuric acid

Ca10(P04)6F2+20HN03 \longrightarrow 10 Ca (N03)₂+ 6 H₃ PO₄ + 2 HF

Most of fluorine in the phosphate rock is retained in the product , while about (5%) only of this fluorine is evolved during the processing of nitrophosphate . The fluorides in the effluent gases are scrubbed with water. The scrubber liquor contains a very dilute solution of (H2SiF6), therefore it is neutralized and discharged

Ammonium Phosphates

Ammonia fumes, ammonium phosphate particulates and fluorides are evolved during the production of the different types of ammonium phosphate fertilizers, from ammonia and phosphoric acid. Ammonia fumes from neutralizer, granulator and drier are recovered in **venture** scrubbersfor reuse. Fluorides are absorped and the resulted liquor is neutralized before discharge. Ammonium phosphate particulates from cooling and screening equipment of the product are collected by a battary of cyclones and recycled.

Complex Fertilizer (NPK) production

There are different methods for production of NPK fertilizers starting from combinations of various raw materials.

For dust recovery, hot gases from drier, product cooler, coater, as well as air from dust points such as elevators and screens are drawn through cyclones by fans. Recovered dust is recyled to the granulatory vents are washed with weak acid solution to recover nutrients and to avoid any environmental pollution.

Ammonia and fluorides evolved in the neutalizer and granulator are washed by scrubbing with water, or scrubbed in a scrubbing tower irrigated with phosphoric acid. The scrubber liquor can be recycled to the granulation unit

liquid effluents from (N P K) plant contain fluorides, phosphates and ammoniacal nitrogen. These effluents have to be treated before disharge.

3- Pollution Regulations and Legislations in Fertilizer Industry

The ill-effects of pollutants emitted or discharged from fertilizer plants to air or water are well-known at present time. For example, fluorine concentration in air of (2p p m) cause damage to the plants and to human tissues , while higher concentrations cause corrosion of teeth and bones.Sulphurdioxide concentrations in air more than (5 ppm) injure nose, eyes, and lungs Low concentration even less than (0.5 ppm) cause vegetation damage ,and corrosion of steel structures. The reddish brown blume of nitrogen oxide rising from stacks in nitric acid plants, often provokes public denunciation as a source of air pollution, principally because it is so visible . High concentrations could under certain conditions result in damage to vegetation and accelerate corrosion of man-made structures . Nitrous and nitric oxides from fertilizer industry and otles sources are thought to be responsible for a sizable proportion of natural ozone depletion. With this depletion the intensity of harmful ultraviolet light at the earth surface would increase resulting in effects very dangerous on life itself.

Polluta 's in liquid discharges from fertilizer plants can also cause big difficulties. Ammoniacal nitrogen in this effluent is very toxic to fish life. It can lead to oxygen depletion, excessive growth of algae and corrosion. Urea can be hydrolised to ammonia which is toxic for fish. Sulphides and sulphur compounds are toxic. They create odour and corrosion problems. Fluorides phosphate, suspended matter and oils , all are undesirable and must be removed before the discharging of effluents to water bodies.

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Therefore many countries have laid down legislations and regulations to restrict the total discharge of pollutants in the atmosphere and natural waters. In fact, stringent regulations are now adopted by industrially developed nations. Environmental Protection Agency of U.S.A.has restricted emissions from fertilizer plants by issuing certain standards regarding the air quality criteria surrounding the plant, and accordinglu laid down regulations on quantities of pollutants emitted to the atmosphere. Similar actions also have been taken regarding water bodies.

Several years ago different Organizations and Agencies investigated the existing legislations in order to formulate suitable international standards and guidelines and to determine whether existing standards in developed countries were suitable and could be adapted to developing occuntries.

In the Arab Region, as the case in many developing countries the regulations and legislations concering pollution control in the fertilizer industry are not yet adopted. No uniform guidelines or standards for gaseous and liquid effluents from fertilizer industry have been established. However, since industrialization have intensified markedly in the last decade, most of Arab Countries pay great attention to pollution control, and pollution committees in a number of them have been formed. Recently these committees have issued maximum allowable concentrations for major pollutants in ambient air and permits con⁺rolled discharge of liquid effluents as guidelines for pollution control. The following tables give two examples for these guidelines in two industrial areas in the Arab Region:

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Table (6) Allowable Concentrations for major pollutants in the ambient air at Shuaiba Industrial Area-Kuwait

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Pollutants	Community maximum allowable concn(ppm) (One hour)	Long term average concn- ppm(annual mean)
Ammonia	2,3	0,13
Carbon Monoxide	35	2,0
Chlorine	C,1	
Hydrogen Sulphide	0,1	
Total mercaptans	0,05	
Nitrogen oxide	0,5	0,025
Oxidant as ozone	0,06	
Sulphur oxides	0,5	0,025

(Table 7)	Particulate	Emission F:	gures	for	new	plant	in
	Shuaiba	Industrial	area-	Kuwa	it_		

Pollutants	Source	Emission figure mg/m3
UREA	Fertilizer plant	130
Sulphuric acid	Sulphuric acid plant	230
Others :		
Cement dust	grinding & crushing	100
Heavy metals	As the element	23
Total solid particulate matter: Dust & Grit larger than 10 micron	Miscellaneous , incinerators, process furnace	460
Fines, fumes less than 10 micron	New electric generating plant	115

The above figures should not be concidered as regid standards but as guide lines to best practicable means for Shuaiba Industrial Area

Regarding the discharge of liquid effluents and in order to protect the inshore waters against eutrification by the nitrogen products, the waste water from urea plants which equals about (0.7 m3) per ton urea and contains (200 - 5000) mg/m3 ammonia and (7000 - 10000) mg/m3 urea is treated and pumped(1ℓ)km from the plant site and diluted with **Bweet** water to be used for irrigation. In addition, the Technical Committee at Shuaiba Area Authority has recommended the quality criteria for the discharge of liquid effluents to the Arabian Gulf at Shuaiba , Kuwait as given in Table (8):

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	Desirable	Maximum /Minimum	Reference Discharge
	Enviromental	Threshold Hazard	Load Tonnes/day from
Paramerter	Value(DEV)	Value(T H V)	Total Industrial Un-
			polluted sea water
PH	8.0	5.5 to 9.0	_
Dissolved oxygen	5.4ppm	2.0 ppm	-
BOD	2.0	4.0 ppm	-
COD	2.0	4.0 ppm	15 dependent on
	<u></u>		receiving water
Total H. C	N.d	0.5 as in water bulk	0
Phenolics	0.05ppm	0.1 ppm	0.25
Detergents	0.05ppm	0.2 ppm	0.25
Sulphides	0.005 ppm	0.01ppm	0.025
Ammoniacal Nitrogen			Total Nitrogenous
(NH3 & NH4)	0.0.02 ppm	0.2 to 0.5 ppm	Load 2.75
Oxidized Nitrogen	0.40 ppm	0.8 pr.n	
Total Nitrogen	0.5 ppm	1.3 ppm	
Inorganic Phosphate	0.001 ppm	0.02ppm	0,005 to 0.10
Cyanide	N.d	0.01ppm	0
Alkyl Mercury	N.d	0.0001 ppm	0
Total Mercury	N.d	0.0001 ppm	0
Arsenic	0.01 ppm	0.05 ppm	0.05
Cadmium	0.001 to 0.01	0.03 ppm	0.005
Lead	0.01 ppm	0.05 ppm	0.05
Chromium	0.05 ppm	0.10 ppm	0.25
Copper	0.001 to 0.01	0.05 ppm	0.005
Zink	0.001 to 0.05	0.10 ppm	0.005
Iron	0.05 ppm	0.30 ppm	0.25
Manganeze	0.02 ppm	0.10 ppm	0.10
Nickel	0.002	0.10 ppm	0.010

Table(8)Recommended Ambient Marine Environment Quality Criteria for

In-Shore Waters around Shuaiba

The Bechnical Committee at Homs Industrial Area Syria has recommended maximum allowable concentration of pollutants in the discharged liquid effluents to Settena Lake as given in table (9). Settena Lake supplies cooling waters for all plants in the area in the same time all liquid effluent from these plants are discharged after treatment to the lake. The nitrogen and phosphate fertilizer complexes in Homs discharge about (500 - 1000) m³/hr of wast water to the lake.

Table(9) Recommended Specifications for the discharged liquid effluents to Qattena Lake

Parameter	Maximum allowable limit
Temperature	35 C
РН	6 - 9
CL	400 mg/L
so ₄	400 mg/L
Suspended matter	80 mg/L
0i1	10 mg/L
BOD	20 mg/L
COD	30 mg/L
TDS	1000 mg/L
NH ₃	10 mg /L
NO3	45 mg/L
Fluorides	5 - 8 mg/L

COUNTRY	Standards mg /m3 (daily average)								
	Farticu-	NH3	so2	so3	NO2	Hcl	Fluorides	CO	H.C
	lates								
U. S. A.	0.75	-	0.8	-	1.0	-	0.00 7	100*	** 1.6
JAPAN	0.1	-	1.1	-	0.4	-	•	-	-
ITALY	0.3	-	0.19	-	0.39	0.05	0.02	-	-
GERMANY (8hr average	-	-	4.0	_	3.0	-	-	-	-
CANADA (Industrial) areas	_	-	-	-	-	-	0.026	-	-
FRANCE	0.15	-	0.25		-	-	-	-	-
BELGIUM	-	-	0.28	_	-	-	-	-	-
CZECHOSLOVA- KIA	-	-	-	- -	-	-	0.1	-	_
U.S.S.R		-	-	-	-	-	0.1	-	-
Recommended air quality	_	1.0	3.65	1.0	_	_	0.1	-	_
<u>standards</u>	L	L	L	L	L	L		L	L

Table(10)Ambeint air quatity standards in some developed Countries

* Maximum 8 - hr Concentration

** Maximum 3 - hr Concentration

The pollution standards or guidelines in any country are formulated according to local conditions and its need in respect of pollution level, techno-economic suitabilities, etc. Therefore we find that standards for pollution control adopted by developing countries are not as stringent as in developed countries. It is because the reason that developed countries are highly industrialized and have large size manufacturing units whose effluents are also considerably large in quantity. Consequently the environment surrounding them has larger quantities of pollutants in comparison to other places in developing countries. Table (10) gives the quality standards of ambient air in some developed countries.

From this table we can see tha lack of uniformity between air quality standards in diffirent countries.

To meet the air quality standards it is necessary to control the emissions from fertilizer plants according to certain limits or standards. Table (11) gives the emission standards specific to fertilizer plants in some developed and developing countries.

While Tables (12),(13),(14) give examples for standards of water and Liquid effluents

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Country	Source	Pollutants	Emission Limit			
	Nitric acid	Nitrogen oxides as NO ₂	1.5 Kg/T 100 % acid,			
U.S.A.	(30- 70% HNO.)	Opacity	10%			
	H ₂ SO ₄ plants		2 Kg/T 100 % acid			
	2 4 -	Laid mist as H SO	0.075 Kg/E 100% poid			
		Acid mist as H ₂ 504	10 %			
	Wet process phosphoric acid	Total Fluorides	10.0 gf/T of equivalent P205feed			
	TSP plants	Total Fluorides	100 gf/T of equivalent P2 ⁰ 5 feed			
	D. A. P	Total Fluorides	30 gf/T " " " "			
	HNO3 plants	Nitrogen oxides	1 g No/m ³ of tail gas			
	H ₂ SO ₄ plants :	so ₂	Conversion efficiency99%			
	(DCDA)	Acid mist	0.4 Kg SO3/T H2SO4			
	SC SA	so2	Conversion efficency 97.5%			
Germany	when SO ₂ in the gas 6%	Acid mist	0.6 Kg SO3/T H2SO4			
	H ₂ SO ₄	SO2	Minimum Conversion 97.5%			
	metallurgicalplants	Acid mist	2Kg SO3/T H2 SO4			
	H- SO4 Chamber	so	5 mg/ m3			
	plants	NO2	1.2 g/ m3			
	Phosphate fertilizer plan	Fluorides	20 mg/m ³ as HF			
	Different Sources	Dust	50 - 150 mg/m3			
India	H ₂ SO ₄ plants	so ₂	12 - 16 Kg/T acid 100%			
	New H ₂ SO ₄ plant	so,	4 - 12 Kg/T acid 100%			
	Existing and new plants 200	so ₃	0.5 - 5 Kg/T acid 100%			
	H ₃ PO ₄ plants	Fluorides	0.65-1.5 Kg/T of P2 05			
	TSP plants	Flucrides Dust	0.075-0.3 Kg/T product 4 Kg/T product			
	SSP plants	Fluorides Dust	0.1 -0.5 Kg/T product 500 mg/Nm3			
	New HNO _z plants	Nitrogen Oxides as NO ₂	3 Kg/T of 100 % HNO3			

Table(11) Standards for ellowable emissions from fortilizor

plants in some developed and developing contries

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	Tolerance lim:	its re	
	River water &	Effluents	Effluents
	industrial	discharged	discharged int:
Effluents Characteristics	Water	into surface water	open sewerage
ΤSS,		20	-
Temperature C, max	25	30	60
РН		6.5-5,8	6.5 - 9.0
BOD	4	20	*
COD	N.W	*	*
Dissol v ed o xy gen	6	6	-
Oil, fats and grease	N.W	20	-
Ammoniacal Nitrogen as N	0.5	*	_
Free ammonia as N	0.1	-	
Nitrate (as NO ₃)	25	-	-
$Sulphates(as SO_4)$	100	*	300
Sulphides (as S)		0.1	1
Russides (as F)	1	10	10
Chlourides (as CL)	100	*	1
Cyanides (as CN)	0.01	0.5	0.5
Lead (as PB)	0.05	0.5	0.5
Zinc (as Zn)	0.2	2	2
Copper (as Cu)	0.01	0.2	1
Nickel (as Ni)	0.05	2	2
Cadmium (as Cd)	0.005	0.1	0.01
Mercury (as Hg)	0.001	0.01	0.01
Arsenic (as As)	0.01	0.1	0.5
Iron (as Fe)	1	2	20
Phenolic compound as 6 5 OH	0.005	0.05	5
Residual (as C1)		0.05	0.5 -3
Barium (as Ba)	0.5	5	*
Trivalent Cr.(as Cr ³)	0.05	2	2
$D \cdot O \cdot C \cdot S(as C)$	2	10 - 15	*

Table(12)Swiss standards for waters and liquid effluents as example

from developed countries

N.W = Not worth

.

* = Decided case by case

Effluents characte	ristics	Teleren		me/T nev
		1	2	3
 T S S		100		
TDS				
Temperature C		40		
РН		5.5 - 9.0	5.3 - 9.0	5.5 - 9.5
BOD		30		
COD		250		
Dissolved oxygen				
Cils and grease		10		
Ammoniacal nitroger	n (as N)	50		100
Free ammonia	(as NH ₃)			5
Nitrates	(as No _z)			
Sulphates	(as So ₄)			
Phosphates	(as P)	15	5	
Sulphides	(asS)	2		
<u>Fhorides</u>	(as F)	2	15	
Chlorides	(as Cl)			
Cyanides	(as CN)	0.2		
Leads	(as Pb)	0.1		
Selenium	(as Se)	0.5		
Zink	(as Zn)	5		
Copper	(as Cu)	3		
<u>Nik</u> el	(as Ni)	3		
Cadmium	(as Cd)	2		
Chromium	(as Cr ⁶)	0.1		
Mercury	(as Hg)	0.01		
Arsenic	(as As)	0.2		0.2 new plants
Sodium	(as Na)			
Phenolic compounds				
(as C6H50H)		1		
Resedual chlorine	(as Cl)	1		

Table(13) Indian standards for liquid effluents discharged into inland

surface water as example from developing countries

1- General. 2- For phosphatic industry.

3-

p.,

For nitrogeneous fertilizer industry.

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	Tol	erence	limits	ppm or	mg/L;	max
Effluent Characteristics	врс	T C A	ВАЗ	EA	new S	ources
	1	2	1	2	1	2
A-Phosphate sub-category		l				
Total phosphorus (as P)	105	3 5	105	35	105	3 5
Fluorides (as F)	75	25	75	25	75	25
TSS	150	50	150	50	150	50
B-Ammonia Sub-category						
Ammonia (as N) PH	187 . 5 6 - 9	62.5 6 - 9	50 6 - 9	25 6 - 9	110 6 - 9	55 6 - 10
C1-Urea sub-category(not prill)	ed)					
Ammonia (as N) Org.nitrogen (as N) PH	75 125 6 - 9	37.5 62.5 6 - 9	30 50 6 - 9	15 25 6 - 9	65 75 6 - 9	32.5 37.5 6 - 9
C2- Urea_sub-category(prilled)						
Ammonia (as N) Org.nitrogen (as N) PH	100 250 6 - 9	50 125 S - 9	60 75 6 - 9	15 37.5 6 - 9	65 125 6 - 9	32.5 62.5 6 - 9
D1-Ammonium nitrate(prilled or	granulat	ed				
Ammonia (as N) Nitrates (as N) PH	200 220 6 - 9	100 110 6 - 9	150 250 6 - 9	7.5 12.5 6 - 9	100 50 6 - 9	50 25 6 - 9
D2-Ammonium nitrate (as aqueous	a solutio	m)				
Ammonia (as N) Nitrate (as N) PH	75 6 6 - 9	3 7.5 6 - 9	15 25 6 - 9	7.5 12.5 6 - 9	50 25 6 - 9	25 12.5 6 - 9
E1-Nitric acid (using gaseous	NH ₃)					
Ammonia (as N) Nitrate (as N) PH	7 330 6 - 9	0.7 44 6 - 9	4.5 170 6 - 9	0.45 23 6 - 9	4.5 170 6 - 9	0.45 23 6 - 9
E2-Nitric acid (using liquid	NH ₃)					
Ammonia (as N) Nitrate (a s N)	80 and P H	8 the same	80 ne as E 1	8	80	8

Table(14)U.S.A Standards for liquid effluents from fertilizer plants

Example fromdeveloped countries

B P C T C A: Best practicable control technology currently available B A T E A : Best available technolgy economically achievable . 1 : Daily average , 2: Monthly average of 30 daily values.

4- Pollution Control Techniques and cost :

Various methods for pollution control in fertilizer industry have been recognized by developed countries more than one decade ago. The cost of such methods will depend on many factors such as: size of the plant, status, location, and the degree of pollution control required. A good pollution control method should be cheap to install, easy to operate and should not generate products which are likely them selves to create further pollution or disposal problem.Pollution control methods can be categorized as follows :

1- Air pollution control methods :-

a- SO2, SO3, acid vapour, acid mist and nitrogen orides

from sulphuric acid plants

 $\frac{SO_2}{2}$: The most common SO_2 emission control technique is the double contact double absorption process "DC/DA" . Considering the current environmental regulations in developed countries, it seems necessary for sulpaurie acid plants to employ " DC/DA " process. Such plants will cost (10 %) more than " SC/SA " plants. For existing plants which must be modified to meet emission regulalions(most " SC/SA " plants based on sulphur burning and high SO₂ strength wet gas plants), and when their equipment are of good design. It is possible to convert a " SC/SA " plant into " DC/DA " plant. This will need addition of gas to gas heat exchanger, a new absorption tower, mist eliminator and acid cooler. Rough estimation shows that for (1000) tonnes per day plant, the direct operating cost for a " DC/DA " is only about (5 0.2) / tonne more than for a " SC/SA " plant. If we consider the increase in the production that will be produced from the same raw material we may be able to find about (\$ 0.8)/ tonne advantage in direct unit operating cost for " DC/DA ". Ammonia scrubbing of stack gas is another alternative. It can compete economically with "DC/DA " $\!\!\!$ process if ammonia cost can be recovered . Ammonia scrubbing process offers a substantial capital cost advantage over " DC/DA " process for (5 % SO₂) plants. Also to decrease the concentration $of(SO_2)$ in the stack gases by increasing conversion efficiency, the cost of the "DC/DA" plant may increase considerably ,where as the cost of scrubbing plant will not.

SO.,

The reduction of (SO_2) in the tail gas from a sulphuric acid plant is the matter of the absorption efficiency in the absorption tower. Efficiency more than (99.9%) can be reached by controlling acid concentration and temperature in the absorption tower.

Acid vapours: Operating at acid concentration less or more than(98.5%) results in the formation of acid vapour. The reason is that (98.5%) sulphuric acid used in the absorption tower exerts a minimum vapour pressure.

- Acid_mist_ __: Acid mist is an aerosol of fine drops of sulphuric acid with particle sizes up to (10) microns. It is formed either by condensation of sulphuric acid vapour as the gas is cooled, or by reaction between (SC_z) gas and water vapour at a temperature at which sulphuric acid can condence. Escaping (SO_x) in the tail gas also will react with the moisture in the atmosphere to form acid mist. It is also formed in any acid plant with wet purification section. Acid mist is visible and can be easily detected. Therefore elimination of this mist is very important. Electro static precipitator is used to remove acid mist particularly in the wet purification section of the acid plant, high installation cost is the main disadvange. venturi scrubber can also be used, but high power consumption is the major disadvantage. Mist eliminators of different types are the most efficient equipment used at present time for mist elimination in sulphuric acid plants.
- <u>Nitric oxide</u>: During the normal combusion of sulphur, nitric oxides are formed. The formation of(NO) is influenced by temperature, (SO_2) and (O_2) concentrations. Formation of (NO) can be avoided by using a modified system for burning sulphur. The investment cost is not higher than that for normal combusion plants.

b- Nitrogen oxides from nitric acid plants:

Absorption techniques :

The most satisfactory method of recovering more nitric acid from the tail gas is by means of extending the absorption capacity. This method is a good one for high pressure plants but is fairly expensive.

- Wet scrubbing techniques:

The scrubbing with aqueous ammonia to produce a dilute ammonium nitrate solution seems to be a good way if this by-product can be used. Scrubbing with urea solution is a new alternative which is now used by Norsk Hydro. It is also used to control nitrogen oxides formation in nitrophosphate manufacture by adding urea in the digestion stage. The installed cost of the equipment for the use of solid urea for a (500) t.p.d. medium pressure nitric acid plant is about (\$30000). Operating cost is roughly balanced by credits.

- Catalytic reduction :

The alternative to recovering of nitrogen oxides values is to destroy them and the main method of doing this is the catalytic reduction with gaseous reducing agent (natural gas or purge gas from ammonia plant). Ammonia can also be used as reducing agent and in this case avoiding the fromation of explosive ammonium nitrate is very important.

- Molecular sieve adsorption :

Amolecular sieve anarytant / catalyst is used to convert (NO) to (NO_2) in presence of oxygen and then selectively absorbs the NO_2 , which is desorbed and recycled to the nitric acid plant absorber.

Rough estimation shows that additional unit operating cost for (300) tonne per day plant will be (\$7) per tonne for catalytic reduction, (\$5) per tonne for molecular sieve and (\$3.3) for absorption.

c- <u>Dust from urea plants</u> :

One of the main sources of pollution is the air discharged from the top of the prilling tower, which may contains, a considerable quantity of urea powder (more than 300 mg/Nm²). A dedusting system with misteleminator can reduce urea powder in the discharging air to less than (30 mg/Nm³). The obtained urea solution (15 - 20 %) urea is recycled back to the urea plant for further utilization. The investment for such dedusting system in a (1000 tonne) per day urea plant will be around (0.5)million dollars ,while the amount of urea recovered may reach (1000 ton...es) per year. In one of our member companies the prilling system was modified and fitted with a new designed prilling bucket and the dust emission is now meeting the current guidelines for the industrial area.

The elternative to the dedusting system is the replacing of the prilling tower by rotary drum granulater. Several new plants have adopted the granulation process.

Regarding dust control from urea cyclones of the conveyor and drying system of urea, impingement type scrubber is used now in one of our member companies with dust collection overall efficiency of (99.6%).

d- Dust and funes from ammonium nitrate plants

The air leaving the top of the prilling tower contains A.N dust and A.N fumes. The dust is formed either by attrition of solid prills and microprills or from the break-up of solid prills on impact at the bottom of the tower, while fumes is formed by chemical reaction of ammonia and nitricacid vapours resulted from dissociation of solidand liquid ammonium nitrat at elevated temperatures.

The great difficulty with purifying prill tower effluent is its very great volume, the low concentration of fumes and the very small particle sizes of this fumes.

Granulation facilities have been installed in some plants to overcome the problem of prill tower emissions, while other plants have applied the internal shroud system with brink mist eliminator, this system has proven to be effective. The capital cost of internal shroud system to control pollution in ammonium nitrate plant with 1000 M T/day capacity is about \$ 1.5 million. The total saving as result of ammonium mitrate recovery is 0.2 - 0.6 \$ per tonne.

e- Dust control from ammonium Sulphate Plant:

The removal of ammonium sulphate dust in the off-gas from dryer requires special dust catcher to meet with the allowable low pressure drop of the system.

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f- Dust and fluorides:

Single and triple super phosphate

The conventional scrubblers and packed towers for absorping fluorides from exhaust gases by water are not suitable, as they are liable to be clogged by precipitated silica which is formed as a result of hydrolysis of (Sif 4). Therefore the various improved types of scrubbing systems have been suggested such as venturi scrubbers viod towers, etc. To obtain good absorption of fluorides, H. SiF 6 liquor having a strength of 17 to 23% H_ Si F6 is used for recirculation in the scrubber. A suitable system of cyclones or cloth filters should be installed before the gas scrubber to collect the finely ground particles of rock pnosphate which is the main source of P_0 contamination in H_ Si F6. Collected solids can be recycled to the process.

- Phosphoric Acid

Fluorides evolved at the concentration stage amount to 30 - 40% of the fluorine in the rock feed. A void tower is used to absorp these fluorides from off gases by H_2 SiF6 solution. The strength of the recovered fluosilicic acid can be from 17 to 23% with P_2o_5 contamination not exceeding 100 ppm.

Nitro phosphate

The fluorides concentration in the exhaust gases is very low. They are scrubbed with water. The scrubber liquor contains a very dilute solution of H_2 SiF6. This is neutralized with lime before discharge.

- Ammonium_Phosphate

A venturi scrubber is used for ammonia recovery from exhaust gases from reactor and granulator, a cyclonic spray tower is used to absorp fluorides using water as absorbing solution. Ammonia in the flue gas from dryer is removed in a venturi scrubber and another venturi scrubber is used for particulate removal from the air stream of the dry cyclone on the product cooling and screening equipment. Others

Ammonia in purg gas from an ammonia plant

This ammonia is usually recovered by washing purge gas with water in a recovery unit and reuse of the obtained liquor.

SO2 in flue gas from steam boilers and primary reformer

It is possible by venting the flue gas from a tall chimney 90m to obtain a satisfactory dispersion. The cost of reducing SO2 emissions from an ammonia plant using fuel oil with high sulphur content is relatively high.

Gases and vapours discharged during emergency per.od It is necessary to provide the plants with two or three flares; one for wastes containing carbon dioxide and a 2nd for wastes containing ammonia. A third flare may be to serve ammonia storage and

shiping area. Ammonia vapours from storage tanks is usually recovered in a refrigeration unit. Dust from storage, handling and transfere systems

A variaty of control devices are used to control dust emissions from such systems such as cyclones, cloth filters, bag filters, etc. Sulphur which is an important raw material for fertilizer industry is transported now as liquid sulphur. This will offers many advantages such as: easy handling, no dust emission, clean surrounding and high purity.

2- Control and treatment methods of liquid effluents:

The fertilizer industry consumes huge quantities of water, mainly for cooling purposes, and discharges a variety of liquid effluents mainly as waste water with different degree of contaminations. The various waste water effluents may be classified as follows:

- Clean streams relatively uncontaminated e.g.. once through cooling water.
- Contaminated streams e.g: cooling tower blow down, process water from ammonia and urea plants, acidic and alkaline effluents from demineralized water plant, leaks, gland cooling water, effluent from compressor house, blown down from boilers, barometic condenser water. etc..
- Streams containing soluble fluoride and phosphatic contaminants. Usually uncontaminated waste waters are kept seperate and used for dilution of treated and untreated effluent streams to maintain pollutants within tolerance limits. Most of waste waters can be treated and recycled for reuse. The methods of treatment ir general include sedimontation, flocculation, precipitation, neutralization filteration, steam or air stripping, hydrolysis, ionexchange and others. The following are some examples of liquid effluent treatments in fertilizer industry:-
 - Oil and grease can be removed from waste streams e.g: gland cooling water or effluent from compressor house of ammonia/urea plant by gravity type seperator. The oil content can be reduced to less than 0.5 ppm.

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- The removal of heavy metal ions, suspended solids and acidity can be achieved by lime addition to raise the PH up to 9.0 followed by settling, thick ening and vacuum filtration.
- For chromates removal from cooling tower blowndown, two effective methods are available. The first one involves the acidification of the blowndown stream to bring down the PH to 3 and then the toxic hexavalent chromium is reduced to nontoxic trivalent by reducing agent. The chromium is then precipitated as hydroxide by treatment with lime, and then removed and disposed. In the second method ion-exchange technique is used for complete recovery of chromates. The treated water is recycled back to the cooling system.
- The acidic and alkaline effluents obtained during the regeneration of cation and anion resin beds in the demineralized water plant are mixed in neutralization tank where the PH is adjusted and then the effluents are pumped out. These effluents can also be used for the adjustment of the PH of the final effluent.
- Ammonia content in the process condensate from ammonia plant can be reduced to 20 ppm NH3 by steam or air stripping. The ion-exchange technique can also be used either alone or in combination with a stripper. In the later case, the process condensate is fed to a steam-heated stripping tower, to remove the volatile ammonia and Co2. The vapours from the stripper are condensate is pumped through the ion-exchanger where the heavy metal ions are removed and replaced with ammonium ions. The water from the ion-exchanger is used as boiler feed water, using such systems the ccst of treatment may range from \$ 1.1. to^{1.4} per tonnes of product.
- * Ammonia and urea content in the process water from urea plant can be reduced to 50 ppm of NH3 and 200 ppm of urea by hydrolysis and steam stripping. The ammonia vapours and CO2 will be fed back to (LP) carbamate condenser, while the treated process water can be used for irrigation.

The cost of such treatment may range from \$ 1.7 to \$ 2.3 per tonne of product.

* The removal of ammonium and nitrate ions contained in process water from ammonium nitrate plant can be achieved by ion-exchange technique. Using moving bed ion-exchanger, the waste water is completely demineralized and is recycled to steam boilers. The ammonium and nitrate ions are recovered as ammonium nitrate solution which is concentrated and recycled. The cost of such treatment may range from \$ 2 to 3 per tenne of product.

- The effluents from sulphuric acid and nitric acid plants are acidic in nature. They are mainly generated due to accidental spillages and leakages from various units. These effluents usually are treated with lime to adjust the PH before discharge.
- Treatment with lime is usually used to precipitate fluorides and phosphate in waste waters from phosphoric acid and phosphate fertilizer plants . All contaminated waste waters usually discharge to the gypsum pond. The pond water discharge is then treated with lime neutralization in order to reduce the fluoride and phosphate ion concentration to acceptable level. As an alternative to gypsum pond disposal, special scrubbers can be installed to recover fluorine as hydrofluesilicic acid which is used as raw material for manufacturing of useful by-products like aluminium fluoride and cryolite. The cost of complete fluoride removal for a phosphoric acid plant at a modern fertilizer complex in a developed site with water recirculation is more than \$ 4 per tonne of P₂O₅ produced.
- * The waste water from NPK plant is usually neutralized with lime to precipitate fluoride and phosphate in a clariflocculator. The overflow from clariflocculator is treated for removal of ammoniacal nitrogen.
- <u>Solid Wastes</u>: The most important solid waste from fertilizer industry is the phosphogypsum, resulting as by-product from manufacture of phosphoric acid. If this by-product is not economically utilized in manufacturing of valuable products such as cement and sulphuric acid, ammonium sulphate .. etc., It will be disposed of in the sea or on the land. Usually phosphogypsum is disposed as solid or slurry. In the later case phosphogypsum as discharged from the filter in the phosphoric acid plant is slurried and pumped to a pond near the phosphoric acid plant. The liquor seperating from settled phosphogypsum is recycled back to the plant for slurrying fresh phosphogypsum. The cost of transport phosphogypsum for a 2 km is about \$ 5 per ton of P₂O₅.
- 6- Conclusions and recommendations:
 - 1- The harmful effects of pollutants, resulting from the fertilizer industry, on the environment can not be ignored. The discharge of pollutants to the atomosphere and water bodies is forbidden in several countries and effluents must be treated effectively to abide with regulations before discharge.
 - 2- Recycling and reuse of waste waters in fertilizer plants or its dilution for irrigation seems to be vital for countries with scarce water resources, even it adds to the cost of production.

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3-	The treatment of effluents in a fertilizer complex using
	the integrated approach looks to be the best solution to
	minimize pollution by making use of the different charac-
	terisitics of effluents emissions and by products
<u>ц</u> _	Consideration should be given to pollution control during
1 -	the design store . On the athen hand establishment of
	the design stage. On the other hand establishment of
	a department of pollution control and safety for a ferti-
	lizer complex must be done as soon as possible in order
	to undertake information collection, research. and
5-	training of specialized personnel for pollution control. For regional cooperation and coordination in the field
	of pollution control, a technical field study to all
	nitrogen fertilizer plant in the Arab Countries should
	be carried out to define closely pollution problems,
	ways and means of cooperation, and future activities in
	this field. After completion of the study an expert group
	meeting should be convened
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5-	"The Fertilizer Association of India (FAL)". FAI - "Pollution control and Monitoring Techniques in
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8-	Johnson K.T. "Pollution Control in Fertilizer Industry"
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11_	Second World-Wide study on the Fertilizer Industry 1975 - 2000
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	o

2- "Recent Developments in Environmental Aspects in Indian" Fertiliser Industry"

Abstract

Environmental aspects - air, liquid and solid - of the Indian Fertiliser Industry and the pollution control measures already adopted are briefly discussed. The air and liquid pollution control standards as formulated by the ISI, State and Central Pollution Control Boards for the existing and new plants are given along with a sample estimate of the cost of pollution control in a plant. The ongoing research and development oriented to minimise the pollution in fertiliser industry and the role of FAI' are mentioned.

Man's stability depends on his ability to manage the earth's resources to avoid sudden discontinuities in supply before alternatives are available. If the economic growth is assessed primarily by the rate of conversion of raw materials into manufactured goods, then it cannot continue indefinitely. The growth will simply be halted by a confrontation with environmental limits, unless we learn to adjust in a deliberate and controlled manner. At the same time we cannot accept either slow growth or no growth control. Pollution is an unavoidable adjunct of industrial growth. Eventhough all-out efforts are made to control the more abnoxious and harmful constituents of effluents and at the same time improve the plant viability through recovery of more expensive byproducts, pollution carnot be totally removed. Even a life saving drug like penicillin is not free from undesirable side effects. It is interesting that the higher the standard of living of a society, the greater is its concern with pollution. Several reviews, monographs etc. are available in the literature on the abatement of pollutants in chemical industries (5,6,7,12,14-16).

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By:Dr. V. Pachaiyapan (FIE, MAIChE, LMIIChE) Director (R&D) Fertiliser Association of India

The Indian Fertiliser Industry, beginning in 1906 at Ranipet, with the production of SSF, has been continuously expanding embracing a whole range of fertiliser technology, using a wide spectrum of feedstocks and producing a vast array of products. Today, the fertiliser industry occupies a pivotal position in the country, occupying the 4th position in nitrogenous fertiliser production in the world. This has reversed our tradition of regular import of foodgrains to self-sufficiency and even exporting foodgrains to our neighbours. The fertiliser situation in India for the coming years is given in Table $1^{(2)}$. Such an impressive growth also has its side effect, namely, the environmental problems. The consequential atmospheric pollution has not yet assumed a serious proportion in India, though it could do so at some future dete.

								(.00	U tonni	es)
	C	apacity	Pro	duction	Cc	nsumpt	ion		Gap	
	<u>N</u>	P2 ⁰ 5	N	P2 ⁰ 5	N	P205	^к 2 ⁰	N	P205	к ₂ 0
VI Plan										
1980-81	4586	1333	2200	820	3742	1172	637	1542	352	637
1981-82	5313	1646	3456	1055	4734	1356	754	1278	301	754
1982-83	5385	1699	3733	1146	5270	1485	830	1537	339	830
1983-84	5597	20 8 8	3941	1360	5837	1620	910	1896	2 6 0	91 <u>0</u>
1984-85	6567	2366	4382	1556	6434	1761	994	2052	105	993
VII Plan										
1985 -86	76 6 2	2566	5046	1751	7062	1908	1081	2016	157	1061
1986- 87	235ه	2846	56 39	194 4	7625	2062	1172	20 86	111	1172
1987-88	8580	2846	6056	2030	8411	2221	1267	2355	191	1267
1988-89	927 0	2846	6487	2072	9,1 31	2387	1366	2645	315	1366
1969-90	961 5	2846	6815	2072	9883	2558	1468	30 6 8	486	1468

Table 1: Estimates of Capacity, Production, Consumption and Gap of N,P,K

The Govt. of India has enacted the Water (Prevention and Control of Pollution) Act 1974, Water (Prevention and Control of Pollution) Cess Act 1977 and Air (Prevention and Control of Pollution) Act 1981. Relevant statutory agencies at the Centre (like Indian Standards Institution - ISI -

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and Central Board for Prevention and Control of Water and Air Pollution) and in the States (Anti Pollution Boards) have fixed standards for various industrial effluents and are monitoring the implementation of measures for achieving these standards. The ISI has prescribed standards for tolerance limits, both for air and liquid effluents of chemical industries including the fertilisers, as given in Table 2 and $3^{(15)}$ respectively. These standards are intended to provide guidelines to the State/Central authorities to decide suitable restrictions in effluent disposal and to the industry for choosing suitable technology, site and degree of treatment required prior to the disposal of the effluents. The Indian standards, for liquid effluents, as prescribed by the State Boards, are given in Table 4⁽¹⁵⁾.

Table 2 : Indian Standard for Gaseous Effluents

۱.	IS : 8635 - 1977	Indian Standar from Sulphuric Industries	rd L c Ac	imits for Gaseous Emissions id and Phosphatic Fertiliser
	(i) Fluorine (as F ₂)			
	(a) Phosphoric acid	plants:		
	- Existing		:	1.50 kg/te of P ₂ 0 ₅
	- New		:	$0.65 \text{ kg/te of } P_0 Q_e$
	(b) SSP Plants :			~ 25
	- Existing - New		:	0.5 kg/te of product 0.1 kg/te of product
	(c) TSP Plants :			
	- Existing - New		:	0.3 kg/te of product 0.075 kg/te of product
	(ii)Particulate Matter	when emitted	thro	ough stacks
	SSP Plants TSP Plants		:	500 mg/Nm ³ 4 kg/te of product
	(iii) Sulphur Dioxide			
	(a) Planta upto 200) tpd	1	16 kg/te of product (100% H_504)
	(b) Plants about 20	00 tpd	1	12 kg/te of product (100% H_50)
	(c) New Plants upt	o 2 00 tp d	:	12 kg/te of product (100% H,50)
	(d) New Plants abov	ve 200 tpd	:	4 kg/te of product (100% H ₂ 50,
	(iv) Sulphur Trioxida (a) Existing Plants (b) New plants upto	s 5 200 tpd	:	5 kg/te of 100% H ₂ 504 5 kg/te of 100% H ₂ 504
	(c) New plants abo	ve 200 tpd	:	0.5 kg/te of 100% H ₂ 50 ₄

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2.	IS : 9005 - 1978	Indian Standard Limits for Emissions from Nitric Acid and Litrogenous fertiliser Industries
	(i) Nitrogen Oxides (as	NG ₂)
	Existing Units	: 24 kg/te of 100% HNC
	New Units	: 3 kg/te of 100% HNG ₃
	(ii) Hydrocarbons (as CH) : 5 kg/te cf ammonia
(iii) Particulate Matter	
	Existing Units	: 6 kg/te of product
	New Units	: 0.5 kg/te of product

<u>Table 2</u>: <u>Indian Standard for Gaseous Effluents</u> (concluded)

The exact quantity and content of various substances as ammonia from ammonia, urea, AS, ammonium nitrate and AP plants and urea from urea plants, biocides, chromates, etc., from cooling water, arsenic, K_2CO_3 , caustic sode and salts of Fe, Cu, Mn, Mo, Co, etc., acids like PA, HNO₃, H₂SO₄ as spillages of acid plants and alkalies from regeneration of ion exchange units and plants, aldehydes, etc. from gas compressors etc., phosphates, fluorides from PA, NPK, SSP and TSP Plants, will vary with size of plant, nature of raw materials used, the process employed and the type of products produced.

In view of the likely impact of these effluents on the quality of environment and its effects on human health, ecological imbalance etc., the fertiliser industry is taking steps to curb the effect of effluents to the extent possible. It can be safely said that in India we achieved greater success in pollution abatement issue. Theoretically it is very good to say that processes for treatment of effluents are available and hence the industry should invest in these to make the effluents totally pollutant free. However, in practice, this is not easy and sometimes impossible to achieve.

In a conflict between industrial activity and zero pollution, the extremists would rather opt for the latter. The emphasis today is on R&D to firstly evolve processes which will reduce pollution at the design stage itself, and then to institute measures which will suitably treat the effluents so that the harmful ingredients can be brought down to

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acceptable level at a reasonable cost. The two i.e. the extent of pollution control necessary and its cost have to be suitably harmonised. From this endeavour have emerged the concepts of "Best Available Control Technology" leading to "Economically Available Control Technology". No longer is "Zerc Pollution" the standard even in most industrialised countries. The recent cost-benefit analysis by the United Nations Environment Programme clearly brought out the fact that the relation between cost and efficiency is an exponential one and the region of minimum total cost is not at pollution level zero. Hence countries like India which are midway between the two must learn from the experience of other countries and avoid pitfalls. It is axiomatic that "prevention is better than cure" and it is easier to build in suitable safety guards at the stage of planning and construction than super imposition at a later stage. Of coarse, for existing units there would be no alternative to instituting suitable measures gradually in a phased manner. The new units may have to instal control equipment which will be capable of conforming to the present laws or may be even to the anticipated future laws.

It is visualised that "pollution is a visible sign of corporate inefficiency... Lots of wastes are useful in themselves... It is money that is going up the chimney..." ⁽¹¹⁾. An appraisal and control evaluation of possible impact on the environment of all the present and planned products due to their chemical and physical structure, general toxicity, stability and biodegradability, are being planned. To start with, we are directing our attention to important aspects like heavy metals (arsenic, Cr...) and chelating agents (that keep the toxic metals dissolved in water), stable halogenated compounds, non-biodegradable synthetic organic chemicals etc. An off-shoot effollution abatement and control is the opportunity that offers for utilising all the materials with the least wastage. Attempts are made wherever possible to recycle or recover many expensive ingredients, thus adding to the economic viability of the unit.

Adopted Control Measures

The pollution abatement technology in the fertiliser industry the world over is of recent origin, still in an evolutionary stage and of a more complex nature than that of the chemical and petrochemical industries.

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Unlike many other major industries, large single treatment plants are not an enswer to pollution control problems in the fertiliser industry. What is required is to implement a phased programme in terms of firstly minimising pollution through prevention and recycling; secondly, recovery of wastes and thirdly, treating the effluents. In a country like Incia, the major emphasis in regard to pollution control in fertiliser industry has been on prevention, recycle and reuse of waste and finally waste treatment.

Briefly, the salient features of a few of the pollution cuntrol measures adopted by the fertiliser industry are given below.

Major components contributing to the atmospheric pollution are SO_2 (from fuel oil, coal, naphtha, $H_2SO_4...$), NO_x (from HNO_3 , coal burning...), dust and the vapours of ammonia. The SO_2 emission is considerably reduced by the introduction of DCDA system having 99.5 per cent conversion efficiency in H_2SO_4 plants. Special mist eliminators are provided before any gas is vented through a tall stack for better dispersion. The NO_x can be controlled by many methods like catalytic combustion, acidic liquid urea scrub and alkaline wash method. The aresenic, from leakage or spillage, is collected, concentrated and packed in concrete containers and buried. One company has had to instal a 3-km long PVC pipe line into the sea so as to discharge any harmful effluent into the sea. The company is also having an aquarium to study the harmful effects of effluents on varieties of fish so that the effluent content from the plant is well below the safe level.

In most of the plants, the ammonia and urea plant effluents are treated by one of the following well known methods : air stripping of ammonia, high pressure stripper/hydrolyser stripper and biochemical removal of nitrogen. A pilot scale air stripping unit was designed by an unit and the operation was economical when combined with lime treatment for removal of phosphates from a complex plant, though air stripping may become less acceptable in future as air pollution control regulations become more stringent.

Several companies have already carried out studies to measure the gaseous and solid pollutants from the urea plant in different zones, covering about 1000 metres radius, with the prill tower as the centre. Some of the units near big towns plan to monitor pollution levels at various places

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•For cooling waste waters	as (1) mg 1; max.	piux	Phenolic compounds (as C.H.OH) mg/l:	Sodium (as Na) per cent; max.			max.	mg/1; max. Arxenic (as As), mg/1;	Mercury (as Hg),	(as Cr)+* mg 1; max.	mg/l, max.	Cadmium (as Cd),	MIGREI (AS INI), FU g ir, Mâx.	max.	Copper (as Cu), mg/1;	Z SUG (MS Z JI), SUBJU; JMAN,	max. Zing (as Za) and I:	Selenium (as Se), mg/1;	'Lead (as Pb), mg/1; max.	me i: mar.	mg/l; max.	Chlorides (as Cl),	Fluorides (as F).	mg/l; max.	ng 1; max.	Phosphates (as P),
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Sulphates (as SO4) mg/l;	Nitrates (as NO ₃)	Free atomionia (as NH ₃) mg/l; max	Ammonical nitrogen (a, N), mg/l; max.	Oils and grease, mg/l; a	Dissolved oxygea, mg/l; min.	CUD, mg/1; max.	BOD, mg/1; max.	pH	Temperature, C: max		micron; max.	TSS, Mg I; max.	E/Ruent characteristic					
induk.	8	i	I	мя. 0.1	دما	1	3.0	6.0-9.0	t I	l	I	ļ	For public water supply and for bathing ghats IS: 2296-1974	For inland su subject to				
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Table 3 : I.S.I. Standard for Liquid Effluents and Inland Surface Waters(15)

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Table 4 : Indian Standards for Liquid Effluents as Prescribed by State Boards for Prevention and Control of Water Pollution (15)

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				TOLERAN	CE LIMI	TS		-
	Enlumt characteristic			Maharashira		Uttar Pr	adesh	
		Karnataka	Kerale	Disposal into saline waters	Rajasthan	Disposal into Inland surface water	Disposal on land for irrigation	West Bengal
1.	TSS, mg/l; max.	100	100	100		100	-	100
2.	Particle size of TSS, Micron; inax.	\$50		_		850		50
3.	TDS, mg/l; max.		-		-		2100	-
4.	Temperature, *C; max.	40	40	_	-	41)		40
5.	pH	5,59.0	5.57.0	5.5-9.0	-	5.5-9.0	5.5-9.0	5.5-9.0
6.	BOD, mg/l; max.	3 0	30	100	-	30	500	30
7.	COD, mg/1; max.	250	250	250	-	250		250
8.	Distolved oxygen mg 1; min.			5	_	_	_	-
9.	Oils and grease, mg/1; max.	10	10		-	10	30	10
10,	Ammon ¹ cal nitrogen (as N), mg/1: max,	50	50	50	_	50	-	50
11.	Free ammonia (as N), mg/l; max.	1.2	1.2	_	-		-	
12.	Nitrates (as NO2), mg/1; max.	-		-	50	_		—
13.	Sulphates (as SO ₄), mg/1; max.	_	-	5		_	100	-
14.	Phosphates (as P), mg.1: max.	1.5	5.0	_		-		
15.	Sulphides (as S), mg/l; max.	2.0	_	-		2.0	_	2.0
1 6 ,	Fluorides (as F), mg/1; max.	2.0	2.0	10		2.0		2.0
17.	Chlorides (as Cl). mg/l; max.	1	-	_	-	_	600	_
[8 .	Cyanides (as CN), mg·1; max.	0.2	_			0.7	•	0.7
19.	Lead (as Pb), mg/1; max.	0.1	_	-		0.2		0.2
20 .	Selenium (as Se), mg/1; max.	0.05	_			0.05		0.15
21.	Zinc (as Zn), mg/l; max.	5	5	_		5	_	0.05 5
22.	Coppir (as Cu), mg/l; max.	3.0	-	_	_	3.0	_	3.0
23.	Nickel (as Ni), mg 1; max.	3.0	-	_		3.0		3.0
24.	Cadmium (as Cd), mg/l; max.	2.0	-	_		2.0	_	2.0
25 .	Hexavalent chromium (as Cr ⁺⁴), mg/1; max.	0.1	0,1	-		0:	_	0.1
26 .	Mercury (as Hg), mg/1; max.	0.01	_	-	_	0.01		0.01
27	Arsenic (as As.) mg/1; max.	0.2	0.2			0.2	_	0,2
28 .	Per cent solium (as Na); Max	-			_		60	
29.	Iron (as Fe), mg/1; max.	→		_	0.3	_		_
30 .	Free carbon dioxide (as COg), mg/1; max.	-	-	90	_	_		_
31	Phenolic compounds (as C_H_OH) ing/.; max.	1.0			~	1.0	_	1.0
32.	Residual chlorine (as Cl), mg/l: max.	1	1.0		-	t		1
33.	Barium (is Bi), mg/l; max				0.3	-		•
14,	Manadium (as V) - mg/t; max.	0.1	_ -		_		-	
				5—				

by giving suitable instruments to the local people and thus create a better image of the fertiliser units, rather than initiating action after complaints build up. One company has adopted the continuous air quality monitoring system. Its essential components are stack monitoring, in situ monitoring, air quality monitoring both mobile and air quality net work. The company measures relevant data and correlates it with meterological parameters like wind velocity, wind direction, humidity, temperature etc., for the following purposes : to check pollution level to comply with stipulated standards; to determine the material loss and to follow the trend to correlate the events with their causes to find suitable remedies; to identify the worsening, of emission control for preventive maintenance and as a record of defence in a pollution episode. Considerable attention has been paid to the training of personnel for the operation and maintenance of continuous monitoring with recording. This company has adopted the total systems approach to bring down to the bare minimum level of the concentration of pollutants. It has had planted over 25,000 trees in and around the plant by supplying saplings, agricultural inputs and technical knowhow free of cost to the residents in and around the factory with the dual purpose of growing more trees and to dispel the false notion that trees are difficult to grow in and around the factory. Another fertiliser company has set up a small agricultural farm to demonstrate to the neighbouring community that the partly treated effluent in lagoons etc., can be usefully deployed for increasing agricultural production. Their extensive pot culture experiments and field trials with varieties of crops have been highly successful. The company is working out the economics of the pollution control methods to be implemented shortly as given in Table $5^{(9)}$.

Table 5 : Economics of Pollution Control Measures

1.

		Rs. (million)
Installation Cost		
A. Main Effluent]	Disposal Scheme	
(a) Consultant	cy fee to various organisations	0.025
(b) Construct: effluen	ion of ammonia effluent tank, main t tank, pumping systems, atc.	1.935
(c) Construct: system,	ion of urea effluent tank, pumping formation of lagoons, etc.	0.700

Table 5 : Economics of Pollution Control Measures (contd.)

2.

- - ---- - ----

		Rs.	(million)
B. Wa	iter Treatment Plant		
(ε	a) Pre-neutralisation tank		0.140
(b) Neutralisation tank and connected facility		0.383
C. Am	monia Plant		
(a) Arsenic waste collection & treatment system		0.385
(ь) Condensate recovery system		1.400
(c) Chromate removal system		C.75C
D. Ur	ea Plant		
(a) Oil separator		0.011
(5) Urea crystalliser cooling tower and pumps		0.900
E. Su	lphuric Acid Plant		
(a) Sulphur dioxide recovery system		1.950
(Ь) Cost towards increasing chimney height from 50 m to 70 m		0.250
F. Ph	csphoric Acid Plant		
(a) Fluorine recovery system, line neutralisation and pumping facility		2.850
(ь) Improvements to neutralisation facility		0.300
G. Ef	fluent Reuse		
(a) Pot culture studies on reuse of effluent water		• .
	and field studies		0.016
(Ь) Effluent farm under implementation		0.500
(c) Modifications to water supply system to farm		
	removal system	_	0.200
		1	2.695
		-	
Cost o	f Schemes under Consideration		
(a) F	luorine recovery plant (c ryolite manufactura)		8.000
(Ь) 5	team stripper for urea plant affluent	<u>र</u> =	4.500

Table 5: Economics of Pollution Control Measures (concluded)

Rs. (million)

•	Operatin g/Maintenance Cost (per year : approximately)		
	(a)	Neutralisation of water treatment plant effluent	0.825
	(Ь)	Neutralisation of acid group of plant effluent	2.000
	(c)	Effluent pumps maintenance and operating cost	0.215
	(d)	Sulphur recovery system and fluorine removal system	ŋ.200
	(e)	Steam consumption in steam stripper	3.800
	(f)	Effluent farm and lagoon maintenance	0.160
	(g)	Chromate removal plant	0.400
			7.600

3

Another plant in the west (3) has adopted the following measures : replacement of arsenic based CO, recovery system by glycine system; replacement of reciprocating pumps (carbamate pumps) by centrifugal pumps; pumping back barometric condensate water to cooling towers in urea plant thereby reducing consumption of fresh water; plant modifications such as prilling nozzles, modification of plunger pump house, replacement of centrifuges, installation of mechanical seals on pumps, recovery scheme for CFD washings thereby reducing effluents and specially ammoniacal nitrogen from the urea plant; installation of polyethylene lined lagoon for collection and evaporation of effluents from the urea plant; use of AS plant effluent for repulping of chalk; use of bleed water from chalk pond for pan filters of PA plant, thereby minimising bleed from chalk pond to effluent; use of chalk pond water for Dust Scrubber in the grinding section of PA plant thereby reducing consumption of fresh water; use of sewage from factory and factory canteens as nutrient to the BDD Reduction plant reducing consumption of phosphorous; modifications in the Caprolactam plant such as provision of mechanical seals for all pumps, replacement of oil seals and oil cupa, replacement of better material and better design to minimise leakages; phosphetes and fluoride reduction; dust recovery from DAP plant; expansion of BOD plant etc. to meet the statutory norms and, if possible, to reach the ideal zero discharge of effluents.

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Research in Pollution

In recent years, enormous interest has been focussed on R&D in fertiliser industry all over the world, particularly in India, to utilise the effluents to inter alia improve the economic viability of the industry. These and other developments have been reviewed "lsewhere⁽⁷⁾. In India, most of the fertiliser companies have attempted to set up their own R&D to cater to their needs for which incentives are also available from the Govt. of India, in the form of tax concessions. Attempts are made to recover the effluents in the form of useful, saleable materials, rather than breaking into elements. The biological treatment method for urea, the arsenic treatment method and the electro-biolysis method tried/ suggested in India are available in the literature⁽⁸⁾.

Fluorine emanating from phosphatic plants (PA, SSP, TSP, etc.) has been successfully controlled by converting F into cryolite and AlF, based on their own inhouse R&D in the companies independently. Attempts are being made in several research laboratories to reduce No, level much more effectively. The use of fluocculants to recover carbon from carbon slurry of gasification processes and other pollution methods presently followed in various units are available in a recent publication (13). A few companies are attempting to recover uranium from PA/Rock Phosphate with the dual purpose of recovery of uranium and control of any possible pollution hazard. The importance of uranium recovery in phosphatic industries to reduce dependence on imported uranium supply needed for our nuclear reactors has been brought out in a review (7). Byproduct gypsum is being successfully used for the production of ammonium sulphate in 3 plants, based on the Indian know-how. In a plant, it is planned to use gypsum for the production of low grade cement. Possibility of using gypsum as a coating agent with/without rockphosphate on urea has been investigated and encouraging results have been obtained. One plant in the east has installed an Ion Exchange type unit, developed indigenously to treat effluent with an ammonia concentration of 1000 ppm, costing the ammonia to AS.

A cheap reduction technique to convert Cr⁺⁶ to Cr⁺³, by using boiler flue gas with the added benefit of reducing part of ammonia from the effluent water, was developed in a company. According to that company, its method using packed scrubber, is claimed to be cheaper than the other methods available, such as ferrous sulphate addition, vanturi scrubber, electro chemical systems and ion exchange method. In 1976, a continuous

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semi commercial unit was set up. The specifications as recommended by the company are given in Table $6^{(17)}$.

Cooling water flaw	:	136 m ⁸ /hr.
Ammonia liquid flow	:	3.5 m ³ /hr.
Flue gas flow	:	2 x 17000 NM ³ /hr
Gas temp.	:	200 °C
Head required for blower	:	50 cm W.C.
Motor H.P.	:	60
Packing	:	5 cm Ceramio rachig rings
MATERIALS OF CONSTRUCTION		
Steel (bottom) (top)	:	Acid proof brick lined MS Apoxy printed MS
Grating (top & bottom)	:	n
Gas duct	:	Ceramic tile lined steel (outside)
Water outlet line	:	Rubber lined steel
Estimated cost	:	Rs. 0.4 million

Table 6 : Flue Gas Scrubber Specifications

The scrubbing liquid (cooling water) containing 20-400 ppm of chromate is fed from the top. Flue gas (0.2 per cent SO_2) is pushed into the packed bed counter-currently, at an optimum gas/liquid ratio of 24. The ${\rm Cr}^{+3}$ leaves the packed bed as soluble ${\rm Cr}_2(SO_4)_3$ and this is converted into insoluble hydroxide (totally free from toxic effect) by treating with waste ammonia liquid (purge gas liquor) thereby bringing down the effluents to conform to ISI stendard. The commercial scale adoption, the company claims, will be an "appropriate technology" suited to the one's own needs at an optimum cost.

Role of FAI

The FAI - national representative body of the fertiliser industry in India - is doing useful work in the field of pollution control also. Its Pollution Control Advisory Committee is actively involved in constantly monitoring the status of pollution problems of the fertiliser industry. It periodically reviews the existing effluent statutory control measures based on techno-economic considerations. Periodically group discussions are

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arranged, inviting selected experts in the field, preferably at one of the plant sites, to discuss industry problems in depth by choosing for each meeting, a specific well defined area. Guidelines in the form of an action plan are suggested for consideration and adoption by different units based on shared experience. Thus, useful and practical information is disseminated for the benefit of the entire industry at the minimal cost. The FAI is represented on the ISI and other Regulatory Boards and thus acts as a bridge between these agencies and the industry so that industry's views and experience in the field of pollution are adequately appreciated.

In conclusion, in conformity with the country's requirement in pollution abatement, fertiliser industry is in the vanguard. A wide diversity of measures have been adopted by various units depending upon the technology adopted for product manufacture. These and other details are brought out periodically and disseminated by the FAI through group discussions $\binom{(8-10)}{}$, publications $\binom{(12)}{}$ and books $\binom{(4,15)}{}$ to make the industry aware of the developments in India and elsewhere so that the life of the peeple, more particularly the neighbourhood, can be made pleasant.

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3- EFFLUENTS AND MEASURES OF POLLUTION

CONTROL IN JFI'S FERTILIZER COMPLEX

IN AQABA, JORDAN

1. INTRODUCTION

The construction of JFI's Fertilizer Complex in Aqaba began in mid 1978, and commercial production is expected to commence in the second half of 1982. The complex includes:

- A sulfuric acid plant designed to produce 1,800 t/d of sulphuric acid from each of two identical units,
- . A phosphoric acid plant designed to produce 1,250 t/d of P_2O_5 .
- A fertilizer granulation plant which consists of two units each sized for the production of 1,200 t/d of diammonium phosphate (DAP) or monoammonium phosphate (MAP).
- A utilities plant to supply the complex with electricity, steam, water, compressed air and other required services,
 A sea water intake station which provides sea water for
- A sea water intake station which provides sea water for plant cooling at a rate of about 19,000 m³/h, and
 A deep water dock which is used to load bulk granular fertilizer and phosphoric acid and off load fuel oil, liquid ammonia, and molten and dry sulfur.

2. SITE LOCATION AND POLLUTION CONTROL

The site is located at Wadi-2, 15 km. south of the port of Aqaba. Wadi-2 is further located as the second valley north of the coastal border of Saudi Arabia. The gulf of Aqaba is about 160 km. long and 16-26 km. wide, narrowing to about 5 kms. at its northern end. The gulf is remarkably deep for its width, reaching a maximum of 1829 m. The 400 fathom isobath defines two basins, a northern shallower one of 1100 m depth and the southern one with typical depths of 1400 m. The gulf is separated from the Red Sea by a submarine sill that varies in depth from 175 m to 350 m. This

Prepared by : Najem Hammadi. Presented by: Hassan Sha'sha'a. combined with the fact that the Strait of Tiran is quite narrow, means that the deeper waters of the gulf of Aqaba are largely cut off from circulation with the Red Sea.

Aqaba is Jordan's main port. In addition, it is Jordan's sole water access. It is also an important tourism center, as the gulf of Aqaba is renowned for its clear waters, corals and rare sea life forms.

The need to preserve and protect the natural environment in the area is thus obvious.

On this basis, the Aqaba Fertilizer Complex was designed, engineered and constructed to very stringent emission and effluents criteria.

3. AIR POLLUTION CONTROL

Bunker C fuel oil is used as fuel in the auxilliary boilers of the utilities plant. The resulting gaseous effluents are rented to the atmosphere through two concrete stacks each 86 m high. Further, the combustion process itself is constantly monitored and controlled to ensure appropriate burning of the fuel oil.

The sulphuric acid units were designed such that the gaseous effluents contain less than one ppm of SO_3 and 0.03% by volume of SO_2 . The stacks in this plant are 70 m high.

The washing columns of the gases produced in the attack unit of the phosphoric acid plant were designed such that the fluorine emitted into the atmosphere does not exceed 350 grams per hour. The stacks in this plant are 47 m high.

In the granulation plant, the washing columns of the gaseous effluents resulting from the reaction of phosphoric acid are designed such that the amount of fluorine that is released to the atmosphere does not exceed 15 kg/per day. The stacks are 42 m high.

Special washing columns and stac's were designed and constructed for gases which might be emitted from the phosphoric acid storage tanks. All storage tanks are covered to avoid fluorine

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emission directly into the armosphere.

Phosphate rock unloading facilities are supplied with filters to cleanse the air from dust and to prevent it from escaping into the atmosphere.

4. WATER POLLUTION CONTROL

Sea water is utilized for the major cooling requirements in the complex, namely steam condensation in the utilities plant and the sulphuric acid plant. Provision was made to ensure that the temperature of the sea water returned to the gulf will not be increased by more than 10° C and thus the temperature of the gulf waters in the vicinity will not be increased by more than 2° C.

Very small quantities of waste water will be released into the gulf after being neutralized and treated, such that the amount of suspended solids will not exceed 30 mg/litre and the BOD will not exceed 20 mg/litre.

Almost 43,000 tons of Fluosilicic acid per year will be produced as a by-product in the phosphoric acid plant. Fluosilicic acid will be extracted during the concentration process of phosphoric acid, and will be partly used to produce aluminium fluoride, whereas the remainder will be neutralized and then disposed of with the gypsum which will be discussed later here.

Water used in the phosphoric acid and fertilizer granulation plants will be returned to a cooling pond of capacity 29,000 m³. Suspended solids will be treated in an evaporation pond of capacity 22,000 m³ to avoid polluting the sea and neighbouring areas.

JFI has gone to great lengths not to pollute the gulf of Aqaba and preserve its sea life forms and the purity of its waters. Large sums of the project's budget were dedicated to the construction of water treatment facilities and to prevent leakage of waste waters into the gulf or the underground waters inspite of the fact that many plants in developed countries dispose of their wastes directly into rivers or the sea.

5. LAND POLLUTION CONTROL

Almost 2 million tons per year of gypsum are produced as a by-product in the phosphoric acid plant, and have to be disposed of safely. It was thus necessary to look for a place, far from the sea, where gypsum could be stored safely for many years to come. Following several investigations conducted into this problem, it was decided to store the gypsum in a valley, 3 km. east of the site. Preliminary studies showed that five to ten years of the gypsum production could be stored there.

This solution, inspite of the extremely high cost associated with it, was found to be the most suitable since that area is uninhabited and does not contain underground waters, and thus our goal of preserving the environment will be achieved. Solid gypsum will be transported from site to the valley by a conveyor belt. Means are provided to distribute the gypsum in the valley.

6. CONCLUSION

It can thus be seen that the complex has been designed and constructed in accordance with very stringent pollution control criteria, in order to preserve the environment and prevent its pollution.

JFI did not spare any costs to achieve this goal.

Finally, our laboratories have been especially equipped to monitor and control the complex's effluents during production, and a special branch was founded within the Safety Department to make certain that the pollution control criteria we have set are being observed during production, as an additional guarantee to achieve our goal.

4- STEPPING FORWARD TO ENVIRONMENTALLY BALANCED FERTILIZER COMPLEXES BY INTEGRAL PLANNING EFFECTIVE OPERATION AND PREVENTIVE MAINTENANCE

SUMMARY

Our todays environmental problems are very seldom caused by the missing technology for environmental protection but are very often originated in the missing integral view of the management.

This paper tries to assist the planning engineer of a fertilizer complex in obtaining an integral view by supplying him with information on processes and their by-products possible by-product processing within the complex, i.e. "integral planning" as well as to show the importance for the management to obtain additional support from the production management by "effective operation" and the maintenance management by "preventive maintenance".

With this index of an integral view one should be able to stepp forward to an environmentally balanced fertilizer complex.

INTRODUCTION

The present environmental pressure varies very much for different locations of fertilizer complexes, but the existing pollution problems are demanding the application of proper environmental standards (see slide No. 1 and OP 1) for all fertilizer complexes to avoid disasters when expanding your fertilizer complex in the future.

Chemie Linz e.g. have been under an increasing environmental pressure over the last 40 years, since the Chemie Linz plant is facing on the one side the river Danube and on the other side a residential area of the city of Linz. (Slide No. 2 gives you an impression about this situation.) With this background Chemie Linz was forced to:

With this background chemie Linz was forced to:

- follow an integral planning taking into account all products and byproducts and to find optimal recycle-conditions
- 2. improve the supervision of the plants to avoid off-spec streams and uncontrolled shut-downs, which means <u>effective operation</u>
- work with the preventive maintenance philosophy to limit plant shutdowns due to faulty materials.

Chemie Linz is prepared to make available this know how to other companies and in the following chapters some of the aspects are discussed.

(Chemie Linz AG, Austria)

By: H. D. Schneider

INTEGRAL PLANNING

1.

The integral planning i.e. the consideration of all possible processes including available by-product processes for a fertilizer complex by the planning engineer will consequently lead to a fertilizer complex with environmental and economical feasible solutions.

Slide No. 3 is showing an interlocking matrix for the major processes of a fertilizer complex, which can be used as a checklist in finding out possible combinations. Such a matrix should be kept continuously up dated as a real tool for the planning department of your company. The following process survey provides the information, which is

necessary for the integral planning.

The figures are generalized and they should show only the tendency. For an exact overall balance for a complex the actual used raw materials and the process particularities have to be taken into account. OP 2 is showing us the data on basic processes:

1.1 BASIC PROCESSES

1.1.1 PHOSPHORIC ACID PROCESS

1.1.1.1 Dihydrate process

(acid from 28 to 32 % P₂0₅ will be obtained) Available processes: DORR-OLIVER FISONS PRAYON PSG-UCB (PECHINEY SAINT GOBAIN - UNION CHIMIQUE BEDRIJVEN S.A.) SINGMASTER & BREYER RHONE - POULENC

By-products:

- a) Phospho-gypsum, approx. $5 t/t P_2 O_5$ (as dry dihydrate)
- b) Fluosilicic acid, approx. 7 kg/t P₂0₅ (as F from attack section)
- ad.a) Special know-how (e.g. from Chemie Linz) is necessary to reduce the fluorine and P_2O_5 content to allow further use of the phospho-gypsum in the sulphuric acid and cement as well as for the ammonium sulphate production. The phospho-gypsum may be also used for adjusting the retard setting of the cement. If the phospho-gypsum gets recrystallized it will be also accetable for the production of wall boards and plaster of Paris.

- ad.b) This fluorine is normally emitted with the waste water, but in a balanced complex it may be well utilized as an additional raw inaterial source for aluminium fluoride or fluosilicate production.
- 1.1.1.2 Hemihydrate-dihydrate process

 (acid from about 30 % will be obtained)
 Available processes:
 MITSUBISHI
 NISSAN
 NKK

By-products:

- a) Phospho-gypsum, approx. 5 t/t P₂0₅ (dry dihyrate)
- b) Fluosilicic acid, approx. 7 kg/t P₂0₅
 (as F from attack section)
- ad.a) Normally this phospho-gypsum may be used without any special treatment for adjusting the retard setting of the cement or for the production of sulphuric acid and cement as well as after partial calcination as plaster of Paris.
- ad.b) Comments equal to the ones for the dihydrate process.

Acid with 42 % - 50 % $P_2^{0}_5$ will be obtained directly with the newer processes from FISONS (HDH) or NISSAN C. Experience about the possible conversion of this by-product-gypsum is not available.

1.1.1.3 Hemihydrate process

(acid from about 38 to 42 % or more will be obtained)

Available processes:

there are developments from

ALBATROS, FISONS, HEURTEY, LANDSKRONA, NORDENGREN.

The older processes have been causing some operational problems and they have been seldom applied inspite of the advantage of the more concentrated acid.

By-products:

- a) Phospho-gypsum, approx. 3,9 t/t P₂0₅ (as dry hemihydrate)
- b) Fluosilicic acid, 7 kg/t P₂0₅ (as F from attack section)
- ad.a) Special know-how for reducing the fluorine and P_2O_5 content is essential for further use in gypsum sulphuric acid plant. The high impurities (mainly P_2O_5) may also cause problems when used for the conversion to ammonium sulphate (filter stage).
- ad.b) Comments equal to the ones for the dihydrate process.

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With the newer <u>dihydrate-hemihydrate process</u> (e.g. PRAYON-CENTRAL GLASS) one get similar by product conditions as mentioned under 2.1.1.2.

New processes of OCCIDENTAL and FISONS are producing directly up to 50 % P_20_5 . Experience for the conversion of this by-product-gypsum is not available.

1.1.2 PHOSPHORIC ACID CONCENTRATION PROCESS (Concentration of acid from 30 to 54 %) By-product:

fluosilicic acid, 55 kg/t P_20_5 (as F)

This process is the main source for fluorine for conversion to aluminium fluoride (AIF₃), cryolite or fluosilicates.

For the concentration of the acid from a hemihydrate process with about 40 % to 54 % the by-product fluorine will be less, related to

the higher initial concentration.

1.1.3 SINGLE SUPERPHOSPHATE PROCESS (SSP) By-product:

fluosilicic acid, approx. 5,5 kg/t SSP (as F)

The Chemie Linz AlF₃-plant is based on the recovered

fluorine from SSP-production.

1.1.4 TRIPLE SUPERPHOSPHATE PROCESS (TSP)

By-product:

fluosilicic acid, 4 kg/t TSP (as F)

The fluorine recovery is very small and will be only of interest if it will be combined with other fluorine sources of a complex.

There are other process steps where fluorine is evolved but it

will be rather difficult or nearly impossible to recover the fluorine.

1.1.5 DRYING AND CALCINING OF GYPSUM

No fluorine can be recovered, since the amount of released fluorine is very small related to the off gas.

1.1.6 DRYING OF COMPOUND AND COMPLEX FERTILIZERS

Fluorine recovery from the off gas from compound and complex fertilizer production will be impossible due to high dust load and also chemical impurities (e.g. chlorine).

Only the drying stage of fertilizers with a single $P_2^{0}_5$ component could supply fluorine for a recovery as fluosilicic acid. Care must be taken to find for the recovery economical and physical conditions (temperature and concentration).

- 1.2 GYPSUM ACCEPTING PROCESSES
- 1.2.1 PLASTER, GYSPUM BOARD AND GYPSUM PANELS

Phospho-gypsum for this application should be with low

impurities regarding the P_2O_5 and fluorine content. Phosphoric acid and other phosphates cause retardation of early setting and at this time lowers the strength of the hardened body. Fluorine compounds shorten setting time, and although there is a tendency for lowering the strength, the effect is small.

Due to that fact phospho-gypsum from hemihydrate-dihydrate process is superior for this application where phospho-gypsum will be obtained with as low as $0.15 \ \% P_2 O_5$ and $0.18 \ \%$ fluorine concentration which needs no neutralization.

Phospho-gypsum from dihyrate process needs special treatment (e.g. defluorination by Chemie Linz know-how) repulping and possible neutralization.

There are some processes for reprocessing the phosphogypsum (GIULINI, ICI) which are giving also suitable gypsum for above purposes.

1.2.2 GYPSUM FOR RETARD SETTING OF CEMENT

Phospho-gypsum from dihydrate processes is needing special treatment before drying according to ONODA or CHEMIE LINZ knowhow, but phospho-gypsum from the hemihydrate-dihydrate process can be used with less difficulty.

1.2.3 PRODUCTION OF CEMENT CLINKER AND SULPHURIC ACID

Production of cement clinker and sulphuric acid bases on phospho-gypsum from dihydrate, hemihydrate-dihydrate and dihydratehemihydrate (PRAYON/CENTRAL GLASS) from phosphoric acid process is solved.

Chemie Linz is operating its sulphuric acid and cement clinker plant, based originally on natural gypsum since 1966 with phospho-gypsum from PRAYON-dihydrate process and a licenced plant is operating at Phalaborwa in South Africa based on phospho-gypsum from PRAYON/CENTRAL GLASS process since 1972 very successfully.

Special know-how allows to lower the P_2O_5 and fluorine content from dihydrate phosphoric acid process down to 0,5 % P_2O_5 and 0,15 % fluorine based on dry dihydrate, which is essential for a proper cement.

Phospho-gypsum from the hemihydrate-dihydrate process with its lower impurity content is used also widely for the production of cement and sulphuric acid.

The co-production of cement clinker and sulphuric acid makes it necessary to evaluate the credit for one of the two products. If you know the credit for the cement clinker you can calculate the total production cost for the sulphuric acid.

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The investment costs are considerable higher than for a single sulphuric acid plant based on brimstone but in spite of that fact CISA/South Africa and Chemie Linz are operating their plants economically and successfully. With rising brimstone prices this process will gain further importance.

The consumption figures are shown in OP 3. By this process you can solve your wrste gypsum disposal problem and at the same time you will decrease the dependance of your complex from outside raw material supply.

1.2.4 AMMONIUM SULPHATE PROCESS

The well-known ammonium sulphate process (Merseburgprocess) was modified by Chemie Linz to use phospho-gypsum instead of natural gypsum or anhydrite. The Chemie Linz plant with 180 000 t/a based on natural gypsum was modified in 1967 for use of phospho-gypsum and the process has been licenced already to India and California.

There will be no problem with the phospho-gypsum from dihydrate and hemihydrate-dihydrate and dihydrate-hemihydrate processes but with phospho-gypsum from hemihydrate processes care has to be taken to avoid filtration problems due to calcium phosphate formation.

The consumption figures are shown in OP 4. This by-product calcium carbonate can be further used in the calcium-ammonium nitrate fertilizer production or in the cement production.

By the conversion of phospho-gypsum to ammonium sulphate one can avoid the installation of a disposal site. The third group of processes are the

1.3. FLUORINE ACCEPTING PROCESSES

1.3.1 PRODUCTION OF ALUMINIUM FLUORIDE

The Chemie Linz aluminium fluoride process based on fluosilicic acid accepts fluorine from various sources within a phosphoric acid and fertilizer complex. The specification should be as follows:

clear liquid

1)

no suspended matter

This limit was set to reach only 100 ppm P₂0₅ in the final product. It may be actually accepted higher from the side of

the aluminium industry. On the other side a new fluorine absorption unit should be designed with minimum possible P_20_5 level in fluosilicic acid (approx. 50 ppm) to make maximum mother liquor recycle (decrease of consumption figures) possible.

Higher chlorine contents (up to 20 g/l) are increasing the consumption figures and are influencing the selection of the material for the equipment.

The consumption figures are shown in OP 5.

By-products:

Silicic acid may be recycled to the phosphoric acid and the fertilizer complex, for what Chemie Linz may offer also detailed advice for a general improvement.

Effluent:

Mother liquor as mer.ioned before. Recycling to the fluosilicic acid absorption unit will be possible. Otherwise neutralization of the mother liquor is necessary.

Waste water from the scrubber may be used as make up water in the phosphoric acid complex.

1.3.2 PRODUCTION OF CRYOLITE

Regarding the fluosilicic acid for the production of cryolite based on the Chemie Linz process the specification will be similar to the one for the production of aluminium fluoride (see 2.3.1). The consumption figures are shown in OP 6.

The by-product silicic acid and the waste water may be reused for the aluminium fluoride process as mentioned before.

1.3.3 PRODUCTION OF SODIUM FLUOSILICIC AND POTASSIUM FLUOSILICATE Sodium fluosilicates are often used in water fluoridation (also

fluosilicic acid). Processes are available for the production of these fluosilicates and they are also used in the production of opal glass, vitreous enamel, wood preservations, etc.

1.3.4 (NEUTRALIZATION OF FLUOSILICIC ACID)

If there is no use for the released fluorine as described in items 2.3.1 to 2.3.3 the fluorine has to be neutralized. As a guide 2,4 kg $Ca(OH)_2/kg F$ will be necessary for neutralization. These costs should be also credited to the fluorine accepting processes.

2)

1.4

OTHER PROCESSES WHICH OFFER USEFUL COMBINATIONS WITH ABOVE PROCESSES

1.4.1 TAIL GASES FROM MELAMINE PROCESSES

Melamine processes based on urea produce an off gas con-

taining NH₃ and CO₂, which may be separated in its components for further use in the urea plant by the "Chemie Linz off gas treatment process If there is an ammonium sulphate plant in the same chemical

complex the ammonium carbonate solution which is gained in the

off gas treatment process of the melamine process can be utilized

directly for the ammonium sulphate production.

From the Chemie Linz melamine process the following amounts of NH_3 and CO_2 are recovered:

	per t melamine
NH ₃	1,2 t
co,	1,1 t

1.4.2 OTHER NH₃/CO₂ TAIL GAS PROCESSES

There are many other processes which are delivering

 NH_3/CO_2 tail gases as

organic pigment processes based on urea

production of nuclear fuel

phenosolvan process

coal gasification processes

which may be separated by the Chemie Linz/Lurgi process or partly used as feedstock for the preparation of ammonium carbonate solution for the ammonium sulphate process.

1.4.3 UREA PROCESS

Off gas from urea plants are containing NH_3 and CO_2 which have to be recovered either for the preparation of ammonium carbonate or separated by the Chemie Linz process into NH_3 and CO_2 .

1.4.4 REUSING SiO₂ FROM AIF₃ AND CRYOLITE PROCESS

The by-product SiO_2 from AIF_3 and cryolite process has a very high activity and can be recycled to the phosphoric acid plant to control the fluorine content of the by-product gypsum.

There are also many other acceptors for silicic acid but they are only interesting under favourable conditions (because of low bulk density and high water content of the silicic acid).

1.4.5 REUSING CALCIUM CARBONATE FROM AMMONIUM SULPHATE PRODUCTION

If there is a calcium ammonium nitrate fertilizer production within the fertilizer complex the calcium carbonate from ammonium sulphate production can be used as the calcium component or may be utilized for the cement production.

1.5 SOME INTERESTING COLIBINATIONS OF ABOVE MENTIONED PROCESSES FOR SOLVING THE POLLUTION PROBLEMS

A chemical complex normally includes a number of above mentioned processes and I would like to show you some interesting combinations with by-product processes.

1.5.1 STRAIGHTFORWARD CONVERSION OF PHOSPHO-GYPSUM AND EMITTED FLUORINE INTO USEFUL PRODUCTS SHOWN ON A 1 000 t/d P₂0₅ DIHYDRATE UNIT WITH A P₂0₅ CONCENTRATION TO 54 % Slide No. 4 details the possible by-product conversion for a

1 000 t/d $P_2 0_5$ plant. The following remarks should be considered to find out whether the conversions are economically sound or not:

a) For gypsum sulphuric acid plant:

The credit for the cement!

Raw material supply for the sulphuric acid production!

Availability of natural gypsum!

- b) For ammonium sulphate production:
 - Ammonium sulphate market (additional supply from processes with by-product ammonium sulphate)!

Availability of ammonium carbonate solutions within the complex!

Calcium carbonate demand!

c)

For aluminium fluoride and cryolite production:

Production of AIF_3 or cryolite of this magnitude will be difficult to market on a free low priced market. Fixed market contracts with the aluminium industry will be necessary (see also cooperation with other industrial complexes par. 4).

1.5.2 ADDITIONAL ADVANTAGES IN COMBINATION WITH PROCESSES DETAILED UNDER 2.4

Slide No. 5 is showing the possible integration of other plants as detailed under item 2.4 and the recycling of converted or recovered by-products.

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At first there will be an interesting solution in combining the NH_3/CO_2 tail gases of e.g. a melamine and urea plant to recover partly ammonium carbonate in an amount as necessary for the ammonium sulphate production, while the remaining NH_3/CO_2 will be separated in a separate step of the particular Chemie Linz process for recycling.

The phospho-gypsum will be used after filtration first for the ammonium sulphate production and the remaining amount after calcination may be combined with natural gypsum to produce the total required sulphuric acid for the whole complex.

1.5.3 CHEMIE LINZ COMPLEX AS AN EXAMPLE

A chemical complex is normally developing over a number of years and therefore a concept for the integration of future plants is rather difficult.

Chemie Linz was founded 1939 and started 1942 with the production of ammonia and calcium ammonium nitrate.

In 1954 the production of sulphuric acid and cement clinker from anhydrite on the basis of an own anhydrite mines started. The sulphuric acid was partly used for the production of 280 000 t/a SSP and the rest was sold.

The SSP plant caused soon a severe environmental problem with the evolved fluorine and therefore the own research department got the task to find a process for utilization of the free fluorine.

1963 the Chemie Linz AIF_3 -plant was taken into operation and produced AIF_3 äquivalent to the evolved fluorine of the SSP (2000 t/a AIF_3).

In 1966 a PRAYON phosphoric acid plant of 60 t/d P_20_5 was started. Subsequently the gypsum sulphuric acid plant was adapted to use phospho-gypsum also as feed stock for the sulphuric acid plant.

Alternatively the know-how for the use of the phosphogypsum for the ammonium sulphate production was developed. This gave a considerable flexibility to the Chemie Linz complex in respect to the rather instable ammonium sulphate market.

The old use plant delivered first the ammonium carbonate for the $(NH_{4})_2SO_4$ production.

The successive installations of melamine 1, 2 and 3 plant (total capacity 35 000 t/a) and the new urea plant (1977) called for the separation of the NH_3/CO_2 containing tail gases since ammonium sulphate production was down in these years. Here also flexibility to use cheaper secondary sources at any time is a considerable advantage.

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SSP-production dropped by the well known reasons and left the AIF_3 -plant recently with only sporadic supply of fluosilicic acid. Chemie Linz takes also advantages of this situation and uses now its AIF_3 -plant to prove the results of the continuous research work in a technical scale. By this way the Chemie Linz AIF_3 process represents always updated technology. A training program for licencees is offered which gives the opportunity of real trouble shooting.

If a company is considering a grass root fertilizer or phosphoric acid complex or even an expansion of it the engineers responsible for the planning should know about all these possibilities as detailed before to avoid costly investments, which are worthless for later byproduct recovery and represent an economical burden which makes it later on difficult to gain the important flexibility.

Chemie Linz is at any time prepared to assist companies in the integral planning of fertilizer complexes on the background of its successful experiences.

2. <u>EFFECTIVE OPERATION</u>

Effective operation will increase the economy of the process at one side and at the other side it will improve also the environmental situation by reducing the effluents.

The following measures will support effective operation:

- Exact definition of the waste streams
- Provision for suitable measurements for the waste streams
- Proper process control
- Extensive training of the operators
- Regular computation of the mass balance based on actual measured values by the materials and energy department and discussion of deviations with the production management.

From the above listed measures some should get executed already in the design stage of the plant.

2.1 Exact definition of the waste streams

The definition of the waste streams is normaly an essential work to be done for obtaining the permission from the authority for the errection and the operation of a chemical plant but it is also the basis for a mass balance which should assist the plant management to figure out possible deviations of the waste streams. Following documentation should be worked out:

- a) Data on the input-materials (s. OP 7)
- b) Data on the output-inaterials (s. OP 8)
- c) Data on the state of emission (s. OP 9)
- d) Data on the waste stream cleaning equipment (s. OP 10)

2.1.2 Provision of suitable emission measurements for the waste streams

Depending on the importance of the different waste streams well placed sample points have to be provided and proper analyses methods have to be determined. Flow measurements with acceptable accuracy have to complete the data on the waste streams.

2.1.3 Proper process control

Based on the process flow sheet and having in mind possible misoperation one has to select additional control measures taking into account good engineering practice.

2.1.4 Extensive training of operating personnel

An aprenticeship for chemical plant operators is today desirable. During this time the operator gets the basic knowledge about the operation units and the understanding for plant data. The special training for a particular plant must be provided well before the start up and it is desirable that the training is performed in a similar plant.

These measures are the basis for proper collection of data during operation of the plant which are later on evaluated by the material and energy department.

2.1.5 The material and energy department

This department handles normally also environmental affaires. The mass balance is here computed (s. OP 11) and deviations are discussed with the production managements to find its cause and measures to avoid any detriment to the evironment.

This department is fully independent from the production, which ensures a neutral control function.

3. PREVENTIVE MAINTENANCE

Unexpected shut downs are causing often uncontrolled environmental pollution and therefore they have to be avoided.

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Typical causes for unexpected shut downs are

break downs of equipment and leaks by corroded pipes or equipment.

These are failures which can be limited by preventive maintenance, a philosophy which saves money and protects the environment. To be able to follow this philosophy some organisational measures have to be taken.

3.1 Recording of all failures in the plant

It is of immense importance that every plant is keeping a repair book where all troubles are recorded. The maintenance engineer should everyday discuss the recorded troubles with the operators concerned and complete this information by the experience of daily personal visits to the plant. Together with the material testing department, possible trouble spots regarding corrosion should be determined and sufficient material samples for corrosion tests placed inside the process.

3.2 Evaluation of necessary spare parts and determination

of preventive maintenance cycles

With the information under 3.1, the recommendations of the purchase of the equipment and taking into account previous experiences one can select and order the necessary spare parts.

The spare part cycle starting with the order, following the delivery, the storing and the use during plant repairs has to be closely controlled to avoid shut downs without spare parts.

From the evaluation of the faults (wear, corrosion, fatigue, aging) the cycles for preventive maintenance are determined and special spare part philosoph as for groups of machines can be developed. (see OP 12)

E.g.: for pumps which show corrosion or cavitation spare impellers are ordered for turbocompressors complete set as recommended by the purchaser. One impeller always ready for installation etc.

3.3 The planned annual shut down

During the year the maintenance engineer is computing all repairs or changes which could be carried out during a more or less fixed shut down. This shut down will also give the opportunity to investigate the general condition of the plant. It should deliver important data for the preventive maintenance for the next year. Therfore the findings should be carefully documentated (by photographies and analyses). During normal operation a plan should be available to the plant operator for plant maintenance by the operator (lubrication etc.).

	_, <u>,</u>	flugri g/m	ne kg/t P	suspended CaSO ₄ 2 ⁰ 5 g/m ²	mg/Nm ³ flu	total F/t P205	fluorine as gas mg/Nm
ons	USA	15	0,18	1)	1)	10 g	1)
	Europe (BRD)	20	1)	30 - 100	20	1)	0,05 HF
T C P L L	UdSSR	1,5	1)	1,5	1)	1)	0,005
4 5 5	Convential phosphoric acid plant (54 % P ₂ O ₅) environmen*ally	max.47	0 62	max.30 000	-	300 g	-
	balanced phosphoric acid plant (54 % P ₂ 0 ₅) 2 ⁰ 5	max.20	2) _	max.100 ³⁾	50	18 g	-
	1) not avai}able	2) F	luorine j	s recovered for con	version	3) CaSO ₄ is convert	e d or dumped

Restrictions on fluorine emission and for suspended solid in waste water

Natrix for the interlock of processes with by-products accepting processes														
Freeses with by-products	By-products			B y- product	acceptin	g proces	ses							
	emission	disposal	2.2.1	2.2.2	2.2.3	2.2.4	2.3.1	2.3.2	2.3.3	2.4.3	2.4.5			
	Cast Fluorire Sic Caso Caso Caso Caso	CaSO, Caf, (Neutralization)	Plaster Gypsum board Gypsum parels	Gypsum for re- tard setting of cement	H ₂ S0 Ceent	(NH4) 207	Alf ₃	Cryalite	Fluosílicates	Urea piant	Calcium Ammonium nitrate or cement	H_SiF6 Abcorption	P.0. Production	
2.1.1.1 Dihydnate process	•	•	•	•	• •	•	•	•	•			•		
1.1.1. Henibydrate-dibydrate process	••	•	•	•	••	•	•	•	•			•		}
	••	• •				•	•	•	•			•		
2.1.2 Phosphonic acid concentration process	•	•					•	•	•			•		
	•	•					•	•	•			•		
2.1.6 150	•	•						•	•			•		
1.1.5 Inving and calcining of gypsum	•	•									_			[
	•	•												
2.571 Tail gases from melamine processes	•					•				•				
	•					•				•				
2.4.3 Unea processes	•					•				9				
2224 Alf, and cryolite	•	•										•	•	
1.4.5 Ammonjum sulphate process	•										•		Γ	
1.1.4 Neutralization of fluorine		•												
There the $h(\rho_{i})$ reparation process	•					•				•				
			<u>_</u>			<u> </u>							<u> </u>	

By-Product conversion:	Hz	2 ⁵⁰ 4 Ce	ment-clinker	(NH ₄) ₂ SO ₄	H ₂ SiF ₆ (100 %)	Alf ₃	Cryolite
By-products:	r	·					
$Caso_4 \times 2H_2O$ ary	5 000 2	564	2 564	(3 760)			
Fluorine from attack section	-			I			
from concentration section combined	<u>55</u> 62					71	(104)
Necessary raw materials:							
$4_2 SO_4 (100 \text{ s}) = 3.000 =$	436 + 25	64				Á	
A1 (OH) (100 t)	80					ł	≜
(100 %)	$\begin{bmatrix} 42\\ 88\end{bmatrix}$						
Production			2 564	(3 760)		71	(104)
Aluminium melting unit	1 000 t/d						
aluminium fluoride	consumption					30	
sryalite.	approx.						20 ')



		<u>PHOSPHO-GYPS</u> IN T/T P.O.	<u>MUM</u>	<u>FLUORINE AS F</u> IN KG/T P.O.
		AS DRY DIHYDRATE	AS DRY HEMIHYDRATE	205
2.1.	BASIC PROCESSES			
2.1.1	PHOSPHORIC ACID PROCESS	ES		
2.1.1.1	DIHYDRATE PROCESS	5		7
2.1.1.2	HEMIHYDRATE-DIHYDRATE PROCESS	5		> 7
2.1.1.3	HEMIHYDRATE PROCESS DIHYDRATE - HEMIHYDRATE		3,9	>7
2.1.2	PHOSPHORIC ACID CONCENT PROCESS (30 TO 54 %)	RATION		55
2.1.3	<u>SSP</u>			5.5 KG/T SSP
2.1.4	<u>TSP</u>			< 4 KG∕T TSP

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CONSUMPTION FIGURES FOR THE CHEMIE LINZ GYPSUM SULPHURIC ACID PROCESS

<u>CEMENT FROM</u>		ANHYDRITE	DIHYDRATE DR HEMIHYDRATE (PHOSPHO-GYP	Y OR DIHYDRATE WET WET (PHOSPHO-GYPSUM) SUM)
<u>UNITS:</u>		1 T CE	EMENT + 1	T SULPHURIC ACID
RAW MATERIALS:				
ANHYDRITE UR				
GYPSUM	KG	1 550	1 950	2 430
COKE BREEZE	KG	95	95	95
CLAY, FLY ASH				
OR SHALE	KG	140	140	140
SAND	KG	80	80	80
IRON OXID	KG	8	8	8
UTILITIES:				
HEAT CONSUMPTION	GJ	6.4	7,8	10
ELECTRIC				
ENERGY	KWH	250	250	250
WATER FOR COOLING	M 3	45	45	45

CONSUMPTION FIGURES FOR THE CHEMIE LINZ AMMONIUM SULPHATE PROCESS

RAW MATERIALS:	UNITS			
BY-PRODUCT-GYPSUM				
(AS CASO ₄ ,2H ₂ O DRY)	T/T	1.33 (ENTERS	THE PROCESS	FILTER WET)
AMMONIA (100 %)	T/T	0,27		
CO ₂ (100 %)	T/T	0,35		
SULPHURIC ACID (100 %)	T/T	0.06		
		BY-PRODUCT		
<u>UTILITIES:</u>		FILIER WEI	DRYED	
PROCESS WATER	T/T	1,5	1,5	
COOLING WATER	T/T	50	50	
STEAM (6 BAR)	T/T	0,65	0,65	
ELECTRIC POWER	KWH/T	50	50	
INSTRUMENT AIR	NM ³ /T	10	10	
FUEL	GJ/T	0,32	1,8	
<u>EFFLUENT:</u>				
WASTE WATER				
(0.4%.(NH ₄) ₂ SO ₄)	T/T AS	1,5		
<u>BY-PRODUCT:</u>				
CACO ₃ DRY	T/T	0,75		

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CONSUMPTION FIGURES FOR THE CHEMIE LINZ ALUMINIUM FLUORIDE PROCESS

RAW MATERIALS:	PER T_ALF 3
ALUMINIUM HYDROXYDE (100 %)	1,12
$H_2S_1F_6$ (100 %)	1,10
<u>UTILITIES:</u>	
ELECTRIC ENERGY	200 KWH
FUEL	5 GJ
LOW PRESSURE STEAM	2 T
CUOLING WATER	20 M ³
SCRUBBER WATER	MAX. 50 M ³
STEAM CONDENSATE	1 M ³
INSTRUMENT AIR	APPROX. 300 NM ³

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CONSUMPTION FIGURES FOR THE CHEMIE LINZ CRYOLITE PROCESS

RAW MATERIALS:	PER T CRYOLITE
ALUMINIUM HYDROXYDE (100 %) FLUOSILICIC ACID (100 %)	0.4 T 0.75 T
NATRIUM CARBONATE (100 %)	0.85 T

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UTILITIES:	
PROCESS WATER	
(CA-FREE)	12 M^3
COOLING WATER	50 M ³
STEAM	3.5 T
ELECTRICAL ENERGY	A CRYOLITE PLANT SHOULD BE NORMALLY COMBINED WITH A
FIF	ALUMINIUM FLUORIDE PLANT TO BE MORE ECONOMICALLY.

DATA ON INPUT MATERIALS

OPERATION UNIT:

i

CAPACITY:

STREAM ¹⁾	DESSIGNATION	FLOW	COMPOS	ITION MIN WZ MAY
NO.	UF THE STREAMS		SUBSTANCE	
	RAW MATERIALS ADDITIVES FUEL ETC.			

1) FROM PROCESS FLOW SHEET

DATA ON OUTPUT MATERIALS

OPERATION UNIT:

CAPACITY:

STREAM ¹⁾	DESSIGNATION	FLOW	COMPOS	ITION
No.	OF THE STREAMS	UNIT/H	SUBSTANCE	MIN 🌈 MAX
	PRODUCT			
	BY-PRODUCT			
	EFFLUENTS			

1) FROM PROCESS FLOW SHEET

DATA ON THE STATE OF EMISSION

OPERATION UNIT:

CAPACITY:

STREAM	OPERATIONAL	FREQUENCY	WAST	E GAS	5	SUBSTANCES	ENITTE	D	MEASUREMENT
No.	STATE	AND DURATION	FLOW		TEMP.	SUBSTANCE	CONCEN	TRATION	FOR THE
		OF EMMISSIONS	UNIT	/H	^о С		MG	/M 3	EMMISSION
		H. DAYS, MONTHS	MIN	MAX			MIN	MAX	
·								1	

1) FROM PROCESS FLOW SHEET

DATA ON THE EFFLUENT CLEANING EQUIPMENT

OPERATION UNIT:

CAPACITY:

DEVICE	OF EQUIP	ENT No.	DESIGNATION ¹⁾ OF EQUIPMENT	TYPE OF CLEANING DEVICE	PRINCIPLE OF CLEANING	EFFLUENT DESIGN LOAD UNIT/H AT ^O C	EFFICENCY OF CLEANING DEVICE	PRECIPITATED SUBSTANCE	EFFICENC FOR SUBSTANCI
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1) FROM PROCESS FLOW SHEET

DLOCK 25 KS112D5 P-SAURE

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JE T P205 IN P-SAEURE-----

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₩64: 0	P-SAEURE PRD- DUKTION T P203 Y100	TATO P205 WAEHREHD DETRIEDS- ZEIT V119	BETRIEPS- ZEIT X YI18	PRO- DUKTIONS- SAEURE X P2OS Y117	ROH- PHOSPHAT (MEHL) Y Y101	H2 504 (100 %) T Y102	KIESELGUR KG Y104	DELBAEURE Kg V105	P-GIPS ANFALL T CASO4 JE T P205 Y106	NH3- WA1SER Kg N Y103
1981 31	3813	131	94.0	23.8	3.03	2.65	6.1		3.59	1.6
1981 02	3413	136	91.2	23.5	3.04	2.75	7.2	3.5	3.76	1,6
1981-03	3805	131	24.1	23.7	3.03	2.80	5.8	3.5	3.66	1.6
1981 04	3 . 4 2	120	20.3	23.4	2.95	2.07	3.8	2.9	3.66	1.9
1981 05	3020	124	94.0	23.7	2.92	2.62	2.6	۲.8	3.38	1.7
1981 06	3627	128	74.6	23.7	3.03	2.70	••.9	3.4	3.47	1.6
1281 07	3581	123	93.7	23.3	3.05	2.64	6	3.5	3.45	1.7
1981 08	3749	129	93.8	23.5	3.03	2.64	10.2	3.6	3.51	1.7
1981 DV	3060	126	80.6	23.7	3.03	2.60	12.2	3.6	5.53	5.0
rer	31915	127	91.8	23.6	3.01	2.68	8.0	3.2	3.56	1.7
VORSCHAJ	44000	123	93.9	U	3+07	2.45	20.0	4.0	3.49	1.7
VCRJANR	44005	128	93.8	23.9	\$.05	2.65	11.6	3.4	5.51	1.6

RLOCK 26 KST1205 P-SAEURE GESAMT JE T P205------

M642	FLUWA	DAMP F	STROM (6 KV)	STROM (500/38D)	DRUCK- Luft	1NSTRU- MENTEN- Luft	
r	H 3 Y 1 0 7	T Y 1 0 8	K WH 4109	КЫН Ү110	NH3 4111	NM 3 V112	
1981 01	41.9	0.29	85.6	80.3	567	4.4	
1981 02	43.2	0.32	93.5	105.4	586	5.3	
1981 03	42.9	0.27	20.1	92.5	577	5.8	
1981-04	45.6	0.28	98.5	103.3	403	7.2	
1931 05	43.3	0.23	27.3	98.2	371	6.2	
1981 06	44.8	0.11	89.7	94.1	565	6.4	
1981 07	44.0	0.10	91.0	97.8	588	7.5	
1281 08	44.5	0.11	74.2	91.8	553	7.1	
1261 09	53.3	0.10	13.6	90.2	528	8.2	
PiR	44.7	0.20	88.2	95.5	526	6.4	
VORSCHAU	37.5	0.18	84.5	96.1	556	U	
VORJAHR	42.2	0.20	82.5	95.8	568	6.0	

NUR DAU 627 JE T P205-----BLOCK 27 DAMPE M644 FLUDA STROUSOOV INSTRUM. M 3 ۲ КМН LUFT JE T P205 JE T P205 JE T P205 NH3 JE T P205 e 01 82 83 84 -------------74.1 1981 01 40.4 0.29 4.4 1781 02 41.7 0.32 98.8 5.3 1981 03 41.4 0.27 5.8 86.1 1981 04 43.7 0.28 96-1 7.2 1951 05 41.6 0.23 90.9 6.2 1981 06 43.5 0.11 87.4 6.4 1981 07 42.4 7.5 0.10 90.9 43.5 1981 08 0,11 86. 2 7.1 1981 07 52.0 0.10 93.7 8.2 PER 43.2 0.20 89.0 6.4 VORSCHAU 36.0 0.18 90.0 u 40.8 6.9 0.20 VORJAHR 89.3

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GK.HUMBOLDI	NOFHER TE I	P103		
GH-MUEHLE	FLUNA	STROM	STROM	DRUCK-
FUER 627		(6 KV)	(500/380)	LUIT
RP-MEHL				
STUTO	M 3	Кын	KWH	N# 5
¥1131	¥113	¥114	1115	¥116
19.5	1.31	78.0	5.65	539
21.1	1.24	77.4	5.33	509
19.1	1.33	81.5	5.76	549
20.1	0.90	\$2.8	3.84	264
18.0	0.77	43.8	3.33	222
19.4	1.26	72.8	5.45	\$20
19.5	1.30	74.8	5.63	537
19.7	1.51	74.2	5.65	535
20.4	1.27	73.6	5.50	525
19.5	1.19	70.0	5.14	469
20.7	1.25	71.1	5.07	507
20.9	1.24	68.6	5.36	510

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CYCLES OF PREVENTIVE MAINTENANCE

5- LOWER NITROGEN ETFLUENT FROM UREA PLANTS *

SUMMARY

Urea plant effluents containing nitrogen compounds represent process inefficiency and environmental pollution. Reduction of the nitrogen content of the effluent streams by continual development and process improvement is discussed with reference to prilling tower air, process condensate, inert gas purge and operational discharges in the Snamprogetti Urea Process. A note is added on the advantages of granulation from the pollution standpoint.

Also noise pollution has been considered together with a short description of the method used by Snamprogetti to study this problem.

INTRODUCTION

Nitrogenous fertilizer factories discharge effluents containing nitrogen in the form of ammonia, urea and nitrate.

Industrial growth n any country is associated with an increase in problems caused by effluents: the importance of these problems vary from one country to another depending on many factors and in the same country from one area to another, being more acute in those areas that are more densely populated and poorer of natural open waters. So every country has different laws, more or less stringent, that request treatments involving considerable amounts of money (particularly for existing plants) to reach a satisfactory reduction of pollutant effluents. In general, methods used can be biochemical and chemico-physical: the first ones do not lead to the recovery of nitrogen compounds, the second

Author: F. Granelli Snamprogetti - Italy. ones can involve the recovery with a consequent benefit on the specific cost per ton of produced fertilizer.

Having in mind the enormous world nitrogen fertilizers production it is easy to state that also the losses are large. Just an example of the importance of the problem: it has been reported that the discharge of nitrogen from the river Rhine into the North Seahas been estimated, years ago.at 750 MTD a figure that is self-explanatory.

Such a large amount of losses justify the efforts made to reduce them not only from the pollution point of view: easy to say that those artipollution systems leading to a recovery of nitrogenous compounds would be preferable. But of course each case has to be examined in its own environment along with the socio-economic aspects before choosing the best method.

In fact many experts ask for flexible requirements to reflect local environmental considerations instead of rigid standards, although the same experts suggest similar regulations for different countries.

Going closer to an urea plant, pollutants are represented by ammonia (in vents or in aqueous solutions) and urea (as dust or in aqueous solutions). It is not easy to calculate the quantity of ammonia (as ammonia or as urea) released by a certain urea plant. In fact the amount depends on many factors such as process, engineering, proper operation and maintenance of the plant, unawareness or indifference to hazards of pollution, control of pollutants by the factory management and/or the authorities, lack of legislation (inside or outside the factory) and of course the presence of the antipollution systems.

But, just to give an idea of the amount of ammonia that is lost in the air or in the water, it is sufficient to mention that the stoichiometric content of ammonia in one ton of urea is about 567 kg and the actual specific consumption of ammonia, considering long periods of plant operation is 575-580 kg (and even more), leading to an amount of losses from 1.3 to 2.3%.

For a plant capacity of 1500 MTD the total loss is between 12 and 21 MTD as ammonia or between 20 and 30 MTD as urea, being the losses a part of ammonia and a part of urea.

The damages that can arise from pollutant effluents of a fertilizer plant and more specifically of an urea plant are those to the human lives (both for the workers inside the factory and for the inhabitants in the surrounding areas), the vegetation and the marine and fresh-water fauna. Undoubtedly the major problem is toxicity of ammonia to aquatic organisms.

This explains the fact that the first attempts against pollution in nitrogenous factories have been made (and in many cases they are still the only ones) to reduce the quantity of ammonia in liquid effluents, a problem that becomes technically more difficult when less ammonia is requested in the discharge.

On the basis of the above matters it is clear that it is (and it must be) a continuous objective of Snamprogetti, in common with other urea process owners and designers, as well as plant owners, to reduce or eliminate loss of nitrogen in the interest of both plant efficiency and environmental pollution.

The sources of such losses are by now well known and well documented. For example we can refer to several of the papers presented at the recent British Sulphur Corp. Fourth Internation Conference (1), (2), (3). It is also clear that the search for improvements has become "a war of attrition" in which much effort has to be expended for each small gain. A year or so ago we published some information about a plant which was at that time the latest Snamprogetti plant to go onstream - for 1FFCO at Phulpur (India)(4). Figures 1 and 2 attached are copied from that article, in which we mentioned the antipollution measures taken. We now report further progress on some of these topics - firstly on effluents from the prilling tower, by reference to the most recent of our plants now starting up in India - for RCF at Trombay; secondly on waste water treatment by reference to plant scale development work, based on laboratory trials, recently carried out and applied in several commercial plants now being designed. We also want to emphasise two of the pollution-avoiding benefits which are built in to Shamprogetti's fundamental design, relating to inert gas scrubbing and to inventory losses.

Finally we indicate some of the benefits of the granulation technology which we can now offer as an alternative to prilling. In addition to chemical pollution also noise pollution is by now a major problem for industrial plants. Snamprogetti has developed a computer programme which allows to foresee the plant noise level since the design phase. Thus lower costs and better results are obtained, as compared to the case where actions are taken on plants already built.

EFFLUENTS FROM THE PRILLING TOWER

The air pollution problem due to the urea dust contained in the air from a prilling tower is very uneasy to eliminate because of the large volume of air and the small size of particles to be caught. The effect of this emissions on the environment is not very clear: in the vicinity of a plant the effect on vegetation can even considered as beneficial, but the prevailing winds can concentrate the dust in a small area to cause scorching on vegetation.

Most Snamprogetti plants which produce prilled urea are provided with a natural draft prilling tower. Apart from the savings in running costs and maintenance by avoiding the use of induced draft fans, we have found a reduction in the amount of dust carried out of the tower. For example, measurements carried out several years ago on prilling towers of two otherwise similar 1000 MTD plants without any supplementary de-dusting showed the following results:

·	Natural Draft	Forcea Diaft
Air	300.000 Nm3/h	600.000 Nn3/h
Urea dust content	90 mg/Nm3	150 mg/Nu:3

TOTAL DUST

27 kg/h

90 kg/h

Although these figures are not typical of the best modern practice, we were encouraged to continue our development along the lines of natural draft towers. It was next found that with external air exhaust vents at the top of the tower (the smaller tower in Figure 3) at no-spheric air movements (winds) caused irregular air flow patterns inside the tower, leading to increased dust carry-over. This problem was

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eliminated when the top of the tower was re-designed, to have the exhaust air vents on a concentric inner wall (the larger tower in Figure 3). The re-design of the top of the tower was a consequence of the development of our wet scrubbing system, which was first tested in a pilot plant installed on the top of Manfredonia urea plant prilling tower. The air, from the inside of the prilling tower, was sucked by means of a scrubber Venturi. The energy to suck the air is provided by a pump recirculating the solution which absorbs the urea dust from the air as shown in the attached diagram, Figure 4.

The dust content measured at the inlet of the dedusting unit (point

A	of	the diagram) min.	was:	39	mg/Nm3
		average		63	**
		max.		80	**

Liquid/air ratio

6.4 1/Nin3

Discharge presame of the recircul	ating pump	€ kg/cm2
Pressure at nouzle inle*		4.5 kg/cm2
Liquid temperature in the tank		19°C
Air temperature at dedusting unit (point K of the diagram)	inlet	50°C
Air temperature at dedusting unit (point B of the diagram)	outlet	22°C
Ambient air temperature	min/max	14/24°C
Average quantity of water evapora	ited	14 l/h

The results o	f the tests were:	
Test	Urea concentration in the recirculating solution	Absorption efficiency
nr	%%	%
1	0.0	99
2	5.0	95
3	20.0	92







MICROCOPY RECOLUTION TEST CHART

In applying this system of wet-scrubbing to all the air in large diameter prilling towers the top of the tower is re-designed as shown in Figure 5. The IFFCO plant at Phulpur has the inside windows with the possibility to install the scrubbing system in future. The RCF plant at Trombay has the full system installed which operates as follows: Air rising through the prilling to er enters the annular duct (A) where inside windows have been provided which allow the air to be discharged directly to atmosphere if the de-dusting system is not in operation. Air is drawn from this annular duct by a ring of liquid jets arranged in the annular space (E), which provide the energy required to overcome the pressure drop through the system. These liquid jets break into fast moving droplets which have a high collection efficiency for the very fine dust contained in the air.

Now purified and saturated with the liquid droplets, the air rises in the duct (C) which is sized to reduce speed and thus allows the separation of a good part of the entrained liquid. It is then discharged after passing through demister packings which retain the mist. Fresh make-up water is sprayed into the demisters for washing purposes whilst the jet nozzles are fed with the urea solution which coulects in the annular basin (D). Surplus solution is returned to the urea plant.

This dedusting system has an electrical power consumption of 9 Kwh/ MT The design performance for the Trombay plant is as follows:

air quantity	500.000 Nm3/hr
guaranteed dust content	30 mg/Nm3

It must be pointed out that the system described above allows also to catch a part of ammonia that, although in low concentration, is contaiited in the air leaving the prilling tower.

Thet Snamperogetti's approach to the problem is effective can be shown by two practical examples. At the new Manfredonia plant, (the larger tower in Figure 3) many measurements have been made, and values of about 40 mg/Nm3 are found, even without the de-dusting system. This

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figure for dust content is consisten with the results obtained from routine checks carried out on air panples taken at fixed points inside and cutside the factory at ground lovel. At Chemie Linz where the factory is very close to the town centre, no complaints are made concerning dust emissions from the prilling tower.

A confirmation comes also from the HFCO usea plant at Phulpur. According to the Owner of the plant the quantity of dust is about 50 mg/Nm3 and "the visual observations show that this prill tower has lower dust losses than forced draft towers currently being used in the country".

After such a result the Management has decided that no dedusting system, although foreseen, will be installed.

WASTE WATER TREATMENT

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The origin, composition and methods of treating the process condensate discharged from a Urea plant have already been described in detail by others.

We refer to reference (3) (and the earlier publications referred to in that paper) and particularly to reference (6).

In the last paper the authors have presented the stripper hydrolysis method, but they have also indicated some other methods: biological oxidation, reverse osmosis, oxidation with hypochlorite, ion exchange resins and reaction with nitrites.

As already said in the introduction of this paper, those methods that lead to a recovery of nitrogenous compounds are preferable.

So we are in favour of the stripper-hydrolysis method, but we point out that in many usea plants the only existing anti-pollution system is that used to reduce the ammonia contained on the so called "process water" represented by a stripping with air (or with steam depending upon prevailing economics to individual units): in any case this method was probably the first one used in usea (and ammonia) plants. The reason is due to the fact that a imonia is considered the most se-

ricus of pollutants. Its harmful effects (both ionised and unionised forms) in effluent waters discharged into inland surface waters are well known.

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This knowledge has led to stringent specifications and so the stripping process is one of the nitrogen removal processes that actually has been used in waste water treatment.

The process mainly involves raising the pH of the effluent to values above 11.0 using lime to bring all the ammonia present to the unionised form and to strip the ammonia in a tower with air.

Useless to say that the pollution problem is transferred from water to air (where ammonia can form smog with aciaic gasecus effluents vented from other fertilizer plants in the same factory) unless ammonia is fixed in an absorption system producing an ammonium salt.

Although the proper solution can be different from case to case it seems to us that a better solution is a stripping of ammonia followed by a recovery of it as a solution that can be recycled to the urea plant. This avoids any auxiliary chemicals and can be easily coupled with a thermal hydrolysis, where also urea (that doesn't pose toxicity problem, but has in many countries received fixed tolerance limits) can be decomposed back to ammonia and carbon dioxide and recovered to urea plant. Two examples of ammonia (Phulpur plant) and both ammonia and urea

(Gujarat plant) recovery are described herebelow.

The waste water treatment section of the Phulpur plant shown in Fig. 2 consists only of a stripping column to rec ver ammonia. Any hydrolysis of urea is incidental, and the effluent water contains 300 ppm ammonia and about 0.5 % urea.

The 1800 metric tens per day Snamprogetti Urea plant for Gujarat, which is soon to be started up for the first time, represents an improvement on the Phulpur plant. The flow scheme is shown in Figure 6. This is the Snamprogetti version of the generally used system of hydrolysis, preceded and followed by stripping of the ammonia and carbon dioxide. The offluent water quality is sufficient to meet the usual environmental stardards as can be seen from the following data:

					1	\mm	non	ia			Urc	<u>a</u>		
Process	condensate	before	treatm	nent	1	-	5	Ń			up	to	1	% %
Treated	effluent:	Expecte	d	50	Ինա				150	Ppr	m			
		Guarant	eed	100	ppm				200	ppr	n			
				_	-92—									

This treated condensate is at present discharged to drain, after cooling. The next step is to make it sufficiently pure for further use, as for example Boiler Feed Water.

Like other designers (3) we recognise the need to avoid back-mixing in the hydrolyzer, if the theoretical iow levels of urea are to be achieved in practice in full scale commercial plants. Therefore our most advanced hydrolyzer design, which adheres to the principles of physical chemistry and to the time/temperature/concentration relationships established by our own laboratory work, pe.mits a much more complete hydrolysis and lower residual levels of urea in the treated condensate. The hydrolyzer is illustrated diagrammatically in Figure 7. It provides plug flow, thus avoiding back-mixing, and also the continuous removal of the hydrolysis reaction products, to encourage the decomposition of urea to proceed further to completion. This new hydrolyzer is provided in several new plants new in the design phase, including three 1725 MTD plants for RCF in India. With steam available at 40 Ata for the hydrolyzer, the composit¹ n of the treated process condensate is:

	Guaranteed	Expected
Urea	5 ppm	negligible
Ammonia	30 ppm	24
	· · · · · · ·	

It is planned to publish the results of our laboratory work and industrial scale tests fully at a later date.

INERT GAS SCRUBBING

The principal feature of the Snamprogetti Urea process is the use of ammonia for stripping the uncoverted carbamate from the product urea solution within the isobaric reaction loop. Thus the presence of excess ammonia and operation at relatively mild reactor conditions, combine to minimize corrosion in the reactor. Furthermore, we use titanium tubes in the stripper which are also more resistant to corrosion than stainless steel. One consequence of these facts is that the quantity of passivating air introduced into the reaction loop can be minimised and is less than for other processes.

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The passivating air is eventually discharged from the plant, via the inert gas scrubber (item C-3 of Figure 2) which serves to prevent losses of ammonia.

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Since the total amount of inert gases is less, the amount of ammonia lost with the inert gases is less. On the other hand it is usual to allow some ammonia to remain in the inert gases in order to keep outside the explosive limits of the mixture of oxygen and hydrogen. In the Snamprogetti process this ammonia residue can be less because the oxygen content is less. In the majority of cases a very complete scrubbing of ammonia can be performed with consequent minimum pollution, and it is only ir the case of abnormally high hydrogen content of the carbon dioxide feedstock that the possibility of explosive mixtures in the inert gas scrubber has to be given special consideration. Even so, it is often possible to arrange for maximum recovery of ammonia by substituting some additional inert gas in the scrubber. This can be steam, nitrogen or even ammonia plant synthesis gas, which is then used for fuel. In the latter case the gas mixture is outside the explosive limits on the high side with hydrogen. A typical inert gas scrubber effluent is:

H2	25.0 %	vol.
N2	44.0	"
СО	2.0	••
C114	12.0	••
NH3	1.0	**
O2	11.0	
H2O	5.0	"

For a urea plant of 1500 MTD the total amount of inerts discharged to the atmosphere is 600 Nm3/h, corresponding to less than 0.03 kg of ammonia per ton of urea product.
INVENTORY LOSSES

Pollution is usually thought of as the small quantities of process materials which escape unavoidably and continuously from the plant as contaminants of what would otherwise be an inert stream of fluid e.g. cooling air, steam condensate and inert gases in the three examples described (bove. Much attention is devoted to reducing the levels of such contaminants. But the process fluids which may be released into the environment due to occasional leakage, spillage and other accidents can be equally or even more polluting, especially if they are more concentrated. How, therefore, to contain the process fluids within the plant at all times?

Obviously good maintenance of flanged joints, pump glands etc. is important. But more than that, the very design principles and design details of the Snamprogetti process make the most important contribution to a pollution-free usea plant. It is during start-up and shutdown and during other periods of integular operation that lesses of process fluids form the plant are most likely to occur. At such times the storage of solutions in the large quantities required may present a serious problem. The problem may be alleviated by:

- (1) less frequent plant stoppages
- (2) less frequent emptying of the plant
- (3) lower inventory of materials in process.

Less frequent stoppages derive from the fact that the plant is very flexible in operation and can run at 40% capacity. Even if production is stopped, the process fluids within the high pressure loop can be "blocked-in" for several days without risk of correction damage. And if the plant has to be drained down, the inventory of process fluids is minimal, firstly because the reaction loop volume is smaller for a given plant capacity due to the high reactor conversion (about 67%) and secondly because the extensive use of falling film exchangers in the decomposition sections minimizes the use solution inventory. Therefore the need to discharge use ammonia-carbamate solution, at plant shutdowns, is not necessary and the pollution problems caused by such discharges are therefore avoided.

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GRANULATION

Air

The primary reason for preferring granulation to prilling would be the particular qualities of the product, i.e. granule size and hardness, but granulation processes may also have advantages in reducing pollution, or in achieving the same pollution levels at lower capital cost for pollution control equipment. Nevertheless there are some owners of urea plants (7) which claims that, just to reduce the problem of urea dust pollution from a prilling tower, they installed a granulation section after some years of operation with a prilling tower. Snamprogetti has not had the occasion to develop its own granulation process, but has nevertheless maintained a close contact with developments in this field in order to assure its clients of the best available technology. The Snamprogetti urea technology has already been associated with the well-known "Spherodizer" granulation process of C&I GIRDLER. This process is particularly suitable for single streams up to 500 MTD.

Recent projects now in the design phase include the newly developed NSM granulation process (5) which uses the fluid bed principle, and is being used for up to 1750 MTD in a single stream.

In two particulars granulation gives lower effluent quantities than prilling. Firstly with regard to process condensate the amount is less because some of it is evaporated into the air passing through the granulator and the scrubbei.

Secondly the quantity of polluted air is less and can be satisfactorily cleaned in cyclones because of larger dust size.

The overall quantities of effluents for a complete urea production plant including NSM granulation, compared to prilling, are typically the following per metric ton of product urea:

	Granulation	Prilling
r quantity	5.500 Nm3	10.000 Nm3
Dust content	30 ppm guaranteed 20 ppm expected	

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Process	condensate
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210 kg

440 kg

Urea dust size distribution in microns (*)

> 3	97	18
1 ÷ 3	2	66
< 1	1	16

(*) Dust emission from granulator only, sizes from cooler even larger.

NOISE CONTROL

Exposure to noise can cause irreversible damages to the human ear. The extent of these damages depends on noise characteristics and level and exposure length. In any case noise pollution has become a major problem for industrial plants and therefore Snamprogetti has developed a method for studying and foreseeing sound levels. Definitions (8)

Although sound may occur within large ranges of frequencies and magnitude, we are only concerned with it as far as it is audible to a healthy human ear.

<u>Frequency</u> (number of air vibrations per second) is expressed in Hertz (Hz). The audible range for human beings is between 20 and 20,000 Hz. <u>Magnitude</u> (or amplitude) is expressed in decibels (dB).Since sound is practically a pressure variation of air, this pressure is usually expressed in Newtons per square meter (N/m^2) , i.e. Pascals (Pa).As pressure variations related to acoustic phenomena are in the range 2×10^{-5} to 63.5 Pa, decibel has been introduced in order to have a simplified scale.

Sound pressure level (SPL) in dB is defined as follows:

SPL = 20 $\log_{10} (P/P_o)$ where $P_o = 2 \times 10^{-5} Pa$

Isophonic curves are de ned as lines of equal impression.

Each curve is formed by points representing the same impression on an **average** human ear. On the basis of tests carried out on several persons it can be said for instance that 50 dB of noise at 1000 Hz have the same effect or loudness as 82 dB at 31.5 Hz.

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For semplification ISO (International Standard Organization) has recommended to rectify these curves (noise rating or NR curves). Each curve is called according to its dB value at 1000 Hz.

dB(A) value. Noise levels can be measured with an instrument including a filter which simulates the human ear and calculates a corrected dB value which is called the dB(A) value. dB(A) values correspond to 150 curves approximately according to the following pattern:

ISO	NR	dB (A)
55		60
85		90
90	i	95
92		97

The following examples give an idea of the correspondance between dB(A) values and everyday situations.

110 ": jet landing at 250 meters

100 " : ball mill in cement factory at 1 meter

90 " : train pacsing at 120 Km/h at 25 meters

70 " : electric typewriter at 1 meter

60 " : normal conversation

30 ": reading room in a public library

10 ": falling leaf

0 " : threshold of hearing

METHODS FOR STUDYING AND FORESEEING NOISE LEVELS

In order to meet the noise limits fixed by environmental rules, two types of actions can be offered:

- to act on running plants

- to act on plants under design

It has been demonstrated in several cases that actions of the first type involve very high costs along with results which are not always appreciable, whereas actions during the design phase can have lower costs and certainly better results.

During the design phase the equipment position is schematically drawn, that means a preliminary 'ay-out is prepared.

A noise spectrum is then attributed to each apparatus and this is assumed on the basis of a series of data obtained from previous tests. Tests can be carried out by suppliers or Snamprogetti themselves.

These data are worked out by programme NEW NOISE which has been studied for this purpose. Programme NEW NOISE determines S.P.L. (sound pressure levels) figures in several positions (hearing points) as a sum of contributions of all the noise sources and depending on the following parameters:

- temperature, pressure and ambient humidity conditions

- source types (points, lines or planes)

- distances of sources from the hearing points

- atmospheric absorption

- ground absorption

- reverberation effect if the calculation is carried out for an indoor case

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The calculation is carried out for the main frequencies, viz. 62.5,125,250, 500,1000,2000,4000 and 8000 Hz.ln addition to S.P.L. figures in dB, also S.P.L. figures in dB(A) are calculated. The programme allows then to draw the isophonic curves for the area of specific interest.

In order to give evidence to the characteristic properties of sound sources, three types of models have been considered:

- point sources

- defined linear sources with constant SPL

- defined plane sources with constant SPL

Generally speaking the following assumptions are made:

- points sources are those with an enveloping surface smaller than 40 m² (e.g. pumps and electric motors)

- linear sources are for instance pipes

- plane sources are the remaining ones (e.g. furnaces, cooling towers, compressors, turbines etc.)

Once the preliminary map of isophonic curves has been drawn (the computer prints both a curves map and a SPL table by points), it is possible to determine areas with a noise level exceeding the acceptable limits and locate the apparatus which is the main responsible for noise in the considered points. Thus an action is taken by limiting the noise of a certain apparatus (enclosures, screens,dampers,silencers), otherwise protected areas are provided for personnel (acoustic shelters).

Main appliances of programme NEW NOISE are the following:

- Melilli refinery (Italy)
- Tabriz refinery (Iran)
- Basrah refinery (Iraq)
- Pembroke refinery (Wales, U.K.)
- Rabigh refinery (Saudi Arabia)
- Lavera refinery (France)
- Gela polyethylene plant (Italy)
- Hamburg polyethylene plant (West Germany)
- Kavala urea plant (Greece)

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- (5) B.S.C. Conference Paper 13 - "NSM's Fluidized Bed Urea Granulation Process" [.P. Bruynseels
- V. Laganà and Pascarella "How Snamprogetti has solved pollution problem from urea plants" - Semina: on Technical and Economic Aspects of the Fertilizer Industry Helsinki 11-15 August 1975
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Figure 1.

BLOCK SCHEMATIC DIAGRAM



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Figura 3 - Old and new prilling towers at Manfredonia plant



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Figure 5 - Top of prilling tower designed to incorporate wet scrubbing of cooling air



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Figure 6 - Waste water treatment at G.N.F.C. - Gujarat (India)



Figure 7 - Diagrammatic illustration of plug-flow horizontal hydrolyzer

6- PROCESS CONDENSATE PRE-TREATMENT .

A NEW SYSTEM DESIGNED FOR AMMONIA PLANTS IN KUWAIT.

ABSTRACT

A new process Condensate Pre-Treatment System was designed and shall be implemented in Kuwait to treat the condensate from P.I.C.'s two existing 800 T.P.D. Ammonia Units and one new 1000 T.P.D. Unit .

The system replaces simple atmospheric degasification by a more elaborate distillation step. The quality of water is improved tremendously and most of the pollutants are recycled to process unit.

The system is relatively expensive to install, but it results in a reduction of make-up water to the plants as well as a large reduction in the frequency of regeneration of subsequent ion-exchange thus reducing liquid effluents and permitting smaller water treatment facilities. The paper offers a description of the existing and future treatment systems and their impact on the environment. The economics of the new system are also discussed, it's applicability to other sites has to be evaluated in the light of local Costs and Pollution Control requirements.

1 - Introduction,

In an effort to reduce effluents from it's Ammonia Plants, Petrocemical Industries Company of Kuwait decided to implement a new process Condensate Pre-treatment System .

The system has been designed in detail by our company and shall be implemented as part of P.I.C.'s fourth Ammonia Project. The existing treatment facilities at P.I.C. already includes recycling of process condensate as well as Steam Condensate to conserve expensive make-up water. With three Ammonia Units as Shuaiba and a fourth on the way, P.I.C. had however a good incentive to undertake additional measures to reduce pollution to the lowest possible limits. The system was proposed by the Licensors, Messrs HALDOR TOPSOE A/S of Denmark, who had already tried out similar system in other plants. The advantages achieved are :

- A reduction in steam losses to the atmosphere .
- A large improvment in the quality of process condensate at the inlet of the demineralization unit, resulting in less frequent regeneration and therefore reducing liquid effluents from the unit.
- A large reduction in total make-up water to the plants and in the consumption of chemicals, resulting in a reduced cost of Boiler Feed Water.

By : Mostafa Badr El-Din. Abdel Raouf M. Nada. Petrochemical Industries Consulting Office. Kuwait. The system was designed to minimize Utility requirements particularly Cooling Water, and includes a large Air-Cooled Condenser. The increased capital cost is justified at the conditions prevailing in Shuaiba, but alternative designs may be utilized to acheive similar pollution control results in other locations.

In the following section the existing system at P.I.C.'s plant "B" is described and compared with the new design. The basic idea is very simple, using proper distillation to recover most of the pollutants in a concentrated form and recycling them back to the process, instead of direct degasification.

II - General Description

For clarification please refer to the attached drawings .

Figure 1: Shows the sources of water supplies to the Eoiler Feed Water Treatment Unit for the generation of High Pressure Sceam utilized in the Ammonia Plants. The figures represent the consumption of 2 x 800 M.T.P.D. Ammonia Plants operating at a 4.5 s/c ratio. It is evident that the process condensate collected from the gas preparation section of the Ammonia Plants represents approx 25% of the total Boiler Feed Water requirements. A typical analysis of the untreated process condensate is shown .

Process Description :

The process Condensate collected from the gas preparation section of the Ammonia Plants flows to the process condensate degasifiers where most of the CO_2 and part of the NH_3 and CH_3OH are stripped off and emitted to the atmosphere by means of Low Pressure Steam . The degasifier is a vessel containing one bed of Pall rings , the condensate is introduced at the top over a distributor and steam is introd-The stripped process condensate is cooled and uced at the bottom . filtered from mechanical impurities then flows to the Cation Exchangers , where (NH_{4} +) cations are removed and replaced by hydrogen $ions (H_3O+)$. The condensate is then aerated to remove the dissolved Co, and mixed with the steam condensate and the Raw Water make-up. The mixed stream is sent through the mixed ion exchangers for final purification . It's worth noting that the cation exchange resin is regenerated with dilute sulphuric acid effluent water from regeneration contains NH_3 and excess of H_2SO_4 . The mixed bed exhange resin is regenerated by dilute sulphuric acid followed by diluted sodium hydroxide ; the effluent water from regeneration is slighly alkaline. Both effluents flow to a neutralizing pit where they are neutralized then pumped out of the plant to a remote area .

Figure 2: Shows a flow diagram of the new approach developed for the process condesate pre-treatment which replaces the degasifiers. The demineralization section remains unchanged and is common for all Plants. The Process Condensate Treatment here serves for 2 x 800 Plus 1 x 1000 M.T.P.D. Ammonia Plants. The process Condensate collected from the gas preparation section of the three Ammonia

Plants flows to the CO. Flash Drum where most of the CO. is sepera-ted by flashing , the condensate from the flash drum is introduced to the process condensate Stripper, which is a tower containing 22 Bubble cap trays condensate, enters on tray number 15. The downflowing condensate is stripped countercurrently against an upflow of low pressure steam that is introduced at the bottom of the tower . The stripped uprizing vapours are rectified against a ruflux flow introduced at the top of the tower. The stripped process condensate is drawn off from the bottom of the tower and cooled in a plate exchanger with cooling water then pumped to the demineralization section. The overhead vapours are drawn off the top of the tower and isothermally condensed in an air cooled condenser then subcooled with cooling water in a tubular exchanger ; the cooled overhead product which is a concentrated aqueous solution of NH₃, CO₂ and CH₃OH flows to a seperator where the disassociated gases are feleased. Part of the overhead is returned to the top of the tower as reflux viz a reflux pump and the remaining is injected to the process steam inlet the primary reformer of the fourth Ammonia Plant .

III - Material Balances :

<u>Figure 1</u> :	Shows a material balance around the degasifiers curren- tly employed for the two 800 M.T.P.D. Ammonia Plants . The rates of pollutants emitted to the atmosphere are as follows :
	NH ₃ 16 Kg/Hr
	Сн ₃ он 59 кg/нг
	CO ₂ 524 Kg/Hr
	The rate of undesired Materials to be removed in the demineralization section are :
	NH ₃ 58 Kg/Hr
	Сн он
<u>Figure 2:</u>	CO 65 Kg/Hr Shows a material balance around the newly developed process condensate treatment system serving the two 800 M.T.P.D. and the one 1000 M.T.P.D. Ammonia Plants . The rate of pollutants emitted to the atmosphere are as follows :
	NH ₃ 35 Kg/Hr
	СН он 214 Кд/нг
	CO2752 Kg/Hr
	The rate of undesired materials to be removed in the demineralization section are :
	NH ₃ 2.5 Kg/Hr
	Сн_он5.0 Kg/Hr Co ₂ 2.5 Kg/Hr

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The rate of pollutants recycled back to the process are as follows :

NH ₃ 70	Kg/Hr
сн ₃ он103	Kg/Hr
co ₂ 103	Kg/Hr

The large reduction in ammonia feed to the demineralization section from 58 Kg/Hr to 2.5 Kg/Hr results in reducing the rate of effluents in the wash stream during regeneration .

The amount of steam vented to the atmosphere is also reduced from 23575 to 8800 NM^3/Hr , thus pring approx. 12 Tons/Hr of steam lost to the atmosphere .

Although the new system consumes a larger quantity of steam (approx. 37 Tons/Hr or 40 Kg/M³ of treated condensate) this does not cause any problem since low pressure steam is available in excess in most similar fertilizer complexes and in any case is usually recycled as steam condensate to reduce the need for expensive make-up water .

IV - Comparisons

In order to compare the performance of the two systems in question and the contribution given towards environmental protection, the following points will be discussed.

- A Ground level concentration of Ammonia.
- B Cut-down regeneration effluents .
- C Disposal of pollutants .

It will be seen that although in the new system the treated capacity has been increased by 46 %, the total pollution load is reduced compared to the old system.

A - Ground level concentration of Ammonia.

The Bosanquet-Pearson equation is used assuming a wind velocity of 5 m/sec, and a moderate turbulance factor of 0.5. The height of emission for the old system is taken as 10 meters and the height of emission in the new system is taken as 25 meters. (Both heights are actual) The results are as follows:

Old system	New system
mg/M ³	mg/M ³
Ammonia concen. 1.7	0.594

The new system reduces the Ammonia ground level concentration inspite of the increase in the total Ammonia discharged to the atmosphere (from 16 to 35 Kg/Hr). This is due to the increased height of the vent stack .

B - Cut-down on regeneration effluents .

Since the reaction taking place on the cation exchange resin is directly porportional to the cation concentrations in the treated process condensate, the following is concluded : (NH_4 +) cation concentration decreases from 400 ppm to 10 ppm. Saving on cation exchange regeneration time for equivalent flow rates = 400/10 = 40 times. This means that effluent rate from the cation exchange resin during regeneration is cut-down by 97.5 %, cutting down the disposed effluent pumping rate by an average of 95%.

<u>C</u> - <u>Disposal of pollutants</u>.

In the old system the pollutants are disposed of in two manners; emission to the atmosphere and as industrial effluents, whereas in the new system they are disposed of in the same manners at relatively lower concentrations, in addition to a recycle stream containing highly concentrated pollutants that are injected back to the process. Out of the total ammonia pollution load of 107.5 Kg/Hr, 70 Kg/Hr are recycled, giving a recycle ratio of approx. 65 %. The Ammonia remaining as a liquid effluent was essentially eliminated in the new system.

<u>V</u> - <u>Design Considerations</u>.

The process design of the new system is relatively diffcult due to the lack of published data on equilibrium constants for multi-phase systems at the low concentrations encountered in the process conden-In 1975 Thomas J. Edward, John Newman and John M. Prausnitz sate . established a thermodynamic frame-work to calculate equilibrium vapour-liquid composition for dilute aqueous solutions of one or more volatile weak electrolytes , the parameters required for multisolute systems are estimated from corrolations , coupled with chemical equilibria . The weak electrolyte in the liquid phase exists in two forms , molecular and ionic , the chemical equilibria between these two forms is described by dissociation equilibrium constant; and at high dilution vapour liquid equilibrium is characterized by Henry's Law . Therefore the thermodynamic analysis of such systems is based on two descriptions , a Macroscopic (Bulk) basis and Microscopic (Molecular) basis.

The parameters involved are :

- 1 Dissociation equilibrium.
- 2 Mass balance .
- 3 Solution electro-neutrality.
- 4 Vapour-Liquid equilibrium.
- 5 Molecule-Ion and Ion-Ion interaction parameters. (Including dissociation equilibrium for water.)

In the case of process codensate collected from the gas preperation section of Ammonia Plants , ten distinct species are present :

$$NH_3$$
 (Molecular), CO_2 (Molecular), NH_4^+ , HCO_3^- , CO_3^{--} ,

These ten species result in 18 equations as follows:

- Five chemical equilibria.
- Three Mass balance.
- One Elctro-neutrality .
- Eight Activity coefficients .

These 18 equations must be solved simultaneously using the itera \rightarrow tive Newton-Raphson technique utilizing a computer. The process design was conducted in association with Messrs HALDOR TOPSOE, who

had access to such programs and had actual performance data from operating units of their design . The basic and detailed mechanical design was handled by our company , the main difficulties encountered were related to limitation in available area and Utilities for the unit. It had to fit properly in a site surronded by existing facilities , and there was a need to minimize piping changes . Since our head office is in Kuwait , we were able to optimize the design quickly by frequent visits and discussions with the client .

VI - Economic Considerations.

A new pre-treatment sys em similar to the one described ,together with related cation facilities; is estimated to cost some 300,000 to 400,000 K.D. more than the simpler existing system with a larger cation exchange requirments. This results in an additional depreciation charge in the range of 30 to 40 fils per meter cube of treated water, (Based on 10 years depreciation).

To claculate the total cost per meter cube of treated water , it would be recessary to add the cost of extra steam , power, and cooling water and to substract the costs of saved regeneration chemicals , wash water and steam losses to the atmosphere. They would therefore differ from plant to plant due to differences in utility costs .

In Kuwait , as in most Gulf Countries, make-up water is expensive, while cooling water and power are relatively cheap. The total cost per meter cube of treated water proved to be cheaper in the new system. An idea of the relative importance of different cost elements can be given by assuming some typical values as shown on the next page .

It can be seen that the main extra cost in the new system is due to extra Low-Pressure steam and cooling water consumption.

Value in fils/M³

			Existing System.	New System.
<u>1</u>	-	Variable Costs:		
	-	Chemicals.	180	7,5
	-	L.P steem feed.	30	75
	-	Steam/Cond. Losses.	23	6
	-	Regeneration wash water.	12	0,5
	-	Cooling water & Power.	30	101
		Total Variable costs.	275	190
2	-	Fixed Costs:		
	_	Depreciation.	5	25
	-	Maintenance.	5	20
	-	Other costs.(Operatione	tc) 5	15
		Total Fixed costs.	15	60
**	*	Total cost Per M ³	290 Fils	250 Fils

If Low Pressure steam is in excess . which is the case in most chemical plants, it's value would tend to zero , if vented to atmosphere for example. To make use of surplus low pressure steam it would have to be condensed, thus increasing cooling water consumption . In such a situation , the new system would result in significantly lower cost per meter cube of treated water .

Finally, we can conclude that the new system would either be cheaper or have the same order of magnitude of cost for water treatment in most Arab Gulf countries. The system is being adopted im many locations in view of increasing concern about the environment, it represents the best technical means of reducing pollution from ammonia plants process condensate to the lowest possible level.

	<u>PROCESS</u> CONDENSA LOW PRES STEAM CO RAW WATH	<u>TE</u> SURE STEAM	(<u>160600</u>) (<u>160600</u>) (<u>163663</u>)		PROCESS CONDENSATE DLGASIFIER CONDEN CODLERS		EILTE	HSATE EXCHANGERS	CATION/ANION EXCHANGERS SENDO SENDO BOILER FEED WATER
	PDS.	- <u></u>			2		3		
	H20	146416	\$9.40	16944	9 5, 94	141472	99.00	CONSULTING OFFICE.	
H20 146416 \$9.40 10944 95.94 141472 99.80	≖ N H 3	74	0,05	16	0.08	58	0.04	PICO KUWAIT.	
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H20 146416 \$9.40 10944 95.94 141472 99.80 ± NH3 74 0.05 16 0.08 58 0.04 ± C02 589 0.40 524 2.68 ES 0.05 CH3DH 221 0.15 55 0.30 162 0.11	TOTAL	147300	100,00	19543	100.00	141757	100.00	F	

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Discussions:

Q: Badr El-Din, PICO, Kuwait:

What do you mean by integrated approach to effluent treatment in a fertilizer complex? Most people have determined that the treatment of each effluent separately at its source is a better ap proach.

A: M.Ezzat, AFCFP, Kuwait:

The integrated approach for treatment of effluents in a fertilizer complex looks to be the best solution to minimize pollution by making use of the different characteristics of effluents and emissions, e.g. the gaseous pollutants like hydrogen sulphide, nitrogen and sulphur oxides and hydrogen fluoride are acidic innature and some of them have reducing property, while the ammonia bearing effluent is basic and chromate bearing effluent is oxidizing in nature. Scrubbing these gaseous pollutants by chromate bearing effluent and ammonia bearing effluent successively in seperate scrubbers can lead to reduction of chromate, removal of a part of ammonia and arresting the gaseous pollutants.

Q: S.R. Ahmad, Core Lab., Bahrair:

What are the major pollution problems in transporting sulphur and what are the advantages of transporting it in liquid form?

A: M. Ezzat, AFCFP, Kuwait:

Sulphur is a dusty product, dust is considered a nuisance when loading or unloading vessels or cars. Molten sulphur is not dusty and is also not corrosive. Corrosion can take place only by solid sulphur being in contact with water.

Q: R. Anders, Lurgi, Germany:

Is there a similar institution in the Arab Countries as for instance in U.S.A., the Environmental Protection Agency? Who sets the pollution levels? Who determines pollution levels of SO_2 , SO_3 , F ...etc. for new plants to be built?

A: M.Ezzat, AFCFP, Kuwait:

Such institution is not yet established. Recently technical committees have been formed in some of the Arab Countries. These committees have laid down guide-lines for pollution in fertilizer plants. Of course, these committees take into consideration the regulations adopted by developed and developing countries and also they follow the recommendations laid down by plants designers. Mr. F. Al-Ma'ayouf, session chairman, commented that in each Arab Country there is its own committee for environmental protection and that in the near future similar agency will be formed in the Arab Region.

Q: Seif El-Din Atfeh, Ministry of Industry, Syria:

Which system do you apply for controlling water thermal pollution?

A: <u>H. Sha'asha, JFI, Jordan</u>:

It is very obvious that you can control thermal pollution by regulating the amount of water flow. So, if you find out that the temperature of water returned to the sea exceeds, say 10° C, than the ambient temperature, then you simply increase the flow. Design calculations are based such that increase in temperature will not be more than ambient temperature by 10° C.

Q: <u>Mahmoud Al-Attal</u>, <u>Ministry of Health</u>, <u>Bahrain</u>:

What about dangers from SiO₂ dust?

A: <u>H.D.Schneider</u>, Chemie Linz, Austria:

The Silica(SiO₂) is known as a by-product from the production of aluminium fluoride from fluosilicic acid. This precipitated SiO₂ is considerably finer than the SiO₂ which is found in nature. Chemie Linz is having already experiences with this by-product since 1963,(start up of the ALF₃plant) and there have been no health problems observed on workers exposed to this product. So in my opinion, the traces of SiO₂ present in the final fertilizer product should be also of no problem when handled by workers or in the agriculture. But I will certainly consult our experts to be able to correct this view if necessary.

Q: Seif El-Din Atfeh, Ministry of Industry, Syria:

What about the viability of production of sulphuricacid from gypsum?

A: H.D. Schneider, Chemie Linz, Austria:

The gypsum-sulphuric acid process is a coproduction of cement clinker and sulphuric acid. Therefore one has to know first the credit for the cement to calculate the production cost of sul phuric acid. Other influencing factors are:-

- Availability of sulphur in the country.
- Other raw materials for the production of cement.
- Availability and price of energy.

With this information one can only calculate the actual production cost, and some recent projects for India, Bangladesh and U.S.S.R. are showing that there are economically solutions for the elimination of the phospho-gypsum problem.

Chemie Linz would be pleased to check also your case, to add more to the already operating units in Linz and in South Africa.

Q: M.Ezzat , AFCFP, Kuwait :

Is it possible to apply the Shroud System for the prilling tower in urea plants since it is now applied successfully in ammonium nitrante plants ?

A: Mr.F.Granelli , Snamprogetti , Italy:

In principle I think that it can be applied to the prilling tower in urea plants, but the problem is entirely different between ammonium nitrate and urea. So I beleive that in urea plant you have simply to catch and possibly to avoid from the very begining the formation of small particles in the prilling tower itself and that can be done by using a system which avoid a formation from the begining itself and during the impingenment at the bottom of the prilling tower but in principle we may use such system for urea prilling tower.

Q: Mr. F.Sehweil , PIC, Kuwait :

Can we practically use the effluent from the hydraulizer in a urea plant as a boiler feed water make-up in a high pressure system ? what is the content of ammonia and urea in this case ?

A: Mr. F.Granelli , Snamprogetti , Italy :

Yes, you can use the effluent from hydmaulizer as make-up boiler feed water even from the high pressure steam system, since the content of ammonia and urea in the effluent are within the acceptable limits.

Q: <u>Mr. F. Sehweil</u>, <u>PIC</u>, <u>Kuwait</u>:

Does the natural draft tower reduce the dust particles , and how tall the tower which we need especially when we have high capacity plant ?

A: Mr. F.Granelli , Snamprogetti , Italy :

The natural draft tower by itself by definition does not solve or reduce the problem . It is the result of a combination of proper design of the prilling tower and use of a special prilling busket, because if you can reduce the formation of very small particles during the action of spraying by this way you achieve half of the results because you do not get these particles entrained in the outlet of prilling tower . The height of the prilling tower is mainly affected by the temperature of the air around and it does not make so much difference if you have induced draft tower or natural draft tower . The cross section " diameter " of the prilling tower depends to a very large extent on the device you are using for spreading, as uniform as possible, the powder on the cross section, so even if you use an induced draft tower you can not decrease very much , but only marginally the diameter of your tower for a certain capacity , because otherwise you risk to have impingement of droplets still in melt conditions on the inner walls of the prilling tower itself , so you get a build up of this material on the prilling tower inner walls which can become dangerous problems afterwords , so I should split the two aspects, you know and all these experiences of ours about the two types of towers have brought us to the conclusion that the effort of having induced draft towers does not pay-off in any case and it is just on the opposite usually a problem because you have increased operating cost due to the fans and maintenance cost and so on . Moreover paradoxically when we tried to make very close analysis of of the flow pattern of the air inside of the tower we have came to conclusion that you get a less uniform distribution of the air in an induced draft tower rather than in the natural draft tower . But as far as the size , there is a very small difference unles you are talking about very large plants, but even in this case, we have built what is nowadays I think the largest urea plant in the world 1800 MT/day in india and it is a natural draft tower even if the climate conditions are not specially favourable even in such case the difference in size of the two types is really very marginal. It is much more important the spining busket itself and speed of rotation for that, which determines the minimum diameter , that is independent of natural draft or forced induced draft tower .

Q: M. Ezzat, AFCFF, Kuwait:

Do you recover ammonia from the gas discharged to the atmosphere from the flash drum?

A: Mr. Mostafa Badr El-Din, PICO - Kuwait:

No, this gas is mainly carbon dioxide and vapour. It contains some ammonia, but this is unavoidable. There is no cheap way of recovering it. It can however be recommended if desired.

Q: M. Ezzat, AFCFP, Kuwait:

Is it possible to combine urea process condensate with ammonia plant process condensate in the same treatment system?

A: Mr. Mostafa Badr El-Din :

Theoretically, if urea is totally dissociated in a hydraulizer, this can be done, but boiler-feed water must not contain any urea and in practice hydraulizer effluent can not be recycled as boiler-feed water.

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• SECOND DAY: Monday, November 16th.

<u>Chairman</u>: Mr. Hassan Sha'asha, JFI, Jordan <u>Rapporteur</u>: Mr. M. Ezzat, AFCFP, Kuwait

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- * Morning Session:
 - 7- Pollution Monitoring and Control Programme at SAFCO.
 - 8- Remarks on Pollution Problems in the Syrian Fertilizer Complex.
 - 9- Controlling Water Treatment to Combat Water Pollution.

* Afternoon Session:

- 10- Emission Control in Fertilizer Industry.
- 11- The Effluent Situation at QAFCO with Reference to Local Regulations.
- 12- Pollution Abatement at PIC, Kuwait
- * <u>Discussions</u>

7- PULLUTION MONITORING AND CONTROL PROGRAM AT SAFCO

This paper elucidates the pollution control strategy adopted at SAFCO, i.e. pollution monitoring and control system, plant improvements undertaken to reduce pollution and future action plan.

Introduction

The SAFCO plant is situated half way between Dammam and Al-Khobar at a distance of 2 Kilometers from the main highway. When the plant was constructed there was hardly any population or housing schemes for miles around. The commissioning of the urea plant took place in 1969. Tremendous problems were encountered during the start up period and SAFCO early years of operation. These factors were responsible for a rather low key management attention to pollution monitoring and controls at SAFCO.

The first five years of SAFCO operations were very trying but fortunately the plant was able to over-ride all the technical difficulties and headed for a steady course. The plant was able to make great strides in all areas including production and related functions and systems. However, during the last six years the area around the plant has witnessed a rapid progress in development and construction. SAFCO now has neighbours such as King Faisal University, Petromin and other concerns. SAFCO housing project adjacent to plant premises is underway and will be ready by the end of 1982.

As a logical sequence to these developments the pollution monitoring and control program at SAFCO has been revitalised and receives active management support.

I. Pollution Monitoring and Control

The monitoring of SAFCO effluents and emissions is carried out on a regular programmed basis. The work is undertaken by an active group in the Laboratory headed by the Pollution Control Coordinator.

The program started with identification of effluent and emission sources and establishing standard methods of monitoring the pollutions. The sources of emissions and effluents are listed in Table-1.

By : Arshad A. Al-Saleh & Moh'd. Abul Huda. Suadi Arabian Fertilizer Company. Dammam, Saudi Arabia. SAUCO has its own weather station and parameters such as atmoshperic temperature, pressure, wind direction and velocity are continuously recorded.

The SAFCO pollution monitoring and control program is aimed at two main objectives:

- a) To sustain a suitable environment for people working in plant areas and this is achieved by regular monitoring of sources of emission and endeavours to improve conditions whenever reasonably feasible. Pollutants, such as, NH3 SO2, H2S, dust and sound levels are assessed regularly. Results obtained so far comply with industrial hygiene threshold limit values recommended by the Americican Conference of Governmental Industrial Hygienists for workers exposures of 8 hours per day, 40 hours per week.
- b) SAFCO has a moral responsibility to ensure that the ambient air quality and liquid effluents discharged to the Gulf are within the approved standard limits.

Ambient Air Monitoring

Initially 15 posts defining sampling locations were established on the boundary of the SAFCO plant. The gaseous contaminants which are mainly ammonia, sulfur dioxide and hydrogen sulphide were sampled using'Midget Impinger'with a hand pump. The drawbacks of this system were:

- a) Time consuming
- b) Sample size and period were limited
- c) Tedious to carry around the necessary sampling equipment.

However, the system was advantageous in assessing peak levels where-ever required.

Monitoring system currently adopted comprises of four fixed stations located round the SAFCO periphery. These stations consist mainly of sampling equipment housed in well ventilated cupboard. The measuring equipment essentially consists of bubblers with suitable reagents, pumps for drawing atmospheric air and gas meters for volume measurement.

The system works on 24 hours basis. The results collected so far on both systems have constantly shown to be well below the limits set by EPA and other environmental regulation agencies. The ambient air quality with respect to SO2, urea dust, and ammonia has greatly improved after executing major projects such as new sulphuric acid plant, urea revamp and third stage decomposition etc. Table-2 shows the levels of pollutants in ambient air and how favourably they compare with approved standards.

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Liquid Effluents

SAFCO takes active interest in monitoring and controlling liquid effluents parameters. SAFCO also collaborated with University of Petroleum and Minerals in their efforts to assess the water pollution levels in the Gulf.

The liquid effluents in SAFCO are classified into two main categories. The first category is the nitrogenous effluents which are contributed from various streams in the urea unit and end up in the evaporation pond which is remotely located from the operating facilities. The effluent to the evaporation pond is checked frequently to assess ammonia and urea levels. The effluent to pond does not pose any serious problem since the level in the pond stays low and no discharge of the nitrogenous effluent outside the plant is required. Furthermore the ammonia emissions round the pond are within approved limits.

The second category is the non nitrogenous effluent contributed mainly from cooling water, evaporators and boilers blow down alongwith other streams from the ammonia and sulfuric acid plants. This effluent is finally discharged into the sea. Water quality parameters such as PH, TDS, Chromium, Phosphate etc. are monitored on a continuous basis. Range of SAFCO effluent to sea is shown in Table-3.

- II. Action taken to reduce Pollution
 - Safco Cooling Water System

Prior to 1975 SAFCO employed a chromate/polyphosphate treatment for its 900,000 gallons hold up and 90,000 GPM circulation capacity cooling tower. The chromate control limits were in the region of 20 - 30 ppm. This in effect meant that about 240 lbs of chromate per day was dumped into the sea because of cooling tower blow down. It was realized that this situation could have serious ill effects on aquatic life. Strenuous efforts were made by SAFCO to curtail this pollution trend and steps were taken in 1975 to change the cooling water treatment.

The chromate levels in the cooling water effluent were reduced in 1977 from 20 ppm to 3 ppm by adopting a new low chromate/zinc plus phosphate chemical treatment. The new corrosion control treatment has also proved to be very efficient in inhibiting corrosion and deposits in cooling water exchangers.

2. Urea Revamp Project

The 1000 MeTons per day urea unit was originally designed with facilities for crystallizing urea from the solution after two stages of decomposition. The urea prills were processed by way of crystallization centrifuging, drying, remelting and spray heads prilling. The process utilized a large variety of heavy mechanical equipment like centrifuges, dryers, conveyors, melters, cyclone separators and prill coolers etc. Operation of the above equipment gave rise to frequent mechanical failures and unsafe conditions and a continuous/ steady production could not be maintained. But above all, the urea fallout due to crystals handling and poor prilling was a crucial problem. Weather conditions such as high humidity and temperature escalated the problem even further.

The urea back-end revamp project was iniated by SAFCO Management with a view to replace the old urea unit backend facilities. The new back-end facilities were installed in 1977-78 at an expense of SR. 15.5 million and commissioned in 1978.

The new system consists mainly of two falling film evaporators, air heaters, melt pump and prilling Tuttle bucket. Operation of the new system helped in eliminating pollution problems and the urea fallout now is almost negligible. Other advantages of the system include no dust collection system is required, tremendous improvement in prills size distribution, smoother operation and an overall very high service factor. 3. Third Stage Decomposition

The urea plant was initially designed by Chemico with two stages of decomposition. The effluent from the second decomposer was expected to have 0.77% ammonia whereas in actual operation the effluent contained 1.5 - 1.7% ammonia. Due to this deficiency in design the plant sustained about 22 MeTons of ammonia loss against the design loss of 12 MeTons per day. In addition to loss in production the situation was considered unacceptable because of sizable ammonia discharge into the atmosphere.

The third stage decomposition and recovery system was initiated by SAFCO Management with the view to recover ammonia losses and to drastically curtail ammonia escape to atmosphere. The system was installed and commissioned in July 1981 at an expense of SR. 4.5 million.

The facilities essentially includes:

- a) 3rd Stage Stripper
- b) Low pressure condenser
- c) Low Pressure Separator.

Operation of the above system efficiently removes ammonia from the urea solution sent to evaporators for concentration before prilling. The ammonia content in the 3rd Stripper bottom solution is about 0.6% as against 1.5 - 1.7% experienced earlier. On an average, about 12 MeTons of ammonia are actually recovered per day. The recovery of ammonia has improved ammonia to urea conversion rates and also eliminated a significant pollution hazard.

Ammonia Vapour Recovery System

SAFCO has two atmospheric ammonia storage tanks with a capacity of 10,000 and 2,500 MeTons respectively. Initially a Yorkshipley refrigeration unit was incorporated in the design to recover ammonia vapours from the main storage tank. The unit however proved to have inadequate capacity and also required more than normal maintenance to operate. As a result, ammonia vapours from the main storage tank had to be frequently flared. This pollution and production loss situation persisted from 1974 - 1977. A higher capacity HTI Refrigeration Compressor was installed in 1977 which allowed complete recovery of ammonia vapours from the atmospheric ammonia storage tanks amounting to about 8 MeTons of ammonia per day.

5. The New Sulphuric Acid Plant

SAFCO had initially a single absorption 50 ton capacity Sulphuric Acid Plant with an overall conversion efficiency of 95 - 96%. The SO2 and SO3 in the exit stack were running at higher values than those set by EPA thus causing a pollution problem.

The new 300 MeTons Sulphuric Acid Plant project was initiated by SAFCO Management with the view to meet market demands and to implement the latest technology available to ensure minimum emissions of sulphur oxides.

The new Sulphuric Acid Plant was commissioned in the first quarter of 1980. The plant was designed with double absorption which means an addition of an intermediate absorption tower and a heat exchanger ahead of the final stage of conversion resulting in overall conversion efficiency of 99.7 - 99.8%. The height of the sulphuric acid stack is 125 ft. which allows for better diffusion and dilution of the vent gases. Acid mist eliminator equipment is provided. An infra red analyzer is incorporated to allow for continuous analysis of SO₂ levels in the exit stack. Current stack emissions in the new Sulphuric Acid Plant as compared with old one is shown in Table-4.

Design guarantee and subsequent test values of SO2 and SO3 in the exit stack meet United States EPA standards quite favourably. The old Sulphuric Acid Plant was put out of service after commissioning of the new unit. The provisions made in the new Sulphuric Acid Plant have helped significantly in improving SO2 ambient air quality.

6. General Plant Improvements

Frequent shutdown and start ups were experienced in the early years of SAFCO operation due to technical problems. This also resulted in frequent venting and draining of the equipment. As a results of the many improvement project executed since 1975 the service and capacity factors are now around 94% (including the yearly turnaround of 13 - 15 days duration). As a result of long continuous operational runs the plant emissions and effluent generally stay low with no peak excursion.

III. Future Action Plan

1. Purge Gas Recovery System

The purge gas from the ammonia synthesis loop is currently burnt and utilized in the Primary Reformer furnace as a source of fuel. Based on design and test values, 2 - 2.5 MeTons of ammonia are lost per day. The recovery of ammonia is an economically viable proposition and plans are underway to install a purge gas ammonia recovery unit to eliminate ammonia and hydrogen losses. This will also eliminate any traces of NOx in the atmosphere.

2. Scrubbers for Evaporators Stack

With the operation of the urea revamp system the urea fall out has been drastically reduced and is almost negligible. However, efforts are underway to examine possibility of scrubbing the stack from the evaporators. An in line scrubbing facility is already in operation recovering a good part of urea entrainment from air exit the evaporators. Further improvement to the system is being developed.

TABLE - 1

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A. <u>Sulphur Emissions</u> H₂S, SO₂, SO₃/Acid mist

Contributing Sources

H₂S flare

Acid Plant Absorption Tower Stack MEA-H₂S/CO₂ Removal System Claus Sulphur Recovery Unit Sour Gas Line

B. <u>Ammonia Emissions</u> NH₃

C. Particulate Matter

fall out dust

D. Effluents

E. Noise

Suspended dust, urea

Nitrogenous and non

nitrogenous effluents

Contribution Sources

Ammonia and Carbamate Pumps Urea Unit Drains Urea Unit Vent Stack NH₃ Storage Tank/HTI Plant Leakages

Contributing Sources

Air (Suspended dust) Prill Tower Fans Evaporators Stack

Contributing Sources

Cooling Tower Blowdown Boilers Blowdown MSF Evaporators Blowdown Plant Drainage Urea Drains

Contributing Sources

Primary Reformer Furnace Compressors Boilers (F.D.Fans) Power Generators Steam Ejectors.

TABLE - 2

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AMBIENT AIR QUALITY AROUND SAFCO PLANT PERIPHERYPollutantRange H_2S (ppm)N.D. - 0.006 SO_2 (ppm)N.D. - 0.05NH3 (ppm)Nil - 0.1Particulate matter
(Suspended dust Mg/m³)150 - 250

N.D. - Not Detectable

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TABLE - 3

NORMAL RANGE OF SAFCO EFFLUENT TO THE SEA

PH	7 - 9
Temperature	28 – 29 ⁰ C
Ammonical nitrogen	50
Chromium (Cr.)	0.3 - 0.7
Phosphate as (PO ₄)	0.2 - 0.7
Arsenic (As)	0.001 - 0.003
Zinc (Zn)	0.3 - 0.7
Total Suspended Solids (TSS)	65 - 85

Results are expressed in mg/l.

TABLE - 4

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SULPHURIC ACID STACK EMISSIONS

Sulphur Oxides Levels Ex Stack	* New H ₂ SO ₄ Plant	Old H2SO4 Plant	Maximum Allowable
SO ₂ (ppm)	100 - 170	1900 - 2500	380
SO ₃ and Acid mist	12 - 25	140 - 180	37

* The new sulphuric acid plant meets stringent EPA regulations.
8- <u>REMARKS ON POLLUTION PROBLEMS IN</u> THE SYRIAN FERTILIZER COMPLEX

The paper discusses the importance of water resources in the western part of syria, especially for agriculture, and therefore industrial activities that consume water will be on the expense of agricultural needs and this is considered dangerous. The pollution problems in Homs are centered in one area where three fertilizer plants and the Electric Station are located. One the main pollution problems facing the fertilizer plants at present is the phosphogypsum.

Technical Committee in syria studied thoroughly the phosphogypsum problem and the possibilities of utilizing it in cement-sulphuric acid process or ammonium sulphate production or others.

The committee decided to apply the phosphogypsum pumping because it was almost 50 % less in cost than other methods

Dr. M. Seif El-Din Atfeh , Ministry of Industry , Syria . ** This is a brief summary of the paper because the full text of the paper was not received from the auther.

9- CONTROLLING WATER TREATMENT TO COMBAT WATER POLLUTION

1. <u>Preface</u>

- 1.1. The plant No. 2 of State Enterprise of Fertilizers, Basrah has been designed to produce 120 M / HR of domin water for the production of 800 Tons / Day Ammonia and 1300 Tons / Day Urea.
- 1.2. The Design of the system has been based on 1972 1973 specification of raw water from Shatt Al-Arab River .
- 1.3. The plant went into operation in 1976. The salinity of water of Shatt-Al-Arab increased over the years due to several reasons. Consequently, the operation of water treatment had to undergo various modifications resulting in increased consumption of chemicals. This had created additional water pollution problems in the area.
- 1.4. Attempts have been made to overcome this problem , taking into consideration the stringent anti-pollution regulations of government of Iraq , the pollutants in this case coming from water treatment chemical Ammonia and Urea .
- 1.5. In this report, we propose to give an idea of the modifications we intend to carry out to minimise the water pollution by making necessary changes in the design and operation of the water treatment section.
- 2. Design Specification of Water Treatment Section.
- 2.1. The plant was designed to operate in accordance with the raw water specification given in table 1.
- 2.2. The material balance for water tretment is summarised in figure 1.
- 2.3. Figure 2 gives the figures for the waste water produced from primary treatment, cooling water treatment, blow down of boilers, etc.
- 3. Influence of Modified Raw Water Specification .
- 3.1. The increase in salinity of Shatt-Al-Arab has been attributed to the following reasons:-

(i) Development of irrigation in the country.

(ii) Presence of excess flood waters to Suphrates on account of Tartar Project .

- 3.2. Such factors as above have been beyond the control of the Fertilizer project and this had resulted in the following problems.
 - By: Eng. Maan Rashad

State Enterprise of Fertilizers - Basrah - IRAQ

Table (1)

Desgin	Fig. of	Feed	Water
P.H	7.8	3	
E.C	1711 -	Mr/cm	
T.H	560	P.Pm a	s CaCO ₂
са.н	339	H H	н
Mg H	221	н н	11
M.ALK	190	H H	H
CI [®]	406	M 11	н
SiO2	17	P.P.m	as SiO ₂
T.D.S.	1250	mg/	L
S.S	300	P.P.m	
TURB	100	*	

3.2.1. Increased Consumption of Chemicals:

Table 2 gives an idea of the increase in chemical consumption in comparison to the original design figures for primary treatment.

3.2.2. Cooling water treatment : it is to be noted here we did encounter different operational philosophies of the main contractor and the supplier of cooling water treatment chemicals . While the supplier of chemicals suggested to operate the unit based on 15 ppm of acid inhibitor in circulating water at a concentration ratio of 2, the main contractor insisted according to his research work, to use 35 ppm of inhibitor keeping concentration ratio same .

3.3. Operation of Soda-Lime Process:

3.3.1. The Operation of Soda-Lime process has been found to be very troublesome in the face of the changed specification of raw water .

4. <u>Conclusions</u>:

- 4.1. The following steps have been considered for implementation in the project to minimise water pollution .
- 4.1.1. To install a reverse osmosis unit of 140 M^3 / HR capacity in between the existing filtered water section and demineraliser.
- 4.1.2. To change the present system of cooling water from acidic to alkaline treatment in order to have an opportunity to work with a high concentration of calcium hardness with possible reduction of the blow-down by about 1/3RD
- 4.1.3.Delete the present Soda-Lime process operation and operate it only as coagulant process using aluminum sulphate in the clarifier.

4.1.4.Neutralisation of waste by sulphric acid, Etc.

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FIG : 1

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ITEM	1977	1978	1979
F-W as 70% of Design	630	630	630
CaO Tan	.1120	1239	1287
Na ₂ CO ₃ Tan	944	1279	1953
ALUM Tan	193	237	259
D-W-P-as 92% Design	963	963	963
H ₂ SO ₄ Tan	1915	2105	2473
NaOH Tan	1277	1600	2156

TABLE SHOW THE INCREASE OF CHEMICAL CONSUMPTION FOR THE YEARS FROM 1977 to 1979

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TABLE 3

ITEM	CONSUMPTION 1979	SUGESTED CONSUMPTION
CaO /Tan	1838	Zero
Na ₂ CO ₃ /Tan	2790	Zero
ALUM /Tan	370	300
H ₂ SO ₄ /Tan	2 688	850
NaOH /Tan	2340	600
F-W / M ³	9x10 ⁶	7.6x10 ⁶
D-W / M ³	10.4x10 ⁴	10.4x10 ⁴
C-W / M ³	6.88x10 ⁶	5.76×10 ⁶
T-W-W / M ³	3.44×10 ⁶	2.32×10 ⁶

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ANALYSIS OF RAW WATER 1980

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Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
P.H	7.72	7.8	7.78	7.65	7.7	7.6	7.6	7.7	7.86	7.77	7.81	7.69
E.C (14 V/a	2073	1906	1908	1950	2081	1905	2261	1645	1950	2341	2268	2066
T.C(CaCO)	1084	1013	1015	-	-	-	-	789	975	1209	1235	1153
ca. H(")	347	330	337	370	324	253	284	221	304	341	357	355
Mg.H(")	401	301	255	281	334	299	314	234	277	323	316	324
Na ⁺ (")	336	391	424	-	-	-	-	334	394	545	562	474
M.ALK(")	167	172	169	157	151	170	166	184	180	171	159	144
CI (")	481	442	443	382	422	413	496	368	469	580	572	554
so ₄ (")	436	400	404	400	360	331	373	237	326	458	503	455
Si0 ₂ (P.P.	M)3.4	3.3	2.2	1.45	3.1	4.55	7.8	6.2	11.9	7.7	5.9	2.97
T.D.S(")	1237	1267	1123	1275	1243	1309	1301	1090	1550	1473	1386	1195
Turb(")	11.1	7.7	4.6	3.7	6.1	3.4	4.4	6.75	6.5	4.73	4.63	6.49
s.s (")	8.1	11.5	8.4	4.4	7.25	9.2	5.8	13.1	4.7	7.3	5.8	8.6
C.O.D(")	9.5	7.6	5.7	8.3	5.6	6.3	7.8	7.85	4.9	5.48	5.13	6.3
Fe (")	0.3	0.36	0.19	0.15	0.32	0.26	0.22	0.99	2.5	0.26	0.23	0.32

1978

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Date	Jan	Feb	Mar	Apr	Мау	Jun	Jul	Aug	Sep	Oct	Nov	Dec
P.H	7.78	7.79	7.65	7.79	7.73	7.73	7.67	7.82	8.0	7.71	7.58	7.87
E.C (#1/4	1720	1581	1590	1550	1423	1417	1875	2468	3286	2655	2432	2353
T.C(CaCOs)	944	799	824	796	743	763	834	1178	1461	1425	1265	1175
Ca.H(")	308	249	268	296	27⊥	260	296	381	414	438	3938	353
Mg.H(")	287	295	231	226	229	287	273	338	432	381	412.5	458
Na (")	349	255	325	274	243	216	265	459	621	606	459	364
MALK(")	179	156	163	157	149	144	167	160	146	136	141	158
CI (")	407	339	344	320	300	331	381	550	642	641	575	527
so ₄ (")	358	304	317	319	294	288	332	469	664	648	549	491
SiQ(P.P.M	2.93	2.33	2.11	2.4	3.1	6.74	7.0	8.1	10.5	11.4	6.1	4.5
T.D.S(")	1311	1051	998	1053	962	. 995	1168	1538	1747	1547	16 56	1564
TURB(")	7.03	9.96	5.69	5.53	5.49	9.73	14.2	10.3	4.6	6.5	7.0	5.6
s.s (")	9.2	12.2	6.22	7.6	6.2	43.4	8.8	15.2	7.2	9.1	9.1	7.0
COD (")	5.47	6.31	5.58	6.47	6.6	5.52	6.8	6.4	7.9	10.6	6.6	5.7
Fe (")	0,24	0.31	0.28	0.33	0.3	0.75	0.46	0.52	0.33	0.23	0.27	0.19

ANALYSIS OF RAW WATER 1979

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FIG : 3

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5. Expected Improvements From Such Modifications:

- 5.1. It is our opinion after certain period of studying different water treatment processes that it is not strictly necessary to follow a conventional pattern in the design of water treatment units. The Following General Improvements we expect to achieve by our proposed modifications.
- 5.1.1. Reduction of Sludge quantity.

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- 5.1.2. Reduction in required quantity of treated water to produce the required quantity of domin water .
- 5.1.3. Longer operation life for the lagoon because lesser quantity of waste input.
- 5.1.4. Elimination of the cumbersome chemical feeding devices for lime and soda .
- 5.1.5. Establishing steady operating conditions since the bottle neck of the tight soda-lime process is eliminated .
- 5.1.6. Possible neutralisation effects between reverse osmosis effluents with cooling Tower blow down water (Partial Neutralisation) .
- 5.2. Table 3 and Fig, 3 gives a summary of the expected (Above Mentioned) advantages for the modified system.

10-EMISSION CONTROL IN

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FERTILIZER INDUSTRY

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1	INTRODUCTION
2	WHAT IS A MIST ?
3	WHAT DOES A MIST DO ?
4	COLLECTION MECHANISM
5	COMMON FEATURES OF BRINK MIST ELIMINATORS
6	EMISSION CONTROL IN AMMONIUM NITRATE PROCESS
	PROCESS DESCRIPTION :
6.1	- NEUTRALISER
6.2	- CONCENTRATOR
6.3	- PRILLING TOWER
6.4	- SHROUD SYSTEM TO REDUCE FLOW
6.5	- BRINK SYSTEM
6.6	- CAPITAL AND OPERATING COSTS
7	EMISSION CONTROL ON UREA PROCESS
7.1	- PROCESS DESCRIPTION
7.2	- EMISSION PROBLEM
7.3	- BRINK SYSTEMS
7.3.1	SC/HE SYSTEM
7.3.2	MESHPAD/HP SYSTEM
8	EMISSION CONTROL IN SULPHURIC ACID
8.1	- INTRODUCTION
8.2	- DRYING AND STRIPPING TOWER
8.3	- INTERPASS ABSORPTION TOWER
8.4	- FINAL ABSORPTION TOWER
9	EMISSION CONTROL AND CATALYST RECOVERY IN N'TRIC ACID
9.1	PROCESS DESCRIPTION :
	- PT RECOVERY
	- ABSORPTION TOWER

* Presented by : Mr. P. Goossens from Amafilter b.v., Alkmaar, Holland.

1 INTRODUCTICA

BRINK MIST ELIMINATORS are used in systems throughout the world to remove both liquid and soluble solids from practically any gas stream. Whatever your manufacturing process, it is possible that small and sub-micron particles are present in the process or stack gas stream. These particles form a dense mist which will cause a variety of problems varying from air pollution to production losses.

Unfortunately these small mists with a particle diameter in the range of 0.1 to 3.0 micron have a high light scattering effect and produce stack plumes giving great visibility and persistance. The BRINK MIST ELIMINATOR was developed to remove and collect these troublesome particles.

2 WHAT IS MIST ?

The term mist is commonly applied to liquid particles suspended in a gas stream. This broad definition can be dangerous, because it can lead to an erroneous determination of the problem and a costly error in the choice of a solution. If liquid droplets are present in a gas stream, the diameter of the individual particles may vary considerably. In order to determine the exact nature of your problem and accurately determine an effective and economical solution, it is important that particle size distribution be characterized for the gas stream in question.

- <u>SPRAY</u>: is commonly defined as liquid particles 10 microns or larger in diameter. Sprays are not too difficult to remove and a wide variety of equipment is available for this purpose.
- MISTS : are defined as liquid particles smaller than 10 microns in diameter (a micron is 1/1,000 of a millimeter, or 1/25,400 of an inch). True mist is extremely difficult to remove, requiring highly specialised equipment.

It is virtually impossible to produce a mist by mechanical means and they are normally formed in manufacturing processes in one of two ways :

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- 1.: Cooling of gases occurs and the liquid or solid mist condenses to form mist or dust particles.
- 2.: Chemical reaction of two or more gases forms a product which has a relatively low vapor pressure at the reaction temperature and condenses from gas.

Typical examples would be cooling of hot oil vapour which forms a dense blue mist or the reaction of SO₃ vapour with water vapour to form sulphuric acid mist. Both these form a mist with a particle diameter less than one micron.

3 WHAT_DOES MIST DO ?

True mists cause problems in both process gas streams and in exit stack gases.

Spray particles can be removed fairly easily, but the mist particles that are not collected by conventional equipment will still result in serious problems if they are not effectively removed and collected.

Air Pollution

Removal or collection of spray particles from stack effluents may reduce emissions of a pollutant to acceptable levels but a plant may still be faced with a serious pollution problem. Mists, especially sub-micron mist particles, generate visible, persistent plumes, which can trail off for great distances from a stack. The weight of these particles per cubic meter of exhaust gas may not be economically significant from product loss standpoint, or from a kg-per-hour emission limit, but these mists are in fact the major cause of stack plume opacity as well as plume persistence! Mist particles with diameters of 0.1 to 1.0 microns have the greatest light scattering effect : therefore, they cause the greatest plume opacity. Brink systems can be designed for an essentially invisible stack plume, provided there are no condensable vapours in the stack gas.

In-Process gases

The presence of true mists in process gas streams can cause problems in product purity, safety, decreased process onstream time (due to fouling of catalysts or equipment) and increased maintenance costs. These mists can also affect

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both the design and operation of a process by requiring more expensive materials of construction for equipment and by dictating operating conditions (to minimize mist formation) which are unfavorable for maximum output or yield. Brink mist eliminator systems have succesfully solved many such process problems.

4 COLLECTION MECHANISMS

Inertial impaction

The momentum of larger particles (normally greater than three microns) prevents them from following the gas as it streamlines through the fibre bed. These particles impact on a fibre and are thus collected.

Collection efficiency below 3 microns is limited. Direct interception

Particles may follow a gas streamline and be collected without inertial impaction, if the streamline is relatively close to a fibre. Consider a particle 1.0 micron in diameter which follows a gas streamline passing within 0.5 microns of a fiber. The particle will touch the fiber and be collected by direct interception.

Brownian movement

The BRINK MIST ELIMINATOR utilizes brownian movement to achieve high collection efficiencies in the range of 100%. Brownian movement, or diffusion is defined as the random back and for movement of the fine particles caused by their collision with gas molecules.

A particle 0.1 micron in diameter will have approximately five times the Brownian displacement of a 1.0 micron particle, and 15 times that of a 5.0 micron particle.

Thus as the particle size decreases, the probability that these particles will collide with a fibre and be collected increases. As a result, BRINK MIST ELIMINATORS utilizing Brownian movement actually increase in collection efficiency as the particle size decreases.

BRINK MIST ELIMINATORS utilize all three mechanisms to give approximately 100% removal of all particles greater than 3 microns and a very high collection efficiency on particles below 3 microns.

The collection efficiency by interception and impaction falls off below 3 microns. The collection efficiency by Brownian Movement becomes significant on particles smaller than one micron resulting in a high overall efficiency for all small particles.

	<u>nE</u> (HIGH EFFI- CIENCY)	HP (HIGH PER- FORMANCE)	HV (HIGH VELOCI TY)	<u>SC</u> (SPRAY CATCHER)
Controlling Mechanism for Mist Collection	Inertial 1m- paction Direct Inter- ception Brownian Move- ment	Inertial Im- paction Direct inter- ception	Inertial Im- paction Direct inter- ception	Inertial Impaction Direct in- terception
Efficiency on particles > 3 µ Efficiency on particles > 3 µ	100% 94 to 99.95%	100% 70 to 99%	100% 50 to 97%	100% 15 to 30%
Pressure drop (mm wc)	100 to 400	250	200	50
STRUCTURE OF ELIMINATOR	CYLINDRICAL	CYLINDRICAL	RECTANGULAR	RECTANGU- LAR

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5

COMMON FEATURES OF BRINK MIST ELIMINATORS

All Brink mist eliminators consist of a vertically packed fibre bed retained between two screens. The fibre bed may be packed between two concentric cylindrical screens or between two parallel flat screens. Structural parts are made from any weldable metal or certain plastic materials.

All mist climinators operate in a similar manner. Gases containing mist and spray particles pass in horizontal direction through the fibre bed.

Clean gases emerge from the bed and rise upwards to exit from the system.

The liquid particles are collected on the fibres in the bed and coalesce into liquid film which are moved horizontally through the fibre bed by the drag of the gases and then downward by gravity. The collected liquid drains off the downstream face of the fibre bed and out through the drain.

There are four basic types of mist eliminators produced by Amafilter.

SC - SPRAY CATCHER

HV - HIGH VELOCITY

HP - HIGH PERFORMANCE

HE - HIGH EFFICIENCY

In addition, through a programme of constant research, Amafilter expects to be introducing shortly some significant technical advance which will extend our product range.

H-E : HIGH EFFICIENCY

Extremely Efficient on Submicron Particles uses all 3 Collection Mechanisms but principally diffusion.
Constant Efficiency on Particles Below 3 microns.
Pressure drop depending on design: 100 MM - 500 MM WC
High flexibility Efficiency independent from flow rate
Cylindrical shape
Efficiency increases if gas flow decreases

H-P : HIGH PERFORMANCE

. Excellent Efficiency on Particles

- between 0.5 1 micron
- . Treats large volumes with small size Installation
- . Design pressure drop:
 - 200 250 MM WC
- . Guaranteed Efficiency ± 95 %
- . Easy to install . Cylindrical Shape

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H-V : HIGH VELOCITY

- . Very Efficient on Particles
 - 1 3 microns
- . Large Flow per surface unit
- . Pressure drop:
 - 150 200 MM WC
- . Small height required
- . Rectangular shape
- . Assembly in modules or polygon

S-C : Spray Catcher

- . Very low pressure drop 25 - 50 MM WC
- . Large flow per unit surface
- . 100 % Efficient on particles
- above 3 microns. . Used often as prefilter for
- insoluble solids
- . Rectangular shape assembly Module or Polygon.

6 EMISSION CONTROL IN AMMONIUM NITRATE PROCESS

Each of the numerous vents in a modern fertilizer production plant is a potential source of serious pollution. The ammonium nitrate plant can be the worst air polluter: emissions arise from the neutraliser, the evaporator and prill tower. Whilst a variety of proprietary manufacturing processes for ammonium nitrate have been developed by leading engineering companies, each of which uses different concepts of neutralising, evaporation, drying and conditioning methods, all of them are based on the production of ammonium nitrate by the neutralisation of nitric acid with gaseous ammonia. Pure ammonium nitrate is highly hygroscopic, a characteristic which is of primary <u>importance</u> for the separation processes to be described.

6.1 NEUTRALISER

In the atmospheric process, the ammonium nitrate produced during neutralisation is subject to strong turbulence as a result of heat generated in the exothermic reaction. This causes some of the product to enter the atmosphere directly in aerosol form, thus, we have an air pollution problem. In pressurized or vacuum systems, steam has to be condensed before released to the environment, creating in general a waste water problem. Emissions from several neutralisers have been examined and exit loadings near 10.000 mg/Nm3 of steam with following particle size distribution have been found:

larger than 3 μ	25 % (by weight)
1 – 3 да	25 %
0.5 - 1 A	40 %
0.1 - 0.5 µ	8 %
smaller than 0.1 µ	2 %

We propose our HV elements in SS 304 L with teflon fiber to solve this pollution problem giving global efficiency of 85 to 95% on the NH4NO3 mist. The recovered products allow a pay-off of this installation, within a reasonable period.

6.2 CONCENTRATOR

Depending on the type of process, the concentrator presents emission problems similar to those of the neutraliser, although the ammonium nitrate mist loading of the waste gas depends on the type of evaporator.

Sampling done on low concentrators indicates emissions around 3000 mg/Nm3 with 99% of particles above 3 micron. Sampling on high concentrators indicates loading of 1.500 mg/Nm3, roughly half of which is smaller than 3 micron.

6.3 PRILLING TOWERS

Depending on the application, two types of products are prilled, namely low-density ammonium nitrate of 95% and high-density of 99.5 to 99.8 %. Low density contains 3-5 % water and is prilled at 140°C.

This is just approaching the temperatures at which submicron particles are produced. So low density prill towers usually do not have severe emission problems. High density prill towers typically spray 175-185[°]C molten ammonium nitrate at a prill deck near the tower's top. The spray stream breaks up into droplets which are cooled and solidify into prills as they fall through cooled air flowing up from the bottom of the tower. Sometimes "satellite" connected prills and "micro prills" are formed as the spray stream breaks up. Smaller microprills will be carried out of the cower by the cooling air creating a nuisance problem. Emissions will vary with ambient temperatures but typically will be 100-150 mg/Am3 with the following particle size distribution: Particle Size Weight percent

	Larger than 3 µ	30	8
	1 – 3 _/ u	20	8
	$1/2 - 1 \mu$	35	8
	smaller than 1/2 µ	15	8
6.4	SHROUD SYSTEM TO REDUCE	FLOW	

The effluent air from prilling towers represents the bulk of the emission problem in ammonium nitrate production. Since the amount of fume generated is a function of temperature, it follows that if one can reduce the amount of air containing the fume by isolating that portion of the prill air which cools the prills to a temperature below which mist is not formed, then collection of the mist becomes simpler and less costly. This is the principle of the shroud system whereby only the air passing in the vicinity of the prill head is treated by mist eliminators.

A computer program has been established which takes into account all variables such as the effect of various prill sizes, changing air temperatures and air velocities, to design the most economically sized collection duct (shroud). Collection duct length may vary from 6 m to 20 m and air flows from 1/8 to 1/4 of the total air flow depending on spray temperature.

Pilot work was done to find the right type of scrubber to meet mass and opacity regulations from Enviromental Protection Agency in the U.S. The first full scale unit with the

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collection duct and the impingement type scrubber did not meet the cpacity limits although the collection duct worked properly.

The Scrubber was replaced in 1974 by a Brink Mist Eliminator system which is still performing well and meeting opacity limits. The flow from the collection duct, the evaporator and neutraliser were combined to one flow to the Brink System thus solving the total emission problem.

6.5 BRINK SYSTEM

The incoming air from the prilling tower passes through a prefilter stage f.i. spray catcher (SC) elements, where insolubles, microprills and other relatively large particles are removed. These elements are heavily irrigated with acidified solution to dissolve the micro-prills and flush off any insolubles. As the air turns up toward the HE elements it passes atomizing nozzles, which spray process condensate as a very fine fog. The HE elements collect the fogged mist along with those ammonium nitrate particles which are small enough to pass the prefilters. The Brink Mist Eliminator collects the dissolved fume and drains it down the sump.

Performance tests have confirmed the design efficiency of 97.5 %. The Shroud system is capable of reducing the quantity of air requiring treatment but it requires higher collection efficiencies than does a system treating the total flow (97.5 % vs 91 %) thus the Shroud system reduces the Brink system (Element and vessel) costs by 50 % and makes the total system more practical for controlling prill tower emissions. 13 of such abatement systems are operating at present and more are scheduled to start. The operating experience indicates that Brink Mist Eliminators are the only succesful method of controlling prill tower emissions.

6.6 CAPITAL AND OPERATING COSTS

1. Capital Costs.

The installed cost of a system can vary from one plant to another. Typical items that cause cost variations are:

1. Volume of the air flow.

Use of the shroud system can reduce the flow requiring treatment to 25-30% of the total.

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- 2. Customer or authorities collection efficiency requirements.
- 3. Installation at the top (generally for new plant only) or at the bottom of the prilling tower.
- 4. Modification of the tower to support the equipment if installed on top.
- 5. Available plot area.
- 6. Installation during plant construction or later.

Capital cost data have been obtained from plants when systems have been installed or where installations are planned. When the plant size increases, as expected, the cost per unit of production decreases.

2. Operating Costs.

The operating costs incurred are principally the electrical power for the system, blower and circulation pumps. As the elements are self cleaning no special maintenance is required. The quantity of ammonium nitrate collected (40-50% solution) is normally sufficient to pay for these operating costs.

7 EMISSION CONTROL IN THE UREA PROCESS

7.1 Process Description

Urea is manufactured by reaction ammonia and carbon dioxide at a pressure in the range of 200 - 300 bars and at a temperature in the range of $170 - 210^{\circ}$ C. The first reaction, in which ammonium carbamate is formed, is exothermic and goes rapidly to completion.

 $Co2 + 2NH3 \rightarrow NH4 COO NH2 + 31 Kcal$

The second is endothermic and relatively slow.

NH4 COO NH2 \rightarrow NH2 CO NH2 + H2O - 5 Kcal

Two important $si^{4}\epsilon$ reactions are the formation of biurct by the combination of two urea molecules and the hydolysis of urea to ammonia and carbon dioxide.

7.2 Emission problem

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During prilling (and granulating), microprills prill
     fragments and thermally generated sub-microns urea fumes
     are formed in the prill tower (or granulator) by the air
     used to cool down the molten urea.
     Several sampling and pilot tests have been done in U.S.
     and Europe.
     It has been found that loading varies between 75 mg/m3 and
     600 mg/m3.
    The size distribution of the particles depends on the pro-
    cess, the spray system and the temperature.
    Nevertheless, different types of distributions can be recognised
    in two population one greater than 10 micron and one less than 1 micron
    Greater than 10 µ 30 - 50 %
    Smaller than I µ 50 - 30 %
    In order to obtain a clear stack, the dust load must be reduced
    below 10 mg/Nm3.
    To select the Brink system, we must know
         - the mistload
         - the particles size distribution
         - the available pressure drop
         - the allowed outlet load
         - the objectives the customer has
           set for his pollution abatement system.
    Depending on these, we will propose one of the following systems:
7.3 Brink systems
7.3.1. SC-HE SYSTEM
    The basic system consists of irrigated glass fiber packed
    Spray Catcher (SC) element followed by irrigated glass fiber
    packed High Efficiency (HE) elements (see sketch 1 & 2).
    Characteristics of the SC-HE System.
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- very high efficiency (>97.5%)
- mist free emission
- pressure drop 350 mm WC
- exit load less than 10 mg/Nm3
- recovery of 25% urea solution

(a) Irrigated SC elements

The BRINK SC elements are irrigated by soray nozzles to humidify the gas stream and dissolve the urea.

The purpose of this section is to collect the particles that are larger than 3 microns. The spray liquor is recycled 25% urea. Process condensate is used as liquid make-up.

(b) Irrigated HE elements

The BRINK HE elements collect 97.5% of the particles smaller than 3 microns. Hydraulic atomizing nozzles provide sufficient fresh water to complete the humidification and wet the element surfaces. The remaining urea is collected, dissolved and drained to the vessel sump.

7.3.2. MESHPAD BRINK HP SYSTEM

The basic lay-out of this system is an irrigated meshpad followed by irrigated glass fiber High Performance (HP) type elements.

Characteristics.

- High efficiency : 70-80%
- Faint plume
- Pressure drop : 200-250 mm WC
- Exit load : less than 30 mg/Nm3
- Installed at the top or bottom of the tower
- Concentration of urea solution : 25%
- The system consists of irrigated meshpad to humidify the gas stream and dissolve urea followed by glass fibre packed HP elements (see sketches 3).
- (a) The irrigated MESHPAD

The meshpad is irrigated by spray nozzles to cover the whole surface to humidify the gas stream and dissolve the urea.

(b) Irrigated HP elements

The BRINK HP elements collect nearly all of larger than 3 microns particles and enough of the smaller than 3 microns particles that the exit loading is in a range that produces an opacity less than 20%. The liquid collected from the HP section is drained and

recycled to the meshpad irrigation sprays. A bleed of urea solution (25%) is drained from the sump. Fresh water is added as needed.

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SELECTION OF REFERENCES IN AMMONIUM NITRATE AND UREA PRILLING TOWERS

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COMPANY	LOCATION	CAPACITY
ATLAS	JOPLIN, MISSOURI - U.S.A.	400 TPD.
C.F.C.A.	LAWRENCE, KANSAS - U.S.A.	1) 600 TPD
(Farmland Industries)		2) 1.000 TPD
C.F.I.	TERRE HAUTE, ILLINOIS - U.S.A.	600 TPD
ILLINOIS NITROGEN	MARSEILLES, ILLINOIS - U.S.A.	400 TPD
MONSANTO	ELDORADO, ARKANSAS - U.S.A.	2 x 750 TPD
	LULLING, LOUISIANA - U.S.A.	2 x 1.000 TPD
ST PAUL AMMONIA	SOUTH ST PAUL, MINNESOTA - U.S.A.	500 TPD
S.A.I.	SCOTLAND - UK	350 MTPD
I.C.I.	BILLINGHAM - UK	1000 MTPD
AMERICAN CYNAMID	HANNIBAL, MISSOURI - U.S.A.	600 MTPD
COLUMBIA NITROGEN	AUGUSTA, GEORGIA - U.S.A.	800 MTPD
POLIMEX	POLICE - POLAND	1200 MTPD
C.D.F.	MAZINGARBE - FRANCE	900 MTPD

TYPICAL DATA FOR DIFFERENT BRINK SYSTEMS IN UREA APPLICATION

Inlet Mistload	Type of Mist	Collection	Pressure	Concen-	Outlet
	<u>eliminator</u>	efficiency	drop	tration	<u>mist</u>
				<u>of recy-</u>	<u>lo</u> ad
				cled urea	
90-110 mg/Nm3	SC	<u>+</u> 50 %	50-75 mmWC	25 %	<u>+</u> 50 mg/Nm3
90-110 mg/Nm3	meshpad/HP	<u>+</u> 80 %	200-250 mmWC	25 %	+ 25 mg/Nm3
90-110 mg/Nm3	SC-HE	97.5 %	350 mmWC	25 %	10 mg/Nm3

This data is based on a particle size distribution of /

30% > 10 Microns

50% < 1 Micron

EMISSION CONTROL IN SULPHURIC ACID PROCESS 8

8.1 Introduction

BRINK MIST ELIMINATORS are used extensively by all major constructors in the control of mists in sulphuric acid plants. When not installed as original equipment they may be added later. The expected life of an element is more than 10 years. BRINK MIST ELIMINATORS can be found in the following locations on an acid plant: 1. Mist from wet gas before the drying tower. 2. Mist from the exit gases of the: - interpass tower - drying tower

- cross flow stripping tower
- final absorbing tower
- oleum tower
- 3. In addition, mist eliminators are used to control oleum mist from storage tanks and tanker loading bays.

As the type of mist varies depending on the application, the type of equipment installed is carefully chosen to provide the best solution.

8.2 Drying and stripping tower

The type of mist encountered in wet gases entering the drying tower, the gases leaving the drying tower and the gases leaving the cross flow stripping tower are all relatively large, generally in the 1-5 micron range. For this reason, we normally install SC (Spray Catcher) elements or HP (High Performance) elements depending on the pressure drop available which combine good efficiency (both 100% on particles greater than 3 microns) with acceptable pressure drop.

8.3 Interpass Absorption Tower

This tower is installed part way through the catalytic conversion process and produces fine mists of submicron size due to vapour phase reaction of sulphur trioxide with water vapour and shock condensation. It is essential that these mists are removed if corrosion of down-stream heat exchangers and damage to the catalyst mass is to be avoided.

Because of the need to remove these fine submicron mists Amafilter recommends the installation of HE, High Efficiency Mist Eliminators with 97.5% efficiency on particles less than

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3 microns. The HE mist eliminator is not dependent on gas flow rate which means that full protection is obtained even at low production rates.

If oleum is produced before the interpass tower the amount of mist produced is even greater and smaller in size. In this case we would offer mist eliminators with 99.0% efficiency.

8.4 Final Absorption Tower

In the previous applications we have discussed, the mist eliminators have been installed to protect equipment from corrosion and to stop costly damage of the catalyst masses. In the final absorption tower the mist eliminators are installed for pollution control. For this reason, acid plants are fitted with HP, HV and HE elements depending on the degree of pollution control required. Most popular is now the HP high performance element. This provides excellent and economic collection efficiency on particles greater than 3 microns with good efficiency below 3 microns. When oleum is produced before the final tower, HE mist eliminat are fitted either to the oleum tower or the final absorption tower as the proportion of submicron mists is much higher.

9 EMISSION CONTROL AND CATALYST RECOVERY IN NITRIC ACID PLANTS

9.1 Platinum recovery

In the conventional "DuPont" type nitric acid process, the conversation of ammonia to nitrogen oxides is usually in the range of 95% to 97% with new platinum gauzes. When the ammonia and air streams are not sufficiently cleaned, i.e., when unfiltered, the gauzes are fouled and/or poisoned rather rapidly and the conversion not only decreases two or three percent within a few weeks, but it continues to decrease at this or a more accelerated rate to a level at which continued operation is uneconomical. As a result of this rapidly decreased conversion and the corresponding increased operating costs, many nitric acid plant operators change their platinum gauzes frequently. Brink mist eliminators may be used on both air and ammonia gas streams.

Brink platinum recovery filters in nitric acid plants

The Brink Platinum Recovery Filter is the leading product on the market for collecting platinum dust "burnt-off" the catalyst gauze in nitric acid plants. It has a firm stable bed which does not collapse and or through. Depending on the user's requirements and practices, the Brink Platinum Filter can be kept in operation for several months before changing out and replacing with a spare unit. The range is about four to nine months, with most units lasting at least six months. The change-out time is a matter of economics depending on maximum allowable pressure drop, overall recovery efficiency and cost of carrying platinum in process. The efficiency actually improves as time goes on and the pressure drop builds up. Our filters start with a clean bed drop in the range of 1/2 to 1 psi and are allowed to build up to a pressure drop of 2 to 3 psi. Running to pressure drops as high as 4 to 5 psi leads to the danger of rupturing the bed. It is recommended that an accurate differential pressure indicator be used across the bed.

We expect 55-60% overall recovery.

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"Losses" from the gauze other than "burn-off", from the filts cannot be collected since these "losses" never reach the filter. Losses can occur due to handling the gauzes in and out of the reactor, pickling the partially spent gauze, packaging the spent gauze for return to the processor, handling and accounting at the processors' plant.

If the platinum is cleaned out of the filter housing each time, it should be added to the platinum collected in the fiber bed for accounting purposes, since the "filter system" did stop and collect the catalyst particles. We have found that in some cases the catalyst cleaned out of the housing was not credited to the filter, but was credited to the gauze to reduce the gauze loss. This arbitrary accounting procedure does not credit the filter with the complete job that it does and results in lower calculated efficiencies.

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We would expect the filter system to collect as much as 90% or more, depending on particle sizes, length of time in operation, etc., of all the catalyst dust reaching it. If accounting does not seem to show a 55-60% overall recovery, a visual check may be made on the filter performance. When removing the filter for recovery of platinum, observe the inside or core side of the bed. It should be virtually white indicating essentially no visible catalyst particles have penetrated through. Our experience has shown that the outside will be black with catalyst with a gradual transition through snades of grey to virtually white in the first 25 to 30 mm of the bed.

Any platinum filter user with a little care and effort cannot only establish that the filter is doing an excellent job of recovering catalyst, but can also increase his overall recovery of catalyst.

In the design of platinum filters utilizing our glass fibers, we usually assume that the process gas will consist of reasonably completely reacted (90% or higher conversion) ammonia and air from a properly operated converter. We also assume that the filter will be started-up with cold (less than 150° C) gases passing through the filter media. If the process contains a high pressure boiler, ahead of the filter, or other features which permit "hot" start-ups, our design incorporates special ceramic fibers (instead of glass) with a melting point of over 1600° C.

The special ceramic fibers are more expensive than our glass fibers, therefore, we utilize them only when required in these special cases.

9.2 Absorption tower

Brink Nitric Acid Mist Eliminator

A cylindrical H-V (high velocity) design Brink Mist Eliminator, fabricated of stainless steel and special glass fibre packing, is used to collect nitric acid mist and spray carried over in the gas stream from the absorption tower. These elements are normally installed following the absorption tower in a separate carbon steel tank lined with stainless steel.

In operation, the mist laden gases entering the Brink tank below the tube sheet pass upward through the cores of the Brink elements and through the packed fibre bed. The acid particles are removed from the gas stream by coalescing on the fibres and the clean gas passes out the through the top of the tank (See Fig. 6).

A film of agglomerated acid droplets is formed on the downstream face of the fibre bed. This liquid film continuously drains downward onto the tube sheet and out of the tank through a side drain back to the process. Another drain is provided in the bottom of the tank to remove the accumulation of large acid drops that fall out by gravity and do not reach the elements.

While particle size distribution of the entrainment is not known with certainty, the cylindrical H-V system has given excellent results (overall efficiencies of over 99%) in this service. Corrosion to the downstream piping, heat exchange equipment and expansion turbine is greatly reduced at a minimum cost.

The Brink Mist Eliminator requires virtually no maintenance. The elements are self-draining and small amounts of solids will normally be flushed through the bed with the collected acid.

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REGULATIONS

Background

Qatar Fertiliser Company operate two 900 t/d Ammonia Flants and two 1000 t/d Urea Plants. Related facilities include desalination plants, ammonia and urea storage, and a power station.

The present Qafco plant was built in two stages. The first Ammonia plant and an MTC Urea plant were designed in the late sixtees and came an stream in the early seventies. At that time there were no regulations governing emissions to the environment in Qatar. Consequently no facilities were installed to treat unwanted effluent streams from the plant.

In the middle of the seventies the Qafco plant was expanded. There had been no change in the pollution regulations in Qatar since the first plants were built so the new Ammonia plant was a copy of the old one. A Stamicarbon Urea plant was built this time however, but reduction of emissions was not the reason for the change of process.

The new plants came on stream in 1979. Today in 1981 the situation is the same. There are no regulations governing emissions in Qatar and Qafco have made no systematic effort to map the emission sources or quantify them.

The only work that has been done in the field was commissioned by IDTC - The Industrial Development Technical Centre in Doha in 78. A consultancy firm in the UK -Atkins Research & Development investigated the pollution situation in the Industrial Area of Umm Said and summarized their findings in a report which they presented to the IDTC. The following summary of emissions from Qafeo is based on that report. (1)

By: Keith Duns - Chief Process Engineer. Mohammed Al-Bakir - Senior Process Engineer. Qatar Fertilizer Company (S.A.Q.)

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Discharge from Gafco

The principal pollutants were found to be sulphur dioxide from the gas turbines, boilers, heaters and the de-sulphurisation flare stack, ammonia from process vent stacks and relief valves, and usea dust from the prill tower and drying systems.

Natural gas is partly used as a feedstock for the process and partly as a fuel for gas turbines, boilers and heaters. Gas used as feedstock is first de-sulphurised and the separated gases sent to flare. This results in an emission of sulphur dioxide to atmosphere continuously. The fuel gas combustion products add to the level of sulphur dioxide continuously emitted from the plant.

Under normal operating conditions the only significant sources of ammonia emissions to atmosphere will be from the area plant vents and the area prill tower, where, although the concentration of ammonia is very low, the level is significant because of the large volume of gas from the tower.

Other significant sources of pollution emanate from the urea prilling tower an. package dryers. Wind-blown urea dust will also result from handling operations including bulk export of urea.

Under normal shut down conditions, and in emergency situations venting to atmost phere will occur.

There will also be continuous low-level emissions of a number of other gasebis polluturts including nitrogen oxides, carbon monoxide, and hydrocarbons but, their concentrations will be very low.

The Present Situation

During the week of 26 September to 2 October 1981 Qafco produced 12000 tons immonia and 10000 tons of Grea. Consumption of associated gas was 730 million SCF. The sulphur contained in this gas during the period in question was of the order of 230 tons, most of which would be emitted to atmosphere from the desulphurization vents, and the boiler & turbine exhaust stacks.

The Future

The associated gas availability from on-shore oil has dropped during the last year so that insufficiant is available to operate both ammonia plants at full load.

Off shore associated gas containing a higher sulphur content is available and Qafco plan to use 20 million SCF per day of this from the spring of 1982 which could increase up to about 80 million SCF in 18 - 24 months time. The use of off shore gas will mean that sulphur emission from Qafco will increase by up to 50 %

From the point of view of pollution control \sim regulations IDTC have established a laboratory in the Umm Said area and will began to **monitor** emissions from the industrial sites **Boon.** It is therefore probable that regulations on emissions will come to Qatar within the coming years.

Reference

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- 1) The Impact of Atmosphere Pollutants upon Flour Mill Production at the Qatar Flour Mills Company.
 - Alkins Research & Development- Report to IDTC January 1978.

12- POLLUTION ABATEMENT AT PIC DURING THE LAST DECADE

The modern definition of pollution has become so broad that it includes every element which harms the human life, his well-being, or the environment in which he lives. It covers noise pollution, atmospheric pollution, water pollution, Solid wastes pollution, nuclear & thermal pollution. Some sociologists even go further to consider any act or behaviour which is not accepted by majority of a community as a pollutant.

PIC has crossed a long way in pollution abtement during the last decade. Many antipollution measures are marked on the top priority list. PIC contains a huge fertilizer complex which produces around 2100 Tons of Ammonia / Day, 2000 Tons of Urea / Day, in addition to sulphuric acid and Ammonia sulphate plants. It contains a water treatment unit and ammonia storage facilities. It is located in the heavily industrialized Shuaiba area. The main electric power and water generation plants of KUWAIT are on the next door of our plants. These Electric power generation plants are very sensitive to atmospheric pollution mainly urea dust and Amm. We cannot afford to let our plants be the cause of interruption of Electric supply to the Many stringent antipollution measures have been taken by PIC. Several country. Projects were successfully executed to reduce the pollution and to improve the production capacity of the plants or save the Raw materials and chemizals used in the plant.

I. NOISE POLLUTION:

1.1. PIC Plants were constructed with inadequate number of noise silencers. None of the vents of the four high press steam boilers had a Silencer. The vents were very short. Steam used to be vented at a pressure of 110 kg/cm² and 510 °C at a tremendous noise level. Similarly, the other MPS (Medium pressure steam) and LPS (Low pressure Steam) boilers have no silencers. Proper silencers have been fixed during the last two years. Other silencers were installed on the synthesis gas vents of Amm. plants front end.

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By : Fahed F. Sehweil. Petrochemical Industries Company (PIC). Kuwait.

1.2. In order to save energy and reduce the noise pollution, the process feed Natural Gas ($6 \times 10^6 \text{ NM}^3/\text{ Yr}$) which used to be wasted as a vent is now being recycled to the suction of process Natural gas compressor.

2. ATMOSPHERIC POLLUTION:

Each of the numerous vents in the fertilizers industry is a potential source of serious pollution and environmental nuisance. This following were among the executed projects.

- 2.1. The project of Ammonia recovery from the purge gas was successfully executed. It minimized Ammonia pollution to the atmosphere and saved about 4000 Tons of Ammonia /Year. Reuse of the remaining purge gas as a fuel and / or recovery of its Hydrogen is being studied as one of the top priority projects.
- 2.2. The urea dust in the air of cyclone separators was minimized to give an almost clean air by executing a dedusting water scrubber. The urea dust in the effluent of fans of prilling tower is about 80 mg/M³. However, we aim at reducing it further to less than 6 mg/m³ by implementing mist eliminators or other similar devices.
- 2.3. Flares were installed on the knock out condensates, which are associated with combustible gases, and on the stripped Hydrogen sulphide from N.G.
- 2.4. The above mentioned vented N.G. circulation through the compressor has minimized N.G. pollution.
- 2.5. Stacks of sulphuric acid plant were elevated, thus decreasing the intensity of pollution but, of course, not the amount of pollution.

3. WATER POLLUTION:

3.1. Urea Hydrolyzer project brought down the urea & Ammonia contents in the waste effluent of urea plants to less than 200 PPM and 50 PPM respectively. Thus, it allowed water to be safely pumped to irrigate the forestry which we have at a distance of about 16 kms from our plant. Again, this water is being thought of to be treated for further use as

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boiler feed water. This project has also helped in saving 16 Tons of urea / day and in saving energy by using much less direct steam for desorption system.

- 3.2. A new pretreatment system of the process condensate of ammonia plants will replace the existing system. The new system will result in less ammonia content in the process condensate & hence reduce the regeneration water & regeneration chemicals. Slightly, more ammonia will be vented to atmosphere but the stack will be higher. Again, there will be a net economical saving in the cost of treated boiler feed water.
- 3.3. Oil pollution was minimized through dirty oil recovery project, degassification project of seal oil and finally installing oil skimmers on the closed sewer of oil contaminated water. It is to be noted that PIC is using a lot of oil for the many centrifugal Compressors which are driven by steam turbines. The speed of these Compressors range from 8500-14000 r.p.m. oil is used as lube oil, and control oil.
- 3.4. Chemicals such as potassium carbonate and MEA, which used to leak, from packing of pumps and drains of sight glasses etc, and then go to the sea through sewers are now being recovered into pits and reused. Thus reducing pollution and saving chemicals cost.
- 4. Well prepared preventive maintenance specially during turn-a-rounds of the plant will help in reducing the abnormalitities of equipments which lead to excessive pollution.
- 5. I would like to stress on the fact that the intensity of pollution depends on the stability of plant operation. Therefore, the maximum pollution rate is usually experienced during the startups and shut downs of the plants. Thus, increasing the ON-STREAM FACTOR will certainly reduce the pollution.

6. Proper training of plant operators and giving more attention to the wrong practices of plant operation would help in minimizing the pollution. For example, we used to open the seal water of Benfield solution pumps at a pressure much higher than what it should be. This resulted in frequent failure of the pumps and its packing and thus increasing the pollution. Another practice was opening the vent of N.G. machine to avoid the surge of the machine during abrupt changes of sp.gravity. These vents used to remain open unnecessarily most of the time resulting in loss of 6 million NM³/Yr as a pollutant & energy loss.

7. CONCLUSION:

Pollution is rarely due to lack of available Technology. It is mostly due to less attention paid to pollution while planning & designing a new plant. PIC has a growing concern for environmental preservation. We have a committee for pollution abatement. The whole heavily industrialized area of Shuaiba is under the control of shuaiba area authority (S. A. A.) who traces all sources of pollution from any nearby industry. S. A. A. sends the respective warning and askes for an immediate corrective measure to minimize the pollution.

PIC has so far executed several projects for pollution abatement. Many of these project had a comparatively very low investment. They resulted in economical saving of the product in addition to the tremendous reduction of pollutants. The pay back time of several projects was less than two years. However, many other pollution abatement projects are on the top priority list of PIC plants.

Finally, let us remember that we can only command nature by obeying her only.
Discussions:

Q: Sameh Gharaiba, Environment Authority, Jordan:

What about recovery of purge gas at SAFCO?

A: Abul Huda, SAFCO, Saudi-Arabia:

The purge gas recovery at SAFCO is now under study and is going to be executed shortly. Most of the purge gas is burnt in the primary reformer as a source of fuel and the losses of ammonia in purge gas is about 2-3 tonnes per day.

Q: Jalil Zaynal, Bahrain:

Is the discharge outlet located away from the shore in the deeper water or is it directly discharged near the plant in the shallow water?

A: Abul Huda , SAFCO, Saudi-Arabia:

It is a good practice in many cases to have the discharge away from the shore in the deeper water for washing away the pollutants. The discharge from SAFCO fertilizer complex is carried out in a big pipe to the sea but not in the deeper waters. There is a programme at SAFCO to extend the pipe of discharge.

Q: Mustafa Badr El-Din, PICO, Kuwait:

It appears that liquid effluents at SAFCO are not treated which means large losses of both ammonia and water. As technology now exists to recover ammonia and recycle water at low cost, do you plan to implement a pollution control project in that field?

A: Abul Huda, SAFCO, Saudi-Arabia:

We have noticed , in particular, 50 mg of ammonia/litre in the water discharged to the sea is higher than limits in many countries.Furthermore, the water facilities which we have at SAFCO are guite sufficient for both steam and water production. have multi flash evaporators "two units" and six boilers. We Recovery of water of course at present time is not necessarily as SAFCO is concerned. Regarding the 50 mg/litre, this actually is the upper limit, we have much less than that at SAFCO. It is not economical to recover the ammonia at present time. The only treatment we have for treating effluents at present time is internal treatment for blown down from cooling tower to reduce chromate level from 20 to 3 ppm. The suspended solids are within acceptable level while pH is in the normal range and all other parameters are in lines.

Q: Dr. Pachaiyapan, FAI, India:

In the phosphogypsum disposal, have you considered the UNIDO report submitted by Mr. Schmidt to the Syrian Government around 1978 for cement-sulphuric acid production? If not, what are the difficulties you encountered in using your phosphogypsum? Did you carry any laboratory scale investigations on phosphogypsum? You may attempt the method developed by Madras Fertilizer Ltd. using flue gas. We are ready to supply more details.

A: Seif El-Din Atfeh, Ministry of Industry, Syria:

Mr. Schmidt suggested to the Syrian Government to transport the phosphogypsum by rail about 40 km to the east of the site , but we noticed that any transport by rail or truck is not viable, then the technical committee decided to apply the phosphogypsum slurry pumping because it was almost 50% less in cost than any other method.

The second point about Mr. Schmidt report was that he indicated that there is a connection between the water accumulating in certain depressions near by the proposed site for phosphogypsum and the lake itself. I did not agree at all with this opinion. Per haps Mr. Schmidt was not able within a very short time to examine the geological and hydrogeological situation in the area, because of the impermeable structure of the surface bed, there is no connection between surface water accumulated in depressions and the lake which is about 12 m lower than the level of phospho gypsum site. From this point of view there is no fears at all from underground pollution.

Regarding air pollution indicated by Mr. Schmidt, we believe that there will be no air pollution, because phosphogypsum is transported as slurry.

Regarding utilization of phosphogypsum to produce either cementsulphuric acid or others. This point was discussed by the technical committee where they noticed that to wash phosphogypsum they will need 4-5 cubic meter of water per ton of phosphogypsum, so if you consider full capacity, you will need 1.2 million cubic meter of water, and then you need drying. Since water is scarce in Syria, and natural gypsum geographically distributed in very convenient places of the country, therefore we think that there is no necessity to use phosphogypsum as additives in cement production. The production of ammonium sulphate, however we have surplus ammonia in Syria, but water balance is not helpful. Regarding the recovery of Sulphur from phosphogypsum, The present price of Sulphur "160 \$ / ton" and expected increase may encourage to investigate this process. We would be grateful if Dr. Pachaiyapan could supply us by any information about this process.

Q: Mustafa Badr El-Din, PICO, Kuwait:

Does the ammonia/ urea plant include liquid effluents treatment system? or do you entirely depend on the biological treatment system for all effluents?

A: Seif El-Din Atfeh, Ministry of Industry, Syria:

The proposal waste water treatment system includes a biological section to remove the oxidizable carbonaceous contaminants, and at the same time hydrolize the urea into ammonia and CO_2 . Ammonia and nitrates are subsequently removed by means of selective cation and anion exchanger in which resins are protected against eventual solids build up by sand high pressure filter.

Q: Dr. Ali Shyoukh, Arab Potash Company, Jordan:

What is the silica content of water feed to the reverse asmosis unit?

A: <u>Ma'an Rashad, State Enterprise for Fertilizers, Iraq</u>:

Actually this question is specific especially in the Middle East and , before I answer this question I would like to introduce something about silica content in the region. Most of our Middle East area, the water contains high silica. In my country the silica content seasonaly of low change but the highest, the peak point is around 10-15 ppm, and as to treat such water by reverse osmosis, this figure has a relation with the recovery rate by the reverse osmosis unit itself. In Saudi-Arabia(e.g.) nowadays for the area of International Airport, they use water from the well containing around 22ppm of silica and they want recovery rate of more than 85%.I was in Japan and discussed this thing there, but contractor can not exceed the recovery rate at this figure, 22ppm, because there is a connection between silica content in the feed water and the recovery rate of the whole \circ smosis unit .

So in the design specifications we can not reach more than 140ppm of silica in the brine water"140ppm of silica is the maximum". Silica content in the feed water also has a relation with temperature, so in the Middle East, we have another problem for reverse osmosis process. Of Course, there is a new membrane to deal with temperature more than 30° C " $30-35^{\circ}$ C". In Iraq we are at the safe side, because our recovery rate is calculated according to the total hardness and not to the silica content which reach 15ppm while the total hardness is 800ppm which was taken as design figure. It means that we can operate our plant with 85% recovery rate with no problems in the brine solution.

 Several questions were raised on the paper of Mr. P. Goossens from Amafilter, Holland. The following are the questions and their answers:

- Q: Where do you find limitation in the installation of your brink mist eliminators in existing plants?
- A: There will always be some limitation in installing our brink mist eliminator, hereby we think at space, energy loss, efficiency cost but there also are a lot of other factors (catalyst, less corrosion, less efficient and less power consuming installation) which can easily solve the above limitation factors.
- Q: at is the necessary pressure drop in the brink mist eliminators to reach the high efficiency quoted in your paper?
- A: We do not need a pressure drop in our brink mist eliminators in order to achieve the high efficiency. Different factors affect the pressure drop noted in our system:

-	Internal factors	:									
	- Fiber		size: diame	te	r/ 10	ength					
		-	material :	gla	ass,	teflo	on ,	,]	polyprop	oylene,	
				ce	rami	2					
	- <u>Packing</u>	-	thickness								
		-	density								
		-	design								
~	External factors	:									
	- <u>Ga</u> s	-	flow, veloc	it	Y						
		-	properties	of	the	gas	:	-	viscosi	ty	
								-	velocit	:y	
	- Mist	-	properties	of	the	mist	:	-	liquid	tension	
									surface	2	
								-	liquid	viscosi	ty
								-	liquid	density	_
			mist loadin	a						-	

- particle size of mist

- Q: Would you also install the "shroud system" on prill towers in new projects? If so is your anti-pollution installation a real environmental protection or is it an optical surgery?
- A: Yes, the shroud system was installed on newly build prill towers as in our references at: - ICI (Imperial Chemical Industries- Billingham) - SAI (Scottish Agricultural Industries- Edinburgh) - CDF (Chemie de France) As for the second question: No, our anti-pollution installation is not an optical surgery but is only a real effective environmental protection system. The limit of 10mg/Nm3 and 20 percent capacity which we indicated is a standard limit set by the EPA in the USA (Enviromental Protection Agency) and accepted by European Antipollution authorities for new plants.
- Q: What are the advantages of BME over Venturi scrubber and ESP Which are less common equipment for removal of mist from a sulphuric acid plant.

- A: Having in mind absorption towers, nowadays 90 percent of these towers are equipped with mist eliminators and only 10 percent with Venturi scrubbers, when almost no electrostatic precipitator(ESP) was installed in the last ten years. The advantage of the mist eliminator versus the Venturi lays in easy handling, maintenance, easy installation, reliability, high efficiency, lo. pressure drop and long life (more than 10 years).
- Q: Advice what the proper situation is to allocate the Brink Mist eliminators in sulphuric acid plants(single or double absorption process) or to use the scrubbing ammonia technique to control pollution.
- A: The difference between the two systems depends on the final goal which should be achieved regarding SO₂,SO₃, H₂, SO₄ emissions. While the mist eliminators would reduce SO₃ and H₂ SO₄ emissions, the scrubbing ammonia system would reduce the SO₂ emissions. But mist eliminators would be used in the last case to reduce the emission from the scrubbing tower in the ammonia scrubbing system.
- Q: Does Brink mist eliminators remove acid vapours?
- A: Yes, Brink mist eliminators remove acid vapours but note that in this case the fiber bed would be sprayed by a recerculating solution.
 Examples for SO₃, HCl, oleum are already designed with success.
- Q: What is the period after which the BME should be maintained and cleaned in a well operated sulphuric acid plant equiped with such equipment.
- A: The answer is relatively simple. Once the BME are installed no further maintenance is required.
- Q: M. Murad, State Enterprise for Phosphates, Iraq.

Have you measured the ground level concentration of the pollutants $(SO_2, NO_{x...etc.})$ before and after your improvements achieved by reducing the total quantity of pollutants as shown by you? and what was the result if any?

A: K.Duns, QAFCO, Qatar:

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I think these measurements have been done and I will try to obtain the results.

Q: <u>M. Ezzat, AFCFP, Kuwait</u>:

Could you give us some information regarding the liquid effluent at QAFCO and what is the effect of gaseous pollutants on the neighbouring area?

A: <u>K. Duns, QAFCO, Qatar</u>:

QAFCO uses sea water for cooling. The condensates from urea and ammonia plants are recycled and used again in the complex. There is small amount of liquid effluent, e.g. blow down and ion exchange regeneration effluent which are dumped into the outlet sea water. The effluent to the Gulf is monitored. There is no evidence that pollutants from QAFCO are troubling the extended area 11 km away from the plant.

Q: Abul Huda, SAFCO, Saudi-Arabia:

The flaring of acid gases from the sulphur removal unit will create a serious pollution hazard. Do QAFCO intend to utilize H_2S to produce sulphur?

A: <u>K. Duns, QAFCO, Qatar</u>:

QAFCO is considering at present time building a third sweetening plant to treat off-shore associated gas. Sulphur recovery has been discussed in connection with this as phase two of the project.

- Q: Regarding ammonia recovery from purge gas at PIC, to what limit ammonia is reduced? Are you thinking of recovering hydrogen from purge gas?
- A: Fahed Fahmi, PIC, Kuwait:

Ammonia concentration in purge gas is brought down from 3-6% to 0.2-0.4%. The recovery of hydrogen from purge gas is under our top priority study. We may use it also as a direct fuel gas. Hydrogen recovery can be done through selective absorption system (molecular sieve) which we are trying to find out whether it is economically justifiable.

Q: <u>M. Ezzat, AFCFP, Kuwait</u>:

Could you tell us about the condensate treatment at PIC?

A: Fahed Fahim, PIC, Kuwait:

All process condensates from ammonia plants are treated and utilized as boiler feed water, while process condensates and other waste water of urea plants are being treated in hydraulizer. All effluents from hydraulizer are pumped 16 km away from the plant to be used for irrigation. THIRD DAY: Tuesday , November 17th.

<u>Chairman</u>: Dr. Mohamad Seif El-Din Atfeh, Ministry of Industry, Syria. <u>Rapporteur</u>: M. Ezzat, AFCFP, Kuwait.

* <u>Morning Session</u>:

- 13- Fluorine Recovery in the Phosphate Fertilizer Industry.
- 14- Pollution Aspects in Pan Granulation of Straight Nitrogen Fertilizers.
- 15- The Wet Gas Sulphuric Acid Process for Treatment of Lean H₂S Gases and Other Sulphurous Off-Gases.
- 16- Anti-Pollution Performances in Sulphuric Acid Plants.
- 17- Possibilities of Improving the Conversion Efficiency in Existing Sulphuric Acid Plants Designed as Double Catalysis and Based on Sulphur Combustion.
- * Discussions:
- Afternoon Session:
 - Recommendations

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in the Phosphate Fertilizer Industry

A. Abstract

This paper presents important facts and parameters to be considered when planning a fluorine recovery unit for the phosphate fertilizer industry.

Typical processes and their technical parameters will be highlighted, the use of fluosilicic acid will be discussed and some information on the economic aspect of such units will be provided. Introduction

In the past, little attention was paid to the emission of gasous fluorine compounds in the fertilizer industry. Today fluorine recovery is absolutely necessarc because of strict environmental regulations which demand drastic reductions in the quantities of volatile and toxic fluorine compounds emitted with the waste gas. These compounds have now to be recovered and to be converted into either harmless by-products for disposal or - more desirable into marketable products.

Most phosphate rocks mined today, contain an average of 3 - 4 % fluorine as an undesirable impurity. When they are processed to phosphoric acid (see figures 1, 2) fluorine compounds (SiF₄ and HF) are relased at various process stages. During the production of phosphoric acid from rock phosphate and sulphuric acid the calcium fluoride present in the rock is converted, by reaction with the silica into fluosilicic acid (see equations of figure 3).

There are 3 main areas in a phosphoric acid plant where fluorine has to be recovered:

Reaction, filtration and evaporation.

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By : Reinhard Anders. Lurgi. Chemie / Germany.

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Approx. 20 - 30 % of the fluorine which enters the phosphoric acid plant in the rock phosphate remains in the product phosphoric acid (54 % P_2O_5). Of the remainder about 5 - 10 % is evolved from the reactor, approx. 30 % leaves the process with the gypsum and approx. 40 % is evolved from the concentrators (see figure 4).

Reactors and filters are usually exhausted to maintain a slight vacuum in order to prevent fumes from escaping into the environment. These fumes in addition to SiF_4 and HF contain droplets of acid, slurry, occasionally entrained foam and in the case of the reactor some phosphate dust. The corresponding gas cleaning is executed at ambient pressure. In the acid concentration section or in the evaporation cooler, the vapours contain mainly SiF_4 and HF, but may also carry - depending on operating condition - droplets of acid and slurry and/or some foam. As these vapours have to be cleaned before reaching the condenser, scrubbing is done under vaccum.

C. Fluorine Recovery (Typical processes)

1. Fluorine recovery at atmospheric pressure (as used in single and triple superphosphate plants and in weak phosphoric acid production). - Process I. The gases from the above mentioned plants containing fluorine mainly in the form of silicon tetrafluoride (SiF_A) are extracted from the reaction vessel and fed to a venturi scrubber in which the silicon tetrafluoride is absorbed, forming, fluosilicic acid (H_2SiF_{κ}) and silica (SiO₂) (Fig. 5). The scrubbing liquid is diluted fluosilicic acid. To increase the scrubbing efficiency (up to 99 %) two or more venturi units are arranged in series. Dust can be eliminated first, if necessary, in a special scrubber. Precipitated silica will be removed from the product by filtration. The concentration of the formed fluosilicic acid, depending on its use, is maintained between 18 and 25 %. The higher the concentration of the acid, the lower is the washing efficiency of a single stage scrubbing unit.

The P_2O_5 content of the fluosilicic acid amounts to approx. 100 ppm (18 % H_2SiF_6). The maximum throughput of a single stream plant is approx. 50,000 Nm³/h.

2. Fluorine recovery under vacuum used in the concentration of phosphoric acid from 30 - 50 P₂O₅ and in evaporative cooling during phosphoric acid production The superheated vapours from the flash vessel of the phosphoric acid concentration plant first pass through a high-efficiency entrainment separator. This is essential to reduce the P_2O_5 contamination of the vapours and is particularly important if the product fluosilicic acid is to meet a high purity standard. The collected mixture of dilute phosphoric and fluosilicic acid from the entrainment separator is sent back to the concentration unit and thus does not represent a loss of either fluorine or P_2O_5 . The cleaned vapours are then fed to a fluorine scrubber, where silicon tetrafluoride and hydrogen fluoride are absorbed using circulating fluosilicic acid as scrubbing liquor. Fluosilicic acid (18 % - 25 %) is withdrawn continuously under density control and the corresponding amount of water is introduced into the system (Fig. 6). For economic reasons, it is desirable to achieve the required fluorine recovery with one scrubbing stage only.

The attainable fluorine recovery largely depends on the fluorine content of the incoming vapour as well as the concentration and the temperature of the fluosilicic acid produced. The P_2O_5 content of the fluosilicic acid is mainly dependent on the P_2O_5 :F ratio in the vapours from the flash vessel and on the efficiency of the P_2O_5 separator. Figure 7 shows the fluorine recovery efficiency versus the fluorine content of the vapours for a single stage scrubbing unit at different concentrations of circulated fluosilicic acid.

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D. Marketable products

1. Fluosilicic acid

Today fluosilicic acid has only limited applications for direct use but it can be used as a raw material for the production of aluminium fluoride and cryolite (as described later). Its direct use is restricted (sterilizing and impregnating agent in breweries and for wood protection and for fluoridation of drinking water) because of its low concentration and the relatively high amount of impurities, as shown below for a typical acid composition;

H ₂ SiF ₆	18 - 25 %	
P205	100 p.p.m.	
Fe ₂ 0 ₃	70 p.p.m.	
so ₄	1,000 p.p.m.	
Cl	1,000 p.p.m.	

2. Aluminium fluoride

Aluminium fluoride (AlF_3) and cryolite (Na_3AlF_6) are used to reduce the melting point of alumina in electrolysis plants producing aluminium metal. Approx. 20 - 30 kg aluminium fluoride and about the same amount of cryolite are consumed per tonne of aluminium, depending on the specific process conditions. The P₂O₅ content of these flux materials should be as low as possible in order to minimize losses of electrical energy.

The modern processes using fluosilicic acid are devided into the acid and the ammonia process. The acid process is described below as it is already commercially used since 1960.

For the AlF₃ production aqueous fluorosilicic acid is heated up to reaction temperature and fed together with the corresponding amount of aluminium hydroxide to the reactor, (see figure 8). Under careful control of temperature, pH-value and time of the exothermic reaction, silica is precipitated.

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After the reaction the slurry is fed to a centrifuge where the silica is separatet and the clear aluminium fluoride solution is discharged to one of the crystallizers (batch-operation). The by-product silica can be used as filler material in the plastic industry. After completion of the cristallization the slurry is fed to a belt filter where the solid aluminium fluoride trihydrate is separated and discharged into a drier/calciner.

The calcination is carried out under special conditions to minimize hydrolysation of the AlF_3 (see figure 9).

The anhydrous aluminium fluoride is cooled and packed as final product. The liberated water vapour and the offgases pass through a cyclone, a bag filter and a scrubber, before they are released to the atmosphere. The separated product dust material is fed back to the calciner and to the cooler respectively.

The largest single stream plant on line has a capacity of 15,000 tpy AlF_3 . The lowest economically feasible plant capacity is 3,000 typ AlF_3 .

3. Cryolite

There are no significant differences between the various processes for manufacturing cryolite.

In one of them fluosilicic acid is neutralized with aluminium hydroxide and soda ash forming aluminium fluoride solutions which after separation of the precipitated silica react to cryolite (see figure 10).

- Hydrofluoric acid and fluorspar A number of processes have been developed, but none has so far been used industrially.
- E. Economic aspects

The investment cost of a 150,000 tpy phosphoric acid plant are increased by approx. 5 % when adding fluorine recovery units as described under processes I and II.

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The increase of the production cost of the phosphoric acid plant is negligible in case the fluosilicic acid can be sold as by-product.

Examples of production cost calculations are shown in figures 11 and 12.

F. Conclusion

Due to the present pollution standards (fluorine containing gases of new phosphoric acid plants are limited to max. 5 mg F/Nm^3 exit gas and those of existing phosphoric acid plants to max. 20 - 50 mg F/Nm^3 exit gas) the installation of a fluorine recovery unit becomes mandatory in most countries of the world.

For the production of phosphoric acid, fluosilicic acia and aluminiumfluoride the following relation of the production figures can be provided (see diagram 13).



FLIESSCHEMA FÜR DIHYDRAT-VERFAHREN

FLOW DIAGRAM FOR DIHYDRATE PROCESS

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FLIESSCHEMA PHOSPHORSÄURE-KONZENTRIERUNG



FLOW DIAGRAM PHOSPHORIC ACID CONCENTRATION



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FLUCRIME RECOVERY HUDER ATMOSPHERIC PRESSURE FLOURE 5

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Fluorine recovery under vacuum







MICROCOPY REPORTION TEST CHART HATCHARTS HEALTER CHARTAR MICROCOPULATER MEDIA MICROCOPULATER MEDIA MICROCOPY REPORT FLUORINE RECOVERY EFFICIENCY OF A SINGLE-STAGE FLUORINE SCRUBBER IN RELATION TO THE FLUORINE CONTENT OF THE VAPOURS

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Figure 7



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SUMMERY EQUATIONS FOR ALUMINIUM FLUORIDE

 $2 \text{ AL}(\text{OH})_3 + \text{H}_2\text{SIF}_6 + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ ALF}_3 \cdot 3\text{H}_2\text{O} + \text{SIO}_2$

FIGURE 9

SUMMERY EQUATIONS FOR CRYOLITE

 $\begin{array}{rcl} H_{2}SIF_{6} + 2 & AL & (0H)_{3} \longrightarrow 2ALF_{3} + SIO_{2} + H_{2}O \\ H_{2}SIF_{6} + 3NA_{2}CO_{3} \longrightarrow 6NAF + SIO_{2} + 3CO_{2} + H_{2}O \\ 2ALF_{3} + 6NAF \longrightarrow 2NA_{3}ALF_{6} \end{array}$



Production cost for a 9,000 tpy (100 %) fluosilicic acid plant (if H_2SiF_6 is sold as by-product)

· -

		Approx.	450,000 DM
7.	RAW MATERIAL		-
6.	Labour		-
5.	Insurance, fees	APPROX.	30,000 DM
ų.	UTILITIES (POWER, WATER)	APPROX.	200,000 DM
3.	REPAIR AND MAINTENANCE (4 %)	APPROX.	40,000 DM
2.	Depreciation (7%)	APPROX.	120,000 DM
1.	Interest charges on loan capital (10 %)	APPROX.	60,000 DM

Related to the production cost for a 150,000 try phosphoric acid plant (approx. 600 DM/t), an increase of 3 DM/t $(\frac{450,000 \text{ DM}}{150,000 \text{ try}})$ is calculated (less than 1 %).

FIGURE 11

IN CASE THE FLUOSILICIC ACID (9000 TPY) HAS TO BE NEUTRALIZED, THE FOLLOWING PRODUCTION COST CALCU-LATION CAN BE MADE

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1.	INTEREST CHARGES ON		
	LOAN CAPITAL (10 %)	APPROX.	80,000 DM
2.	DEPRECIATION (7 %)	APPROX.	160,000 DM
3.	REPAIR AND MAINTENANCE (4 %)	APPROX.	60,000 DM
4.	UTILITIES	APPROX.	230,000 DM
5.	Insurance, Fees	APPROX.	40,000 DM
6.	Labour	APPROX.	80,000 DM
7.	RAW MATERIAL (LIME)	APPROX.1	,000,000 DM
		APPROX.1	,650,000,- DM

Related to the production cost for a 150.000 tpy phosphoric acid plant (approx. 600.- DM/t), an increase of approx. 11.- DM/t ($\frac{1.650.000 \text{ DM}}{150.000 \text{ TPy}}$) is calculated (less than 2 %)

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FIGURE 12



14- POLLUTION ASPECTS IN PAN GRANULATION OF STRAIGHT NITROGEN FERTILIZERS BY THE NORSK HYDRO HIGH TEMPERATURE PAN GRANULATION (HTPG) PROCESS

SUMMARY

The Norsk Hydro High Temperature Pan Granulation (HTPG) process for ammonium nitrate, urea, calcium ammonium nitrate and calcium nitrate presents a number of advantages such as low investment and operating costs, high product quality and low air pollution compared to prilling and other granulation techniques.

In the HTPG process fertilizer melt is sprayed on a moving bed of granules in the inclined, rotating pan. The pan has a classifying action, and the recycle ratio is low. The agglomeration process near the crystallization temperature gives a very rapid particle growth, resulting in small equipment requirements. One train of equipment in sufficient up to 800 mtpd capacity.

The process is very flexible to changes in product size specifications. 2 - 4 mm products and products larger than 10 mm may be produced in the same plant only by small changes. The crushing strength of the product granules is normally 2 - 3 times higher than with prilling, and dust formation is low both in the production plant and during handling. Conditioning of pan granulated products may be omitted in some cases, even with bulk transports.

BY : Egil Holte Norsk Hydro a.s , NORWAY In the HTPG process haze from concentrated melts is only mixed with a small amount of venting air and is completely recovered in an economic way. As wet recycle is minimized and no product drying is necessary, the energy consumption is low.

The HTPG process has been in commercial operation for several years in the Norsk Hydro Rjukan Works on forest grade ammonium nitrate, as well as on fertilizer grade ammonium nitrate and calcium ammonium nitrate. Two licensed plants for urea, one for AN and one combined unit for AN/CAN are under construction.

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- 1. INTRODUCTION
- 2. PROCESS DESCRIPTION
- 3. PROCESS FEATURES
- 4. PRODUCT PROPERTIES
 - 4.1 General
 - 4.2 Urea
 - 4.3 AN and CAN
- 5. ECONOMIC ASPECTS
 - 5.1 Investment costs
 - 5.2 Utilities for consumption
- 6. STATUS OF PAN GRANULATION TECHNOLOGY

Enclosure: Principle flow diagram

INTRODUCTION

1.

Forest fertilization in Scandinavia is carried out by aerial spreading. For such purposes Norsk Hydro developed a non dusting, coarse grade (7 - 11 mm) ammonium nitrate (AN) process based on high temperature pan granulation of 99.5% AN-melt. The first production plant for coarse grade AN was started in 1971 at Norsk Hydro's Rjukan Works in Norway.

The coarse grade AN pan granulation process turned out to be a success. The pan granulation technique was therefore extended to other fertilizer products and particle sizes. Today, the pan granulation process is fully developed to produce all nitrogen fertilizers like urea, ammonium nitrate (AN), calcium ammonium nitrate (CAN) and calcium nitrate (CN) on an industrial scale. In addition to Norsk Hydro's own production, the pan granulation process is licensed internationally, and there are two plants for urea and two for AN/CAN under construction.

2. PROCESS DESCRIPTION

The pan granulation of urea, AN, CAN and CN have so much in common that all processes will be described in one. Reference is made to the attached principal flow diagram. Dry solids, normally consisting of recycled material, are fed at a controlled rate to the inclined, rotating pan granulator. In the granulator, a hot, nearly moisturefree fertilizer melt is sprayed on the moving bed of solids. The melt solidifies on the cold particles, and round granules are formed by an agglomeration mechanism. As the granules increase in size, they move upwards in the rotating pan and finally roll over the rim. This classifying action of the pan gives an unusually high granulation efficiency.

The pan temperature is controlled by the rate of solids fed to the pan. An optimum temperature giving fertilizer melt as liquid for the agglomeration with a resulting high growth rate of the particles is found in the range $5-25^{\circ}$ C below the solidification temperature of the fertilizer melt. The recycle ratio controlled in this way is about 1:1 for urea and 0,5:1 for AN and CN.

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The granules leaving the pan are plastic and have a somewhat irregular surface. From the pan they enter the polishing drum where they are exposed to mild mechanical forces and smoothened. A certain cooling also takes place, due to a small vent air quantity and heat losses. No haze is liberated from the granules leaving the polishing drum.

Cooling down to the desired product temperature is performed in normal cooling equipment like a fluid bed cooler or a rotary drum cooler. Cooling may take place in one or more stages. The cooling air may be ambient or conditioned, depending on the climatic conditions at the plant site and the desired product temperature. The dust contained in the exit air is effectively recovered in dry cyclones and recycled to the pan granulator.

The cooled granules are conveyed by a bucket elevator to the product screen. This is a conventional designed screen and could be a double deck, vibrating type screen, with mesh openings to fit the required screen analysis of the product.

Oversize material from the screen is fed to a crusher to reduce the particle size. The crushed material, undersize granules, dust from the cyclones and a balance of on-size material is recycled to the pan via the recycle elevator and the recycle bin.

The product may be sent to the warehouse without further treatment in some cases, or if required it may be conditioned by conventional means.

When a solid filler is required to obtain the desired product formulation, like limestone with CAN, the filler may be added as a dry material directly to the pan. <u>PROCESS FEATURES</u>

1.

The high granulator temperature gives a high net production rate. A commercial size one train pan granulation plant has a capacity in excess of 600-800 mtpd. The pan and other equipment are standard commercial types. As the recycle load is low, the equipment size is minimized. All this leads to low investment cost.

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Operation of the pan is simple and easy to control. The desired pan operating temperature is automatically controlled by instruments, and visual observations are simple because the pan is partly open. Dedusting is performed by a vent hood.

Necessary equipment to meet arti-pollution requirements will be relatively simple because the only particles in the lower- and sub-micron range are contained in a small vent air stream from the pan which is treated in a scrubber. This air stream contains only small dust quantities. The main air flow coming from the cooler contains no "blue haze", and the solids are efficiently collected in dry cyclones.

In a situation where an existing prilling plant is to be revamped, the pan granulation process has proved to be very simple to tie into existing facilities, thus improving product quality and air effluents at a very favourable investment cost.

4. **PRODUCT PROPERTIES**

4.1 General

The granules are well rounded and have no sharp edges. They are well suited both for bulk blending as well as direct application by conventional equipment. The particle size distribution of the products can be controlled within wide ranges by minor changes of operating parameters. In the same plant, normal fertilizer grade, i.e. 2-4 mm granules, can be made, as well as a 7-11 mm forest grade product.

The mechanical strength of the products is much superior to prilled materials, and less dust is created during handling. Further, the bulk density of pan granulated fertilizers is very high.

Storage tests show that pan granulated products have excellent storage properties. Depending on the climate, conditioning of the products may even be omitted in some cases.

4.2 Urea

Addition of formaldehyde to the urea melt can be applied but is not needed. Mechanical strength tests have shown that pan granulated urea without formaldehyde is more

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than 2 times harder than prills of similar size with formaldehyde. Granules with formaldehyde are more than 3 times harder than similar prilled particles. Due to the short retention time of hot material in the pan, undesired side-reactions are greatly suppressed. For urea, the increase in biuret content from melt to final product is concistently lower than 0.1% absolute. Another feature of the pan products is the low water content. For urea this is normally between 0,05 and 0,1% due to evaporation of water from the pan.

For slow-release fertilization of water-logged rice areas, so-called urea "Super Granules" are presently being field tested with promising indications. These granules with mean diameter from 11 mm to 16 mm are sucessfully produced in the pan granulation process.

4.3

Ammonium nitrate and calcium ammonium nitrate

Forest grade AN product has been produced by Norsk Hydro since 1971. The same plant has been modified to produce both AN and CAN with the normal fertilizer grade particle size of 2-4 mm. For AN, bulk density of 1000 kg/m³ and hardness values of 2,5 kg are obtained. For CAN, corresponding values are 1030 kg/m³ and 3,0 kg. With magnesium nitrate as a melt additive, excellent storage properties are obtained with a moisture level of 0,25-0,30%.

5. <u>ECONOMIC</u> ASPECTS

5.1 Investment costs

The investment cost of a pan granulation plant is relatively

- low due to the following facts:
- Single train capacity up to 800 t/d
- Recycle ratio is lower than 1:1
- No need for product dryer
- Low air volumes that require scrubbing

Compact arrangement of equipement

Typical total investement costs for a grass roots pan granulation plant taking battery limits at the supply line for concentrated melt and at the conveyor for product to store, would be about US \$ 5,5 mill. for a 750 mtpd plant and about US \$ 8,0 mill. for a 1200 t/d plant. The figures are general for all the products, assuming European conditions, and will

of course depend on the actual conditions of the specific project. In revamping cases, i.e. when an existing prill tower is replaced by a pan granulation plant, the investment may be considerably reduced, depending on the use of available equipment.

5.2 Utilities consumption

The only steam consumption of a pan granulation plant is for evaporation of scrubber solution and conditioning of cooling air, when required. However, the latter amount is the same as for other prilling and granulation processes. For scrubber solution, a maximum of 1% of the net product is recycled to the evaporation section. This means a considerable saving in steam consumption over other granulation processes.

The electric power consumption is low due to low recycle ratio and low energy consumption needed to recover effluents. A typcal consumption figure would be 25-30 kWh per ton of fertilizer product.

Process and cooling water is only needed for the reconcentration of scrubber solution, which is less than for other granulation processes. Maximum values are 0,01 tons of process water per ton of product and 0,5 m³ of cooling water ($t = 10^{\circ}$ C) per ton of product. Depending on the size and integration with other sections of the fertilizer plant, 1.5 - 2 operators are needed per shift for the pan granulation plant. As all equipment is of standard design and only one or at maximum two production trains are needed, the maintenance costs of a pan granulation plant are moderate and less than for other conventional granulation technologies. To sum up, the utilities consumption for pan granulation is low, and it is in most cases lower than the consumption of prilling and other granulation processes.

6. STATUS OF PAN GRANULATION TECHNOLOGY

Norsk Hydro has operated a plant of 400 t/d capacity for forest grade ammonium nitrate since 1971. Several industrial scale production runs in this plant has proved the ability of the process to produce fertilizer grade ammonium nitrate and calcium ammonium nitrate as well. A 25 t/d pilot plant for urea has been operated by Norsk Hydro on all urea qualities during several years.

A combined 600 t/d AN and 800 t/d CAN is under construction with the Norsk Hydro HTPG technology by Uhde for Phosphoric Fertilizer Company in Kavalla, Greece.

A plant for 300 sh.tons of urea per day is under construction for the American N-Ren Company in Sudan, Africa, and an identical urea plant is also under construction by N-Ren in Madagascar, Africa.

A plant for 800 t/d AN fertilizer grade is under construction by Cofaz in Pierrefitte-Nestalas, France.

Pan granulation technology for production of nitrophosphates and calcium nitrate are presently being studied by Norsk Hydro. Pan granulation is expected to be an economic interesting alternative, also of these products, in the near future.


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NORSK HYDRO PAN GRANULATION PROCESS FOR UREA, AN, CAN AND CN. PRINCIPLE FLOW DIAGRAM.

"W S A"

15- <u>The Wet Gas Sulfuric Acid Process</u> <u>for</u> <u>Treatment of Lean H₂S Gases and</u> <u>Other Sulfurous Off-Gases</u>

The Topsøe WSA process is a "wet sulfuric acid" technology which can recover up to 99% of the sulfur from practically any kind of sulfurous off-gases, as 94 to 98% concentrated sulfuric acid. The heart of the process is the WSA tower which can be used together with either of two optional Topsøe sub-processes: Catalytic Incineration of combustibles in the gas or Dust-Tolerant Conversion for treatment of dust-laden off-gases from roaster and furnace operations.

In comparing WSA with conventional sulfuric acid processes, the most important difference is that the SO_2 process gas is <u>not</u> dried in the WSA process. This means that there is no minimum limit of sulfur concentration in the feed gas and no maximum water concentration for the process gas, and that SO_3 as well as SO_2 is accepted in gases from roaster and furnace operations. WSA also avoids the formation of dilute acid and the large heat losses involved in cooling and scrubbing the gas upstream of the drying tower in conventional sulfuric acid plants.

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With the catalytic incineration option, all combustibles in the feed gas, such as hydrogen sulfile, hydrocarbons, organic vapors, cyanides, ammonia etc., are, as a first step in the process, oxidized completely with air to CO_2 , H_2O , SO_2 , and N_2 over a non-noble metal oxidation catalyst. Thermal incineration can be used only when the heating value of the gas is high enough to support combustion by itself. All the heat of combustion of the gas, heat of oxidation of SO_2 to SO_3 , and even most of the heat of hydration of SO_3 to H_2SO_4 (gas) are recovered in the form of high-pressure steam. Furthermore, WSA plants are autothermal (i.e. use no support fuel) for gases with a content of combustibles corresponding to heating values as low as 250 kJ/Nm³, equivalent to about 1% H_2S .

Table 1 compares the ranges of SO_2 -concentrations in practice for various SO_2 off-gas processes. The table also applies in principle for any other off-gases after incinetation of sulfur compounds to SO_2 . The WSA process is usually the most economic alternative for cleaning gases with 0.3 to 7% SO_2 plus SO_3^- . For desulfurization of more dilute offgases, such as flue gas from power stations burning fuels with 1 to 2.5% sulfur, limestone absorption processes are usually cheaper. Production of sulfuric acid by burning liquid sulfur is more economic by conventional acid processes than by WSA.

APPLICATIONS OF THE WSA PROCESS

- <u>Gasification Plant Off-Gases</u>: When producing synthesis gas from coal or heavy oil for use in manufacturing ammonia, methanol, hydrogen, SNG, etc., the sulfur present in the fuel will appear in the raw gas mainly as H_2S and to a lesser extent as COS. These are removed together with the CO_2 by scrubbing the gas with physical or chemical solvents. The stripped off-gas (consisting mainly of these compounds

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and water vapor) can be fed directly to a WSA plant which recovers the sulfur values as concentrated sulfuric acid and the heat values as high-pressure steam. In contrast to Claus plants, WSA does not require that the H_2S off-gas be concentrated or pretreated upstream of the plant.

- <u>Coke-Oven Off-Gases</u>: Coke ovens produce complex gas mixtures containing H_2S , COS, organic sulfur, and large concentrations of NH₃ and HCN, which can be fed directly into a WSA plant. The cleaned ff-gas will contain only CO₂, H₂O, N₂ and normally less than 1000 ppm SO₂.

- <u>Natural-Gas-Treating Off-Cases</u>: When the CO₂:H₂S ratio of the off-gas from natural gas treating plants is so high that it gives problems in conventional sulfur-recovery plants, WSA can be used to make sulfuric acid directly for the local market.

- <u>Claus Plant Off-Gases</u>: While it is desirable to recover the bulk of the sulfur in the form of elementary sulfur, it is expensive to obtain very high yields at low throughputs in a sulfur-recovery plant. The optimal solution may be to put the off-gas from the Claus plant to a WSA plant.

- <u>SO₂-Laden Off-Gases</u>: Furnace and roasting operations, combustion of low-grade, high sulfur fuels and incineration of spent acid and wastes etc. all produce dirty off-gases which only need to be dry dedusted to 100-200 mg dust/Nm³ before entering the "dust-tolerant conversion" process step in the WSA plant. There are no limitations on the SO₃ concentration or the H₂0:SO₂ ratio of the feed gas.

TWO WSA PLANTS NOW IN OPERATION

Two 18 MTPD Topsøe WSA units with catalytic incineration have been successfully on stream since January and June 1980 respectively at SUPRA AB's plants in Kvarntorp and Köping, Sweden. These units clean sulfurous off-gas streams, typically with 10% H_2S + COS in CO₂, from gasification of high-sulfur fuel oil used as feedstock for production of ammonia. At least 99% of the sulfur is recovered in the form of 98.5% concentrated sulfuric acid. The cleaned off-gases, from the WSA plants contain typically less than 600 ppm SO₂ and less than 20 mg/Nm³ of acid mist.

PROCESS DESCRIPTION

The Topsøe WSA process for off-gases containing combustibles comprises three steps: Catalytic or thermal incineration, oxidation of SO_2 to SO_3 and, finally, absorption and concentration of the product acid in the WSA tower.

Fig. 1 shows a typical process scheme and operating conditions for WSA with catalytic incineration treating sulfurous off-gases with heating values up to $8000-10,000 \text{ kJ/Nm}^3$. Operating conditions refer to a case where the plant is used for treating an off-gas with 12.5% H₂S + COS in CO₂ as produced in the casification of 500 MTPD heavy fuel oil with 3.5% S.

In the first step, the feed gas is mixed with air before it is fed directly (without preheating) into the saltcooled tubular reactor for <u>catalytic incineration</u> (and the subsequent catalytic conversion of SO_2 into SO_3). A surplus of air is required in order to obtain the desired conversion (typically 98 to 99%) of SO_2 into SO_3 .

In the upper section of the reactor all combustible compounds in the gas are oxidized to CO_2 , H_2O , N_2 , and SO_2 over a special sulfur-resistant catalyst which is loaded in tubes surrounded by molten heat-transfer salt. The oxidation starts when the gas has been heated to about $200^{\circ}C$ in the tubes. No fuel other than the combustibles in the gas is

needed to maintain complete autothermal oxidation of hydrogen sulfide, carbonyl sulfide, organic sulfur compounds, ammonia, cyanides or other combustible compounds, provided the total content of combustible materials is equivalent, in terms of heating value, to a content of 1-1.5% $\rm H_2S$ in the off-gas feed.

The second step is the <u>catalytic conversion</u> of sulfur dioxide into sulfur trioxide, reaction (2) in Table 2. 90-95% of the conversion takes place on a vanadium catalyst placed in the lower section of the salt-cooled catalyst tubes, below the incineration catalyst. Most of the remaining SO₂ is then converted in an adiabatic layer of vanadium catalyst placed in the same reactor below the catalyst tubes. The special ring shaped, low temperature vanadium catalyst requires a minimum operating temperature of 410° C which is maintained by controlling the inlet temperature of the salt used to cool the reactor.

Downstream of the incinerator/converter the gas is cooled to 270-280°C with molten salt in the heat exchanger. The temperature of the coolant (salt) must be kept a safe margin above the sulfuric acid dew point of the gas. In the heat exchanger most of the SO₃ is hydrolyzed to H_2SO_4 in the gas phase, reaction (3) in Table 2.

A large part of the heat of SO₃ hydrolysis is utilized for steam production in the WSA process, while in conventional acid plants it is all lost as low-grade heat in the acid coolers.

In the third step, the gas passes from the gas cooler/SO₃ hydrolyzer to the <u>WSA tower</u> in which hot absorption and mist agglomeration take place in the upper section of the tower, and concentration to commercial-grade concentrated acid takes place in the lower section. The acid them flows down

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through an internal weir between the two sections. The heats of absorption and of cooling the gas to $80-90^{\circ}$ C are removed by circulating acid (of approx. 90% strength) which in turn is cooled in an acid cooler. The heat is given off to cooling water either directly or through an intermediate, closed cooling water loop in order to avoid the risk of polluting the external cooling water with acid.

Fig. 2 shows another version of the WSA process with thermal incineration for off-gases with heating values higher than about 9000 kJ/Nm³. The SO₂ conversion can take place either in a salt-cooled reactor (with only vanadium catalyst), or in a converter with four intercooled adiabatic beds. In the latter case, salt or boiling water at 50-80 bar can be used as coolant in the gas coolers between the beds.

Fig. 3 shows the WSA lay-out for treating dilute H_2S cff-gases (from chemical plants or Claus plants) with heating values corresponding to about 2% H_2S . Here the catalytic incineration and conversion of SO_2 can take place in two adiabatic beds, the excess heat being used directly for generation of high-pressure steam. Conventional acid processes could hardly be used because the SO_2 concentration is too low to produce sufficient acid to dry the process gas.

ADVANTAGES OF WSA

Concentrated Product Acid

The concentration of the product acid depends to some extent on the water concentration in the gas phase. With less than 5-8% of surplus H_2O in the gas, the concentration is around 98% H_2SO_4 , but even with 30 to 50% H_2O in the gas phase product acid concentrations from 94 to 93% H_2SO_4 respectively can be obtained.

Mist-Free Stack Gas

Under normal operating conditions there will be about 100 mg (or less) of acid mist and acid vapor per Nm³ in the gas leaving the absorption zone. However, a high-efficiency mist filter is installed in the top of the WSA tower in order to prevent mist emission during start-up or misoperation of the plant. At normal conditions the filter reduces the H_2SO_4 concentration to about 10 mg/Nm³ of mist and acid vapor in the stack gas.

Easy Operation

The operation of a WSA plant is insensitive to large variations in feed gas composition and load. The critical parameters - salt inlet temperatures to gas cooler and reactor, acid exit temperature from the weir and gas exit temperature from the absorption zone - are controlled automatically. If the concentration of combustibles falls below the limit for autothermal operation, an electric heater in the salt tank or a burner in the inlet gas is started.

The simplicity of the process and the relatively few process steps - compared to the alternatives: Claus plants and conventional acid plants - also make it easy to operate the plant. The plant may be monitored from the central control room of the main plant and usually does not require additional operators.

Maximum Energy Efficiency

The total amount of heat released in producing 99% concentrated sulfuric acid from H_2S and air is the sum of the heat produced in each of the reaction steps listed in Table 2. This means that the theoretical total heat production is 4.68 MW_t (Megawatt thermal) in the case shown in Fig.l , i.e., for treatment of 4000 Nm³/h CO₂-gas with 12.5% H_2S , assuming all inlet and outlet streams have the same temperature, say 50°C.

In the WSA plant on Fig. 1, about 3.20 MW_t or 68% of the total theoretical heat production of 4.68 MW_t is utilized for the production of medium pressure steam (15-60 bar), giving with 30 bar steam system a net production of 116 t of steam per day. Of the remaining 32% of the total heat release, about 27% are taken up in cooling water, 3% are lost in stack gas (at 80°), and 2% is lost by conduction.

The heat recovery could be increased from 68% to about 76% using the heat produced in the WSA tower for preheating air.

For comparison, the principle features of a conventional sulfuric acid plant, operating on the same feed gas as in Fig. 1, with thermal incineration and drying of the SO, gas are shown on Fig. 4. The conventional plant needs external fuel equivalent to about 100 kg/h of fuel oil for thermal incineration. Furthermore, there would be a net loss of heat to cooling water in the conventional plant which is about 0.83 MW_{+} higher than in the WSA case, due firstly to quench cooling of the SO₂ gas prior to the drying step, secondly to the loss of all SO, hydration heat to cooling water, and thirdly to the extra dilution of process gas by the primary air $(1100-1200 \text{ Nm}^3/h)$ required for the oil burner. All this means that the net steam production for export would be about 84 tons/day of 30 bar steam (after deducting the steam value of the support fuel oil at 16 kg steam/kg oil), which is only about 70% of the steam yield of a WSA plant treating the same gas.

The energy losses as well as production costs would be even higher than in Fig. 4 if sulfuric acid is produced by first producing elemental sulfur in a sulfur-recovery unit and then producing acid from this sulfur in a sulfuric acid plant.

Construction Materials

Carbon steel may be used for all the equipment located upstream of the WSA tower, where the operating temperatures are well above the acid dew point. For the tower section, acid pumps, and acid coolers, acid-resistant ceramics, glass and teflon-lined materials are used. Hastalloy can also be used for the acid coolers.

WSA-PROCESS FOR SO, CFF-GASES

Another important field of application of the WSA process is the treatment of off-gases with 0.2 to 8.0% SO, plus SO, from furnace and roasting operations. Here the first process step is conversion of SO2 into SO3. In the frequent case where the off-gas also contains 20-200 mg dust per Nm³ after dry electrostatic dedusting at 300-420°C of the offgas, the "Topsøe Dust-Tolerant Conversion" process step is used. In this process the dust is separated out as a dry powder at the same time that the SO, is converted into SO,, and none ends up later in the product acid. Fig. 5 shows the principle features of the WSA process combined with Dust-Tolerant Conversion for desulfurization of dust-laden offgases. The overall advantage of the WSA process is obvious compared to conventional acid processes in which the gas must be cooled and scrubbed and the SO3 removed as dilute "black acid" prior to drying the SO₂ gas. Furthermore, the conventional processes cannot be used on gases with less than 4 to 5% SO_2 .

Process:

Stack gas to the atmosphere



SO₂-absorption with regeneration of the absorbent

WSA process (recovers also SO₃)

Conventional sulfuric acid processes





% SO₂ in off-gas



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(1) H₂S + 1 ½ O₂	→ H ₂ O (g) + SO ₂	+518kJ/MOLS
(2) $SO_2 + \frac{1}{2}O_2$	↓ SO ₃	+ 98 kJ/MOL S
(3) $SO_3 + H_2O$ (g)	→ H₂SO₄ (g)	+ 100 kJ/MOL S
(4) H ₂ SO ₄ (g) + 0.11 H ₂ O (g)	→ H ₂ SO ₄	
	(liq., 98%)	+ 57 kJ/MOL S
(5) H ₂ S + 2 O ₂ + 0.11 H ₂ O (g)	→ H ₂ SO₄	

+ 98 kJ/MOL S	+ 100 kJ/MOL S		+ 57 kJ/MOL S		+ 760 kJ/MOL S	
SO ₃	H₂SO₄ (g)	H₂SO₄	(liq., 98%)	H ₂ SO ₄	(liq., 98%)	

Table 2



Fig. 2





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Fig. 3

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Fig. 4



Fig. 5



16- ANTI - POLLUTION PERFORMANCES

IN SULPHURIC ACID PLANTS

1, <u>SUMMARY</u>

MECHIM, AS AN ENGINEERING COMPANY LINKED TO THE NON-FERROUS METAL INDUSTRY, ACQUIRED EXTENSIVE EXPERIENCE IN SULPHURIC ACID PLANT DESIGN. CONSCIOUS OF THE ENVIRON-MENTAL PROBLEMS CAUSED BY THIS TYPE OF INDUSTRY, MECHIM HAS, SOME YEARS AGO, SELECTED TO PROMOTE THE RALPH M.PARSONS DOUBLE CATALYSIS/DOUBLE ABSORPTION PROCESS; AFTER CAREFUL EVALUATION, THIS ORIGINAL PROCESS HAS PROVED TO BE THE MOST ADAPTED ONE TO SOLVE THE AMBIENT POLLUTION PROBLEMS. NOWADAYS, THE INDUSTRIAL EXPERIENCE GAINED BY MECHIM, IN PERU DEMONSTRATES THE MERITS OF OUR CHOICE. HIGH SO₂ TO SO₃ CONVERSION EFFICIENCY, LIKE 99.8 %, AND GREAT FLEXIBILITY IN OPERATION OF THE SULPHURIC ACID PLANT IN PERU ARE THE KEY POINTS OF OUR SUCCESS AND THE GUARANTEES FOR AN ACTIVE FIGHT AGAINST AMBIENT SO₂ CONTAMINATION.

NO DOUBT THAT WE SHALL GET SAME EXCELLENT RESULTS IN TRAK FOR THE LARGE FERTILIZER COMPLEX OF AL-KAIM, WHERE MECHIM IS SUPPLYING STATE ORGANIZATION OF MINERALS WITH THREE SULPHU-RIC ACID PLANTS LINES TOTALIZING A 4,500 MT/D PRODUCTION AND USING THE RALPH M. PARSONS TECHNOLOGY.

By : Dr. J.L. Corbiau from Mechim . S.A. - Belgium

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2. LOCATION OF MECHIM'S RECENT EXPERIENCE

A LARGE INDUSTRIAL COMPLEX HAS BEEN BUILT AT CAJAMARQUILLA, AT 30 KM FROM LIMA IN PERU. THIS PLANT IS ESSENTIALLY AN ELECTROLYTIC ZINC REFINERY, WHICH PRODUCES 101,500 MT SUPER-HIGH GRADE ZINC PER YEAR, AS WELL AS A SULPHURIC ACID PLANT WITH A NOMINAL DAILY PRODUCTION OF 567 MT. THIS INVESTMENT CONSTITUTES AN IMPORTANT INJECTION OF CURRENCY FOR THE ECONOMY OF PERU. FOR THE ENGINEERING AND REALIZATION OF THIS COMPLEX, MECHIM HAS USED THE MOST UP-TO-DATE TECHNICS IN THE MATTER.

The sulphuric acid unit, described in this paper, works following the double catalysis-double absorption process developed by R.M. PARSCNS. It is to be pointed out that the MINERO PERU plant is the first one where the PARSONS process is used for the conversion of sulphurous gases delivered by a zinc concentrate roaster.

THE EXCELLENT SO_2/SO_3 conversion efficiency ENABLES TO RESPECT PERFECTLY THE VERY STRICT ANTI-POLLUTION LAWS APPLIED IN PERU : IN NORMAL OPERA-TION, THE SULPHUR DIOXIDE EMISSION LEVEL AT THE STACK IS ABOUT 200 PPM.

The major demand for H_2SO_4 in Peru is for use in metallurgical plants, installed in different parts of the country. Up~to-now, a part of the acid was

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IMPORTED. THE ENTIRE PRODUCTION OF THE NEW PLANT SHALL BE USED IN PERU WITH, CONSEQUENTLY, AN IMPOR-TANT SAVE OF CURRENCY.

The concentrates coming from several mines of the Andes are roasted in a VIEILLE-MONTAGNE type furnace. The produced calcine is leached by the Jarosite process of ASTURIANA DE ZINC. The purification, electrolysis and melting and casting areas have been developed following the VIEILLE-MONTAGNE/MECHIM know-how.

3. PLANT PERFORMANCES

IN NORMAL CONDITIONS, THE MINERO PERU SULPHURIC ACID PLANT IS ABLE TO REACH PERMANENTLY A HIGH CON-VERSION EFFICIENCY OF 99.75 % - 99.8 % WITH NEW OPERATING PERSONNEL.

- MORE EXPERIENCED PERSONNEL ARE ABLE TO MAIN-TAIN A CONVERSION BETWEEN 99.8 % AND 99.85 % AND REACH LESS THAN 200 PPM SO₂ AT THE CHIMNEY.
- THE VERY GOOD DESIGN OF THE ACID DISTRIBUTION SYSTEM IN THE ACID TOWERS AS THE ADEQUATE CHOICE OF VERY PERFORMANT MIST ELIMINATORS ALLOW A VERY GOOD SO₃ RECOVERY (99,998 %).
- THE GREAT FLEXIBILITY OF THE PLANT MUST ALSO BE POINTED OUT AS IT WAS ABLE TO RUN WITH HIGH CONVERSION EFFICIENCY WITHIN THE FOLLO-WING ACID PRODUCTION RANGE : FROM 515 MT/ DAY TO 600 MT/DAY OF 100 7 SULPHURIC ACID (DESIGN ACID PRODUCTION BEING 567 MT/DAY).

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4. GAS PURIFICATION

THE SULPHUROUS GASES FROM THE ROASTING FURNACE ARE TREATED IN THE WET GAS PURIFICATION SECTION. SPE-CIAL ATTENTION HAS BEEN PAID TO THIS SECTION THE GOOD WORKING OF WHICH BEING OF A UTMOST IMPORTANCE FOR THE BEST PERFORMANCES AT THE CONVERSION AND ABSORPTION AREAS.

AFTER THE GASES HAVE PASSED THROUGH THE EMPTY TOWER AND THE SCRUBBING TOWER, THEY ARE PURIFIED IN THE ACID MIST PRECIPITATORS WHICH ARE THE MOST IMPORTANT EQUIPMENTS OF THIS SECTION.

For this section, we have chosen to install four electrofilters working in parallel. These equipments, each one of them with an individual transfo-rectifier group, have been largely dimensioned so that even during shut-down of one unit, during the cleaning period, a gas purification efficiency of 97 % may still be expected for the whole installation. Afterwards, the gases, optically clear, go through the drying tower which dries the gases up to 0.1 g H₂0/Nm³.

A group a two blowers, working in parallel, blow the total gas flow (max. $80,000 \text{ Nm}^3/\text{H}$) to the catalyst section.

A VERY EFFICIENT NOISE-INSULATION REDUCES TO A MINI-MUM THE NOISE-LEVEL OF THESE EQUIPMENTS.

5. <u>CATALYST SECTION</u>

THE DRY AND COLD GAS LEAVING THE MAIN BLOWERS IS HEATED UP IN 3 HEAT-EXCHANGERS IN SERIES AND SENT TO THE FIRST BED OF A MULTI-STAGE (3 + 1) VANADIUM PENTOXIDE CATALYST CONVERTER,

Exit gas from each of the first 2 beds is split into two streams, each of them being sent to a different heat-exchanger in order to preheat the SO_2 gas stream fed into the first oxidation bed and the exit gas from the intermediate absorption tower. After heat-exchange, the two streams are fed into the next oxidation bed.

EXIT GAS FROM THE FIRST OXIDATION STAGE (THIRD BED), AFTER EXCHANGING HEAT WITH SO₂ GAS FED TO THE FIRST CONVERTER BED, IS SENT TO THE INTERMEDIATE ABSORP-TION TOWER.

BEFORE REACHING THE 4TH CATALYTIC BED, THE GAS IS HEATED UP BY THE GAS LEAVING THIS BED AND BY ONE PART OF THE HEAT GENERATED IN THE FIRST TWO BEDS (AS EXPLAINED HEREABOVE).

AFTER THE SECOND CONVERSION STAGE, THE PROCESS GAS IS COOLED BY HEAT TRANSFER WITH RETURN GAS STREAM FROM THE FIRST ABSORPTION STAGE AND SENT TO THE SECOND ABSORPTION STAGE,

6. PROCESS CHARACTERISTICS OF THE PLANT

THE MINERO PERU SULPHURIC ACID PLANT HAS TWO MAIN PROCESS CHARACTERISTICS WHICH ALLOW TO REACH VERY HIGH EFFICIENCY AND CONFER IT A VERY HIGH THERMAL STABILITY QUITE SIMILAR TO A SINGLE CATALYSIS/ SINGLE ABSORPTION PLANT.

The first characteristic is that the first cata-LYTIC stage is thermically autonomous as the SO₂ Gas fed to the converter is heated up by heat supplies coming from the first catalytic stage. The second characteristic is that the gas going to the second catalytic phase is heated up in three heat-exchangers, two of them transferring heat generated in the first catalytic stage where heat level is high and not disturbed. These two heatexchangers are in fact acting as "external heaters" and allow an excellent control of the Last converting stage where a great driving force is available because of high oxygen to sulphur dioxide ratio and the absence of sulphur trioxide.

THEREFORE A VERY HIGH CONVERSION EFFICIENCY IS OBTAINED REDUCING DRASTICALLY THE AMOUNT OF UNCON-VERTED SULPHUR DIOXIDE LEAVING THE EXIT STACK. GENERALLY SPEAKING, THE PRESENCE OF THE 6 HEAT-EXCHANGERS ENABLES TO ADJUST VERY CLOSELY THE IN-LET TEMPERATURE IN EACH BED AND TO RUN CONTINUOUSLY IN WORKING CONDITIONS ENSURING THE MAXIMUM EFFI-CIENCY.

7. TEST RUN DATA

A 72-HOUR PERFORMANCE TEST HAS BEEN REALIZED IN JULY 1981. THE DATA OBTAINED FROM THE PLANT DURING THIS TEST RUN ARE SUMMARIZED HEREAFTER AND COMPARED TO THE CONTRACTUAL GUARANTEES.

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	UNIT	OFFICIAL TEST-RUN RESULTS	CONTRACTUAL GUARANTEE
- H ₂ SO ₄ PRODUCTION (100 %)	мт/р	590	567
- SO ₂ EMISSION AT THE STACK	PPM	201	500
- CONVERSION PERCENTAGE SO ₂ /SO ₃	ማ ነን	99,78	99.5
- SO ₃ absorption percentage	, J Q	99,99	85 99,95
- H ₂ SO ₄ CONCENTRATION	%	98,58	98.5 ± 0.2

ALL THESE DATA ARE LARGELY WITHIN THE PARTICULAR SPECIFICATION, PARTICULARLY AS TO THE RESIDUAL SO₂ EMISSION AT THE STACK, WHICH WAS LIMITED TO 500 PPM.

8. <u>COMPARISON WITH CONVENTIONAL PROCESS</u> First of all, it is important to set out the characteristics inherent in both processes, R. PARSONS D/C/DA Process (Flow-sheet 1)

There are 6 heat-exchangers and intermediary absorption of the SO_3 formed occurs after the third catalyst bed. It is seen that the first catalytic phase comprises three catalyst beds, that this first

CATALYTIC PHASE IS THERMICALLY AUTONOMOUS, AS THE cold gases containing SO_2 reach the converter after HAVING FLOWN THROUGH EXCHANGERS 1, 2, 3 IN WHICH THE HEAT EXCHANGES TAKE PLACE BY THE HEAT SUPPLIES COMING EXCLUSIVELY FROM THIS FIRST CATALYTIC PHASE. So, this particular arrangement ensures the R. PARSONS DC/DA UNITS GREAT STABILITY IN OPERATION, COMPARABLE TO THAT OF A SINGLE CATALYSIS PLANT, ON THE OTHER HAND, HEATING UP OF THE GASES AFTER INTERMEDIARY ABSORPTION BEFORE THE SECOND CATALYTIC PHASE OCCURED BY PASSING SUCCESSIVELY THROUGH EXCHAN-GERS 6, 5 AND 4 WHERE, MORE PARTICULARLY IN EXCHANGERS 5 AND 4 THE HEAT SUPPLIES HAVE BEEN GENERATED IN THE FIRST TWO CATALYST BEDS BELONGING TO THE FIRST CATALYTIC PHASE (CONSEQUENTLY, WITH HIGH TEMPERATURELEVELS), IT MAY BE STATED THAT EXCHANGERS 5 AND 4 ACT LIKE "OUTSIDE HEATERS" WITH RESPECT TO THE HEATING UP OF THE GASES TO THE SECOND CATALYSIS. Conventional DC/DA Process (Flow-sheet 2) THERE ARE 4 HEAT-EXCHANGERS AND INTERMEDIARY ABSORP-TION OF THE SOZ FORMED OCCURS AFTER THE SECOND CATALYST BED. It is seen that the cold gases containing $\mathrm{SO}_{\mathbf{Z}}$ reach THE CONVERTER AFTER HAVING PASSED SUCCESSIVELY THROUGH EXCHANGERS 4 AND 1 WHERE HEAT EXCHANGES OCCUR : 1°) IN EXCHANGER 4 BY HEAT SUPPLIES OF THE SECOND

PHASE OF CATALYSIS,

2°) IN EXCHANGER 1 BY HEAT SUPPLIES OF THE FIRST PHASE OF CATALYSIS (HEAT SUPPLY FROM THE FIRST CATALYST BED). (As a matter of fact, fxchanger 3 is very small and operates in parallel with exchanger 4. In exchanger 3, a small cold gaseous flow containing SO₂ receives a heat supply from the second catalytic phase).

So, in this process, the heat supplies resulting from BOTH CATALYTIC PHASES CONTRIBUTE SUCCESSIVELY TO THE HEATING UP OF THE COLD GASES FLOWING TO THE FIRST PHASE OF CATALYSIS.

ON THE OTHER HAND, HEATING UP OF THE GASES AFTER INTERMEDIARY ABSORPTION BEFORE THE SECOND CATALYTIC PHASE OCCURS BY THE PASSING INTO EXCHANGER 2 WHERE THE HEAT SUPPLY TAKES PLACE, WHICH HAS BEEN GENERATED IN THE SECOND CATALYST BED.

THIS CHARACTERISTIC OF THE CONVENTIONAL PROCESS RESULTS IN LOWER CONVERSION EFFICIENCY, AS IT IS NECESSARY, IN ORDER TO ACCOMPLISH HEAT EXCHANGE, TO REACH A SUFFI-CIENTLY HIGH TEMPERATURE AT OUTLET OF THE SECOND catalyst bed, by injection of fresh SO_2 gas, whatever THE CONSEQUENCE ON THE TOTAL CONVERSION EFFICIENCY MAY BE. AFTER THIS BRIEF COMPARATIVE DESCRIPTION, LET US NOW EXAMINE THE THERMAL STABILITY OF A SULPHURIC ACID PLANT BUILT ACCORDING TO EITHER OF THE FLOW-SHEETS. WE SUPPOSE THAT THE WORKING CONDITIONS ARE ESTABLISHED, BOTH FOR GASEOUS FLOW AND SO2 CONTENT IN THE GASES. LET US IMAGINE A DISTURBANCE, WHICH FOR INSTANCE REDUCES THE SO2 CONTENT BELOW THE THEORETICAL VALUE ENSURING THE AUTOTHERMICITY OF A DOUBLE CATALYSIS. IN FITHER OF THE FLOW-SHEETS CONSIDERED, THIS WILL RESULT IN VERY REDUCED, OR EVEN, PRACTICALLY NO OPERATION OF THE SECOND CATALYSIS, WHICH WILL PRODUCE ALMOST NO MORE HEAT.

WHAT IS GOING TO HAPPEN ?

1) IN THE PARSONS CASE As the first catalysis is autonomous, it will go on operating perfectly without trouble, while the gases, leaving the converter to exchanger 5, by cooling will bring about a temperature drop for the gases passing through this exchanger inside tubes. But as theses gases must pass successively through exchangers 5 and 4, where temperature levels are high and not disturbed, the result will be that after all, their temperature will be only very little reduced when they reach the fourth catalyst bed. So, as soon as disturbance in the SO₂ is finished, the temperatures will very <u>Quickly</u> become normal again at all the catalyst beds. The PARSONS system is not sensitive to disturbance.

2) IN THE CONVENTIONAL CASE

As the first catalytic phase is not autonomous, the disturbance affecting the second catalysis will directly affect the heat exchange in exchanger 4, the cold gases to be heated up will be quickly at a lower temperature than the normal one when they reach exchanger 1 and as this exchanger becomes quickly insufficient, one will be compelled, even if the SO₂ disturbance lasts only a little while, to stop the plant and put in operation the contact plant heater. This "great sensitivity" which shows itself in the CONVENTIONAL Case, results from the particular manner in which the heat exchanges are accomplished :

THERE IS NO THERMIC AUTONOMY BETWEEN THE TWO CATALYTIC PHASES : THEY ARE CLOSELY CONNECTED TO ENSURE HEATING OF THE FIRST CATALYSIS GASES.

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17- Possibilities of Improving the Conversion Efficiency in Existing Sulphuric Acid Plants Designed as Double Catalysis Plant and Based on Sulphur Combustion

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Possibilities of Improving the Conversion Efficiency of Double Catalysis Sulphuric Acid Plants based on Sulphur Combustion

This paper presents the essential parameters influencing the SO_2 conversion efficiency of double catalysis plants.

The following possibilities of improving the conversion efficiency and their economical aspects will be discussed:

- Influence of converter inlet temperatures and use of low bite catalyst
- 2. influence of the specific catalyst quantity
- 3. O_2/SO_2 ratio of converter gas
- Arrangement of the intermediate absorption
 (2 + 2 versus 3 + 1 or 3 + 2 system)
- 5. Increase of conversion in a 5-bed converter system
- 6. Peracidox tail gas treatment
- 7. Economic aspects
- 8. Conclusions

By : Reinhard Anders, Lurgi / Chemie. Germany.

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B. INTRODUCTION

The subject of this paper "possibilities of increasing the conversion efficiency of sulphuric acid plants" is limited to the particular aspect of double catalysis sulphuric acid plants based on sulphur combustion. It will therefore not be necessary to further discuss in detail the differences and substantial increase in conversion efficiency achieved by changing from normal (98 % conversion) to double catalysis design (99.5 - 99.7 % conversion).

It is rather the intention of this paper to present some alternatives for improving the SO₂ conversion in already existing double catalysis plants with regard to increasingly stricter enforced emission controls.

As more than 60 % of the world's sulphuric acid plants are operated on sulphur combustion, we based the following observations on the technical parameters of such a plant working according to the double catalysis system (see figure 1).

The combustion of elemental sulphur (see figure 2) requires the same amounts of sulphur and oxygen. When using atmospheric air for sulphur combustion, a theoretical SO_2 concentration of max. 20.5 % could be achieved. However the catalyst used in the converter (for the conversion of SO_2 to SO_3) allows only SO_2 concentrations up to 10.5 vol% SO_2 (temp.limit.) Sulphur trioxide (SO_3) is formed in the converter by oxidation of sulphur dioxide (SO_2) with atmospheric air in the presence of a vanadium pent-oxyde containing catalyst and sulphuric acid is formed by absorption of SO_3 in sulphuric acid by the addition of H_2O (see figure 2)

C. Improvement of SO₂ conversion in existing double catalysis plants

 Influence of the converter inlet temperatures and use of low bite catalyst

> The chemical equilibrium between SO_2 and SO_3 depends, on the one hand, on the concentrations or the partial pressures of the individual reaction components in the -229

gas phase $(P_{SO_2}, P_{O_2} \text{ and } P_{SO_3})$ and, on the other hand, on the equilibrium constant (K_P) corresponding to the chemical law of mass action (see figure 3).

The equilibrium constant Kp is a direct function of temperature, on the assumption of constant pressure.

Consequently, for each gas composition a temperature – equilibrium – conversion function can be established in accordance with the initial SO_2 and O_2 concentration. With a view to obtaining a maximum overall SO_2 conversion efficiency it is essential to perform the catalytic SO_2 oxidation in several steps, cooling the gas to the most favourable temperature before it enters the next catalyst bed.

The reaction heat evolved in the exothermic SO₂ oxidation reaction leads to an equivalent temperature rise of the gas during its passage through the catalyst bed under adiabatic conditions. The maximum conversion that can be achieved in each bed is thus limited by the gas inlet temperature at which the catalyst still enables a thermally stable operation and by the temperature conversion function predetermined by the initial gas composition. (see temperature - conversion diagram in figure 4).

The preliminary conversion attained in the first converter beds before the intermediate SO₃ absorption, will determine the new temperature conversion equilibrium function which is decisive for the conversion attainable in the converter beds following the intermediate absorption and especially for the final conversion efficiency of the entire plant.

However, an operation at the desirable low gas inlet temperatures highly depends on the specific reaction properties of the catalyst type used.

The use of so called low temperature or low-bite catalyst would be of particular advantage for raising the overall conversion efficiency.

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The use of such a catalyst would be the most elegant and technically the simplest solution for achieving an increase of conversion efficiency in existing as well as in new plants.

However, as long as sufficient long-term experience with such catalyst types is not available, this remains still a rather theoretical possibility.

2. Influence of the specific catalyst quantity

Apart from the thermodynamics and reaction kinetics mentioned before, the physico-technical parameters such as the gas velocity, gas distribution and retention time or space velocity play a decisive role in achieving optimum conversion, especially in industrial units.

The gas distribution in the individual converter beds depends essentially on the gas velocity and catalyst bedheigth as well as on the resulting pressure drop. The gas retention time in the catalyst bed or its reciprocal value, the space velocity, is a co-determining factor for a maximum approximation of the practically attainable conversion efficiency with respect to the theoretical temperature-conversion relation.

In practice, the requisite specific catalyst quantity is defined as liters of catalyst per tpd H_2SO_4 monohydrate (Mh) production capacity of a plant.

Figure 5 shows the final SO₂ conversion efficiency as a function of the specific catalyst quantity determined by computer programs and based on practicable experience for • double catalysis plant with a (2 + 2) system. Although this function may vary for each catalyst type, the general character of the curve is nevertheless typical. While the lower part of the curve shows a relatively great influence of the specific

catalyst quantity on the final SO2 conversion, the upper

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curve range indicates an asymptotic approximation to the maximum attainable conversion. This means that no further significant improvement of the final conversion can be expected even if the specific catalyst quantity would be increased considerably.

When comparing the attainable SO₂ conversion efficiency for a specific catalyst quantity of 160 1/tpd Mh in relation to 180 l/tpd Mh it might be concluded that such a small conversion increase of 0.02 %, which is practically within measuring accuracy, does not justify more than 10 % additional costs of catalyst. However not only operating conditions with relatively constant optimum gas conditions are to be considered when designing a plant. A higher heat capacity of the first converter bed is especially important for a plant start-up. Therefore, as a general rule, the catalyst quantity of the first bed should be higher than actually required for achieving the optimum conversion equilibrium. Another point to be considered in this connection is a certain decrease of catalyst activity over the years. Taking into consideration the aforementioned facts it is recommended to distribute the catalyst equally (25 % 25 % 25 % 25 %) over the 4 catalyst beds of the converter vessel.

3. $0_2/SO_2$ ratio of the converter gases

The O_2/SO_2 ratio of the feed gas has a decisive influence on the final conversion efficiency achievable in the contact plant, as can be seen from the theoretical dependence (figure 6).

Figure 6 shows that the relative rate of increase in conversion decreases significantly at higher $0_2/SO_2$ ratios so that even when further lowering the SO_2 concentration by air dilution an additional improvement of conversion cannot be expected.

A shifting of the Ω_2/SO_2 ratio from 1.0 to 1.2 which may often be within the range of actual operating fluctuations, actually means an increase of the theoretically attainable final conversion by more than 0.1 % in a double catalysis plant with a (2 + 2) system. This difference may already be decisive when fixed emission standards have to be complied with.

4. Arrangement of the intermediate absorption (2 + 2 versus 3 + 7 system)

Intermediate absorption can be arranged either after tray No. 2 or after tray No. 3 of the converter.

The following advantages or disadvantages are related to either version

- a) <u>2 + 2 arrangement</u>
 - overall conversion $(SO_2 \text{ to } SO_3) \text{ 0.05 } \$$ -point lower with 3 + 1 version than
 - Intermediate heat exchanger area smaller than with 3 + 1 version (less investment cost)
 - slightlylower steam production since more heat
 - is lost in the intermediate absorption system.
- b) 3 + 1 arrangement

Overall conversion (SO₂ to SO₃) approx. 0.05 point than with 2 + 2 version.

- intermediate heat exchanger area bigger than with
 2 + 2 version(higher investment cost)
- slightly higher steam production since less heat is lost in the intermediate absorption system.

5. Increase of conversion in a 5 bed converter system Apart from the possibility of designing a plant for lower SO_2 concentrations and a higher O_2/SO_2 ratio another alternative for improving the conversion efficiency is to use a converter with 5 beds instead of a 4 bed system. This is also demonstrated in figure 6. The theoretically possible increase in final conversion by an additional catalyst layer in a (3 + 2) system compared with a (2 + 2) system at the same gas composition, for example with an O_2/SO_2 ratio of 1.0, roughly corresponds to the previously considered difference in conver-

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sion when increasing the O_2/SO_2 ratio from 1.0 to 1.2 in a conventional (2 + 2) system. In order to illustrate the significance of the O_2/SO_2 ratio a comparison of several SO_2 concentrations at the converter vessel inletwith the corresponding theoretical SO_2 conversion figures are shown in figure 7. In view of the previously discussed dependence on conversion in a (2 + 2) converter system, a change of the O_2/SO_2 ratio from 0.98 to 1.19 means a reduction of the SO_2 feed gas concentration from 10.5 to 9.5 % SO_2 with an expected increase in conversion from 99.49 to 99.65 % i.e. a difference of 0.16 %-point

6. Peracidox tail gas treatment system

The oxidative SO $_2$ tail gas scrubbing process, the so-called Peracidox process represents another alternative for improving the overall conversion in double catalysis plants (see figure 8). As per experience from an existing plant the SO₂ content in the exit gas can be reduced up to 50 ppm. The very simple arrangement and operation of the Peracidox system with H_2O_2 is demonstrated in figure 9. The tail gas leaving the final absorber of the contact plant passes through a tail gas scrubber and a packed tower. The oxidant is added to the acid circuit of the scrubber. By simple overflow, the sulphuric acid formed during SO₂ oxidation is passed on to the sump of the scrubber where the remaining H_2O_2 content is consumed before the dilute sulphuric acid produced is conveyed to the sulphuric acid plant. In the acid system of the final absorber it is practically used instead of process water, thus being added to the main production flow. A technical advantage of the Peracidox system is its little space requirement and its easy installation in existing acid plants as an add-on unit. Another variant of the Peracidox process is the use of peroxisulphuric acid instead of hydrogen peroxide as oxidant. Such a system where peroxisulphuric acid is produced electrolytically (from sulphuric acid), only differs from the system with H_2O_2 by the integrated electrolysis. For this alternative only electric power and a small quantity of cooling water is required.

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Control and maintenance of these add-on units are simple and unproblematic. They are operated by the sulphuric acid plant personnel and may also be used especially for the start-up operation of contact plants, for the purpose of reducing temporarily increased SO₂ emissions until the individual converter beds have reached their optimum operating temperatures.

For such a temporary use of an oxidant, the utilization of H_2O_2 is in any case the more economic alternative because the relatively high capital cost for the electrolyzer can be saved.

D. Economic aspects

When discussing increases in conversion efficiencies in H_2SO_4 -plants in the order of only 0.1 \$-point, this might seem virtually uninteresting and negligible to a non-expert. Herewer based on the requirements for pollution control the SO₂ emmission may have to be improval from 99.6 \$ overall conversion to 99.7 \$. The extra investment and operating cost for achieving such improvements are quite considerable and not any longer negligible. This can be seen from the diagram (figure 10) in which the relative capital costs are represented as functions of the $\$O_2$ feed gas concentration.

<u>The capital cost</u> of a double catalysis plant based on sulphur combustion (1000 tpd) with a (2 + 2) system for SO₂ gases of 9.5 % are about 7 % higher than for a plant operated with 10.5 % SO₂. (Difference in conversion efficiency 0.16 %). On the other hand, the additional capital cost of a (3 + 1) system amounts to about 8 % and of a (3 + 2) system to about 10 % (comparing plant designs of 10.5 % SO₂ and 9.5 % SO₂).

Figure 11 shows the relative <u>operating cost</u> as a function of the SO_2 content in the feed gas of double catalysis plants based on sulphur combustion. It can be noted that the relative operating cost between a 2 + 2 and a 3 + 1 system (at the same SO_2 concentration of converter inlet) differs by approx. 1 %. However between the 2 + 2 and a 3 + 2 system exists already a difference of approx. 3 %.

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Figure 12 shows the specific operating cost of a tail gas treatment unit as a function of the SO2 removal when using H_2O_2 as an oxidant. The specific operating cost expressed in DM/t Mh also refers to a practical example of a 1000 tpd double catalysis plant and includes the cost of H202 consumption and electric energy. When processing feed gas of 10.5 % SO₂ instead of 9.5 % the decrease in final conversion efficiency of 0.16 % corresponds to a reduction of the SO₂ tail gas concentration by using the Peracidox system of approx. 150 ppm SO2. For this example, the implied additional cost of the acid plant amount to approx. 3.50 DM/t Mh. Furthermore the diagram shows that the operating cost of the Peracidox system is a linear function of the SO₂ removal. This is due to the stoicheiometric relation of the H_2O_2 consumption to the amount of SO_2 to be oxidized (approx. 0.6 kg H_2O_2 per kg SO₂ to be removed). When comparing the different possibilities of increasing the conversion, the tail gas scrubbing system has an essential advantage as it allows a great flexibility and also an adaptation to changing operating conditions of the acid plant. However a higher removal of SO $_{2}$ (300 ppm and more) causes substantial extra cost which is not justifiable

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Conclusion

for purely economic reasons.

The discussion of the various dependencies of SO₂ conversion shows that even in existing plants it is often possible to achieve further and, sometimes decisive, increases in conversion by a careful optimization of the contact plant operation.

The comparison of various technical possibilities (see figure 13) shows the consequences for obtaining even a relatively small conversion efficiency increase. The present pollution standards of most countries in the world require for H_2SO_4 plants based on sulphur combustion a maximum of 4 lbs SO_2/t of Mh produced (approx. 270 ppm SO_2 in the tail gas.

This figure can be safely and in the most economic way achieved by designing a double catalysis plant with less

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than 9.5 \$ SO₂ (3 + 1 system for the double absorption) and 180 l/t of Mh catalyst in the converter.

Existing plants can be modified by using built-in systems or add-on-systems. However each particular case has to be investigated for the different alternatives in order to find the optimum solution under the aspects of technical feasibility as well as economics.



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SULPHUR COMBUSTION

$$S + O_2 \longrightarrow SO_2 (297 \text{ KJ/mol})$$

CATALYTIC OXIDATION
 $2 SO_2 + O_2 \longrightarrow 2 SO_3 (98 \text{ KJ/mol})$
SULPHUR TRIOXIDE ABSORPTION
 $SO_3 + H_2O \longrightarrow H_2SO_4 (137 \text{ KJ/mol})$

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Figure 2

EQUILIBRIUM CONSTANT

$$K_{P} = \frac{P_{SO_{3}}}{P_{SO_{2}} : P_{O_{2}}} \frac{1/2}{1/2}$$

$$K_{P} = \frac{5186.5}{T} + 0.611 \log T - 6.75$$

Figure 3



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THEORETICAL SC_2 - CONVERSION EFFICIENCY OF DOUBLE CATALYSIS PLANTS (2 + 2 SYSTEM) AS A FUNCTION OF THE CONTACT GAS COMPOSITION

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Vo∟ % SO ₂	Vo∟ % 0 ₂	0 ₂ /S0 ₂ ratio	THEOR. Conversion %
9,0	11,8	1,31	99,73
9,5	11,3	1,19	99,65
10,0	10,8	1,08	99,58
10,5	10,3	0,98	99,49

FIGURE 7

REACTION EQUATIONS FOR

PERACIDOX PROCESS

 $SO_2 + H_2SO_5 + H_2O \longrightarrow 2 H_2SO_4$ $SO_2 + H_2O_2 (+ H_2SO_4) \longrightarrow 2 H_2SO_4$ FIGURE 8

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Figure 10

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Figure 12



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Type of System	Type of Improvement	Increase in Conversion Efficiency	Changes in Plant Operation	Changes in Investment Volume	Additional Operating Cost #	Additional Investment Cost *
Built-in Systems	Use of low bite catalyst	0.10 %		different catalyst		negligible
	Increase in cata- lyst quantity 180 l/t instead 160 l/t	0.02 %	Increase in Pressure drop additional power consumption	Additional catalyst addi- tional blower n capacity	-	approx. 1 %
	Improved 0 ₂ /SO ₂ ratio 1.2 instead 1.0	0.15 %	Increase in gas volume additi- onal power consumption	Increased Equipment Size	approx. 1 %	approx. 7 %
	Arrangement of intermediate ab- sorption step 3 + 1 versus 2.2	0.05 %	higher steam production	Bigger heat exchanger area for in- termediate heat exchan- ger	slightly lower due to credit for steam prod	approx. 1 %
	5 bed converter system 3 + 2 versus 2 + 2	0.16 %		Additional Equipment like 1 more conver- ter bed,addi- tional heat ex- changer, ducts	approx. 3 %	approx. 3 %
Add-on System	Peracidox Tail Gas Treatment	0.16 %	H ₂ O ₂ consump- tion,additio- nal power con- sumption	Additional scrubber, to- wer, pumps, tank ducts and pipes	approx. 4 %	approx. 4 %

* Based on a 1000 tpd H₂SO₄ Double Catalysis Plant Designed for 10.5 % SO₂ 160 1/t Mh Catalyst and

2 + 2 system for the double absorption

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(conversion 99.5 %)

Figure 13

Discussions:

- Q: Dr. V. Pachaiyapan, FAI, India:
 - 1- You have not compared the economy using prilling tower vs. granulation. Could you give us some comparison?
 - 2- High temperature operation you mentioned also, is energy consuming. Is it not contradicting?

A: Eqil Holte, Norsk Hydro, Norway:

1- The investment cost of a prilling plant vs. granulation plant will depend very much on the local conditions. Thus comparison of this has to be done on a real case basis. Coming to the operating cost, the following can be indicated for granulation process:

Power consumption = 20-25 kwh/ton product. Process water = 0.01 ton/ ton product. Cooling water at $10^{\circ}C=0.5$ m³/ ton product. Operators = 1-2 man/ shift. The power consumption in prilling, normal process 15-20 kwh/ton product, but with antipollution measures, it will increase by 10-15 kwh/ton.

2- No extra energy is added to the melt. The high temperature term refers only to the operational temperature in the pan.

- Q: Dr. V. Pachaiyapan, FAI, India:
 - 1- Your DC/DA need 2 additional heat exchangers. What about the additional cost? Is it offset by the efficiency claimed by you?
 - 2- Great sensitivity is also good for better inter-relation, though not for stability . Could you comment?
 - 3- 72 hrs performance should not be used for contractual guarantees .
- A: Dr. Y.L. Corbiau, Mechim, Belgium:

1- First of all, it must be pointed out that my paper is relative to the performances of sulphuric acid plants working on metallurgical gases and not on sulphur burning.

This is true we need 2 additional heat exchangers but the surface area needed is not as the ratio of number of heat exchangers, i.e. $\frac{6}{4}$. The additional cost is less than 1% and this is largely compensated by the decrease in atmospheric pollution (200 ppm in DC/DA Parsons case against 500 ppm in DC/DA Conventional case). 2-In sulphuric acid plants treating metallurgical gases, flexibility is an important factor as the raw feed material is always changing. A process, which is less sensitive to variations like the DC/DA Parsons process, does not require that operating personnel conduct the plant at high temperature levels so as to ensure that they will not loose catalyst activity. The result is that, with lower temperature at the inlet of each bed, the performance of the plant will be higher.

3- A 72 hrs performance test is a normal rule in world contracts. This 72 hrs performance test is achieved only when plant is in stable operation (not including start-up period).

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Afternoon Session: Recommendations:

- 1- Promotion of Industrial Awareness in the field of pollution from the fertilizer industry and the importance of its control to protect the environment.
- 2- Pollution regulations should be established regarding all pollutants from the fertilizer industry.
- 3- Fertilizer plants should follow the established pollution regulations and ensure that pollutants are within the acceptable limits.
- 4- Future planned projects should include pollution control units during the design stage.
- 5- Well-trained and qualified personnel in the field of pollution control and the establishment of a department of pollution control in the company is considered necessary.
- 6- Encouragement of cooperation among Fertilizer plants in the field of pollution control.
- 7- Encouragement of the utilization of spent or liquid effluents which contain acceptable percent of nutrients in agriculture in particular in countries with deficient water resources.
- 8- A technical field study on the pollution problems of nitrogen fertilizer industry in the Arab Countries should be undertaken by AFCFP,AIDO, and UNIDO, followed by an expert group meeting to discuss the report of the field study.

• OTHER TECHNICAL PAPERS: *

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18- The Gaseous, Liquid and Solid Effluents Emitted from the Phosphoric Fertilizer Complex in Al-Qaim and the Techniques Applied to Limit and Control them.

19- Pollution at Arzew Nitrogen Fertilizer Complex.

These Papers were prepared for hte Seminar but were not presented in Bahrain .

16- THE GASEOUS, LIQUID, & SOLID EFFLUENTS EMITTED FROM THE PHOSPHATIC FERTILIZER COMPLEX IN AL-KAIM, AND THE TECHNIQUES APFLIED TO LIMIT AND CONTROL THEM.

<u>A B S T R A C T</u>

As far as the gaseous effluents are concerned, namely the SO₂, Fluorides and NC_x, besides the application of good designs to get the minimum possible pollutants concentration emitted through the stacks (using double contact/double absorption technology for Sulphuric Acid production as an example). The principle of not exceeding an allowable threshold limit value on ground level was also followed by a computrized studying to survey all the possible meteorological conditions and calculating the maximum concentration of pollutants on ground level and making sure that they are not exceeding a predefined threshold limit value.

For liquid and solid effluents a complete project is constructed to handle and to treat them. The project includes the construction of two separate storages. One for acidic effluents lined with high density polyethylene to prevent the penetration of these effluents to the underground water; the solid materials (mainly the phosphogypsum) will be stacked upto a height of 40 metre. The second storage is for basic effluents (calcium hydroxide mainly) which results from the washing of the calcined phosphate rock, the height of the solid material in this storage could reach 18 metre.

By : M.A. Murad. Atate Enterprise for Phosphate. Al-Kaim. 1 aq.

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The excess acidic effluent drained from the gypsum stack (as the most part of the acidic water will be recycled to the Complex to be used for gypsum dilution produced in the Phosphoric Acid unit in order to make it suitable for pumping through pipelines to the gypsum storage) will be neutralized with the excess basic effluents in two stages in series, then the neutralized water is disposed to the nearby wadi with a PH and fluorine content within the accepted values detailed in the next pages.

INTRODUCTION The phosphatic fertilizer companies are con-

sidered among the companies which throw to the environment different kinds of pollutent effluents, gaseous, liquid and solid in huge quantities. During the design and the construction stages of the Fertilizer Complex in Al-Kaim, the pollution problems were reflected directly on the designs executed by the Contractor(s) companies after defining the required limits and criteria. In some cases we were obliged to follow special solutions to take care of the liquid and solid effluents as the Complex is located in a desert area near the Euphrates river and throwing these effluents directly without treatment will lead certainly to the pollution of the underground water and the River. BRIEF DESCRIPTION OF THE COMPLEX, ITS PRODUCTION UNITS AND EFFLUENTS DISCHARGED FROM EACH UNIT :

1. Beneficiation Unit

It discharges liquid and solid effluents (basic effluents) resulted from the washing operation of the calcined phosphate rock. It discharges also gaseous effluents mainly SO₂ which comes from the sulfur content of the fuel used for the calcination furnaces.

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2. Sulfuric Acid Units

They discharges SO_2 and SO_3 as pollutents to the atmosphere.

3. Phosphoric Acid Unit

Its liquid and solid effluents (phosphogypsum) are considered the most important pollutents in phosphatic fertilizer industries due to their large quantities and their poisonous effect (fluoride ions mainly). This unit also discharge fluorine compounds as gaseous effluent to the atmosphere.

4. Fertilizer Units (TSP, NPK, MAP) & Fluoride Salt Units (AlF3, Na3AlF6).

> They discharge fluorine compounds as gaseous effluent to the atmosphere and also acidic liquid effluents contains fluorides mainly. Ammonia Plant

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5. <u>Ammonia Plant</u>
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6.

A small Ammonia Unit is going to be constructed within the Complex, it is going to discharge gaseous effluents mainly NO_X and a very small quantity of SO_2 . Utilities Units

Gaseous effluents mainly SO₂ is discharged from the stacks of power house and other drying furnaces in the Complex (its source is the sulphur content of the fuel), acidic liquid effluent from the water demineralization unit is discharged also.

The gaseous effluents discharge to the atmosphere will be discussed first.

A. The Gaseous Effluents :

As mentioned above they include SO₂, SO₃, Fluorides and NO_X. A.1. SO₂ and SO₃ :

The Sulfuric Acid units are the main source of these effluents and the first step to minimize pollution with these gaseous is a design step by choosing the double contact/ double absorption technology which has become common recently and its lesser pollution is reflected directly on its efficiency for example. Alkaim Sulfuric Acid units are designed to convert not less than 99.25% of the burned sulfur to sulfuric acid and they discharge through their stacks not more than the following rates :

SO₂ 400 ppm equivalent to 2.3 kg SO₂/ton H₂SO₄ SO₃ 40 ppm equivalent to 0.29 kg SO₂/ton H₂SO₄

which use fuel of certain sulfur content, and in order to study the influence of all stacks together, it was decided to use the criteria of a threshold limit value represented by the ground level concentration of SO2 and the figure selected was 40 pphm (0.4 ppm) for 15 minutes recommended by G. Nonhebel in his article

"Recommendation on heights for new industrial chimenys"

journal of Institute of Fuel, October, 1960, page 479 - 511 and following C.H. Bosanquet method for calculation of plume rise as indicated in the article

"Rise of a hot waste gas plume"

journal of Institute of Fuel, June, 1957, page 322 -328 and since other factors (besides the emission parameters discharged from the stacks) like ambient temperature, wind stability, wind speed, direction of winds, and physical height of stacks affect the ground level concentration, and it is clear that the four meteorological factor mentioned can not be controlled and the emission parameters are fixed following design requirement (being understood that each individual stack is not discharging to the atmosphere more than the allowable limit in the country of origin) then the only factor which remains under control is the physical heights of the stacks which should be sized to minimize the SO2 concentration on ground level. The involved calculation is lengthy and complicated specially there are 13 stacks in Alkaim Complex discharging SO2 to the atmosphere, therefore, the calculation was carried-out using a computor programme applying a mathematical model by assuming the presence of 121 receptors uniformly distributed all over the Complex and the surrounded area to find out the ground level concentration at each receptors surveying all the possible climatic conditions.

The meteorological parameters of the model werethe following :

- (a). Ambient temperature, the most unfavourable hypothesis is assumed which is the maximum temperature recorded in the area.
- (b). Wind stability classes, six cases are covered :
 - Class A Very unstable.
 - Class B Unstable.
 - Class C Slightly unstable to neutral.
 - Class D Neutral to slightly stable.
 - Class E Moderately Stable.
 - Class F Very Stable.
- (c). Wind speed, six values are assumed between the range 1 to 15 m./sec.
- (d). Wind direction, 16 wind origin direction classes are assumed to cover the all possible wind direction (360°) between each direction and the other 22.5°.

i.e. a total of 6 X 6 X 16 = 576 particular situations are covered and the concentration at each receptor is determined. The above model is applied three times with a 7.5 angle between two consequence

wind directions, i.e. the wind direction covered is 16 X 3 = 48 direction in order to give more precise picture of the ground level concentration and to enable the tracing of a map of iso - max. concentration curves covering the whole Complex. Moreover it was assumed that the most unfavourable type of fuel will be used as far as the sulfur content is concerned (all the furances of the Complex are designed to use one of the three alternatives, natural gas, crude oil, and fuel oil) and the calculation is based on the assumption of using fuel oil which has the highest sulfur content. In addition to that no absorption effect of the ground (by the soil, asperities, vegetation, etc.) is assumed i.e. perfect reflection of the polluting agents on the ground is assumed to be on the safe side.

According to the above assumption and while the whole stacks are operating with their full capacity, it was found that the maximum ground level concentration will range between 0.2 - 0.3 ppm for most part of the Complex, and the <u>absolute</u> maximum concentration for few parts will reach to 0.4 ppm at an unlikely occurring conditions (as these conditions require an ambient temperature above 40° C and a wind direction blowing from south to south-east and the probability of this meteorological situation to take place is very rare). In the above study the probability of occurrence of the meteorological data was not taken into consideration so even the very unlikely ones are considered which put us on the safe side also.

A.2. Fluorine Pollutant.

The following design figures have been taken as a maximum limits for the concentration of fluorine gases allowed to be emitted from stacks to the atmosphere after passing the scrubbers and they actually represent the limits which the engineering companies are abide to in their countries (Western EuropeanCountries) :

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- i. Phosphoric Acid Unit 25 mg/Nm3.
- ii. Fluorine Salts Units 25 mg/Nm3.

35 mg/Nm3. Fertilizers Units 111. And again to study the influence of the whole stacks working together at their full capacity a criteria of an allowable threshold limit value is defined, the ground level concentration selected is 2.5 mg F/m^3 (as an allowable limit of exposure for 8 h/day and 5 days/week), this represents the limit to which the workers may be exposed repeatedly, day by day, without adverse effect following the recommendation of the "American Conference of Governmental Industrial Hygienists for 1977". The ground level concentration has been calculated in the same way of calculating the SO2 concentration explained in para A.1 covering all the possible meteorological conditions and it was found-out that the absolute maximum concentration of fluorine on ground level will not exceed 0.16 mg \overline{F}/m^3 .

A.3. NOx Pollutants

The maximum ground level concentration of NO_x gases was taken not to be exceeding the U.S. Federal Regulations of 100 micrograms/cubic metre (0.05 ppm) the calculated value was found to be $38.5 \mu g/m^3$.

B. The Liquid and Solid Effluents

Since huge quantities of liquid and solid effluents are going to be discharged from the Complex some of which are acidic and containing poisionous ions (Fluorine ions for example) and since the Alkaim Fertilizer Complex is located in a desert area (away from sea-shore where usually these effluents are discharged) and the nature of the soil is calcite i.e. highly permeable to acidic solutions as these solution attack this kind of soil easily and in order to protect the enviornment from pollution by these solutions represented by the underground water and consequently the river (as the level of

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the underground water is higher than the level of the river) it was decided to construct a complete Project to store and to treat these industrial effluents and hereunder given a brief description of this Project. The effluents can be classified into two types :

B.1. <u>Acidic Effluents of PH < 3</u>

- B.1.1. Phosphoric Acid effluents (mainly phosphogypsum) which contain high concentration of fluorine ions besides other impurities like P205 etc. (the phosphogypsum is pumped to the gypsum stack as a slurry of 22% solid).
- B.1.2. Fertilizers, Fluorine Salts and demineralization Units Effluents which contain Fluorine ions, P205, H2S04 and others.
- B.2. <u>Basic Effluents of PH > 12</u>

They are formed as a result of washing the calcined phosphate rock and the solid content is mainly calcium hydroxide and other impurities like mud.

Project Section :

The Project is consisted mainly of three sections, acidic effluents storage and its accessories, slime storage and its accessories and neutralization section besides the piping network connecting the Project to the Complex (see the attached sketch).

I. <u>Acidic Effluents Storage :</u>

It is foreseen to store the solid materials (mainly the phosphogypsum) by lining the storage ground properly with high density polyethylene HIPE to prevent acidic seepage to the underground water, the solid materials will be stacked upto a height of 40 metre in an area enough for 20 years operation which is going to be constructed into four equal stages and the first stage is now under construction. In the gypsum stack area alotted drain-pipes are embedded towards cahnnel lined with HDPE as well, then towards an acidic water pond which also lined with HDPE. This pond serves as a buffer tank to rationalize the operation of the Complex units and the neutralization section due to implant large capacity. Most of the acidic

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water is recycled towards the Complex to the Phosphoric Acid unit in order to dilute the gypsum cake after filteration and make it in a slurry form of 22% by wt. solid which is pumped through piplines to the gypsum storage. The excess acidic water will be neutralized as willbe shown later.

II. Slime Storage :

The basic effluents are stored in a separate area, the ground of which is adequately compacted in order to minimize the slime water seepage into the ground during the first stage of operation as the slime material later-on will form an isolation layer highly preventing the seepage of slime water. A slime water pond is integrated with the slime storage, the pond is lined with HDPE (as there is no possibility of forming impervious layer of slime as in the case of slime storage).

III. Neutralization of Acidic Effluents :

Neutralization of excess acidic effluents is carried on in two consequence stages with the excess basic water from the slime storage, each stage consists of neutralization basin and thickeners; the first stage is lined with rubber and carbon bricks and the second stage (after rising the PH) is epoxy lined. The fluorine ions are precipitated as insoluble CaF₁ and the PH is rised to acceptable limit, the formed precipitations are separated by the thickeners and transported to the gypsum and the slime storage respectively. The neutralized effluent is discharged towards a pond (called clear water pend in the attached sketch) lined with HDPE as an extra precaution then discharged to the near-by WADI 7 Km. far away from the river.

The main characteristics of the neutralized effluent are :

PH about 9.5

Dissolved Fluorine less than 10 mg/litre.

The excess acidic effluents are calculated taking into consideration the annual rate of evaporation and the rate of rains, and during the summer season when the rate of evaporation is increased a mixture of slime water and slime solid could be used to get the same neutralization results. Also it has taken into consideration the probability of stoppage of some of the units of the Complex for more than two weeks and consequently a shortage might occur either in the acidic or in the basic effluents and this will be faced by addition of Sulfuric Acid or lime as the provision of storing and feeding these materials is included in the Project.

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× 2.

And in order to ensure utmost security, any possible change, in the quality of the underground water and in the river will be recorded by drilling wells near the gypsum stack and in the way of discharged neutralized water and also carrying on periodical analysis to the river water at two points before and after the discharge point to the river to record any possible adverse change one year before the start-up of the Project.



19- POLLUTION AT ARZEW NITROGENOUS FERTILIZERS

COMPLEX

I. INTRODUCTION :

As to the Arzew Nitrogenous Fertilizers Complex_among all the polluants we briefly present herein after in this report, ammonium ion is the one that caused us the most problems as to the running of units composing this complex and certain neighbouring complexes.

It should be noted that in view of the future running of new units, the problem of sea water pollution by ammonium ion will gain more importance, thus reducing on one part the reliability of the exploitation and production of the complex and of neighbouring plants on the other, in terms of wind direction.

The dominant wind direction being the west, the LNG plants are then the most affected because the ammonia discharges are located in the west with regard to the S.W ammonia pumping unit and in the east with regard to that of LNG.

The industrial sewages of the complex are thrown into the sea, without preliminary treatment, other than the partial neutralizing of acid condensates in the chalk pit.

By : Dr. A. Mahi. Ministry of Energy and Petrochemical Industries. Algeria.

li. <u>Among all the polluants</u>, the free or combined ammonium ion conveyed to the sea through water, steam and the air causes problems in :

2.1. The ireshening units : Water, boiler feeding is obtained by :

2.1.1. <u>Distillation of sea water</u> in the distillation blocks The control of water purity is made through measuring its conductivity.

In this way, the increase of ion ammonium concentration in distilled water implies an increase of its conductivity therefore an automatic sewage disposal.

The lack in boiler feeding water is often due to this phenomenon. The presence of ammonium ions in the distilled water will reduce the cycles of demineralization resins, which are not fitted to the treatment ammonium ion :

of

The resins used are :

Amberlite IR 120 L, Anionic Resin Amberlite IR 400 C, Cationic Resin.

An ion exchanger resin specific to ammonium ion would prove necessary.

The ammonium ions concentration in distilled water is five to six times larger than that in sea water.

In the LNG 1, the distilled water being used in the boilers without previous demineralization. The ammonium conveyed by steam will affect the turbines condenser and other equipment made out of copper alloy.

2.2. Cooling system by sea water :

Several exchangers in contact with sea water are made out of a dimetallic alloy, copper/aluminium and copper/ nickel. However when in the presence of ammonium ions,

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these exchangers are bhighly corroded. Therefore it has proved necessary to determine the tolerable ammonium ion content in such equipments.

2.3. Chlorine injection to the system of cooling sea water:

Chlorine injection is used as a "biocide" agent at a rate where the free chlorine concentration in circulating water is 0,5 Mg/1,

The presence of ammonium ion entails a chlorine dissociation, therefore a more important chlorine injection (see table 1). For example, for a 0.5 Mg/l ammonium ion concentration in sea water, chlorine injection must be done at a 4 Mg l concentration in order to keep a 0.5 Mg/l free chlorine rate in circulating sea-water, instead of a chlorine injection at 2 ppm in the case of an absence of ammonium ion. The ammonium ion pollution was more important, with the new units, therefore the chlorine requirements will be enormous.

The shock injection at high chlorine concentration in case of high ammonium ion concentration is a solution to reduce the chlorine needs.

TABLE 1

0.5	4.0
1.0	8.0
1,5	12,0
2,0	16,0
2,5	20,0
3,0	24,0
3,5	28,0
4,0	32,0
4,5	36,0
5,0	40,0
5,5	44,0
6,0	48,0
	1,0 1,5 2,0 2,5 3,0 3,5 4,0 4,5 5,0 5,5 6,0

CHLORINE INJECTION RATES WITH AN AMMONIUM ION CONCENTRATION

111. Presentation of the Arzew Nitrogenous Fertilizers Complex :

The Arzew Nitrogenous Complex comprises : 3.1. Units operating since 1969 3.1.1. Ammonia Unit : with a capacity of 1000 tons ϵ day "Chemic." Process. 3.1.2. Nitric Acid Unit : 400 tons day 100 🐔 Acid - "Chemico" Process. 3.1.3. Ammonium Nitrate Unit : 500 tons day "Chemico" Process. 3.1.4. Urea Unit : with yet no conclusive results after starting tests. 400 tons day "Chemico" Process. 3.1.5. Necessary utilities and offsites : 3.2. Units due to start soon 3.2.1. Ammonia Unit : with a capacity of 1000 tons day "Kellog" Process. 3.2.2. Two Nitric Acid Lines : 400 tons day x 2 acids at 100 % "Chemico" Process. 3.2.3.-20 (twenty) ammonium nitrate lines : with a capacity of 500 tons day x 2 "Chemico" Process.

3.2.4. Necessary Utilities and offsites.

In consideration of the over mentioned processes and utilities and the non-treatment of discharges either locally or globally, except for acid condensates which are partially. neutralized together with basic condensates in a chalk pit pollution, particularly ion ammonium's hinders not only the runniong of our complex but also that of neighbouring plants, of which LNG, which is the most affected in view of the dominant west wind direction.

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The consequence of which direction vehicles the entire ammonium ions to their sea-water (S.W.) pumping unit.

IV. Pollution Sources :

Sea water pollution is due to process condensates on the one part because of equipment washing and leaks and atmosphere steam on the other part (chimney, ventilator, steaming) depending on wind direction.

4.1. Sea water pollution through condensates :

Condensates would contain several impurities contaminants namely :

4.1.1. the ammonia

4.1.1.1. Ammonia Unit :

It is formed at the level of the primary converter due to an iron-based catalyst on one part and to an excess of steam in the running in order to avoid carbon formation. Il is dissolued in CO2 saturated water.

4.1.1.2. Ammonium Nitrate Unit : The ammonia which does not react in the C. 3101 is dissolved in the condensates.

4.1.1.3. Nitric Acid Unit : This plant does not constitute a pollution source in ammonium ion.

4.1.1.4. Urea Unit :

During the starting tests, high concentrations of ammonia have been observed due to defective operation. Being presently at rest, it does not constitute a source of pollution. In the future, il would be useful to take corrective measures and to avoid any solution purge.
Compared to other processes, our plant does not show process condensates. The water resulting from the reaction : $2 \text{ NH3} + \text{CO2} \longrightarrow (\text{NH2})2 \text{ CO} + \text{H2O} + \text{Q}$ is insufficient for absorption. Therefore it is necessary to recourse to topping up water, the latter will have to evaporate in the E 4401 evaporator.

4 1.2. Ammonium Nitrate : 4.1.2.1. Ammonia, nitric acid and urea Units : This set does not constitute a source of pollution in ammonium nitrate.

4.1.2.2. Nitrate Unit : Process condensates in the C 3101 neutralizor

4.1.3. Urea :4.1.3.1. Ammonia, nitric acid and urea Units :Do not constitute a pollution source in urea.

4.1.3.2. Urea Unit :

Under normal conditions, whatever the unit working order (starting or normal running), we should not have a process condensate containing urea or process water due to the fact that over~mentioned reaction is insufficient for absorption.

This absomption requires topping up water the excess of which will be evaporated in the evaporator.

Thus, this heavy urea concentration in the purges is due to the ill mastering of unit bringing on stream. Before its starting up, it is necessary to take up corrective steps and to avoid any urea-ammonia solution purge to the sea. 4.1.4. Carbonate : see above unsteady element during its creeping. It may turn to urea-ammonia and CO2.

4.1.5. Nitric Acid :

4.1.5.1. Ammonia Unit : Here, ammonium nitrate and urea are not a source of pollution in nitric acid.

4.1.5.2. Nitric Acid Unit : The acid condensates of this unit combined with those of the utilities are neutralized in a chalk pit.

4.1.6. : Methanol :

It is produced in a substantial quantity in the secondary converter, the catalyst of which is copper base. Then, only the ammonia unit is a source of pollution in this product.

4.1.7. The Amines :

Ammonia reaction with methanol. Only ammonia unit is a source of pollution in this composite.

4.1.8. The formaldehyde :

In small quantity. Only the ammonia unit is a source of pollution in this product.

4.1.9. The metals :

All the units are a source of pollution in these polluants, namely sodium, iron, copper, zinc, calcium, magnesium and silicium originating from the heat proof catalyst of pipes and equipment walls.

4.2. Sea water pollution due to washing and leakage.

4.2.1. Ammonia :

As to all the units of pollution in ammonia, due to washing or leakage, further to a tube breakage or from a flange, or to the accidental opening of relief valve. The washing being done periodically (once a month is, the highest frequency) and the leakage in terms of gravity they will either be water-tighted at the next shut down or shut for repair.

4.2.2. Ammonium Nitrate :

The nitrate unit is the only source of pollution in nitrate following plugging and washing of the bottom of tower and drying section.

It should be noted that it is the main source of pollution in ammonium ions. Then it is recommended not to use water when washing the nitrate units because the nitrate solution corrodes the foundations and increases the embrittlement of the equipments and lines, the material of which is carbon steel or a low alloy base such as in the steam lines.

Furthermore, in addition to increasing air moisture for a same temperature, washing reduces the evaporation of nitrate in the atmosphere and increases the air water absorption by nitrate.

This phenomenon is the cause of plugging problem.

During the washing, air moisture is about 100%, this increasing at that rate the difficulties in plugging.

4.2.3. Urea :

The urea unit is the only source of pollution in urea, notably when washing the bottom of tower and drying section. It was not possible to lollow the intensity and regularness of this problem since all the tests done were unconclusive.

4.2.4. Nitric Acid :

The acid unit is the only source of pollution in nitric acid, due to leakage.

It is an accidental pollution which entails stopping.

4.2.5. Conclusion :

In all units, pollution due to leakage is accidental and entails a shut down of said unit. However, nitrate and unea pollution, probably due to washing and plugging following an increase in relative air moisture, itself a consequence of a big water use, is important.

4.3. Sea water pollution by atmosphere :

Depending on wind direction, the atmosphere contributes to sea water pollution through chimneys, ventilators and steam transmitters.

4.3.1. Ammonia :

4.3.1.1. Ammonia and nitric acid units : These units do not constitute a pollution source.

4.3.1.2. Ammonium nitrate unit :

In ammonia steams released by the E 3201 dehydrator and those drawn with the air by the ventilator of the granulation tower.

4.3.1.3. Urea unit :

In ammonia drives released from the B 4201 tank breather plug of the C 4202 absorber and the chimney placed at the outlet of the E 4204.

4.3.2. Nitrate :

Only the nitrate unit is a source of pollution in nitrate. The nitrate dusts are carried along with the steam to the dehydrator E 3201 together with the air released by the ventilators of the granulation tower K 3201 and the cooling ventilators K 3204.

4.3.3. Urea :

Only the urea unit is a source of pollution in urea. The urea dusts are carried along from the dehydrator E 0403, the ventilators of the K 4402 granulation tower and those of the K 4404 coolers.

4.3.4. Nitrogen monoxyde and dioxyde (NO.NO2) : Only the nitric acid unit is a source of pollution in NO.NO2 through the chimneys located behind the absorption tower.

Has a negative effect on the animal reign, acts notably on ozone playing the role of screen to the ultraviolet rays.

4.4. Atmospheric pollution :

Depending on wind direction and on turbulence, air pollution contributes either to marine pollution as shown in 4.3. or to its own pollution - ref. to par. 4.3 for the sources of pollution.

V. Treatment of the pollution problem :

Treatment of the global discharge : 5.1. Treatment of the global discharges : In view of the huge sea water volume discharged, this treatment is realistically impossible. Moreover, comparison of tables 2 and 3 shows that the treatment of global discharge is : a) Technically impossible : no available technology fitted for so low concentrations as shown in table 3.

b) Economically impossible : high cost,table 2 shows the methods of treatment together with the corresponding cost as well as the level of residual polluant after treatment, table 03 indicates the rate of pollution in sea water as to ammonium ions :

It should be noted that even when the pollution rate reaches its maximum value, that is to say when all the running units with a wind direction favourable to pollution, five to six times bigger concentration than those indicated remain too low for the available technologies.

5.2.Treatment of the effluents, source of pollution per type : This method encounters the above-mentioned

difficulties.

5.2.1. Condensates recovery :

To use it as boiler water seems economically impossible in consideration of the low volume comparatively with the freshming facilities and the operation cost. An economic survey is necessary before taking any action whatever.

5.2.2. The pollution products are not always recoverable.

5.2.3. The technologies such as the biologic treatment units are difficult to handle and operate at very low concentration rates only.

5.2.4. The handling cost of big volumes is often very high.

5.3. The use of polluted waters in the artificial meadows (prairies) : Aftractive solution. We should look at the availability

of the area, if it is not used in other projects.

For such a solution, the recoverable waters are : a) condensates, washwater and purges. b) rain water

In consideration of the technical difficulties linked to the running of the units and to the volume limitation, we must provide for other make up.

5.4. Improvment of process on the level of the units such an option requires :

a) setting up of new equipments

b) working in the most absolute conditions which is not always possible.

c) an adequate zone of storage where the losses are inevitable (eg. nitrate and unea drying zone). This type of pollution elimination when acting on the process, presents the foilowing advantages :

- available technology

more economical than the global S.W. treatment and relatively close to the treatment per type of effluents.
 saving_industrial water consumption with the use of process condensates of the nitrate and ammonia units.

VI. <u>Description of the various technologies adapted</u> to the elimination of ammonium ions :

6.1. Biochemical process :

In this process, the ammonia nitrogen is eliminated in two phases with the property of bacteria.

PROCESSES FOR THE DISCHARGE TREATMENT AND THEIR COSTS FOR FERTILIZERS PLANTS

TAPLE 02

plant	process of +.eating	investment in US \$ (**)	discharge debit CU.M/h	concentra- tion result Mg/l	annual operating costs US \$
	ammonia condensate stripment	217 920	63.4	25 NH3-N	243-660
ammoniaintegrated conden- sate stripment NH3112 700biological treatment nitrification110 000ammonia condensate air stripment (*)96 600	112 700	63.4	25 NH3-N	144-135	
	98.7	5 NH3-N 5 NH3-N	55 950		
	96 600	63.0	JO NH3-N	23 415	
urea	urea hydrolises	231 000	15.0	50 NH3-N 100 ORG-N	198 910
ionic exchanger 580 000	228.6	40 NH3-N 40 N03-N	418 000		
ammonia	biologic treatment	as for ammoni	a treatment by	biological p	process
nitrate	nitrate discharge treatment	132 020	18.2	_	57 585

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- (*) Does not fit with our case. Air emission of NH3 penetrates into the sea in the concluding stage.
- (**) All the data are those of august 1971, Data source: Environmental Protection Agency U.S.A.

TABLE 03

IONS LEVELS (NH4+) IN SEA WATER DISCHARGES OF CEA - Z

SUMMARY TABLE OF NH4+ IONS IN SEA WATER U. 90

DATE	TIME	PUMP-ENTRY	OUTLET/DISCHARGE
19.11.78	14.00	0.736 (Mg/1)	1.368 (Mg/l)
20.11.78	10.00	0.400	3.554
21.11.78	09.00	0.900	1.400 *
22.11.78	14.00	1.100	1.500
23.11.78	08.30	1.000	1.400
25.11.78	10.30	0.300	0.500
26.11.78	14.00	0.400	2.880
28.11.78	10.30	0.500	0.700
29.11.78	10.05	0.340	1.000
30.11.78	08.30	0.800	1.100
02.12.78	10.00	0.270	1.000
03.12.78	09.00	0.400	0.400
05.12.78	12.00	0.050	0.200
07.12.78	10.00	1.300	1.800
12.12.78	15.00	0.106	0.422
16.12.78	10.00	2.750	4.000
23.12.78	12.00	0.050	0.400
25.12.78	10.45	0.100	0.500
26.12.78	10.00	0.200	0.450
27.12.78	11.00	0.158	0.632

In a first phase, the ammonia nitrogen is oxidized in nitrite then in nitrate under the effect of nitrifying bacteria in aerobian medium (environment) initrification process.

In the second phase, the nitrates are turned into nitrite and nitrogen. This process is performed in a low or non-oxygenated environment (anoxy phase), the bacteria using the oxygene contained in the nitrates : denitrification process.

These effluents containing no carbon organic products, we must add to it a carbonacious product, for eg. methanol with 4,5 g/g nitrogen.

This biological process does not seem indicated in consideration of :

a) High ammonia ions concentration may have sometimes a toxic effect over the bacteria.

b) energy and make up carbonacious products consumption would increase the operation cost.

c) Uneasy control due to different ammonium ions concentrations.

6.2. Ammonium ions retention in ion exchanger resin.

The ammonium ions can be maintained in a cationic exchanger by nitric acid regeneration. Thus, we obtain a nitrate solution. The ammonium ions are not eliminated in this process, which enables to concentrate them for future use. This process could be completed by the use of an anionic resin where the nitrate ion will be hold back. The regeneration will be done with ammonia and then we get a second ammonium nitrate solution. To hold back urea, we must first make a hydrolyse before its passage on the resins.

6.3. Stripping process :

Stripping will be done either with air or water. For a high ammonium ion elimination, the PH of the effluent must be increased under normal conditions, stripping does not eliminate urea.

A new stripping process allows simultaneous hydrolyse and urea making which is done at substantially high temperature and pressure.

6.4. Other processes allowing an elimination of ammonium ions and urea :

6.4.1. Urea oxydation by hypochlorite : NACLO.

Co (NH2)2 + ·3 Na OCL → Co2 + N2 + 3Nacl + 2H2O

This reaction consumes a big quantity of hypochlorite.

6.4.2. Ammonia oxydation by chlorine. Here also the chlorine consumption would be important.

6.4.3. Use of ammonia waters as water in the artificial meadows (see 5.3).

VII. CONCLUSION :

It is not so easy to eliminate nitrogen from the effluents. It should be noted that stripping is not enough and therefore should be completed by treatment on ion exchanger resins depending on projects and water availabilities.

Then, the use of ammonia waters in the artificial meadows is the best solution.

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تقريـــــر الندوة الأقليمية حول مشاكل التلوث الناجمة عن صناعة الأسمدة الكيماوية في الدول العربيـــة البحريـــز 18-16 تشرين ثاني 1981

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الجانب الأنجليزى



سعادة الدكتور على فخرو وزير الصحة ووزير التربية والتعليم بالوكلَّة اثناء القاء كلمته امس في ندوة التلوث التي تنظمها جمعية المندسين . المقسيدمية

قام بتنظيم الندوة : المنظمة العربية للتنمية الصناعية (بفداد) والا تحاد العربى لمنتجى الاسدة الكيماوية (الكويت) بالتعاون مع جمعية المهند سين البحرينية ووزارة الصحــة البحرينيـــة. بتعويـــل : منظمة الام المتحدة للتنمية الصناعية " اليونيد و فيينا " نيابة عن البرنامج الانمائـــي للام المتحدة " نيويورك "

افتتحت الندوة برعاية سعادة الدكتور على فخرو وزير الصحة ورئيس المهيئة الوطنية العليا لحماية البيئة فى دولة البحرين ، حيث رحب سعادته بالضيوف المشاركين واك على ضرورة الاهتمام بمثاكل التلوت وحماية البيئة ، وأشار سعادته الى أننا تأخرنـــا كثيرا فى ذاك المجال ، الذى سبقتنا اليه كثير من الدول المتقدمة منذ سنوات عديــدة وبات علينا أن نبذل جمود ا متواصلة فى شتى المجالات حتى نلحق بالركب .

كما أشار المهند من حسن فخرو رئيس جمعية المهند سين البحرينية ورئيس مجلمسس اد ارة شركة نفط البحرين الوطنية في كلمة الافتتاح الى الدور الذي تلعبه جمعيسسة المهند سين البحرينية في متابعة قضايا التطور والتكولوجيا والمحافظة على البيئسسة وتحسين نوعية الحياة ، وتساهم بقدر استطاعتها في كل الموتعرات والتجمع العلمة التي تعتبر بلاشك الملتقي الحقيقي لتبادل الخبرات والمعارف حول القضايسا ألهامة التي تعس حياتنا وخاصة ما يتعلق منها بتصنيع ثرواتنا النفطية والغازية وسسسا يتبعها من صناعات مختلفة كالاسمدة والبتروكيا ويات والتي أصبحت توثر على البيئسسة وتفسد ها بسبب ما تلفظه من ملوئات عديدة . ثم تحدث المهند من / فاروق المعيوف _ الامين العام للاتحاد العربي لمنتجى الاسمدة الكيماوية فأشار الى التوسع المهائل الذى حدث فى صناعة الاسم____ ة الكيماوية فى المنطقة العربية خلال العقدين الماضيين والمتوقع خلال العقد الحالى وبين كيف أصبحت مشاكل التلوث الناجعة عن هذه الصناعة تساهم بشكل لا يمك_ن غض النظر عنه فى افساد البيئة وتلوثها وحث فى كلمته على ضرورة تضافر الجه___ود لتلافى أى نتائج سلبية على نوعية البيئة جائت كنتيجة حتمية للتقدم الصناعى الـــذى نسعى الى تحقيقه ، وقال ان الاتحاد يعول كثيرا على هذه الند وة والا ستسفر عنه من نتائج من خلال مشاركة هذا الحشد الكبير من الخبراء العرب والا جانب .

ثم جائ كلمة الدكتور/ غانم جاسم معثل المنظمة العربية للتنمية الصناعية ليوكد بدوره على أهمية موضوع الندوة وكيف توليه المنظمة اهتماما بالغا من خلال متابعــة وتنغيذ برنامج تطوير وتنمية صناعة واستخدام الاسمدة الكيماوية فى الدول العربيـــة والتى تأتى هذه الندوة المتخصصة والتى تعقد لمناقشة مثل هذا الموضوع المحــام لا ول مرة ـ كأحد نشاطاته لعام 1981 وأشار الى التعاون الوثيق بين الاطـــراف المعنية بتنغيذ هذا البرنامج والمنظمة العربية للتنمية الصناعية ، والذى بلاشــــك سوف نتمكن من خلاله من احراز كثير من النجاحات سوا من تم يطوير صناعة الاسمــدة الكيماوية أو فى حماية البيئة من أضرار التلوث الناجمة عنهــــا.

حضر السيد / عبد الروموف شكرى _ ممثل اليونيد و ومدير برنامج تطوير وتنميــــة صناعة واستخدام الاسمدة الكيما وية في الدول العربية _ اليوم الاخير من النـــــد وة وحضر الجلسة المسائية وشارك في وضع التوصيات،

عقدت أول جلسات عمل الندوة في الساعة الع^رشرة صباحا حيث انتخب السيد / فاروق المعيوف الامين العام للاتحاد العربي لمنتجي الاسمدة الكيماوية رئيســـــا للندوة لليوم الاول والسيد / حسان شعشاعه من شركة صناعة الاسمدة الاردنيــــة ليترأس جلسات الندوة لليوم الثاني والدكتور / محمد سيف الدين عطفه مستشـــــار وزير الصناعة في الةطر السوري رئيسا للندوة لليوم الثالث ، كما تم اختيار كل مــــن



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جانب من الحضور في زبارة شركة باناجاز ــ البحرين



جانب من الحضور بعد الجلسة الختامية وصياخة توصيات الندوة

الدكتور / غانم جاسم _ مثل المنظمة العربية للتنمية الصناعية والسيد / محمود عزت من الاتحاد العربي لمنتجى الاسمدة الكيماوية مقرريسين للنسب وة .

شارك في الندوة بالحضور والقا^ع البحوث 20 مشاركا من الغنيين المتخصصين في مشاكل التلوث في شركات الاسمدة الكيماوية أعضا^ع الا تحاد العربي من ثمـــان دول عربية الى جانب ₁₅ خبيرا من الشركات العالمية العاملة في مجال صناعــــة الاسمدة الكيماوية وحماية البيئة بالاضافة الى عدد كبير من المهتمين بصناعة الاسمدة الكيماوية وحماية البيئة من بعض المنظمات والمكاتب الاستشارية في دولة البحريــــن والدول العربية .

قام المشاركون فى نبهاية الندوة بزيارة معالم البحرين الصناعية وأهمها شــــركــه بانوكو وشركة باناجاز والحوض الجاف ، هذا وقد أعرب المشاركون عن شكرهم وتقديرهم لدولة البحرين أميرا وحكومة وشعبا ، كما أعربوا عن شكرهم الجزيل لجمعية المهند سين البحرينية ووزارة الصحة لرعايتها للنك وة وتوفيرها كاغة التسهيلات كما أعرب المشاركـون عن شكرهم للاتحاد العربى لمنتجى الاسمدة الكيما وية والمنظمة العربية للتنمسيسية الصناعية واليونيد ولما قدموه من جهد لعقد وانجاح هذه الند وة . كلمة الدكتور/ على محمد على فخرو ... وزير الصحة ... رئيس المهيئة الوطنية لحما ي................................. البيئة في البحرين •

بسم الله الرحمن الرحيم

أصحاب السعادة:

أخى رئيس جمعية المهندسين البحرينية أيها السيدات والمادة أخى الامين العام للاتحاد العربي لمنتجي الاسمدة الكيماوية ·

يطيب لى أن أرحب بضيوفنا في البحرين وأن أرفع اليكم تحيات وتعنيات صاحب السمو أمير البلاد المعظم – وسمو رئيس مجلس الوزرا^ع – وسمو ولى العهد كما أحيى الاخو ة أعضا^ع جمعية المهند سين البحرينية لنشاطهم الدو²وب في حقل المحاضرات والمؤ تمرات العلمية التى ترتبط مباشرة بحاضر ومستقبل التقدم العلمى في الوطن البحرينى بصورة عامة وفي للدان الخليج بصورة خاصة ٠

أيبها السيدات والسادة :

اننى لن أعلن عن ملوثات البيئة من جرا صناعة المخصبات والاسمدة فتلك أمور ستبحثوه! في اليومين القاد مين وانما دعونى اغتنم فرصة هذا اللقا لأعرضعلى ندوتكم بعضا مسن جوانب الصناعة وتلوث البيئة التى أعتقد أنها تحتاج الى اهتمام منكم •

ومنذ أكثر من ربع قرن دخل الكمبيوتر المجتمع الغربي ، بد ¹أ بالصناعة والتجارة وانتها^ع في وقتنا الحاضر بدخول مئات الالوف من المنازل ، وبأنه أصبح جز⁴ من البرامج التعليمية في المدارس الابتدائية والثانوية ، أما في وطننا العربي فان عدد الجامعات التي لديها برنامج تعليم لعلم الكمبيوتر لا تزيد على أصابع اليد ، وسنحتاج على ما أظن الى سنيين طويلة قبل أن تستجيب مؤ سساتنا التعليمية الى واقع ومتطلبات هذا الوجه الجديد من حضارة اليوم وحضارة المستقبل .

ومنذ عشر منوات انعقد مؤتمر (استكهولم الشهير) حول البيئة وما أن انتهى حتى بدأت المؤسسات التعليمية وغيرها في الغرب تهتم بعلم البيئة وتطوره ، أما نحن فان احساسنا بأهمية هذه المشكلة لم يتعد بعد ملامسة السطح ، ولا تزال غالبية مؤسساتنا التعليمية غير راغبة أو غير قادرة على ادخال هذا العلم الجديد في مناهجها .

ومنذ خمس سنوات ، وبعد أن تغجرت مشكلة الطاقة في وجه العالم بدأ الغرب يتحدث عن الصناعة التقليدية العتيةة التي تحتاج الى طاقة كبيرة ، والتي تلوث البيئة تلوثا كبيرا والتي كفائتها الانتاجية تعتبر منخفضة وترك مثل هذه الصناعات للعالم الثالث ليقسوم بها «مستعملا ما لديه من أيد عاملة رخيصة متوسطة التدريب «مبذرا الطاقة التى لديه « ملوثا بيئته، ومواجها المشاكل الكلاسيكية الغنية والادارية والاجتماعية لصناعة القرن التاسع عشر والنصف الاول من القرن العشرين «أما نحن فاننا نسير في ذلك الدرب المرســــوم لنا دون مقاومة ودون تهيئة طويلة المدى على الاقل للخروج من هذا المصير •

أيها السيدات والسادة:

هذه أمثلة ثلاث تبرز كيف أن المجتمع العربي يظل دائما يلهث وراً المنطلقات الحديثة والقضايا الجوهرية بسببعدم الشفافية والحساسية الذهنية عند الكثيرين من السؤ ولين عن تسيير الامور التقنية والاقتصادية والاجتماعية في دولته ، وتبرز هذه الاسئلة: _

- الا يستطيع هذا المجتمع حقا أن يخطط ليقفز فوق الثغرة التى فصلته عن المجتمعات المتقدمة ، ويستشرف آفاق المستقبل، ويبدأ من هناك؟
 - الانستطيع أن نبدأ من حيث يتكلم الغرب عن الصناعة الجديدة ونخطط لقيامهــــا في بلداننا في المستقبل المنظور دون مرور طويل ومؤلم عبر الصناعات القديمة ؟
 - ألا نستطيع أن نركر على مشارف المستقبل الذي يتطلع الى صناعة الفضا وصناعـــة استغلال ثروات البحار والصناعة الخفيفة الحركة العالية الكفائة إ
 - واذا كنا لا نملك التكنولوجيا ولا العلم الذى يسمع بذلك الآن، أقلم يؤن الأوان ... لكى نضع جهدا مكتفا بالتعاون مع المسؤ ولين عن التعليم والتدريب لكى تنصــب جهودنا في قنوات من التعليم الحديث والتدريب المكتف والبحث العلى المتواصل لكى توصلنا إلى مشارف علوم ذلك المستقبل ؟ فمثلا إذا كان علم البيولوجى سيصبح علم القرن الواحد والعشرين، ليحل محـــل علوم الكيمياء والفيزياء في الاهمية، فماذا تنتظر مؤ سماتنا النعليمية والحكوميـــة لكى تعطيه الاهمية القصوى والدفع القومى ٠
 - وأخيرا عاذ! كان بنا؟ قاعدة دائمة صناعية يحتاج إلى مورد دائم للطاقة جديـــدة تكون متوافرة لدينا بعد أن تنضب المصادر الحالية؟ متى سنستعمل جزاً غيرهــا بخلاف خيرات طاقتنا الحالية للاستعداد لفترة طاقات المستقبل ؟

أيها السيدات والسادة:

تلك كانت أسئلة مرتبطة بالصناعة، وينطبق الأمر على البيئة أيضا ١٠ ان نظام تقييم تأثـــير الصناعة على البيئة لم يدخل في حياتنا العربية الا باستحيا مديد ، ولا يزال مغه ومنا للمؤ ثرات على البيئة مقتصرا على التأثيرات الملوثة للبيئة المادية فقط، وننسى أن تأثير الصناعات والمشاريع الكبيرة على الجوانب الاجتماعية والاقتصادية تحتاج الى انتبــــاه شديد ، اننا نبنى المصانع والمشاريع الضخمة دون أن نهيئ القوى الانسانية القادرة على أن تسير تلك المشاريع ، القادرة على أن تطور تلك المشاريع ، القادرة على أن تحسل مشاريع أخرى محل مشاريع اليوم عندما تصبح في المستقبل عديمة الجدوى أو الفاعلية ، بل اننا لا نقوم بأى جهد قانونى أو اجتماعى أو ادارى لمواجهة مشاكل هذ ، المشاريسع اننا بدلا من ذلك نكتفي باستيراد القوى العاملة من خارج حدودنا ، ونعتقد مخطئين بالطبع ، أن باستطاعتنا أن نستعر بهذ ، الصورة معتمدين على الفائض المالى القريسب لدينا ، وننسى أن حضارات كثيرة بنيت في الماض بهذ ، الصورة قد أصبحت مدنها بعسد حين مدن أشباح ، ينعدق فيها البوم وتذروها الرياح .

وبعد فان رفع هذه الاسئلة والمخاوف لا يقصد منها التعجيز ولا ثبط الهم، فلأن بينكم من هم أصحاب اتخاذ القرار، ومن هم أساتذة في المؤسسات التعليمية، ومن هــــــم علماء في البحوث، نعتقد أن بامكان مؤتمركم هذا، وبأفكار مؤتمرات مستقبلية أخــــرى أن تنظر في بعض منها، ونحاول حلها.

اننى أشعر أن بعض الكلمات التى قلتها مطؤة بالمرارة الكنها أيها الاخوة مرارة الذى يعلم أن المجتمع العربى يزخر بالامكانيات الضخمة العظيمة، ومع ذلك يراها تهــــدر يوميا في مسالك عقيمــة وتنحر يوميا في صراعات قبيحة شخصية أو قبلية أو عقائد يــــة جوفاً • •

رالسلام عليكم ورحمة الله وبركاته ، ،

كلمة السيد / حسن عبد الله فخرو ـ رئيس جمعية المهند سين البحرينية

بسم الله الرحمن الرحيم

أصحاب السعاد ة، سيداتي وسادتي ،

انه لمن سؤ الحظ في مسيرة التطور الغير مسبق هذه ،عدم اهتمامنا ان لم يكن تجاهلنا التام بظروف البيئة التى تحيط بنا في كل جانب ونرعية الحياة التى نحياها كل يوم . واليوم حيث ينتابنا ويبهرنا هاجس اللحاق بالتطور الغربى بكل أنواعه فكاد آن ننســـخ منهاجا لا يعطينا سوى القشور في حين أن الغرض الاساسى من التقدم في الغرب كانت ولا تزال هى التندية وتحسين ظروف الحياة المعيشية نما في ذلك من مرد ود على الانسان وهو بيت القصيد ــ نجد أنفسنا نتجاهل أو نجهل هذه الحقيقة الاولى والاولية بالذات. ان ذلك لمن دواعى السخرية المحزنة .

ولكن السخرية الأهم بعد ذلك هو فشلنا في فهم والاستفادة من القوانين الطبيعيـــة والنظم والتشريعات المتراكمة التى أنتجها المجتمع المتقدم على مر السنين • فكــــان بالامكان تطويع تلك القوانين لصالحنا متى أحسن ادراكها واستيعابها •

ان تلك الحقيقة الاخرى تنعكس وبشكل خاصعاى معظم ما شيدنا من مصانع ونظــــم وعمارات شاهقة وبعضمدننا الجديدة في وقت كان مناسبا وممكنا اخضاعها لشـــروط ومقاييس صحيحة منذ البداية • وتلك الحقيقة تتعلق أيضا بشكل خاص بصناعاتنا النغطيــة والغازية وما يتبعها من صناعات مختلفة وأخص بالذكر مشاريع الاسمدة والبتروكيما ويات •

ان ذلك في نظرى مأساة جيلنا الحالى ١٥ن تلك لأكبر بلية نراها بأم أعيننا ٥ وهى ــ فشلنا في التمييز بين ما هو مهم وآهم ٥ أنه بالاحرى فشل في تحديد الاوليات، تنافس متواصل فيما بيننا لبنا الاكبر والأكثر ضجيجا ٥ كأن شروط الحياة غير متوفرة على وجـــه الخليقة ٥ وكأن أنجع وسيلة لتربية طفل هى في جهاز كبير ٥ وكأن مقاييس البنايات هـــو في طوابقها الخمسين وكثرة زجاجها ومدى انارتها ليلا خوفا من عدم رؤيتها في وضبع النهار ٠

اننى لأعجب إلى متى نواصل ما نحى فيه • إلى متى لا نعى ثمن تلويث الهوا السندى نتنفسه والما الذى نشربه ونغتسل به والارض التى نعيش عليها ونأكل منتوجها ــ هـــل يا ترى سنرى النور يوما ؟ ومتى سنعرف الثمن لكل ذلك؟ نحن في جمعية المهندسين البحرينية نتابع قضايا التطور والتكنولوجيا في حين انقلـــق ونتألم في كوننا من ضمن القلائل المهتمين بضرورة المحافظة على شروط البيئة وتحســـين الرعية الحياة 1 ولهذا السبب نشارك بتواضع في هذا المجتمع 1

في هذا الوقت أود أن أقدم تحية تقدير وعرفان لشخصفي هذا البلد يتغانى في خدوض هذا المضار نحو فرضقوانين أكثر صرامة في مجال التلوث ءانه وزير الصحة سعسسادة الدكتور على فخرو

فنحن نفخر بوجوده معنا اليوم لمواصلة محاولاته الدوّوبة في هذا الطريق وبوجوده معنا لما يعثله من عناصر الخير في هذا المجتمع • وما وجوده هنا اليوم معنا الادلالـــــة أخرى على اهتمامه المستمر بهذا الموضوع •

كما أود أن أغرب عن امتنانا للاتحاد العربي لمنتجى الاسمدة الكيماوية لعبادرته الطيبة. بالمساهمة الكبيرة في تنظيم هذا المؤتمر ومساغد تهم المخلصة في سبيله • وأشكر كذلك المساهمة الجليلة الاخرى من قبل اليونيدو ووزارة الصحة والمنظمة العربية للتنميسية. الصناعية لمساعداتهم القيمة •

وأود أن الشكر كذلك المتحدثين والمشاركين في هذا المؤتمر على اهتمامهم والوقت المذى بذل في سيسيسيل تطور هذا الموضوع • واتمنى للجميع الاستغادة وحسن الاقاميسة في بلدنا العزيز •

وليكن هذا المؤتمر خطوة أخرى في الطريق الصحيح ،

والسلام عليكم ورحمة الله ، ، ،

كلم---ة السيد / فاروق المعيـوف الأمين العام للأتحاد العربي لمنتجي الأسمدة الكيماويسة

بسم الله الرحين الرحيـــــم مسلسسسسسسسسسسسسس حاد قالد كتور/ على فخرو وزير الصحة درئيس الهيئة العليا لحماية البيئة الأخوات والأخوة المشاركين الأفاضـــل

يسعدنى ان أرحب بكم اجعل ترحيب باسم الأتحاد العربى لمنتجى الأسمدة الكيماوية ، شاكسرا ومقدرا تلبيتكم حضور هذه الندوة التى تأتى ضمن أبرز نشاطات البرنامج الأقليمى لتنمية وتطويسر صناعة واستخدام الأسمدة الكيماوية فى الدول العربية لعام 1981 ، انه أول لقا^م متميز يسسخم نخبة معتازة من الخبرا^ء المتخصصين العرب والأجانب لمناقشة مظا هرومشاكل التلوث فى صناعسسة الأسمدة فى الدول العربية ، كما ان المساهمة الفعالة فى أعماله من واقع التجربة والخسسبرة العملية والتطور التقنى فى هذه الصناعة والبحوث الميدانية سوف تساعدنا كثيرا فى تغم مشاكسل التلوث التى تواجهنا فى هذه الصناعة والبحوث الميدانية سوف تساعدنا كثيرا فى تغم مشاكسل فيما بيننا لحل هذه المشاكل بدرجة عالية من الكها^مة .

ان تلوت البيئة بات يمتبر من أهم المشاكل التى تواجه العالم فى العصر الحاضر ، واذ ا جاز لنا ان نطلق هذا التعبير " تلوت البيئة " فاننا نقصد بذلك كل ما يقوم به الأنسان بطريقة مباشرة أو غير مباشرة بادخال مواد ضارة تتسبب فى افساد البيئة وتهدد حياة الكائنات الحيـــة بما فيها الأنسان نفســه ، وقد تُنْتَج بعض هذه المواد الضارة أو ما نسميها بالملوثات رغـــما عن الأنسان أو بطريقة حتمية كمواد ثانوية فى عمليات التصنيع المختلفة ، ولاشك ان هذا التلوت جا أحد النتائج السلبية لأندفاع العالم نحو التصنيع سعيا ورا التقدم ، وصناعة الأســـــدة الكيماوية وهى جزء من المجمعات الكيماوية الضخمة التى أقيمت فى العصر الحديث ، ومن أبــــرز

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سمات التقدم التكولوجي فيه ، فهى وان كانت لا تشكل مدر الخطر الأساسي أو الوحيد فسي تلوث البيئة وافساد ها ، الا ان التوسع المهائل فيها باعتبارها أحد العناصر الرئيسي................. لتأمين انغذا ، واستغلال الثروات الطبيعية التي منحها الله لناوصل الى درجة لا يمكن معه غض النظر عما تلفظ مالمصانع من اضرار للحرث والنسل ، من أجل ذلك نجد ان المصانع الحديثة للأسعدة الكيماوية أصبحت تأخذ بعين الأعتبار عوامل التحكم في التلوث وحماية البيئة واختيار الموقع المناسب منذ اللحظة الأولى لدراسة المشروع ، وتضع في حسبانها ما يضيفة ذل...ك من أعباء اقتصادية على كلفة الشروع وما يتطلبه من استخدام للطرق التكولوجية المتقد مسة ، من أعباء اقتصادية على كلفة المشروع وما يتطلبه من استخدام للطرق التكولوجية المتقد مسة ، أن العالم ينفق الكثير من أجل المحافظة على نظافة البيئة وتأمين الرفاهية للسكان ولمقد في العالم خلال عام 1980 برقم تراوح بين (3 سرح) بليون دولار ، صحيح ان جزءا في العالم خلال عام 1980 برقم تراوح بين (3 سرح) بليون دولار ، صحيح ان جزءا الى العالم خلال عام 1980 برقم تراوح بين (3 سرح) بليون دولار ، صحيح ان جزءا في العالم خلال عام 1980 برقم تراوح بين (3 سرح) بليون دولار ، صحيح ان جزءا البيرا من هذا الأنفاق يتم استرجاعه كردود لقيمة الملوثات بعد ان يتم استماد تها وتحويلها ومدى الجهد اللازم لحماية النان ذلك يعكس الأهمية التي الماء من عامة الماء من المناء ولماء المناء ومدى الجهد اللازم لحماية البيئة من التلوث الناجم عن مناعة الأسمدة الكيماوي......

لقد تطورت صناعة الأسعدة الكيماوية تطورا هائلا في الوطن العربي خلال العقد ين الماضيين ، واصبحت هناك مجمعات للأسعدة الكيماوية في معظم الأقطار العربية ، تغــــــم مصانع لأنتاج جميع انواع الأسعدة النيتروجينية والفوسغاتية والعركبة المعروفة في العــــالم بطاقات انتاجية سنوية عالية تربو حاليا على (3) عليون طن نيتروجين ، (2) مليسون طن خامس أكسيد الفوسفور رمن العتوقع ان تتضاعف هذه الطاقات في منتصف هذا العــــقد ، كما تغم هذه المجمعات مصانع لأنتاج المنتجات الوسطية اللازمة لصناعة الأنواع المختلفة من هذه الأسعد ة كحامض الفوسفوريك وحامض الكبريتيك وحامض النيتريك والأمونيا كما تضم المن ذلك وحدات لمعالجة العياء وانتاج البخار وفيرها من العرافق الخدمية ، الفاقة السبي وحدات استخراج وتعدين خامات الفوسفات والكبريت وما يتطلبه ذلك من نقل وتداول لكبيات هائلة من هذه الخامات ها معانية المنتجات الوسطية الماتفات المات المات المعالية السبي المات في مناب ذلك وحدات لمعالجة العياء وانتاج البخار وفيرها من العرافق الخدمية ، النواع المختلفة من وحدات استخراج وتعدين خامات الفوسفات والكبريت وما يتطلبه ذلك من نقل وتداول لكبيات هائلة من هذه الخامات الغامات الغوسفات والكبريت وما يتطلبه ذلك من نقل وتداول لكبيات وحدات استخراج وتعدين خامات الغوسفات والكبريت وما يتطلبه ذلك من نقل وتداول لكبيات هائلة من هذه الخامات ، معا ينجم عنه بالتالي تصاعد كتـــير من الأتربة التي تسبب تلوت جو العمل والبيئة المحيطة اذا لم تتوفر الأجهزة المناسبة لجمع هذه الأتربة ومنع تصاعدها في الأجوا

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المحيطة 10 انتاج المنطقة العربية من هذه الخامات يزيد على (30) مليون طن من خام الفوسفات و (7ر1) مليون طن من خام الكبريت ومن المتوقع أن تتضاعف هذه الطاقـــات بحلول عام 1985 ٠

لا أريد ان اتحدث عن موضوع انتم أخبر منى به ولكم أجد لزاما على ان أرجوكم التركيبز على ما يسلى : <u>المنصرفات الغازيمة</u> كأكاسيد النيتروجين وأكاسيد الكبريت وأبخرة الأمونيا ومركبات الغلورين وفبار السماد المتصاعد من معدات تجهيز المنتج النهائى . <u>والمنصرفات السائلة</u> وهذه تحتوى على كعيات كبيرة من العلوثات كالأمونيا واليوريا والأحمـــماض والمنصرفات السائلة وهذه تحتوى على كعيات كبيرة من العلوثات كالأمونيا واليوريا والأحمـــماض والمنصرفات السائلة وهذه تحتوى على كعيات كبيرة من العلوثات كالأمونيا واليوريا والأحمـــماض والمنصرفات السائلة وهذه محتوى على كعيات كبيرة من العلوثات كالأمونيا واليوريا والأحمـــماض والمنصرفات الصلية وأهمها الفسفوجيسم الذى ينتج بكعيات هائلة من حامض الفوسفوريـــك المصنع بالطريقة الرطبة من الصخر الفوسفاتي وحامض الكبريتيك ويتوقع أن يبلغ الأنتاج العربي من هذا الفوسفوجيسم أكثر من (20) مليون طن سنويا في منتصف الثمانينات .

ان التأثير الضار لهذه الملوثات أصبح معروفا للجميع ، فالغازات والأبخرة والأتربسة المتصاعدة من مصانع الأسمدة الكيماوية تؤثر تأثيرا ضارا على النبانات وسائر الكائنات الحيسة وحتى المنشآت الحديدية •

كما ان صرف السوائل المختلفة من هذه المجمعات بالوقت الذى يؤثر تأثيرا ضــارا على الكائنات الحية المائية ويؤدى الى تلوث المياه التى لا غنى للأنمان عن استخدامها فى شتى نواحى الحياة ، فان الخسائر الأقتصادية الناجمة عن عدم معالجة واسترجاع مابها من مــــواد كيماوية نافعة تضيف بعدا جديدا للمشكلة وما بها من هدر ، حيث تجد المنصرفات الصـــلبة من الفوسفرجبسم طريقها الى البحار فى كثير من المصانع التى تقع بالقرب منها ، ولا يخفى على أحد التأثير الضار الناجم عن ذلك على الكائنات البحرية لما يحتويه الفوسفوجبسم من ملوثات أهمها الفلورين والمواد المشعة من اليورانيوم •

من أجل ذلك بادرت الدول المتقدمة ولحقت بها بعض الدول النامية فى سمسسسن قوانين وتشريعات لحماية البيئة من التلوث ، وعلى ضو هذه القوانين والتشريعات تحمد مددت المواصفات القياسية لنوعية الهوا فى المصنع والمناطق المجاورة ، ثم جات قوانين أخرى تحمد د --21--- النسب المسموحة للملوثات الغازية والأتربة وكذلك المواصفات القياسية للمنصرفات السائلة مسسن مصانع الأسعدة الكيماوية وللحد من تلوث البيئة وافسادها ، ولا شك ان هذ ، المواصفات زما يتعلق بها من تشريعات وقوانين تختلف من قطر الى آخر أعتماد اعلى كثير من العوامل ، أهمها العوامل الأقتصادية والأجتماعية ، الا اننا نجد ان هذ ، القوانين أشد صرامة فى الدول المتقدمة عنها فى الدول النامية نظرا للكتافة العالية من التصنيع التى وصلت اليها الدول المتقدمة وما ترتب عليه من نتائج سلبية على نوعية البيئة .

ان الأتحاد العربى لمنتجى الأسمدة الكيماوية انطلاقا من وعيه التام لهذه المسسألة وتأثيرها يعول كثيرا على ما ستسفر عنه مناقشاتكم فى هذا اللقا، وسوف تحظى توصياتكم بكامسسل اهتمامه فهى بالتأكيد ستنير الطريق وتهدينا الى ما يجب ان نفعله وما ينبغى ان تتضمنه الخسطط والمشاريع المستقبلية لنشاطات الأتحاد المختلفة فى الجانب الصناعى كما أننا وبتنسيق تام مسع المنظمة العربية للمواصفات والمقاييس والمنظمة العربية للتنمية الصناعية وبالتعاون مع جسسميع المنظمة العربية للمواصفات والمقاييس والمنظمة العربية للتنمية الصناعية وبالتعاون مع جسسميع ومتابعة ما تقترحونه من حلول وتوصيات .

وفى الختام لا يسعنى الا ان أتقدم بالشكر والتقدير لدولة البحرين الشقيقة أمسيرا وحكومة وشعبا لكرم الضيافة وحسن الأستقبال ،كما يسرنى أن أتقدم بالشكر الجزيل لسمستادة الوزير الدكتور / على فخرو لرعايته الكريمة هذه الندوة وتفضلة بافتتاحها ،كما لا يفوتنى التنويسه بخالص الشكر والعرفان للأخوة العاملين فى جمعية المهندسين البحرينية وعلى رأسهم الأخ / حسن فخرو والأخ / يوسف فخرو على ما بذلوه من جهود لتنظيم هذه الندوة •

كما أسجل شكرى وتقديرى للمنظمة العربية للتنمية الصناعية ومنظمة الأم المتحدة للتنمية الصناعية والبرنامج الأنمائى للأم المتحدة لما قدموه من دعم وتغطية مالية لتكاليف هذه النسسدوة كما لا يفوتنى أخيرا أن أتقدم بخالص شكرى للخبرا^ع العرب والأجانب الذين ساهموا ببحوثهم القيمة بانجاح الندوة ، راجيا للجميع طيب الا^ققامة ولندوتنا كامل النجاح ·

> وفقنا الله لما فيه خير وصالح وتقدم أمتنا العربية المجيدة والسلام عليكم ورحمة الله وبركاته -13

كلمة الدكتور/ غانم جاسم (ممثل المنظمة العربية للتنمية الصناعية)

بسم الله الرحمن الرحيم

صاحب السعادة وزير الصحة ورئيس اللجنة الوطنية لحماية البيئة ــ الدكتور / علــــــى محمد نخرو ، أصحاب السعادة / السيد رئيس جمعية المهندسين البحرينيــــــة المهندس/ حسن فخرو ، السيد / الامين العام للاتحاد العربى لمنتجى الاسمــــدة الكيماوية ــ المهندس/ فاروق المعيوف ، أيها السب ت والسادة :

يشرفني بالنيابة عن السيد / المدير العام للمنظمة العربية للتنمية الصناعية ، والــــذي كان توامًا للمشاركة شخصيا في هذا الحغل الكريم الا أن ظروفا اقاهرة حالت دون ذلك، وبالاصالة عن نفسي أن اعبر عن اسمى آيات الشكر والتقدير لدولة البحرين الشقيــــقة لاستضافة هذه الندوة والتي تعقد بتضافر الجهود المخلصة لكل من وزارات الصحة ، والاتحاد العربي لمنتجى الاسمدة الكيماوية وجمعية المهندسين البحرينية لمعالجة احدى المواضيع الحبوية التي تواجه المتصنيع في حقل الاسمدة الكيماوية وتأتى هـــذه الندوة كاحدى ثمار نشاط عام 1981 البرنامج الاقليمي لتنمية وتطوير واستخسيدام الاسمدة الكيماوية بالدول العربية والذي أشرف على اعداده كل من المنظمة العربيـــة للتنمية الصناعية والبرنامج الانمائي للام المتحدة ، وذلك لخدمة المنطقة العربيــــة خلال المنوات 1979-1983 عن طريق تنفيذ أنشطة مختلفة في مجال التدريب وتوفير الخبرا والمستشارين لحل المشاكل التي تواجه صناعة الاسمدة الكيماوية مسمسه عقد اجتماعات وندوات في مجالات فنية متنوعة، ولقد برزت أهمية انتاج واستخميه ام الاسمدة الكيماوية بالاستناد الى عاملين أساسيين الاول : ... باعتبار الاسمدة ه..... المدخل الاساسي لتحقيق لامن الغذائي العربي وتوفير الغلة الزراعية والثاني وفسيسرة العواد الخام اللازمة لاقامة هذه الصناعة في الوطن العربي كالغوسغات _ الكبري____ الغاز الطبيعي وغيرها ، وانطلاقا من ذلك فقد سارت صناعة الاسمدة الكيماوية بوتا فسسر نعو عالية حيث بلغ الانتاج العربي من الاسمدة عام 1980 حوالي (2,5) مليون طين الانتاج بمعدلات أكبر لتلبية الطلب المتزايد سواعد اخل المنطقة العربية أو لاغــــراض التصدير للأسواق العالمية ، وعند الحديث عن تنمية صناعة الأسمدة الكيماوية ، يجبب الا ينحصر النقاش حول متطلبات تنمية اهذا الفرع من الصناعة ضمن زاوية توجيـــــه الاستمارات أو تسويق الانتاج أو تأهيل الكوادر وغيرها فحسب، بل يجب أن يشــــمل موضوع لا يقل أهمية عن هذه العوامل وهو التأثيرات البيئية جرا انتاج الاسمدة ســـوا

أيها السيدات والسادة:

ختاما باسم المنظمة العربية للتنمية الصناعية أتقدم مرة أخرى بالشكر والتقدير الى دولة البحرين أميرا وحكومة وشعبا على كرم الضيافة وحسن الاستقبال ، والى وزارة الصحـــة وعلو, وجه الخصوص سعادة وزير الصحة لتشريفه حفلة الافتتاح والى جمعية المهند سين البحرينية للاعداد والتنظيم الجيدين والى الاتحاد العربى لمنتجى الاسمدة الكيماوية لما أبداه من نشاط ملحوظ في حشد هذه الطليعة من الخبرات العربية والاجنبيـــة وللبرنامج الانمائى للام المتحدة ، ومنظمة الام المتحدة للتنمية الصناعية وللاخــــوة معتلو الدول العربية والخبراء العرب والاجانب للمشاركة في اعداد البحوث وتجشمهـــم عناء السفر والحضور متمنين للندوة كامل التوفيق والنجاح .

والسلام عليكم ورحمة الله وبركاته ، ، ،

توصيميمات النمسيك وة ب

- 1- السعى لا يقاظ الوعى لدى العاملين في مجال صناعة الاسمدة الكيماوية بمخاطــر التلوث الناجم عن صناعة الاسمدة الكيماوية في العالم العربي وأهمية السيطـــرة عليه حفاظا على سلامة البيئـــــة.

 - 3- ضرورة التزام مصانع الاسعدة الكيماوية بمراعاة هذه المعايير وتأمين الاساليمميب العلمية والتكولوجية الحديثة لعدم تجاوزها .
 - 4- عند وضع التصاميم الهند سية لمصانع الاسعدة المخطط لاقامتها مستقبلا يراعى وجود وحدات للسيطرة على تلوث البيئــــة.
 - 5- العمل على اعداد كوادر متخصصة والاهتمام بتدريبها في مجال السيطرة على 5- العمل على المنشأة.
 - 6- تشجيع التعاون العربى فى مجال صناعة الاسمدة وتبادل الخبرات حول مشاكل التلميميون.
 - مرورة الاستفادة من المنصرفات السائلة والتي تحتوى مخصبات بنسب مقبولـــة
 في المجال الزراعي في البله، إن التي تعانى نفصا في موارد المياه الطبيعية .
أسماء المشاركين في الندوة

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الوظيفة	أسم الشركسة وعنوانهممم الشركس	الا	رتم
	هيئة حباية البيئة.ص و1799عما ن/إلارد ن	دكتور / سامح غرابيسة	-1
	شركة صناعة الاسمدة الارد ني ة.الارد ن	السيد / حسان شعشاعه	-2
	شركة البوتاس العربية _الارد ن	ں کتور /علی أحمد شيوخ	-3
	شركةالا سمدة العربينا لسعودية (سافكو)	السيد / ارشاد الصالح	-4
	شركة الاسعد مالعربية السعو ^ر ية (سافكو)	السيد /محمد أبوالهدى	5
مہند سکیمائی	شركة الجبيل للأسمدة مدينة لجبيل الصناعية مي 1 1 م 1 السعو ^ر ية	السيد /عبد المحسن الدار س	- 6
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-	شرکة اما فلتر _ هولند ا	Mr. P. Goossens	<mark>-</mark> 2 ک
مدير مبيعات منطقة الشرق الا وسط	شرکة اما فلتر ـ هولند ا	Mr.Jan Ten Bosch	-21

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