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IN-PLANT POLLUTION CONTROL WORK IN AN ORGANIC AND INORGANIC CHEMICAL PLANT[1]

by

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by

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## ABSTRACT

In this study two case histories are presented, one for the control of liquid effluents from a refinery   plant and the other for the control of gaseous effluents from a fertilizer plant.  In-plant control, that is control at source of pollutants, is being emphasized as being the most important one to abate pollution from industrial production plants to  protect the surrounding environment.

It is the responsibility of industrial policy makers and plant managers to maintain close control of their operations.  Control measures recommended for adoption include the following methods:

a)    Engineering and process design consideration;
b)    Recovery and utilization;
c)    Local treatment;
d)    Good housekeeping;
e)    Effluent treatment.

The above methods are to serve as guide to management of chemical industry in developing countries so as to avoid making the same mistakes as industrial countries have made in the past.

INTRODUCTION

In industry generally two main approaches to the problem of pollution and environmental damage warrant careful examination. One is the development or adoption of new technologies which reduce pollution and other undesirable side-effects; the second is the location for new industrial plants in areas where there is not already a large concentration of industry and the environment therefore retains its capacity to absorb and dispose of pollutants. UNIDO in its programme to assist developing nations with their programme of industrialization has and is giving consideration to these matters which require the attention of policy makers and industrial management.

In this paper, both corrective and preventive measures are discussed as main strategies for environmental management to be pursued within an organic chemical producing plant and inorganic chemical producing plant.

## Pollution Control in the Refinery Industry

As early as 1928 the American Petroleum Institute organized the first technical committee on waste disposal. Later in 1930 this committee was replaced by a committee on disposal on refinery wastes, which promptly initiated an agressive plan of action for the accumulation and dissemination of water pollution control. Manuals were published on good practices on waste water containing oil. The latter contained design information on the API oil water separator. The committee also sponsored research project at the University of Wisconsin. The result of these research findings was the basis on the design of the gravity differential type oil-water separator.

The waste disposal problems confronting the refinery are those of the control of pollution by free and emulsified oil, both acidic and alkaline chemicals; taste and odour producing and toxic constituents and those materials exerting both an immediate and bio-chemical oxygen demand.

The various types of waste originate from a multitude of refinery processes including fractionating, cracking, polymerization, isomerization, alkylation, chemical treating and selective solvent refining of oil stocks (see figure 1, which gives a simplified presentation of the origins of wastes within a refinery Ref.(1)

### Control Methods

The control of water pollution by wastes originating within a refinery is accomplished by

      a)    engineering and process designing consideration:

      b)    recovery and utilization;

      c)    local treatment;

      d)    good housekeeping;

      e)    effluent treatment.

The above measures are all in-plant control measures that should be taken by plant management.

## a) Engineering and process design consideration

Under engineering and process design comes the design of a multiple sewerage and collection system provided to collect clean cooling water and storm drainage, thereby separating it from a system designed to collect polluted process drainage with a third system to collect sanitary wastes.

Surface drainage from enclosed process areas is drained to the process sewerage system. All other surface drainage is drained to a clean water sewer. Simple devices such as gravity differential oil-water separators will generally prevent water pollution by wastes that may be accidentally spilled and obtain access to the clean water sewerage system.

Cooling water discharges to sewers are reduced to minimum by installing cooling towers. Pretreatment facilities such as septic tanks are the minimum provided for sanitary wastes.

The use of dirty water collection systems for basically different types of wastes occurring within a unit is a common practice. Dirty water recirculation systems ar cooling towers for barometric condensers and vacuum pumps jets have reduced water control problems associated with vacuum distillation units. Waste control has been accomplished by providing surface condensers in place of barometric condensers for vacuum jet pumps. This applies also to various solvent refining processes.

Emulsion losses at a typical wax deoiling plant have been reduced by the use of dirty water recirculation and cooling tower system. Emulsion accumlation is prevented by the use of a demulsifying agent.

Furfural which is used as an extracting agent for various petroleum fractions have to be kept to minimum. In order to keep losses of furfural refining units to a minimum, the use of minimum boiling point azeotropic distillation and phase separation has been adopted. The recovery system provides for a solvent drying tower, a stripping tower and a separator with essential appurtenances. The solvent drying tower produces dry furfural at the bottom and minimum boiling point azeotrop at the overhead. Upon looking this overhead a phase separation occurs to produce furfural rich and a water rich layer. The furfural rich layer is returned to the drying tower as reflux and the water rich layer is pumped to stripping tower. In this tower steam stripping produces a bottom of minimal furfural content and a minimum boiling point azeotrop as overhead. This overhead is combined then from the furfural drying tower (see figure 2.).

Generally the design of continuous instead of batch
treatment processes has aided in pollution control by eliminating
peak discharge of wastes.  The use of processes which include
regeneration of the active chemicals for sweetening, hydrogen
sulphide removal and mercaptan  extraction may avoid or appreciably
reduce the problems associated with the disposal of waste caustics.

b)     Recovery and utilization

The recovery of sulphuric acid from acid sludges produced in the
treatment of oils is one good example for recovery and reuse of waste
produced in a refinery.  The hydrolysis of sludges produces dilute
black acid.  The sludge conversion-contact acid method can produce
white acids of 98-104.5 per cent concentration.  Black acids of the
same strength can be produced by feeding weak acids (obtained
by hydrolysis) to the towers in the  place of clean water.

Spent alkylation acid is reused for treating various oils and
waxes and is regenerated in local and outside acid plants.

Some refineries adopt a chemical flocculation plant using
aluminium chloride as a coagulant that has been recovered from
aluminium chloride-hydrocarbon sludge.  The hydrolysis of the
sludge produces aluminium chloride, hydrocarbon and benzol.
Each component will be recovered and utilized.

Water treating plant sludge from boiler feed water treatment has
been collected and handled in a separate system and used for the
neutralization of acidic waste waters.  In numerous cases various types
of acidic and alkaline wastes are combined for mutual neutralization.

Processing chemicals such as phenols, methyl ethyl ketone,
benzol, furfural etc., lost through pump gland leakage, sample collection,
spills etc., are collected in a separate drainage system and sump
and recovered from dilute waste solutions.  Special stills are
provided for chemical recovery and waste control

Refinery waste water is separated to remove free oil, clarified and softened using lime, soda ash and ferrosulphate, filtered through high rate sand filters, acid treated to control **pollution and stabilized** using polyphosphate. The treated water is returned to the refinery for reuse. The sludge is pumped to lagoons.

All refineries have slop oil recovery systems where large quantities of oil originate at a single source, such as two stage pipe stills with barometic condensers.

Slop oils collected from waste water separators and bottoms of storage tanks are usually treated by heating the presence of an alkaline treating agent. In some cases emulsion breaking organic sources can be appreciably reduced by the use of precoat vacuum filter for slop oil treatment.

## c)    Local treatment

The most commonly adopted local treatment is that of the use of oil and water separators for separation and collection of oil at individual units. The use of local separators has the advantage that contamination can be kept to a minimum, thereby decreasing the cost of conditioning the wasted oil and returning it to the process.

"White water" emulsions containing 1-3% oil are normally treated locally. They are formed in the water washing of acid treated lubricating stocks. The emulsions may be treated using heat and calcium chloride. The water layer is satisfactory for discharge to plant sewers. The oil or soap layer makes fuel of high ash content.

Waste caustics are treated using various methods. Those waste caustics high in organic matter content are usually neutralized to "spring" the "acid oils" i.e. the phenolic and **naphtenic** materials insoluble at pH value 8 using sulphuric acid. Spent alkylation acid, hydrolized **black** acid, and fluid acid sludges are also used for treatment. The hydrogen sulphide released in this process is burned or utilized for sulphuric acid production.

Waste caustics high in **mercaptans** are usually regenerated by steam stripping with open steam in a bubble tray column.

Waste caustics high in sulphides are treated by contact with
steam and air and by stripping procedures.  The sulphides in the
waste caustic contacted with air and steam are converted to thiosulphates.
This type of system operates with 95 per cent conversion.

Condensate waters high in ammonia and hydrogen sulphide are
treated in some cases using steam stripping(figure 2). A typical system
is shown in Figure 3.  The ammonia and sulphide appear to exist
in these solutions as polysulphides.  These polysulphides are
decomposed in the process so that ammonia and hydrogen sulphide are
stripped overhead. The overhead gases are usually burned.  The
condensate waters may be treated by aeration.  Ammonia and small
amounts of hydrogen sulphide are released by the aeration of colloidal
sulphur which is precipitated.  pH control is sometimes needed as
an adjunct to this process.

At the fluid catalytic cracking units the usual practice is to
inject part of the condensate or accumulator waters into the
catalyst regenerator gas stream. This can be done before or after
the electrostatic precipitators.  The temperature of the gas stream
is high to destroy the polluting materials.

Phenolic waters and waste caustics have satisfactorily disposed
of by injection into furnaces or stacks.

Phosphoric acid catalysts have been satisfactorily handled by dumping into
leach pit covering with water leaching at a slow continous rate by
displacing water from the pit, draining of the water and disposing
of the neutral Kieselguhr   as a fill.

Numerous devices and processes are used in the local treatment
of refinery wastes as one can see from the above description.
There are many detailed modifications of various basic processes to
fit local situations.

Continuous research is being conducted to improve the waste
control facilities in refineries. Recently the introduction of an
air floatation treatment of refinery waste water was introduced to conserve
water and reduce pollution (Ref.3).  The system was installed between
the primary API separators and impounding basin of the refinery
waste water treatment train.  The latter acting as secondary separator
providing one or two day residence time allowing further separation of
emulsified oil and suspended solids.

Air is introduced into the system by saturating a pressurized stream of water with air. The stream is mixed with waste stream in an open floatation basin. The pressure release causes an immediate oversaturation of air in the water. This air in excess of saturation is precipitated as millions of very fine bsubbles having size range of 20 - 120 microns. In processing oil refinery wastes recycle flow is most widely used because oil floc tends to be very unstable when subjected to high shearing forces. With recycle flow the feed water is not subjected to high shearing forces after floculation has occurred and this reemulsification is minimized. A larger floatation basin is needed then with the recycle flow, but better performance is obtained then with a split flow in which only part of the feed stream is pressurized because floc can be formed in the entire feed stream.

The skimmed material from the induced aire floatation unit averaged about 65 per cent of the feed rate. It responded very well to centrifuging. All the coagulated oil and solids compacted at the bottom of the centrifuge. The skimmings from the floatation unit were also separable by gravity settling. Eventually the floated material settled due to further coagulation or loss of entrapped air. The induced air floatation unit averaged 81 per cent oil removal and 71 per cent suspended solids removal.

d) <u>Good housekeeping</u>

Good housekeeping is most important to cut down pollution. Operating personnel has to be educated to endeavour to reduce spilling product to the plant sewers establishing a co-operative relationship between production and waste control personnel. This has to be inspired by management of each plant. Most refineries have an individual or group responsible for control activities, depending on the size of the plant. Regular sampling of effluents and their analysis in special waste control laboratories on a routine basis help to introduce a waste consciousness at all plant levels. Local facilities for collection of lost products are frequently provided to encourage good housekeeping and control losses.

## e)  Effluent treatment

Most of the refinery wastes pass through gravity differential type oil-water separators prior to discharge to receiving waters. Separator designs of various types are available in the publications of the American Petroleum Institute(**ref.4**) **The use of vertical slotted** baffles at the inlet structure has gained preference over the conventional API inlet structure. The design droplet diameter should be reduced from 0.02 to 0.013 **cm** for design basis. The sludge that accumulates in these separators is generally disposed as fill.

In several cases this treatment alone was found to be inadequate. Portion of the oil content of refinery waste water is not susceptible to gravity-differential separation and cause taste and odor, toxicity and biochemical oxygen demand. The adoption of treatment processes includes filtration through sand, floatation and chemical flocculation.

The filtration of separator effluents through a porous media such as sand is particularly applicable to cases in which oils of higher specific gravity are being separted, alternatively to those cases in which there is a definite correlation between oil and suspended solids content. This process is expected to be effective in removing only suspended solids and oil.

Dissolved air floatation processes both with and without flocculation have been used as already mentioned. The reports indicate that air floatation aided by coagulant and a coagulant aid such as activated silica will produce an effluent conditioning oil concentration of 10 ppm or less, also reducing the BOD of oil field wastes.

As described earlier chemical flocculation has been used for refinery wastes. Reports indicate at an effluent with average oil concentration of less than 5 ppm can be produced.

The sludge produced is disposed of into lagoons for drying then used for fill or disposed **into incinerator facilities. Incineration** can be accomplished in a single hearth furnace.

Storm waters are collected in a water basin with a capacity to store one year storm to reduce pollution during storm periods.

The stored storm water is treated along normal dry weather flow.

The foregoing illustrates some of the waste control practices at petroleum refineries taken by industry. There is a continuing research being carried out by refineries to study wastes control and devices to bring about an economical solution. It is this in-plant control measures enforced by management in an effort to be a good neighbour and to preserve the water resources that have been stressed throughout the industry.

## In-plant Control of Pollution in an Inorganic Chemical Plant

To illustrate the in-plant control work in an inorganic chemical plant we have chosen the manufacture of phosphoric acid plant coupled with a triple superphosphate fertilizer plant.

There are presently a large number of these plants under construction in developing countries having indigenous phosphate rock.

As the fertilizer industry utilizes well over half of the phosphoric acid produced, we have chosen the classical dihydrate "wet phosphoric acid" process from which the major contaminant to the environment is gaseous fluorine.

The estimated total world production of phosphate fertilizers will reach 32.49 million tons (ref.5) in 1977/78 using phosphate rock containing between 3 - 4.5 per cent fluorine by weight.

There are three major pollutants discharged from phosphoric acid production plants:

1) Fluorine compounds in tail gases;
2) Calcium sulphate, so-called phosphogypsum;
3) Phossy water and other wastes which occur in comparatively small quantities.

## a) Process design consideration

In the production of phosphoric acid phosphate rock is acidulated with sulphuric acid, releasing fluorine mostly in the form of silicon tetrafluorides $(SiF_4)$. About 5 per cent of fluorine is released in the digester

where the reaction takes place.  Since silicon tetrafluorides readily
hydrolize to form fluosilicic acid and silica,

$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2$$
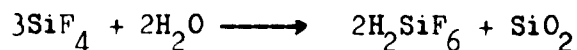
fluoride recovery in the scrubbers usually exceeds 95 per cent and in some region
air pollution control regulations make greater than 98 per cent recovery necessary.
When economics dictate fluoride may be recovered as fluosilicic acid for sale.
Two types of scrubbers have been used successfully.

- cyclonic scrubbers using water injection in a cylindrical chamber;
- cross flow spray chambers with packed sections.

The slurry produced in digester is then filtered to remove gypsum formed
which contains about 30 per cent of the fluorides.  For every ton of
$P_2O_5$ produced about 5 tons of gypsum is produced as calcium sulphate containing
calcium fluorides.  In the newer plants fume exhaust systems have been
installed to remove the dilute fluorine containing gases from this
filtration process.

The filtrate that is phosphoric acid containing 36 - 37 per cent
$P_2O_5$ which for commercial purposes is concentrated to 54 per cent acid.
This concentration is achieved in multiple effect evaporators.  In this
evaporation about 40 per cent fluorine is evolved with the vapours
that amanate overhead in the evaporators.

The collection of these vapours is accomplished by condensation.
In order to recover the fluorine for the manufacture of artificial cryolite used
in the electrodes for the manufacture of aluminium, it is necessary to concentrate
these solutions of fluosilicic   acid to at least 15 per cent concentration
which is acceptable to the aluminium industry for recovery purposes.
The concentration is achieved by recirculating the scrubbing solution of
fluosilicic acid.  Impurities such as $P_2O_5$ has to be kept below 250 ppm
in the recycled fluosilicic aḥid solution to be suitable for recovery
and production of artificial cryolite.  This can be accomplished by
droplet separation and subsequent washing system based on partial condensation
(ref.6).

In the TSP manufacturing process in which phosphate rock is reacted
with phosphoric acid, the fluorides released are collected and first
passed through cyclonic separators to remove entrained dust before
being passed through wet scrubbing facilities.  Similarly gases containing

fluorides can be exhuasted from the green    triple superphosphate curing
building and passed through wet scrubbers in which fluosilicic acid solution
is recirculated building up the fluoride concentration to 15 - 25 per cent
concentration.

The proposed environmental standards by EPA issued to the phosphate
trade (ref.7) limits the emission of fluorides in gases discharged into
the atmosphere as follows:

- wet phosphoric acid plants:      10 grms/metric ton of equiv.$P_2O_5$ feed.
- triple superphosphate plants      100 grms/metric ton of equiv.$P_2O_5$ feed
- green triple superphosphate curing/storage     0.25 grms/metric ton  of
equiv.$P_2O_5$ feed

## b)   Recovery and utilization

The recovery of fluorine from gases can result in the manufacture
of the following products:  fluosilicic acid and fluosilicates, aluminium
fluorides and cryolite.   The latter two products are used as flux agents in the
aluminium smelters.  At present 30 kg of $AlF_3$ and 30 kg of $Na_3AlF_6$ are
needed per ton of aluminium as flux agent.  The percentage of $Na_3AlF_6$ is
expected to be reduced in the future due to an increased washing  out
of fluorine containing waste gases in aluminium smelters and their
recovery in the form of NaF.

According to an estimate at the beginning of 1980 the world production of
aluminium will be in the order of 15 million tons and the demand for flux agents
0.6 million tons can be expected.

When the presently used fluorspar raw materials become short in supply
the phosphate fertilizer industry will be able to offer themselves as
an ideal raw  material source. (ref. 6)

The fluorine-yield can be increased by recycling of the by-product silicic
acid from aluminium fluoride

| | | |
|---|---|---|
| $H_2SiF_6$ | | 17 - 30 per cent |
| $P_2O_5$ | max. | 250 mg/liter |
| $F_2O_3$ | max. | 70 mg/liter |
| $SO_4$ | max. | 1  g/ liter |
| Cl | max. | 1  g/ liter |

Clear liquid free of suspended material, this acid can be used for drinking water fluorination but preferably for the production of fluorine compounds such as

| | |
|---|---|
| sodium fluosilicate or other | sodium fluoride |
| silico fluorides | cryolite |
| aluminium fluoride | hydrogen fluoride |
| calcium fluoride | hydrogen fluoride |

The reaction of fluosilicic acid with aluminium hydroxide (Bayer hydrate) produces primarily a super saturated metastable solution of aluminium fluoride which is separated by centrifuging from the precipitated silicic acid.

$$H_2SiF_6 + ? \ Al(OH)_3 \longrightarrow 2 \ AlF_3 + 4 \ H_2O + SiO_2$$
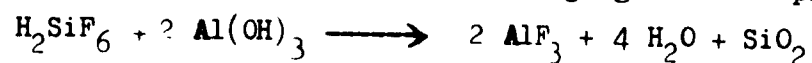
$AlF_3$ is precipitated as the trihydrate out of the metastable $\alpha AlF_3$ solution at increased temperature within 5 hours in crystallizers after the conversion into $\beta$ modification of $AlF_3$. The subsequent drying and calcination result in the final product of approximately 98 per cent $AlF_3$, provided the conditions leading to a hydrolisis of the $AlF_3$ are avoided, Thus obtaining quality product, the drying and calcination can be performed in fluidized calciner which is indirectly heated to about $600^{o}C$ as designed by Chemie Linz.

The simplest way of utilizing the silicic acid by-product by recycling within the plant: there are further possibilities to be used by construction industry and by the detergent industry.

Phosphogypsum which is produced in large quantities as a by-product in the production of phosphoric acid (about 5 tons of gypsum for every ton of $P_2O_5$ produced as acid) has been disposed of in lagoons or by dumping into the sea, as it is soluble in sea water.

Attempts to recover the gypsum have been successful by certain fertilizer manufacturers located inland where the lack of space prevented lagooning.

Phosphogypsum as a filter cake leaving the phosphoric acid plant containing about 20 per cent water can be calcined after blending with coke and clay. This is done to drive off the water of gypsum crystallization in the kiln operating between $900^{o} - 1000^{o}C$ temperature. In the Chemie Linz process calcium sulphate is reduced to calcium sulphide which reaches with the remaining unchanged calcium sulphate to produce sulphur dioxide and Portland cement. The sulphuric dioxide gases containing 8 - 10 per cent $SO_2$ after removal of

solids are used in a sulphuric acid plant as feedstock.

Cement produced in this way contains residual amounts of phosphates and fluorides. Phosphate content should not rise above 1 per cent in the clinker;otherwise it will lower the initial strength of the cement appreciably. Fluorine in the gypsum is released as gaseous fluoride compounds mixed with the sulphur dioxide kiln gas. Fluorine has to be removed by wet scrubbing in the gas cleaning section. Fluorine remaining in the clinker has a beneficial effect because it counteracts the effect of the phosphates by providing an alternative route by which tricalcium silicate can be formed by way of fluosilicates. Indeed, calcium fluoride is used as a mineralizer in cement made from phosphatric lime stone for just this purpose.

Fluorine levels in the phosphogypsum feed have been restricted to 0.15 per cent (ref.8).

Apart from reutilization of phosphogypsum as cement it can be used as substitute for natural gypsum after suitable treatment. The biggest use has been found in the manufacture of plaster, plaster products for the building industry and cement additives (ref.9).

Unfortunately phosphogypsum contains a number of soluble and insoluble impurities which have detrimental effect on the properties of plaster and it is for this reason that phosphogypsum has not in the past been widely used as a material for plaster. Soluble impurities such as mono and di-calcium phosphates and fluosilicates reduce the setting rate of the plaster. Insoluble impurities such as silica, insoluble phosphates and fluoride compounds and organic materials which not only discolour the product but also can delay setting and have adverse effect on the ultimate strength of the plaster. These impurities occur to lesser extent in phosphogypsum produced from hemihydrate phosphoric acid plants.

A number of process have been developed to make use of the dihydrate process phosphogypsum. One of these processes is the Rhône-Poulenc process in which phosphogypsum is converted into calcium sulphate $\beta$ hemihydrate for use in the construction industry by fabricating plaster blocks.

Other processes developed by Knauf, ICI and the Giulini as well as CdF Chimie/Air Industry have been adopted by industry for commercial operation (ref.4 and 10).

Among these processes the ICI process was found uneconomic and production was abandoned.

The above mentioned processes can be identified by the manner in which the dehydration is affected. This step can be carried out either in dry or wet phase like in the Giulini process. Similarly the type of hemihydrate produced is dependent of dehydration; in the dry plate $\beta$ hemihydrate is produced and in the wet phase $\alpha$ hemihydrate is the product. The soluble impurities in the phosphogypsum are removed by washing in hydrocyclones or floatation from which the phosphogypsum suspension is filtered or centrifuged to reduce free water content to the lowest possible level before entering the thermal section in order to minimize waste of fuel in the subsequent drying and calcination stages. In particular, the Knauf process used for manufacture of plaster boards has the advantage of simplicity and low energy consumption.

The CdF Chimie/Air Industry process is capable of accommodating phosphogypsums of different compositions without modification of the process or the equipment used. The purification process is carried out in the aqueous phase at atmospheric pressures by reslurrying the phosphogypsum from the acid filter. The removal of soluble impurities takes place in series of hydrocyclones. A lime solution being used to neutralize the phosphogypsum vacuum filtration produces a solid cake containing 15 - 20 per cent moisture, the filtration being reused in the washing tanks. The thermal stage of this process is carried out in three air driers arranged in series. The first unit is for drying the second for calcining and the third for rehydrating the gypsum. The plaster produced in this process is particularly suited for use in prefabricated products as wall slabs, plaster boards and has good mechanical and physical properties.

c) Local treatment

Effluents bearing a phosphoric acid plant are normally lagooned or collected in ponds. They are acidic, containing hydrofluorosilicic acid originating from coolers, barometric condensors and slurried gypsum lake (if it is not reprocessed). Provisions have to be made to neutralize these wastes, should the lagoon/pond overflow due to

unusually high precipitation. Normally two stage neutralization systems with the addition of lime are required to enable the discharge of such acidic wastes to public receiving waters. In the first stage neutralization of the pH of the effluent is increased from 1.5 to 4.0 and in the second stage the effluent is neutralized to a pH of 6 - 7.

## d) Effluent treatment

As mentioned before fluoride containig effluent gases are normally scrubbed with water or solution of fluocilicic acid to remove the fluorides from the gas. The gases are exhausted from the digestor system and passed through a two stage scrubbing system. Many plants have been equipped with Doyle scrubbers having an overall efficiency of 97.5 per cent for fluorine removal. Other plants have used Tellerette packed scrubbing boxes. Tellerette polyethylene packing has been found particularly suitable being self cleaning and having a low pressure drop across the scrubber.

In the manufacture of triple superphosphate (0-48-0) where phosphoric acid is reacted with phosphate rock again, it is necessary to collect the vented gases containing fluorine. The exhausted gases from the equipment such as granulators or setting belts are first cleaned to remove solids in cyclonic separators, before being admitted to scrubbers. Cyclonic scrubbers or floating bed scrubbers have been used, recovery fluosilicic acid by recirculating the scrubbing solution. It is particularly difficult to maintain the required low $P_2O_5$ content required for the recovered acid to be used for the manufacture of cryolite. In some cases manufacturers permitted 1.5 per cent max. $P_2O_5$ concentration for a 15 per cent $H_2SiF_6$ solution to be used for that purpose.

In order to establish the possible yields from this treatment it is necessary to make a fluorine material balance for the entire plant.(see figure 3)

In Florida where there is an exceptionally large concentration of phosphate industry, it is mandatory to present the plans for fluorine treatment before permission is granted by the state authorities to construct such a plant at a chosen site.

## Summary and Conclusions

As one can see from the aforegoing, each industry has its own particular problems. The most important aspect of pollution control for a plant manager and chemical engineer in all industries is in-plant control. There are several disciplines or measures to control pollution within a plant prior to waste treatment or discharge. Some of these are changes in the manufacturing processes, material salvage including water reuse and by-product recovery, good plant housekeeping and collection segregation and equalization of wastes.

In this paper we have illustrated the problems and some of the solutions available for the control of liquid wastes from a refinery and the gaseous wastes from a phosphoric acid plant coupled with a TSP plant.
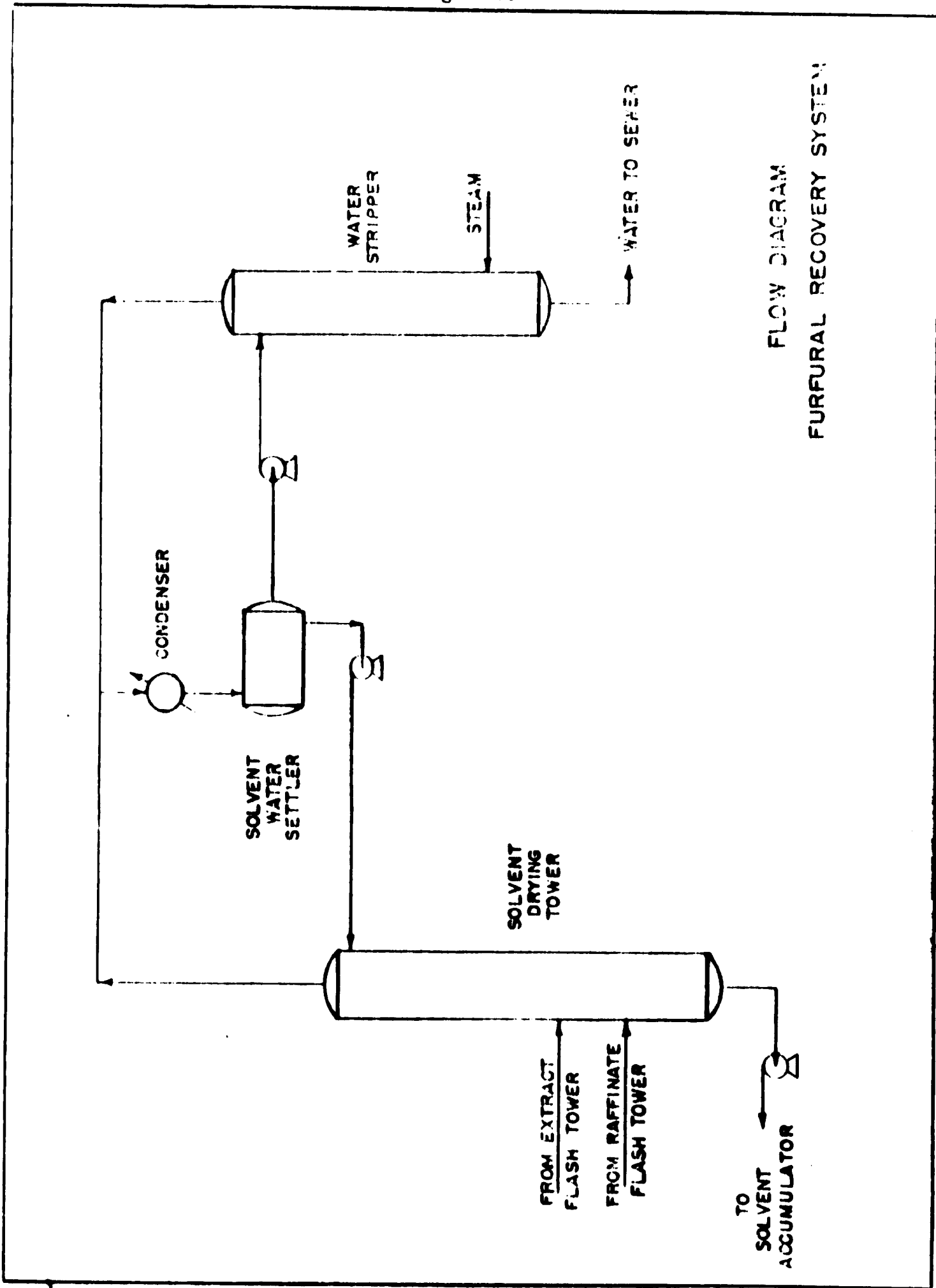
It is the responsibility of plant management to maintain control over their operation and production as well as abate pollution to maintain good neighbourly relation and take the necessary steps not to spoil the environment surrounding the plant.

Figure 1.
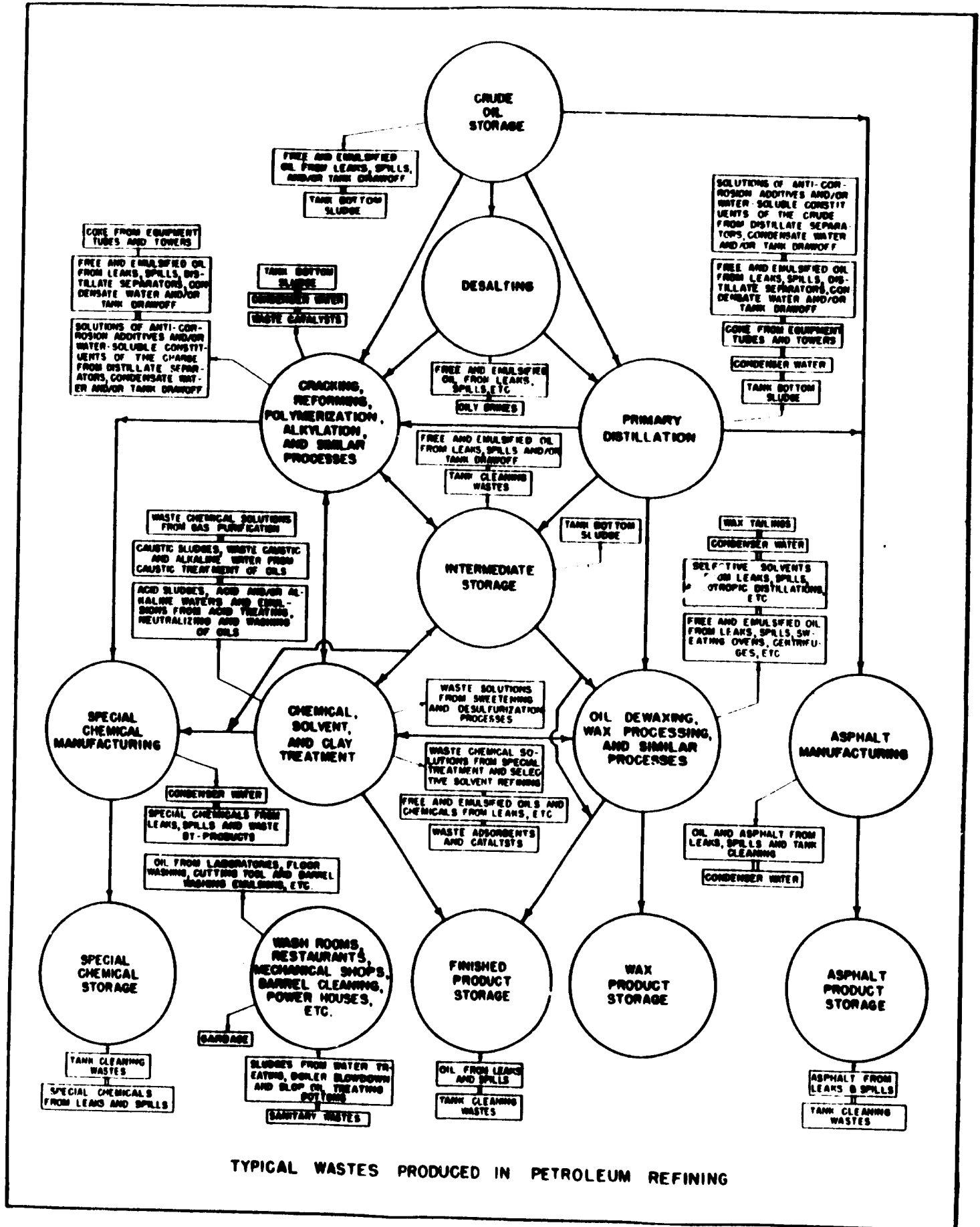


TYPICAL WASTES PRODUCED IN PETROLEUM REFINING

Figure 2.



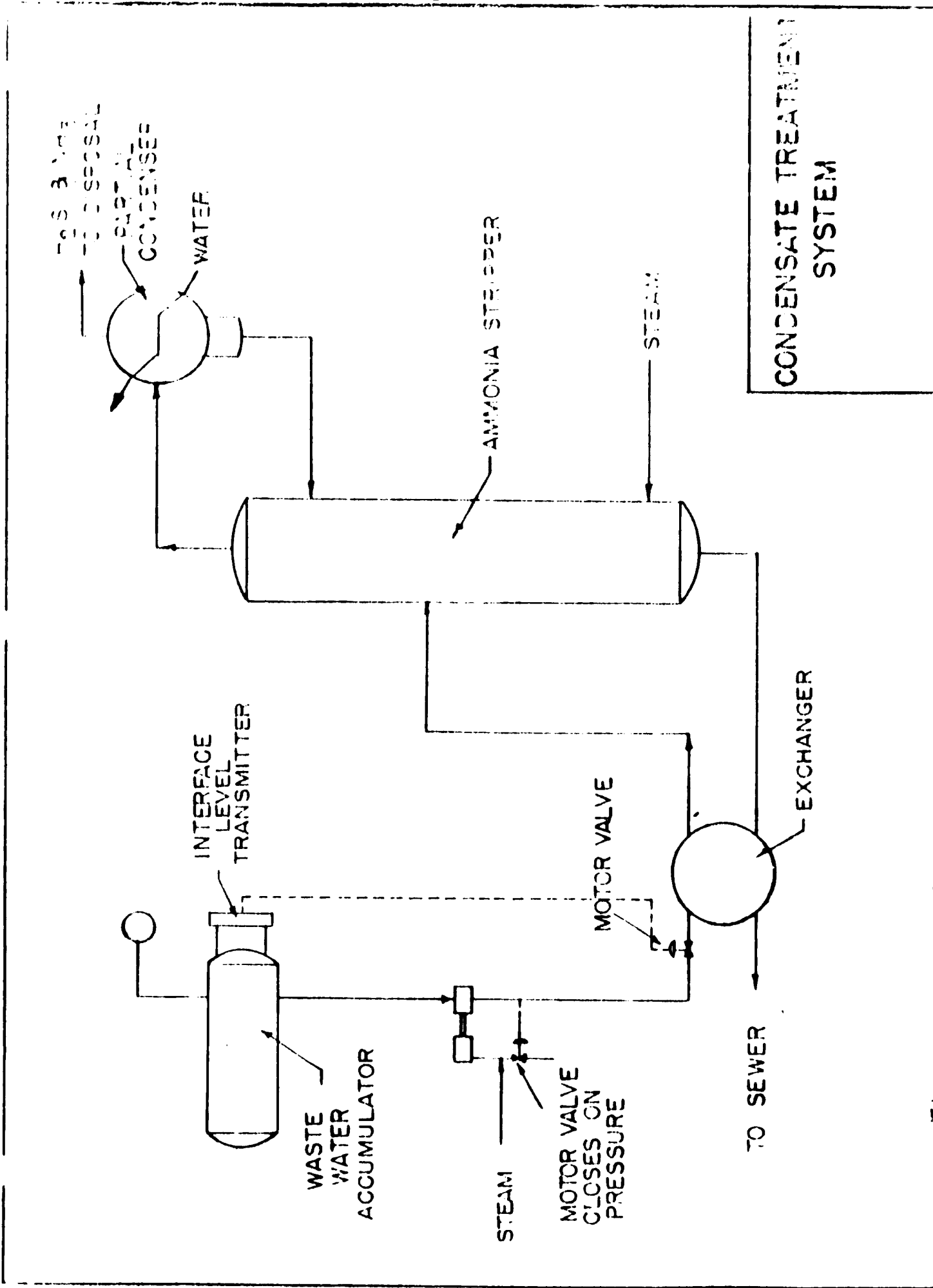FLOW DIAGRAM
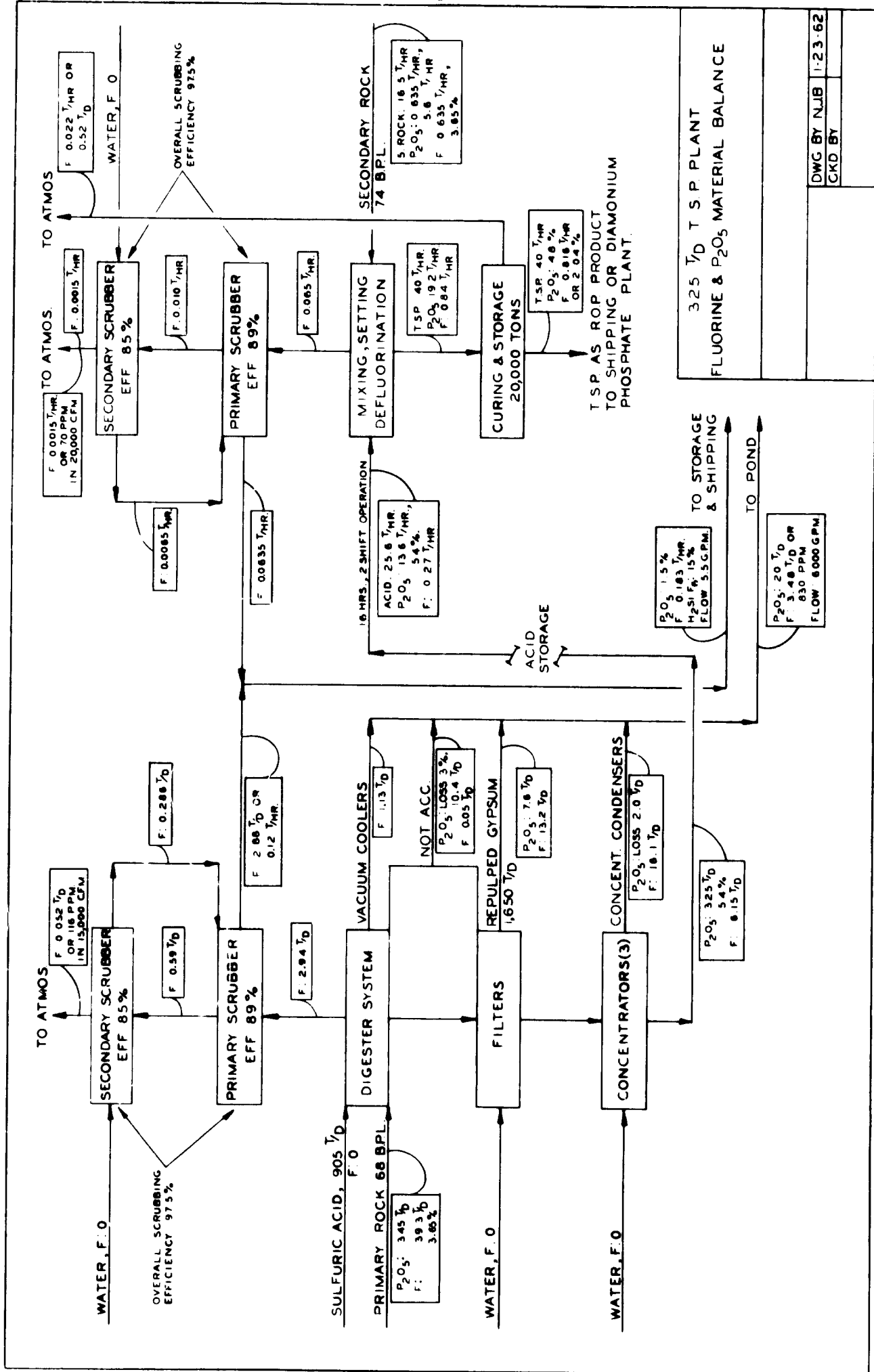FURFURAL RECOVERY SYSTEM

Figure 3.



CONDENSATE TREATMENT SYSTEM

325 $T_D$ T S P PLANT
FLUORINE & $P_2O_5$ MATERIAL BALANCE
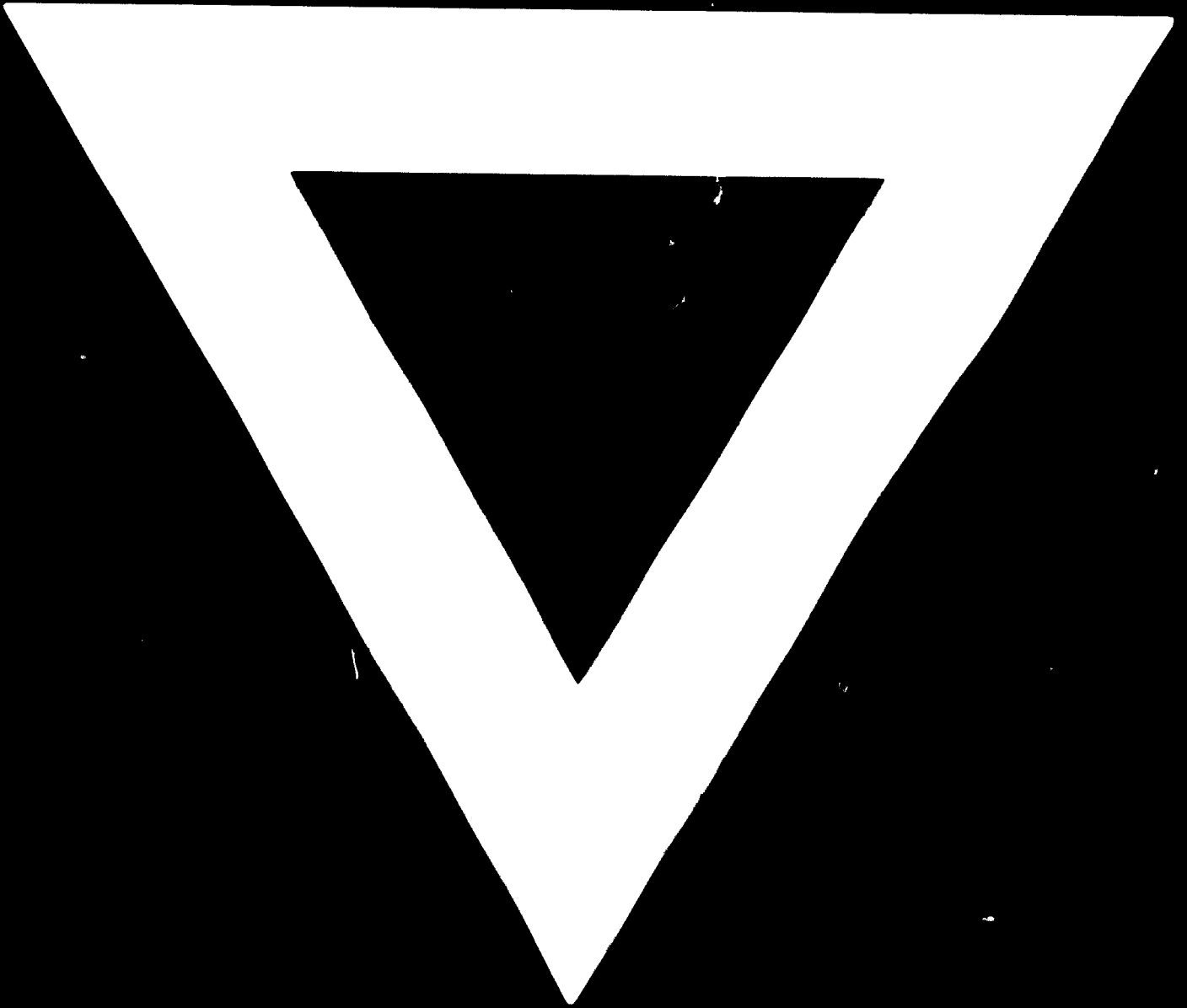
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# References

1)  Weston Roy F.,    Waste Control at Oil Refineries
                        Chemical Engineering Progress, Vol.48
                        No. 9, pp. 459 - 467;

2)  Albright John C., Petroleum Processing 3, 11, 1116 (1948);

3)  J.L. Steiner; G.F. Bennett; E.F. Mohles and L.T. Clere
                        Sun Petroleum Products, Toledo, Ohio,
                        Chemical Engineering Progress, December 1978;

4)  American Petroleum Institute Manual on Disposal of Refinery
    Waste Water containing Oil,American Petroleum Institute, 4th Edition(1948);

5)  UNIDO/FAO/World Bank Working Group Estimates, June 1978;

6)  United Nations Economic and Social Council
    ECE Chemical Industry Committee Ad-hoc Expert Group Meeting for
    Study on Utilization of Wastes in and by Chemical Industry
                        Paper CHEM/AG.7/R-2/ADD.4, 10 May 1978;

7)  C/Marketing, October 28, 1974, pp. 4, 7, 21
    Fluoride Emission Standards on Five Fertilizer Categories
    issued to the Phosphate Trade;

8)  Getting Rid of Phosphogypsum II
    Portland Cement and Sulphuric Acid
                        Phosphorous and Potassium, No. 89 May/June 1977
                        British Sulphur Corporation Ltd.;

9)  Getting Rid of Phosphogypsum III
    Conversion to Plaster and Plaster Products
                        Phosphorous and Potassium, No.98 March/April 1978
                        British Sulphur Corporation Ltd.;

10) Neven B., "Valorization of Phosphogypsum"
                        The Charbonages de France Chimie-Air Industry
                        Process, Paper presented at ISMA Technical
                        Conference, The Hague, September 1976

11) Wall Blocks from By-product Gypsum
    Knapsack AG takes Giulini Licence
                        Phosphorous and Potassium, No.63, January/February
                                                                    1973

                        British Sulphur Corporation Ltd.;

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