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*pollution control  
fertilizer plant  
urea*

POLLUTION ABATEMENT IN A UREA PLANT <sup>1/</sup>

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## INTRODUCTION

Major pollutants from a urea plant are ammonia and urea. If these pollutants are caught and recycled back to the process in efficient manner, then the emission of pollutants to atmosphere and drainage can be reduced with additional merits that the raw material consumption, especially ammonia consumption per ton of product urea, will be improved at the expense of slight increase of utilities consumption.

First of all, sources of pollution in a urea plant were reinvestigated and classified into a kind of pollutants—namely, urea, ammonia and oil etc. —, a kind of pollution — either to air — water —, and duration of pollution — whether continuously or intermittently. Based on the above philosophy, various pollution control methods and systems have been scrutinized, tested and developed by us. The pollution control systems thus developed and incorporated into the standard design of our urea process, which meet the recent requirements for environmental protection, are introduced hereinafter.

A major concern of air pollution in a urea plant is urea dust contained in the effluent from the prilling tower. The most difficult point to handle this pollution problem is that very fine dust of urea is carried in a huge amount of hot air through the prilling tower which is about 400,000 - 500,000 Nm<sup>3</sup>/hr for a 1,000 MTPA urea plant. The newly developed dedusting system by us, wet scrubbing method in principle, now reduces urea dust content to less than 30 mg/m<sup>3</sup> effluent air.

A major concern of water pollution in a urea plant is process condensate water from a vacuum generating system of either a crystallizer or evaporator. In urea synthesis, one molecule of water is formed to one molecule of urea,

which is to be separated in either a crystallizer or evaporator together with the water used as absorbent in a recovery section. The above separated water usually entrains very small amount of urea mist, ammonia and carbon dioxide, which has been a major concern of water pollution in a urea plant. By our sophisticated design of the vacuum generating system, two kinds of process condensate can be obtained, namely, a condensate rich in urea which is used as a scrubbing urea solution in the above mentioned dedusting system and the balance rich in ammonia and carbon dioxide which is used as an absorbent solution in the recovery section or sent to a stripper for recovery of ammonia and carbon dioxide by steam stripping. By this way, the reduced amount of condensate to drainage contains less than 200 ppm of ammonia.

Thus, by combining our newly developed prilling tower dedusting system with sophisticated design of the vacuum generating system, two major pollution problems in a urea plant are now solved simultaneously in a very efficient manner. This system has been successfully proven in our 1,500 MTPD urea plant, in Osaka, Japan which was started up in 1969.

## 1. UREA PROCESS DESCRIPTION IN GENERAL

To assist understanding of the following main description, urea process is very briefly explained herein taking Mitsui Toatsu Total Recycle C-Improved Process as example which is shown in Figure 1.

For the convenience of explanation, urea process can be divided into three sections, namely, synthesis, decomposition/recovery and finishing section.

In synthesis section, urea is synthesized by the highly exothermic reaction of ammonia fed from ammonia pumps, carbon dioxide fed from CO<sub>2</sub> compressor and recycle carbamate solution to form ammonium carbamate with subsequent slightly endothermic dehydration of the ammonium carbamate to form urea. The reactions are reversible and can not be completed in one-pass.

The principal variables affecting the reaction are temperature, pressure, feed composition and reaction time. It can be generally said that higher temperature and pressure favor the conversion, as do more excess ammonia and less water in the feed. Reaction conditions in commercial installations range between 180-220°C and 150-420 atm. with NH<sub>3</sub>/CO<sub>2</sub> mole ratio in the feed between 2.6-5. The resulting one-pass conversion of carbon dioxide to urea varies between 55-80%.

Accordingly, the reaction products consist of urea, ammonium carbamate, water and excess ammonia. Subsequent processing is required in decomposition/recovery section to separate urea from the reaction products, and to recycle ammonium carbamate and excess ammonia back to the synthesis section.

Basic differences among the various existing urea processes lie in the methods of separating un-converted ammonium carbamate and excess ammonia from

the urea solution and in the forms of recycling those separated ammonium carbonate and excess ammonia back to the reactor.

Generally, the solution from the urea reactor must be heated to decompose and remove ammonium carbonate.

The decomposition products are evolved as a hot, gaseous mixture of ammonia, carbon dioxide and water. Undesirable side reaction - urea hydrolysis and biuret formation - should be minimized during this step.

To condense the mixed gas by cooling with some addition of water and to recycle the resulting condensate solution back into the reactor is now the standard for new plants. Although there are obvious disadvantages that conversion is reduced by recycling water to the reactor and that the recycle solution pump is required, various processes have been developed.

These various processes have apparently similar major steps. The reaction products are heated through two or three stages of decomposition at stepwisely lower pressure levels. In each stage, the evolved gas mixture is absorbed in weak solution condensed in a later stage and the resulting solution are pumped back to the reactor. The excess ammonia passes through the absorbers, and is finally condensed in ammonia condensers to be recycled back to the reactor. The inert gas accompanied in make-up CO<sub>2</sub> gas is finally vented to atmosphere after scrubbing ammonia in it.

There are, however, considerable differences among those processes from the viewpoints of pressure and temperature levels, equipment arrangement and process flow. The recent version is to use stripping gas, either ammonia, carbon dioxide or inert gas in some stage of decomposition.

In finishing section, about 75 wt.% urea solution leaving the decomposition section is further processed to the product. The choice of two processes,



either direct prilling (evaporation - prilling) or crystallization (crystal remelt - prilling) depends solely upon the requirements for product quality and grade. In any case, the urea solution is concentrated up to 99.7 wt.% under vacuum or in combination of vacuum and atmospheric hot air stripping. Urea melt of more than 99.7 wt.% concentration is formed to prills while descending through the prilling tower as droplets and being cooled counter currently by ascending air.

## II. SOURCES OF POLLUTION IN A UREA PLANT

Sources of pollution in a urea plant are briefly reviewed below.

### A. Continuous Source

- (a) Condensate drain from CO<sub>2</sub> compressor; which is contaminated by dissolved carbon dioxide and oil and to be collected into oil separation pit before being drained to sewer.
- (b) Gland cooling water from NH<sub>3</sub> feed pumps; which is contaminated by ammonia and oil and to be collected into process water pit for oil separation before being recycled to the process for recovery of ammonia. The total amount of gland cooling water and degree of contamination depend on type of pump and maintenance.
- (c) Gland cooling water from various centrifugal pumps; which is contaminated by trace of urea, ammonia, carbon dioxide and oil and to be collected into process water pit for oil separation before being recycled to the process. The total amount of gland cooling water and degree of contamination depend on type of seal used for the pumps and their maintenance.
- (d) Process condensate from a vacuum concentrator; to be discussed later in this paper.
- (e) Urea dust in pneumatic conveyor effluent; to be treated together with effluent of the prilling tower.
- (f) Urea dust in prilling tower effluent; to be discussed later in this paper.
- (g) Purge gas from the ammonia recovery absorber; the inert gas (mainly nitrogen and hydrogen) accompanied in make-up CO<sub>2</sub> as impurity gas and air injected for corrosion protection are finally vented to atmosphere after recovering ammonia in the ammonia recovery absorber. So, total

amount of gas vented to atmosphere and accompanying loss of ammonia with it depend on purity of make-up CO<sub>2</sub> and amount of air injected for corrosion protection. The loss of ammonia vented to atmosphere will range from 0.2 MTPD where titanium is used for reactor lining to 0.6 MTPD where air is heavily injected to protect stainless steel equipment operated under synthesis pressure. It should be further mentioned that more ammonia rich gas is vented to atmosphere in order to avoid explosive gas mixture if heavy air injection is used.

B. Intermittent Source

- (h) Washing water from urea filter (if installed).
- (i) Floor washing water.
- (j) Blow from safety valve.
- (k) Start-up and shutdown draining from process equipment.

The frequency of above cases depends on stability of plant operation and process design itself. If the composition of solution is so designed to have high freezing point and corrosive nature, the solution in high pressure vessels should be dumped into atmospheric holding tank after dilution even during short time shutdown.

### III. PRILLING TOWER DEDUSTING SYSTEM

The size of urea dust in the prilling tower effluent distributes from 200 microns to a couple of microns, as shown in Figure 11. The origin of these urea dust is atomized molten urea and undersized or crushed prills. These are carried away by a higher air velocity of ascending air through the tower. The particle size of the latter is relatively large, but the former almost resembles a fume. Both sizes of dust can cause air pollution resulting in direct harm to plants or low visibility. The amount of urea dust contained in the emitted air varies within a range of 500 to 1,000 mg/Nm<sup>3</sup> at the tower exit without any treatment. Naturally, higher dust content will be carried with higher air velocities.

Various primitive and simple devices have been tried to abate pollution from the natural draft towers where the maximum allowable pressure drop is only a few millimeters of water gauge. One of the relatively successful measures for control of the pollution is an impinger-type device with baffle plate and a water curtain system as shown in Figure 12. The exhaust air is first impinged with the baffle plate to turn its direction downward toward the surface of the water sump, and then passed through a water curtain before venting to the atmosphere. This system is simple and effective for relatively larger size of particles, which are easy to separate by the gravitational sedimentation, and requires very small pressure drop. Therefore, it is generally applied to natural draft towers. The efficiency of this system, however, for small dust loading is low; 200 - 400 mg/Nm<sup>3</sup> of urea is still contained in the effluent air.

The modification of urea prilling tower dedusting systems is limited by certain technical and economical factors:

- (a) The amount of air to be handled is massive.

- (b) Urea dust contains extremely fine particles partially under 10 microns in diameter.
- (c) The pressure drop available or allowable in such a system is very small; only a few millimeters in natural draft towers, and approximately 50 mm water gauge in forced ventilation towers.

It is, therefore, essential that maximum collection efficiency with minimum pressure drop at lowest cost be designed into this system. For handling a hygroscopic and water-soluble material such as urea in a dust separator, a wet-type separator is normally preferable to avoid plugging which occurs in the dry-type. A dry cyclone is not so effective for very fine dust such as prilling tower effluent in spite of a fairly high pressure drop requirement.

In a wet-type system, on the other hand, effective separation of secondarily emitted mist is very important, as is the washing efficiency. The experimental spray tower, with the minimum pressure drop, was selected for further study as shown in Figure IV. Proper selection of the second stage mist eliminator was very important. A simple construction such as wire mesh had too low an efficiency, and a fibrous bed required too high a pressure drop. After a series of trials, a new material, porous resin foam, was found as one of the best materials for mist-eliminator. With this material, small droplets were coalesced in the porous foam and resultant large droplets were separated at the fore or rear surface of the filter. Uncollected dust in the spray zone was dissolved into the coalesced droplets at the same time. It was found that these functions could be achieved with relatively small pressure drop.

The successful results of the pilot plant test were immediately applied to the modification of the existing scrubber in the 1,500 MTPD our Osaka urea

plant. The following design basis was used to arrive at a dust content of 30 mg/Nm<sup>3</sup> at the scrubber exit:

Flow rate of air .....	500,000 Nm <sup>3</sup> /hr
Liquid/gas ratio .....	1.5 - 2.0 lit/Nm <sup>3</sup>
Collection efficiency in spray zone .....	90 - 96%
Overall collection efficiency .....	95 - 99%

A sketch of this improved dedusting apparatus is shown in Figure V. The followings are the performance data derived in the apparatus.

Flow Rate of Air Nm <sup>3</sup> /hr	Urea Dust Content mg/Nm <sup>3</sup> Inlet	Exit	Overall Collection Eff. %	Total Pressure Drop mm H <sub>2</sub> O
550,000 .....	1,330 .....	28 .....	98 .....	39
500,000 .....	398 .....	11 .....	97 .....	35

This improved dedusting apparatus has been running quite satisfactorily since 1970 and the same system has also been used since 1972 in a 1,000 MTPD urea plant in Japan with similar operating efficiency. Since then, the same dedusting system has been incorporated into the standard design of the prilling tower and is installed in the concentric circle opening of effluent air exit at the top of the prilling tower.

Such effluent as that from a urea crystals pneumatic conveyor to the top of the prilling tower which again contains fine crystals of urea and/or as that from a hot air stripping type urea solution evaporator which contains urea mist, can be led into the above system for dedusting at the same time.

Ammonia, being formed by biuret formation and emitted to air from droplets while falling through the prilling tower, can not be recovered in this dedusting system, because its concentration is so low as less than 20 mg-NH<sub>3</sub>/Nm<sup>3</sup> effluent air from the prilling tower which corresponds to less than 0.2 MTPD NH<sub>3</sub> loss.

#### IV. PROCESS CONDENSATE FROM A VACUUM CONCENTRATOR

In urea synthesis, one mol. of water is formed to one mol. of urea. This by-produced water is to be separated in a evaporation system together with the water used as an absorbent to recover unreacted ammonia and carbon dioxide in the recovery section. The above water evaporated usually under vacuum in a concentrator entrains very small amount of urea mist, ammonia and carbon dioxide.

In the original design, the above evaporated water was condensed by direct contact with common circulating cooling water. Accordingly, the blow-down of such cooling water contained and was contaminated by urea and ammonia in the form of nitrogen compound.

Our newly developed design has following two alternatives to avoid such water pollution.

##### Alternative I: Independent Cooling Water System for Barometric Condenser

A small cooling water system independent from the cooling water system for heat exchangers is installed for barometric condensers of the vacuum concentrator. The cooling water of this system will be circulated only between the barometric condensers and the cooling water tower. The blow-down of this system is used partly as absorbent of the recovery section and the balance as make-up water of the prilling tower dedusting system, which is explained already.

The combination of this independent cooling water system and the prilling tower dedusting system can reduce remarkably both air and water pollution.

The defect of this system, however, is that some parts of ammonia condensed into the cooling water escapes to the atmosphere while being circulated

through the cooling water tower.

Alternative II: Surface Condenser and Dehumidifier System

More sophisticated system has been developed to cover the defect of Alternative I, namely, ammonia emission from the cooling water tower.

A series of surface condensers with a mist separator replace the barometric condensers for a concentrator of Alternative I. In the first surface condenser with a mist separator, almost all of entrained urea with water vapor from the crystallizer is separated and dissolved into the condensate of which amount is so designed as to be equivalent to the process water required partially as absorbent of the recovery section and mostly as make-up water to the prilling tower dedusting system.

The remaining water vapor and accompanied small amount of ammonia and carbon dioxide gases are condensed and recovered in the second and third surface condenser. The condensate is sent to the dehumidifier (or stripper) where ammonia and carbon dioxide in the said condensate are stripped out by heating directly with low pressure steam and recovered as overhead gases to be absorbed in a low pressure absorber. The clean condensate from the bottom of the dehumidifier, with contamination of less than 200 ppm of ammonia, can be drained out to the sewer.

By this alternative, virtually no water pollution can be achieved. Such contaminated cooling water from the gland packings of pumps and temporary washing water from process equipment can be sent to this dehumidifier, if necessary.

It is possible but very impracticable to try to hydrolyze urea in the process condensate. Our study shows it needs following time, assuming initial concentration of 0.5% urea, to get 80% of the urea to be hydrolyzed at various



temperatures.

<u>Temperature</u>	<u>Required Time</u>
°C	Minutes
120	1,000
140	240
160	76

## V. CONCLUSIONS

By combining the various above-explained pollution abatement processes and equipment into a system, the following schemes for pollution control system as shown in Figure VI and VII are considered as most effective and economical, and have been used in recent urea plants.

An overall pollution in a 1,000 MTPD urea plant will be reduced to as below;

### (a) Air pollution

Urea .....	prilling tower .....	less than 0.3 T/D
Ammonia .....	prilling tower .....	less than 0.2 T/D
" .....	ammonia recovery absorber..	less than 0.2 T/D
<hr/>		
Total ammonia .....		less than 0.4 T/D

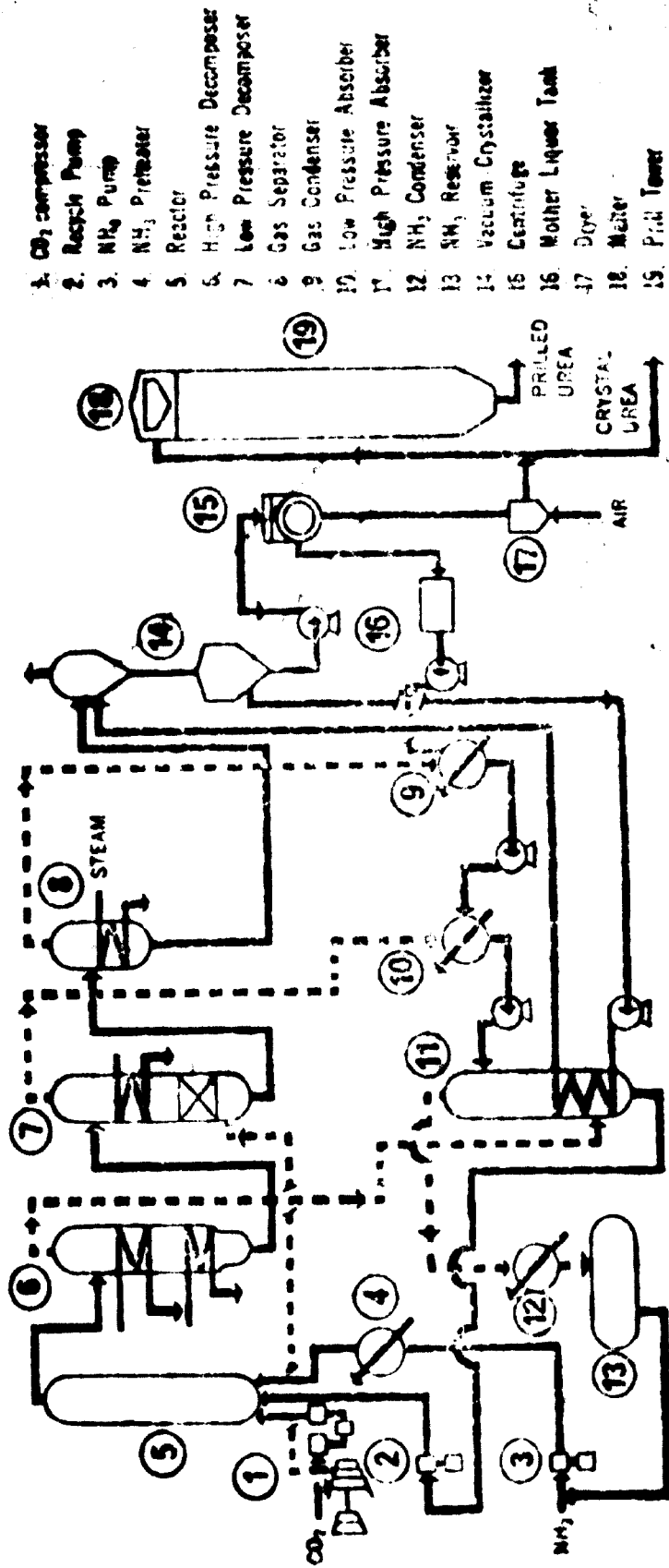
### (b) Water pollution

Ammonia .....	dehumidifier .....	0.06 - 0.1 T/D
---------------	--------------------	----------------

Naturally, the amount of water evaporated in the prilling tower dedusting system varies by seasonal change of ambient air, which finally affects the amount of cleaned condensate from a dehumidifier to the sewer.

If more strict pollution regulation is applied, more sophisticated and heavy dedusting system and ammonia recovery system using sulfuric acid can be applied. Biochemical method is also one of possible methods to solve water pollution more completely.

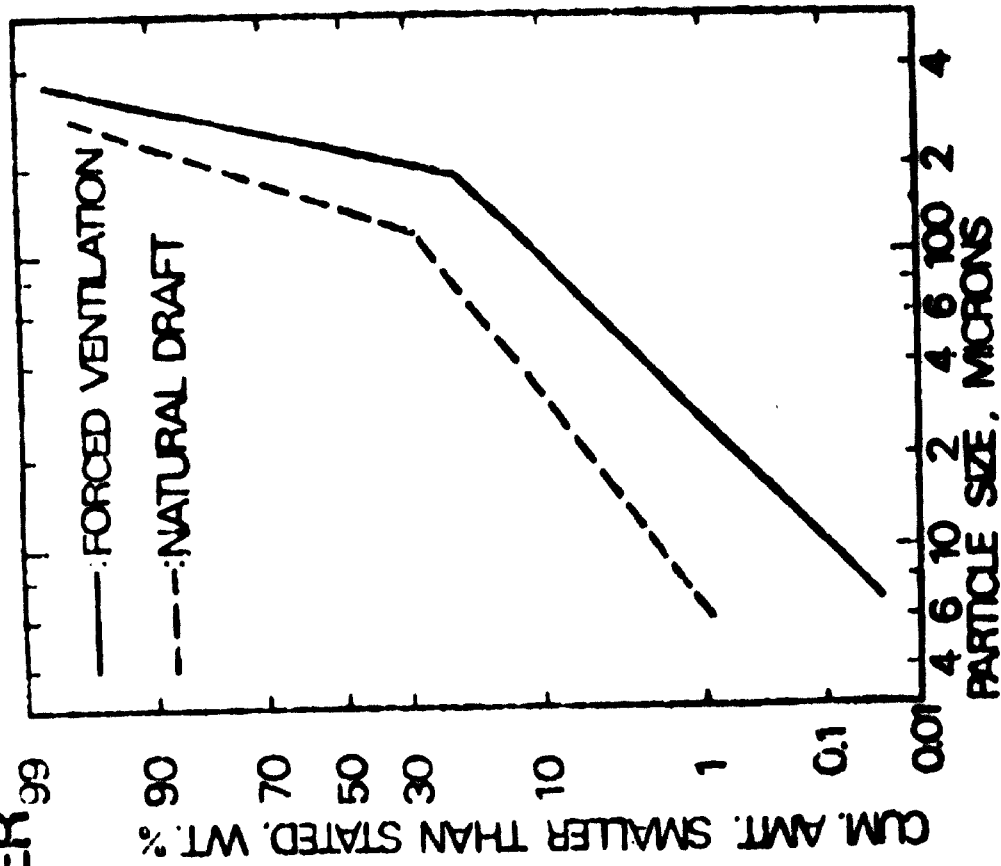
FIG. 1 TOTAL RECYCLE C IMPROVED PROCESS



1. CO<sub>2</sub> compressor
2. Recycle Pump
3. NH<sub>3</sub> Pump
4. NH<sub>3</sub> Preheater
5. Reactor
6. High Pressure Decomposer
7. Low Pressure Decomposer
8. Gas Separator
9. Gas Condenser
10. Low Pressure Absorber
11. High Pressure Absorber
12. NH<sub>3</sub> Condenser
13. NH<sub>3</sub> Reservoir
14. Vacuum Crystallizer
15. Centrifuge
16. Mother Liquor Tank
17. Drier
18. Water
19. Puff Tower

16  
 1912

FIG. 1 SIZE DIS. OF UREA DUST FROM PRILLING TOWER<sup>99</sup>



**FIG. III IMPINGER-TYPE DEDUSTING SYSTEM FOR  
A NATURAL DRAFT TOWER**

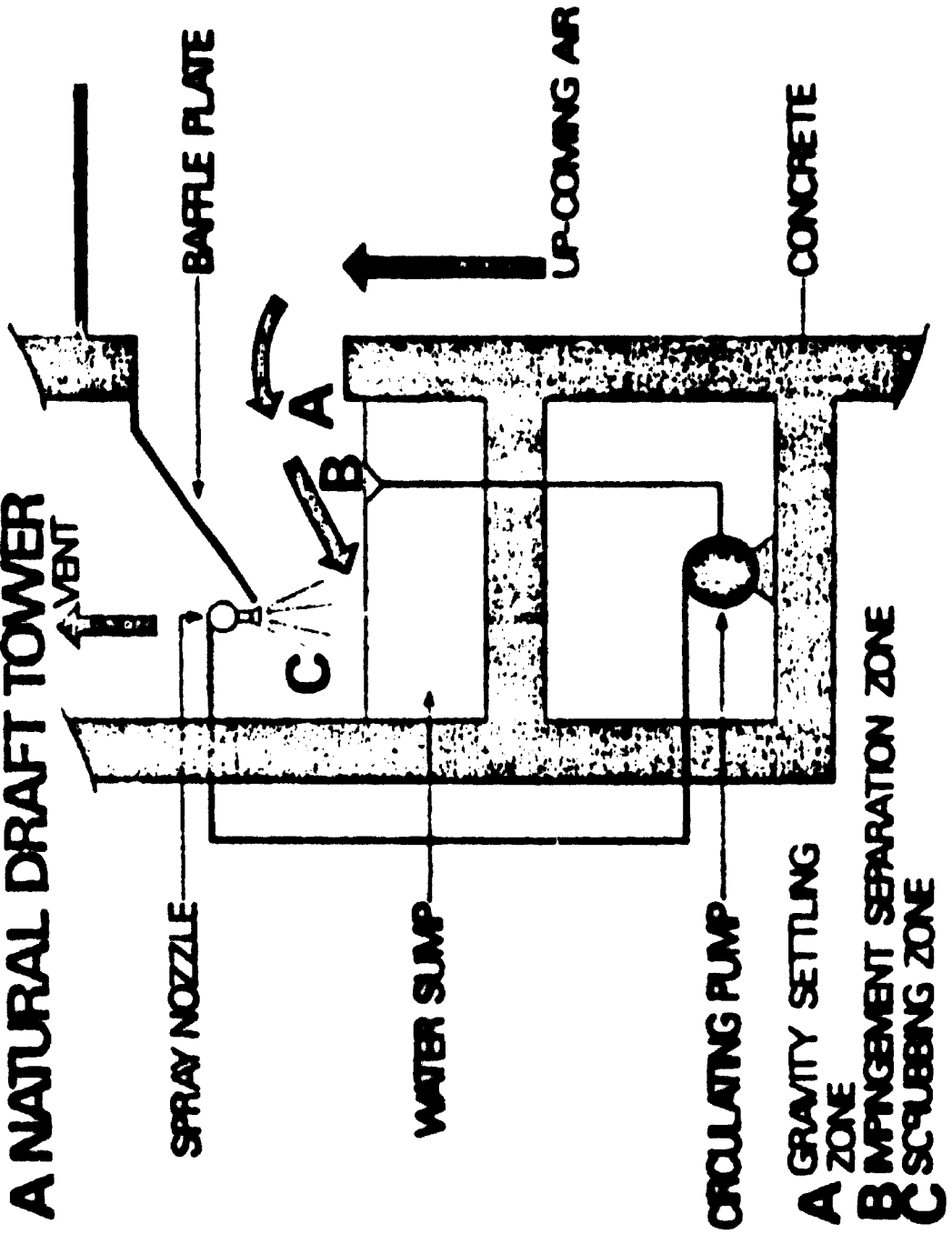


FIG. IV SCHEMATIC DIAGRAM OF THE EXPER. APPARATUS

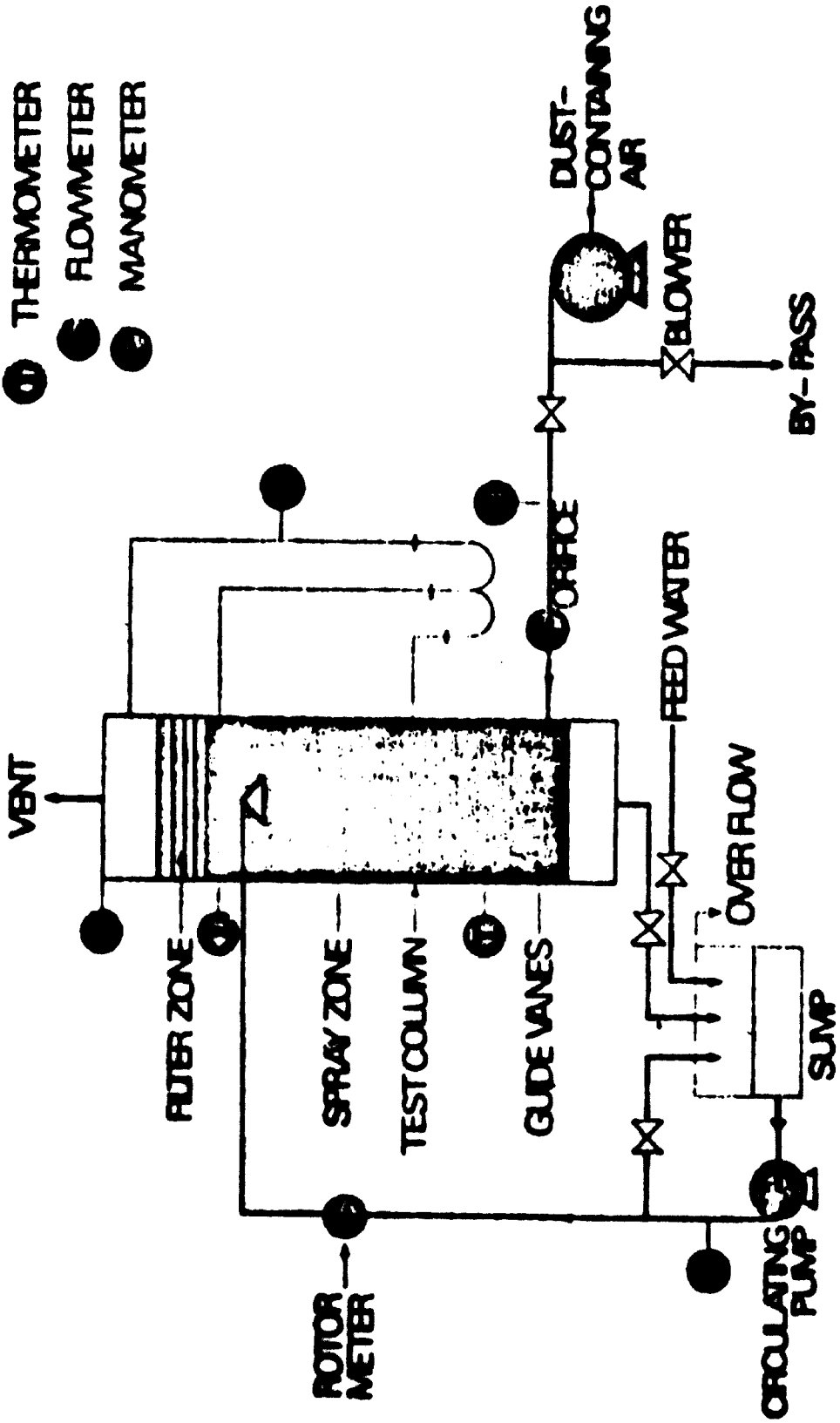


FIG. V SKETCH OF IMPROVED DEDUSTING APPARATUS

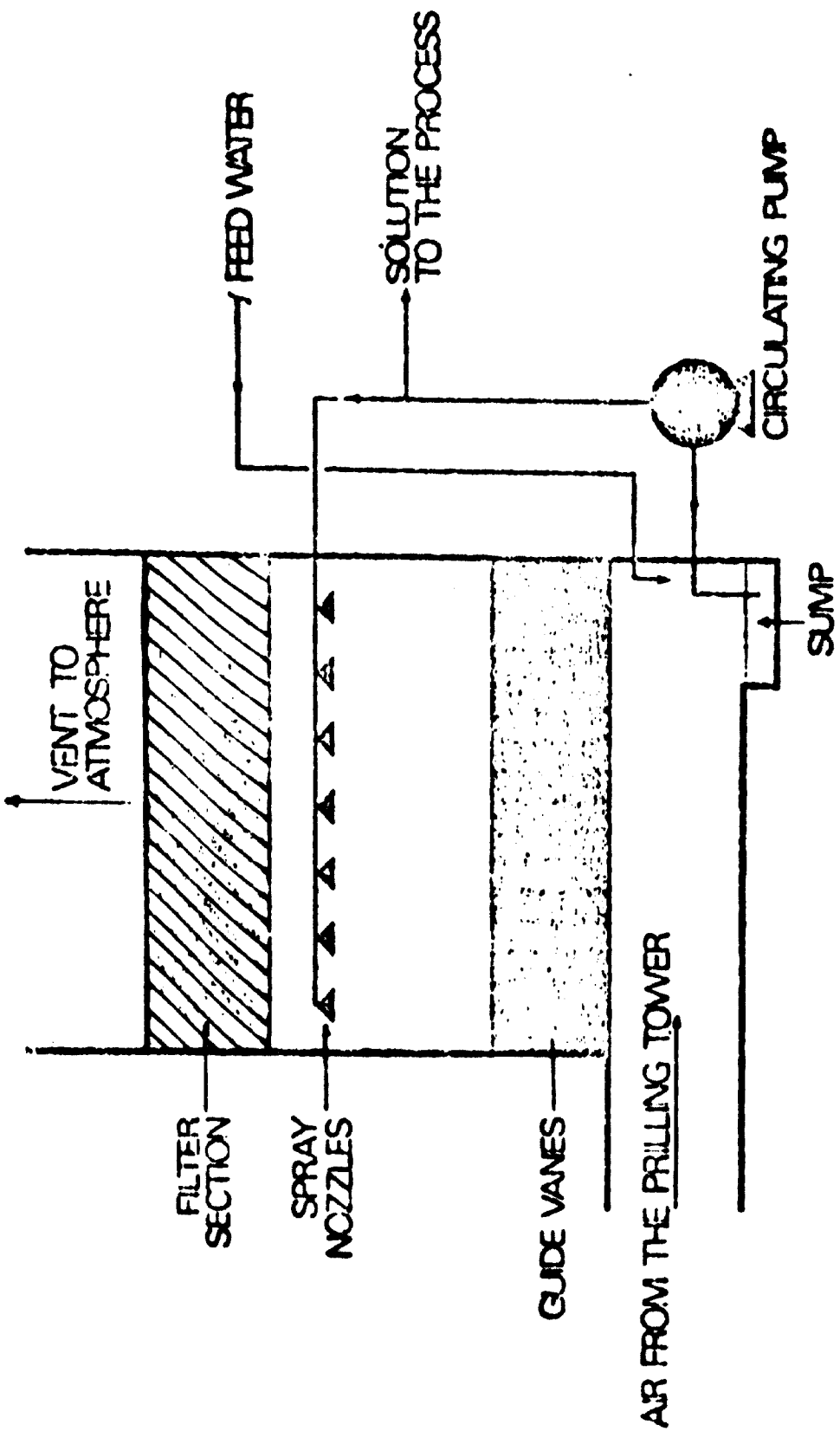


FIG. VI FLOW SCHEME FOR POLLUTION CONTROL SYSTEM  
( ALTERNATIVE I )

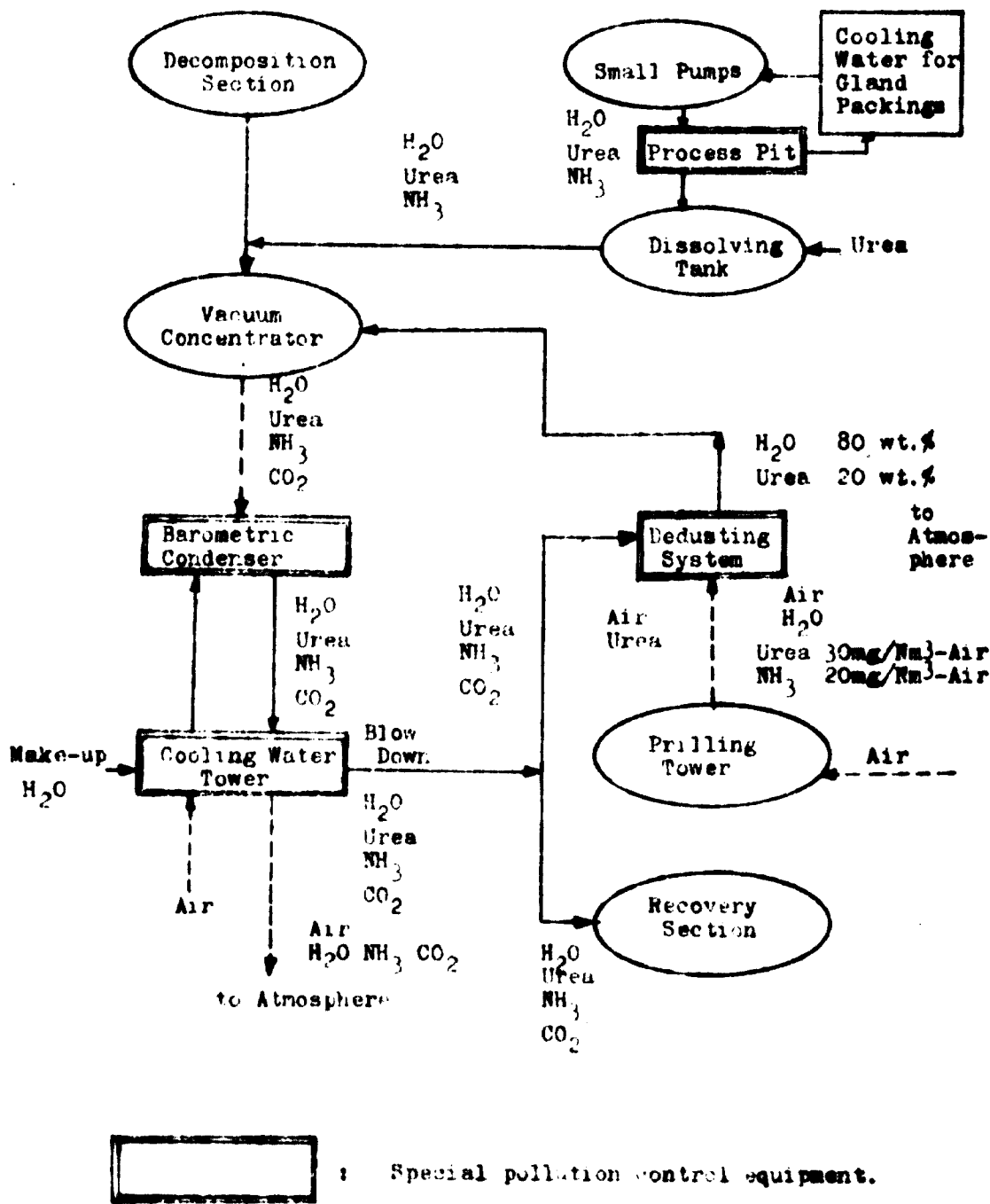
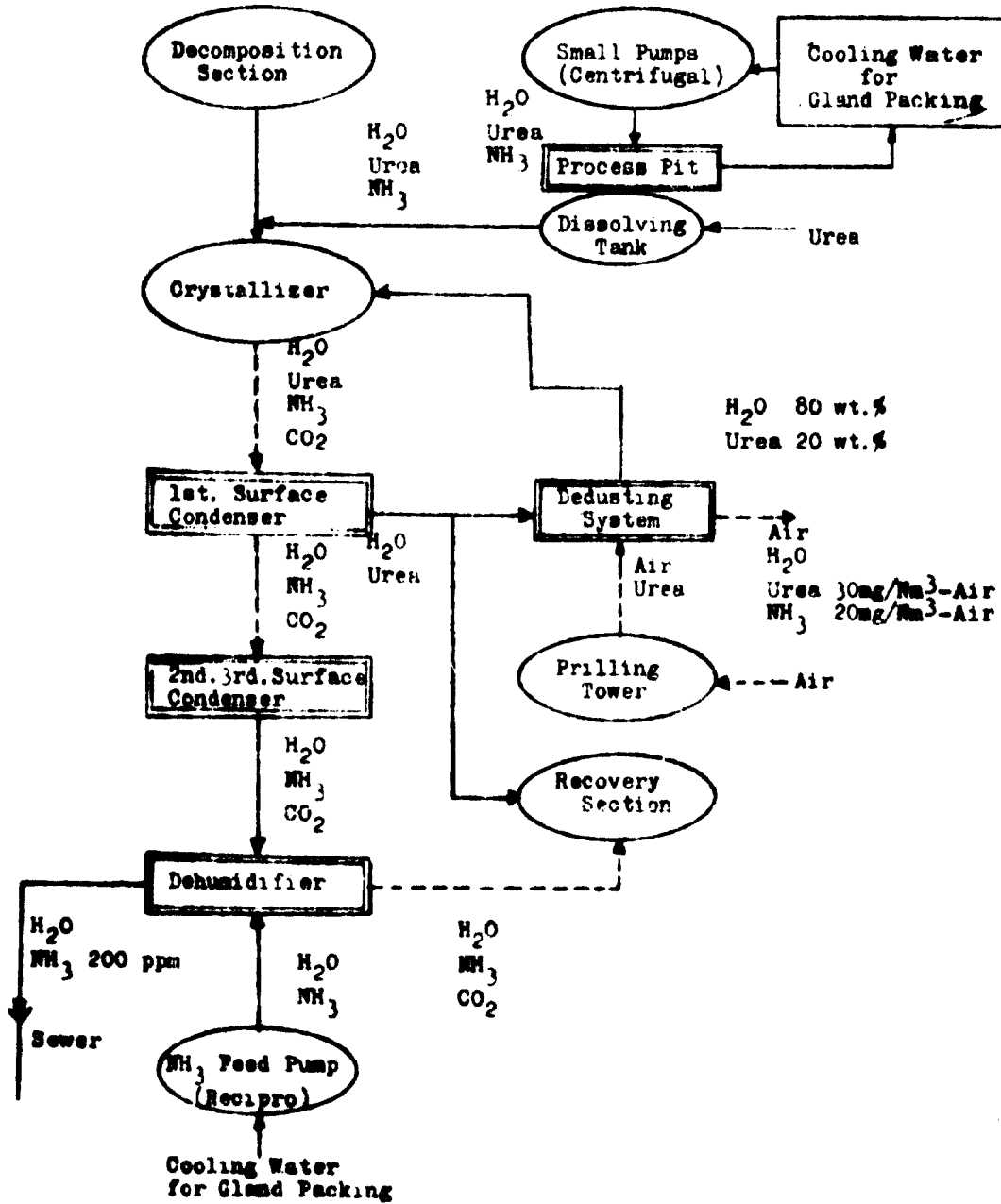

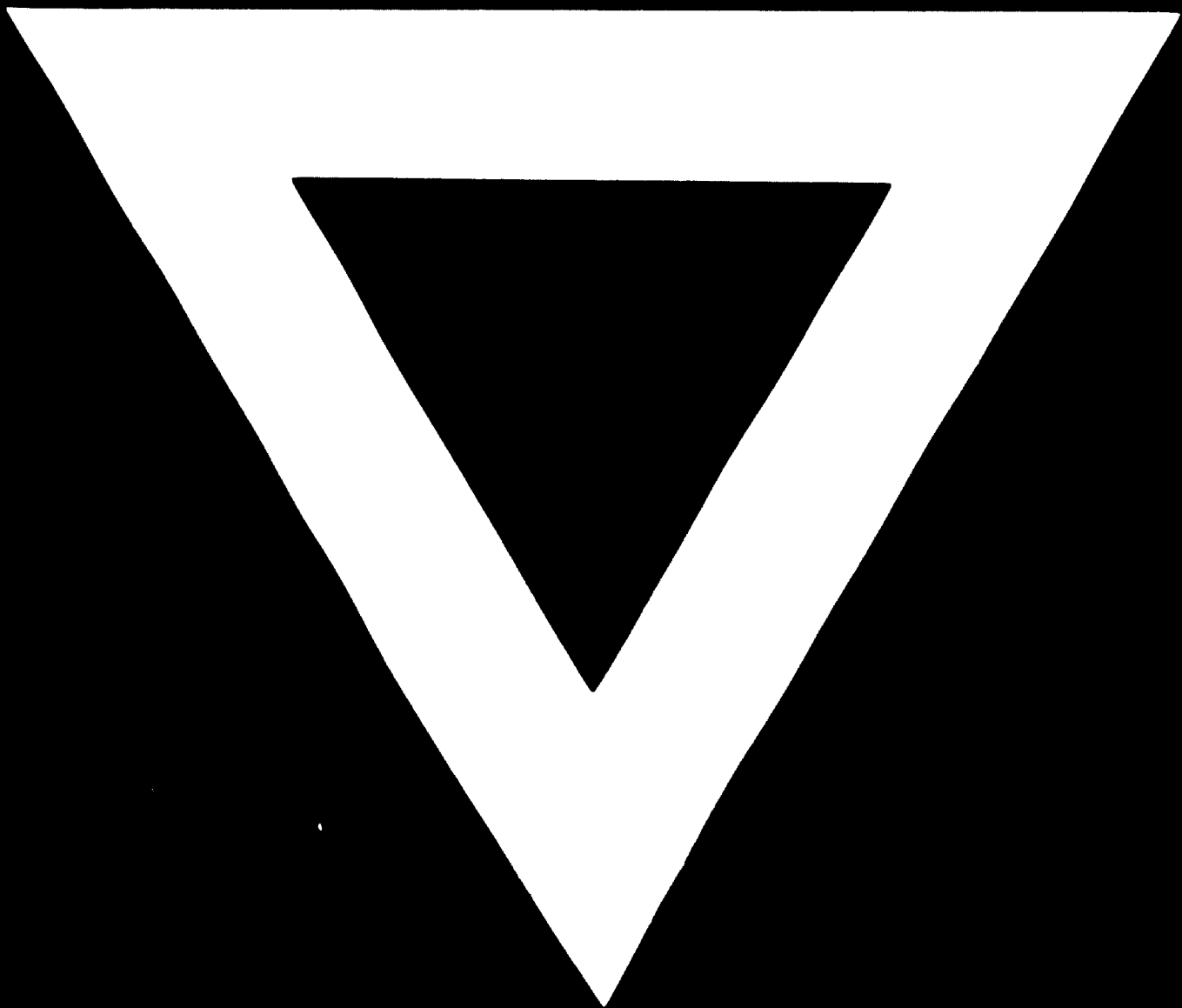




FIG. VII FLOW SCHEME FOR POLLUTION CONTROL SYSTEM  
( ALTERNATIVE II )



 : Special pollution control equipment.



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