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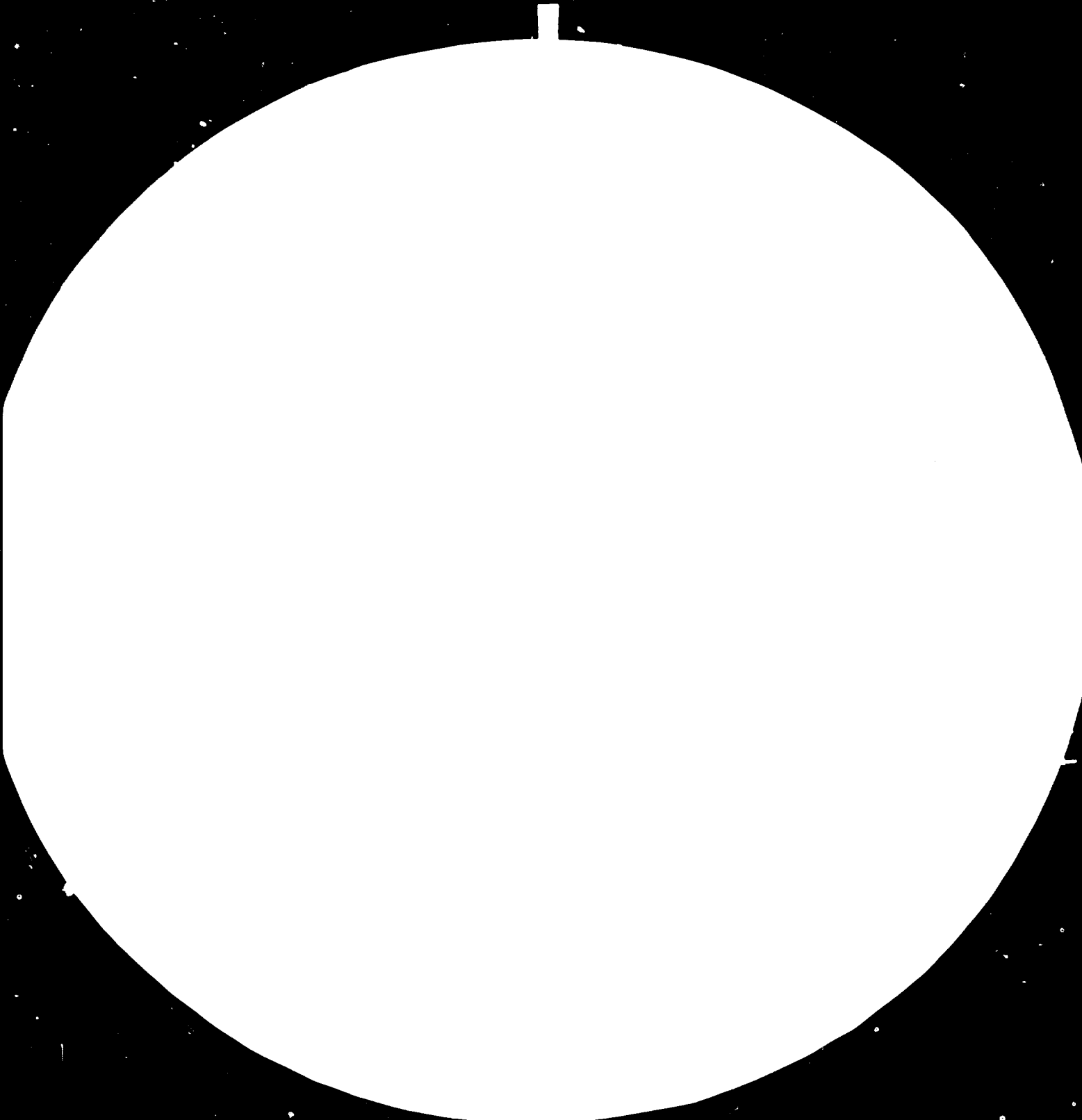
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Resolution Test Chart, NBS 1010-A, 1963 Edition

U.S. GOVERNMENT PRINTING OFFICE: 1963



10061



Distr.
LIMITED
ID/WG.333/1
10 October 1980

United Nations Industrial Development Organization

ENGLISH

Interregional Meeting on Safety in Production,
Transportation and Storage of Fertilizers
New Delhi, India, 8 - 10 December 1980

EXPLOSION HAZARDS IN UREA PLANTS AND ITS PREVENTION*

by

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Introduction

Urea is synthesized from ammonia and carbon dioxide which reactants are both produced in ammonia plants.

Carbon dioxide is recovered from the ammonia synthesis gas mixture containing hydrogen and nitrogen as the major components. In the carbon dioxide absorption solution small quantities of hydrogen and nitrogen will simultaneously dissolve with the carbon dioxide.

In the stripper in the ammonia plant these components will be stripped off together with the carbon dioxide. The resulting carbon dioxide feed gas for the urea plants will thus contain hydrogen and nitrogen as the major impurities.

The ammonia condensed from the ammonia converter off-gas may also contain hydrogen and nitrogen in a concentration depending on the treatment of the condensed ammonia prior to feeding it to the urea plant.

The nature of the reaction products in the urea plants is such that the materials of construction in these plants must be highly corrosion resistant. The applied materials are normally stainless steel and titanium.

Both metals require an oxidizing environment for protection against corrosion, though the required quantity of oxygen might be different.

In order to provide such an environment, oxygen or air must be introduced into the system.

After reaction the remaining non condensable components (H_2 , O_2 and N_2) must be purified, either at urea synthesis pressure, or atmospheric pressure, or any pressure in between, depending on the process used, in order to reduce losses of ammonia to the atmosphere.

After purification a hydrogen-nitrogen-oxygen mixture will result with a composition being well within the explosive limits.

In several urea plants, applying different type processes, ignition of these mixtures have occurred.

Examples of some purified non condensable gas mixtures

The different processes use different oxygen quantities.

The concentration is generally expressed as a percentage of the CO_2 feedgas, in which the oxygen or air is introduced, because by this introduction one has the simplest way to feed the required oxygen to the urea plant.

The oxygen concentration in the carbon dioxide range from 0.1 to 0.8% of oxygen. Let us examine the two above mentioned concentrations as examples. Normal compositions of carbon dioxide feed gas at the battery limits of the urea plant are:

CO₂ 99.0 % (mole)
H₂ 0.6 % (mole)
N₂ 0.4 % (mole) including A, Ne etc.

Example 1

If we need 0.1 % of oxygen in this gas mixture and we feed this as air the final composition of the non condensable components becomes:

H ₂	0.6 moles		H ₂ = 40 % (mole)
N ₂	0.4 moles	or	N ₂ = 53 % (mole)
Air	<u>0.1 O₂ + 0.4 N₂</u>		O ₂ = 7 % (mole)
Total	1.5 moles		

This mixture is within the explosion limits as can be seen from fig. 1 (point A).

Example 2

If we need 0.8 % of oxygen in the above mentioned CO₂ gas mixture, the final purified gas composition will become:

H ₂ =	0.6 moles		H ₂ = 12 % (mole)
N ₂ =	0.4 moles	or	N ₂ = 72 % (mole)
Air =	<u>0.8 O₂ + 3.2 N₂</u>		O ₂ = 16 % (mole)
Total	5 moles		

This mixture is also within the explosive limits (fig. 1 point B).

All of the carbon dioxide gas mixtures with oxygen concentrations between 0.1 and 0.8 % mole will be within the explosive limits.

We may thus conclude that each high ammonia efficiency urea process will end up with a hazardous gas mixture, unless provisions are being made to remove the hydrogen from carbon dioxide and if the ammonia contains hydrogen, to remove this hydrogen as well.

Experience

There are many plants, running during normal operation or upset conditions, emitting gas mixtures within the explosion limits.

A great many plants however have never experienced explosion. In those plants all of the conditions required for an explosion (an explosive gas mixture and an ignition source simultaneously) did not occur so far. The potential danger is there however as practice has shown.

In a few plants Stamicarbon has experienced explosions in the 18 ats purification step of conventional urea plants as well as in the 140 ats purification step in CO₂ stripping urea plants.

Stamicarbon's approach to solve the explosion hazard

When Stamicarbon started the design for purification of the off gases in the high pressure (140 ats) section of the CO₂ stripping plant, the design of this purification step was adapted in such a way that if an explosion step would take place damages were restricted to simple vessel internals. The vessel itself would not rupture, thus not creating a dangerous situation for the plant operators or not damaging major equipment in the plant itself.

In figure 2 a simplified version of the purifier is shown.

In the upper part of the purifier, the non condensables (H₂-N₂-O₂) are freed from ammonia and carbon dioxide in the packed section.

The volume V1 thus contains the explosive gas mixture.

On ignition of this mixture the pressure in V1 will rise very rapidly and the packed section drum will rupture.

The volume V2 is chosen such, that the pressure rise in V2 is kept minimal after the rupture, and thus no harm is done to the shell enclosing the volume V2.

This design has shown in the past to be very successful. In the few explosions which occurred the relatively cheap packed section was damaged without harming the shell of the vessel itself.

Since a few years Stamicarbon removes the hydrogen catalytically from the carbon dioxide as a standard design feature. The removal of the hydrogen from the carbon dioxide at synthesis pressure in large scale plants has demonstrated to very efficient in avoiding the risk of having an explosion.

As said before the hydrogen is removed from the carbon dioxide at synthesis pressure. In the discharge of the carbon dioxide compressor (145 at) a vessel is installed, in which a layer of platinum catalyst (Pt on aluminium oxide as a carrier).

On the suction side of the compressor sufficient air is introduced to provide the oxygen necessary to accomplish complete combustion of hydrogen (and other flammable components) and the additional oxygen required to maintain an oxidizing atmosphere in the urea synthesis section.

The discharge temperature of the carbon dioxide compressor is sufficiently high to maintain the combustion reaction. The hydrogen concentration in the carbon dioxide after combustion is so low that it is analytically undetectable. Temperature and oxygen concentration in the outlet of the combustion vessel are monitored.

An additional advantage of this system is a very rapid detection of any increase of the hydrogen in the carbon dioxide from the ammonia plant (detection of leakages in heat exchanger in the ammonia plant) through increased hydrogen reactor exit temperature.

As an additional safety measure Stamicarbon still incorporates in its design the explosion resistant scrubber (fig. 2) for the case that unexpected situations might arise. These could e.g. develop when an increased amount of hydrogen is present in the ammonia or in the highly unlikely situation that the hydrogen in the carbon dioxide would not be converted completely and slip through unnoticed.

Summary

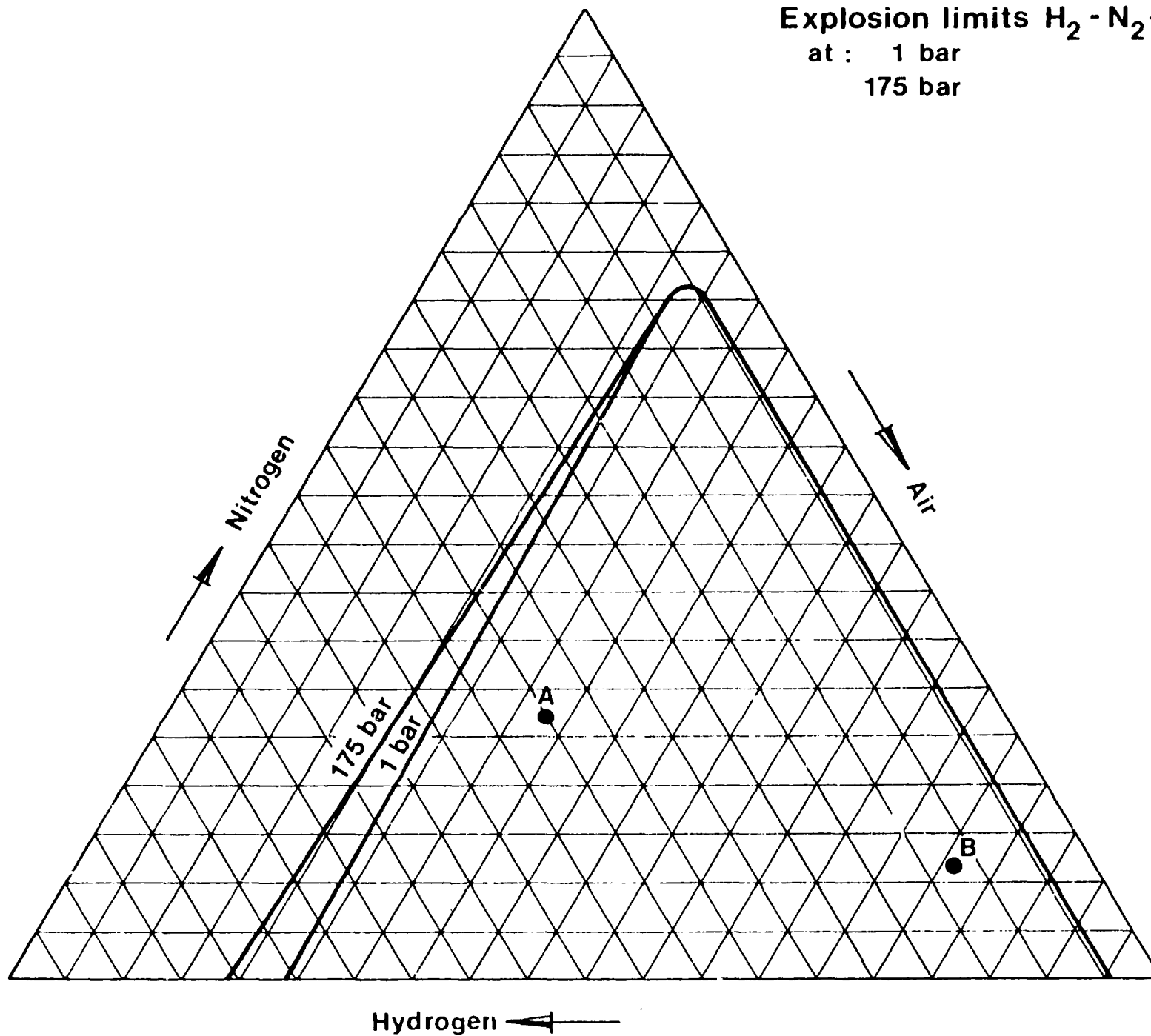
1. In every urea plant where no special precautions have been taken to avoid the presence of hydrogen, explosive gas mixtures will show up if the non condensable gases are purified thoroughly to prevent ammonia losses or to minimize emission of ammonia into the atmosphere.

2. Stamicarbon removes the hydrogen from carbon dioxide catalytically at synthesis pressure. If necessary the hydrogen could be removed from the ammonia as well.

3. Stamicarbon builds its equipment in such a way that if in severe process upsets an explosive gas mixture might be formed, no major equipment damage will occur if this gas mixture would be ignited for some reason.

4. The hydrogen removal system is an excellent warning system that there is a heat exchanger leakage problem in the NH_3 plant.

Explosion limits $H_2 - N_2 - \text{air}$
at : 1 bar
175 bar



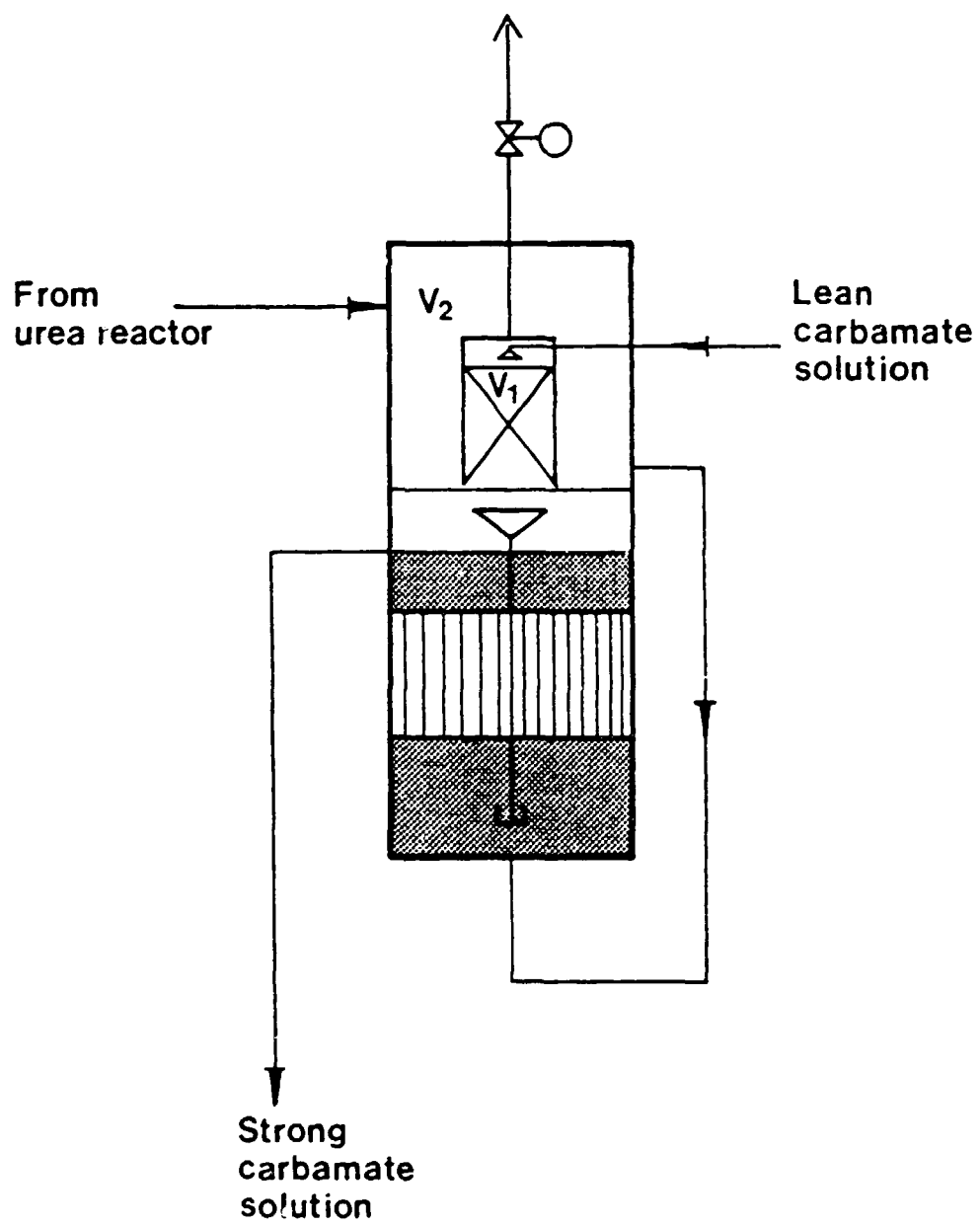


Fig. 2

