Chemical process industries

lecture 3

HNO_3 production

By

Dr.Intisar Khalaf

NITRIC ACID

INTRODUCTION

Nitric acid (HNO_3), also known as aqua fortis (strong water) and spirit of niter, is

- a highly corrosive strong mineral acid.
- The pure compound is colorless, but older samples are yellowish in color due to the accumulation of oxides of nitrogen.
- Commercially available nitric acid having concentration of 68% HNO_3, while the solution containing more than 86% HNO_3, is referred to as fuming nitric acid.
- Depending on the amount of nitrogen dioxide present, fuming nitric acid is further characterized as white fuming nitric acid or red fuming nitric acid, at concentrations above 95%.

Commercial grade of HNO3

36 Be	**sp.gr 1.33**	**52.3%**
40 Be	**sp.gr 1.381**	**61.4%**
42 Be	**sp.gr 1.408**	**67.2%**

MANUFACTURES

Nitric acid is manufactured by three methods.

1. From Chile saltpetre or nitrate
2. Arc process or Birkeland and eyde process
3. Ostwald's process or Ammonia oxidation process

1. From Chile saltpeter or nitrate

It is the first commercial process of manufacture of nitric acid from sodium nitrate extracted from Chile saltpeter. The process is now become obsolete since second decade of nineteenth century.

Raw materials

Sodium Nitrate
Sulfuric acid

Sources of raw material

Sulfuric acid can be obtained by contact process, Sodium nitrate can be obtained from caliche ore.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

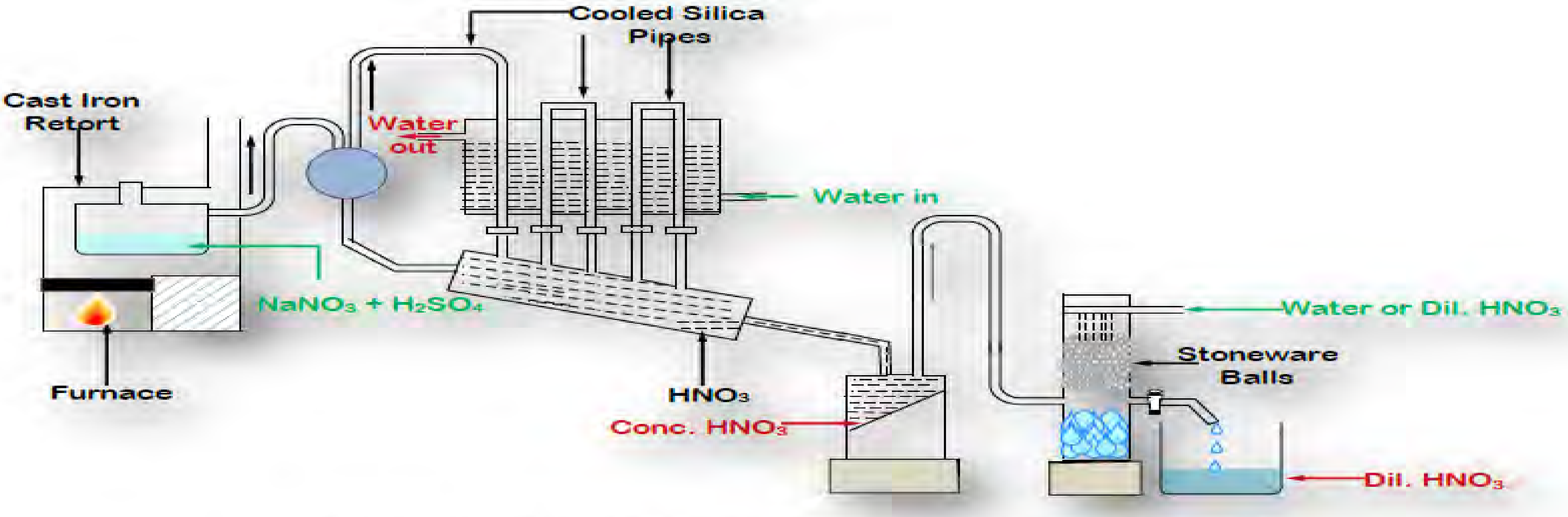


Figure: Manufacture of nitric acid from chile saltpetre or nitrate

$NaNO_3 + H_2SO_4$

Reactor → Condenser → Cocentrator → Conc. HNO_3 → Dilution Tank → Dilute HNO_3

Figure: Manufacture of Nitric Acib by Chile Saltpetre

2. Arc process or Birkeland and eyde process:

Raw materials

Basis: 1000kg Nitric acid (98% yield) , Air ,Water

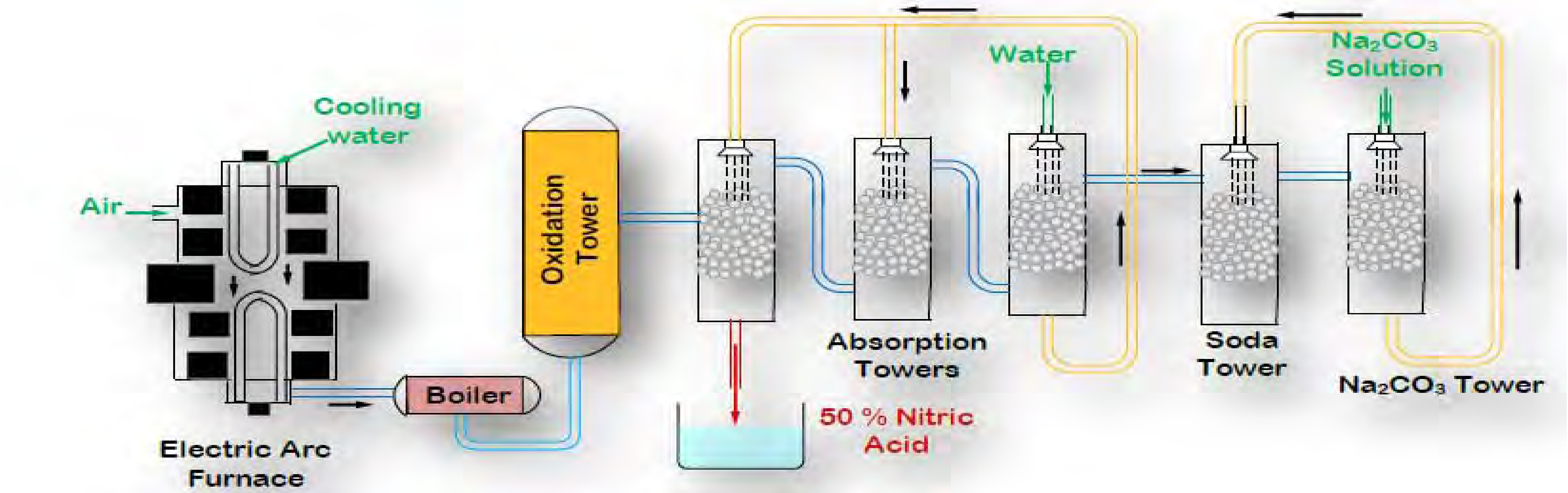
Reaction

$N_2 + O_2 \rightarrow 2NO$ ΔH = + 43.2 kcals

$2NO + O_2 \rightarrow 2NO_2$ ΔH = - 26.92 kcals

$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$

Manufacture



3. Ostwald's process or Ammonia oxidation process:

Raw Materials

Ammonia , Air, Platinum , Water , Steam

Sources of raw material

Ammonia can be synthesized by Haber – Bosch or Modern process

Major reactions

$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$ $\Delta H = -216.6$kcals ---- (1)

$2NO + O_2 \rightleftharpoons 2NO_2$ $\Delta H = -27.1$kcals ---- (2)

Side reactions

$4NH_3 + 3O_2 \rightleftharpoons 2N_2 + 6H_2O$ $\Delta H = -302.7$kcals ---- (3)

$2NH_3 \rightleftharpoons N_2 + 3H_2$ $\Delta H = +26.7$ kcals ---- (4)

$2NH_3 + 2O_2 \rightleftharpoons N_2O + 3H_2O$ $\Delta H = -65.9$kcals ---- (5)

$4NH_3 + 6NO \rightleftharpoons 5N_2 + 6H_2O + 432.25$kcal $\Delta H = -431.9$kcals ---- (6)

Manufacture

Nitric acid is made by the oxidation of ammonia, using platinum or platinum- 10% rhodium as catalyst, followed by the reaction of the resulting nitrogen oxides with water.

- Compressed air is mixed with anhydrous ammonia, fed to a shell and tube convertor designed so that the preheater and steam heat recovery boiler-super heater are within the same reactor shell. The convertor section consists of 10-30 sheets of Pt-Rh alloy in the form of 60-80 mesh wire gauge packed in layers inside the tube. Contact time and of the gas passes downward in the catalyst zone 2.5 X 10-4sec and are

- Product gases from the reactor which contain 10-12% NO, are s heat recovery units consisting of heat recovery boiler, super heate unit for rapid cooling to remove large fraction of product heat, and -absorber system.

- Air is added to convert NO to NO_2 at the more favourable tempe environment of the absorption system.

- The equipment in the absorption train may be series of packed o sieve tray vertical towers or a series of horizontal cascade absorbe

- The product from this water absorption system is 57- 60% HNO which can be sold as or concentrated as follow:

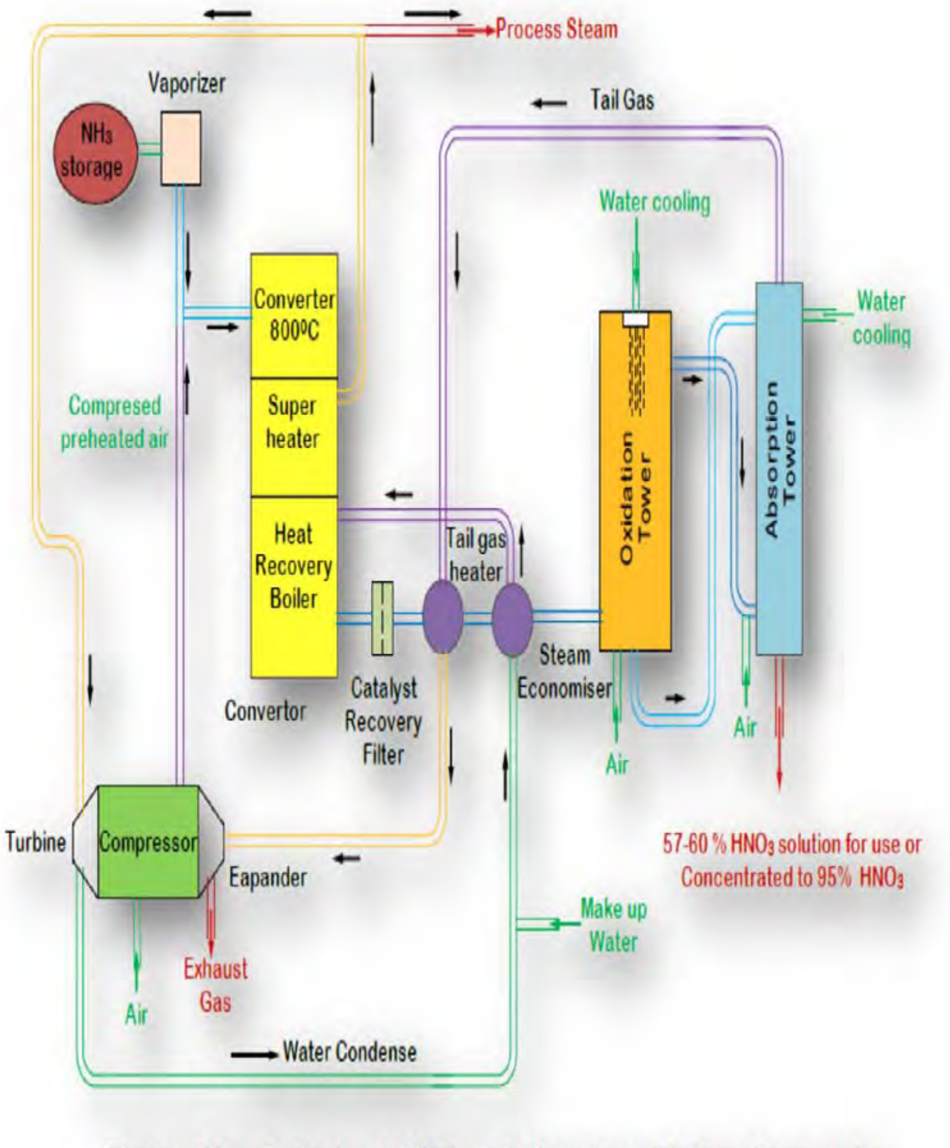


Figure: Manufacturing of Nitric acid from by oxidation of ammonia

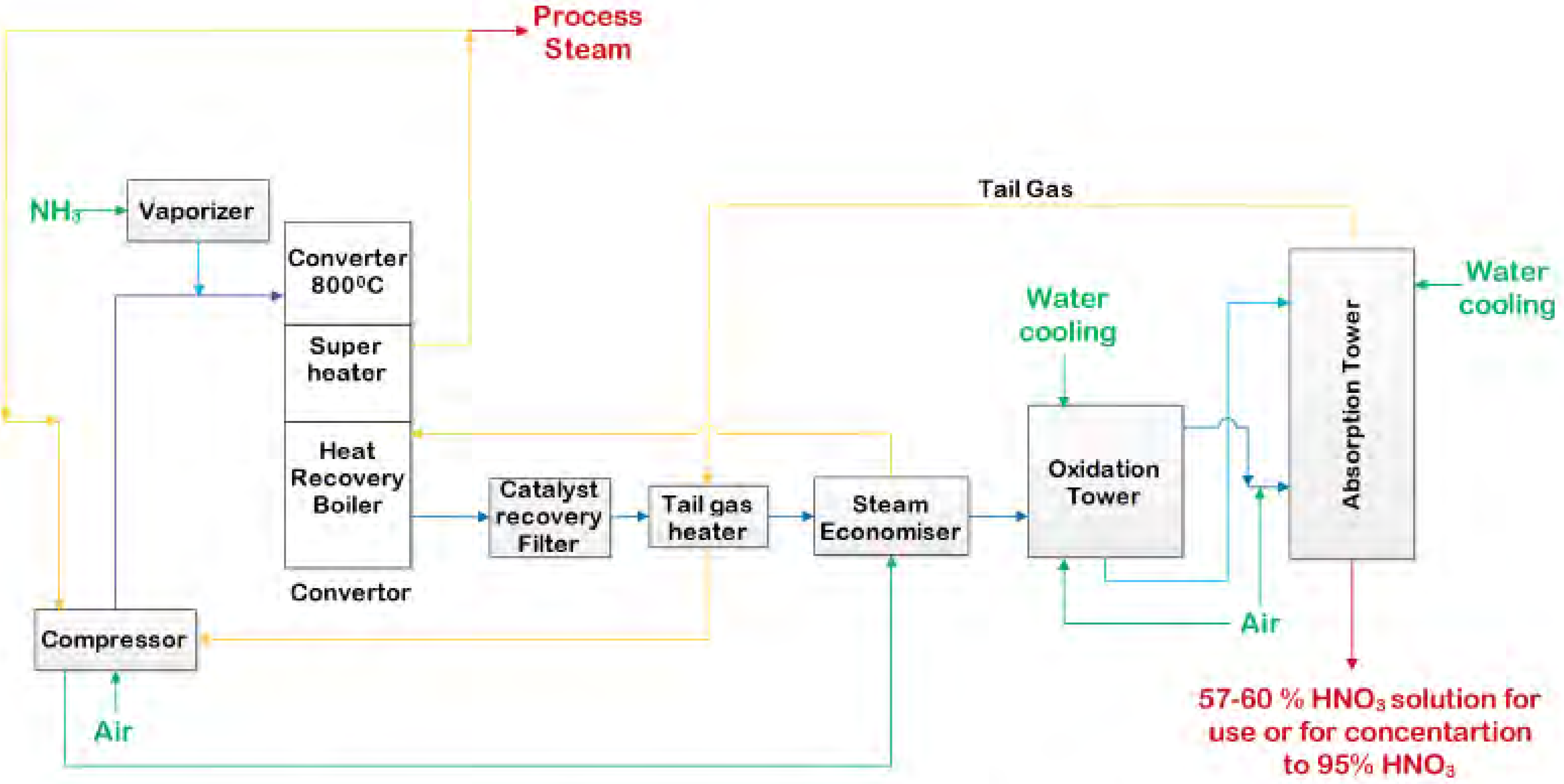


Figure: Manufacturing of Nitric acid by oxidation of ammonia

The process involves four steps :

1. Catalytic oxidation of ammonia with atmospheric oxygen to yield nitrogen monoxide .

2. Oxidation of the nitrogen monoxide product to nitrogen dioxide or dinitrogen tetroxide.

3. Absorption of the nitrogen oxides to yield nitric acid.

4. Concentration of nitric acid .

Concentration by H_2SO_4
Concentration by $Mg(NO_3)_2$

Engineering aspects

Thermodynamics and kinetics

$4NH_3 + 3O_2 \rightleftharpoons 2N_2 + 6H_2O$ $\Delta H = -302.64$kcal ---- (12)
$4NH_3 + 6NO \rightleftharpoons 5N_2 + 6H_2O$ $\Delta H = -432.25$kcal ---- (13)
$2NO \rightleftharpoons N_2 + O_2$ $\Delta H = -43$kcal ---- (14)

All the above exothermic reaction takes place in more or less extent.
Reaction 12 and 13 occurs with decrease in enthalpy with increase in number of moles followed by increase in entropy.

$4NH_3 + 5O_2 \rightleftharpoons 4\,NO + 6H_2O$

Ammonia oxidation reaction has an extremely favourable equilibrium constant so that one step, high temperature converter design may be used.

Further, ammonia air mixture exhibit explosion limits. At STP it is 15.6% ammonia, while temperature above 600°C and 1atm pressure, the limit is lowered to 10.5%
The following condition should be fulfilled to convert NH_3 into NO

- **Explosion limit**

The explosion limits are avoided by employing quantity of air such that the amount of ammonia **Reaction kinetics in ammonia oxidation stage**

☐Rate of reaction is directly proportional to system pressure
☐Alloying of platinum with rhodium improves yield at given set of conditions
☐Reaction to form NO is favoured by increasing temperature until an optimum is reached which increases with higher velocities. This results from the prevention of back diffusion of NO into higher NH_3 concentration region. If this occurs the following reaction is quite probable and should be avoided for high NO yield.

$$4NH_3 + 6NO \rightleftharpoons 5N_2 + 6H_2O$$

☐Rate of NO formation very nearly corresponds to diffusional transport of ammonia molecules to the catalyst surface

There is slight equilibrium advantage to operation at atmospheric pressure. This is more than offset by increased capacity in a given reactor volume with subsequent catalyst and reactor savings when operating high pressures (3-8atm.)
Oxidation of nitrogen oxide does not have as large equilibrium constan ia mixed with it is less than 10.5vol% of total volume.

Thermodynamics

The thermodynamics of competing reactions (12) and (13) are rendered unfavourable by working above 5000C, while the reaction (14) are not favoured if the process is carried out under 1200°C

Catalyst for oxidation of ammonia

- Platinum/rhodium alloy containing 10% rhodium is the only industrially viable catalyst.
- Rhodium not only improves the catalytic properties of platinum but also improves mechanical and anti-abrasive properties of material under the operating condition such as to counter the severe corrosion and oxidation atmosphere.
- 4–10 % of rhodium used in Pt/Rh supported catalyst. Higher efficiencies and smaller platinum losses can be achieved by knitted gauzes.

- The metallic alloy catalyst is prepared into very fine threads of diameter 0.05mm which are woven into meshes with more than 1000stiches/cm_2. Two to four or even more of these meshes are placed on top of one another inside the reactors when these are put into operation.
- Catalyst threads are smooth, bright and less active at initial stage, as the time progresses they becomes dull and wrinkled whereupon their activity rises to the maximum. Finally they become spongy with activity falling off.
- When it is in most active state, ammonia oxidation yields up to 98% of NO are obtained.

- Ammonia conversion efficiency is a function of **pressure and temperature**.
- As the pressure increases, higher temperatures are needed to obtain the high conversion efficiency.

An increased flow rate and the presence of several layers of the catalyst help to minimize undesirable side reactions. However, high flow rates increase the catalyst loss which leads to search for non-platinum catalysts for ammonia oxidation. The most prospective non-platinum catalysts are based on oxides of Co, Fe or Cr.

Catalyst poison

- **Sulfates, H_2S, chlorides, Arsenic and its oxide, Si, P, Pb, Sn and Bi** are permanently poisoning the catalyst. These elements lead to the formation of inactive compounds in the wires resulting in decreasing of the catalytic activity.

- Traces of **acetylene, ethylene, Cr, Ni and Fe** temporarily reduce the conversion efficiency which can be restored by treatment with HCl. There so air should be freed from all above impurities along with suspended particles of lubricants, fats, fine dust and abrasive powder. Also, suspension of Fe_2O_3 from ammonia is removed. For that efficient filtration system along with magnetic separators are provided.

PROPERTIES

Physical Properties

- Molecular formula : HNO_3
- Molecular weight : 63.013gm/mole
- Appearance : Colourless liquid
- Odour : Pungent
- Boiling point : 121°C (68% HNO_3 solution)
- Melting point : -42°C
- Density : 1.5129gm/mL (liquid)
- Solubility : Miscible with water in all proportions
- The impure nitric acid is yellow due to dissolved oxides of nitrogen, mainly NO_2.
- It has a corrosive action on skin and causes painful blisters.

Chemical Properties

- **Acidic properties:** It is a strong monobasic acid and ionization in aqueous solution.
- **Oxidizing properties:** It acts as a powerful oxidizing agent, due to the formation of nascent oxygen.
- **Action on metals:** It reacts with almost all the metals, except noble metals, like Pt and Au. The metals are oxidized to their corresponding positive metal ions while HNO_3 is reduced to NO, NO_2. N_2O, NH_2OH or NH_3, depending upon the conditions such as temperature, nature of metal and concentration of the acid.

- Nitric acid has ability to separate gold and silver.

USES

- As a starting material in the manufacture of nitrogen fertilizers such as ammonium nitrate, ammonium phosphate and nitrophosphate. Large amounts are reacted with ammonia to yield ammonium nitrate.
- Weak acid are used to digest crude phosphates.
- As a nitrating agent in the preparation of explosives such as TNT, nitroglycerine, cellulose polynitrate, ammonium picrate
- In manufacture of organic intermediates such as nitroalkanes and nitroaromatics.
- Used in the production of adipic acid.
- Used in fibers, plastics and dyestuffs industries
- Used in metallurgy and in rocket fuel production
- As the replacement of sulfuric acid in acidulation of phosphate rock.