

OVERVIEW OF PRODUCTION OF NITRIC ACID

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Abstract: - Nitric acid is considered as one of the strongest inorganic acid and one of the important chemicals in industries. The use of nitric acid involves various fields like their use in fertilizer industry, polyurethanes, fibres and many more. The formation of nitric acid depends upon various factors and involves different types of techniques depending upon the use of raw materials. This paper discusses two different types of techniques i.e. Non-Selective Catalytic reduction and Selective Catalytic Reduction and their role in nitric acid plant. This paper also emphasizes upon the Nitric Acids Pressure plants i.e. Single Pressure Plant and Dual Pressure Plant. A depiction of block diagram is created in order to explain the process efficiently.

Keywords: - Nitric acid, fertilizer industry, polyurethanes, selective catalytic reduction, pressure plant, fibres

1. INTRODUCTION

With the rapidly growing scenario of chemical industries, the most growth in demand has come from the production of polyurethanes, fibers and ammonia nitrate-based explosives (Splinter, 2003). The common chemical used in these industries is nitric acid (C. Sharma R. S., 2017). The colorless to yellow or red liquid which sometimes fumes as reddish-brown vapors with suffocating odor is used in large areas. The production of nitric acid involves the major challenges and hereby required a complete discussed process in order to face the problems that must be addressed by mankind.

Nitric acid is commonly called as strong water (aqua fortis) by middle ages and is considered as strong inorganic acid which is produced in large volumes (T., 1964, G.Speight, 2017). It is used in the production of various chemicals but mostly played role in fertilizers industry (Markham, 1958, Arvin Mosier, 2013). Other than this, it is also used in formation of agricultural chemicals, corrosion inhibitors, intermediates, water treatment products, personal care products, anti-scaling agents, oxidizing agents and many more (Carlos A. Grande, 2018, Maslan, 1969).

For the most part, the consumption and manufacturing of nitric acid is about 60%. But, concentrated nitric acid is required for the production of chemicals like isocyanates and nitrobenzene, that are commonly used as the initial materials in diverse chemical (Hocking, 2005). Nitric acid is considered as the most powerful oxidizing agent that reacts violently by many organic materials. Their oxidation depends upon the acid

concentration, temperature and reducing agents (Harold F, 2015). Hereby, by observing the growing importance of nitric acid, the production of nitric acid requires a proper procedure.

2. LITERATURE REVIEW

Various researches have been done discussing about the production and importance of nitric acids. One such research report has been made by chemical industry committee (T., 1964) which discusses about the manufacturing of nitric acids by the ammonia oxidation process and the production of concentrated acid by considering the air pollution aspects of the process.

Another work by (V.A. Sadykov, 2000), which describes the role of oxide catalyst in the nitric acid production. They studied about the factors that affect the performances of precious metals and the oxides during high temperature in ammonia oxidation process. They also analysed the synthesis of mixed oxide systems which also includes the perovskites that control the nitric acid selectivity and stability in high temperature during the ammonia oxidation process.

Similarly, (Armistead G. Russell, 1985), discussed about the dynamics of nitric acid production and performed the modelling for the fate of nitrogen oxides emission. Their main focus was on the reactions that are responsible for the production of nitric acids. Study describes that maximum amount of NO from the air parcel are removed by the process of dry deposition at the ground which involves the contribution of nitric acid at the large scale.

(J.Roironb, 1989) studied about the selective catalytic reduction in order to reduce NO_x emissions from Nitric Plants. They presented the data collected upon commercial vanadium oxide-alumina catalyst (DN-110) which gets active at low temperature. Operating temperature, space velocity as well as gas compositions are also studied by them. Mechanisms are proposed for both NO and NO₂ reductions which explains the experimental results. Optimization of operating cost of NO_x abatement were also performed using coupling of SCR by high proficiency absorption.

(P.Avila, 1993) worked upon the behaviour of V₂O₅/WO₃/TiO₂ phosphorated catalyst, in the Selective Catalytic Reduction (SCR) using equimolar NO+NO₂ mixture. Their main aim was to analyse its industrial utilisation in order to treat nitric acid plant stack gases. Molar ratio of NO/NO₂ and oxygen concentration were

the variables which were also studied during the research.

Working on the catalyst part, (Mowla, 2009) studied about the selective catalytic reduction (SCR) of nitric oxide with abundance smelling salts within the presence of oxygen on silica-supported vanadium oxide in a packed bed reactor, and a numerical model was proposed for the cycles happening in the reactor. Trial information were introduced for assessment of the precision of the proposed model. They also examined various boundaries, for example, feed temperature, inlet feed structure, and gas hourly space speed (GHSV) on the transformation of NO over V₂O₅/SiO₂ impetus for reasonable application. They concluded that high NO transformation happened at temperatures of 280°–300°C, GHSV under 2000 h⁻¹ (STP), and O₂ focus more noteworthy than 10% v/v.

Another research by (Yibo Cao, 2019) used water or nitric acid for the washing of the waste V₂O₅-WO₃/TiO₂ denitrification catalyst from the coal fired power plant which is further followed by different contents of impregnating different contents of V₂O₅. They also investigated that the additional amount of vanadium that can be used on the low-temperature selective catalytic reduction process, under the conditions of high concentration of Sulphur dioxide as well as the water. Inductively coupled plasma, optical emission spectrometry, nitrogen adsorption/desorption and x-ray power diffraction were characterization of catalyst. They concluded that the optimum activity was achieved approximately by using point 8 mole per litre HNO₃ solution. They also concluded that the nitric washing can remove the ammonium salts which was deposited on the waste catalyst and hence can help in production of crystalline WO₃.

Hereby, this paper discusses the different techniques of production of concentrated nitric acids and classification of plants by oxidation pressure and absorption pressures.

3. GENERAL SCHEME FOR MANUFACTURE OF CONCENTRATED NITRIC ACID

- Ammonia oxidation in presence of Pt/Rh Catalyst

The catalyst systems at present being used in the oxidation of ammonia to nitric oxide are minor departure from a kind of metal catalyst first utilized more than 60 years prior. With the appearance of high-pressure alkali oxidation plants, catalyst misfortune turned into a genuine monetary issue. Consequently, alloys, other than being utilized for strengthening were presently read for their potential in bringing down catalyst loss by evaporation. At present consequently, apparently varieties of the Pt/Rh impetus framework actually offer the most prudent technique for creating nitric corrosive,

given platinum loss can be additionally decreased (James Anthony Busby C. Chem, 1975). The catalytic oxidation of ammonia salts over platinum is a key step, both in modern assembling of nitric and in ecological science where alkali is taken out in the so-called specific catalyst reduction (SCR). Nitric corrosive is created through NO in the Ostwald cycle where ammonia is passed along with air a Pt/Rh gauze as catalyst (R. Imbihl, 2007).

- Oxidation of NO to NO₂
NO oxidation is a key response in lean NO_x reduction advancements and in the Ostwald cycle for nitric acid creation. In Ostwald's cycle, NO oxidation is completed as a non-catalytic measure and the forward response is supported by the evacuation of heat and by giving adequate habitation time. Utilizing a catalyst for NO oxidation may prompt intensification of the nitric acid plant. Along with accelerating the oxidation cycle, it might decrease capital expenses and increment heat recovery. Attempts have been made to discover an impetus viable under modern conditions; yet achievement so far has not been (Ata ul Rauf Salman S. M., 2019). In the Ostwald cycle, normal gas piece at the exit of the ammonia ignition step is 10% NO, 6% O₂ and 15% H₂O. Gas stage oxidation of nitric oxide happens in tubing and heat exchangers downstream of the NH₃ oxidation reactor (Ata ul Rauf Salman B. C., 2018).
- NO₂ absorption in water to form nitric acid.
The absorption of a gas by a fluid is a fundamental designing unit operation which has been very much examined. At the point when it is desired to structure an item, as on account of nitrogen dioxide absorption by water to frame nitric acid, or to clean an emanating gas stream of a specific pollutant, the unit activity is ordinarily alluded to as "cleaning" (Herrmann, 1977). NO₂ is retained quicker in the weakened nitric corrosive than in water. The bigger beginning weight (>90 kPa) and the higher convergence of nitric acid (>7wt%) both lead to a huge ascent of the absorption productivity. The deteriorating part of HNO₂ arrives at greatest when the molar proportion of NO₂ to water is 0.024 (Zhang Feng, 2013).
- Reaction with NO₂ or distillation is done for concentrating the weak nitric acid. Simple distillation cannot be used due to the formation of azeotrope with water at about 68% concentration. Nitric acid structures an azeotrope with water at about 68wt% of nitric acid and a breaking point at pressure of 122°C. So as to defeat a fluid azeotrope concentrated

highly hygroscopic sulfuric acid is an ideal alternative as an extractive specialist. It tends to be effortlessly isolated from nitric corrosive just as from water and is fluid over the total working temperature range which facilitates activity, fire up and shut down of a plant. Various studies show that azeotrope vanishes past a sulfuric acid centralization of 50wt%. So as to limit the efforts to reuse the weakened sulfuric acid, the nitric acid ought to be pre-concentrated (System, n.d.).

4. PROCESS OVERVIEW

Today, ammonia oxidation is the premise of all business nitric corrosive creation. Plant limits range between around 100 and near 3000 tons/day (Weiland, 2018). Monopressure measures working at 0.7–1.4 MPa abs limit capital venture, though double pressures measure with ammonia oxidation at 0.3–0.6 MPa abs and retention at 1.0–1.4 MPa abs upgrade ammonia conversion effectiveness furthermore, catalyst use. These cycle variations produce "powerless" nitric corrosive (55–68 wt%). Corrosive fixations in the reach 50–60 wt% are ordinarily used to fabricate ammonium nitrate for compost and mining dangerous creation. Higher focuses up to 68 wt% are utilized in natural and organic nitrations. "Solid" nitric acid (up to 99 wt%) is needed for some natural and organic reactions of modern significance (Lefers, 1980).

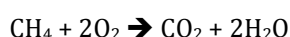
Discussion of production process involves raw materials as its important part. For producing nitric acid, ammonia and cooling water are the main components (United States Patent No. US7118723B2, 2008).

Two techniques are generally used during the process i.e. Non-Selective Catalytic Reduction and Catalytic Reduction.

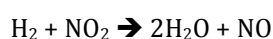
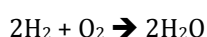
4.1. Non-Selective Catalytic Reduction

During this process, the reaction between the hydrogen or natural gas or naphtha and NO_x takes place in the presence of free oxygen during the waste gas over catalyst like platinum, rhodium or palladium (M Heck, 1999, Maurer, 2008). Initially, the nitrogen dioxide is reduced and if the reduction is not taken further, the process merrily decolourise the gas according to the reaction given below.

(When methane is considered as the reactant)

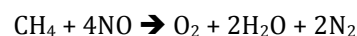


(When hydrogen is considered as the reactant)

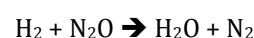
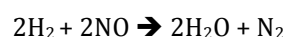


Excess amount of the reducing agent is required in order to reduce nitrogen oxide to nitrogen. As a result, formation of high temperature gas take place which contains methane and naphtha as constituents (Jihui Wanga, 2015). When hydrocarbons are used, the release of carbon monoxide and hydrogen takes place into the atmosphere according to the following reaction.

(When methane is considered as the reactant)



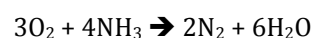
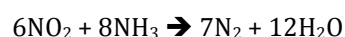
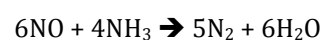
(When hydrogen is considered as the reactant)



Tail gas removed from the absorber is again preheated to a minimum of 300°C with hydrogen or 550°C with methane in order to operate the catalyst efficiently. The gas resulted from the reaction after mixing with the preheated tale gas, is passed through the catalytic bed reactor. NSCR has advantage because of substantial N₂O reduction but this technique is not usually followed as during the use of hydrocarbon as reducing agent, gases like ammonia, carbon monoxide, carbon dioxide and unburnt hydrocarbon takes place. Other than this, in absence of hydrogen, the temperature of tail gas would be high since it is used a reducing agent for cooling of gases.

4.2. Selective Catalytic Reduction

During this process, the reaction between the ammonia with NO and NO₂ takes place in the presence of minimum amount of oxygen. The reactions involved are



Catalysts like radium pentoxide, platinum, iron, chromium oxide and zeolites are commonly used during the reaction (B. J. Adelman, 1996, Dinyar K. Captain, 1998). Catalyst efficiency and gas temperature are the two factors on which the leakage through the catalyst bed depends upon. Temperature during the operation is generally kept more than 200°C whereas, efficiency of ammonia is minimally affected by the pressure.

The tail gas obtained from the absorber is preheated to minimum temperature for the proper functioning of the SCR catalyst (Ken-ichi Shimizu, 1998). The aggregate of reactant gas and the preheated tale gas is passed through the catalytic bed reactor (Shijian Yang, 2014). Unlike NSCR, there is negligible increase in tale gas temperature and use of oxygen in the SCR. Since the nitric acid plant contains the ammonia in large amount, SCR is highly preferred than NSCR (Sang Wook Bae, 2006). Although,

the major disadvantage of SCR is that it works only at the high temperature initially.

5. DESCRIPTION OF PRODUCTION PROCESS IN THIS PLANTS

Oxidation pressure and absorption pressure are the two factors on which production process in plants are based upon. Hence, it is classified as: -

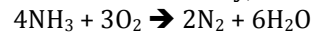
1. Dual Pressure Process
 - Low Pressure/Medium Pressure
 - Medium Pressure/High Pressure
2. Single Pressure Process
 - Medium Pressure/Medium Pressure
 - High Pressure/High Pressure

5.1. Process Bases

The oxidation section of nitric acid plants involves a reaction between ammonia with air, in the presence of platinum/rhodium alloy catalyst. Formation of Nitric Oxide and water takes place according to the reaction (United States Patent No. US7118723B2, 2008),



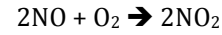
Simultaneously,



5.2. Catalyst

Due to presence of several factors like air pollution, contamination from ammonia, poor gas distribution across catalyst and poor mixing of ammonia can poison the catalyst. Hereby, it is important to have a catalyst recovery system, hence, a palladium alloy ("Getter" or

"Catchment") helps in recovery of 60-80% catalyst. Hence, the enthalpy from hot gas reaction helps in the heating of the tail gases, before discharging them to the atmosphere (R.W. van den Brink S. B., 2001). The water obtained after this is cooled in condenser and transferred to the counter flow absorption column. Simultaneously, oxidation of nitric acid takes place to NO_2 .



Gas obtained from ammonia oxidation is mixed with secondary air in order to increase the oxygen content up to 2-4 % in the waste gases leaving from the plant (Paul N.Cheremisinoff P.E., 1995). The reaction between the NO_2 and nitric acid depends upon temperature and pressure and usually takes place at low temperature and high pressure.



Hence, since, the reaction being exothermic, continuous cooling is provided within the absorber. The nitric acid in absorber involves dissolved nitrogen oxide and will be further bleached by secondary air (Grzegorz Giecko, 2008).

5.3. Medium Pressure, Single Pressure Plant

Figure: - 1 represents the block diagram, describing the various sections of processes. Some of the sections are explained below

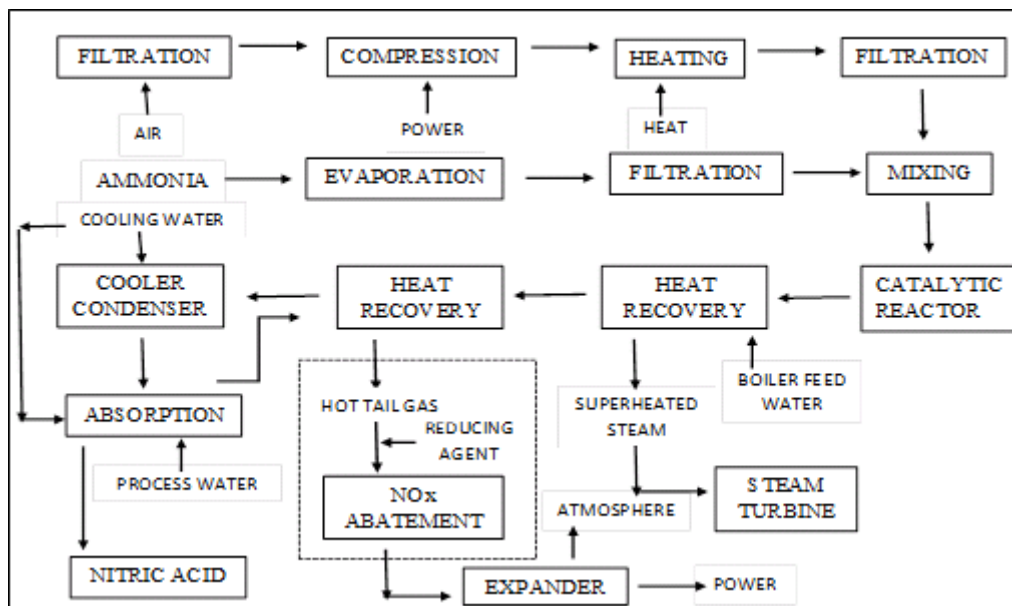


Figure 1: - Block Diagram of Single Pressure Plant

Liquid ammonia from storage is evaporated using water or condensates and superheated to prevent any liquid carryover. Gaseous ammonia is filtered to remove any rust from carbon steel equipment. Some plants also use a magnetic field on the liquid ammonia. By using 2-3 stage filtration units, air of high purity is obtained.

For some reasons the blower expander set might be viewed as the core of a nitric acid cycle. To an enormous degree it sets the energy effectiveness and working adaptability of the cycle and speaks to somewhere in the range of 35% and 45% of the complete gear cost. In little mono pressure plants, the air blower is regularly a multistage radial unit with intercoolers, while for enormous limit plants, axial flow compressors are regularly utilized for the underlying phases of compression. A double weight plant generally has a hub air blower.

Compressor is driven by a tail gas expanded and by steam condensing turbine. Modern plants use static mixers to give the high-quality mixture which is essential in maintaining good catalyst operation. The catalytic reactor is designed to give a uniform distribution of the air/ammonia mixture over the catalyst gases (R.W. van den Brink, 2002, Twigg, 1989). Maintenance of the catalyst operating temperature is very important for the NO yield. This is achieved by adjusting the air/ammonia ratio and ensuring that lower explosive limit for ammonia in air is not exceeded. The catalytic reactor is typically mounted as the upper part of the vessel which contains the first heat recovery section. A set of gas or gas heat exchanger transfer the energy from the gas leaving the boiler set, to the tail gas. A cooler condenser ensures final cooling down to 50°C after the final heat recovery. Weak acid solution is formed and is separated and pumped to the absorption tower. The modern absorber design uses counter current flow circulation with high efficiency trays which are usually sieve trays

or bubble cap trays. The tray spacing increases progressively from the bottom to the top of the absorber. Many of the trays are fitted with internal cooling coils to remove the heat of reaction. The absorption section consists of one or more columns in series.

Demineralised water demineralised water or steam condensate is added at the top of the tower as makeup. Process condensate from the manufacture of ammonium nitrate may be used after acidification. The acid solution leaving the absorption section is rich in dissolved nitrogen oxides and is passed to a bleaching tower where it is contacted with the counter-current flow of secondary air. The secondary air and the nitrogen oxides which have been stripped out are mixed with the gases leaving the cooling section and recycled to the absorption section. Gas from the absorber is passed through the heat recovery and expand the sections for energy recovery and then passed to the stack. The steam turbine is also used for plants at start up. In some plants the energy makeup comes from an electric motor and generated steam is exported.

5.4. High Pressure, Single Pressure Plants

A typical high pressure, single pressure plant is similar in layout to the medium pressure, single pressure plant as shown in Figure: - 1. The process parameters differ from the higher operating pressure.

The main differences include a higher operating catalyst temperature and pressure with the lower NO yield and a greater loss of catalyst. A higher inlet pressure to the gas expander allowing a higher inlet temperature and has more energy recovered in the expander and a small steam turbine. A higher operating pressure in the absorber with the lower tail gas NO_x content (Holger C. Andersen, 1961).

5.5. Dual Pressure Plant

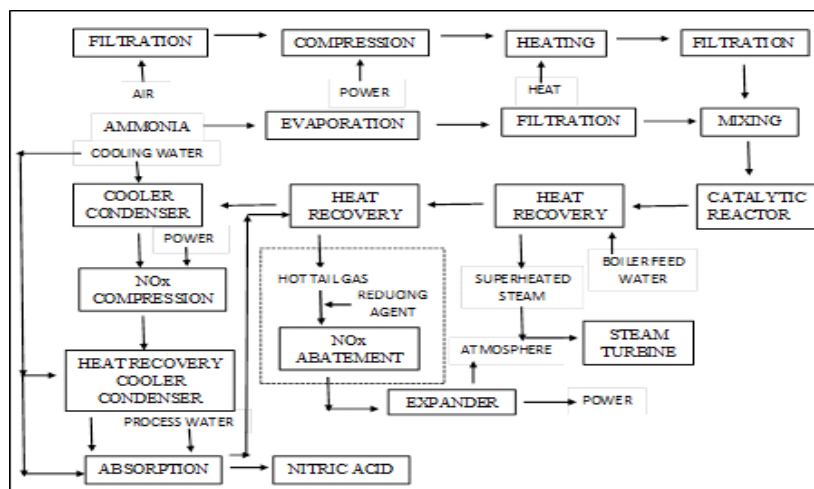


Figure 2: - Block Diagram of Dual Pressure Plant

Figure: - 2 shows the block diagram for dual pressure plant which is similar to the single pressure plant.

Air is provided to the cycle from a blower that is controlled by an expander and a makeup driver, all having a typical shaft. The expander is a turbine that recoups energy from the tail gas remaining after the NO_x retention venture as it is diminished to environmental weight. The make-up driver, generally a steam turbine or all the more infrequently an electric motor, meets the balance of any force prerequisite for air pressure (and on account of the double weight measure, NO_x gas pressure) (Miles, 1961). Alkali and air are separated and blended with the end goal that there is an overabundance of oxygen and are passed over a platinum/rhodium catalyst in the alkali burner to create nitric oxide, water fume, and much warmth. The coming gases are cooled, tail gas heating and creating steam that can be sent out or used to control the steam turbine (J. Eimers, 1985). As the cycle gases cool, nitric oxide is additionally oxidized to form nitrogen peroxide.

After the cooling section, in dual pressure plants the gases leaving the cooling section are mixed with the air and the nitrogen oxides from the bleaching of the acid solution and compressed to a higher pressure for the absorption stage. The heat of compression is removed from the compressed gases by heat recovery into the tail gas or the boiler feed water. A second cooler condenser reduces the temperature of the gases to about 50°C and the acid solution formed is mixed with the product acid.

The acid solution from the absorption section is passed to a column working at the pressure of the air compressor discharge, where it is stripped of the nitrogen oxide by a flow of air from the air compressor. The air and the stripped nitrogen oxides return to the NO_x gas compressor.

ADVANTAGES

Nitric corrosive is a key synthetic for some ventures. Exactly 60 million tons are created yearly, of which 80% goes into nitrate creation for composts and explosives, the last mainly for mining. (Groves, 2020). Nitric acid creation is mostly determined by fertiliser industry. Nitric acid is utilized in the creation of ammonium nitrate and calcium ammonium nitrate which discover applications as fertilisers. Ammonium nitrate is additionally utilized in the assembling of urea ammonium nitrate (UAN) utilized in compost definitions (C. Sharma R. S., 207).

Some nitric acid is utilized to make intermediates in the polymer business, strikingly in the production of hexanedioic corrosive (adipic corrosive) to make polyamides and TDI (toluene diisocyanate or methylbenzene diisocyanate) and dinitrobenzene. Two of a scope of reagents used to make polyurethanes. Nitrobenzene is utilized to make aniline which is a key

reagent for making colors. Nitric corrosive is utilized as a middle in the assembling of nitrobenzene and nitrochloro benzenes among others (The essential chemical industry-online, 2016).

Nitric acid is utilized widely in industry to nitrate aliphatic and sweet-smelling compounds. In numerous occasions, nitration requires the utilization of sulfuric acid as a getting dried out specialist or catalyst; the degree of nitration accomplished relies upon the centralization of nitric and sulfuric acids utilized. This is of modern significance in the production of nitrobenzene and dinitrotoluene, which are intermediates in the assembling of polyurethanes (Hanson, 1976). Dynamite is an unstable. Different isomers of mononitrotoluene are utilized to make optical brighteners, herbicides (qv), and bug sprays.

CONCLUSION

Two different techniques have been shown i.e. Non-Selective Catalytic reduction and Selective Catalytic Reduction. It has been concluded that SCR (Selective Catalytic Reduction) is commonly used in industries due to its high efficiency. Production of nitric acid can be classified as single pressure plant and double pressure plant depending upon the oxidation and absorption pressure. The block diagrams of both the plants presented above shows that latter does involve two extra sections then the former in order to reduce the final temperature and increasing the performance. Due to increased demand of nitric acid, it has become important to first analyze and more important to study the process effectively.

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