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Role of nitrous acid decomposition in absorber and bleacher in nitric acid plant

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ABSTRACT

The stringent statutory regulation for clean environment makes the absorber and the bleacher in the nitric acid plant two very important equipments. The NOx finally released to the atmosphere from the absorber, is based on the mathematical calculations of the nitric acid and nitrous acid concentration profiles along the length of the absorber. The present work focuses on the role of HNO_2 decomposition in the absorber and the bleacher in the nitric acid plant. The decomposition of HNO_2 is a heterogeneous reaction resulting into the formation of nitric acid and desorption of nitric oxide. At high nitric acid concentration (40–50 wt.%), the reversibility of HNO_2 decomposition due to NO oxidation with nitric acid is important. The model for bleacher column is presented, which takes into account the de-colorization of the product acid from the absorption column and makes it free from the nitrous acid. The model for the bleacher also takes into account the decomposition and oxidation of HNO_2 with dissolved oxygen. The models proposed for absorber and bleacher are validated from the data collected from a mono-pressure nitric acid plant as well as the data present in open literature.

1. Introduction

Ever growing stringent statutory regulations for clean environment makes the absorption column in the nitric acid plant very important piece of equipment. The absorption column helps to achieve the desired strength of nitric acid as well as controls the emission of NOx gases. Considerable research efforts have produced a greater understanding [1–6] on the various aspects of NOx absorption, such as: (i) NOx gases consist of several components NO, NO_2, N_2O_3, N_2O_4, HNO_2, HNO_3, etc. and the liquid phase contains two oxyacids (i.e. nitric acid and nitrous acid), (ii) several reversible and irreversible reactions occur in both gas and liquid phases, (iii) absorption of multiple gases is accompanied by multiple chemical reactions, (iv) desorption of gases occur preceded by chemical reaction, (v) heterogeneous equilibria prevail between the gas and the liquid phase components, (vi) heat effects of the absorptions and the chemical reactions. Considerable modeling of various pieces of equipment of a nitric acid plant has been carried out and a modeling, simulation and optimization strategy has been proposed in a recent work by Chatterjee and Joshi [7]. In this work as well as practically by all the studies reported in the published literature [8–18], the depletion of aqueous nitrous acid in the absorber and the bleacher in a nitric acid plant has not been adequately modeled.

The depletion of nitrous acid in the aqueous solutions is an integral part of nitrogen oxide absorption from gas streams. In the bleacher, nitrous acid decomposes to nitric acid and also oxidation of nitrous to nitric acid occurs with the help of air. The decomposition of nitrous acid is a heterogeneous reaction resulting into the formation of nitric acid and the desorption of nitric oxide (NO). The nitric oxide desorbed then oxidizes in the environment of secondary air, which is passed into the bleacher as a side stream from the air compressor. The oxidation leads to the formation of NO_2, N_2O_3, N_2O_4, etc. which are further absorbed in nitric acid. The liquid phase HNO_2 and the dissolved NO can also get oxidized with dissolved oxygen. The process is therefore complex and an adequate mathematical model is essential to represent the various physico-chemical phenomena occurring in the absorption and bleacher processes.

Though the published literature has addressed the above mentioned (i)–(vi) components of the NOx absorption mechanism, two additional components need to be duly considered. These are: (a) kinetics of decomposition of HNO_2 and (b) the liquid phase oxidation of HNO_2 and NO. The objective is to obtain colorless and practically HNO_2 free nitric acid. The above mentioned two components have been included in the present work for the estimation of overall rate of reaction and have been used to model the absorber and bleacher units in a nitric acid plant.

2. Mathematical model

Except HNO_2 decomposition and oxidation, the NOx absorption has been duly addressed in the published literature [7,16]. The following discussion addresses HNO_2 decomposition and oxidation.

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Nomenclature

$\underline{a}$	interfacial area ($m^2\,m^{-3}$)
E_a	activation energy (J/mol K)
G	molar flow rate of inert ($kmol\,s^{-1}$)
H_i	Henry's coefficient for species i ($kmol\,m^{-3}\,kN\,m^{-2}$)
$[i]$	concentration of species i ($kmol\,m^{-3}$)
k_1	forward rate constant for nitric oxide oxidation (kPa^{-1})
k_b	3rd order reaction rate constant in Eq. (10) ($kg\,m^{-2}\,s^{-1}\,Pa^{-1}$)
k'_b	reverse reaction rate constant in Eq. (11) ($kg\,m^{-2}\,s^{-1}\,Pa^{-1}$)
k_d	decomposition rate constant in Eq. (11) ($m^3\,kmol^{-1}\,s^{-1}$)
k	mass transfer coefficient in liquid ($m\,s^{-1}$)
k_o	Arrhenius constant for Eq. (14)
K'	constant in Eq. (4)
K_n	equilibrium constant for Eqs. (30)–(33) (n = 2–5) ($kPa^{-2}\,s^{-1}$)
K_6	parameter defined by Eq. (25) ($kPa^{-1/2}$)
L	molar flow rate of water ($kmol\,s^{-1}$)
p_i	partial pressure of gas phase species i (kPa)
P	operating pressure (kPa)
R	gas constant ($kJ\,kmol^{-1}\,K^{-1}$)
Ra_i	volumetric rates of mass transfer for species i ($kmol\,m^{-3}\,s^{-1}$)
R_d	rate of HNO_2 decomposition ($kmol\,m^{-3}\,s^{-1}$)
r_{NO}	rate of NO oxidation ($kmol\,m^{-3}\,s^{-1}$)
R_o	rate of HNO_2 oxidation ($kmol\,m^{-3}\,s^{-1}$)
S	cross-sectional area (m^2)
T	temperature of operation (K)
V	volume (m^3)
W_i	weight percent of species i
X_N^*	mole of reactive nitrogen per mole of water
Y_i	moles of species i per mole of inert
$Y_{H_2O}^*$	moles of water per mole of inert
Y_N^*	moles of reactive nitrogen per mole of inert
Y_{NO}^*	moles of divalent nitrogen per mole of inert
$Y_{O_2}^*$	moles of oxygen per mole of inert
z	length (m)

Greek letters

ε	hold-up

Subscripts

G	gas phase
L	liquid phase
n	stage number

Superscripts

b	heterogeneous equilibrium value
i	interface value
o	bulk gas phase

The overall equation for the liquid phase nitrous acid decomposition is given by:

$$3HNO_2(l)\overset{k_d}{\rightleftarrows}HNO_3(l)+2NO(g)+H_2O(l) \tag{1}$$

The kinetics of nitrous acid decomposition has been studied by Abel and Schmid [19,20], and proposed the following rate expression assuming the N_2O_4 hydrolysis as the rate-determining step:

$$R_d = 3.93\times10^{-6}\left(\frac{[HNO_2]^4}{[NO]^2}\right) \tag{2}$$

Komiyama and Inoue [21] related the rate of HNO_2 depletion to the desorption rate of NO, by considering the N_2O_4 hydrolysis as the rate-determining step and presented in the form of following equation:

$$R_d = \frac{3}{2}k_L a[NO] \tag{3}$$

The liquid phase NO concentration is a function of the mass transfer characteristics of the equipment and HNO_2 concentration, which is obtained by combining Eqs. (2) and (3) as:

$$[NO] = 1.26\times K'\times(k_L a)^{-1/3}[HNO_2]^{4/3} \tag{4}$$

Komiyama and Inoue [21] studied the decomposition kinetics by substituting Eq. (4) into Eq. (2) and the overall rate is thus given by:

$$R_d = k_d(k_L a)^{2/3}[HNO_2]^{4/3} \tag{5}$$

The value of k_d is $2.528\times10^{-2}\,m^3\,kmol^{-1}\,s^{-1}$ [21].

The decomposition of nitrous acid in aqueous solution is a complex phenomenon. The reaction (1) is considered to account for the depletion of nitrous acid. Substantial contribution in this field has led to the understanding of the following facts: (i) a critical concentration exists for strong solutions of nitrous acid, above which the rate of decomposition is very rapid and slower for concentrations below the critical value; (ii) the critical concentration is a function of temperature and pressure, and the value increases for low temperature and high pressure [22]; (iii) the reaction (1) is reversible [23], but the reverse reaction proceeds extremely slowly with dilute solutions of nitric acid [24,25]; (iv) the rate of chemical decomposition of the nitrous acid is practically doubled [23] for every 20 °C rise in temperature and (v) when nitric oxide gas is passed into nitric acid a greenish-blue solution is produced which shows the formation of nitrous acid [23] given by the following equation, which is reverse of Eq. (1):

$$2NO(g) + HNO_3(l) + H_2O(l) \rightleftarrows 3HNO_2(l) \tag{6}$$

In case of the absorber in the nitric acid plant, the NOx gases from oxidizer are introduced at the bottom tray and passed in the solution of nitrous and nitric acid on the tray. The calculation of absorption column starts at the bottom of the column. At the bottom plate, nitric acid concentration is high and it progressively decreases along the height of the column. Tereshchenko et al. [26] showed that, at lower temperatures and 50–60 wt.% HNO_3 concentrations, the liquid phase NO oxidation with HNO_3 (Eq. (6)) takes place according to following equation:

$$NO(g)+2HNO_3(l)\overset{k_b}{\rightleftarrows}3NO_2(g)+H_2O(l) \tag{7}$$

The mechanism proposed for liquid phase NO oxidation is as follows:

$$NO + HNO_3 \rightleftarrows HNO_3{\cdot}NO \tag{8}$$

$$HNO_3{\cdot}NO \rightleftarrows HNO_2 + NO_2 \tag{9}$$

The overall reaction can be represented by Eq. (7). The solubility of NO increases substantially, with an increase in the concentration of HNO_3 in the liquid phase and has been attributed to the formation of $[HNO_3{\cdot}NO]$ associated group [27]. They also noted high concentration of $HNO_3{\cdot}NO$ in the solution at HNO_3 concentrations between 55% and 60% HNO_3. The rate of NO oxidation with HNO_3 [26] can be written as:

$$r_{NO,L} = k_b(W_{HNO_3})^2 p_{NO} \tag{10}$$