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A SIMPLIFIED MODEL OF THE ABSORPTIVE-REGENERATIVE PROCESS IN THE TECHNOLOGY OF NITRIC ACID PRODUCTION

UPROSZCZONY MODEL PROCESU ABSORPCYJNO-REGENERACYJNEGO W TECHNOLOGII KWASU AZOTOWEGO

Abstract

This paper presents a method of calculating the physical absorption of low concentrated gaseous nitrogen oxides in liquid nitric acid solutions. This absorption is used in the absorptive-regenerative process (AR process) to reduce the nitrogen oxide content in the exhaust gas from nitric acid plants. This method consists of the calculation of the effectiveness of the absorption in dependence on the liquid/gas ratio, the number of theoretical shelves adequate to the absorption system and other parameters of the process. The paper presents some results of calculations based on, for example, the accepted values of the initial parameters of the process. Conclusions formulated in this paper result from the calculations and concern the rational formation of the AR process as a whole and especially, the stage of regeneration.

Keywords: *nitric acid*, *nitrogen oxides*, *exhaust gas*, *physical absorption*, *regeneration*

Streszczenie

Przedstawiono sposób obliczenia procesu fizycznej absorpcji nisko stężonych tlenków azotu w wodnym roztworze kwasu azotowego, służący w tzw. procesie absorpcyjno-regeneracyjnym („proces AR”) do zmniejszenia strat azotu związanego w gazie wylotowym z instalacji produkcyjnych kwasu azotowego. Sposób polega na obliczeniu wydajności absorpcji w zależności od stosunku gaz/ciecz, liczby półek teoretycznych jakim odpowiada układ absorpcyjny i pozostałych parametrów procesu. Przedstawiono wyniki obliczeń na przykładowo założonych wartościach parametrów wyjściowych. Wnioski wynikają z przedstawionych obliczeń dla racjonalnego ukształtowania procesu AR zwłaszcza dla etapu regeneracji.

Słowa kluczowe: *kwas azotowy*, *tlenki azotu*, *gaz wylotowy*, *absorpcja fizyczna*, *regeneracja*

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1. Introduction

Under the absorptive-regenerative process (AR process) in the technology of nitric acid production, one understands a method of increasing the efficiency of nitric oxide absorption whilst at the same time, reducing losses of bound nitrogen in exhaust gases by subjecting exhaust gases to absorption in a nitric acid solution of an appropriately chosen concentration in which nitric oxides are ‘physically’ absorbed. The solution containing the dissolved nitric oxides then undergoes a change to a regenerative operation consisting of the removal of the dissolved nitrogen oxides (by any method), and at the same time, restoring the ability of the solution to absorb nitrogen oxides. After this, the solution returns to the absorption stage.

For the first time, the essential idea of the AR process was shown in Polish patent Nr 51804 applied in 1963 [1] and two substantially identical papers [2–3]. A wide summary of these papers was published in Brit. Chem. Eng. [4]. The scheme of the AR process idea quoted there is shown on Fig. 1.

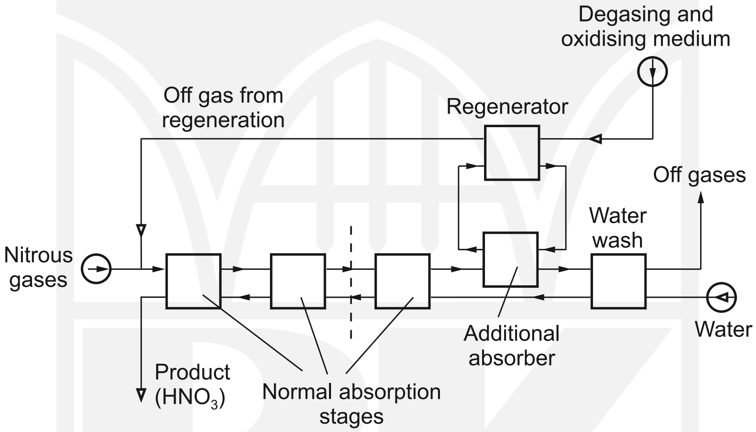

Fig. 1. Idea scheme of the AR process quoted in Brit. Chem. Eng. [18], copied from Polish papers [16, 17]. The inscriptions are replaced by English ones

In the following years, many publications and patent descriptions appeared concerning different varieties of the AR process and methods of its realization [5–21], as well some its theoretical bases [22–27].

This paper presents a simplified calculation method of the absorption stage of the AR process, the results of which seem to throw significant light on the AR process in general. The calculations are preceded by a presentation of the detailed composition of diluted nitrogen oxides standing in chemical equilibrium with a nitric acid water solution of a given concentration.

2. Detailed composition of the gas phase containing dilute nitric oxides standing in chemical equilibrium with the nitric acid solution

In the absorption stage of the AR process, the dilute nitrogen oxides are in contact with the nitric acid solution of a given concentration which is significantly higher than that occurring in the final stages of the traditional absorption process. The cause of this is that, although we call it ‘physical’ absorption, it is a complex process: dilute nitrogen oxides consisting mainly of NO must be oxidized at the cost of nitric acid, the absorbed NO occurs in the liquid phase mainly as NO_2, N_2O_4 or nitrous acid HNO_2.

Fig. 2 is a diagram showing the detailed composition of diluted gaseous nitrogen compounds in equilibrium with a 30% solution of nitric acid as a function of its total content (including HNO_3) in the gas phase. A similar diagram for the composition of diluted gaseous nitrogen compounds in equilibrium with a 55% HNO_3 solution is easy to calculate, but is of no real significance for further reasoning and will not be shown here.

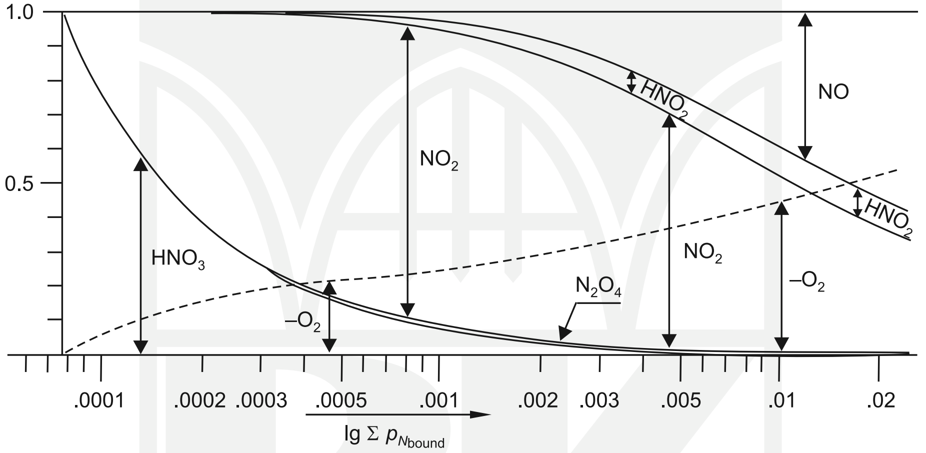

Fig. 2. Shows in a little demonstrative manner the detailed composition of diluted gaseous nitrogen oxides in equilibrium with 30% HNO_3 solution at 30°C. The sum of vapor pressures of all nitrogen compounds (including P_{HNO_3}) are marked in a logarithmic scale on the horizontal axis. Vertical distances between the curves relate to the part of a given compound in fractions of unity. The partial pressure of a given compound is received by multiplying the sum of partial vapor pressures red from the horizontal scale with its share red on the vertical scale. The broken line relates to the ‘oxygen demand’ that is the partial pressure of O_2 which would be needed to oxidize all nitrogen compounds to derivatives of N_2O_5

The following data was accepted for the calculations:

For reactions in the gas phase, for $T = 30°C$ (303 K), the following values of equilibrium constants were accepted:

$2\ NO \leftrightarrow N2O4$ $K_p = 5.325$ [28–29]

$NO + NO_2 \leftrightarrow N_2O_3$ $K_p = 0.394$ [30–32]

$$NO + NO_2 + H_2O \leftrightarrow 2\ HNO_2 \qquad K_p = 1.246 \qquad [33–34]$$

For the equilibrium between the gas phase and the HNO_3 solution at 30°C, the data in Table 1 was accepted.

Table 1

Concentration of the HNO_3 solution, %	30	55
Density, g/cm^3	1.18	1.339
‘Partial equilibrium constant’, $K_2 = (p_{NO}/(p_{NO2})^3$	30200.0	75.9
Vapor pressure of water, bars	0.03173	0.01626
Vapor pressure of HNO_3, bars	0.0000773	0.001104

The value of the K_2 constant is the subject of many publications [33, 35–42]. Considerable disagreements are caused by a difficulty to analytically distinguish between the different nitrogen compounds. A special publication is devoted to this problem [43]. Vapor pressures of H_2O and HNO_3 were taken from partially extrapolated Taylor’s data [44]. A diagram of the gaseous nitrogen oxides in equilibrium with HNO_3 is shown on Fig. 2

3. Calculation of the absorption stage in the AR process

The calculations and their results presented below present some practical aspects of the ‘physical’ absorption of nitrogen oxides having essential significance for the reasonable design of the AR process as a whole. The calculations are based on determining the number of theoretical shelves necessary for gaining the desired effectiveness of the absorption in dependence of other parameters in the process.

The ‘theoretical shelf’ is a definite notion in the field of chemical engineering. It does not mean that in a filled tower to a theoretical shelf suits still one and the same segment of the filling. That depends on many process parameters, such as pressure, velocity of the gas phase, density of the liquid supply and others. Nevertheless, defining the effectiveness of the absorption as a function of the number of the theoretical shelves is sensible and it allows for a better understanding of the specifics of the process.

In the calculations, the following assumptions and dates were accepted:

Instead of converting the absorbed nitric oxides to a given nitrogen compound such as NO_2 or HNO_2, in order to determine their amount in the liquid phase, a substitute parameter was used – the demand for oxygen, expressed in the number of moles of O_2 stoichiometrically needed to oxidize all lower oxidized nitrogen compounds to a derivative of N_2O_5[1]). This parameter will be symbolized here with the letter *S*. A similar parameter for the gas phase, which is the oxygen demand for oxidizing NO and NO_2 to N_2O_5, follows from the following stoichiometric equations:

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[1] In [45] appears a description of a separate determination of N_2O_3, NO_2 and HNO_2 in the liquid phase. The author proposed to the editorial of this journal a publication assuming this method as totally wrong, but the editorial replied evasively.

$$NO + 0.75\ O_2 = NO_{2.5}$$

$$NO_2 + 0.25\ O_2 = NO_{2.5}$$

From which results the oxygen demand in the gas phase symbolized here by the letter *Z*:

$$Z = 0.75\ NO + 0.25\ NO_2 \tag{1}$$

Evidently, the oxygen demands in both phases S and Z must be balanced within each theoretical shelf.

A scheme of balance equations of the absorption system composed of N theoretical shelves is presented in Fig. 3.

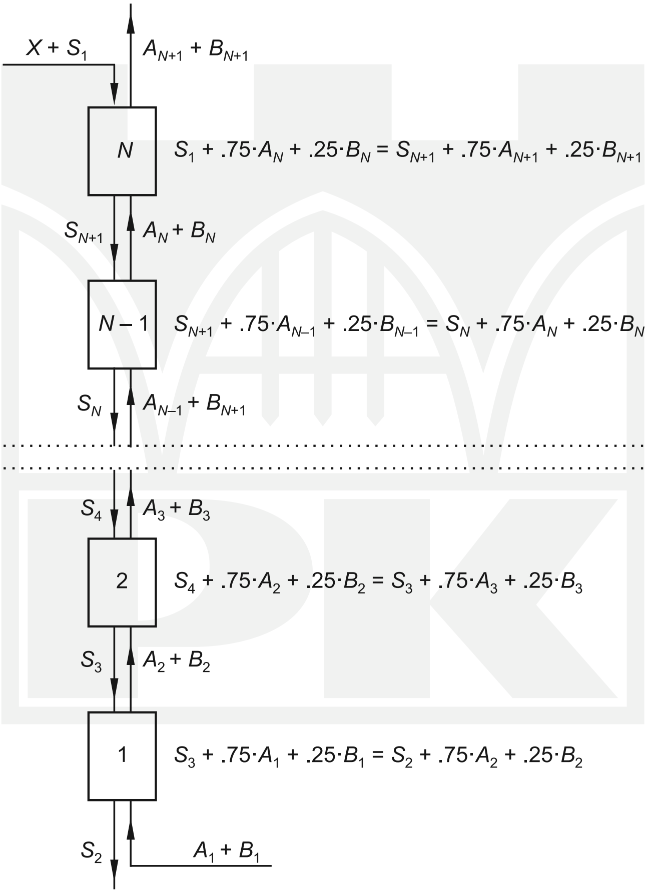

Fig. 3. Balance scheme of an absorption stage composed of N theoretical shelves. A balance equation of the 'oxygen demand' is given for each symbol of the shelf. At phases flowing from one shelf to another, the balance constituent of the phase is given. The letters have following meanings: *A* – the number of NO moles in the gas phase, *B* – the number of NO_2 moles in the gas phase, *S* – the oxygen demand in the liquid phase in one mole of O_2. Further comments and supplements are to be found in the text

In order to be able to use the balance of oxygen demands in both phases for calculating the absorption as a whole, they are complemented with dependencies between the oxygen demands S and Z and the NO and NO_2 contents in the gas phase A and B one rests on the following assumptions and simplifications:

1) Considering the small quantity of exchanged compounds in comparison to the size of both phases, small changes of sizes of both phases resulting from the process are neglected and their sizes remain constant. Due to the intense circulation of the nitric acid solution, its concentration in the quite absorption stage remains constant. For the same reason, the temperature in the quite system also remains constant.
2) The partial pressures p_{NO} and $p_{\mathrm{NO_2}}$ are agreeing with the so called 'partial equilibrium constant' of the reaction:

$$3\,NO_2 + H_2O \leftrightarrow 2HNO_3 + NO$$

$$K_2 = p_{\mathrm{NO}}/(p_{\mathrm{NO_2}})^3 \tag{2}$$

The value of K_2 depends on the concentration of the nitric acid solution with which the gaseous phase is in equilibrium and on the temperature.

Taking into account

$$p_{\mathrm{NO}} = P\cdot(A/L) \text{ and } p_{\mathrm{NO_2}} = P\cdot(\mathrm{B}/L), \tag{3}$$

where P = total pressure and L = number of moles of the gaseous phase, one gets:

$$B = ((A \cdot L^2)/(K_2 \cdot P^2))^{1/3} \tag{4}$$

3) Between the values of S and Z exists a dependence similar to Henry's law

$$S/V_C = f \cdot Z/V_G$$

That is:

$$S = f \cdot Z \cdot (V_C/V_G). \tag{5}$$

where V_C and V_G mean the volumes of the liquid or the gas phases, and f is a proportional coefficient meaning the multiplicity of the gas phase volume to the liquid phase volume by which the oxygen demands in both phases are the same, while

$$V_C = X/d, \tag{6}$$

where X is the amount of the nitric acid solution in one kg falling for L moles of the gas phase while d is its density in g/cm^3.

The volume of the gas phase is expressed by the equation:

$$V_G = (L \cdot T \cdot 22.4)/(273 \cdot P) \tag{7}$$

where L is the number of moles in the gas phase, T is the absolute temperature and P is the total pressure.

Currently, only an approximate value of coefficient f is known. Data from paper [2], as well as an approximate extrapolation of Bode's data [46], and own unpublished fragmentary research, for T = 30°C and 30% acid, the value of f = 30 and for a 55% acid solution, the value of f = 40 was accepted. Specifying coefficient f for different temperatures and acid concentrations requires careful laboratory examination. It is assumed that the values of the coefficient f accepted here are sufficiently close to the real values in order to show the problem of a reasonable formation of the absorption stage in the AR process.

4) As nitrogen compounds in the gas phase, only NO and NO_2 are taken into account. All other compounds, such as HNO_2, N_2O_4 etc., are considered to be composed of the two first named here and were eventually neglected.
5) All gaseous compounds behave as ideal gases.

According to the definition of the theoretical shelf, phases leaving the shelf are in mutual equilibrium. In order to avoid mistakes about the balance on Fig. 3, both phases leaving the shelf are marked with the same number. Taking into account the dependencies resulting from equations (1)–(4), (6) and (7) and putting the values to equation (5), one gets finally:

$$\mathrm{S} = (X \cdot (f \cdot 273 \cdot P)/(d \cdot T \cdot L \cdot 22.4))\cdot(0.75 \cdot A + 0.25\cdot(L^2 \cdot A \cdot K_{2-1} \cdot P^{-2})^{1/3}) \tag{8}$$

Inserting equations (4) and (8) into the set of equations presented on the balance scheme on Fig. 3, the coefficient values, and other values accepted for a given account we get a set of equations, allowing the calculating at accepted of the content of nitrogen oxides in exhaust gases after the absorption stage. $(A_{N+1} + B_{N+1})$ being a function of the number of theoretical shelves corresponding to the absorber system and of the supply of nitric acid solution at a given supply of L moles inlet gas By comparing that with the initial nitrogen oxide content $(A_1 + B_1)$, the efficiency of the absorption in % can be calculated.

The absorption in a system with very numerous or an unlimited number of shelves is calculated separately. In such a situation as shown in Fig. 4, the entering gas is in equilibrium with the liquid phase leaving the absorption system in accordance with equation (5):

$$S_2/V_C = f \cdot (0.75\cdot A_1 + 0.25\cdot B_1)/V_G \tag{9}$$

Inserting the formula for S_2 into the balance equation in Fig. 4:

$$S_2 = X \cdot (0.75\cdot A_1 + 0.25\cdot B_1)\cdot 273 \cdot f \cdot P/(22.4 \cdot d \cdot L \cdot T) \tag{10}$$

Observing the dependence between B_2 and A_2 according to equation (4):

$$B_2 = ((A_2 \cdot L^2)/(K_2 \cdot P^2))^{1/3} \tag{11}$$

and inserting values of terms composed of parameters which are constant in a given series of calculations:

$$G_1 = L^2/(K_2 \cdot P^2) \text{ and } G_2 = (273 \cdot f \cdot P)/(22.4 \cdot d \cdot L \cdot T) \tag{12}$$

Finally, the balance equation for an absorbing system with an unlimited number of theoretical shelves is as follows:

$$S_1 + 0.75A_1 + 0.75B_1 = X \cdot (0.75A_1 + B_1) \cdot G_2 + 0.25\cdot(A_2 \cdot G_1)^{1/3} \tag{13}$$

In equation (13), the only unknowns (A_2, B_2) will be calculated according to A_2, indentified with equation (11). From these two items of data, one gets the content of nitrogen oxides in the gas leaving the absorption stage, whilst at the same time, the effectiveness of the process as a function of X. This is the highest permissible effectiveness which can be attained by a given liquid/gas ratio improving the absorption system.

In the calculations below, the following initial parameters and some combinations of them have been accepted:

Pressure: 1.013 respectively 7.093 bars.

Temperature: 30°C (303 K), the same in all cases.

The initial content of nitrogen oxides in the entering gas: 10 respectively 2 moles $NO + NO_2$ per 1000 moles of gas (1% respectively 0.2% vol.). In all cases it is assumed that the nitrogen oxides at the entry are exclusively in the form of NO. This is of no significance because the balance equations (see Fig. 3) are not related to the content of nitrogen oxides but to the 'oxygen demand'. The calculation with an assumed 3% NO_2 at the entry would give the same result as in the case of an assumed 1% NO. The concentration of the circulating solution of nitric acid is assumed to be constant in the whole system: 30% or 55% by weight.

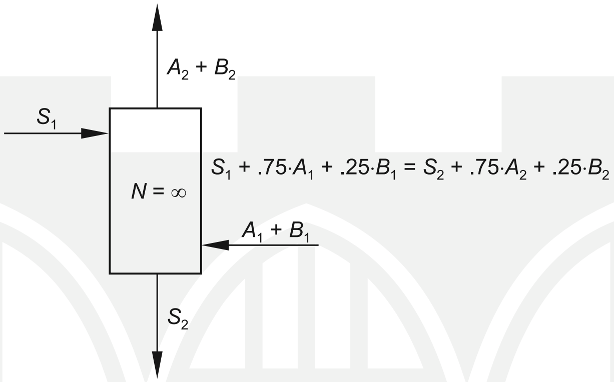

Fig. 4. Scheme of an absorption system with an unlimited number of theoretical shelves. Further explanations are presented in the text

The results of the calculations are presented below in graphic form. For better transparency and comparability, the same quantity of gas was assumed for all calculations: 1000 moles ($L = 1000$). Figs. 5–7 show concentrations of nitrogen oxides in moles $NO + NO_2$ per 1000 moles of gas leaving the absorption stage as a function of the liquid/gas ratio (X kg HNO_3 solution per 1000 moles of gas) and the number of theoretical shelves presented by the absorption system. For all three graphics, the common initial conditions are: the total pressure $P = 1.013$ bars; the inflowing gas contains nitric oxides only in form of NO ($B_1 = 0$); the HNO_3 solution given to the absorber contains no lower oxidized nitrogen compounds ($S_1 = 0$). Graphics illustrating similar dependencies under the pressure of 7.091 bars are presented in Figs. 8–12. For place saving reasons, in the graphic subscriptions the initial conditions are marked by following symbols: t: °C, P: bars; A: moles NO; B: moles NO_2; S: oxygen demand of the liquid phase in moles O_2; M: concentration of the circulating nitric acid solution in weight %% of HNO_3. Axis X stands for the liquid/gas ratio in kg HNO_3 per 1000 moles gas, axis Y stands for the number of $NO + NO_2$ moles in 1000 moles of gas leaving the absorption stage.

A review of the graphs in Figs. 5–7 justifies the following remarks and conclusions:

- The runs of curves presenting concentrations of nitrogen oxides in gases leaving the absorption stage are similar to each other in all three cases. The runs of curves for a given number of shelves (up to five), the curves for an unlimited number of shelves

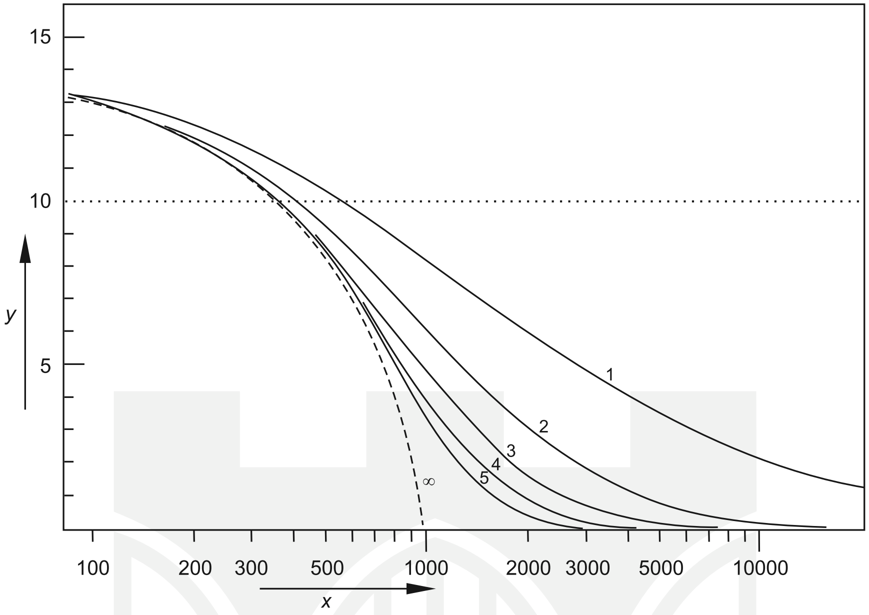

Fig. 5. Nitric oxide concentrations in gas leaving the absorption stage. Initial conditions: T = 30°C (303 K); P = 1.013 bar; A_1 = 10; B_1 = 0; M = 30%; S_1 = 0. Continuous lines present the results for absorbing systems appropriating successively to 1, 2, 3, 4 and 5 theoretical shelves. The broken line corresponds to an absorbing system with an unlimited number of theoretical shelves (the entering gas is in equilibrium with the nitric acid solution leaving the absorption stage). The dotted horizontal line shows the level of the initial content of NO + NO_2

(broken lines) and their mutual positions seem to be logical and convincing. Curves for shelve numbers greater than five will increasingly approach the curve for an unlimited number of shelves.

- In all three presented cases, the content of nitrogen oxides in gas leaving the absorption stage as a function of the liquid/gas ratio are passing fluently from the area in which the nitrogen oxides content is higher than initial to the area in which it is lower than initial. The cause of this is simple: in all presented cases, only NO in the entering gas phase is assumed. In the efflux gas from the traditional nitric acid plants, there is normally an excess of NO in comparison to NO_2. At low liquid/gas ratios, the amount of HNO_3 is sufficient to oxidize a large proportion of the NO to NO_2, but is too little to absorb it. The increase of nitrogen oxide content at low liquid/gas ratios is higher when using a 55% nitric acid solution as opposed to when using one of 30%.
- From the presented examples, it follows that having a sufficiently effective absorption system (corresponding to an adequate number of theoretical shelves) and having at one's disposal a nitric acid solution with no oxygen demand, it is possible to remove nitrogen oxides from the gas phase to any low level. The theoretical border is the vapor pressure of HNO_3, but this ingredient is easy to remove with the final water wash (see Fig. 1).

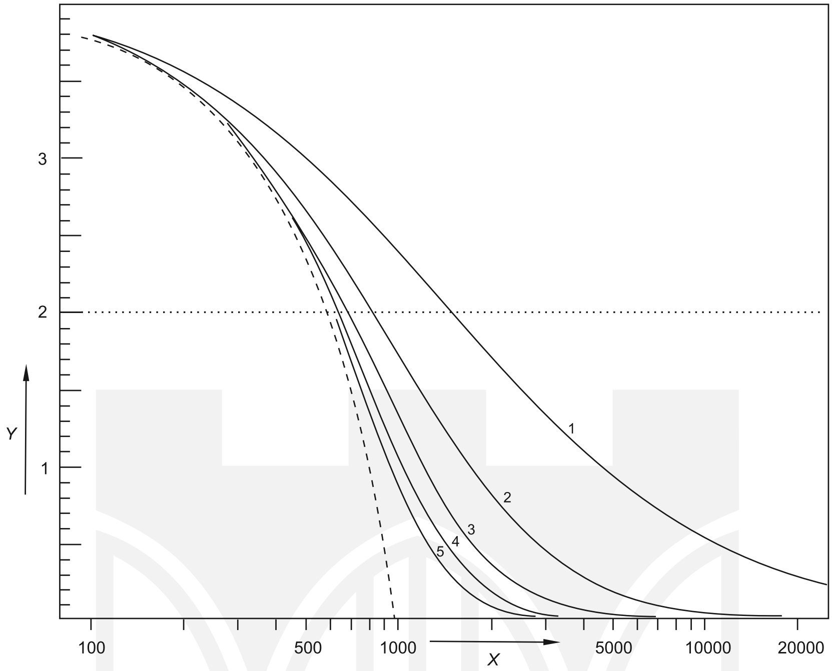

Fig. 6. Nitric oxide concentrations in gas leaving the absorption stage. Initial conditions: $A_1 = 2$. All other parameters are the same as in Fig. 5. The level of 0.2% vol. of nitric oxides in the tail gas is not typical for a non-pressure nitric acid process. Such an initial condition was only chosen for the purpose of comparability. The high similarity with the graph in Fig. 5 is as a result of the fivefold extended scale of the *Y*-axis

The effectiveness of the absorption stage highly depends on pressure. Fig. 9 shows the comparison of two cases differing only in pressure. From this graph, it could be read that for removing 90% nitrogen oxides from the gas containing an initial 0.2% NO in an absorbing system, adequate to five theoretical shelves under the atmospheric pressure 1600 kg of 30% nitric acid solution is needed, whereas under the pressure of 7.09 bars for the same result only 230 kg of this solution per 1000 moles of gas are sufficient.

What is interesting about the absorption systems which are adequate for several theoretical shelves is the shape of the gas composition after each shelf in a sequence, depending on the liquid/gas ratio. In order to present this, two extreme cases were chosen – the absorption of gas with 1% NO under atmospheric pressure using a 30% solution of nitric acid compared with the absorption of gas with a content of 0.2% NO under higher pressure (7.093 bars) using a 55% solution of nitric acid. Both cases are shown in Fig. 9 and 10.

Neither graph is fully comparable because all three values of X shown in Fig. 9 are lying in the 'effective' area. At the lower liquid/gas ratios, which are not shown here, appears the phenomenon of increasing the content of nitrogen oxides and not its lowering as a result of double function of nitric acid as an absorbing and oxidizing agent. A different situation is shown on Fig. 10 where the range of *X* values is wider and the increase in the nitrogen oxide

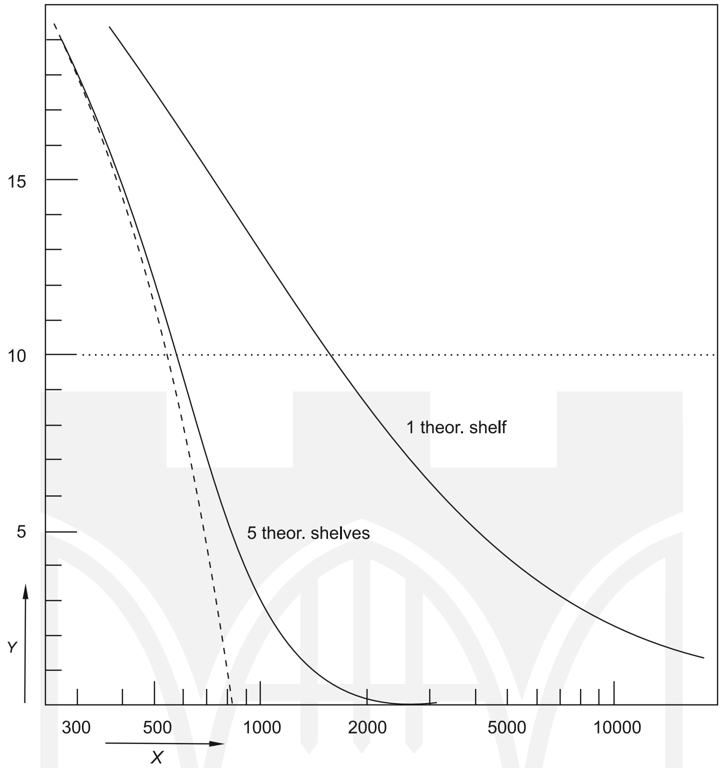

Fig. 7. Concentration of nitric oxides in gas leaving the absorption stage. Initial conditions: P = 1.013 bar; A_1 = 10; M = 55% HNO_3. Curves for two, three and four theoretical shelves are not shown

content at lower X values is quite distinct. The case of X = 200 on Fig.10 shows that even if the absorption after five theoretical shelves is effective (about 90%), a significant increase in the nitrogen oxide content in the gas phase can appear after the first shelve. It is also remarkable that if in the case presented in Fig. 10 one assumed 0.6% NO_2 instead of 0.2% NO ($A_1 = 0, B_1 = 6$) in the entering gas, the image would remain the same – only the horizontal line of initial NO_X would lie on level 6 instead of 2. A similar image would appear on Fig. 9. The reason for this is that balancing the oxygen demand by one mole of NO counts as much as balancing the oxygen demand by three moles of NO_2, please check that I've not accidentally changed the intended meaning whereas as a loss of bound nitrogen, both oxides count equally. Fig 11 presents a comparison of the absorption of nitrogen oxides in two nitric acid solutions of different concentrations under identical conditions.

On the graph in Fig. 11, for the growing liquid/gas ratio, both pairs of curves are passing from the area of increasing to the area of decreasing content of nitrogen oxides in the gas phase. The increase of nitrogen oxide content is distinctly bigger in the case of 55% HNO_3 than in the case of the 30% solution; passing to the decreasing area demands a twice higher liquid/gas ratio. Both curves are crossing. By further increase of X, the superiority

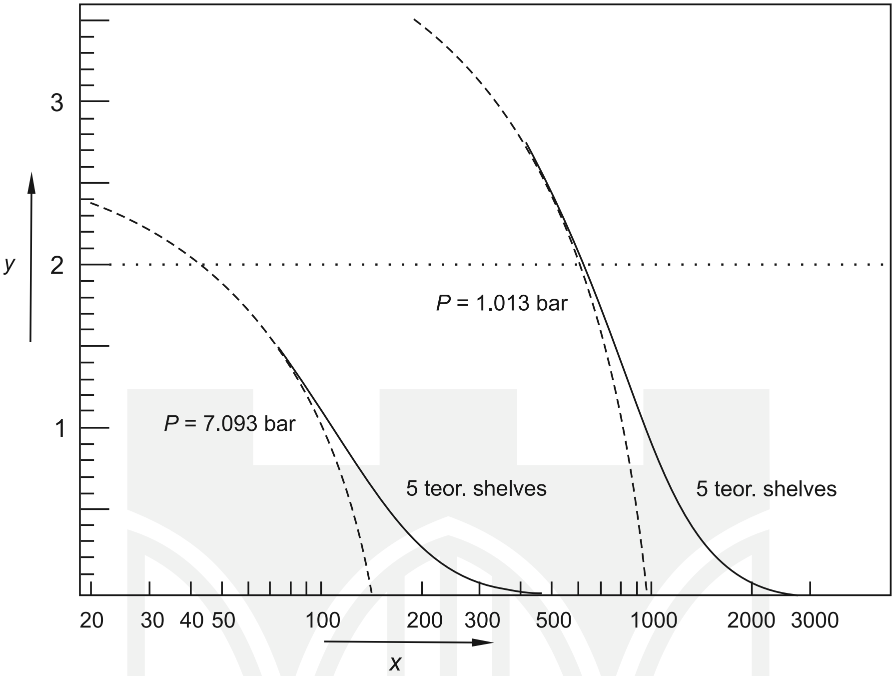

Fig. 8. Comparison of nitric oxide concentration in gas leaving the absorption stage under atmospheric pressure and under higher pressures. Common conditions: T = 303 K; $A_1 = 2$; $B_1 = 0$; $S_1 = 0$; M = 30%. The absorption system is adequate for five theoretical shelves (continuous lines), broken lines correspond to an unlimited number of theoretical shelves. The right pair of curves relates to the atmospheric pressure, the left pair relates to a pressure of 7.093 bars

of the 55% solution becomes higher and the co compensation of these superiority demands an about 30% bigger supply of the weaker solution.

In the examples given above, it was always assumed that the nitric acid solution put to absorption is free from any lower oxidized nitrogen compounds ($S_1 = 0$), which means, it is ideally. Such an assumption is not fully realistic. A non-fully accomplished regeneration must be taken into account. Fig. 12. shows a comparison of the absorption of nitrogen oxides by using both a fully and a non-fully regenerated HNO_3 solution.

The assumed oxygen demand of 0.0005 moles O_2 per kg of solution corresponds to the traditionally calculated manner 0.109 g NO_2 per litre. At a circulation of X = 400 kg per 1000 moles of gas, that would correspond to a regeneration degree of 90%. Increasing the supply of the nitric acid solution showing a given oxygen demand one cannot achieve a total removing of nitrogen oxides from the gas phase. In the example shown above, assuming a stable value of S_1, the content of NO_X would at increasing circulation establish on ca. 0.015% vol., which regarding the industrial conditions, could be recognized as a very good achievement. However, it is unknown how an increasing circulation would change the value of S_1 – no certain assumptions can be made regarding this.

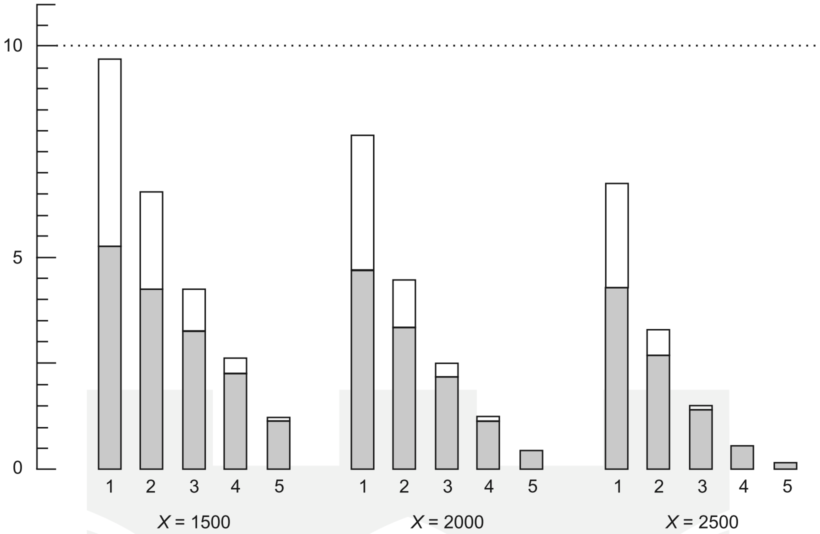

Fig. 9. Nitrogen oxide content after each shelf in an absorption system adequate to five theoretical shelves. Initial conditions: T = 303 K; P = 1.013 bars; M = 30%; A_1=10 (1% vol.); B_1 = 0; S_1 = 0. The height of the numbered bars is the measure of the nitrogen oxide content after each shelf (shelf numbers are given below the bars). The dotted parts of piles stand for NO_2, no dotted parts stand for NO. The values of X indicate kg of nitric acid solution per 1000 moles of gas

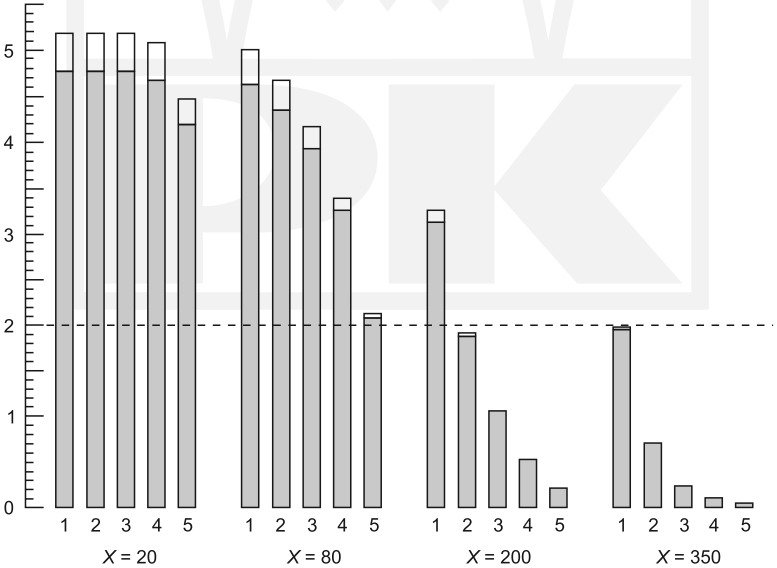

Fig. 10. Nitrogen oxide content after each shelf in an absorption system adequate to five theoretical shelves. Initial conditions: T = 303 K; P = 7.093 bars; M = 55%; A_1 = 2 (0.2% vol.); B_1 = 0, S_1 = 0. For further explanation, see Fig. 9

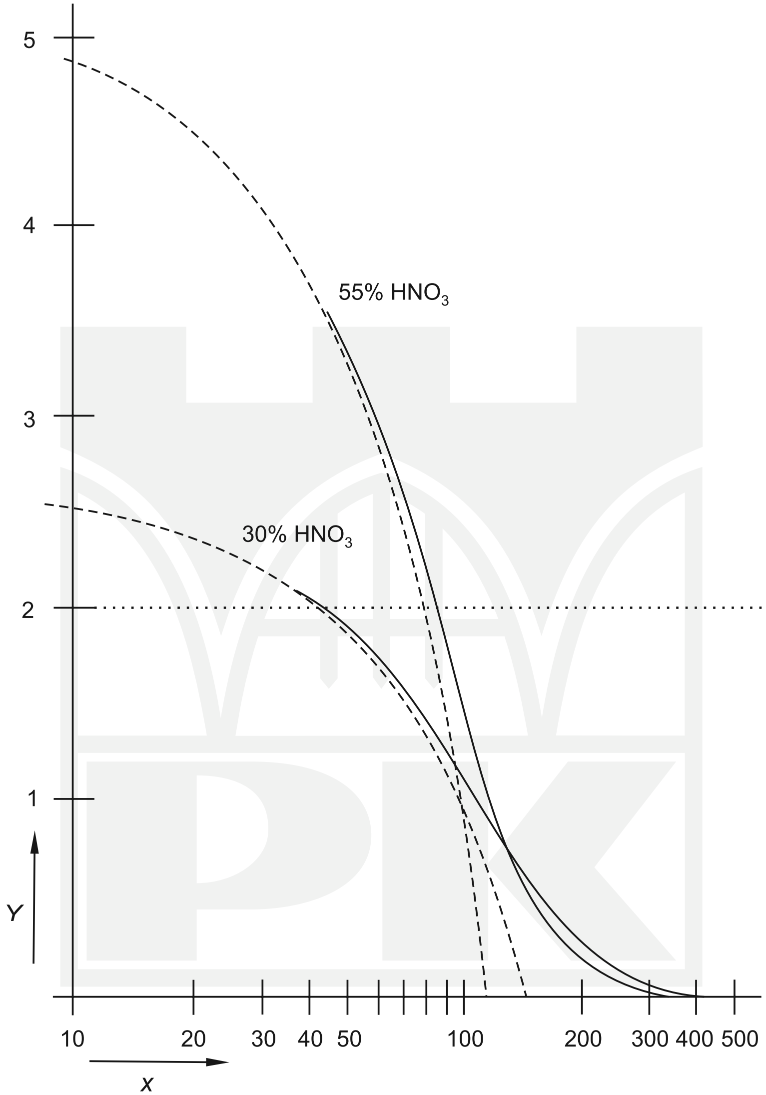

Fig. 11. Comparison of nitrogen oxide content in gases after absorption in nitric acid solutions of two different concentrations – 30% and 55%. Common conditions: $T = 303$ K (30°C); $P = 7.093$ bars; $A_1 = 2$; $B_1 = 0$; $S_1 = 0$. Both continuous lines relate to nitric oxide content after absorption in a system adequate to five theoretical shelves; broken lines relate to a system with an unlimited number of shelves

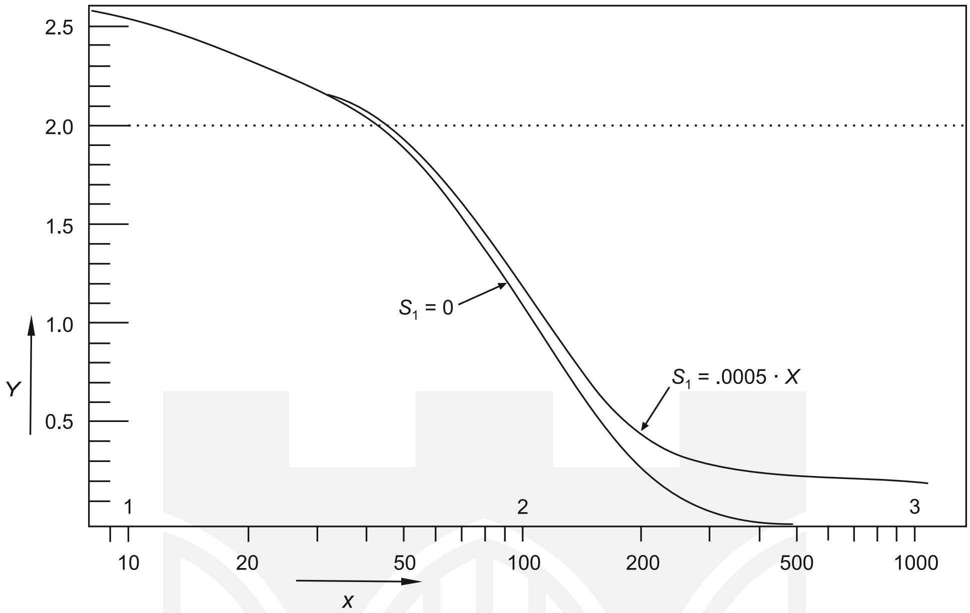

Fig. 12. Comparison of nitrogen oxide content in the gas phase after absorption in a 30% HNO_3 solution free of dissolved nitrogen oxides (S_1 = 0) with nitrogen oxide content in the gas phase after absorption in a solution showing an oxygen demand of 0.0005 moles of O_2 per kg of solution (S_1 = 0.0005 · *X*). Common conditions: $T = 30°C$; $P = 7.093$ bars; $A_1 = 2$; $B_1 = 0$; $M = 30\%$. All curves were calculated for a system adequate to five theoretical shelves

4. Conclusions

The results of calculating the absorption stage in the AR process presented above provide in total, a coherent and logical picture. Having rationally constructed absorption equipment at one's disposal enables the application of a sufficient high liquid/gas ratio. It is in principle, possible to reduce the nitrogen oxides from the outlet gas to any low level. However, the essential condition for this is as follows: the nitric acid added at the absorption stage cannot contain dissolved nitrogen oxides (the oxygen demand must be S_1 = 0). The effectiveness of the AR process as a whole thus mainly depends on the effectiveness of the regeneration of the HNO_3 solution. An additional conclusion follows from this: absorption can be effectively made at a fairly broad range of concentrations of the nitric acid solution. Thus, the choice of this concentration should be made regardless of the optimization of the absorption, but with regard to optimizing its regeneration.

5. Remarks

The regeneration of the nitric acid solution containing absorbed nitrogen oxides consists of their removal and in this way, restoring the initial ability of the solution with regard to absorbing nitrogen oxides. The stage of absorption is relatively transparent. It consists of two elements: of the absorption as such, and of the NO/NO_2 ratio dictated by the concentration of the nitric acid solution contacting with the gas phase. In comparison to that, the stage of regeneration is not so obvious. Methods of regeneration can be quite different. Under these methods two main categories can be distinguished:

1. ‘Physical’ removal of the dissolved nitrogen oxides using their significant fugitiveness in comparison to two other main components of the solution (H_2O and HNO_3) and
2. Oxidation of the absorbed nitrogen oxides, for instance according to summaric equations:

$$4NO_2 + O_2 + 2H_2O = 4HNO_3 \qquad \text{or} \qquad 2HNO_2 + O_2 = 2\ HNO_3$$

Both categories of methods, if effective and tolerating expenses related to it, are useful. Different combinations of both main directions are possible too. Physical regeneration can consist of ‘boiling away’ or ‘blowing through’ with gas or of combining both measures. The ‘boiling away’ approach demands a significant energy expense and extended heat exchangers, which increases costs. For ‘blowing through’ only the so called ‘second air’ can be used, which accounts for not more than 30% of the total gas volume and is needed for bleaching the product, therefore, its use demands a significant raising of temperature. An interesting (but, in the author’s opinion, a not very attractive) example is the ‘Bolme’ process [14–15]. In that process, outlet gas nitrogen oxides are absorbed in nitric acid of the same concentration as that of the product which circulates between absorption and regeneration by ‘blowing through’ at high temperature. The circulation is fed by the raw product from the rich end of the traditional absorption line, an appropriate part of the regenerated solution is led off as ready product.

The second direction, which is regeneration by oxidization, is more diversified. Air as an oxidant is rather unuseful. A possible method for its use is shown in a Polish patent [1]. It is a combination of oxidization and ‘blowing through’, but its applicability is limited to multi-tower, non-pressure systems. Oxygen is more useful - its consumption does not significantly exceed the stoichiometric one, but a near complete removal of the nitrogen oxides from the solution (decreasing its oxygen demand to almost zero) would need sizable, thus expensive regenerators.

For years, much attention was paid to hydrogen peroxide H_2O_2 as a strong oxidizer of nitrogen oxides in the liquid phase [6, 11, 20, 21] – it can be used as an exclusive or as a supplementary oxidizer. Hydrogen peroxide is certainly very effective as an oxidizer, as a low fugitive substance can be introduced directly to the solution guided to the absorption. However, there is no information about its industrial realizations.

In last years interest is directed to ozone O_3 as an intensifying factor of the process of converting nitrogen oxides into nitric acid. Intensive research works on its application in nitric acid technology are led in Polish industrial and high school research institutions. The papers concerning these works [47–53] are distinguished by a high theoretical level, but an image of technological realization of their results is not shown.

The author of this thesis dares to express his conviction that the introduction of ozone into the technology of nitric acid production will bring about significant technical and economical, as well as ecological, progress.

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