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Treatment of Nitrous Off-Gas from Dissolution of Sludges

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Abstract: Several configurations have been reviewed for the NO_x removal of dissolver off-gas. A predesign has been performed and operating conditions have been optimized. Simple absorption columns seems to be sufficient.

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TREATMENT OF NITROUS OFF-GAS FROM DISSOLUTION OF SLUDGES

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NOx treatment
HANFORD

MP/IL

TECHNICAL NOTE

TREATMENT OF NITROUS OFF-GAS FROM DISSOLUTION OF SLUDGES

Rev.	Written	Checked	Approved
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TABLE OF CONTENTS

1.	PURPOSE.....	5
2.	BASIC DATA.....	6
2.1.	CHARACTERISTICS OF THE FLUX TO BE TREATED.....	6
2.2.	DISPOSAL CONSTRAINTS.....	7
3.	CHOICE OF A NOX TREATMENT PROCESS	8
4.	GENERAL METHODOLOGY FOR THE PRELIMINARY DESIGN OF THE NOX ABSORPTION UNIT.....	10
4.1.	HYDRAULIC PRELIMINARY DESIGN.....	10
4.2.	OPTIMISATION OF EFFICIENCY.....	10
5.	DESCRIPTION OF THE HYDRAULIC PRELIMINARY DESIGN METHOD AND OF THE NOX ABSORPTION COLUMN MODEL.....	11
5.1.	METHOD FOR HYDRAULIC PRELIMINARY DESIGN [1]	11
5.2.	DESCRIPTION OF THE NOX ABSORPTION COLUMN MODEL	12
5.2.1	Modeled phenomena.....	12
5.2.2.	Used software	13
5.2.3.	Qualification of the model	14
6.	PRELIMINARY DESIGN OF THE NOX ABSORPTION UNIT : RESULTS	15
6.1.	HYDRAULIC PRELIMINARY DESIGN.....	15
6.1.1.	Oxygen brought by air.....	15

6.1.2.	Oxygen brought by enriched air	15
6.2.	DEFINITION OF STUDIED CONFIGURATIONS	16
6.2.1.	Oxygen brought by air	16
6.2.1.1.	Configuration ① : one water column.....	16
6.2.1.2.	Configuration ② : two water columns.....	16
6.2.1.3.	Configuration ③ : one water column and one caustic soda column.....	17
6.2.2.	Oxygen brought by enriched air (Configuration ④).....	18
6.3.	OPTIMISATION OF EACH CONFIGURATION : OPERATING CONDITIONS AND RESULTING PERFORMANCE	18
6.3.1.	Configuration ①	18
6.3.2.	Configuration ②	20
6.3.3.	Configuration ③	21
6.3.4.	Configuration ④	23
6.4.	SUMMARY	25
7.	GENERAL CONCLUSION : RECOMMENDATIONS	27
	REFERENCES	29
	APPENDIX 1 : INFLUENCE OF PACKING HEIGHT ON NOX DISCHARGE FOR CONFIGURATION ①	30
	APPENDIX 2 : INFLUENCE OF PACKING HEIGHT ON NOX DISCHARGE FOR CONFIGURATION ④	31

1. PURPOSE

NHC is in charge of the treatment of sludges containing mainly uranium dioxide and metallic uranium.

The process is based on the following processing steps :

- a dissolution step to oxidise the pyrophoric materials and to dissolve radionuclides (uranium, plutonium, americium and fission products),
- a solid/liquid separation to get rid of the insoluble solids (to be disposed at ERDF),
- an adjustment of the acid liquor with neutronic poisons,
- a neutralization of the acid liquor with caustic soda.

The dissolution step generates a flow of nitrous fumes which was evaluated in a previous study [7].

This NOx flow has to be treated.

The purpose of this report is to study the treatment process of the nitrous vapours and to perform a preliminary design.

Several treatment configurations are studied and the most effective process option with respect to the authorised level of discharge into atmosphere is discussed.

As a conclusion, recommendations concerning the unit preliminary design are given.

2. BASIC DATA

2.1. CHARACTERISTICS OF THE FLUX TO BE TREATED

The maximum NOx flowrate generated by dissolution in the best operating conditions is 3 Nm³/h (NO and NO₂) [7].

At the dissolver outlet, the nitrous vapours flow through a condenser before feeding the NOx removal system.

The temperature of the flux at the outlet of the condenser is considered to be 40°C.

In order to perform the preliminary design of the treatment unit, all the nitrous species NOx are supposed to be in the form of NO (penalizing condition). Moreover recombination in the upstream condenser and in the piping is not considered.

The species CO₂ (from the air) is not considered (in case of absorption by caustic soda, the risk of precipitation will be examined). The presence of H₂O in the gas is neglected (a major fraction of the H₂O has been condensed in the condenser).

The amount of oxygen which has to be added in the dissolver head to the NOx flux is calculated by considering an excess of 50% as compared to the stoichiometric quantity (3/4 mole O₂ for 1 mole NO for absorption in water : see details of chemical reactions in § 5.2.1.). This assumption leads to a flowrate of 3.375 Nm³/h O₂.

Oxygen is added by the way of air or of oxygen-enriched air.

As a result, the composition of the flux considered for the preliminary design is the following one :

- in the case of air :

total flowrate :	19.1 Nm ³ /h
NO :	15.7 % (157300 vpm)
O ₂ :	17.7 %
N ₂ :	66.6 %

So the air flowrate to be added in the dissolver head is 16.1 Nm³/h.

Some part of this flowrate will be provided by leakages : indeed the dissolver and its annexes (for instance the powder feeding system) cannot be perfectly tight.

- in the case of oxygen-enriched air (40 % vol. O₂ in air) :
 - total flowrate : 11.4 Nm³/h
 - NO : 26.2 % (262000 vpm)
 - O₂ : 29.5 %
 - N₂ : 44.3 %

So the enriched-air flowrate to be added in the dissolver head is 8.4 Nm³/h.
As in case of air a part of this flowrate is provided by leakages.

The treatment unit operates at atmospheric pressure.

2.2. DISPOSAL CONSTRAINTS

The limit for NO_x release on the Hanford site is 40 t/year (about 10 t/year for the dissolution unit and the remaining for the vitrification units).

Moreover, if the NO_x emissions are higher than 2 lbs/h or 17000 lbs/year (about 1 kg/h or 8500 kg/year), a dispersion modeling analysis has to be done to calculate the concentration at the site boundary (site boundary is defined as any area that does not have restricted or controlled public access). This calculation needs to show that the concentration at the site boundary is less than the Acceptable Source Impact Level (ASIL) for nitric oxide (which is 100 micrograms/m³ averaged over 24 hours), otherwise the design has to be modified.

Finally, it will be necessary later on to prove that the NO_x treatment system has been chosen using the Best Available Technology (BAT) process. This selection process should include the following steps :

- review of all the possible alternatives for the NO_x treatment,
- estimation of the cost for the various options,
- choice of the technology which represents the best compromise between costs and technical performances (breakpoint on a curve showing the variations of cost with respect to NO_x released).

3. CHOICE OF A NOX TREATMENT PROCESS

NOx treatment can be achieved through several technologies : the main ones are described hereafter.

The nitrous oxides can be reduced using ammonia or urea by the SCR (Selective Catalytic Reduction) or the SNCR (Selective Non Catalytic Reduction) methods. They can also be removed through absorption processes.

Absorption processes are less efficient as they only allow to reduce NOx concentration to a few thousands vpm (when operating at atmospheric pressure). Reduction technologies as SCR or SNCR allow to obtain lower levels of NOx discharge.

However these reduction technologies present some drawbacks :

- they use ammoniac or urea,
- they need relatively high temperature (~ 400°C for SCR and ~ 900°C for SNCR), so they consume energy and need heat exchangers.

N.B : They are well suited to hot offgas from an incinerator for instance, but not suited to "cold" off-gas from a dissolver.

- SCR process generates a solid waste, resulting from irreversible poisoning of (costly) catalyst.

These characteristics lead to a relatively expensive process (investment + operation) as compared to the absorption process.

Moreover, in the studied case, the NOx flowrate from dissolution is not very important (a few Nm³/h). Therefore a few thousands vpm NOx at the outlet of absorption columns lead in fact to a low NOx flowrate which can be compatible with the authorized annual discharge. It also allows to recover nitric acid which can be reused in the dissolution process.

So an absorption process seems to be a good choice to treat NOx from the dissolver. Therefore, this process is first examined in this study.

Then, if efficiency is not high enough, additional or alternative technology will be recommended.

It is worth noticing that the great experience of SGN about NOx absorption will lead to an optimised efficiency of absorption columns.

Indeed several NOx recovery units of reprocessing plants (UP1 at Marcoule, UP2 and UP3 at La Hague, Tokai-Mura and Rokkasho-Mura in Japan) have been designed by SGN. These units process off-gases from various origins :

- dissolver off-gas,
- off-gas of high active liquid waste concentration,
- vitrification off-gas,
- ...

SGN has also studied columns of the uranium refining plant of Comurhex (the French company specialised in conversion of uranium ore to natural UF_6). The optimisation of these columns have led to a drastic reduction of NOx emissions.

Besides the model used to design columns has been qualified by comparison with experimental results (see § 5.2.3.).

It is worth noticing that the final choice of a technology has to be performed through an analysis based on the "Best available technology" approach. The first approach developed in this paragraph must be considered as leading to a preliminary choice.

4. GENERAL METHODOLOGY FOR THE PRELIMINARY DESIGN OF THE NOX ABSORPTION UNIT

The preliminary design of the absorption unit includes the determination of the number of necessary columns, of optimised operating conditions and of column(s) predesign for several configurations. According to the obtained results , recommendations concerning the most effective option are made.

No oversizing factor is taken into account.

4.1. HYDRAULIC PRELIMINARY DESIGN

On the basis of the characteristics of the gas that feeds columns, the hydraulic predesign leads to a first estimation of :

- the packing characteristics,
- the column diameter,
- the range of necessary internal liquid flowrate.

These parameters are calculated so as to fit the following main criteria [1] :

- an acceptable gas velocity with respect to flooding and residence time,
- an acceptable wetting rate on packing.

4.2. OPTIMISATION OF EFFICIENCY

In a second time, a sensitivity study (using the SGN model) allows to optimise the efficiency of columns in order to minimise the NOx discharge into the atmosphere. Results are checked with respect to the hydraulic criteria.

This step leads to the determination of the number of necessary columns (using water and/or caustic soda) and of the optimised operating conditions.

In particular, the use of oxygen-enriched air is examined as it is favorable to NOx recombination.

Several configurations are studied and then recommendations are given.

N.B : Columns operating at pressure higher than atmospheric pressure (favorable to NOx recombination) are not studied as this operating condition is not easily compatible with safety requirements relative to this unit.

5. DESCRIPTION OF THE HYDRAULIC PRELIMINARY DESIGN METHOD AND OF THE NOX ABSORPTION COLUMN MODEL

5.1. METHOD FOR HYDRAULIC PRELIMINARY DESIGN [1]

Hydraulic predesign is carried out from the flooding rate.

Gas velocity :

The flooding velocity is estimated using the correlation of Lobo, which requires :

- the packing characteristics (specific surface, free volume, packing factor, nominal dimension),
- the liquid and gas flowrates,
- the liquid and gas densities and liquid viscosity.

The gas velocity is estimated as a percentage of the flooding velocity. Optimum absorption efficiency is known to be about 70% of flooding (for Pall rings). However, since NO oxidation requires an important residence time, it is necessary to choose a gas velocity which represents a compromise between efficiency and residence time. This compromise is chosen according to the know-how of SGN.

The choice of a gas velocity leads to the calculation of the column diameter.

Packing dimension :

Pall rings (stainless steel) are chosen (they are the most commonly used random packing in industry).

In order to avoid liquid flowing on the column wall, the nominal dimension of packing must be lower than a limit value depending on the column diameter.

The ratio $\frac{\text{column diameter}}{\text{packing dimension}}$ is recommended to be greater than 10 for the Pall rings.

Wetting rate :

The wetting rate is defined by the following relation :

$$M = \frac{Q_L}{Ac.a}$$

With :

M	: wetting rate	(m ³ /s.m)
Ac	: column cross-section	(m ²)
a	: packing specific surface	(m ² /m ³)
Q _L	: liquid volumetric flowrate	(m ³ /s)

The wetting rate must be high enough to allow a good wetting of the packing but must not be too important to avoid drowning of surfaces.

The condition (relative to an absorption column) is the following :

$$2,78.10^{-3} < M < 1,95.10^{-4} \text{ m}^3/\text{s.m}$$

This criterion leads to the estimation of the liquid volumetric flowrate.

The different criteria are reached by varying the packing characteristics, the internal liquid flowrate (recycling) and the column diameter.

5.2. DESCRIPTION OF THE NOX ABSORPTION COLUMN MODEL

5.2.1 Modeled phenomena

A rigorous steady-state model (proprietary) is used.

This model accounts for the interphase liquid/vapour mass and heat transfer processes, the equilibrium and kinetically controlled chemical reactions, and the liquid/vapour equilibrium at the interface [2].

Mass and heat transfer

The model uses correlations of Onda (adapted to random packing columns) to calculate mass transfer coefficients for the vapour and the liquid phase, and interfacial areas. These correlations, given in document [3], have been corrected according to the experimental results obtained during the model qualification.

The heat transfer coefficients are calculated using the Chilton-Colburn analogy [3].

Chemical reactions

The chemical mechanism taken into account for absorption in water is the following one :

Gas phase

Liquid phase

The laws describing the kinetics of reactions $\textcircled{1}$ and $\textcircled{4}$ and the equilibria of reactions $\textcircled{2}$ and $\textcircled{3}$ are given in document [2].

On the other hand, in the case of absorption in caustic soda, nitrous and nitric acids are neutralised. So reaction $\textcircled{4}$ doesn't take place.

Liquid/vapour equilibrium

Equilibrium between liquid and vapour phases is given by the equality of the fugacities in the two phases.

The vapour phase fugacity is given by the equation of state of SRK (Soave Redlich Kwong) [4].

The liquid phase fugacity is given by the activity coefficient model Electrolytes NRTL (Non Random Two Liquids), which takes into account the non-ideality of ionic solutions.

The liquid/vapour equilibrium for non-condensable species (NO , NO_2 , N_2 and O_2) is represented by a Henry's law.

5.2.2. Used software

The model is developed using ASPEN Plus V 9.3 software (RATEFRAC module).

5.2.3. Qualification of the model

The NOx column model has been qualified by comparison to experimental values [5].

The conditions of validation were the following ones :

- 2 columns in series (1st : water, 2nd : caustic soda),
- 5 to 6 kmol/h NOx for 800 Nm³/h gas (140000 to 168000 vpm),
- bottom temperature : 24 to 48°C,
- bottom acidity : 2 to 4 N HNO₃ (1st column) - pH $\approx$ 10 (2nd column),
- Pall rings (stainless steel).

The results relative to efficiency obtained with the model are compared with the experimental values, for 3 experiments, in the following table :

	Global efficiency	
	Experience	Simulation
Test 1	98.5	97.5
Test 2	98	96.5
Test 3	98	95

These comparisons show that the model is in good agreement with the experience for the conditions of validation.

Calculated global efficiency is slightly underestimated.

6. PRELIMINARY DESIGN OF THE NOX ABSORPTION UNIT : RESULTS

6.1. HYDRAULIC PRELIMINARY DESIGN

6.1.1. Oxygen brought by air

In the case of air, the gas mass flowrate flowing in the column is $19.1 \text{ Nm}^3/\text{h}$ ($\sim 25 \text{ kg/h}$). The characteristics of the vapor flux allow to estimate the column diameter, to choose the packing size and to determine the range for recycling liquid flowrate, in order to be in agreement with hydraulic criteria.

The selected packing is constituted of stainless steel PALL rings, with the following characteristics :

Size $d = 15.875 \text{ mm}$ (0.625 in)
 Specific area $a = 341.21 \text{ m}^2/\text{m}^3$
 Packing factor $F = 229.656 \text{ m}^{-1}$
 Void fraction $\varepsilon = 0.93$

A column diameter of 0.21 m is chosen to cope with the compromise between efficiency and residence time.

The range of recycling liquid flowrate which leads to a correct wetting ratio is about 1150 to 8300 l/h at 20°C . The choice of flowrate will be performed during the optimisation of efficiency.

6.1.2. Oxygen brought by enriched air

The enriched air considered contains 40% vol. of oxygep.

In this case, the gas mass flowrate flowing in the column is $\sim 11.4 \text{ Nm}^3/\text{h}$ (15 kg/h).

The selected packing is the same as in the previous case (6.1.1.).

The column diameter is 0.2 m .

The range of recycling liquid flowrate which leads to a correct wetting ratio is about 1050 to 7500 l/h at 20°C . The choice of flowrate will be performed during the optimisation of efficiency.

6.2. DEFINITION OF STUDIED CONFIGURATIONS

Studied configurations (corresponding to the most commonly used according to SGN experience) are presented below.

6.2.1. Oxygen brought by air

6.2.1.1. Configuration ① : one water column

The simplest configuration consists in one water column, with oxygen brought by air.

Figure 1 : Configuration ①

6.2.1.2. Configuration ② : two water columns

This configuration involves two columns using water, with recycling of the bottom effluent of the second column towards the first column. Oxygen is brought by air.

Figure 2 : Configuration ②

6.2.1.3. Configuration ③ : one water column and one caustic soda column

This configuration involves two columns using respectively water and caustic soda, with two liquid effluents generated. Oxygen is brought by air.

Figure 3 : Configuration ③

6.2.2. Oxygen brought by enriched air (Configuration ④)

Configuration ④ : two water columns

This configuration involves two columns using water, with recycling of the bottom effluent of the second column towards the first column (similar to configuration ②). Oxygen is brought by oxygen-enriched air (40% vol. O₂).

6.3. OPTIMISATION OF EACH CONFIGURATION : OPERATING CONDITIONS AND RESULTING PERFORMANCE

For all the studied configurations, an optimisation of operating conditions has been performed, always checking hydraulic criteria. The optimised and recommended conditions and predesigns are presented below with the resulting performance. Moreover influence of packing height is given when it can be useful.

For each configuration, the fresh water flowrate is set so as to reach 5 N to 6 N in the bottom tank. In this condition, the acid liquid effluent can be recycled to the dissolution operation. Besides it is worth noticing that this water flowrate can be slightly modified (in order to reach another bottom acidity) without any significant change of the NO_x concentration discharge.

6.3.1. Configuration ①**a) Geometric characteristics**

- Packing : PALL rings (stainless steel) 0.625 in
- Column internal diameter : 0.21 m
- Packing height : 10 m
- Volume of bottom tank : 1 m³

b) Operating conditions and reached performance

- Atmospheric pressure
- Gas effluent
 - flowrate 14.5 Nm³/h
 - NO_x concentration 16200 vpm
 - temperature 21 °C
- Liquid effluent
 - flowrate 26 kg/h (22 l/h)
 - acidity 5.5 M HNO₃
 - temperature 24 °C

- Internal recycling flux : 1400 kg/h (1210 l/h), cooled at 20°C
- Water flux added for balance in the column : 20 l/h at 25°C
- Power to be evacuated in the heat exchanger (on the recycling flux or/and in the bottom tank) :
5 kW

c) Influence of packing height

Since the available height in the room can be an important constraint, it is useful to know the influence of the column height. So a sensitivity study has been realised concerning height packing of the water column (see appendix 1).

It shows for instance that reducing packing height from 10 to 8 m increases the NOx level in the gaseous effluent from 16200 vpm to 18200 vpm.

d) Conclusion

Performance reached with configuration ① is summarised in the following table :

Efficiency	NOx concentration discharge	NOx discharge * (operating 200 days/year)
92.2 %	16200 vpm	2.3 t/year (equivalent NO ₂) 480 g/h

Table 1 : Performance of configuration ① with 10 m packing

* : considering dissolution continuously generating a NOx flowrate of 3 Nm³/h, which is in fact the maximum value

Even with this simple configuration (which reaches ~ 92% efficiency), the discharge is widely lower than the disposal constraint of 10 t/year, and lower than 1 kg/h.

6.3.2. Configuration ②

a) Geometric characteristics

For each of the two columns, design characteristics are the following ones :

- Packing : PALL rings (stainless steel) 0.625 in
- Diameter : 0.21 m
- Packing height : 10 m
- Volume of bottom tank : 1 m³

b) Operating conditions and reached performance

- Atmospheric pressure
- Gas effluent
 - flowrate 14.3 Nm³/h
 - NOx concentration 6600 vpm
 - temperature 20 °C
- Liquid effluent
 - flowrate 27 kg/h (22 l/h)
 - acidity 5.7 M HNO₃
 - temperature 24 °C
- Internal recycling flux: 1400 kg/h (1210 l/h), cooled at 20°C
- Water flux added in the 2nd column : 20 l/h at 25°C
- Powers to be evacuated (heat exchangers on the recycling flux and/or in the bottom tanks) :
 - 1st column : 4.9 kW
 - 2nd column : 300 W

c) Conclusion

Performance reached with configuration ② is summarised in the following table :

Global efficiency	NOx concentration discharge	NOx discharge * (operating 200 days/year)
96.8 %	6600 vpm	930 kg/year (eq NO ₂) 195 g/h

Table 2 : Performance of configuration ② with 2 x 10 m packing

* : considering dissolution continuously generating a NOx flowrate of 3 Nm³/h, which is in fact the maximum value

The discharge is widely lower than the disposal constraint of 10 t/year, and lower than 1 kg/h.

6.3.3. Configuration ③

a) Geometric characteristics

For each of the two columns, similar design characteristics are presented below :

- Packing : PALL rings (stainless steel) 0.625 in
- Diameter : 0.21 m
- Packing height : 10 m
- Volume of bottom tank : 1 m³

b) Operating conditions and reached performance

- Atmospheric pressure
- Gas effluent
 - flowrate 14.4 Nm³/h
 - NOx concentration 5500 vpm
 - temperature 20°C
- Liquid sodic effluent
 - flowrate 30 kg/h (~ 29 l/h)
 - 0.7 M NaOH
 - 0.12 M NaNO₃
 - 0.12 M NaNO₂
 - temperature 20°C
- Liquid acid effluent
 - flowrate 26 kg/h (22 l/h)
 - 5.5 M HNO₃
 - temperature 24°C
- Internal recycling flux : ~1210 l/h (1st column) and 1360 l/h (2nd column), cooled at 20°C
- Water flux added for balance in the 1st column : 20 l/h at 25°C

- The caustic soda flux to be introduced in the 2nd column is determined from the inlet gas composition. An excess of 130 % with respect to the required stoichiometric quantity is considered. The resulting flowrate is 30 kg/h of NaOH 1N (~ 29 l/h), at 25°C.

N.B : The NaOH excess can be less important : it would generate a less concentrated effluent or a smaller flowrate of effluent but would reduce the margin relative to NaOH amount in case of an uncontrolled NOx flowrate increase.

- Powers to be evacuated (heat exchangers on the recycling flux and/or in the bottom tanks) :

1st column : 5 kW

2nd column : 300 W

c) Checking of non-precipitation of carbonate in the 2nd column

Carbon dioxide present in air is well absorbed by caustic soda, giving sodium carbonate and carbonate hydrogen. Carbonate hydrogen NaHCO_3 may not be present (as the reaction conversion into Na_2CO_3 is instantaneous). However, since NaHCO_3 is little soluble (9.6 g/l at 20°C [6]), it is necessary to evaluate the precipitation risk if all CO_2 is absorbed in the form NaHCO_3 .

As CO_2 molar fraction in air is ~ 0.06%, the CO_2 flowrate entering the columns is evaluated to about 0.43 mol/h.

Making the assumption that all CO_2 is absorbed in the 2nd column and taking into account the liquid flowrate in the column, the calculated concentration of NaHCO_3 is ~ 1.1 g/l, which is far lower than the solubility limit.

Therefore, with the proposed operating conditions of the 2nd column, there is no risk of carbonate precipitation.

d) Conclusion

Performance reached with configuration ③ is summarised in the following table :

Global efficiency	NOx concentration discharge	NOx discharge * (operating 200 days/year)
97.4 %	5500 vpm	780 kg/year (eq. NO_2) 160 g/h

Table 3 : Performance of configuration ③ with 2 x 10 m packing

* : considering dissolution continuously generating a NOx flowrate of 3 Nm^3/h , which is in fact the maximum value

The discharge is widely lower than the disposal constraint of 10 t/year, and lower than 1 kg/h.

The use of caustic soda leads to a higher efficiency than water but produces a sodium effluent. However, the calculated sodium effluent flowrate is small (~ 29 l/h), and it is possible to recycle this flux (containing excess NaOH) towards the neutralization step.

6.3.4. Configuration ④

a) Geometric characteristics

For each of the two columns, proposed design characteristics are the following ones :

- Packing : PALL rings (stainless steel) 0.625 in
- Diameter : 0.2 m
- Packing height : 6 m
- Volume of bottom tank : 1 m³

b) Operating conditions and reached performance

- Atmospheric pressure
- Gas effluent
 - flowrate 6.4 Nm³/h
 - NOx concentration 4300 ppm
 - temperature 20 °C
- Liquid effluent
 - flowrate 27 kg/h (23 l/h)
 - acidity 5.8 M HNO₃
 - temperature 24 °C
- Internal recycling flux : 1300 kg/h (~ 1120 l/h), cooled at 20°C
- Water flux added for balance in the 1st column : 20 l/h at 25°C
- Powers to be evacuated (heat exchangers on the recycling flux and/or in the bottom tanks) :
 - 1st column : 5.1 kW
 - 2nd column : 250 W

c) Influence of packing height

The above results concern a packing height of 2 x 6 m. A sensitivity study has been realised concerning the packing height of the columns (see appendix 2). With two columns containing 10 m packing each, the outlet NOx concentration reaches 3100 vpm.

d) Conclusion

Performance reached with configuration ④ is summarised in the following table :

Global efficiency	NOx concentration discharge	NOx discharge * (operating 200 days/year)
99.1 %	4300 vpm	270 kg/year (eq. NO ₂) 60 g/h

Table 4 : Performance of configuration ④ with 2 x 6 m packing

* : considering dissolution continuously generating a NOx flowrate of 3 Nm³/h, which is in fact the maximum value

The discharge is widely lower than the disposal constraint of 10 t/year, and lower than 1 kg/h.

The use of oxygen-enriched air allows to reach a higher efficiency with a moderate packing height.

Two columns containing packing heights of 6 m each (~ 7 m for the column without the bottom tank, without any oversizing factor) allow to reach ~ 4300 vpm.

6.4. SUMMARY

The following table gives the main characteristics of each studied configuration.

	Air			O ₂ enriched air
	Configuration ① 1 water column	Configuration ② 2 water columns	Configuration ③ 2 water/caustic soda columns	Configuration ④ 2 water columns
Column (each)	Diam. 0.21 m Pack. height 10 m	Diam. 0.21 m Pack. height 10 m	Diam. 0.21 m Pack. height 10 m	Diam. 0.2 m Pack. height 6 m
Liquid effluent	22 l/h 5.5 M HNO ₃	22 l/h 5.7 M HNO ₃	22 l/h 5.5 M HNO ₃ +29 l/h 0.7 M NaOH	23 l/h 5.8 M HNO ₃
Gas effluent	14.5 Nm ³ /h NOx 16200 vpm 2.3 t/year * (480 g/h)	14.3 Nm ³ /h NOx 6600 vpm 930 kg/year * (195 g/h)	14.4 Nm ³ /h NOx 5500 vpm 780 kg/year * (160 g/h)	6.4 Nm ³ /h NOx 4300 vpm 270 kg/year * (60 g/h)

Table 5 : Characteristics of studied configurations

* : considering dissolution continuously generating a NOx flowrate of 3 Nm³/h, which is in fact the maximum value

For all of the studied configurations, the annual discharge is largely lower than the 10 t/year limit and the discharge is lower than 1 kg/h. Moreover the discharge will be actually lower since the unit operates scarcely at maximum flowrate of NOx (in fact the sludges contain other products that do not generate NOx).

The obtained performance is satisfactory, especially in the option involving oxygen-enriched air (configuration ④). According to these results no additional technology is necessary.

However an analysis based on "Best available technology" approach is necessary to confirm the choice of a process option.

The connections between the absorption unit and the whole process are represented on the figure 4.

Figure 4 : Scheme of the whole treatment unit

Air (or enriched air) is introduced in the head of the dissolver in order to favour the nitrous recombination. Since part of this flowrate will be provided by leakages, it will be necessary to quantify the leakage amount.

The condenser has to be oversized so as to be efficient in case of a sudden increase of vaporized water flowrate. Besides, in case of an electricity loss, the cooling water feed is stopped : the condenser thermal inertia has to be large enough to achieve the condensation of the dissolution off-gas until vapour generation from dissolution stops. The condensate flow can be recycled towards the dissolver.

Absorption columns need heat exchangers on their internal recycling flux.

The HNO_3 effluent from the bottom of the first column can be continuously recycled towards the dissolver. The recovered acid effluent contains also HNO_2 . Therefore if recovered acid is stored before being recycled at the dissolution step, a preliminary stripping of HNO_2 is necessary to avoid generation of NO_x from storage tank.

The sodium effluent (if caustic soda is used in the absorption columns) can be recycled towards the neutralization unit.

7. GENERAL CONCLUSION : RECOMMENDATIONS

Absorption has first been studied for the dissolution off-gas treatment. Indeed this process seems to be adapted to the present case according to the low NOx flowrate and to the authorized level of discharge. Besides, absorption columns represent one of the simplest technologies and allows to recycle recovered nitric acid.

Several configurations have been studied for the dissolution off-gas treatment. For each of them, the predesign has been performed, the operating conditions have been optimised and the resulting efficiency has been calculated.

The results have shown that absorption process allows to reduce in a significant way the annual discharge : 2.3 t/year (equivalent NO₂) with the simplest process option, involving a single water column. Besides the daily discharge is lower than 1 kg/h.

The choice of one process option among the presented ones depends on the constraints related to the effective limit of discharge in atmosphere and to the available height in the room.

The use of two tall columns (~ 12 m with 10 m packing each) using water and caustic soda (configuration ③) allows to reach ~ 5500 vpm of NOx and 780 kg/year (to compare with 6600 vpm and 930 kg/year in the case of two water columns, configuration ②).

It is worth noticing that the use of caustic soda generates sodium effluents, which can be recycled towards the neutralization process.

On the other hand, if the available height is not sufficient, it is possible to use smaller columns and/or to improve efficiency by operating with oxygen-enriched air. In particular, with enriched air, two water columns of ~ 7 m (6 m packing each) allow to reach ~ 4300 vpm and 270 kg/year (configuration ④).

Finally, the process option involving oxygen-enriched air seems to be interesting. Indeed, columns can be smaller and no sodium effluents are generated.

According to these results, it seems that there is no need to use an additional technology as a final treatment. However an analysis based on "Best available technology" (BAT) approach has to be performed in order to confirm the choice of the process option.

All these results correspond to a maximum NOx production flowrate from dissolution. For a lower flowrate, the discharge concentration is reduced (for a NOx flowrate divided by ten, configuration ② leads to ~ 2700 ppm and configuration ④ to ~ 2000 ppm). Besides, since the maximum flowrate actually corresponds to a short production time as compared to the total annual production time, the calculated annual discharge (based on the maximum flowrate) is overestimated.

- N.B :
- The present results don't include any oversizing factor.
 - All the studied configurations have been considered at atmospheric pressure.
 - It will be necessary later on to check that the air leakage flowrate from dissolution is not too large with respect to the air flowrate needed for the treatment unit.

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APPENDIX 1 : INFLUENCE OF PACKING HEIGHT ON NOX DISCHARGE FOR CONFIGURATION ①

APPENDIX 2 : INFLUENCE OF PACKING HEIGHT ON NOX DISCHARGE FOR CONFIGURATION ④

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