UMONS
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L'usage du peroxyde d'hydrogène (H_2O_2) dans les techniques industrielles de réduction des polluants atmosphériques (NOx, SOx, COVs,…)

The use of hydrogen peroxide (H_2O_2) for the purpose of reducing industrial gaseous pollutants (NOx, SOx, VOCs,…)

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POLYTECH MONS

Atmos'Fair
Paris – 21-22 juin 2011

Hydrogen Peroxide H_2O_2 – properties/characteristics

- ✓ Agent for oxidation process
- ✓ Zero waste
- ✓ « easy » liquid for solution aq+H_2O_2
- ✓ Oxidations/reductions/organic and inorganic compounds formation /addition compounds formation

✓ Oxidizing agent according to:
- Ionic reactions
- Oxygen transfer
- Electron transfer
- Radical mechanisms

☹ stability (pH, t°,..)

☹ Cost

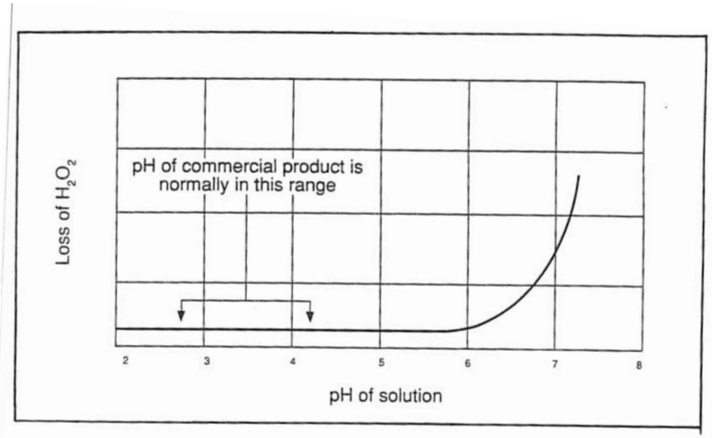


Figure 4.1: Effet du pH sur la stabilité du H_2O_2

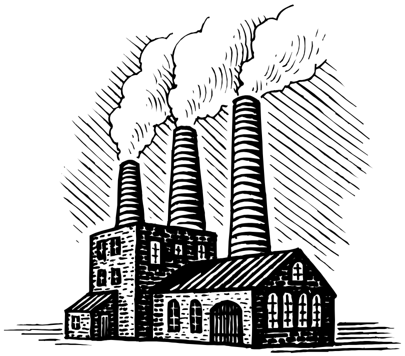
Uses of hydrogen peroxide H_2O_2

		Wastewater	Air pollutant	Soil / Groundwater
Organic Compounds	COD / BOD / TOC	◆		◆
	Phenol	◆		◆
	Formaldehyde	◆		
	Hydrocarbon	◆		◆
	Organohalogen	◆		◆
Inorganic Compounds	Hydrogen sulfide	◆	◆	
	Mercaptan	◆	◆	
	Sulfur dioxide		◆	
	Available chlorine	◆		
	Nitric oxide		◆	
	Nitrogen dioxide	◆	◆	
Others	Sludge reduction	◆		
	Odor	◆	◆	
	Color	◆		

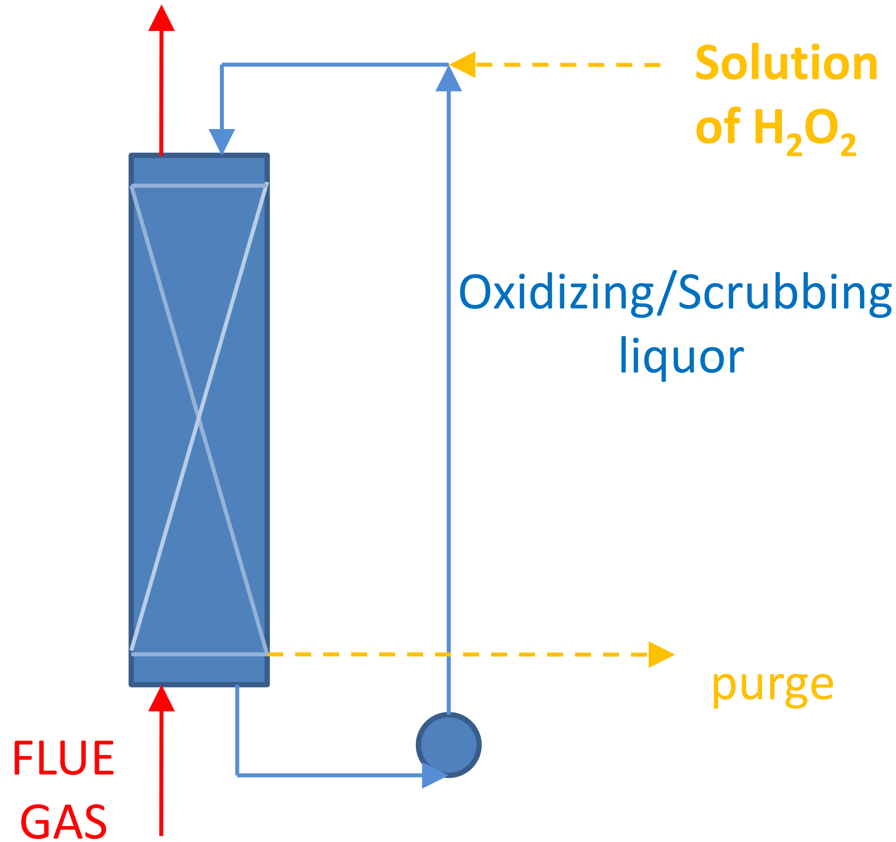
◆ Use of Hydrogen Peroxide

→ Context of the conference

Environnemental Applications for the reduction of **NOx**, **SOx**, **H_2S**, **COV** in industrial flue gases



Absorption Process



Two aims:

- non hazardous or valorizable liquid effluent
- H_2O_2 concentration profile (kinetics/consumption)

Objectives of the researchs:

- MECHANISMS
- BEST OPERATING CONDITIONS (t°, pH, Ionic Force…)
- DESIGN

Comparison of performances for NOx or SOx reduction

Water
- Low cost
- Medium absorption rates

Alkaline solutions
- SO_2 and NOx absorption rates ↑
- Absorption of CO_2
- Need to treat absorption products (Na_2SO_3, $NaNO_3$...)

Acidic solutions
- NOx and SO_2 absorption rates ↓

SO_2 and/or NO_X absorption into oxido-acidic solutions

Oxido-acidic solutions

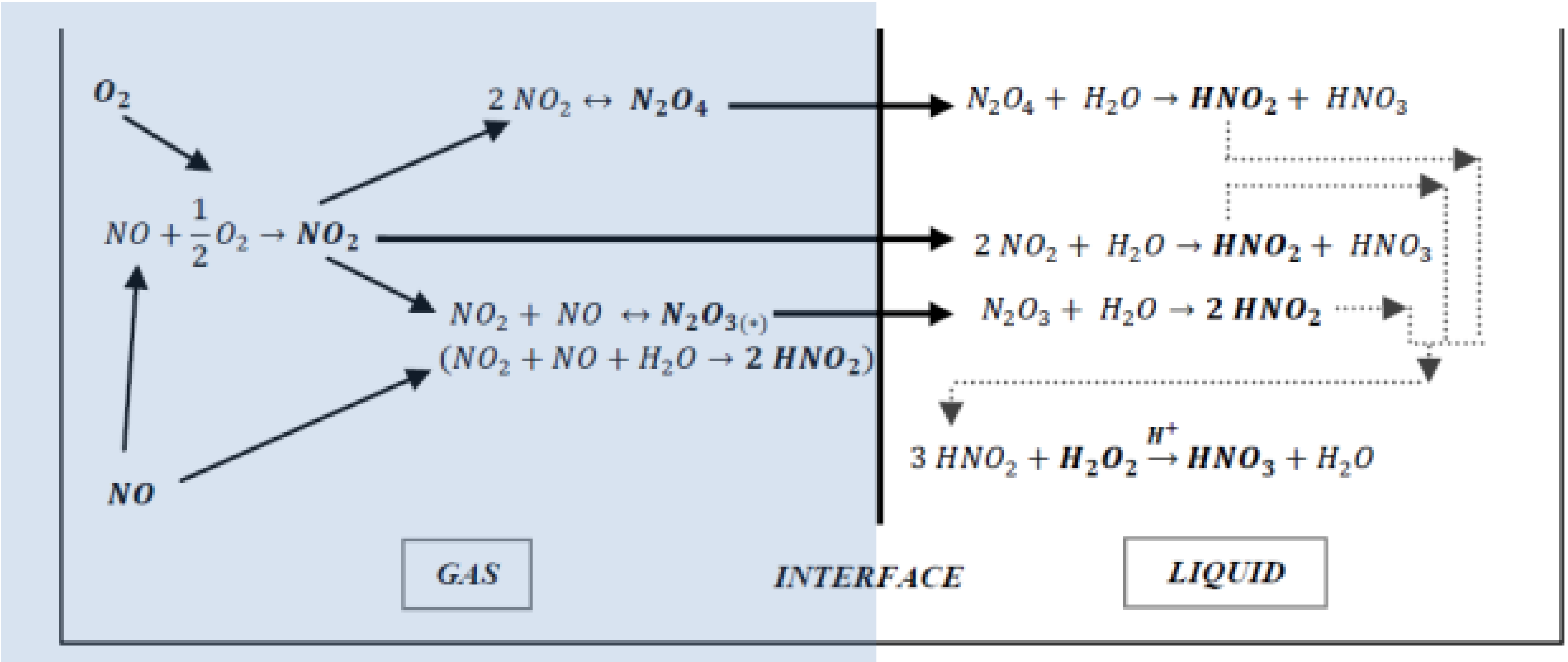
$$SO_2,\ NO_X \xrightarrow{+\,H_2O_2} H_2SO_4,\ HNO_3$$

CO_2 absorption ≈ 0

- Valuable by-products
- Recycled into the system

Reduction of NOx

NO_x in $HNO_3 + H_2O_2$



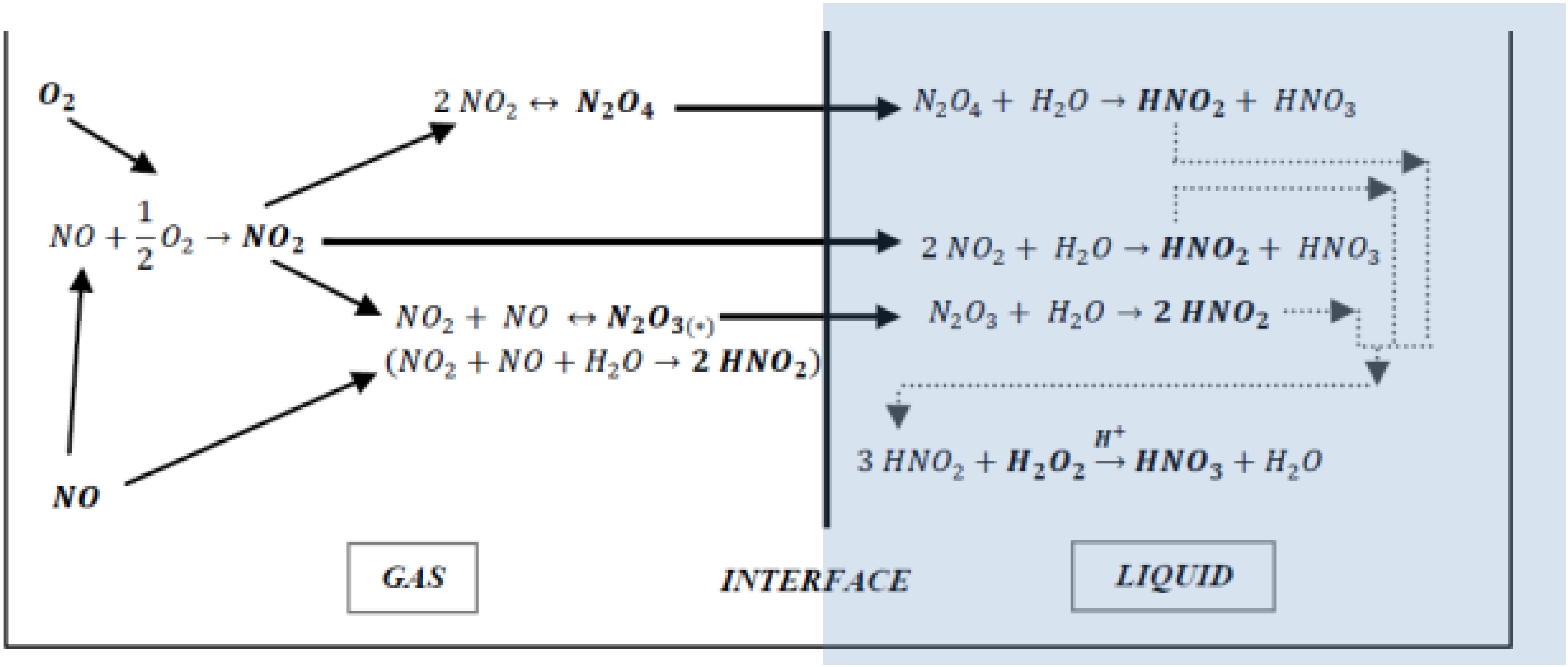
Gaseous mixture : « $NO + NO_2$ »

Characterized by **Oxidation Ratio** (OR) = p_{NO2}^*/p_{NOx}

OR ? combustion flue gases: ~ 5%

various industrial flue gases: 0 < OR < 100%

Reduction of NOx



Absorption mechanism:

1°) **without H_2O_2**: decomposition of HNO_2 (NO release) and low absorption rates

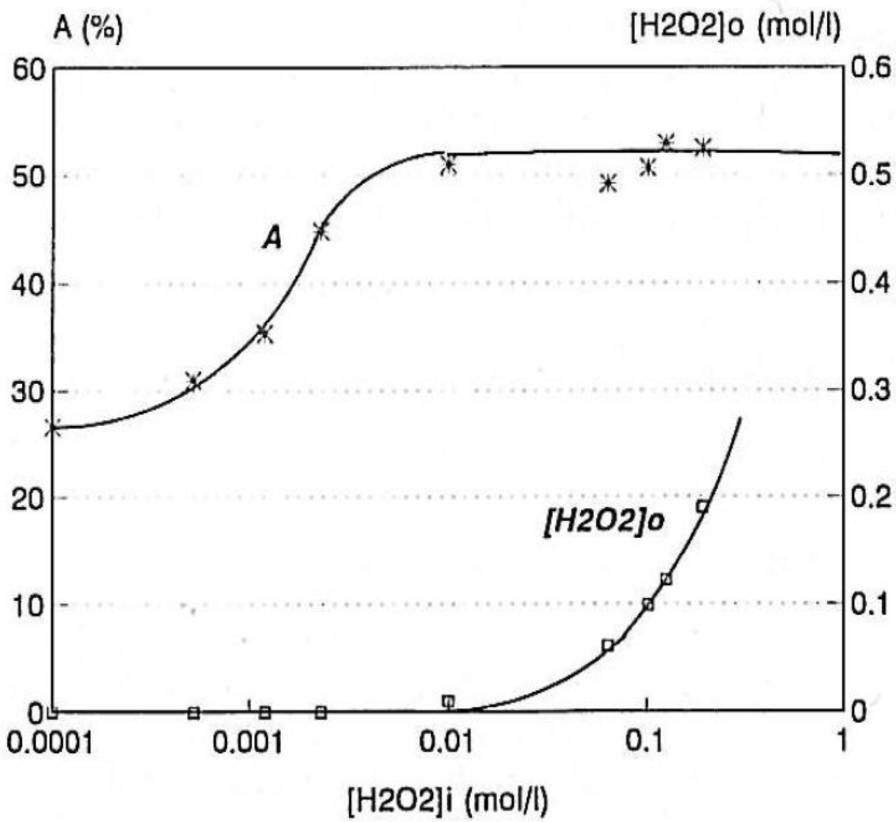
2°) **with H_2O_2**

$$HNO_2 + H_2O_2 \xrightarrow{H+} HNO_3 + H_2O$$

+ autocatalysis by HNO_3

Reduction of NOx

Experimental results



1.

HNO_2 decomposition in NO: prevented in the liquid phase

If C_{H2O2} ↗ : NOx absorption performances ↗ then steady (zero order ÷ H_2O_2)

2.

Increase of the transfer rate of HNO_2 formed in the gaseous phase

If C_{HNO3} ↗ : performances ↗ (auto-catalysis)

Hydrolysis reactions of NO_2, N_2O_4, N_2O_3: fast but limiting

Reduction of NOx

Modelling for NO_x absorption in oxido-acid solutions – Design parameters

Multicomponent absorption/reaction

Enhancement of the mass transfer due to the chemical reaction

NO_2; N_2O_4; N_2O_3: Fast reactions – 1 or 2 order

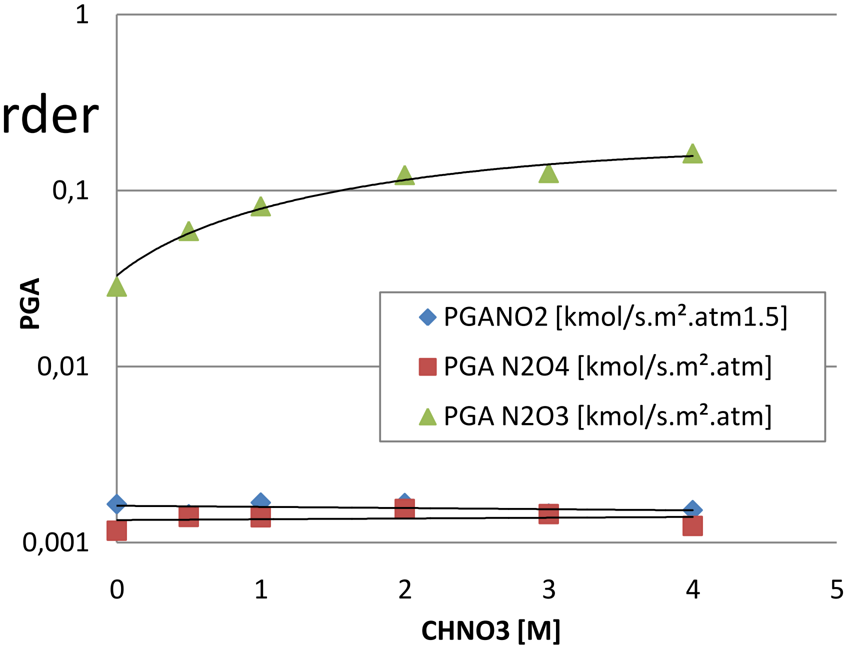
$$R_{NO_2} = PGA_{NO_2}.(p^i_{NO_2})^{3/2}$$

$$R_{N_2O_4} = PGA_{N_2O_4}.p^i_{N_2O_4}$$

hydrolysis

$$R_{N_2O_3*} = PGA_{N_2O_3*}.p^i_{N_2O_3}$$

hydrolysis of N_2O_3 + reaction of HNO_2



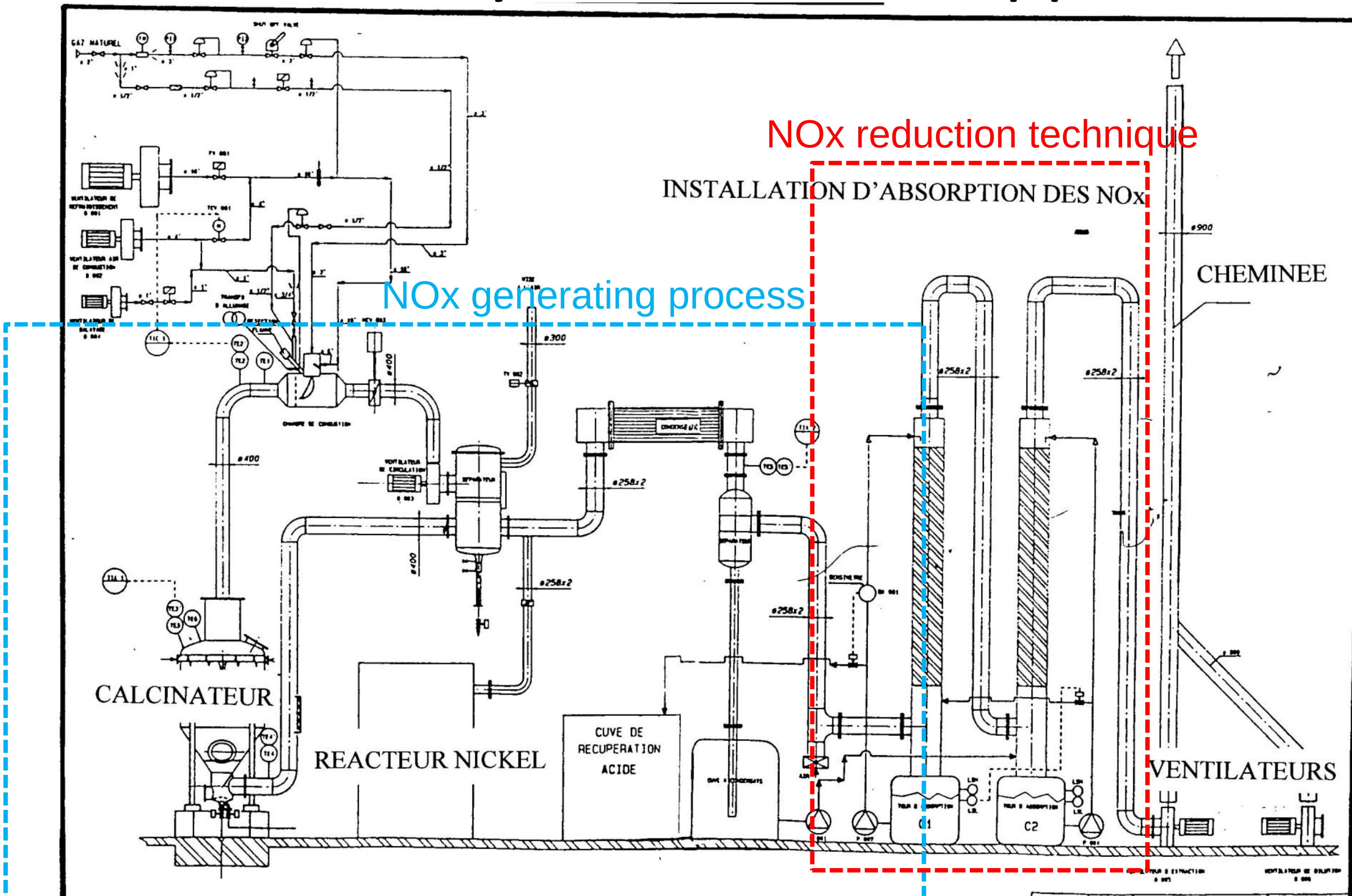
PGA (*'Global Parameter of Absorption'*)
= f (solubility H; diffusivity D and kinetic reaction k)

NO: Physical absorption

$$R_{NO} = k_L . \frac{p^i_{NO}}{H}$$

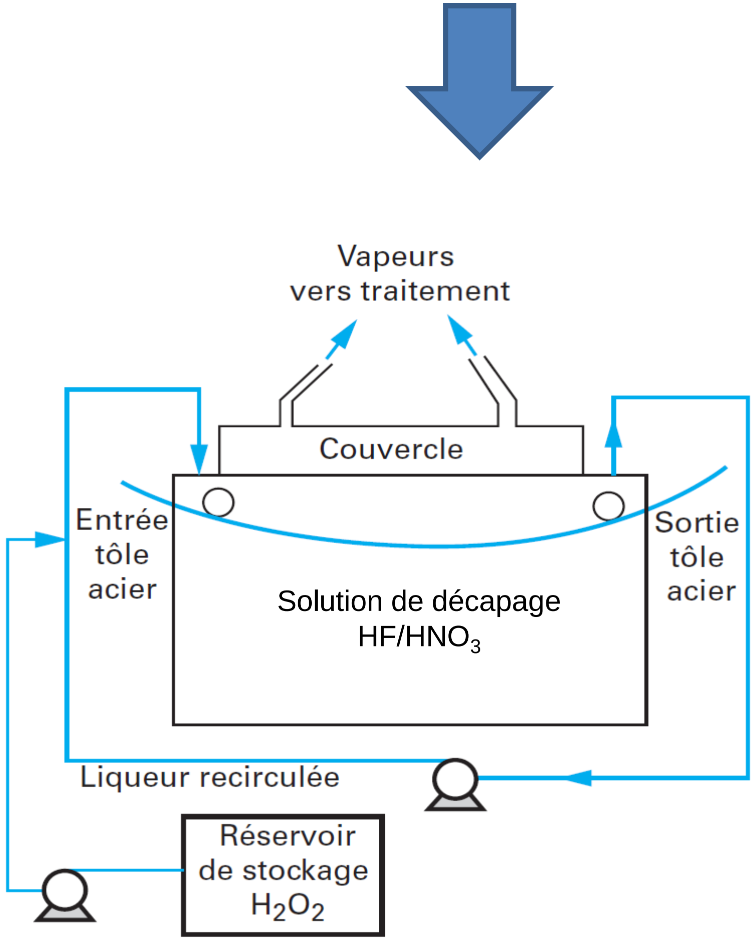
REF:
D. Thomas, S. Brohez, J. Vanderschuren, Trans. IChemE 74B(1996), pp 52-57
D. Thomas and J. Vanderschuren, Chem.Eng.Sci, Vol.51, n 11 (1996), pp 2649-2654
D. Thomas and J. Vanderschuren, Ind. Eng. Chem. Res., Vol 36, n 8 (1997), pp 3315-3322
D. Thomas and J. Vanderschuren, Ind.Eng.Chem.Res., Vol. 37, n 11 (1998), pp 4418-4423

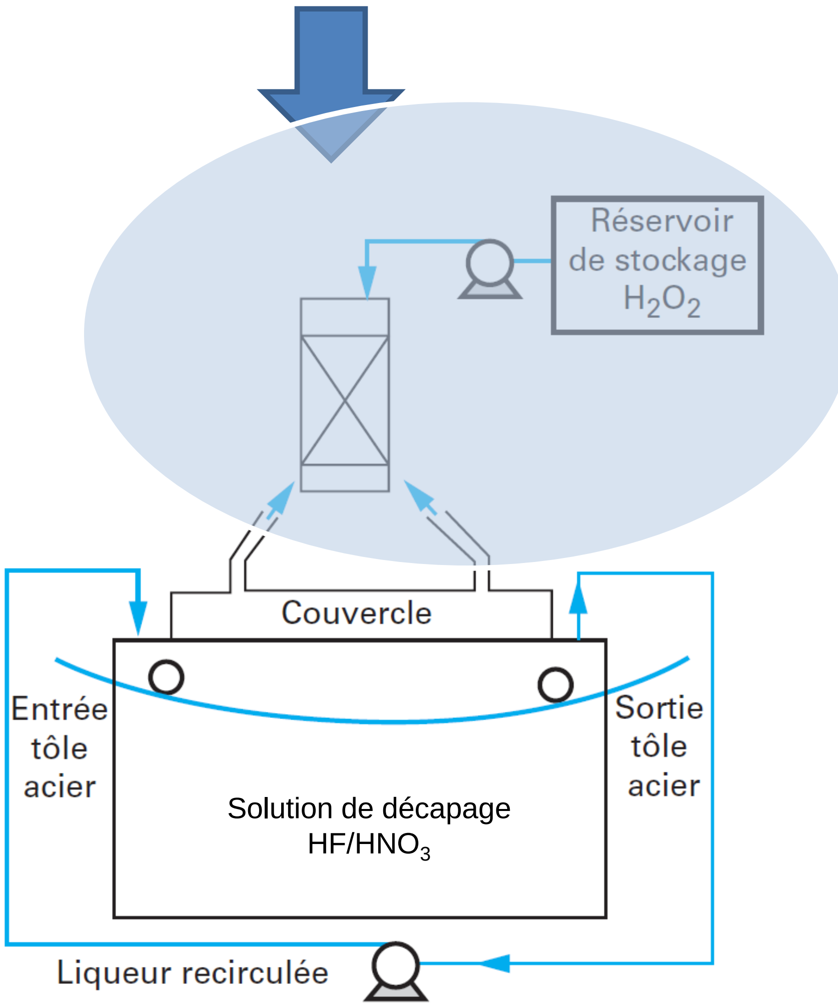
Example 1: NOx reduction in off-gases issued from the production of catalysts for vehicle exhaust pipes



Procédé :
1°) attaque : $3\ Ni + 8\ HNO_3\ (42\%) \rightarrow 3\ Ni(NO_3)_2 + 2\ NO$ ↗
2°) Immersion support poreux dans solution de $Ni(NO_3)_2$
3°) cata / $Ni(NO_3)_2$ -> calcination (250-450°C) -> cata / NiO avec NOx ↗

Example 2: reduction of NOx in flue gases of a pickling unit by addition of H_2O_2





Reduction of SOx

SO_2 in $H_2SO_4 + H_2O_2$

$$SO_2 + H_2O_2 \rightarrow H^+ + HSO_4^-$$

Irreversible reaction

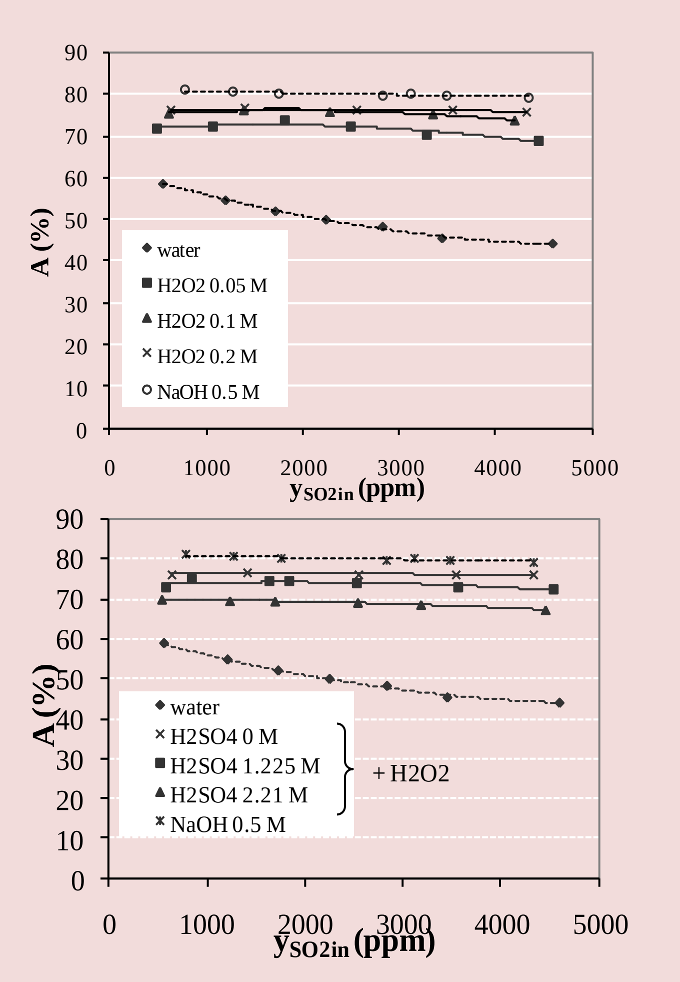
2^d global order

1^{st} order $\div$ H_2O_2 et $\div$ SO_2

$\pm$ fast reactions depending on concentrations

Si C_{H2O2} ↗ : Performances ↗

Si C_{H2SO4} ↗ : Performances ↘



REF:

D. Thomas, S. Colle and J. Vanderschuren, Chem. Eng. Process., Vol. 42, n 6 (2003), pp 487-494

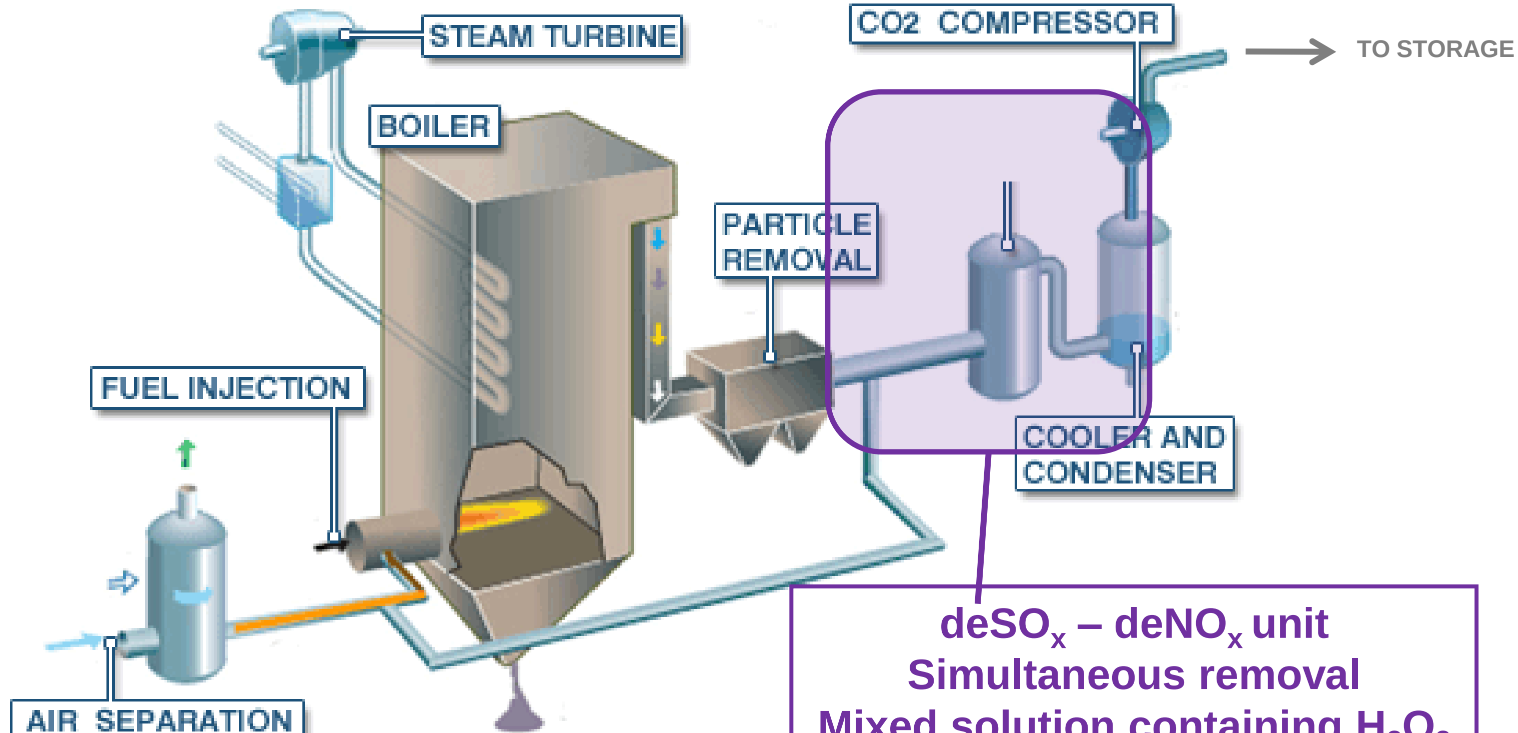
D. Thomas, S. Colle and J. Vanderschuren, Chem. Eng. Technol., Vol. 26, n 4 (2003), pp 497-502

S. Colle, J. Vanderschuren and D. Thomas, Chem. Eng. Process, Vol. 43, n 11 (2004), pp.1397-1402

D. Thomas, S. Colle, J. Vanderschuren, Chem. Eng. Process. Vol. 44 (2005), pp 487-494

S. Colle, J. Vanderschuren and D. Thomas, Chem. Eng. Sci., Vol. 60, n 22 (2005), pp 6472-6479

Reduction with oxido-acid solutions of NOx and SOx contained in oxyfuel flue gases

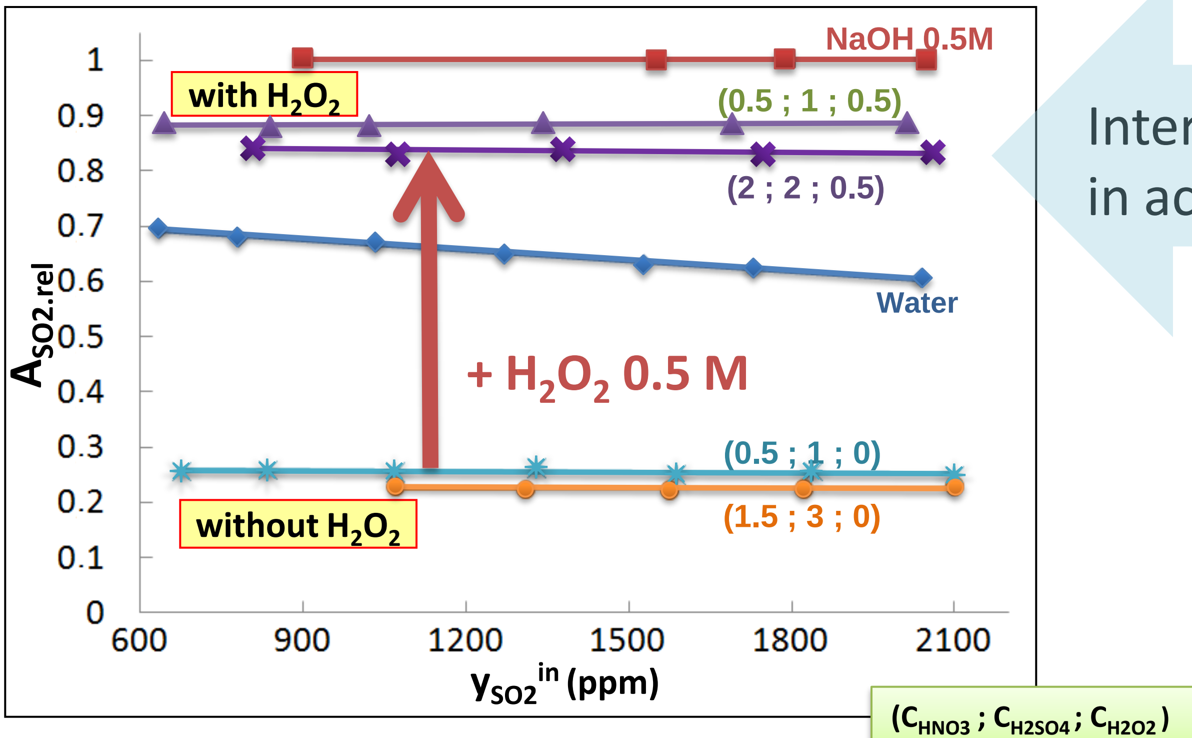


deSO$_x$ – deNO$_x$ unit
Simultaneous removal
Mixed solution containing H_2O_2

SOURCE: Vattenfall

Simultaneous reduction of NOx and SOx in oxido-acid solutions

$$\left.\begin{matrix} SO_2 \\ NO_X \end{matrix}\right. \xrightarrow{+ H_2O_2} \left.\begin{matrix} H_2SO_4 \\ HNO_3 \end{matrix}\right\} \text{Mixed solutions}$$



Interest of H_2O_2 in acid solutions

Simultaneous reduction of NOx and SOx in oxido-acid solutions

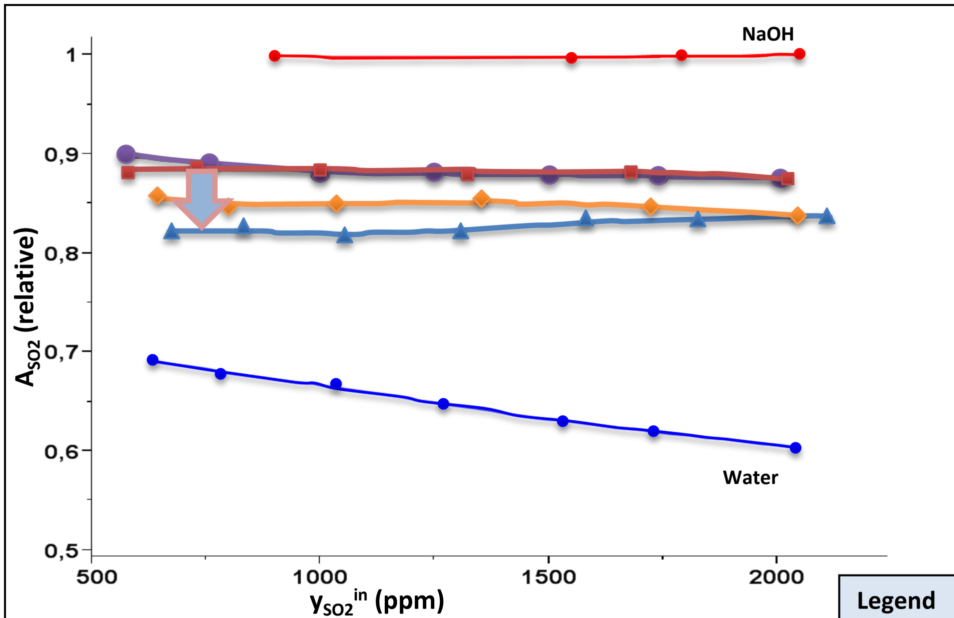
Absorption ↘ when C_{HNO3} ↗

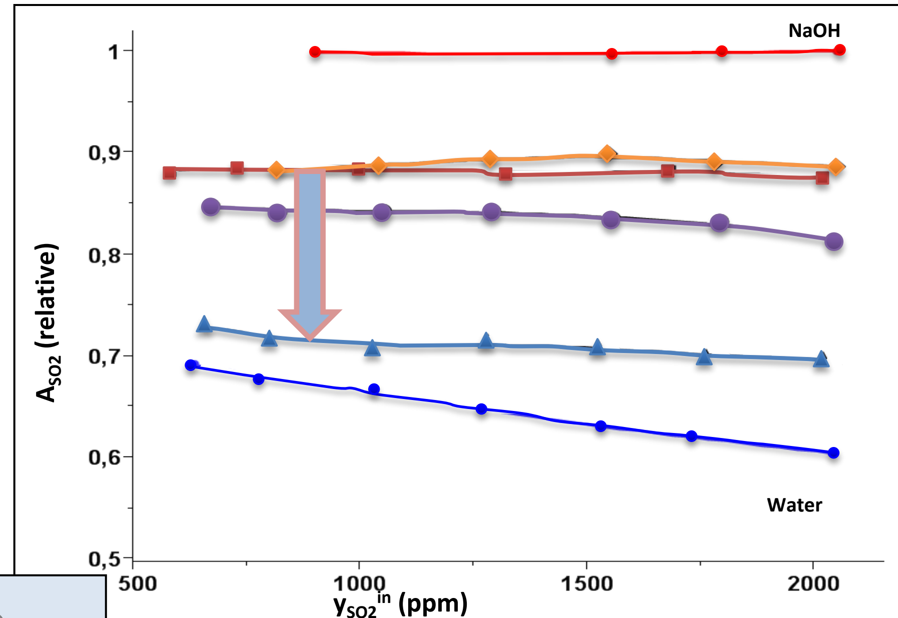
Absorption ↘ ↘ when C_{H2SO4} ↗

HNO_3=A

C_{H2O2} = 0,2 mol/l

H_2SO_4 =A

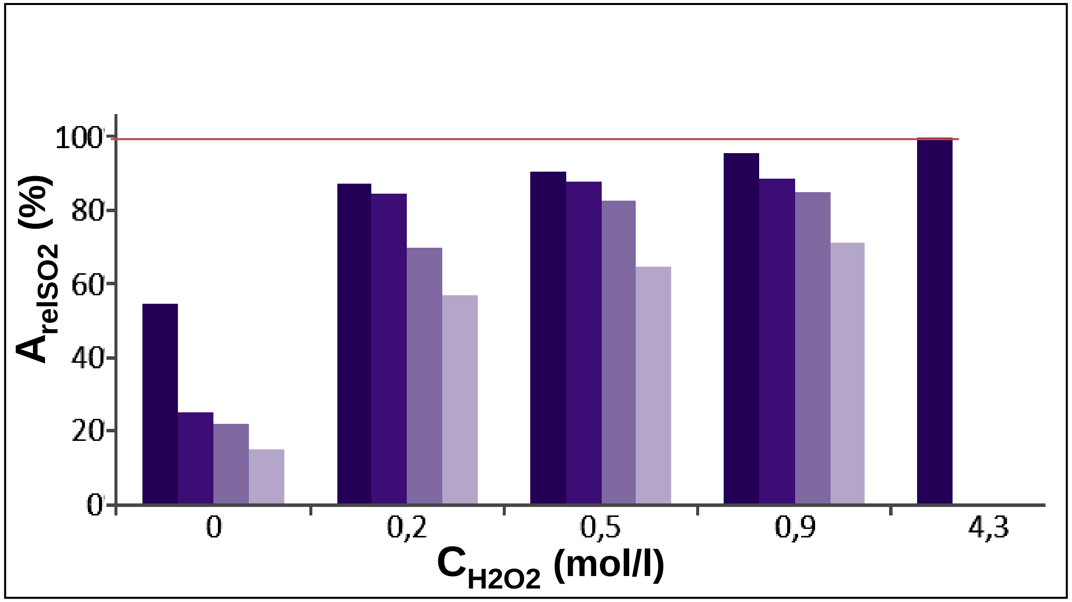




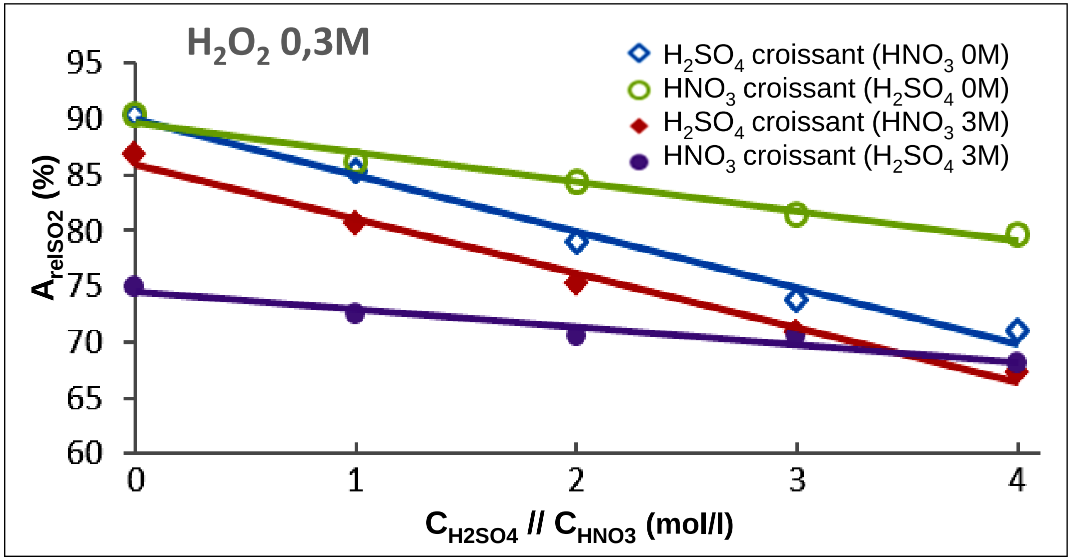
Legend
- ▪ A 0M □
- ◆ A 1M ◇
- ● A 2M ○
- ▲ A 4M △

+B 2M

Simultaneous reduction of NOx and SOx in oxido-acid solutions



A_{SO2} ↗↗ quand C_{H2O2} ↗



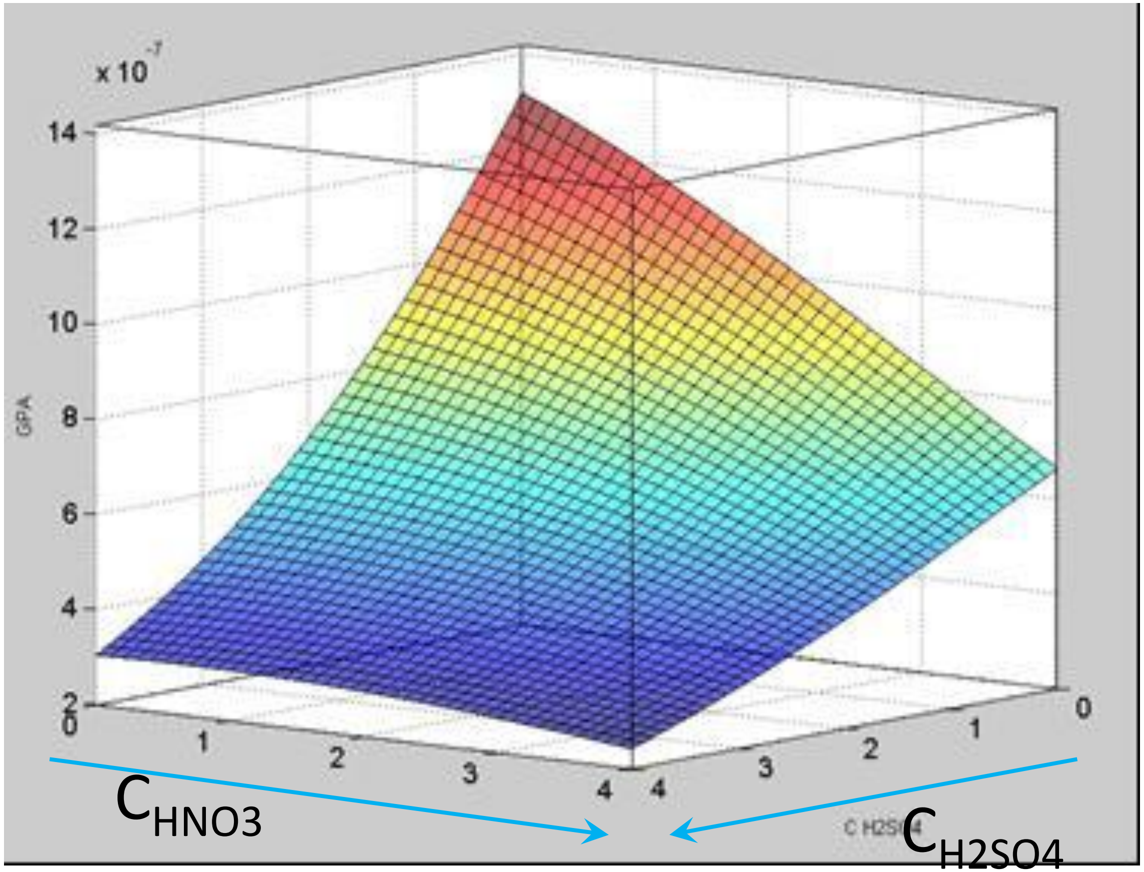
A_{SO2} ↘ quand C_{HNO3} ↗

A_{SO2} ↘ ↘ quand C_{H2SO4} ↗

Simultaneous reduction of NOx and SOx in oxido-acid solutions

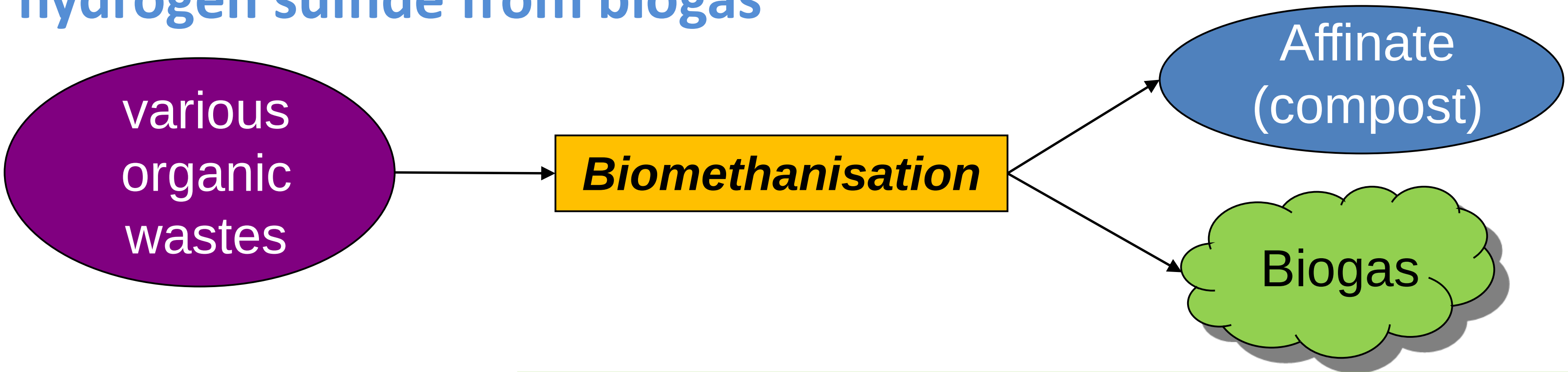
Design parameters

$$R_{SO_2} = PGA_{SO_2} . p^{i}_{SO_2}$$



REF: I. Liémans, B. Alban, J-P Tranier and D. Thomas, Energy Procedia, Vol. 4 (2011), pp 2847-2854

Oxidative scrubbing process for the selective removal of hydrogen sulfide from biogas



Biogas *(variable composition)*

CH_4 : 75 % max
CO_2 : 40 % max
H_2S : 50 à 10^4 ppm

O_2 : 5 %
H_2O : 5 %
Aromatic: traces

H_2S:

- Problems of behaviour of materials
- Environnemental problems

Selective removal of H_2S (versus CO_2)
Conditions ???

REF: L. Dubois and D. Thomas, Chem. Eng. Technol., Vol. 33, n 10 (2010), pp 1601-1609
A. Couvert et al., Chem. Eng. Science, Vol. 61 (2006) pp 7240

Selective removal of H_2S from biogas – Effect of pH

CO_2

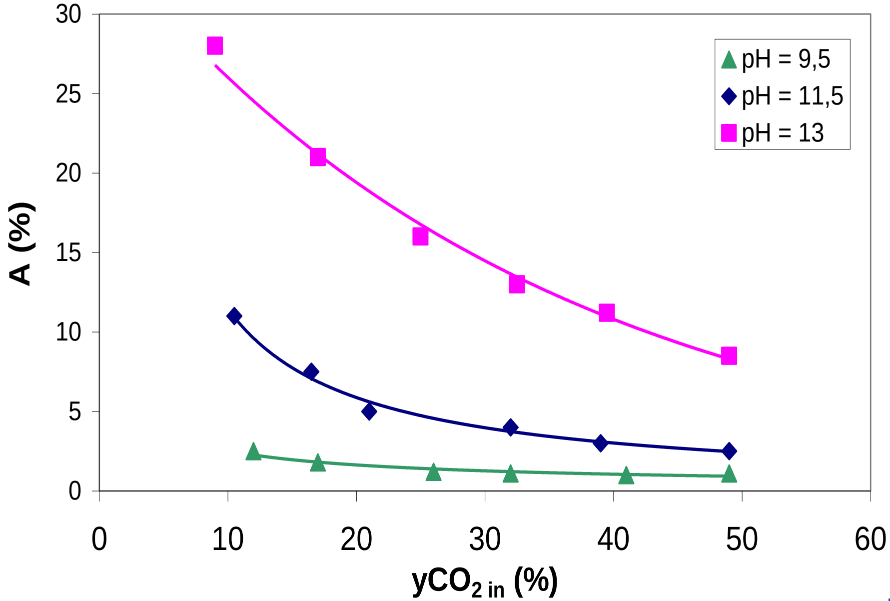
- Consumption of NaOH by CO_2
- Interaction CO_2/ H_2O_2
  & transfer enhancement

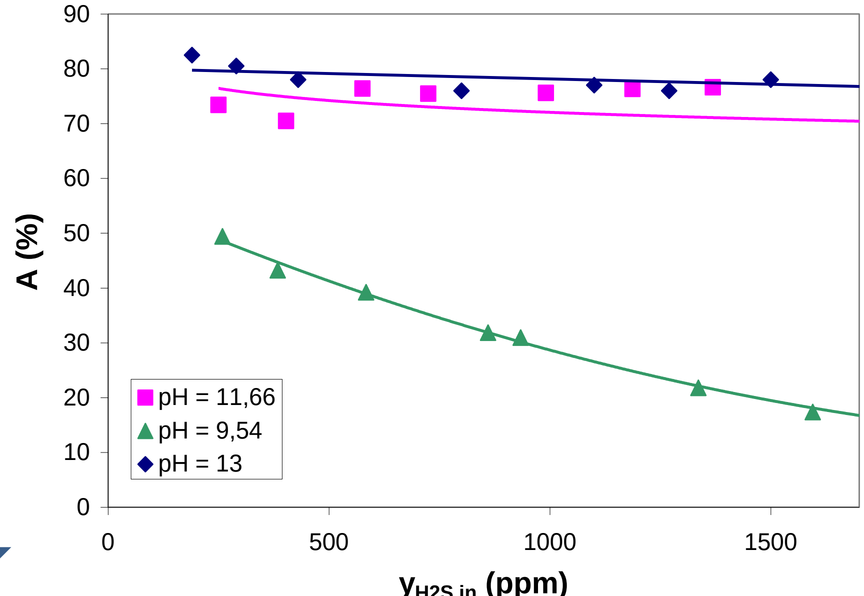
pH ≈ 13

H_2S

- Instantaneous reaction
- liquid film resistance = cancelled

non selective absorption





c_{Na+}= 0,2 M

c_{H2O2} = 0.2 M

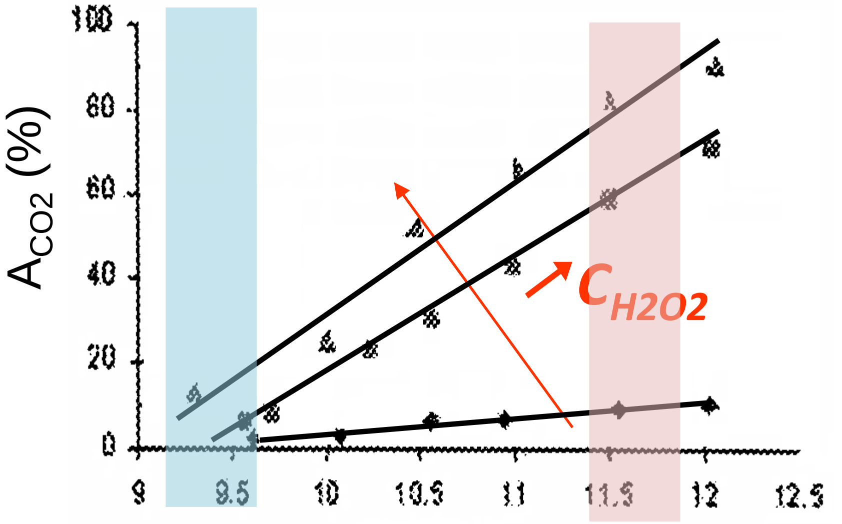
pH ≈ 9,5

Best selectivity conditions

Selective removal of H2S from biogas – Effect of pH and c_{H2O2}

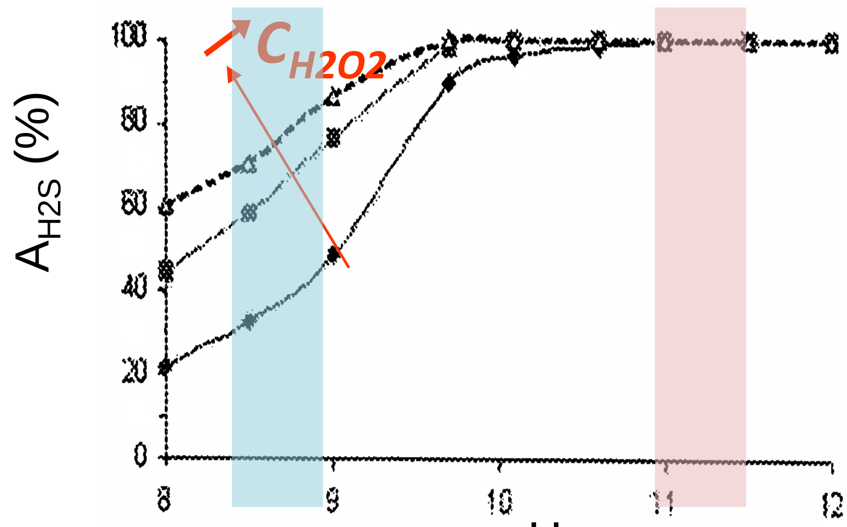
CO_2

y_{CO2} = 400 ppmv



H_2S

y_{H2S} = 7 ppmv



pH >: non selective absorption

pH ↓: best selectivity conditions

Reaction mechanism:

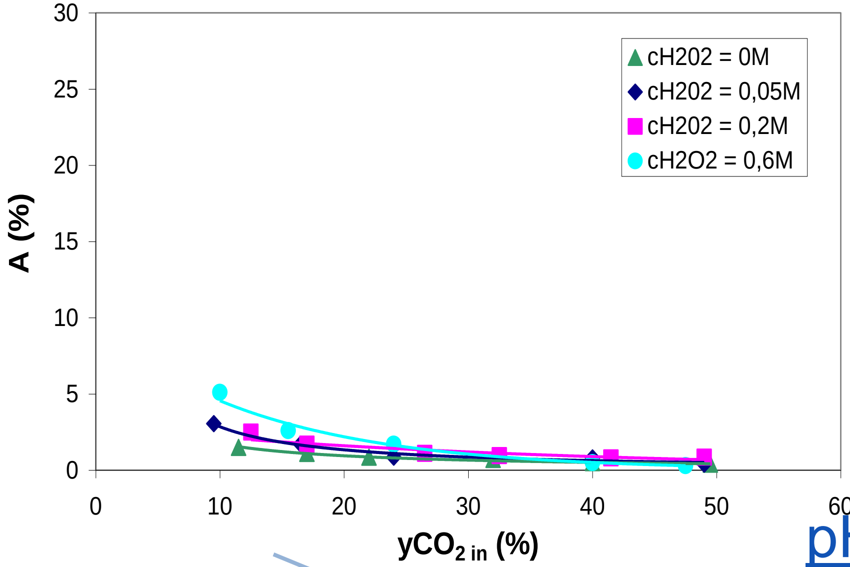
$H_2S(g) \leftrightarrow H_2S(aq)$

$H_2S(aq) + OH^- \leftrightarrow HS^- + H_2O$

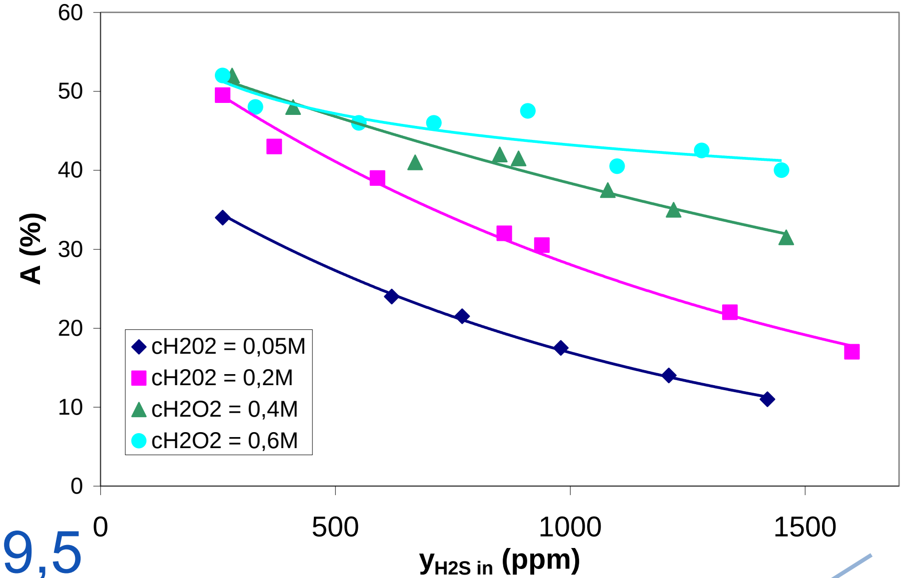
$HS^- + 4\ H_2O_2 \rightarrow SO_4^{2-} + 4\ H_2O + H^+$

Selective removal of H2S from biogas – Effect of c_{H2O2}

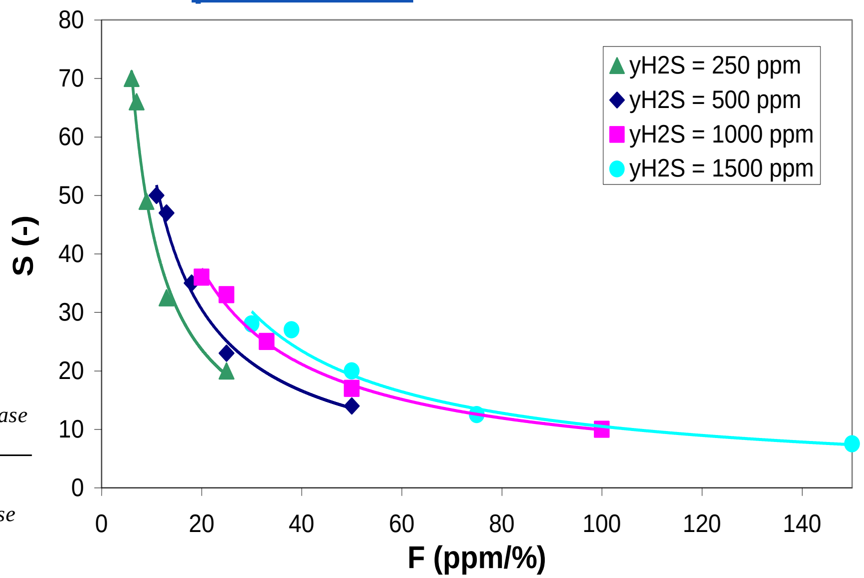
CO_2



H_2S



pH ≈ 9,5



Feed gas ratio **F**

F = $y_{H2S\ in}/y_{CO2\ in}$

Selectivity **S**

$$S = S_{H_2S/CO_2} = \frac{\left(\frac{mol.conc.of\ H_2S}{mol.conc.of\ CO_2}\right)_{liquid\ phase}}{\left(\frac{mol.conc.of\ H_2S}{mol.conc.of\ CO_2}\right)_{gas\ phase}}$$

c_{Na+}=1 M

c_{H2O2}=0.2 M

Advanced Oxidation Process (AOP) for reduction of VOCs

1. Peroxone process ($O_3 + H_2O_2$)

- Dissociation of H_2O_2 and production of HO_2^- :

  $H_2O_2 \rightarrow H^+ + HO_2^-$

- Fast decomposition of dissolved ozone initiated by HO_2^- leading to chain reactions involving free radicals such as $O_2^{-°}$, $HO_2°$ and $HO°$:

  $HO_2^- + O_3 \rightarrow O_2 + HO° + O_2^{-°}$

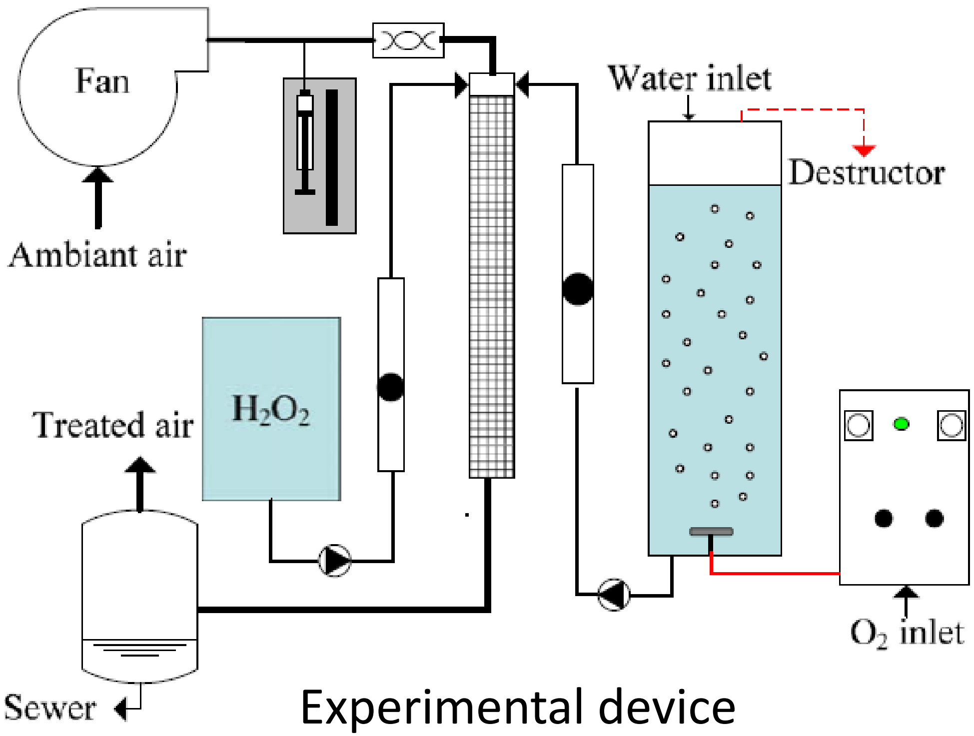
- Oxidation of the VOC by $HO°$

  $\rightarrow$ mineralization to CO_2 and H_2O

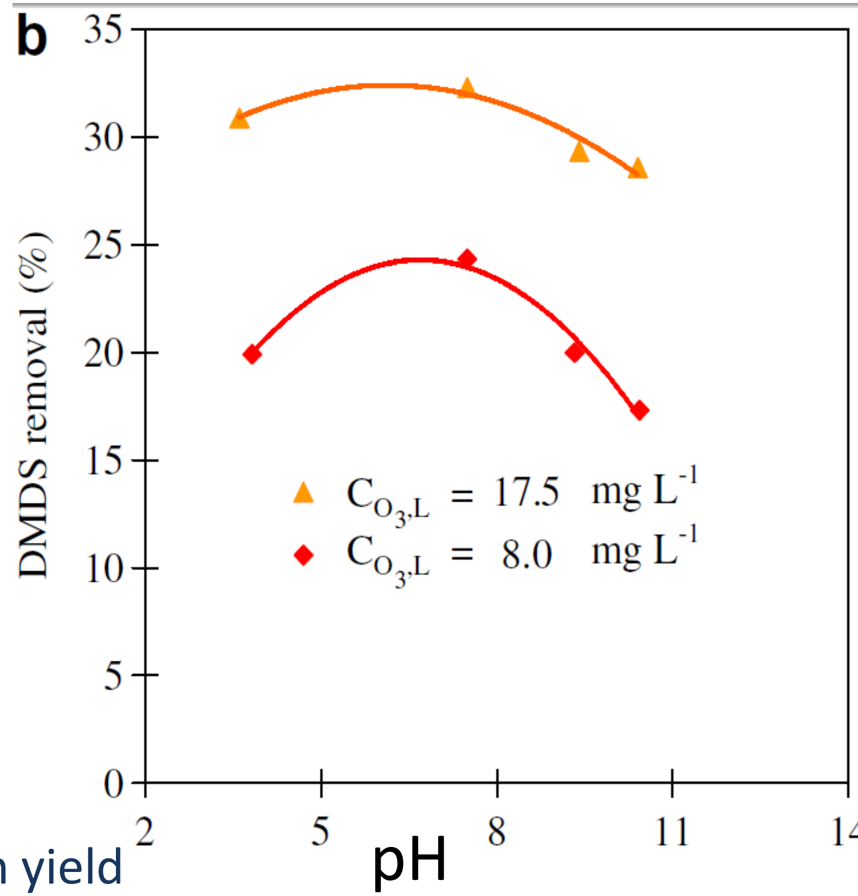
Advanced Oxidation Process for reduction of VOCs

1. Peroxone process ($O_3 + H_2O_2$)

✓ O_3 alone
✓ $O_3 + H_2O_2$



Experimental device



→ F_{H2O2}/F_{O3} ~ 1,5 and pH ~ 8
maximizing the hydroxyl radical production yield

REF: P-F. Biard, A. Couvert, C. Renner and J-P. Levasseur, Chemosphere, Vol. 77 (2009), pp 182-187

Advanced Oxidation Process for reduction of VOCs

2. Fenton + UV process

- Combination of the Fenton reagents (Fe^{2+} and H_2O_2) and light energy generating highly reactive powerful hydroxyl radicals in the liquid phase:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO° + OH^-$$

Fenton reaction-iron catalyzed decomposition of H_2O_2 and oxidation of Fe^{2+}

- Reaction of Fe^{3+} with water which occurs when the light of wavelength 300 to 650 nm is irradiated:

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO° + H^+$$

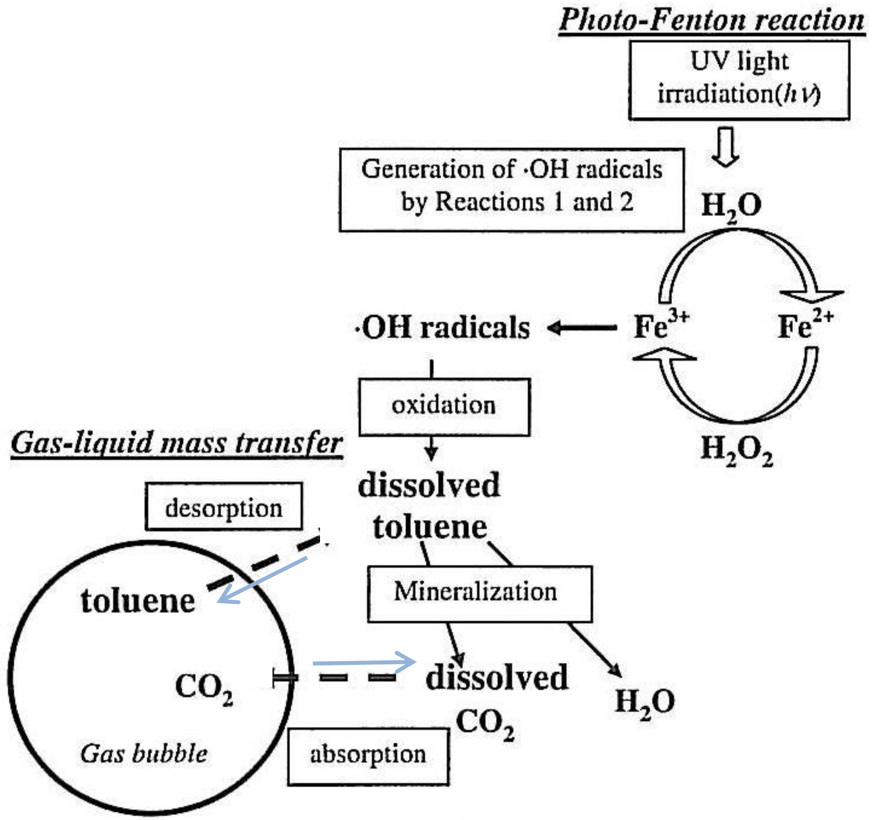
- Fast and non selective attack of VOC molecules by OH°

  → mineralization to CO_2 and H_2O

REF: M. Tokumura, R. Nakajima, H. Tawfeek Znad and Y. Kawase, Chemosphere, Vol. 73 (2008), pp 768-775

Advanced Oxidation Process for reduction of VOCs

2. Fenton + UV process



Conceptual model for degradation of toluene in effluent gas by the photo-Fenton reaction

Concentration in the gas phase

Solubility in the solvent

Mass transfer rate including reaction kinetics of the VOC degradation

→ Powerful photocatalytic degradation technology for VOCs in wastewater

→ Promising technology in the effluent gas treatment

REF: M. Tokumura, R. Nakajima, H. Tawfeek Znad and Y. Kawase, Chemosphere, Vol. 73 (2008), pp 768-775

Advanced Oxidation Process for simultaneous reduction of NOx and SOx - H_2O_2 + UV

Major reaction pathway for removal of NO:

- Photolysis of H_2O_2 producing a lot of HO° free radicals (= initial step)

  $H_2O_2 + h\nu \rightarrow 2\ OH°$

- Oxidation removal of HO° free radicals = leading role

  $NO + HO° \rightarrow HNO_2$

  $NO + HO° \rightarrow NO_2 + H°$

  $NO_2 + HO° \rightarrow HNO_3$

  $HNO_2 + HO° \rightarrow HNO_3 + H°$

- Oxidation removal of H_2O_2 for NO

  $2\ NO + 3\ H_2O_2 \rightarrow 2\ HNO_3 + 2\ H_2O$

- For H_2O_2 concentration exceeding a great value

  → some side reactions

  - example: $HO° + HO° \rightarrow H_2O_2$

REF: Y. Liu, J. Zhang, C. Sheng, Y. Zhang and L. Zhao, Chem. Eng. Journal, Vol. 162 (2010), pp 1006-1011

Advanced Oxidation Process for simultaneous reduction of NOx and SOx - H_2O_2 + UV

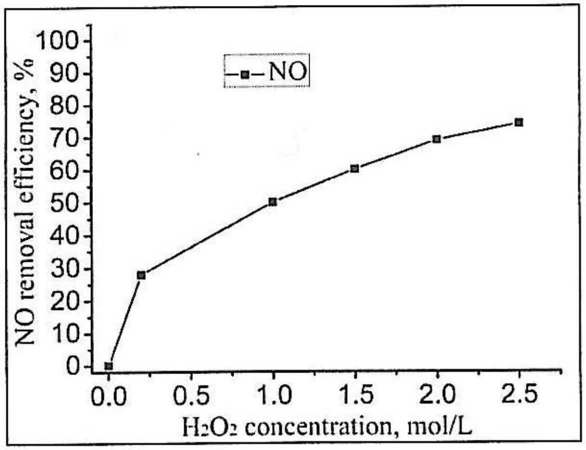


Fig. 3. NO removal efficiencies under different H_2O_2 concentratio

Conditions: UV lamp power, 36W; NO concentration, 456ppm

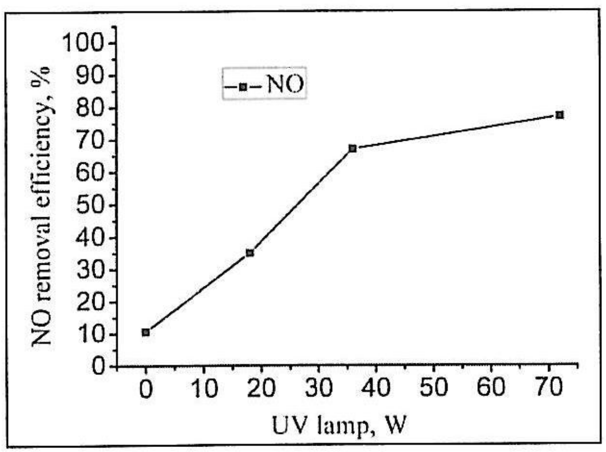
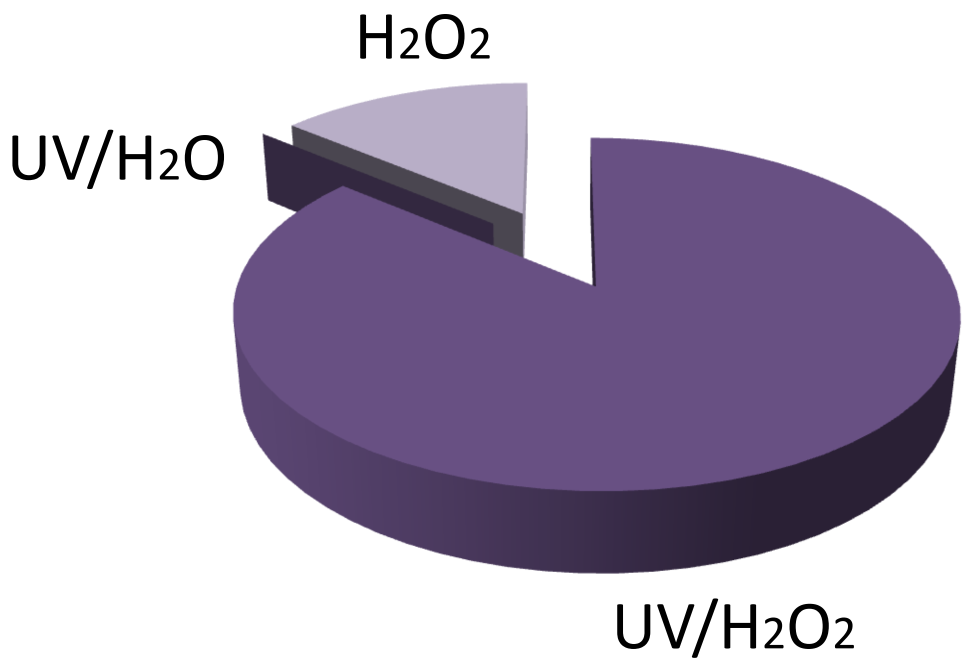


Fig. 4. NO removal efficiencies under different UV lamp powers.

Conditions: H_2O_2, 2.0mol/L; NO concentration, 434ppm.



Removal shares of NO in different run modes

Advanced Oxidation Process for simultaneous reduction of NOx and SOx - H_2O_2 + UV

Major reaction pathway for removal of SO_2:

- Photolysis of H_2O_2 producing a lot of HO° free radicals (= initial step)

  $H_2O_2 + h\nu \rightarrow 2\ OH°$

- hydrolysis reaction of SO_2 in water

  $SO_2 + H_2O \rightarrow HSO_3^- + H^+$

- Oxidation removal of HO° free radicals = leading role

  $SO_2 + HO° \rightarrow HSO_3$

  $HSO_3 + HO° \rightarrow 2H^+ + SO_4^{2-}$

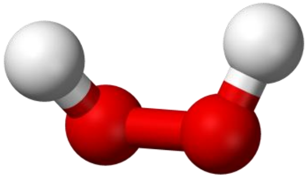
  $HSO_3^- + HO° \rightarrow SO_3^{-°} + OH^-$

  $SO_3^{-°} + HO° \rightarrow SO_4^{2-} + H°$

- Oxidation removal of H_2O_2 for NO

  $SO_2 + H_2O_2 \rightarrow 2\ H^+ + SO_4^{2-}$

CONCLUSIONS



H_2O_2

= interesting agent/additive for wet processes for gaseous pollutants reduction

→ Efficient action (oxygen transfer or reactive radicals)

→ Appliable to various gaseous pollutants

→ Valorizable liquid effluents

or total mineralization

H_2O_2 commercialized processes

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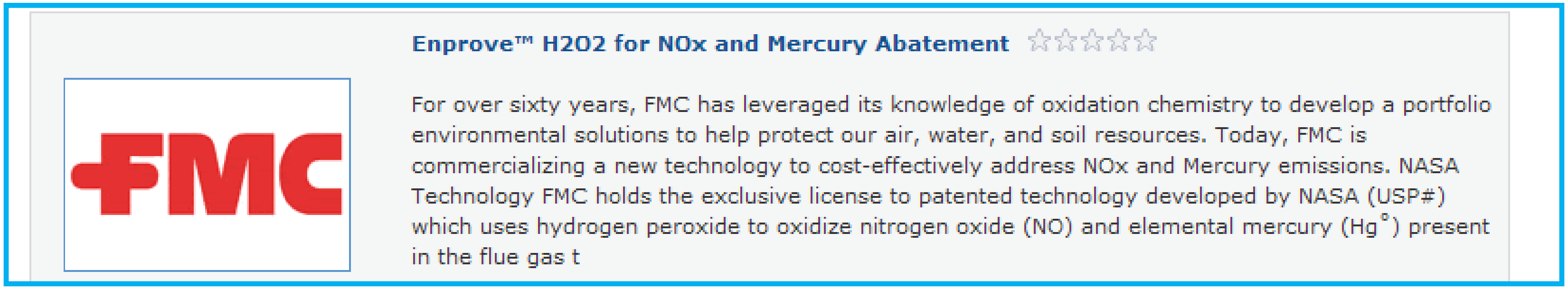
Gas Scrubbing

Control of hydrogen sulfide (H2S) air emissions are a critical part of the design and operation of many industrial operations, including chemical and paper manufacturing, oil refining, and solid waste landfills to name only a few. Hydrogen peroxide has been shown to be a cost effective and environmentally friendly part of H2S gas scrubbing technologies.

Have a question or would like more information?

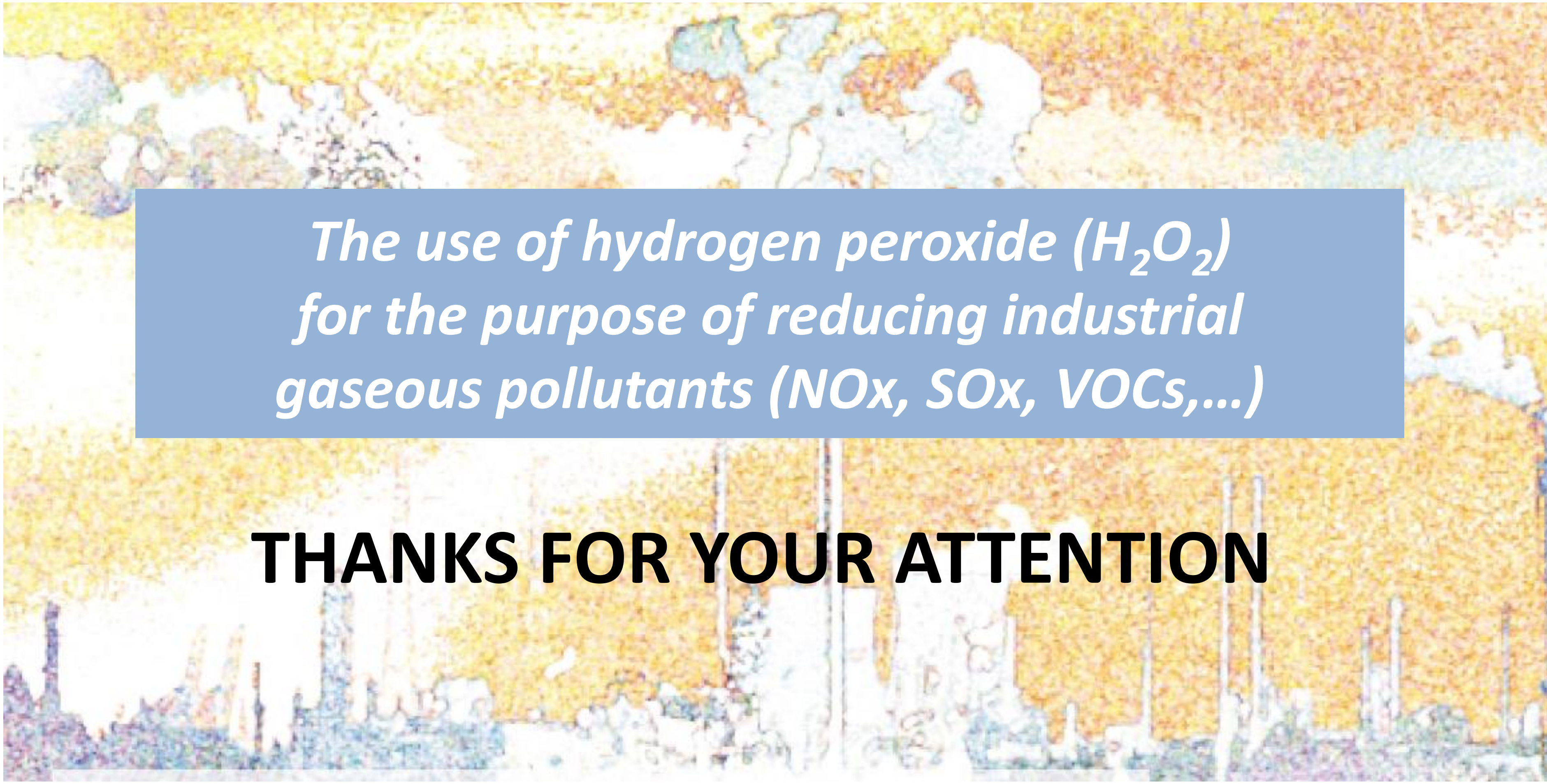
Contact Us Today



FMC

Enprove™ H2O2 for NOx and Mercury Abatement

For over sixty years, FMC has leveraged its knowledge of oxidation chemistry to develop a portfolio environmental solutions to help protect our air, water, and soil resources. Today, FMC is commercializing a new technology to cost-effectively address NOx and Mercury emissions. NASA Technology FMC holds the exclusive license to patented technology developed by NASA (USP#) which uses hydrogen peroxide to oxidize nitrogen oxide (NO) and elemental mercury (Hg°) present in the flue gas t



The use of hydrogen peroxide (H_2O_2)
for the purpose of reducing industrial
gaseous pollutants (NOx, SOx, VOCs,…)

THANKS FOR YOUR ATTENTION

Diane THOMAS

Atmos'Fair

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