

Process Design Technical Note

TECHNICAL NOTE

NO_x SCRUBBING

*P & I Design Ltd.
2Reed Street, Thornaby, Cleveland, TS17 7AF*

*Tel: (01642) 617444
Fax: (01642) 616447
E Mail: jee@pidesign.co.uk*

Contents

- 1.0 Oxides of Nitrogen**
- 2.0 NOx Scrubbing**
- 3.0 Reactions**
- 4.0 Enhanced Oxidation**

NOx scrubbing (Nitric oxide, NO and Nitrous oxide, NO₂)

	NO	NO₂
CAS Number	10102-43-9	10102-44-0
Molecular weight	30	46
Melting Point	-161°C	-9.3°C
Boiling Point	-151°C	21.3 °C

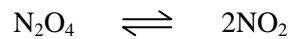
1. Oxides of Nitrogen

The composition of NO_x, Nitrous fumes, normally a mixture of nitric oxide, NO and nitrogen dioxide, NO₂, depends on the source and on the presence or absence of oxygen. Other oxides of nitrogen are not a significant factor in normally encountered NO_x fumes.

The reaction $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ (brown fumes) is instantaneous at normal temperatures.

At 150°C NO₂ starts to decompose to $2\text{NO} + \text{O}_2$ and is complete at 600°C.

Di-nitrogen tetroxide and nitrogen dioxide exist in a strongly temperature-dependent equilibrium.



The pale reddish-brown vapour at 22°C, just above its boiling point, mainly comprises N₂O₄; at 100°C, the darker vapour composition is 90% wt. NO₂: 10% N₂O₄, and at 140°C it is completely dissociated into almost black NO₂ gas.

The **first essential** of any scrubbing of NO_x is to ensure the oxidation of any NO that may be present e.g. from a nitrogen inerted chemical reaction.

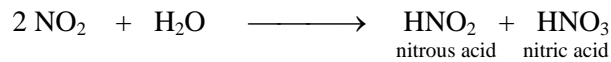
2. NO_x SCRUBBING

There are two main methods of scrubbing nitrogen dioxide; with water or caustic solution. The choice depends on the disposal route available for the spent scrubber liquor. Water is the preferred medium if there is a convenient use for the acid mixture generated, or there is an available waste alkali stream.

3. REACTIONS

3.1 With water

Nitrogen dioxide reacts with water as follows:-

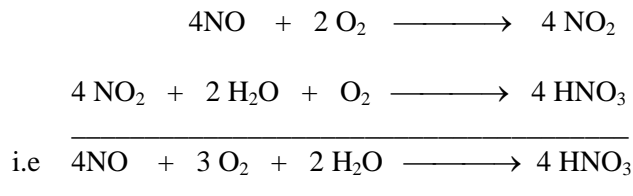


The nitrous acid decomposes rapidly as follows:-



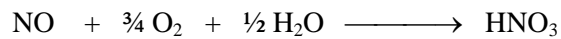
to be followed by further oxidation $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$

Ultimately the overall reaction can be represented by



3.1.1 Heat of Reaction - Water

Heats of formation, ΔH_f @25°C	O_2 (g)	0
	NO (g)	21.60 kcal/gm mole
	(NO_2) (g)	7.96
	H_2O (l)	-68.32
	(HNO_2) (l)	-39.85
	HNO_3 (l)	-41.35

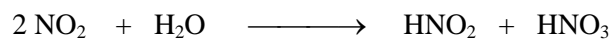


$$\begin{aligned} \text{Heat of reaction} &= -((+ 21.60) + 0.75(0) + 0.5 (- 68.32)) + (- 41.35) \\ &= \underline{-53.91 \text{ kcal/gm mole}} \end{aligned}$$

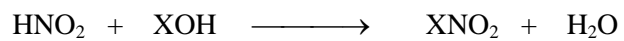
i.e. **54 kcal/gm mole nitric oxide** exotherm

3.2 With alkali solutions

Nitrogen dioxide reacts with water as follows:-

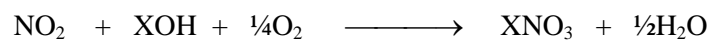


The resulting mixed acids can then react with alkali; both NaOH and KOH



Normally an excess of the nitrate is found, which indicates that some breakdown of intermediate HNO_2 may occur (see section 3.1).

The improbable worst case of total conversion to nitrate would be represented by

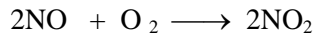


3.2.1 Heat of reaction - sodium hydroxide solution

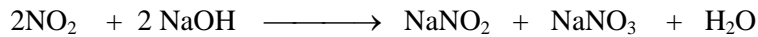
Heats of formation, ΔH_f @25°C	NO (g)	21.60 kcal/gm mole
	NO ₂ (g)	7.96 kcal/gm mole
	NaOH (aq)	-112.19
	NaNO ₂ (aq)	-83.10
	NaNO ₃ (aq 400)	-106.88
	H ₂ O (l)	-68.32

Scrubbing NOx fumes with caustic soda can be represented chemically as follows:-

Case 1



$$\begin{aligned} \text{Heat of reaction} &= - (+21.60 + 0.5(0)) + (+7.96) \\ &= (- 21.60 + 7.96) = \underline{-13.64 \text{ kcal/gm mole}} \end{aligned}$$

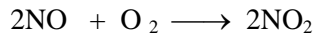


$$\begin{aligned} \text{Heat of reaction} &= - ((2 \times 7.96) + (2 \times (-112.19))) + ((-83.10) + (-106.88) + (-68.32)) \\ &= (208.46 - 258.30) / 2 = \underline{-24.92 \text{ kcal/gm mole}} \end{aligned}$$

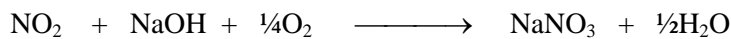
i.e. **25 kcal/gm mole nitrogen dioxide** exotherm

39 kcal/gm mole nitric oxide exotherm

Case 2 – worst case



$$\begin{aligned} \text{Heat of reaction} &= - (+21.60 + 0.5(0)) + (+7.96) \\ &= (- 21.60 + 7.96) = \underline{-13.64 \text{ kcal/gm mole}} \end{aligned}$$



$$\begin{aligned} \text{Heat of reaction} &= - (+ 7.96) + (-112.19) + 0.25(0) + ((-106.88) + (-0.5(68.32))) \\ &= (104.23 - 141.04) = \underline{-36.81 \text{ kcal/gm mole}} \end{aligned}$$

i.e. **37 kcal/gm mole nitrogen dioxide** exotherm

50 kcal/gm mole nitric oxide exotherm

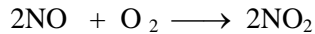
If Case 2 is used as the design case there will be between 0 and a maximum of 25% thermal over-design.

3.2.2 Heat of reaction - potassium hydroxide solution

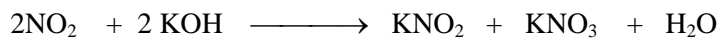
Heats of formation, ΔH_f @25°C	NO_2 (g)	7.96	kcal/gm mole
	KOH (aq 400)	-114.96	
	KNO_2 (aq)	-118.08	
	KNO_3 (aq 400)	-109.79	
	H_2O (l)	-68.32	

Scrubbing NOx fumes with potassium hydroxide solution can be represented chemically as follows:-

Case 1



$$\begin{aligned} \text{Heat of reaction} &= - (+21.60 + 0.5(0)) + (+7.96) \\ &= (- 21.60 + 7.96) = \underline{-13.64 \text{ kcal/gm mole}} \end{aligned}$$



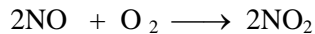
$$\begin{aligned} \text{Heat of reaction} &= - ((2 \times 7.96) + (2 \times (-114.96))) + ((-118.08) + (-109.79) + (-68.32)) \\ &= (214.00 - 296.19) / 2 = \underline{-41.10 \text{ kcal/gm mole}} \end{aligned}$$

i.e. **41 kcal/gm mole nitrogen dioxide** exotherm

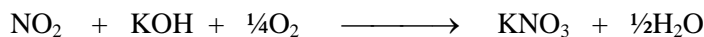
55 kcal/gm mole nitric oxide exotherm

cf 25 kcal/gm mole with sodium hydroxide and NO₂. There would need to be a strong case for preferring KOH over NaOH. e.g. site policy.

Case 2 – worst case



$$\begin{aligned} \text{Heat of reaction} &= - (+21.60 + 0.5(0)) + (+7.96) \\ &= (- 21.60 + 7.96) = \underline{-13.64 \text{ kcal/gm mole}} \end{aligned}$$



$$\begin{aligned} \text{Heat of reaction} &= - (+ 7.96) + (-114.96) + 0.25(0) + ((-109.79) + (0.5(- 68.32))) \\ &= (104.23 - 143.95) = \underline{-39.72 \text{ kcal/gm mole}} \end{aligned}$$

i.e. **40 kcal/gm mole nitrogen dioxide** exotherm

53 kcal/gm mole nitric oxide exotherm

3.3 Solubilities

	Solubility in water @ 0°C g/l	Solubility in water @ 100°C g/l
NaNO₂	721	1632
NaNO₃	730	1800
KNO₂	2810	4130
KNO₃	133	2460

4. ENHANCED OXIDATION

As the first essential of any scrubbing of NOx is to ensure the oxidation of any NO that may be present it may be necessary to enhance the normal air oxidation method by the use of oxidising agents in the scrubbing liquid.

Three practical methods are as follows.

4.1 Hydrogen peroxide

The mechanism can be represented by



The drawback to using this technique is in the storage and handling of the potentially explosive hydrogen peroxide.

4.2 Alkaline potassium permanganate

Nitric oxide is oxidised by potassium permanganate under alkaline conditions to NO₂. Insoluble hydrated MnO₂ is formed, which is an obvious drawback. It is also an oxidising agent, which will react with organic compounds and with HCl to release chlorine.

4.3 Sodium hypochlorite solution

The mechanism can be represented by



This is the preferred method on the grounds of cost, although the handling of the material is not simple and the introduction of Cl⁻ may not be advisable. This will depend on the nature of any other chemical species likely to be present in the system and the difficulty in disposing of the resultant spent chloride-containing liquors.

However, a by-product of this method is the probable formation of nitrous oxide, N₂O, formed by the reduction of nitrite. (Almost pure N₂O can be prepared by heating HNO₃ in the presence of small amounts of Cl⁻).