Process Design Technical Note

TECHNICAL NOTE

CARBON DIOXIDE SCRUBBING

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1.0 Carbon Dioxide Scrubbing

Atomic weight 44.01
Boiling point -78.5 ^{o}C

1.1 Reactions of Carbon Dioxide

1.1.1 Dissolution

The rate at which carbon dioxide comes into equilibrium with carbonic acid and its dissociation products is measurably slow.

$$CO_2 + H_2O \leftrightarrow \underset{\text{carbonic acid}}{H_2CO_3} \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{--}$$

Solubility in water at 760mm Hg pressure:

3.35 g/l	@ 0^{o}C
2.32	@ 10^{o}C
1.69	@ 20^{o}C
1.26	@ 30^{o}C
0.98	@ 40^{o}C
0.02	@ 50^{o}C

1.1.2 Neutralisation

The neutralisation of CO_2 occurs by two paths.

For pH <8

$$CO_2 + H_2O \longrightarrow H_2CO_3 \quad \text{(slow)}$$

$$H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O \quad \text{(instantaneous)}$$

For pH >10

$$CO_2 + OH^- \longrightarrow HCO_3^- \quad \text{(slow)}$$

$$HCO_3^- + OH^- \longrightarrow CO_3^{--} + H_2O \quad \text{(instantaneous)}$$

In the range pH 8 – 10 both reactions are important.

1.1.3 Scrubbing

$$CO_2 + 2\,XOH \longrightarrow \underset{\text{carbonate}}{X_2CO_3} + H_2O$$

This is the principal reaction provided the pH of the scrubbing liquor is kept above pH10.

1.1.4 Caustic solutions

The reaction outlined above take place with NaOH and KOH (X = Na, K).

1.1 Reactions of Carbon Dioxide(Cont.)

1.1.5 Solubilities

	Solubility in water g/l				
	10°C	**20°C**	**30°C**	**40°C**	**50°C**
Na_2CO_3	ca.110				ca.144
$NaHCO_3$	81.5	96	111	127	144.5
K_2CO_3	1080	1105	1137	1169	1212
$KHCO_3$	277	332	391	454	524

If concentrations in the gas are high KOH is preferred to avoid the possibility of crystallisation; otherwise, NaOH is suitable with appropriate scrubber liquor changes before blockages can occur.

1.2 Heat of Reaction

1.2.1 NaOH

Heats of formation, ΔH_f @25°C

$CO_{2\ (g)}$	-94.05	kcal/mole
$NaOH_{\ (aq)}$	-112.19	
$Na_2CO_{3\ (aq)}$	-275.13	
$H_2O_{\ (l)}$	-68.32	

$$CO_2 + 2\ NaOH \longrightarrow Na_2CO_3 + H_2O$$

Heat of reaction = -(-94.05 + (2 x -112.19)) + (-275.13 + (-68.32))
= 318.43 – 343.45
= -25.02 kcal

i.e. **25 kcal/mole carbon dioxide** exotherm

1.2.2 KOH

Heats of formation, ΔH_f @25°C

$CO_{2\ (g)}$	-94.05	kcal/mole
$KOH_{\ (aq)}$	-114.96	
$K_2CO_{3\ (aq)}$	-315.50	
$H_2O_{\ (l)}$	-68.32	

$$CO_2 + 2\ KOH \longrightarrow K_2CO_3 + H_2O$$

Heat of reaction = -(-94.05 + (2 x -114.96)) + (-315.5 + (-68.32))
= 313.97 – 383.82
= -69.85 kcal

i.e. **70 kcal/mole carbon dioxide** exotherm

1.3 Alternative Methods

If carbon dioxide is required for further use monoethanolamine can be used as scrubber liquor as CO_2 is totally soluble and can be subsequently regenerated easily.