Process Design Technical Note

TECHNICAL NOTE

SULPHUR DIOXIDE SCRUBBING

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Sulphur Dioxide

Molecular weight	64.06
Melting Point	-75.5°C
Boiling Point	-10.0°C
Relative density (AIR)	2.264

1. Dissolution

Sulphur dioxide is soluble in water and is present in solution as hydrated SO_2 ($SO_2.H_2O$).

$$SO_2 + H_2O \longrightarrow SO_2.H_2O$$

Solubility in water: 228 g/l @ 0°C,
45 g/l @ 50°C.

It is soluble in sulphuric acid

2. Scrubbing of sulphur dioxide

There are several methods of scrubbing sulphur dioxide. The method selected for a given situation depends on the rate and quantity involved and the availability and site compatibility of the neutralising chemicals required.

2.1 Sodium hydroxide solution

Scrubbing sulphur dioxide with caustic soda can be represented chemically as follows:-

$$SO_2 + H_2O \longrightarrow SO_2.H_2O$$

$$SO_2.H_2O + NaOH \longrightarrow \underset{\text{sodium bisulphite}}{NaHSO_3} + H_2O$$

The **bisulphite** is the predominant species formed in **dilute** solutions.

Further reaction will take place with excess sodium hydroxide:-

$$NaHSO_3 + NaOH \longrightarrow \underset{\text{sodium sulphite}}{Na_2SO_3} + H_2O$$

In the presence of excess sulphur dioxide the following will occur:-

$$2\ NaHSO_3\ (aq) \longrightarrow \underset{\text{sodium disulphite}}{Na_2S_2O_5} + H_2O$$

Under all scrubbing conditions one mole of sulphur dioxide will require one mole of sodium hydroxide for absorption and chemical reaction, irrespective of the final mixture of the sodium salts formed.

2.2 Sodium carbonate solution

Scrubbing sulphur dioxide with sodium carbonate solution can be represented chemically as follows:-

$$2\ SO_2 + 2\ H_2O \longrightarrow 2\ SO_2.H_2O$$

$$2\ SO_2.H_2O + Na_2CO_3 \longrightarrow \underset{\text{sodium bisulphite}}{2\ NaHSO_3} + CO_2 \uparrow + H_2O$$

The CO_2 generated can be vented to atmosphere or to a second scrubber containing sodium hydroxide solution when the following occurs:-

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

The two scrubbers could be switched and the sodium bisulphite solution discarded or further treated with sodium hydroxide solution as follows:-.

$$NaHSO_3 + NaOH \longrightarrow Na_2SO_3 + H_2O$$

2.3 Mixed solution of sodium hydroxide and sodium carbonate

This achieves in a single scrubber the reactions outlined in 2.2. The scrubber will have to be designed for the carbon dioxide absorption case.

2.4 Sodium sulphite solution (Dual alkali system)

Scrubbing sulphur dioxide with sodium sulphite solution can be represented chemically as follows:-

$$SO_2 + H_2O \longrightarrow SO_2.H_2O$$

$$SO_2.H_2O + Na_2SO_3 \longrightarrow \underset{\text{sodium bisulphite}}{2\ NaHSO_3}$$

The resultant bisulphite solution could then be reacted with lime (calcium hydroxide) as follows:-

$$2\ NaHSO_3 + Ca(OH)_2 \longrightarrow Na_2SO_3 + CaSO_4.2H_2O \downarrow$$

The gypsum can be filtered out and the sulphite solution re-used.

This method is suitable for higher emission rates and can be used to scrub a sulphur dioxide / sulphur trioxide mixture.

2.5 Lime slurry

Scrubbing sulphur dioxide with lime slurry can be represented chemically as follows:-

$$SO_2 + Ca(OH)_2 \longrightarrow CaSO_3 + H_2O$$

The calcium sulphite is further oxidised with air

$$2\ CaSO_3 + O_2 \longrightarrow CaSO_4 \downarrow$$ which is filtered off.

3. Heats of Reaction

3.1 Sodium hydroxide solution

Heats of formation, ΔH_f @25°C

SO_2 (g)	-70.94 kcal/mole
$SO_2.H_2O$ (aq)	-146.88
NaOH (aq)	-112.19
$NaHSO_3$ (aq)	*-269.42 (estimated from CODATA)*

$$SO_2\ (g) + NaOH\ (aq) \longrightarrow NaHSO_3\ (aq)$$

Heat of reaction = -(-70.94 + (- 112.19)) + (-269.42)
= 183.13 - 269.42 = <u>-86.29 kcal/mole</u>

i.e **86 kcal/gm mole sulphur dioxide exotherm**

3.2 Sodium carbonate solution

Heats of formation, ΔH_f @25°C

SO_2 (g)	- 70.94 kcal/mole
H_2O (l)	- 68.32
Na_2CO_3 (aq)	-275.13
$NaHSO_3$ (aq)	*-269.42 (estimated from CODATA)*
CO_2 (g)	- 94.05

$$2\ SO_2\ (g) + H_2O\ (l) + Na_2CO_3(aq) \longrightarrow 2\ NaHSO_3 + CO_2 \uparrow$$

Heat of reaction = -(2 x (–70.94) + (-68.32) + (-275.13)) + (2 x (-269.42) + (-94.05)
= 485.33 - 632.89 = <u>-147.56 kcal/mole</u>

i.e**. 148 kcal/gm mole sulphur dioxide exotherm**

3.3 Sodium sulphite solution

Heats of formation, ΔH_f @25°C

SO_2 (g)	- 70.94 kcal/mole
H_2O (l)	- 68.32
Na_2SO_3 (aq)	-264.1
$NaHSO_3$ (aq)	*-269.42 (estimated from CODATA)*

$$SO_2\ (g) + H_2O\ (l) + Na_2SO_3\ (aq) \longrightarrow 2\ NaHSO_3$$

Heat of reaction = -(-70.94 + (-68.32) + (-264.1)) + (2 x (-269.42))
= 403.36 - 538.84 = <u>-135.48 kcal/mole</u>

i.e. 135 kcal/gm mole sulphur dioxide exotherm