ChE 308 Lecture 4

Chlor-Alkali Industries: Caustic soda, Chlorine, **Soda Ash**(cont'd)

Sodium Carbonate Production

SOLVAY TECHNIQUE

• The Overall reaction:

$2 \text{ NaCl} + \text{CaCO}_3 = \text{CaCl}_2 + \text{Na}_2\text{CO}_3$

Besides Soda the Solvay Technique also causes CaCl₂ as a byproduct.

• General bases of the production process:

For the manufacture of 1 ton of Soda Ash by means of SOLVAY TECHNIQUE 1.5 ton salt, approximately 80 m³ water, 1.2 ton limestone and 0.1-0.5 ton coke are required.

SOLVAY TECHNIQUE cont'd

The total process can be divided into the following reaction steps:

1.Brine Cleaning

2.Manufacture of the product

3.Lime Milk preparation

4.NH₃ recovery

1. Brine Cleaning

•Precipitation of Magnesium Hydroxide and Calcium Carbonate by the addition of lime milk and soda solution into the brine:

 $Mg^{2+} + Ca(OH)_2 = Mg(OH)_2 + Ca^{2+}$ $Ca^{2+} + Na_2CO_3 = CaCO_3 + 2 Na^+$

2. Manufacture of the product

• Precipitation of the relatively heavy-soluble bicarbonate (NaHCO3) by the addition of carbonic acid into a salt solution saturated with ammonia:

$$NaCI + H_2O + NH_3 + CO_2 = NH_4CI + NaHCO_3$$

•Thermo decomposition of the bicarbonate:

 $2 \text{ NaHCO3} = \text{CO}_2 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$

3. Lime Milk preparation

•Manufacture of caustic lime:

 $CaCO_3 = CaO + CO_2$

•Manufacture of lime milk:

 $CaO + H_2O = Ca(OH)_2$

4. NH₃ recovery

• Recovery of the ammonia by distillation of ammonium chloride containing mother liquor with lime milk:

$2 \text{ NH}_4 \text{CI} + \text{Ca}(\text{OH})_2 = 2 \text{ NH}_3 + 2 \text{ H}_2 \text{O} + \text{Ca} \text{CI}_2$

•The calcinations also lead to the following parallel reactions, which generate ammonia as well as sodium chloride:

$NH_4CO_3 = NH_3 + CO_2 + H_2O$ $NaHCO_3 + NH_4CI = NH_3 + CO_2 + H_2O + NaCI$

In this side reaction, soda is polluted with sodium chloride

LeBlanc Process

- The LeBlanc process was a batch process in which sodium chloride was subjected to a series of treatments ,eventually producing sodium carbonate.
- In the first step, the sodium chloride was heated with sulfuric acid to produce sodium sulfate (salt cake) and hydrochloric acid gas according to the chemical reaction:

$2 \text{ NaCl} + \text{H}_2 \text{SO}_4 = \text{Na}_2 \text{SO}_4 + 2 \text{ HCl}$

- LeBlanc's contribution was the second step , in which the salt cake was mixed with crushed limestone (calcium carbonate) and coal and fired.
- In the ensuing chemical reaction, the coal (carbon) was oxidized to **carbon dioxide**, reducing the **sulfate** to **sulfide** and leaving behind a solid mixture of sodium carbonate and calcium sulfide (black ash).

 $Na_2SO_4 + CaCO_3 + 2C = Na_2CO_3 + CaS + 2CO_2$

LeBlanc Process cont'd

- Because sodium carbonate is soluble in water, but neither calcium carbonate nor calcium sulfide is, the soda ash was then separated from the black ash by washing it with water.
- The wash water was then evaporated to yield solid sodium carbonate. This extraction process was termed lixiviation.

Uses of sodium carbonate include:

- manufacture of soap, glass, ceramics, paper, sodium hydroxide and sodium hydrogen carbonate (carb. soda)
- petroleum refining
- water softener
- cleaner and degreaser in washing compounds
- removing sulfur dioxide from waste gases in power stations.