MATERIAL FOR EXPERIMENT NO. 10

Continuous process of sodium bicarbonate production by Solvay method

based on: "Podręcznik do ćwiczeń z technologii chemicznej" (Ed. T. Kasprzycka-Guttman), Wydawnictwa UW, Warszawa 1996.
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1. General information.

Sodium carbonate (commonly called as soda ash or washing soda) is the primary product of the chemical industry since the year one. It was used in antiquity for the manufacture of soap and glass, using the mineral appears in some lakes of Africa, Asia and North America being a natural soda, so-called trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$). In Europe, the most important was the soda ash produced in Spain, Normandy and Scotland from the ashes of some marine plants. With the development of industry as well as many wars causing restrictions on trade demand for other methods of producing soda ash grew very rapidly, so that in 1755 the French Academy of Sciences announced a competition for the economical method of producing soda ash from sodium chloride. Only 45 years later, in 1790 the French physician Nicholas Leblanc developed method for satisfying this requirement. His method has been used for over 120 years. Economic considerations supported by modern, for those days, of technical solutions led to new method developed by Ernest Solvay. This method was used for the first time in 1865 in a chemical factory in Belgium Couillet. Leblanc method was completely supplanted by Solvay method which remains to this day, despite the existence of significantly modified its variants, the main means of production of soda ash (about 80% of total production in the world).

It should be mentioned that due to economic and technical aspects plants producing soda ash also produces: caustic soda ($NaOH$), sodium bicarbonate ($NaHCO_3$), crystalline soda ($Na_2CO_3 \cdot 10H_2O$) as well as other products such as $CaCl_2$, $CaCO_3$ and dry ice (CO_2).

The use of soda in different forms mentioned above is very broad. About 30% is used in the manufacture of various inorganic salts such as: borax, sodium sulphite, sodium oxalate, sodium dichromate or sodium nitrate. Soda is used among others in the industry: glass, steel, metal, paper and leather, dyes, rubber, food (approximately 30%) and soap industry and washing powders (about 20%).

2. The process of obtaining soda ash.

The process of obtaining soda ash is, in short, the secretion of a solution composed of water, sodium chloride, ammonia and carbon dioxide sparingly soluble salt of sodium bicarbonate ($NaHCO_3$), but remains in solution of ammonium chloride (NH_4Cl). The order of combining the substrates is as follows: to the saturated aqueous solution of sodium chloride is introduced ammonia, and later in the stage of carbonization the carbon dioxide. The resulting ammonium bicarbonate (NH_4HCO_3) reacts with NaCl to give sparingly soluble $NaHCO_3$ and soluble ammonium chloride (NH_4Cl). The separated sodium bicarbonate is subjected to heating (calcination) and transformed to soda ash and secreted CO_2 is recycled to the process. With NH_4Cl solution ammonia is recovered by adding to a solution of slaked lime ($Ca(OH)_2$) and resulting $CaCl_2$ solution is largely a waste product. As follows from the balance, stoichiometric equation basic raw materials for the production of soda ash are: sodium chloride and calcium carbonate:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$$

In Poland, both of these salts are present in large quantities as the main components of rock salt and limestone.

At various stages of the process consists of the following physical and chemical changes:

1. Preparation of a saturated aqueous solution of sodium chloride:

$$NaCl + H_2O$$

2. Thermal decomposition (calcination) of limestone to carbon dioxide and calcium oxide (burnt lime):

$$CaCO_3 \rightarrow CaO + CO_2$$

3. Preparation of brine solution saturated with ammonia:

$$NaCl + H_2O + NH_3$$

4. The saturation of the resulting solution with carbon dioxide (carbonization). The reaction proceeds in the following stages:

$$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)2CO_3$$
$$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$$

then the resulting ammonium bicarbonate reacts with sodium chloride:

$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$$

5. Filtering and washing the precipitated sodium bicarbonate.

6. Calcination received $NaHCO_3$ to Na_2CO_3:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

7. Regeneration of ammonia from the solution after the separation of $NaHCO_3$:

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

used in this reaction of $Ca(OH)_2$ comes from the next reaction:

8. Receipt of slaked lime:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

As you can see from the above reactions constantly circulating component during production the soda ash is ammonia and it should be to supplement the losses arising from this material, whose size depends on the method of conducting the process.

In the step (1) is produced a saturated solution of sodium chloride by leaching using water, salt bed. Brine used for production of soda ash should have a concentration of approximately 300 - 315 g NaCl/l, contain as little as SO_3 ions and be free of Ca and Mg ions. Too high concentration of Ca and Mg ions leads to a reduction in the quality of the final product. Reducing the concentration of magnesium is obtained by precipitation of magnesium ions in the form of magnesium hydroxide in the reaction of <u>milk of lime</u> (suspension of calcium hydroxide particles in water):

$$Mg^{2+} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{2+}$$

Calcium ions are precipitated by treating a brine with solution of soda ash:

$$Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+$$

Step (2) refers to the unit operation known as the limestone burning. Limestone used in this technology should be of high purity (SiO_2 < 3%, Fe_2O_3/Al_2O_3 < 1.5%). As a result, carbon dioxide is obtained which is used for the carbonization process (step (4)) and calcium oxide used for the recovery of ammonia (step (7)). The operation is being performed in a so-called lime kilns at a temperature of about 1100 °C. The second product, so called burnt lime (CaO) is subjected to the process of the reaction with water (step (8)). This process is carried out in such a way to get a thick slurry of $Ca(OH)_2$ in water (so-called milk of lime).

Step (4) is an essential stage of the production of soda ash. In most modern installations the carbonization is carried out in the counterflow of carbonating columns. The process is carried out at 50 - 60 °C. It should be pointed that there are different views on the mechanism of carbonization, but commonly expressed view is that the summary equation:

$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$$

is the result of several intermediate reactions presented above. Efficiency of carbonization process depends largely on the composition of the crude product precipitating in carbonating columns. And this obviously depends on the solubility equilibrium of these salts. From the perspective of physico-chemical analysis these four salts form a typical configuration of a two reciprocal salt pairs, that is, those within which there is no common ion. In such a system is stable the pair, whose solubility equilibrium is smaller. For the temperature of post-reaction slurry leaving the carbonating column, solubility equilibrium of $NaHCO_3$ + NH_4Cl pair is lower than the solubility equilibrium of NaCl + NH_4HCO_3 pair.

Step (6) is the calcinations of the resulting of $NaHCO_3$. Besides the main reaction:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

there are three side reactions of substances accompanying of sodium bicarbonate:

$$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$$
$$(NH_4)_2CO_3 \rightarrow NH_3 + CO_2 + H_2O$$
$$NaHCO_3 + NH_4Cl \rightarrow NH_3 + CO_2 + H_2O + NaCl$$

Exemplary block scheme of soda production by Solvay method: