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A method of sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) producing by polythermal crystallization from the saturated solution at 100°C which contains NaCl , Na_2CO_3 and NaHCO_3 at the molar ratio $\text{Na}_2\text{CO}_3 : \text{NaHCO}_3 = 2 : 1$ is developed. It is shown that the product of the crystallization represents large crystals of lamellar shape with the length up to 2 mm. Functional scheme of production of $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ based on recycling of mother liquor and mixing with washing water is developed. It allows increasing the product yield from 54.7 to 74.3%.

Introduction. Sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) is mixed carbonate. According to [1, 2], the compound is used in the phosphate-free compositions of environmentally safe cleaning products, in the manufacture of cosmetic products. It is associated with the presence of the positive dermatological effect and its disinfectant properties. Sodium sesquicarbonate is used to desulfurize for acid gas industry, treatment of industrial and municipal waste water, adjusting the pH of water in swimming pools. Large deposits of sodium sesquicarbonate are concentrated mainly in the U.S. and Russia as the trona mineral. However the liberation of a $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ is consuming and energy-intensive, so the interest consists on the obtaining of a synthetic sodium sesquicarbonate. There are some ways to get sodium sesquicarbonate based on a mixture of powdered sodium carbonate and sodium bicarbonate aqueous suspension [3]. The disadvantage of these methods is the presence of the synthesis products $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and NaHCO_3 (in addition to sodium sesquicarbonate) and a low base material. At the same time it has been noted [4] that it is possible to obtain a product containing 96–98 wt % $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ by polythermal crystallization from a saturated solution. However the information about the methods of producing of this very useful for many technical purposes compound (especially for the production of household chemicals) is extremely limited.

The aim of the work was to study the crystallization conditions $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ and a method for its production in the system $\text{Na}_2\text{CO}_3 - \text{NaHCO}_3 - \text{NaCl} - \text{H}_2\text{O}$.

Main part. Sodium sesquicarbonate is prepared in the following way. Carbonate, bicarbonate and sodium chloride are slowly added to the hot water while stirring constantly. The resulting slurry was heated up to 100°C and kept under constant stirring to dissolve the salts. Then the solution was slowly cooled to 35°C for 30 h. This was accompanied by falling of needle-shaped crystals of sodium sesquicarbonate. The resulting product was filtered by suction-type filter and washed with 15%

solution of sesquicarbonate sodium or alcohol to a negative reaction to the Cl^- -ions. The precipitate was dried at room temperature. Mother solution was analyzed for chloride, carbonate and bicarbonate ions and by the addition of NaCl , Na_2CO_3 and NaHCO_3 it was saturated to the desired content. After that the second cycle of crystallization under conditions similar to those in the first cycle of crystallization was carried out.

The content of Cl^- -ions was determined by mercurimetric method, HCO_3^- and CO_3^{2-} – by acid titrimetry [5]. Phase composition was established by XRD diffractometer “DRON-3”, morphology and particle size was determined with a scanning electron microscope Jeol JSM-6510LV (Japan). Thermal analysis of the synthesized products was carried out by the method of differential scanning calorimetry on the measuring apparatus Mettler TOLEDOSTAR. Thermal mapping was carried out at atmospheric pressure in the air in a ceramic crucible at a heating rate of 5 grad/min.

At the Table 1 you can see the solubility [6] of original salts used to produce a saturated solution and crystallization of sodium sesquicarbonate. It shows with the temperature growing the solubility is increasing, while the solubility of NaHCO_3 and NaCl varies slightly. The solubility of sodium sesquicarbonate in terms of anhydrous salt at 30°C is higher than the solubility of NaHCO_3 , but lower than the solubility of Na_2CO_3 . However with the increase in temperature to 100°C solubility of $\text{Na}_2\text{H}(\text{CO}_3)_2$ is close to the solubility of sodium carbonate. On the basis of the Table 1 and the data presented in [4], the composition of saturated solution, which contained 10.7, 4.2, 14.2 wt % Na_2CO_3 , NaHCO_3 , NaCl , respectively at 100°C was calculated. The molar ratio of $\text{Na}_2\text{CO}_3 : \text{NaHCO}_3$ in a saturated solution corresponds to 2 : 1 and exceeds the stoichiometric ratio of these salts in the sodium sesquicarbonate. The presence of excess sodium carbonate content as well as sodium chloride in a saturated solution is devoted to the salting-out effect which they may have as a result of a slight change in their solubility with decreasing temperature from 100 to 35°C (Table 1).

Table 1

Sodium salts solubility

Solubility, wt %	$t, ^\circ\text{C}$							
	30	40	50	60	70	80	90	100
Na_2CO_3	30.2	32.8	32.2	31.6	31.3	31.1	31.0	31.9
NaCl	26.5	26.7	26.8	27.0	27.3	27.5	27.8	28.1
NaHCO_3	10.0	11.3	12.7	14.1	15.5	16.8	18.2	19.6
$\text{Na}_3\text{H}(\text{CO}_3)_2^*$	17.5	19.3	21.1	22.9	24.6	26.4	27.9	29.4

* The solubility of sodium sesquicarbonate in terms of anhydrous salt $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3$.

Nucleation of sodium sesquicarbonate and their growth is possible as a result of supersaturation in the process of cooling the solution because the solubility of the salt when the temperature changes practically twice. The low rate of a saturated solution cooling can bring the crystallization to equilibrium conditions and therefore provide a higher product yield. Calculations show that the yield of sodium sesquicarbonate in the process of its crystallization from a saturated solution equals to 54.7% from sodium bicarbonate.

The composition of the mother solution after the first cycle of crystallization and separation of crystals of sodium sesquicarbonate is presented in Table 2. It shows that the content of sodium chloride and H_2O increases slightly. It shows that the content of sodium chloride and H_2O increases slightly. It can be explained by the change in the weight of the solution as a result of crystallization of $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ crystalline hydrate and formation of precipitation.

After additional saturation at 100°C of mother solution by carbonate, bicarbonate and sodium chloride to a predetermined concentration of sodium salts (Table 2) the solution was cooled in the same way as in the first cycle. The composition of the mother solution after crystallization of the second cycle is shown in Table 2. It shows that the content of sodium salts is on the same level as after the first cycle of crystallization. Calculations show that the returning of the mother solution to the production process reduces the consumption of sodium carbonate and bicarbonate in the production of the saturated solution and increases the product yield to 74.3%.

According to X-ray analysis (Fig. 1) the solid phase obtained in both the first and second cycle contains sodium sesquicarbonate characterized by the presence of the X-ray intensity peaks corresponding to interplanar distances $d = 4.818; 3.26; 3.071; 2.642; 2.506; 2.440; 2.021; 1.954; 1.394 \text{ \AA}$. As a result of an incomplete washing of the product from the mother solution the possible presence of NaCl and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ can take place.

It is shown by the presence of low-intensity reflections corresponding to interplanar distances of the corresponding phases although analytically chloride ions in the solid phase aren't detected.

Table 2

Composition of mother solution

Solution	Components content, wt %			
	Na_2CO_3	NaHCO_3	NaCl	H_2O
Original saturated solution	10.7	4.2	14.2	70.9
– after the first cycle of crystallization	8.4	1.3	15.3	75.0
– after the second cycle of crystallization	8.3	1.2	15.0	75.5

According to the electron microscopy analysis (Fig. 2), sodium sesquicarbonate is some plate-shaped phenocrysts up to 2 mm. There are some small particles (it might be sodium chloride) on their surface. The electron probe microanalysis revealed that the content of NaCl is less than 1.5 wt %.

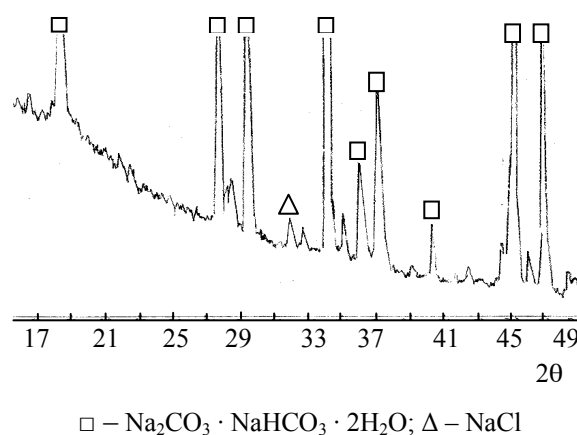


Fig. 1. X-ray pattern of crystallization product

The results of differential scanning calorimetry (DSC) are shown in Fig. 3. The DSC curve indicates the presence of a deep endothermic effect in the temperature range $75\text{--}150^\circ\text{C}$. The weight loss

of the sample is 29.4 wt %. According to calculations the mass loss of sodium sesquicarbonate in the process of its heating is 29.6 wt %. 15.9 wt % are the removing of crystallization water, 13.7 wt % are the decomposition of sodium bicarbonate accompanied by removal of 4.0 wt % of chemically bound water from the structure of sodium bicarbonate and 9.7 wt % of CO_2 . Consequently the product of heating of sodium sesquicarbonate over 150°C is Na_2CO_3 .



Fig. 2. Microphotograph of crystallization product

Based on the experimental data the mass balance of production of 1 t of sodium sesquicarbonate in the first and second cycle of the crystallization was calculated. The results are presented in Table 3. The cited data show that at the implementation of the recycle mother solution allows to reduce the consumption of Na_2CO_3 from 1,750 to 490 kg/t, NaHCO_3 from 680 to

484 kg/t. The introduction to the cycle of additional 20 kg of sodium chloride and 146 kg of H_2O can be explained by the loss of these components during the washing up of the product as well as the expenditure of water on formation of $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$.

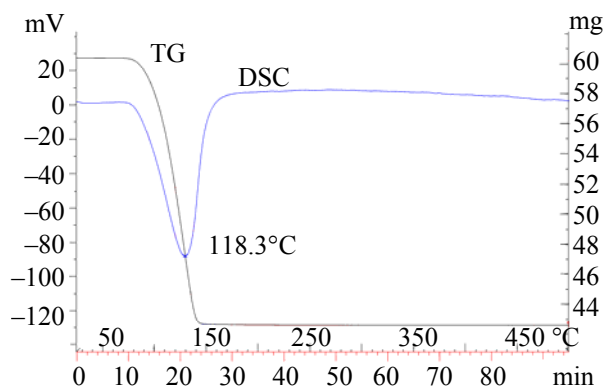


Fig. 3. Dynamic thermogravimetry (TG) and differential scanning calorimetry (DSC) curves of the crystallization product

A functional scheme of the sodium sesquicarbonate production with mother solution recycle which includes saturation of the solution at 100°C with carbonate, bicarbonate, and sodium chloride, polythermal crystallization with a gradual decrease of temperature to 35°C , filtration and washing of the product is proposed on Fig. 4. The precipitation cleaning occurs with a saturated solution of sodium sesquicarbonate at 30°C . The resulted wash water is mixed with mother solution and it is transferred to the additional saturation of the original raw materials.

Table 3

Material balance of sodium sesquicarbonate producing*

Inflow lines	The first cycle, kg	The second cycle, kg	Outflow lines	The first cycle, kg	The second cycle, kg
1. Na_2CO_3	1,750	490	1. Sodium sesquicarbonate	1,000	1,000
2. NaHCO_3	680	484	2. Mother Solution	15,100	15,140
3. NaCl	2,310	20	Including:		
4. H_2O	11,500	146	– Na_2CO_3	1,260	1,257
5. Mother Solution	–	15,100	– NaHCO_3	196	182
Including:			– NaCl	2,290	2,271
– Na_2CO_3	–	1,260	– H_2O	11,354	11,430
– NaHCO_3	–	196	3. Loss of the mother solution in the process of washing	140	100
– NaCl	–	2,290			
– H_2O	–	11,354			
<i>Grand Total</i>	16,240	16,240	<i>Grand Total</i>	16,240	16,240

Notes. The calculation of the material balance excluding product cleaning.

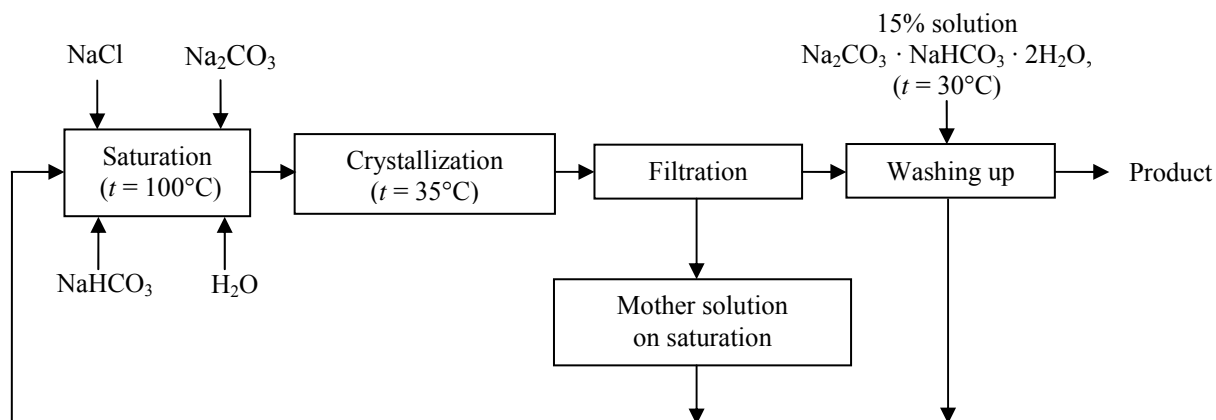


Fig. 4. Functional scheme of the sodium sesquicarbonate producing

Conclusion. A method for sodium sesquicarbonate producing with recycle of mother solution will increase the product yield from 54.7 to 74.3%. It is shown that the implementation of the crystallization process in the polythermal mode and slow cooling of the saturated solution causes the formation of coarse precipitation of sodium sesquicarbonate. Its particles have a plate shape and a length of 2 mm.

References

1. Энергоэкономная технология получения высококачественного кристаллизационного сесквикарбоната натрия [Электронный ресурс]. – Режим доступа: <http://niochim.kharkov.ua/ru/innovations.html#2>. – Дата доступа: 17.08.2010.
2. Порошок на троне [Электронный ресурс]. – Режим доступа: http://www.ecostar.com.ua/index.php?option=com_content&view=article&id=54:2010-07-05-21-47-38&catid=30:the_community&Itemid=2. – Дата доступа: 17.08.2010.
3. Method of producing non-phosphate detergents based on powdered sodium sesquicarbonate: EP 1690923 Ukraine, C 11 D 3/10, C 11 D 11/04 / O. Kachur, W. Lemeshko; BRANDPAT Kancelaria Patentowa; заявл. 15.02.2005; опубл. 16.08.2006 // Bulletin 2006/33 / European Patent Office. – 2006. – № 12/82.
4. Torgeson, D. R. Heats of formation and decomposition of trona / D. R. Torgeson // J. of Industrial and Engineering Chemistry. – 1948. – Vol. 40, № 6. – P. 1152–1153.
5. Шарло, Г. Методы аналитической химии. Количественный анализ / Г. Шарло. – М.: Химия, 1966. – 976 с.
6. Справочник экспериментальных данных по растворимости солевых систем: в 3 т. / сост.: А. Б. Здановский, Е. Ф. Соловьева, Л. Л. Эзрохи, Е. И. Ляховская. – Л.: Гос. науч.-техн. изд-во хим. лит-ры, 1961. – Т. 3. – 950 с.

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