

INORGANIC SYNTHESIS  
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Features of Phase Formation during “Dry” Neutralization  
in the System  $\text{Na}_2\text{CO}_3\text{--H}_2\text{O--H}_x\text{An}$

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**Abstract**—It was found that during the “dry” neutralization of mono- (acetic) and polybasic (orthophosphoric, citric, sulfuric) acids ( $\text{H}_x\text{An}$ ) in the  $\text{Na}_2\text{CO}_3\text{--H}_2\text{O--H}_x\text{An}$  system with a molar ratio  $\text{Na}_2\text{CO}_3/\text{H}_x\text{An} = 1.5\text{--}10.5$  at the interface, sodium sesquicarbonate ( $\text{Na}_2\text{CO}_3\cdot\text{NaHCO}_3\cdot 2\text{H}_2\text{O}$ ) crystallizes as a result of decomposition of  $\text{Na}_2\text{CO}_3$ , dissolution of the resulting  $\text{CO}_2$  in the surface liquid layer and its interaction with  $\text{CO}_3^{2-}$  anions with the formation of an equimolar amount of  $\text{HCO}_3^-$  anions. The hydrated salts formed during the process (phosphates, acetates, citrates, and sodium sulfates) play the role of binders during the aggregation of particles into granules of a 0.106–1.00 mm size.

**Keywords:** dry neutralization, detergents, sodium sesquicarbonate, agglomeration

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Powdered synthetic detergents are multicomponent mixtures, the main share of which (up to 90 wt %) are salts of inorganic and organic acids (builders) [1]. Sodium sesquicarbonate  $\text{Na}_2\text{CO}_3\cdot\text{NaHCO}_3\cdot 2\text{H}_2\text{O}$  is a hypoallergenic and non-caking compound [2, 3], due to which it is increasingly used in builders. Detergents based on this salt are usually produced by simple mechanical blending of sodium sesquicarbonate with other components [4]. In [5] it is shown that  $\text{Na}_2\text{CO}_3\cdot\text{NaHCO}_3\cdot 2\text{H}_2\text{O}$  in the builders can be formed by intensive mixing of a powdery mixture of sodium salts containing  $\text{Na}_2\text{CO}_3$  with a citric acid solution. As the authors note, the reaction mixture upon addition of the acid solution is first moistened, and after a few minutes of blending it turns into a dry powdery state. The “dry” neutralization method consists in preparing powdery builders, when the reaction mixture keeps powdery state upon spraying the acid solutions onto solid alkaline reagents [6].

There are few reports on studies of phase formation in the preparation of builders by “dry” neutralization, although these investigations are of scientific and practical importance. We have found [7, 8] that the

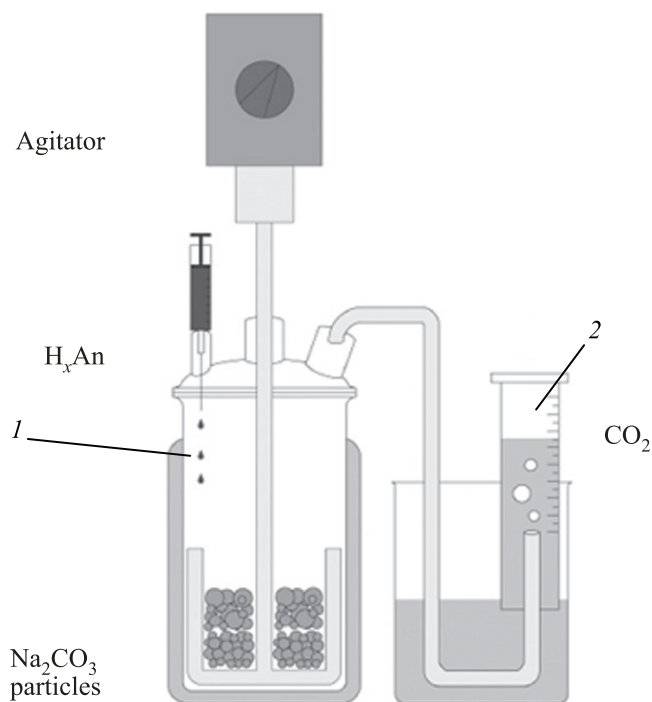
content of sodium sesquicarbonate in builders is determined by such factors as the water content in the reaction mixture, the nature of the acid [acetic, citric, orthophosphoric, sulfuric acid ( $\text{H}_x\text{An}$ )], the  $\text{Na}_2\text{CO}_3/\text{H}_x\text{An}$  molar ratio. It was shown [8] that the formation of the  $\text{Na}_2\text{CO}_3\cdot\text{NaHCO}_3\cdot 2\text{H}_2\text{O}$  structure can occur both by crystallization of sodium sesquicarbonate in the surface liquid layer of  $\text{Na}_2\text{CO}_3$  particles, and by rearrangement of the primary crystal lattice of  $\text{Na}_2\text{CO}_3$  as a result of the substitution of coplanar  $\text{Na}^+$ , coplanar relative to the  $\text{CO}_3^{2-}$  anions, by  $\text{H}^+$  ions.

This work is aimed at studying the phase formation in the  $\text{Na}_2\text{CO}_3\cdot\text{NaHCO}_3\cdot 2\text{H}_2\text{O}$  system during the “dry” neutralization of mono- and polybasic acids.

## EXPERIMENTAL

The initial reagents used were:  $\text{Na}_2\text{CO}_3$  (reagent grade, JSC LenReaktiv),  $\text{H}_3\text{PO}_4$  (food grade, Kazphosphate LLP, food grade), citric, acetic, and  $\text{H}_2\text{SO}_4$  acids (reagent grade, JSC LenReaktiv).

To study the processes proceeding in the  $\text{Na}_2\text{CO}_3\text{--H}_x\text{An--H}_2\text{O}$  system,  $\text{Na}_2\text{CO}_3$  (particle size less than



**Fig. 1.** Setup for “dry” neutralization of  $\text{Na}_2\text{CO}_3$  with acid solutions and determination of the  $\text{CO}_2$  volume. (1) reaction vessel, (2)  $\text{CO}_2$  volume measuring burette.

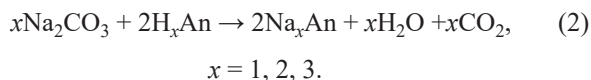
0.1 mm) was brought into reaction vessel 1 (Fig. 1). Using a spray device, an acid solution was supplied in an amount corresponding to the  $\text{Na}_2\text{CO}_3/\text{H}_x\text{An}$  molar ratio of 4.0–10.5 (for tribasic acids), 2.5–6.7 (for diacids), and 1.5–2.0 (for monobasic acids), and the reaction mixture was intensively blended with the same speed in all experiments.

The acid flow was  $2.5\text{--}10.5\text{ mL min}^{-1}$ . The temperature was recorded in the reaction vessel, the volume of evolved  $\text{CO}_2$  was determined from the volume of the displaced saturated  $\text{NaCl}$  solution from burette 2.

The  $\text{CO}_2$  fraction (%) in the gas phase was calculated by the formula

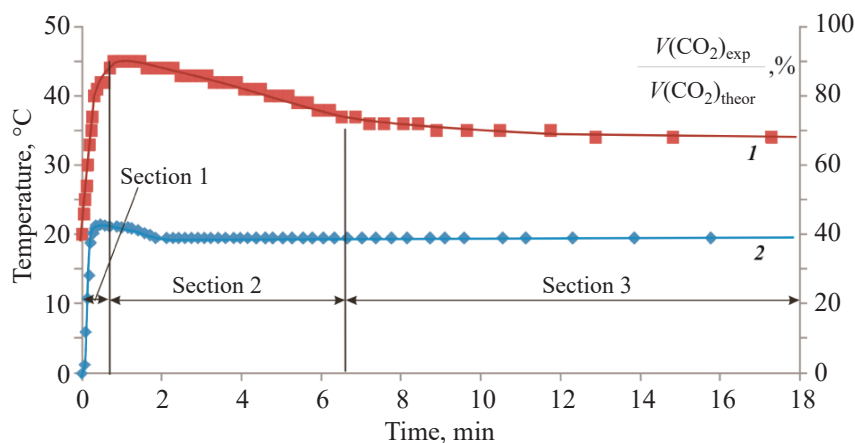
$$v = \frac{V_{\text{CO}_2}^{\text{red}}}{V_{\text{CO}_2}^{\text{theor}}} \times 100, \quad (1)$$

where  $V_{\text{CO}_2}^{\text{red}}$  is the volume of  $\text{CO}_2$  released during the “dry” neutralization, reduced to normal conditions (mL);  $V_{\text{CO}_2}^{\text{theor}}$  is the theoretically calculated volume of  $\text{CO}_2$ , reduced to normal conditions assuming complete decomposition of sodium carbonate in accordance with the process equation

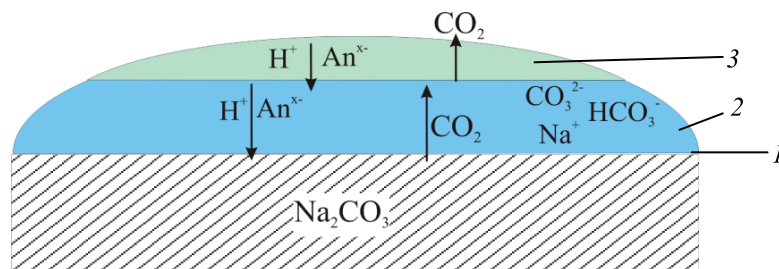


## RESULTS AND DISCUSSION

On the temperature change curve 1 (Fig. 2), three sections can be distinguished, characterizing the stages of “dry” neutralization proceeding at different rates. The first section (40–50 s after the start of the experiment) is characterized by a sharp jump in both the temperature of the reaction mixture from 20 to  $45^\circ\text{C}$  (in terms of 1 mol of  $\text{Na}_2\text{CO}_3$ ) and the volume of released  $\text{CO}_2$ . In the next 6–7 min (second section), a gradual decrease in temperature to  $35\text{--}36^\circ\text{C}$  is observed, after which, within



**Fig. 2.** (1) Temperature in the reaction zone and (2) the proportion of  $\text{CO}_2$  in the gas phase vs. “dry” neutralization time in the system  $\text{Na}_2\text{CO}_3\text{--H}_2\text{O--H}_3\text{PO}_4$ .

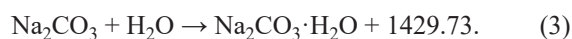


**Fig. 3.** Scheme of the “dry” neutralization process in the system  $\text{Na}_2\text{CO}_3\text{--H}_2\text{O--H}_x\text{An}$ . (1)  $\text{Na}_2\text{CO}_3$  surface, (2) surface liquid layer, (3) liquid phase.

10–15 min (third section), the temperature and volume of released  $\text{CO}_2$  practically do not vary.

The sharp rise in temperature at the first stage is due to the exothermic process of sodium carbonate hydration [Eq. (3)], and the intense release of  $\text{CO}_2$  into the gas

phase occurs as a result of the decomposition of sodium carbonate [Eq. (2)]:



Processes (2) and (3) occur on the surface of

**Table 1.** Solubility of carbonate-containing compounds and sodium salts  $\text{H}_x\text{An}$  vs. temperature

Temperature, °C	Solubility, g/100 g $\text{H}_2\text{O}$							
	$\text{Na}_2\text{CO}_3^a$		$\text{NaHCO}_3^a$	$\text{Na}_3\text{H}(\text{CO}_3)_2^b$	$\text{Na}_3\text{PO}_4^a$		$\text{Na}_2\text{HPO}_4^a$	
	value	solid phase			value	solid phase	value	solid phase
20	21.8	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	9.59	18.3	12.1	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	7.66	$\alpha\text{-Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$
25	29.4		10.38	–	14.0		12.14	
30	39.7		11.1	21.15	16.3		24.2	$\beta\text{-Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$
35	–	–	–	–	–	–	42.9	$\beta\text{-Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$
40	48.8	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	12.7	23.95	20.2	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	55.1	$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$
45	–	–	–	–	–	–	–	–
50	47.3	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	–	26.78	29.4	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	80.2	$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$
55	–	–	–	–	–	–	–	–
60	46.4	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	16.4	22.89	54.3	$\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$	82.9	$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$
65	–	–	–	–	–	–	–	–
70	45.6	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	–	24.56	–	–	87.0	$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$
75	–	–	–	–	–	–	–	–
80	45.1	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	20.2	26.36	68.0	$\text{Na}_3\text{PO}_4 \cdot 6\text{H}_2\text{O}$	92.4	$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$
85	–	–	–	–	–	–	–	–
90	44.9	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	–	27.87	–	–	100.5	$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$
95	–	–	–	–	–	–	105.8	$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4$
100	44.7	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	24.3	29.37	94.6	$\text{Na}_3\text{PO}_4 \cdot 6\text{H}_2\text{O}$	104.1	$\text{Na}_2\text{HPO}_4$

Table 1. (Contd.)

Temperature, °C	Solubility, g/100 g H <sub>2</sub> O					
	Na <sub>2</sub> SO <sub>4</sub> <sup>a</sup>		Na <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ) <sup>c</sup>		C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Na <sup>a</sup>	
	value	solid phase	value	solid phase	value	solid phase
20	19.2	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	33.8	Na <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> )·5.5H <sub>2</sub> O	46.5	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Na·3H <sub>2</sub> O
25	27.9		35.0		–	–
30	40.8		36.4		54.5	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Na·3H <sub>2</sub> O
35	–	–	38.1		–	–
40	48.4	Na <sub>2</sub> SO <sub>4</sub>	39.9		65.5	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Na·3H <sub>2</sub> O
45	–	–	41.8		–	–
50	46.6	Na <sub>2</sub> SO <sub>4</sub>	41.4	Na <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> )·2H <sub>2</sub> O	83	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Na·3H <sub>2</sub> O
55	–	–	41.9		–	–
60	45.3	Na <sub>2</sub> SO <sub>4</sub>	42.5		139.5	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Na
65	–	–	43.2		–	–
70	44.1	Na <sub>2</sub> SO <sub>4</sub>	43.9		146.0	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Na
75	–	–	–	–	–	–
80	43.3	Na <sub>2</sub> SO <sub>4</sub>	–	–	153.0	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Na
85	–	–	–	–	–	–
90	42.7	Na <sub>2</sub> SO <sub>4</sub>	–	–	161.0	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Na
95	–	–	–	–	–	–
100	42.3	Na <sub>2</sub> SO <sub>4</sub>	–	–	170.0	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Na

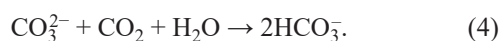
<sup>a</sup> *Spravochnik khimika* (Chemist's Handbook), Nikolsky, B.P., Ed., Leningrad: Chemistry, 1965.

<sup>b</sup> *Spravochnik eksperimental'nykh dannykh po rastvorimosti solevykh sistem* (Handbook of Experimental Data on the Solubility of Salt Systems), Pelsh, A.D., Leningrad: GKHI, 1961.

<sup>c</sup> Apelblat, A., *Citric Acid*, New York: Springer Int. Publ., 2014.

Na<sub>2</sub>CO<sub>3</sub> particles in a liquid film formed at the interface (Fig. 3).

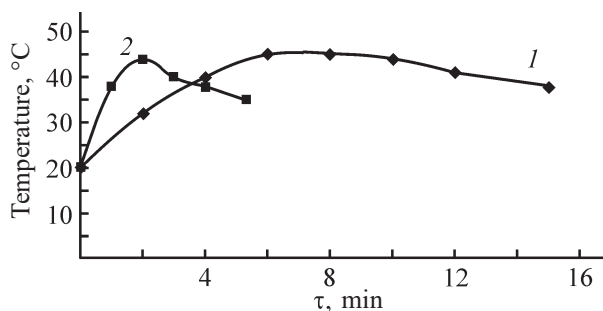
The content of Na<sup>+</sup> and CO<sub>3</sub><sup>2-</sup> ions in the surface liquid layer depends on the temperature, which affects the solubility of Na<sub>2</sub>CO<sub>3</sub>, and the concentration of H<sub>x</sub>An. The released gaseous CO<sub>2</sub> dissolves in the liquid surface layer and interacts with CO<sub>3</sub><sup>2-</sup> anions:



This is assured by experimental data (Fig. 2), according to which the volume of CO<sub>2</sub> in the gas phase does not exceed 40–45% of the calculated one. Consequently, about 55–60% of the produced CO<sub>2</sub> interacts with CO<sub>3</sub><sup>2-</sup> anions. The authors of [9, 10] also

reported the presence of dissolved CO<sub>2</sub> in the liquid film and its partial release into the gas phase in the study of “dry” neutralization of alkylbenzenesulfonic acid with sodium carbonate. The formation of HCO<sub>3</sub><sup>-</sup> ions according to Eq. (4) and the achievement of an equimolar ratio HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> in the liquid layer leads to the formation of a mixed salt of carbonic acid. Similar processes, in particular, the interaction of CO<sub>2</sub> with CO<sub>3</sub><sup>2-</sup> in the liquid film and the formation of sodium sesquicarbonate, also occur during the “dry” neutralization of all the H<sub>x</sub>An acids under study (citric, sulfuric, and acetic).

Saturation and supersaturation of the liquid layer on the surface of sodium carbonate particles with salts of carbonic and other acids leads to their crystallization. NaHCO<sub>3</sub> possesses the lowest solubility



**Fig. 4.** Temperature of the reaction mass vs. the “dry” neutralization time in the system  $\text{Na}_2\text{CO}_3\text{--H}_2\text{O--H}_3\text{PO}_4$ . Acid flow ( $\text{mL min}^{-1}$ ): (1) 2.5, (2) 7.5.

at synthesis temperatures (Table 1), which can crystallize first. Crystallization of  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , due to the close solubility in the temperature range 40–50°C, most likely proceeds simultaneously. As a result of the formation of these phases, the surface of the primary sodium carbonate particles is covered with a layer of crystals of the above salts, and the rate of further interaction of  $\text{H}_x\text{An}$  with  $\text{Na}_2\text{CO}_3$  is determined by the diffusion of  $\text{H}^+$  to the surface of unreacted  $\text{Na}_2\text{CO}_3$ , which limits the process of “dry” neutralization.

The surface area of the solid phase  $\text{Na}_2\text{CO}_3$ , on which the surface liquid layer forms and the reactions proceed, depends on the  $\text{Na}_2\text{CO}_3/\text{H}_x\text{An}$  ratio and is determined by the acid flow. Thus, with an increase in the  $\text{H}_3\text{PO}_4$  solution flow from 2.5 to 7.5  $\text{mL min}^{-1}$ , the heating time of the reaction mixture to 45°C diminishes from 6 to 2 min (Fig. 4).

This dependence is associated with an increase in the reaction zone on the surface of sodium carbonate and, consequently, the interaction rate of the reagents, the achievement of saturation and supersaturation in the  $\text{Na}_2\text{CO}_3\text{--H}_2\text{O--H}_x\text{An}$  system, and the crystallization of sodium salts. With decreasing the temperature, the layer

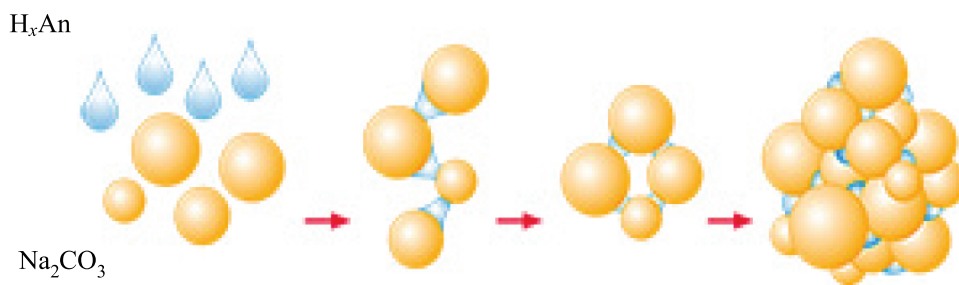
thickness of the crystallizing salts rises as a result of a decrease in their solubility (Table 1). The water supplied with the  $\text{H}_x\text{An}$  solution is spent on the formation of crystalline hydrates of the salts of carbonic and other acids, as a result the synthesis products pass into a powdery state.

It has been shown experimentally [8] that along with physicochemical processes during “dry” neutralization, agglomeration of particles also occurs due to the formation of a binder, derivatives of proton-containing reagents. Upon the  $\text{H}_x\text{An}$  neutralization and the liquid layer saturation with the corresponding salts, the viscosity and the amount of the binder rise, which in turn results in an increase in the deformability of solid particles and the degree of saturation of the powdery reaction mass with the binder. Thus, the formation time of granules is reduced, and granules are formed in the system in accordance with the scheme in Fig. 5. Their size depending on the nature of the binder, the resulting sodium salt of the acid, mainly is of 0.106–1.0 mm.

As noted earlier [8], when using citric acid, the amount of sodium citrate (binder) is formed relatively more than at application of orthophosphoric, acetic, and sulfuric acids. Consequently, the degree of saturation of the powdery mass with the binder and the proportion of the coarse fraction (>1.0 mm) are higher. When free water is bound into crystallization water, the resulting salt bridges are cemented and the bonds between the particles are strengthened, which leads to the stabilization of the granule structure.

## CONCLUSIONS

During the “dry” neutralization of mono- (acetic) and polybasic (orthophosphoric, citric, sulfuric) acids ( $\text{H}_x\text{An}$ ) in the  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$  system with an excess of  $\text{Na}_2\text{CO}_3$ , a mixed salt of carbonic acid  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$  is formed due to the interaction



**Fig. 5.** Granule formation scheme during “dry” neutralization in the system.

of the resulting  $\text{CO}_2$  with  $\text{CO}_3^{2-}$  anions in the liquid layer at the interface, as well as salts of  $\text{H}_x\text{An}$  acids (phosphates, citrates, acetates, sodium sulfates). The mixture of these salts is a powdery product, in which granules with a size of 0.106–1.0  $\mu\text{m}$  predominate. The granule size and size distribution depend on the type of acid salt formed, which acts as binder in agglomerating the particles into granules.

#### CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest requiring disclosure in this article.

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