Synthesis of Li$_5$AlO$_4$ involving a repulpation mixing in a Li$_2$CO$_3$ saturated solution.

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Abstract. Two methods of the pentalithium aluminate synthesis (Li$_5$AlO$_4$) are investigated in the study: by sintering dry mixture of lithium carbonate and hydroxodialuminate and mixture obtained as a result of repulpation mixing in Li$_2$CO$_3$ saturated solution. The pentalithium aluminate synthesis was studied using thermogravimetry and infrared spectroscopy. The researches on the Li$_5$AlO$_4$ synthesis kinetics were carried out using gas chromatography and the pycnometric density, bulk density and tap density were also determined.

1. Introduction
At present time metallic lithium is produced by electrolysis [1]. This method has significant disadvantages. The use of extremely corrosive and hygroscopic salt: lithium chloride, and also the necessity of chloride trapping and neutralizing, the utilization of exhausted electrolyte consisting of eutectic mixture of potassium and lithium chlorides should be referred to them. To obtain a high purity lithium, both initial lithium chloride salt and also electrolyte salts must be additionally purified.

Most of these disadvantages are avoided in the vacuum metal-thermal method of the lithium production. The analysis of studies for the metal-thermal lithium production [2], [3] showed that the use of lithium aluminates, in the place of lithium monoaluminate LiAlO$_2$, and pentalithium aluminate Li$_5$AlO$_4$ as initial materials was outstandingly the most preferable.

It must be pointed out that the method of metal-thermal reduction of lithium monoaluminate has a significant drawback along with the obvious merits: a low lithium content in this compound– 10.45%. From the point of view of the improvement of technical and economic indicators of the reduction process the method of the pentalithium aluminate reduction in which the lithium content amounts to 27.78% is more preferable.

Lithium carbonate sintering with lithium hydroxodialuminate (GODAL) [4] according to the reaction:

$$9\text{Li}_2\text{CO}_3 + \text{Li}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 11\text{H}_2\text{O} \rightarrow 2\text{Li}_5\text{AlO}_4 + 11\text{H}_2\text{O} \uparrow + 9\text{CO}_2 \uparrow \quad (1)$$

should be recognized as the most efficient method to produce pentalithium aluminate.

The application of this method revealed along with the positive side: time decrease of the pentalithium aluminate synthesis to 2 h instead of 16-18 h when using aluminum oxide [5], but also some disadvantages. Original particles sharply differ in particle sizes: Li$_2$CO$_3$ – (1.2 – 2.4) – (1.6 – 3.2)$\times$10$^5$ m; GODAL – (0.3 – 0.06) – (0.4 – 0.02)$\times$10$^5$ m. In this connection the considerable dispersity of fine-dispersed particles of GODAL within the entire capacity of the mixer is observed. Obtaining an homogeneous mixture is then complicated, what results in mechanical losses, the dust loading in the working place requires to use covered gears and a powerful ventilation. Considerable time and high energy consumption are required to reach a proper mixing process. Synthesized pentalithium aluminate has a low bulk density that reduces the efficiency of the vacuum thermal plants upon its aluminothermal reduction.
2. Experimental

Two methods of Li₅AlO₄ synthesis were investigated in this study: on one hand by sintering a dry mixture of lithium carbonate and hydroxodialuminate and on another hand mixture obtained as a result of repulpation mixing in the Li₂CO₃ saturated solution. Repulpation mixing in lithium carbonate–saturated solution prevents solid Li₂CO₃ from passing from the mixture into solution and the solubility of lithium hydroxodialuminate does not exceed 0.005 g/l. Besides, mixing in the saturated lithium-carbonate solution runs considerably more intensively. According to [6], this is mainly attributed to the fact that the liquid injection into the mixture favors the decrease of the electric attraction forces among particles and, consequently, their better dispersion in the mixture. In addition, under the action of capillary forces an increased pressure is formed in thin particles fissures that assists in disengaging particles associated into aggregates and results in component post-grinding. Upon mixing in saturated solution the particle mobility increases that favors, in its turn, a more intensive mixing.

It must also be pointed out that as a consequence of repulpation mixing of original products, their subsequent filtration and drying, every particle of lithium hydroxodialuminate (GODAL) is coated with a lithium carbonate film, i.e. a close contact is formed at the boundaries between powder particles. In this connection the reaction surface sharply increases.

2.1. Synthesis methods

Lithium carbonate of the especially pure grade and “GODAL“ of the following composition: Li₂O = 6.9 mass %; Al₂O₃ = 47.5 mass %; H₂O = 45.6 mass % that complies with Li₂O·2Al₂O₃·10.95H₂O compound were used as initial materials. GODAL was produced according to the method defined in [7], [8].

The amount of initial materials was calculated in compliance with the synthesis reaction equation (see equation 1).

Dry mixing was performed in the mixer of the «drum tumbler» type repulpation one, in lithium carbonate-saturated solution using an agitator. Mixing in saturated solution was performed at a S:L ratio of 1:2; 1:3; 1:4; 1:5. Burden material mixing at a S:L ratio of > 1:4 results in increasing the pulp viscosity and as a consequence, in mixing deterioration. Decreasing the S:L ratio below 1:4 leads to an excessive carbonate solution consumption. Mixing results were controlled by the chemical sample analysis. Samples were treated with water. In this case lithium carbonate having a solubility of 13.3 g/l passes into the solution and GODAL remains in precipitate. The phase relation in samples selected from prepared mixtures was determined by the subsequent solution analysis for lithium and drying up to the GODAL mass consistency and calculating lithium therein. In case of the application of the repulpation mixing technology the burden material homogeneity was achieved in 0.5 h and in case of dry mixing in 5-6 h.

2.2. Analysis

2.2.1. Thermogravimetric analysis.

The thermogravimetric analysis of the mixture of GODAL and lithium carbonate at a molar ratio of 1:1 was carried out in the “DU PONT-1090” plant at the atmospheric pressure. The heating rate was 10 degrees/s. Platinum was used as crucible material. Sensitivity: DTA – 1/5; DTG – 1/15; TG – 200 mg. In the process of linearly programmed heating of the original mixture a series of successive solid-phase chemical transformations takes place which are recorded in curves of the differential-thermal analysis. Within the temperature interval of 100-190°C a low endothermal effect is noted in dry and repulpation mixture that is accompanied by a sample mass loss corresponding to three water molecules and a partial disintegration of the GODAL structure. The second endothermal effect within the interval of 210-295°C is accompanied by the further sample mass loss and corresponds to the complete water removal from the GODAL structure. That well accords with the results of the GODAL differential-thermal analysis performed in study [8]. Within the temperature interval of 310 up to 470°C and of 470 up to 700°C two inadequate exothermal effects are noted in the differential-thermal curve of dry
mixture heating. The first exothermal effect with a minimum at 420ºC is attributed, obviously, to the recrystallization of GODAL X-ray amorphous components obtaining Li and Al oxides mixture from GODAL decomposition products. The second exothermal effect is accompanied by a sample mass decrease corresponding to the CO₂ content in the original mixture that evidences the interaction of lithium carbonate with GODAL thermal decomposition products with the formation of pentalithium aluminate. The process of the α-Li₅AlO₄ synthesis out of the mixture terminates at 700ºC. The further temperature rise leads to an additional exothermal effect in the DTA curve within the temperature interval of 980 – 1,000ºC. This effect is not accompanied by any mass decrease and can be attributed to the polymorphous transformation of α-Li₅AlO₄ to its high-temperature form β-Li₅AlO₄. When comparing the chemical interaction in the dry mixture with the interaction in the repulpation mixture it must be pointed out that the process of repulpation mixing ensures itself the delivery and securing of lithium carbonate particles on the GODAL surface. That assists in activating the solid-phase interaction.

A conclusion can be made on the ground of the analysis results that the synthesis of pentalithium aluminate from dry mixture runs within the temperature interval of 470 up to 700ºC, and from repulpation one within the temperature interval of 310 - 635ºC. Thus, repulpation mixing of initial products (lithium carbonate and GODAL) activates to a significant extent the solid-phase chemical interaction: the reaction rate increases, the pentalithium aluminate synthesis temperature decreases.

2.2.2. Infrared (IR) spectroscopy.

For the IR spectroscopy the reaction mixture was sintered at temperatures of 500, 550, 600, 650, 700, 750, 800, 850 and 900ºC. The sintering time at every temperature was 1 h. Infrared spectra of synthesis products were recorded in the IR spectrometer SPECORD-75JR within the band of wave numbers of 1,600 to 400 cm⁻¹ (6.5 – 25 µm). Samples for taking IR spectra were prepared by mixing weighed specimens with potassium bromide. A pellet of pure potassium bromide was used as a reference standard.

Synthesis products at 500 – 550ºC within the band of 1,480 – 1,410 cm⁻¹ and 1,080 – 1,010 cm⁻¹ have absorption bands characteristic for carbonates [9]. That confirms the data of the X-ray phase analysis that synthesis products at 500 and 550ºC contain Li₂CO₃ residues.

2.2.3. Research of the Li₅AlO₄ synthesis kinetics applying the gas chromatography method.

The interaction reaction of lithium carbonate with GODAL dehydrated as a result of the thermal GODAL decomposition is accompanied by the release of gaseous carbon dioxide. Therefore the rate of the pentalithium aluminate synthesis can be judged by the variation of the CO₂ concentration in the gas phase. The comparative analysis of the pentalithium aluminate synthesis kinetics was performed using gas chromatography.

Inertial argon-carrier gas was let pass through the quartz reactor inside which there is an alumina fiber boat with burden material (4 g) at a given rate.

The reactor was heated in the tube resistance furnace. The temperature was controlled and regulated by means of a chromel-alumel thermocouple. After the set temperature had been achieved, the furnace was moved along the quartz reactor to the area of the boat location and sampling was started. Sampling was carried out in three minutes. The gas mixture analyzed was investigated after drying for the CO₂ content. A strictly controlled sample of 20 cm³ was subjected to analysis. The results of the chromatographic analysis for CO₂ in the form of a D.C. signal were plotted in the data recorder.
2.2.4. Research of physical and technological properties.
When using pentalithium aluminate as initial a raw material for vacuum thermal production of lithium, its physical and technological properties are of a major importance. First of all that applies to the vacuum thermal gear efficiency. To that end a comparative analysis of physical and technological properties of Li$_5$AlO$_4$ powders synthesized from dry and repulpation mixtures was performed at various temperatures.

The pycnometric density was determined in kerosene. The measured pycnometric density of Li$_5$AlO$_4$ synthesized from the repulpation mixture confirms the data of the X-ray phase analysis that α-Li$_5$AlO$_4$ is formed at 635°C and its polymorphous transformation to β-Li$_5$AlO$_4$ terminates at 700°C. Upon the Li$_5$AlO$_4$ synthesis from the dry mixture the crystallization of the α-phase of pentalithium aluminate completes at 700°C and within the temperature interval of 750 - 900°C the process of the polymorphous transformation of α-Li$_5$AlO$_4$ to β-Li$_5$AlO$_4$ takes place. Since lithium carbonate sintering with GODAL both in dry and also in repulpation mixtures was performed for 2 h at every temperature this phenomenon confirms that the repulpation mixing of initial products accelerates the Li$_5$AlO$_4$ synthesis.

**Figure 1.** Li$_5$AlO$_4$ synthesis kinetics (dry mixture)
3. Results
The relation of the tap density and bulk density of pentalithium aluminate as a function of the synthesis temperature was studied here. The obtained results are presented in Figure 1. The both indicators in the samples obtained from the repulpation mixture increase with the temperature rise although the pycnometric density remains unchanged after 700°C. The research of sizes of pentalithium aluminate particles demonstrated that with the temperature rise the particle size increased from \((0.8 – 1.2)\times10^{-5}\) m at 700°C to \((2.0 – 2.4)\times10^{-5}\) m at 900°C. Upon the phase transition the \(\beta\)-\(\text{Li}_5\text{AlO}_4\) «bunches» collective crystallization occurs up to sizes of \((6.8 – 8.0)\times10^{-5}\) m. Besides, particles in the \(\beta\)-phase vary their form changing-over to the isometric rounded.

4. Conclusions
Thus, having conducted the comparative analysis of the pentalithium aluminate synthesis using dry and repulpation mixtures it became obvious that the repulpation mixing of initial products favors a more uniform mixing, provides the delivery and securing of lithium carbonate particles on the GODAL surface that activates to a significant extent the solid-phase chemical interaction:
- the rate of the chemical reaction run increases;
- the temperature of the pentalithium aluminate synthesis decreases;
- the bulk density of pentalithium aluminate increases.

Acknowledgments
This research was carried out with financial support of the National University of Science and Technology “MISiS” Creation and Development Program.

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