THERMODYNAMIC ANALYSIS OF THE FORMATION OF CALCIUM BORATES IN THE $CaCO_3$ – m H_3BO_3 SYSTEM

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Abstract

Agglomeration of phosphorite fines is carried out at a fairly high temperature (1200-1300º) with a consumption of 6-8% of coke breeze per each ton of feedstock. The resulting agglomerate is not very strong. The yield of suitable agglomerate does not exceed 50%. The purpose of this study was to find solutions to reduce the agglomeration temperature of phosphorite fines, which are more fusible compared to calcium silicates. The article presents the results of research on the thermodynamic analysis of the formation of calcium borates in the CaCO3 – m H3BO3 system. The studies were carried out by calculating ΔG^o, as well as using the second order planning method. Found that the formation of calcium borate (CaO. B2O3) is more preferable than calcium silicate (CaO• SiO2). Regardless of the temperature (1000.1100 and 1200ºC), the dependence ΔG^o - f (β) has an extremum at β = 1. In this case (at β = 1) the reaction CaCO3+2H3BO3=CaB2O4+3H2O+CO2 with the formation of CaB2O4 is characterized by a lower thermodynamic probability of all other reactions. To comply with the conditions of the sintering temperature from 1000 to 1200 ° C and ΔG -250 kJ and less, the process must be carried out at β = 0.76-2.0.

INTRODUCTION

The modern phosphorus and phosphate-fertilizer industry is experiencing a shortage of high-quality mineral raw materials and fuel and energy resources. A decrease in the phosphate raw material P_2O_5 and frequent fluctuations in its composition, depending on the deposits, leads to overspending of material and energy costs and other costs, causing a violation of the ecological situation of the environment and a decrease in technical and economic indicators of production, which requires cardinal solutions to these issues. This question was observed in works of such scientists as Kabdrakhmanova S. (2003), Alteev T. (2002), Bakhov J. (2003), Tleuov A.S., Shevko V.M., Tleuova A.Kh. (2002), Arlievsky M.P., Podgornykh A.Yu., Shlyapintokh L.P. (2002), Bugenov E.S., Dzhusipbekov U.Zh. (2005), Tleuov A.S., Tleuova A.Kh. (2001), Dmitrevsky B.A. (2003), Angelov A.I., Ozerov S.A., Sobolev N.V. (2003), Klassen P.V., Brodsky A.A. (2003), Kazakbaeva D.T., Negmatov S.S., Yusupov M.U. (2003), Klassen P.V., Zavertaeva T.I., Adamov E.A. (2003), Khuziakhmetov R.Kh., Khaidarov R.A., Naumkina N.I. et al. (2003), Zhekeev M.K. (2004), Udalova Yu.P. (2000) and others.

Phosphorus is of great importance for human life, since without organophosphorus compounds the process of carbohydrate metabolism in the brain tissues could not take place. In addition, it is necessary as a fertilizer for the soil, as a feed additive for animals, as organophosphate insecticides for the control of agricultural pests.

A significant amount of phosphates is used in food, pharmaceutical, metalworking, phosphoric, petroleum and other industries.

The intensive development of the phosphorus industry in the 70-80s of the last century led to the gradual production of phosphorites with a high content of the target component (more than 28% P_2O_5) and, accordingly, the accumulation of refractory ores of complex mineral and chemical compositions. The use of these ores as raw materials for electrothermal processing requires their preliminary thermal preparation and refinement by removing carbonates and other volatile impurities undesirable for the electric sublimation of lump ore into elemental phosphorus.

In this regard, the developed and improved technologies and processes of thermal preparation of phosphate raw materials, as well as thermal units to achieve these goals must be

effective both from an environmental and economic point of view, ensuring the maximum temperature uniformity throughout the entire layer of the fired material, a high degree of decarbonization phosphorites and the minimum yield of fines return and production safety.

At one time, in the dumps of phosphorus plants of the Republic of Kazakhstan, about 5.5 million tons of phosphorite fines were accumulated, which is not inferior to marketable ore in terms of P_2O_5 content sufficient for the production of more than 400 thousand tons of yellow phosphorus.

For the disposal of phosphorite fines of the 0-10mm class, located in the dumps of the mining industry, which is of great national economic importance from both economic and environmental points of view, in the south of Kazakhstan, the production capacity of the agglomeration process of this fines was mastered to obtain yellow phosphorus, phosphoric acid and technical salts at the Novo-Dzhambul phosphoric plant.

A distinctive feature of this plant from other phosphorus enterprises is that it operates on agglomerate obtained in the process of sintering fine fractions (0-10 mm) in an AKM-312 sintering machine, and not on natural lump ore. With the development of the agglomeration process, the problem of using phosphorite fines formed in the mines of the Karatau basin during the extraction and preparation of commercial ore with various constituent compounds (with different acidity modules) for electrothermal processing into yellow phosphorus was solved. From what has been said, it follows that the issue of the phosphate base for this production is being resolved.

However, the experience of the enterprise showed that the sinter production process is characterized by a low yield of a suitable product and the formation of about 50% of fines return, which requires additional fuel and energy costs for its re-melting in order to obtain a liquid-phase eutectic, which plays the role of a binder when cooling sinter.

The low yield of finished products of the sinter shop of the Novo-Zhambyl phosphoric plant is primarily determined by the insufficient strength of the sinter, which worsens the technical and economic indicators of its production and requires solutions to increase the yield of suitable sinter with a simultaneous decrease in fuel and energy costs.

In this regard, increasing the strength of the agglomerate is the most important task, which requires the development of methods for increasing the strength of the agglomerate and improving the technical and economic indicators of its production.

Within the framework of the production development program for the near future, it is planned to expand the production complex, reconstruct, modernize and expand the production capacities of existing production enterprises, and expand the product markets. At present, the efforts of scientists, designers, designers, as well as engineering and technical workers of chemical plants are aimed at improving the existing methods of preparation and processing of phosphate raw materials for phosphorus, finding new technological methods for obtaining phosphorus, disposing of production waste and creating a waste-free technology. The complexity of the processes is due to the quality of the feedstock sent for processing (Bardin, 1963).

One of the industrially mastered methods of agglomeration of raw material fines, i.e. sintering on sintering machines. Known research and experience in the industrial operation of sintering installations of the firm TVA (USA) for sintering small phosphate materials obtained from Tennessee phosphorites (Shout, 1950).

The history of the development of agglomeration production is quite rich in the proposed methods of agglomeration and the designs of devices for their implementation. For example, a circular sintering machine with a central flue has been developed. Methods and designs have been patented (devices for sintering in rotary kilns. There are proposals for the agglomeration of ores in shaft furnaces and in installations with a suspended bed, patents have been obtained for the production of sinter using electricity, etc. However, the most widespread both in our country and for abroad received agglomeration with air suction from top to bottom on the grate of the conveyor sintering machine (Wegman, 1974).

The advantages of straight conveyor sintering machines include the continuity of the sintering process, which ensures a high utilization rate of equipment in time, a high level of mechanization of the technological process with the possibility of maximum automation of its control and management, a relatively simple machine design that allows, with an increase in its linear dimensions, power.

Since the invention of the sintering process, sintering equipment has changed and the sintering technology has been greatly improved. A great contribution to the development of the theory of sintering, increasing the productivity of sintering plants and improving the quality of the sinter was made by: Soviet scientists and practitioners-sinters. Many activities developed in the CIS have become the property of the world practice: the production of fluxed and highly basic agglomerates, the use of lime to intensify the sintering process, heating-sintering charge, two-layer sintering, combined heating of the sintered layer of the charge, stabilization of the agglomerate by size, cooling-sintering sinter on a sinter and others. Currently, the industry uses methods for the production of an agglomerate of two different basicities, the use of oxygen to intensify the sintering process during the ignition period, heat treatment of the agglomerate (Blann, 1967). Measures are being developed and undergo industrial tests to increase the efficiency of sinter production, such as increasing the height of the sintered layer of the charge, supplying heated air into the layer, preliminary pelletizing or lining of the charge, especially containing finely ground concentrates, rolling part of the fuel and flux onto the surface of the charge granules. Due to the shortage of coke breeze, intensive research is underway to find other types of sinter fuel and industrial tests of effective substitutes for metallurgical coke. It is necessary to develop and master methods for the production of metallized agglomerate, two-zone agglomeration with air enrichment with oxygen, sintering of mixtures under pressure. From foreign practice, research and experience in the industrial operation of sintering plants manufactured by TVA (USA) for sintering small phosphate materials obtained from Tennessee phosphorites are known (Tyurenkov, 1943).

The agglomeration process involved the products of washing and beneficiation of Tennessee phosphorites, the so-called sands of three varieties. On the basis of the positive results of laboratory studies of the agglomeration of phosphorus raw materials in a rotary kiln, one of the rotary kilns for limestone burning was proposed for this process after reconstruction.

The main difficulty arising during agglomeration in rotary kilns is the formation of deposits on the lining of the rotary kiln, which must be removed every 5-6 hours of operation of the unit. Serious difficulties are caused by the formation of cakes, which require stopping the furnace to remove them, as well as high wear of the furnace lining (Blann, 1967).

The TVA company developed a technology for agglomeration of these materials of less than 10 mm class on grate bars with air suction through the sintered layer of charge material. Based on the results of laboratory studies, a plant was designed with a full cycle of phosphorite agglomerate production by this method.

MATERIALS AND METHODS

Agglomeration of phosphorite fines is carried out at a fairly high temperature (1200-1300º) with a consumption of 6-8% of

coke breeze per each ton of feedstock. In this case, the resulting agglomerate does not have high strength. In this regard, the yield of suitable agglomerate does not exceed 50% (Kunaev & Shumakov, 1982). Therefore, at present, it is relevant to search for solutions to reduce the sintering temperature of phosphorite fines (with a simultaneous decrease in coke consumption) and increase its strength. To lower the sintering temperature, the presence of a substance in the charge is necessary, which, when interacting with phosphorite, can form more fusible compounds in comparison with calcium silicates. Such substances include calcium borates ($CaO \cdot B_2O_3$), ($CaO \cdot 2B_2O_3$), ($2Ca \cdot B_2O_5$, ($3CaO \cdot 2B2O_3$) for which the melting point is, respectively: 1159 ° C, 989 ° C, 1311 ° C, 1480 ° C (Roine, 2002). For comparison, the melting point of $CaO \cdot SiO_2$ is 1544 ° C, $2CaO \cdot SiO_2$- 2130º C (Babushkin, Matveev, Mchedlov & Petrosyan, 1986). From a thermodynamic point of view, the formation of calcium borates is more likely than the formation of calcium silicates (Table 1)

Table 1. Influence of temperature on Δ G (kJ / mol) formation of silicate and calcium borate.

Reaction	Temperature, ° C						
	500	700	900	1100	1300	1500	1700
$CaO+B_2O_3= CaO \cdot B_2O_3$	-121,6	-113,2	-110,1	-103,8	-105,2	-111,6	-119,7
$CaO+ SiO_2= CaO \cdot SiO_2$	-90,8	-90,8	-90,8	-90,7	-90,7	91,0	-91,5

In this regard, the use of boron oxide in the agglomeration of phosphate raw materials (phosphorite fines) will reduce the process temperature and save fuel ΔGº.

RESULTS AND DISCUSSION

The article presents the results of a thermodynamic analysis of the formation of calcium borates by the interaction of calcium carbonate with boric acid. The research was carried out using the HSC-5.1 software package (Reaction Egutions subroutine) (Roine, 2002). The influence of temperature on the thermodynamic possibility ΔGº of the formation of calcium borates at the interaction of calcium carbonate with boric acid was determined. The following reactions were considered:

1. $CaCO_3+4H_3BO_3=CaB_4O_7+6H_2O+CO_2$;
2. $CaCO_3+3,5H_3BO_3=0,75CaB_4O_7+ 0,25CaB_2O_4 +5,25H_2O+CO_2$;
3. $CaCO_3+3H_3BO_3=0,5CaB_4O_7+ 0,5CaB_2O_4 +4,5H_2O+CO_2$;
4. $CaCO_3+2,5H_3BO_3=0,25CaB_4O_7+ 0,75CaB_2O_4 +3,75H_2O+CO_2$;
5. $1,25CaCO_3+2H_3BO_3=0,75CaB_4O_7+ 0,125CaB_2O_4 +3H_2O+1,25CO_2$;
6. $1,5CaCO_3+2H_3BO_3=0,5CaB_4O_7+ 0,15CaB_2O_4 +3H_2O+1,5CO_2$;
7. $1,75CaCO_3+2H_3BO_3=CaB_4O_7+ 0,125CaB_2O_4 +2,5H_2O+1,75CO_2$;
8. $2CaCO_3+2H_3BO_3=Ca_2B_2O_5 +3H_2O+2CO_2$;
9. $CaCO_3+2H_3BO_3=CaB_2O_4 +3H_2O+CO_2$;
10. $2,25CaCO_3+3H_3BO_3=0,75Ca_2B_2O_5+ 0,25Ca_3B_2O_6 +3H_2O+2,25CO_2$;
11. $2,5CaCO_3+3H_3BO_3=0,5Ca_2B_2O_5+ 0,5Ca_3B_2O_6 +3H_2O+2,5CO_2$;
12. $2,75CaCO_3+3H_3BO_3=0,25Ca_2B_2O_5+ 0,75Ca_3B_2O_6 +3H_2O+2,75CO_2$;
13. $3CaCO_3+3H_3BO_3=Ca_3B_2O_6 +3H_2O+3CO_2$.

The temperature range of research is 300-1200º C. Figure 1 shows the effect of temperature on ΔGº, and in Figure 2 - ΔHº of the considered reactions. Figure 1 shows that all reactions are possible starting from 300 ° C. With increasing temperature, the equilibrium of the reactions shifts noticeably to the right. For a technological sintering temperature of 1200 ° C, the values of ΔG ° reactions have the following values (table 2).

Table 2. The value of ΔGº reactions at 1200º C.

Reaction	1	2	3	4	5	6	7	8	9	10	11	12	13
ΔG°, kj	-332,7	-309,6	-286,6	-263,5	-240,4	-273,3	-306,2	-339,0	-371,8	-396,2	-420,5	-448,8	-469,2

From Figure 1 it follows that the interaction between $CaCO_3$ and H_3BO_3 in all the considered reactions occurs with heat absorption. The observed thermal effects are associated with the melting of individual calcium borates and their mixtures. According to the obtained ΔGº data, we found a relationship between ΔGº and the molar ratio BaO / CaO = β of reaction 1-13 (Figure 1).

Figure 3 shows that regardless of the temperature (1000.1100 and 1200ºC), the dependence ΔGº - f (β) has an extremum at β = 1. In this case (at β = 1) the reaction $CaCO_3+2H_3BO_3=CaB_2O_4+3H_2O+CO_2$ with the formation of C CaB_2O_4 is characterized by a lower thermodynamic probability of all other reactions.

Bearing in mind the complex nature of the dependence ΔGº– f (T, β), further study of the interaction in the $CaCO_3$-H_3BO_3 system was carried out using the second-order rotational planning method

(Box-Hunter plans) (Akhazarova & Kafarov, 1978). In this case, CaO/B_2O_5 = β and temperature T ° C were independent factors. Optimization parameter - ΔGº. Temperature range 1000-1200ºC. Due to the fact that one second-order equation does not adequately describe the relationship (ΔGº– f (T, β). Planning was carried out in two areas along β (from 0.3 to 1.0 and from 1.0 to 2.0) The matrix of the study is shown in Table 3. Using the obtained values in accordance with (Akhazarova & Kafarov, 1978), adequate regression equations ΔGº = f (T, ß) of the following form were found:

ΔGº(β=0,3-1,0) = - 54,45 -0,586· T+301,5β+2,4·10·T²303β·β²0,341·T·β; (1)

ΔGº (β=1-2) = 523,42 -0,958· T+16,89β+3,47·10⁻⁴·T²⁸,¹⁶³β·β²-0,11·T·β. (2)

On the basis of equation 1.2 according to the method (Ochkov, 2007) volumetric images, response surfaces (ΔGº) and its horizontal sections were built (Figure 4).
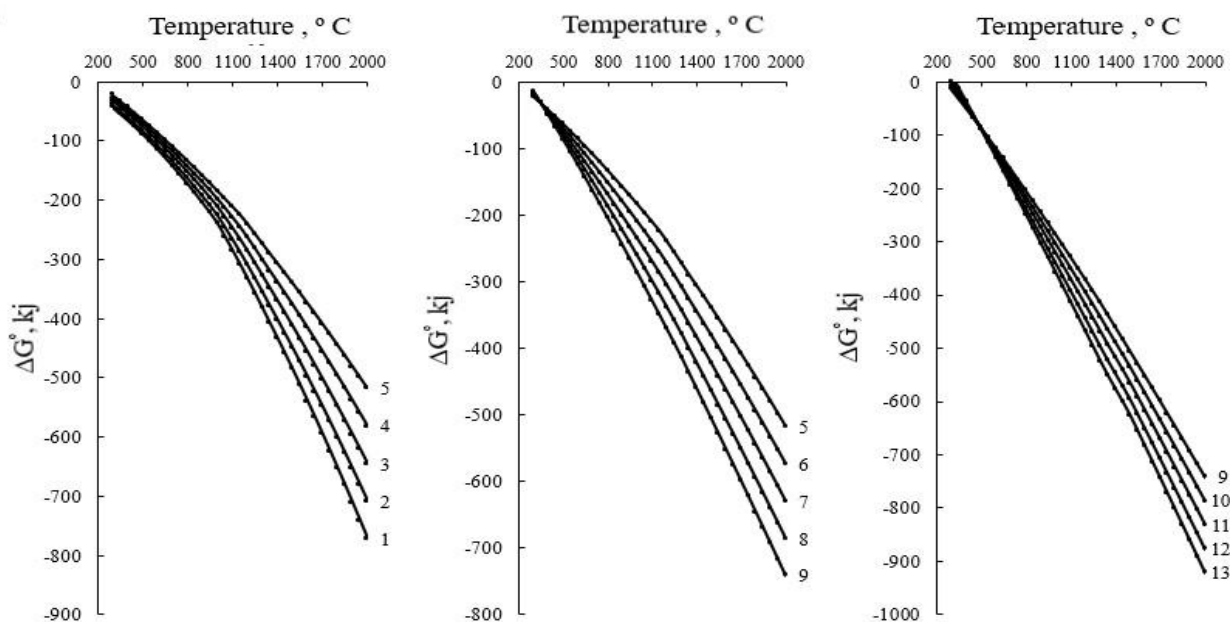
Figure 1. Influence of temperature on ΔG° of reactions of interaction between CaCO₃ and H₃BO3.
Notes: The numbers on the line correspond to the reaction number on the page.
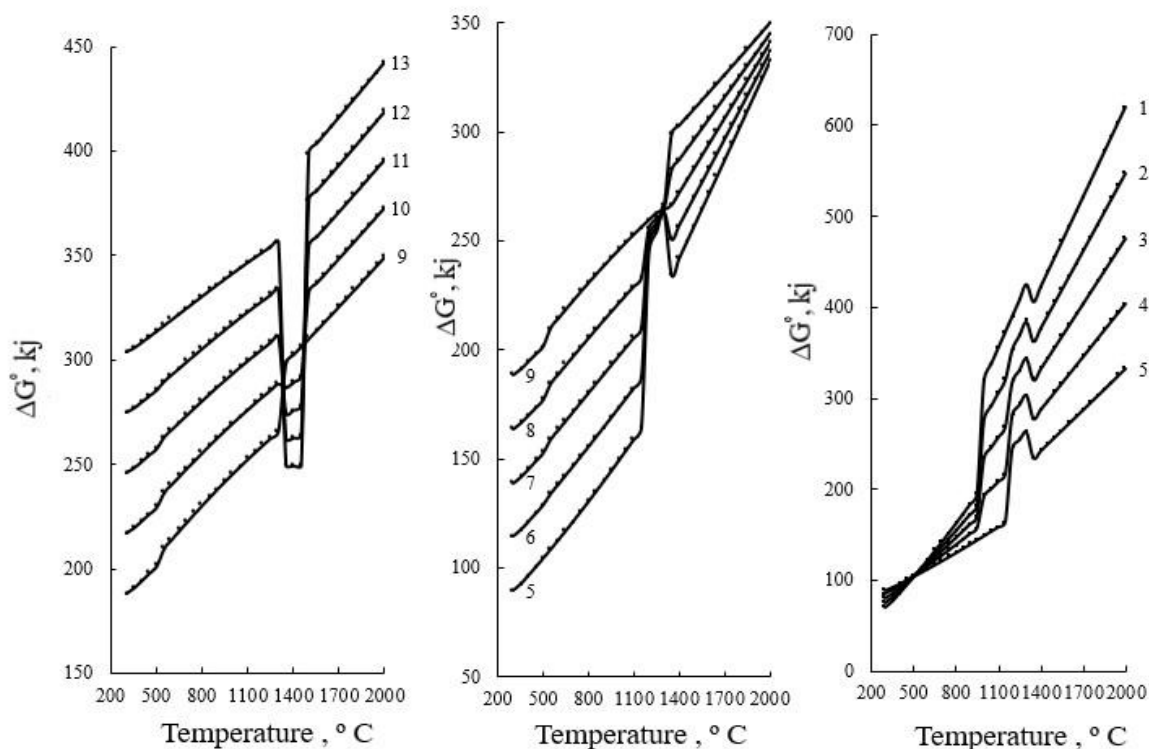
Figure 2. Influence of temperature on ΔH° of interactions CaCO₃ c H₃BO3.
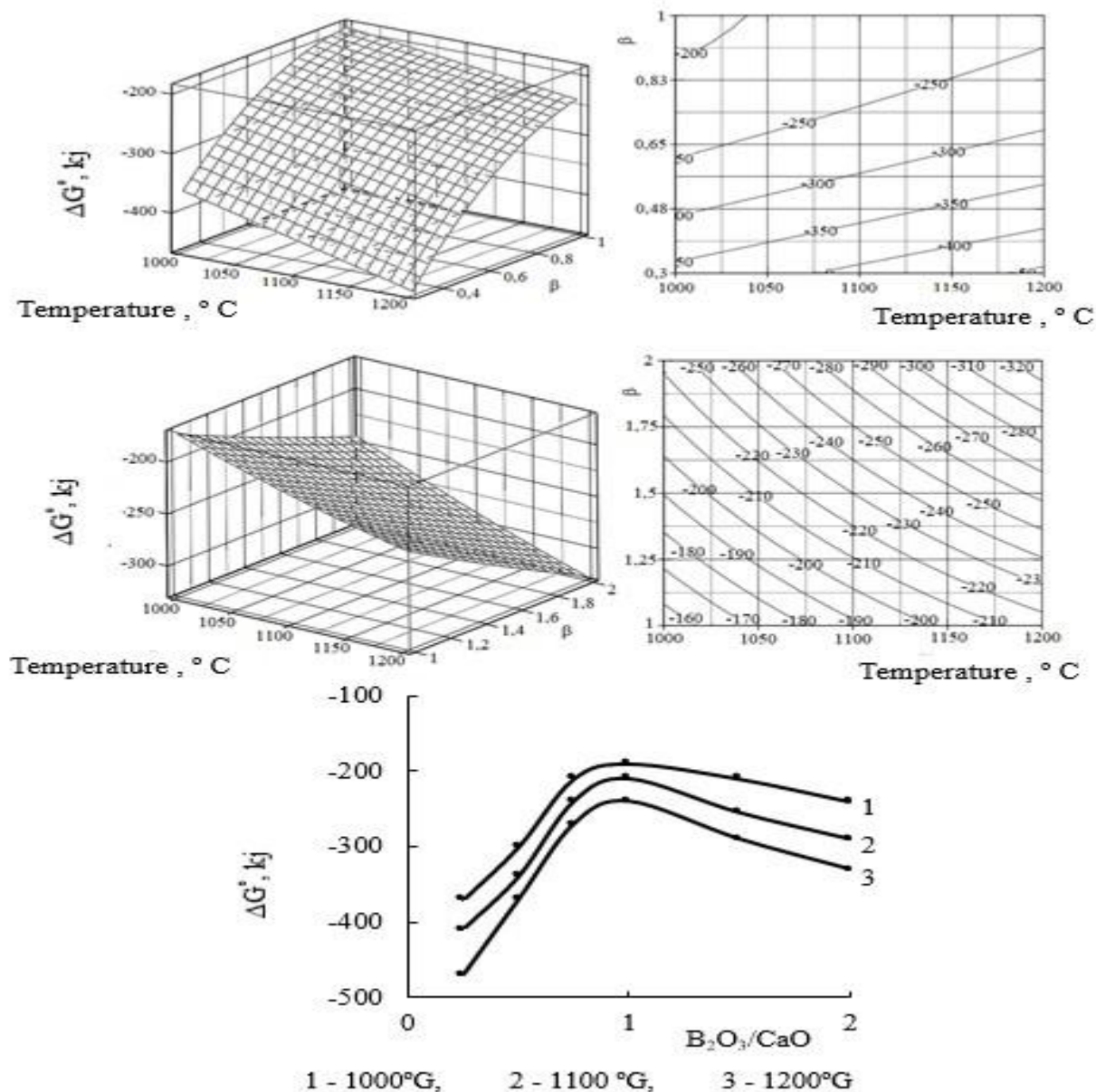
Figure 3. Influence of the BaO/CaO ratio and temperature in the CaCO₃₋ H₃BO₃ system on ΔG^o of reactions 1-13.

Table 3. Research planning matrix and their results on the effect of temperature and CaO/B₂O₃ ratio on ΔG^o in the CaCO₃ – mH₃BO₃ system.

Variables				ΔG^o,kj (ß=0,3-1,0)	ΔG^o, kj (ß=1-2)
Coded view		Original view			
X_1	X	T° C	β		
+1	+1	1171	0,43	-243	-301
+1	-1	1171	0,69	-398	-241
-1	+1	1029	0,21	-204	-246
-1	-1	1029	0,34	-335	-297
+1,41	0	1200	0,43	-312	-285
-1,41	0	1000	0,43	-240	-210
0	+1,41	1100	0,5	+216	-290
0	-1,41	1100	0,3	-412	-208
0	0	1100	0,43	-276	-250
0	0	1100	0,43	-275	-251
0	0	1100	0,43	-276	-251
0	0	1100	0,43	-277	-249
0	0	1100	0,43	-276	-249

Figure 4 shows that with a decrease in β from 1 to 0.3, the value of ΔG^o at 1200° and β = 0.3 become more negative (reaching - 452 kJ). An increase in β from 1 to 2 also leads to a decrease in ΔG^o, but to a lesser extent (only up to 333 kJ at
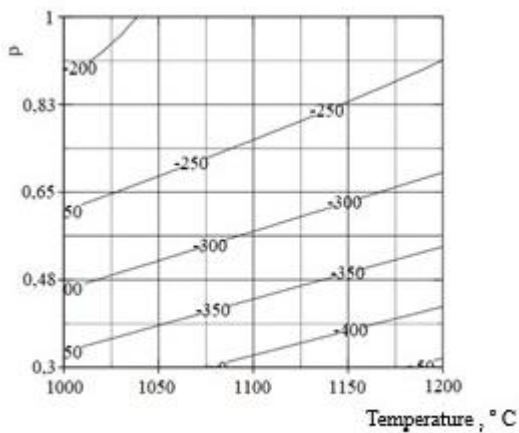
1200º C).

Tmelt.º C	989	1159	1311	1480

The value $\beta = B_2O_3/CaO$ affects the melting point of calcium borates:

This dependence is described by the equation: Tmelt. = 1662.6 - 705 · 8t + 185.07 RT². From the results obtained it follows that the agglomeration of phosphorites can be carried
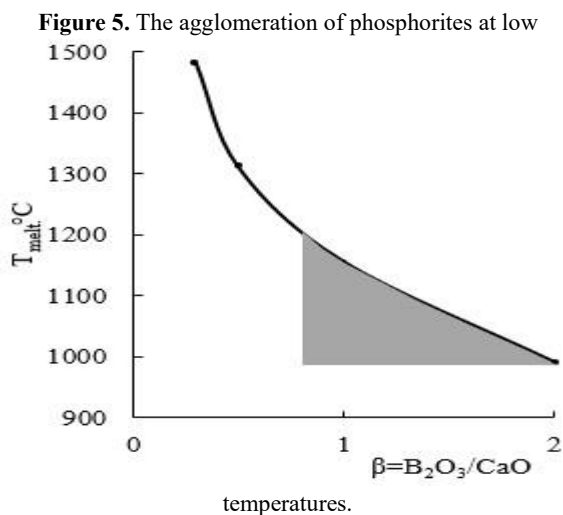

I) for $\beta = 0,3 - 1$

β	2,0	1,0	0,5	0,33
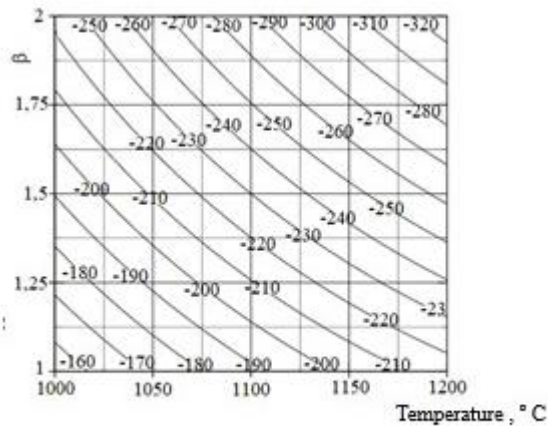
II) for $\beta = 1 - 2$

out at temperatures (990 - 1160 ° C).

Figure 4. Influence of temperature and molar ratio B_2O_3/CaO (β) on ΔG^o interaction in the system $CaCO_3$ – m H_3BO_3

Figure 5. The agglomeration of phosphorites at low

temperatures.

Figure 5 shows that for the agglomeration of phosphorites at low temperatures (990 - 1160º) the value β= CaO• B_2O_3 should be equal to 2 - 1. At β <1, the agglomeration temperature takes an increase making up + 486ºC for β = 0.33. With a decrease in the amount of B_2O_3 in the agglomeration charge to β = 0.76, the process temperature will increase to 1200 ° C.

CONCLUSION

Based on the results obtained on thermodynamic modeling of the interaction of CaO with H_3BO_3, it follows that
- the formation of calcium borate (CaO· B_2O_3) is more preferable than calcium silicate (CaO• SiO_2).
- at a constant temperature (1000, 1100 and 1200 ° C), the reaction with the formation of CaO•B_2O_3 has a higher thermodynamic probability, and a lower one with the formation of $B_2O_3.3CaO$.

- to comply with the conditions of sintering temperature from 1000 to 1160 ° C and ΔG -250 and less kJ, the process must be carried out at β = 1.5-2.0.

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