# Thermochemical Decomposition of Calcium Sulfate in Presence of Carbon and Hydrogen Mix

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## Abstract

Results of research of thermodynamic modeling of thermochemical decomposition of $CaSO_4$ by a mix of carbon and hydrogen are given in the article. Influence of temperature on degree of carbon interchange by hydrogen on a degree of formation in systems CaO, $CaCO_3$, CaS was determined. Interchange of C by $H_2$ reduces formation of $CaCO_3$, CaS, and formation of CaO has an extreme character. With the help of method of research planning adequate equation of regression has been defined and optimum technological parameters (T = 1660 K and 40 % degree of carbon interchange by $H_2$), providing full decomposition of $CaSO_4$ to CaO were determined. The composition of a gas phase of $CaSO_4$ restoration, containing 16 components was established. By reduction of pressure to 0,001 MPa it is possible to lower temperature of process to 1400 K. The chemical equation of $CaSO_4$ interaction with carbon and hydrogen was found.


## Introduction

At heat treatment of phosphogypsum in presence of natural coals basic restoration $CaSO_4$ up to CaO occurs according to reaction [1]:

$$2CaSO_4 + C = 2CaO + 2SO_2 + CO_2 \quad (1)$$

The structure of flying coals includes hydrogen [2, 3] which also restores $CaSO_4$:

$$CaSO_4 + H_2 = CaO + SO_2 + H_2O \quad (2)$$

The purpose of the present research is definition of regularities of restoration $CaSO_4$ by mixtures containing carbon and hydrogen. Research was carried out by a method of thermodynamic modeling employing program complex Astra [4] based on the fundamental principle of entropy maximum [5, 6]. The basis of the information on a database consists of thermodynamic properties of the individual substances systematized at the Institute of high temperatures of the Russian Academy of Sciences and the USA National bureau of standards [7, 8].

## Experimental

The research was carried out at temperature interval of 500 - 1800 K at pressure (P) 0,1 MPa. Proceeding from [9] initial quantity of carbon moles in system comprised 1,5. Influence of the degree of carbon moles interchange by hydrogen (γ) on the degree of formation CaO was determined in the work.

In figure 1 the information about influence of γ and temperature on the process, from which it follows, that the basic compounds in systems are $CaCO_3$, $CaSO_4$, CaS and CaO. $CaCO_3$ is formed at low temperatures. So, at T = 500 K the degree of $CaCO_3$ formation changes as follows:

| $\alpha CaCO_3$, % | 0 | 15 | 50 | 85 | 100 |
|---|---|---|---|---|---|
| γ, % | 49,95 | 42,13 | 28,64 | 12,51 | 0,00 |

That is, with increase of hydrogen amount in the system the degree of transition of Ca from $CaSO_4$ into $CaCO_3$ ($\alpha CaCO_3$) decreases. This regularity is described by the equation:

$$\alpha CaCO_3 = 50,365 – 0,4744 \cdot \gamma \ (R^2 = 0,9882) \quad (3)$$

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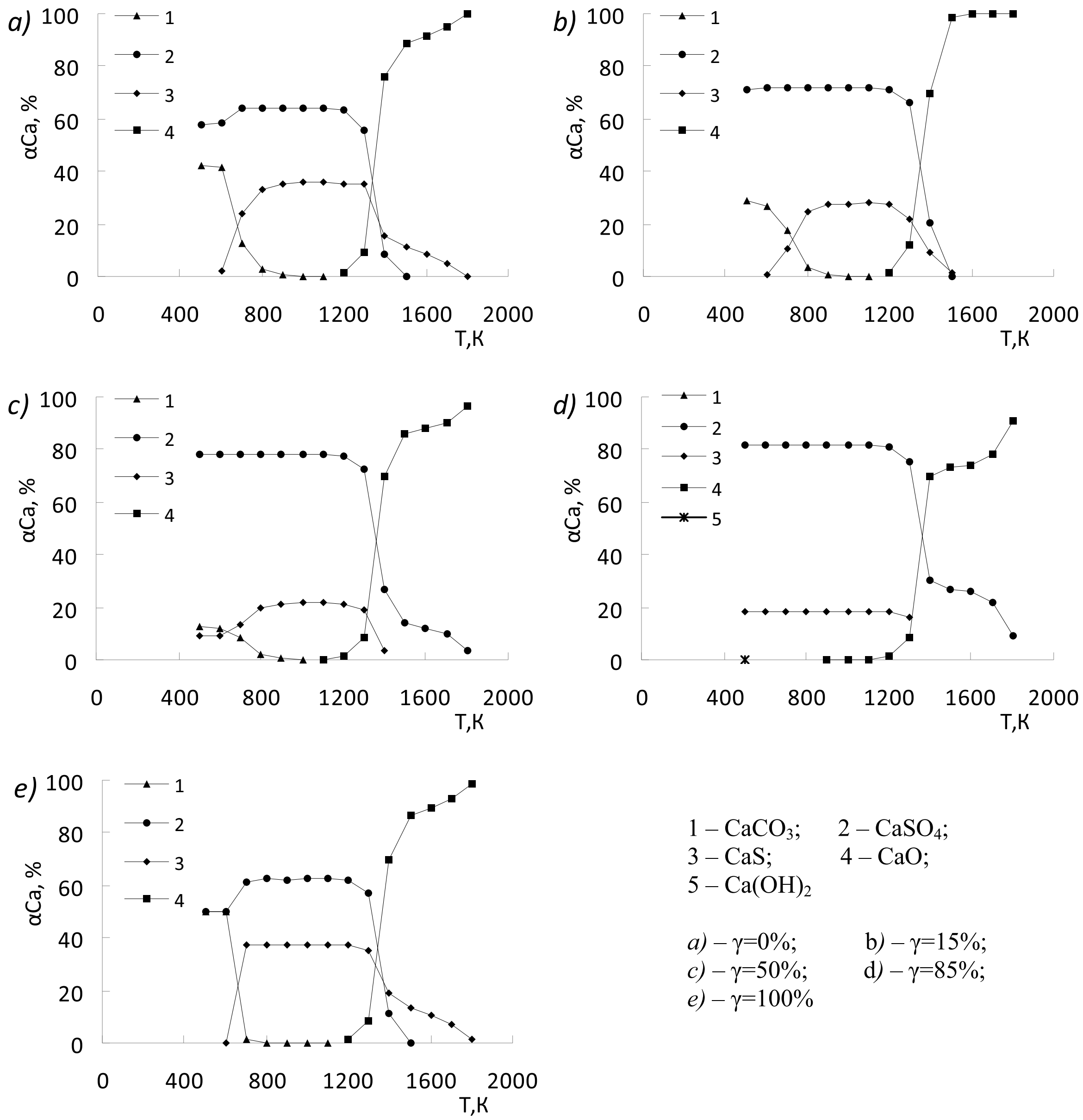



Fig. 1. Influence of temperature and degree of carbon interchange by hydrogen (γ) on the degree of calcium (αCa) distribution in system $CaSO_4$ - C - $H_2$

CaS, sulfide of calcium, is an intermediate product of $CaSO_4$ restoration to CaO. The degree of transition of Ca from $CaSO_4$ into CaS (αCaS) at increase of γ from 0 up to 100 % decreases from 37,9 to 18,5 % obeying the equation:

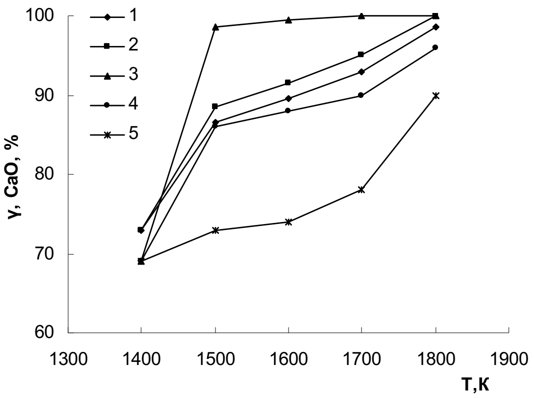
$$\alpha CaS = 38{,}082 - 0{,}1964 \cdot \gamma \; (R^2 = 0{,}9882) \quad (4)$$

CaO in systems appears at T > 1100 K. From figure 2 it follows, that dependence of the transition degree of Ca from $CaSO_4$ into CaO (αCaO) from γ degree of interchange has an extreme character with a maximum αCaO at γ = 50 %. For example, at T = 1600 K αCaO changes as follows:

| αCaCO, % | 0 | 15 | 50 | 85 | 100 |
|---|---|---|---|---|---|
| γ, % | 89,2 | 91,5 | 100 | 87,9 | 74,0 |

Thus the dependence αCaO=f (γ) looks like:

$$\alpha CaO = 0{,}6016 \cdot \gamma - 0{,}0072 \cdot \gamma^2 + 87189 \quad (R^2 = 0{,}9475) \quad (5)$$




1 - γ = 0 %; 2 - γ = 15 %; 3 - γ = 50 %; 4 - γ = 85 %; 5 - γ = 100 %

Fig. 2. Influence of temperature and the degree of mole carbon interchange by $H_2$ (γ) on the degree formation of CaO in $CaSO_4$ - C($H_2$) system at P = 0,1 MPa.

## Research results

To define the optimum parameters of restorating $CaSO_4$ to CaO in $CaSO_4$-C-$H_2$ system we carried out the research using rototable plan of the second order [9]. As independent variables γ and T have been used. Parameters of the plan and the matrix of research planning are given in tables 1 and 2.

**Table 1**

Parameters of the research plan

| Level of variables | The coded kind | | Natural kind | |
|---|---|---|---|---|
| | X1 | X2 | γ, % | T, K |
| Bottom | -1 | -1 | 14,5 | 1544 |
| Top | +1 | +1 | 85,5 | 1756 |
| Zero | 0 | 0 | 50 | 1650 |
| Arm + α | +1,414 | +1,414 | 100 | 1800 |
| Arm - α | -1,414 | -1,414 | 0,0 | 1500 |

Using program Mathcad - 14 [10] we have found the equation of regression in $\alpha CaO = f(\gamma, T)$ in the coded type:

$$\alpha CaO_{(cod)} = 99,2 - 4,3473 \cdot x_1 + 1,68 \cdot x_2 - 7.475 \cdot x_1^2 - 0,675 \cdot x_2^2 - 0,35 \cdot x_1 \cdot x_2 \quad (6)$$

Checking the importance of the coefficient of regression equation by Student's criterion has shown, that all 6 factors of the equation are significant. The equation is an adequate one. Calculated value of Fisher's criterion (5,59) is less than the tabular one (6,59). Thus the coefficient of determination ($R^2$) has comprised 0,988 [10]. In natural scale the adequate equation of regression looks like:

$$\alpha CaO_{(nat)} = -106,888 + 0,62 \cdot \gamma + 0,218 \cdot T - 5,93 \cdot 10^{-3} \cdot \gamma^2 - 6,01 \cdot 10^{-5} \cdot T^2 - 9,3 \cdot 10^{-5} \cdot \gamma \cdot T \quad (7)$$

**Table 2**

The plan and results of research

| № | The coded type | | Natural type | | αCaO, % (res). | αCaO, % (calc). |
|---|---|---|---|---|---|---|
| | X1 | X2 | γ, % | T, K | | |
| 1. | -1 | -1 | 14,5 | 1544 | 92,0 | 93,30 |
| 2. | 1 | -1 | 85,5 | 1544 | 86,2 | 85,37 |
| 3. | -1 | 1 | 14,5 | 1756 | 97,3 | 97,43 |
| 4. | 1 | 1 | 85,5 | 1756 | 90,1 | 88,03 |
| 5. | 1,414 | 0 | 100 | 1650 | 76,2 | 78,10 |
| 6. | -1,414 | 0 | 0 | 1650 | 91,6 | 90,39 |
| 7. | 0 | 1,414 | 50,0 | 100 | 99,0 | 10,22 |
| 8. | 0 | -1,414 | 50,0 | 0 | 96,0 | 95,47 |
| 9. | 0 | 0 | 50,0 | 1650 | 100 | 99,20 |
| 10. | 0 | 0 | 50,0 | 1650 | 99,3 | 99,20 |
| 11. | 0 | 0 | 50,0 | 1650 | 97,7 | 99,20 |
| 12. | 0 | 0 | 50,0 | 1650 | 99,4 | 99,20 |
| 13. | 0 | 0 | 50,0 | 1650 | 99,6 | 99,20 |

Results of calculating αCaO according to the equation (7) are given in table 2. Absolute maximum mistakes are within the limits of 0,2 - 2,06 % and relative ones are in the limits from 0,2 to 2,49 %. The surface αCaO=f (γ, T) is constructed on the basis of the equation (7) - figure 3 and its horizontal sections (figure 4.)

From figure 3 it follows, that the surface is characterized by a maximum. The maximum of αCaO = 100 % is in the area of FMN surface (figure 4).

That is, at γ = 26 - 52 % and T = 1660 - 1750 K. At the minimal temperature (1660 K) for αCaO = 100 % value γ comprises 40 %. For αCaO = 98 % the temperature can be reduced up to 1570 K, and for αCaO = 97 % - 1530 K.

The composition of the gas phase of the system at γ = 40 % is given in figure 5 from which it follows, that $SO_2$, $H_2S$, $CO_2$, $H_2O$ and CO are the principal components of the gas phase. At T = 1600 K the gas phase, for example, contains 16 substances: 24,02 % $CO_2$; 54,15 % $SO_2$; 16,73 %

$H_2O$; 2,27 % CO; 1,57 % $S_2$; 0,42 % SO; 0,32 % $H_2$; 0,15 % $H_2S$; 0,002 % $S_3$; 0,0015 % S; 0,02 % SH; 0,028 % CaS; $0{,}39 \cdot 10^{-3}$ H; $0{,}26 \cdot 10^{-3}$ $SO_3$; 0,069 % $S_2O$; $0{,}3 \cdot 10^{-4}$ % $SOH^-$.

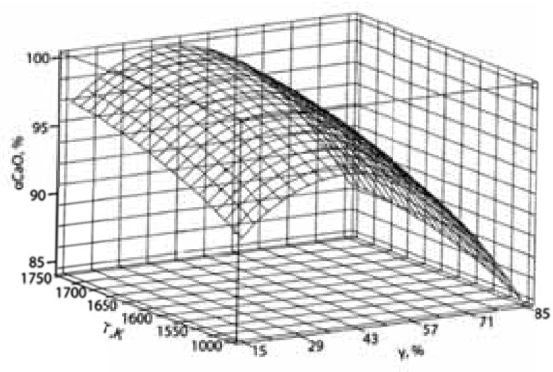
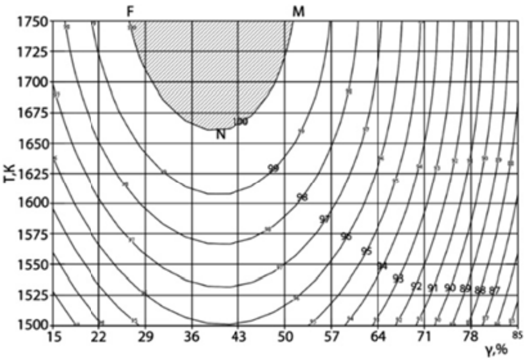
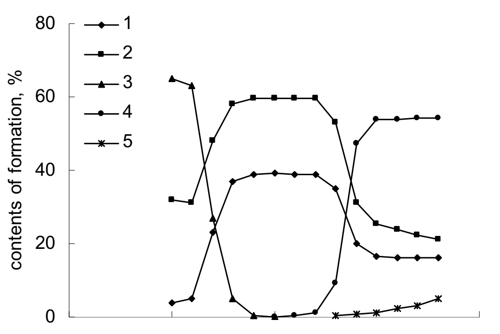



Fig. 3. The form of response surface αCaO of the $CaSO_4$-C-$H_2$ system at P=0,1 MPa




Figures on lines - αCaO, %

Fig. 4. Horizontal section views of response surface




1 - $H_2O$; 2 - $CO_2$; 3 - $H_2S$; 4 - $SO_2$; 5 - CO

Fig. 5. Influence of temperature on the content of components in a gas phase of system $CaSO_4$-C-$H_2$ at P = 0,1 MPa and 40 % of carbon interchange by hydrogen.

If to reduce the pressure to 0,001 MPa, then it is possible to lower temperature of full (100 %) transition of Ca from $CaSO_4$ into CaO to 1400 K, that is by 260 degrees. Thus interaction will be described by the following chemical equation:

$$4CaSO_4 + 1{,}5C + 1{,}5H_2 = 4CaO + 3{,}707\,SO_2 + 0{,}128\,S_2 + 0{,}026\,SO + 0{,}004\,H_2S + +0{,}0013\,S_2O + 1{,}354CO_2 + 0{,}146CO + 1{,}424H_2O + 0{,}07H_2 \quad (8)$$

## Conclusions

On the basis of conducted research on interaction in $CaSO_4$-C-$H_2$ system it is possible to draw the following conclusions:

- the degree of formation of intermediate products ($CaCO_3$ and CaS) decreases in process of carbon interchange in system by hydrogen;
- the degree of CaO formation depending on temperature and degree of carbon interchange by hydrogen has an extreme character;
- a maximum of CaO formation (≈ 100 %) can be achieved at T=1660 K and γ = 40 %;
- by reducing pressure from 0,1 to 0,001 MPa the temperature of full decomposition of $CaSO_4$ to CaO dicreases to 1400 K.

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*Received 1 October 2009.*