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

V.K. Bishimbayev*, A.A. Yerubay

M.Auezov South-Kazakhstan State University
Tauke-khan avenue 5, Shymkent, 160012, Kazakhstan

Abstract

Results of research of thermodynamic modeling of thermochemical decomposition of CaSO₄ by a mix of carbon and hydrogen are given in the article. Influence of temperature on degree of carbon interchange by hydrogen on degree of formation in systems CaO, CaCO₃, CaS was determined. Interchange of C by H₂ reduces formation of CaCO₃, 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 H₂), providing full decomposition of CaSO₄ to CaO were determined. The composition of a gas phase of CaSO₄ 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 CaSO₄ interaction with carbon and hydrogen was found.

Introduction

At heat treatment of phosphogypsum in presence of natural coals basic restoration CaSO₄ up to CaO occurs according to reaction [1]:

\[ 2\text{CaSO}_4 + \text{C} = 2\text{CaO} + 2\text{SO}_2 + \text{CO}_2 \] (1)

The structure of flying coals includes hydrogen [2, 3] which also restores CaSO₄:

\[ \text{CaSO}_4 + \text{H}_2 = \text{CaO} + \text{SO}_2 + \text{H}_2\text{O} \] (2)

The purpose of the present research is definition of regularities of restoration CaSO₄ 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 CaCO₃, CaSO₄, CaS and CaO. CaCO₃ is formed at low temperatures. So, at T = 500 K the degree of CaCO₃ formation changes as follows:

| γ, % | 49,95 | 42,13 | 28,64 | 12,51 | 0,00 |
|---|---|---|---|---|---|
| αCaCO₃, % | 0 | 15 | 50 | 85 | 100 |

That is, with increase of hydrogen amount in the system the degree of transition of Ca from CaSO₄ into CaCO₃ (αCaCO₃) decreases. This regularity is described by the equation:

\[ α\text{CaCO}_3 = 50,365 - 0,4744 \cdot γ \left( R^2 = 0,9882 \right) \] (3)

*corresponding author. Email: sksu_kaz@mail.ru
CaS, sulfide of calcium, is an intermediate product of CaSO₄ restoration to CaO. The degree of transition of Ca from CaSO₄ into CaS (αCaS) at increase of γ from 0 up to 100 % decreases from 37,9 to 18,5 % obeying the equation:

$$\alpha_{CaS} = 38,082 - 0,1964 \cdot \gamma \, (R^2 = 0,9882)$$  \hspace{1cm} (4)

CaO in systems appears at $T > 1100$ K. From figure 2 it follows, that dependence of the transition degree of Ca from CaSO₄ into CaO (αCaO) from γ degree of interchange has an extreme character with a maximum αCaO at $\gamma = 50 \%$. For example, at $T = 1600$ K αCaO changes as follows:

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

Thus the dependence $\alpha_{CaO}=f(\gamma)$ looks like:

$$\alpha_{CaO} = 0,6016 \cdot \gamma - 0,0072 \cdot \gamma^2 + 87189 \hspace{1cm} (R^2 = 0,9475)$$  \hspace{1cm} (5)
Fig. 2. Influence of temperature and the degree of mole carbon interchange by $\gamma$ on the degree formation of $\gamma$ 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 rotatable plan of the second order [9]. As independent variables $\gamma$ 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 |
|--------------------|----------------|--------------|
| Bottom             | -1             | -1           | 14,5 | 1544 |
| Top                | +1             | +1           | 85,5 | 1756 |
| Zero               | 0              | 0            | 50   | 1650 |
| Arm $+\alpha$      | +1,414         | +1,414       | 100  | 1800 |
| Arm $-\alpha$      | -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:

$$\alpha\text{CaO}_{(\text{cod})} = 99,2 - 4,3473 \cdot x_1 + 1,68 \cdot x_2 - 7,475 \cdot x_1^2 - 0,675 \cdot x_2^2 - 0,35 \cdot x_1 \cdot x_2$$  \hspace{1cm} (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:

$$\alpha\text{CaO}_{(\text{nat})} = -106,888 + 0,62 \cdot \gamma + 0,218 \cdot \gamma^2 - 5,93 \cdot 10^3 \cdot \gamma^3 - 6,01 \cdot 10^5 \cdot T^2 - 9,3 \cdot 10^5 \cdot \gamma \cdot T$$ \hspace{1cm} (7)

**Table 2**
The plan and results of research

| No | The coded type | Natural type | $\gamma$, % | $T$, K | $\alpha$CaO, % (res.) | $\alpha$CaO, % (calc.) |
|----|----------------|--------------|-------------|--------|----------------------|------------------------|
| 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 $\alpha$CaO 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 $\alpha$CaO=F($\gamma, T$) 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 $\alpha$CaO = 100 % is in the area of FMN surface (figure 4).

That is, at $\gamma = 26 - 52$ % and $T = 1660 - 1750$ K.

At the minimal temperature (1660 K) for $\alpha$CaO = 100 % value $\gamma$ comprises 40 %. For $\alpha$CaO = 98 % the temperature can be reduced up to 1570 K, and for $\alpha$CaO = 97 % - 1530 K.

The composition of the gas phase of the system at $\gamma = 40$ % is given in figure 5 from which it follows, that SO$_2$, H$_2$S, CO$_2$, H$_2$O 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 %
H₂O; 2.27 % CO; 1.57 % S₂; 0.42 % SO; 0.32 % H₂; 0.15 % H₂S; 0.002 % Si; 0.0015 % S; 0.02 % SH; 0.028 % CaS; 0.39*10⁻³ H; 0.26*10⁻³ SO₃; 0.069 % S₂O; 0.3*10⁻⁴ % SOH.

If to reduce the pressure to 0.001 MPa, then it is possible to lower temperature of full (100 %) transition of Ca from CaSO₄ into CaO to 1400 K, that is by 260 degrees. Thus interaction will be described by the following chemical equation:

\[ 4CaSO₄ + 1.5C + 1.5H₂ = 4CaO + 3.707 SO₂ + 0.128 S₂ + 0.026 SO + 0.004 H₂S + 0.0013 S₃O + 1.354CO₂ + 0.146CO + 1.424H₂O + 0.07H₂ \]  

(8)

Conclusions

On the basis of conducted research on interaction in CaSO₄-C-H₂ system it is possible to draw the following conclusions:
- the degree of formation of intermediate products (CaCO₃ 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 CaSO₄ to CaO decreases to 1400 K.

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Received 1 October 2009.