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Reduction of $PbSO_4$ by ($CO + CO_2$) mixture

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Abstract

This paper includes experimental results of $PbSO_4$ reduction. The experiments were carried out within temperature range 923–1073 K and for varying CO/CO_2 ratio. The obtained results allow to determine the influence of the temperature range and gas composition on the quantity and constituents of the resulting products. It shows the distribution of lead sulphate on two reactions, concerned with the direct transformation of lead sulphate ($PbSO_4$) to lead sulphide (PbS) and with the reaction of $PbSO_4$ with PbS which takes place at a phase $PbSO_4$–PbS boundary.

Keywords: Reduction; Lead sulphate; Lead sulphide; Reaction in solid state

1. Introduction

The reduction of metal sulphates as well as the reduction of metal oxides is an important problem in chemistry and metallurgy. In carried out industrial processes metal sulphates are converted into metal oxides by means of thermal decomposition or metal sulphides in case of reducer attendance. Owing to the effect produced by reducers on metal sulphates, there are formed phases that depend on a temperature and types of metals. In this case such phases can be formed as: metallic phases (Pb, Cu, Ag); sulphidic phases (ZnS, PbS, K_2S, Na_2S) as well as oxidic phases, e.g. MgO [1]. It is shared view that the reduction of metal sulphates by means of hydrogen (H_2) or carbon monoxide (CO) runs in lower temperatures than their thermal decomposition. The work [2] assumed that the reaction of MSO_4 reduction by means of H_2 runs according to the following scheme:

$$2MSO_4 + 5H_2 = MO + MS + 5H_2O + SO_2 \quad (1)$$

$$MO + H_2 = M + H_2O \quad (2)$$

If we assume that the equation (Eq. (1)) is possible the obtained products should always contain two phases MO and MS (in various mole ratio) or M and MS in case when the reaction (Eq. (2)) occurs. It seems that the reaction of MSO_4 reduction runs in a more complex way including converting MSO_4 to MS as well as the reaction at the phase boundary between MSO_4 and MS which produces metal oxide. The direct reduction of MO to M is also possible in this case. These reactions can be described according to the following equations:

$$MSO_4 + 4CO(H_2) = MS + 4CO_2(H_2O) \quad (3)$$

$$MS + 3MSO_4 = 4MO + 4SO_2 \quad (4)$$

$$MO + CO(H_2) = M + CO_2(H_2O) \quad (5)$$

The quantity and type of the resulting products depend on the differences of the reaction (Eqs. (3)–(5)) rate. If in the conditions of carried out MSO_4 reduction processes, reactions (Eqs. (4) and (5)) do not occur, just MS will only be obtained. Whereas, in case when the reaction (Eq. (5)) does not occur, the products of the MSO_4 reduction will only contain MS and MO, but their participation depends on the differences of reactions (Eqs. (3) and (4)) rate. In case of the high rate of the reaction (Eq. (4)) the only product of the process is MO. The occurrence of a metallic phase as a result of the reaction (Eq. (5)) is possible only in the appropriate conditions.

The hypothesis about the presented above courses of the reactions can be confirmed thanks to the following investigation and the experimental results:

- The reduction of $SrSO_4$ by means of gaseous ($CO + CO_2$) mixtures in the range of temperatures 1121–1240 K

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directly to SrS as the only product of this reaction [3–5].

- $CaSO_4$ reduction by means of hydrogen in the range of temperatures 1023–1088 K to CaS [6,7].
- Whereas $MgSO_4$ reduction by means of CO in the range of temperatures 873–1048 K resulting in MgO in the final products [8].

The conducted thermodynamic analysis of the reaction between MSO_4 and MS showed that especially for strontium and calcium mentioned reaction does not occur in the considered range of temperature, therefore the only product in this case is a metal sulphide. In the event of magnesium occurrence coursing of these reaction is possible, therefore MgO occurs in the final products. In the considered conditions the reduction of MgO does not occur, therefore metallic magnesium does not appear in the final products. In order to confirm this hypothesis we can refer to the work [9] in which the reduction of $ZnSO_4$ was conducted. The temperature of this process was 948 K. The obtained results contained in this work showed the occurrence of ZnO and ZnS in the final products. It results from the fact that reactions at the phase $ZnSO_4$–ZnS boundary run in considered conditions.

This work is aimed to determine the influence of the temperature range and the gaseous $(CO + CO_2)$ phase composition on the quantity and composition of obtained products.

2. Experimental results

The investigation of $PbSO_4$ reduction was conducted by thermogravimetric method. The investigated samples in the form of powder were placed on a special pan of Al_2O_3, which was suspended on the electronic balance. This made possible the continuous registration of mass changes during the process with the accuracy of 1×10^{-3} g. The apparatus used for investigations consisted of the vertical electric furnace tube with the regulation of temperature by means of Pt–PtRh thermocouple from below of the furnace and kept immediately under the examined sample. The gaseous phase of the constant amount and of predetermined composition which was controlled by means of the rotameter, flowed from below of the furnace to its top. The gaseous phase with the flow rate of 60 dm^3/h was passed through the furnace. This rate was adjusted in order to prevent its influence on the speed of the process. The experiments were carried out within the temperature range 893–1073 K and for varying CO/CO_2 ratio ranging from 20 to 100% of CO. The measurements were conducted to an amount in which samples reached the constant mass. On the basis of registered mass changes of the samples during the reduction process relative mass changes were calculated, which as a function of time for different conditions were presented in Figs. 1–4. The obtained products were subjected to X-ray phase analysis, which showed only Pb and PbS presence. Due to this fact on the presented figures the relative mass changes were indicated. They correspond to Pb or possibly PbS occurrence in the sample after the end of the process. The sigmoidal character of the obtained relations points to the autocatalytic course of process; such a process course can be either a result of the reaction surface developing or of an increased participation of secondary reactions in the process in question whereas those secondary reactions proceed among substrates and transitory reaction products being formed and it is possible that they can increase the summary rate of the entire process.

It should be mentioned that the total mass decrease depends on both: the process temperature and the gaseous phase composition. Making a comparison between relative mass decreases in temperature equal to 973 and 1048 K it should be noticed that the time of the process is considerably influenced by the CO concentration in the gaseous phase. Also simultaneously with the increasing CO concentration,

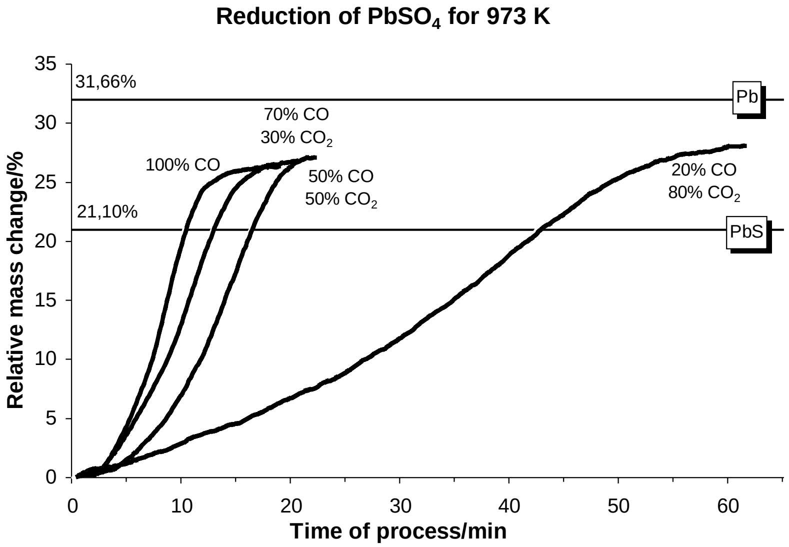

Fig. 1. The influence of gaseous phase composition on the relative mass changes for temperature 973 K.

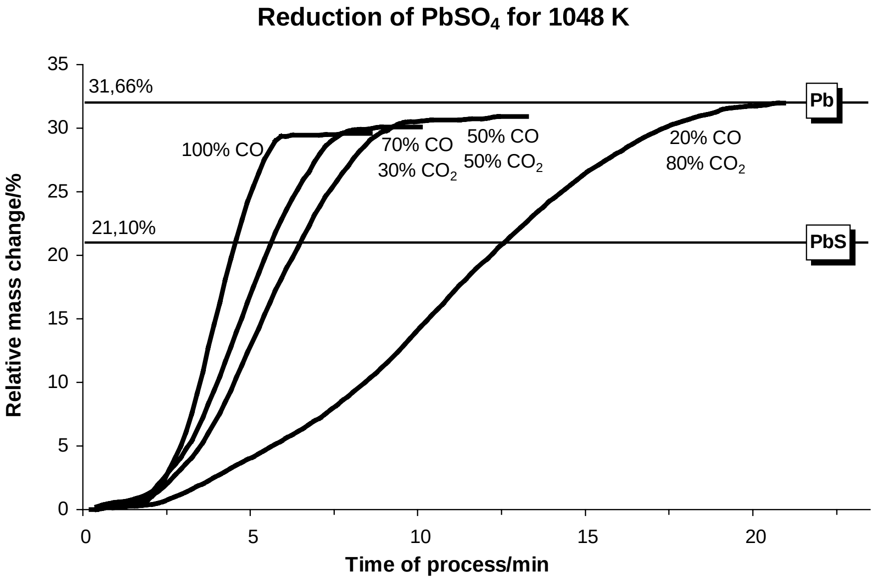

Fig. 2. The influence of gaseous phase composition on the relative mass changes for temperature 1048 K.

the total mass changes decrease, which could suggest the rising quantity of PbS in the final products. The influence of temperature on the relative mass changes for constant CO concentration in the gaseous mixture is presented in Figs. 3 and 4. For CO concentration equal to 50% (Fig. 3) simultaneously with the increasing temperature, the total mass change also increases and reaches the value of mass decrease which corresponds to the formation of metallic lead. In case when the process is carried out in pure CO, the quantity of PbS in the final products increases.

3. Results and discussion

Having the mass of the preparation after the process and the relative mass change, the mass calculations of metallic lead and lead sulphide in the final products were performed according to the following relations:

$$\%\mathrm{PbS} = \frac{(\Delta m_t/m_0)_{\mathrm{PbSO_4}\to\mathrm{Pb}} - (\Delta m_p/m_0)}{(\Delta m_t/m_0)_{\mathrm{PbSO_4}\to\mathrm{Pb}} - (\Delta m_t/m_0)_{\mathrm{PbSO_4}\to\mathrm{PbS}}} \times 100$$

where %PbS is the contents of PbS in preparation after the process (%); $(\Delta m_t/m_0)_{\mathrm{PbSO_4}\to\mathrm{Pb}}$ the relative $PbSO_4$ mass change in case when the only product is Pb, is equal to 31.66%; $(\Delta m_t/m_0)_{\mathrm{PbSO_4}\to\mathrm{PbS}}$ the relative $PbSO_4$ mass change in case when the only product is PbS, is equal to 21.10%; $(\Delta m_p/m_0)$ the registered relative change of the mass of the sample during the process.

The results of the PbS and Pb quantity calculations in the preparation after the process are presented in Table 1.

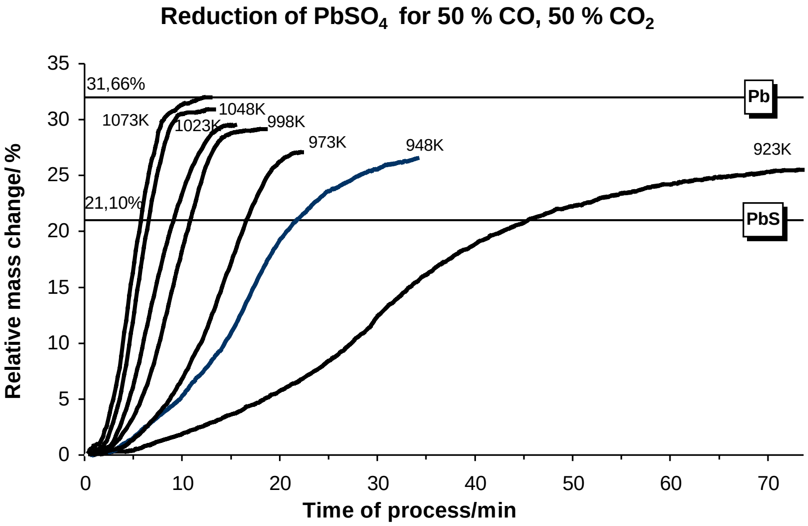

Fig. 3. The influence of temperature on the relative mass changes for gaseous mixture composition 50% CO, 50% CO_2.

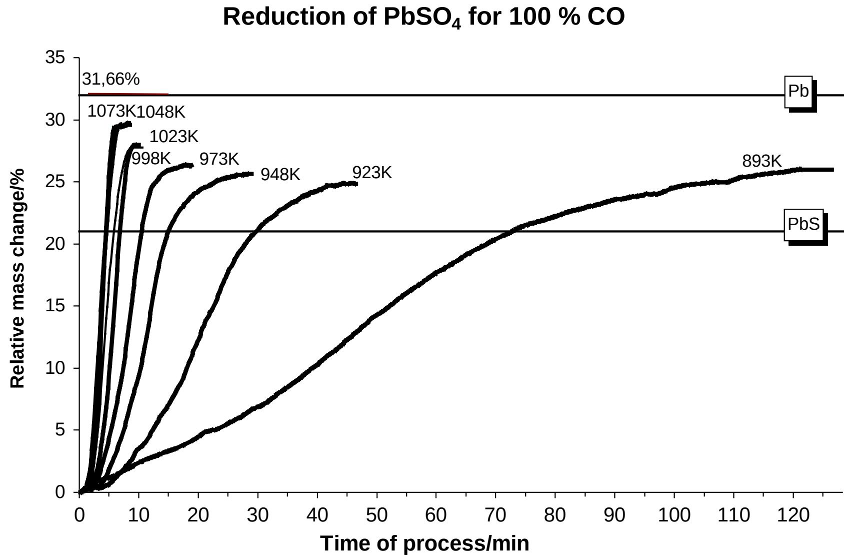

Fig. 4. The influence of temperature on the relative mass changes for gaseous mixture composition 100% CO.

Making the analysis of obtained results we can claim that in the constant temperature of the process, simultaneously with increasing CO concentration in the gaseous phase the participation of PbS in the final products increases. Whereas, taking into consideration the influence of temperature on the constitution of obtained products at constant CO concentration in the gaseous phase, the received data of the $PbSO_4$ reduction show that simultaneously with the increasing

Table 1
Mass fraction of PbS and Pb in the end products for different process conditions

Temperature (K)	Concentration of CO (vol.%)	Mass fraction in the end product (%)		$\Delta m/m_0$
		PbS	Pb	
923	50	58.33	41.67	25.50
	70	54.83	45.17	25.87
	100	65.53	34.47	24.74
948	50	40.72	59.28	27.36
	70	46.40	53.60	26.76
	100	57.01	42.99	25.64
973	20	33.90	66.10	28.08
	50	42.71	57.29	27.15
	70	44.32	55.68	26.98
	100	48.48	51.52	26.54
998	20	15.34	84.66	30.04
	50	23.77	76.23	29.15
	70	33.62	66.38	28.11
	100	35.13	64.87	27.95
1023	20	12.50	87.50	30.34
	50	19.98	80.02	29.55
	70	34.38	65.63	28.03
	100	36.84	63.16	27.77
1048	20	0	100	31.66
	50	7.20	92.80	30.90
	70	15.06	84.94	30.07
	100	21.12	78.88	29.43
1073	20	0	100	31.66
	50	0	100	31.66
	70	6.53	93.47	30.97
	100	18.84	81.16	29.67

Table 2
Distribution of $PbSO_4$ to the particular reactions

Temperature (K)	Concentration of CO (vol.%)	Distribution of $PbSO_4$ (%)		
		$PbSO_4 + 4CO = PbS + 4CO_2$	$3PbSO_4 + PbS = 4PbO + 4SO_2$	$PbSO_4$ not reacted
893	100	62.29	36.62	1.09
923	50	66.16	32.78	1.06
	70	63.46	35.46	1.09
	100	71.71	27.30	0.99
948	50	52.89	46.05	1.07
	70	57.09	41.81	1.10
	100	65.14	33.78	1.07
973	20	47.95	51.06	0.99
	50	54.38	44.54	1.08
	70	55.58	43.33	1.09
	100	58.67	40.23	1.10
998	20	35.09	64.33	0.58
	50	40.83	58.36	0.81
	70	47.80	51.21	0.99
	100	48.87	50.12	1.01
1023	20	33.17	66.34	0.49
	50	38.26	61.03	0.71
	70	48.35	50.66	1.00
	100	50.07	48.90	1.03
1048	20	25.26	74.71	0.03
	50	29.68	70.01	0.30
	70	34.87	64.56	0.57
	100	37.88	61.42	0.70
1073	20	25	75	0
	50	25	75	0
	70	29.25	70.47	0.28
	100	37.46	61.86	0.68

temperature, the contamination of PbS decreases and metallic Pb increases. Thermodynamic accounts testify that the occurrence of metallic lead is caused by the reduction of PbO by means of CO, whereas PbO was formed by the reaction at $PbSO_4$–PbS phase boundary. According to the literature data [10] the reaction between $PbSO_4$ and PbS occurs, forming basic sulphates which in reducer attendance are subjected to the reduction resulting in Pb and PbS as products. Obtained PbS reacts again with $PbSO_4$ at the PbS–$PbSO_4$ phase boundary. Due to this fact, the following reactions of $PbSO_4$ reduction have been assumed:

$$PbSO_4 + 4CO = PbS + 4CO_2 \tag{6}$$

$$PbS + 3PbSO_4 = 4PbO + 4SO_2 \tag{7}$$

$$PbO + CO = Pb + CO_2 \tag{8}$$

On the basis of coursing of the reactions (Eqs. (6) and (7)) the distribution of $PbSO_4$ to the particular reactions was calculated. Results are presented in Table 2. The formation of metallic lead according to the reaction: $PbS + 2PbO = 3Pb + SO_2$ was left out.

The data obtained by the distribution calculations indicate that participation of the reaction (Eq. (6)) in the reduction progress increases for the preset temperature and increasing CO concentration in the gaseous phase, whereas this participation decreases with the increasing temperature for constant CO concentration. Differences of the reactions rate determine the quantity of PbS in the final products. In case when the rate of the reactions (Eq. (6)) is higher in comparison to the reaction (Eq. (7)) a considerable part of $PbSO_4$ is subjected to the reduction to PbS (it is if we assume that the reaction (Eq. (8)) runs with an appropriate rate the whole quantity of PbO is reduced to PbS). The increasing of the process temperature influences on the growth of the reaction rate at the $PbSO_4$–PbS phase boundary to a higher degree than on the reaction reduction. In this case reaction has a considerable participation (Eq. (7)), it also springs from the final products composition. If the rate of this reaction is efficiently high in proportion to the reaction (Eq. (6)) rate, resulting PbS will immediately react with not reacted $PbSO_4$ resulting in Pb presence. The last column in Table 2 presents the quantity of not reacted $PbSO_4$ which springs from the performed mass balance.

4. Conclusion

The obtained experimental results of the $PbSO_4$ reduction by means of gaseous $(CO+CO_2)$ mixture and the performed calculations allow to formulate the following conclusions:

1. In the reduction process simultaneously three reactions take place; the direct reduction of $PbSO_4$ to PbS; reaction at a phase boundary of $PbSO_4$–PbS in which PbO is formed; PbO reduction to metallic lead.
2. The constituents of obtained products including only lead sulphide (PbS) and metallic lead (Pb) depend on differences of the reaction (Eqs. (6) and (7)) rate.
3. The concentration increase in the gaseous phase of CO at a constant temperature causes an increase in the $PbSO_4$ to PbS reduction rate, and the result is the increased PbS fraction in the reaction products. Provided the CO content in the system is constant, an increase in a temperature influences the rate of reaction at a phase boundary of $PbSO_4$–PbS to a higher degree than the rate of the direct reduction of PbO_4 to PbS, and the result is that a metallic Pb content in the reaction products grows.
4. The obtained dependencies show a sigmoidal character of the reaction. This refers especially to a lower temperature range and a lower CO concentration in the gaseous phase.

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