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ANALYSIS OF THE REACTION BETWEEN $PbSO_4$ and ZnS

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The reaction between ZnS and $PbSO_4$ has been studied at different mole ratios. It has been found that the reaction is multistage. The products of the first stage of the reaction consist mainly of ZnO, PbS and $PbSO_4$ in different amounts, depending on the mole ratio of the substrates. The following stages consist in the interaction of PbS formed in the first stage with $PbSO_4$. It has been found that the reaction rate depends on the temperature and on the $PbSO_4$: ZnS mole ratio (up to 3 : 1).

It is thought that chemical reactions between sulphides and sulphates have a great influence on the roasting of zinc-lead concentrates. Some information concerning the reactions between the sulphide and sulphate of the same metal can be found in the literature [1–7], but no reports on this process between the sulphide and sulphate of different metals have been found. The reaction between ZnS and $PbSO_4$ can play some role in the roasting process of zinc-lead concentrates, which led the authors to investigate this problem.

The preliminary thermogravimetric studies, carried out in an argon atmosphere, at increasing temperatures, on mixtures with varying mole ratios, showed that the reaction between $PbSO_4$ and ZnS has a multistage character (Fig. 1). To determine the phases formed, the direction of the chemical reaction, and the influence of the temperature and the $PbSO_4$: ZnS mole ratio on the reaction rate, isothermal studies were carried out. Samples of 1 g were used and a heating rate of 25 deg/min was applied.

Phase analysis and chemical analysis of the materials after a definite mass reduction showed that in the $PbSO_4 + ZnS$ mixture, independently of their mole ratio, the $ZnS \rightarrow ZnO$ transformation and PbS formation take place. The next stages are connected with the chemical reaction between the PbS formed and some lead sulphate in an amount exceeding the stoichiometric composition. Let us consider the problem of how $PbSO_4$ and ZnS react with each other. Analysis of this problem leads to two schemes of reaction:

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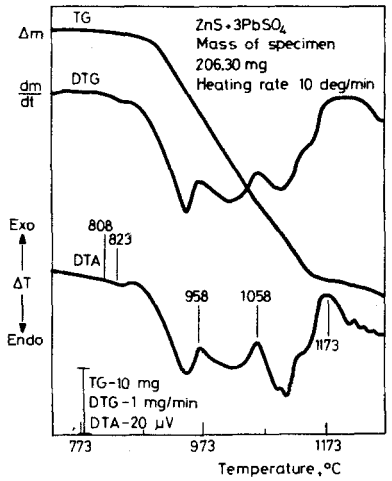

Fig. 1 Thermal curves of ($ZnS + 3\,PbSO_4$) reaction. TG = 10 mg, DTG = 1 mg/min, DTA = 20 μV. Sample size: 206.3 mg, Heating rate: 10 deg/min

1. Reduction according to the equation

$$3/4\ PbSO_4 + ZnS = 3/4\ PbS + ZnO + SO_2$$

2. Gradual decomposition of lead sulphate $PbSO_4$ to basic sulphate $PbO \cdot PbSO_4$, with sulphur dioxide and oxygen evolution. Oxygen combines with zinc sulphide, and zinc oxide is formed. Simultaneously, the exchange reaction occurs between lead sulphide and the oxide in the basic sulphate. This can be presented as follows:

$$2PbSO_4 = PbO \cdot PbSO_4 + 1/2\ O_2$$

$$ZnS + 3/2\ O_2 = ZnO + SO_2$$

$$ZnS + PbO \cdot PbSO_4 = ZnO + PbS + PbSO_4$$

Table 1 Theoretically calculated composition of products after the first stage of the reaction

Mixtures	Composition, %						Theoretical mass reduction, %
	Zn	Pb_{total}	$Pb_{(PbSO_4)}$	$S_{SO_4^{2-}}$	S_s	S_{total}	
$3ZnS + 2PbSO_4$	26.95	56.93	—	—	10.26	10.26	18.99
$ZnS + PbSO_4$	19.42	61.55	15.38	2.38	7.13	9.51	15.98
$ZnS + 2PbSO_4$	10.22	64.79	40.48	6.25	3.75	10.00	9.09
$ZnS + 3PbSO_4$	6.93	65.92	49.44	7.64	2.55	10.19	6.36
$ZnS + 4PbSO_4$	5.25	66.51	54.04	8.54	1.92	10.26	4.88

The chemical compositions of the products after stage I of the reaction have been calculated according to the above assumptions. The calculation results are presented in Table 1. The chemical compositions of the samples after stage I of the reaction are presented in Table 2. Very good conformity of the Zn, Pb and S_{total} contents is observed if the data in Tables 1 and 2 are compared. Some discrepancy

Table 2 Chemical composition of products after the first stage of reaction

Mixture	Composition, %					
	Zn	Pb_{total}	$Pb_{(PbSO_4+PbO)}$	$S_{SO_4^{2-}}$	S_s	S_{total}
$3ZnS+2PbSO_4$	27.19	55.37	7.03	0.45	9.50	9.95
$ZnS+PbSO_4$	19.27	61.11	20.60	2.47	6.81	9.28
$ZnS+3PbSO_4$	6.91	65.44	53.54	7.82	2.18	10.00
$ZnS+4PbSO_4$	5.49	65.62	56.95	8.44	1.68	10.12

occurs in the cases of $Pb_{(PbSO_4)}$ and $Pb_{(PbSO_4+PbO)}$. This discrepancy is caused by the fact that a certain amount of PbO is present in the material after the reaction. This proves the reaction of PbS with $PbSO_4$. The decrease of the PbO content in the reaction products with $PbSO_4$: ZnS ratio increase (which corresponds to the $PbSO_4$: PbS ratio in the reaction products) is in accordance with [8, 9]. The conversion has been calculated as the ratio of the recorded mass reduction to the theoretically calculated one, and is presented in Fig. 2.

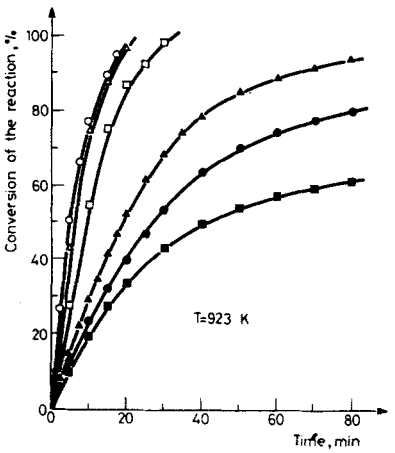

Fig. 2 Influence of $PbSO_4$ · ZnS ratio on conversion of reaction at 923 K. ■ $3ZnS+2PbSO_4$, ▲ $ZnS+PbSO_4$, □ $ZnS+2PbSO_4$, △ $ZnS+3PbSO_4$, ○ $ZnS+4PbSO_4$, ● $PbS+2PbSO_4$

Conclusions

1. The multistage character of the studied reaction has been found. The ZnS → ZnO transformation and the formation of an equivalent amount of PbS proceeds in the first stage of the reaction, while the following stages are connected with the $PbS + PbSO_4$ reaction.

2. The $PbSO_4 : ZnS$ reaction up to 3 : 1 and the temperature have a significant influence on the conversion in the first stage of the reaction. The conversion is directly proportional to the $PbSO_4 : ZnS$ ratio, while a temperature increase of 25 K results in almost a doubling of the conversion.

3. The $ZnS + PbSO_4$ reaction proceeds at a higher rate than the $PbS + PbSO_4$ reaction.

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Zusammenfassung — Die Reaktion von ZnS mit $PbSO_4$ wurde bei verschiedenen Molverhältnissen untersucht. Man fand, daß die Reaktion in mehreren Schritten abläuft. Die Produkte des ersten Schrittes sind hauptsächlich ZnO, PbS und $PbSO_4$, deren Mengen vom Molverhältnis der Reaktanten abhängen. Die folgenden Reaktionsschritte bestehen aus den Zusammenwirkungen von dem primär gebildeten PbS mit $PbSO_4$. Dabei hängt die Reaktionsgeschwindigkeit von der Temperatur und vom Molverhältnis $PbSO_4 : ZnS$ (bis zu 3 : 1) ab.

Резюме — Изучена реакция между сульфидом цинка и сульфатом свинца при их различном молярном соотношении. Найдено, что данная реакция является многоступенчатой. Главными продуктами разложения на первой стадии реакции являются оксид цинка, сульфид свинца и сульфат свинца, количество которых зависит от молярного соотношения исходных компонент. На последующих стадиях происходит взаимодействие сульфида свинца с сульфатом свинца. Установлено, что скорость отдельных стадий реакций зависит от температуры и молярного соотношения сульфата свинца и сульфида цинка (верхный предел 3 : 1).