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The Possibility Assessment of Complex Processing of Technogenic Formations Containing Zinc Sulfide

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Abstract

The comprehensive methodology for the zinc extraction from sulfide compounds into the oxide form with possible further reduction to metal is presented in this study. It was demonstrated in laboratory conditions during sludge treatment with Zn and ZnO obtaining. The remaining silicate products. It is proposed to recycle this material into Portland cement clinker to ensure a waste-free process.

Keywords: zinc sulfide, zinc oxide, sludge recycling, Portland cement clinker, waste-free recycling

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Zinc in oxide form (ZnO) can be found in arc and blast furnaces dust. To extract zinc from oxide forms waelz process is used carried out in rotary kilns. In its conditions a carbon-containing material is added to the raw mixture, which provides zinc oxide reduction and its sublimation at 1100 °C. The waelz process is based on the zinc oxide reduction to metal zinc using a carbon-containing material by reaction (1):

$$2ZnO + C = 2Zn\uparrow + CO_2\uparrow \quad (1)$$

In some technogenic formations, such as synthetic fibers production sludge from, zinc is in sulfide form (ZnS). Extraction of zinc from such man-made materials using waelz process is difficult. Figure 1 presents results of thermodynamic calculations of Gibbs energy change as a function of temperature.

Since zinc is in sulfide form, its reduction by carbon is possible by the reaction (2):

$$2ZnS + C = 2Zn\uparrow + CS_2 \quad (2)$$

Thermodynamic calculation results presented in Figure 1 indicate that the reaction (2) is possible only above 1900 °C. Special high-temperature units using will be required to implement such reaction in practice. It is not economically feasible.

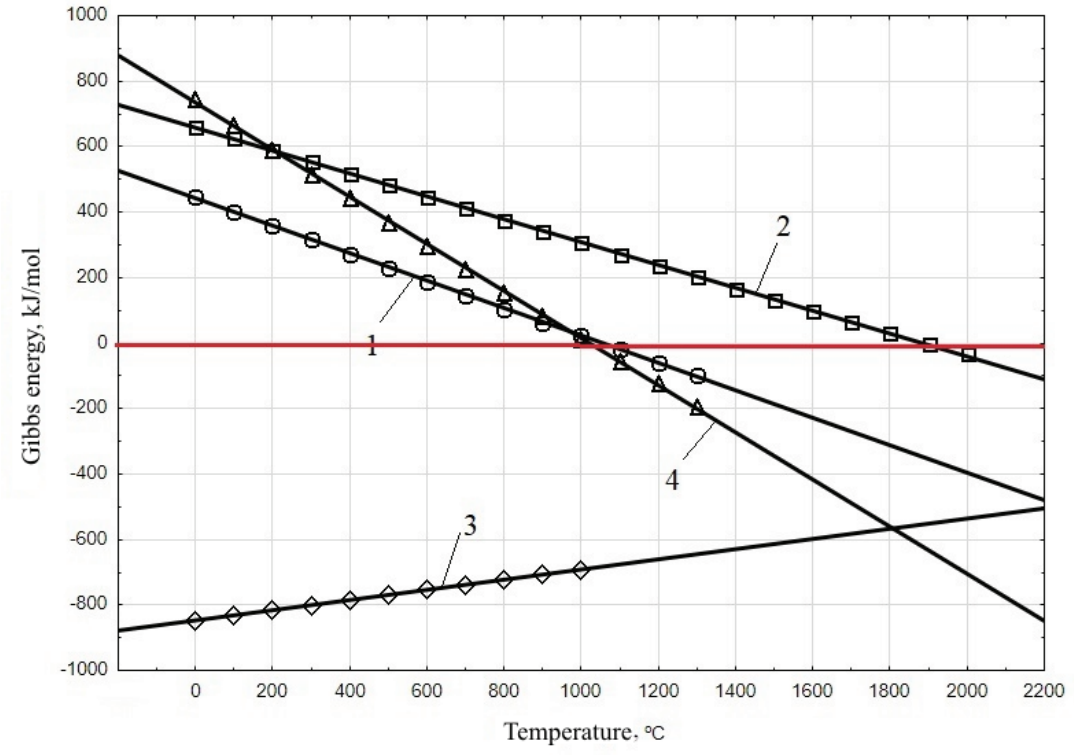

Figure 1: Gibbs energy changes for reactions (1) - (4) as a function of temperature

Sulfur removal from zinc sulfide forms is possible by oxygen purging, while sulfur is removed as gas (SO_2), and zinc passes into the oxide form by reaction (3):

$$2ZnS + 3O_2 = 2ZnO + 2SO_2\uparrow \quad (3)$$

When implementing such a sulfur removal scheme, zinc remains in the mixture in oxide form and the reduction stage will be required for its sublimation, so it is necessary to introduce additional carbon-containing material in the mixture. This means that this technology is implemented only in two stages, since the carbon-containing material introduced into the mixture before oxygen purging will burned out without reducing zinc oxide.

The most attractive for the sulfide-oxide zinc form conversion are limestone, magnesite and dolomite. When using limestone for the decomposition of sulfide and zinc sublimation, the reaction (4) proceeds:

$$2ZnS + 2CaCO_3 + C=2Zn\uparrow + 2CaS + 3CO_2\uparrow \quad (4)$$

The results of thermodynamic calculations indicate that the reaction (4) is possible above a temperature of 1100 ° C, at which the Gibbs energy becomes negative. Also, the calculation results indicate a thermodynamic preference for the reaction (4) relative to reaction (1) at a temperature of 1100 ° C.

Evaluation of the decomposition parameters of zinc sulfide (in a technogenic formation), was carried out by heating the sludge from the production of synthetic fibers located in the Balakovo city, Saratov region. In this sludge, the concentration of zinc sulfide depends on the occurrence depth, therefore, Table 1 shows the average chemical composition of the sludge.

Table 1: Average chemical composition of the sludge

Content, mass. %						
CaO	SiO_2	Al_2O_3	Fe_2O_3	ZnS	SO_3	Oст.
20,4	9,1	3,6	2,5	22,7	32,6	9,1

The phase analysis data (Table 2) indicate that the slurry, in addition to zinc sulfide, contains a significant amount of limestone, which will contribute to the decomposition of zinc sulfide by reaction (4). According to the stoichiometry of reaction 4, for its complete implementation, an additional small amount of limestone (2%) and about 3% carbon should be added. The raw mixture was prepared based on the presented ratio of the components.

Table 2: Phase composition of the sludge

Phase name	Chemical formula	Content, mass. %
Limestone	$CaCO_3$	55,41
Gypsum dihydrate	$CaSO_4 \cdot 2H_2O$	18,24
Zinc sulfide	ZnS	12,77
Quartz	SiO_2	13,58
In total:		100,00

The components of the raw mix were thoroughly mixed by co-grinding and briquetted with the addition of water at a pressure of 50 MPa. Briquettes were fired at temperatures of 1100, 1200 and 1300 ° C without isothermal exposure. The firing was carried out in a chamber high-temperature electric furnace brand SKV 12/14-V. Calcined samples were subjected to quantitative phase analysis.

Table 3 shows the summary results on the content of zinc phases in the sample at realized firing temperatures.

The results of a phase analysis of firing products (Table 3) indicate that with increasing firing temperature, the amount of zinc sulfide in the samples decreases, and zinc oxide increases. Hence the conclusion about the correctness of theoretical conclusions and the possibility of implementing the proposed technology for the extraction of zinc from the sulfide form.

Table 3: Sample Phase Content

Firing temperature, ˚C	The content in the sample, mass. %			Zinc sublimation, mass. %
	ZnS	ZnO	ZnS+ZnO	
0	34,4	0	34,4	0
1100	15,3	9,3	24,6	9,8
1200	10,0	14,8	24,8	9,6
1300	6,87	17,6	24,5	9,93

After zinc extraction, a significant amount of silicate products remains in the firing products, which, to ensure complex processing of sludge, it is advisable to convert into commercial products, such as Portland cement clinker.

A significant amount of gypsum anhydrite is presented in the firing products (Table 4). From the practice of production of Portland cement it's known that it's difficult to obtain high-quality clinker from a raw mix, containing a significant amount of gypsum anhydrite, which is a source of SO_3. According to [1, 2], with an increase in the content of SO_3 in the feed mixture, the amount of dicalcium silicate C_2S increases, and the dicalcium silicate C_3S decreases. Since tricalcium silicate is the most active and refractory component of Portland cement clinker, its reduction leads to a decrease in refractoriness and activity of the clinker. It was found [3] that with an increase in the content of SO_3 in the Portland cement clinker, not only the content of C_3S, but also C_3A decreases. No reasons have been found for a decrease in the content of tricalcium silicate in Portland cement clinker with an increase in the content of SO_3 in it.

Table 4: Phase composition of firing products

Phase name	Chemical formula	Content, mass. %
Gelenite	$2CaO{\cdot}SiO_2{\cdot}Al_2O_3$	23,50
Zinc sulphide	ZnS	15,3
Mayenite	$12CaO{\cdot}7Al_2O_3$	6,75
Zinc oxide (Zincite)	ZnO	9,27
Larnith	$2CaO{\cdot}SiO_2$	22,07
Gypsum anhydrite	$CaSO_4$	9,11
Zinc sulfide oxide (Wurtzite)	$Zn(S_{0,988}\ O_{0,12})$	14,0
In total:	100	

To identify the causes of inhibition of alite formation in the high sulfate clinker, raw material mixtures were calcined to obtain a typical Portland cement clinker with modular characteristics KN = 0.92, n = 2.3 and p = 1.69.

For the preparation of Portland cement clinker, a raw mix, based on limestone, clay, quartz sand and natural gypsum was used. The total amount of gypsum in the mixture

was 5%. The components of the raw mix were thoroughly mixed by co-grinding for 30 minutes. The averaged mixture was moistened and pressed at a pressure of 50 MPa. Samples were fired at temperatures from 1100 to 1300 ° C. The phase analysis data for firing products are shown in Figure 2.

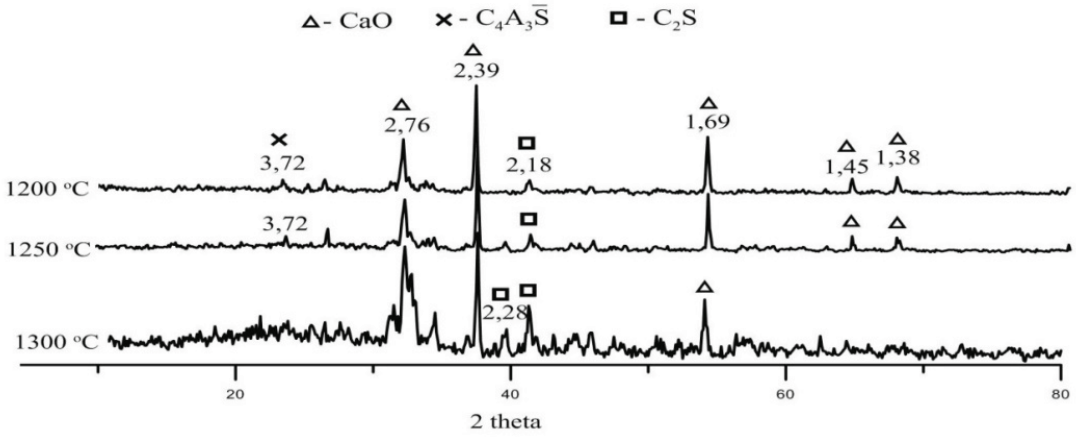

Figure 2: Results of a phase analysis of clinker, based on a raw mix with the addition of 5% gypsum

The test results indicate that tricalcium silicate is not formed in the firing products, and the formed clinker contains a significant amount of free lime (Table 5).

TABLE 5: The content of free lime in clinker

Material name	The content of free CaO. in clinker, wt. %, at firing temperature, ° C		
	1100	1200	1300
Raw mix clinker with 5% gypsum	14,0	13,84	11,6

Thermodynamic analysis of clinker formation reactions in the presence of gypsum anhydrite showed that, in the absence of SO_3 the synthesis of C_3A and C_4AF is thermodynamically possible from simple minerals - CaO, Al_2O_3 and Fe_2O_3, and in the presence of SO_3, the formation of calcium sulfoaluminate $C_4A_3\bar{S}$ is thermodynamically preferable. Calcium sulfoaluminate is formed from calcium monoaluminate CA, which is synthesized at a temperature of about 900 ° C. In the presence of calcium monoaluminate, the formation of C_3A and C_4AF is thermodynamically impossible. Therefore, if the calculation of the raw mixture is carried out to form highly basic minerals C_3A and C_4AF in a clinker containing SO_3, in fact, low basic aluminates and calcium ferrites are formed in such a clinker, then due to the difference in the lime content in these minerals, a significant amount of free lime is formed. Well-crystallized free lime prevents the formation of tricalcium silicate.

Based on the results obtained, a methodology for calculating the composition of the raw mix containing gypsum anhydrite, which allows the formation of a significant amount

of tricalcium silicate in Portland cement clinker was developed. The phase analysis data (Figure 3) indicate that in the firing products based on sludge from the production of synthetic fibers, it was possible to form typical phases of Portland cement clinker.

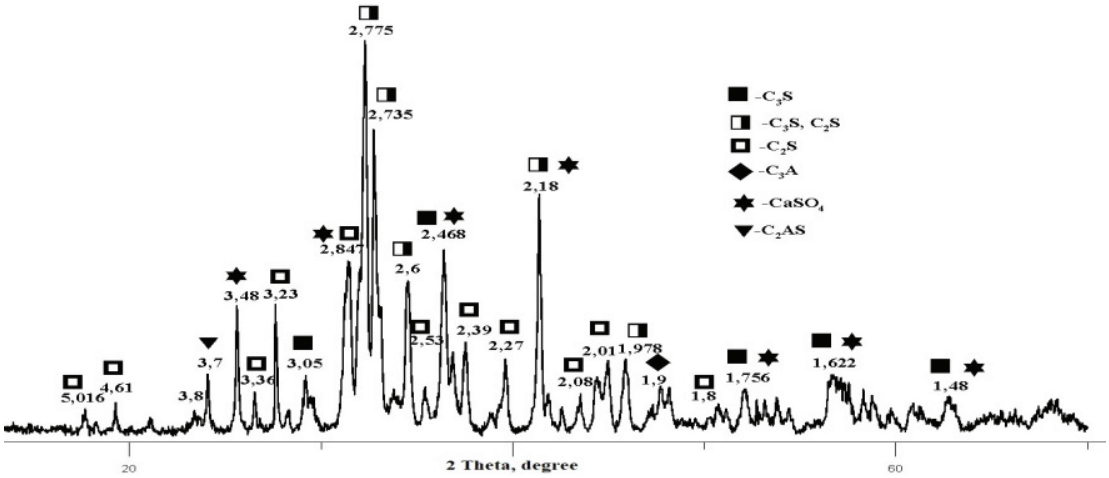

Figure 3: Phase Analysis Data

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References

[1] Javed, I. B. (1995). *Role of Minor Elements in Cement Manufacture and Use*. Skokie: Portland Cement Association.

[2] Horcoss, S., Ltief, R. and Rizk, T. (2011). Influence of the Clinker SO_3 on the Cement Characteristics. *Cement And Concrete Research*, vol. 41, pp. 913-919.

[3] Horcoss, S., Ltief, R. and Rizk, T. (2010). Calculation of the C_3A Percentage in High Sulfur Clinker. *International Journal of Analytical Chemistry*, vol. 2010, Article ID 102146, p. 5.