

PHASE CONTENT OF SEMI-FINISHED PRODUCTS IN ZINC PRODUCTION

B.Boyanov, R.Dimitrov - Plovdiv University,
Bulgaria

SUMMARY

Zinc calcine, cakes, waelz and fuming oxides, etc. are investigated, applying DTG and thermogravimetric analysis, X-ray phase analysis, Mössbauer spectroscopy, chemical and chemical phase analyses. Their phase contents are defined. The phase ZnO , 2ZnSO_4 occurs in some semi-finished products in addition to ZnO , $\text{ZnO}\cdot\text{Fe}_2\text{O}_3$, Zn_2SiO_4 , ZnSO_4 and ZnS . The obtained results are of great importance to the improvement of the indices of the technological processes in zinc production by the hydrometallurgical method.

INTRODUCTION

The multicomponent content of the starting materials in zinc hydrometallurgical production determines the obtaining of semi-finished products of complex chemical phase contents. The knowledge and control of their phase content are important for carrying out the processes at optimum conditions and their control /1-5/. It is object of the present work, using different methods, to characterize more completely the different semi-finished products from zinc production and pay attention to zinc sulphates.

RESULTS AND DISCUSSION

Most semi-finished products contain ZnSO_4 and the problem of its decomposition is still interesting. The investigations show, that in dynamic conditions $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ releases 6 water molecules at 115°C and one molecule at 285°C . In quasi isobarothermal conditions these temperatures are 108°C and 310°C , respectively. At 740°C $\alpha\text{-ZnSO}_4 \longrightarrow \beta\text{-ZnSO}_4$ and partial decomposition of ZnSO_4 takes place. That leads to decrease of the exo-effects of the transition $\beta\text{-ZnSO}_4 \longrightarrow \alpha\text{-ZnSO}_4$. At 840°C - 850°C a clearly expressed turn in the TG and evolved SO_3 curves is observed, related to the different rates of ZnSO_4 decomposition and $\text{ZnO}\cdot 2\text{ZnSO}_4$ obtained at that temperature.

$\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ heated up to 600°C - 700°C absorbs 0,5-1 water mo-

lecule from the air, after cooling, which is clearly seen on the derivatogram. That explains why in zinc calcine /2/ and in some fluid bed furnace /6/ crusts, the existence of $ZnSO_4 \cdot H_2O$ is pointed out, though they are obtained at high temperatures.

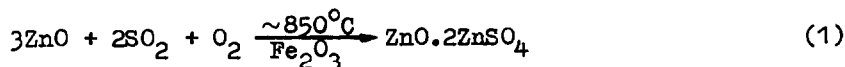
The value of ΔH° for $ZnSO_4$ - 4290 cal/mol, which agrees with references /3/, was calculated using the value of ΔH° (2140 cal/mol) for K_2SO_4 with phase transition at $583^\circ C$ and the peak area for a mol of K_2SO_4 and $ZnSO_4$.

When heating $ZnSO_4$ up to $800^\circ C$ the peaks of the X-ray patterns coincide with those of $ZnSO_4$ and some $ZnO \cdot 2ZnSO_4$ lines appear. When heated up to $900^\circ C$ the X-ray pattern has all $ZnO \cdot 2ZnSO_4$ peaks /3/. It is very similar to some X-ray patterns for crusts from the fluid bed roaster for zinc concentrates.

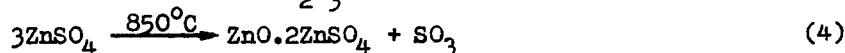
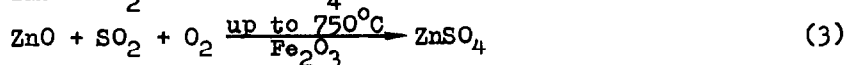
When $ZnSO_4$ is heated to $900^\circ C$, cooled, held in air and reheated, a new endoeffect is established at $370^\circ C$, what is observed with some semi-finished products from zinc production, too. The third effect is explained by the presence of lead compounds /2/. It may be concluded from $ZnO \cdot 2ZnSO_4$ and zinc semi-finished products derivatograms, that the endoeffect at $360^\circ - 380^\circ C$ is due to the presence of $ZnO \cdot 2ZnSO_4$. According to us, $ZnSO_4$, heated to $900^\circ C$, changes its content and a third coordination sphere of the crystallization water appears.

$ZnO \cdot 2ZnSO_4$ lines are observed on the X-ray patterns of some crusts from the fluid bed furnace. In roasting conditions it may be obtained by different ways:

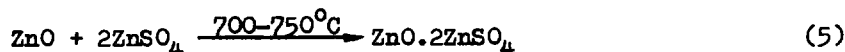
a) directly



b) by $ZnSO_4$ decomposition



c) by solid phase interaction



The possibility of obtaining $ZnO \cdot 2ZnSO_4$, established on the grounds of chemical potentials /7/ diagrams, in determined conditions in the roaster, is experimentally confirmed.

Sulphate zinc content of zinc calcine is 2-3% /2/. That is why, it is difficult to determine the presence of $ZnO \cdot 2ZnSO_4$ by X-ray phase analysis. Indirect conclusion for its presence may be drawn by means of the calcine derivatograms at the availability of endoeffect at 360° - $380^{\circ}C$ which disappears or decreases during its water extraction.

As for the cakes from extraction, the observed effects are mainly due to $ZnSO_4 \cdot H_2O$ inclusions. Two endoeffects at 825° and $890^{\circ}C$, in addition to the endoeffect due to water removal, are observed in neutral stage cakes, containing ZnO also, while in acid stage cakes there is one endoeffect at $840^{\circ}C$. Two effects, at 810° - $820^{\circ}C$ and 875° - $885^{\circ}C$, are observed again when ZnO or Zn calcine are added to the last cake. This fact may be used in the qualitative analysis of semi-finished products of similar origin for determining the presence of undissolved zinc calcine.

The observed zinc phases in some of the investigated samples are represented in the following table.

No	Material investigated	Zinc content, %				
		sulphate	oxide	silicate	sulphide	ferric
1	calcine	2,35	47,14	2,46	0,58	2,71
2	neutral stage cake	7,84	5,17	1,44	0,77	5,80
3	acid stage cake	6,74	0,79	1,05	0,97	5,88

The results represented show that $ZnSO_4$ phase is available in zinc production cakes. Its reduction by improving washing and filtering will better the process indices /5/. $ZnSO_4$ lines were observed in the taken IR spectra, too.

$ZnO \cdot Fe_2O_3$ doublet and α - Fe_2O_3 sextet are observed in zinc semi-finished products by Mössbauer spectroscopy.

The unroasted waelz and fuming oxides contain impurities, which as per DTA and TG curves are eliminated at the temperatures of 650° - $700^{\circ}C$. Aiming at the intensification of the process and more complete impurities removal, it is advisable to increa-

se the temperature up to 1000°C and to carry out roasting at a state, called by us "falling" /7/.

CONCLUSIONS

Zinc semi-finished products phase content established on the grounds of the performed investigations is the following:

Zinc calcine: ZnO , $ZnO \cdot Fe_2O_3$, $ZnSO_4(ZnO \cdot 2ZnSO_4)$, $2ZnO \cdot SiO_2$, β -ZnS, $CaSO_4$.

Neutral stage cake: $ZnO \cdot Fe_2O_3$, ZnO , $PbSO_4$, $ZnSO_4 \cdot H_2O$, $2ZnO \cdot SiO_2$, β -ZnS, $CaSO_4$, Fe_2O_3 . The same phases and insignificant quantities of ZnO are observed in the acid stage cake.

Crusts from the fluid bed furnace walls: $ZnSO_4$, $ZnO \cdot 2ZnSO_4$, ZnO , $ZnO \cdot Fe_2O_3$, $2ZnO \cdot SiO_2$, β -ZnS, $PbSO_4$, PbO , PbS , Fe_2O_3 . Some Pb (metal), $PbO \cdot SiO_2$, $CaSO_4$, SiO_2 (α -quartz) were found also in the hearth crusts.

Some concrete recommendations for improving the practical performance of the processes in zinc production are made on the grounds of the obtained results.

REFERENCES

- 1 L.S.Getskin, V.I.Jarigin, U.S.Remizov, L.A.Abramovskaja, Physical and Chemical Investigations in Lead and Zinc Metallurgy, Ust-Kamenogorsk, 1980, 3.
- 2 V.Riesenkampf, E.Gerasimova, V.Zhabinski, Metallurgia(Bulgaria), 4(1974) 25.
- 3 T.R.Ingraham, H.H.Kellogg, Trans.Met.Soc.AIME, 227(1963) 1419.
- 4 E.V.Margulis, Izv.VUZ, Tsv.Metallurgia, 1(1983) 44.
- 5 A.S.Bagaev, Izv.VUZ, Tsv.Metallurgia, 2 (1984) 47.
- 6 R.Dimitrov, B.Boyanov, Izv.VUZ, Tsv.Metallurgia, 6(1983) 28.
- 7 R.Dimitrov, I.Dokuzov, A.Hekimova, T.Genevska, Yearbook, Institute for Non-Ferrous Metallurgy (Bulgaria), XX (1982) 60.
- 8 R.Dimitrov, D.Khadzhistavrev, B.Boyanov, V.Vasilev, Author's certificate, Bulgaria, class C 22 B 1/00, № 24323 (1977).