Thermochimica Acta, 93 (1985) 733-736
Elsevier Science Publishers B.V., Amsterdam

PHASE CONTENT OF SEMI-FINISHED PRODUCTS IN ZINC PRODUCTION

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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, $ZnO.Fe_2O_3$, 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 $ZnSO_4.7H_2O$ releases 6 water molecules at 115°C and one molecule at 285°C. In quasi isobaro-isothermal conditions these temperatures are 108°C and 310°C, respectively. At 740°C α-$ZnSO_4$ $\longrightarrow$ β-$ZnSO_4$ and partial decomposition of $ZnSO_4$ takes place. That leads to decrease of the exo-effects of the transition β-$ZnSO_4$ $\longrightarrow$ α-$ZnSO_4$. At 840°-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 $ZnO.2ZnSO_4$ obtained at that temperature.

$ZnSO_4.7H_2O$ heated up to 600°-700°C absorbs 0,5-1 water mo-

Proceedings of ICTA 85, Bratislava

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 $ZnSO_4.H_2O$ is pointed out, though they are obtained at high temperatures.

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

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

When $ZnSO_4$ is heated to 900°C, cooled, held in air and reheated, a new endoeffect is established at 370°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 $ZnO.2ZnSO_4$ and zinc semi-finished products derivatograms, that the endoeffect at 360°-380°C is due to the presence of $ZnO.2ZnSO_4$. According to us, $ZnSO_4$, heated to 900°C, changes its content and a third coordination sphere of the crystallization water appears.

$ZnO.2ZnSO_4$ 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

$$3ZnO + 2SO_2 + O_2 \xrightarrow[Fe_2O_3]{\sim 850^oC} ZnO.2ZnSO_4 \qquad (1)$$

b) by $ZnSO_4$ decomposition

$$ZnS + 2O_2 \xrightarrow{750^oC} ZnSO_4 \qquad (2)$$

$$ZnO + SO_2 + O_2 \xrightarrow[Fe_2O_3]{\text{up to } 750^oC} ZnSO_4 \qquad (3)$$

$$3ZnSO_4 \xrightarrow{850^oC} ZnO.2ZnSO_4 + SO_3 \qquad (4)$$

c) by solid phase interaction

$$ZnO + 2ZnSO_4 \xrightarrow{700-750^oC} ZnO.2ZnSO_4 \qquad (5)$$

The possibility of obtaining $ZnO.2ZnSO_4$, 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 $ZnO.2ZnSO_4$ 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 $ZnSO_4.H_2O$ 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.

$ZnO.Fe_2O_3$ 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 increase 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, $ZnO.Fe_2O_3$, $ZnSO_4(ZnO.2ZnSO_4)$, $2ZnO.SiO_2$, β-ZnS, $CaSO_4$.

Neutral stage cake: $ZnO.Fe_2O_3$, ZnO, $PbSO_4$, $ZnSO_4.H_2O$, $2ZnO.SiO_2$, 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: $ZnSO_4$, $ZnO.2ZnSO_4$, ZnO, $ZnO.Fe_2O_3$, $2ZnO.SiO_2$, β-ZnS, $PbSO_4$, PbO, PbS, Fe_2O_3. Some Pb(metal), $PbO.SiO_2$, $CaSO_4$, 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.

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