J. Int. Environmental Application & Science, Vol. 4 (2): 198-206 (2009)

Slag Valorisation of Reductive Smelting Process by Shaft Furnace in the Lead Metallurgy of "Trepça" Complex with Economical and Environmental Effects

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Received April 14, 2009; Accepted June 09, 2009

Abstract: Slag exploration using reductive smelting of the lead agglomerate to many manufacturers as well as to the lead smelter of "Trepça" is a process followed by economical and environmental effects. Main objective of this paper consists in determining of useful metals in slag, in selecting of the technological process and corresponding equipments for the slag treatment in the recycle process. Based on analyses of the chemical composition for solid slag (around 2.5 million ton) and data collected by the slag of process, as a more rational technological process has been taken the fuming process. There are done 354 samples, as a result is concluded that the obtained values for the slag chemical composition are within the permissible limits. Determination of technological parameters for the process is completed through the material balance. Quantity of useful metals in slag (Pb, Zn, Cu, Ag, Tl, In, Ge *etc*) is favourable in order to meet economical effects of the process. Advancement of such a study consist in the fact that the product gained through fuming process will be processed further, until obtaining high purity metals, what can be achieved by using present equipments in the sector of zinc metallurgy plant of Trepça complex. On the other hand, the remaining slag can be used in the construction industry, this way has been achieved the full scale use of raw material including environmental positive effects.

Keywords: Fuming, slag, reductive, smelting, furnace**.**

Introduction

World general tendencies for application of economical technologies in the lead metallurgy enabled application of some slag processing processes of the reductive smelting process. For the first time in history, slag processing started in the USA, in the company „IST-HELEN" in 1927.

During the reductive smelting process of lead concentrates, in slag is transformed approximately 80%Zn, 20%Cu, and 1-1.8% Pb, considering the case when there are disorders during the reductive smelting process, resulting in a higher quantity of lead.

Turns into slag up to 65% Ge, 55% Tl, 45% In, 30% Te *etc*., whereas other elements are rare and scattered. Based to reports of the lead metallurgy „Trepça" in the last 25 years have been stored more than 2.5 million tons of slag from the process of reductive smelting in shaft furnaces, which has the following average chemical composition: ZnO(10-12%), Pb(1-2%), Cu(0.1-0.20%), Ag(10-15g/t) CaO(15-18%), FeO(30-38%), SiO_2(21-24), MgO(2.0-3.0%), Al_2O_3(2.0-5.0%), and a quantity of rare metals (Rizaj *et al.*, 2008).

Experimental

Chemical analyses

Distribution of slag components (Figure 1), is analysed based on the statistical model and the obtained results are with accepted confidence. There are done chemical analyses in the slag and then compared to the results of the statistical model (King & Flojd, 1990; Kelmendi & Zeqiri, 2007; Girone & Salvemini, 2000). The chemical composition of the lead metallurgy slag has presented in Table 1, from Trepça" and "Plovdiv" smelters.

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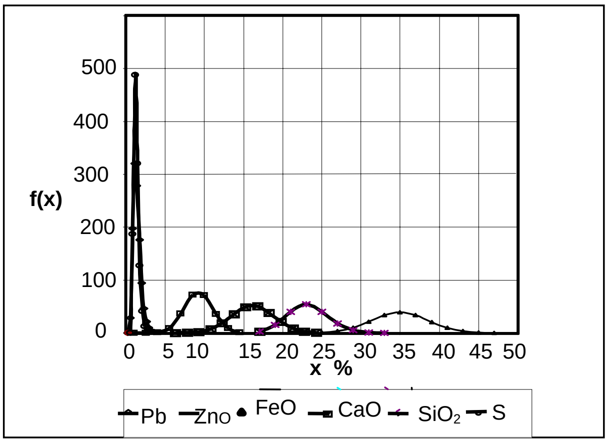

Figure1. Distributions of slag components (Pb; ZnO; FeO; CaO; SiO_2 and S)

Table 1. Chemical composition of slag in lead metallurgy "Trepça"

Pb %	ZnO %	FeO %	CaO %	SiO_2 %	S %	Cu %	MgO %	Al_2O_3
2.75	11.20	37.05	13.60	21.30	-	0.12	2.57	7.34
2.22	10.70	36.42	16.78	20.60	-	0.13	3.30	7.34
1.5-2	7-12	32-34	20-22	18-20	1.5	-	3.30	7.34
2.24	7.09	37.42	15.93	24.50	1.20	0.14	3.04	8.28
0.5-1.5	10-14	30-35	18-21	21-24	-	-	3.55	7.95
2.05	10.15	36.30	16.40	20.70	-	0.17	3.04	8.28
1.41	9.00	28.72	18.42	23.17	1.38	0.14	2.70	9.48
0.87	9.39	37.14	17.46	25.10	1.65	0.13	3.08	8.10
2.06	9.45	32.76	18.62	24.43	1.87	0.24	3.95	8.80
1.90	12.23	34.46	9.37	19.14	0.91	0.16	-	-
1.91	8.10	35.75	15.87	30.70	1.93	0.10	2.82	6.38
1.73	5.81	37.12	14.85	24.33	1.90	0.21	3.30	6.22

Table 2. Chemical composition of slag in lead metallurgy "Plovdiv"

Components	Sample-1, %	Sample- 2, %
FeO	38.00	38.00
CaO	12.00	13.00
SiO_2	24.00	19.00
ZnO	16.00	12.00
Pb	1.00	2.10
Cu	-	0.30
MgO	2.00	2.20
Al_2O_3	3.00	3.80
S	-	2.00

Table.3. Chemical composition of slag in lead metallurgy„Plovdiv" after fuming process

Components	Sample-1, %	Sample- 2, %
FeO	40.35	41.05
CaO	12.00	12.00
SiO_2	25.03	20.26
Zn	2.10	2.23
Pb	0.10	0.10
Cu	-	0.23
MgO	2.38	2.30
Al_2O_3	4.27	5.15
S	-	0.90

Slag treatment according to fuming process

Basic processes of the lead-zinc slag processing are as follows: fuming, vells, elektrothermic and sajrosmelt process. Considering our case, the most acceptable process is chosen the fuming process.

Fuming process accomplished through the blowing of the smelted slag with mixing air and reducing agents under pressure. In the reductive space available under such conditions in temperature 1200-1300 ° C, metal oxides there will be reduced and stems of these metals will turn into a gaseous state.

The process basic reactions are:

$$C + O_2 = CO_2$$
$$CO_2 + C = 2CO$$
$$ZnO + C = Zn + CO$$
$$ZnO + CO = Zn + CO_2$$
$$PbO + CO = Pb + CO_2$$

The equilibration constant of this reaksion is as follows:

$$K = P_A \cdot [PbO]_{zgj} / P_B$$
$$P_A / P_B = K / [PbO]_{zgj}$$

P_A, P_B, and $(PbO)_{sl}$- are the partial pressure of CO, CO_2 and PbO (Gjokiç, 1982) Metalurgija sirovog olova u topionici „Trepçe" (Zveçan, 1982). From the above mentioned reaction can be concluded that in order to reduce PbO or another oxide from the slag the higher concentration of CO is needed in the gases of the process how the lower is oxide concentration in the slag. During the reduction process will be formed steams of zinc and lead which on the liquid bath space and in the gas-pipeline, steams of such metals are oxidised with the air oxygen towards the corresponding oxides.

$$2Zn + O_2 = 2ZnO$$
$$2Pb + O_2 = 2PbO$$

Zinc oxide formed during the oxidisation as powder is taken out along with the gases of the process. The fuming process of the slag takes 2 to 3 hour duration. More of Pb and Cd is extracted in a few minutes. Copper and precious metals during the fuming process are mixed with the slag, this way they are considered as a disadvantage of the fuming process (Loskutov, 1991). In such cases when the concentration of zinc in the slag is up to 8%, its activity coefficient in smelting is approximately one.

During evaporation process of zinc, blowing pressure have an important role. Dependence of lead steams' pressure and its components from temperature nearly can be given through the following expression.

$$\lg p_{Pb\,(1)} = 6210 / T + 6{,}34 ;$$
$$\lg p_{PbO\,(1)} = -7640 / T + 8{,}04 ;$$
$$\lg p_{PbS\,(ng)} = -7850 / T + 9{,}19$$

During the fuming process, flow of zinc evaporation varies within a wide range (15-50kg/min) depending mostly from the slag composition. Specific productivity of the fuming shaft furnace is 45 to 55 t/m^2 of slag (Abdejev *et al*., 1985).

In Trepça smelter, large lead production is made in shaft furnace. Two of them had capacity of 260t/24h (for each). Whereas, the other one after reconstruction have capacity of 360 t/day.

Slag production varied from time to time and its production ranged form 55.000- 60.000t/year. For slag processing intending to exploit useful components both the fresh one and recycling from the store, in continuity with optimal parameters obtained from the program is determined the unit capacity of the fuming furnace. Production of a fuming furnace is 60 tpd and a ratio between the fresh slag and old one is 3 :1 (weigh ratio).

Fuming furnace capacity is calculated based on the following parameters: 30 days of annual repair, number of working days 335, operation utility factor is 0.87. For the capacity of a furnace 60 tpd is taken the optimal value of technological parameters, such as: oxygen percentage in the air flow and the quantity of slag processed.

Material balance

Material balance is determined based on input and output quantities of fuming furnace, what proves the mass conservation law. Calculation is done based on the companies (KCM- Plovdiv) balance which have similar with chemical composition of slag to that of Trepça complex, based on interpolation is obtained a certain number of the given values. Using approximate methods are obtained mathematical equations.

Material balance for fuming process is given in the following tables, for the slag in the lead metallurgy of „Trepça" and input parameters given such as: air blown temperature 540 °C ; air enriched by oxygen O_2= 23% ; carbon percentage in coal C= 70% and slag quantity for a cycle of 70t.

In the following tables are given the main parameters of the fuming process.

Table 4. Input selected values

Oxygen percentage, %	23.000
Air temperature, °C	600.000
Coal quantity, t	60.000
carbon percentage, %	70.000
zinc percentage, %	9.131
lead percentage, %	1.362
copper percentage, %	0.211

Table 5. Chemical composition of sublimation

Components	sublimate	
	kg	%
Zn	7.4254	59.9011
Pb	1.3048	10.5256
Cu	0.0148	0.1192
SiO2	0.2133	1.7206
FeO	0.1059	0.8541
CaO	0.3020	2.4359
MgO	0.0334	0.2693
Al2O3	0.1220	0.9845
S	0.2252	1.0000
Remain	2.6494	21.3729

Table.6. Chemical composition of the slag output after fuming process

Components	Waste slag	
	kg	%
Zn	1.5086	1.6013
Pb	0.0472	0.0501
Cu	0.1962	0.2083
SiO_2	22.8749	24.2801
FeO	34.7360	36.8699
CaO	15.8088	16.7800
MgO	2.9727	3.1553
Al_2O_3	7.2002	7.6425
S	1.1043	1.1721
Remain	7.7635	8.2404

Table 7. Chemical composition of gases

Components	Gases	
	kg	%
Zn	0.1970	0.2393
Pb	0.0100	0.0121
SiO_2	0.0186	0.0225
S	0.1501	0.1823
H_2	0.2531	0.3075
N_2	53.7763	65.3149
CO	13.3439	16.2070
CO_2	6.0228	7.3150
H_2O	4.1660	5.0599
Remain	4.3962	5.3394

Table 8. Main parameters for the fuming

The time blown for one cycle	min	132.500
Process length	min	162.500
Number of the cycle in the day	cycle/day	8.862
The surplus coefficient of air		0.500
Coal quantity for one cycle	kg	10779.000
Coal quantity for one cycle	kg/min	81.351
Coal quantity for one day	t	95.519
Coal quantity for one year	t	31903.187
Temperature of output gases	C	1282.000
Speed of rectified Zn	kg/min	3.371
Day's production of the furnace	t/day t	531.692
Yearly production of the furnace	t/(year m^2)	35.722
Quantity of the processed slag in day	t	531.692
Quantity of processed slag in year	t	177.585
Sublimation quantity for one cycle	kg	7437.643
Sublimation quantity for one day	t	65.909
Sublimation quantity for one year	t	22013.593
The general quantity of the air	kg	42586.491
The general quantity of the air	kg/min	262.071
The general quantity of the air	m^3/min	202.716
The general quantity of the gases	t	49.400
Zinc quantity for one cycle	kg	4455.232
Zinc quantity for one day	t	39.480
Zinc quantity for one year	t	13186.391
Lead quantity for one cycle	kg	782.856
Lead quantity for one day	t	6.937
Lead quantity for one year	t	2317.061
Copper quantity for one cycle	kg	8.862
Copper quantity for one day	t	78.531
Copper quantity for one year	t	26.229

Table. 9. Input quantities in the material

Components	Slag	powder coal		Air		Sum
	kg	kg	%	kg	%	kg
Zn	9.131	-	-	-	-	9.131
Pb	1.362	-	-	-	-	1.362
Cu	0.211	-	-	-	-	0.211
SiO_2	23.107	-	-	-	-	23.107
FeO	34.842	-	-	-	-	34.842
CaO	16.111	-	-	-	-	16.111
MgO	3.006	-	-	-	-	3.006
Al_2O_3	7.322	-	-	-	-	7.322
S	1.300	0.180	1.000	-	-	1.480
Remain	3.608	1.976	11.000	1.056	1.488	17.736
C	-	12.576	70.000	-	-	12.576
O_2	-	1.617	9.000	16.325	23.000	17.942
H_2	-	0.898	5.000	-	-	0.898
N_2	-	0.180	1.000	53.597	75.512	53.776
CO	-	-	-	-	-	-
CO_2	-	-	-	-	-	-
H_2O	-	0.539	3.000	-	-	0.539
Sum	**100.000**	**17.965**	**100.000**	**70.978**	**100.000**	**188.943**

Table 10. Output quantities in the material balance

Components	Sublimation		Waste slag		Gases		Sum
	kg	**%**	**kg**	**%**	**kg**	**%**	**kg**
Zn	7.425	59.901	1.509	1.601	0.197	0.239	9.131
Pb	1.305	10.526	0.047	0.050	0.010	0.012	1.362
Cu	0.015	0.119	0.196	0.208	-	-	0.211
SiO_2	0.213	1.721	22.875	24.280	0.019	0.023	23.107
FeO	0.106	0.854	34.736	36.870	-	-	34.842
CaO	0.302	2.436	15.809	16.780	-	-	16.111
MgO	0.033	0.269	2.973	3.155	-	-	3.006
Al_2O_3	0.122	0.985	7.200	7.643	-	-	7.322
S	0.225	1.000	1.104	1.172	0.150	0.182	1.480
Remain	2.649	21.373	7.764	8.240	4.396	5.339	14.809
C	-	-	-	-	-	-	-
O_2	-	-	-	-	-	-	-
H_2	-	-	-	-	0.253	0.308	0.253
N_2	-	-	-	-	53.776	65.315	53.776
CO	-	-	-	-	13.344	16.207	13.344
CO_2	-	-	-	-	6.023	7.315	6.023
H_2O	-	-	-	-	4.166	5.060	4.166
Sum	**12.396**	**100.000**	**94.213**	**100.000**	**82.334**	**100.000**	**188.943**

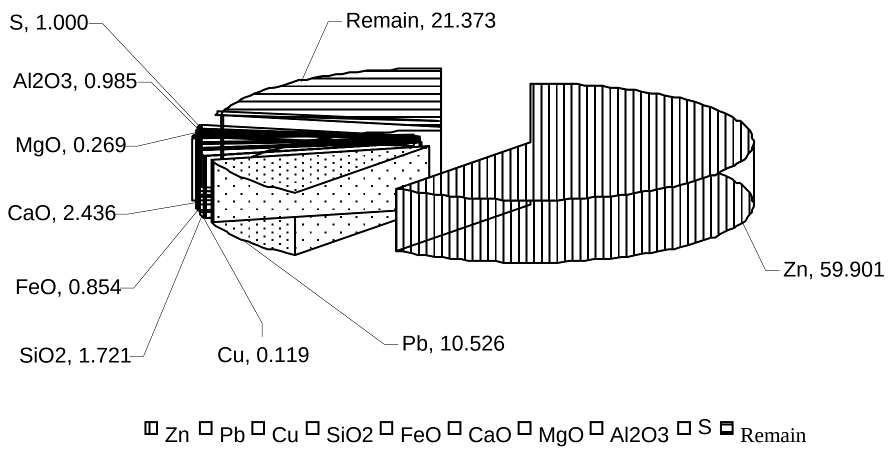

Figure 2. Chemical composition of the obtained product (sublimation)

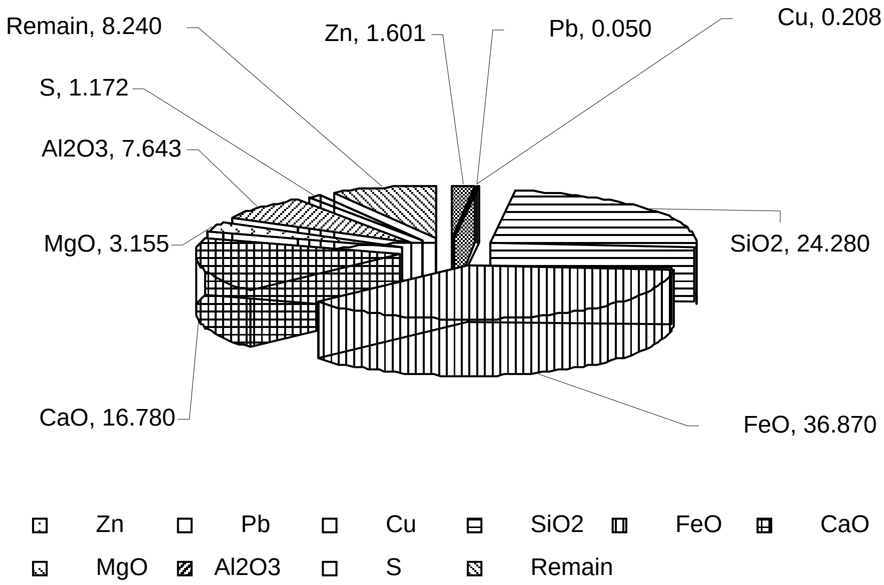

Figure 3. Chemical composition of the slag output of fuming process, %

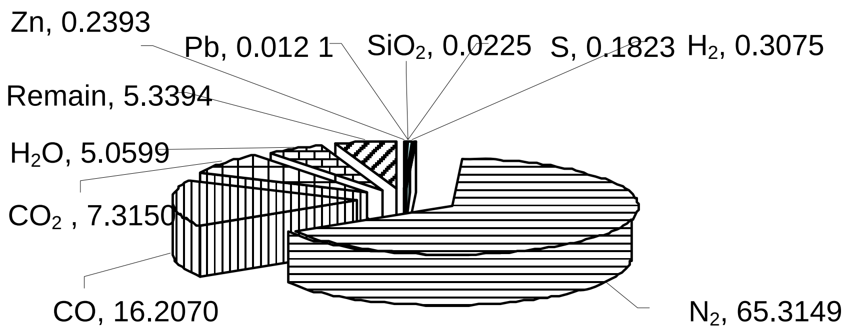

Figure 4. Chemical composition of the output gases (Zn, Pb, SiO_2, S, H_2, N_2, CO, CO_2, H_2O, Remain)

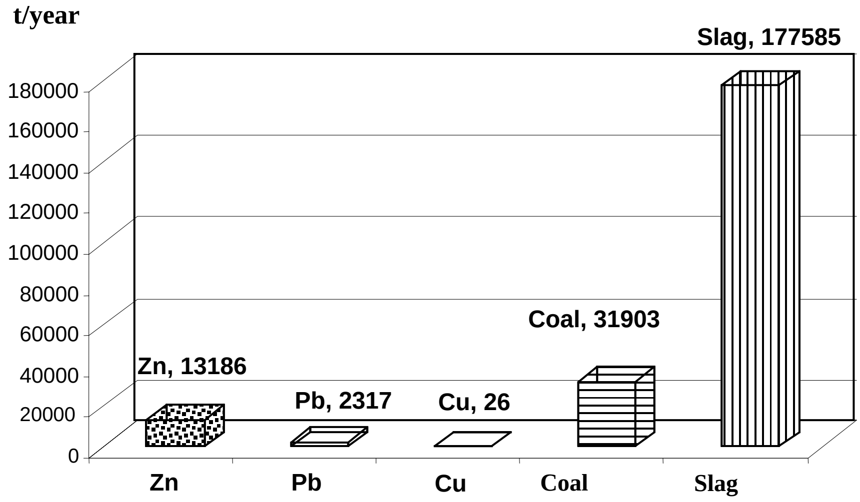

Figure 5. Pb, Zn,Cu and slag quantity for one year

Conclusion

In this paper is intended to have knowledge of chemical composition and determination of the amount of slag in the slag store (around 2.5 million ton). Since, it is supposed that there is a qualitative raw material (Pb, Zn, Cu, Ag etc.) which can be processed with the fuming process, therefore there are presented comparative data to some manufacturers of different countries that use almost the same technology for smelting the lead agglomerate. Based on the raw material available, we suggest:

a) The fuming process, as a technological process of many advantages for the treatment of melted slag and solid slag from the store.
b) Slag, apart from the above mentioned components has an amount of rare metals, such as: Ge, In, Tl, *etc*. A positive impact in the economic parameters of the process will be achieved by using them.
c) Slag quantity used for the fuming process is of mixed type, the ratio between the fresh slag and slag from the dam will be 3:1 (or 60 to 70 % fresh and 40 to 30 % from the dam).
d) Therefore, slag quantity gained during the reductive smelting process in the lead metallurgy of „Trepça” (55.000-60.000 tpy) is sufficient for normal development of fuming process.
e) Given data show of reductive smelting process in “Trepça” has the lowest smelting level compared to the slag in Plovdiv, so it has a higher level for the advancement of fuming process.
f) Through a special program compiled with „Pascal” language is conducted the material balance of process, what represents quantitative difference of the participating components’ level during the technological process development.
g) Suggested basic input parameters, which enable us to have the most optimal characteristics of the process, are as follovs:

g^{I} - air temperature which is blown is 540 °C ;
g^{II} - pure air with 23% O_2;
g^{III}- carbon percentage in coal 70 % and
g^{IV}- slag quantity per cycle is 70 t.

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