THE CHOICE BETWEEN PRODUCTION OF LEAD SELECTIVE CONCENTRATE OR RECOVERY OF LEAD AND ELEMENTAL SULPHUR FROM GALENITE DOMESTIC ORES

Prof. Dr. Blagoj Golomeov[1], Prof. Dr. Boris Krstev[1], Prof. Dr. Mirjana Golomeova[1], Dr. Aleksandar Krstev[2]
Goce Delcev Universiry, Faculty of Technical&Natural Sciences
Goce Delcev Universiry, Faculty of Informatics
2000 STIP, The Republic of Macedonia

Abstract: *The polymetallic galena-sphalerite domestic ores in Republic of Macedonia are treated by conventional flotation and renewed selective technology. In the meantime, investigations are directed to the new possibilities of treatment as leaching methods. The paper is result of these technologies and investigations carried out for recovery of lead and present sulphur in the mentioned galena-sphalerite ores. The average recoveries from flotation process in the lead concentrate were cca 90% for lead, 80-85%. The average recoverie from acid HF leaching were cca 92-93% for lead, 80-90% for sulphur.*
KEYWORDS: *LEAD, SELECTIVE, FLOTATION, LEACHING, RECOVERY*

1. Introduction

The ores from Sasa mine at the Svinska Reka, Kozja Reka and Golema Reka ore bodies occur in three chief textural minerak types, such as most distributed compact ore , banded ore and least distributed impregnated ore. The main minerals are galena, sphalerite and pyrite, althought pyrhotine, chalcopyrite, magnesite, hematite, ceruzite, marmatite and other occur in small amounts as well. The gange minerals are quartz, calcite, chlorite, epidote etc. The galena and sphalerite rarely occur in the form of free grains ranging in size from 10 to 270 micrometers, while the free sphalerite christal grains can reach a size even to 350 micrometers and galena and sphalerite ratio aproximativelly is 1:1.

Flotation separation and recovery of lead and zinc concentrates from ores containing galena (PbS) and sphalerite (ZnS) is well established and generally achieved quite effectively. Silver often provides highly significant economic value, if not the greatest value, with the silver most often associated with the galena mineralization which is fortuitous since smelters pay more for silver in lead vs. zinc concentrates. Lead flotation collectors and frother are conditioned before lead flotation which is conducted typically at near neutral to slightly elevated pH which can be increased in the cleaner circuit to ensure iron sulphide rejection. Sometimes cyanide, if can be used, is added to help depress iron sulphides. Because silver typically is mineralogically associated with galena, most of the silver values are carried with and report to the galena concentrate.

2. Lead and zinc concentrates and result from flotation in Sasa mine

Lead-zinc ores in the Republic of Macedonia is processed in three flotation plants and mines: Zletovo mine, Sasa mine and Toranica mine. Former Sasa concentrator flowsheet gave the following technological results: Pb+Zn collective concentrate with average 32-34% Pb and 21-23% Zn with appropriate recoveries of 92-94% Pb and 77-80%Zn.

The recent Sasa concentrator has changed flowsheet from collective to selective flotation of galena concentrate and sphalerite concentrate with following contents in concentrate from average 73-75%Pb (2,5-3,0%Zn) and average 49,5-51%Zn (1-1,5%Pb), with appropriate recoveries from cca 89-91%Pb and 89-91%Zn.

Table 1.

Reagents and Materials (kg/t)	January		February		March		April	
	Plan	Fact	Plan	Fact	Plan	Fact	Plan	Fact
CaO	5,100	3,644	3,700	3,954	3,700	3,790	3,600	2,801
KEX	0,100	0,095	0,095	0,118	0,095	0,095	0,095	0,076
KAX	0,030	0,022	0,027	0,025	0,027	0,026	0,027	0,017
DOW 250	0,060	0,049	0,055	0,046	0,055	0,049	0,055	0,052
NaCN	0,060	0,057	0,060	0,050	0,060	0,043	0,060	0,032
$CuSO_4$	0,530	0,453	0,490	0,458	0,490	0,400	0,420	0,349
$NaSO_3$	0,190	0,179	0,180	0,173	0,180	0,142	0,170	0,064
$ZnSO_4$	0,160	0,145	0,160	0,155	0,160	0,110	0,160	0,081
RODS φ100	0,400	0,479	0,400	0,411	0,400	0,461	0,400	0,309
BALLS φ60	0,300	0,224	0,300	0,310	0,300	0,250	0,300	0,276
BALLS φ20	0,030	0,000	0,027	0,031	0,027	0,013	0,027	0,015

Table 2.

Reagents and Materials (kg/t)	May		Jun		July		August	
	Plan	Fact	Plan	Fact	Plan	Fact	Plan	Fact
CaO	3,600	2,985	4,000	2,219	3,400	1,806	3,400	1,822
KEX	0,095	0,088	0,095	0,104	0,105	0,101	0,105	0,093
KAX	0,027	0,022	0,027	0,021	0,033	0,026	0,033	0,023
DOW 250	0,055	0,031	0,040	0,037	0,040	0,035	0,040	0,038
NaCN	0,060	0,057	0,060	0,050	0,060	0,043	0,060	0,032
$CuSO_4$	0,420	0,350	0,480	0,340	0,400	0,270	0,400	0,280
$NaSO_3$	0,170	0,005	0,060	0,125	0,140	0,101	0,140	0,111
$ZnSO_4$	0,160	0,066	0,100	0,097	0,110	0,094	0,110	0,087
RODS φ100	0,400	0,369	0,400	0,313	0,400	0,345	0,400	0,400
BALLS φ60	0,300	0,246	0,300	0,252	0,300	0,267	0,300	0,299
BALLS φ20	0,027	0,041	0,027	0,017	0,027	0,031	0,027	0,029

Table 3.

Reagents and Materials (kg/t)	September		October		November		December	
	Plan	Fact	Plan	Fact	Plan	Fact	Plan	Fact
CaO	2,200	1,807	2,400	2,076	2,400	2,090	2,400	2,401
KEX	0,105	0,089	0,100	0,102	0,095	0,095	0,095	0,076
KAX	0,033	0,024	0,030	0,024	0,027	0,026	0,027	0,017
DOW 250	0,067	0,056	0,060	0,048	0,055	0,049	0,055	0,055
NaCN	0,040	0,033	0,045	0,035	0,045	0,043	0,045	0,032
$CuSO_4$	0,340	0,296	0,380	0,324	0,380	0,340	0,380	0,349
$NaSO_3$	0,125	0,107	0,130	0,090	0,130	0,100	0,130	0,065
$ZnSO_4$	0,100	0,077	0,110	0,078	0,100	0,085	0,100	0,085
RODS φ100	0,400	0,480	0,400	0,433	0,400	0,420	0,400	0,365
BALLS φ60	0,300	0,474	0,300	0,315	0,300	0,250	0,300	0,300
BALLS φ20	0,027	0,015	0,027	0,015	0,027	0,013	0,027	0,015

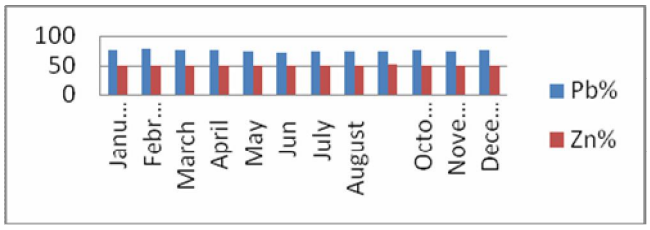

Fig 1. Pb% and Zn% in appropriate concentrates

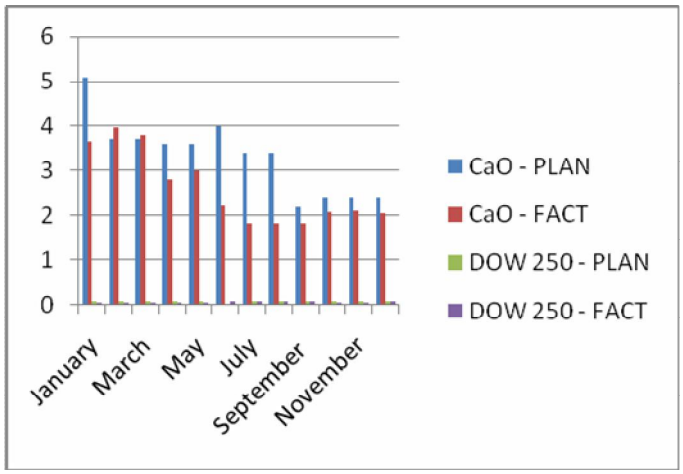

Fig 2. The ratio of CaO and DOW 250 by planning and true consumption

A major cost factor in the sintering and smelting process for producing Pb is the control needed to meet existing environmental standards for Pb emissions. Another issue is the current concern over acid rain, which will in all probability result in even more stringent controls on emission of sulfur gases.

Processing of the galena concentrates is developed as an effctive low-temperature leaching-electrowining method to produce Pb metal and elemental sulfur from galena concentrates. The method reduces Pb emissions and totally eliminates the formation of sulfur gases. The elemental S produced is more economical to store and ship than the sulfuric acid (H_2SO_4) generated by the high-temperature smelting process.

This hydrometallurgical method consists of leaching galena concentrates in waste fluosilicic acid (H_2SiF_6) with hydrogen peroxide (H_2O_2) and lead dioxide (PbO_2) as oxidantsat 95°, electrowinning the ($PbSiF_6$) solution at 35° to produce *99,99%Pb* metal, and solvent extraction to recover S, leaving a residue containing eventually present Cu, Ag, and other metal values.

$$2PbS+3H_2SiF_6+H_2O_2+PbO_2 \Rightarrow 3PbSiF6+4H_2O+2S^o \quad (1)$$

$$PbSiF_6+2H^++2e^- \Rightarrow Pb+H_2SiF_6 \quad (2)$$

$$PbS+2H^++[O] \Rightarrow Pb^{2+}+S^o+H_2O \quad (3)$$

$$PbS+8H^++8[O] \Rightarrow PbSO_4+4H_2O \quad (4)$$

$$PbS+2H^+ + \Rightarrow Pb^{2+}+H_2S \quad (5)$$

$$PbS+H_2O_2+H_2SiF_6 \Rightarrow PbSiF_6+2H_2O+S^o \quad (6)$$

$$PbS+PbO_2+H_2SiF_6 \Rightarrow PbSiF_6+PbO+H_2O+S^o \quad (7)$$

$$PbO+H_2SiF_6 \Rightarrow PbSiF_6+H_2O \quad (8)$$

Several galena leaching processes have been investigated, including processing using ferric chloride, ferric sulfate, nitric acid and ammonium acelate solutions. The leached $PbCl_2$ and $PbSO_4$ salts have a very limited solubility in aqueos solution, making aqueos electrolysis difficult. Lead metal was recoverable from $PbCl_2$ by molten-salt electrolysis operated at 450°. It's known that elecrowinning of Pb in HNO_3 and H_2SiF_6 solutions yields Pb metal at the cathodes and at the same time PbO_2 at the anodes.The next text will explain the oxidative leaching-electrowinning process.

Reaction *(3)* shows that oxidative leaching of PbS will yield Pb salt and elemental S. Reaction *(4)* suggests $PbSO_4$ may form if the redox potenial of the solution is too high, and reaction *(5)* indicates H_2S will form when leaching in acid solution if the redox potential is too low. To avoid the generation of H_2S one-fourth of the required oxidant have to be added to the H_2SiF_6 solution prior to the addition to the PbS. The reaction is exothermic and it's necessary to add H_2O_2 slowly through a birette to avoid overheating the leach solution. After adding the H_2O_2, PbO_2 was added slowly to control the redox potential. The reacions occuring during the oxidative leaching of PbS synthetic mixures or concentrates with H_2SiF_6 are shown below. At the end of leaching, the mixture was filtered to separate the leachate from the residue. The residue consisted of elemental S and other metal values. The leachate is sent to electrowinning to recover pure Pb metal.

3. Previous investigations

As leaching parameters were investigated: *PbS* samples of 98% on the –400 mesh or 96% on the as-received concentrates if H_2O_2 and PbO_2 were used as oxidants (the possible oxidants may be air, oxygen, ozone, HNO_3 and MnO_2); leaching temperature from 50-95°; leaching time from 35-335 min. The results of carried out investigations follow:

Table 1. *Effect of various amounts of oxidants*

Test	H_2O_2 35% ml	PbO_2 gr.	Pb%
1	0,0	16,0	92,0
2	2,5	17,0	95,0
3	5,0	9,8	95,0
4	7,5	8,1	96,8
5	10,0	5,7	95,1
6	19,0	0,0	96,0

Table 2.*Effect of time and temperature*

Leach temperature T°C	Leach time, (min)	Pb%
50	335	62,3
70	240	91,5
80	90	76,0
90	75	90,1
90	90	97,5
95	35	96,0
95	75	96,5

Table 3. *Effect of leach time in Pb extraction*

	Leach time, *min*		
	30	60	90
Pb%	92,3	95,6	96,4
Leachate,g/l:	163,500	176,700	180,300
Pb.	62,900	55,400	52,300
H_2SiF_6	0,540	0,619	0,683
Zn	0,369	0,415	0,091
Fe	0,050	0,091	0,109
Cu	0,006	0,007	0,007
Co	0,012	0,014	0,007

Table 4. *Effect of H_2SiF_6 concetration*

	H_2SiF_6 technical-grade acid (g/l)			
	175	200	250	300
Pb%	89,0	97,5	95,4	95,7
Leachate g/l:	80	179	184	177
Pb	32	56	94	133
H_2SiF_6	0,57	0,75	0,82	1,00
Zn	0,53	0,61	0,61	0,67
Fe	0,12	0,13	0,13	0,18
Cu	0,00	0,00	0,00,	0,00
Co	0,02	0,02	0,02	0,02

The effect of using different combinations of oxidants of H_2O_2 and PbO_2 on PbS leaching was insignificant. Previous leaching experiments showed that H_2O_2 was a more efficient oxidizer to initiate the leach reaction. Also, it was less expensive than PbO_2. Thus, it is beneficial to use H_2O_2 to leach PbS and only use PbO_2 at the end of the leach to void oxidizing PbS into $PbSO_4$.

Leaching temperatures had a great influence on reaction rate and Pb extraction. When leaching below 80°C, the reaction rate was thought to be too slow for any practical pplication. Lead extraction was 96% when leaching at 95°C for 35 min using H_2O_2 and PbO_2 as oxidants. The leach-ing rate increased greatly and the required leaching time was reduced from 90 min to 35 min as the temperature increased from 90°C to 95°C. Lead extraction was increased from 92% to 96% as leaching time increased from 30 min to 60 min at 95°C. Initial leaching was rapid, but the elemental sulfur formed and coated the PbS particles, further reaction was probably diffusion controlled and the leach rate was reduced. However, the efect of the sulfur coating was not critical, because of the fine particle size of the PbS.

The amounts of *PbS,* PbO_2 and H_2SiF_6 used in a leach test determined the concentration of $PbSiF_6$ and free H_2SiF_6 in the pregnant leachate. Increasing the concentration of free H_2SiF_6 above 60 g/lit had no significant effect on the Pb extraction, extraction of impurities decreased with decreasing concentration of free H_2SiF_6.Lead extraction of 96%, 91% and 96% were achieved using H_2SiF_6 solutions made from technical-grade, waste, and recycled acid. Waste H_2SiF_6 contained HCl and H_2SO_4 as impurities, which formed some insoluble Pb salts during leaching, resulting in lower Pb extraction. Recycled electrolyte, in which impurities were removed during prior leaching, was as reactive as technical-grade H_2SiF_6.

4. Conclusions

Lead-zinc ores in the Republic of Macedonia is processed in three flotation plants and mines: Zletovo mine, Sasa mine and Toranica mine. Former Sasa concentrator flowsheet gave the following technological results: Pb+Zn collective concentrate with average 32-34% Pb and 21-23% Zn with appropriate recoveries of 92-94% Pb and 77-80%Zn.

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Above mentioned combined hydrometallurgical and electrometallurgical methods are de- veloped to produce lead and elemental S from synthetic mixures or concentrates with high purity. Contemporary, this process eliminates S gases and Pb emissions. The elemental S produced is easier to transport and store than is the H_2SO_4 generated by the pyrometallurgical methods.

Investigated experiments and tests included oxidative leaching of PbS in synthetic mixures with H_2SiF_6, electrowinning the leach solution to produce high-purity lead metal, carbon treatmet of spent electrolyte for recycling, and S removal from the leach residue. Investigated experiments by PbS synthetic mixures show satisfactory Pb extraction and appropriate possibility for treatment of natural ore samples and concentrates produced in industrial mineral processing lead-zinc plants in the Republic of Macedonia.

5. References

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