LEACHING METHOD FOR PRODUCING LEAD AND ELEMENTAL SULFUR FROM DOMESTIC GALENA CONCENTRATES

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ABSTRACT:

In this pape will be shown possibilities to produce lead metal and elemental sulfur by leaching domestic galena concentrates. In our invesigations we treated lead concentrate from the Zletovo mine which contains around 70% Pb and lead-zinc concentrate fromthe Sasa mine which contents around 35%Pb.

These investigations were based on preliminary laboratory experiments carried out on the domestic galena concentrates

Keywords: leaching, lead, sulfur, concentrates

1. INTRODUCTION

Lead-zinc ores which are mined in the Republic of Macedonia belong to typical lead-zinc ores with relatively favourable structural properties in which galena and sphalerite occur as basal ores and economically important minerals. Lead-zinc ores in Republic of Macedonia is processed in three flotation plants and mines: the Zletovo mine, Sasa and Toranica mines.

Zletovo concentrator flowsheet give the following technological results: Pb concentrate with average 72-74%Pb and 1,9-3,0%Zn with recovery of 92-94%Pb; Zn concentrate with average 51-54,5%Zn and 1,3-3,0%Pb with recovery of 77,0-78,0%Zn.

Sasa concentrator flowsheet give the following technological results: Pb+Zn collective concentrate with average 32-34%Pb and 21,0-23,0%Zn with recovery of 92-94%Pb and recovery of 77,0-80,0%Zn.

Toranica concentrator flowsheet give the following technological results: Pb+Zn collective concentrate with average 15%Pb and 35,0%Zn with recoveries of 32%Pb and 90%Zn; Pb selective concentrate with average 73,0%Pb and 4,3-5,0%Pb with recoveries of 61,0%Pb and 5%Zn.

Processing of the galena concentrates is developed as an effective low-temperature leaching-electrowinning method to produce Pb metal and elemental sulfur from galena mixures or 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 oxidants at 95^o, electrowinning the ($PbSiF_6$) solution at 35^o to produce *99,99%Pb* metal, and solvent extraction to recover S, leaving a residue containing eventually present Cu, Ag, and other metal values.

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

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

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 soluton, making aqueos electrolysis difficult. Lead metal was recoverable from $PbCl_2$ by molten-salt electrolysis operated at 450°. It is 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.

2. GENERAL

The chemical equations for PbS leaching in acid solution with and without oxidants follow:

$$PbS+2H^{+}+[O]\Rightarrow Pb^{2+}+S^{o}+H_2O \qquad (3)$$
$$PbS+8H^{+}+8[O]\Rightarrow PbSO_4+4H_2O \qquad (4)$$
$$PbS+2H^{+}+\Rightarrow Pb^{2+}+H_2S \qquad (5)$$

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 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 exotermic and it is 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 reactions occuring during the oxidative leaching of PbS sinthetic mixures or concetrates with H_2SiF_6 solution follow:

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

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

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

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.

2.1 Previous investigations

As large-scale 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; leaching time. The results of carried out investigations follow:

Table1. Large-scale leaching tests[*]

	Test 1	Test 2	Test 3
Test parameters;			
H_2SiF_6.....lit	40	50	75
H_2O.....lit	44	26	14
PbS.....kg	12	12	7,5
H_2O_2(35%)....lit	4,5	4,1	4,1
PbO_2.....kg	3,5	3,8	0,39
Temp.....°C	95-98	95,98	95-98
Time.....h	2,5	2,5	2,0
Results:			
Pb-extraction...%	93,6	91,1	95,6
Partial analysis:			
Leachate:			
Volume.....lit	83,3	75,1	95,6
Pb.....g/lit	137,2	147,3	83,7
H_2SiF_6.....g/lit	98,4	103,4	93,4
Zn.....g/lit	0,36	0,36	0,50
Fe.....g/lit	0,34	0,34	0,71
Cu.....g/lit	0,09	0,02	0,04
Residue:			
Weight.....kg	3,11	3,79	1,74
Pb.....%	25,6	28,4	23,3
S^{o}.....%	43,7	31,5	49,0
S^{T}(total).....%	54,0	37,3	59,3
Zn.....%	4,03	2,43	3,20
Fe.....%	4,00	3,39	4,40
Cu.....%	2,18	1,70	2,50
Ni.....%	0,34	0,29	0,31
Co.....%	0,22	0,19	0,22
Ag.....%	0,01	0,01	0,01

*Test 1: Technical H_2SiF_6 contaning 396 g/lit H_2SiF_6
Test 2: Waste H_2SiF_6 contaning 305 g/lit H_2SiF_6
Test 3: Recycled H_2SiF_6 contaning 396 g/lit H_2SiF_6

1. EXPERIMENTAL TESTS

The conditions by the leaching process of the galena concentrates (*PbS*)- Zletovo mine and Sasa mine with gangue mineral's compounds (*ZnS*, *CuS*, *NiS*, *CoS*, *CaO*, *MgO*, Fe_2O_3, SiO_2) and oxidants addition H_2O_2 and PbO_2, leaching temperature (°C) with retaining leaching time (min) in the presence of technical H_2SiF_6 is shown on the following tables.

Table 2. Effect of various amounts of oxidants

Test *(Pb-70%)*	H_2O_2-35% ml	PbO_2, gr	Pb (%)
1	0,0	15,0	85,2
2	2,5	15,0	91,0
3	5,0	9,5	92,0
4	7,5	8,0	92,8
5	10,0	5,0	94,0
6	19,0	0	93,5

Table3. 35% H_2O_2 (10 ml); PbO_2 (5 gr);90°; 90 min; Zletovo concentrate

	H_2SiF_6			
	175 gr/l	*200 gr/l*	*250 gr/l*	*300 gr/l*
Pb(%)	82,0	90,5	95,0	95,5
Analysis of leachate, gr/l				
Pb.....	160	170	180	175
H_2SiF_6.....	50	65	80	100
Zn.....	2,00	1,75	1,60	2,00
Fe.....	0,50	0,60	0,60	0,65
Ni.....	0,00	0,00	0,00	0,00
Cu.....	0,00	0,00	0,00	0,00

Table 4. 35% H_2O_2 (7,5 ml); PbO_2 (8 gr); H_2SiF_6 (200 gr/l); Zletovo concentrate

Pb%	*T°C*	*t(min)*	*Pb%*
70%	90	90	93,6
		100	95,2
		110	95,6
		120	96,2
		130	96,5

Table 5. Effect of various amounts of oxidants, Sasa concentrate

Test *(Pb-30%)*	H_2O_2-35% ml	PbO_2, gr	Pb (%)
1	0,0	7,5	76,0
2	2,5	7,5	80,0
3	5,0	10,0	85,0
4	7,5	10,0	89,5
5	10,0	5,0	89,0
6	19,0	0	87,0

Table 6. 35% H_2O_2 (10 ml); PbO_2 (5 gr);90°; 90 min; Sasa concentrate

	H_2SiF_6			
	175 gr/l	*200 gr/l*	*250 gr/l*	*300 gr/l*
Pb(%)	75,0	85,5	90,0	90,5
Analysis of leachate, gr/l				
Pb.....	80	105	120	155
H_2SiF_6.....	20	35	60	80
Zn.....	2,00	2,00	2,00	2,00
Fe.....	0,50	0,60	0,50	0,50
Ni.....	0,00	0,00	0,00	0,00
Cu.....	0,00	0,00	0,00	0,00

Table 7. 35% H_2O_2 (7,5 ml); PbO_2 (8 gr); H_2SiF_6 (200 gr/l); Sasa concentrate

Pb%	*T°C*	*t(min)*	*Pb%*
30%	90	90	89,0
		100	90,5
		110	90,8
		120	91,5
		130	92,2

Conclusion

The new trends and developments in mineral processing especially mentioned combined hydrometallurgical-electrowinnng methods are developed to produce lead and elemental S from synthetic mixures or concentrates with high metal purity. Contemporary, this process eliminates S gases (SO_2) and Pb emissions in environment. 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 different cncentrates with H_2SiF_6, electrowinning the leach solution to produce high-purity lead metal, carbon treatment of spent electrolyte for recycling, and S removal from the leach residue.

Investigated experiments by PbS concentrates from the domestic concentrators: Zletovo, Sasa and Toranca (R. Macedonia) show satisfactory Pb extraction and appropriate possibility for treatment of natural ore samples and concentrates produced in industrial mineral processing lead-zinc plants in R. Macedonia.

The average Pb extraction by leaching method about Zletovo concentrates is up to 90% (93,6-96,5%), and the average Pb extraction by leaching method in Sasa concentrates is up to 90% (89,0-92,2%),

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