

THE PRODUCING OF LEAD AND ELEMENTAL SULFUR BY NEW TECHNOLOGIES FROM GALENITE ORES

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Abstract

These investigations have developed an effective hydrometallurgical method to recover high-purity lead metal and elemental sulfur from simulated galena synthetic mixtures eliminating sulfur gases and lead emissions, in contrast to the current high-temperature smelting technology.

The method consists of different operations: oxidative leaching with production of solution with residue containing elemental sulfur., electrowinning by the solution with metal production.

The obtained results determined the optimal parameters for possible processing of natural domestic galena ores.

Keywords: leaching, lead, sulfur, synthetic mixtures

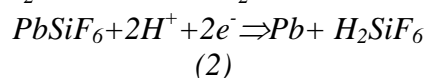
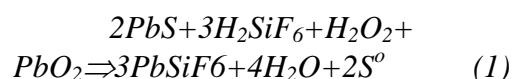
Introduction

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 mixtures or concentrates is developed as an effective low-temperature leaching-electrowinning method to produce Pb metal and elemental sulfur from galena mixtures 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 synthetic mixtures or concentrates in waste fluosilicic acid (H_2SiF_6) with hydrogen peroxide (H_2O_2) and lead dioxide (PbO_2) as oxidants at 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.



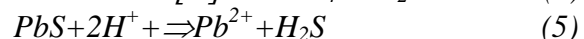
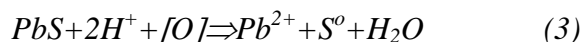
Several galena leaching processes have been investigated, including processing using ferric chloride, ferric sulfate, nitric acid and ammonium acetate solutions. The leached $PbCl_2$ and $PbSO_4$ salts have a very limited solubility in aqueous solution, making aqueous electrolysis difficult. Lead metal was recoverable from $PbCl_2$ by molten-salt electrolysis operated at 450°. It's known that electrowinning 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. The parameters

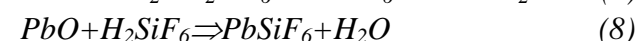
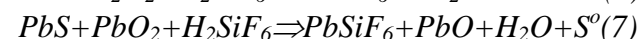
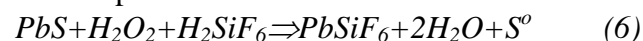
for leaching process about synthetic mixtures were investigated in laboratory experiments.

1. General

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



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 potential 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 burette to avoid overheating the leach solution. After adding the H_2O_2 , PbO_2 was added slowly to control the redox potential. The reactions occurring during the oxidative leaching of PbS synthetic mixtures 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.



2.1 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%
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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		
	30 min	60 min	90 min
Pb%	92,3	95,6	96,4
Leachate, g/l:			
Pb.....	163,500	176,700	180,300
H_2SiF_6	62,900	55,400	52,300
Zn.....	0,540	0,619	0,683
Fe.....	0,369	0,415	0,091
Cu.....	0,050	0,091	0,109
Co.....	0,006	0,007	0,007
Ni.....	0,012	0,014	0,007

Table 4. Effect of H_2SiF_6 concentration

	H_2SiF_6 -technical-grade acid			
	175 g/l	200 g/l	250 g/l	300 g/l
Pb%	89,0	97,5	95,4	95,7
Leachate, g/l				
:	180	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
Ni.....				

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 $80^\circ C$, the reaction rate was thought to be too slow for any practical application. Lead extraction was 96% when leaching at $95^\circ C$ 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 $90^\circ C$ to $95^\circ C$. Lead extraction was increased from 92% to 96% as leaching time increased from 30 min to 60 min at $95^\circ C$. 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 effect 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 .

1. Experimental tests

The conditions by the leaching process of the synthetic galena mixures (PbS) 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 ($^\circ C$) with retaining leaching time (min) in the presence of technical H_2SiF_6 is shown on the following tables.

Table 5. Chemistry composition of the synthetic mixures

Compounds	Synthetic mixures (%)		
	I	II	III
Pb	50.000	60.000	
PbS	57.740	70.000	80.830
ZnS	5.000	5.000	5.000
CuS	1.000	1.000	1.000
	0.050	0.050	0.050
Fe_2O_3	1.010	1.050	1.020
SiO_2	29.200	16.900	6.100
Al_2O_3	2.000	2.000	2.000
CaO	2.000	2.000	2.000
MgO	2.000	2.000	2.000
Total	100.000	100.000	100.000

Table 6. Effect of various amounts of oxidants

Test (Pb-70%)	H_2O_2 -35% ml	PbO_2 , gr	Pb (%)
1	0,0	15,0	90,0
2	2,5	15,0	95,0
3	5,0	9,5	95,0
4	7,5	8,0	96,5
5	10,0	5,0	95,0
6	19,0	0	96,0

Table 7. 35% H_2O_2 (7,5 ml); PbO_2 (8 gr)

	H_2SiF_6			
	175 gr/l	200 gr/l	250 gr/l	300 gr/l
Pb(%)	85,0	97,5	95,0	95,5
Analysis of leachate, gr/l				
Pb.....	180	175	185	175
H_2SiF_6	30	55	90	130
Zn.....	0,55	0,75	0,80	1,00
Fe.....	0,50	0,60	0,60	0,65
Ni.....	0,10	0,10	0,10	0,2
Cu.....	0,015	0,02	0,02	0,02

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

Pb%	$T^\circ C$	t(min)	Pb%
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50%	70	30	52,5
		60	56,5
		90	65,3
	80	30	54,2
		60	58,5
		90	67,0
60%	70	30	55,6
		60	60,2
		90	68,7
	80	30	57,2
		60	63,3
		90	71,5
70%	70	30	57,0
		60	61,0
		90	73,5
	80	30	60,5
		60	63,8
		90	75,0
90	80	30	65,0
		60	72,0
		90	79,0
	90	30	87,6
		60	95,3
		90	97,6

Conclusions

Above mentioned combined hydrometallurgical and electrometallurgical methods are developed to produce lead and elemental S from synthetic mixtures 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 H₂SO₄ generated by the pyrometallurgical methods.

Investigated experiments and tests included oxidative leaching of PbS in synthetic mixtures with H₂SiF₆, 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 synthetic mixtures 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.

References

1. Cole, E.R. (1985). Production of Lead from Sulfides. U.S. pat. 4,500,398.
2. Cole, E.R. (1985). Update on Recovering Lead from Scrap Batteries. *Journal Metall.*, vol 37, pp 79-83.
3. Cole, E.R. (1985). Recovery of Lead from Battery Sludge. *Journal Metall.*, vol 35, pp 42-46.
4. Haver, F.P. (1970). Recovery of Lead and Sulfur from Galena Concentrate Using a Ferric Sulfate Leach. BuMines RI 7360, pp 13.
5. Lee, A.Y. (1984). Electrolytic Method for Recovery of Lead from Scrap Batteries. BuMines RI 8857, pp 20.
6. Lee, A.Y. (1986). Hydrometallurgical Process for Producing Lead and Elemental Sulfur from Galena Concentrates. BuMines RI 9055, pp 13.
7. Wong, M.M. (1983). Integrated Operation of Ferric Chloride Leaching, Molten-Sat Electrolysis Process for Production of Lead. BuMines RI 8770, pp 21.

