

# HYDROMETALLURGICAL PROCESSING OF GALENA SYNTHETIC MIXURES FOR PRODUCING LEAD AND ELEMENTAL SULFUR

Blagoj GOLOMEOV, Boris KRSTEV, Aleksandar KRSTEV

Faculty of Mining & Geology-Stip, R. Macedonia,  
2000 Stip, R. Macedonia  
blagojg@rgf.ukim.edu.mk, borisk@rgf.ukim.edu.mk

## 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.*

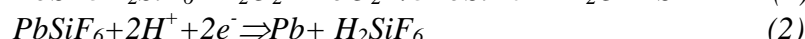
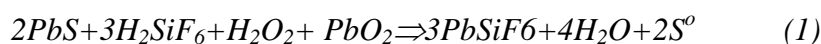
**Keywords:** leaching, lead, sulfur, synthetic mixtures

## 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  $95^\circ$ , electrowinning the ( $PbSiF_6$ ) solution at  $35^\circ$  to produce 99,99% Pb metal, and solvent extraction to recover S, leaving a residue containing eventually present Cu, Ag, and other metal values.

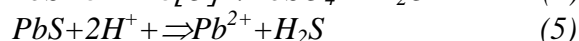
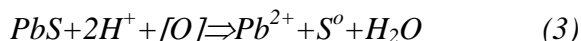


Several galena leaching processes have been investigated, including processing using ferric chloride, ferric sulfate, nitric acid and ammonium acetate solutions. The leached  $PbCl_2$  and  $PbSO_4$  salts have a very limited solubility in aqueous solution, making aqueous electrolysis difficult. Lead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

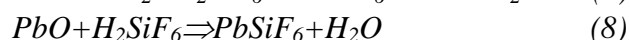
## 1. General

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%
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:				
Pb.....	180	179	184	177
$H_2SiF_6$ ....	32	56	94	133
Zn.....	0,57	0,75	0,82	1,00
Fe.....	0,53	0,61	0,61	0,67
Cu.....	0,12	0,13	0,13	0,18
Co.....	0,00	0,00	0,00,	0,00
Ni.....	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 application. Lead extraction was 96% when leaching at 95°C for 35 min using  $H_2O_2$  and  $PbO_2$  as oxidants. The leaching 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 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 mixtures (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 (°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 mixtures

Compounds	Synthetic mixtures (%)		
	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 <sub>2</sub> O <sub>2</sub> -35% ml	PbO <sub>2</sub> , 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<sub>2</sub>O<sub>2</sub> (7,5 ml); PbO<sub>2</sub> (8 gr)

	H <sub>2</sub> SiF <sub>6</sub>			
	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 <sub>2</sub> SiF <sub>6</sub> .....	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<sub>2</sub>O<sub>2</sub> (7,5 ml); PbO<sub>2</sub> (8 gr); H<sub>2</sub>SiF<sub>6</sub> (200 gr/l)

Pb%	T°C	t(min)	Pb%
50%	70	30	52,5
		60	56,5
		90	65,3
	80	30	54,2
		60	58,5
		90	67,0
	90	30	56,5
		60	59,1
		90	70,0
60%	70	30	55,6
		60	60,2
		90	68,7
	80	30	57,2
		60	63,3
		90	71,5
	90	30	57,0
		60	61,0
		90	73,5
70%	70	30	60,5
		60	63,8
		90	75,0
	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  $H_2SO_4$  generated by the pyrometallurgical methods.

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

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