THE CHOICE BETWEEN PREPARATION OF ELEMENTAL LEAD OR LEAD POWDER FROM GALENA CONCENTRATES FROM FYROM MINES

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Abstract:

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 flu silicic acid or flu boric acid(H_2SiF_6 – HBO_4) with oxidants at 95^o, electrowinning the ($PbSiF_6$) solution at different T^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.Hence, a new approach of preparing $PbSO_4$ from galena concentrates in the sulfuric acid (H_2SO_4) and ferric chloride media coupled with selective purification and chemical sedimentation was proposed.

KEYWORDS; LEAD, LEAD POWDER, FLUOSILIC, FLUOBOR

1. 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 mixures or concentrates is developed as an effctive low-temperature leaching-electrowining 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 synthetic mixures or concentrates in waste fluosilicic acid (H_2SiF_6) with hydrogen peroxide (H_2O_2) and lead dioxide (PbO_2) as oxidantsat 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 sulphate, 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^o. It's known that electro winning 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-electro winning process. The parameters for leaching process about synthetic mixtures were investigated in laboratory experiments.

2.General and important characteristics

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

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

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 biretta 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 electro winning to recover pure Pb metal.

$$PbS+H_2O_2+H_2SiF_6 \Rightarrow PbSiF_6+2H_2O+S^o \quad (6)$$
$$PbS+PbO_2+H_2SiF_6 \Rightarrow PbSiF_6+PbO+H_2O+S^o \quad (7)$$
$$PbO+H_2SiF_6 \Rightarrow PbSiF_6+H_2O \quad (8)$$

2.1Previous investigations and discusions

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

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 concetration

	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 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 sulphur formed and coated the PbS particles, further reaction was probably diffusion controlled and the leach rate was reduced. However, the effect of the sulphur 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.

2.2 Previous investigations and discussions

The hydrometallurgical recovery of lead from galena based concentrates is carried out by means of the FLUBOR Process. Generally speaking the main peculiarities of this process are the following: Production of elemental Pb and S; Slag and SO_2 emissions cutting; Environmental impact reduction to very low values; Very small consumption of fuel, and Environment safeguard in the workplace.

The FLUBOR Process operates with HBO_4 based electrolyte, as an excellent solvent for Pb, and composed by the following units: ***The leaching:*** The acidic oxidizing selective leaching where galena is contacted with solution containing HBO_4 and ferric fluoborate. The sulphur of the galena is oxidized to elemental sulphur while lead is taken in solution as lead fluoborate. The present metals more noble than lead are kept into the leaching residue. ***The electro winning:*** The solution coming out of the leaching unit is sent to a diaphragm divided cell in which in the cathodic compartment the lead is plated while, in the anodic compartment, the iron is oxidized to regenerate the leaching solution. ***The bleed treatment:*** Based on the precipitation of metal sulphates of the inpurities less noble than lead. In this unit the HBO_4 consumed during the leaching by these elements is recovered to the process. ***The residue treatment:*** The S contained in the residue is removed and recovered making this new residue available for the recovery of the other values contained in it.

All carried out extensive laboratory and pilot investigations and testing showed very good performances with: *Lead extraction rate higher than 97%; The produced lead cathodes have a Pb content of 99,99% free of Bi, Ag, Se, Te and Operating costs are very attractive and sensibly lower of the one of the thermal processes used nowdays.*

2.3 Previous investigations and discussions

Lead sulfate ($PbSO_4$) as an important chemical product can be widely used in white pigment, lead storage battery and so on. [1-2] Fire metallurgy is the process which produce $PbSO_4$ from lead concentrates and electrolysis of the crude lead to produce electrolytic lead, then chemical synthesis [3-5]. Thus, there is serious pollution due to the emission of SO_2 and lead vapor as well as filled dust during processes of the lead metallurgy and electrolysis. These emissions of pollutants not only do harm to the health of operators, but also result in local atmosphere and water pollution. Under the current pressures of strict environmental regulations, seeking much efficient ways to produce $PbSO_4$ is very necessary. Many researches have done extensive work on hydrometallurgical lead production process. The ferric chloride leaching of galena has received considerable attention over the last 20 years or so [6-10]. This process is based on the rapidly of the reaction between $FeCl_3$ and PbS on the predominant formation of elemental sulphur, and on the elevated solubility of $PbCl_2$ in hot concentrated chloride media. It can be found that the methods of hydrometallurgical lead production process mainly involve lead sulfide concentrates leaching in some medium, followed by fused-salt electrolysis to produce electrolytic lead. All mentioned methods lead to the conversion of lead sulfide concentrates to lead sulfate, and to demonstrate the feasibility of realizing a green route to prepare lead sulphate.

On account of the lowest valence state of sulphur in PbS, the insoluble PbS can be transformed into soluble lead salts by strong oxidation of ferric chloride with rapid reaction and the moderate solubility of lead chloride in concentrated chloride media. During this leaching process chloride ion plays an important role, especially in saturated NaCl solution system. Ferric attack of mineral:

$$PbS + 2\,Fe^{3+} + 2Cl^- = PbCl_2 + 2Fe^{2+} + S^o \qquad (9)$$

$$PbCl_2 + 2Cl^- = PbCl_4^{2-} \qquad (10)$$

$$PbS + 2\,H^+ + 2Cl^- = PbCl_2 + H_2S \qquad (11)$$

$$2FeCl_3 + H_2S = 2\,FeCl_2 + 2\,H^+ + 2Cl^- + S^o \qquad (12)$$

The reaction mechanism to prepare $PbSO_4$ with $PbCl_2$ is as follows.

$$PbCl_2 + H_2SO_4 = PbSO_4 + 2\,HCl \qquad (13)$$

The are several factors, affecting the leaching processes, which involve stirring speed, reaction time, reaction temperature and lixiviate concentration. The maximum leaching rate of $PbCl_2$ from galena concentrate is 98%. The optimum leaching conditions are 250 gr/L NaCl, 75 gr/L $FeCl_3x6H_2O$, o,1 mol/L HCl, 40 min, L/S= 20, pH<2, 1600 r/min.

2. Conclusion

The 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^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.

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Hence, a new approach of preparing $PbSO_4$ from galena concentrates in the sulfuric acid (H_2SO_4) and ferric chloride media coupled with selective purification and chemical sedimentation was proposed. Compared with traditional process, this new method will simplify the production process and decrease the energy consumption, as well as realize leaner production of $PbSO_4$. The aim is to investigate the conversion of lead sulfide concentrates to lead sulfate, and to demonstrate the feasibility of realizing a green route to prepare lead sulphate.

4. Literature

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