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An Investigation on the Kinetics of Lead Recovery from Smelting Furnace Slag Using Hydrochloric Acid¹

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Abstract—With regard to the large amount produced from this type of slag in flash lead smelting furnace of Ghaniabad plant and considerable lead content of the slag, the recovery of lead is of prime importance. This research work was under taken to study the lead recovery from the mentioned slag using a hydrometallurgical process. Solving in water is done on slag for 30 minutes. XRD analysis showed that PbS is the main mineral in the slag and the difference between washed and unwashed samples is lack of Na₂O in washed one so that before washing this compound existed. The slag sample was first crushed and washed in distilled water. The residue was classified into different sizes. The slag powder was then leached in Hydrochloric acid under different conditions to evaluate the effect of such parameters as pH, temperature and slag particle size on the dissolution rate of lead. It was depicted that the most critical parameter affecting the leaching rate is pH whereby the decrease of down to negative number the leaching rate increased pH significantly. Finally kinetic study of slag leaching showed that the diffusion of in the solid particle controlled the lead leaches process. This was confirmed by calculation of activation energy where was obtained as 9.47 kJ mol⁻¹ calculated.

Keywords: lead, leaching, the smelting furnace slag, hydrochloric acid, negative pH number

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1. INTRODUCTION

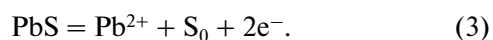
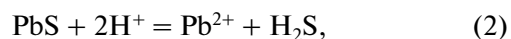
Factories producing lead in all over the world excrete wastes and tailings in a great volume in clued lead-melting furnace slag, furnace dust and grit, liquid wastes and so on every year. Considering a large amount of lead and poisoning status of lead compounds, wastes and tailing have destructive and irreparable effects on environment [1]. To recycle lead of lead-melting factories wastes and tailing is economical as well [2, 3]. A great percent of resulted lead is used in wet batteries. Getting to end of shelf life, batteries are wastes and to recycle lead, they apply secondary melting approaches [2].

Over 70% of lead is resulted through recycling useful materials specially leaded acidulous batteries [4]. The batteries are easily collected and recycled and they are main source for secondary lead producing [5, 6]. Extending secondary refining is established on reject materials and batteries which are the main source for production secondary lead [5].

Lead is just soluble in concentrated acidic solvents and thus has high corrosion resistance against acids and salts. This feature is one of the most important instances for applying lead in industry [7]. Some heavy metals are recycled by solving these in acids like sulphuric acid and hydrochloric acid [8]. Everett [9]

states that galena can solve in hydrochloric acid selectively in certain conditions by solving lead sulphids selected among ferro sulphid, zinc sulphid, lead sulphid and copper sulphid.

We believe the feature of being selective is related to galena high tendency to react than other sulphids, strong complexion power of lead ion with chloride electrolyte as well as the fact that solubility of some metals in the presence of hydrogen sulphid is lowered by reversible reaction [10]. Studying hydrochloric acid leaching behavior represents that achieving the highest efficiency for lead solving, pH < 1.5 and reduction oxidation potential >600 mV are needed [11]. To get lead concentrate solving thermodynamically conditions by chloride solutions, we can see pourbaix diagram (pH–Eh). Figure 1 illustrates Pb-S-H₂O with condition of 25°C and chloride ion = 1 mol. The vectors represent possible methods to solve lead sulphor by three reactions:



Sulphor in lead sulphid in oxidation conditions can oxidize thermodynamically in form of sulphate or bisulphate even in little pH. But in natural condition sulphor resulted from reaction (3), doesn't have outstanding

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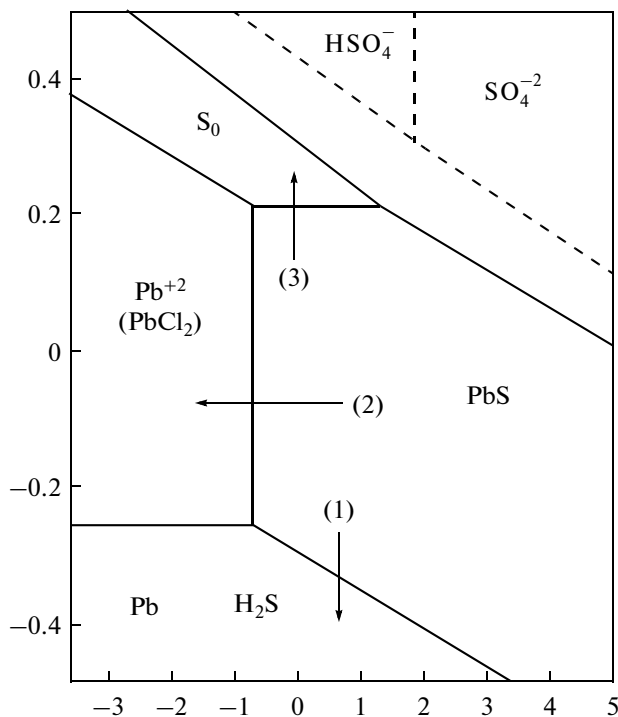


Fig. 1. pH-Eh diagram for Pb-S-H₂O system at 25°C and density of chloride ion = 1 mol.

reduction for kinetics barriers which is probably resulted from hydrophobic elemental sulphur [12].

About the leaching of lead slag, there is a few publication; therefore the aim of this research was to study the leaching phenomena of Ghaniabad slag with HCl solution.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and Characterization

Ghaniabad lead smelting furnace slag's are screened by mesh 30 (590 μm), 60 (250 μm) and 100 (149 μm), respectively, after crashing. To recognize compounds in slag as well as appoint amount of existing lead percentage, some slag's with the mesh grading -100 (<149 μm) were selected to XRD & XRF analyses. XRD analyze was applied by Joel 8030-cu kα and XRF analyze was done by Philips 1480. Then, solving in water was performed on slag for 30 minutes. All solving experiments were accomplished in 1 liter beakers. Hot plate was used for mixing and warming solution whose solutions were over than room's temperatures. pH was measured by laboratory digital pH-meter (with 0.01 accuracy). The resulted solutions were chemically analyzed by GBC Avanta with the method of atomic absorption. Mixer rotation speed was fixed about 1000 r/min for all experiments.

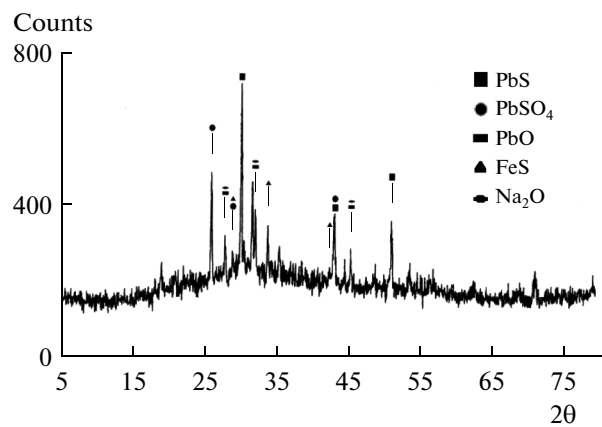


Fig. 2. X-ray diffraction pattern of slag before washing.

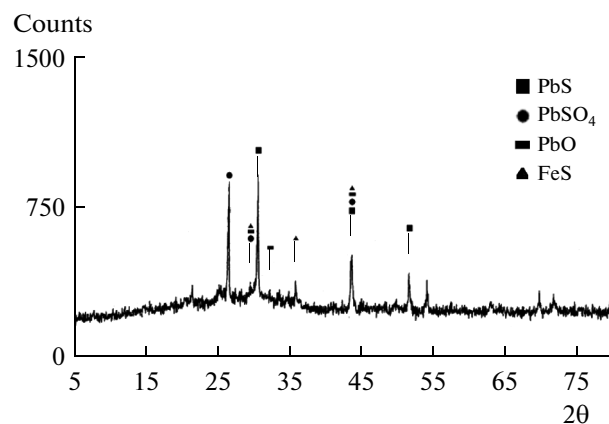


Fig. 3. X-ray diffraction pattern of washed slag.

2.2. Leaching Process

The amount of slag for every experiment was measured by digital balance with 0.01 g Accuracy. 100 mL HCl + H₂O was arranged in the certain pH level by pH-meter. In the experiments with high temperature the prepared solution were put on Hot plate and when they reached selected temperature, mixer began to work and proper rotation was arranged. Then the slag amount added to solution and it was the first time of experiments. Reappointed times peaks was sampled from solution by 4 mL bubble pipette. The sample cleared and chemically analyzed by atomic absorption method. To chemically analyze, a certain amount of samples were taken by clean pipettes after clearing and cooling and diluted. Standard samples with density of 1, 2, 3 and 4 ppm were prepared from solving net lead in Nitric acid with volume of standard solutions 1000 mg in 100 mL lead.

3. RESULTS AND DISCUSSION

Figures 2 and 3 show XRD pattern of slag before and after washing, respectively. As can be seen the

XRF analysis of slag before washing and washed slag

Element	Slag before washing	Washed slag
	wt %	wt %
Pb	21.97	25.55
Fe	30.14	37.43
Na	18.84	4.28
Cl	1.8	1.34
S	3.42	8.86
Si	3.46	5.11
Other elements	20.37	17.43

main component in washed and unwashed slags is galena (PbS) and other compounds afterwards include PbSO_4 , PbO and FeS.

The difference between washed and unwashed samples is lack of Na_2O in washed one so that in sample before washing this compound exists and its origin is ammonium chloride which is used in factory for slag-making. Decreasing of Na_2O percent in washed sample showed sodium value in this slag was decreased and as a result lead percent of slag increased. In fact with washing treatment phase concentration was performed.

Table shows chemical analyze by X-ray spectrometer (XRF) for slag before washing and washed slag. By washing with water, lead weight percent has increased from 21.97 to 25.55%.

3.1. pH Effect

Figure 4 shows effect of hydrochloride acid concentrate on lead leaching process. Decreasing pH number or increasing acidity has much effect on lead leaching in slag and during experiment has a great effect on reacted fraction so that when pH decreased from 0.65 to 1.88 the reacted fraction was changed

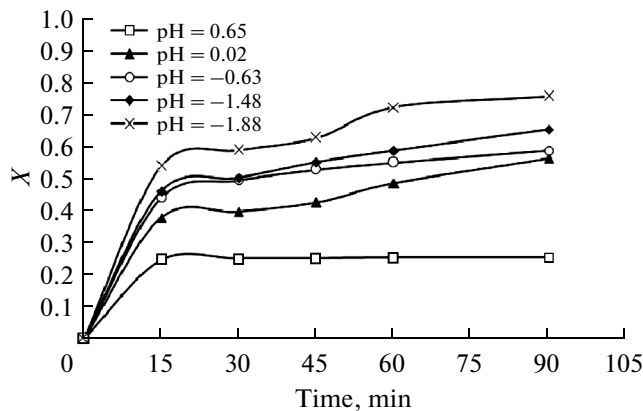


Fig. 4. Reacted fraction versus leaching time at various pH (Pulp density 50 g/L, $T = 50 \pm 2^\circ\text{C}$ and mesh -100).

about 3 times but reacted fraction by pH decreasing from -0.63 to -1.88 changed only 0.15.

According to Fig. 1, in low pHs numbers, the reaction is $\text{PbS} = \text{Pb}^{2+} + \text{S}_0 + 2\text{e}^-$ and Fig. 4 shows, with pH reduction reacted fraction will be increased to 0.75.

3.2. Temperature Effect

According to Fig. 5, there's no difference between reacted fractions at 28°C and $50 \pm 2^\circ\text{C}$. But by temperature increasing to $70 \pm 2^\circ\text{C}$, leaching rate has a great increase i.e. gets to 0.6 after 15 minutes, which shows 20% increase compare to other temperatures. But with temperature increase to this end, there is no much change in reacted fraction after 90 minute.

3.3. Slag Particle Size Effect

Figure 6 shows reacted fraction with mesh screen -30 + 60 gets to 0.23 after 90 min while fraction with mesh -100 gets to 25% in the same time which shows slag particles reduction to this size hasn't great effect on reacted fraction.

3.4. Kinetic Study of Slag Leaching

In leaching process, one of three mechanisms, diffusion reaction in the liquid boundary layer, diffusion reaction in the solid particle and chemical reaction, has the least rate which is leaching kinetics controller. To assign leaching kinetics controller, equation diagram of these three theories drawn. It was done for times at the initial 15 minutes and found that diagrams of diffusion reaction in the solid particle, $1 - 2/3X - (1 - X)^{2/3} = K_d \cdot t$ (Fig. 7) represents more linear relation than two other diagrams which indicates in the initial stage the diffusion reaction in the solid particle, this reaction: $\text{PbS} = \text{Pb}^{2+} + \text{S}_0 + 2\text{e}^-$, has controlled the leaching process.

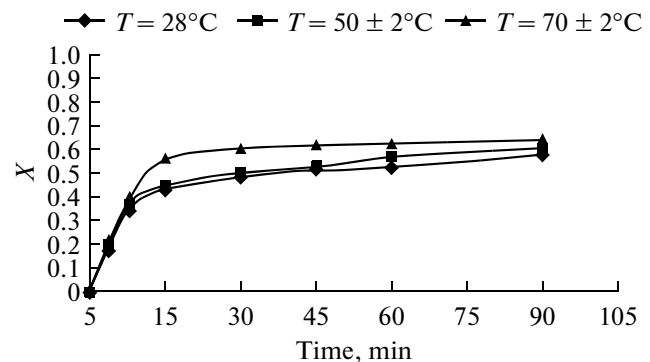


Fig. 5. Reacted fraction versus leaching time at various temperature (Pulp density 30 g/L, pH = -0.65 and mesh -100).

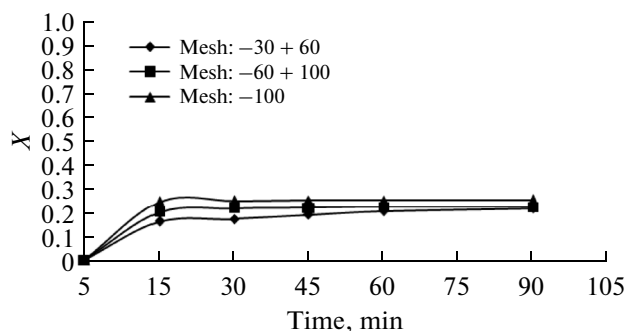


Fig. 6. Reacted fraction versus leaching time at various particles size ($T = 50 \pm 2^\circ\text{C}$, $\text{pH} = -0.65$ and Pulp density 50 g/L).

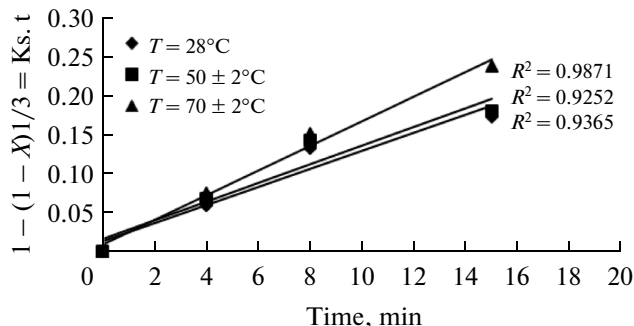


Fig. 7. $f(X)$ as function of time for the first 15 minutes (diffusion reaction in the solid particle).

To evaluate this model, rate constants of this equation ($1 - 2/3X - (1 - X)^{2/3} = K_d \cdot t$) was estimated from Fig. 7 and Arrhenius diagram ($-\ln k = -\ln A + Ea/RT$) was drawn. According to diagram slope, activation energy was evaluated 2.26 kcal/mol (9.47 kJ/mol) which is related to diffusion control theory and confirms model accuracy. Therefore, it can be concluded that ions diffusion into solid layer formed was slowest stage and so leaching process controller.

CONCLUSIONS

Among resulted data from slag dissolution experiments in hydrochloride acid, the following conclusions can be made:

—By washing slag in water Na_2O existing in slag solved and lead percent in slag increases about 4%.

—Slag particles size until $149 \mu\text{m}$ hasn't great effect on slag leaching rate, while by increasing temperature from room temperature to 70°C , leaching rate will be increased about 20%.

—Solution acidity (pH reduction) has a great effect on leaching rate which is evident in pH near to zero and negative, so that pH reduction from 0.65 to 0.02 increases leaching rate from 0.2 to 0.35 equals 75% at 15 min.

—Kinetic study of slag leaching at the first 15 minutes showed that diffusion reaction in the solid particle controlled this leaching process.

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