Leach Optimization of "Tumurtiin-Ovoo" Zinc Concentrate in $NaNO_3$ and H_2SO_4 Mixture

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***Abstract*— Samples were taken from "Tsairt Mineral" LLC's zinc concentrate, Mongolia. The company develops the "Tumurtiin-Ovoo" zinc project in Sukhbaatar province in Mongolia. This zinc concentrate contains 51.529% Zn, 30.87% S, 5.712% Fe, 4.31% Mn, 0.752% Pb, and 6.827% other elements [1]. The zinc concentrate consists sphalerite (ZnS) 76.63%, magnetite (Fe_3O_4) 0.79%, pyrite (FeS_2) 14.40%, chalcopyrite and chalcocite ($FeCuS_2$+Cu_2S) 0.83%, galena (PbS), 1.6%, and non-ore minerals 5.76%** [2].

The results of a study on optimization of leaching parameters of "Tumurtiin-Ovoo" zinc concentrate in $NaNO_3$ and H_2SO_4 mixture. The effect of leaching time, temperature, zinc concentrate and 1.5 mol/l H_2SO_4 solution's solid-liquid ratio, stirring speed, the ratio of zinc concentrate and $NaNO_3$, were investigated.

The best condition of leaching was found to be: leaching time 1 hour, temperature between 60-80^{0}C, zinc concentrate and 1.5 mol/l H_2SO_4 solution's solid-liquid ratio was 1:20g/ml, stirring speed of leaching process was 400 rpm, the weight ratio of zinc concentrate and $NaNO_3$ was 1:1.02 g/g. The zinc recovery was 99.46% at optimal leaching condition.

Keywords: Direct leaching, zinc sulfide, leaching of sphalerite

I. INTRODUCTION

"Tsairt Mineral" LLC joint venture was established in 1998, and the mine and zinc concentrate plant went into production in 2005. The company mines 350-400 thousand tons of ore per a year, and sells about 90-110 thousand tons of 50% zinc concentrate a year for export [3]. But our country doesn't produce value-added products such as zinc sulfate, zinc oxide, electro winning zinc from zinc concentrate. Producing value-added product will be helpful for economy of our country. Producing zinc from zinc concentrate has conventional methods usually follow roasting-leaching and electro winning steps [4]. Our previous study is shown "Tumurtiin-Ovoo" zinc concentrate was roasted at 900^{0}C, before sulfuric acid leaching process [5].

But direct leaching method of zinc concentrate has increased in recent years. There doesn't emit gaseous SO_2, when direct leaching process. So this method is environment-friendly.

The leaching purpose into $NaNO_3$ and H_2SO_4 mixture was: sulfide sulfur was changed into elemental sulfur, detect leaching optimization conditions, maximum zinc recovery when leaching process.

Some researchers noted, elemental sulfur was floated on solution surface of zinc concentrate leaching into $NaNO_3$ and H_2SO_4 mixture [4]. The kinetics and mechanism of sphalerite leaching from complex sulfide concentrate with sulfuric acid and sodium nitrate solution at standard conditions was presented in some paper [4], [6], [7], [8]. But there haven't Tumurtiin-Ovoo zinc concentrate's leaching investigation in $NaNO_3$ and H_2SO_4 mixture. Therefore, this paper presents the result of leaching kinetic study of Tumurtiin-Ovoo zinc concentrate in $NaNO_3$ and H_2SO_4 mixture.

I. II. METHODOLOGY

When dissolving ZnS in $NaNO_3$ and H_2SO_4 mixture, elemental sulfur separates on surface of solution. From these results and literature data it seems as if the dissolution process can be represented by one of the following chemical reactions:

$$ZnS + 2/3NaNO_3 + 4/3H_2SO_4 = ZnSO_4 + 1/3Na_2SO_4 + S^0 + 2/3NO + 4/3H_2O \quad (1)$$

$$ZnS + 2NaNO_3 + 2H_2SO_4 = ZnSO_4 + Na_2SO_4 + S^0 + 2NO_2 + 2H_2O \quad (2)$$

$$ZnS + Fe_2(SO_4)_3 = ZnSO_4 + 2FeSO_4 + S^0 \quad (3)$$

$$FeSO_4+1/3NaNO_3+2/3H_2SO_4=1/2Fe_2(SO_4)_3+1/6Na_2(SO_4)_3+1/3NO+2/3H_2O \quad (4)$$

NO gas that produced is oxidized by the air into NO_2, which dissolves in the solution and reacts with water to form HNO_3 [4]. So leaching process, we separated elemental sulfur and it will be use for producing pure sulfur, our further investigation.

Sample of zinc concentrate from Tumurtiin-Ovoo zinc concentrate plant and detected chemical composition by XRF devices and results are shown table 1 [1].

TABLE 1. CHEMICAL COMPOSITION (%WT) OF ROASTED AT 900^{0}C ZINC CONCENTRATE

AI	Si	S	Ca	Mn
0.177	0.131	30.870	0.436	4.310
Fe	Cu	Zn	Pb	O
5.712	0.282	51.529	0.752	5.801
Total 100%				

We also detect zinc content by titration method with Na2H2EDTA (complexon III) and Eriochrome Black T. Before detecting zinc in the zinc concentrate, sample was dissolved in mixture of HCI and HNO_3 completely. The solution contains certain amount of iron and manganese. Therefore solution was separated from iron and manganese before detecting zinc content. By adding ammonium solution until pH= 9, iron and manganese were precipitated from the solution. Bases of iron and manganese were separated from solution by filtration process.

Zinc was determined by complexon III in the presence of Eriochrome Black T. Eriochrome Black T (EBT) forms a wine-red colored complex with Zn^{2+} ions in solution at a pH of about 10 (obtained by adding ammonia solution). Na2H2EDTA forms a stronger complex with the Zn^{2+} ions and liberates free EBT, which has a blue color. One mole of Na2H2EDTA complexes react with one mole of Zn^{2+} ions and liberate free EBT.

$$Na2H2EDTA + Zn^{2+} \rightarrow ZnH2EDTA\ (complex) + 2\ Na^{+} \quad (5)$$

Before detecting zinc content added sodium fluoride in the solution for covering some ions (such as Al^{3+} and Ca^{2+}). Zinc recovery calculates by following formula.

$$Zn_{\%} = \frac{N_1 \cdot V_1 \cdot V_{flask} \cdot Э_{Zn}}{m \cdot V_{aliquot} \cdot 1000} \cdot 100\% \quad (6)$$

There: N_1 -normal concentration of Na2H2EDTA

V_1 -volume of Na2H2EDTA, ml

V_{flask} -volume of flask, ml

$Э_{Zn}$ - equivalent weight of zinc

m -sample mass, g

$V_{aliquot}$ -volume of aliquot, ml

The results of zinc content determination are shown in the table 2.

TABLE 2. DETERMINATION OF ZINC CONTENT BY TITRATION METHOD

Sample mass g	V_{flask} ml	$V_{aliquot}$ ml	V_1 ml	Zinc content of sample, %	Average zinc content of sample, %
0.5171	250	5	3.24	51.85	51.85
		5	3.24	51.85	
		5	3.24	51.85	
0.5048	250	5	3.10	50.82	50.82
		5	3.10	50.82	
		5	3.10	50.82	
0.5100	250	5	3.20	51.92	51.92
		5	3.20	51.92	
		5	3.20	51.92	
Average zinc content according by titration method					51.53%

Zinc content's instrumental investigation result was 51.529% in the zinc concentrate. On the other hand zinc content's titration investigation result was 51.53%. The results fitted very well each other. Therefore, we used the titration methods, further study for detecting zinc content.

For leaching in $NaNO_3$ and H_2SO_4 mixture by used 0.098 mm zinc concentrate sample. When leaching process, sulfuric acid concentration was 1.5 mol/l. We changed leaching time 1-4 hour, temperature 25-80^{0}C, zinc concentrate and sulfuric acid ratio 1:5-1:60 g/ml, stirring speed 200-600 rpm, zinc concentrate and sodium nitrate weight ratio 1:0.34-1:1.36 and studied leaching process. Determination of zinc in the leach liquor was done by titration analysis methods.

III. RESULTS AND DISCUSSION

A. Effect of time

Leaching best conditions was used to study effect of time investigation. During experiment conditions were: zinc concentrate weight-3g, powder size-0.098 mm, 1.5 mol/l sulfuric acid's volume-60 ml, magnetic mixer speed-500 rpm, 3.06g-$NaNO_3$. At first 250 ml glass beaker poured 60 ml sulfuric acid (1.5 mol/l) and heated 80^{0}C, then added 3.06g $NaNO_3$ and 3g zinc concentrate and stirred by magnetic mixer. Leaching process continued from one to four hour, by one hour step. After leaching the solution filtered and detected zinc content by titration method. From a plot of zinc in the solution at different times, the time that gives the maximum extraction during leaching was determined. Results of leaching of zinc concentrate at 80^{0}C in 1.5 mol/l sulfuric acid solution for different periods of time as determined the content of zinc in the leach liquor, is shown in Table 3, Fig.1.

TABLE 3. THE ZINC RECOVERY DEPENDING ON LEACHING TIME

№	Leaching time, hour	Aliquot volume, ml	V_1 ml	Zinc content of sample, %	Zinc recovery of solution, %
1	1	1	4.5	51.25	99.46
2	2	1	4.5	51.25	99.46
3	3	1	4.5	51.25	99.46
4	4	1	4.5	51.25	99.46

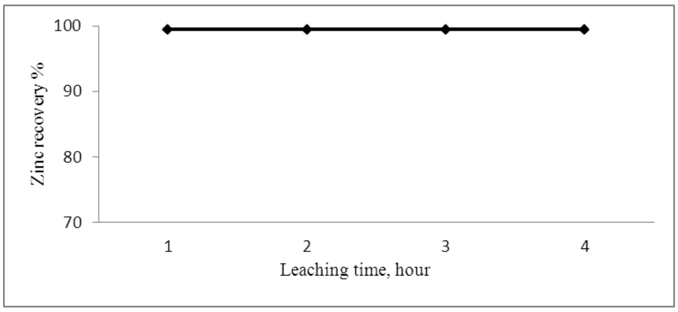

Fig. 1. Effect of leaching time on zinc recovery

You can see from Table 3, Fig.1, leaching time was 1-4 hour, zinc recovery same 99.46%. So one hour enough for leaching process.

B. Effect of temperature

Maximum extraction of zinc's leaching conditions was used effect of temperature investigation. The temperatures investigated were 25, 40, 50, 60, 70, 80 ^{0}C. At first 250 ml glass beaker poured 60 ml sulfuric acid and heated different temperature, then added 3.06g $NaNO_3$ and 3g zinc concentrate and stirred by magnetic mixer 500 rpm and leaching was continued 1hour. After leaching process, filtered the solutions and detected zinc content by titration method. The temperature plot gave the maximum zinc extraction during leaching in sodium nitrate and sulfuric acid mixture. Investigation result is shown Table 4, Fig.2. With increasing temperature, the dissolution rate of zinc is increased more. Example: zinc recovery was 11.04% when leaching at 25^{0}C, further heated to 40^{0}C and zinc recovery increased until 14.37%. Solution heated 60-80^{0}C, zinc recovery also increased until 99.46%.

TABLE 4. THE ZINC RECOVERY DEPENDING ON LEACHING TEMPERATURE

№	Leaching temperature ^{0}C	Sulfur slag on the solution	Aliquot volume ml	V_1 ml	Zinc content of sample, %	Zinc recovery of solution, %
1	25	Wasn't	1	0.5	5.69	11.04
2	40	Wasn't	2	1.3	7.40	14.37
3	50	Wasn't	0.2	0.8	45.56	88.41
4	60	Was	0.2	0.9	51.25	99.46
5	70	Was	0.2	0.9	51.25	99.46
6	80	Was	0.2	0.9	51.25	99.46

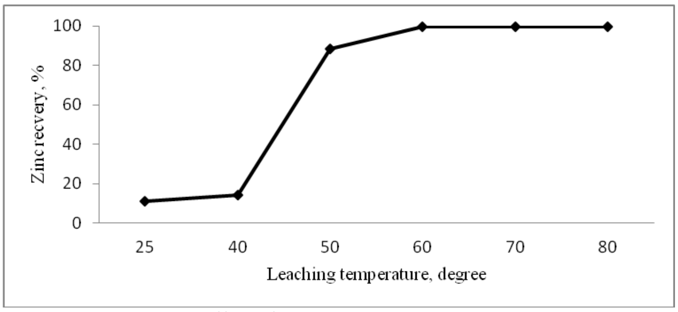

Fig. 2. Effect of temperature on zinc recovery

You can see from Table 4, Fig.2 maximum zinc content was recovered at 60-80^{0}C and it reached until 99.46% of zinc recovery and sulfur slag presented on the solution surface.

C. Effect of zinc concentrate and 1.5 mol/l sulfuric acid's solid liquid ratio

250 ml glass beaker poured 1.5 mol/l sulfuric acid solutions by different volume and heated 60^{0}C. Than added 3.06g sodium nitrate, 3g zinc concentrate sample. Leaching process continued one hour by 500 rpm stirring speed. During experiment, zinc concentrate and 1.5 mol/l sulfuric acid's solid liquid ratio was 1:5, 1:10, 1:15, 1:20, 1:40, 1:60 g/ml. experiment result is shown Table 5, Fig.3.

TABLE 5. THE ZINC RECOVERY DEPENDING ON SAMPLE AND SULFURIC ACID'S SOLID LIQUID RATIO

Sample Mass g	1.5 mol/l H_2SO_4 Volume ml	Solid liquid ratio g/ml	Aliquot volume ml	V_1 ml	Zinc content of sample, %	Zinc recovery of solution, %
3	15	1:5	1	2.8	31.89	61.88
3	30	1:10	1	3.3	37.58	72.94
3	45	1:15	1	3.7	42.14	81.78
3	60	1:20	0.2	0.9	51.25	99.46
3	75	1:25	0.2	0.9	51.25	99.46

Maximum zinc recovery was 99.46% when leaching at zinc concentrate and 1.5 mol/l sulfuric acid's solid liquid ratio increased from 1:20 to 1:25. From this result is given 1.5 mol/l sulfuric acid volume was 20 ml for 1g solid zinc concentrate was selected as the optimum condition and was applied to subsequent experiments.

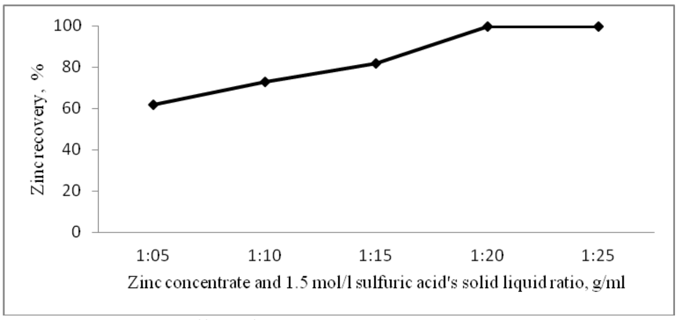

Fig. 3. Effect of solid liquid ratio on zinc recovery

D. Effect of stirring speed

When leaching process, the magnetic mixer speed changed four steps. Example: non stirring, with 200, 400 and 600 rpm. 250 ml glass beaked poured 60 ml sulfuric acid (1.5 mol/l) and heated until 60^{0}C then added 3.06g $NaNO_3$ and 3g zinc concentrate sample. During leaching process continued one hour and with different stirring speed. We detected optimum stirring speed when leaching process from the investigation. The zinc recovery depending on stirring speed is shown in Table 6, Fig.4.

TABLE 6. THE ZINC RECOVERY DEPENDING ON STIRRING SPEED

Sample mass g	Stirring speed rpm	Aliquot volume ml	V_1 ml	Zinc content of sample, %	Zinc recovery of solution, %
3	non	1	3.6	41.00	79.57
3	200	1	3.7	42.14	81.78
3	400	0.2	0.9	51.25	99.46
3	600	0.2	0.9	51.25	99.46

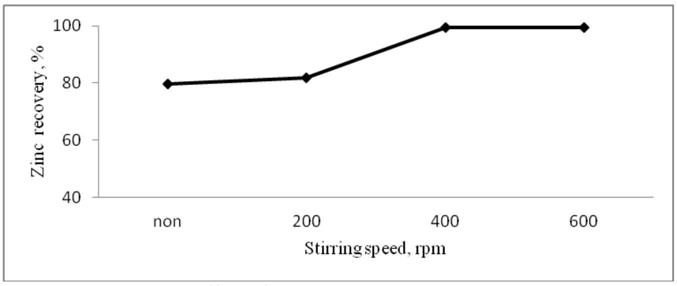

Fig. 4. Effect of stirring speed on zinc recovery

With increasing speed of mixer the dissolution rate of zinc is increased. 400 rpm mixer speed was selected as optimum retention mixer speed and zinc recovery was 99.46%.

E. Effect of zinc concentrate and sodium nitrate's weight ratio

For this investigation we used previous optimal leaching conditions and changed zinc concentrate and sodium nitrate's weight ratio 1:0.34, 1:0.68, 1:1.02, 1:1.36. The investigation result is shown Table 7, Fig.5.

This investigation was shown that zinc recovery depending on sample and $NaNO_3$ weight ratio. When the ratio was 1:1.02, maximum zinc recovery was 99.46% and the optimal ratio was ascertained from this experiment (Table 7, Fig. 5).

TABLE 7. THE ZINC RECOVERY DEPENDING ON SAMPLE AND $NANO_3$ MASS RATIO

Sample mass, g	Weight of $NaNO_3$ g	Sample and $NaNO_3$ ratio	Aliquot volume ml	V_1 ml	Zinc content of sample %	Zinc recovery of solution, %
3	1.02	1:0.34	1	0.5	5.69	11.05
3	2.04	1:0.68	1	3.7	42.14	81.78
3	3.06	1:1.02	0.2	0.9	51.25	99.46
3	4.08	1:1.36	0.2	0.9	51.25	99.46

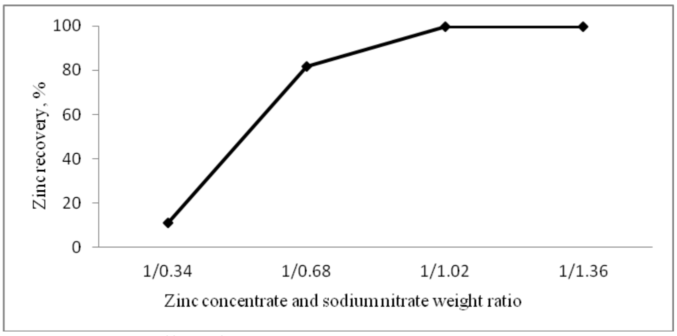

Fig. 5. Effect of zinc concentrate and $NaNO_3$ weight ratio on zinc dissolution

IV. CONCLUSION

The dissolution kinetics of Tumurtiin-Ovoo zinc concentrate in $NaNO_3$ and H_2SO_4 was studied. The effect of leaching time, temperature, zinc concentrate and 1.5 mol/l H_2SO_4 solution's solid-liquid ratio, stirring speed, the weight ratio of zinc concentrate and $NaNO_3$, were investigated. The best condition of leaching was found to be: leaching time 1 hour, temperature between 60-80^{0}C, zinc concentrate and 1.5 mol/l H_2SO_4 solution's solid-liquid ratio was 1:20g/ml, stirring speed of leaching process was 400 rpm, the weight ratio of zinc concentrate and $NaNO_3$ was 1:1.02 g/g. Zinc recovery was 99.46% at optimal leaching condition.

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