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EXTRACTION OF LEAD FROM GALENA CONCENTRATES USING FLUOSILICIC ACID AND PEROXIDE

EKSTRAKSI TIMBAL DARI KONSENTRAT GALENA MENGGUNAKAN ASAM FLUOSILIKAT DAN PEROKSIDA

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ABSTRACT

A study on lead extraction from lead concentrate had been conducted. Galena is usually associated with other sulfide ores such as sphalerite.The lead concentrate was able to be extracted and purified into its metal through a leaching process using a selective solvent of fluosilicic acid (H_2SiF_6). Parameters used in this process include ratio (dose) of reactant (H_2SiF_6:H_2O_2), temperature (without heating; 30; 50; 70; 80; and 90°C) and particle size (-100+150#, -150+200#, -200+325, dan -325#).The best extraction was achieved using the particle size of -325 mesh. The amount of extracted lead was increased due to the rise of temperature and dose of fluosilicic. The amount of peroxide addition was determined by its optimum influence on the lead extraction because its excess would produce $PbSO_4$. The influence of H_2SiF_6 and H_2O_2 doses was calculated using ANOVA.

Keywords: galena, leaching, fluosilicic acid, peroxide, precipitation.

ABSTRAK

Pemrosesan konsentrat Pb telah dilakukan untuk memperoleh logamnya. Galena pada umumnya berasosiasi dengan mineral sulfida lainnya seperti sphalerit. Konsentrat tersebut dapat diekstraksi dan dimurnikan untuk memperoleh logam melalui proses pelindian menggunakan pelarut selektif seperti asam fluosilikat (H_2SiF_6). Parameter dalam proses pelarutan adalah jumlah pereaktan (H_2SiF_6:H_2O_2), temperatur (tanpa pemanasan, 30; 50; 70; 80 dan 90°C dan ukuran partikel -100+150#, -150+200#, -200+325, dan -325#). Persen ekstraksi terbaik diperoleh menggunakan ukuran partikel -325#. Jumlah Pb yang terekstrak meningkat seiring dengan kenaikan temperatur dan jumlah fuosililat. Jumlah peroksida harus ditentukan jumlah optimumnya karena jika berlebihan tidak akan meningkatkan persen ekstraksi secara signifikan karena pembentukan $PbSO_4$. Pengaruh dosis H_2SiF_6 and H_2O_2 dihitung dengan ANOVA.

Kata kunci: galena, pelindian, asam fluosilikat, peroksida, presipitasi.

INTRODUCTION

Galena is one of the lead ores that can be used as a raw material to obtain the lead. Naturally, the mineral is associated with sphalerite (ZnS), chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) (Zárate-Gutiérrez, Lapidus and Morales, 2012). One of lead separation methods is flotation to obtain a lead concentrate (Idiawati, Triantie and Wahyuni, 2013). Indonesia has totally 387.280 million tons of lead reserves (Kementerian Energi dan Sumber Daya Mineral, 2013) and some of them have been processed to obtain the lead concentrates. However, according to the provisions of Regulation No 4 of 2009, the concentrate cannot be exported unless it has been processed through further refinery in Indonesia.

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Generally, lead manufacturing for commercial use is conducted by pyrometallurgy method (Zárate-Gutiérrez, Lapidus and Morales, 2012). The process is extracting the ores using high-exothermic temperature and transforms the material from solid to melted form. Separation process with pyrometallurgy method requires relative short time, but it must be conducted at high temperatures that can reach thousands degrees Celsius. In addition, obtaining metals such as lead by pyrometallurgy method must be conducted to high-grade ore and can be used for a large production capacity. However, if the process is carried out to low-grade ores, pyrometallurgy is ineffective and inefficient because it produces toxic gasses such as SO_2 that harms to the environment. The method also requires greater energy consumption and enormous dust production (Habashi, 2013). Moreover, the cost of controlling the gas effect to meet the environmental requirement of the process is high (Krstev *et al.*, 2012). In order to pursue the environment regulations, an alternative method of hydrometallurgy is introduced to replace the sulfur dioxide production to inert sulfur elemental (Baba and Adekola, 2013).

Lead extraction process using hydrometallurgical method has been conducted by previous researchers using leachate solutions such as sulfuric (H_2SO_4), nitric (HNO_3) and hydrochloric (HCl) acids. Using these acids will cause some problem in leaching process, as the sulfuric acid will form a $PbSO_4$ precipitate that will be difficult to be separated from the leaching solution results. Nitric acid as leaching solution can be used but the process is uneconomical. HCl may be applied as leaching solution but it will produce a $PbCl_2$ that only soluble in hot water (Li *et al.*, 2016). Furthermore, the $PbSO_4$ and $PbCl_2$ salt are difficult to solve in an aqueous solution that results aqueous electrolysis is hard to do. An alternative electrolysis of $PbCl_2$ salt can be conducted in the molten-salt system at 450°C which is required higher energy. Another more selective solution towards Pb is fluosilicic acid (H_2SiF_6). The Pb metal will produce at the cathodes and PbO_2 at the anodes as the $PbSiF_6$ solution is electrolyzed (Golomeov *et al.*, 2003).

Research on lead extraction using fluosilicic acid had also been conducted by Golomeov, Krstev and Krstev (2004). They found that a combination of PbO_2 and H_2O_2 as oxidizing agents gave insignificance results. The efficient process was accomplished by using only H_2O_2 as oxidant and added PbO_2 at the end of the reaction. Sulfur precipitated to be a free compound as a result of H_2S oxidation produced by H_2O_2 reduction in acid. Their research confirmed that increasing fluosilicic acid concentrations above 60 g/l did not show increasing of extracted lead. It is mentioned that the best condition of leaching time was 30-60 minutes and at a temperature of 95°C. The amount of extracted lead was 96%.

The experiment weakness of Golomeov, Krstev and Krstev (2004) is no reduction process for impurities/other metal ions that are usually present in galena such as Cu, Zn and Fe as sulfide compounds. Those metal ions were also dissolved in extract solution. Moreover, extracted Pb solution performed directly to the electrowinning process. Besides H_2O_2, the possible oxidants that can be used are air, oxygen gas, ozone, HNO_3 and MnO_2.

Based on previous studies, this lead extraction research was conducted using a concentrated acid solution of fluosilicic acid and H_2O_2 as oxidant. Leaching process was accomplished by controlling some experiment variables such as temperature, particle size, reactant stoichiometric ratio and oxidant. The reaction of Pb extraction using fluosilicic acid is as follows (Golomeov *et al.*, 2011):

$$PbS\,(s) + H_2O_2(l) + H_2SiF_6(aq) \rightarrow PbSiF_6(aq) + 2H_2O\,(l) + S\,(s)$$

Besides Pb, fluosilicic acid is also able to dissolve zinc (Zn) but the kinetics of zinc extraction using the acid is lower than that of lead extraction. Therefore, fluosilicic acid is suitable for extracting the lead-zinc sulfide complex (Wu, 2010).

Another important parameter to understand the influence of fluosilicic acid and peroxide doses on lead extraction is temperature. The behavior of those parameters of Pb leaching process needs to be confirmed by multivariate analysis known as ANOVA to distinguish an average of more than two group's data by comparing variances. Analysis of variance is widely used in survey research and experimental research

(Henson, 2015). The analysis of variance was included in parametric statistical categories. As a parametric statistical tool, to be able using ANOVA formula, it is necessary to test the normality assumptions including, heteroscedasticity and random sampling (Ghozali, 2011). Furthermore, ANOVA can describe the significance of parameters on the leaching efficiency statistically that show through the F-value. The bigger F value signifies the huge influence of the parameter (Behnajady *et al.*, 2012).

METHODOLOGY

The leaching experiment was conducted to lead concentrates derived from a mining company in Bogor area. The sampling process was carried out to the concentrates to obtain representative samples. The samples were then prepared in terms of getting certain sizes. A few samples were analyzed chemical and physical characters by X-Ray diffraction (XRD), optical microscope, scanning electron microscope (SEM) and nuclear absorption spectrophotometry (AAS). After sample characteristics were known then leaching was performed using fluosilicic acid (H_2SiF_6) as a solvent medium. In addition to solvent media, the process also requires an oxidant of H_2O_2 30%. The fluosilicic acid can dissolve glass material, so it requires a reactor that made from the Teflon material. Leaching process was performed using several controlled parameters namely temperatures (22; 30, 50, 70, 80, 90 °C), particle sizes (-100+150; -150+200; -200+325 and -325 meshes) and doses of reactant (H_2SiF_6: H_2O_2). The amounts of Fluosilicic acid and hydrogen peroxide were determined by a stoichiometric mole ratio of lead (Pb), zinc (Zn) and iron (Fe). The arrangement of process equipment can be seen in Figure 1. After the two-hour reaction, resulted solution was filtered to separate solution and residue. All filtrates were stored within plastic bottles. Meanwhile, the residue was washed using distilled water to reduce reactants that were still remained on its surface. The washed residue was then dried in an oven for 24 hours. The independent variables were observed by ANOVA (analysis of variance) method.

Figure 1. The layout of the instrumentations for leaching process

RESULTS AND DISCUSSION

Lead Concentrate Characterization

Physical characterization of the sample was obtained by XRD, optical microscopy and SEM-EDS analysis. According to the XRD analysis, the lead concentrate comprised of galena, sphalerite and chalcopyrite as shown in Figure 2. The majority of those three minerals can be recognized through the optical microscope as seen in Figure 3. Galena (white color) was compared to other minerals within the section such as chalcopyrite (yellow color).

SEM result in Figure 4 shows several cubistic materials that were assumed as lead minerals (galena). Lead (Pb) is dominant while zinc (Zn) serves as a minor element.

The Chemical composition of lead concentrate was examined through AAS as shown in Table 1. It depicted that the concentrate was dominated by lead (Pb) and sulfur (S). Zinc (Zn) and irons (Fe) were not too high. The chemical analysis confirms that the sample was lead concentrate.

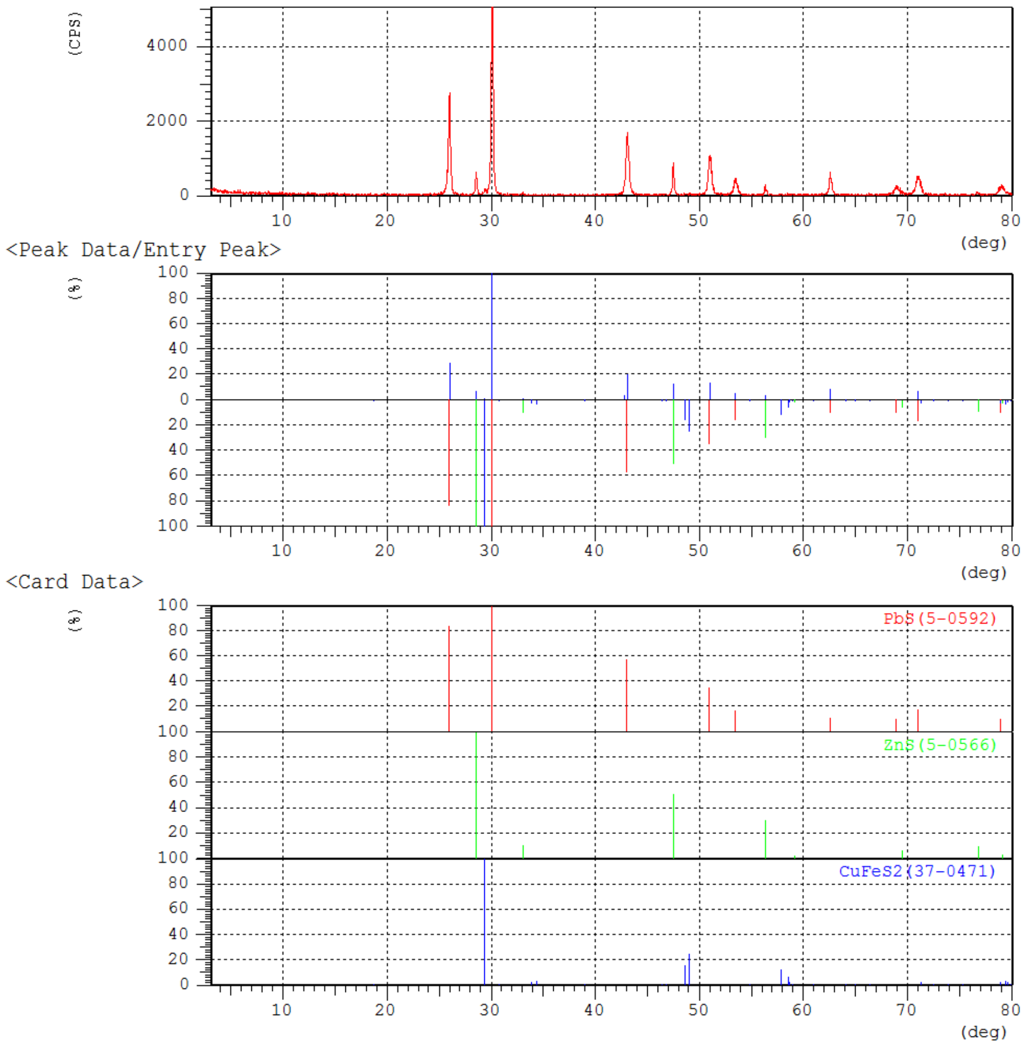

Figure 2. XRD result of the sample

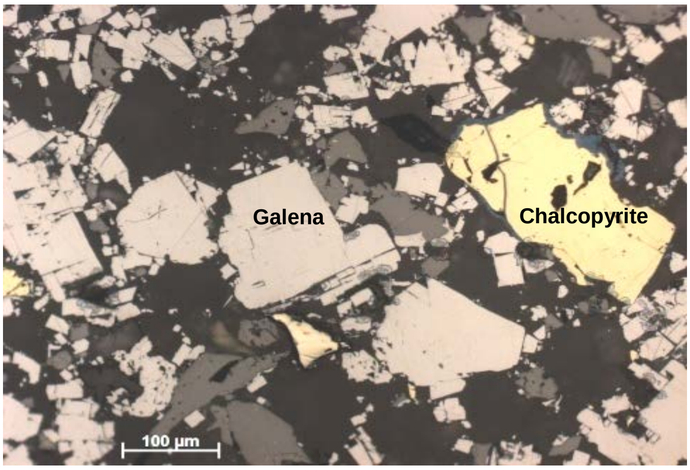

Figure 3. Result of optical microscope analysis showing galena as the main mineral and chalcopyrite as the minor one

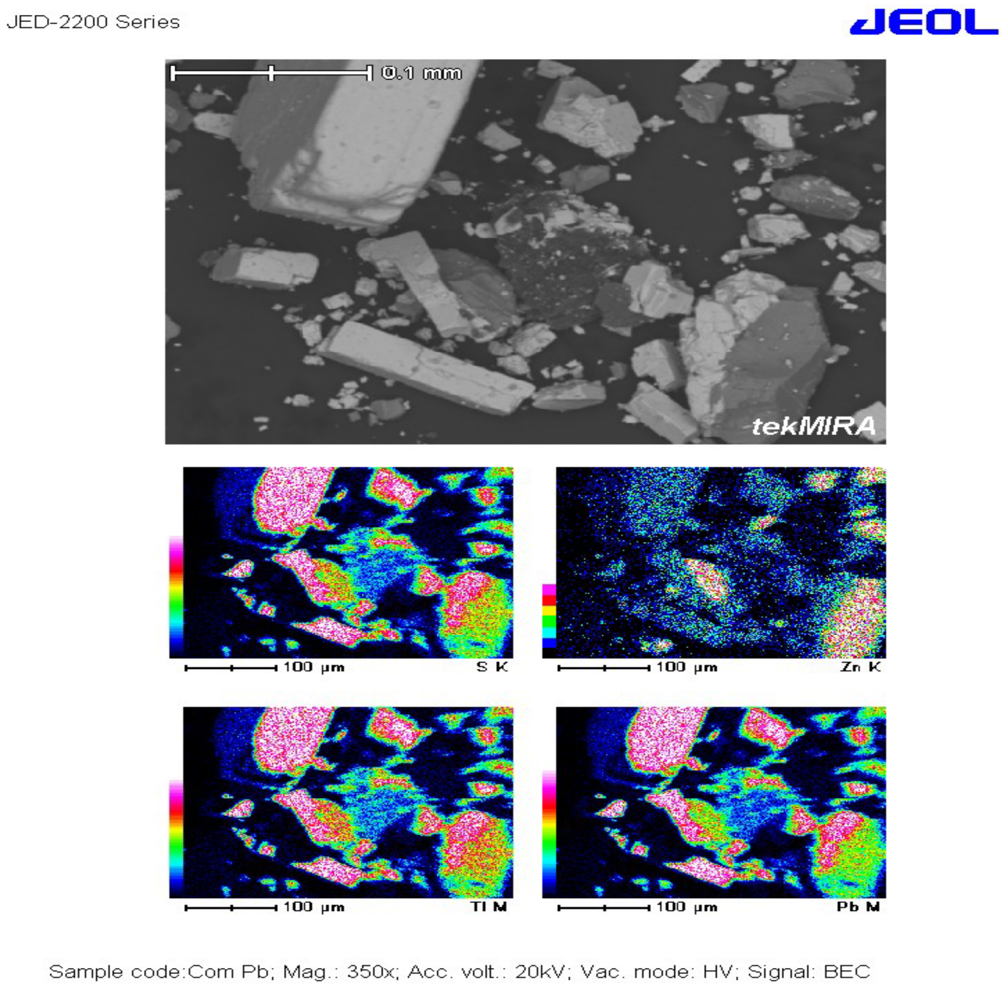

Figure 4. Result of SEM-EDS analysis showing Pb, Zn and S as the component of galena and sphalerite

Table1. Chemical composition of the sample

Element/Oxides	Content (%)
SiO_2	0.53
Al_2O_3	0.079
TiO_2	0.015
MnO	0.023
MgO	0.058
Fe Total	0.74
S Total	13.52
Cd	0.081
Co	0.029
Cu	0.65
Ni	0.003
Pb	73.35
Zn	9.40

Lead Concentrate Leaching

An appropriate temperature for lead leaching is important to be determined. Hence, the first observation of lead leaching was conducted at several temperatures (22; 30; 50; 70; 80 and 90°C) using a solution of H_2SiF_6 and H_2O_2 with ratio 2:1.5 respectively. The experiments used sample size of -200+325# and such experiment accomplished for 2 hours. The result of this condition is described in Table 2 and Figure 5, where extraction of lead increased as the temperature increased. The data correlation of temperature effect on extraction percentage was observed through the polynomial line. The line on the graph (Figure 5) has an R^2 value of 0.972. It means that the data had a good correlation with the equation approached.

It is noted that the room temperature became higher to 35°C. The phenomenon proved that the reaction is exothermic as verified by the delta enthalpy value of reaction at room temperature (67.950 kcal) (Anonymous, 2015).

Table2. Lead extractions at different temperatures using -200+325# particle size.

No.	Temperature (^oC)	Extracted lead (%)
1	22	9,32
2	30	12,90
3	50	39,10
4	70	43,20
5	80	44,71
6	90	45,34

From Table 2 it can be seen that the best extraction was achieved at 90°C. Such a temperature was then chosen as the fixed temperature for the next experiments. The influence of particle size of the sample on the lead extraction was investigated using H_2SiF_6 and H_2O_2 solution with ratios of 1.5:1.5 for 2 hours. The best extraction was achieved using a particle size of -325 mesh as seen in Figure 6. The size reduction increased the liberation degree of them and release the gangue materials from physical bonding as shown in Figure 7. The finer the particle size the bigger surface area of the sample and the larger the contact between the material and the solvent that results in increasing extraction.

The particle sizes of -325 mesh were then used in the next experiment to observe the influence of reactants (H_2SiF_6 and H_2O_2) on the lead extraction. The influence of H_2SiF_6 amounts (1; 1.2; 1.5 and 2 times stoichiometric) was examined through leaching with the constant amount of H_2O_2 and 1.5 times stoichiometry at 90°C for 2-hours. The extraction of Pb got higher when the amount of H_2SiF_6 increased as seen in Table 3.

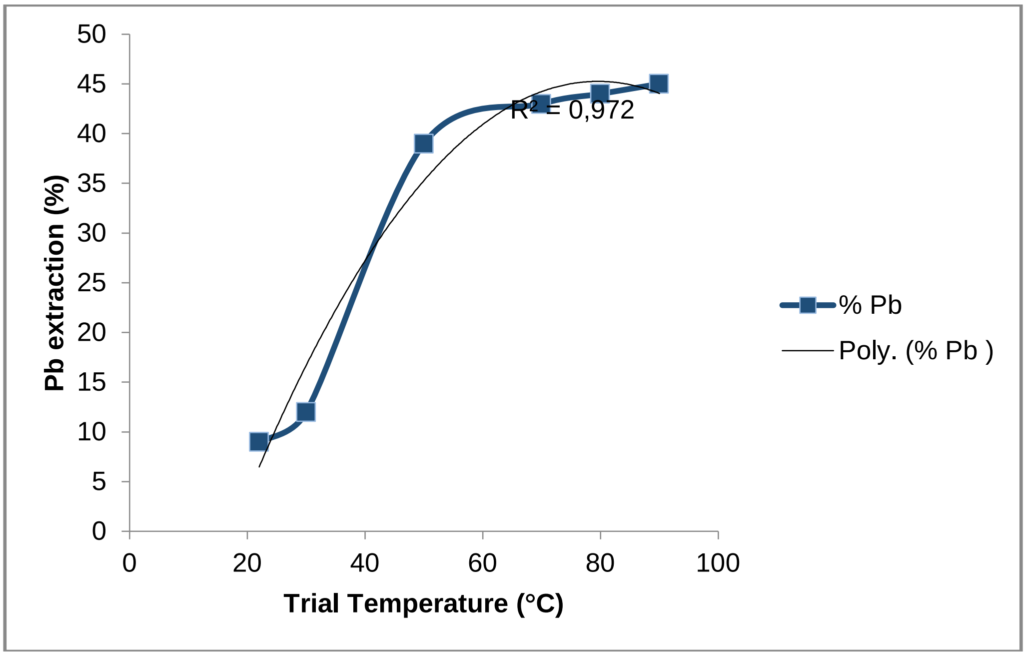

Figure 5. The influence of temperature (°C) on lead extraction

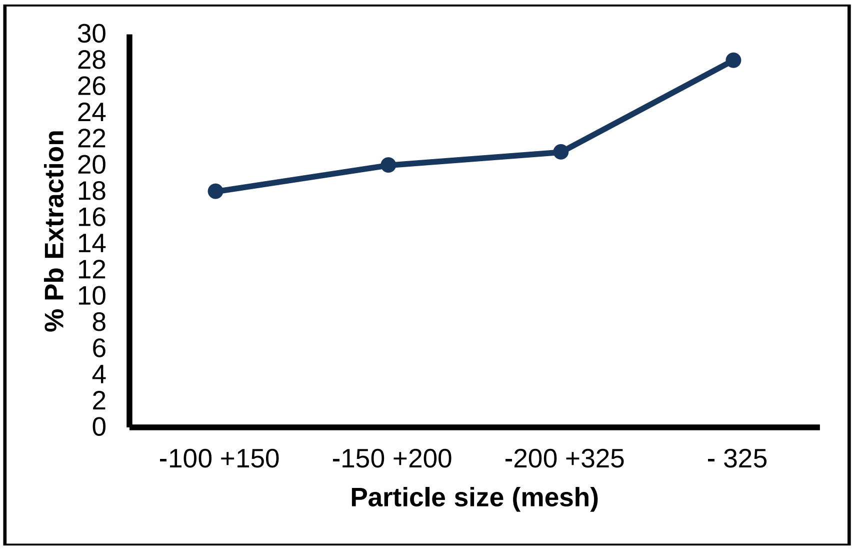

Figure 6. The influence of particle size on Pb extraction

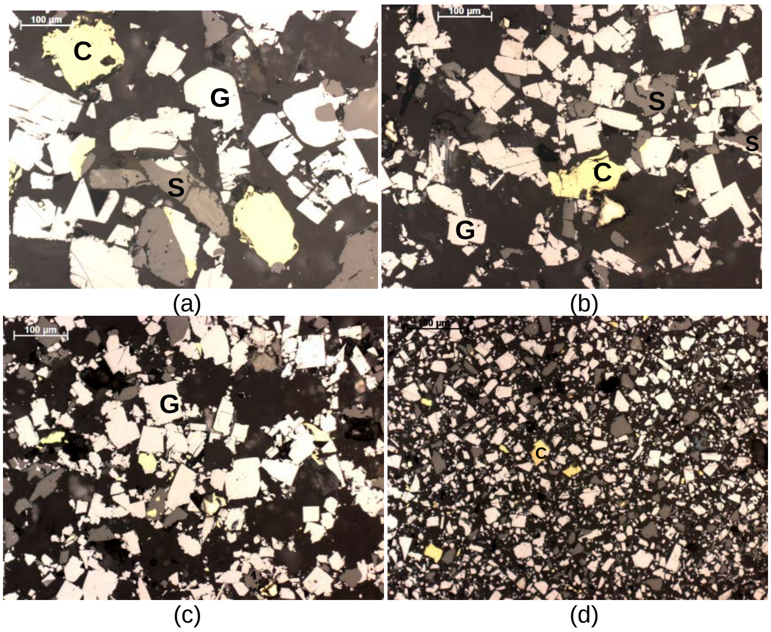

Figure 7. Liberated particle within sample: (a) -100+150# showing galena (G) attached to sphalerite (S); (b) -150+200# partial apparent of galena (G) had been liberated; (c) -200+325# emerging large parts of galena (G) had been liberated; (d) -325# emerging almost whole parts of galena (white) had been liberated.

Table 3. The influence of H_2SiF_6 on % Pb extraction on -325# sample

No	Stoichiometry Variation (x)		% Pb Extraction
	H_2SiF_6	H_2O_2	
1	1	1.5	50.87
2	1.2	1.5	56.01
3	1.5	1.5	58.95
4	2	1.5	66.27

The more H_2SiF_6 used, the more extracted Pb were obtained. Reactant amounts affected the reaction because H_2SiF_6 also reacted with Zn and Fe, therefore the process required H_2SiF_6 in large amounts. The influence of H_2SiF_6 was calculated using ANOVA. ANOVA was used to determine the effect of factors to variability that occurs in response. The results of data processing using ANOVA can be seen in Table 4. The

ANOVA test was carried out on two factors, H_2SiF_6 stoichiometry variations (A) and H_2O_2 stoichiometry variations (B). Each factor consists of 4 levels, thus the response of data experiment consists of 16 responses. F value generated was 37.95, and greater than F table value (1.92795) thus H_0 and H_1 accepted. Where the value of H_0 is $\mu1 = \mu2 = \mu3 = \mu4$ and H_1 is $\mu1 \neq \mu2 \neq \mu3 \neq \mu4$. The results suggest that the amount of H_2SiF_6 affected Pb extraction. In addition, the P value was <0.05. Small P Value indicates that there was a significant effect between factor and response.

The residual plot can be used to analyze the influence of H_2SiF_6 besides applying variance analysis table. The residual plot illustrates data distribution. The residual plot in this experiment was focused on C7 which is dependent variable column that illustrate the Pb extraction. Moreover, normal probability plot of the residual illustrates a point that coincides the line forms of a normal distribution. Bell-shaped histogram describes the data that are normally distributed. The better assessment are arisen if the residual value against fitted values as well as residual values against data order resulted in a specific pattern. The experiment using a variation on H_2SiF_6 doses did not obtain a particular pattern so the analysis results are convincing. Figure 8 and 9 shows a graphical display of variety factors influence to observe the responses.

Table 4. Anova test result for H_2SiF_6 variation

Analysis of Variance

Source	DF	AdjSS	AdjMS	F-Value	P-Value
Model	6	846,17	141,029	37,94	0,000
Linear	6	846,17	141,029	37,94	0,000
A	3	423,21	141,069	37,95	0,000
B	3	422,97	140,989	37,93	0,000
Error	9	33,45	3,717		
Total	15	879,63			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)	S
1,92795	96,20%	93,66%	87,98%	1,92795

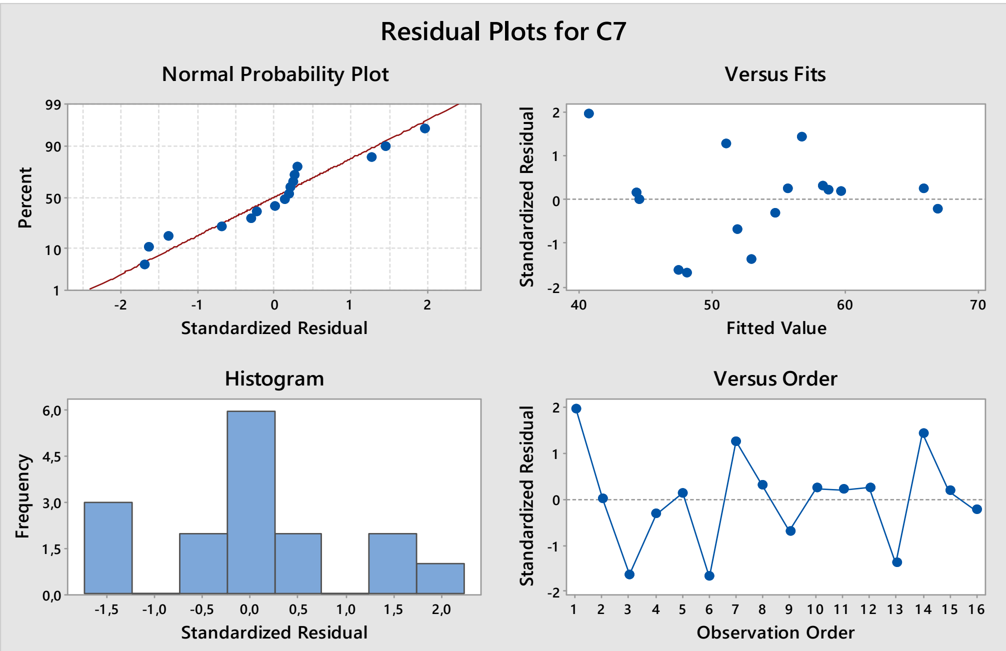

Figure 8. Response of residual plot graph

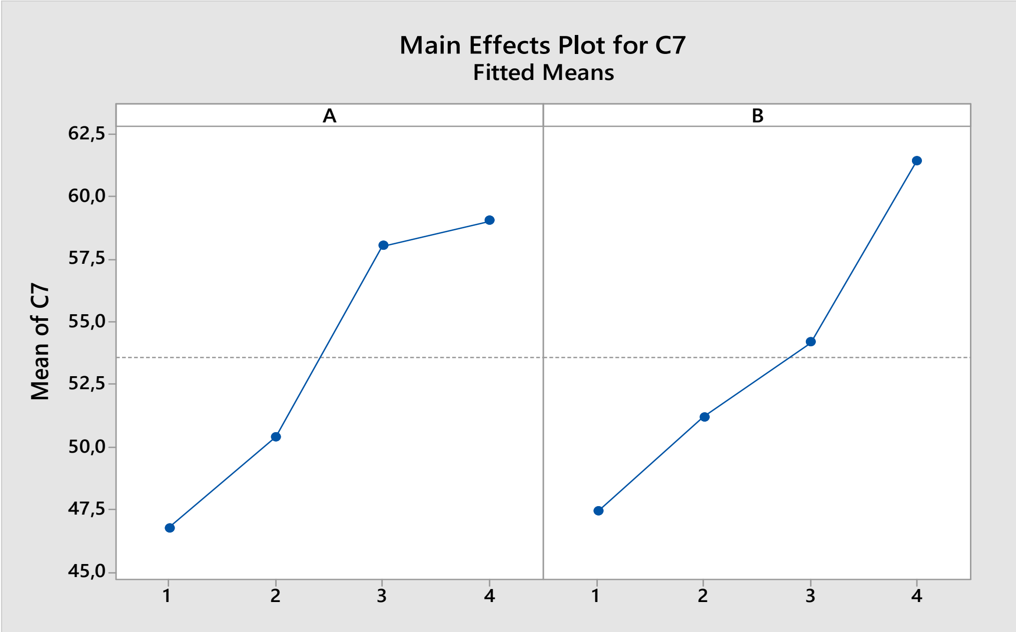

Figure 9. Response of main effects plot

The effect of H_2O_2 doses on Pb extraction also needs to be investigated. The experiments were performed by varying stoichiometry of H_2SiF_6 (1.0, 1.5, and 2.0 times) and the amount of H_2O_2 (1.0, 1.2, 1.5 and 2.0 times) at 90°C for 2 hours. The results are given in Table 5. Figure 10 shows that the addition of H_2O_2 up to 1.5 times of stoichiometry increased Pb extraction and tends to be nearly steady after adding H_2O_2 twice of stoichiometry. It was arisen due to a $PbSO_4$ formation that can be seen from XRD analysis of the leaching residue (Figure 11). The $PbSO_4$ was generated from soluble Pb that reacted with SO_4^{2-} which produced from the oxidation of PbS by H_2O_2.

ANOVA test was also conducted to the experiments using H_2O_2 stoichiometry variation. The F-value of 37.94 was obtained from the test (Table 5) that much greater than that of the F-value from the table (1.92795) while the P-value was very small (< 0, 05). It can be concluded that H_2O_2 had a significant effect on Pb extraction. Experimental data for the variations of the H_2O_2 amount is normally well distributed (bell-shaped histogram). Referring to Figure 12, the data were considered good because they did not form a specific pattern on both graphs.

Table 5. Variation of H_2O_2 doses

No	Particle Size	Stoichiometry variation		% Pb extraction
		H_2SiF_6	H_2O_2	
1	-325 #	1×	1×	43.48
2		1×	1.2×	44.47
3		1×	1.5×	50.87
4		1×	2×	50.90
5		1.5×	1×	45.04
6		1.5×	1.2×	52.87
7		1.5×	1.5×	58.95
8		1.5×	2×	59.93
9		2×	1×	54.20
10		2×	1.2×	58.72
11		2×	1.5×	66.27
12		2×	2×	66.59

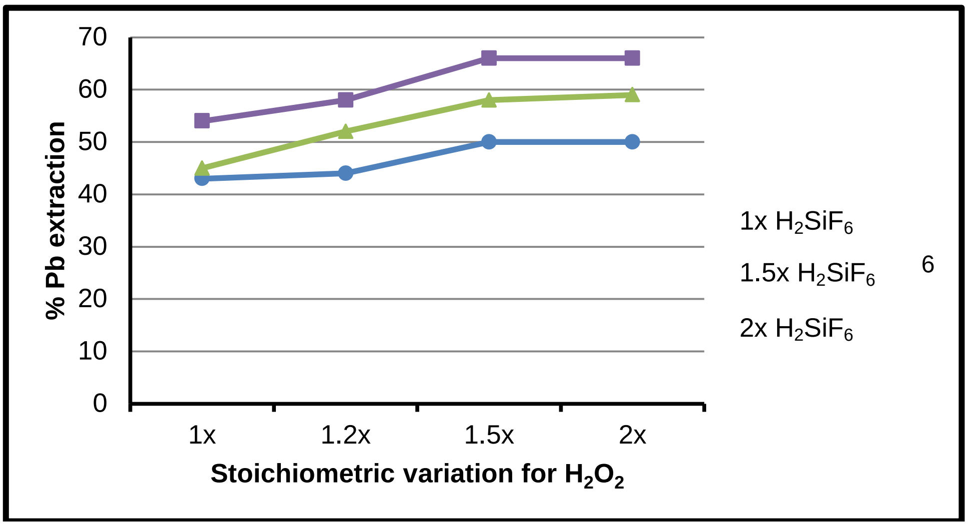

Figure 10. Effect of H_2O_2 dose on Pb extraction

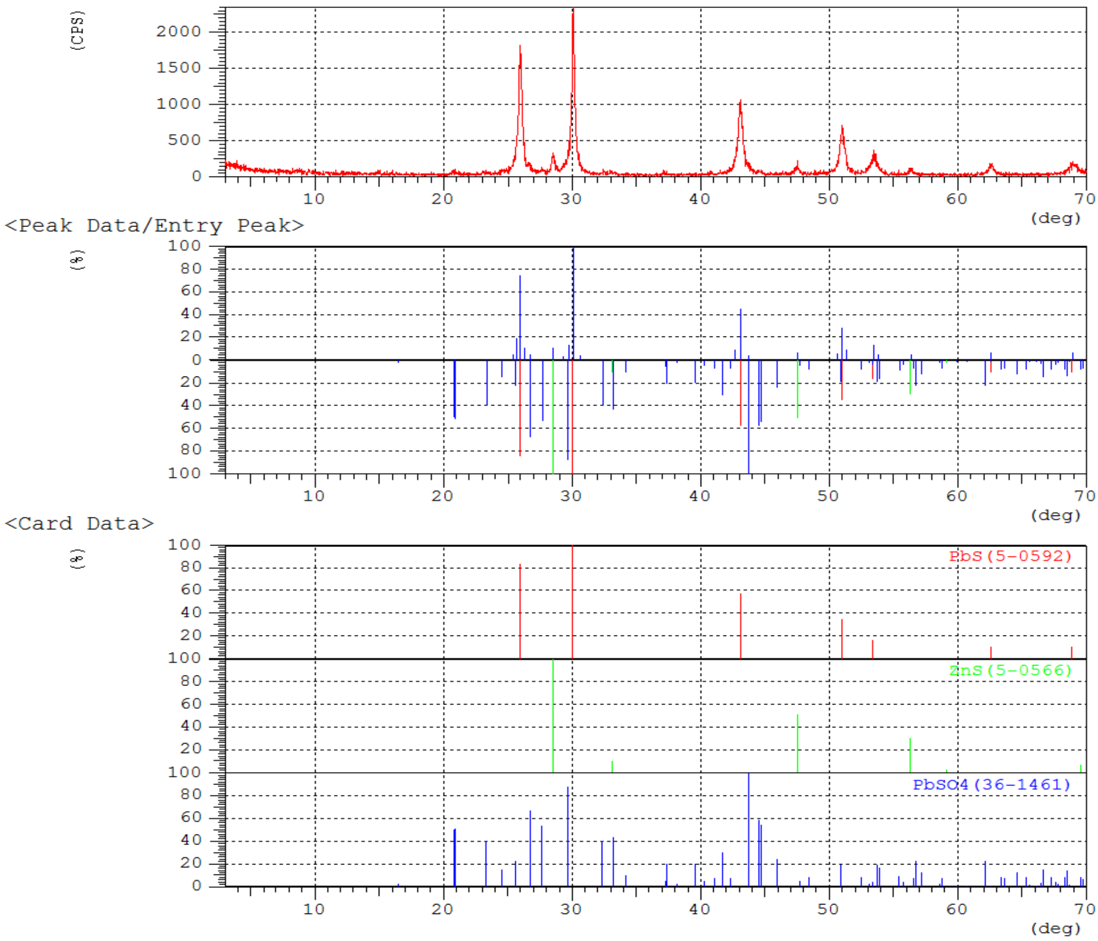

Figure 11. XRD analysis for leaching Pb result

Table 6. Anova test result for H_2O_2 stoichiometry variation

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	6	846,17	141,029	37,94	0,000
Linear	6	846,17	141,029	37,94	0,000
A	3	422,97	140,989	37,93	0,000
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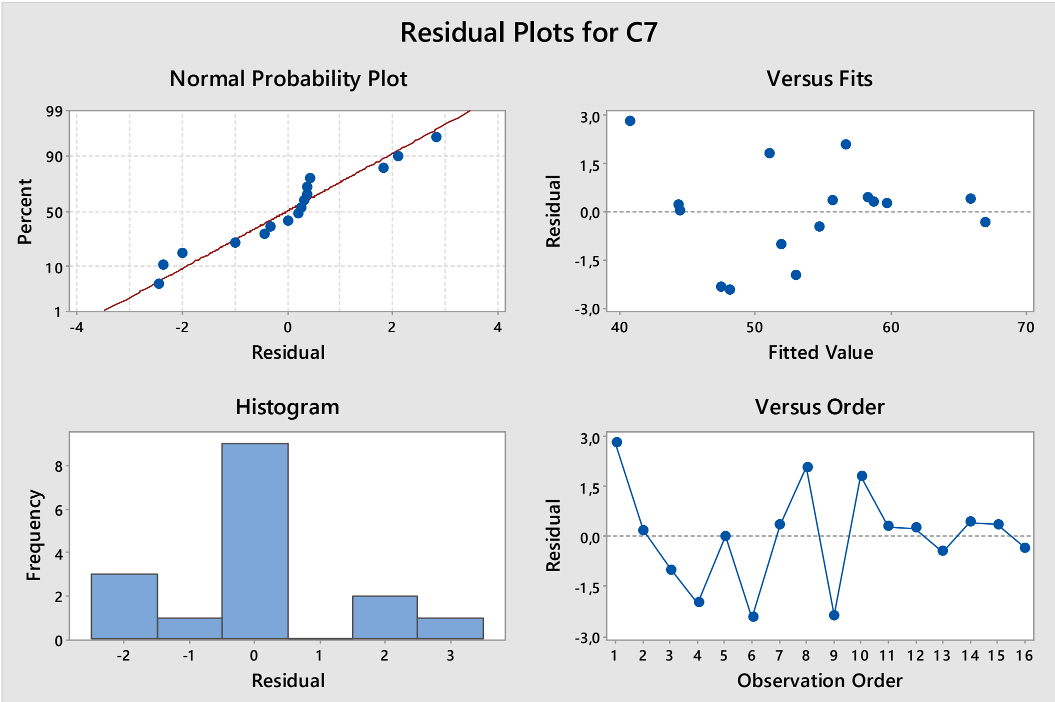

Figure 12. Response of residual plot graph (dependent variable)

CONCLUSION AND SUGGESTION

Fluosilicic acid (H_2SiF_6) and peroxide (H_2O_2) as the oxidant can dissolve Pb. However, the Pb extraction has not reached to 99% due to some lead precipitation into lead sulfate. Based on ANOVA, the doses of H_2SiF_6 and H_2O_2 significantly affect the Pb extraction. The greater the H_2SiF_6 and H_2O_2 used, the greater the Pb extraction percentage. The similar appearance to temperature observation, the higher the temperature, the greater the extracted Pb.

Hence, for the further experiment, the reactant doses should be increased to get higher Pb extraction. In addition, to reduce the lead precipitation, PbO_2 could be added to prevent precipitation due to its higher reactivity compared to lead.

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