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PYROMETALLURGICAL PROCESS FOR ZINC ANALYSIS IN SPHALERITE APPLYING XRD AND XRF

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Abstract

This paper has analyzed dominant zinc element in sphalerite naturally found together with galena in mineral ore. Since pyrometallurgical route related to roasting process is very common to mineral dressing, therefore, this investigation has studied the effect of varied roasting time (30 min, 60 min, and 90 min) and temperature (500^oC, 600^oC, and 700^oC) on zinc mineral examination using XRD (X-Ray Diffraction) and zinc element using XRF (X-Ray Fluorescence) analyses. Previous studies usually applied cheaper AAS (Atomic Absorption Spectrometer) for zinc analysis in aqueous solution, however, sphalerite is a solid matrix and therefore, this study has applied XRF to analyze zinc. Pyrometallurgical process of zinc mineral in sphalerite is related to mineral transformation in the form of $ZnSO_4$, ZnS, and ZnO that cannot be detected by XRF. Therefore, this study has used XRD that can observe mineral transformation. The XRD pattern shows four intense peaks at 2θ (28^o, 47^o, 56^o, and 76^o) justified sphalerite (ZnS) sample with little amount of pyrite (FeS_2) and galena (PbS) as impurities. The XRF analysis shows from 30 min to 90 min, the Zn content has increased remarkably at 700oC and Zn content looked stagnant at 500^oC, while Zn content increased dramatically from 60 min to 90 min at 600^oC. During roasting process at high temperature, ZnS mineral converted to ZnO and expelled SO_2 gas due to oxidation reaction causing weight reduction. The study is valuable for mineral processing in searching for optimization.

Keywords: *Roasting Temperature, Roasting Time, Zinc Analysis, XRD, XRF.*

1. INTRODUCTION

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Sphalerite or zinc blende mineral is a zinc sulfide rich mineral with its chemical formulas as (Zn, Fe) S [1]. Sphalerite ore (Figure 1) is the important source for zinc. It is primarily found in sediment deposits. Moreover, it is usually found in association with galena, pyrite, chalcopyrite, and other sulfides minerals. Besides sphalerite is a substantial source of zinc, sphalerite is also a mineral ore of indium, cadmium, and gallium.

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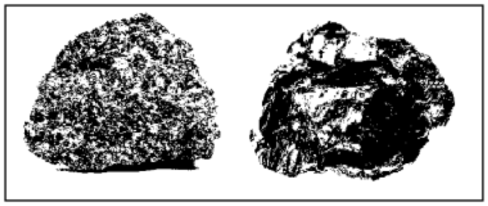


Figure 1. Sphalerite ore

Sphalerite has face centered cubic crystal structure, which is similar with the crystal structure of diamond. Zinc takes as position ion in sphalerite crystal lattice, sometimes substituted by lead, cadmium, indium, gallium, and germanium as impurities, as well as mercury and manganese [2, 3]. Cadmium may replace zinc up to 1%, while manganese is usually found in high iron sphalerite [3]. On the other hand, sulfur as negative ion generally replaced by selenium and tellurium. As already mentioned, Zn and Pb found primarily as sphalerite (ZnS) and galena (PbS) in nature due to their thiophilic properties [4].

Previous works reported several routes of sphalerite recovery and zinc separation from sphalerite concentrate. Previous studies reported zinc recovery from sphalerite concentrate as reductant with sulfuric acid leaching [5]. The investigation studied the leaching effects on acid concentration, particle size, leaching time and temperature in sulfuric media [5]. Recently, a study reported a literature review on flotation method for sphalerite recovery [6]. According to this literature review, flotation route has attracted worldwide scientists as the most remarkable technique for sphalerite recovery [6]. A study found a negative correlation between sphalerite recovery and grain size in the study of sphalerite flotation in the presence of manganese and iron in Zn-Pb-Cu complex ore [7]. Addressing to sphalerite separation from galena, a research work applied non toxic pectin based on selective depressant [4]. More-over, this work studied the interaction characteristics between pectin and both minerals of sphalerite and galena and found physical interaction between pectin and galena, while stronger chemisorption between pectin and sphalerite due to formation of -OH and -COOH groups with Zn sites [4]. On other occasion, a study reported separation of sphalerite from galena applying $KMnO_4$ and carboxylated chitosan that $KMnO_4$ oxidized sphalerite faster resulting faster interaction between carboxylated chitosan and sphalerite through chemisorption causing sphalerite depression [8]. At the same time, a sphalerite study applied hyaluronic acid as depressant through chemisorption of carboxyl and N-acetyl groups with Zn sites on the separation of sphalerite from galena for the study of flotation and adsorption mechanism [9].

It is apparent that previous reports on zinc recovery from sphalerite are still a few, although the re-ports corresponding with separation of sphalerite from galena are still limited. With regard to this matter, Figure 2 shows the concept of respective zinc and lead recoveries from mineral ore such as galena coexisted with sphalerite [10]. An Indonesian mining company located in West Java Province has been successful to recover ZnS (sphalerite) and PbS (galena) from mineral ore applying flotation method [11].

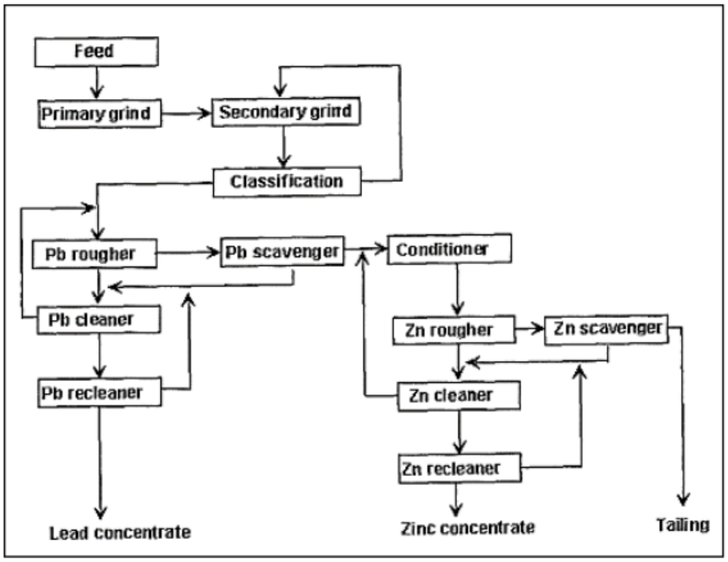


Figure 2. Flowchart of zinc and lead recovery from mineral ore [10]

In relation to mineral recovery, there are three types of metallurgical routes, i.e., pyrometallurgical, hydrometallurgical, and electrometallurgical techniques. This paper has only observed on pyrometallurgical route since this route is significant for high grade ores such as zinc in sphalerite or lead in galena. In fact, pyrometallurgical route may generate disadvantage result related to toxic gas emission generating environmental pollution. Although pyrometallurgical process has some drawbacks, many investigations have applied integrated routes of pyrrometallurgical and acid leaching to obtain zinc recovery from sphalerite. This study has only limited to the examinations of XRD and XRF on sphalerite yielded from pyrometallurgical process. With regard to zinc recovery from sphalerite, the pyrrometallurgical process is not the ending investigation, it needs other processes such as modified acid leaching or froth floatation route that is beyond the scope of this paper.

However, pyrometallurgical route is still fascinating to mineral recovery in mining field due to its low production cost. There are four types in pyrometallurgical techniques, i.e. (i) calcination, (ii) roasting, (iii) smelting, and (iv) refining. Since zinc is the major element in sphalerite and lead in galena, this study has selected the roasting method for zinc examination. The roasting method has conducted at 500^{o}C, 600^{o}C, and 700^{o}C respectively, for 30 min, 60 min, and 90 min at each temperature. XRD and XRF analyses have been applied to investigate zinc in sphalerite mineral.

2. EXPERIMENTAL METHOD

2.1. Material and Glassware

The raw material is a mineral ore sampling taken from Bogor Residence, West Java Province, as shown in Figure 1 that 100g sample was used for roasting process with the particle size in the range of 60 – 200 mesh. The material and glassware used in this study are presented in Table 1 as follows:

Table 1. Material and glassware used in the study

No.	Material and glassware	Notation
1	Mineral ore	Sampling location: Bogor Residence, West Java Province
2	Particle sizes for roasting	60 – 200 mesh
3	Petri dish	Sample plate
4	Mortar and pestle	Sample grinding and refining
5	Oven	Sample drying ≈ 100°C
6	Sieve shaker	Sample screening
7	Analytical balance	Sample weighing
8	Muffle furnace	Sample roasting >> 600°C

2.2. Roasting Method

The roasting process was conducted for mineral ore at varied temperatures (500°C, 600°C, and 700°C) and varied roasting times (30 min, 60 min, and 90 min). During roasting process, the possible chemical reactions was described as follows:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \quad (1)$$

$$ZnS + 2O_2 \rightarrow ZnSO_4 \quad (2)$$

The pyrometallurgical process generated sulfur dioxide gas and mineral zinc sulfate as described in the chemical reaction (1) and (2). It is interesting that oxidation reaction during roasting at high temperature may yield other mineral such like $ZnSO_4$ as shown by chemical reaction (2). Therefore, three types of zinc mineral may exist together after roasting process, i.e., ZnO, $ZnSO_4$, and ZnS. The existence of the three zinc minerals will be shown in the XRD spectra (Figure 9).

2.3. XRD Examination

A PANalytical type X'Pert PRO using Cu-Kα emitted ray at 1.542 A provided with fully ceramic X-Ray tubes and hybrid pixel detector was used to examine mineral ore obtained from Bogor Residence, Jawa Barat Province, before and after roasting process. A sieve shaker was used to screen samples with given particle size after roasting in muffle furnace at given time and temperature. The XRD examination was applied to investigate type of minerals in sphalerite in association with galena samples. The diffraction peaks are determined by Bragg's Law, i.e., $\mathbf{n}\lambda = \mathbf{2d}\ \mathbf{sin}\theta$. Where n = number of repeating units; λ = light wavelength; d = distance between lattice planes; θ = diffraction angle. The light reflections through crystal lattices followed the Braggs' Law are illustrated in Figure 3 [12].

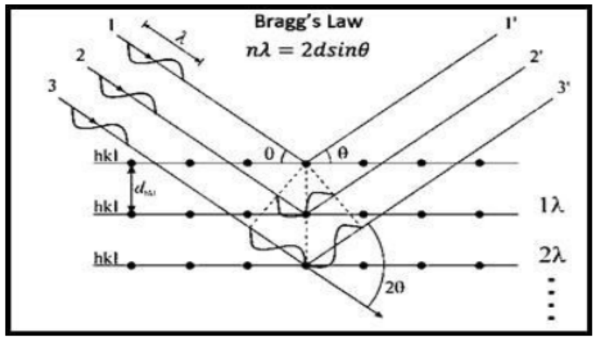


Figure 3. Conceptual theory of X-Ray Diffraction (XRD) with Bragg's Law [12]

2.4. XRF Examination

A PANalytical, type Minipal 4 XRF (X-Ray Fluorescence) Spectrophotometer with silicon drift detector was used to analyze qualitatively and quantitatively elements in mineral ore before and after roasting process. A sieve shaker was used to get sample with given particle size (≤ 200 mesh) after roasting mineral ores in a muffle furnace for 500°C, 600°C, and 700°C. The roasting times were conducted at 30 min, 60 min, and 90 min at each given temperature, respectively. As mentioned above, the sample was obtained from Bogor Residence, West Java Province and stored in Galena Maju Karya Mandiri company. 100g sample with ≤ 200 mesh was used for XRF examination. The XRF examination was applied to determine concentrations of several representative elements in sphalerite mineral, such as zinc, lead, iron, copper, and molybdenum. Figure 4 illustrates the electron excitation to higher energy level if an atom attacked by X-Ray. The energy of incident X-Ray is used by electron to jump up to higher energy level.

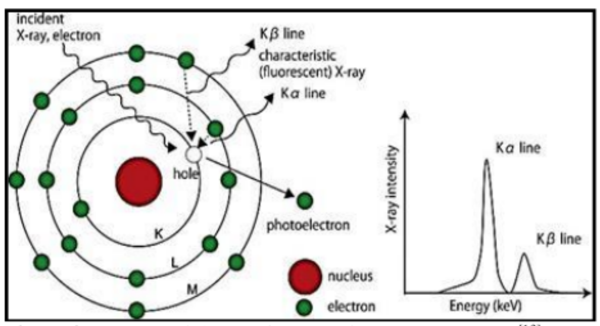


Figure 4. Conceptual theory of X-Ray Fluorescence (XRF) [13]

2.5. Experimental Steps

The given size sample ore was consecutively dried, screened, and roasted at given temperature and time followed by examinations using XRD and XRF. The experimental steps in this study are presented as flowchart shown in Figure 5 as follows:

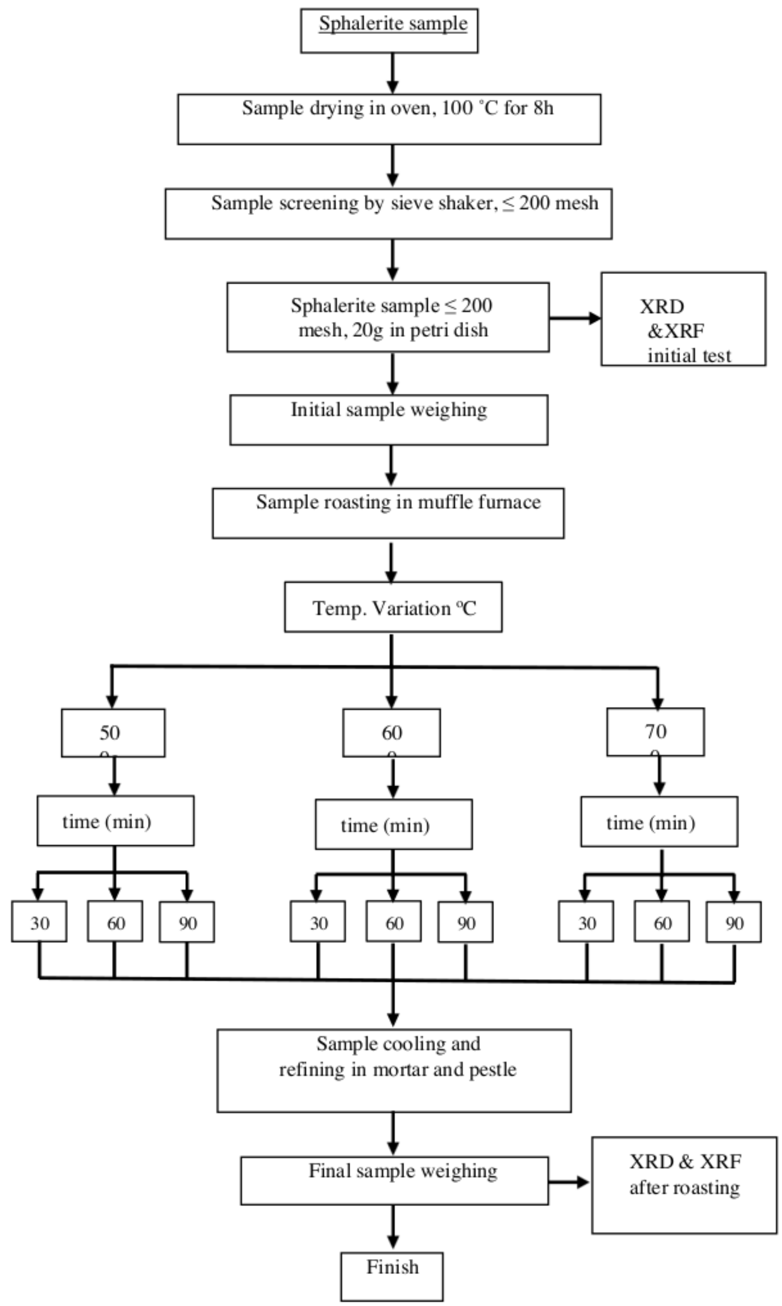


Figure 5. Flowchart of this study

3. RESULTS AND DISCUSSION

3.1. Sample Screening Results

The sample ore taken from sampling area needs to be screened to obtain the given size. The mineral sample used in this study followed the given size, i.e. ≤ 200 mesh using a sieve shaker. Previous investigation reported that finer sample grains may give better roasting result [14]. There were eight samples available for screening process to obtain sample with given size ready for roasting. Table 2 shows the result.

Table 2. Sample screening applying sieve shaker for roasting process

Sample	Sampel weight (g)	Sample weight (g)		
		+175 mesh	+200 mesh	-200 mesh
1	500	175	20	305
2	485	180	20	285
3	500	190	30	280
4	490	205	35	250
5	500	180	30	290
6	480	175	45	260
7	500	180	40	280
8	490	190	35	265

3.2. Roasting Results

Roasting at high temperatures (500°C, 600°C, and 700°C) may cause oxidation due to oxygen consumption from the environment. The oxidation reaction oxidizes zinc blende (ZnS) to give ZnO and emitted SO_2 gas resulting mass reduction of the sample. The chemical reaction (1) illustrates the conversion of zinc blende to zinc oxide. In addition, the zinc blende can also convert to yield zinc sulfate as shown by chemical reaction (2) if the roasting process takes longer time at higher temperature. Table 3 shows the result.

Tabel 3. Sample screening applying sieve shaker for roasting process

Variable		Initial mass (g)	Final mass (g)	Mass removal
Temp (°C)	Time (min)			
500	30	65,03	63,47	2,40%
	60		62,38	4,08%
	90		61,74	5,06%
600	30	65,01	62,85	3,32%
	60		61,44	5,48%
	90		61,49	5,41%
700	30	65,10	61,23	5,95%
	60		59,10	9,21%
	90		58,95	9,45%

3.3. XRD Results

The XRD analyses were conducted for mineral samples before and after roasting process at varied temperatures (500°C, 600°C, and 700°C). The roasting times are varied at 30 min, 60 min, and 90 min. In order to verify the sphalerite sample used for XRD examination, this study applied a standard sphalerite sample based on previous study [15] shown by Figure 6. Moreover, Figure 6 shows four intense peaks at 2θ 28°, 47°, 56°, and 76° as characteristic peaks of pure sphalerite sample not mixed with other minerals.

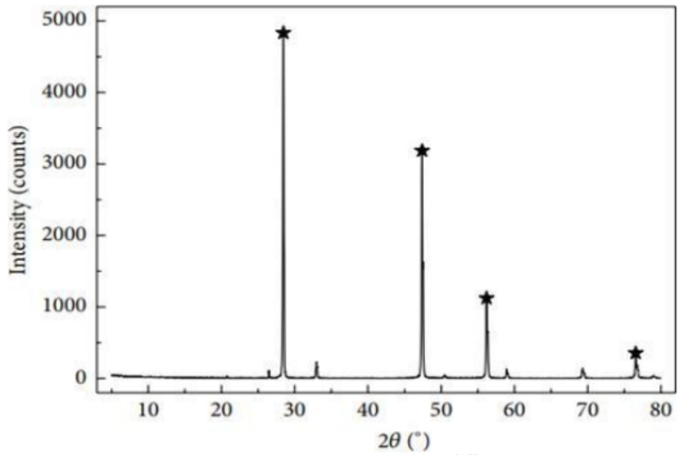


Figure 6. XRD pattern of standard sphalerite sample [15]

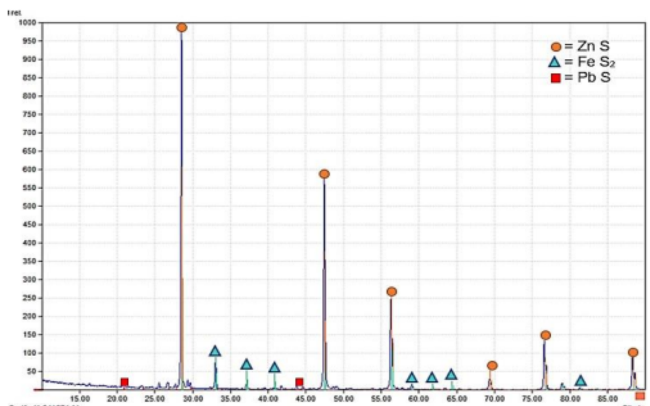


Figure 7. XRD pattern of mineral sample used in this study

Furthermore, Figure 7 shows the XRD pattern of mineral sample applied in this study. There are four intense diffraction peaks at 2θ 28°, 47°, 56°, and 76° attributed to sphalerite sample as shown by Figure 6. Figure 7 also shows other diffraction peaks of pyrite (FeS_2) and galena (PbS). This matter verified that the sample used in this study is dominated by sphalerite as major mineral in association with other minor pyrite and galena minerals. Figure 7 shows the XRD pattern of sphalerite sample before roasting. Figure 8 (a – c) shows the XRD patterns of mineral sample with sphalerite dominant after roasting time of 90 min addressing to 500°C, 600°C, and 700°C, respectively. XRD examination is valuable especially for structure analysis. With regard to process examination conducted at different temperature treatment, an XRD analysis was used to investigate provskite structure of electrochemical cathode at sintering temperatures of 1000°C and 1100°C [16]. XRD analysis was applied to examine the size, shape, and morphology of SnO_2 crystal structure using sol gel method [17].

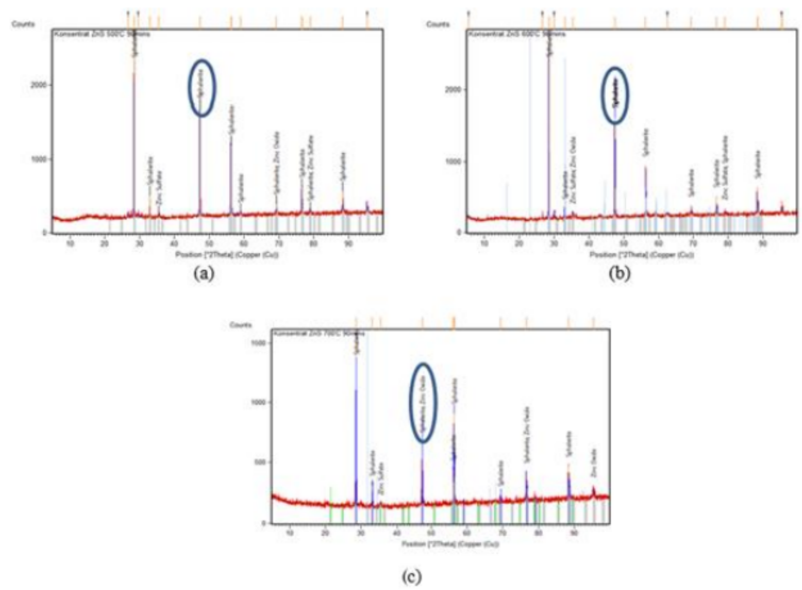


Figure 8. XRD patterns of roasting mineral samples at (a) 500°C, (b) 600°C, and (c) 700°C. Roasting time 90 min

Figure 8 (a) shows the XRD patterns of sphalerite at 500°C, (b) at 600°C, (c) at 700°C with roasting time 90 min. An interesting matter should be noted at diffraction peak (2θ) of 47° the sphalerite peak overlapped with ZnO peak after roasting at 700°C, 90 min, while both at 500°C and 600°C (90 min) the diffraction peak 2θ at 47° only attributed for sphalerite. It is an indication when the roasting temperature increased from 500°C or 600°C to 700°C, a transformation or partial oxidation of ZnS to form ZnO occurred.

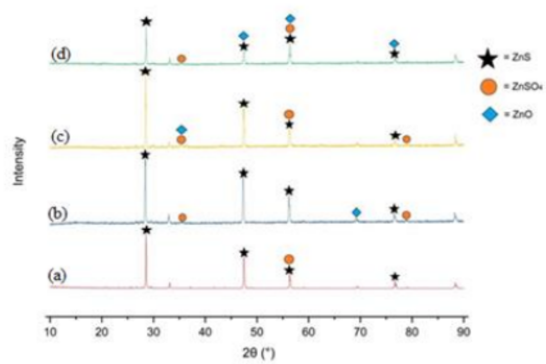


Figure 9. Overlay of XRD patterns of roasting minerals (a) non roasting , (b) 500°C, (c) 600°C, (d) 700°C. Roasting time 90 min

Figure 9 shows the overlay patterns of XRD addressing to varied conditions, i.e., non roasting, 500°C, 600°C, and 700°C for 90 min roasting time. As seen, the non roasting mineral sample was dominated by sphalerite, then at 500°C roasting, $ZnSO_4$ and ZnO were generated due to air oxidation converting partial zinc blende to form $ZnSO_4$ and ZnO. As the roasting temperature elevated to 600°C, more $ZnSO_4$ generated due to continued oxidation, and as the roasting temperature increased to 700°C, more production ZnO rather than $ZnSO_4$, it showed that most of sulfur was removed as SO_2 gas yielding both reduction of ZnS and $ZnSO_4$ to form ZnO, as well as the residual Zn oxidized to ZnO. All these roasting processes were conducted at 90 min. Therefore, the roasting process gave effects on mineral transformation between ZnS, $ZnSO_4$, and ZnO.

3.4. XRF Results

As XRD analysis examined the type of minerals, the XRF analysis investigated the type of elements existed in mineral samples. The concentrations of sulfur and zinc are significant in Table 4 that should be highlighted in red square brackets due to their concentrations change in relation to condition changes (non roasting and varied roasting times, i.e., 30 min, 60 min, and 90 min at 500°C). The sulfur content decreased slowly, i.e. 8.9% - 8.3% - 8.2% - 7.8%, consecutively. On the other hand, the zinc content increased slowly, i.e., 51.04% - 51.30% - 51.82% - 51.87%, consecutively. Both are attributed to red square brackets.

Table 4. XRF records for elemental analysis in mineral samples

Compound	Si	S	Ca	Cr	Mn	Fe	Ni	Cu	Zn	As	Y	Zr	Nb	Mo
Conc	0,51	8,9	0,20	0,059	0,18	8,52	0,062	1,27	51,04	0,31	1,2	1,3	8,3	14
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%	%

Compound	La	Eu	Yb	Pb
Conc	0,1	0,09	0,28	3,8
Unit	%	%	%	%

non roasting

Compound	Si	S	Ca	Cr	Mn	Fe	Ni	Cu	Zn	As	Y	Zr	Nb	Mo
Conc	0,68	8,3	0,17	0,052	0,18	9,26	0,061	1,21	51,30	0,32	1,4	1,3	7,4	14
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%	%

Compound	La	Eu	Yb	Pb
Conc	0,09	0,10	0,30	3,8
Unit	%	%	%	%

roasting 500°C 30 min

Compound	Si	S	Ca	Cr	Mn	Fe	Ni	Cu	Zn	As	Y	Zr	Nb	Mo
Conc	0,54	8,2	0,17	0,058	0,18	9,9	0,067	1,28	51,82	0,33	1,4	1,5	7,3	13
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%	%

Compound	La	Eu	Yb	Pb
Conc	0,09	0,06	0,28	3,8
Unit	%	%	%	%

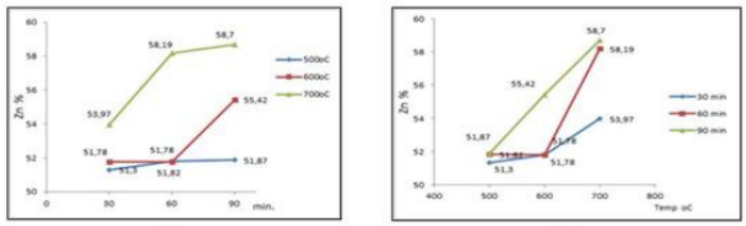
roasting 500°C 60 min

Compound	Si	S	Ca	Cr	Mn	Fe	Ni	Cu	Zn	As	Y	Zr	Nb	Mo
Conc	0,61	7,8	0,17	0,055	0,17	10,57	0,056	1,27	51,87	0,31	1,3	1,3	7,4	13
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%	%

Compound	La	Eu	Yb	Pb
Conc	0,10	0,1	0,29	3,7
Unit	%	%	%	%

roasting 500°C 90 min

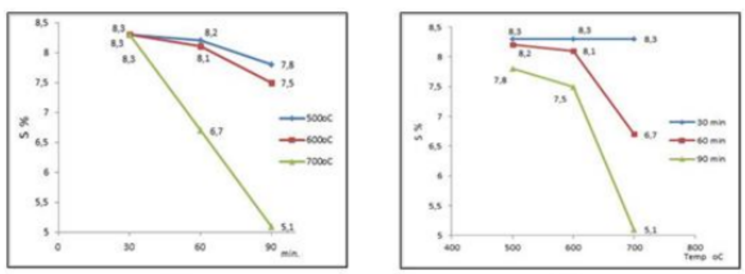
The findings are related to higher roasting temperature (500°C) and longer roasting time (30 min, 60 min, 90 min) causing sulfur loss due to volatility of SO_2 gas. The air oxidation converted sulfur in sphalerite to form SO_2 gas resulting sulfur reduction in mineral sample. On the other hand, the zinc content increased slowly due to formation of $ZnSO_4$ and ZnO besides the zinc blende ZnS residual presence in sphalerite mineral. The formation of $ZnSO_4$ and ZnO is closely related to air oxidation of zinc blende in the mineral sample as shown by chemical reactions (1) and (2) mentioned above. This phenomenon is shown clearly in XRD illustrations (Figure 9) where Figure 9 shows the phenomenon due to roasting temperature effect. It is apparent that longer roasting time gave little effect on the conversion of concentrations of both sulfur and zinc in given mineral sample. This finding will be shown clearly in next XRF presentations. In addition, Figure 9 also shows data of rare earth elements (REE), i.e. lanthanum (La), europium (Eu), and ytterbium (Yb) with insignificant changed due to pyrometallurgical process. Up to date, REE has become fascinating and experienced fast development due to their substantial applications for renewable energy.



(a) (b)

Figure 10. Data XRF for Zn (%) based on (a) varied roasting time and (b) varied roasting temperature

In order to compare the effects of roasting temperatures (500°C, 600°C, and 700°C) and roasting times (30 min, 60 min, and 90 min) on Zn concentrations in mineral samples, Figure 10 present this phenomenon. It is apparent that the effects of both 90 min and 700°C gave the highest responds on Zn concentrations. On the opposite way, the effects of both 30 min and 500°C gave the lowest responds on Zn concentrations. The effects of 60 min and 600°C yielded the moderate responds on Zn concentrations. In general, increased trends are presented for all given conditions as both increased roasting times and temperatures. However, the trend is almost flat at increased roasting times from 30 min to 90 min at 500°C as shown at Figure 10 (a).



(a) (b)

Figure 11. Data XRF for S (%) based on (a) varied roasting time and (b) varied roasting temperature.

As Figure 10 present the effects of roasting time and temperature on zinc concentrations in sphalerite samples applying XRF analysis, Figure 11 present the same effects on sulfur concentrations. Figure 11 (a) shows remarkable reduction of sulfur concentration as roasting times increased from 30 min to 90 min at the highest given roasting temperature (700°C) attributed to green line. The same trend is also shown at Figure 11 (b) addressing to remarkable reduction of sulfur content as the roasting temperatures increased from 500°C to

700°C at the longest given roasting time (90 min). At the moderate given conditions (600°C and 60 min) the sulfur reductions are moderately decreased as shown at both Figure 11 (a) and (b). Figure 11 (b) shows interesting feature that increasing roasting temperatures from 500°C to 700°C gave no significant change of sulfur concentrations at roasting time of 30 min attributed to blue line. Generally, low given roasting temperature (500°C) and time (30 min) gave no significant effect on sulfur reduction. This condition gave inversed performance showed by the highest given roasting temperature (700°C) and time (90 min) that yielded remarkable effect on sulfur reduction. This finding gave a consistency between roasting condition (temperature and time) and sulfur reduction. It is reasonable since high roasting temperature and long roasting time yielded high removal of SO_2 gas due to air oxidation as shown by chemical reaction (1) above. The findings are emphasized on zinc mineral and sulfur concentration since the discussion involved with sphalerite samples with ZnS as dominant mineral and other minerals such as galena and pyrite, as well as other elements shown in Table 3 existed in minor quantity. In order to enhance sphalerite and zinc recovery from ores, usually the roasting route is followed by flotation technique applying carboxylated chitosan and permanganate oxidant or pectin organic compound as sphalerite depressant [8, 18].

4. CONCLUSION

This study shows interesting features in relation to element and mineral transformations in sphalerite mineral due to the effects of pyrometallurgical process addressing to roasting temperatures and times. In the case of zinc mineral concentrations, the zinc blende (ZnS) experienced transformation to $ZnSO_4$ as the roasting temperature and time increased followed by transformation to ZnO at higher temperature and longer roasting time. In the case of sulfur concentration, sulfur mineral experienced air oxidation to form SO2 gas yielding sulfur reduction in sphalerite mineral. Moreover, the experimental results show that given roasting temperatures (500°C, 600°C, and 700°C) perform the most influential factor on the sulfur content at longer roasting time (60 min and 90 min). This study is useful related to information of pyrometallurgical process for mineral and elemental recovery. In the context of research development, a scavenger system should be included to reduce the effect of polluted toxic gasses yielded from high roasting temperature.

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PYROMETALLURGICAL PROCESS FOR ZINC ANALYSIS IN SPHALERITE APPLYING XRD AND XRF

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Abstract

This paper has analyzed dominant zinc element in sphalerite naturally found together with galena in mineral ore. Since pyrometallurgical route related to roasting process is very common to mineral dressing, therefore, this investigation has studied the effect of varied roasting time (30 min, 60 min, and 90 min) and temperature (500ºC, 600ºC, and 700ºC) on zinc mineral examination using XRD (X-Ray Diffraction) and zinc element using XRF (X-Ray Fluorescence) analyses. Previous studies usually applied cheaper AAS (Atomic Absorption Spectrometer) for zinc analysis in aqueous solution, however, sphalerite is a solid matrix and therefore, this study has applied XRF to analyze zinc. Pyrometallurgical process of zinc mineral in sphalerite is related to mineral transformation in the form of $ZnSO_4$, ZnS, and ZnO that cannot be detected by XRF. Therefore, this study has used XRD that can observe mineral transformation. The XRD pattern shows four intense peaks at 2θ (28º, 47º, 56º, and 76º) justified sphalerite (ZnS) sample with little amount of pyrite (FeS_2) and galena (PbS) as impurities. The XRF analysis shows from 30 min to 90 min, the Zn content has increased remarkably at 700oC and Zn content looked stagnant at 500ºC, while Zn content increased dramatically from 60 min to 90 min at 600ºC. During roasting process at high temperature, ZnS mineral converted to ZnO and expelled SO_2 gas due to oxidation reaction causing weight reduction. The study is valuable for mineral processing in searching for optimization.

Keywords: *Roasting Temperature, Roasting Time, Zinc Analysis, XRD, XRF.*

1. INTRODUCTION

Sphalerite or zinc blende mineral is a zinc sulfide rich mineral with its chemical formulas as (Zn, Fe) S [1]. Sphalerite ore (Figure 1) is the important source for zinc. It is primarily found in sediment deposits. Moreover, it is usually found in association with galena, pyrite, chalcopyrite, and other sulfides minerals. Besides sphalerite is a substantial source of zinc, sphalerite is also a mineral ore of indium, cadmium, and gallium.

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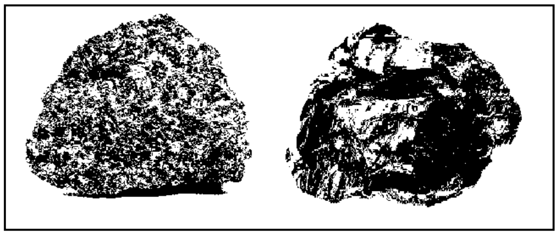


Figure 1. Sphalerite ore

Sphalerite has face centered cubic crystal structure, which is similar with the crystal structure of diamond. Zinc takes as position ion in sphalerite crystal lattice, sometimes substituted by lead, cadmium, indium, gallium, and germanium as impurities, as well as mercury and manganese [2, 3]. Cadmium may replace zinc up to 1%, while manganese is usually found in high iron sphalerite [3]. On the other hand, sulfur as negative ion generally replaced by selenium and tellurium. As already mentioned, Zn and Pb found primarily as sphalerite (ZnS) and galena (PbS) in nature due to their thiophilic properties [4].

Previous works reported several routes of sphalerite recovery and zinc separation from sphalerite concentrate. Previous studies reported zinc recovery from sphalerite concentrate as reductant with sulfuric acid leaching [5]. The investigation studied the leaching effects on acid concentration, particle size, leaching time and temperature in sulfuric media [5]. Recently, a study reported a literature review on flotation method for sphalerite recovery [6]. According to this literature review, flotation route has attracted worldwide scientists as the most remarkable technique for sphalerite recovery [6]. A study found a negative correlation between sphalerite recovery and grain size in the study of sphalerite flotation in the presence of manganese and iron in Zn-Pb-Cu complex ore [7]. Addressing to sphalerite separation from galena, a research work applied non toxic pectin based on selective depressant [4]. More-over, this work studied the interaction characteristics between pectin and both minerals of sphalerite and galena and found physical interaction between pectin and galena, while stronger chemisorption between pectin and sphalerite due to formation of -OH and -COOH groups with Zn sites [4]. On other occasion, a study reported separation of sphalerite from galena applying $KMnO_4$ and carboxylated chitosan that $KMnO_4$ oxidized sphalerite faster resulting faster interaction between carboxylated chitosan and sphalerite through chemisorption causing sphalerite depression [8]. At the same time, a sphalerite study applied hyaluronic acid as depressant through chemisorption of carboxyl and N-acetyl groups with Zn sites on the separation of sphalerite from galena for the study of flotation and adsorption mechanism [9].

It is apparent that previous reports on zinc recovery from sphalerite are still a few, although the re-ports corresponding with separation of sphalerite from galena are still limited. With regard to this matter, Figure 2 shows the concept of respective zinc and lead recoveries from mineral ore such as galena coexisted with sphalerite [10]. An Indonesian mining company located in West Java Province has been successful to recover ZnS (sphalerite) and PbS (galena) from mineral ore applying flotation method [11].

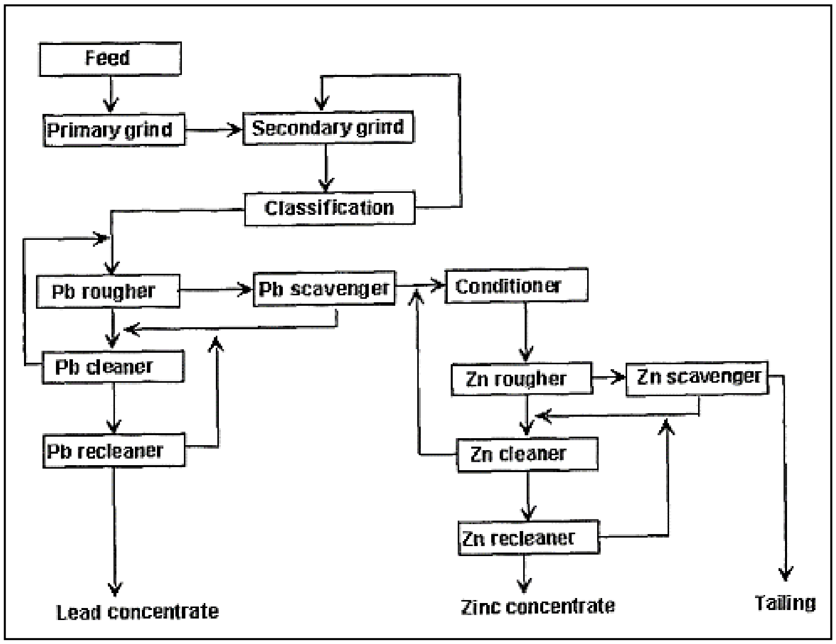


Figure 2. Flowchart of zinc and lead recovery from mineral ore [10]

In relation to mineral recovery, there are three types of metallurgical routes, i.e., pyrometallurgical, hydrometallurgical, and electrometallurgical techniques. This paper has only observed on pyrometallurgical route since this route is significant for high grade ores such as zinc in sphalerite or lead in galena. In fact, pyrometallurgical route may generate disadvantage result related to toxic gas emission generating environmental pollution. Although pyrometallurgical process has some drawbacks, many investigations have applied integrated routes of pyrrometallurgical and acid leaching to obtain zinc recovery from sphalerite. This study has only limited to the examinations of XRD and XRF on sphalerite yielded from pyrometallurgical process. With regard to zinc recovery from sphalerite, the pyrrometallurgical process is not the ending investigation, it needs other processes such as modified acid leaching or froth floatation route that is beyond the scope of this paper.

However, pyrometallurgical route is still fascinating to mineral recovery in mining field due to its low production cost. There are four types in pyrometallurgical techniques, i.e. (i) calcination, (ii) roasting, (iii) smelting, and (iv) refining. Since zinc is the major element in sphalerite and lead in galena, this study has selected the roasting method for zinc examination. The roasting method has conducted at 500ºC, 600ºC, and 700ºC respectively, for 30 min, 60 min, and 90 min at each temperature. XRD and XRF analyses have been applied to investigate zinc in sphalerite mineral.

2. EXPERIMENTAL METHOD

2.1. Material and Glassware

The raw material is a mineral ore sampling taken from Bogor Residence, West Java Province, as shown in Figure 1 that 100g sample was used for roasting process with the particle size in the range of 60 – 200 mesh. The material and glassware used in this study are presented in Table 1 as follows:

Table 1. Material and glassware used in the study

No.	Material and glassware	Notation
1	Mineral ore	Sampling location: Bogor Residence, West Java Province
2	Particle sizes for roasting	60 – 200 mesh
3	Petri dish	Sample plate
4	Mortar and pestle	Sample grinding and refining
5	Oven	Sample drying ≈ 100ºC
6	Sieve shaker	Sample screening
7	Analytical balance	Sample weighing
8	Muffle furnace	Sample roasting >> 600ºC

2.2. Roasting Method

The roasting process was conducted for mineral ore at varied temperatures (500ºC, 600ºC, and 700ºC) and varied roasting times (30 min, 60 min, and 90 min). During roasting process, the possible chemical reactions was described as follows:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \quad (1)$$

$$ZnS + 2O_2 \rightarrow ZnSO_4 \quad (2)$$

The pyrometallurgical process generated sulfur dioxide gas and mineral zinc sulfate as described in the chemical reaction (1) and (2). It is interesting that oxidation reaction during roasting at high temperature may yield other mineral such like $ZnSO_4$ as shown by chemical reaction (2). Therefore, three types of zinc mineral may exist together after roasting process, i.e., ZnO, $ZnSO_4$, and ZnS. The existence of the three zinc minerals will be shown in the XRD spectra (Figure 9).

2.3. XRD Examination

A PANalytical type X'Pert PRO using Cu-Kα emitted ray at 1.542 A provided with fully ceramic X-Ray tubes and hybrid pixel detector was used to examine mineral ore obtained from Bogor Residence, Jawa Barat Province, before and after roasting process. A sieve shaker was used to screen samples with given particle size after roasting in muffle furnace at given time and temperature. The XRD examination was applied to investigate type of minerals in sphalerite in association with galena samples. The diffraction peaks are determined by Bragg's Law, i.e., $\mathbf{n}\lambda = \mathbf{2d}\ \mathbf{sin}\theta$. Where n = number of repeating units; λ = light wavelength; d = distance between lattice planes; θ = diffraction angle. The light reflections through crystal lattices followed the Braggs' Law are illustrated in Figure 3 [12].

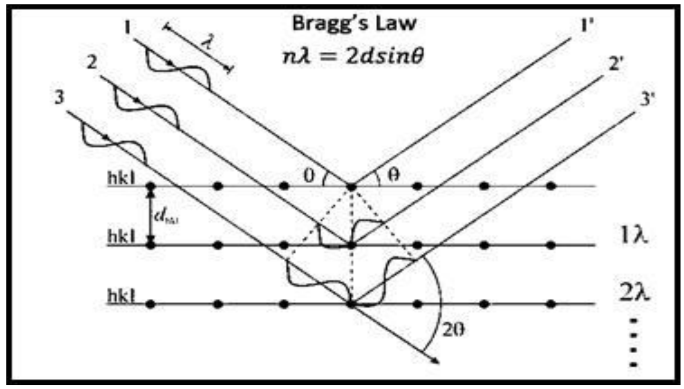


Figure 3. Conceptual theory of X-Ray Diffraction (XRD) with Bragg's Law [12]

2.4. XRF Examination

A PANalytical, type Minipal 4 XRF (X-Ray Fluorescence) Spectrophotometer with silicon drift detector was used to analyze qualitatively and quantitatively elements in mineral ore before and after roasting process. A sieve shaker was used to get sample with given particle size (≤ 200 mesh) after roasting mineral ores in a muffle furnace for 500°C, 600°C, and 700°C. The roasting times were conducted at 30 min, 60 min, and 90 min at each given temperature, respectively. As mentioned above, the sample was obtained from Bogor Residence, West Java Province and stored in Galena Maju Karya Mandiri company. 100g sample with ≤ 200 mesh was used for XRF examination. The XRF examination was applied to determine concentrations of several representative elements in sphalerite mineral, such as zinc, lead, iron, copper, and molybdenum. Figure 4 illustrates the electron excitation to higher energy level if an atom attacked by X-Ray. The energy of incident X-Ray is used by electron to jump up to higher energy level.

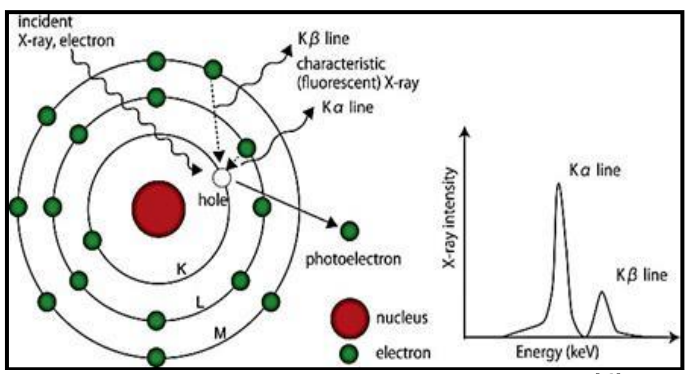


Figure 4. Conceptual theory of X-Ray Fluorescence (XRF) [13]

2.5. Experimental Steps

The given size sample ore was consecutively dried, screened, and roasted at given temperature and time followed by examinations using XRD and XRF. The experimental steps in this study are presented as flowchart shown in Figure 5 as follows:

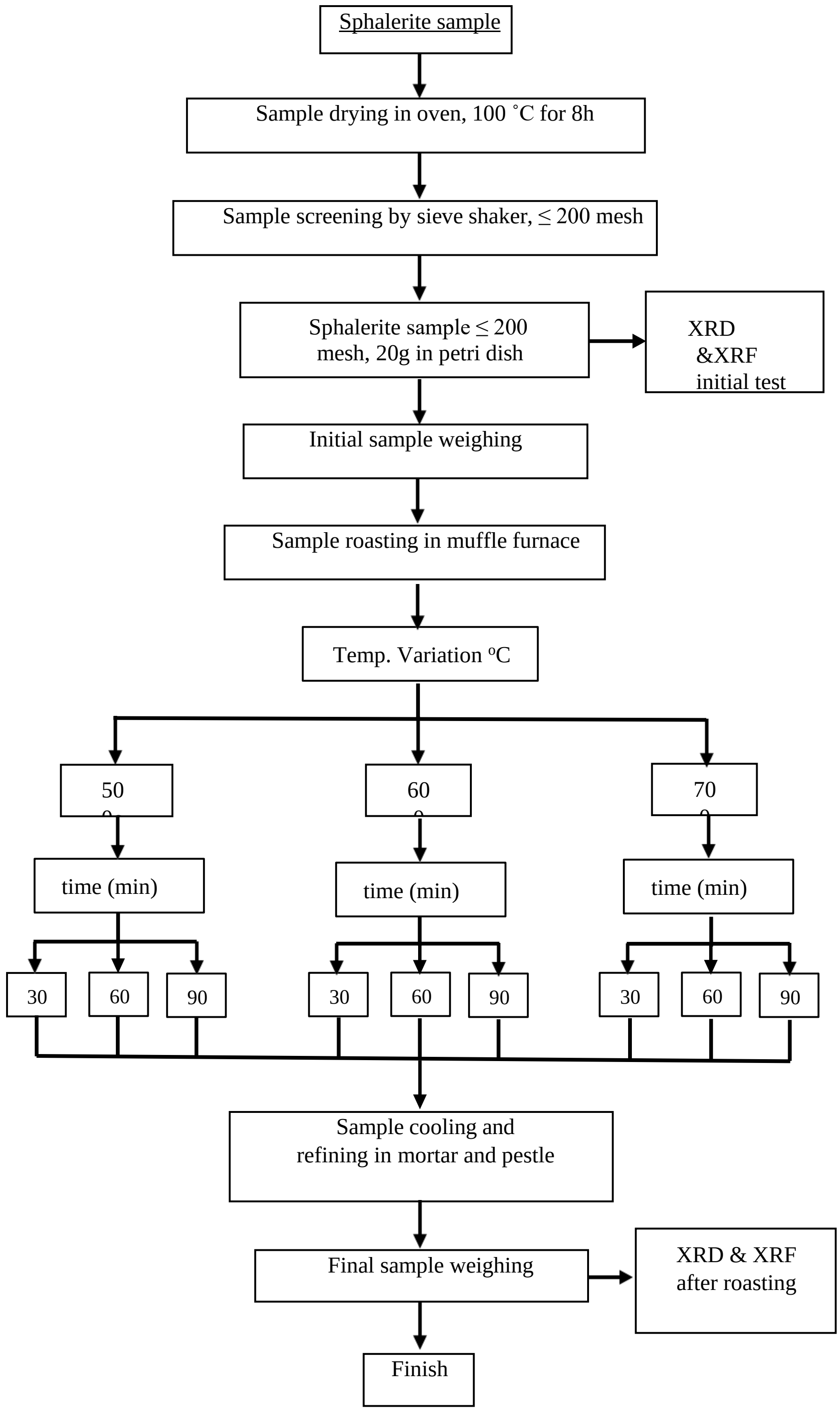


Figure 5. Flowchart of this study

3. RESULTS AND DISCUSSION

3.1. Sample Screening Results

The sample ore taken from sampling area needs to be screened to obtain the given size. The mineral sample used in this study followed the given size, i.e. ≤ 200 mesh using a sieve shaker. Previous investigation reported that finer sample grains may give better roasting result [14]. There were eight samples available for screening process to obtain sample with given size ready for roasting. Table 2 shows the result.

Table 2. Sample screening applying sieve shaker for roasting process

Sample	Sampel weight (g)	Sample weight (g)		
		+175 mesh	+200 mesh	-200 mesh
1	500	175	20	305
2	485	180	20	285
3	500	190	30	280
4	490	205	35	250
5	500	180	30	290
6	480	175	45	260
7	500	180	40	280
8	490	190	35	265

3.2. Roasting Results

Roasting at high temperatures (500ºC, 600ºC, and 700ºC) may cause oxidation due to oxygen consumption from the environment. The oxidation reaction oxidizes zinc blende (ZnS) to give ZnO and emitted SO_2 gas resulting mass reduction of the sample. The chemical reaction (1) illustrates the conversion of zinc blende to zinc oxide. In addition, the zinc blende can also convert to yield zinc sulfate as shown by chemical reaction (2) if the roasting process takes longer time at higher temperature. Table 3 shows the result.

Tabel 3. Sample screening applying sieve shaker for roasting process

Variable		Initial mass (g)	Final mass (g)	Mass removal
Temp (°C)	Time (min)			
500	30	65,03	63,47	2,40%
	60		62,38	4,08%
	90		61,74	5,06%
600	30	65,01	62,85	3,32%
	60		61,44	5,48%
	90		61,49	5,41%
700	30	65,10	61,23	5,95%
	60		59,10	9,21%
	90		58,95	9,45%

3.3. XRD Results

The XRD analyses were conducted for mineral samples before and after roasting process at varied temperatures (500ºC, 600ºC, and 700ºC). The roasting times are varied at 30 min, 60 min, and 90 min. In order to verify the sphalerite sample used for XRD examination, this study applied a standard sphalerite sample based on previous study [15] shown by Figure 6. Moreover, Figure 6 shows four intense peaks at 2θ 28°, 47°, 56°, and 76° as characteristic peaks of pure sphalerite sample not mixed with other minerals.

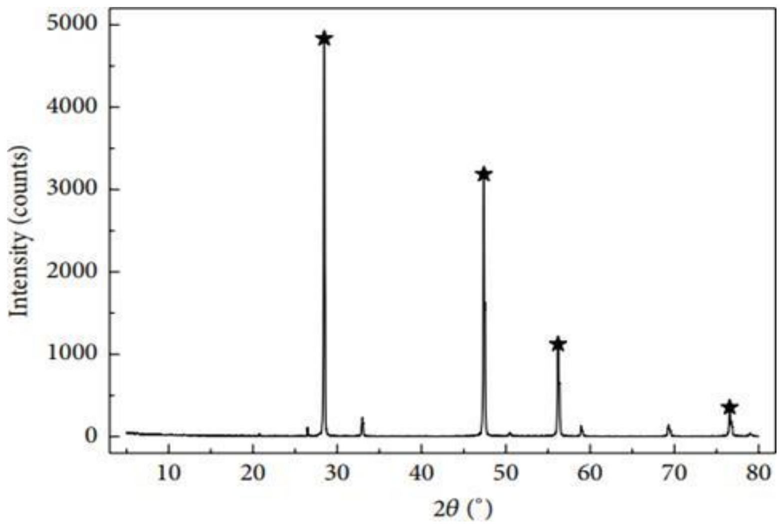


Figure 6. XRD pattern of standard sphalerite sample [15]

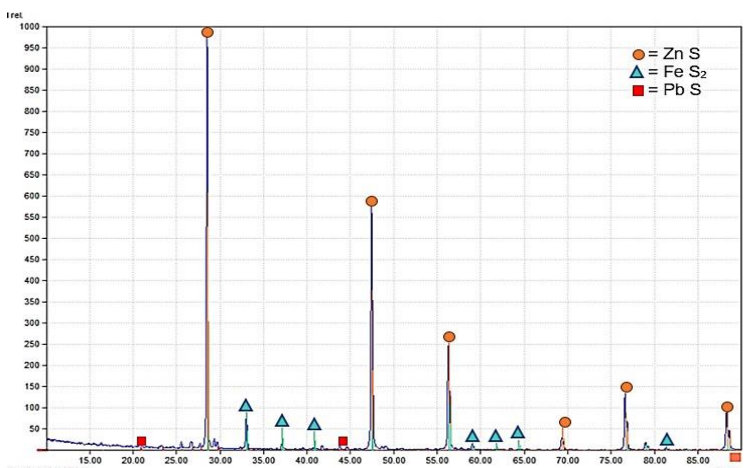
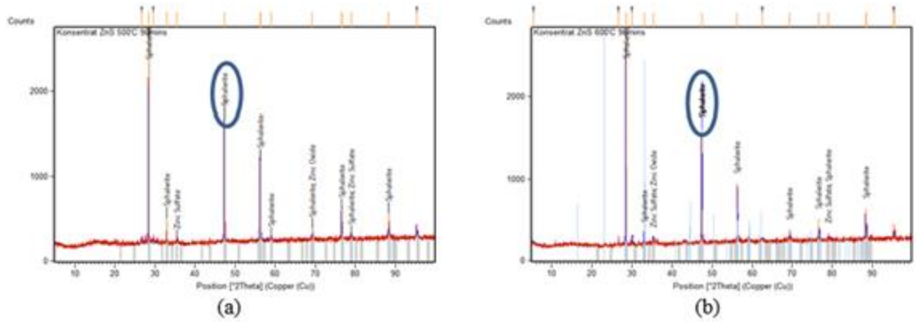


Figure 7. XRD pattern of mineral sample used in this study

Furthermore, Figure 7 shows the XRD pattern of mineral sample applied in this study. There are four intense diffraction peaks at 2θ 28°, 47°, 56°, and 76° attributed to sphalerite sample as shown by Figure 6. Figure 7 also shows other diffraction peaks of pyrite (FeS_2) and galena (PbS). This matter verified that the sample used in this study is dominated by sphalerite as major mineral in association with other minor pyrite and galena minerals. Figure 7 shows the XRD pattern of sphalerite sample before roasting. Figure 8 (a – c) shows the XRD patterns of mineral sample with sphalerite dominant after roasting time of 90 min addressing to 500ºC, 600ºC, and 700ºC, respectively. XRD examination is valuable especially for structure analysis. With regard to process examination conducted at different temperature treatment, an XRD analysis was used to investigate provskite structure of electrochemical cathode at sintering temperatures of 1000ºC and 1100ºC [16]. XRD analysis was applied to examine the size, shape, and morphology of SnO_2 crystal structure using sol gel method [17].



(c)

Figure 8. XRD patterns of roasting mineral samples at (a) 500ºC, (b) 600ºC, and (c) 700ºC. Roasting time 90 min

Figure 8 (a) shows the XRD patterns of sphalerite at 500ºC, (b) at 600ºC, (c) at 700ºC with roasting time 90 min. An interesting matter should be noted at diffraction peak (2θ) of 47º the sphalerite peak overlapped with ZnO peak after roasting at 700ºC, 90 min, while both at 500ºC and 600ºC (90 min) the diffraction peak 2θ at 47º only attributed for sphalerite. It is an indication when the roasting temperature increased from 500ºC or 600ºC to 700ºC, a transformation or partial oxidation of ZnS to form ZnO occurred.

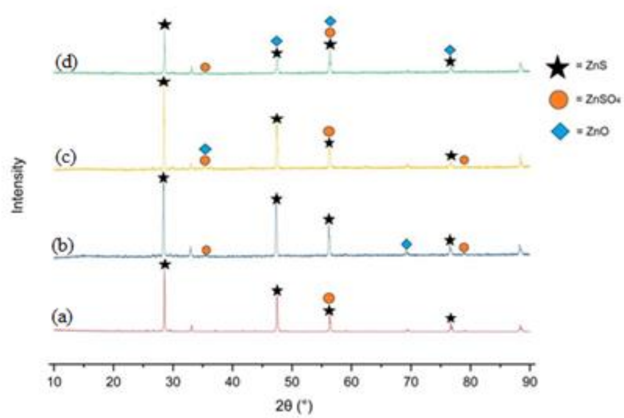


Figure 9. Overlay of XRD patterns of roasting minerals (a) non roasting , (b) 500ºC, (c) 600ºC, (d) 700ºC. Roasting time 90 min

Figure 9 shows the overlay patterns of XRD addressing to varied conditions, i.e., non roasting, 500ºC, 600ºC, and 700ºC for 90 min roasting time. As seen, the non roasting mineral sample was dominated by sphalerite, then at 500ºC roasting, $ZnSO_4$ and ZnO were generated due to air oxidation converting partial zinc blende to form $ZnSO_4$ and ZnO. As the roasting temperature elevated to 600ºC, more $ZnSO_4$ generated due to continued oxidation, and as the roasting temperature increased to 700ºC, more production ZnO rather than $ZnSO_4$, it showed that most of sulfur was removed as SO_2 gas yielding both reduction of ZnS and $ZnSO_4$ to form ZnO, as well as the residual Zn oxidized to ZnO. All these roasting processes were conducted at 90 min. Therefore, the roasting process gave effects on mineral transformation between ZnS, $ZnSO_4$, and ZnO.

3.4. XRF Results

As XRD analysis examined the type of minerals, the XRF analysis investigated the type of elements existed in mineral samples. The concentrations of sulfur and zinc are significant in Table 4 that should be highlighted in red square brackets due to their concentrations change in relation to condition changes (non roasting and varied roasting times, i.e., 30 min, 60 min, and 90 min at 500ºC). The sulfur content decreased slowly, i.e. 8.9% - 8.3% - 8.2% - 7.8%, consecutively. On the other hand, the zinc content increased slowly, i.e., 51.04% - 51.30% - 51.82% - 51.87%, consecutively. Both are attributed to red square brackets.

Table 4. XRF records for elemental analysis in mineral samples

Compound	Si	S	Ca	Cr	Mn	Fe	Ni	Cu	Zn	As	Y	Zr	Nb	Mo
Conc	0,51	8,9	0,20	0,059	0,18	8,52	0,062	1,27	51,04	0,31	1,2	1,3	8,3	14
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%	%

Compound	La	Eu	Yb	Pb
Conc	0,1	0,09	0,28	3,8
Unit	%	%	%	%

non roasting

Compound	Si	S	Ca	Cr	Mn	Fe	Ni	Cu	Zn	As	Y	Zr	Nb	Mo
Conc	0,68	8,3	0,17	0,052	0,18	9,26	0,061	1,21	51,30	0,32	1,4	1,3	7,4	14
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%	%

Compound	La	Eu	Yb	Pb
Conc	0,09	0,10	0,30	3,8
Unit	%	%	%	%

roasting 500ºC 30 min

Compound	Si	S	Ca	Cr	Mn	Fe	Ni	Cu	Zn	As	Y	Zr	Nb	Mo
Conc	0,54	8,2	0,17	0,058	0,18	9,9	0,067	1,28	51,82	0,33	1,4	1,5	7,3	13
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%	%

Compound	La	Eu	Yb	Pb
Conc	0,09	0,06	0,28	3,8
Unit	%	%	%	%

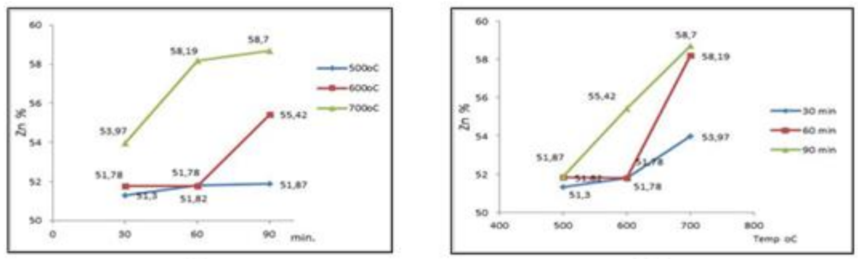
roasting 500ºC 60 min

Compound	Si	S	Ca	Cr	Mn	Fe	Ni	Cu	Zn	As	Y	Zr	Nb	Mo
Conc	0,61	7,8	0,17	0,055	0,17	10,57	0,056	1,27	51,87	0,31	1,3	1,3	7,4	13
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%	%

Compound	La	Eu	Yb	Pb
Conc	0,10	0,1	0,29	3,7
Unit	%	%	%	%

roasting 500ºC 90 min

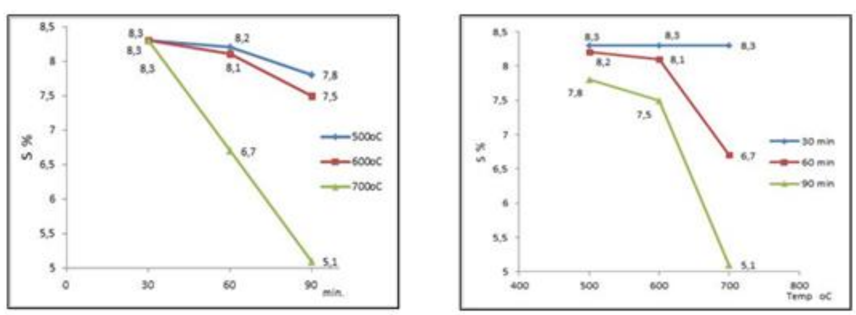
The findings are related to higher roasting temperature (500ºC) and longer roasting time (30 min, 60 min, 90 min) causing sulfur loss due to volatility of SO_2 gas. The air oxidation converted sulfur in sphalerite to form SO_2 gas resulting sulfur reduction in mineral sample. On the other hand, the zinc content increased slowly due to formation of $ZnSO_4$ and ZnO besides the zinc blende ZnS residual presence in sphalerite mineral. The formation of $ZnSO_4$ and ZnO is closely related to air oxidation of zinc blende in the mineral sample as shown by chemical reactions (1) and (2) mentioned above. This phenomenon is shown clearly in XRD illustrations (Figure 9) where Figure 9 shows the phenomenon due to roasting temperature effect. It is apparent that longer roasting time gave little effect on the conversion of concentrations of both sulfur and zinc in given mineral sample. This finding will be shown clearly in next XRF presentations. In addition, Figure 9 also shows data of rare earth elements (REE), i.e. lanthanum (La), europium (Eu), and ytterbium (Yb) with insignificant changed due to pyrometallurgical process. Up to date, REE has become fascinating and experienced fast development due to their substantial applications for renewable energy.



(a) (b)

Figure 10. Data XRF for Zn (%) based on (a) varied roasting time and (b) varied roasting temperature

In order to compare the effects of roasting temperatures (500°C, 600°C, and 700°C) and roasting times (30 min, 60 min, and 90 min) on Zn concentrations in mineral samples, Figure 10 present this phenomenon. It is apparent that the effects of both 90 min and 700°C gave the highest responds on Zn concentrations. On the opposite way, the effects of both 30 min and 500°C gave the lowest responds on Zn concentrations. The effects of 60 min and 600°C yielded the moderate responds on Zn concentrations. In general, increased trends are presented for all given conditions as both increased roasting times and temperatures. However, the trend is almost flat at increased roasting times from 30 min to 90 min at 500°C as shown at Figure 10 (a).



(a) (b)

Figure 11. Data XRF for S (%) based on (a) varied roasting time and (b) varied roasting temperature.

As Figure 10 present the effects of roasting time and temperature on zinc concentrations in sphalerite samples applying XRF analysis, Figure 11 present the same effects on sulfur concentrations. Figure 11 (a) shows remarkable reduction of sulfur concentration as roasting times increased from 30 min to 90 min at the highest given roasting temperature (700°C) attributed to green line. The same trend is also shown at Figure 11 (b) addressing to remarkable reduction of sulfur content as the roasting temperatures increased from 500°C to

700ºC at the longest given roasting time (90 min). At the moderate given conditions (600ºC and 60 min) the sulfur reductions are moderately decreased as shown at both Figure 11 (a) and (b). Figure 11 (b) shows interesting feature that increasing roasting temperatures from 500ºC to 700ºC gave no significant change of sulfur concentrations at roasting time of 30 min attributed to blue line. Generally, low given roasting temperature (500ºC) and time (30 min) gave no significant effect on sulfur reduction. This condition gave inversed performance showed by the highest given roasting temperature (700ºC) and time (90 min) that yielded remarkable effect on sulfur reduction. This finding gave a consistency between roasting condition (temperature and time) and sulfur reduction. It is reasonable since high roasting temperature and long roasting time yielded high removal of SO_2 gas due to air oxidation as shown by chemical reaction (1) above. The findings are emphasized on zinc mineral and sulfur concentration since the discussion involved with sphalerite samples with ZnS as dominant mineral and other minerals such as galena and pyrite, as well as other elements shown in Table 3 existed in minor quantity. In order to enhance sphalerite and zinc recovery from ores, usually the roasting route is followed by flotation technique applying carboxylated chitosan and permanganate oxidant or pectin organic compound as sphalerite depressant [8, 18].

4. CONCLUSION

This study shows interesting features in relation to element and mineral transformations in sphalerite mineral due to the effects of pyrometallurgical process addressing to roasting temperatures and times. In the case of zinc mineral concentrations, the zinc blende (ZnS) experienced transformation to $ZnSO_4$ as the roasting temperature and time increased followed by transformation to ZnO at higher temperature and longer roasting time. In the case of sulfur concentration, sulfur mineral experienced air oxidation to form SO2 gas yielding sulfur reduction in sphalerite mineral. Moreover, the experimental results show that given roasting temperatures (500ºC, 600ºC, and 700ºC) perform the most influential factor on the sulfur content at longer roasting time (60 min and 90 min). This study is useful related to information of pyrometallurgical process for mineral and elemental recovery. In the context of research development, a scavenger system should be included to reduce the effect of polluted toxic gasses yielded from high roasting temperature.

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