Article

A Study on Reduction of Copper Smelting Slag by Carbon for Recycling into Metal Values and Cement Raw Material

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Abstract: Copper smelting slag is a solution of molten oxides created during the copper smelting and refining process, and about 1.5 million tons of copper slag is generated annually in Korea. Oxides in copper smelting slag include ferrous (FeO), ferric oxide (Fe_2O_3), silica (SiO_2 from flux), alumina (Al_2O_3), calcia (CaO) and magnesia (MgO). Main oxides in copper slag, which iron oxide and silica, exist in the form of fayalite ($2FeO \cdot SiO_2$). Since the copper smelting slag contains high content of iron, and copper and zinc. Common applications of copper smelting slag are the value added products such as abrasive tools, roofing granules, road-base construction, railroad ballast, fine aggregate in concrete, etc., as well as the some studies have attempted to recover metal values from copper slag. This research was intended to recovery Fe-Cu alloy, raw material of zinc and produce reformed slag like a blast furnace slag for blast furnace slag cement from copper slag. As a results, it was confirmed that reduction smelting by carbon at temperatures above 1400°C is possible to recover pig iron containing copper from copper smelting slag, and CaO additives in the reduction smelting assist to reduce iron oxide in the fayalite and change the chemical and mineralogical composition of the slag. Copper oxide in the slag can be easily reduced and dissolved in the molten pig iron, and zinc oxide is also reduced to a volatile zinc, which is removed from the furnace as the fumes, by carbon during reduction process. When CaO addition is above 5wt.%, acid slag has been completely transformed to calcium silicate slag and observed like blast furnace slag.

Keywords: copper smelting slag; pig iron; fayalite; recovery

1. Introduction

Since the beginning of the industrial revolution, by-products as the metallurgical slags left over when metals are produced from natural and secondary raw materials, have been considered waste. The copper slag is produced during manufacturing of copper that for every ton of copper production about 2.2 tons of copper slag is generated and 1.5 million tons of copper slag is generated in Korea every year [1-5]. Dumping or disposal of copper slag causes wastage of metal values and leads to environmental problems. In particular, the dumping requires wide area and leads many negative impacts such eroding and damaging land surface, solid and gas substances polluting the atmosphere [6]. In actually, South Korea is a small land country with a high population. Therefore, South Korea refuses to landfill the metallurgical slags and promotes zero waste through the re-use and recycling of these waste materials. Recently, some scientists all over the world had paid special attention to recycle the copper slag and developed several technologies. The common management options for copper slag are recycling of production of value added products such as abrasive tools, roofing granules, cutting tools, abrasive, tiles, glass, road-base construction, railroad ballast, asphalt pavements and etc,. The potential uses of copper slag are a partial substitute in cement and aggregate

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in concrete [7, 8]. Nevertheless, these methods cannot efficiently recover high content of iron and valuable metal in copper smelting slag.

Copper slag differs by chemical composition and structure, depending on the type of processing. Copper smelting slag usually contains about 1 wt.% of copper and 40 wt.% of iron depending on the initial ore quality and the furnace type. Significant amounts of SiO_2, FeO, CaO, Al_2O_3 and minor amounts of other elements (e.g., zinc, titanium, and lead) are also associated with copper slag [9]. Main components of copper slag are iron oxide and SiO_2, these exist in copper slag mainly in the form of fayalite ($2FeO{\cdot}SiO_2$).

The processing technologies are different depending on the metals to be recovered from copper slag. Hydrometallurgical treatment is widely used on copper recovery from copper slag that including direct leaching in sulphuric acid, leaching in sulphuric acid through H_2S gas or ferric chloride [10, 11], but leaching of the copper slag may be too expensive because it requires high consumption of strong acid and reagents, and very toxic. Magnetic separation and reduction smelting method are used to recover and separate the iron from copper slag. Magnetic separation cannot efficiently recover the iron from copper slag due to its difficult processing of fayalite. Although the reduction smelting requires a large amount of energy during smelting process, it is possible to recover the Fe-Cu alloy from the copper slag. Copper is used as an additive element to improve mechanical properties such as hardness, abrasion resistance and corrosion resistance in the cast iron products [12, 13]. Therefore, our study is focused on manufacture of foundry pig iron with Cu content from copper slag using high-temperature reduction smelting and investigate utilization of by-products as reformed slag and furnace ash containing zinc. The by-products as the furnace ash containing zinc and reformed slag give additional value to the recycling which recovery of zinc and preparation of value added products like a cement and concrete.

2. Materials and Methods

2.1. Experimental Materials

In this study, waste copper slag from G Company was used. The molten slag were rapidly quenched into cool water, consequently, cooling rate tend to obtain a glassy phase, and ground for further applications. Figure 1 shows the results of XRD analysis of the copper smelting slag. XRD data collection of the slag sample was conducted with a scanning range of 10 to 90° and a time of 10 min under step size of 0.02°. Although peaks of peculiar to amorphous phase of glass were indicated, several peaks of fayalite ($2FeO{\cdot}SiO_2$) and monticellite ($CaMgSiO_4$) were observed. X-Ray fluorescence was also used to analyze the components of the copper slag as shown in Table 1. The results of XRF analysis on the particle of the copper slag indicated that it contains about 40 wt.% of Fe_2O_3, about 21 wt.% of SiO_2, and 16 wt.% of CaO, and about 7 wt.% of Al_2O_3.

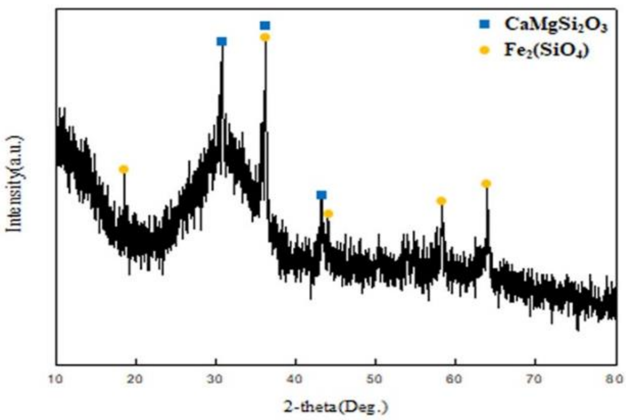

Figure 1. XRD pattern of the copper smelting slag.

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Table 1. The chemical composition of copper smelting slag by XRF.

Element	Fe_2O_3	SiO_2	CaO	Al_2O_3	ZnO	MgO	CuO	MnO	P_2O_5	Na_2O	TiO_2	K_2O	Cr_2O_3
Content,wt.%	38.51	21.17	16.25	7.75	6.27	2.61	2.09	1.34	1.11	1.02	0.72	0.58	0.58

2.2. Experimental Apparatus

The reduction smelting experiments were performed in a high-frequency induction furnace. The high-frequency induction furnace consisted of a cooler, controller and heater box. The installation space was small and the additional equipment such as dust collector was miniaturized to reduce the difficulty and cost of the process. The temperature of the high-frequency induction furnace was controlled by regulating the voltage. Figure 2 is a schematic diagram of a heater box where high-frequency induction. The heater box enclosed the equipment and eliminated dust and flue gases from the furnace. Electricity was conducted through the thermo-generator using the graphite crucible, where it was placed inside the heater box, and the temperature was measured using a thermocouple.

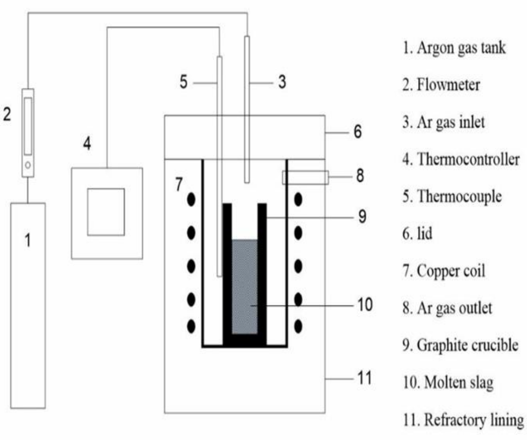

Figure 2. Schematic diagram of experimental apparatus.

2.2. Experimental Procedures

For the experimental process, the copper slag with irregular fine irregularities of 1 mm to 3 mm and reducing agent activated carbon were mixed with the sample at the ratio of 9 g per 100 g, and then charged into the carbon crucible. CaO additives were 5, 10, 15, 20 and 25 g per 100 g of copper slag under the ratio B = %CaO/%SiO_2 = 0.8, 0.9, 1.0, 1.1 and 1.2. The experiment was conducted at a necessary temperature of 1600°C for 180 minutes and reduction smelting continued for 30 minutes of holding. Then, the slags were left inside furnace to cool down to room temperature naturally. Ar gas was introduced at a rate 300 cc/min during the process. In this experiment, when copper slag may smelts at high temperatures up to 1600°C, Fe_2O_3, CuO and some oxides can be reduced and formed a metal phase as the molten pig iron while unreduced oxides such as SiO_2, CaO, and Al_2O_3 etc, form to the reformed slag and this slag floats on the molten pig iron.

3. Results and Discussion

3.1. Reduction Smelting for Makingiron

The reduction smelting experiments on the recovery of iron from copper slag were performed by reduction agent carbon at high-temperatures under the holding temperature and holding time factors. In the reduction smelting process of copper slag, the iron oxide might be reduced from decomposition of the fayalite by direct reduction with solid carbon and indirect reduction with CO gas following the reaction:

$$Fe_2SiO_4 + CO = 2Fe + SiO_2 + CO_2 \quad (1)$$

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$$FeO + CO = Fe + CO_2 \quad (2)$$

$$Fe_2SiO_4 + 2C = 2Fe + SiO_2 + 2CO \quad (3)$$

$$FeO + C = Fe + CO \quad (4)$$

Copper smelting slag was used in this study contains 16 wt.% of CaO. Therefore, it was considered that slag consists of Fe_2SiO_4 (fayalite), Ca_2SiO_4 (calcium orthosilicate) and $CaFeSiO_4$ and Fe_2O_3 [14, 15]. The CaO impacts on the decomposition of the fayalite and reduction of iron oxide, and changing chemical composition of slag. Copper oxide can be easily reduced and also dissolved into molten metal phase, and zinc oxide is reduced to a volatile zinc, which is removed from the furnace as the fumes, by carbon at a temperature of 980~1000°C during reduction process.

$$Fe_2SiO_4 + 2CaO + 2C = Ca_2SiO_4 + 2Fe + 2CO \quad (5)$$

$$Cu_2O+CO=2Cu+CO_2 \quad (6)$$

$$2Cu_2O+C=4Cu+CO_2 \quad (7)$$

Reduction behaviour of iron oxide to be reduced from fayalite decomposition was examined by thermodynamic analysis using HSC 5.1 chemistry software. It determined that as the results of the thermodynamic analysis in Figure 3, iron can be reduced from the decomposition of fayalite in reduction smelting process at high temperatures above 1400°C, and moreover, due to impact of CaO, reduction of iron in fayalite is more intensified. As above illustrated, reduction of CuO can be reduced by CO gas at low temperatures, it is shown in Figure 3.

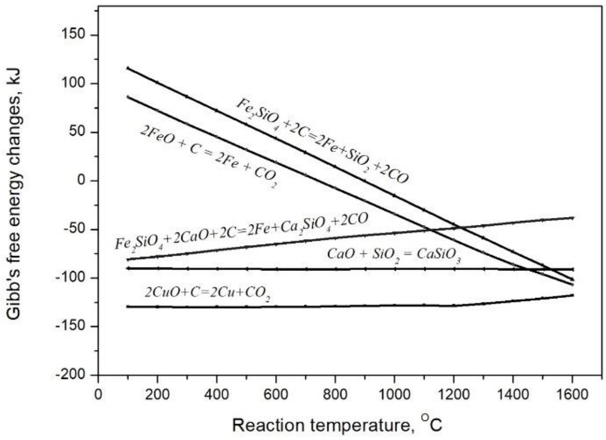

Figure 3. Gibb's free energy changes of reduction of components in copper slag by reducing carbon.

In reduction smelting experiment with carbon additives, Fe and Cu completely reduced from the slag, and then formed to a metal phase, where are separated by the specific gravity difference with slag consisting of SiO_2, CaO, Al_2O_3 and etc, at 1600°C for 30 minutes of holding. Besides, the reformed slag with a relatively specific grafity floats on the molten pig iron. Table 2 shows the XRF results of the chemical composition of the reformed slag from copper slag by high temperature reduction according to the changes of reaction temperature condition for 30 minutes of holding. The main constituent elements were measured such as oxides of SiO_2, CaO and Al_2O_3. The iron oxide content in the slag was decreased from 24.62 wt.% to 16.13 wt.% according to the increasing reaction temperature from 1400°C to 1500°C, respectively. At the reaction temperature of 1600°C, Fe in the slag could not be measured that indicating complete separation from the slag. The recovery rate of pig iron varied greatly depending on the reaction temperature. As shown in Table 3, it was found that the Fe_2O_3 content in the slag was decreased according the increasing reaction time, when reaction time was of 30 minutes, Fe_2O_3 was non detected, whereas SiO_2 content was increased. The Cu content in the slag was not detected that it was completely dissolved into molten pig iron. Furthermore, the ZnO was removed with the furnace gas awhile smelting of copper smelting slag.

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Table 2. Chemical composition of the reformed slag separated from copper slag using high temperature reduction according to the changes of reaction temperature condition by XRF.

Reaction temperature, °C	Element, wt.%								
	SiO_2	CaO	Fe_2O_3	Al_2O_3	MgO	Na_2O	K_2O	TiO_2	Cr_2O_3
1400	35.20	19.80	24.62	13.07	2.85	1.69	0.39	0.51	1.87
1500	37.90	21.30	16.13	14.83	3.12	1.55	0.61	0.84	3.72
1600	44.50	23.55	ND	19.46	4.24	1.44	0.67	0.93	4.81

Table 3. Chemical composition of reformed slag according to the timeslot at 1600^{0}C temperature by XRF.

Reaction time, min	Element, wt.%												
	SiO_2	CaO	Fe_2O_3	Al_2O_3	MgO	Na_2O	ZnO	MnO	Cr_2O_3	P_2O_5	K_2O	TiO_2	SO_3
5	35.94	21.26	19.55	11.19	3.53	2.39	2.01	1.45	1.0	0.87	0.77	-	-
10	39.05	22.56	14.32	12.53	3.69	1.93	0.57	1.43	1.21	0.72	0.86	1.09	-
15	42.45	25.55	8.68	12.97	4.46	1.98	-	1.86	1.17	1.17	0.85	-	-
20	44.92	26.11	4.47	14.35	4.09	2.14	-	1.51	0.72	-	1.02	-	0.61
25	46.24	26.56	2.69	14.48	3.88	2.55	-	1.62	0.75	-	-	0.99	-
30	46.25	26.57	ND	14.49	3.92	2.70	-	1.70	1.25	0.90	0.99	0.72	0.50

Table 4 shows EDS results of the chemical composition of the pig iron separated from copper smelting slag by high temperature reduction according to the change of reaction temperature condition. It was confirmed that there was no significant difference according to the changes of the reaction temperature conditions, and about 86 wt.% of Fe and 3 wt.% of Cu were recovered indicating the formation of Fe-Cu alloy.

Table 4. Chemical composition of the pig iron separated from copper smelting slag by high temperature reduction according to the changes of reaction temperature condition by EDS.

Reaction temperature, °C	Element, wt.%					
	Si	C	Cr	Mn	Cu	Fe
1400	5.53	3.84	1.33	1.43	3.11	84.75
1500	4.09	4.00	0.99	1.12	3.62	86.17
1600	2.94	4.62	1.25	0.81	2.93	87.45

In the reduction smelting by solid carbon, the iron was completely reduced, and formed to liquid pig iron at 1600℃ temperature for 30 minutes. The reformed slag contains about 46 wt.% SiO_2, 26 wt.% CaO and 14 wt.% Al_2O_3, which was an acid slag. Therefore, next experiment with CaO additives was conducted to change the chemical composition of reformed slag under the ratio B = %CaO/%SiO_2 = 0.8, 0.9, 1.0, 1.1 and 1.2 at the 1600°C temperature for 30 minute.

As the reduction smelting with CaO additives, the fayalite (2FeO·SiO_2) in the copper slag is decomposed under high temperature and reduction process, and iron oxide is reduced and separated to the liquid pig iron according to the reaction (1) to (5) in order. In this case, it might be seen that the remaining oxides such as the SiO_2, CaO, Al_2O_3 and MgO interact with each other, and hence generate the reformed slag. This reformed slag might be consisted on the considering typically eutectic compounds as the CaO·SiO_2, 2CaO·SiO_2, 3CaO·2SiO_2, CaO·Al_2O_3·2SiO_2, 2CaO·Al_2O_3·SiO_2, CaO·MgO·SiO_2, and etc [14, 15]. The basic slag with high content of CaO transforms into calcium silicates slag by CaO additives, and hence changing of chemical composition of the slag may be effectively conducted in the reducing process. Chemical compositions of the slag reformed from copper slag in the reduction smelting with CaO additives were determined by X-ray flourescene (XRF) to evaluate the difference according to the CaO additives as shown in Table 5. As the XRF results, it was found that the SiO_2 content in the slag was decreased according to the increasing the CaO content in the slag. When the CaO additives are upto 15 wt.%, the chemical compositions of reformed slag observed similar chemical composition of the Blast Furnace slag (BFS). The chemical composition of the BFS is a significant factor in potential performance of cementitious uses. Chemical

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analysis both of the produced slag and Blast-Furnace slag show that the major oxides as the CaO, SiO_2, MgO and Al_2O_3 are contained up about 95% of the total in accordance with requirements of BFS for cement material, as shown in Table 5. The application and recycling of the BFS for cement and concrete materials were also developed about 100 years ago with attention paid to effective utilization of a slag in steel industry [16, 17]. Therefore, the produced slag with upto 15 wt.% of CaO additives seems that is achievable as a raw material for Portland cement. Table 6 shows EDS results of the chemical composition of the pig iron separated from copper smelting slag by high temperature reduction according to the changes of CaO additives. It was still confirmed that there was no significant difference according to the changes of the CaO additions and contained about 86 wt.% of Fe and 3 wt.% of Cu that is indicating the formation of Fe-Cu alloy.

Table 5. Chemical composition of reformed slag by XRF.

Type		Element, wt.%											
		SiO_2	CaO	Al_2O_3	MgO	Na_2O	TiO_2	K_2O	MnO	SO_3	BaO	Fe_2O_5	SrO
BFS		32 to 42	32 to 50	7 to 16	5 to 15	-	-	-	0.2 to 1.0	1 to 2	-	0.1 to 1.5	
CaO addition, g per 100 g of copper slag	**5**	40.05	37.50	13.45	5.00	1.52	0.91	0.635	0.61	0.30	-	-	-
	10	37.42	42.54	13.12	4.40	0.54	0.41	0.18	0.23	0.28	0.66	0.10	0.07
	15	31.80	50.86	12.42	4.14	-	.0.24	-	-	0.46	-	-	0.08
	20	28.82	53.94	11.80	3.49	-	0.21	-	-	0.45	0.49	0.70	0.07
	25	22.36	60.91	11.24	3.50	-	-	-	-	0.55	-	1.14	-

Table 6. Chemical composition of the pig iron separated from copper slag by EDS.

CaO addition, g per 100 g of copper slag	Element, wt.%					
	Si	C	Cr	Mn	Cu	Fe
5	4.56	3.95	1.12	1.82	3.01	85.54
10	4.10	4.09	1.03	1.56	3.17	86.05
15	4.23	4.35	1.25	1.27	3.19	85.71
20	3.63	3.95	0.87	1.30	3.06	87.19
25	2.94	4.62	1.25	0.81	2.93	87.45

3.2. Mineralogical analysis of reformed slags

Cooling method is impacted on the crystallization of slag that rapidly cooling tends to form a glassy as noncrystalline material and slower cooling leads to crystallization of several slag minerals such as akermanite, gehlenite, wollastone, dicalcium silicate, anorthite and etc [16]. The mineralogical composition of reformed slag were obtained by identification of precipitated crystalline phases with powder X-ray diffraction analysis (XRD). As shown in Figure 4, glass and quartz phases were presented in the slag sample without CaO additives, it was indicated that slag was like glass. When the CaO addition was 5 wt.%, diffraction peaks of the glass like slag were not detected and glass matrix has been transformed to diopside aluminian $Ca(Mg)(Al,Si)SiO_7$ and akermanite-gehlenite series $Ca_2(Al,Mg)(Si,Al)SiO_7$ phases in which indicating that glass slag has been completely formed to calcium silicate phases. For slag with 10 wt.% CaO, akermanite-gehlenite series were still appeared, but the diopside aluminian was transformed to calcium aluminosilicate $Ca_2Al_2SiO_7$. When the CaO additives were of 15 and 20 wt.%, only akermanite-gehlenite series were observed, but at the CaO additive was of 25 wt.%, diffraction peaks of the gehlenite were still appeared while dicalcium silicate Ca_2SiO_4 was also observed. It is indicated that dicalcium silicate phases are produced due to increasing of CaO content. To summarize, the glass like slag can be greatly transformed to new phases as the calcium silicate when CaO addition is above 5 wt.%.

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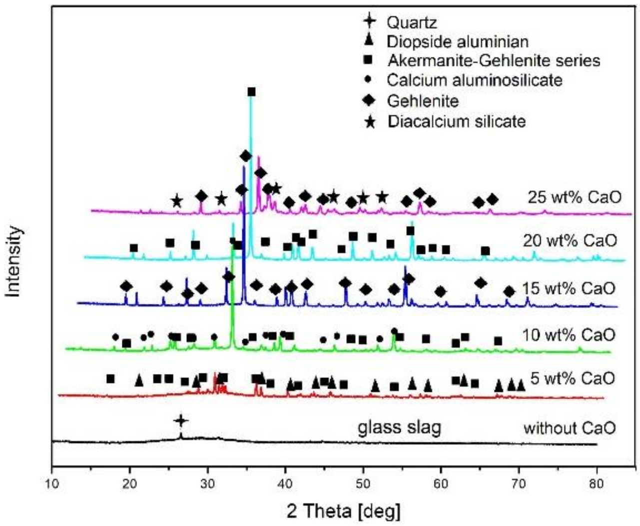


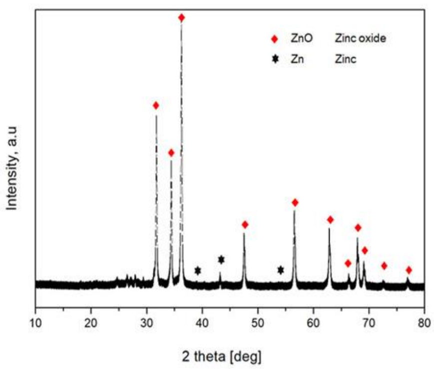
Figure 4. XRD patterns of the reformed slag without and with CaO additives.

3.3. Zinc ash characterization

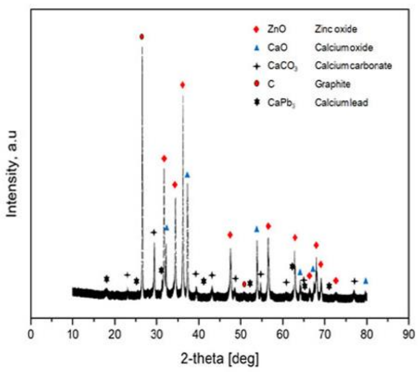
During the reduction smelting, the zinc oxide in the copper slag can be easily reduced, and removed with the fumes from the furnace. It was confirmed that there was no detected zinc content in the reformed slags after 10 minutes in the reduction smelting experiment as shown in Table 3. In this study, the zinc ash generated during reduction smelting were two type due to reduction smelting preformed without and with CaO additives. Table 7 shows the compositions of zinc ash powder. It was found to contaminated with main impurities as the Ca, Fe, Si and Pb. The zinc amount in zinc ash powder generated during reduction smelting was found to be rich at rate of 52 to 81%. This level is like concentrates of zinc employed for primary production of zinc [18, 19]. Figure 5 shows the XRD patterns of the zinc ash powder which indicates that the zinc in the zinc ash generated during reduction smelting without CaO additives is in the form of ZnO and observed few points of metallic zinc (in Figure 5a). However, the zinc ash generated during reduction smelting with CaO additives contained several impurities such as calcium oxide, calcium carbonate and calcium lead (in Figure 5b).

Table 7. Chemical composition of the zinc ash powder by XRF.

Element	Fe_2O_3	SiO_2	CaO	Al_2O_3	ZnO	MgO	CuO	MnO	P_2O_5	Na_2O	TiO_2	K_2O	Cr_2O_3
Content,wt.%	38.51	21.17	16.25	7.75	6.27	2.61	2.09	1.34	1.11	1.02	0.72	0.58	0.58



(a)



(b)

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Figure 5. XRD patterns of the zinc ash powder.

5. Conclusions

Copper smelting slag contains significant amount of components such as iron, copper and zinc, which susceptible to be recovered using pyrometallurgical process could be employed to obtain final products. The feasibility of a high-temperature reduction technology to improve benefication of metallic elements and reformed slag from copper slag using reduction smelting was investigated, and following results were achieved:

1. Iron in the copper slag was completely reduced and separated through iron alloy at the emperature of 1600°C and the holding time of 30 minutes using the reduction smelting as well as the copper in the copper slag was also dissolved into the pig iron during the reduction smelting. The produced iron alloy contained about 3 wt.% of copper that it is possible to use at the cast iron containing copper for excelent casting alloys have significant properties including strength, toughness and corrosion resistance, and etc.
2. The reformed slag in the reduction smelting without CaO additives was acid slag. Therefore, next reduction smelting with CaO additives was performed to transform the slag structure. When CaO addition was upto 15 wt.%, the chemical compositions of reformed slag were similar with Blast-Furnace slag, which it is potentially an cement raw material.
3. Zinc in the copper slag was completely removed with furnace fume from furnace that it was confirmed no detected zinc content in the reformed slags during reduction smelting. The zinc amount in zinc ash powder generated during reduction smelting was found to be rich at rates of 52 to 81%, which it can be used primary production of zinc.

Author Contributions: U.E. organized the study plan, performed the experiments, and JP.W. reviewed and checked the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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