



Article A Thermodynamic and Experimental Assessment of the Recovery of Copper, Iron, Zinc, and Lead from Copper Slag

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Abstract: With the increases in the costs of iron and copper ores, the incongruity between the significant imports of these ores into China and the ongoing accumulation of unused copper slag has greatly increased. Even so, there are few low-value methods for the utilization of copper slag. The present work demonstrates the processing of this material via reduction whilst smelting wear-resistant cast iron. This system is able to recover copper, iron, zinc, and lead. The FactSage software package was used to calculate the reduction thermodynamics of the copper slag, and suitable conditions for the processing of this slag were experimentally investigated. The thermodynamic calculations indicated that copper, zinc, and lead oxides could all be readily reduced whereas the reduction of sulfides was more difficult than that of oxides. The most suitable conditions for the reduction of copper slag comprised a temperature of 1450 °C, an alkalinity of 1.2, and a reducing agent ratio of 0.225. This newly developed process was found to recover 95.49% of copper and iron from the slag along with 83.54% of lead and 98.30% of zinc. The copper-containing molten iron obtained could be used to create wear-resistant cast iron.

Keywords: copper slag; reduction; FactSage; thermodynamic

1. Introduction

Copper smelting processes incorporating intense oxidation have become dominant because these processes reduce the smelting time, are highly efficient, and provide a product with a high matte grade. During smelting, copper slag is generated in the form of matte and a higher copper content in the slag will give a higher matte grade. Even after dilution, the copper content in slag can remain above 0.5% and copper slag can contain iron at levels higher than those found in mined iron ore [1–4]. Copper slag is also typically mixed with a certain amount of zinc. Copper slag is a secondary resource with a high value. At present, copper slag is primarily used as a source of copper by recovering the copper in this material through flotation methods; the zinc and iron in the slag are normally discarded [5–8].

With the ongoing development of the economy of China, the demand for copper and iron has greatly increased. Unfortunately, the copper and iron ores that are mined in China tend to be of low grade and so the utilization cost of these raw materials is high. Ninety percent of the copper ore used in China is imported; China is also the largest importer of iron ore in the world. Simultaneously, as the utilization of refined copper in China has increased, the output of copper slag has also greatly increased and presently amounts to more than 20 million tons per year. As noted, copper slag contains residual copper, iron, and zinc as well as lead; thus, unused slag represents a significant waste of resources and energy.

Traditionally, copper slag is utilized by either extracting iron or copper from the material. The recovery of iron from slag is primarily based on techniques involving magnetism to obtain iron and iron oxides whereas copper is typically extracted by dilution [6,9–11].



Citation: Zhang, B.; Zhang, T.; Dou, Z. A Thermodynamic and Experimental Assessment of the Recovery of Copper, Iron, Zinc, and Lead from Copper Slag. *Minerals* 2022, 12, 496. https://doi.org/ 10.3390/min12050496

Academic Editors: Carlos Hoffmann Sampaio, Weslei Monteiro Ambros and Bogdan Grigore Cazacliu

Received: 10 March 2022 Accepted: 15 April 2022 Published: 19 April 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Riveros Urzua investigated the recovery of copper and molybdenum from slag [12]. The thermodynamics were studied using FactSage software and the relationship between the stirring speed and the refractory wear in electric furnaces was quantified. Heo et al. investigated the reduction behavior of FeO in copper slag at 1773 K [13]. The Fe recovery was about 90 wt%. Busolic et al. investigated the feasibility of Fe recovery from copper flash slag at 1723 K [14]. They obtained Fe–Cu alloys, but their aim was to reduce the Cu content and only obtain iron. Erdenebold et al. investigated the reduction and recovery of iron from copper slag as well as the preparation of building materials from tailings [15–17]. There are few studies on the simultaneous recovery of copper and iron. The flotation methods used to extract resources from copper slag cool the slag and thus waste the heat that it contains [8,9,18].

On this basis, the present work devised a process in which copper slag was reduced whilst smelting copper-containing wear-resistant cast iron. Both zinc and lead were collected from the reducing gas and, after ferrochrome was added, usable cast iron was obtained.

2. Experimental Procedures

2.1. Materials

The copper slag used as the raw material in this work was obtained from a copper plant in Liaoning, China. The composition of the slag is summarized in Table 1. The electron microscopy and EDS results of the copper slag are shown in Figure 1. The main components were Fe_3O_4 , fayalite, silica, and matte inclusions [19,20].

Table 1. The composition of copper slag.

Element	CaO	SiO ₂	Al_2O_3	MgO	T _{Fe}	M _{Fe}	FeO	S	Cu	Zn	Pb
Wt.%	3.03	35.30	6.52	1.68	37.23	1.60	40.22	1.17	0.73	1.71	0.12



Figure 1. Electron microscopy and EDS results of copper slag (wt.%).

The phase analysis results of the copper slag are shown in Figure 2a. These results indicated that the main phases of the copper slag were fayalite and ferric tetroxide. The inclusion content of the copper matte was too low to show diffraction peaks. The dilution method for the copper slag was to add a small amount of reducing agent to reduce the Fe_3O_4 to FeO, which reduced the melting point of the slag, increased the fluidity of the

slag, and promoted the sedimentation of the matte inclusions. The copper matte did not react in the dilution process. The main phases of the matte obtained by dilution were consistent with the matte contained in the copper slag. The phase analysis of the copper matte, obtained by dilution, is shown in Figure 2b. The main phases of the copper matte were Cu_5FeS_4 and Cu_2S .



Figure 2. The phase analysis results for copper slag and copper matte. (a) copper slag (b) copper matte.

2.2. Experimental Procedures

The experiments were carried out in an electric resistance furnace. In each trial, copper slag particles with diameters of less than 147 μ m were thoroughly mixed with calcium oxide and coke and then transferred into an alumina crucible (48 (40) mm \times 120 mm). A graphite sleeve was placed around the crucible to prevent the slag from escaping and the crucible was held under an Ar atmosphere. The slag was subsequently heated at rates of 10 °C/min to 1200 °C, 8 °C/min from 1200 to 1400 °C, and then 5 °C/min to the desired reaction temperature. During each experiment, the molten slag was stirred with a graphite cross paddle at 20 rpm. The reaction time was 150 min, wherein the holding time was

30 min, the stirring time was 90 min, and the settling time was 30 min. The slag was subsequently cooled at a rate of 10 $^{\circ}$ C/min to 1200 $^{\circ}$ C and then allowed to naturally cool in air to room temperature. A diagram of the experimental apparatus is provided in Figure 3.



Figure 3. Experimental device.

During the reduction process, the lead and zinc in the slag were volatilized. As parts of the volatilized metals remained on the crucible wall and on the surface of the sleeve, and because collecting all the gas was difficult, the content of zinc and lead in the flue gas could not be precisely defined under the experimental conditions. According to the content of zinc and lead in the raw materials as well as in the metals and slag, the amounts of lead and zinc in the flue gas were calculated according to the mass balance. The amounts of lead and zinc in the flue gas were subsequently determined to calculate the percent recoveries of both metals. The copper and iron in the raw slag were reduced to copper-containing molten iron and the amount of this material was determined in order to ascertain the recovery of each metal. The amounts of metal and oxides were determined using atomic emission spectrometry and a fluorescence spectrometer, and the amounts of C and S were determined using a carbon sulfur analyzer. During these trials, the effects of temperature as well as the amount of reducing agent added (that is, the ratio of added reducing agent to slag) and the alkalinity (the mass ratio of calcium oxide to silica) were all investigated.

2.3. Characterization Methods

The phases of the slags and matte samples were monitored using X-ray powder diffraction (XRD; D8, Bruker Ltd., Karlsruhe, Germany, Cu K α 1 radiation) in the range of 10–90° (2 θ). The compositions of the alloy samples were detected by inductively coupled plasma atomic emission spectrometry (Prodigy, Optima 4300 DV, Lehman, NY, USA). The compositions of the slag samples were detected using an atomic absorption spectrophotometer (SU-Z2700, Hitachi, Tokyo, Japan). The C and S contents in the slag and metal samples were detected using a carbon sulfur analyzer (G4 ICARUS, Bruker Ltd., Karlsruhe, Germany). The microstructures of the alloy and slag samples were monitored by SEM coupled with energy-dispersive X-ray spectroscopy (SU-8010, Hitachi, Tokyo, Japan). Thermodynamic calculations were carried out using FactSage (FactSage 7.5, Thermfact/CRCT and GTT-Technologies, Canada and Germany) with the pure substances (FactPS), oxides (FToxid), alloys, and sulfides (FTmisc) databases [21].

- 3.1. Thermodynamics of the Reduction Process
- 3.1.1. Presence of Oxides and Sulfides in the Slag

The processing of the copper slag in this work included the reduction reactions of sulfides as well as copper, iron, zinc, and lead oxides. The slag also contained oxides of calcium, magnesium, aluminum, and silicon. Among these components, iron oxides were the most common and the other oxides were combined with these iron oxides to form a large number of complex compounds. Copper slag is typically discharged between 1150 and 1250 °C, so the FactSage software package was used to generate maps of the various binary oxides expected to be present at 1200 °C, as shown in Figure 4 [21,22].



Figure 4. Cont.



Figure 4. Advantageous area maps (1200 °C) of oxides and sulfides in copper slag (**a**): Fe—Cu—C—O, (**b**): Fe—Zn—C—O, (**c**): Fe—Pb—C—O, (**d**): Fe—Mg—C—O, (**e**): Fe—Al—C—O, (**f**): Fe—Ca—C—O, (**g**): Fe—Si—C—O, (**h**): Cu—Fe—S—O.

The primary phases in the copper slag were Fe_3O_4 and fayalite, as indicated in the region outlined in red in Figure 4g, which demonstrated the oxygen potential of the copper slag in this area of the map. These maps also indicated the presence of other oxides, either alone or in combination with iron oxides. These phases consisted of FeO, Fe_3O_4 , $(Cu_2O)(Fe_2O_3)$, $ZnFe_2O_4$, ZnO, $PbFe_{10}O_{16}$, PbO, MgO, Al_2O_3 , $Fe_2Al_2O_6$, $FeAl_2O_4$, CaO, $CaFe_4O_7$, $CaFe_2O_4$, $Ca_2Fe_2O_5$, Fe_2SiO_4 , and SiO₂. Among these, CaO, MgO, Al_2O_3 , and SiO₂ were relatively unreactive under the reducing conditions applied in the present work. Thus, the copper, iron, zinc, and lead oxides were the primary reactants. Copper slag was produced during the smelting process and primarily consisted of Fe_3O_4 , FeO, and copper matte. The data shown in Figure 4h demonstrate that the copper matte was composed of Cu_2S and Cu_5FeS_4 .

3.1.2. Reduction Reactions of Copper Slag

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During the reduction process, the carbon added to the slag reacted with the various metal oxides to form CO and CO_2 ; some of this CO_2 reacted with the carbon to generate CO. The thermodynamics of the CO reduction process were calculated based on the reactions:

$$Fe_3O_4 + 4CO(g) \rightarrow 3Fe + 4CO_2(g) \tag{1}$$

$$FeO + CO(g) \rightarrow Fe + CO_2(g)$$
 (2)

$$(Cu_2O)(Fe_2O_3) + 4CO(g) \rightarrow 2Cu + 2Fe + 4CO_2(g)$$
(3)

$$ZnO + CO(g) \rightarrow Zn + CO_2(g)$$
 (4)

$$ZnFe_2O_4 + 4CO(g) \rightarrow Zn + 2Fe + 4CO_2(g)$$
(5)

$$PbO + CO(g) \rightarrow Pb + CO_2(g)$$
 (6)

$$PbFe_{10}O_{16} + 16CO(g) \rightarrow Pb + 10Fe + 16CO_2(g)$$
 (7)

$$Fe_2Al_2O_6 + 3CO(g) \rightarrow 2Fe + Al_2O_3 + 3CO_2(g) \tag{8}$$

$$FeAl_2O_4 + CO(g) \rightarrow Fe + Al_2O_3 + CO_2(g)$$
(9)

$$CaFe_4O_7 + 6CO(g) \rightarrow 4Fe + CaO + 6CO_2(g)$$
(10)

$$CaFe_2O_4 + 3CO(g) \rightarrow 2Fe + CaO + 3CO_2(g)$$
(11)

$$Ca_2Fe_2O_5 + 3CO(g) \rightarrow 2Fe + 2CaO + 3CO_2(g)$$
(12)

$$Fe_2SiO_4 + 2CO(g) \rightarrow 2Fe + 2SiO_2 + 2CO_2(g)$$
(13)

$$FeS + CO(g) + CaO \rightarrow Fe + CaS + CO_2(g)$$
 (14)

and

$$Cu_5FeS_4 + 4CO(g) + 4CaO \rightarrow Fe + 5Cu + 4CaS + 4CO_2(g)$$
(16)

As demonstrated in Figure 5, in the standard state at 1450 °C, the oxides of Zn, Pb, and Cu were more readily reduced when combined with iron. In addition, the ΔG^{θ} values for the reactions of iron oxides with CaO, MgO, Al₂O₃, and SiO₂ were positive whereas the reduction of sulfide did not readily proceed. The reaction with the gas participating in the general case was a non-standard condition that was affected by the partial pressure of the gas. The Gibbs free energy change for copper slag reduction could, therefore, be calculated as:



Figure 5. ΔG^{θ} of the reactions and the equilibrium partial pressure under non—standard state (**a**,**c**): oxides, (**b**,**d**): sulfides.

During the reduction process, the gas phase inside the furnace included both CO and CO_2 . The amount of coke in the slag was minimal and it was generally produced on the

surface of the slag, meaning that reactions also occurred on the surface. As this was an open system, the pressure in the furnace was a standard atmospheric pressure and the partial pressure of CO was assigned a value of *a*, with the partial pressure of CO₂ being (1 - a). The results obtained for the gas partial pressure at a reaction equilibrium are shown in Figure 5c,d.

The Cu, Pb, and Zn oxides in the slag were all easily reduced; thus, as the temperature increased, the partial pressure of the CO required for the reduction rapidly decreased. $CaFe_4O_7$ and $FeAl_2O_4$ readily reacted at low temperatures, meaning that as the temperature increased and the partial pressure of CO increased, these reductions became more difficult. Both Fe_3O_4 and FeO were also highly reactive at low temperatures. Following the reduction, the slag was primarily a silicon calcium slag suitable for use as a cement ingredient. The sulfides could not be directly reduced during the present experiments because these species require both a sulfur carrier and oxygen donor for a substitution-based reduction [12]. Thus, CaO was added as a sulfur carrier. The data shown in Figure 5 indicated that the CO partial pressure required for the reduction of the sulfides was relatively high, with a value of close to 1 required for Cu_5FeS_4 . Consequently, the oxides in the slag were reduced prior to the sulfides.

3.1.3. Effects of Carbon and Calcium Oxide Additions on Oxide Reduction

During the present slag reduction, the amounts of carbon and calcium oxide added were important factors. Specifically, a sufficient amount of reducing agent provided a high CO partial pressure that ensured the complete reduction of oxides and sulfides in the slag. Thus, if the CO partial pressure was low, the reducing agent had to be added in excess. Copper slag is also acidic and contains a significant amount of SiO_2 along with Al_2O_3 . These oxides can combine with iron oxides to form compounds that are difficult to reduce. The addition of calcium oxide adjusted the alkalinity of the slag by reacting with SiO_2 and Al_2O_3 to produce calcium silicate and calcium aluminate, which is also the primary raw material in cement and contributes to the realization of no secondary tailings in comprehensive applications of copper slag. The iron oxides generated by the decomposition of iron silicates were more easily reduced, which improved the iron recovery. FactSage software was used to perform the calculations to ascertain the effects of varying the amounts of calcium oxide and carbon added; the results are shown in Figure 6.

The primary oxide in the copper slag was Fe_2SiO_4 and a phase diagram for Fe_2SiO_4 , C, and CaO at 1450 °C was generated (Figure 6a). Note that, in this plot, the area indicated in red did not contain oxides. With the addition of carbon, the iron in the phase diagram gradually transitioned from Fe_2SiO_4 to Fe and Fe_3C . The calcium oxide reacted with the Fe_2SiO_4 to generate calcium silicate. Thus, the reduction of iron oxides required a certain amount of calcium oxide and carbon. If the moles of calcium oxide added were equal to the moles of Fe_2SiO_4 in the slag, CaSiO₃ was formed and the slag had a composition along the line labeled CD in Figure 6. The phase changes of the copper slag with increasing amounts of carbon additions were calculated and the results are presented in Figure 6b. At point C, the phases comprised $CaSiO_3$ and FeO, but the incorporation of carbon gradually reduced the FeO such that the amount of Fe increased. It should be noted that CO and CO₂ were also present. The addition of 50 moles of carbon caused the FeO phase to completely disappear along with the formation of Fe₃C. At this point, if the carbon utilization rate was 100%, carbon was present in excess. The line labeled AB demonstrated that, under these same conditions, the phase composition changed with increases in the amount of calcium oxide added. The results are presented in Figure 6c. As more calcium oxide was incorporated, the proportions of the Fe₂SiO₄ and SiO₂ phases were continually lowered. When 25 moles of CaO were added, which was equal to the moles of Fe_2SiO_4 , all Fe_2SiO_4 was removed from the slag and the CaSiO₃ content reached a maximum. As further CaO was added, CaSiO₃, Ca₃SiO₇, Ca₂SiO₄, and Ca₃SiO₅ disappeared and appeared in turn.



Figure 6. Phase diagram and equilibrium composition of iron oxide reduction. (a) C–CaO–Fe₂SiO₄; (b) $(50 - 0.5A)CaO + (50 - 0.5A)Fe_2SiO_4 + (A)C$; (c) $(A)CaO + (50 - A)Fe_2SiO_4 + 50C$.

3.1.4. Influence of Carbon and Calcium Oxide Additions on the Sulfide Reduction of Copper Slag

The phase diagrams for the Cu₅FeS₄, C, and CaO systems at 1450 $^{\circ}$ C were calculated using FactSage software, as presented in Figure 7a. The region indicated in red in this

plot did not contain sulfides. From the calculated results (Figure 7b), it was evident that the addition of carbon and CaO decomposed Cu₅FeS₄ into Cu₂S and FeS. Specifically, the incorporation of 15 moles of both carbon and CaO decomposed all Cu₅FeS₄ and provided the maximum amounts of Cu₂S and FeS. In addition, FeS reacted with CaO to generate Fe, after which Cu₂S was reduced and Cu began to appear. Based on the desulfurization reaction, the sulfur in the molten iron was easily removed whereas the sulfur in Cu₂S was less reactive. The addition of 40 moles of both carbon and CaO caused the sulfides to completely disappear. Thus, the amounts of calcium oxide and carbon added to the slag had to be more than four times the molar amount of Cu_5FeS_4 . The line labeled CD in Figure 7c indicates the changes in composition with the addition of calcium oxide. These data showed the formation of Cu₂S, FeS, and CS₂ at point C following the addition of carbon, all of which were reduced after the incorporation of calcium oxide. Specifically, the addition of 45 moles of CaO completely removed the sulfides. The line labeled EF in Figure 7d shows the changes in composition with the addition of carbon. At point E, the phases were Ca₂Fe₂O₅, Cu₂S, and CaO, confirming the presence of Cu₅FeS₄. The FeS was reduced to FeO and combined with CaO to produce Ca₂Fe₂O₅ whereas the Cu₂S did not react with CaO without the addition of carbon. In the presence of carbon, Ca₂Fe₂O₅ and FeO disappeared and appeared in turn, after which Cu₂S was reduced.



Figure 7. Phase diagram (**a**) and equilibrium composition of sulfide (**b**): the compositions varie along the AB line, (**c**): the compositions varie along the CD line, (**d**): the compositions varie along the EF line.

3.2. Experiment of the Reduction Process

3.2.1. Effects of Temperature

Experimental trials were performed in which 88.2 g of copper slag was combined with a mass of the ratio of added reducing agent to slag of 0.225, using an alkalinity value of 1.2 and a reaction time of 150 min. The results of these trials are presented in Figure 8. The data showed that as the temperature increased, the metal yield gradually increased to a maximum of 98.30% at 1500 °C whereas the concentrations of residual Zn and Pb in the slag decreased. The Zn and Pb recoveries reached maximums of 98.61% and 85.95%, respectively, at this same temperature. At higher temperatures, greater amounts of Zn and Pb were volatilized into the gas phase; thus, the elevated temperatures promoted the extraction of these metals.



Figure 8. The effect of temperature on the reduction of slag (**a**): metal recovery, (**b**): element content in metal and slag.

The S content in the slag decreased with increases in temperature and reached its lowest value of 0.89 wt% at 1500 °C. Simultaneously, the S content in the metal product initially decreased and then increased. The target product was wear-resistant cast iron HBW600Cr20Mo2Cu, in which the S content was required to be less than 0.06%. A high temperature accelerated the fluidity of the slag, promoted the contact between the oxides

and sulfides in the slag and the reducing agent, and improved the reduction rate of the metals. The melting points of zinc and lead were relatively low and they quickly volatilized into the flue gas after being reduced to form a metal element; only a small part remained in the slag and metal. At a certain temperature range, a temperature increase was helpful to the reduction process. After the temperature reached the appropriate value, the influence effect was greatly reduced whereas the energy consumption and the corrosion of the refractory materials increased. Based on assessing both the sulfur content in the wear-resistant cast iron product and the metal recovery at various temperatures, the most suitable temperature was determined to be 1450 $^{\circ}$ C.

3.2.2. Effects of the Addition of a Reducing Agent

Additional trials were performed using 88.2 g of copper slag at a temperature of 1450 °C, an alkalinity of 1.2, and a reaction time of 150 min. The results are shown in Figure 9.



Figure 9. The effect of the addition of a reducing agent on the reduction of slag (**a**): metal recovery, (**b**): element content in metal and slag.

With continuous increases in the amount of reducing agent added, the metal recovery also gradually increased and the highest yield of 95.49% was obtained at a reducing

agent ratio of 0.225. The highest yields of Zn and Pb recovery were 98.30% and 83.54%, respectively. A small amount of zinc and lead existed in the form of unreduced oxides in the slag and dissolved solution in the copper–iron alloy. The addition of the reducing agent promoted the reduction of oxides and sulfides and ensured the reducing atmosphere of the system. Due to the low density of coke, it was easy to suspend on the surface of the slag under high temperature conditions and part of it volatilized with the gas. Therefore, the reducing agent was added in excess. Changing the amount of reducing agent had only a minimal effect on the Zn recovery, indicating that the reducing agent had little impact on the evaporation of Zn. In contrast, the recovery of Pb rapidly increased. As more of the reducing agent was added, the S content in the slag initially increased and then decreased, such that the value was within the standard range required for wear-resistant cast iron. Considering the metal recovery data, the suitable reducing agent ratio was determined to be 0.225.

3.2.3. Effects of Alkalinity

These trials employed 88.2 g of copper slag with a reducing agent ratio of 0.225, a temperature of 1450 °C, and a reaction time of 150 min. The results obtained are shown in Figure 10.



Figure 10. The effect of alkalinity on the reduction of slag (**a**): metal recovery, (**b**): element content in metal and slag.

With increases in the alkalinity, the metal recovery first increased and then decreased. At an alkalinity of 1.4, the metal recovery reached a maximum of 97.01%. The recoveries of Zn and Pb also initially increased and then decreased. The alkalinity reflected the amount of calcium oxide added. The main phase of the iron in the copper slag was fayalite, which is difficult to decompose and reduce. The addition of calcium oxide can promote the dissociation of ferrous oxide, which can then be reduced to a metal element. Calcium oxide can also be used as the carrier of sulfide. CaS was generated during the reduction process, which immobilized the sulfur in the slag. The alkalinity affected the viscosity of the slag, which in turn modified the flow of the molten material. With an increase in alkalinity, the fluidity of the slag improved, but high melting point compounds were formed after an excessive addition. In general, the alkalinity value affected the recoveries of all metals. The S content in the slag first increased and then decreased with changes in alkalinity, providing a concentration suitable for wear-resistant cast iron. Considering the metal recovery rates, the ideal alkalinity value was found to be 1.2, and this value provided a Cu and Fe recovery of 95.49%, Zn recovery of 98.30%, and Pb recovery of 83.54% whilst providing a S concentration of 0.061% in the metal.

These trials indicated that copper-containing molten iron and tailings after reductions could be obtained via the reduction of copper slag. The SEM image of the metal and the XRD result of the slag are shown in Figures 11 and 12, respectively. The reduction results of the copper slag under suitable conditions were simulated by FactSage software. The simulated compositions were: CaO, 42.36 g; MgO, 1.68 g; Al₂O₃, 6.52 g; SiO₂, 19.71 g; C, 19.85 g; Fe₃O₄, 9.08 g; Fe₂SiO₄, 53.02 g; Cu₅FeS₄, 1.15 g; ZnO, 2.13 g; PbO, 0.13 g; and S, 0.88 g. The compositions of the metal and slag are shown in Tables 2 and 3. According to the results, it could be concluded that the phases of the tailings were mainly calciumsilicon slag, calcium–aluminum slag, and CaS. In addition, there was some coke floating on the surface of the molten slag. As an alumina crucible was used as a reaction vessel, which could be eroded into the slag, the alumina content in the actual experiment was higher than that in the thermodynamic calculation. There was still a small part of fayalite that was not reduced. The C content in the metal was lower than the calculated result because in the actual process, there was volatilization and a burning loss of C. From these data, it was apparent that the levels of copper, iron, zinc, and lead in the slag were very low after processing. It should also be noted that the wear-resistant cast iron obtained from this system contained minimal Cr; thus, the addition of ferrochrome to the product was required.



Figure 11. Metal and slag under suitable conditions.



Figure 12. The phase analysis results of tailings.

Table 2. The composition of tailings.

Wt.%	CaO	SiO ₂	Al_2O_3	MgO	S (CaS,SiS ₂)	Cu (Cu ₂ O)	Fe (FeO)	Zn (ZnO)	Pb (PbO)
Thermodynamic calculation	49.00	39.08	7.54	1.94	1.21	0.021	0.026	$2.29 imes 10^{-4}$	$5.55 imes 10^{-6}$
Experiment	42.18	34.35	14.27	1.82	1.29	0.017	1.19	0.011	0.004

Table 3. The composition of copper-iron.

Wt.%	С	Si	Mn	Р	S	Cu	Fe	Zn	Pb
Thermodynamic calculation	4.62	1.75	-	-	0.031	1.70	91.90	-	$6.43 imes 10^{-4}$
Experiment	2.78	1.21	0.88	0.075	0.061	1.86	91.66	0.091	0.043

4. Conclusions

The present data indicate that the use of solid waste should be based on its composition and that such waste can be used to prepare high-value target products. It is apparent that phase separation and enrichment can allow the full utilization of the metal elements in copper slag. This work studied the reductive processing of copper slag as a means of utilizing this high-value waste product. The following conclusions were obtained.

(1) The copper slag was primarily composed of iron oxides and fayalite together with a lesser amount of matte and could be processed based on the reduction of oxides and sulfides. The thermodynamic calculations indicated that the reduction of copper, zinc, and lead oxides would be expected to proceed readily whereas the iron oxides were determined to be more difficult to reduce and the reduction of sulfides was even more challenging. From the calculated results, Cu_5FeS_4 was found to decompose into FeS and Cu_2S during the reduction process, with FeS undergoing a rapid reduction followed by the reduction of Cu_2S based on the addition of carbon.

(2) The most suitable conditions for the reduction of copper slag were found to consist of a temperature of 1450 °C, an alkalinity of 1.2, and a reducing agent ratio of 0.225. These conditions extracted 95.49% of the copper and iron from the slag together with 83.54% and 98.30% of the Pb and Zn, respectively. The S content in the resulting metal was 0.06%.

Author Contributions: Conceptualization, B.Z. and T.Z.; investigation, B.Z.; resources, B.Z. and Z.D.; software, T.Z.; writing—original draft, B.Z.; writing—review and editing, B.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Natural Science Foundation of China (52004284) and the fundamental research funds from the Central University of the Ministry of Education of China (2020QN55).

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

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