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Recovery of Cu-Fe Alloy from Copper Smelting Slag

Yi Qu [1,2], Keqin Tan [3], Baojun Zhao [1,2] and Sui Xie [1,2,*]

[1] Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China
[2] International Institute for Innovation, Jiangxi University of Science and Technology, Nanchang 330013, China
[3] Dongying Fangyuan Nonferrous Metals Co., Ltd., Dongying 257091, China
* Correspondence: xiesui21@126.com

Abstract: Copper smelting slag usually contains 1–6 wt% copper, which can be recovered by pyrometallurgical and flotation processes. However, the tailing slags still consist of 0.3–0.7 wt% Cu and 35–45 wt% Fe equivalents to those in the copper and iron ores, respectively. Most of the research was focused on the recovery of iron from the tailing slags. Copper can increase the mechanical strength, corrosion resistance and antibacterial property of some steels. A new process to recover copper and iron directly and fully from hot copper smelting slag is proposed to produce Cu-Fe alloy for steel production. Effects of flux, temperature, reaction time, reductant type and addition on the recovery of copper and iron were investigated by high-temperature experiments and thermodynamic calculations. It was found that, with 5% CaO and 13–16% carbon additions, most of the copper and iron can be recovered from copper smelting slag at 1350–1400 °C. The copper and iron contents of the reduced slag are lower than 0.1% and 0.5%, respectively, at optimum condition. The new process has the advantages of low energy consumption, low flux addition and high recovery of copper and iron.

Keywords: copper smelting slag; smelting reduction; Cu-Fe alloy; FactSage

1. Introduction

80% to 90% of copper is produced through a pyrometallurgical process from concentrates around the world [1]. Copper smelting slag is a by-product of the pyrometallurgical process. 2–3 tons slag is generated for producing per ton of copper [2]. Approximately 35.2 million tons were produced globally in 2022 [3]. In the modern smelting process, copper smelting slag contains 1–6% copper and 35–45% iron [1]. Most of the copper in the slag is present as entrained matte and can be recovered by the cleaning process [2,4]. Pyrometallurgical cleaning [5–9] and flotation cleaning [10–13] are the main methods to recover copper from the smelting slag. The tailing slag contains 0.7% Cu from the pyrometallurgical cleaning [5–9] and 0.3% copper from the flotation cleaning. In addition, 35–45% iron in the cleaning slag is not recovered.

The contents of copper (0.3–0.7%) and iron (35–45%) in the cleaning slags are close to the grades of copper ores and iron ores, respectively. Extensive studies have been conducted to recover iron from the cleaning slags through reduction process [14–22]. For example, a tailing copper smelting slag containing 0.24% Cu and 38.23% Fe was used to recover iron at 1100–1300 °C [15]. 16% CaO and 20% coke fines were mixed with the tailing slag and pelletized for reduction. After reduction, the sample was ground, and the alloy powder was recovered by magnetic separation. The alloy contained 91% Fe and 0.18% Cu together with 0.1–0.6% Al_2O_3, CaO, MgO, Na_2O and SiO_2. This process used tailing slag powder for low-temperature reduction, which saved ground and heating energy. However, the maximum recovery of iron was only 92%, and the alloy cannot be directly used to produce steel due to the high impurities. Smelting separation at 1500 °C was used to remove the impurities, which increased the cost of the alloy [21]. The smelting reduction at 1500 °C was undertaken with additions of CaO and MgO. The maximum recovery of 90% Fe was

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achieved with 20% CaO and 10% MgO [14]. Copper recovery was not mentioned in these studies as the Cu content in the slags was low. The smelting reduction can separate the alloy from the oxide slag completely to obtain a clean product. However, this process did not consider the recovery of copper, and the smelting conditions such as flux addition and temperature need to be optimized to increase the recovery of the metals. All copper smelters have a slag cleaning process to recover copper from the slags. Most of the research was focused on the recovery of iron from the cold tailing slags. The recovered alloy was not suitable for general steel production because the copper in the alloy is considered an impurity in most of the steels. All proposed processes to recover iron from copper cleaning slags are not commercialized due to the high cost and high level of impurities.

In most of the steels, copper is considered an impurity that induces severe microstructural distortions in the steel and decreases its tensile strength, impact energy and hardness [23]. On the other hand, it was found that 2.5–4% copper in steel increases the mechanical strength, corrosion resistance and antibacterial property of steel [24–30]. Copper metal is usually used to produce Cu-containing steels. However, the cost is high to use high-purity copper, and the distribution of copper in the steel is not uniform, which limits the applications of the Cu-containing steels. Hao et al. studied the possibility of producing antibacterial stainless steel from copper cleaning slag via smelting reduction [31]. The optimum condition was found at 1450 °C with 20% CaO and 13% carbon additions. The overall metal recovery was 91.76% at optimum condition. The contents of Cu and Fe in the reduced slag were 0.015% and 0.29%, respectively. The copper content in the alloy was 1.65%, which is lower than that required for antibacterial stainless steel. Extra copper metal needs to be added to the steel production. A new process to recover iron and copper directly from copper smelting slag is developed in the present study. The molten slag as a feed can be used in the reduction process to save energy. The new technology omits the cleaning process and produces a Cu-Fe alloy with high Cu, which can be directly used as a feed for the production of Cu-containing steels. Effects of the parameters including flux, temperature, reaction time, reductant type and addition on the recovery of copper and iron from copper smelting slag are investigated in this study.

2. Materials and Methods

2.1. Materials

The copper smelting slag was provided by a smelter, and the composition of the slag measured by an XRF (X-ray Fluorescence Spectrometer) is shown in Table 1. The iron in the slag includes both Fe^{2+} and Fe^{3+}. For presentation purposes, all iron is expressed as “FeO”. It can be seen that “FeO” and SiO_2 are the main components in the slag. 6.83% Cu_2O and 8.52% ZnO are also present in the slag. In the high temperature experiments, coke and graphite were used as reductants and CaO (analytically pure) was used as a flux.

Table 1. Composition of the smelting slag measured by XRF.

“FeO”	MgO	CaO	SiO_2	Al_2O_3	ZnO	Cu_2O	S
54.67	2.53	3.22	20.54	2.23	8.52	6.83	1.46

2.2. Experiments

The equipment used in this study is shown in Figure 1. The experiments were carried out in a vertical tube furnace heated by $MoSi_2$ heating elements. A Pt/Pt-13%Rh thermocouple inside an alumina sheath was placed in the hot zone of the furnace to accurately measure the temperature of the sample. The sample, consisting of the required slag, reductant and flux was mixed in an agate mortar for 30 min and pelletized. The pelletized mixture was placed in a corundum crucible and suspended at the bottom of the furnace. The furnace was properly sealed, and ultrahigh purity argon was flushed for 30 min to remove the air inside. The crucible with the mixture was raised from the bottom to the hot zone of the reaction tube for the required reaction time. The sample was quenched in water after the reduction was finished. The experimental conditions are shown in Table 2. Alloy and slag were separated after the reduction and quenching. The compositions of the alloy and slag were measured by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer; Agilent 5900, Palo Alto, CA, USA), and the microstructures of the quenched slag were observed by SEM (Scanning electron microscopy; FEI, Hillsboro, OR, USA).

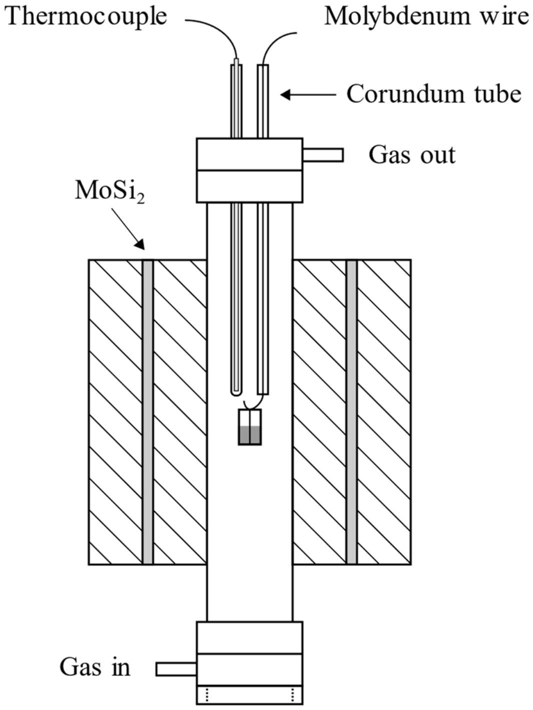

Figure 1. Schematic diagram of the experimental system used in this study.

Table 2. Experimental conditions.

Exp	Slag/g	CaO/g	Carbon/g	C Type	Temperature/°C	Time/min
1	10	0.5	1.3	Graphite	1250	120
2	10	0.5	1.3	Graphite	1350	120
3	10	0.5	1.3	Graphite	1450	120
4	10	0.5	1	Graphite	1400	120
5	10	0.5	1.3	Graphite	1400	120
6	10	0.5	1.6	Graphite	1400	120
7	10	0.5	1.4	Graphite	1350	120
8	10	0.5	1.3	Graphite	1400	60
9	10	0.5	1.3	Graphite	1400	120
10	10	0.5	1.3	Graphite	1400	180
11	10	0.5	1	Coke	1400	120
12	10	0.5	1.3	Coke	1400	120
13	10	0.5	1.6	Coke	1400	120

2.3. Thermodynamic Predictions

The thermodynamic software FactSage has been widely used in the fields of materials and metallurgy [32]. The latest version, FactSage 8.2 (Thermfact/CRCT and GTT-Technologies), was used in the present study to predict the reactions and plan the experiments. The databases “FactPS“, “FToxid“ and “FTmisc“ were used in the “Equilib” module. The solution phases selected in the calculations included “FTmisc-FeLQ”, “FTmisc-CuLQ”, “FTmisc-FeCu”, “FTmisc-MATT”, “FToxid-SLAGA”, “FToxid-SPINC”, FToxid-MeO”, “FToxid-cPyrA”, “FToxid-WOLLA”, “FToxid-bC2SA”, “FToxid-aC2S”, “FToxid-Mel_A”, “FToxid-OlivA”.

3. Results and Discussion

The overall reaction in the present study to recover valuable metals from the copper smelting slag includes the following:

$$\text{Slag1}(Cu_2O, FeOx, SiO_2, Al_2O_3, MgO)(l) + CaO(s) + C(s) \rightarrow \text{Cu-Fe}(l) + \text{Slag2}(Cu_2O, FeOx, ZnO, SiO_2, Al_2O_3, MgO)(l)$$

Slag1, in the previous studies, is a tailing slag which after cleaning contained little copper. In the present study, Slag1 is a smelting slag containing relatively more copper. CaO is a flux that can be added as $CaCO_3$ or CaO. C is a reductant to be added as graphite, coal or coke. The Cu_2O and FeOx in Slag1 can be reduced to form the Cu-Fe alloy. Other components from Slag1 react with the flux to form Slag2, which is a tailing slag. The variables in the reaction include the ratios of flux and reductant to Slag1, temperature and reaction time, which will be discussed in the following sections.

3.1. Control of Liquidus Temperature of Reduced Slag

When the copper smelting slag reacts with carbon, the oxides of copper, iron and zinc can be reduced to form the Cu-Fe-C alloy, and zinc is vaporized from the condensed system. Most of sulfur in the slag is also present in the alloy. After reduction, the remaining slag contains only CaO, MgO, Al_2O_3 and SiO_2. The liquidus temperature of the alloy Cu-Fe-C is low. It is essential to keep the reduced slag fully liquid to separate the alloy from the slag completely. The effect of flux addition on the liquidus temperature of the reduced slag is calculated by FactSage 8.2 and shown in Figure 2. It can be seen that the liquidus temperature of the reduced slag without flux is 1560 °C. Both CaO and MgO can decrease the liquidus temperature of the reduced slag. 5% CaO can rapidly decrease the liquidus temperature to 1270 °C. If the CaO addition is more than 7%, the slag will enter the $CaSiO_3$ primary phase field and the liquidus temperatures will increase. MgO can only decrease the liquidus temperatures to 1380 °C, showing that CaO is a more effective flux to control the liquidus temperature of the reduced slag.

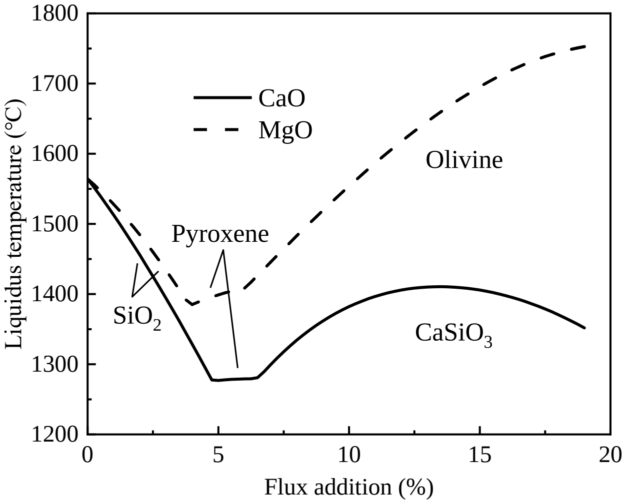

Figure 2. Effect of flux addition on the liquidus temperature of slag.

Figure 3 shows the appearance of the alloy from experiments 1 to 6 in Table 2. It can be seen from the figure that, after the reduction at 1250 °C (Exp 1), both alloy and slag were not liquid and they were not separated. As the reduction temperature was increased to 1350 °C (Exp 2), the alloy was separated from the slag. However, there are still slag and pores present inside the alloy, indicating that it was not completely melted. A dense alloy was obtained from experiments 3–6 indicating that the reduction temperature of 1400 °C is suitable to produce a dense alloy.

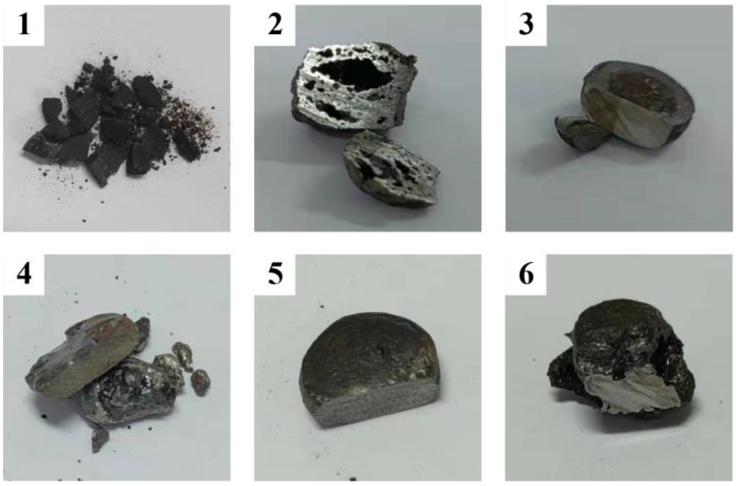

Figure 3. Appearance of the alloy after reduction: (**1**) 1250 °C, 13% C; (**2**) 1350 °C, 13% C; (**3**) 1450 °C, 13% C; (**4**) 1400 °C, 10% C; (**5**) 1400 °C, 13% C; (**6**) 1400 °C, 16% C.

Figure 4a shows the typical microstructure of the quenched sample after reduction at 1250 °C. The black phase shown in Figure 4a is graphite, the grey phase is slag, and the white phase is alloy. It seems that the alloy was not liquid at 1250 °C because it did not separate from the graphite and slag. Figure 4b shows the typical microstructure of the quenched sample after reduction at 1350 °C. It can be seen that the slag was fully liquid at a high temperature and converted to a homogeneous glass on quenching. The microstructures shown in Figure 4 confirm the observations shown in Figure 3 and the prediction shown in Figure 2. With the support of thermodynamic predictions, high temperature experiments show that only a 5% addition of CaO can decrease the liquidus temperature of the reduced slag to approximately 1300 °C. This result provides the possibility of low-temperature smelting reduction compared to those (1450–1500 °C) previously reported in the literature [14,31]. 5% CaO addition not only decreases the flux cost but also reduces the volume of the reduced slag by approximately 30% compared to the previous studies [14,31] where 20% CaO was added.

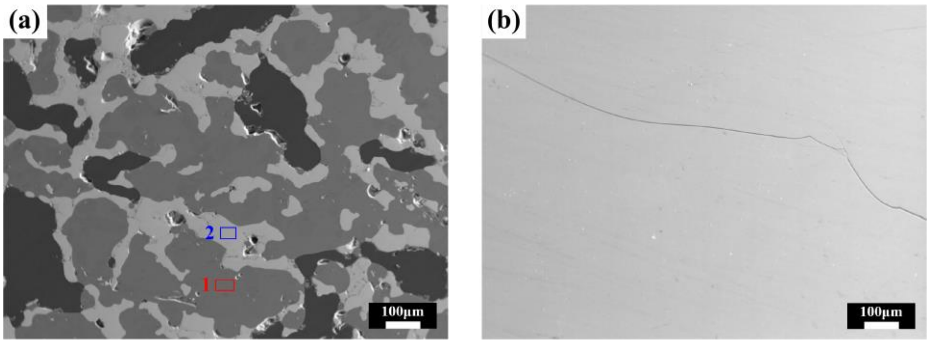

Figure 4. Typical microstructures of the quenched slags after reduction, (**a**) 1250 °C; (**b**) 1350 °C.

3.2. *Effect of Reductant on the Recovery of Copper and Iron*

The effect of carbon addition on amounts of the phases during the reduction of the copper smelting slag was calculated by FactSage 8.2, and the results are shown in Figure 5. 100 g of copper smelting slag was used as a base, and the temperature and CaO addition were 1400 °C and 5%, respectively, for the calculations. It can be seen that the proportion of the slag phase decreases with increasing carbon addition as "FeO", Cu_2O and ZnO in the slag were reduced from the slag. As a result, Fe and Cu form an alloy, and Zn vaporizes as a gas. Zinc can be collected in flue gas as a dust which is an extra advantage of this technology. According to the prediction, ZnO in the slag is completely reduced with the

2.5% carbon addition. All iron and copper oxides are reduced with a 14% carbon addition. Further addition of carbon causes the formation of graphite.

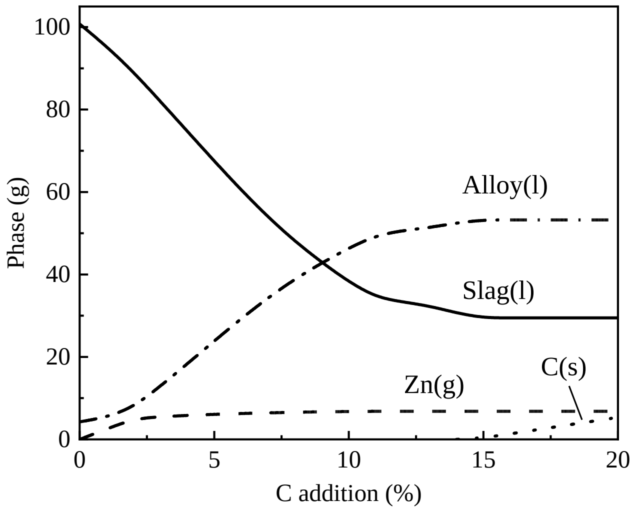

Figure 5. Effect of carbon addition on the amounts of the phases during reduction at 100g slag, 1400 °C and 5% CaO addition.

Figure 6 shows the experimental results on the copper and iron contents remaining in the reduced slag after reduction at 1400 °C with 5% CaO addition. As can be seen from Figure 6, after reduction by 10% graphite, the copper and iron contents in the remining slag are 0.14% and 16%, respectively. The copper and iron contents of the remining slag decrease with increasing carbon addition. As the carbon addition increased to 16%, the copper and iron in the reduced slag decreased to 0.06% and 0.5%, respectively. The experimental results confirmed the reductant ratio predicted by FactSage and that reported by Hao et al. [31]. The exact requirement of the reductant depends on the proportions of the reducible oxides in the slag, the types of the reductants and the reaction temperature.

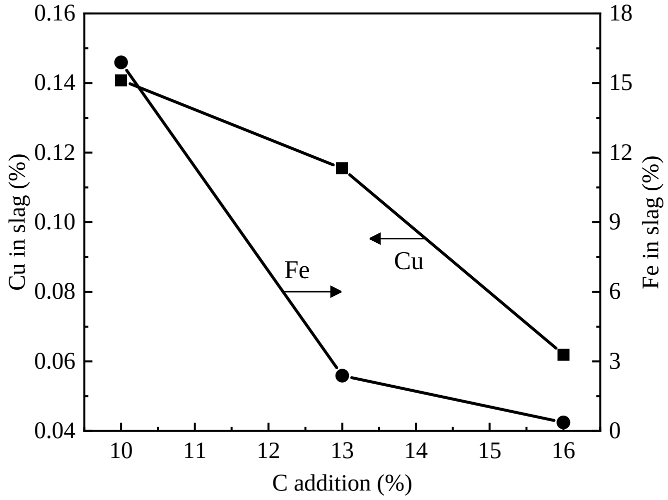

Figure 6. Experimentally determined copper and iron contents in the reduced slag at 1400 °C with 5% CaO addition.

Figures 7 and 8 show the effect of carbon type on the copper and iron contents in the reduced slags after reduction at 1400 °C and 5% CaO addition. It can be seen from Figure 7 that the copper content in the reduced slag decreases with increasing graphite and coke additions. The coke (which contains 85% carbon) is a more effective reductant than the graphite due to its higher reactivity and surface area. With 13% graphite and coke (13% caron equivalent) addition, the copper content in the reduced slag is 0.12 and 0.053%, respectively. To decrease the copper content to 0.06%, 16% graphite is required. It can be seen from Figure 8 that 13% carbon equivalent coke addition can reduce the iron in the slag to 0.2%. The same amount of graphite addition only reduced the iron content in the slag to 2.5%. Similarly, more than 16% graphite is required to reduce the iron content in the slag to 0.2%.

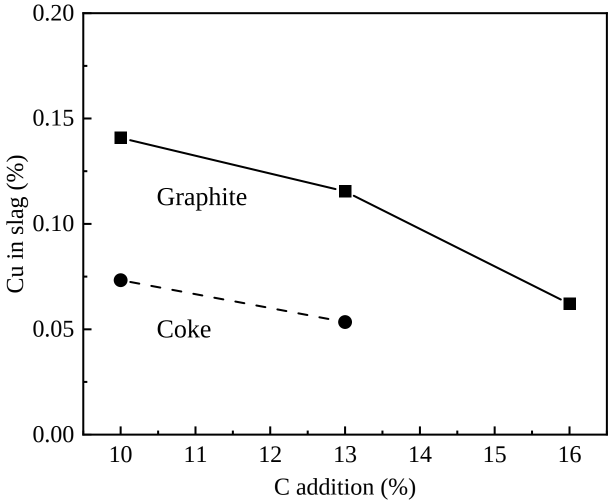

Figure 7. Effect of carbon type on copper content in the reduced slags after reduction at 1400 °C and 5% CaO addition.

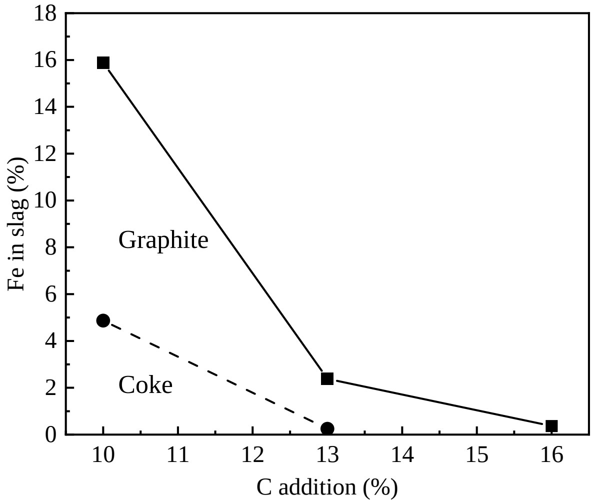

Figure 8. Effect of carbon type on iron content in the reduced slags after reduction at 1400 °C and 5% CaO addition.

3.3. *Effect of Temperature on the Recovery of Copper and Iron*

The effect of temperature on the copper and iron contents in the reduced slag, predicted by FactSage 8.2, is shown in Figure 9. From 1350 to 1410 °C, the amount of iron in the reduced slag decreases slowly with increasing temperature. Above 1410 °C, the iron content of the reduced slag decreases rapidly with increasing temperature. In contrast, copper in the reduced slag increases with decreasing temperature below 1410 °C. Above 1410 °C, the copper content of the reduced slag decreases rapidly with increasing temperature. The increase of copper in the slag can be explained by the sulfur in the slag. It can be seen from Figure 9 that sulfur in the slag first increases and then decreases with increasing temperature. When the sulfur is high in the slag, the chemical bond Cu-S is strong, which affects the reduction of copper from the slag.

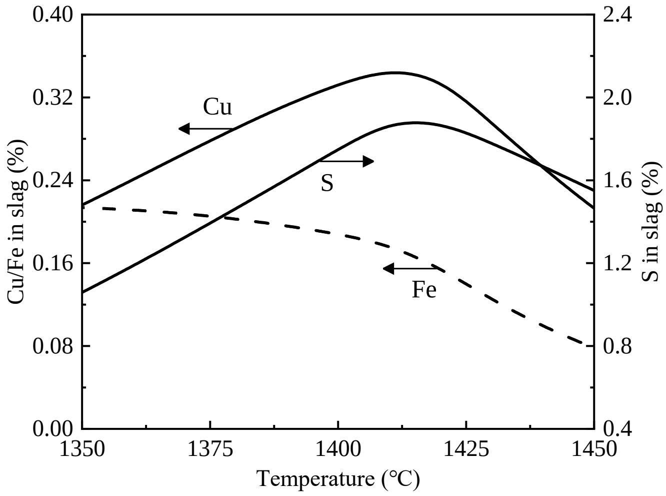

Figure 9. Effect of temperature on the copper and iron contents in the reduced slag, predicted by FactSage 8.2: 13% carbon and 5% CaO.

Figure 10 shows the experimental results about the effect of temperature on the copper and iron contents in the reduced slag with 5% CaO and 13% graphite. It can be seen that the iron content of the slag decreases slowly at lower temperatures and fast at higher temperatures, which shows the same trend as that predicted by FactSage. In the temperature range investigated (1350–1450 °C), copper in the slag continuously increases, which is different from that predicted by FactSage as shown in Figure 9. An optimum temperature should be selected to maximize the recovery of copper by considering the liquidus temperatures of the alloy and slag and the copper content in the reduced slag. Hao et al. [31] reported that the copper content in the reduced slag decreased from 1400 to 1450 °C and then increased from 1450 to 1500 °C, followed by a decrease from 1500 to 1550 °C. They also reported that the iron content of the reduced slag increased from 1400 to 1500 °C, followed by a decrease from 1500 to 1550 °C, but the reasons for the observed trends were not mentioned.

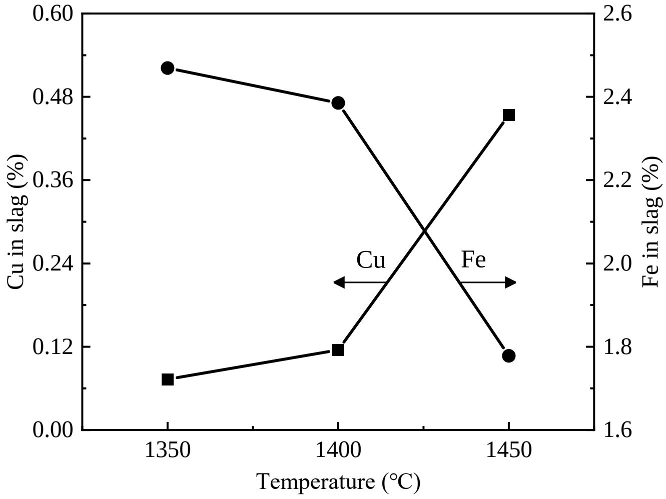

Figure 10. Effect of temperature on the copper and iron contents in the reduced slag by experiments, 5% CaO and 13% graphite.

3.4. Effects of Reduction Time on the Recovery of Copper and Iron

The effect of reduction time on the copper and iron contents in the reduced slag was studied by experiments at 1400 °C with 5% CaO addition and 13% graphite. As can be seen from Figure 11, the copper and iron contents of the slag decrease with increasing reduction time. It seems that the reduction of copper approached equilibrium because thre was only a small decrease in the copper content from 120 min to 180 min. On the other hand, the iron content in the slag continuously decreases, indicating that the reduction of iron did not reach equilibrium in 180min. A proper reaction time is determined economically, as a long reaction time increases the fuel cost and reduces productivity. Heo et al. [14] reported that the iron content in the reduced slag decreased linearly with the reaction time up to 60 min which showed the same trend as the present study. However, in the study of Hao et al. [31], the contents of copper and iron in the reduced slag showed a fluctuating upward trend with the reaction time between 15 and 60 min.

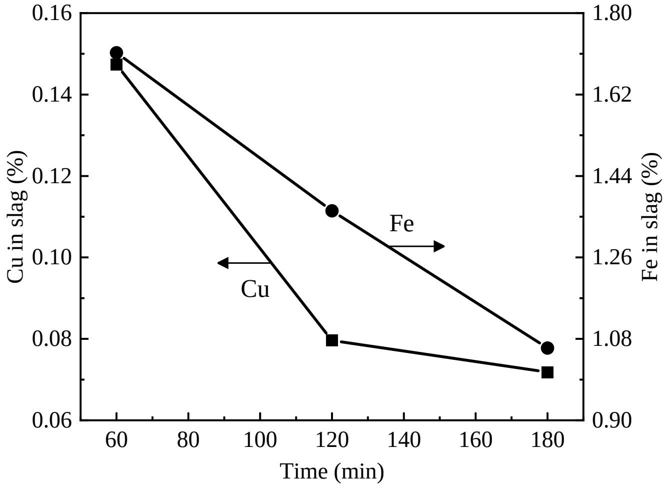

Figure 11. Effect of reduction time on the copper and iron contents in the reduced slag at 1400 °C, 5% CaO and 13% graphite.

Laboratory research is a systematic study to identify the optimum conditions to maximize the recovery of valuable metals from the copper smelting slag with a minimum cost. Copper smelting slag is around 1200 °C when it is tapped from the smelting furnace. In most of the smelters, the slag is slow-cooled and ground to recover copper through a flotation process. The previous research was focused on the recovery of metals (mainly iron) from the tailing slag. In the present study, a novel process is proposed to recover valuable metals directly from the hot copper smelting slag. This process does not need a flotation plant and fully uses the heat from the molten slag. In one single step, copper, iron and zinc can be recovered through smelting and reduction. The present study demonstrates that the optimum conditions to achieve a good recovery of the metals from the copper smelting slag include 5% CaO and 13–16% carbon additions, 1350–1400 °C, and a 60 min reaction. These conditions are specifically for the as-received copper smelting slag and available flux and reductants. In an industrial operation, maximum recovery is not the target, and economic factors need to be taken into account. For example, higher temperatures and longer reaction times can increase the recovery but also increase the cost of the fuel and refractory. The optimum conditions in the laboratory study may not be the best when they are applied to an industrial operation. The research is only used as a guideline to support the industry in adjusting the operating parameters to maximize the economic benefits.

4. Conclusions

Cu-Fe alloy has wide applications in the production of Cu-containing steels. A new process to produce Cu-Fe alloy directly from hot copper smelting slag. Effects of flux, temperature, reaction time, reductant type, and amount on the recovery of copper and iron were studied by thermodynamic calculations and high temperature experiments. Optimal flux and reductant additions have been determined. High temperatures decrease the iron content but increases the copper content in the slag. Coke is a better reductant than graphite to reduce copper and iron from the slag. In optimal conditions, over 99% of copper and iron can be recovered from the copper smelting slag. Zinc in the slag can also be recovered from the dust. The proposed process has the potential to replace the existing slag cleaning plant in the copper smelter to produce a Cu-Fe alloy suitable for steel production.

Author Contributions: Methodology, B.Z.; software, B.Z.; resources, K.T.; writing—original draft preparation, Y.Q.; writing—review and editing, K.T., B.Z. and S.X. All authors have read and agreed to the published version of the manuscript.

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References

1. Zuo, Z.L.; Feng, Y.; Dong, X.J.; Luo, S.; Ren, D.D.; Wang, W.H.; Wu, Y.X.; Yu, Q.B.; Lin, H.; Lin, X.Q. Advances in Recovery of Valuable Metals and Waste Heat from Copper Slag. *Fuel Process. Technol.* **2022**, *235*, 107361. [CrossRef]
2. Tian, H.Y.; Guo, Z.Q.; Pan, J.; Zhu, D.Q.; Yang, C.C.; Xue, Y.X.; Li, S.W.; Wang, D.Z. Comprehensive Review on Metallurgical Recycling and Cleaning of Copper Slag. *Resour. Conserv. Recycl.* **2021**, *168*, 105366. [CrossRef]
3. U.S. Geological Survey. *Mineral Commodity Summaries 2022*; U.S. Geological Survey: Reston, VA, USA, 2022. [CrossRef]
4. Zhou, W.T.; Liu, X.; Lyu, X.J.; Gao, W.H.; Su, H.L.; Li, C.M. Extraction and Separation of Copper and Iron from Copper Smelting Slag: A Review. *J. Clean. Prod.* **2022**, *368*, 133095. [CrossRef]
5. Zhou, S.W.; Wei, Y.G.; Shi, Y.; Li, B.; Wang, H. Characterization and Recovery of Copper from Converter Copper Slag Via Smelting Separation. *Metall. Mater. Trans. B* **2018**, *49*, 2458–2468. [CrossRef]
6. Zhang, J.; Qi, Y.H.; Yan, D.L.; Xu, H.C. A New Technology for Copper Slag Reduction to Get Molten Iron and Copper Matte. *J. Iron Steel Res. Int.* **2015**, *22*, 396–401. [CrossRef]
7. Zhang, H.P.; Li, B.; Wei, Y.G.; Wang, H.; Yang, Y.D. Effect of CaO on Copper Loss and Phase Transformation in Copper Slag. *Metall. Mater. Trans. B* **2022**, *53*, 1538–1551. [CrossRef]
8. Guo, Z.Q.; Pan, J.; Zhu, D.Q.; Zhang, F. Green and Efficient Utilization of Waste Ferric-Oxide Desulfurizer to Clean Waste Copper Slag by the Smelting Reduction-Sulfurizing Process. *J. Clean. Prod.* **2018**, *199*, 891–899. [CrossRef]
9. Zuo, Z.L.; Yu, Q.B.; Wei, M.Q.; Xie, H.Q.; Duan, W.J.; Wang, K.; Qin, Q. Thermogravimetric Study of the Reduction of Copper Slag by Biomass: Reduction Characteristics and Kinetics. *J. Therm. Anal. Calorim.* **2016**, *126*, 481–491. [CrossRef]
10. Shang, X.K.; Lan, Z.Y.; Zhang, Q.F.; Li, T.T. A Comprehensive Recovery of Copper-Iron Experimental Research in the Copper Smelting Slag. *Adv. Mater. Res.* **2014**, *926*, 4197–4200. [CrossRef]
11. Roy, S.; Datta, A.; Rehani, S. Flotation of Copper Sulphide from Copper Smelter Slag Using Multiple Collectors and Their Mixtures. *Int. J. Miner. Process.* **2015**, *143*, 43–49. [CrossRef]
12. Meng, X.Y.; Li, Y.; Wang, H.Y.; Yang, Y.D.; Mclean, A. Effects of Na_2O Additions to Copper Slag on Iron Recovery and the Generation of Ceramics from the Non-Magnetic Residue. *J. Hazard. Mater.* **2020**, *399*, 122845. [CrossRef] [PubMed]
13. Liu, R.Q.; Zhai, Q.L.; Wang, C.; Li, X.; Sun, W. Optimizing the Crystalline State of Cu Slag by Na_2CO_3 to Improve Cu Recovery by Flotation. *Minerals* **2020**, *10*, 820. [CrossRef]
14. Heo, J.H.; Kim, B.-S.; Park, J.H. Effect of CaO Addition on Iron Recovery from Copper Smelting Slags by Solid Carbon. *Metall. Mater. Trans. B* **2013**, *44*, 1352–1363. [CrossRef]
15. Long, H.; Meng, Q.; Chun, T.; Wang, P.; Li, J. Preparation of Metallic Iron Powder from Copper Slag by Carbothermic Reduction and Magnetic Separation. *Can. Metall. Q.* **2016**, *55*, 338–344. [CrossRef]
16. Guo, Z.Q.; Zhu, D.Q.; Pan, J.; Yao, W.J.; Xu, W.Q.; Chen, J.N. Effect of Na_2CO_3 Addition on Carbothermic Reduction of Copper Smelting Slag to Prepare Crude Fe-Cu Alloy. *JOM* **2017**, *69*, 1688–1695. [CrossRef]
17. Guo, Z.Q.; Zhu, D.Q.; Pan, J.; Zhang, F. Innovative Methodology for Comprehensive and Harmless Utilization of Waste Copper Slag via Selective Reduction-Magnetic Separation Process. *J. Clean. Prod.* **2018**, *187*, 910–922. [CrossRef]
18. Wang, J.-P.; Erdenebold, U. A Study on Reduction of Copper Smelting Slag by Carbon for Recycling into Metal Values and Cement Raw Material. *Sustainability* **2020**, *12*, 1421. [CrossRef]
19. Łabaj, J.; Blacha, L.; Jodkowski, M.; Smalcerz, A.; Fröhlichová, M.; Findorak, R. The Use of Waste, Fine-Grained Carbonaceous Material in the Process of Copper Slag Reduction. *J. Clean. Prod.* **2021**, *288*, 125640. [CrossRef]
20. Du, J.L.; Zhang, F.X.; Hu, J.H.; Yang, S.L.; Liu, H.L.; Wang, H. Direct Reduction of Copper Slag Using Rubber Seed Oil as a Reductant: Iron Recycling and Thermokinetics. *J. Clean. Prod.* **2022**, *363*, 132546. [CrossRef]
21. Pan, L.T.; Zhu, D.Q.; Guo, Z.Q.; Pan, J. Preparation of a Master Fe–Cu Alloy by Smelting of a Cu-Bearing Direct Reduction Iron Powder. *Metals* **2019**, *9*, 701. [CrossRef]
22. Gorai, B.; Jana, R.K. Premchand Characteristics and Utilisation of Copper Slag—A Review. *Resour. Conserv. Recycl.* **2003**, *39*, 299–313. [CrossRef]
23. Sekunowo, O.I.; Durowaye, S.I.; Gbenebor, O.P. Effect of Copper on Microstructure and Mechanical Properties of Construction Steel. *Int. J. Chem. Mol. Nucl. Mater. Metall. Eng.* **2014**, *8*, 839–843.

24. Takaki, S.; Fujioka, M.; Aihara, S.; Nagataki, Y.; Yamashita, T.; Sano, N.; Adachi, Y.; Nomura, M.; Yaguchi, H. Effect of Copper on Tensile Properties and Grain-Refinement of Steel and Its Relation to Precipitation Behavior. *Mater. Trans.* **2004**, *45*, 2239–2244. [CrossRef]
25. Hong, I.T.; Koo, C.H. Antibacterial Properties, Corrosion Resistance and Mechanical Properties of Cu-Modified SUS 304 Stainless Steel. *Mater. Sci. Eng. A* **2005**, *393*, 213–222. [CrossRef]
26. Vaynman, S.; Fine, M.E.; Chung, Y.-W.; Hahin, C. *Low-Carbon, Cu-Precipitation-Strengthened Steel*; Association for Iron & Steel Technology: Warrendale, PA, USA, 2011; pp. 181–188.
27. Yokoi, T.; Maruyama, N.; Takahashi, M.; Sugiyama, M. Application of Controlled Cu Nano-Precipitation for Improvement in Fatigue Properties of Steels. *Nippon Steel Tech. Rep.* **2005**, *91*, 49–55.
28. Ren, L.; Nan, L.; Yang, K. Study of Copper Precipitation Behavior in a Cu-Bearing Austenitic Antibacterial Stainless Steel. *Mater. Des.* **2011**, *32*, 2374–2379. [CrossRef]
29. Yin, Y.; Zhang, X.; Wang, D.; Nan, L. Study of Antibacterial Performance of a Type 304 Cu Bearing Stainless Steel against Airborne Bacteria in Real Life Environments. *Mater. Technol.* **2015**, *30*, B104–B108. [CrossRef]
30. Zhang, X.R.; Yang, C.G.; Yang, K. Contact Killing of Cu-Bearing Stainless Steel Based on Charge Transfer Caused by the Microdomain Potential Difference. *ACS Appl. Mater. Interfaces* **2020**, *12*, 361–372. [CrossRef]
31. Hao, J.; Dou, Z.H.; Zhang, T.A.; Jiang, B.C.; Wang, K.; Wan, X.Y. Manufacture of Wear-Resistant Cast Iron and Copper-Bearing Antibacterial Stainless Steel from Molten Copper Slag via Vortex Smelting Reduction. *J. Clean. Prod.* **2022**, *375*, 134202. [CrossRef]
32. Bale, C.W.; Bélisle, E.; Chartrand, P.; Decterov, S.A.; Eriksson, G.; Gheribi, A.E.; Hack, K.; Jung, I.-H.; Kang, Y.-B.; Melançon, J.; et al. Reprint of: FactSage thermochemical software and databases, 2010–2016. *Calphad* **2016**, *55*, 1–19. [CrossRef]