

DIRECT REDUCTION OF SARCHESHME COPPER SULFIDE CONCENTRATE WITH CARBON IN THE PRESENCE OF LIME

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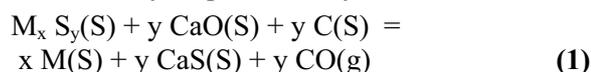
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Abstract: The direct reduction of copper sulfide concentrate from Iranian Sarcheshme deposits with carbon in the presence of lime was investigated in the temperature range of 800-1000 °C. The reduction kinetics was determined by means of weight loss measurements. It was found that the rate of reaction increased considerably with increasing the temperature. The kinetics was also improved when large excesses of lime and carbon were present in the mixture. The effects of catalytic additives of Na₂CO₃ and K₂CO₃ were also investigated. It was realized that the rate of reaction increased by higher concentrations of additives. X-ray diffraction analysis of reduced samples revealed that sulfur was fixed as solid CaS, and metallic copper was formed.

1. INTRODUCTION

Production of metals Cu, Ni, Co, and Pb from their sulfide ores, via conventional pyrometallurgical routes involves different steps of roasting, smelting, and converting. The sulfur dioxide gas evolved during these steps causes major environmental problems. Therefore, the industries related to these nonferrous metals in general, and copper industry in particular, are under intense pressure to reduce emissions of sulfur oxides. In older methods, generally the SO₂ concentration in off-gases is too low to permit an economical production of sulfuric acid. In modern processes although the SO₂ concentration is higher and sulfuric acid can be produced economically, but the huge amount of the gas creates new problems. So, in recent years, many attempts have been made to develop new processes for treating copper sulfide concentrates that do not cause appreciable air pollution by SO₂ emission [1-8]. An alternative method for production of metals from sulfide minerals in which no sulfur oxide gases are produced, is direct reduction of sulfide with carbon in the presence of lime [3-4]. Thermodynamically, copper sulfides could not be reduced to metal in absence of lime. But, it has been shown that in the presence of lime, the equilibrium constant is considerably more than unity for carbothermic reduction reaction of copper sulfide at temperatures near 1000 °C, making the reaction feasible [1]. During this

process, sulfide is reduced to metal and the sulfur is fixed as the solid CaS. The overall reaction may be presented by :



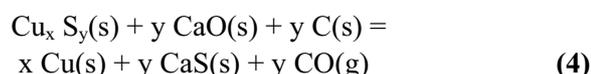
Two steps are involved in this process [2]. In the first step, there is an exchange of sulfide and oxide anions :



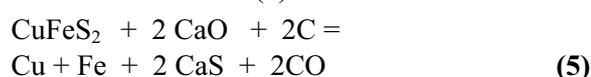
Metal oxide produced in this way is then reduced to metal in the presence of carbon in the second step, which may be shown by :



The sum of these two reactions (2 and 3) is the overall reaction presented above as reaction (1). In the case of copper sulfide, the overall reaction of carbothermic reduction in the presence of lime may be shown by reaction (4), in which the stoichiometric ratios of S/CaO/C is 1/1/1.



In the case of chalcopyrite (CuFeS₂) as copper sulfide mineral, the overall carbothermic reduction reaction in the presence of lime is in the form of reaction (5) shown below:



Although, considerable attention has been given to this method in recent years by many investigators, most of these research works have

been done using high purity chemical grades of metal sulfides, synthesized in laboratory [1,2].

2. MATERIALS AND METHODS

In the present work, copper sulfide concentrate from Iranian Sarcheshme deposits was used, and carbothermic reduction of sulfide in the presence of lime was studied in the laboratory scale. Reduction experiments were performed in air. Kinetics of overall reduction reaction was measured by weight loss using a gravimetric method. In order to protect the mixture during reduction process against oxygen of air, samples were covered with a protective layer of coal. The weight loss due to this layer of coal was measured in a separate crucible containing the same amounts of coal in samples subjected to reduction process in all experiments. The separation of metallic copper from reduced concentrate was not part of this investigation. The catalytic effects of Na_2CO_3 and K_2CO_3 additions on reduction reaction was also studied. Copper sulfide concentrate used in this study, was obtained from Sarcheshme deposits located in the southern part of Iran. The chemical composition of the concentrate was: 29.8% Cu, 25% Fe, 35.5% S, 2.6% CaO, and 6.4% SiO_2 , by weight. In this concentrate, Cu exists mainly as chalcopyrite. Details concerning its mineralogy and physicochemical characteristics can be found in Ref. [9]. Spectrographically pure graphite (- 104 to + 75 μm) was used as a reducing agent. In order to produce pure lime, analytical reagent grade calcium carbonate was calcined at 1000 °C in air long enough to obtain 44 % weight loss as a result of CO_2 evolving. The calcined lime was kept in a desiccator to prevent its hydrolysis and carbonation from ambient air.

Moreover, in each experiment, all materials (calcined lime, graphite, copper concentrate, and catalytic additives) were separately dried for at least one hour at 110 °C, before mixing. In order to study the effects of catalytic additives on reduction reaction, Na_2CO_3 and K_2CO_3 of 99%+ purity, were also used. In all reduction experiments, the samples were prepared by mixing 10 grams of copper concentrate with appropriate amounts of graphite, calcium oxide, and additives (if present) in a laboratory scale ball mill for 5 minutes. The required amounts of

CaO and C in the samples were calculated based on sulfur content of concentrate according to stoichiometric reaction (1).

Reduction experiments were performed in an electric furnace at temperatures of 700 to 1050 °C in air under atmospheric conditions. In order to protect the samples from oxidation, a protective layer of charcoal of +60 mesh was used. A gravimetric method was applied and the progress of reduction reaction was measured by weight loss due to the evolution of CO gas. Relative weight loss was calculated at each experiment using Eq. (6).

$$\text{Relative weight loss } (-) = \Delta W_t / \Delta W_{\text{max}} \quad (6)$$

ΔW_t and ΔW_{max} are the weight loss at time t, and the theoretical weight loss, respectively. It must be noted that each individual point on the curves in “Results and Discussion” section is the result of test carried out on an individual sample.

3. RESULTS AND DISCUSSION

In the first series of experiments, reduction of sulfide in the concentrate with carbon in the presence of lime was studied without using any catalytic additives. The effects of temperature and molar ratio of the components in the samples on the reduction reaction were studied. The results obtained are given below.

3.1. Effect of Temperature and the Relative Proportions of S, C, and CaO

In Fig. 1, the effect of reduction temperature on the relative weight loss of samples due to the reduction reaction are shown, where the S/CaO/C ratio was 1:1:1. As can be realized from this Fig., the average rate of weight loss increases with increasing temperature. It means that the rate of reduction reaction is greatly improved with increasing temperature.

The effect of excess amounts of CaO and C in the mixture was examined in a series of experiments, and is shown in Figs. 2 to 6. In each figure, the results of reduction experiments are compared for the samples in which the S/CaO/C ratio varied from 1:1:1 to 1:4:4 and reduced at the same temperature. At any given temperature, the kinetics of reduction reaction improved with increasing S/CaO/C ratio in the sample. As it can be understood from these figures., the reduction kinetics are greatly improved with excess CaO and C in the mixture.

But, this rate improvement is quite considerable when S/CaO/C ratio increases from 1:1:1 to 1:2:2. While, this ratio becomes less important upon further increase to 1:3:3 and 1:4:4. The reaction mechanism is solid-solid system which generates gaseous CO.

Generally, when there are excess amounts of the solid reactants CaO and C in the mixtures, the conditions become more favorable for generation of the gaseous CO which enhances

the reduction kinetics. It must be noted that, as can be seen in the figures, in some cases the amount of relative weight loss is slightly more than 1.

This could be due to the evolution of volatile matter in the copper concentrate and/or some unknown reactions occurring between the components during reduction experiments. In any case, this weight loss is not considered in the calculation of maximum weight loss.

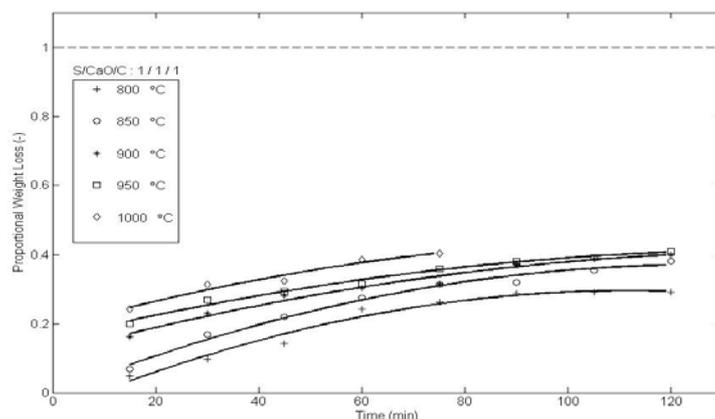


Fig. 1. Effect of temperature on the reduction kinetics of uncatalyzed concentrate:graphite:lime mixture.

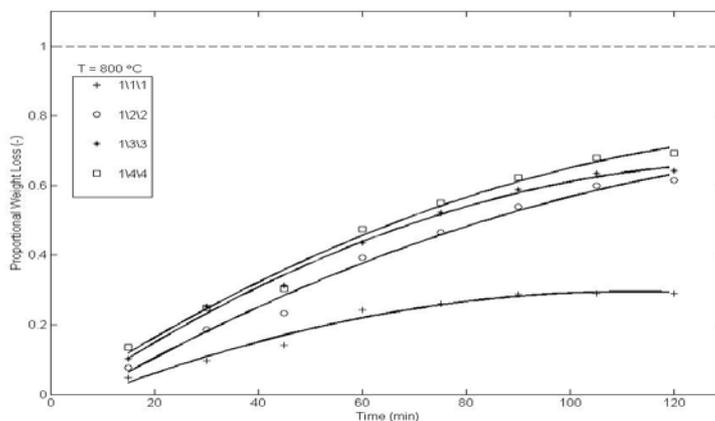


Fig. 2. Effect of S/CaO/C ratio on the reduction kinetics of uncatalyzed mixtures at 800 °C.

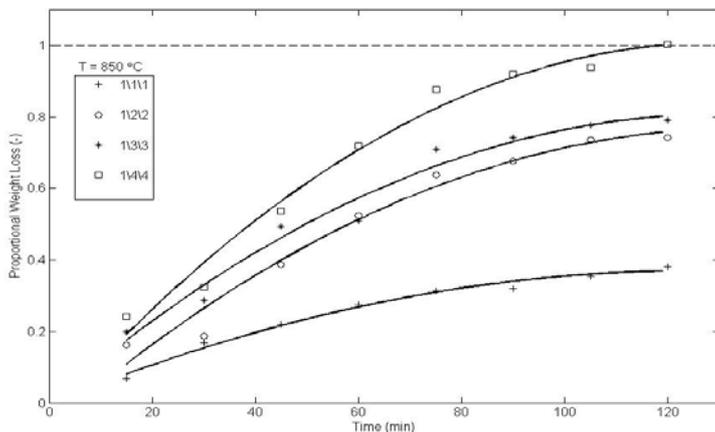


Fig. 3. Effect of S/CaO/C ratio on the reduction kinetics of uncatalyzed mixtures at 850 °C.

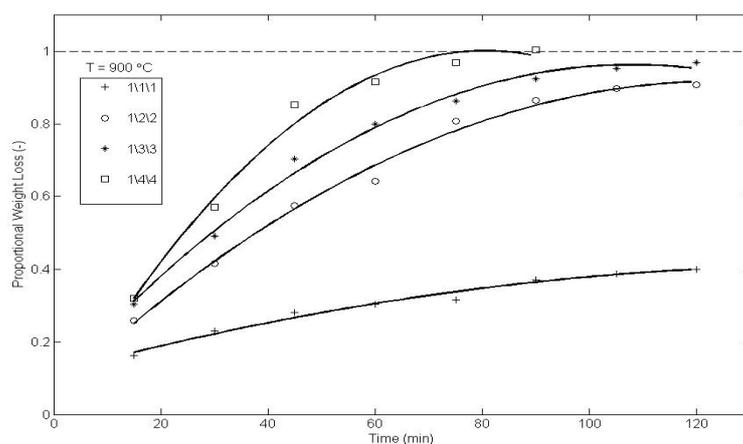


Fig. 4. Effect of S/CaO/C ratio on the reduction kinetics of uncatalyzed mixtures at 900 °C.

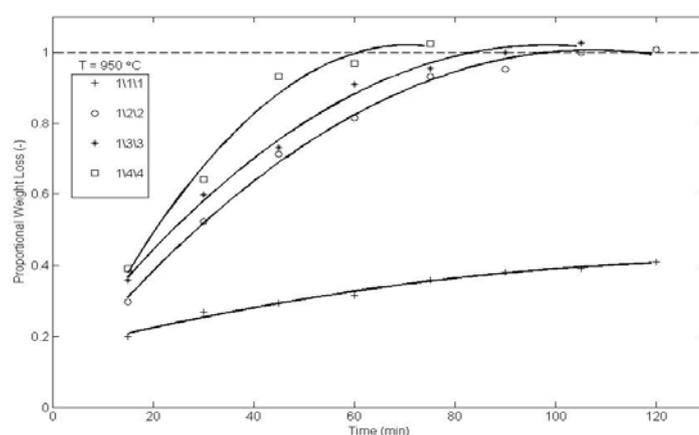


Fig. 5. Effect of S/CaO/C ratio on the reduction kinetics of uncatalyzed mixtures at 950 °C.

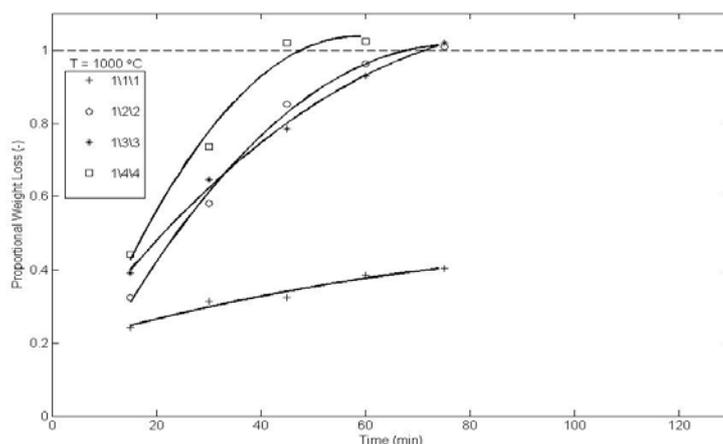


Fig. 6. Effect of S/CaO/C ratio on the reduction kinetics of uncatalyzed mixtures at 1000 °C.

3.2. Effect of Catalytic Additives

The catalysts used in the experiments included Na_2CO_3 and K_2CO_3 . Different amounts of 1 wt%, 2.5 wt%, and 5 wt% additives were used. At each concentration, the reduction tests were performed at temperatures of 800, 850, and 900 °C. The results are shown in Figs. 7-9 for Na_2CO_3 and 10-12 for K_2CO_3 . It can be realized

from these figures that the addition of small amounts of each additive has a great influence on improvement of reduction kinetics, in comparison with uncatalyzed samples. Using more catalysts, up to 5 wt%, has less effect on improvement of reduction kinetics. Comparing Figs. 7, 8 and 9, it can be concluded that increasing temperature also improves the

reduction kinetics. Considering the curves related to the same amounts of catalyst containing samples, it could be realized that the

relative weight loss increases with increasing temperature.

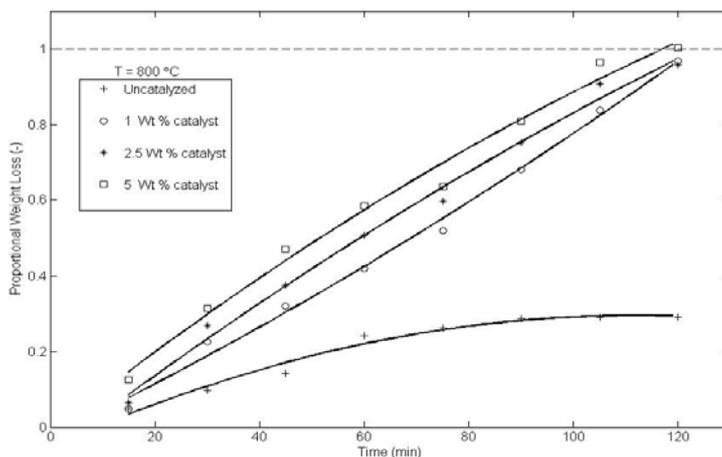


Fig. 7. Effect of Na_2CO_3 catalyst coccentration on the reduction kinetics of mixtures of $\text{S}/\text{CaO}/\text{C} = 1:1:1$ at $800\text{ }^\circ\text{C}$.

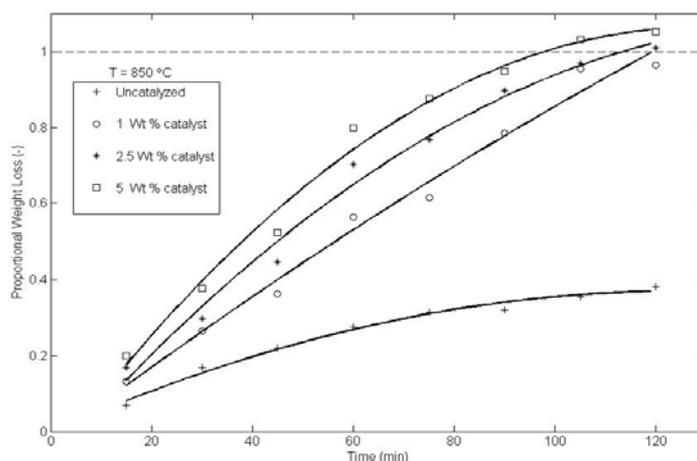


Fig. 8. Effect of Na_2CO_3 catalyst coccentration on the reduction kinetics of mixtures of $\text{S}/\text{CaO}/\text{C} = 1:1:1$ at $850\text{ }^\circ\text{C}$.

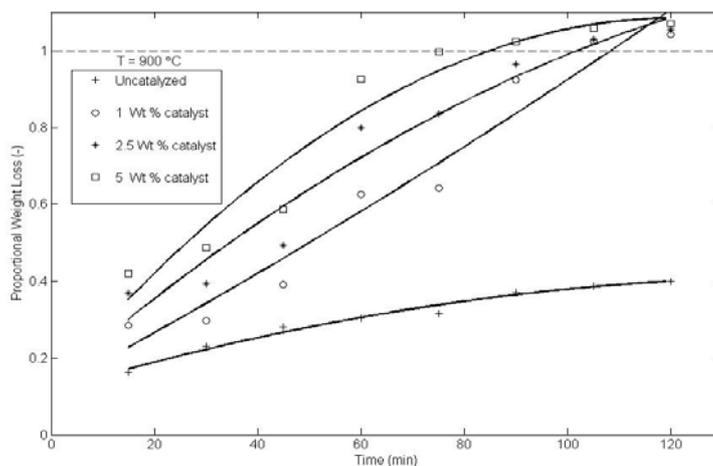


Fig. 9. Effect of Na_2CO_3 catalyst coccentration on the reduction kinetics of mixtures of $\text{S}/\text{CaO}/\text{C} = 1:1:1$ at $900\text{ }^\circ\text{C}$.

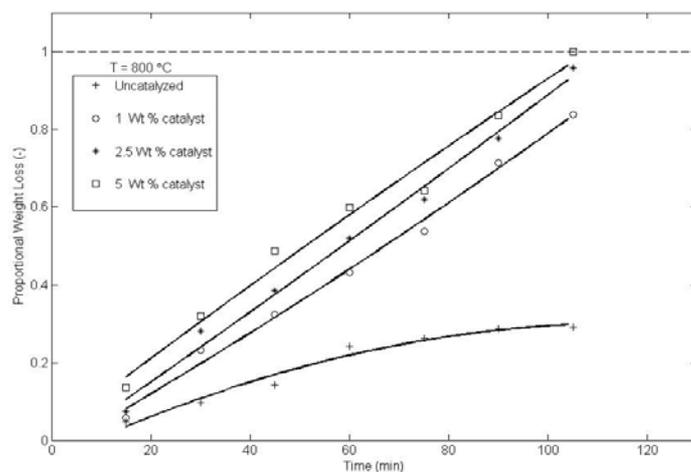


Fig. 10. Effect of K_2CO_3 catalyst coccentration on the reduction kinetics of mixtures of $S/CaO/C = 1:1:1$ at $800\text{ }^\circ\text{C}$.

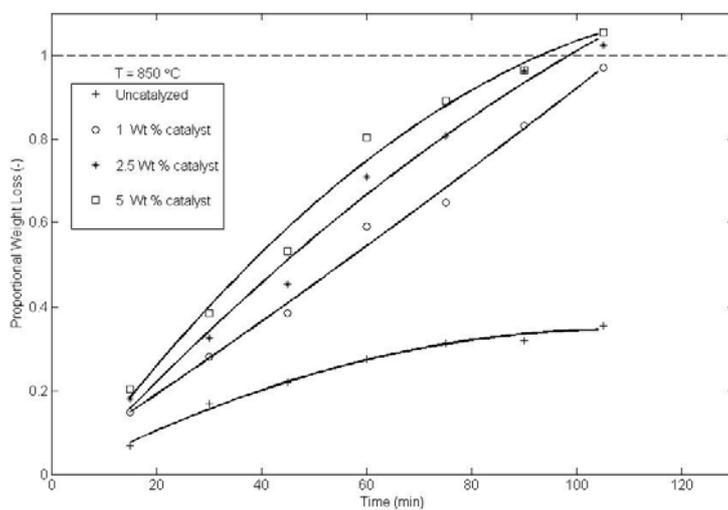


Fig. 11. Effect of K_2CO_3 catalyst coccentration on the reduction kinetics of mixtures of $S/CaO/C = 1:1:1$ at $850\text{ }^\circ\text{C}$.

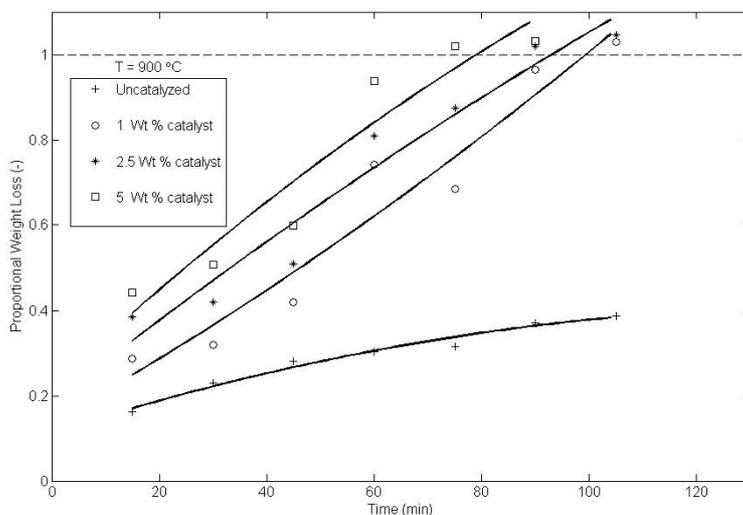
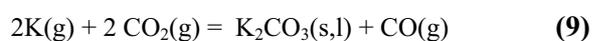
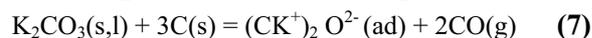


Fig. 12. Effect of K_2CO_3 catalyst coccentration on the reduction kinetics of mixtures of $S/CaO/C = 1:1:1$ at $900\text{ }^\circ\text{C}$.

Comparing the two types of catalysts, it could be observed that K_2CO_3 is more effective than Na_2CO_3 in improving the reduction kinetics. The reduction mechanism in the presence of carbonate catalysts seems to involve the catalysis of the Boudouard reaction. The addition of catalytic substances resulted in enhanced reduction potentials in the gas-phase which is possible only through the catalysis of the Boudouard reaction [2]. In the case of K_2CO_3 catalyzed Boudouard reaction, the mechanism can be explained by following Eqs.



Adding the above reactions yields the Boudouard reaction which is enhanced in the presence of carbonate. The similar mechanism is valid for addition of sodium carbonate. But, K_2CO_3 acts more effectively than Na_2CO_3 as a catalyst. M. Moinpour and Y. K. Rao [2] studied

the catalytic effects of different additives on carbothermic reduction of high purity chemical grades of copper sulphide (Cu_2S) in the presence of lime. Their results also showed that Potassium carbonate was the best catalyst for the direct reduction process.

3.3. Analysis of Reduction Products

The sample with 1:2:2 proportions of S:CaO:C, was subjected to X-ray diffraction analysis, after completion of reduction reaction at $900^\circ C$. This reduced sample, was subjected to magnetic separation followed by X-ray analysis. The phases identified in both samples, included metallic copper, metallic iron, C, CaO, and CaS. There was no evidence of initial phases of concentrate like chalcopyrite or other copper sulfides in the reduced mixture. The magnetically separated reduced sample contained significantly more metallic iron and copper. The results of X-ray diffraction analysis are shown in Figs. 13 and 14.

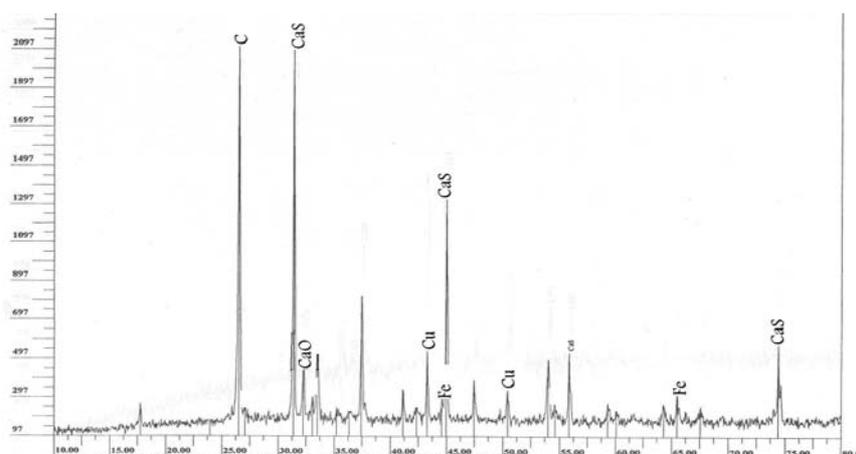


Fig. 13. X-ray pattern of S/CaO/C = 1:2:2 mixture reduced at $900^\circ C$.

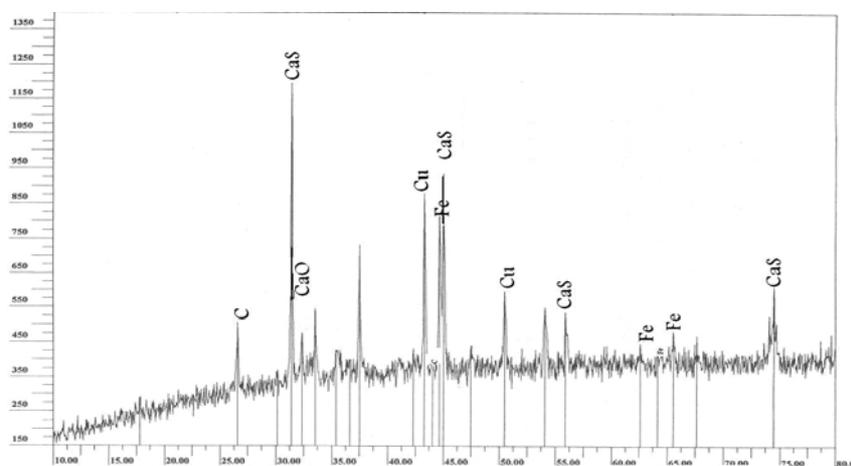


Fig. 14. X-ray pattern of S/CaO/C = 1:2:2 mixture reduced at $900^\circ C$ and subjected to magnetic separation.

4. CONCLUSIONS

In this work, direct reduction of copper sulfide concentrate, from Iranian Sarcheshme deposits, with carbon and lime was investigated. It was found that the process was more feasible at elevated temperatures. The experiments were performed in the temperature range of 800-1000 °C. The progress of reduction reaction and its kinetics was determined by means of weight loss measurements. It was found that the rate of reaction increased considerably with increasing of temperature. The kinetics of reduction reaction was also improved when excess amounts of lime and carbon were used in the mixture. The effects of catalytic additives of Na₂CO₃ and K₂CO₃ were also investigated. It was realized that the rate of reaction increased by higher concentrations of those additives, and that K₂CO₃ was more effective than Na₂CO₃. X-ray diffraction analysis of reduced samples revealed that sulfur was fixed as solid CaS, and metallic copper was formed during reduction.

ACKNOWLEDGMENT

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