

Thermodynamic analysis of copper(I) sulfide chlorination by calcium chloride in the presence of oxygen

RAJKO Ž. VRAČAR and KATARINA P. CEROVIĆ

*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O.Box 494,
YU-11000 Belgrade, Yugoslavia**

(Received 21 December 1998, revised 8 February 1999)

This paper presents a thermodynamic analysis of possible, but insufficiently studied, chemical reactions occurring during the chlorination of copper(I) sulfide by calcium chloride in the presence of oxygen. It formed the basis for assessing the probability and priority of their occurrence. Phase stability diagrams have been plotted for the Cu–S–O–Cl system in the coordinates $\log p(\text{S}_2)$ – $\log p(\text{O}_2)$ – $\log p(\text{Cl}_2)$ in the temperature range from 473 to 773 K.

Key words: thermodynamic analysis, Cu–S–O–Cl system, chlorination, calcium chloride.

Many polymetallic ores and potential mineral raw materials containing non-ferrous metals are not exploited nowadays due to the fact that existing processing methods cannot solve the problems of their chemical, mineralogical and textural features in order to obtain the concentrates with high contents of base metals and low contents of impurities to enable their further metallurgical processing.^{1,2}

From the technological viewpoint, new pyrometallurgical processing methods, used in the production of non-ferrous metals, are very complex and applied to relatively rich ores. However, for processing poor ores and other raw materials these processes are unacceptable either from the point of view of techniques or economics. For these reasons, there has been increased effort worldwide over the last few years, on the research and development of new processes that are more selective than the classical ones and that could enable a successful metallurgical processing of such raw materials. Chlorination is one of the processes being investigated worldwide.

The chlorination of metals in their ores and concentrates is based on the great activity chlorinating agents towards metals, sulfides, oxides and other composites, so that chlorination occurs at significantly lower temperatures than it is the case with other pyrometallurgical processes (oxidation and reduction). The chlorides are obtained with a high vapor pressure at relatively moderate temperatures, enabling either their easy separation from the waste, or they are easily dissolved, and can, thus be further treated hydrometallurgically.

* E-mail: cer@Eunet.yu

Chlorine, hydrochloric acid and metal chlorides, especially of alkaline-earth and alkaline metals, and, on the first place, calcium chloride are used as chlorinating agents.²⁻¹¹

Calcium chloride can only be used as the chlorination agent in the presence of oxygen at sufficiently high temperatures to enable its decomposition. However, the decomposition of calcium chloride occurs at lower temperatures in the presence of SO₂ and SO₃, obtained during the oxidation of metal sulfides.^{1,2,4-7,9-11}

The chlorination of metal sulfides by calcium chloride in the presence of oxygen is particularly interesting from the aspect of using the energy obtained during the oxidation of sulfides and from the environmental point of view because of binding sulfur into dissoluble calcium sulfate. The calcium sulfate can be retreated by hydrometallurgical processes and converted into chloride again, enabling the simultaneous recycling of calcium chloride, which is another contribution to reducing the production cost.^{1,2,7-10}

Bearing all this in mind, as well as that copper(I) sulfide is an important mineralogical component of copper in natural raw materials and a semiproduct of existing technologies, this paper aims at investigating the thermodynamics of the chlorination of copper(I) sulfide by calcium chloride in the presence of oxygen. The obtained information was used as the basis to assess the probability and priority of the occurrence of possible chemical reactions which have not been studied sufficiently.

EXPERIMENTAL

Copper(I) sulfide chlorination by calcium chloride was carried out as follows. Homogenized mixture of copper(I) sulfide (10 g) and 20% of calcium chloride (dried to its constant weight in a drying oven in order to remove humidity) more than stoichiometrically required for the chlorination of copper(I) sulfide to copper(II) chloride was put on a silica vessel in an even layer. Then, it was put into a silica tube, which had been preheated in an electrical furnace to the investigation temperature. A constant flow of oxygen (20 dm³/h) was introduced into the reaction area through a gas purification system and a rotameter. From that moment the reaction time was measured.

The X-ray diffraction of chlorinated samples was carried out on a Simens automatic powder diffractometer model D 5000 with CuK α radiation $\lambda=0.154051\mu\text{m}$. Ni filter, the voltage of 40 kV and the current of 3 A were used for X-ray analysis. X-ray analysis was carried out in angle range from 10° to 80° with step of 0.02 and constant time of 0.25. Before X-ray analysis the chlorinated samples which had been sintered in the process were ground to the particle size 100% –100 mesh. The obtained X-ray recordings of chlorinated samples were analyzed by using "Diffract At" softer which has a data base for identifying phase composition of chlorinated samples.

RESULTS AND DISCUSSION

Thermodynamic analysis

Chemical reactions of the chlorination process. The chemical reactions of copper(I) sulfide chlorination by calcium chloride in the presence of gaseous oxygen have been little and insufficiently investigated without being uniformly determined. Therefore, in order to carry out a thermodynamic analysis, the possible chemical

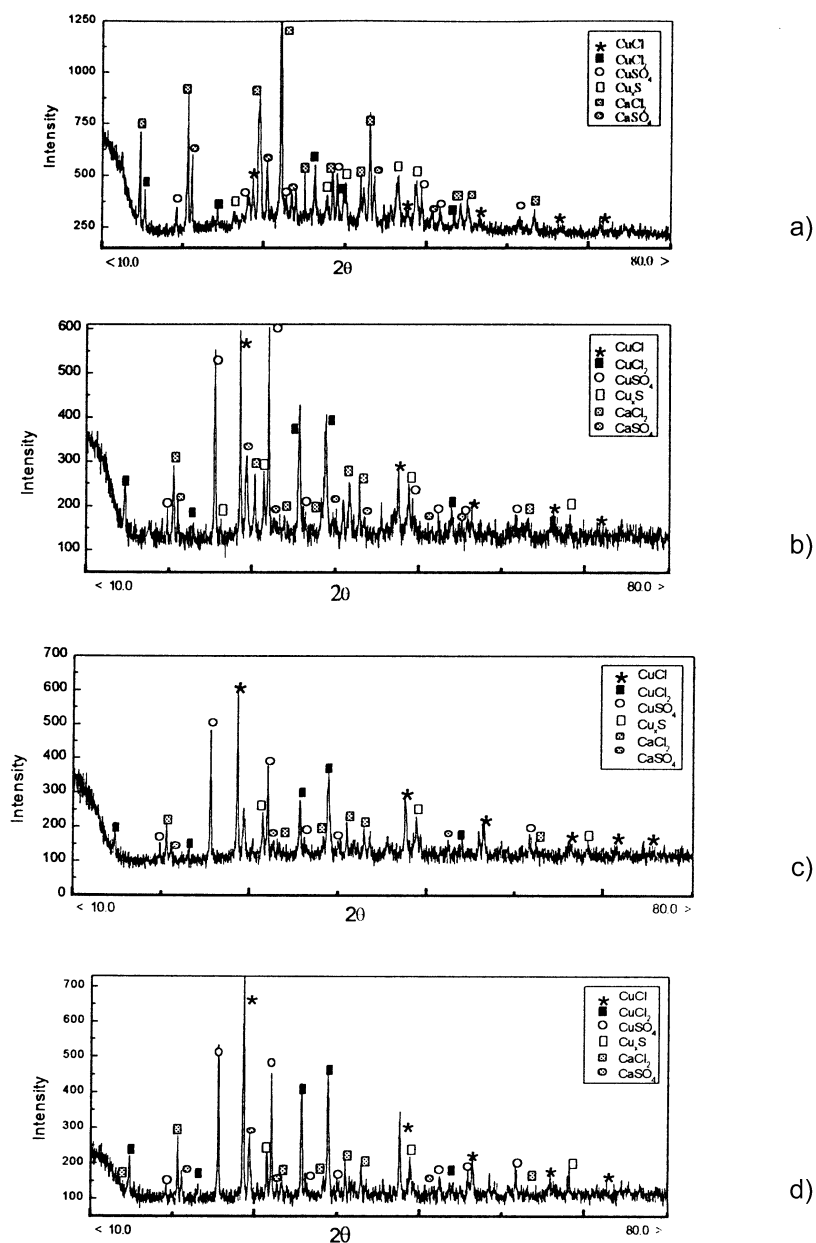


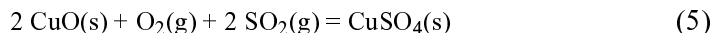
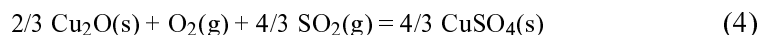
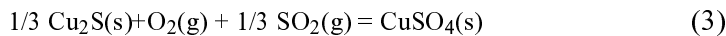
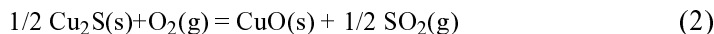
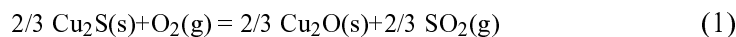
Fig. 1. X-ray diffractograms of the products of the chlorination of copper(I) sulphide by calcium chloride in the presence of oxygen for 30 min at for temperatures a) 473 K, b) 573 K, c) 673 K, d) 773 K.

reactions have been assumed whereas the conclusion of their probability has been drawn from the analysis itself.

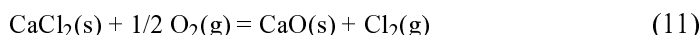
The chemical reactions were assumed on the basis of literature data^{1,2,4,7-15} as well as on X-ray analysis of the chlorination products obtained in the performed experiments (Fig. 1).

On the basis of the above and in accordance with the stability of copper sulfides, oxides and sulfates, *i.e.*, the chemical affinity of copper towards sulfur, oxygen and chlorine, it has been accepted that the chemical process starts with oxidation reactions of copper(I) sulfide to copper(I) oxide, copper(II) oxide and copper(II) sulfate and the oxidation of the copper oxides to copper(II) sulfate in the presence of the formed SO₂. Oxidation-reduction reactions of copper(I) sulfide with oxygen and copper(I) oxide to elementary copper have also been studied thermodynamically where the reaction of copper(I) sulfide with copper(I) oxide is known in copper metallurgy.

Therefore, oxidation reactions within the studied chlorination system investigated thermodynamically are as follows:

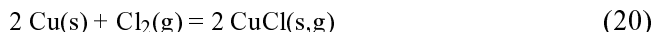
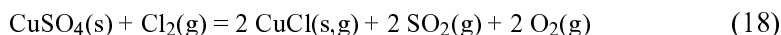
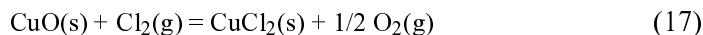
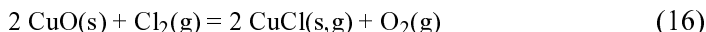
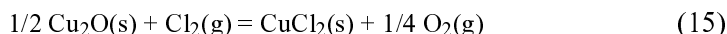
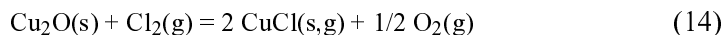
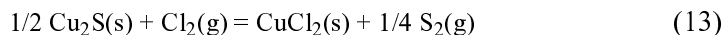
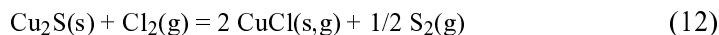


The oxidation products continue to take part in the chlorination, where the chlorine required for chlorination is either formed by decomposition of calcium chloride in the presence of SO₂ and SO₃, or in direct oxidation of calcium chloride by oxygen. In accordance with that Gibbs energies have been calculated for temperature range from 298 to 973 K for the following reactions:

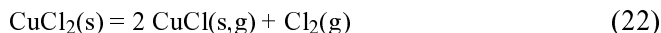


The final results of copper chlorination within the investigated system are copper chlorides: copper(I) chloride and copper(II) chloride (identified on X-ray recordings), the first being insoluble in water and the later soluble. The probability

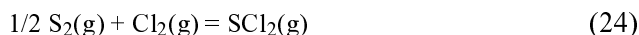
of stable copper(I) sulfide being chlorinated directly, as well as if less stable oxides, copper(I) oxide and copper(II) oxide, and the even more unstable copper(II) sulfate, *i.e.*, elementary copper, are chlorinated, has been shown by thermodynamic analysis of the following reactions:



The dissociation reaction of CuCl_2 to CuCl and Cl_2 was analyzed with particular interest as both products have been experimentally found:



Reactions 12 and 13 show that the formation of elementary sulfur in the vapor state, can be expected in the utilized temperature range. Some authors¹² state that the sulfur vapors can react with gaseous O_2 and Cl_2 and for this reason the following reactions were included in the thermodynamic analysis:



Gibbs energy of the investigated reactions

Thermodynamic analysis of given reactions in the studied system was made with the help of HSC Chemistry software and its data base of thermodynamic values required for the calculation of the change in the values of the Gibbs energy for the reactions in temperature range from 298 to 973 K.

The calculated values of the change of the Gibbs energy are given in Fig. 2,

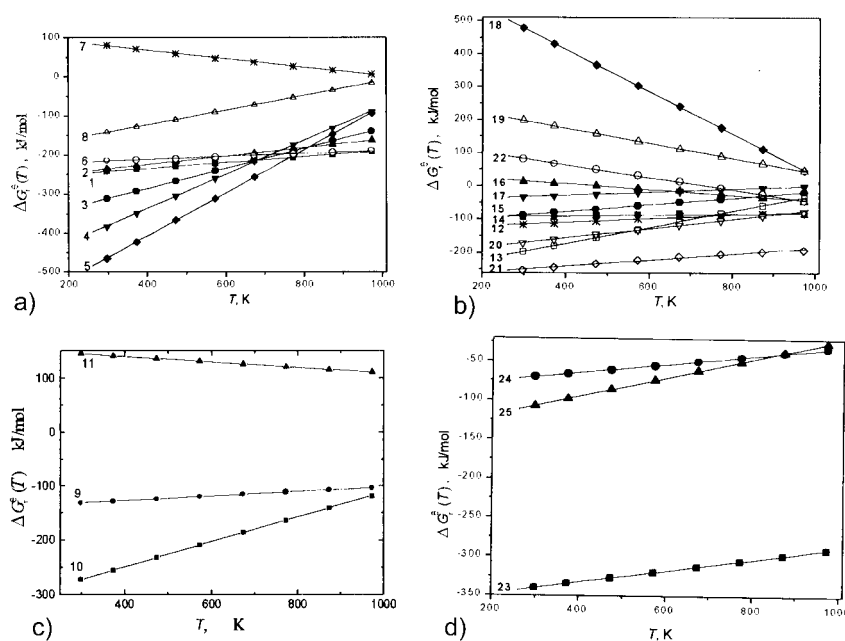


Fig. 2. $\Delta G_r^\circ(T)$ Values as a function of temperature of the analyzed chlorination reactions of copper(I) sulfide by calcium chloride in the presence of oxygen: a) oxidation reaction; b) decomposition reaction of calcium chloride and formation of chlorine; c) reaction of copper chloride formation; d) reactions of sulfur reacting with oxygen and chlorine.

in accordance with an interpretation of certain reaction segments, their character and importance in the process.

The values of $\Delta G_r^\circ(T)$ for the reactions from 1 to 8 (Fig. 2a) show that all, except No. 7, are thermodynamically possible and that their occurrence can be expected in the process. The negative value of the change of the Gibbs energy of these reactions compared to the change in the value of all other reactions, prove the expectations that they have priority and that the overall sequence of chemical reactions starts with their occurrence. In the same way, the more negative values of reactions leading to the formation copper sulfate 3–5 at low temperatures than the values for the direct formation of Cu_2O and CuO oxides, as per reactions 1 and 2, comply to the industrial practice that copper sulfate is formed up to 923 K, whereas above 973 K the sulfate dissociates rapidly forming CuO . The positive values of the change of Gibbs energy for reaction 7 show that it is not thermodynamically possible within the given temperature range, as opposed to the occurrence of the same oxidation reaction of Cu_2S (white matte) in converters in the pyrometallurgical process of obtaining raw blister copper. However, the conversion is performed at higher temperatures (1673 K) and different conditions under which reaction 7 is intensive. This fact is also indicated by the decrease in the value of Gibbs energy with temperature (Fig. 2a).

The assumption that gaseous chlorine, formed by decomposition of calcium chloride, is a chlorinating agent is confirmed by the change in the Gibbs energy of reactions 9 and 10 (Fig. 2b). However, the formation of chlorine by the direct oxidation of calcium chloride by gaseous oxygen is not probable thermodynamically because the corresponding reaction 11 has a positive value of the change of the Gibbs energy. At the same time, reactions 9, 10 and 11 point to the fact that the presence of SO_2 and SO_3 , formed in the oxidation of copper(I) sulfide, is necessary for chlorine to be formed. Thus, it proves again that the oxidation reactions of copper(I) sulfide are the initial chlorination reactions in the $\text{Cu}_2\text{S}-\text{CaCl}_2-\text{O}_2$ system. From the diagram (Fig. 2b) it can be clearly seen that reaction 10 has a more negative change of Gibbs energy than reaction 9 and, therefore, a greater probability of occurrence.

According to given chemical reactions, there arises the question of what is the thermodynamic probability and what is the chlorination priority of the oxidation products like Cu_2O , CuO , CuSO_4 and Cu , *i.e.*, of the initial copper(I) sulfide and of the formation of the final chlorination products, CuCl and CuCl_2 . The answers to these questions are given in the changes of the Gibbs energies of the corresponding reactions, shown in Fig. 2c, from which it can be seen that the chlorination of Cu_2S (12 and 13), Cu_2O (14 and 15), CuO (16 and 17) and Cu (20 and 21), in temperature range from 293 to 973 K, are feasible. However, the positive values of the Gibbs energies for the chlorination reactions of CuSO_4 (18 and 19) show that these reactions do not occur. This is in accordance with literature data¹² and has been shown by our experiments.

Elementary copper and its oxides have not been found by X-ray analysis of the experimentally obtained chlorination products (Fig. 1), which proves that they are completely chlorinated according to reactions 14–17, 20 and 21. The small negative values of the Gibbs energies for the chlorination of copper oxides (CuO , Cu_2O), according to reactions 14–17, indicate the possibility of shifting the balance of their occurrence to the left. However, the shifting of reactions 14–17 in the direction of oxide formation is prevented by the formation of S_2 , according to reactions 12 and 13. On the one hand this is due to the fact S_2 can react with Cl_2 , according to reactions 24 and 25, forming the thermally unstable chlorides S_2Cl_2 and SCl_2 which dissociate at temperature over 300 °C,¹² forming active chlorine atoms which take part in the chlorination. On the other hand, S_2 can react with oxygen according to reaction 23, whose values of the Gibbs energy change of which is significantly lower than the changes for reactions 24 and 25 (Fig. 2d). The formed SO_2 decreases the possibility of reactions 14–17 being shifted to the left, *i.e.*, in the direction of oxides formation. Basically, S_2 reacts here as a reducer and decreases the oxygen concentration in the reacting gas.

Even though the values of Gibbs energies within the investigated temperature range for the oxidation reactions of copper(I) sulfide, 1–3 and 6 (Fig. 2a), are more negative than the values for the chlorination of copper(I) sulfide by chlorine, reactions 12 and 13 (Fig. 2c), these reactions occur simultaneously. The simultane-

ous occurrence of the oxidation and chlorination of copper(I) sulfide results from chlorine ($t_b(\text{Cl}_2) = -35^\circ\text{C}$, $t_b(\text{Cl}_2)$ is boiling temperature of Cl_2) having higher adsorption properties than oxygen ($t_b(\text{O}_2) = -185^\circ\text{C}$, $t_b(\text{O}_2)$ is boiling temperature of O_2), as it is known that gases with low boiling temperatures adsorb on a solid surface with more difficulty than gases with high boiling temperatures.

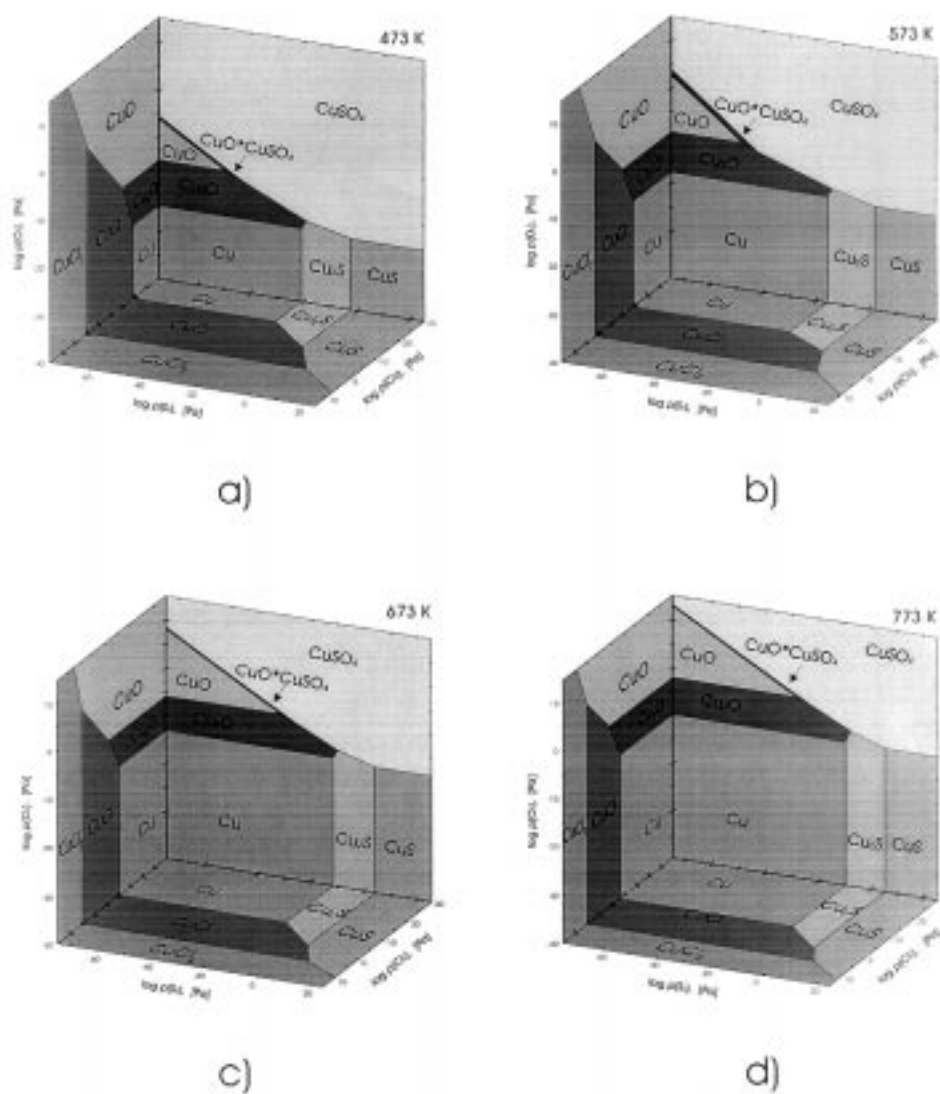


Fig. 3. Phase stability diagrams for the Cu-S-O-Cl system in the coordinates $\log p(\text{S}_2)$ - $\log p(\text{O}_2)$ - $\log p(\text{Cl}_2)$, a) 473 K; b) 573 K; c) 673 K; d) 773 K.

Phase stability diagrams

The HSC-Chemistry thermodynamic analysis software and its data base of thermodynamic values required for the calculation of Gibbs energy changes were used for making the isothermal phase stability diagrams for the Cu–S–O–Cl system shown in Fig. 3 in the coordinates $\log p(\text{S}_2)$ – $\log p(\text{O}_2)$ – $\log p(\text{Cl}_2)$ for the temperature range from 473 to 773 K. The diagrams show that the presence of particular phases and the size of the phases area changes with temperature. To be more precise, the diagrams show that increasing the temperature has a positive influence on the chlorination, as the size of the phase stability area of CuSO_4 , not taking part in the chlorination, decreases with temperature.

CONCLUSION

1. Thermodynamic analysis, based on the calculation of the Gibbs energy changes, of the chlorination reactions of copper(I) sulfide by calcium chloride in the presence of oxygen, the following most important thermodynamic possibilities, *i.e.*, probabilities have been determined:

- The initial starting reactions occurring in the investigated temperature range (298 – 973K) are oxidation reactions of copper(I) sulfide, whereby Cu_2O , CuO , CuSO_4 , Cu and SO_2 are formed.

- Gaseous chlorine, formed by the decomposition of calcium chloride, is the chlorinating agent.

- The decomposition of calcium chloride with the release of chlorine occurs only in the presence of oxygen, as well as SO_2 or SO_3 formed during copper(I) sulfide oxidation.

- Copper chlorides, either the insoluble in water CuCl , or the soluble CuCl_2 , are both, as final products of chlorination, formed in the chlorination of copper(I) sulfides, formed oxides (Cu_2O , CuO) and elementary copper, whereas copper sulfate is not chlorinated.

- Elementary $\text{S}_2(\text{g})$, formed by sulfide chlorination, reacts on the one hand, with chlorine forming the thermally unstable compounds SCl_2 and S_2Cl_2 , the decomposition of which forms active chlorine atoms, and is, on the other, bound in SO_2 , reducing the possibility of oxidation of the formed oxides.

- Increasing temperature reduces the phase stability of CuSO_4 which has a positive effect on the chlorination process.

Acknowledgements. Particular thanks are due to Slavica Zec MSc and the staff of the Vinča Institute of Nuclear Sciences, for invaluable help in carrying out X-ray analysis.

ИЗВОД

ТЕРМОДИНАМИЧКА АНАЛИЗА ХЛОРОВАЊА БАКАР(I)-СУЛФИДА
КАЛЦИЈУМ-ХЛОРИДОМ У ПРИСУСТВУ КИСЕОНИКА

РАЈКО Ж. ВРАЧАР и КАТАРИНА П. ЦЕРОВИЋ

Технолошко-металуршки факултет, Карнегијева 4, 11000 Београд

У раду је дата термодинамичка анализа могућих, а недовољно изучених хемијских реакција које се одвијају у току процеса хлоровања бакар(I)-сулфида калцијум-хлоридом у присуству кисеоника и на тој основи изведена је оцена вероватноће и приоритета њиховог одигравања. Урађени су развијени дијаграми стабилности фаза за систем Cu–S–O–Cl у координатама $\log p(\text{S}_2)$ – $\log p(\text{O}_2)$ – $\log p(\text{Cl}_2)$ за температурни интервал од 473 до 773 K.

(Примљено 21. децембра 1998, ревидирано 8. фебруара 1999)

REFERENCES

1. A. Holmstrom, *Scand. J. Metall.* **17** (1988) 248
2. G. Morizot, G. Barbary, *Extraction Metallurgy*, London Int. Min. Metall. (1980) 151
3. K.L. Luthra, H. S. Ray, D. Kumar, *J. Inst. Eng. India* **53** (1973) 58
4. E. M. L. Peek, *Ph. D. Thesis*, TU Delft, Nederland, (1996)
5. N. Rajmohan, K. T. Jacob, *Min. Metall.Process.* **8** (1992) 141
6. N. Rajmohan, K. T. Jacob, *Min. Eng.* **5** (1992) 235
7. A. Dashed, S. Seetharman, K. T. Jacob, *Scand. J. Metall.* **21** (1992) 242
8. T. K. Mukherjee, C. K. Gupta, *Min. Process. Tech. Rev.* **1** (1983) 111
9. R. Vračar, K. Cerović, *J. Serb. Chem. Soc.* **61** (1996) 903
10. I. Iwasaki, *AIIME Annual Meeting*, New York (1971), p. 1
11. J. K. Gerlach, F. E. Pawlek, *Trans. Am. Inst. Min. Eng.* **239** (1967) 1557
12. F. Haupt, J. Korb, K. Hein, *Erzmetall* **36** (1983) 192
13. T. Rosenqvist, *Principles of Extractive Metallurgy*, McGraw-Hill International Editions, 2nd, Singapore, Sydney, London, 1988
14. V. V. N. S. Ramakrishna Rao, K. P. Abraham, *Metall. Trans.* **2** (1971) 2463
15. M. E. Wadsworth, K. L. Leiter, W. H. Porter, J. R. Lewis, *TMS-AIIME*, **218** (1960) 519.