THE COPPER LOSSES IN THE SLAGS OBTAINED BY PLASMA REDUCTION PROCESS

Ivan Imris & Alexandra Klenovcanova
Technical University of Kosice, Slovak Republic

ABSTRACT

The chemical industries are using different type of catalysts, which after application usually produced many tons heap of residues. One of them is cupric oxide catalyst with high content of copper and silica. The recovery of copper from the waste has become major interest from a viewpoint of environmental protection and recycling of resources. The thermodynamic analysis and experimental results suggest that the copper from cupric oxide catalyst can be extracted by plasma reduction process. By plasma reduction process the crude copper and inert slag is obtained. The copper recovery from cupric oxide catalyst are depending mainly on the copper loses in the slags. In this work, the copper losses in the slags from Plasma Reduction Process has been studied and described.

INTRODUCTION

The chemical industries use many different type of catalysts, which after application usually originated many tons heap of residues. One of them is used cupric oxide catalyst ESM 461 with following chemical composition: 30% CuO, 32% SiO_2, 4% MgO, 4,5% CaO, 4,5% Fe_2O_3, 0,012% Ni+Co and 20% C, with density 750,0-900,0 $kg.m^{-3}$. The recovery of copper from the waste has become major interest from a viewpoint of environmental protection and recycling of resources. The thermodynamic analysis and experimental results suggest that the copper from cupric oxide catalyst can be extracted by plasma reduction process. By Plasma Reduction Process the inert slag and crude copper could be obtained.

The copper recovery from cupric oxide catalyst by Plasma Reduction Process is depending mainly on the copper loses in the slags so in this work, the copper losses in the slags from Plasma Reduction Process has been studied and described.

THERMODYNAMICS OF THE Cu-Si-Ca-O-C SYSTEM

When components of low concentration in used cupric oxide catalyst ESM 461 such as iron, nickel and cobalt and neutral slag making oxide MgO are neglected, the reduction behaviour of copper and iron from used cupric oxide catalyst can be considered as equilibrium in the system Cu-Si-Ca-O-C, where the copper, silica, calcium, and oxygen are main catalyst components and the carbon is reductant. The temperature and partial pressure of oxygen have been chosen as the independent variables for the system.

From thermodynamic calculation has been predicted that the decomposition of CuO to Cu_2O by reaction:

$$2CuO_{(s)} = Cu_2O_{(s)} + 1/2O_{2(g)} \qquad \Delta G^o_T = - 142610 + 103.85.T \tag{1}$$

is running at much lower temperature (1100°C) as is temperature of plasma reduction process (1600°C), so the stability regions of the phases in the system Cu-Si-Ca-O-C can be calculated from standard free energies summarized in Table 1 [1, 2]. The results of calculation are presented in Figure 1 in log $p_{CO2}/p_{CO} - 10^4/T$ coordinates.

Table 1: Standard free energy values for reactions considered in Figure 1

No.	Reaction	(J.mol-1)
(2)	$Cu_2O_{(s)} + CO_{(g)} = 2Cu_{(s)} + CO_{2(g)}$	$\Delta G^o_T = -116\,665 + 19.25.T$
(3)	$Cu_2O_{(s)} + CO_{(g)} = 2Cu_{(l)} + CO_{2(g)}$	$\Delta G^o_T = -101\,720 + 8.745.T$
(4)	$Cu_2O_{(l)} + CO_{(g)} = 2Cu_{(l)} + CO_{2(g)}$	$\Delta G^o_T = -163\,215 + 49.56.T$
(5)	$SiO_{2(s)} + 2CO_{(g)} = Si_{(s)} + 2CO_{2(g)}$	$\Delta G^o_T = 337\,390 - 0.01.T$
(6)	$SiO_{2(s)} + 2CO_{(g)} = Si_{(l)} + 2CO_{2(g)}$	$\Delta G^o_T = 388\,042 - 30.15.T$
(7)	$CaO_{(s)} + SiO_{2(s)} = CaO.SiO_{2(s)}$	$\Delta G^o_T = -83\,300 + 3.43.T$
(8)	$2\ CaO_{(s)} + SiO_{2\ (s)} = 2CaO.SiO_{2\ (s)}$	$\Delta G^o_T = -126\,420 - 5.02.T$
(9)	$2\ CO_{(g)} = C_{(s)} + CO_{2\ (g)}$	$\Delta G^o_T = -170\,790 + 174.55.T$

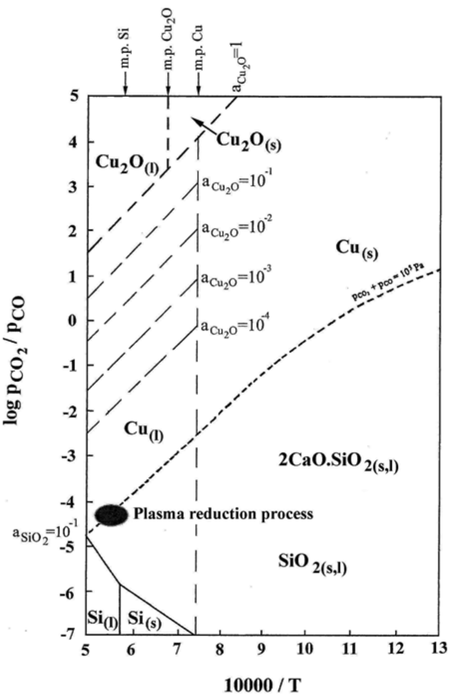

Figure 1: Predominance area diagram of the system Cu-Si-Ca-O-C

If plasma smelting temperature is 1600°C and the system is saturated by carbon then the equilibrium in the furnace atmosphere will be the same as the equilibrium for the Bell - Boudouard´s reaction (9) and the condition for plasma reduction process in Figure 1 can be indicated as dashed area. Under these smelting conditions the copper oxides will be reduced and form the liquid copper phase and slag making oxide such as SiO_2, CaO and MgO will be melted into the liquid slag phase as is documented in Figure 2 [3]. This means that the copper extraction from used cupric oxide catalyst by reduction plasma reduction process, consisting from two essential steps - chemical reactions followed by liquid phases separation, can be described by equilibrium between two liquid phases - copper and silica slag and gas phase assuming that the copper recovery will be limited by copper losses in the slag.

The copper losses in the silicate slag can be divided into two main forms mechanical and physico-chemical losses [4]. The mechanical copper losses in the slag can be considered as particles of mechanically entrapped or floating unsettled droplets of the coexisting copper phase, their size varying from several millimeters to a few microns, is very difficult to predict. The physico-chemical losses in the slag are caused mainly by solubility of copper in oxide forms. According to the phase diagram Cu_2O-SiO_2 presented in Figure 3 [5] and data of Altman and Kellogg [6] and Björkman [7] the final form of the dissolved copper in the acid solution is cuprous ions, which forms the orthosilicate Cu_4SiO_4 by reaction:

$$2Cu_2O_{(s)} = SiO_{2(s)} = Cu_4SiO_{4(l)} \qquad \Delta G^o_T = -\,295075 - 200.25.T \qquad (10)$$

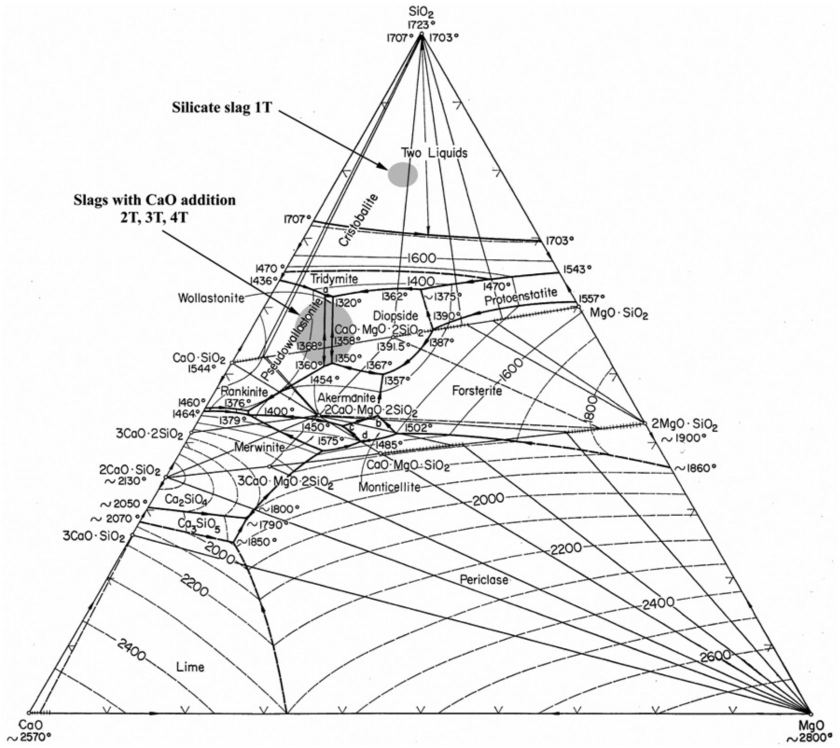

Figure 2: Phase diagram SiO_2-CaO-MgO

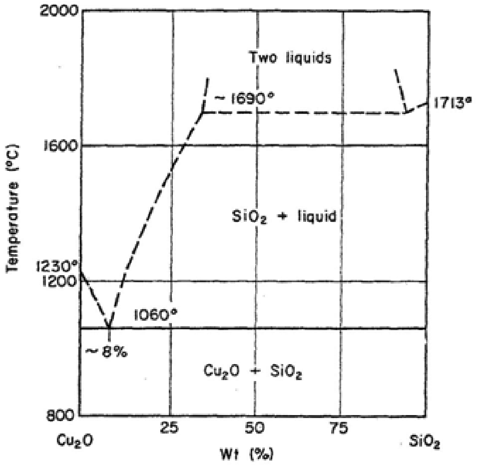

Figure 3: Phase diagram Cu_2O-SiO_2

To increase the copper recovery by decreasing the copper oxide solubility in the silicate slag some basic flux addition, such as CaO is needed. This assumption is in good agreement with experimental data summarized by Mackey [8], which show that the CaO addition lowering the copper oxide solubility in silica-saturated slags.

PLASMA REDUCTION PROCESS

To verify the thermodynamic calculations and assumptions two type of plasma reduction smelting tests were carried out on pilot scale 80 kVA DC transfer plasma arc reactor with single hollow graphite electrode. The diagram and the photograph of pilot scale plasma reactor are shown in Figure 4.

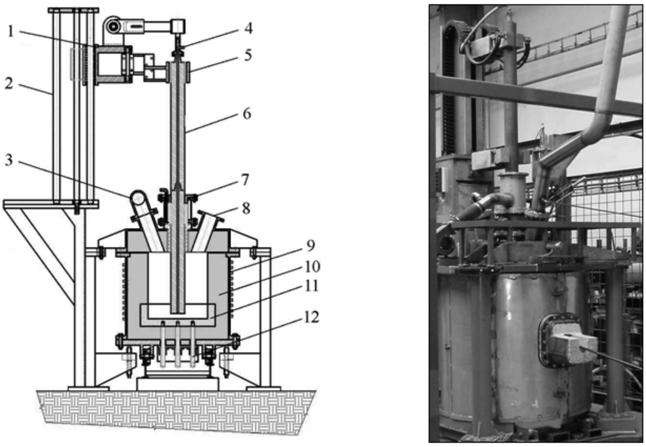

Figure 4: The diagram and view of the 80 kVA DC transferred plasma arc reactor. 1-cathode motion mechanism, 2-rack, 3-off-gas port, 4-plasma forming gas-nitrogen, 5-cathode clamp, 6-hollow graphite electrode–cathode, 7-water- cooled cathode sealing, 8-materials feeding port, 9-steel shell, 10-alumina lining, 11-graphite crucible-anode, 12-anode connection.

The plasma reactor consists from cylindrical steel shell lined with a castable alumina ended with the graphite crucible, serves as the reactor hearth and the anode. Three stainless steel rods are used for connection of graphite crucible anode to air-cooled copper clamps. The taphole is located in the graphite crucible near the hearth. The cathode is the central graphite hollow electrode, with 100 mm diameter, arranged in a vertical configuration with sufficient mechanical movement, which provides up and down movement of the electrode during the operation of plasma reactor. During operation the nitrogen gas flow through the hollow graphite electrode is used as plasma forming gas and the charge in the size range from 0.1 to 5.0 mm is continuously feeding directly under gravity through the feed port into the bath near plasma arc column without any air penetration into the plasma reactor. The reactor is supplied with an 80-kVA ± 20% three-phase transformer and AC-DC tyristor controlled rectifier. Variable power intensity can be selected. The running of the plasma reactor is monitoring and control by electrical computerized control system.

For first series of plasma reduction smelting tests the mixture of used cupric oxide catalyst ESM 461 and carbon reductant with stochiometric amounts of carbon required for copper oxide reduction. As carbon reductant was used very fine carbon residue from electrode production with following composition: 12.25% Cu and 87.75% C.

For second bunch of plasma reduction smelting tests the mixture of used cupric oxide catalyst ESM 461 with stochiometric amounts of carbon reductant and 10% addition of calcium oxide flux with following chemical composition: CaO+MgO min. 90%, MgO max. 5% and CO_2 max. 4% has been used.

The smelting condition for all tests was constant. During all reduction smelting tests the nitrogen gas flow through the hollow graphite electrode with flow rate 8.5 $dm^3.min^{-1}$ has been used as plasma forming gas. The smelting temperature in plasma reactor 1873 K was keeping in constant level by operational power rating varied from 55 to 60 kVA and by the feed rate of the charge. After smelting approximately 60 – 70 kg of the charge, the liquid copper and slag were tapped from the plasma reactor into the mould where the copper slag separation takes place. The cooled products – copper and slag were separated and weighed and samples from both phases were analysed using various physical and chemical methods. The typical chemical composition of copper and slag are summarized in Table 2. The slag sample was polished and observed by microscopic examination. The results of microscopic examination are documented by micrograph in Figures 5-10.

Table 2: Typical chemical composition of copper and slag

No.	**Products**	**Flux**	**Chemical composition (wt.%)**						**Distribution**
			Cu	**Fe**	**SiO_2**	**CaO**	**MgO**	**Al_2O_3**	**Cu (%)**
1-Cu	Copper	-	99.04	0.042	-	-	-	-	57.74
1T	Slag	-	21.60	6.48	64.96	8.97	4.84	1.89	42.26
2-Cu	Copper	CaO	98.79	0.204	-	-	-	-	94.71
2T	Slag		2.18	4.37	51.49	25.58	6.32	2.10	5.29
3-Cu	Copper	CaO	98.76	0.24	-	-	-	-	95.84
3T	Slag		1.85	4.63	55.57	25.34	11.19	0.94	4.16
4-Cu	Copper	CaO	98.61	0.39	-	-	-	-	99.78
4T	Slag		0.081	4.40	45.74	39.99	7.78	1.90	0.22

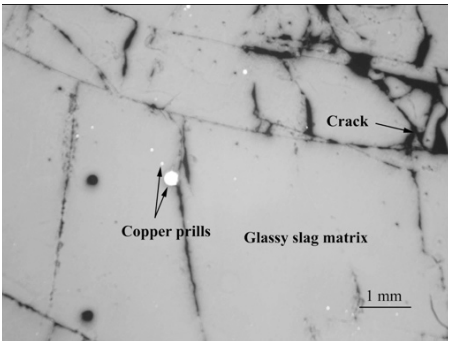

Figure 5: Microstructure of fast cooling slag 2T

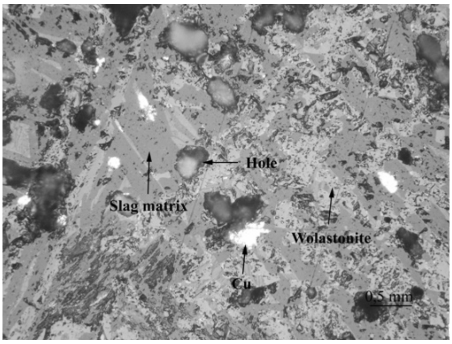

Figure 6: Microstructure of slow cooling slag 2T

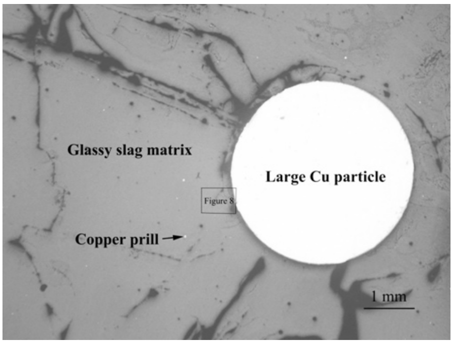

Figure 7: Microstructure of fast cooling slag 3T

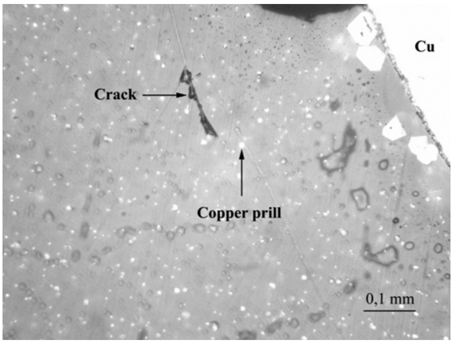

Figure 8: Microstructure of fast cooling slag 3T
(Detail of Figure 7)

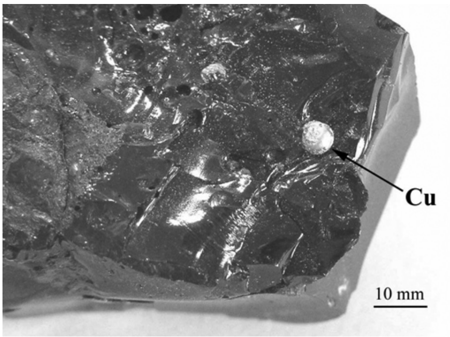

Figure 9: View on copper particle in fast cooling slag 1T

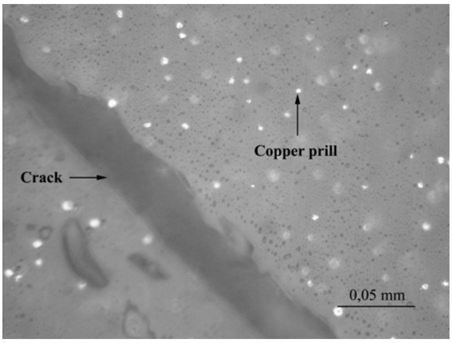

Figure 10: Microstructure of fast cooling slag 4T

DISCUSSION

The thermodynamic analysis and experimental results suggest that the copper from cupric oxide used catalyst can be extracted by plasma reduction process. In agreement with thermodynamic calculations the cupric oxide was reduced to liquid copper and slagmaking oxides such as SiO_2, CaO and MgO was melted into the liquid slag phase.

The microscopic examination of quenched and slowly cooled slags shows that the calcium siliceous slags contain some pseudowolastonite or wollastonite crystals distributed in glassy slag matrix with limited amount of copper prills. The size of phases in solidified slag is depending on the slag composition and cooling rate. Fast cooling rate renders the amorphous slag structure. Slow cooling rate promotes the formation and growth of crystalline phases. The difference between microstructure of quenched and slowly cooled slags is evident from Figures 5 and 6.

During slow cooling rate of the slag the pseudowolastonite or wollastonite is first crystallizing, forming skeleton-dendrites. The slag matrix and copper phases with lowest melting points are solidified last. Therefore the mechanical copper loses in slow cooling slag are presented by solid metals particles at the boundaries of earlier solidified pseudowolastonite or wollastonite crystals as is documented in Figure 5. If the slag-cooling rate was very fast and slag was quenched the mechanical copper losses in solid slag are represented by spherical copper prills in the amorphous slag matrix as is presented in Figures 6-8. Figure 9 shows example of the large copper particle entrapped in the slag (1-T) with high silica content. And Figure 10 is presented the structure of slag (4-T) with low concentration of copper and silica too.

The microscopic examination of polished samples of the slags from Plasma Reduction Process showed that the copper losses in the slag are mainly as mechanically entrained copper prills there sizes varying from several millimeters to a few microns. Stokes' law may theoretically calculate the settling rate of copper prills mechanically entrapped or floated in the slag:

$$\nu = \frac{2}{9} \cdot \frac{g.(\rho_1 - \rho_2).r_D^2}{\mu_2} \tag{11}$$

Assuming that the variation of the densities of slag and copper prills on composition is negligible low and the diameter of copper prills is constant, the main factor to influence the rate of copper prills settling will be the slag viscosity. The significant effect for viscosity of the slag had silica content and the largest copper prills were observed in the slag 1-T with highest silica content (Figure 9) and only very fine copper prills was observed in the slag 4-T with lowest silica content in the slag (Figure 10). The mechanical copper losses in the slags are difficult to predict but the effect of slag viscosity is significant. Therefore there is a reason to believe that good slag composition with low viscosity will result the lowest mechanical copper losses in the slag.

The copper oxide solubility in the system Cu_2O-SiO_2 (Figure 2) is relatively high so the copper recovery in first series of plasma smelting tests, where the mixture of used cupric oxide catalyst with carbon reductant was used, was very low as is documented in Table 2. In the second series of plasma reduction smelting tests, when the calcium oxide flux has been added into the charge and the pseudowolastonite or wollastonite was formed in the slag, the copper recovery was higher as it is seen from Table 2. This is in good agreement with experimental data summarized by Mackey [8], which shows that the CaO addition lowering the copper oxide solubility in silica-saturated slag and with thermodynamic calculation, which shows that, the standard free energy for reaction (8) is more negative ΔG°_{1873} = -135820 J.mol^{-1} as for reaction (10) ΔG°_{1873} = -79990 J.mol^{-1}.

On the basis of this thermodynamic and experimental data and microscopic examination of the slag samples the suggestion can be made that high copper recovery from cupric oxide used catalyst ESM 461 by plasma reduction process could be made only with calcium oxide addition. To minimize the mechanical copper losses in discharge slag, the plasma reactor has to be switch off for some period of time before tapping, to improve copper prills separation from the slag by settling process.

CONCLUSIONS

The thermodynamic analysis and experimental results suggest that the copper from cupric oxide used catalyst ESM 461 can be extracted by plasma reduction process. By plasma reduction process following products may be extracted:

- Copper with low concentration of minor elements
- The inert slag with low concentration of copper which can be used in civil engineering.

The copper recovery from cupric oxide catalyst are depending mainly on the copper loses in the slags which can be divided into two main forms mechanical and physico-chemical copper losses.

The mechanical and physico-chemical copper losses in the slag can be minimazed by calcium oxide addition into the charge and correctly made smelting and tapping process.

NOMENCLATURE

ν = Rate of settling, cm.s^{-1}.
ρ_1 = Density of matte, g.cm^{-3}.
ρ_2 = Density of slag, g.cm^{-3}.
μ_2 = Viscosity of the slag, P.
r_D = Diameter of the particle, cm.

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