

## CHEMICAL, PHASE COMPOSITION AND MORPHOLOGY OF COPPER CAKE AS A SECOND MATERIAL FOR PURE COPPER ELECTROEXTRACTION

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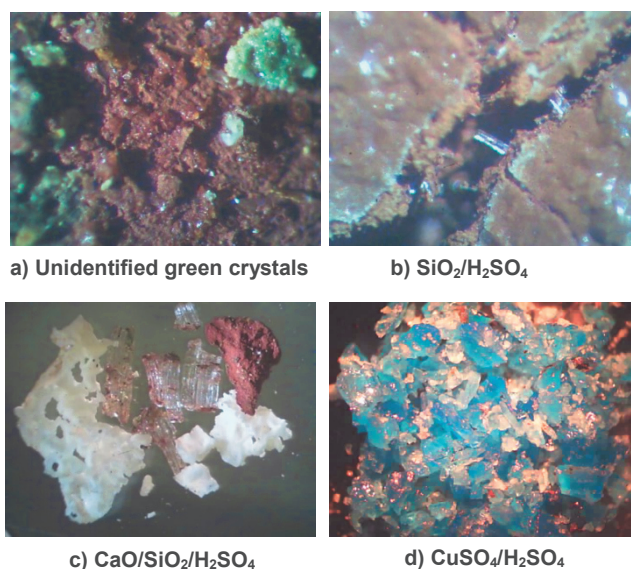
### Abstract

In this study were investigated the surface morphology, chemical content and phase composition of two sorts of copper cakes from zinc plant of KCM-Plovdiv, Bulgaria. The aim of this research is the utilization of valuable copper from copper cakes and reduction the amounts of the specific secondary wastes from hydrometallurgy plants. The copper cake with low chlorine content was tested for leaching with diluted 12% sulphuric acid. The very first results indicate that at simple leaching the cake suspension with the mineral acid generates a substantial amount of dissolved copper sulphate. The leaching process, respectively the concentration of the copper sulphate, has the potential to be further optimized for direct formation of copper sulphate electrolytes from this specific waste product.

**Keywords:** copper cake, surface morphology, cuprite, sulphuric acid leaching

### 1. INTRODUCTION

The copper and copper-Cl cake under investigation are dense red-brown colour filtrates from zinc plant of KCM-Plovdiv, Bulgaria. The first type cake is a product from roasting line of the zinc plant and contains predominantly 66 % cuprous (I) oxide ( $\text{Cu}_2\text{O}$ ). The second type waste is a product from "Waelz" zinc line and contains 45 %  $\text{Cu}_2\text{O}$  and 4 %  $\text{CuCl}$  [1,2]. The copper (I) oxide forms the mineral cuprite which is a raw material in mine industry. In principle, copper cakes are product of cementation process and they consist of very small submicron particle aggregates [1,2]. These specific wastes have very complex chemical composition including mainly different copper, zinc and lead compounds, as well as a large variety of metal impurities. Most of them formulate in the cake different oxide-, sulphate- and mixed chemical structures.



**Fig. 1** Crystallization products from copper cakes

Fresh copper cakes contain large amount of water and have grease consistency. After deposition they loose water rapidly by capillary mechanism. The process of water evaporation is very intensive especially on the cake surface or in open flaws and this leads to appearance of different crystallization products (**Fig. 1, a-c**). This fact as well as the complex chemistry, they specify the copper cakes as a dynamic hazardous waste product at storage conditions. For example the main component copper oxide (I) is extremely toxic for aqua species [3]. Presently, the Bulgarian pyro- and hydrometallurgy industry does not utilize the copper cakes from KCM zinc plant [1,2]. The company for pure zinc and lead metal production disposes the copper cake as a product for industrial applications. In this study the copper cake was regarded as a new starting material for pure copper metal recovery by cathode

electroextraction. For this reason we recall the well known fact that the copper (I) oxide is a soluble compound in dilute sulphuric acid by formation copper (II) sulphate [4]. Presently, the extracting ammoniacal alkaline solutions are more effective than mineral acids [5]. However, the sulphuric acid was chosen as leaching agent accordingly the current technology of the industrial plant. The waste cakes were produced by cementation of copper ions with zinc powder in sulphuric acid solutions [1]. The sulphuric acid finds broad applications as leaching agents of metal copper for example in waste printed circuit boards [6], metal recovery from waste slags and cakes [7], leaching of copper chloride from ores and concentrates [8]. The combination of leaching process of valuable metals with sulphuric acid followed by electroextraction is also a perspective method for pure copper metal production [9].

## 2. EXPERIMENTAL PART

Copper cake was stored at laboratory conditions in wet grease form or dried powder form. The wet form of fresh cake was displaced in open and close glass dishes for gravimetric measurements of water evaporation intensity and morphology observation of crystallization products. The powder cake was obtained after several drying procedures in a laboratory furnace in the temperature interval between 60 to 120 °C. The duration of each heating step was two hours and procedure was repeated until reaching constant weight at room temperature. The samples were stored in an exicator to prevent mass changes from atmospheric humidity. The dry powder was used for X-ray analyses, whereas the wet form was used for acid leaching.

The observations of morphology and crystallization processes on waste surface were performed by stereomicroscope M5C-09 and digital eyepiece camera DEC-18 equipped with ScopePhoto software.

The elemental analysis of waste cake was performed in the KCM-Plovdiv by atomic absorbance spectroscopy. The amounts of copper and copper-Cl cakes were afforded for further investigations directly from the zinc plant together with daily routine analyses.

The X-ray analysis was performed in the Crystallographic Laboratory of the Institute of Mineralogy - Bulgarian Academy of Sciences. The distribution of chemical elements in different phases in copper cake was determined by conventional X-ray powder diffraction from prepared thin sample films on a membrane holder. The cake samples were performed according the procedure shown on **Fig. 3** after full drying of appropriate cake amounts in glass dishes. The sintered cake probes from drying procedures were gently grinded to fine powder and thoroughly homogenized.

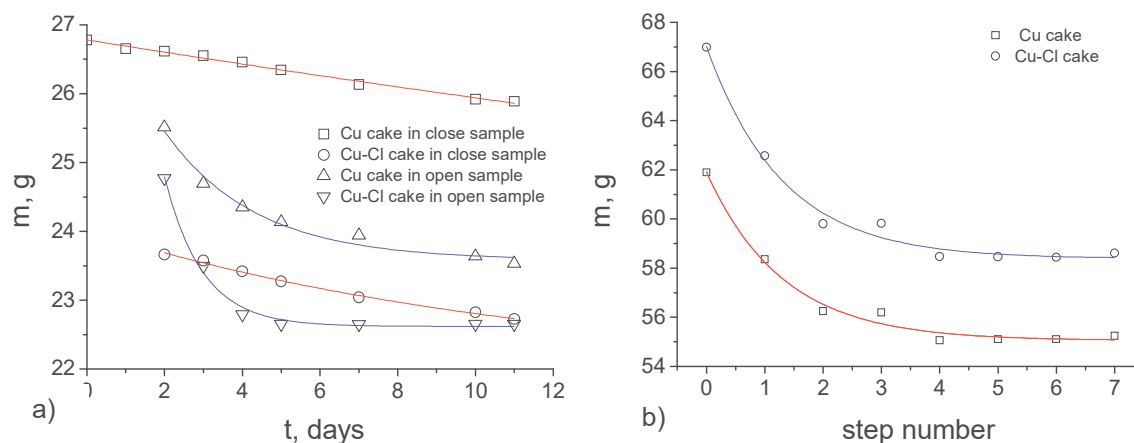
The leaching procedure was performed as follow. A small quantity of the fresh cake was weighed and placed in a cylindrical glass equipped with Teflon stirrer. The diluted sulphuric acid solution (12 %) was added very gently in small 20 ml portions. With the very first portions the dense cake became fluidized and gradually turned in to liquid suspension by the help of a glass stirrer. At this point the magnetic stirrer device was switched on to homogenize the bulk solution with the next fresh leaching portions. The characteristic colour of obtained suspension was dark brown mixed with dark blue due to fine dispersed submicron copper oxide particles in the leaching solution and simultaneous formation of blue copper sulphate. The used mineral acid predominantly dissolves the rests of elementary copper present in the cake as well as other soluble chemical impurities. The leaching procedure was also carried out by gradually increasing the temperature up to 90 °C for two hours. The leaching was finished by switching the stirring off and procedure for sedimentation of copper oxide particles. The sediment copper cake after leaching procedure was collected for additional gravimetric and analytical analyses. The centrifugation was performed by laboratory centrifuge model T 23D at 3500 rpm for 30 min. The leaching suspensions were separated in centrifugation glass tube with dimensions 98 mm (high) x 22 mm (inner diameter). The obtained clear supernatant solution was particularly separated from the bottom sediment and the moderate blue solution was used for analytical determination of copper and zinc ion concentrations.

The concentrations of copper and zinc ions in the leaching solutions were determined by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES). The analysis was performed in the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences. Purposely the probes were appropriately diluted and were prepared calibrating solutions containing copper and zinc ions. The accuracy of ICP-AES analysis was checked by comparison of the results with reference solution, containing 1.0 g/l CuSO<sub>4</sub>.

### 3. RESULTS AND DISCUSSION

#### 3.1 Waste evaporation kinetics and drying

The study of evaporation process was conducted to predict the behaviour of the cakes at storage conditions. The rates of water evaporation from both wastes are shown in **Figs. 2a, b**. The all experimental curves (**Fig. 2a**) depict the kinetics of mass decrease of cake samples at laboratory conditions. The closed samples (the parallel red curves) loose water monotonically with the time whereas the open samples (blue curves) loose water more intensively in the first two days. The open sample of copper-Cl cake evaporates most intensively than other samples. After the intensive evaporation process in the case of open samples the mass of waste cakes remains constant for 5 - 6 days. From this point the mass of all samples starts to increase slowly.



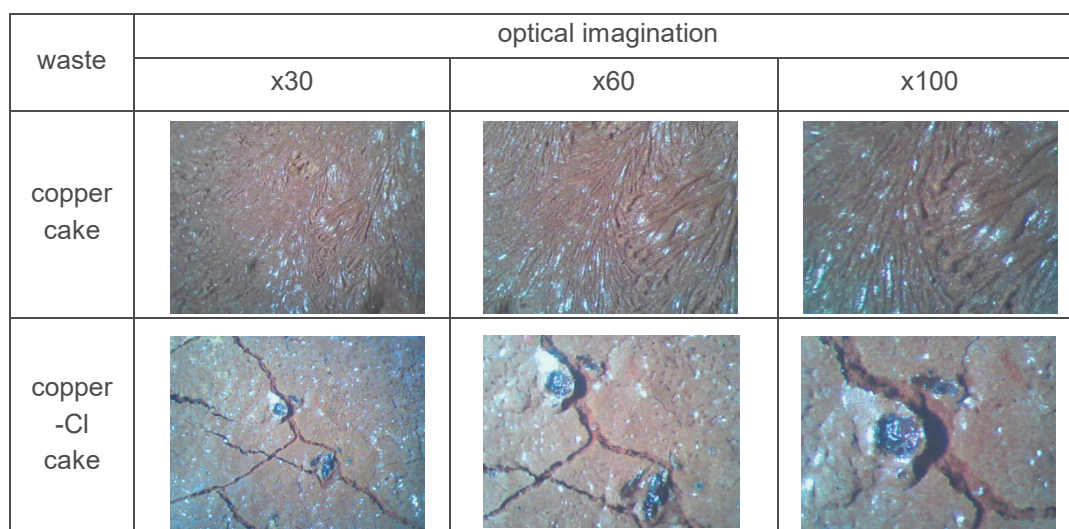
**Fig. 2** Kinetics of water evaporation: a) at room temperature in close and open samples; b) forced drying in the temperature interval 60 - 120 °C

The process of forced drying in the temperature interval 60 - 100 °C of the two wastes is similar to a great extends. In **Fig. 2b** are shown the measured masses of cake samples after each single step heating procedure in a laboratory furnace. In comparison with the evaporation experiment the forced one has the same profile as the open samples. After the first 3 step procedures the mass became constant until the 7<sup>th</sup> step where the masses of the two samples start to increase.

#### 3.2 Copper cake morphology at storage conditions

The process of evaporation of water from the waste cakes leads to crystallization and appearance of different products on the cake surface. The wet brown surface of fresh cake in short terms becomes covered by colourless and white crystallites (**Fig. 1 a-c**). Besides, many often could be observed greenish (**Fig. 1a**) and dark blue (**Table 1**, copper-Cl cake) salting objects. Rarely, even red crystals appear in the samples. In the **Table 1** are shown snapshots at subsequent imaginations of the surface morphology of copper and copper-Cl cake stored in glass dish at close conditions for low rate evaporation. The surface morphology fully corresponds to the result from **Fig. 2a** where the copper-Cl cake evaporate very fast and this leads to

appearance of deep surface flaws. The crystallites appear not only on the cake surface but in the bulk of the waste. The crystallization process is especially intensive in the bulk cracks where growth elongated well faceted single crystals (**Fig. 1b**). Despite the carried out chemical and phase analyses in the next subchapter there is an obstacle to predict the chemical content of all crystallites. It is worth pointing that in the used sulphuric acid solution there are many soluble impurities from the beginning of the technological process whereby leaching are dissolved the roasted ores and "Waelz" - oxides.



**Fig. 3** Comparison of the morphology of two type copper cakes during evaporation

### 3.3 Chemical composition of the fresh copper cakes

The analysis of the chemical content of the waste copper cake was supported by laboratory tests of KCM-Plovdiv. In **Tables 1-3** are represented the presence of different metal and impurities contents in the two type waste products. Summary, the cake contains in a great extend tree main metals which are copper, lead and zinc (**Table 1**). The sours of these metals are the initial lead-zinc ores in which the copper is concomitant element. After the roasting process the copper forms with other metals complex structures and enters in the zinc hydrometallurgy plant by sulphuric acid leaching of the zinc pulp.

**Table 1** The main components in fresh waste copper cakes (wt.%)

Cake/content	Cu (%)	Fe (%)	Pb (%)	Zn (%)	Moisture (%)	Specific density (kg/dm <sup>3</sup> )
Copper cake	55.7	-	5.23	4.25	24.58	1.7
Copper-Cl cake	47.12	-	4.94	2.58	21.28	1.61

**Table 2** Impurity metal contents of copper cakes (wt.%)

cake/content	Ag (g/t)	As (%)	Bi (%)	Cd (%)	Hg (g/t)	Na (%)	Ni (%)	Sb (%)
copper cake	88.0	0.063	0.008	0.79	4.00	0.11	-	0.009
copper-Cl cake	90.5	0.024	0.001	0.07	1.00	0.07	0.002	0.003

**Table 3** Impurity non-metallic contents of copper cakes (wt.%)

cake/content	Cl (%)	F (%)	S (%)	Si (%)
copper cake	0.04	0.013	9.30	not determined
copper-Cl cake	6.63	0.012	7.65	not determined

Besides the main valuable metal contents the cake consists of other undesired metal impurities (**Table 2**). For example the presence of As and Cd over permissible concentrations specify the copper cake as an extremely hazardous waste material. The principal difference between the copper and copper-Cl cake could be seen from **Table 3** where are exposed the non-metallic contents in the two copper wastes. The copper-Cl cake contains substantial amount of chlorine element and it is a product from purification of the zinc leach solutions only from "Waelz" process. Since the last one processes wide range raw and waste materials the leaching solutions contains large amount of chlorine anions which are removed by mixing the solution with fresh copper cake from the roasting cycle of the zinc plant.

### 3.4 Phase composition of copper cake powders

The results of X-ray analysis are shown in **Tables 4** and **5**. It is obvious that the main part of copper content appears in the cake as the mineral cuprite which corresponds with the theory and practice of the cementation of copper ions with pure metal zinc powder [10]. In the **Table 5** as a consequence appears copper chloride compound which is a product from the interaction between elementary copper from fresh copper cake and chlorine anions from "Waelz" leaching solutions. Surprisingly, the analysis does not detect elementary copper present in the fresh cake. This is true also for the most impurity contents present in the **Table 2**, which does not take part in the phase compositions of both copper cakes. A feasible reason could be the small quantities of elemental copper and impurity elements or technological full cementation of copper ions to copper (I) oxide. The presence of elementary copper requires additional analytical evidences.

**Table 4** X-ray analysis of copper cake powder

Index	Amount (%)	Name	Formula sum
A	66.3	Cuprite	Cu <sub>2</sub> O
B	21.2	-	CaH <sub>1.25</sub> O <sub>4.625</sub> S
C	9.3	Zinc arsenate oxide	Zn <sub>4</sub> As <sub>2</sub> O <sub>9</sub>
D	3.2	Anglesite	PbSO <sub>4</sub>

**Table 5** X-ray analysis of copper-Cl cake powder

Index	Amount (%)	Name	Formula sum
A	45.7	Cuprite	Cu <sub>2</sub> O
B	42.5	Bassanite	Ca <sub>2</sub> H <sub>2</sub> O <sub>9</sub> S <sub>2</sub>
C	7.5	Anglesite	PbSO <sub>4</sub>
D	4.3	Nantokite	CuCl

### 3.5 Sulphuric acid leaching of copper cake

The first type copper cake from roasting zinc plant was tested for low temperature copper leaching up to 90 °C with 12 % diluted sulphuric acid. The second type copper-Cl is not suitable for preparation of copper electrolytes due to the presence of Cl ions which deteriorate the cathode copper. The concentrations of the dissolved copper and zinc ions are shown in **Table 6**.

**Table 6** Actual concentration in according with the dilution for Cu and Zn in copper cake leaching samples and relative standard deviation (RSD) % obtained by ICP-AES ( $n = 5$ ,  $P = 95$  %)

Analysis lines, pm Cu I 327 396, pm Zn II 206 200

Samples	Concentration (g/l)	(%)	RSD (%)
Cu	7.043	0.71	3
Zn	1.135	0.1	3

The results from **Table 6** show that the copper cake treatment with dilute sulphuric acid could be used for direct preparation of copper sulphate electrolytes. The concentration of copper ions in the leaching solution is sufficient for conducting copper electroextraction. Interestingly, the zinc ions appear in the leaching solution in a large amount. Probably, the zinc impurity compounds in the cake are more dissolvable than copper (I) oxide. The concentration of copper ions has the potential to be increased by improving the leaching process and fully utilization of cuprite particle in the cake. Another possible way is the concentration of leaching solutions by membrane techniques or evaporation. On **Fig. 1d** are shown copper sulphate blue crystals as a product from copper cake leaching solutions.

## CONCLUSION

The carried out investigations on chemical and physicochemical properties of copper cakes from hydrometallurgy is a necessary step for formulation of strategy for waste storage, preservation and treatment. The process of dehydration and related with this process of crystallization could be used for separation of new valuable products from the waste cake or removing and collecting the hazardous one. In this study was demonstrated sulfuric acid leaching of copper cake, containing large amount of copper (I) oxide and formation of copper (II) sulphate with appropriate concentration for pure copper electroextraction. The shortcomings of the method were the concomitant impurity metals and non-metallic substances. Zinc ions from the copper cake were detected in large amounts in the leaching solution. In this respect the sulphuric acid leaching solutions from copper cake treatment are suitable candidate for separate electroextraction of copper ions in the presence of other more electronegative metal ions by application of low current densities and organic additives.

## ACKNOWLEDGEMENTS

***The authors are grateful to KCM-Plovdiv for the fresh copper cakes supply. This study and the visit of zinc plant of KCM-Plovdiv were fully supported by the Project BG051PO001-3.3.06-0038.***

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