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FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING
DOCTORAL SCHOOL IN CHEMICAL ENGINEERING

DISSOLUTION PROCESS MODELING FOR RECYCLING DIFFERENT METALS FROM SOLID WASTE

(The Summary of the Ph.D. Thesis)

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2015

Acknowledgements

With the completion of this stage in my life, I would like to express a few words of gratitude to those who guided me and gave me their support during this PhD thesis.

First of all, I want to thank of my scientific coordinator, **Prof. Dr. Eng. Petru Ilea** for his unwaivering guidance, support and encouragement throughout the preparation and drafting my doctoral thesis. Equally, I would like to thank **Dr. Eng. Tamás Varga**, who introduced me to the world of mathematical modeling and consistently supported me during my doctoral studies.

Further, I wish to express my gratitude to the evaluation committee members of this thesis: **Prof. Dr. Eng. Călin-Cristian Cormoş, Prof. Dr. Eng. Nicolae Vaszilcsin, Prof. Dr. Eng. Dănuţ-Ionel Văireanu, Prof. Dr. Eng. Vasile Mircea Cristea**, for their advice and suggestions.

I want to thank the guidance committee: **Prof. dr. Liana Maria Mureșan**, **Dr. eng. Árpád Imre-Lucaci**, **Dr. eng. Sorin Dorneanu**, for their ideas and advice offered to me in process engineering approach.

Thanks to **Dr. Eng. Chován Tibor** and his wonderful team from the Institute of Chemistry and Process Engineering from Veszprém, Hungary for their support during internships mobility.

Special thanks to all my colleagues in the research group. An especial thanks to my dear colleagues **Nicoleta**, **Emilia**, **Ligia** and **Zsolt** for all their moral support during difficult times, but also for the beautiful moments spent over my PhD years.

Special thanks to my good friend **Victor**, who supported me unconditionally throughout my doctoral studies.

Above all, I would like to give special thanks to my family, especially to my mother and father for their invaluable support and their, emphasis on the importance of a good education. I would also like, to thank my sister **Iulia** and my nephew **Eric**, for all their unconditional love. I dedicate this thesis to you.

Cluj-Napoca, 2015 Ioana-Alina Popescu

I would also like to thank the financial support of projects:

Sectorial Operational Program for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project number POSDRU/159/1.5/S/132400 with the title „Young successful researchers – professional development in an international and interdisciplinary environment".

Romanian-Hungarian Bilateral Program under project no. 673/2013, TET_12-RO-1-2013-0017 and by the European Union and the State of Hungary, cofinanced by the European Social Fund in the framework of TÁMOP-4.2.2/A-11/1/KONV-2012-0071 project.

Contents

INTRODUCTION

In the last few years, specialized literature has recorded numerous studies dedicated to the recycling of **w**aste **e**lectrical and **e**lectronic **e**quipment (WEEE) for the recovery of metals (Jaiswala și col., 2015).

The management and capitalization of waste is particularly important, from the point of view of environmental protection and natural resource conservation. Furthermore, the national and international regulations are becoming more stringent in relation to WEEE (Lui și col., 2015).

WEEE contains 60 % metal (platinum, gold, silver, palladium, copper, ruthenium, tin, zinc, nickel, indium gallium, etc.), also found in metallic components ranging from printed circuit boards - PCB (2 %), crystal liquid display equipment - LCD (12 %), cables and metal-plastic mixtures (7 %), plastic (15 %), and others waste (4 %) that contain glass or ceramic material (Bakas și col., 2014). Consequently, recycling has a high potential to increase the amount of available metals for society, provided there is appropriate recycling technologies.

Waste from LCD represents an interest category of WEEE due to (Savvilotidou şi col., 2015):

i. high accumulation rate, which is proportional to the evolution of modern technologies in TV sets and monitors;
ii. high content of toxic and harmful substances;
iii. inadequate storage and the large volume it occupies;
iv. lack of available data regarding the construction and material content of this equipment;
v. lack of complex technologies for recycling, that not pollute the enviroment.

To recover valuble metals from WEEE various methods were investigated: mechanical, uncontrolled open burning, pyrometallurgical, pyrolysis, biometallurgical and hyrometallurgical, in various stages of implementation.

The latest enviromental regulations and European energy policy, stimulates reseach on the development of green and energy efficient recycling processes (Bigum şi col., 2012; Hong şi Valix, 2013; Sanyal şi col., 2013). These requirements are fulfilled by hydrometallurgical processes, which are less polluting processes. They lead to superior performance compared to the pyrometallurgical, since can be achived with lower energy consumption, are flexible, with high selectivity and economic to use (Virolainen, 2013).

Development of an efficient recovery method requires the construction of appropiate mathematical models which describe the overall processes that a phenomena that can occur in the metals dissolution process from WEEE.

The models developed in the art for recovery of metals from WEEE cover only certain aspects of the dissolution process.

Presently, with the development of computer capacity and specific chemical engineering programs, more resources are available to researchers, providing necessary support to the overall approach of various engineering problems.

One such tool is the numerical methods applied in kinetic modeling and experimental design methods. Through their use, it becomes possible to acquire more knowledge in identifying the parameters involved in the process, and the information obtained can help to solve engineering problems in the design, development or operation of process technologies (Alaoui şi col., 2015; Perumal şi col., 2013).

Development of detailed kinetic models is necessary for the design and optimization of complex chemical systems. These models are also used to determine the rate step in a complex reaction mechanism (Zapico şi col., 2015).

This thesis aimed to study the advisability of using a hydrometallurgical processed - based on persulfate leaching, enabling the effective dissolution of metals and / or alloys from WEEE. Several mathematical model were applied for experimental design and kinetic process description.

Considering the complex composition of WEEE and economic potential of these secondary sources of metals, the research strategy of the thesis considers the implementation of hydrometallurgical processes which allows the efficient dissolution of metals and/or alloys.

In this sense, our studies have resorted to using a strong oxidizing agent with redox systems ($S_2O_8^{2-}/SO_4^{2-}$). Using persulfate ion as an oxidiser agent in dissolving WEEE has the advantage that can be regenerated electrochemically (Liu şi col., 2014; Turan şi Altundoğan, 2013).

The research undertaken in this thesis focused on the recovery of metals such as Cu and Zn from WEEE using solutions based on persulfate, by attending different stages, which will be further detailed:

i. statistical evaluation of factors affecting the dissolution process of metals from WEEE using persulfate;
ii. development of mathematical models capable of accurately describe the dissolution process of copper, zinc and brass from WEEE in persulfate environment;
iii. detailed study of metal dissolution from specific components from WEEE, in our case the material used was the PCB found in LCDs;
iv. developing a mathematical model meant to describe the metals dissolution from the LCD boards.

At the end of thesis we can find the summarised conclusions and personal contribution regarding the conducted research and also a comprehensive assessment of the subject developed during the thesis.

Keywords: DEEE, LCD, BBD, SCM, ANOVA, process dissolution, copper, zinc, nickel, platinum, tin, brass, persulfat, experimental design, kinetic modelling, cost analysis.

THE STRUCTURE OF THE PAPER

The paper is structured on nine important chapters; the first four are dedicated to the bibliographic research, and the other five chapters address the original research ending with the general conclusions of the paper. The content of the thesis is extended on 154 pages.

THEORETICAL CONSIDERATIONS

The first three chapters addresses as exhaustively as possible the specialty literature configuring the starting phase in the original research of the present thesis. Chapter four presents the general conclusions of the bibliographic study.

4. Partial conclusions

Rising consumer demand for the newest and most innovative devices has resulted in an accelerated production of electrical and electronic equipment (EEE) in turn, generating a significant amount of WEEE in the last couple of years (Khaliq şi col., 2014). WEEE is composed mostly of discarded electronic appliances, of which TV sets, monitors, computers and mobile telephones are disproportionately abundant because of their short lifespan (Robinson, 2009). The global volume of DEEE generated is expected to reach 93.5 million tons in 2016 from 41.5 million tons in 2011, which can seriously pollute the environment if not properly disposed (Bales şi col., 2014). Therefore, many countries and organizations have drafted national legislation which aims to prevent the generation of electrical and electronic waste and to promote reuse, recycling and other forms of recovery, in order to reduce the quantity of WEEE disposed in landfills (Bereketli şi col., 2011).

Globally, the increased demand for LCD equipment has generated a considerable amount of WEEE, due to the rapid replacement of CRT equipment, with LCDs (Peeters şi col., 2013). LCDs are classified as high risk elements because of various other hazardous substances they contain, such as Hg, Be, Pb, Cd, As, Sb, etc. Likewise, LCDs contain a considerable amount of precious metals (Au, Ag, Pd and Pt), base metals (Fe, Cu, Al, Ni, Zn, Sn, etc.) and rare metals (In, Ga) (Savvilotidou şi col., 2015).

Recovery of metals from WEEE can provide an attractive additional income, in the process of disposing of discarded electronic devices. The profitable processing of the WEEE can be represented by Pt, Au, Ag and Cu recovery, with important profits for processors (Kumar şi col., 2013; Birloaga şi col., 2013).

Thus far, the most effective methods in order to recover valuable metals from WEEE are pyro- and hydro- metallurgical processes. Hydrometallurgical methods are more accurate, more predictable and more easily controlled than pyrometallurgical processing for recovery of metals. Generally, hydrometallurgical processes present lower running costs and can be operated economically even on a small-scale (Zhou şi Qiu, 2010).

The most used leaching agents for metals recovering from DEEE are: "aqua regia" (HCl, HNO_3), H_2SO_4, HNO_3 și HCl (Petter şi col., 2014; Jung Oh şi col., 2012; Kumar şi col., 2014), but because of strict environmental regulations and their corrosive nature, these types of reagents are considered inappropriate for hydrometallurgical processes (Jha şi col., 2011; Yang și col., 2011a; Parga şi col., 2007).

A potential alternative to acid and alkaline leaching of metals is to use persulfate ($S_2O_8^{2-}$) as an oxidizing agent (Liu şi col., 2014). Persulfate is one of the strongest oxidants and provides the following advantages over other oxidants: higher stability, high water solubility, relatively low cost and environmentally friendly (Havlik şi col., 2010; Yang şi col., 2011a; Liu şi col., 2014).

The effective operating parameters on metals dissolution are: pH, solid/liquid ratio, dissolution medium, temperature and hydrodynamic conditions (Long Le şi col., 2011; Park şi Fray, 2009). Development of efficient technologies for recovery metals requires inclusion of these parameters in appropriate mathematical models, which describe the overall processes and phenomena in the dissolution process of metals from WEEE (Li şi Miller, 2007; Rivero şi col., 2010; Souza şi col., 2007).

The statistical methods of experimental design and kinetic modeling are the most common in the dissolution process of metals from WEEE. Through their use, becomes possible more extensive knowledge and identifying the parameters involved in the process, and the information obtained can help to solve engineering problems in the design, development or operation of process technologies. The development of detailed chemical kinetic models is necessary for the design and optimization of complex chemical

systems. These models are also used for determining the rate step in a complex reaction mechanism (Zapico şi col., 2015).

The kinetic models developed in the literature for metals recovery from WPCBs covers only certain aspects of the dissolution process. In addition, most papers were based on global kinetic expressions, rather than expressions that allow the determining influence of operating conditions, which are very useful for the design of complex chemical systems. Furthermore, kinetic models to describe the dissolution process of metals from LCD boards, cables, batteries, etc., using persulfate as oxidizing have not been reported in the literature thus far.

ORIGINAL CONTRIBUTIONS

5. Statistical evaluation of factors affecting the leaching process of WEEE using $Na_2S_2O_8$

5.1. Aims of the study

The purpose of this study is to develop multiple models that adequately describe the behavior of the factors affecting the rate of the dissolution process used in recovery of electrical and electronic equipment process. Statistical evaluation and optimization of parameters affecting the leaching performance, such as temperature, sodium persulfate concentration and leaching time, were performed on leaching of copper, zinc, and brass (alloy composition (35% zinc and 65% copper). The main effects and the interactions on these three factors were studied at three levels using a BBD experimental design method, which provides a second-order mathematical model and optimal values for leaching parameters. A fourth factor is introduced in order to analyze how metal content of copper and zinc affects the dissolution rate and to make possible the design of pilot scale leaching equipment.

5.2.1. Material

The materials used in the leaching process derive from WEEE; shape, size, weight and composition were chosen to highlight specific components of the dissolution kinetics. The first set of experiments aimed at investigating the usage of $Na_2S_2O_8$ in copper dissolution. The material used in these experiments was metallic copper wire. For the study of zinc dissolution in persulfate environment, a rectangular block of zinc was chosen. Five facets of the block were varnished and one facet has been left untouched to interact with the persulfate solution, since the zinc block sinks to the bottom of the reactor. The material used for copper and zinc dissolution from brass is a cylindrical rod of brass. The composition of the alloy (65% copper and 35% zinc) was determined by complete dissolution of the metal in nitric acid and analysis of the components was performed using an atomic absorption spectrometer.

5.2.2. Experimental process

The leaching experiments were performed in a 150 mL isothermal stirred batch reactor. The reactor was equipped with a thermometer and a mechanical stirrer. The temperature was kept constant (at 30, 45 and 60 ºC) using an electric thermostat. 100 mL of persulfate solution was added to the reactor. When the desired stirring speed and reaction temperature were reached, the solid sample was added into the reactor. 1 mL of sample solution was withdrawn at specific time (5 min intervals) for analysing the concentration of copper / zinc by an atomic absorption spectrometer Avanta PM GBC Australia (AAS). Metals Cu, Zn or brass samples remaining after the leaching process were dried and weighted after each experiment.

5.3. Dissolution reactions

The global reactions describing the leaching process of copper and zinc using sodium persulfate as an oxidizing agent are presented in Eqs. (5.1 and 5.2). The same reactions have been proposed for the dissolution process of zinc and copper from brass.

$$Cu + Na_2S_2O_8 \rightarrow CuSO_4 + Na_2SO_4 \quad (5.1)$$

$$Zn + Na_2S_2O_8 \rightarrow ZnSO_4 + Na_2SO_4 \quad (5.2)$$

The experiments were conducted to separately investigate the performance and efficiency of the $Na_2S_2O_8$ solution in the leaching of samples on copper, zinc, and brass respectively. The effect of temperature, concentrations of sodium persulfate, leaching time, and copper content were determined on the rate of the process steps.

In the following section, we will present a detail analysis for M6, M7 and M8, which presents a more interesting approach in describing the dissolution process: all experimental data is used as input and metal content of waste as a fourth main factor.

5.8. The ratio of the combined mass of dissolved copper and zinc from pure metals and brass (M6)

M6 is based on the full experimental set of data, in which the number of the inputs is increased with the initial composition of the solid. The purpose of this model is to describe the dissolution of any copper-zinc alloys.

The chosen factors affecting the dissolution process were temperature, oxidant concentration, leaching time and the copper content of the solid.

Statistical analysis of variance (ANOVA) was performed to see whether process parameters are statistically significant or not.

Table 5.15. presents the T statistic and P values of the regression coefficients of the independent variables and their interaction (Coef.) in the regression analysis on the BBD. The T statistic is the coefficient divided by its standard error. The standard error is an estimate of the standard deviation of the coefficient (SE Coef.), the amount it varies across cases. Based on these results, the first order prediction equation can be written. With the performance characteristics and ANOVA, the optimal combination of process parameters can be determined. The optimal level of the quantity process in regard to the influence of the factors can be obtained for a temperature of 30 °C at a leaching time of 5 min for an oxidant concentration of 0.1 M.

Table 5.16. contains the analysis of variance and indicates the relative importance of the first-order sources respect to the sum of squares (Sum Sq). The mean squares (Mean Sq) are formed by dividing the sum of squares by the associated degrees of freedom (DF). The F values represents the variance of the group divided by the mean of the within group variances. A high values of F implies that the effect of the treatment is relevant. R^2 in Table 5.15. means that the reduced model can describe 97.4% of the total variation in the dissolved quantities of metal (copper and zinc, copper and zinc from brass) and all factors affecting the dissolution process have been take into account. The order of factors from high to low influence on the dissolution process is leaching time, temperature, copper content and oxidant concentration if only main effects are taken into consideration.

Table 5.15. Estimated regression coefficients for general model M6 (reduced)

Term	Coef.	SE Coef.	T	P value (<0.05)
Constant	21.736	6.578	3.304	0.004
X_1	-0.580	0.137	-4.224	0.001
X_2	-66.276	25.326	-2.617	0.019
X_3	-0.484	0.111	-4.371	0.000
X_4	-0.140	0.046	-3.080	0.007
$X_1 \cdot X_2$	1.573	0.512	3.075	0.007
$X_1 \cdot X_3$	0.014	0.002	6.779	0.000
$X_1 \cdot X_4$	0.004	0.001	4.062	0.001
$X_2 \cdot X_3$	0.778	0.303	2.570	0.021
R^2: 97.4 %				

Table 5.16. Analysis of variance for general model M6

Source	DF	Sum Sq	Mean Sq	F value	P value (<0.05)
Main effects	4	125.459	31.365	13.320	0.002
X_1	1	42.006	42.006	17.839	0.001
X_2	1	16.125	16.125	6.848	0.019
X_3	1	44.988	44.988	19.105	0.000
X_4	1	22.340	22.340	9.487	0.007
Way interaction	4	184.867	46.217	19.627	0.001
$X_1 \cdot X_2$	1	22.262	22.262	9.454	0.007
$X_1 \cdot X_3$	1	108.210	108.210	45.953	0.000
$X_1 \cdot X_4$	1	38.843	38.843	16.496	0.001
$X_2 \cdot X_3$	1	15.552	15.552	6.605	0.021
Residual error	16	37.675	2.355		

5.9. The dissolution of copper from pure metal and brass (M7)

Estimated regression coefficients and related statistical terms, obtained in the first simulation, were subjected to null hypothesis. The effects which were statistically insignificant compared to other effects were neglected one by one and the related statistics were then recalculated with remaining variables. Table 5.17. shows the results for the reduced model in the only terms which have significant effect on the dissolved mass of the copper.

R^2 presented in Table 5.17. means that 94.5 % of the total variation of dissolved copper can be attributed to the studied experimental factors and their interaction. Based on obtained results, we can conclude the model for the dissolution process of copper can be described by a first order equation.

Table 5.17. Estimated regression coefficients for model M7 (reduced)

Term	Coef.	SE Coef.	T	P value (<0.05)
Constant	19.633	7.031	2.792	0.014
X_1	-0.424	0.145	-2.919	0.011
X_2	-38.635	26.582	-1.453	0.167
X_3	-0.340	0.105	-3.237	0.006
X_4	-0.254	0.061	-4.164	0.001
$X_1 \cdot X_2$	0.829	0.542	1.530	0.147
$X_1 \cdot X_3$	0.007	0.002	3.262	0.005
$X_1 \cdot X_4$	0.004	0.001	4.252	0.001
$X_2 \cdot X_4$	0.252	0.158	1.595	0.132
$X_3 \cdot X_4$	0.003	0.001	4.376	0.001
R^2: 94.5 %				

To observe the effective parameters and their confidence levels on the dissolution process, the analysis of variance was performed. The results of ANOVA are presented in

Table 5.18. Usually, the larger F value the greater effect on the dissolution value due to changes of process parameter.

Table 5.18. Analysis of variance for model M7

Source	DF	Sum Sq	Mean Sq	F value	P value (<0.05)
Main effects	4	101.636	25.409	9.612	0.009
X1	1	22.520	22.520	8.519	0.011
X2	1	5.584	5.584	2.113	0.167
X3	1	27.700	27.700	10.479	0.006
X4	1	45.832	45.832	17.338	0.001
Way interaction	5	139.466	27.893	10.552	0.005
$X_1 \cdot X_2$	1	6.188	6.188	2.341	0.147
$X_1 \cdot X_3$	1	28.130	28.130	10.641	0.005
$X_1 \cdot X_4$	1	47.797	47.797	18.081	0.001
$X_2 \cdot X_4$	1	6.727	6.727	2.545	0.132
$X_3 \cdot X_4$	1	50.625	50.625	19.151	0.001
Residual error	15	39.652	2.644		

From Table 5.18. we can conclude that the most influential factor regarding main effects in the dissolution process is copper content of the solid waste, followed by dissolution time temperature and oxidant concentration. From the interaction terms, the interaction of copper content and dissolution time has the biggest impact on the leaching process, followed by the interaction of temperature and dissolution time.

The fact that the dissolution percentages from the confirmation experiments are within the calculated confidence intervals (see Table 5.18.) shows that the calculated results are within ± 5 % in error.

5.10. The dissolution of zinc from pure metal and brass (M8)

Regression equation obtained from the ANOVA performed on the leaching reaction as a function of temperature, persulfate concentration, dissolution time and Zn content can be written from Table 5.19., in the case of the reduced model. R^2 at a value of 94.5% means the found model can adequately describe the dissolution process and all effects have been included in the analysis. The obtained model is a second order function, where only the zinc content of solid has the second order term.

As it can be seen in Table 5.20. the content of Zn and the interactions between Zn and leaching time have significant effects on the dissolution process.

Table 5.19. Estimated regression coefficients for model M8 (reduced)

Term	Coef.	SE Coef.	T	P value (<0.05)
Constant	-2.564	7.021	-0.365	0.721
X_1	-0.155	0.140	-1.112	0.286
X_2	-10.095	27.263	-0.370	0.717
X_3	-0.068	0.118	-0.577	0.574
X_4	0.260	0.064	4.047	0.001
X_4^2	-0.001	0.000	-4.640	0.000
$X_1 \cdot X_2$	0.744	0.520	1.429	0.177
$X_1 \cdot X_3$	0.007	0.002	3.266	0.006
$X_1 \cdot X_4$	0.000	0.001	-0.436	0.670
$X_2 \cdot X_3$	0.421	0.308	1.365	0.195
$X_2 \cdot X_4$	-0.356	0.152	-2.344	0.036
$X_3 \cdot X_4$	-0.003	0.001	-4.761	0.000
R^2: 94.5%				

Table 5.20. Analysis of variance for model M8

Source	DF	Sum Sq	Mean Sq	F value	P value (<0.05)
Main effects	5	96.544	19.309	7.924	0.030
X_1	1	3.013	3.013	1.236	0.286
X_2	1	0.334	0.334	0.137	0.717
X_3	1	0.812	0.812	0.333	0.574
X_4	1	39.913	39.913	16.378	0.001
X_4^2	1	52.472	52.472	21.532	0.000
Way interaction	6	104.596	17.433	7.154	0.030
$X_1 \cdot X_2$	1	4.977	4.977	2.042	0.177
$X_1 \cdot X_3$	1	25.994	25.994	10.667	0.006
$X_1 \cdot X_4$	1	0.464	0.464	0.190	0.670
$X_2 \cdot X_3$	1	4.539	4.539	1.863	0.195
$X_2 \cdot X_4$	1	13.392	13.392	5.496	0.036
$X_3 \cdot X_4$	1	55.230	55.230	22.664	0.000
Residual error	13	31.680	2.437		

5.12. Cost analysis

M7 and M8 have been chosen to perform an optimization study of the leaching process because both models can adequately describe the dissolved mass of Zn and Cu based on all experimental data. The aim of using these two models was to outline the content of solid for Cu and Zn. We have taken into consideration four factors affecting the dissolution process: temperature (X_1), oxidant concentration (X_2), leaching time (X_3) and solid metal content (X_4). The reduced models after applying BDD method are presented in the following equations where y_{Cu} and y_{Zn} represent the outputs of the models for copper and zinc, respectively:

$$y_{Cu} = 19.63 - 0.42 \cdot X_1 - 3.63 \cdot X_2 - 0.34 \cdot X_3 - 0.25 \cdot X_4 + 0.82 \cdot X_1 \cdot X_2 + 0.007 \cdot X_1 \cdot X_3 + 0.005 \cdot X_1 \cdot X_4 + 0.25 \cdot X_2 \cdot X_4 + 0.003 \cdot X_3 \cdot X_4 \quad (5.8)$$

$$y_{Zn} = -2.57 - 0.16 \cdot X_1 - 10.1 \cdot X_2 - 0.07 \cdot X_3 + 0.25 \cdot X_4 - 0.001 \cdot X_4^2 + 0.74 \cdot X_1 \cdot X_2 + 0.007 \cdot X_1 \cdot X_3 - 0.0004 \cdot X_1 \cdot X_4 + 0.42 \cdot X_2 \cdot X_3 - 0.36 \cdot X_2 \cdot X_4 - 0.003 \cdot X_3 \cdot X_4 \quad (5.9)$$

An economical approach has been used for the optimization of the leaching process. To obtain optimal conditions for parameters affecting the dissolution process, the following equation of profit calculation can be used:

$$y = y_{Cu} \cdot C_{Cu} + y_{Zn} \cdot C_{Zn} - F_l \cdot X_2 \cdot C_{Na_2S_2O_8} - f(X_1) \cdot C_e - I \cdot f(V)/t \quad (5.10)$$

where, y is the output of the profit function, $y_{Cu} \cdot C_{Cu}$ represents the total income from copper recovery and $y_{Zn} \cdot C_{Zn}$ represents the total income from zinc recovery. The second part of the function refers to costs of manufacturing; $F_l \cdot X_2 \cdot C_{Na_2S_2O_8}$ represents the total cost with the persulfate solution, $f(X_1) \cdot C_e$ describes the cost of electricity and $I \cdot f(V)/t$ relates to the investment cost over a defined period of time.

The cost for the persulfate solution can be calculated using the following function:

$$f(X_2) \cdot C_{Na_2S_2O_8} = F_l \cdot X_2 \cdot C_{Na_2S_2O_8} \quad (5.11)$$

where, the liquid flow rate F_l can be obtained as a relationship between mass flow of the liquid m_s and solid-liquid ratio α.

To estimate electricity consumption the conservation law of energy can be used, where the amount of energy input in the process $f(X_1)$ is the quantity of energy resulting from the process, which in our case, represents the sum of heat loss (Q_{loss}) and heat introduced (Q_{in}) in the dissolution process:

$$f(X_1) = Q_{\text{thermostat}} = Q_{loss} + Q_{in} \quad (5.12)$$

The heat loss is mainly a function that describes dissipated heat from the heat transfer process correlated to the difference between the temperature of the mixture (*T*) and the ambient temperature (T_o) which is room temperature in our case. By taking into consideration the heat transfer rate (U) and the contact surface (*A*) the equation can be written as:

$$Q_{loss} = U \cdot A \cdot (T - T_o) \quad (5.13)$$

Transferred heat can be defined as a function of the flow of mass and the change in temperature. In our case, we can split the equation into two parts, addressing separately the two states of our mixture, fluid and solid, as in the following equation:

$$Q_{in} = F_s \cdot \rho_s \cdot Cp_s \cdot (T - T_s^{in}) + F_l \cdot \rho_l \cdot Cp_l \cdot (T - T_l^{in}) \quad (5.14)$$

where F_l – liquid flow rate ($m^3 \cdot month^{-1}$); F_s – solid flow rate ($m^3 \cdot month^{-1}$); T_l^{in} – initial temperature of the liquid (ºC); T_s^{in} – initial temperature of the solid (ºC) ; T – temperature of the mixture (ºC); ρ_S – solid density of the plastic ($kg \cdot m^{-3}$) ; ρ_l – liquid density ($kg\ m^{-3}$); Cp_S – heat capacity of the solid ($J\ kg^{-1}\ K^{-1}$) ; Cp_l – heat capacity of the liquid ($J\ kg^{-1}\ K^{-1}$).

The last term in the profit function is related to the investment cost for the used equipment in the experimental setup, in our case we included only the reactor vessel. The cost function is expressed as a correlation between the used material and volume of the recipient (V), as shown in the Eq. (5.15) (Walas, 1990):

$$f(V) = F_M \exp[2.631 + 1.3673(\ln V) - 0.06309(\ln V)^2] \quad (5.15)$$

F_M represents the cost factor for the type of material used.

The resulted quantities of copper and zinc have been obtained using models M7 and M8 for the output data from an assumed quantity of processed WEEE per month. Table X shows the content of the investigated WEEE. Values for the fourth factor in the optimization process have been chosen as 20 % Cu content of solid and 1 % Zn content of total solid content of WEEE (see Table 5.22.).

Table 5.22. Characteristic material composition of WEEE (Gramatyka et al., 2007)

WEEE	Plastic	Oxides	Cu	Fe	Sn	Ni	Pb	Al	Zn	Ag	Au	Pd
%	30.23	30.23	20.12	8.11	4	2	2	2	1	0.2	0.1	0.01

Profit calculation is done based on the following conditions:

- Copper price: 119.04 (euro kg^{-1})
- Zinc price: 56.24 (euro kg^{-1})
- Sodium persulfate cost: 9.81 (euro kg^{-1})
- Electrical energy price: 0.12 (euro kWh^{-1})
- Assumed quantity of processed WEEE in kg: 1000 (kg)
- Initial quantity of copper from WEEE (20%): 200 (kg)
- Initial quantity of zinc from WEEE (1%): 10 (kg)
- Solid/liquid ratio: 20 ($kg\ m^{-3}$)

- Mass flow rate of the liquid: 1000 (kg $month^{-1}$)
- Initial temperature of the liquid: 25 (ºC)
- Initial temperature of the solid: 25 (ºC)
- Ambient temperature: 25 (ºC)
- Solid density of the plastic: 400 (kg m^{-3})
- Liquid density: 1000 (kg m^{-3})
- Heat capacity of the solid: 1670 (J kg^{-1} K^{-1})
- Heat capacity of the liquid: 4182 (J kg^{-1} K^{-1})
- Rate of heat transfer: 10 (W m^{-2} K^{-1})
- Volume rate of the waste: 2.5/720 (m^3 h^{-1})
- Cost factor of stainless steel, 304: 1.7
- Index cost multiplier: 1.8

Simplified equation of profit:

$$y = 4484.16 - 94.9 \cdot X_1 - 12599399 \cdot X_2 - 140.87 \cdot X_3 - 58.98 \cdot X_4 + 201.58 \cdot X_1 \cdot X_2 + 2.56 \cdot X_1 \cdot X_3 + 1.06 \cdot X_1 \cdot X_4 + 57.97 \cdot X_2 \cdot X_4 + 0.63 \cdot X_3 \cdot X_4 + 0.007 \cdot X_4^2 + 2.36 \cdot X_2 \cdot X_3 - 0.025 \cdot \exp(2.631 + 1.26 \cdot \ln(0.0035 \cdot X_3) - \ln(0.0035 \cdot X_3)^2) \quad (5.16)$$

Results obtained from calculation of profit function on all experimental data have been compared and parameter values have been chosen where profit output had the biggest value. The optimal conditions are 45 ºC for reaction temperature, 0.1 M for oxidant concentration and 35 min for leaching time. Since optimal conditions determined by BBD method in laboratory experiments are reproducible in real production environment as well, the finding of the present study can be very useful for processing in industrial scale.

6. Kinetic models based on analysis of the dissolution of copper, zinc and brass from WEEE in a $Na_2S_2O_8$ environment

6.1. Aims of the study

The present study aims to analyze the dissolution kinetics of copper, zinc and brass from WEEE in sodium persulfate environment in order to take the first step in the design process of a technology which can recover precious metals from waste. The first phase involves testing individually the efficiency of sodium persulfate in the dissolution process of copper, zinc and brass, respectively. Based on experimental data, we propose three kinetic models with different complexity, which adequately describes the leaching process of the investigated materials at a macro scale. These models can be used for different purposes as we summarize in the results section.

6.2. Material and experimental procedure

The materials used in the leaching process derived from WEEE; shape, size, weight and composition (Table 6.1.) were chosen to highlight specific components of the dissolution kinetics. The first set of experiments aimed at investigating the usage of $Na_2S_2O_8$ in copper dissolution. The material used in these experiments was metallic copper wire. For the study of zinc dissolution in persulfate environment, a rectangular block of zinc was chosen. Five facets of the block were varnished and one facet has been left untouched to interact with the persulfate solution, since the zinc block sinks to the bottom of the reactor. The material used for copper and zinc dissolution from brass is a cylindrical rod of brass. The composition of the alloy (65% copper and 35% zinc) was determined by complete dissolution of the metal in nitric acid and analysis of the components was performed using an atomic absorption spectrometer.

Table 6.1. Material description

Material	Weight (g)	Length (cm)	Diameter (cm)	Surface (cm^2)
Cu	2	3	0.3	-
Zn	3.2 - 5	-	-	1.62 - 1.98
Alamă	3.6 - 5.6	1.4 - 2	0.6	-

The chemical leaching experiments were carried out in a150 mL isothermal stirred batch reactor. The reaction vessel was connected to a thermostatic circulating water bath with a controlling temperature accuracy of ± 0.1 °C. Agitation was provided by a magnetic stirrer. 100 mL of $Na_2S_2O_8$ solution was added to the reactor. When the desired stirring speed and reaction temperature were reached, the solid sample was added into the reactor.1 mL of sample solution was withdrawn at specific time intervals and copper/zinc concentration was analysed using an atomic absorption spectrometer (AAS). Metals (Cu and Zn) or brass samples remained after the leaching process were dried and weighed after each experiment.

6.3. Results and discussions

The global reactions describing the leaching process of copper and zinc using sodium persulfate as an oxidizing agent are presented in Eqs. (5.1) and (5.2).The same reactions have been proposed for kinetic analysis and parameter identification.

The experiments were conducted to separately investigate the performance and efficiency of the $Na_2S_2O_8$ solution in the leaching process of copper, zinc and brass respectively.The effect of temperature and concentrations of sodium persulfate were determined on the rate of the dissolution process.We kept the following parameters constant: leaching time (2 h) and stirring speed (350 rpm). The initial pH was low (3.8) in the reactor and it was not controlled during the dissolution process. Specific kinetic parameters were identified for each set of experimental data.

6.4. Kinetic modelling

In literature, there are multiple methods which can calculate the reaction rates of the copper and zinc leaching process. The first group contains very complex models which

can accurately describe the changes of the surface at a micro scale (Ouden et al., 2013). The other group contains simplified shrinking core models in which the simplifications are usually based on the assumption that the dissolution process is under reaction control (Perumal et al., 2013). In this paper we propose three models which describe the dissolution process at a macro scale and accurately calculate the variation in the surface of the solid due to the dissolution process.

Since the dissolution of solid is a mass transport process, via the interaction surfaces between the solid and liquid phases, the rate of the dissolution process is hardly dependent on the size of that surface. Hence, such a model, which can describe the dissolution process, should calculate the changes of the interaction surface. We investigated two kinds of solid geometry. In both cases we proposed that the dissolved volumes in each direction of the investigated geometry are proportional to the surface of the solid in that direction.

6.4.1. Kinetic model of zinc dissolution

In the pure zinc dissolution experiments, the block has only one facet where the mass transport process can take place; hence, due to the shrinking, only the height (h) of the block changes. We assumed that the reactor solution is well mixed, so the reaction mixture around the block is homogenous. The changes in the height of the block can be easily calculated with the following expression based on the change in the mass of the block:

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{\mathrm{d}m/\mathrm{d}t}{\rho_{Zn} \cdot l \cdot w} \tag{6.1}$$

where, *l* and *w* are the length and the width of the block, respectively. The change in the total mass of the solid can be expressed as follows:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -A \cdot r \cdot M_{Zn} \tag{6.2}$$

where, *A* is the surface where the mass transport process takes place, *r* is the dissolution rate of the zinc and M_{Zn} is the molecular mass of the zinc. To calculate the dissolution rate an Arrhenius type correlation is applied:

$$r = k_{0,r} \cdot e^{-Ea_r/RT} \cdot (c_{Zn^{2+}}^{sat} - c_{Zn^{2+}})^{n_r} \tag{6.3}$$

The aim for this stepis to describe an overall reaction equation which can be used in the design process. For this, three unknown parameters are introduced: $k_{0,r}$ – pre-exponential factor, Ea_r – activation energy, n_r – reaction order. Experimental measurements have been used to determine the saturated Zn^{2+} ion concentration ($c_{Zn^{2+}}^{sat.}$) for each temperature and persulfate concentration. The actual Zn^{2+} ion concentration increases with the same rate as the $S_2O_8^{2-}$ ion concentration decreases:

$$\frac{\mathrm{d}c_{Zn^{2+}}}{\mathrm{d}t} = A \cdot \frac{r}{V} = -\frac{\mathrm{d}c_{Na_2S_2O_8}}{\mathrm{d}t} \tag{6.4}$$

As it can be seen in Fig. 6.6., the measured dissolved zinc mass shows an interesting characteristic. If we apply mild conditions (low temperature and reagent concentration) there is an inflection point on the profile. This means there must be another process next to the reaction step, which takes control over the transition periods. It can be the increase of the interfacial area due to the formation of a porous layer on the solid. We supposed this increase was due tothe function of the temperature, the reagent concentration, and of course the surface of the block (A_g) which can be calculated from the sizes:

$$\frac{\mathrm{d}A}{\mathrm{d}t} = k_{0,A} \cdot e^{-Ea_r/RT} \cdot (n_A \cdot A_g - A) \cdot c_{Na_2S_2O_8} \tag{6.5}$$

where, three more unknown parameters $k_{0,A}$, Ea_A, n_A are applied. The last parameter determines what can be the maximal surface in the formed porous layer.

The introduced model was implemented in MATLAB and solved with Runge-Kutta method. In numerical analysis the Runge-Kutta methods are used in temporal discretization for the approximation of solutions of ordinary differential equations. For an effective parameter identification, we incorporate the Runge-Kutta method into the Particle Swarm Optimization algorithm (PSO). After comparing the discrepancy of obtained value and the true value, we construct an unstrained optimization problem, where the objective function is the “discrepancy” and PSO is used to minimize the objective function. The model error is calculated as the sum of square error in case of all the nine experiments (see Fig. 6.6.). The proposed model describes the dissolution of zinc block with acceptable precision. The identified model parameters are: $k_{0,r}= 1.4\cdot10^{-3}$ $m^3m^{-2}s^{-1}$, $Ea_r= 0.1$ J mol^{-1}, $n_r= 0.646$, $k_{0,A} = 1.98$ m^3 $mol^{-1}s^{-1}$, $Ea_A= 3.5\cdot10^4$ J mol^{-1}, $n_A= 0.466$. The first identified model for zinc dissolution presented an error of 4 %. We looked to further improve the model and took in consideration the formation of a porous layer on

the surface of the zinc. The improved model presented a better fit between the measured and calculated values of dissolved zinc, with a correlation coefficient (R^2) of 0.96. The accuracy of the model was improved and the initial error (Error = 4 %) has been lowered to a more acceptable value (Error = 2.18 %).

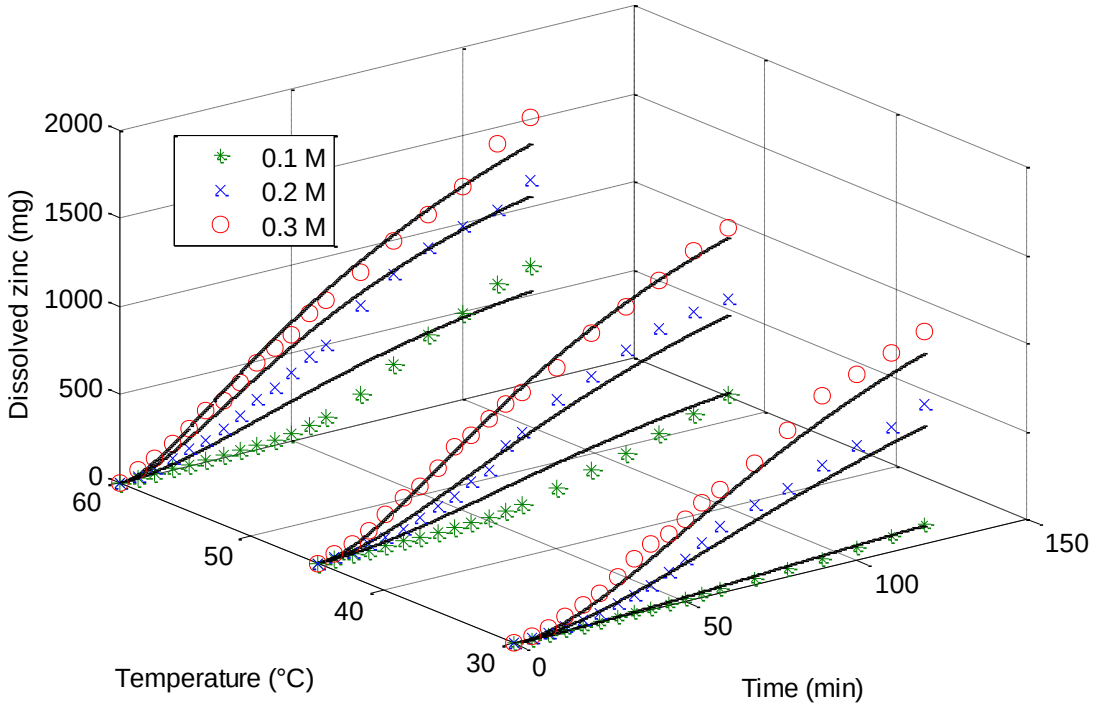

Fig. 6.6. The measured (markers) and the calculated (continuous line) dissolved zinc mass at different experimental conditions

6.4.2. Kinetic model of copper dissolution

In the pure copper and brass experiments the investigated geometry was a cylinder (diameter – *d*, length – *l*). To define the exact geometry changes shrinking core model can be used. In our case a two dimensional method was developed to calculate the diameter and length changes in time and kinetics which have been extended to include the surface dependency. The geometry can change its size in both ways proportional to the material transport area on that direction:

$$\frac{\mathrm{d}l}{\mathrm{d}t} = \frac{4 \cdot \mathrm{d}m/\mathrm{d}t}{\rho_i \cdot (1+2l/d) \cdot d^2 \pi} \tag{6.7}$$

$$\frac{\mathrm{d}d}{\mathrm{d}t} = d - d^{0.5} \cdot \left(-\frac{\mathrm{d}l}{\mathrm{d}t}\right)^{-0.5} \cdot \left(d \cdot l - d \cdot \frac{\mathrm{d}l}{\mathrm{d}t} - 2 \cdot l \cdot \frac{\mathrm{d}l}{\mathrm{d}t}\right)^{0.5} \tag{6.8}$$

The reaction rate for the dissolution process of pure copper can be expressed using the Arrhenius expression as follows:

$$r = k_0 \cdot e^{-Ea/RT} \cdot \left(c_{Na_2S_2O_8}\right)^n \quad (6.9)$$

The rate of the dissolution process represented in Eq.(6.9) is dependent on the area between the solid and the liquid phases. The changes of copper mass can be expressed as a relation between the surface area where the mass transport process takes place *A*, the dissolution rate of the copper *r* and the molecular mass of the copper *M*.

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -A \cdot r \cdot M_{Cu} \quad (6.10)$$

The component balances for Cu^{2+} and $Na_2S_2O_8$ are shown in Eqs.(12) and (13), respectively, where V_0 refers to the actual volume.

$$\frac{dC_{Cu^{2+}}}{dt} = \frac{A\cdot(r_1 - r_2)}{V_0} \quad (6.11)$$

$$\frac{dC_{Na_2S_2O_8}}{dt} = \frac{-A\cdot(r_1 - r_2)}{V_0} \quad (6.12)$$

The balance switch is used to determine the changes in concentration and solid phase mass in case of Cu leaching in persulfate solution. For this case three parameters must be calculated; the pre-exponential constant (k_0), activation energy (E_a) and reaction order.

We defined the objective function as the sum of square error between the measured and calculated concentration profiles. In Fig. 6.8., continuous line represents the values obtained through modelling and points correspond to the experimental data. The identified model parameters are: $k_0 = 9.52\cdot10^3\ m^3\ mol^{-1}s^{-1}$, $Ea_A = 5.2\cdot10^4\ J\ mol^{-1}$, $n_A = 1.$

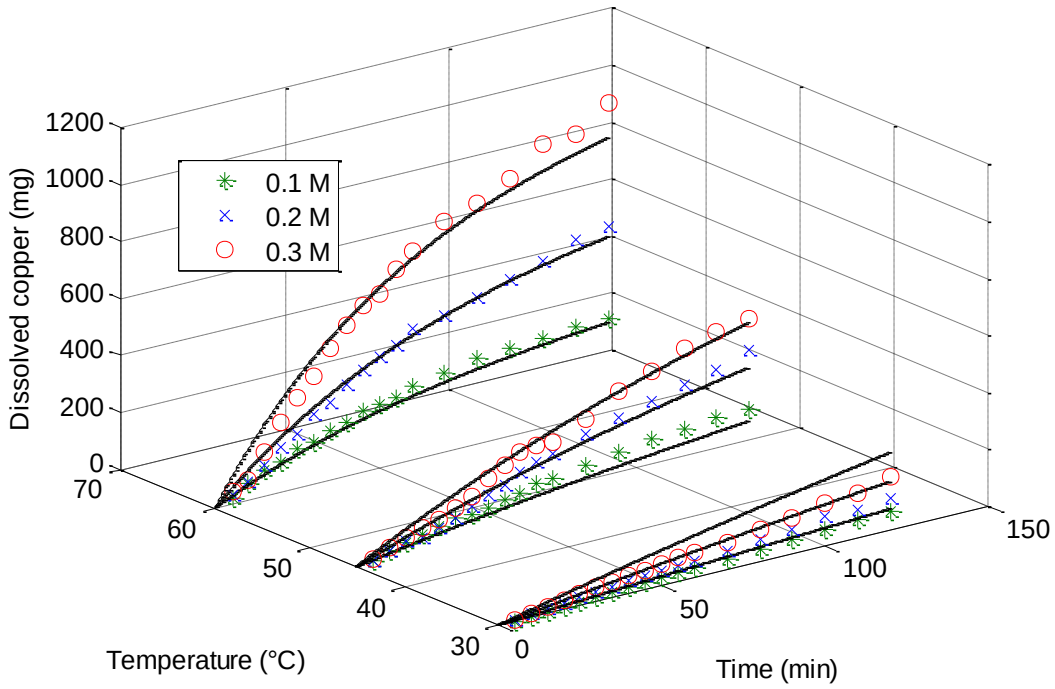

Fig. 6.8. The measured (markers) and the calculated (continuous line) dissolved copper mass at different experimental conditions

The apparent rate constant for copper dissolution increases by increasing the temperature. Generally, a high value of activation energy indicates that the process is strongly influenced by temperature and therefore, the rate-controlling step has reaction at the solid surface. The evaluated activation energy was found to $5.2 \cdot 10^4$ J mol^{-1} and confirms that the dissolution rate is surface dependent. Furthermore, the agreement between the calculated and dissolved copper mass is linear with a regression coefficient (R^2) of 0.97 and a model error of 1.26 %.

6.4.3. Kinetic model of brass dissolution

The component mass balance for Cu and Zn from brass is based on the proposed reaction given by Eqs. (5.1) and (5.2) and the rates of the reactions calculates with the following equations:

$$r_i = k_{0,i} \cdot e^{-Ea/RT} \cdot \left(c_{Na_2S_2O_8}\right)^{n,i} \tag{6.14}$$

where *i* represents the number of the reaction (i.e. if *i=1* the expression gives the rate for copper dissolution; if *i=2* the expression gives the rate for zinc dissolution). In Eq. (6.14) we see that the reaction rate is strongly influenced by the reactant concentration depending on the reaction order. Initial volume of the sample varies linearly with the mass variation which is described in Eq. (6.15):

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -(A_{Zn} \cdot r_{Zn} \cdot M_{Zn} + A_{Cu} \cdot r_{Cu} \cdot M_{Cu}) \tag{6.15}$$

where, *M* (kg/mole) represent the molar mass of each metal and A_i (m^2) is the specific metal surface ratio from the total.

$$A_i = A \cdot x_i \tag{6.16}$$

where, *A* is total surface at a certain time and x_i is metal mass fraction in material.Variations of ion concentrations includingvariation of the reactant in time, and the variations of the dissolved mass concentration in solution, are described in the following equations:

$$\frac{\mathrm{d}C_{Na_2S_2O_8}}{\mathrm{d}t} = \frac{-(A_{Zn} \cdot r_{Zn} + A_{Cu} \cdot r_{Cu})}{V_0} \tag{6.17}$$

$$\frac{\mathrm{d}C_{Zn}}{\mathrm{d}t} = \frac{A_{Zn} \cdot r_{Zn}}{V_0} \tag{6.18}$$

$$\frac{\mathrm{d}C_{Zn}}{\mathrm{d}t} = \frac{A_{Cu} \cdot r_{Cu}}{V_0} \tag{6.19}$$

To calculate the actual volume of the solutionV_0, we took into account the initial volume (100 mL) and the fact that at a certain time 1 mL of solution was taken out for analysis. Eqs. (6.20) and (6.21) describe the mass balance equationsfor the liquid phase:

$$\frac{\mathrm{d}m_{Zn}}{\mathrm{d}t} = \frac{\mathrm{d}c_{Zn}}{\mathrm{d}t \cdot V_0 \cdot M_{Zn}} \tag{6.20}$$

$$\frac{\mathrm{d}m_{Cu}}{\mathrm{d}t} = \frac{\mathrm{d}c_{Cu}}{\mathrm{d}t \cdot V_0 \cdot M_{Cu}} \tag{6.21}$$

In this case the model error is calculated based on the difference of the measured and calculated dissolved mass profiles of zinc and copper (Fig. 6.9.), and defined as the sum of squares of these differences. Although the overall agreement between the measurements and output data of the model is good, we can still observe some differences especially at a low temperature. The proposed model has a better fit to the measurements than in case the dissolution of pure zinc.The identified model parameters for zinc and copper from brass are: $k_{0,1} = 4.26 \cdot 10^4\ m^3 m^{-2} s^{-1}$, $Ea_1 = 5.68 \cdot 10^4\ J\ mol^{-1}$, $n_1 = 1$, $k_{0,2} = 9.5 \cdot 10^3\ m^3\ m^3 m^{-2} s^{-1}$, $Ea_2 = 5.27 \cdot 10^4\ J\ mol^{-1}$, $n_2 = 1$.

According to literature data we can state that the rate determining step is controlled by chemical reaction, due to an activation energy greater than 40 kJ/mol (Hollagh et al. 2013). Therefore, better model fit for higher temperatures (60 °C) can be associated to the reaction mechanism which governs the leaching process. Given that this trend can be observed for both copper and zinc dissolution from brass, changes in the reaction mechanism involves different oxidant reactions correlated with temperature. For instance, Acton (2013) found that persulfate radicals are generated at temperatures above 49 °C. At temperatures below 49 °C, persulfate hydrolyzes to form H^+. However, it should be noted that the proposed model can describe with sufficient accuracy (Error = 1.3 %) the copper and zinc dissolution from brass based only on the general reaction. If we plot the dissolved and calculated mass of zinc and copper versus time we get a correlation coefficient (R^2) of 0.97, which only confirms that the proposed model can accurately describe the dissolution process of brass in sodium persulfate.

According to the result it can be stated that the dissolution kinetics of pure copper and copper from brass are approximately the same, while in the case of pure zinc and zinc from brass there are significant differences. It seems like the activation energy and reaction order for pure zinc leaching are only half of the values obtained for zinc dissolution from brass.

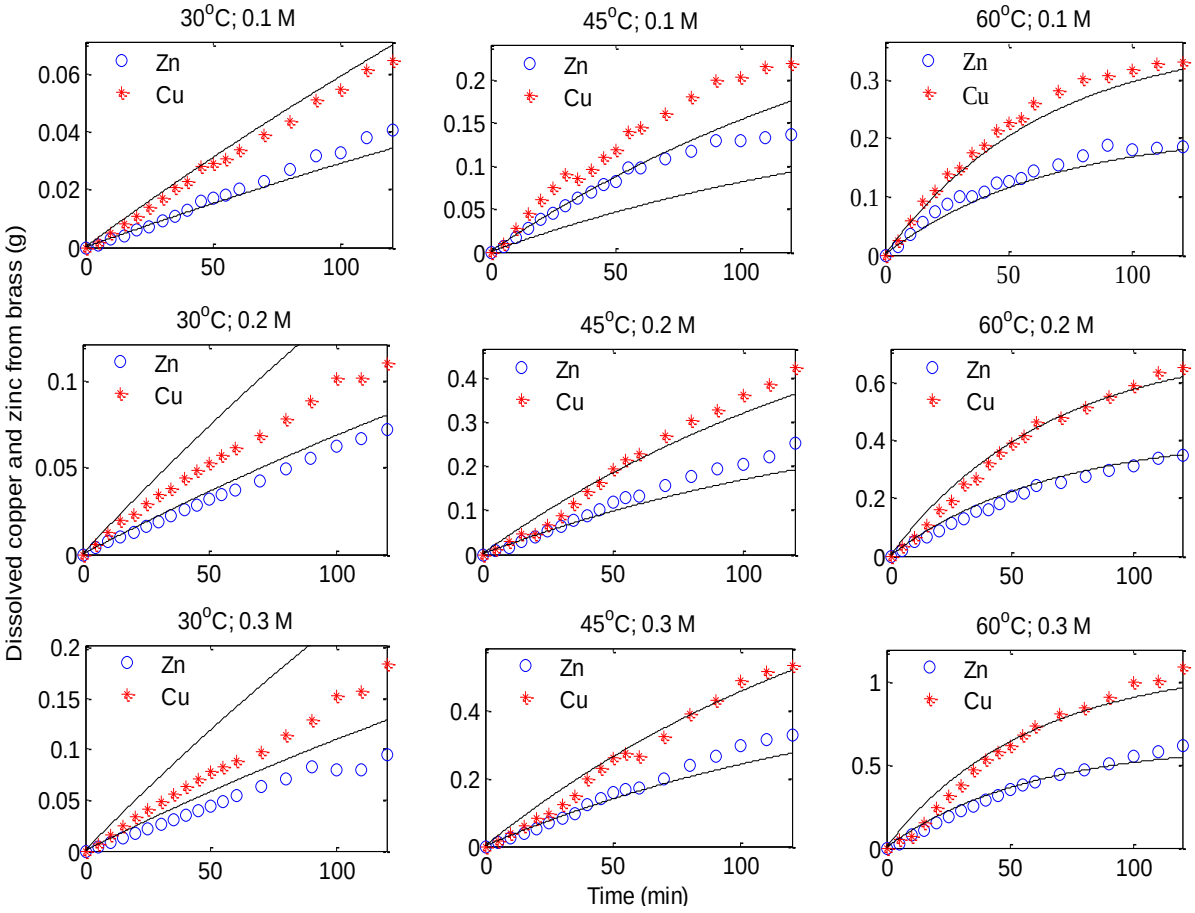

Fig. 6.9. The measured (markers) and the calculated (continuous line) dissolved zinc and copper from brass at different experimental conditions

9. Final conclusions

The bibliographic study presented in **Chapters 1 - 4** of the thesis illustrates a synthesis of the literature data on current progress in technological processes for the recovery of metals from WEEE.

The scientific information presented in **Chapter 1** highlights the level of awareness on WEEE pollution, at a national and international level. It can be concluded that WEEE is both a major source of environmental pollution, if not treated properly, and a source of valuable raw material because of the high metal content (60%).

Chapter 2 contains the description of specific steps related to WEEE recycling, focusing on DPCI-LCD waste due to their rapid rate of accumulation (1.6% annually) and high content of toxic and harmful substances.

Taking into account the latest environmental regulations and European energy policies that stimulates the development of green and energy efficient recycling processes, we introduced a detailed study on the hydrometallurgical processes, which are part of less polluting processes.

In **Chapter 3**, we can found a detailed analysis on numerical methods applied in kinetic modeling and experimental design methods. Using this type of methods can broaden our knowledge and the obtained information can help solve engineering problems found in design, development or operation of a technological processes.

Personal contributions from **Chapter 5** led to the development of eight original mathematical models based on surface response methodology. The presented models adequately describe the impact of factors affecting the dissolution process of metals from WEEE. Statistical evaluation and optimization of parameters (temperature, concentration of $Na_2S_2O_8$, during leaching and metal content) affecting the performance of the dissolution process were carried out by testing the dissolution of Cu, Zn, and brass (alloy composition: 35% Zn and 65% Cu) of WEEE. The experimental variables were assessed at three levels: low (-1), central (0) and high (+1) and the experimental matrix was developed based on Box-Behnken experimental design method. The models were developed for the following cases: the separate dissolution of pure copper and zinc metal (M1 and M2), the separate dissolution of copper and zinc from brass (M3 and M4), the

combined ratio of dissolved copper and zinc from brass (M5), the ratio of the combined mass of dissolved copper and zinc from pure metal and brass (M6), and the dissolution of copper and zinc from pure metal and brass (M7 and M8).

According to experimental results and statistical analysis, the most significant parameter in the dissolution process was leaching time, followed by temperature for models M1 - M6, and metal content for models M7 and M8. Cost analysis allowed evaluating the economic impact of the various parameters influencing the dissolution process.

The optimal parameters are:

- ✓ Temperature: 45 ºC;
- ✓ Concentration: $Na_2S_2O_8$: 0.1 M;
- ✓ Leaching time: 35 minute.

Kinetic analysis of the dissolution process of Cu, Zn and brass from WEEE, described in **Chapter 6** enables the design of modern technologies for metal recovery from solid waste. Individual testing was carried out to verify the efficiency of $Na_2S_2O_8$ in the dissolution process of Cu, Zn and brass, varying temperature and oxidant concentration.

Based on experimental data we propose three new kinetic models that adequately describe the leaching process of metal from WEEE.

For an exact description of the geometry changes that occur in the process, we developed a shrinking core model (SCM). After analyzing the kinetics of the dissolution process of Cu and Zn we can state that the temperature had the most pronounced effect on the leaching process, and activation energies obtained for copper and zinc from brass leaching (5.68•104 J mol^{-1} and 5.27•104 J mol^{-1}) indicate that the processes are controlled by chemical reaction on the solid surface.

To our knowledge, dissolution of Cu, Zn and brass of WEEE using a persulfate solution has not been reported in the literature so far.

Based on studies presented in thesis we can state that sodium persulfate can successfully dissolve Cu, Zn and brass from WEEE.

The proposed models described, with acceptable accuracy, the dissolution of copper and zinc for two types of solid geometry. The third model, which describes the dissolution of brass, gave the best results (Error = 1.3%).

Chapter 7 presents a study on the effect of pH, temperature and concentration on the dissolution of metals from LCD plates in medium persulfate. The results indicate that the rate of metal dissolution is significantly affected by pH. The decrease in pH (< 2) leads to an increase in the reaction rate of the persulfate.

Applying appropriate operating conditions it was found that, after 120 minutes of leaching, persulfate can dissolve successfully Cu (100%), Zn (99%), Pt (98%), Au (83%) and Ni (76%).

On the other hand, a low solubilization was obtained for Pb (6%), Sn (21%) and Ag (47%). However, it can be concluded that sodium persulfate is a suitable oxidizing agent for leaching of metals from DPCI-LCD.

The experimental results from **Chapter 8** show that the reaction kinetics is first-order, with identified activation energies of 29 924, 11 871, 22 434, 38 401 J mol^{-1} for Cu, Sn, Ni, and Pt, respectively. Kinetic analysis indicated that these processes are controlled by the chemical reaction on the surface of the particle.

Proposed reactions for the dissolution of metals from LCD PC have been validated by the proposed kinetic model. Error model was calculated as the sum of squares for all experiments (mean error of the model is 4.92%).

A good agreement between calculated and measured data shows that the proposed model can accurately describe the dissolution of metals from DPCI - LCD.

Finally we can say that there is good agreement between simulated and measured values for all models proposed in this thesis, which means that the proposed models can be applied in the design of similar technologies.

This thesis aimed to study the advisability of using a hydrometallurgical processed - based on persulfate leaching, enabling the effective dissolution of metals and / or alloys from WEEE. Several mathematical model were applied for experimental design and kinetic process description.

The common starting point for all new recycling methods and mathematical models described in this work was correlated with the need to develop green and energy efficient recycling processes, and also to develop appropriate kinetic models that describe the overall processes and phenomena that may occur in the dissolution of metals contained in WEEE.

This thesis represents a formalization of the theoretical and practical contributions in the highly complex field of metal recovery from WEEE, using original mathematical models to process collected experimental data.

Papers and conferences participation

The results obtained in this thesis were published in 5 journals and presented in 6 national and international conferences.

Popescu, I. A., Varga, T., Fogarasi, S., Imre-Lucaci, Á., Ilea, P. Statistical evaluation of factors affecting the leaching process of waste electrical and electronic equipment using sodium persulfate. **Chemical Engineering Communications** In press (2015a) DOI: 10.1080/00986445.2015.1012256 (**articol**).

Popescu, I. A., Varga, T., Egedy, A., Fogarasi, S., Chovan, T., Imre-Lucaci, Á., Ilea, P. Kinetic models based on analysis of the dissolution of copper, zinc and brass from WEEE in a sodium persulfate environment. **Computers & Chemical Engineering** In press (2015b) DOI: 10.1016/j.compchemeng.2015.05.002 (**articol**).

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Popescu, I. A., Egedy, A., Varga, T., Fogarasi, S., Ilea, P. Kinetic modelling of copper leaching process using $FeCl_3$ For recycling waste electrical and electronic equipments. **Bulletin of Romanian Chemical Engineering Society** 1-1 (2014b) 74-82 (**articol**).

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