REVIEW

Of the Dissertation (PhD Thesis) submitted for obtaining the educational and scientific degree "Doctor" in professional field 5.13. "General Engineering" in the scientific specialty "Technology for Utilization and Treatment of Wastes"

Author of Dissertation: **Eng. Dimitar Borisov Borisov, MSc**
Title of Dissertation: **"Determination of Technological Opportunities for Minimization, Utilization and High Temperature Treatment of Industrial Wastes"**

Reviewer: **Prof. Dr DrHC (UCTM) John Patrick Robinson, London, UK,** Member of the Jury, Order No P-OX-40/06.02.2015 by the Rector of the UCTM, Sofia

1. Short biography data for the candidate

Eng. Dimitar Borisov Borisov, MSc was born in 1976. In 1999 he graduated from the University of Chemical Technology & Metallurgy (UCTM), Sofia, Faculty of System and Chemical Engineering, Department of Automation as an MSc Engineer in Information and Managing Technologies and Automation. In 2000 he also graduated from UCTM with an European Masters Degree in "Environmental Protection and Sustainable Development". He has been working at UCTM since 2005 till the present as an Assistant Professor in the Department of "Programming and Use of Computation Systems".

Eng. D. Borisov has declared in his Curriculum Vitae his Scientific Research to be in the following fields: Environmental Technologies in Metallurgy, Energy and Ecology Optimization of Combustion Processes, Incineration and Pyrolysis of Hazardous Wastes, Energy Efficiency and Utilization of Energy from Waste, Mathematical Modeling in Furnaces Processes, Heat and Mass Transfer, Information Technologies and General Process Optimization.

2. Review of Dissertation and analysis of the results

The aim of this PhD investigation has been the development of a methods and technologies for minimization, utilization and high temperature treatment of industrial wastes generated during production operations in metallurgical and chemical technologies.

The main tasks in Dissertation are concerned to the following:

- Choosing a method for waste minimization in metallurgical and chemical industry;
- Developing a mathematical model, which can be used for minimization of the quantity of solid wastes generated in the process of metallurgical smelting;
- Developing an algorithm and software for use in mathematical model solving;
- Verifying the mathematical model;
- Proving the possibility of using the model for process optimization and operational process control in order to minimize the quantity of wastes;
- Investigating the possibility of adapting the mathematical model for other particular technological processes and operations.

The written thesis consists of 169 pages, including 24 pages of supplements, with 24 tables and 45 figures. It is organized into 4 Chapters, an Executive Summary and a Conclusions section.

Chapter 1 is made up of a literature survey concerned with the problem and the thesis goals and tasks are also described. The basic strategies of waste management are discussed and appropriate conclusions made.

The literature observation and analysis are based on 246 literature sources, including 5 Internet sources. Of the total number of referenced articles 151; 62.7 %, were published since the year 2000 and 90; 37.3 %, before 2000 and 233 are written in English and 8 in Cyrillic.

The literature analysis is very comprehensive, critical and extremely relevant. It describes the historical development of approaches to the problem of industrial waste management and details the challenges that currently remain. A significant proportion of the literature review focuses on advanced new strategies for managing industrial wastes. These strategies are primarily based on minimization of waste generation and the current techniques available are critically discussed and analyzed.

On the basis of the extensive literature survey the PhD candidate formulated an extremely intelligent, balanced approach to the goals of the thesis and tasks to be completed to attain these goals.

In Chapter 2 the basic requirements for developing a balanced mathematical model formulation to describe the particular properties of the technological processes in addressed in the thesis are determined. A modeling algorithm for solving the thesis aims and tasks is constructed. The currently available processes for minimization, high temperature stabilization and utilization of smelting wastes have been analyzed and evaluated.

The basic physical and chemical parameters for calculating the necessary material and heat balances for the ore smelting reactions that take place in the essentially fluidized bed environment in the flash smelter are formulated. These original formulations are the basis of the algorithm that is developed to describe minimization, utilization and high temperature stabilization of industrial wastes. They also form the basis of the choice of the Gauss elimination method for solving the system of independent balanced equations that form the mathematical model.

The “Maple” commercial software product was chosen as the program environment for mathematical model implementation.

In Chapter 3 the flow chart describing the general structure of the mathematical model for minimization, utilization and high temperature stabilization was elaborated. An original computational model based on the physico–chemical properties of the three phase Cu – Fe – S system and on the mass concentrations of the elements in the system has been created for assessment of the phases in sulphide copper concentrates and ores.

Equations for material balance of the components included in basic physico–chemical conversions during oxidation and melting of copper sulphide ore in the flash burning phase have been calculated.

Five specific systems of independent balance linear equations, depending on the phase composition of the input solid phase ore are formulated. The rate of the sold-phase product output flows are determined through numerical solution of the system of balanced equations using the Gauss method. Balanced equations for the gas

phase including the carbon fuel combustion have been developed to determine the quantities of each of the components of the solid phase input that go into gas phase.

An algorithm flow-sheet has been created, on which the mathematical model for determining the phase distribution in stocks containing Cu, Fe and S has been programmed.

An analytical mathematical model of the complete process of flash melting of sulphide copper concentrates has been created and on the basis of this analytical model a number of simplified models for optimization and operational purposes are described.

In Chapter 4 the ability of the model to provide results that allow minimization of the quantity of the waste product slag by adjustment of the composition of the input materials, as well as for use of non standard input materials such as waste products from mines and coal production, energy production and other industrial sources is proved.

To facilitate the computational procedure for control of the operational process, the analytical model for the high temperature processes proposed in Chapter 3 is approximated by numerical experiments carried out on restricted regions of the domain in the “composition – property” simplex diagrams. The experimental design approach of McLean-Andersen has been used for investigation of the Cu - Fe – S system. Three experimental design plans for these numerical experiments have been proposed for three different composition domains of the Cu - Fe – S input material and the best approximate model is chosen.

Graphical nomograms have been prepared for rapid evaluation of the expected quantity of waste slag and product; matte or “shtein” for various combinations of Cu - Fe – S in the raw input materials.

A set of Pareto-optimal solutions for input material composition that achieve simultaneously minimum quantities of slag and maximum quantities of matte have been determined.

Each Chapter contains a summary of the appropriate conclusions from the work described in the Chapter. The thesis conclusion includes an overall summary of the thesis including the principle achievements. Some recommendations for further are also included.

In this Thesis the PhD candidate has demonstrated an extraordinary breadth of and depth of scientific and technical knowledge in an interdisciplinary study that encompasses environmental protection, sustainable development, physical and inorganic chemistry, thermodynamics, metallurgy, economics, mathematics and high-level computer programming. The PhD candidate has combined his profound interdisciplinary skill-set to apply up-to-date approaches for algorithm creation, mathematical modeling, parameter estimation, design of numerical experiments, optimization methods and optimal decision making methods to the complex and important technical problem of waste minimization and product maximization in flash smelting of sulphidic copper ores.

The Thesis conclusions as set out allow me to state with confidence that the original thesis goals and objectives have been completely achieved and in fact significantly over-achieved. In the thesis the PhD candidate proposed and developed a systematic, methodical approach for characterization and evaluation of flash smelting as a technology with the potential to both minimize the quantity of solid wastes

generated from copper production and to provide high temperature treatment of solid industrial wastes generated in metallurgical and chemical industries.

The Thesis is extremely well written, well illustrated and very informative. The list of abbreviations and notations is comprehensive as are the lists of Tables and Figures.

In my opinion the scientific and technological work evidenced by the thesis is of the highest quality. The thesis itself is also prepared to the highest international standard and will, in my opinion provide a valuable basis for important future research and technological developments.

3. Evaluation of correspondence between the Summary (Autoreferat) and the PhD Thesis

The presented 50 page Extended Summary (Autoreferat) is comprehensive, very informative and fully reflects the contents of the Thesis.

4. Characterization and evaluation of the scientific contributions of the Dissertation

This dissertation describes an important scientific contribution to the understanding of complex chemical and physical processes in a particularly complicated environment. In addressing such a complex problem the candidate has produced a piece of work that is an example of what can be achieved when an interdisciplinary understanding the chemical and physical characteristics of an environmental problem is combined with a high level of mathematical and computing ability. The approach has the potential to be generalized and applied to a wider range of industrial and natural environments.

The work has significant applied importance in the metallurgical and chemical industries both in process modeling and waste management. By providing simplified, accurate approximation models for predicting waste formation as a function of process management it provides a powerful tool for simplifying and therefore facilitating environmental management in the chemical and metallurgical industries. Again it seems to me that the approach used in the dissertation has the potential to be developed for a much wider application.

(a) Scientific contributions

(1) A mathematical description of the complex physical and chemical transformations taking place in a high temperature industrial smelting process has been developed. A general mathematical model that takes account of more than 180 physical and chemical variables including material and energy balances, chemical reaction equilibria and chemical reaction rates has been created.

(2) The model has been algorthmized to give an analytical mathematical model that has been implemented using the programming environment of “Maple” software.

(3) The main computational modules of the program are:

- Determination of the phase distribution of the components of the charge for a wide range of component concentrations;
- Estimation of the amount of primary fuel required to provide the necessary smelter temperature by calculation of the heat balance in the flash smelting furnace;

- Calculation of the mass flows of the slag waste and matte product phases and the flow rate and composition of the gas phase.

(4) An algorithm using the method of Gaussian elimination has been developed for implementation of the mathematical model and for numerical solution of the independent balanced equations obtained from the model.

(5) The model can be used to predict the quantities of solid waste - “slag” and product - “matte” formed in the flash process for sulphidic copper ore smelting. The quantities of slag and matte can be calculated from the mass proportions of copper, iron and sulphur in the initial “charge” material introduced into the smelter. It can also be used to predict the effect on the amount of slag and matte of addition of certain industrial wastes into the charge.

(6) An important application of the model is for the minimization of industrial waste produced in flash smelting of sulphide copper raw materials. Five examples of independent balanced equations for typical proportions of copper, iron and sulphur in the of the input solid charge stream have been presented.

(7) Software for a shorter mathematical approximation model was developed for predicting conditions for the minimization of waste slag was developed. This model was verified by virtual numerical experiments using a limited factor space approach as being applicable over the input ore composition range of $10 \leq Cu \leq 35$; $15 \leq Fe \leq 45$; $10 \leq S \leq 40$ (mass %).

(b) Applied contributions

(1) Based on a complex model of the reactions in the flash smelter environment, mathematical approximation software has been developed. This approximation sotware is a valuable, practical tool that can be used by flash smelter operators to predict the amounts of matte product and waste slag formed for a given mass composition of Cu - Fe – S input material. This contribution has major significance for production efficiency and solid waste reduction in the smelting industry by providing a convenient method for optimizing product and minimizing slag waste. The minimization of waste is in accord with the EU hierarchy of waste management.

(2) The comprehensive calculations of enthalpy of reaction and energy balances in the analytical model of the process of flash smelting can be used to predict the effect of treating certain wastes from the chemical and smelting industries by adding them to the combustion chamber. Again this represents a powerful, practical tool for waste treatment and can also contribute to reducing the carbon footprint of the smelting process.

(3) Graphical nomograms have been prepared for rapid evaluation of the expected quantity of waste slag and product; matte or “shtein” for various combinations of Cu - Fe – S in the raw input materials.

5. Analysis of the publications on the Dissertation subject

To date five articles describing the dissertation work, co-authored with PhD supervisors have been published by the candidate. Two are journal publications in the English language. One is in the International Journal of Pure and Applied

Mathematics, Vol.38, No. 3, (2007) and the second in the Journal of Chemical Technology and Metallurgy, 49, 1, (2014). Three publications are papers delivered at international conferences and published in the proceedings. One of the articles is in Bulgarian and two are in English.

6. Critical remarks, comments and recommendation for further work

In my opinion this is an excellent example of what can be achieved by an interdisciplinary approach to a practical problem that is based on a deep understanding of chemical and physical sciences. The thesis provides a comprehensive model of the series of complex chemical reactions and thermodynamic and phase transitions that occur in the smelter environment. This complex model is transformed into a practical tool for application in industry.

I have a number of questions stimulated by this thesis:

(1) Have either the initial numerical model or the approximation software model been calibrated against data for slag formation and ore input from an industrial smelter?

(2) Is possible to include in the model information on how any other metallic components of the input material are partitioned between the matte and the slag material?

(3) Can the concentration of sulphur dioxide in the exhaust gases be derived from the analytical model?

(4) What types of waste material from the chemical and metallurgical industries can be added to the input to replace fossil fuels? How would this alter the carbon footprint of the smelting process?

(5) Is it possible to use the analytic model as a platform for developing similar programmes for managing other industrial waste outputs? If so what possible applications does the candidate suggest?

7. Personal impressions for the candidate

I have known the candidate personally since 2000 when he was a student on the European masters degree course at UCTM. I deliver lectures in two modules in the course and I am also a member of the Examination Board of the course. I remember his that Master's Thesis presentation and Thesis defense attracted an excellent mark from the examination panel.

In my opinion Candidate Borisov is an extremely able young scientist with great potential. He has an unusually broad understanding of chemistry, physics and biological chemistry. In addition his skills in information technology and computer modeling equip him with a set of valuable skills rarely found in one person.

I find him to be intelligent, extremely personable and helpful in solving practical problems involving computers.

8. Conclusion

As I have intimated in the sections above this PhD Thesis is of the very highest international quality from both the scientific and applied point of view. The subject matter is environmentally and industrially relevant and significant for both theory and

practice. The Thesis makes considerable scientific and applied contributions to our understanding of an important body of knowledge and fully corresponds to the requirements of Bulgarian Law for Academic Staff Development and the Regulations for Law Application. The PhD Candidate has proved his considerable abilities for carrying out theoretical and practical investigations to solve complex problems by applying up to date methods and instrumentation. All necessary educational requirements have been met by the PhD Candidate.

I have no hesitation in recommending that:

The Scientific Jury award Eng. Dimitar Borisov Borisov the educational and scientific degree "Doctor" (PhD Degree).

Date: 25 February 2015 Reviewer: 

(Prof. Dr. J. P. Robinson)