VTT Technical Research Centre of Finland

Latest in modelling symposium - in honour of professor Pertti Koukkari's 65th birthday

Kangas, Petteri; Pajarre, Risto; Penttilä, Karri; Vahala, Päivi

Published: 12/09/2019

Document Version
Publisher's final version

Latest in modelling symposium - in honour of professor Pertti Koukkari's 65th birthday

September 12, 2019 at GTK, Vuorimiehentie 5, Espoo

Petteri Kangas, Risto Pajarre and Karri Penttilä

VTT

Layout and editing: Päivi Vahala

Cover photo: VTT

Dear friends of process modelling,

It is our pleasure to host the *Latest in modelling symposium* in Otaniemi, Espoo at Thursday 12th September 2019. The day is filled with excellent lectures from academia and process industry. We will start with theoretical and methodological topics during morning and continue with industrial applications of process modelling during afternoon. The latest results from various fields of process industry will be covered, from metallurgy to energy and from chemical to forest industry. In addition, most recent developments of simulation software will be presented.

The symposium will be held *In Honour of Professor Pertti Koukkari's 65th Birthday*. Many of the lectures are related to the rigorous work VTT and especially Pertti have conducted with fellow scholars and industrial experts during years. The symposium presents the academic excellence and industrial impact of modelling and simulation in the field of process industry.

Wish a fine day.

On the behalf of VTT,

Petteri Kangas

Research manager, Dr

VTT Technical Research Centre of Finland

Programme

8:30-9:00	Registration
9:00-10:30	**Session 1 – Theory 1 (Chair: *Dr Petteri Kangas*)**
9:00-9:20	Welcome ***Dr Antti Vasara*** President and CEO, VTT Technical Research Centre of Finland
9:20-9:50	Keynote 1 – ***Prof Tapio Salmi*** Academy Professor, Åbo Akademi University The role of modelling in the development of chemical industry
09:50-10:10	Lecture 1 – ***Prof Alexander Toikka*** Professor, St. Petersburg State University Alternative forms of thermodynamic stability conditions
10:10-10:30	Lecture 2 – ***Dr Susanna Kuitunen*** Associate, Neste Engineering Solutions Industrial needs for modelling thermophysical properties
10:30-11:00	Coffee break
11:00-12:30	**Session 2 – Theory 2 (Chair: *Dr Petteri Kangas*)**
11:00-11:20	Lecture 3 – ***Prof Irina Zvereva*** Professor, St. Petersburg State University Design of photocatalysts based on layered oxides for energy-saving processes of obtaining hydrogen
11:20-11:40	Lecture 4 – ***Prof Daniel Lindberg*** Associate Professor, Aalto University Thermodynamic modelling as a tool to predict behavior of industrial melts
11:40-12:00	Lecture 5 – ***Dr Ville-Valtteri Visuri*** Postdoctoral researcher, University of Oulu Modelling of hot metal desulphurisation in steelmaking
12:00-12:20	Lecture 6 – ***Dr Timo Kankaanpää*** Senior Research Engineer, Freeport Cobalt CFD in Battery Chemical Applications
12:30-13:30	Lunch in Restaurant Maukas (Vuorimiehentie 5, Espoo)

13:30-15:00	**Session 3 – Applications 1 (Chair: Dr Eemeli Hytönen)**
13:30-14:00	Keynote 2 – ***Prof Pertti Koukkari*** Research Professor, VTT Technical Research Centre of Finland Constrained free energy within VTT and industry
14:00-14:20	Lecture 7 – ***Dr Sonja Enestam*** Manager, Valmet Applications of multi-phase chemistry in Valmet
14:20-14:40	Lecture 8 – ***Dr Jukka Rantamäki*** Development Manager, Metsä Fibre Applications of process modelling in kraft pulp mills
14:40-15:00	Lecture 9 – ***Dr Keijo Salmenoja*** Technology Director, Andritz Latest in process modelling in Andritz
15:00-15:30	Coffee break

15:30-17:10	**Session 4 – Applications 1 (Chair: Dr Eemeli Hytönen)**
15:30-16:00	Lecture 10 – ***Prof Klaus Hack*** Founder, GTT Technologies & Dr Stephan Petersen, Managing director, GTT Technologies Application examples of the constrained Gibbs energy theory using FactSage and ChemApp
16:00-16:20	Lecture 11 – ***Dr Alexander Pisch*** Research Fellow, CNRS French National Centre for Scientific Research Thermochemistry in rotary kilns for cement production
16:20-16:40	Lecture 12 – ***Dr Antti Roine*** Technology Director, Outotec HSC Chemistry: Past, present and future
16:40-17.00	Lecture 13 – ***Mr Karri Penttilä*** Senior Scientist, VTT Technical Research Centre of Finland ChemSheet 2.0 - In Honour of ChemSheet 20th Birthday
17:00-17:10	Wrap up and closing ***Prof Pertti Koukkari*** Research Professor, VTT Technical Research Centre of Finland
18:00-22:00	Dinner at Restaurant Arvo (Ekonominaukio 1, Otaniemi, Espoo)

- 18:00 - 18:30 Get together at Arvo
- 18:30 → Dinner
- Speeches and other compliments to Pertti during dinner

Table of contents

Session 1 – Theory 1

Chair Dr Petteri Kangas

Keynote

Prof Tapio Salmi

Åbo Akademi University

Keynote 1

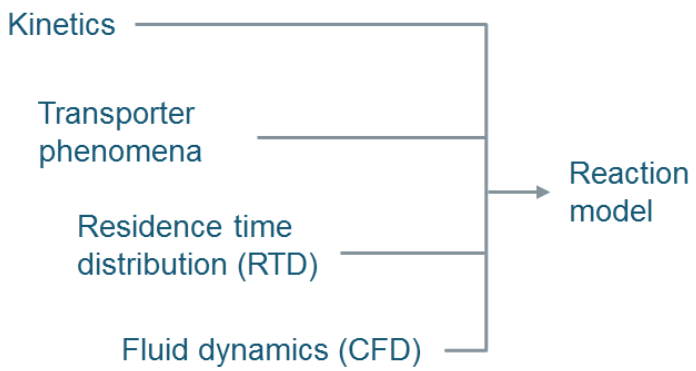
Multiscale modelling of chemical reactors – challenges and opportunities

Tapio Salmi

Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre (PCC), Åbo Akademi, Turku Finland

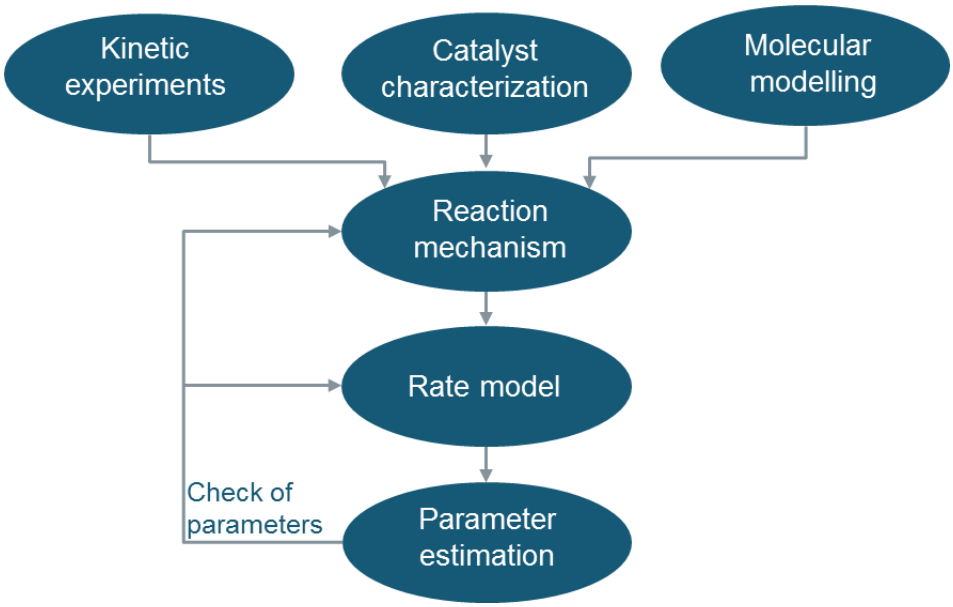
Chemical reaction engineering is a sub-discipline of chemical engineering, concerning the design, operation and optimization of chemical reactors. It is difficult to fix the birthdate of reaction engineering, but a pioneering publication of the great German physical chemist, Gerhard Damköhler should always be mentioned Einflüsse der Strömung, Diffusion und des Wärmeüberganges auf die Leistung von Reaktionsöfen, which appeared before World War II. Damköhler applied mass, energy and momentum balances on continuously operated chemical reactors discovered new dimensionless numbers, nowadays called Damköhler numbers (Da). The title of the article is still very valid – today we would only change Reaktionsöfen to chemischen Reaktoren!

The various elements of modeling of chemical reactors are illustrated below. The concepts of transport phenomena and kinetics – including thermodynamics, of course, form the classical core of chemical reaction engineering. However, it became quite soon clear that ideal flow models based on the concepts of plug flow and complete backmixing do not always correspond to the reality, particularly in industrial scale. The concept of residence time distribution (RTD) introduced by the great British chemical engineer, professor Peter Danckwerts is the key element in understanding non-ideal flow patterns. Theoretical computation of flow patterns (CFD) has been in fashion for a long time, but there are still gaps to be bridged, particularly in case of multiphase flow.



A new challenge is that the mankind has to abandon the rather simple molecules originating from fossil sources and shift to the use of much more – often called over-functionalized – molecules originating from different kinds of biomass. New raw materials with unknown or poorly known physical and chemical properties enter the arena. Chemical reactions, previously not known or uninteresting should be screened, the kinetics and thermodynamics of them should be determined quantitatively. To meet the enormous challenge, an integrated approach, multiscale modelling approach and process intensification is applied.

Quantum chemical calculations have opened a new perspective for modelling of complex molecules on solid surfaces and they can form the basis for the development of kinetic models. The approach improves very much the reliability of the parameters obtained from regression analysis in the classical kinetic modelling applied in academia and in industry. The procedure to be applied in successful chemical reaction engineering is displayed in the scheme below[1].



[1] [1]Salmi T, Wärnå J, Mikkola JP. 2019. Chemical Reaction Engineering and Reactor Technology, CRC Press, Taylor & Francis Group, Boca Raton – London – New York, 2nd Edition, 628p.

[2]Salmi T. 2013. Chemical Reaction Engineering of Biomass Conversion, Advances in Chemical Engineering 42: 195-260.

[3]Freites Aguilera A, Tolvanen P, Sifontes Herrera V, Tourvielle J-N, Leveneur S, Salmi T. 2017. Reaction intensification by microwave and ultrasound techniques in chemical multiphase systems, Process synthesis and Process Intensification – Methodological Approaches (Ben Guang-Rong, ed.), Chapter 3, 111-138, De Gruyter, Berlin.

[4]de Araujo Filho CA, Mondal D, Haase S, Wärnå J, Eränen K, Mikkola J-P, Salmi T. 2016. Dynamic modelling of homogeneously catalysed glycerol hydrochlorination in bubble column reactor, Chemical Engineering Science 149: 277-295.

Alternative forms of thermodynamic stability conditions

Alexander Toikka and Dmitry Gromov

Saint Petersburg State University, Russian Federation

The study of the stability of multicomponent heterogeneous systems is one of the main tasks of general and non-equilibrium thermodynamics. The conditions of thermodynamic stability allow estimating the values of physical and chemical properties, the influence of external forces on thermodynamic states and the changes of the properties during the processes. It is also important that the limits of stability also determine the conditions of spinodal.

The general form of the stability matrix includes the second derivatives of a generalized thermodynamic potential. In our work we analysed some transformations of the stability matrix and variants of mathematical formulations of stability conditions. Previously alternative forms of stability conditions had been discussed in other our works, e.g.[1,2]. We use the opportunity presenting the stability conditions by any thermodynamic potential, i.e. Gibbs and Helmholtz energy, enthalpy, etc. The equivalence of thermodynamic potentials is a well-known fact, but the discussion of the possibility to apply stability conditions presented by different potentials often meets misunderstanding.

Our analysis is based on the system of thermodynamic inequalities and chains of inequalities for multicomponent systems under different external conditions. We also were based on the contact geometric approach for the consideration of the equilibrium energy manifold as an n-dimensional Legendre manifold. Considering the transformation of the stability matrix, we obtained new results concerning transformation of the stability matrix that was indicated by Gibbs[3]: the reduction of the stability matrix due to the replacement of variables. Finally the stability matrix presents as a product of derivatives (not a sum of the products). Such transformation has been verbal described in[3] but our approach gives a new view on the properties of stability matrix and opportunities of stability condition applications, including the equation of spinodal. Resulting thermodynamic relationships could be considered as special cases of theorems of moderation.

Acknowledgement.

This research was supported by the Russian Foundation for Basic Research (grant 19-03-00375).

---

[1]Toikka A. 2010. Stability of chemical and phase equilibrium: alternative forms of equations for thermodynamic analysis. In Mathematical Chemistry, Chapter 11, pp. 509–535. Nova Science Publishers, Inc., NY, USA.
[2]Gromov D, Caines PE. 2015. Stability of composite thermodynamic systems with interconnection constraints. IET Control Theory & Applications, 9(11):1629–1636.
[3]Gibbs JW. 1931. The Collected Works. V. 1. Thermodynamics, Longmans, Green and Co., NY, London, Toronto.

Industrial needs for modelling thermophysical properties

Susanna Kuitunen, Nikolas Tolvanen and Sami Toppinen

Neste Engineering Solutions Oy, Kulloo, Finland

Simulations are typically performed for process design and troubleshooting. In order to produce useful simulations results, the thermophysical properties of the chemical compounds need to be accurately modelled. Accurate modelling requires experimental data, predictive methods, effective model parameter fitting procedures as well as ways to identify the key properties to study experimentally.

Understanding the sensitivity of the design on uncertainties in the model parameters is also valuable. This presentation highlights the importance of industry collaboration, presents some general industry concerns and illustrates the usage of Monte Carlo method for evaluation of reliability of simulation results.

Based on our experience, the experimental data availability for many low molar mass organic compounds is rather good concerning the pure compound properties. If the properties are missing, the issue is tackled (especially in the preliminary concept studies) by estimating the required thermophysical properties. Vast number of estimation methods have been developed for organic compounds in the academia.

According to Gmehling[1], the status of experimental data status for mixtures is quite unsatisfactory. He estimated that there is roughly 1000 chemicals of industrial interest. All binary combinations would result 500 000 vapour-liquid equilibrium sets. Of those only 1.5 % is covered by the literature. Thus, there is often need to rely on predictive methods for interaction of chemical compounds.

Developing reliable predictive methods is a huge effort: vast set of experimental data, sophisticated software and high expertise are needed. In order to make such developments possible, industry sponsored consortia have been established.

Ten years ago the industrial needs for thermophysical properties was surveyed[2]. One issue brought up was the modelling of systems involving electrolytes. The special issue with the electrolytes are the reactions and the long range interactions of the ions. Recently, an industry consortia, EleTher, was established for the development of the best industrial practises to model electrolyte systems[3].

Even though predictive methods are used in preliminary studies, at the later stages of the project it is always recommended to carry out measurements for the key properties. Measurements are expensive and time consuming. To limit the number of required experiments, it is good to focus the work and not to measure everything. To identify the key properties to focus on, one possible option is to carry out Monte Carlo simulations[4]. Such simulations can also be utilized to study the reliability of the simulations.

---

[1] Gmehling J, Constantinescu D. 15th common meeting of UNIFAC consortium and DDBST and 22nd sponsor meeting, presentation, 19.9.2017, Oldenburg, Germany

[2] Hendriks E, Kontogeorgis G, Dohrn R, de Hemptinne J-C, Economou IG, Zilnik LF, Vesovic, V. 2010. Industrial requirements for thermodynamics and transport properties., Ind. Eng. Chem. Res., 49:11131-11141.

[3] EleTher. e-Thermodynamics Joint Industrial Project - 2019 to 2021, http://www.elether.fr/.

[4] Tolvanen N. 2019. The effect of uncertainties in physico-chemical properties on process design, M.Sc. thesis, Aalto University.

Session 2 – Theory 2

Chair Dr Petteri Kangas

Design of photocatalysts based on layered oxides for energy-saving processes of obtaining hydrogen

Irina Zvereva, Ivan Rodionov, Oleg Silyukov

Saint-Petersburg State University, Russian Federation

Photocatalytic production of hydrogen from renewable resources such as water or biomass is regarded as a promising way to deal with the problems of exhaustion of traditional fuel feedstocks and the environment pollution caused by their use. Many inorganic materials were proposed as photocatalysts for hydrogen production under UV- and visible light irradiation. Layered oxides represent a unique class of photocatalysts, which have the abilities to intercalate substrate molecules into the interlayer space[1], to exchange interlayer cations[2],[3] and to undergo the exfoliation with the formation of nanosheets. They are crystalline compounds, which are constructed by the sequential alternation of two-dimensional blocks (layers) of perovskite structure with blocks of other type of structure. The interlayer space of layered oxides is considered as a separate reaction zone, which is responsible for their high photocatalytic activity. Despite many layered oxides have already demonstrated a good performance as photocatalysts for hydrogen production, the process of their interaction with water and aqueous solutions is not fully understood. At the same time, this is essential for the understanding of the mechanism of photocatalysis and for the design of new highly efficient photocatalysts.

Our research is focused on two classes of layered oxides: the triple-layered titanates A2Ln2Ti3O10 (A = K, Rb; Ln = La, Nd) and niobates KCa2Nb3O10. We present results on their synthesis, characterization and photocatalytic properties. A number of new metastable phases with general formula HxA2-xLn2Ti3O10·yH2O was discovered. Some of these phases are readily formed when the layered oxide is dispersed in water. Generally, the photocatalytic activity in the reaction of hydrogen evolution from water-alcohol solutions was found to decrease with the increase of protonation degree (x), which is explained by the fact that the protonation process is accompanied by the contraction of the interlayer distance and by the decrease of the intercalated water content (y). In contrast, the niobates KB2Nb3O10 were found to be stable in aqueous medium and undergo protonation only in acidic solution. Moreover, the intercalation of RNH2 amines (R = Me, Et, Bu, Oc) into the interlayer space of protonated forms was found to be an efficient strategy to improve their photocatalytic activity. Probably, this is due to the strong increase of the interlayer distance.

Research was performed at the Research Park of St.Petersburg State University: Center for Thermal Analysis and Calorimetry, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Chemistry Educational Center. This work was supported by the Russian Science Foundation (grant № 19-13-00184).

---

[1] Rodionov I, Zvereva I. 2016. Photocatalytic activity of layered perovskite-like oxides in practically valuable chemical reactions. Russ. Chem. Rev., 85:248–279.

[2] Rodionov I, Mechtaeva E, Burovikhina A, Silyukov O, Toikka M, Zvereva I. 2018. Effect of protonation on the photocatalytic activity of the K2La2Ti3O10 layered oxide in the reaction of hydrogen production. Monatshefte für Chemie - Chem. Mon., 149:475–482

[3] Rodionov I, Sokolova I, Silyukov O, Burovikhina A, Fateev S, Zvereva I, 2017. Protonation and Photocatalytic Activity of the Rb2La2Ti3O10 Layered Oxide in the Reaction of Hydrogen Production., Int J Photoenergy 9628146.

Thermodynamic modeling as a tool to predict behavior of industrial melts

Daniel Lindberg

Aalto University, School of Chemical Engineering, Espoo, Finland

Thermodynamic modeling is an important tool to predict the chemistry of high-temperature industrial processes. The role of the liquid phase (slag, metal, matte, speiss) is essential in many pyrometallurgical processes, as well as in many combustion processes (black liquor recovery boiler smelt, slag, molten ash). The global trend is to utilize more complicated feed materials in many of these processes, requiring a better understanding of how elements and compounds in trace amounts are distributed between the phases in these processes, especially related to recovery of valuable elements, minimization of harmful emissions and waste, and for optimization of the processes.

Extensive thermodynamic databases exist for liquid metal, both focusing on steels and non-ferrous metals, as well as for the slags associated with the metallurgical processes, have been developed for different thermodynamic software, such as Factsage, Thermo-Calc and MTdata. Databases for molten ashes and recovery boiler smelt has mainly been developed for the Factsage software. Especially the slag and molten salts show a great complexity due to short-range ordering and these have been modeled using various solution models, such as sublattice models, quasichemical models and associate models.

Different modeling approaches to model various phenomena in the industrial processes have been developed over the years, and examples will be given for the for the vacuum tank degasser and ash deposition models connected with stickiness criteria for the molten phase[1].

---

[1] [1]Lindberg D, Backman R, Chartrand P, Hupa M. 2013. Towards a comprehensive thermodynamic database for ash-forming elements in biomass and waste combustion – current situation and future developments. Fuel Proc Technol 105, 129-141

[2]Gisby J, Taskinen P, Pihlasalo J, Li Z, Tyrer M, Pearce J, Avarmaa K, Björklund P, Davies H, Korpi M, Martin S, Pesonen L, Robinson J. 2017. MTDATA and the Prediction of Phase Equilibria in Oxide Systems : 30 Years of Industrial Collaboration. Metallurgical and Materials Transactions B: Process Metall Mat Proc Sci, 48(1), 91–98.

[3]Hupa M, Backman R, Skrifvars B-J, Forssén M. 2001. Liquor-to-liquor differences in combustion and gasification processes: Dust composition and melting properties. J Pulp Paper Sci 27(12), 416-422

Modelling of hot metal desulphurisation in steelmaking

Ville-Valtteri Visuri

Process Metallurgy Research Unit, University of Oulu, Finland

Hot metal desulphurisation serves as the main unit process for removing sulphur in blast furnace based steelmaking. In lance injection, the desulphurisation reagent is injected pneumatically using a submerged lance. In the literature, mathematical models of the process have evolved from simplistic rate equations to phenomena-based models, which provide information on the effect of physical, thermodynamic and operating parameters on desulphurisation efficiency[1]. It has been established that the main reaction mechanisms contributing to desulphurisation are transitory (metal–reagent) and permanent (metal–slag) reaction mechanisms.

At University of Oulu, mathematical modelling of the desulphurisation kinetics has been conducted with phenomenon-based and data-driven modelling approaches. A dynamic phenomenon-based mathematical model was developed based on consideration of the main reaction mechanisms and their microkinetics along with the mass and energy balance of the process. An advantage of the proposed model is that it solves the rate-controlling mechanisms separately for each particle size class. In a preliminary validation, the model was able to predict well differences in desulphurisation efficiency between two lime-reagents with different size distributions[2]. As for data-driven modelling, multiple linear regression (MLR), genetic algorithm (GA) and Nelder–Mead method were tested for fitting a parametrised phenomenon-based model for end-point prediction[3]. Later, a GA-based model selection tool was developed and successfully applied for the selection of an MLR model of desulphurisation with a lime-based reagent[4] and a feedforward neural network model of desulphurisation with calcium carbide[5].

High-temperature metal–slag experiments have been conducted to compare lime-based reagents[6], and to study the potential for resulphurisation after the hot metal desulphurisation[7]. The employed crucible method, which simulates the permanent phase contact, was not found to yield meaningful differences between the studied lime-based reagents[6]. Based on the data-driven mathematical analysis of the observed kinetic behaviour and sulphide capacity of the slag, it was established that the resulphurisation follows first-order kinetics and can be controlled by modifying the slag[7].

On-going computational fluid dynamics modelling is directed at studying the particle–gas jet as well as fluid flows and residence time of particles in the ladle. To validate the results, a 1:3.95 scale physical model was set up at RWTH Aachen University based on dynamic, kinematic and geometric similarity.

---

[1] Visuri VV, Vuolio T, Fabritius T. An overview of modeling studies on hot metal desulfurization, manuscript.
[2] Visuri VV, Sulasalmi P, Vuolio T, Paananen T, Haas T, Pfeifer H, Fabritius T. 2019. Mathematical Modelling of the Effect of Reagent Particle Size Distribution on the Efficiency of Hot Metal Desulphurisation. Proc 4th Eur Steel Technol Appl Days, Düsseldorf, Germany, Stahlinstitut VDEh.
[3] Vuolio T, Visuri VV, Tuomikoski S, Paananen T, Fabritius T. 2018. Data-Driven Mathematical Modeling of the Effect of Particle Size Distribution on the Transitory Reaction Kinetics of Hot Metal Desulfurization. Metall Mat Transact B, 49(5), 2692–2708.
[4] Vuolio T, Visuri VV, Sorsa A, Paananen T, Fabritius T. 2019. Genetic Algorithm-Based Variable Selection in Prediction of Hot Metal Desulfurization Kinetics. Steel Res Int, 90(89), 1900090
[5] Vuolio T, Visuri VV, Sorsa A, Ollila S, Fabritius T. Design of a neural network model for hot metal desulfurization with calcium carbide by making use of a genetic algorithm in variable selection task. manuscript.
[6] Lehtonen P. 2017. An Experimental Study on Desulfurization of Hot Metal with Lime-based Reagents., Master's thesis, University of Oulu.
[7] Vuolio T, Visuri VV, Paananen T, Fabritius T. 2019. Identification of Rate, Extent and Mechanisms of Hot Metal Resulfurization with CaO–SiO2–Na2O Slag Systems. Metall Mat Transact B, 50 (4), 1791–1807.

CFD in Battery Chemical Applications

Timo Kankaanpää

Freeport Cobalt Oy

Freeport Cobalt Oy produces cobalt and mixed metal based battery chemicals (precursors) for lithium-ion batteries. The properties and performance of batteries such as energy density, power density, cycle life and safety are tailored in a wide range by changing e.g. the chemical composition, physical properties and particle morphology of the precursor and thus the cathode active material. These specific and unique properties of the precursors needed in different battery applications are created during several hydro- and pyrometallurgical process stages. CFD modeling offers many additional advantages to study and develop precipitation and lithiation phenomena and applied process technologies as well. In general, mixing reactors and high temperature furnaces can be easily studied, designed and optimized by using single or two-phase CFD simulations. However, modeling becomes a challenging when it is applied to the battery chemicals production that contain several phases and interactions. These have to be known and taken into account in either a direct or an approximated way. In the precipitation, chemical components start to crystallize when temperature, pH and supersaturation of the solution are in a correct range. Here CFD simulation proves its advantage when different mixing and flow pattern situations are studied and optimized together with a certain chemical environment and other process parameters. Nucleation and crystal growth are controlled to obtain a certain type of material for the next pyrometallurgical process stage. After the precipitation, cobalt salt-based precursors are typically fired in a furnace to prepare cobalt oxide material for lithiation. In the lithiation process, cobalt oxide material is fired with a lithium source to form lithium cobalt oxide cathode active material. This process can be also studied and optimized by CFD when gas flow and lithiation reactions are simulated in a high temperature furnace used for the lithiation. It can be concluded that CFD offers an alternative tool to study and develop precipitation and lithiation processes when mixing, nucleation, crystal growth and sintering phenomena are adjusted to an optimum range that the produced precursor can meet the required specifications for different lithium-ion battery applications.

Session 3 – Applications 1

Chair Dr Eemeli Hytönen

Keynote
Prof Pertti Koukkari
VTT

Keynote 2

Constrained free energy within VTT and industry

Pertti Koukkari

VTT Technical Research Centre of Finland

Materials and process research both are pursuing for enhanced functionality and continuously look for new solutions that decrease the want of materials while also ensure energy efficiency and minimum environmental impact. The success of a new application is affected not only by its internal physical and chemical relations but also by the impact on the surrounding environment throughout the life-cycle. With increasing number of chemical elements entering to commercial use the significance of controlling their complex interactions by rigorous quantitative methods has become a necessity in both materials technology and process development. Advanced computational techniques are being used in both fields providing exact formulations and derivations of mass energy balances and their numerical solutions[1],[2].

In 2007, the Best Paper Award of the CAPLHAD Journal was granted to VTT's researchers for the publication on the constrained Gibbs energy minimization method (CFE)[3]. The thermodynamic free energy calculation, conventionally used for multiphase equilibrium balances of chemical substances, is by CFE generalized to include systems subdued to physical or dynamic work factors. Since then the awarded method has been used in several practical applications that have been presented both in VTT's research reports and on international science forums. The new approach has also increased the interest in the use of VTT's thermodynamic calculation software around the world.

Conventional thermodynamic calculation methods focus on phase changes and on products of chemical reactions as function of temperature and pressure. Therefore the methods in wide international use are specifically suited for computing chemical equilibrium compositions and for creating diagrams describing multicomponent phase equilibria. Both approaches are extensively used in chemical technology and material sciences since many decades[4],[5].

However, in practical processes equilibrium is seldom reached, or the composition of the material being processed is affected also by other than purely chemical factors. Accordingly, a new approach was needed for problems in which both the time dynamics of the chemical change and various physical preconditions must be taken into account. The Constrained Gibbs Free energy technique provides a

---

[1] Hack K. 2008. The SGTE Casebook: Second Edition: Thermodynamics At Work, 2nd ed, The SGTE Casebook, 2nd Edition: Thermodynamics At Work. doi:10.1533/9781845693954

[2] Salmi TO. 2018. Chemical Reaction Engineering and Reactor Technology, Chemical Reaction Engineering and Reactor Technology. doi:10.1201/9781439894859

[3] oukkari P, Pajarre R, 2006. Calculation of constrained equilibria by Gibbs energy minimization. Calphad Comput. Coupling Phase Diagrams Thermochem. 30. doi:10.1016/j.calphad.2005.11.007

[4] Petersen S, Hack K. 2007. The thermochemistry library ChemApp and its applications. Int. J. Mater. Res. 98, 935–945. doi:10.3139/146.101551

[5] Roine A. 2015. Outotec, 2015. HSC Chemistry [WWW Document]. URL http://www.hsc-chemistry.com/ (accessed 10.12.15).

quantitative methodology for such chemical and phase changes, which are generally driven by specific physical functions deciphered as thermodynamic work. CFE is straightforward to implement into conventional computation techniques and deals accordingly with the complex systems involving changes in energy and in chemical or phase composition. The salient feature of the method is its ability to incorporate the contribution from generalised work to a multiphase free energy computation, which facilitates quantifiable solutions of intricate problems in multicomponent systems influenced by either internal or external forces due e.g. to surface tension, charge and electric-magnetic factors. The same principle can also be applied to non-equilibrium processes, allowing for the inclusion of 'freezing-in conditions' as well as chemical reaction rates in the form of affinity related constraints in the thermodynamic multiphase analysis. The method uniquely applies the technique of Lagrange in Gibbs energy minimisation, and the potentials defined by work terms and non-equilibrium affinities become solved as the undetermined multipliers.

The computational programs developed by VTT are internationally distributed by the German SME GTT Technologies GmbH [4] which markets thermodynamic calculation software and databases worldwide. VTT's ChemSheet software has been a part of this international product group since 1999[1]. Allowing for the rich multicomponent chemistry in combination with thermodynamic state properties, ChemSheet has provided an efficient and lasting tool also for industrial scientists wishing to connect complex thermochemical calculations with their in-house expert systems. Similarly VTT's specific simulation programs for industrial counter-current reactors and furnaces are being used in more than 20 countries by both research and industry[2].

The thermodynamic method allows for an extensive range of modelling, yet by using basically the same software tools. The applications making use of constrained free energies range from functional behaviour of nanosize particles to features of dynamic superequilibria in large scale industrial reactors [3,4]. Thus the method gives an exceptionally large array of potential uses in process and materials technology, including construction of unconventional phase diagrams for partial and paraequilibrium systems[5] and for systems affected by external fields or constrained by advancement of chemical reactions[6,7] [11,12]. The presentation will summarize the methodology and give some examples of new kinds of phase diagrams.

---

[1]Koukkari P, Penttilä K, Hack K, Petersen S. 2000. CHEMSHEET – An Efficient Worksheet Tool for Thermodynamic Process Simulation. In: Bréchet, Y. (Ed.), Microstructures Mechanical Properties and Processes, pp. 323–330. doi:10.1002/3527606157.ch51

[2] Meyer V, Pisch A, Penttilä K, Koukkari P. 2016. Computation of steady state thermochemistry in rotary kilns: Application to the cement clinker manufacturing process. Chem. Eng. Res. Des. 115, 335–347. doi:10.1016/j.cherd.2016.08.007

[3] Lee Junggoo, Lee Joonho, Tanaka T, Mori H, Penttilä K. 2005. Phase diagrams of nanometer-sized particles in binary systems. doi:10.1007/s11837-005-0235-6

[4] Kangas P, Hannula I, Koukkari P, Hupa M. 2014. Modelling super-equilibrium in biomass gasification with the constrained Gibbs energy method. Fuel, 129:86–94, doi: 10.1016/j.fuel.2014.03.034.

[5] Pelton AD, Koukkari P, Pajarre R, Eriksson G. 2014. Para-equilibrium phase diagrams. J. Chem. Thermodyn. 72, 16–22. doi:10.1016/j.jct.2013.12.02.

[6] Toikka AM, Samarov AA, Toikka MA. 2015. Phase and chemical equilibria in multicomponent fluid systems with a chemical reaction. Russ. Chem. Rev. 84, 378–392. doi:10.1070/rcr4515

[7] Koukkari P, Pajarre R. 2011. A Gibbs energy minimization method for constrained and partial equilibria. Pure Appl. Chem. 83. doi:10.1351/PAC-CON-10-09-36

Applications of multi-phase chemistry in Valmet

Sonja Enestam and Aino Vettenranta

Valmet Technologies Oy

Valmet is one of the main suppliers of technology, automation and services for the pulp, paper and energy industries globally. In the development of efficient, sustainable products and technologies for our customers, a detailed understanding of the processes is a corner stone. Since many of the products and processes in our portfolio involve complex chemistry, either at high temperatures or in water solutions, multi-phase equilibrium modelling has proven to be a very beneficial tool both for understanding the processes and for optimizing their design.

The use of multi-phase chemistry at Valmet dates back to the 1990's where models for predicting the melting behaviour of black liquor recovery boiler smelt and fly ash were developed. The inorganic chemistry of black liquor at high combustion temperatures can be described quite accurately with thermodynamic equilibrium modelling[1], and the models have later been further developed and combined with computational fluid dynamics (CFD) to predict fouling and corrosion of recovery boilers[2].

In the energy sector, one of the main challenges today is to replace fossil fuels with renewable energy sources, such as bio- and waste-based fuels. However, a limiting factor for the efficient use of bio and waste fuels is the corrosion of heat exchanger surfaces. To optimize the use of renewable fuels, Valmet has created an in-house corrosion prediction method, SteaMax. SteaMax is based on multi-phase equilibrium modelling combined with empirical data and is used in the design of new biomass, waste and multifuel boilers and in conversions from coal to biomass[3]. It can also be used to optimize the composition of a fuel mixture, or to troubleshoot corrosion problems.

As the demand for closed pulp mills and lower emissions increases, the need for detailed understanding and optimization of our processes also increases. This need is reflected in increased utilization of multi-phase modelling. Examples of recent applications are models for ash leaching for recovery boilers, wet flue gas cleaning and non-process elements in the pulp mill[4].

---

[1] Lindberg D. 2007. Thermochemistry and melting properties of alkali salt mixtures in black liquor conversion processes. Academic Dissertation, Åbo Akademi University, Finland.
[2] Leppänen A. 2015. Modeling Fume Particle Dynamics and Deposition with Alkali Metal Chemistry in Kraft Recovery Boilers. Tampere University of Technology, Finland.
[3] Enestam S, Niemi J, Mäkelä K. 2008. STEAMAX – A novel approach for corrosion prediction, material selection and optimization of steam parameters for boilers firing fuel and fuel mixtures derived from biomass and waste. in 33rd Int Techn Conf Coal Utiliz & Fuel Syst. Clearwater, Florida.
[4] Penttilä K, Vettenranta, A. 2019. Modelling of non-process elements in a lime kiln burning renewable product gas. Nordic Flame Days,Turku, Finland.

Applications of process modelling in kraft pulp mills

Jukka Rantamäki

Metsä Fibre Oy

Metsä Fibre is a leading producer of bioproducts, bioenergy and sawn timber. The company's brand in the pulp business is Botnia, and in sawn timber, it is Nordic Timber. Metsä Fibre is the world's leading producer of bleached softwood pulp and a major producer of sawn timber. Currently employing approximately 1,200 people, the company's sales in 2018 totaled EUR 2.5 billion. Metsä Fibre is part of Metsä Group.

The motivation for a process industry manufacturing company for using process models is, at the end of the day, to increase bottom line, i.e. make better financial results. Typically, these models are used for problem solving or predicting process change impacts. Typical process models used in Metsä Fibre include e.g. mass & energy balances and black box models generated with and by data mining. Difference between business and academia may be that the results in business need only to be "roughly right" in order to gain benefit. Very often modelling services are purchased and mostly models are static. In house competence is found in using data mining and diagnostic tools, such as Wedge. Mass and heat balances of each mill are used and maintained through their whole life cycle.

Typical manufacturing process models deal with cases such as pulp digester runnability, washing efficiency, process scaling and precipitation forecasting, NPE-(Non Process Element) estimation, energy balances and all around data mining for problem solving. Case examples presented from Metsä Fibre include Metris FOX online pulp quality index, bleaching process simulation and modeling of chip bed packing in a continuous kraft cooking digester.

The present and future challenges in applying process modelling in Metsä Fibre deal with combining data analysis and balances, creating and exploiting dynamic real time simulations ("Digital twins") and especially, ensuring organizational learning using models as a part of organizational memory.

Key references

[1]Laakso S. 2008. Modeling of chip bed packing in a continuous kraft cooking digester, University of Technology, Helsinki, Finland

[2]Rantamäki J, Saarela O. 2015. Diagnosis and economic impact of operational variability – a case from the chemical forest industry. J Quality Maintenance Eng, 21(3), 294-309

Latest in process modelling at ANDRITZ

Keijo Salmenoja, Viljami Maakala, and Jukka Röppänen

Andritz Oy, Helsinki, Finland

ANDRITZ is a world leading provider of Pulp and Paper industry related products and processes. These include e.g. wood yard, fiberline, recovery, and drying machine equipment and processes. ANDRITZ has during the recent years become world's leading supplier of kraft recovery boilers by delivering two of the world's largest recovery boilers. The largest unit in operation have a capacity of 12 000 tds/d and the second largest unit has a capacity of 8 250 tds/d.

Process modeling is utilized in several aspects, such as in basic design, research and development work, trouble shooting, and in different process evaluations. Process modeling is also one of the major tools in designing the world's largest recovery boilers. Process modeling has been utilized in recovery boilers for liquor spraying, combustion enhancement, and for reduction of emission, in particular NOx emissions. To increase power output from recovery boilers, modeling has been used to study heat transfer phenomena in superheater area. Modeling has also rendered possible to design ever larger furnaces, since the flow fields can be reliably visualized with computational fluid dynamic (CFD) models.

In trouble shooting, modeling is a valuable tool in root cause analysis. By combining modeling with practical results, conclusions are easier to draw. Modeling with incorporated dust properties helps to mitigate fouling issues and enables to develop a fouling-free design. Modeling can also be applied in solubility related issues to find out precipitation of different components. This helps to mitigate fouling issues in liquid phases in the processes.

This presentation will concentrate on process modeling used at ANDRITZ. Different applications of process modeling will be briefly reviewed. Examples of applications of process modeling will be reviewed. However, the emphasis will be on recovery boiler related process modeling due to the background of the authors.

Session 4 – Applications 2

Chair Dr Eemeli Hytönen

Application examples of the constrained Gibbs energy theory using FactSage and ChemApp

Klaus Hack, Stephan Petersen and Moritz to Baben

GTT-Technologies, Herzogenrath, Germany

Since the formulation of the Constrained Gibbs Energy Theory by Pertti Koukkari, ChemSheet was used as the main tool at VTT to build application examples and investigate the influence of constraints such as setting kinetic controls for complex equilibrium calculations[1].

Since ChemSheet is built on ChemApp, and the necessary modifications to the thermochemical description of the system are implemented in the Gibbs energy-based data-file read by ChemApp, every software that utilizes ChemApp is able to make use of such kinetic controls, provided that the data-file for the thermochemical system can be edited to make the necessary changes.

The consideration of such custom kinetic controls is even possible in FactSage: In the present version the option of using paraequilibrium permits the application of diffusion kinetic constraints in systems with one or more components which have a much higher mobility than the others. This is typically the case in systems which contain interstitial elements, such as carbon and nitrogen in steels. The "others", i.e. the metallic components, will then on the fly, i.e. without modifications of the contents of the databases, be coupled by appropriate stoichiometric constraints which make them behave like "one element". Examples of this will be discussed in more detail. With one of the coming versions of FactSage it is planned to provide support for the concept of "image system components", thus permitting to include, again on the fly, reaction kinetic constraints as well. A short discussion of how this could be realised will be demonstrated.

Another very useful tool for the investigation into application examples of the Constrained Gibbs Energy Theory is ChemAppPy, a version of ChemApp that integrates into the popular Python environment.

Examples are presented of how kinetic controls are applied in FactSage, ChemApp, and ChemAppPy.

---

[1] [1]Koukkari P, Pajarre R, Hack K. 2008. Setting kinetic controls for complex equilibrium calculations. In K. Hack (Ed.), The SGTE Casebook 2nd ed., pp. 359–367. Cambridge, UK: Woodhead Publishing.

[2]Koukkari P, Pajarre R, Hack K. 2008. Modelling TiO_2 production by explicit use of reaction kinetics. In K. Hack (Ed. The SGTE Casebook 2nd ed., pp. 437–446. Cambridge, UK: Woodhead Publishing.

[3]Bale CW, Bélisle E, Chartrand P, Decterov SA, Eriksson G, Gheribi AE, Hack K, Jung I-H, Kang, Y-B, Melançon J, Pelton AD, Petersen S, Robelin C, Sangster J, Spencer P, Van Ende M-A. 2016. FactSage thermochemical software and databases, 2010–2016", CALPHAD, 54, 35-53.

[4]Petersen S, Hack K. 2007. The thermochemistry library ChemApp and its applications. IJMR 98(10), 935–945.

Thermochemistry in rotary kilns for cement production

Alexander Pisch

University Grenoble Alpes, CNRS, Grenoble INP, SIMaP, France

Cement and Concrete are the most widely used building materials in the world. The production of cement is very energy intensive due to the high temperature process conditions of up to 1500°C and the high content of limestone in the starting materials. In order to optimize the thermal budget of the fabrication process and to minimize the impact of thermal losses, large rotary kilns are used with a clinker production of up to 7500 t/day. The clinker is the active part in the final cement and it is ground together with secondary materials such as slag, fly ash or limestone to reduce the CO2 footprint and a sulphate source to control the setting. The quality of the final cement depends mainly on two parameters: the cement clinker chemistry / mineralogy (impact of natural raw materials, secondary materials, fuel ashes) and the process conditions (burning temperature profile, oxygen partial pressure, cooling conditions).

In order to optimize the production process, the availability of two main tools are desirable:

- A model to predict the clinker mineralogy from the chemical composition
- A simulation tool to evaluate the impact of the process conditions

In both cases, a high quality Calphad type thermodynamic database is necessary. Due to the use of natural raw materials, the chemical system under investigation is complex and may contain up to 12 chemical elements showing a potential impact on the quality of the final cement. Based on the FToxid database implemented in Factsage, an optimized Gibbs energy dataset was produced and a two-step model was set up which allows a reliable prediction of the clinker phases from the chemical composition only. In addition to the mineralogy, the model also predicts some additional key parameters such as the maximum burning temperature and the amount of soluble alkalis. The overall agreement is excellent.

The second step can be tackled using the KilnSimu simulation package developed at VTT[1]. This 1D simulation model of the clinker burning process was used with success to model the impact of a change in burning conditions for a given plant[2].

Some recent approaches to reduce the environmental impact of cement production will also be presented[3] and numerical simulation is a key point to accelerate the development of these promising new solutions.

---

[1] Penttilä K. 1996. A simulation model of TiO2-calcination kiln. M.Sc thesis. Helsinki University of Technology, Finland

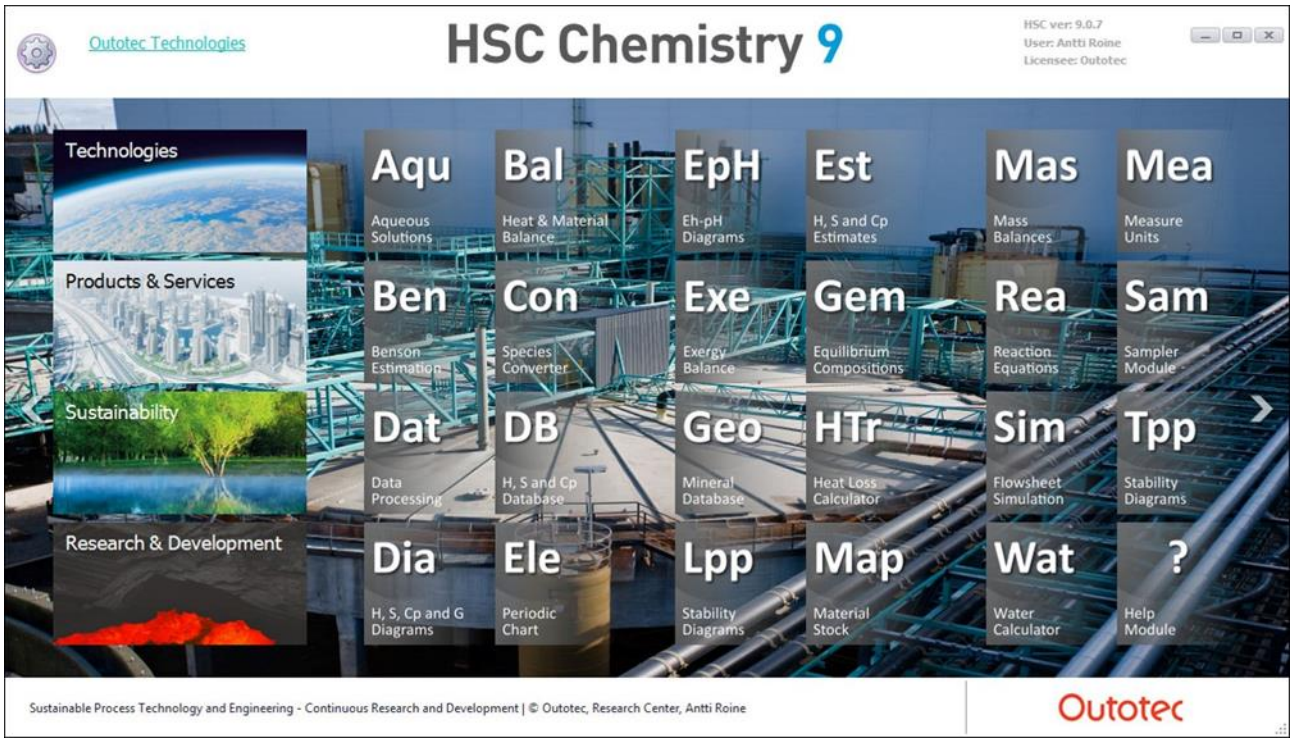
[2] Meyer V, Pisch A, Penttilä K, Koukkari P. 2016. Computation of steady state thermochemistry in rotary kilns: Application to the cement clinker manufacturing process. Chem. Eng. Res. & Design, 115:335-347.

[3] Gartner EM, Gimenez M, Meyer V, Pisch A. 2014. A Novel Atmospheric Pressure Approach to the Mineral Capture of CO2 from Industrial Point Sources. Proc Carbon Capture, Utilization & Storage Conf, Pittsburgh, USA

HSC Chemistry®: Past, present and future

Antti Roine

Outotec (Finland) Oy



HSC Chemistry® development started in 1966 to create R&D tools for the metallurgical process development in Outokumpu Oy, because such software tools did not exist. Within the last 50 years some 24 calculation modules and 13 databases has been integrated into the HSC package. The focus of the development within the last years has been on process flowsheet modelling and simulation, and integrating these process models with the process control and environmental footprint evaluation. The development has been done in close co-operation with several universities and research organizations like VTT. Especially HSC water solution calculations has been developed together with VTT. HSC is widely used in the universities and companies, huge number of scientific papers refer to the HSC software. The presentation will give a brief review of the HSC past, present and future[1].

[1] http://www.outotec.com/HSC

[2]http://www.outotec.com/globalassets/products/digital-solutions/hsc/hsc-chemistry-literature-references.pdf

ChemSheet 2.0

Karri Penttilä

VTT Technical Research Centre of Finland

ChemSheet is one of the software pioneers serving the need of coupling rigorous thermochemical software with more common, easy-to-use interfaces. ChemSheet provides an MS-Excel add-in coupling to the well-known ChemApp Gibbs energy solving library. ChemSheet is already 20 years old and although it has stand the test of times well, it has recently been redesigned with the latest Microsoft Office development tools. New ChemSheet 2.0 is compatibility with current and future 32-bit and 64-bit versions of Excel for Windows desktop. The new version also allows defining constrained thermodynamic equilibrium models easier than ever. Simultaneously new features incorporated to ChemApp are also available in ChemSheet[1].

[1]Hack K, Petersen S, Koukkari P, Penttilä K. 1999. CHEMSHEET an Efficient Worksheet Tool for Thermodynamic Process Simulation. Microstructures, Mechanical Properties and Processes, Bréchet Y., Wiley (Ed.), EUROMAT, 3, pp 323-330.

[2] Penttilä K, Salminen J, Tripathi N, Koukkari P. Chemsheet as a Simulation Platform for Pyrometallurgical Processes. 2014. In Celebrating the Megascale: Proceedings of the Extraction and Processing Division Symposium on Pyrometallurgy in Honor of David G.C. Robertson., Mackey, P. J., Grimsey, E. J., Jones, R. T. and Brooks, G. A., Wiley (Ed.), 377-384.

Professor Pertti Koukkari

Research Professor Pertti Koukkari

Pertti Koukkari is Doctor of Science in physical chemistry from Helsinki University of Technology TKK (today Aalto University). He started career as a university scholar and assistant teacher at TKK, Laboratory of Physical Chemistry and Electrochemistry, where he worked for six years. In 1985, he joined the Finland-based chemical company Kemira Oy as process development specialist, while also continuing academic activities as an R&D coordinator, managing both national and international academy-industry R&D projects. He was assigned to Kemira Inc. USA in 1992-1993 and was stationed in Savannah, Georgia. He defended his doctorate thesis titled A Physico-Chemical Reactor Calculation by Successive Stationary States in 1995, in which the concept of coupling reaction rates with free energy minimization was introduced.

Pertti Koukkari joined VTT in 1995. His career has included positions of Senior Research Scientist, Research Group Leader, Principal Scientist and Research Professor. Currently he is Research Professor for Sustainable Chemical Processes and Systems, leading both national and international research projects.

The speciality field of Pertti Koukkari is multiphase chemical thermodynamics and its applications in process and materials science. His work within industry and research has resulted in several energy and material saving solutions in various fields of process technology. He is the inventor of the internationally recognised Constrained Gibbs Free energy method that is the basis of five advanced process simulation software products developed as team activity, including the widespread ChemSheet and KilnSimu programs. Prof. Koukkari is also co-inventor of several patents and author of over 40 refereed scientific papers with topics ranging from basic thermodynamics to many practical applications in process chemistry and metallurgy.

Prof. Koukkari's awards include Award for Best Published Paper in Computer Coupling of Phase Diagrams and Thermochemistry (2006),

Petteri Forsström Award for Best Published Paper in Materia (2017) and Knight Medal of the 1st Class Finnish Lion (6.12. 2014).

In his spare time Pertti Koukkari maintains the rural family housing and walks wild in nature, either on or off the trails and observes birds.

Scientific papers

1. Koukkari P, Pajarre R, Kangas P. 2018. Thermodynamic affinity in constrained free-energy systems. Monatshefte fur Chemie 149, 381–394. doi:10.1007/s00706-017-2095-5
2. Koukkari P, Paiva E. 2018. Mechanistic and constrained thermochemical modelling in chemical reactor engineering: Ti(IV) chloride oxidation revisited. Chem. Eng. Sci. 179, 227–242. doi:10.1016/j.ces.2018.01.016
3. Meyer V, Pisch A, Penttilä K., Koukkari P. 2016. Computation of Steady State Thermochemistry in Rotary Kilns: Application to the Cement Clinker Manufacturing Process, Chemical Engineering Research and Design, 115, 335-347.
4. Pelton A, Koukkari P, Pajarre R, Eriksson G. 2014. Calculation of parae-quilibrium phase diagrams J. Chem. Thermodynamics 72, 16–22.
5. Blomberg P, Koukkari P. 2011. A systematic method to create reaction constraints for stoichio-metric matrices, Computers and Chemical Engineering 35, 1238–1250.
6. Pajarre R, Koukkari P, Tanaka T, Lee, Y. 2006. Computing Surface Tensions of Binary and Ternary Alloy Systems with the Gibbs'ian Method, Calphad, 30, 196-200.
7. Koukkari P, Pajarre R. 2006. Calculation of Constrained Equilibria by Gibbs Energy Minimization, Calphad, Vol. 30, 18-26.
8. Koukkari P, Liukkonen S. 2002. Calculation of entropy production in process models. Industrial & Engineering Chemistry Research 41(12), 2931 – 2940.

9. Koukkari P, Pajarre R, Pakarinen H. 2002. Modeling of the ion exchange in pulp suspensions by Gibbs energy minimization. J Solution Chem 31(8), 627 – 638.
10. Karlemo B, Koukkari P, Paloniemi J. 1996. Formation of gaseous intermediates in titanium(IV)chloride plasma oxidation. Plasma Chemistry and Plasma Processing 16(1), 59 – 77.
11. Koukkari P; Sippola H, Sundquist A. 1994. Multicomponent equilibrium calculations in process design, A Study of Some Acid Digester Reactors Hydrometallurgy 94. Inst. of Mining and Metallurgy and Society of Chemical Industry, Chapman & Hall, pp. 139 - 157.
12. Koukkari P. 1993. A Physico-Chemical Method to Calculate Time-Dependent Reaction Mixtures, Computers & Chemical Engineering 17(12), 1157 – 1165.

Books and scientific monographies:

13. Koukkari P. 2014. Introduction to Constrained Gibbs Energy Methods in Materials and Process Research, VTT Technology 160, Kopi Jyvä Oy, ISBN 978-951-38-8134-4, 111 pp
14. Koukkari P. (ed). 2009. Advanced Gibbs Energy Methods for Functional Materials and Processes – ChemSheet 1999-2009, VTT Research Notes 2506, Edita Prima Oy Helsinki, Finland, ISBN 978-951-38-7330-1, 145 pp.
15. Koukkari P. 1995. A Physico-Chemical Reactor Calculation by Successive Stationary States, Acta Polytechnica Scandinavica, Chemical Technology Series, No 224, Helsinki, Finland, 60 p. (thesis).

Popular articles:

16. Koukkari P. 2018. Onko Jäämeri ilmastopuskuri vai lämpöpumppu ?, Kemia-Kemi 8, 14-17
17. Koukkari P, Lundström M, Porvali A, Kirillov, S. 2017. Waste heaps may be set to reveal their content of critical metals, Materia 2, 61-65.
18. Koukkari P, Pajarre R, Räsänen E. 2005. pH:n ja alkaliteetin määrittäminen kuitususpensioissa, Paperi ja Puu/Paper and Timber. 87(5), 316 - 321.

SOFTWARES

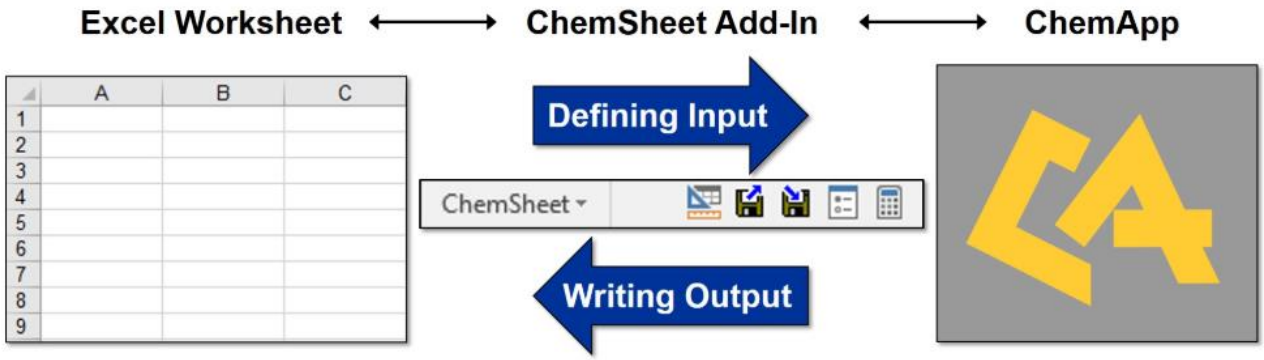
- ChemSheet
- KilnSimu
- Balas
- Apros
- Sulca

https://gtt-technologies.de/ Software/ChemSheet/

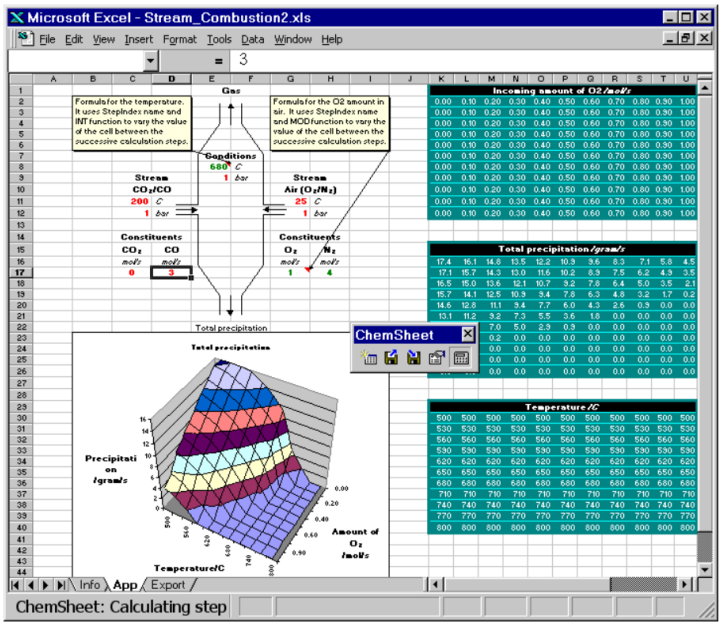
ChemSheet

"ChemSheet combines the flexibility and practicality of spreadsheet applications with rigorous, multi-phase thermodynamic calculations. Each application is defined as an independent worksheet in Microsoft Excel®, in which the entire simulation can be done."

Nowadays, everybody uses spreadsheet programs like Microsoft Excel to collect information on e.g. process conditions (input, output, temperatures…). The great flexibility of spreadsheet programs allows easy basic physical modelling, e.g. of heat transfer, material transport or reaction kinetics. ChemSheet is an Add-In for Microsoft Excel that adds the ability of thermodynamic calculations by linking to ChemApp. This gives the user the ability to combine physical modelling in Excel with thermodynamic modelling in ChemApp. ChemApp is GTT-Technologies' programmer's library for the calculation of multicomponent, multiphase chemical equilibria and their associated energy balances.



The Excel Add-in ChemSheet was originally developed by VTT Chemical Technology, Finland, in cooperation with GTT-Technologies. Check out the various application examples that show how physical modelling and ChemApp calculations can be combined in a single Excel file!



ChemSheet is also available as ChemSheet Light – the free demo version of ChemSheet!

See ChemSheet Model calculation shown as animated gif files to see how easy it is to do different kind of case studies with ChemSheet.

Get in touch with us:
Senior Scientist Karri Penttilä
karri.penttila@vtt.fi.

https://www.simulationstore.com/node/49

KilnSimu – Rotary Kiln Simulator

KilnSimu is used in several industries. Though the technology of rotating drums has been available for over 100 years, it has not been replaced, but remains in active use in many of its traditional applications. The rotary drum provides an effi cient means for both heat and mass transfer in the processing of slurries and other condensed mixtures.

Customer
Pigment and cement manufacturing industries are using rotary drums for the thermal treatment of various materials. In the chemical recovery of kraft pulping rotary drums are applied for lime recycling. Other uses are in themanufacture of oxides (aluminium, zinc, lead), reduction of ores and in waste incineration. Currently KilnSimu has customers in Finland, Japan and Italy.

Challenge
There is increasing interest in the complex chemistry of rotary drums, as many of the raw materials as well as the fuels used as heat sources vary in their chemical composition. This variation may lead to undesired emissions in the off gas or maintenance problems of the kiln. One common problem in lime kiln is the formation of rings due to alkali compounds. An additional challenge is created by the structure of the kilns. Due to the rotating cylindrical steel cover, the monitoring of the kiln interior is difficult. Due to long residence times, which may exceed 10 hours in continuous operation, undesired chemical pathways should be avoided. Thus it is often benefi cial to use a reliable simulation model to depict and control their internal processes.

Solution
Most kilns operate in the counter-current mode, i.e., the condensed material is fed into the kiln from the cold 'feed end', and is then processed to reacted product by heat transfer from the surrounding hot gas, which is introduced into the kiln from its hot 'burner end'. The final material product is removed from the hot end. A fraction of exit gas can be circulated back to the hot end to improve the heat transfer efficiency. As a heat source, a fuel burner operating with the primary air is typically used. In KilnSimu the rotary kiln is divided into number of axial calculation zones, in which the radial temperatures of material bed and gas flows and inner and outer wall of the kiln are assumed constant. The volume elements of material bed and gas in the zones are described as open thermodynamic systems, which transform mass and heat with each other. The chemical composition of the volume elements are calculated by thermodynamics, yet taking into account the time-dependent mass and heat transfer between the elements and their surroundings. The kinetics of the material bed reactions are incorporated by dividing the solid phases into reactive and inert subsystems by using experimental reaction rates. The bed and gas flows of the kiln are calculated in a successive manner until all the energy and mass balances converge to an accurate solution.

Key benefits
The simulation yields axial temperature profi les for the bed, the gas and the inner and outer walls. In addition, axial phase compositions of the bed and gas flows are calculated. Results can be used to optimise fuel consumptions with different material feed capacities and to study the effect of using various fuels. Other uses are optimising the gas circulation and other energy factors including the kiln geometry. KilnSimu is also well suited for kiln scale-up.

Get in touch with us:
Senior Scientist Karri Penttilä, karri.penttila@vtt.fi

https://www.simulationstore.com/balas

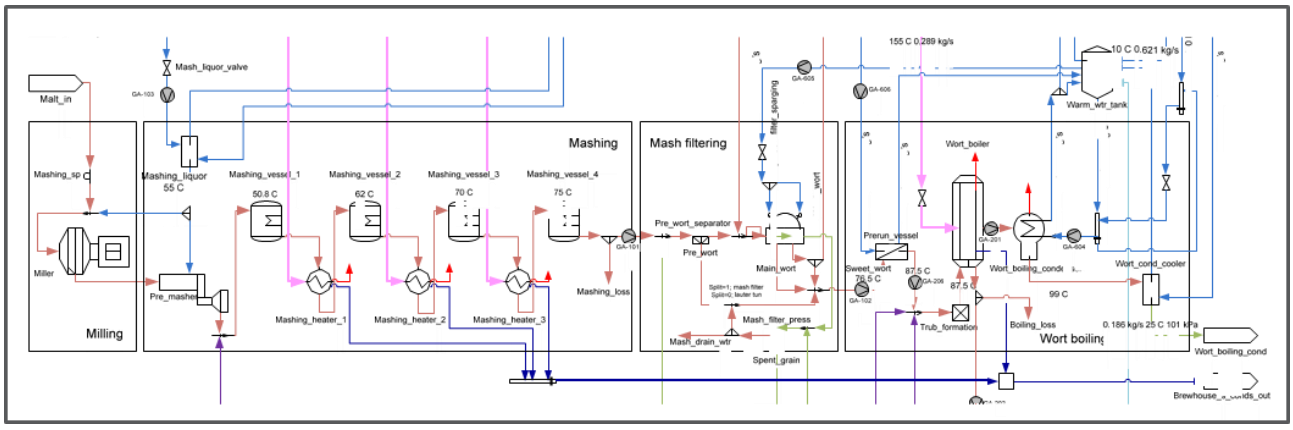
BALAS® – Conceptual process design to optimise your resource efficiency

Process design and analysis is always based on the management of mass and energy balances. BALAS® simulation tool is the most effective way to calculate and optimize complex processes, energy and material streams. With BALAS® you can reduce costs by optimizing the use of chemicals, energy and water in your processes.

BALAS® is a steady-state simulation package for chemical processes with emphasis on pulp and paper, food processing and biochemical processes. The software has been developed at VTT over the last 20 years and many paper mills, engineering companies and equipment manufacturers currently use it.

Efficient and easy to use process simulation
BALAS® has an extensive selection of unit operation modules. These unit operation modules enable the user to model the whole process including raw material handling and processing, reactors, heat recovery, utilities and wastewater treatment. A selection of ready-made model processes are also supplied with the software. Furthermore, the mathematical solvers of BALAS® solve balances for complex process flowsheets efficiently

Easily calculates complex industry processes
BALAS® simulation models are created and maintained through an intuitive user interface. The model is built up in MS Visio by dragging and dropping unit operations from libraries, drawing streams connecting units, and entering input data using dialog windows. MS Excel can be used to further process the balances into usable metrics.



Process simulation model – screenshot of brewhouse flowsheet.

Get in touch with us:
Technology Manager Eemeli Hytönen, Eemeli.hytonen@vtt.fi

http://www.apros.fi/

Apros® dynamic process simulation software

Shorter commissioning, ensured safety and improved performance

Dynamic process simulation is an invaluable tool for producing information about the installation without disturbing the production, and well before procurement and commissioning.

Just imagine what you could do with a digital twin of your plant!

Applications and benefits

- Safety analysis – reduce risks and convince the safety authority
- Engineering support – check up the controls and dimensioning well in advance
- Automation testing – reduce the commissioning time
- Operator training – knowledge transfer by involvement

Products and industries

- Apros Basic for district heating, process industry and shipbuilding
- Apros Thermal for combustion power plants and concentrated solar power plants
- Apros Nuclear for nuclear industry, with add-ons for 3D reactor and containment

Apros advantages

- Wide validity range and solid validation scheme applied to each release
- Comprehensive model libraries for process, automation and electrical systems
- Modern user interface with intuitive graphical access and powerful scripting
- Open interfaces for real time data exchange and use of engineering data
- Stable and continuous development, and active user community

Services by VTT

- Licenses on once paid basis or by rent
- Training mentoring, application development
- Integration to other simulation tools for co-simulation
- Integration to engineering tools and databases

Apros® is a registered trademark of Fortum and VTT

Apros® Thermal is a high-fidelity dynamic simulation product for integrated thermal power plant process and automation design and engineering, and for creating highly realistic plant-specific operator training simulators. It includes complete model libraries to build plant-specific dynamic models of thermal power plants for high-fidelity engineering and training simulation needs. Typical Apros® Thermal users are main process or automation equipment vendors, power plant owner operators, engineering companies, system integrators, and training providers.

Apros® Thermal combines the high-fidelity thermal hydraulic solvers, and modern, easy-to-use fully graphical user interface. The entire power plant model covering the boiler, turbine plant, auxiliary systems including the automation and electrical system can be simulated using a single tool. The openness and supported communication, e.g. OPC UA and OPC DA, it is easily connected to most emulated or virtual DCS and automation HMI on the market.

The thermal hydraulic solvers of Apros® Thermal are verified and validated based on nuclear industry requirements. Apros® Thermal software brings along the same high level of modelling and simulation quality to thermal power plants.

Efficient model configuration and realistic dynamic simulation

Apros® Thermal is currently in active use by several boiler, turbine, and automation system vendors, and has proven efficient and highly realistic dynamic simulation to satisfy dynamic simulation needs of the most demanding customers. Apros® Thermal is completely process and automation system vendor independent. The easy-to-use graphical user interface, the openness to integrate customer's own in-house models, and the features to support customers own model library development makes Apros® Thermal an ideal dynamic simulation tool for boiler, turbine, heat exchanger manufacturers, and engineering companies.

Connection to automation systems for operator training simulators

More than 30 high-fidelity operator training simulators have been successfully delivered internationally based on Apros® Thermal software.

The core of an Apros® Thermal based simulator is a highly realistic dynamic power plant model customized using design data provided by system and equipment vendors.

The connectivity (e.g. OPC UA / OPC DA) of Apros enables the successful integration to most DCS systems on the market; either hardware-in-the-loop, or using the emulated/virtual DCS approach, as most feasible in the customer project.

Get in touch with us:

Product Manager Sami Tuuri, sami.tuuri@fortum.fi

Solution Sales lead Matti Paljakka, matti.paljakka@vtt.fi

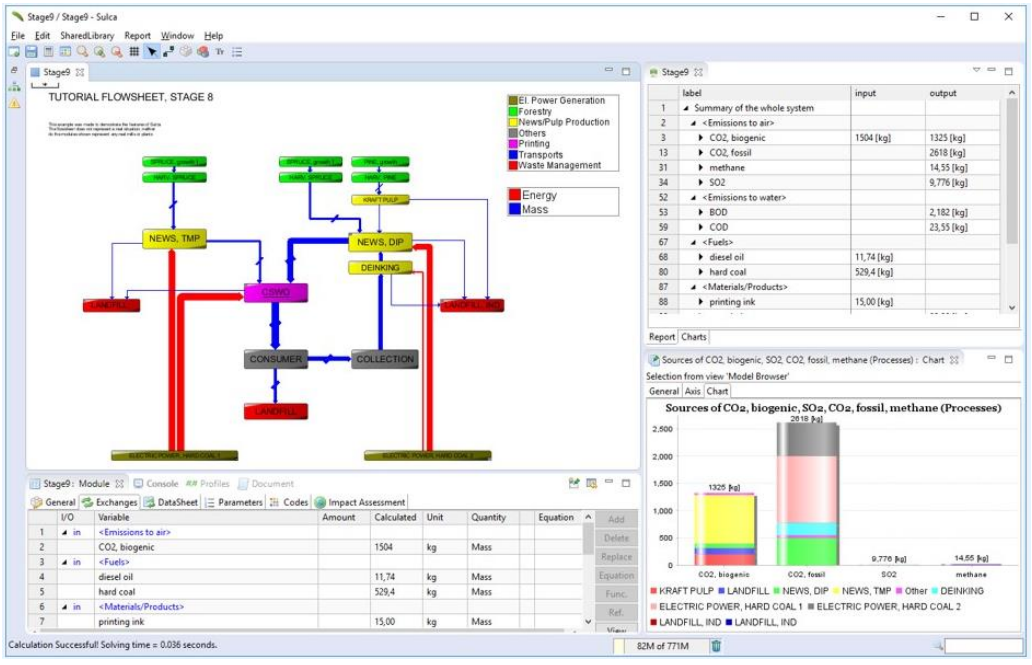
https://www.simulationstore.com/sulca5

Sulca 5.0

SULCA's version 5 is new and the latest version developed at VTT. SULCA 5.0 has the highly visual and easy-to-use features for which the previous versions are well known, along with a new and improved user interface that helps the user to perform reliable and easily understandable LCAs and its' applications. In addition, a lot of new user friendly possibilities to make evaluation and calculation efficient and clear. Special features of SULCA 5.0 include the following:

- Multiple-level flow sheets (agglomerated or non-agglomerated)
- Database compatibility with
    - Ecoinvent v2 and v3,
    - ELCD,
    - Comperhensive Excel Import and Export support.
    - and other databases via the Simantics platform
- A flexible equation editor
- User interface that is
    - fast and flexible,
    - highly visual and easy-to-use
    - efficient for modelling and evaluation
- Enhanced connectivity and data transfer with simulation and design software's in version 5. Thus a new level of connectivity possibilities in the nowadays demand to use several software and databases together!

Sulca software distribution, maintenance and further development is managed by Simantics division of THTH asssociation. There is an annual maintenance fee required in order to use the software. Annual maintenance fee for a single installation is 1500€. Annual fee for unlimited number of installations (including also source code access) is 5000€. With this fee you will also receive a membership in the Simantics Division and possibility to direct further development of Sulca software.



Get in touch with us: Research Scientist Matias Alarotu, matias.alarotu@vtt.fi