

CHEMSHEET AS A SIMULATION PLATFORM FOR PYROMETALLURGICAL PROCESSES

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Abstract

ChemSheet is a thermodynamic multi-phase multi-component simulation software, which is used as an Add-in in Microsoft Excel. In ChemSheet, the unique Constrained Gibbs free energy method can be used to include dynamic constraints and reaction rates of kinetically slow reactions, yet retaining full consistency of the multiphase thermodynamic model. With appropriate data, ChemSheet models can be used to simulate reactors and processes in all fields of thermochemistry. The presentation will cover off-line modeling of Cu-flash smelters and advanced thermochemical simulation coupled with on-line process control of Cu-Ni smelting. The presentation will describe an off-line model of Cu-smelter based on critically assessed properties of the Al-Ca-Cu-Fe-O-S-Si –system (slag, matte and liquid metal) by using the quasichemical model. A four-stage reactor model (shaft, settler, uptake and bath) is used for optimizing process parameters and feed particle distribution. As a second example, an advanced thermochemical model of a Ni-Cu sulphide smelting plant will be given. The on-line model covers the operation of treating Ni-Cu-S concentrate via roasters, electric furnace and converters, producing a high grade Bessemer matte product for further refining. The model integrates the thermochemistry of the roasters and electric furnace, and predicts important process parameters such as degree of sulphur elimination in the fluid-bed roasters, matte grade, iron metallization, slag losses and the iron to silica ratio in the electric furnace slag. Both models can be used to assist process engineers and operators in calculating the addition rates of coke, flux and air for different feed scenarios.

Introduction

The common expectation within industrial companies is that commercial software vendors will supply them with user-friendly software packages that require little or no programming skills. A similar feature is encountered within universities and research institutes, in particular when highly specialized, modular software, compatible with existing 'researcher code' is required. In multiphase thermochemistry, the 'research programs' themselves may be commercialized and appear with their highly specialized databanks. The thermochemical data will then include the necessary interaction models for the complex phase mixtures, which appear as application specific for e.g. different high-temperature operations in metallurgy. To ensure the usage of such data in process simulation software, various interfaces have been developed [1, 2, 3, 4].

ChemSheet [5], when introduced in 1999, was 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 program [3]. Also with ChemSheet the unique Constrained Gibbs free energy method [6] can be used to include dynamic constraints and reaction rates of kinetically slow reactions, yet retaining full consistency of the multiphase thermodynamic model. Thus, with ChemSheet multiphase multi-component thermochemical problems can be worked through the familiar spreadsheet, which is in everyday use by engineers and scientists everywhere in the world. When developing applications, writing macro-code around the basic interface is helpful but for those who do not like programming, the custom made ChemSheet simulation model may appear as just another spreadsheet file.

During its 15-year history, ChemSheet has been adapted by the industrial user, particularly for such purposes where its easy inclusion of Excel features such as special functions, presentation graphics and use of customized spreadsheet interfaces have been beneficial. Figure 1 depicts the Excel spreadsheet connection to ChemApp in ChemSheet.

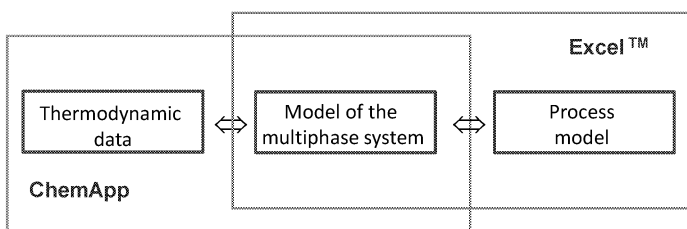


Figure 1. ChemSheet coupling of Gibbsian thermodynamics and spreadsheet calculations

ChemSheet model of the flash smelter

The copper ore (commonly chalcopyrite, CuFeS_2) is crushed and ground before it is concentrated to between 20 and 40% copper in a flotation process. The next major step in production uses pyrometallurgical processing to convert the copper concentrate to 99% pure copper suitable for electrochemical refining. These high temperature processes first smelt the concentrate in a furnace (flash smelting), then oxidize and reduce the molten products to progressively remove remaining sulfur, iron, silicon and oxygen to leave behind relatively pure copper. The feed to flash smelting is known as copper concentrate. It contains copper and iron sulfides, silica and limestone ground to small particles (<100mm). Flash smelting is highly exothermic process. It requires almost no external heat. Concentrate and enriched air are fed to the shaft of the furnace where the iron oxides and the sulfides are converted to liquid slag. Copper sulfides are first partly oxidized and then converted to liquid called matte. At the bottom of the furnace the slag and the matte are collected in a bath and separated from each other by gravity (lighter slag is floating on top of the heavier matte). The gas from furnace consists mainly of nitrogen and sulfur oxide.

The flash smelting process is simulated with a ChemSheet model that contains four calculation steps (see Figure 2). The compositions of the feed flows are shown in Figure 3. The first step calculates the average flow temperature and the composition in the reactor shaft by using an Gibbs energy minimization method and target calculation. The second step calculates the flow temperature and the composition in the settler in a similar manner. Before entering to the settler the solid and the liquid phases are separated (using given separation efficiency) from the flow as

they are assumed to go to the bath at the bottom of the settler. The third step calculates the flow temperature and the composition in the uptake shaft. Again the remaining solid and liquid phases are separated (as gas temperature decreases it is possible that also condensation takes place) from gas. The fourth step calculates the bath temperature and the composition. Flows to bath consists of separated solids and liquids from the reactor shaft and the settler.

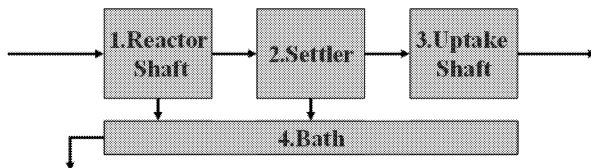


Figure 2. Four steps flash smelter ChemSheet model.

Thermodynamic data-file for copper sulfide flash smelting ChemSheet model was created with FactSage [7]. The thermodynamic properties of the slag, matte, and liquid copper phases in the Al-Ca-Cu-Fe-O-S-Si-system have been critically assessed and optimized over the ranges of compositions of importance to copper smelting/converting based on thermodynamic and phase equilibria information available in the literature and using the modified quasi-chemical model [8]. The thermodynamic system consists of ten elements (the above mentioned seven and C-H-N), 22 gas species, three liquid mixtures (nine species in slag phase, four species in liquid/blister phase and three species in matte phase) and 27 pure condensed phases.

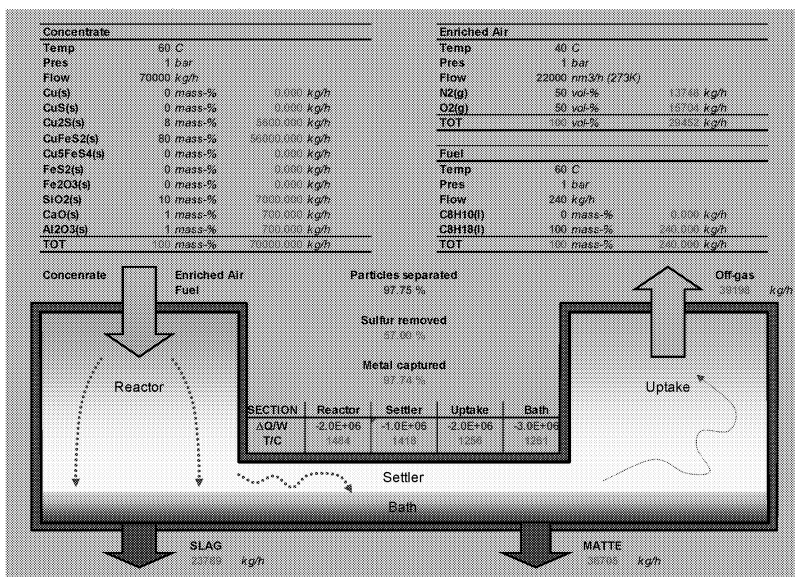


Figure 3. Excel user interface for the flash smelter model (with typical inputs).

Figure 3 shows the user interface of the four steps ChemSheet model for the flash smelter. Excel cells F28:H28 contain the estimated heat losses through the wall in each section and cells F29:H29 contain the calculated average temperatures. Table 1 shows the calculated elementary compositions of the feed and the product flows. Table 2 shows the distribution of elements between the product flows. The off-gas contains 2.25 mass-% of the concentrate feed as dust.

Table 1. Elementary compositions of the feed and product flows (as mass-%).

Composition	Cu	Fe	Ca	S	Si	Al	O	N	C	H
Concentrate	34.09 %	24.34 %	0.71 %	29.57 %	4.67 %	0.53 %	6.08 %	0.00 %	0.00 %	0.00 %
Air+Fuel	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	52.89 %	46.30 %	0.68 %	0.13 %
Matte	63.36 %	13.06 %	0.00 %	23.58 %	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %
Slag	0.28 %	49.86 %	2.06 %	1.03 %	13.44 %	1.52 %	31.80 %	0.00 %	0.00 %	0.00 %
Off-gas	1.38 %	0.98 %	0.03 %	30.10 %	0.19 %	0.02 %	31.62 %	35.07 %	0.52 %	0.10 %

Table 2. Distribution of elements between the product flows.

Distribution	Cu	Fe	Ca	S	Si	Al	O	N	C	H
Matte	97.46 %	28.14 %	0.00 %	41.81 %	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %
Slag	0.28 %	69.61 %	97.75 %	1.18 %	97.75 %	97.75 %	37.90 %	0.00 %	0.00 %	0.00 %
Off-gas	2.26 %	2.25 %	2.25 %	57.00 %	2.25 %	2.25 %	62.10 %	100.00 %	100.00 %	100.00 %

The flash smelter model was further developed to simulate the combustion of a single copper sulfide ore particle. The particle and gas (enriched air) were introduced at the top of the vertical reactor shaft. The superficial gas velocity was solved from ideal gas law and the reactor cross-sectional area and the particle velocity from its momentum equation that includes gravity, drag force and wall friction terms. Neglecting the temperature and composition gradients inside the particle, the model calculates the average temperature and the composition of the particle and the gas flow as function of the axial coordinate in the shaft. Normally the heat balance of flow is given as [9]:

$$\frac{d(\dot{m} c_p T)}{dx} = \dot{Q}_{rad} + \dot{Q}_{conv} + \dot{Q}_{reac} \quad (1)$$

where \dot{m} is the mass flow, c_p the heat capacity and T the temperature of the flow, \dot{Q}_{rad} and \dot{Q}_{conv} the radiation (in radial direction) and convection heat transfer rates between the flow and its surroundings, and the last term is the heat of reactions in the flow. This time it is more convenient to select enthalpy flow as the variable instead of the temperature. Enthalpy is function of temperature, pressure and composition (mass flow rates of species) of the flow. Any changes in the enthalpy of the flow changes its temperature and/or its composition. ChemSheet contains a calculation mode that automatically solves the temperature and the composition of the flow when the enthalpy change is known (extensive property target calculation). Now equation (1) can be given for the particle and the gas flow as:

$$\frac{d\dot{H}_p}{dx} = \dot{Q}_{rad} + \dot{Q}_{conv} - \dot{H}_{pg} \quad (2)$$

$$\frac{d\dot{H}_g}{dx} = \dot{Q}_{rad} + \dot{Q}_{conv} + \dot{H}_{pg} \quad (3)$$

where \dot{H}_p and \dot{H}_g are the enthalpy flow of the particle and the gas in axial direction, respectively, and \dot{H}_{pg} is the net enthalpy flow between the particle and the gas (including the

vaporized gas species). Reactor heat term is no longer needed as it is included in the enthalpy of flow term. The temperatures of the particle and the gas can now be solved from their enthalpies.

Mass transfer rate of gaseous species between the particle and the gas is given as:

$$\frac{dn_i}{dx} = k_i A_p (C_{i,p} - C_{i,g}) \quad (4)$$

where \dot{n}_i is the flow rate of gas species between the particle and the gas, k_i is the mass transfer coefficient, A_p is the total surface area of the particle and C_i is the concentration of the gas species i in the particle and in the gas, respectively. The surface area of the particle is given as:

$$A_p = \frac{6 \dot{W}_p}{\rho_p d_p |v_p|} \quad (5)$$

where \dot{W}_p is the mass flow rate, ρ_p is the density, and d_p is the diameter, and v_p is the velocity of the particle, respectively. The surface area of the particle is also needed when calculating the radiation and convection heat flows between the particle, the gas and the reactor wall.

The system of independent variables consist of velocity, enthalpy and mass flow rates of the components of the particle, and enthalpy and mass flow rates of the components of the gas. The system was solved with an adaptive Runge-Kutta algorithm. The model was implemented in Excel with VBA macros and all the thermodynamic calculations were done with ChemSheet. Normally ChemSheet is operated manually via toolbar commands and dialog controls but for more advance simulations ChemSheet can also be called programmatically from a VBA macro.

Figure 4 shows the calculated particle and gas temperature profiles and the composition of the gas flow (as mass flow rates of main gas species) with average particle diameter 25 μm . The temperature of the reactor wall was set as constant (1800K). The maximum gas temperature in the reactor shaft reaches almost 2400K. Decreasing the particle size increases the combustion rate and the maximum temperature. This also increases the dusting and loss of metals.

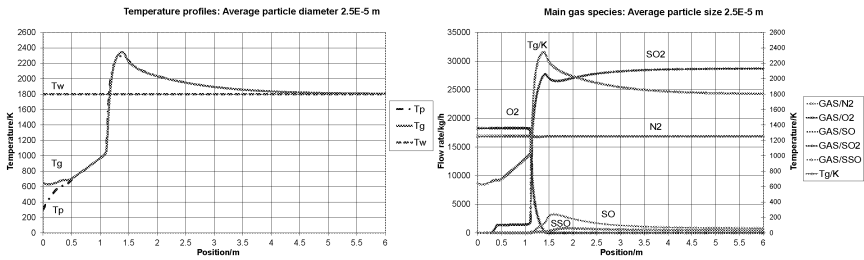


Figure 4. The calculated particle and gas temperature profiles and the composition of the main species in the gas with average particle diameter 25 μm .

On-line model for the XSTRATA Nickel Sudbury Smelter

As a pioneering application in the field of process digitalization, a predictive online thermochemical model was developed for Glencore-Xstrata Nickel's Sudbury smelter. To combine the practicality of a spreadsheet with Gibbs energy solving multiphase routine (FactSage), the ChemSheet platform was used. The model is connected to the PI server to communicate with the plant operation in real time via PI DataLink™. The PI server receives and archives plant measurements, while PI DataLink™ retrieves this data as input to the online model, see Figure 5 below.

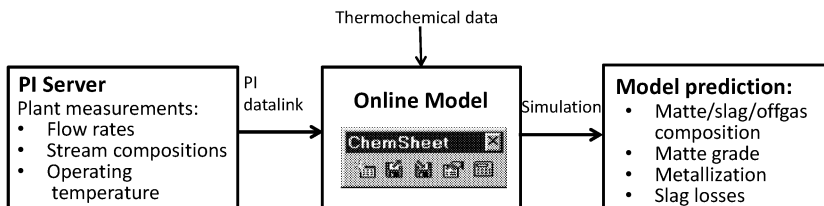


Figure 5. ChemSheet based online model operated in MS-Excel

For effective modeling, the industrial unit operations were again divided into thermochemical modules (see Figure 6). For the roasting operation, the sulphur elimination and sulphate formation steps were separately considered in two different modules. For the sulphur elimination stage, slurried concentrate, flux, revert, custom feed and air were used as the input streams. For the sulphate formation step in the off-gas handling system, dust and air infiltration were given as input streams. Calcine then exits the roasters at 760 °C, but there is a heat loss occurring during calcine transport via drag link conveyors to the electric furnace. Based upon plant measurements, the calcine enters the electric furnace at ca. 500 °C. To account for the heat loss, a separate module was implemented which represents the calcine cooling step during the conveyor transfer in the calculation.

The electric furnace model, respectively, consists of three separate zones – the freeboard, the calcine bank and the smelting zone. To properly account for the heat and mass balance model of the electric furnace, these modules were connected in a countercurrent fashion. The calcine is fed into the electric furnace from the top while reducing gases move up through the calcine layer into the freeboard. This calculating approach allows each zone to coexist with its neighbor under different operating conditions yet still remain thermochemically connected. For example, in the current model of the electric furnace the freeboard is set at a temperature of 500 °C, while the smelting zone is at 1300 °C. The model also takes into account three important process parameters – coke efficiency, degree of calcine oxidation in the freeboard and degree of reduction of the calcine bank by reducing gases from the smelting zone.

The various modules of the model are illustrated in Figure 6. For further details of the on-line model structure and its implementation background see Tripathi and Jabbar [10].

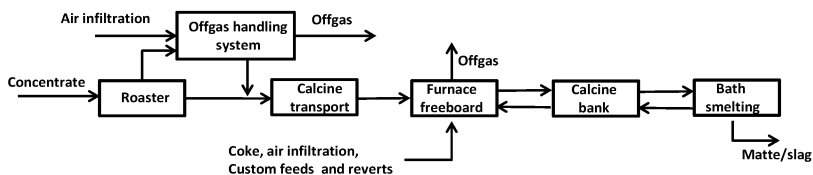


Figure 6. Modular design of the online model with co- and countercurrent connections

Online plant data, such as flow rates, compositions and operating conditions, are dynamically entered into the model. For a given feed scenario, the model converges in ca. 20 s, producing final results for calcine, matte, slag and off-gas compositions. The model could then be employed to predict the plant operating parameters in terms of the historical plant data; for example the degree of sulphur elimination in the roasters, furnace matte grade (see Figure 7) and degree of metallization as well as the composition ratio of Fe and SiO₂ [%Fe/%SiO₂] in the furnace slag.

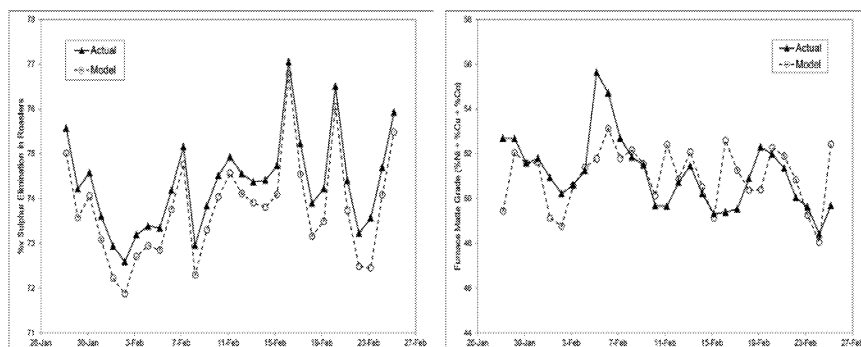


Figure 7. Comparison between the predicted values of sulphur elimination in the roasters, and furnace matte grade with the historical plant data from year 2012. The model predictions follow the plant fluctuations, mainly caused by variation in the feed grade/quality.

The interface of the online model is relatively simple and was found to be easy-to-use. The application of this model is helpful for the plant engineers in calculating the required flow rates of flux, coke and air in achieving the target furnace matte and slag compositions. The combined processing time for roasters and electric furnace is about 35 hours, therefore the model is particularly helpful in addressing plant fluctuations well in advance. The online model is also expected to help in stabilizing the metallurgical performance of the batch converter aisle operation, and is intended for eventual use by plant operations supervision.

Conclusion

Modern simulation programs and advanced thermochemical data are increasingly used for process digitalization and on-line control in metallurgical industry. The advantage of using

thermodynamic models for the simulation of metallurgical processes is their inherent coupling of chemical and enthalpy changes as well as the recovery of calculation data in terms of well-defined, measurable quantities, which allows for checking the model reliability directly with plant historical trends. ChemSheet with its easily customized and application oriented spreadsheet interface provides a practical engineering approach to process modeling with multiphase thermodynamics. The spreadsheet technique allows for development of application specific traits by using Excel features as well as flexible connections with other simulation software. With continuing digitalization in the industry, robust thermochemical modeling tools will have an important role in both supporting plant operations and in supporting their long term development objectives.

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