

DESIGN OF INDUSTRIAL REACTIVE ABSORPTION PROCESSES IN SOUR GAS TREATMENT USING RIGOROUS MODELLING AND ACCURATE EXPERIMENTATION

R Thiele*, R Faber¹, J-U Repke¹, H Thielert², G Wozny¹

¹Technical University of Berlin, Strasse des 17. Juni 135/KWT 9, 10623 Germany,

E-mail: jens-uwe.repke@tu-berlin.de

²Uhde GmbH, Dortmund, Germany

KEYWORDS: packed towers, reactive absorption, gas purification, sour gas treatment

INTRODUCTION

In the industry design of gas purification plants is still often done using empirical methods and simple spreadsheet calculations. Thus, finding an efficient design for the units and optimal operating parameters for the entire process is not possible. In this joint research project between an academic and an industrial partner, reactive absorption and desorption processes are rigorously modelled using thermodynamic and chemical engineering fundamentals taking into account the complex reaction system and its effects on mass and heat transfer [1]. For the validation of the model experiments were carried out in a pilot plant for both absorption and desorption in packed towers. Samples were drawn over the height of the column from the gas, as well as from the liquid phase. These redundant measurements were then processed using a data reconciliation method using a robust estimator, which improved the accuracy of the experimental data significantly and allowed the automatic detection of gross errors. The model could then be validated using these reconciled experimental data and industrial on-site measurements.

Frequently installed processes like the ammonia-hydrogensulfide scrubbing process and amine-based processes have already been modelled with great success [2]. However, models for processes with potash like the VACASULF[®] process are still not available. During the start-up of a recently built industrial VACASULF[®] plant, the experimental results showed a surprisingly large increase in efficiency for a specific alkaline concentration range, which was not predicted by the empirical methods in the design stage.

A literature review revealed that in the past investigations focussed on absorption of CO₂ in highly concentrated solutions. BENSON characterized the CO₂ absorption with high potassium carbonate concentrations [3]. This so-called Benfield Process was for the first time rigorously modelled in 1981 [4] and later extended with the insertion of

* Robin Thiele is now working for BASF AG. The work presented in this paper has been conducted during his previous position at the TU Berlin. Statements and opinions presented in this paper are not done in the name of BASF AG.

dissolved arsenic as promoter for an enhanced CO_2 absorption [5]. In 1990 a model based on kinetic and equilibrium data was developed to calculate the CO_2 absorption and desorption rates in a high loaded potassium solution [6]. A rate-based model for the Benson Process based on effective interfacial area to calculate the mass transfer was also developed by CENTS [7].

In contrary to the extensive modelling of the Benson Process, a model for processes with a low concentrated potash absorbent for the selective removal of H_2S and HCN like the VACASULF[®] process is still not available. Therefore, a rigorous rate-based non-equilibrium model for a more complex electrolyte system ($\text{NH}_3\text{-CO}_2\text{-H}_2\text{S-H}_2\text{O-KOH-NaOH}$) with chemical reactions taking into account the enhancement of mass transfer by the chemical reactions using enhancement factors was built.

RATE-BASED MODEL

For simulating this absorption/desorption process, commercial simulators based on either equilibrium or nonequilibrium models (without reactions), fail to predict the concentrations. Figure 1 shows that an equilibrium model fails to predict the selective removal of H_2S and also seriously overpredicts the absorption of CO_2 compared to both the experiment and the results of the rate-based model presented in this chapter.

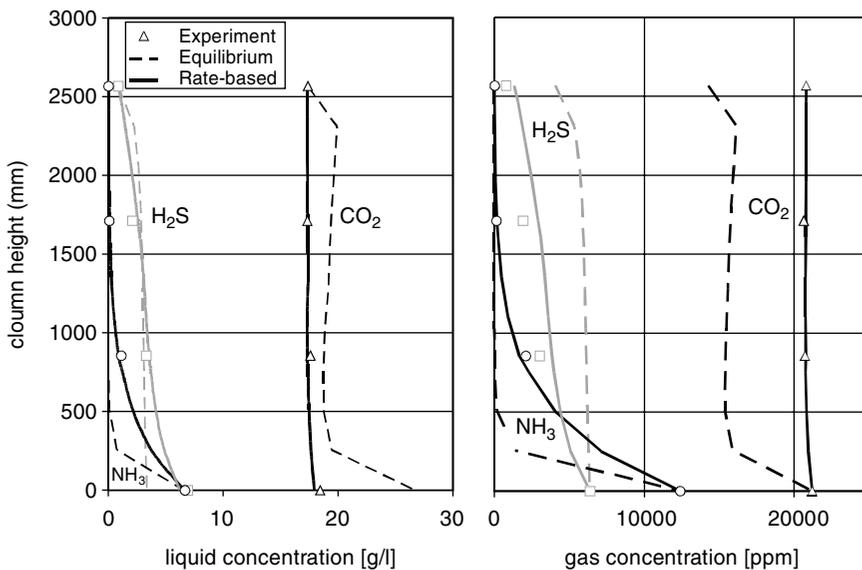


Figure 1. Comparison experiment-model (rate-based & equilibrium), absorption in 32 g/l KOH, $F = 1,8 \text{ Pa}^{1/2}$, $B = 9 \text{ m}^3/\text{m}^2\text{h}$

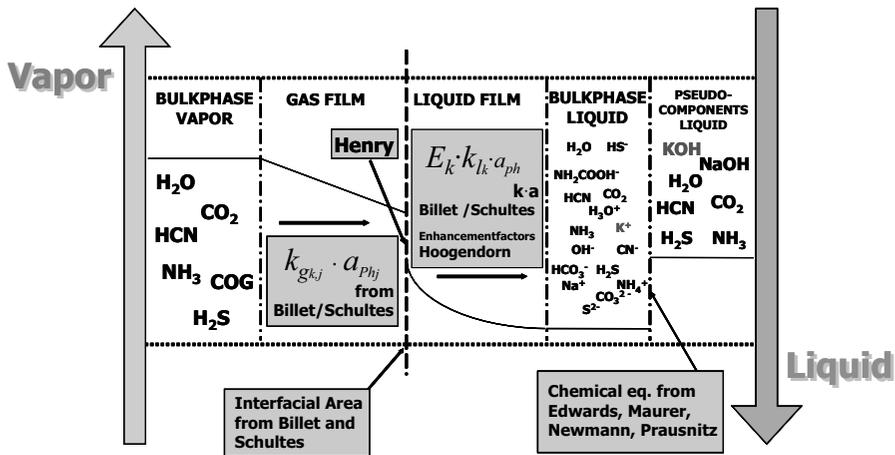


Figure 2. Transfer unit of the rate-based model including chemical reactions

The overestimation of CO_2 -absorption is due to the slow dissociation reactions of CO_2 in water and also due to the kinetically controlled reaction between NH_3 and CO_2 . A selective absorption of H_2S compared to CO_2 during short contact times in packed towers could therefore not be predicted with the above mentioned models. Therefore, the development of the complex heat and mass transfer model taking the interactions of the different chemical species and their reactions into account was conducted using FORTRAN. An overview for one transfer unit of the model is shown in Figure 2 and will only be described briefly here since it has been already presented elsewhere [8, 2, 1].

CHEMICAL AND PHASE EQUILIBRIUM

The given reactive system of weak and strong electrolytes was described by considering all the relevant reactions. To calculate the concentrations of molecular (H_2O , CO_2 , H_2S , NH_3 , HCN) and ionic species (OH^- , H^+ , HCO_3^- , CO_3^{2-} , HS^- , S^{2-} , NH_4^+ , NH_2COO^- , CN^- , K^+ , Na^+) in solution the chemical equilibria are expressed with their dissociation constants K_j and using activity coefficients to consider the non-idealities in the liquid phase. Knowledge of the concentration of the different dissociated species is also especially important to calculate the enhancement factors.

The equilibrium at the interface between the molecular species in the liquid and the gas phase is calculated using the Henry coefficient for dissolved diluted gases as the standard-state fugacity. Activity coefficients are calculated using the correlations and parameters from EDWARDS [10, 11] using a modified PITZER approach, as well as the Henry coefficients and the activity-based dissociation constants K_j .

MASS AND HEAT TRANSFER

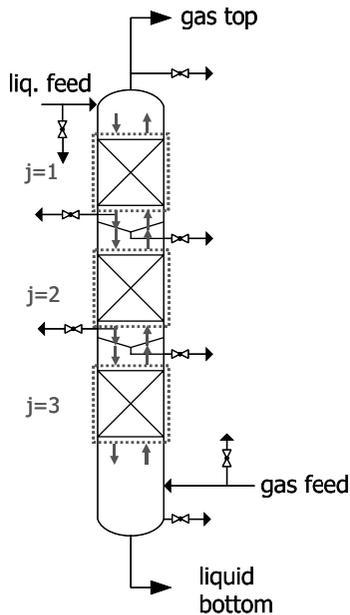
In the non-equilibrium model the column is divided into stages. In each segment the vapor and the liquid phase is considered separately regarding balances for mass, components and enthalpy. Mass transfer between both phases over the interfacial area is evaluated with the film theory. The cross-interactions of the General-Maxwell-Stefan theory can be neglected due to the low concentrations [13]. The convective term is also neglected.

The mass transfer rate J of component i for segment j is then calculated by:

$$J_{i,j} = k_{i,j}^v \cdot \rho_j^v \cdot a_j \cdot (Y_{i,j}^b - y_{i,j}^{\text{int}}) = k_{i,j}^l \cdot \rho_j^l \cdot a_j \cdot E_{i,j} \cdot (x_{i,j}^{\text{int}} - x_{i,j}^b) \quad (1)$$

The mass transfer coefficients $k_{i,j}^v$ and $k_{i,j}^l$ for the gas and liquid film as well as the interfacial area a_j are calculated from correlations developed by BILLET and SCHULTES [14]. The increase in concentration gradients at the interfacial area due to chemical reaction leads to an enhancement of mass transfer which is accounted for by the enhancement factor $E_{i,j}$, calculated from correlations proposed by HOOGENDOORN [12].

Analogous to the mass transfer models, enthalpy balances using heat of formations are formulated separately for the liquid, vapour phase and the interface, thus, considering the heat transfer over the interface.



NUMERICAL METHODS AND IMPLEMENTATION

The entire program is written in FORTRAN and integrated into ChemCAD™ as a User Added Module. This allows to build the entire process of a plant in the flowsheet simulator.

PILOT PLANT

For the experimental validation of the simulation a pilot plant at the TU Berlin was used which has been designed for both absorption and desorption experiments under atmospheric pressure and vacuum conditions. It consists of a stainless steel column ($\varnothing = 100$ mm) equipped with three sections of packings each of 856 mm height. The structured packing used is a SULZER Mellapak 350.Y.

The pilot plant is automated by the process control system Freelance2000™ by ABB. Liquid samples can be taken at three different heights and are analyzed under wet conditions. Gas samples can also be drawn at four different positions and are analyzed by a gas chromatograph. The column is equipped with a glass section for optical examinations. A vacuum pump behind the exhaust gas scrubbers allows pressures down to 70 mbar in desorption mode.

In absorption configuration (Figure 3) the gas stream is mixed inline from gas bottles. The CO₂ concentration is measured online using an infrared CO₂ analyzer from MAIHAK and is kept constant by a controller.

DATA RECONCILIATION

Since all concentrations of both the liquid and the gas phase are known for the three packing segments component balances can be made. This allows the reconciliation of the measurement variables involved, which does not require any process knowledge except that mass is preserved.

$$f_{j,k}(x) = L_j c_{j,k} - L_{j+1} c_{j+1,k} + V_{j+1} y_{j+1,k} - V_j y_{j,k} \quad (2)$$

$$\begin{aligned} k &= \text{KOH, CO}_2, \text{H}_2\text{S, NH}_3 & L &= \text{liquid flow} & c &= \text{liquid concentration} \\ J &= \text{envelope 1, 2 and 3} & V &= \text{gas flow} & y &= \text{gas concentration} \end{aligned}$$

Large deviations in the component balances of up-to 20% which cannot be attributed to measurement errors suggest that the measurements might contain gross errors. It was further assumed that the measurement values which are subject to error are not normally distributed. Thus, a utilization of weighted least squares is not recommendable. Instead a robust estimator, the Fair-function is used [15]. The Data Reconciliation problem can then be formulated as follows:

$$\min J = \sum_{i=1}^{nmv} c^2 \left[\frac{|\varepsilon_i|}{c} - \ln \left(1 + \frac{|\varepsilon_i|}{c} \right) \right] \quad \varepsilon_i = \frac{x_i - \hat{x}_i}{\sigma_i} \quad x_i \in [V, L, c, y] \quad (3)$$

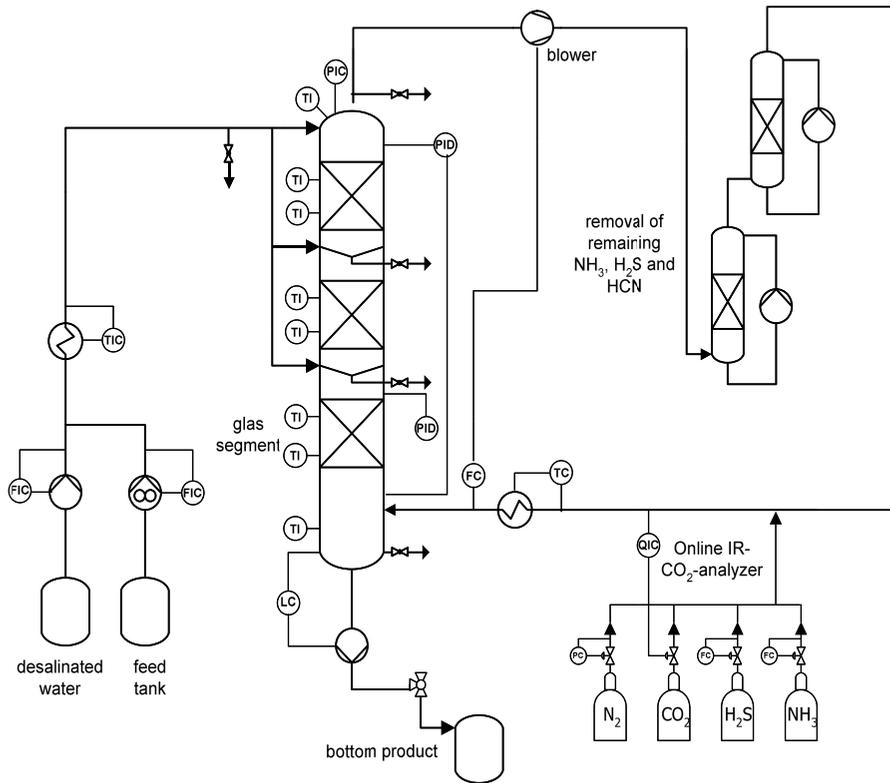


Figure 3. Flowsheet of the pilot plant in absorption mode. Desorption equipment is hidden s.t.

$$f(x) = 0$$

$$Lb \leq x \leq Ub$$

The Fair function introduces simultaneous gross error detection into the data Reconciliation process. This can be shown by the influence function (Figure 4). The contributions from the Fair function for larger standard errors are significantly lower than for the weighted least squares (WLS) function.

EXPERIMENTS

The validation of the enhanced model was carried out with 10 experiments in the packed tower in desorption mode and 8 absorption experiments for which the Data Reconciliation

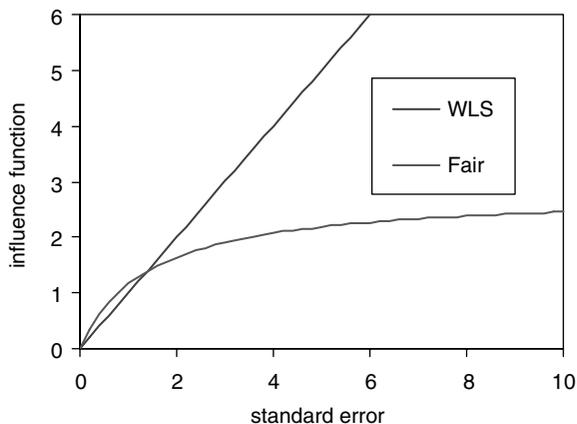


Figure 4. Influence function for different objective functions

was done. Experiments were either conducted under vacuum conditions at 150 mbar or at mean overpressure of about 1100 mbar (abs.), thus, enabling to validate the model in a wide pressure and therefore also in a wide temperature range. The concentration ranges of the components KOH and CO₂ were chosen according to the VACASULF[®] process. At first only a H₂O-KOH-CO₂ solution was used as an absorbent. In further experiments the system was extended with H₂S and finally with NH₃. Thus, the influence of individual components on the model accuracy for both absorption and desorption can also be identified. Exemplarily, one absorption experiment is presented with the data for the process parameters and measured concentrations for feed streams given in Table 1.

The concentration profiles for both the gas and the liquid are given in Figure 5 in comparison to the simulated values achieved by the model. The figure shows both the original measurements, as well as the reconciled variables from the Data Reconciliation. It can be seen that gross errors were detected by the robust estimator for the low concentrated H₂S gas samples. Since the measurement device (gas chromatograph) is operated for these samples outside the usual measurement range it has a high measurement error for these low concentrations which was automatically detected by the data reconciliation method. The absorption results show that a reliable prediction of the chemical absorption using the model is possible.

The complete system H₂O-KOH-CO₂-H₂S-NH₃ was also investigated for desorption under vacuum. Again, the simulation results match well with the experimental data within an average relative error below 20%. The simulated temperature profile also fits closely to the experimental values, hence, confirming enthalpy and heat transfer model.

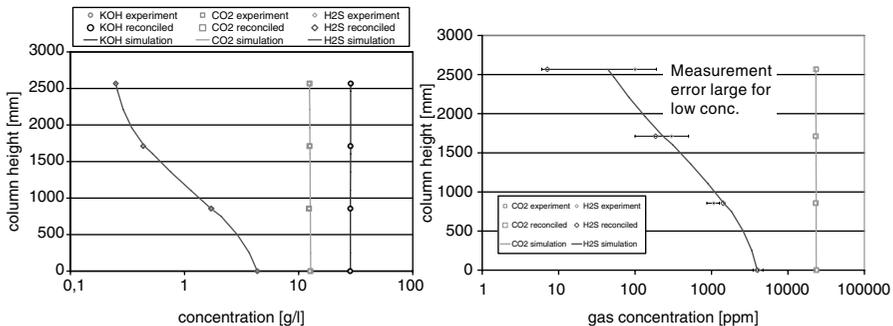
Further investigations also focus on the influence of surface active components on hydrodynamics in packed towers which can cause foaming [16, 17].

Table 1. Experimental parameters for two experimental cases

Process data vapour		Absorption experiment	
		Feed	Outlet
Flow		15 Nm ³ /h	
Temp.	[°C]	25.0	24.9
<i>Liquid</i>			
Flow	[l/h]	69.9	70.8
Temp.	[°C]	25.0	25.8
CO ₂	[g/l]	12.46	12.7
H ₂ S	[g/l]	0.25	4.3
NH ₃	[g/l]	0.0	0.0
KOH	[g/l]	28.6	28.3
<i>Plant Data</i>			
Top Pres.	[mbar]	1095	
Pres. drop	[mbar]	6.45	
F-Factor	[Pa ^{0.5}]	1.80	

INDUSTRIAL PLANT

In addition to our own pilot plant experiments, validation of the model was also done using measurement data from an industrial VACASULF process of Citizens Gas & Coke Utility in Indianapolis, Indiana. The plant has been described in [9]. Measurements were taken in 1997 during a start-up phase by Uhde GmbH. The data was processed using component balances showing that these industrial measurement data are questionable. The best data

**Figure 5.** Absorption case, conc. for the liquid phase with reconciled variables

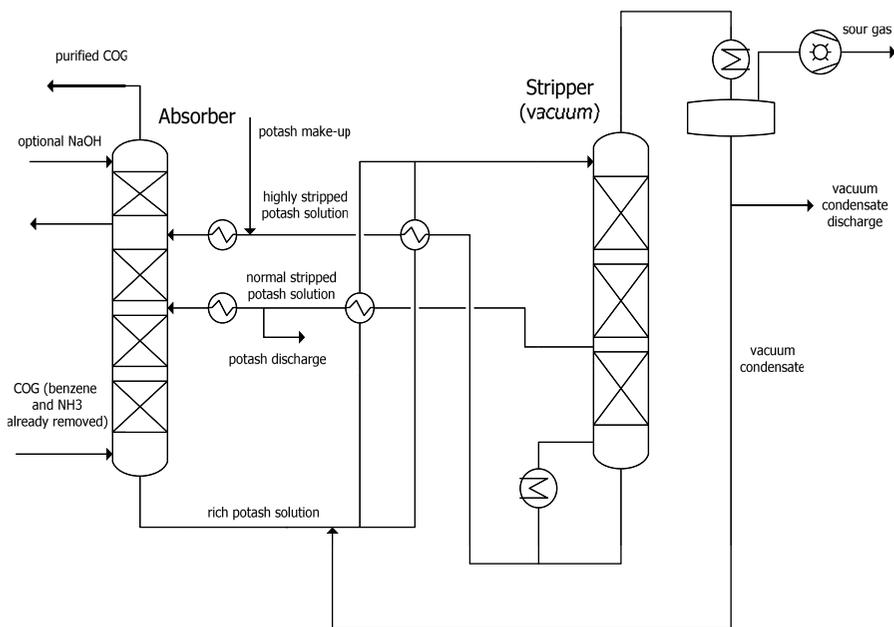


Figure 6. VACASULF process

set, which still showed deviations in the different component balances of up to 30%, was chosen to be simulated using a flowsheet simulation with CHEMCAD with the presented rate-based model as tower units. All design parameters from the process (tower diameters, heights and internal types) were known and put into the simulation. The process can be seen in Figure 6.

The results show that considering the obvious gross errors in the measurements the model is able to predict the industrial process with a good accuracy. The deviations between the predicted and the measured data can be seen in Table 2. Larger deviations do occur for small concentrations, but the associated component streams are considerably small.

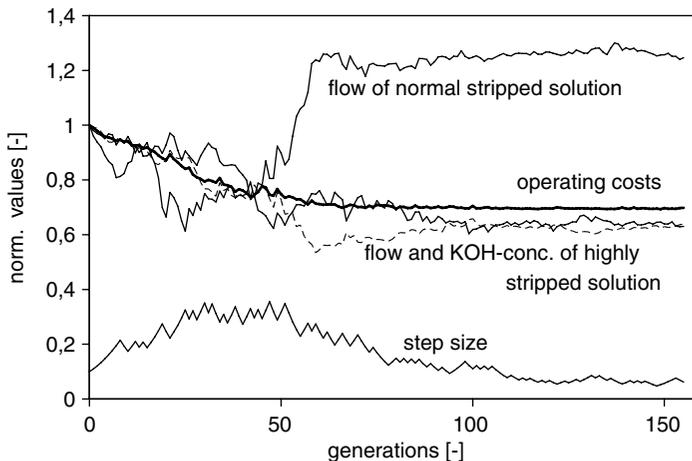
PROCESS OPTIMIZATION BASED ON OVERALL COSTS

The validated rate-based model was then used in the commercial flowsheet simulator CHEMCAD to optimise the entire process. Therefore the flowsheet simulator was connected to an external evolutionary strategy implemented in Visual Basic and Excel which had been developed before in [18]. 10 process parameters (flows, KOH-conc., temp, stripper pressure) and 5 design parameters (absorber and stripper heights, feed

Table 2. Validation using data from the industrial process

		Deviations Simulation ↔ Process
Rich potash solution	c_{CO_2}	-9%
	$c_{\text{H}_2\text{S}}$	1%
	c_{HCN}	23%
Normal stripped Potash solution	c_{CO_2}	-13%
	$c_{\text{H}_2\text{S}}$	6%
	c_{HCN}	65% (low conc.)
Highly stripped Potash solution	c_{CO_2}	-19%
	$c_{\text{H}_2\text{S}}$	-19%
	c_{HCN}	113% (low conc.)
COG H ₂ S gas exit		-53.8% (low conc.)

side stream heights) were chosen as decision variables for the optimisation routine. The objective function was based on annualised costs comprising both investment and operating costs. For an operated industrial VACASULF[®] plant similar to Figure 6 the entire optimisation resulted in a decrease of the operation costs by 30% as can be seen from Figure 7.

**Figure 7.** Optimisation using evolutionary strategies

RESULTS

The model was successfully validated by vapour-liquid equilibrium data from the literature and by the conducted 10 desorption experiments and 8 absorption experiments in the packed tower in desorption mode. The developed experimental procedure including a data reconciliation method improved the accuracy of the measurement data and also automatically detected gross errors. In addition, the model was used in the commercially available flowsheet simulator CHEMCAD as a User Added Module to simulate for the entire VACASULF[®] process. The predicted values compare well with the industrial data. It is now being used in industrial practice for the design of the individual units and the overall process and can also be utilised online for model predictive control. Thus, the project allowed for the first time the simulation of the entire process (VACASULF[®]) with recycles using rigorous models and its application in industrial practice.

Furthermore, the industrial process was systematically optimised regarding annual costs using an evolutionary strategy. This resulted in a decrease of 30% in operating costs still complying with the restrictions for the gas outlet concentration. For a new process the heights of the Absorber and Stripper were significantly reduced resulting also in a decrease in investment costs.

ACKNOWLEDGMENT

The support provided by VDKF e.V. and Chemstations Inc. is gratefully acknowledged, as well as founding by Deutsche Forschungsgemeinschaft for the partner project DFG LI806/4-3 that partially supported this work.

LITERATURE

1. R. Thiele, O. Brettscheider, H. Thielert, G. Wozny, *A Rate-Based Model for Chemical Absorption and Desorption Developed in a Cooperation Between University and the Industry in the Coke Oven Gas Purification Sector*, *Inz. Chem. Proc.* 3 (24) pp. 355–378, 2003
2. O. Brettschneider, R. Thiele, Faber, R., H. Thielert, G. Wozny, *Experimental Investigation and Simulation of the Chemical Absorption in a Packed Column for the System NH₃-CO₂-H₂S-NaOH-H₂O*. *Sep. Pur. Techn.*, 3 (39) pp. 139–159, 2004
3. H.E. Benson, J.H. Field, R.M. Jameson, *CO₂ Absorption: Employing Hot Potassium Carbonate Solutions*. *Chemical Engineering Progress*, 7 (50) pp. 356, 1954
4. S.V. Joshi, G. Astarita, D.W. Savage, *Prediction of Pilot Plant Performance for a Chemical Gas Absorption Process*. *AICHE Symposium Series*, 202 (77) pp. 63, 1981
5. N. Kumar, D.P. Rao, *Design of a Packed Column for Absorption of Carbon Dioxide in Hot K₂CO₃ Solution Promoted by Arsenious Acid*. *Gas Separation and Purification*, (3), pp. 152, 1989
6. R. Pohorecki, E. Kuckarski, *Desorption with Chemical Reaction in the System CO₂-Aqueous Solution of Potassium Carbonate*. *The Chemical Engineering Journal*, (46), 1990
7. A.H.G. Cents, D.W.F. Brillman, G.F. Versteeg, *Gas Absorption in an Agitated Gas-Liquid-Liquid System*. *Chemical Engineering Science*, (56), pp. 1075, 2001

8. H. Thielert, *Simulation und Optimierung der Kokereigasreinigung – Simulation and Optimisation of coke-oven gas purification*, TU Berlin, Department for Process and Plant Technology, 1997
9. J.H. Currey, *New Process for Coke-Oven Gas Desulfurisation*. Iron and Steel Engineering, 1995
10. T.J. Edwards, J. Newman, J.M. Prausnitz, *Thermodynamics of aqueous solution containing volatile weak electrolytes*. AIChE Journal, 2 (21), pp. 248, 1975
11. T.J. Edwards, G. Maurer, J. Newman, J.M. Prausnitz, *Vapor-Liquid Equilibrium in Multi-component Aqueous Solutions of Volatile Weak Electrolytes*. AIChE Journal, 6 (24), pp. 966, 1978
12. G. C. Hoogendoorn, R. D. Abellon, P.J.M. Essens, J.A. Wesselingh, *Desorption of volatile electrolytes in a tray column (sour water stripping)*. Chem. Eng. Res. Des., (66), 483–501, 1988
13. J. Peters, *Modelling and Optimization of the Ammonia-Hydrogensulfide-Scrubbing Process as a process for air pollution control*. Dissertation, TU Berlin, Department for Process and Plant Technology, 1997
14. R. Billet, M. Schultes, *Prediction of Mass Transfer Columns with Dumped and Arranged Packings*. Chem. Eng. Res. Des., (77), pp. 498–504, 1999
15. D.B. Özyurt, R.P. Pike, *Theory and Practice of simultaneous data reconciliation and gross error detection for chemical processes*. Comp. Chem Eng., 2004
16. Thiele, R.; Brettschneider, O.; Repke, J.-U.; Thielert, H.; Wozny, G. *Experimental Investigations of Foaming in a Packed Tower for Sour Water Stripping*. Ind. & Eng. Chem. Res., 7 (42), pp. 1426–1432, 2003
17. Thiele, R.; Wiehler, H.; Repke, J.-U.; Thielert, H.; Wozny, G. *Hydrodynamics of Foaming Systems in Packed Towers*. Conference Proceedings CD, AIChE Annual, Austin, 2004
18. Thiele, R.; Brettschneider, O.; Repke, J.-U.; Thielert, H.; Wozny, G. *An Industrial Case Study in Design and Process Optimization with Rigorous Process Models using Evolutionary Strategies*. presentation at AIChE Annual, San Francisco, 2003