

**DYNAMIC PROCESS MODEL FOR
DENITROGENATION AND DEHYDROGENATION
BY VACUUM DEGASSING**

Paper presented at the Scanmet I Conference

1st International Conference on Process Development in Iron and Steelmaking

7-8 June 1999, Lulea, Sweden

Dr.-Ing. B. Kleimt	Betriebsforschungsinstitut BFI, D-40042 Düsseldorf, Germany
Dr.-Ing. S. Köhle	Betriebsforschungsinstitut BFI, D-40042 Düsseldorf, Germany
Dipl.-Ing. K. P. Johann	Edelstahlwerke Buderus AG, D-35576 Wetzlar, Germany
Dipl.-Ing. A. Jungreithmeier	Voest Alpine Stahl Linz, A-4031 Linz, Austria
Joseba Molinero	Sidenor I+D, E-48970 Basauri-Vizcaya, Spain

ABSTRACT

Based on the principles of thermodynamics and reaction kinetics a dynamic process model for denitrogenation and dehydrogenation was developed. This model was applied to the vacuum tank degassing (VD) and the vacuum circulation (RH) process.

The process model considers the equilibrium conditions for the degassing reactions depending on the vessel pressure and an additional pressure due to the impeded expansion of the gas bubbles near the bath surface. Furthermore the mutual dilution effect of the reaction gases and the dilution by stirring and lift gas is taken into account.

The reaction kinetics are expressed by a time constant for description of the mass transfer in the liquid phase. For denitrogenation the effect of surface-active elements like sulphur and oxygen on the reaction at the liquid / gas interface is additionally taken into account. In case of the RH process the steel circulation through the vacuum vessel is considered.

The process model was installed on a personal computer for dynamic simulation. It was validated with measured process data from two different tank degassing plants and a vacuum circulation plant. Input values for the model are the cyclically measured values of vessel pressure as well as stirring and lift gas flow rate. The simulated behaviour of nitrogen and hydrogen content was compared to analysed nitrogen and hydrogen respectively Hydriis measurement values of samples taken before, during and after degassing. By evaluation of a larger amount of heats representative mean values for the model parameters were estimated. The resulting simulation accuracy is about 8 ppm for nitrogen and 0.2 ppm for hydrogen. The process model was simplified for on-line observation of degassing without considerably reducing its accuracy.

LIST OF SYMBOLS

Symbol	Meaning	Unit
A	effective reaction surface	m ²
A _O	factor of oxygen effect on denitrogenation	1/%
A _S	factor of sulphur effect on denitrogenation	1/%
D _X	Degassing rate of element X (X = H, N)	%/min
f _X	activity coefficient of element X (X = H, N)	1
F _{DH}	conversion factor dehydrogenation rate to H ₂ flow rate	m ³ /%
F _{DN}	conversion factor denitrogenation rate to N ₂ flow rate	m ³ /%
F _{H2}	conversion factor H ₂ partial pressure to H equilibrium	%/bar ^{1/2}
F _{N2}	conversion factor N ₂ partial pressure to N equilibrium	%/bar ^{1/2}
g	constant of gravity	m/s ²
h	distance between inert gas tuyere and steel surface in the vessel	m
H	hydrogen content of steel	%
k _N	mass transfer coefficient of N	m/min
k _{N2}	kinetics coefficient for interface reaction of N	m/min/%
K _X	equilibrium constant of element X (X = H, N)	1
N	nitrogen content of steel	%
O	oxygen content of steel	%
P	pressure	bar
P _{H2}	- H ₂ partial pressure	
P _{N2}	- N ₂ partial pressure	
P _G	- vacuum vessel pressure	
P _Z	- additional pressure due to steel acceleration	
P _{ZE}	- additional pressure at P _G = 0 (parameter)	
Q _L	lift gas flow rate	m ³ /min
Q _M	steel circulation rate	kg/min
Q _P	process gas flow rate	m ³ /min
Q _S	ladle stirring gas flow rate	m ³ /min

R_N	coefficient of denitrogenation kinetics (parameter)	%
R_{VQ}	part of lift gas which has an effect on CO dilution (parameter)	1
ρ	steel density	kg/m ³
S	sulphur content of steel	%
t	time	min
T_{HV}	reaction time constant of dehydrogenation (parameter)	min
T_{NV}	reaction time constant of denitrogenation (parameter)	min
T_{HRH}	effective time constant of dehydrogenation for RH treatment	min
T_{NRH}	effective time constant of denitrogenation for RH treatment	min
V	steel volume	m ³
W	steel weight	kg

Indices

L	in the ladle
V	in the vacuum vessel
Q	at equilibrium
Q0	equilibrium at the bath surface
i	at liquid / gas interface

1. INTRODUCTION

One main purpose of vacuum degassing is the removal of nitrogen and hydrogen from the liquid steel. By evacuation of the steel vessel the partial pressure of the gaseous reaction product (N_2 , H_2) is lowered, which enhances the degassing reaction. Furthermore the partial pressure is diminished by the mutual dilution of the different reaction products, and by dilution from the injected inert gas, which is used for stirring in the tank degassing and as lift gas in the vacuum circulation process.

Different to decarburisation, the progress of dehydrogenation and denitrogenation during degassing cannot be observed on-line from measured waste gas values. The concentration of hydrogen in the waste gas is too low, and nitrogen coming from steel degassing is superimposed by a much higher nitrogen input from the leakage air. Therefore it is usual to elongate the vacuum treatment more than necessary to be sure that the aim values are reached. To overcome the uncertainty with the required degassing duration, a dynamic process model for dehydrogenation and denitrogenation was developed. It can be used for on-line calculation of the current nitrogen and hydrogen content from the cyclically measured values of vessel pressure and inert gas flow rate. In the following the thermodynamic and kinetic fundamentals of this model, its validation with measured process data of two tank degassing and a vacuum circulation plant, and the application for on-line observation are described.

2. FUNDAMENTALS OF THE PROCESS MODEL

The degassing reaction under vacuum can be described by a first order differential equation for the content of element X ($X = N, H$) according to a diffusion process in the liquid steel phase [1]:

$$-\frac{dX}{dt} = \frac{k_X \cdot A}{V} \cdot (X - X_Q) \quad (1)$$

The degassing kinetics are determined by the effective reaction surface A between liquid and gas phase and the mass transfer coefficient k_X of the corresponding element X. In case the resistance at the interface between liquid and gas phase as well as the transport in the gas phase can be neglected, X_Q is the equilibrium content which is determined by the partial pressure of the reaction product (N_2 , H_2) in the gas phase.

For a description of the degassing reaction according to equ. (1) the effective reaction surface A has to be considered. As the reaction mainly takes place at the surface of the inert gas bubbles, which are injected as stirring gas for the tank degassing and as lift gas for the vacuum circulation process, the effective surface depends on the bubble pressure conditions in the steel bath. They are illustrated in **Figure 1** for different reaction heights. The injected inert gas bubbles rise in the liquid steel, and they expand as the ferrostatic pressure decreases. This expansion is enhanced by a lower vacuum pressure P_G above the steel surface, and also by diffusion of the reaction products H_2 and N_2 into the bubbles. Although the concentration of the reaction gas in the ascending bubble increases, the partial pressure decreases with the bubble pressure [2]. Close to the steel surface the gas bubbles expand rapidly because of the low vessel pressure, and they have to accelerate the surrounding steel [3]. Therefore the expansion is impeded, which can be expressed by an additional pressure P_Z .

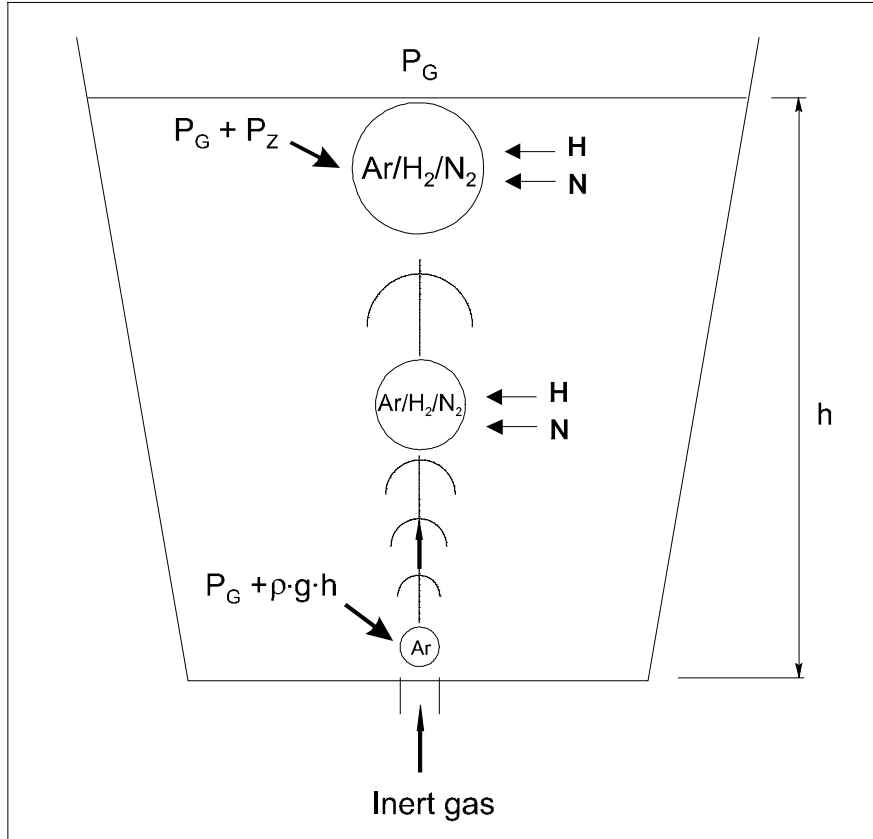


Figure 1: Bubble pressure conditions in the steel bath

As a consequence, together with the bubble pressure also the equilibrium content X_Q of the degassing reaction depends on the height in the steel bath. Furthermore the mass transfer coefficient k_X changes with the radius and the rising velocity of the gas bubble [1]. The evaluation of the therefore height-depending degassing rate according to equ. (1) has to be simplified for an on-line application. For this purpose it is integrated over the height in the steel bath, which gives the total degassing rate [4]:

$$-\frac{dX}{dt} = \frac{1}{T_{XV}} \cdot (X - X_{Q0}) \quad (2)$$

X_{Q0} is the equilibrium content close to the bath surface. The reciprocal value of the product of

- the mass transfer coefficient k_X ,
- the effective reaction surface A related to the steel volume V ,
- and the ratio of the difference between actual and height-dependent equilibrium content $(X - X_Q)$ to its value at the bath surface $(X - X_{Q0})$,

averaged over the bath height, is expressed by the reaction time constant T_{XV} [4]. This reaction time constant can be identified from the degassing behaviour at the respective plant, in case the process conditions in terms of inert gas flow rate and vessel pressure do not vary too much from heat to heat. The calculation of the equilibrium content X_Q close to the bath surface (for simplification the additional index 0 is omitted in the further description) is compiled in **Table 1** for dehydrogenation and denitrogenation.

Table 1: Fundamentals of degassing reactions

	Dehydrogenation	Denitrogenation
Degassing reaction	$[H] = \frac{1}{2} \{H_2\}$	$[N] = \frac{1}{2} \{N_2\}$
Equilibrium constant	$K_H = \frac{\sqrt{P_{H_2}}}{f_H \cdot H_Q} \quad (3a)$	$K_N = \frac{\sqrt{P_{N_2}}}{f_N \cdot N_Q} \quad (3b)$
Equilibrium content	$H_Q = F_{H_2} \cdot \sqrt{P_{H_2}} \quad (4a)$	$N_Q = F_{N_2} \cdot \sqrt{P_{N_2}} \quad (4b)$
Conversion factor: partial pressure to equilibrium content	$F_{H_2} = \frac{0.0025}{f_H} \cdot \frac{\%}{\text{bar}^{1/2}} \quad (5a)$	$F_{N_2} = \frac{0.0434}{f_N} \cdot \frac{\%}{\text{bar}^{1/2}} \quad (5b)$
Conversion factor: degassing rate to reaction gas flow rate	$F_{DH} = \frac{22.4 \text{ m}^3}{2 \text{ kg}} \cdot \frac{W}{100 \%} \quad (6a)$	$F_{DN} = \frac{22.4 \text{ m}^3}{28 \text{ kg}} \cdot \frac{W}{100 \%} \quad (6b)$

The equilibrium content depends on the partial pressure P_R of the reaction product ($R = H_2, N_2$) according to equ. (4). The conversion factor F_R used in this equation can be derived from equ. (3) for the equilibrium constant K_X . Using standard values at 1600 °C for K_X , the conversion factor F_R can be calculated with equ. (5). The activity coefficient f_X can be set to 1 for low alloyed steels.

The partial pressure of the reaction gas

$$P_R = (P_G + P_Z) \cdot \frac{F_{DX} \cdot D_X}{F_{DX} \cdot D_X + Q_P} \quad (7)$$

close to the bath surface results from the vacuum vessel pressure P_G , the additional pressure P_Z , and the concentration of the reaction gas which is diluted by the process gas with the flow rate Q_P . The process gas consists of the gases of the degassing reactions which occur besides the reaction for the element X, and the inert gas which is injected as stirring or lift gas. The reaction gas flow rate is proportional to the degassing rate, abbreviated as D_X ($X = H, N$), with the conversion factor F_{DX} from equ. (6).

As already mentioned, the additional pressure P_Z takes into account that the expansion of the ascending gas bubbles is impeded because they have to accelerate the surrounding steel. From simulation calculations [5] it was found that this additional pressure increases with decreasing distance to the bath surface and with decreasing vessel pressure.

Its value close to the bath surface depends on the vessel pressure P_G according to

$$P_Z = P_{ZE} \cdot \exp \left[- P_G / (2 \cdot P_{ZE}) \right] . \quad (8)$$

The additional pressure P_{ZE} for $P_G = 0$ is a further model parameter, which has to be identified from the behaviour of the individual degassing plant. As will be shown in the following detailed description of model verification for the different degassing processes, its value is much higher than the vessel pressure itself.

2.1 Dehydrogenation

For dehydrogenation within the vacuum tank degassing process equ. (2) can directly be applied to calculate the dehydrogenation rate:

$$- \frac{dH}{dt} = \frac{1}{T_{HV}} \cdot (H - H_Q) \quad (9)$$

The reaction time constant T_{HV} has to be identified from the process behaviour at the respective plant. The equilibrium content H_Q is determined according to equ. (4-8). For calculation of the H_2 partial pressure with equ. (7), the dilution by ladle stirring gas with the flow rate Q_S and the reaction gas flow rate of further parallel degassing reactions has to be considered.

For the vacuum circulation process it has to be taken into account that the degassing reaction takes place in the vacuum vessel, where only a small part of the total steel weight W is treated under vacuum [5]. Therefore the dehydrogenation rates in the vacuum vessel and in the ladle have to be calculated separately. The exchange of the degassed steel between the vacuum vessel (steel weight W_V , hydrogen content H_V) and the ladle (steel weight W_L , hydrogen content H_L) with the steel circulation rate Q_M results in the ladle dehydrogenation rate

$$- \frac{dH_L}{dt} = \frac{Q_M}{W_L} \cdot (H_L - H_V) \quad (10)$$

For calculation of the vessel dehydrogenation rate

$$- \frac{dH_V}{dt} = - \frac{Q_M}{W_V} \cdot (H_L - H_V) + \frac{1}{T_{HV}} \cdot (H_V - H_Q) \quad (11)$$

the dehydrogenation in the vacuum vessel with the reaction time constant T_{HV} and the equilibrium content H_Q has to be considered in addition to the steel exchange.

For the total heat (steel weight W , hydrogen content H) the dehydrogenation rate

$$- \frac{dH}{dt} = \frac{W_V}{W \cdot T_{HV}} \cdot (H_V - H_Q) \quad (12)$$

is given by the weighted mean value of equ. (10) and (11). Substituting H_V from equ. (10) and approximating H_L by H , the total dehydrogenation rate is given by

$$-\frac{dH}{dt} = \frac{1}{T_{HRH}} \cdot (H - H_Q) \quad (13)$$

with the effective time constant

$$T_{HRH} = \frac{W}{W_V} \cdot T_{HV} + \frac{W_L}{Q_M} \quad (14)$$

as an abbreviation, which combines the influence of reaction kinetics and steel circulation [5].

2.2 Denitrogenation

For denitrogenation, in addition to the mass transfer in the liquid phase also the reaction at the liquid / gas interface has to be taken into account. The resistance of the interfacial reaction increases with the concentration of surface-active elements like oxygen and sulphur [1, 2, 6]. This means that similar equations as for dehydrogenation are valid, with the difference that additionally to the equilibrium content N_Q also the interfacial nitrogen content N_i has to be taken into account. As shown in **Figure 2**, the nitrogen content N_i at the steel / gas interface lies in between the content N in the liquid steel and the equilibrium content N_Q .

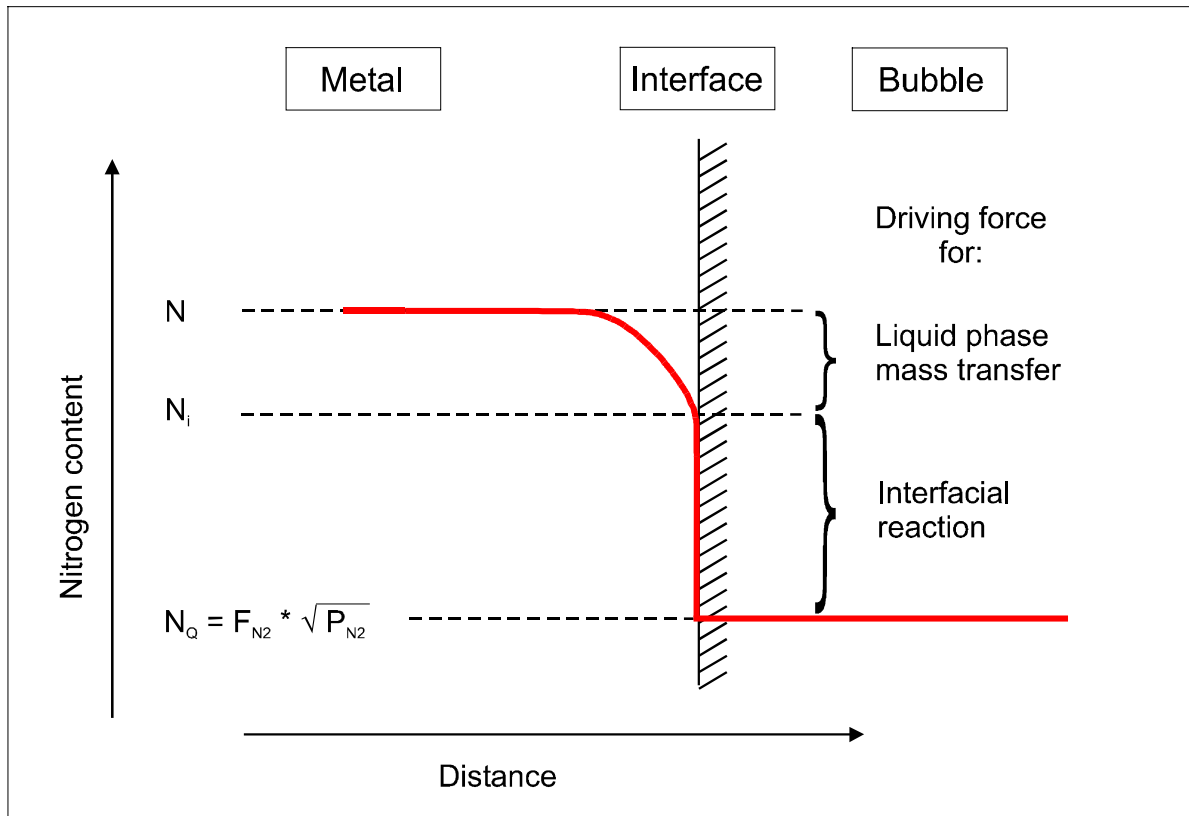


Figure 2: Concentration profile of nitrogen at the interface metal / gas bubble [2]

For description of the mass transfer in the liquid phase, equ. (1) is modified with the interfacial nitrogen content N_i to:

$$-\frac{dN}{dt} = \frac{k_N \cdot A}{V} \cdot (N - N_i) \quad (15a)$$

According to [6] the interfacial reaction and the mass transfer in the gas phase can be described by the following equation, where the coefficient k_{N2} defines the kinetics of this reaction:

$$-\frac{dN}{dt} = \frac{k_{N2} \cdot A}{V} \cdot (N_i^2 - N_Q^2) \quad (15b)$$

For the vacuum tank degassing process the denitrogenation can be described with the corresponding equations by introducing the reaction time constant T_{NV} :

$$-\frac{dN}{dt} = \frac{1}{T_{NV}} \cdot (N - N_i) \quad (16a)$$

and

$$-\frac{dN}{dt} = \frac{k_{N2}}{k_N \cdot T_{NV}} \cdot (N_i^2 - N_Q^2) \quad (16b)$$

The ratio of the two kinetic coefficients k_N and k_{N2} is mainly determined by the content of the surface-active elements oxygen and sulphur and can be described with the following equation:

$$\frac{k_N}{k_{N2}} = R_N \cdot (1 + A_O \cdot O + A_S \cdot S) \quad (17)$$

Values for the influence factors of oxygen and sulphur, A_O and A_S , are given in the literature [2], whereas R_N is introduced as an additional model parameter.

For the vacuum circulation process the vessel denitrogenation rate is given by the first order differential equation, which considers the mass transfer in the liquid phase similar to equ. (11) for dehydrogenation:

$$-\frac{dN_V}{dt} = -\frac{Q_M}{W_V} \cdot (N_L - N_V) + \frac{1}{T_{NV}} \cdot (N_V - N_i) \quad (18a)$$

In addition the interfacial reaction in the vacuum vessel is described by

$$-\frac{dN_V}{dt} = -\frac{Q_M}{W_V} \cdot (N_L - N_V) + \frac{k_{N2}}{k_N \cdot T_{NV}} \cdot (N_i^2 - N_Q^2) \quad (18b)$$

The denitrogenation rate in the ladle is given by the steel exchange between ladle and vessel, as described in equ. (10) for hydrogen.

With the effective time constant

$$T_{NRH} = \frac{W}{W_V} \cdot T_{NV} + \frac{W_L}{Q_M} , \quad (19)$$

the total denitrogenation rate is

$$- \frac{dN}{dt} = \frac{1}{T_{NRH}} \cdot (N - N_i) . \quad (20a)$$

Additionally to equ. (20a), the weighted mean value of the vessel and the ladle denitrogenation rate gives similar to equ. (12) the total denitrogenation rate

$$- \frac{dN}{dt} = \frac{W_V \cdot k_{N2}}{W \cdot k_N \cdot T_{NV}} \cdot (N_i^2 - N_Q^2) \quad (20b)$$

The ratio of the interfacial reaction coefficient k_{N2} and the mass transfer coefficient k_N is defined by equ. (17).

3. PROCESS DATA COLLECTION

The process model was installed on a personal computer for digital dynamic simulation with the help of the MATLAB / SIMULINK software package. It was verified by comparison of simulation results with measured values from two different tank degassing plants and a vacuum circulation plant of the RH type. In **Table 2** the relevant plant data and the process data which are measured at the different plants are compiled.

Table 2: Plant data and measured process data at the different degassing plants

Steel plant	Edelstahlwerke BUDERUS Germany	SIDENOR Basauri Spain	VOEST ALPINE STAHL Linz Austria
Type of degasser	Tank degasser	Tank degasser	RH degasser
Steel weight	95 t	100 t	150 t
Vessel pressure (cyclically measured)	Scan interval $\Delta t = 10$ s Minimum: 1 mbar	Scan interval $\Delta t = 10$ s Minimum: 0.5 mbar	Scan interval $\Delta t = 2$ s Minimum: 0.5 mbar
Inert gas flow rate (cyclically measured)	Average 14 m ³ /h (Ladle stirring)	Average 12 m ³ /h (Ladle stirring)	Average 96 m ³ /h (Vessel lift gas)
Hydrogen content	Gas analysis before and after degassing	---	Hydris measurement before, during and after degassing
Nitrogen content	Gas analysis before and after degassing and at vacuum interrupt	Gas analysis before and after degassing	Leco analysis before, during and after degassing
Material additions	---	---	Nitrogen pickup from alloy materials

4. MODEL VERIFICATION AND SIMULATION RESULTS

The principle of model verification is shown in **Figure 3**: The behaviour of dehydrogenation and denitrogenation was simulated for a heat based on the start values of the analysed respectively measured steel hydrogen and nitrogen content. Input values for the simulation are the cyclically measured vessel pressure and the inert gas flow rate. The accuracy of simulation was judged by the comparison of the simulation results to the analysed respectively measured values of hydrogen and nitrogen content during and after vacuum treatment. The model parameters were adapted by minimising the deviations between simulation and measurement. The simulation results are described and discussed separately for the different types of degassing plants.

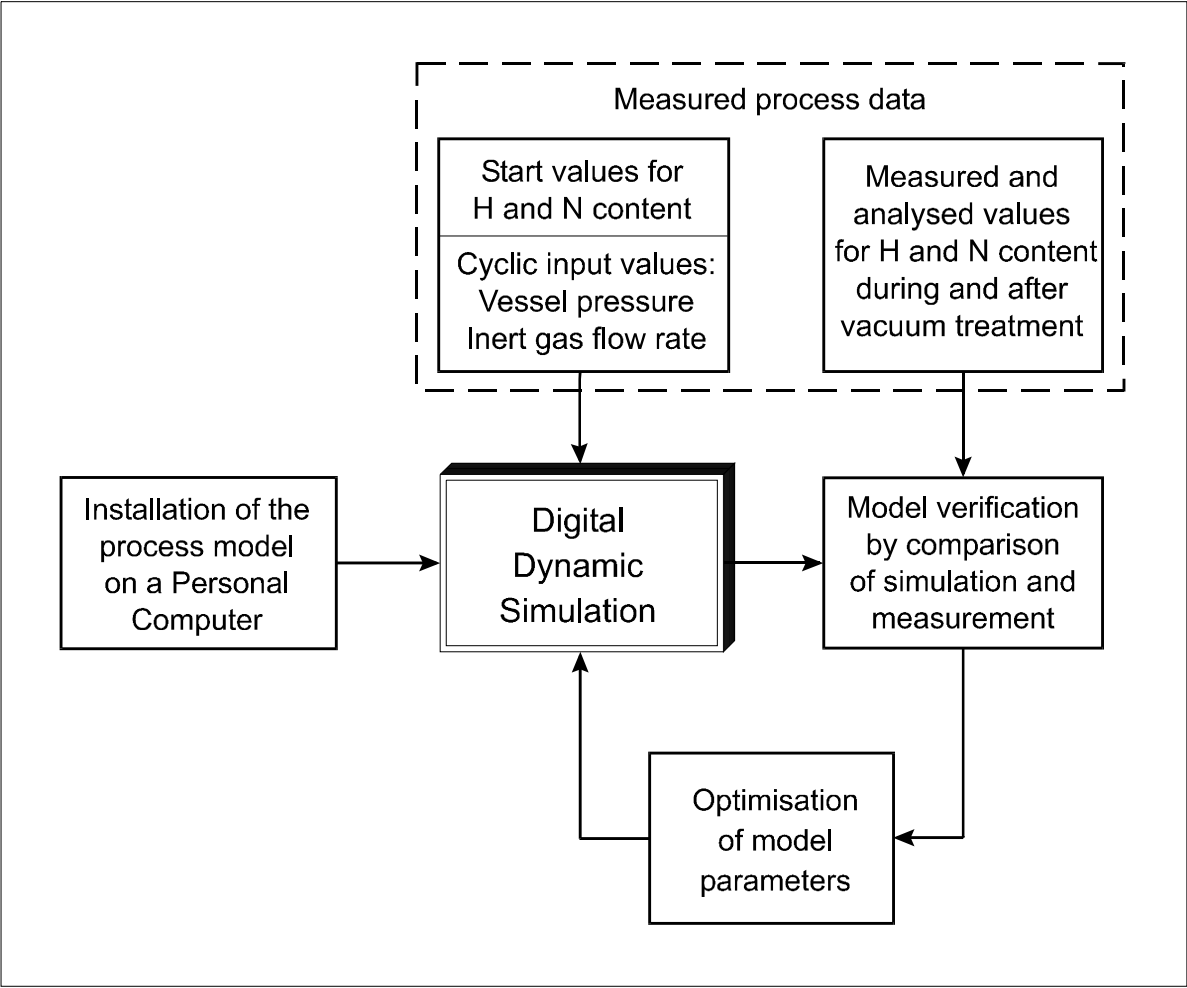


Figure 3: Principle of model verification

4.1 Vacuum tank degassing process

For simulation of the degassing reactions within the vacuum tank degassing process, the process model for dehydrogenation and denitrogenation was applied as described in chapter 2.

For model verification the data of deoxidised heats treated at the tank degassing plant of Buderus were collected. The data of 22 heats include gas analysis values of the hydrogen content before and after vacuum treatment and were used for identifying the model parameters of the dehydrogenation model. For 31 heats gas analysis values of the start and the final nitrogen content were available. During treatment of these heats the vacuum was interrupted after a degassing duration of about 15 minutes, and an additional sample for gas analysis was taken to receive further information on the denitrogenation behaviour.

For 18 heats the analysis data of hydrogen and nitrogen were available, so that the model parameters of the degassing model, i.e. the reaction time constants T_{HV} and T_{NV} , the additional pressure value P_{ZE} and the denitrogenation kinetics coefficient R_N could be optimised at the same time. The optimisation criterion was to minimise the difference between the analysed hydrogen and nitrogen content and the simulated values at the time of measurement.

For the influence parameters A_S and A_O of sulphur and oxygen, values from the literature [2] were taken. To cover the influence of the sulphur content on denitrogenation, a simple simulation model for desulphurisation during the degassing treatment was used. This was necessary because the sulphur content changes during vacuum treatment due to the reaction with the ladle slag. The desulphurisation from an initial content of about 120 ppm to a final content of 20 ppm has a remarkable influence on the denitrogenation behaviour and therefore can not be neglected.

From the parameter optimisation results of the 18 degassing heats, mean values for the model parameters were calculated. They are compiled in **Table 3** together with the parameter values which were identified at the other degassing plants.

Table 3: Model parameter values of the degassing model for the three different plants

Model parameter	Symbol	Value		
		VD Buderus	VD Sidenor	RH Voest
Reaction time constant of dehydrogenation	T_{HV}	1.5 min	1.1 min	4.5 s
Reaction time constant of denitrogenation	T_{NV}	4.0 min	3.0 min	17.5 s
Additional pressure	P_{ZE}	0.038 bar	0.038 bar	0.043 bar
Dilution efficiency of lift gas (only RH)	R_{VQ}	---	---	0.65
Denitrogenation kinetics parameter	R_N	60 ppm	60 ppm	60 ppm
Sulphur effect on denitrogenation [2]	A_S	620 (1/%)	620 (1/%)	620 (1/%)
Oxygen effect on denitrogenation [2]	A_O	770 (1/%)	770 (1/%)	770 (1/%)

The accuracy of the process model was checked using these mean parameter values. **Figure 4**

shows for the 22 Buderus heats with hydrogen analysis data a comparison between analysed and simulated hydrogen content during vacuum treatment. For the final hydrogen content, the mean value of the difference between simulation and analysis is 0.01 ppm with a standard deviation of 0.2 ppm.

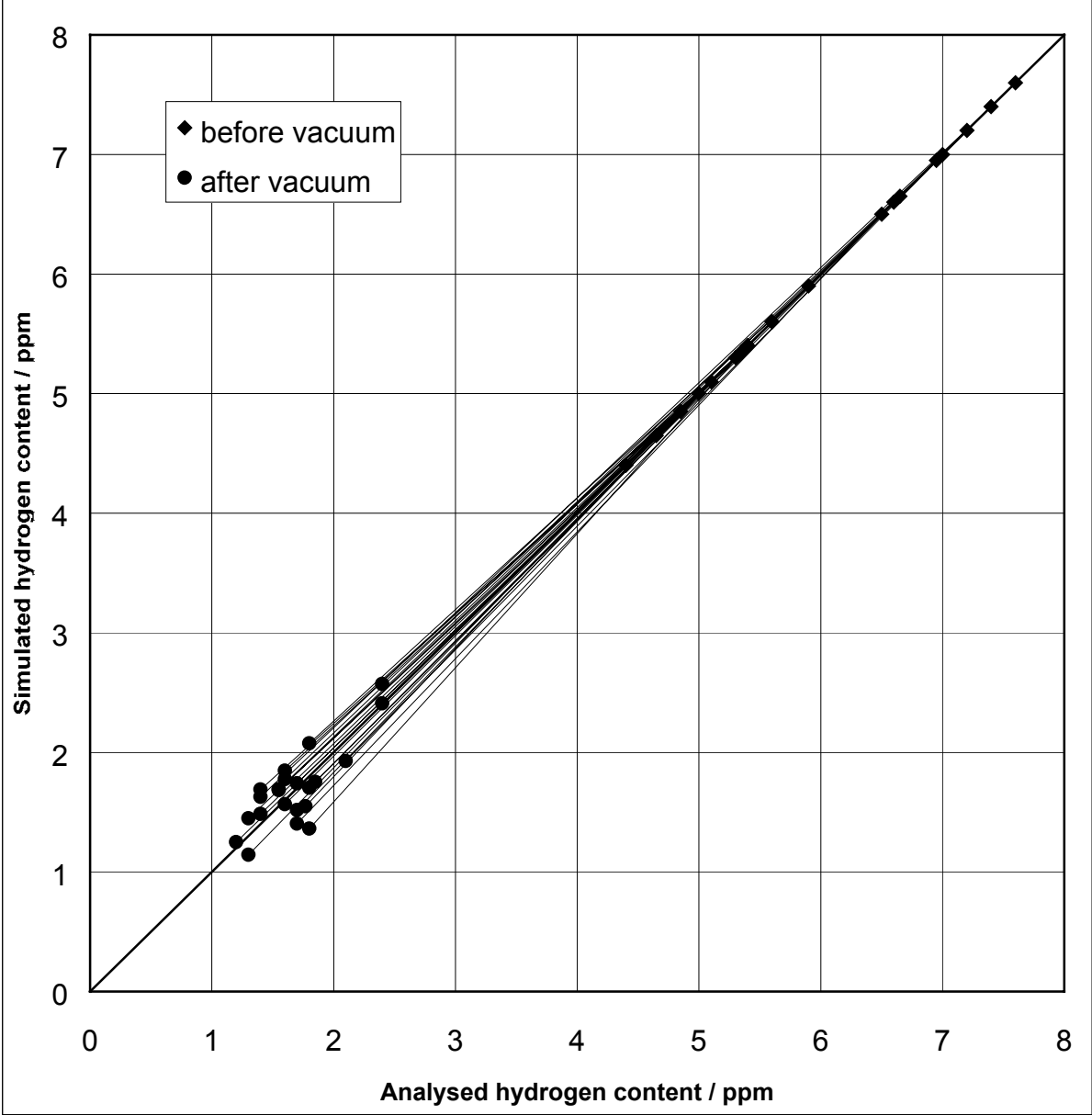


Figure 4: Simulated versus analysed hydrogen content during VD treatment at Buderus plant

In **Figure 5** the corresponding simulation results for the 31 heats with denitrogenation data are displayed. For the final nitrogen content, the mean value of the simulation error is -3.4 ppm with a standard deviation of 9.4 ppm.

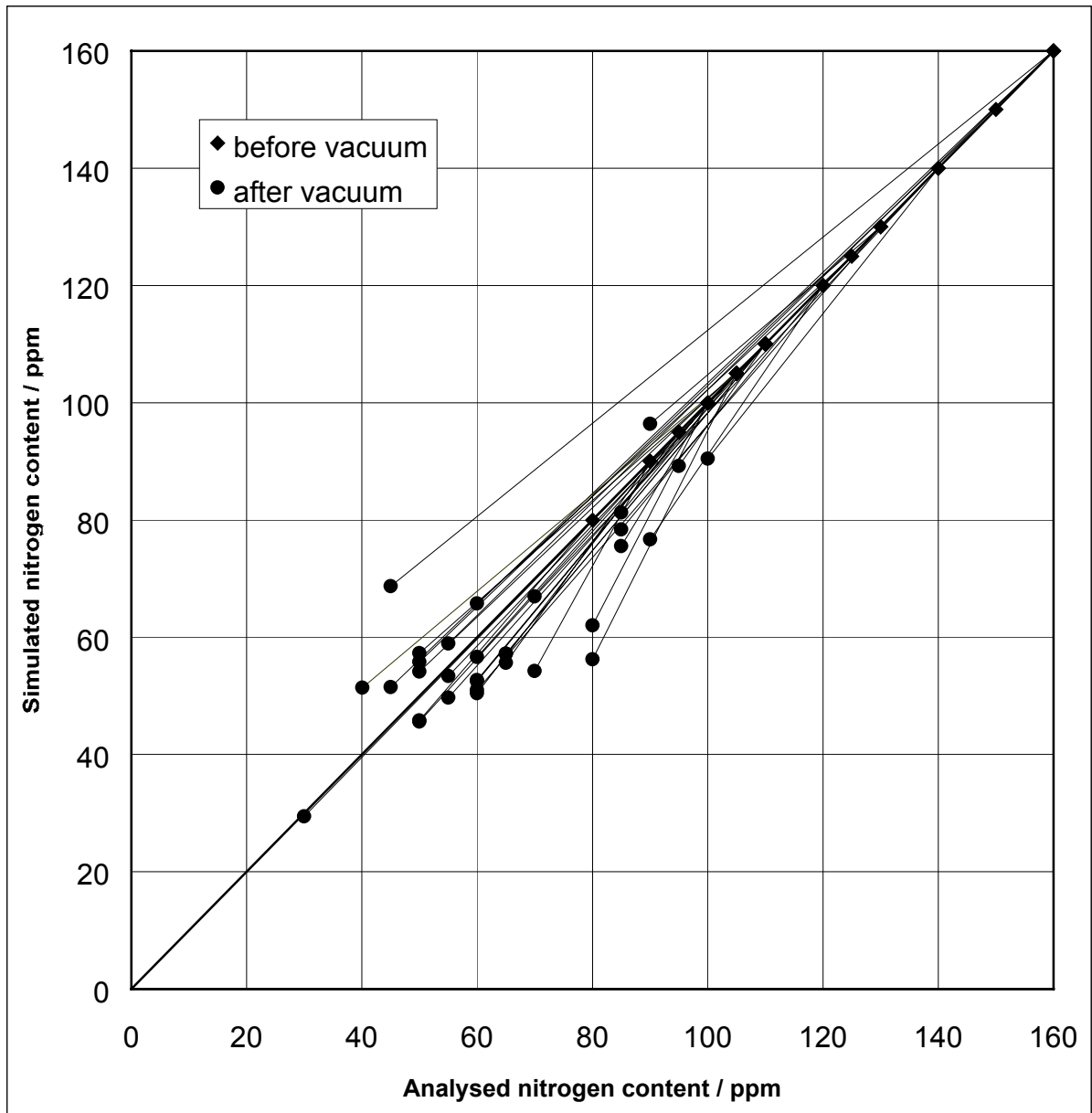


Figure 5: Simulated versus analysed nitrogen content during VD treatment at Buderus plant

At the tank degassing plant of Sidenor the data of 18 heats with nitrogen analysis values before and after vacuum treatment were collected. The evaluation of these data was performed in the same way as for the heats treated at the Buderus plant. As at the Sidenor plant no hydrogen analysis values were available, the reaction time constant T_{HV} for description of the dehydrogenation behaviour could not be identified. To take into account its influence on denitrogenation, the ratio of T_{HV} and T_{NV} was chosen similar to the one identified for the Buderus tank degassing plant. The resulting model parameter values are included in Table 3.

In **Figure 6** the simulated nitrogen content is plotted against the analysed one for the 18 Sidenor denitrogenation heats. The mean value of the simulation error is 2.4 ppm with a standard deviation of 7.1 ppm. In **Table 4** the accuracy of the degassing model is compiled for the two tank degassing plants, together with the values achieved for the vacuum circulation plant.

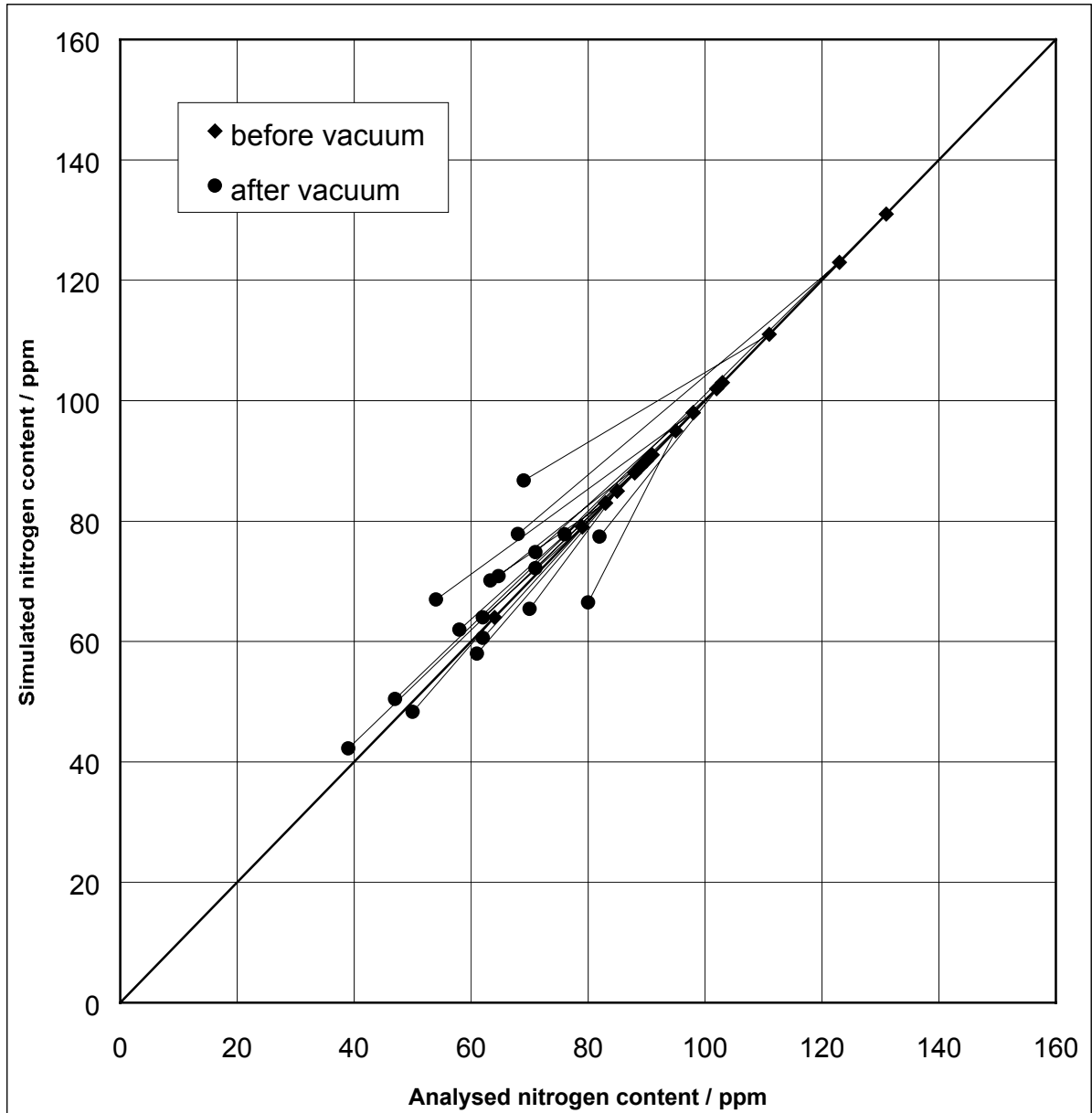


Figure 6: Simulated versus analysed nitrogen content during VD treatment at Sidenor plant

Table 4: Accuracy of the process model for the three different degassing plants

	Simulation error of final content / ppm								
	VD Buderus			VD Sidenor			RH Voest		
	Heats	Mean value	Stand. dev.	Heats	Mean value	Stand. dev.	Heats	Mean value	Stand. dev.
Dehydrogenation	22	0.01	0.20	---	---	---	30	0.00	0.20
Denitrogenation	31	-3.4	9.4	18	2.4	7.1	46	0.0	7.6

4.2 Vacuum circulation process

For simulation of the degassing reactions within the vacuum circulation process, the process model described in chapter 2 had to be extended by some functions.

A detailed evaluation of the decarburisation behaviour [5] had revealed that for the vacuum circulation process a reduced dilution effect of the process gas can be observed. The reason for this is probably that the dilution of the reaction gas mainly occurs in the part of steel which is above the up-leg snorkel of the vacuum vessel. Therefore an additional model parameter R_{VQ} was introduced into equ. (7), to consider this reduced dilution effect when calculating the partial pressure of the reaction gas:

$$P_R = (P_G + P_Z) \cdot \frac{F_{DX} \cdot D_X}{F_{DX} \cdot D_X + R_{VQ} \cdot Q_P} \quad (21)$$

Due to its high flow rate, the main part of the process gas Q_P is given by the lift gas argon Q_L .

Furthermore the calculation of the steel amount in the vacuum vessel W_V and the steel circulation rate Q_M had to be covered by the simulation model, in order to evaluate the degassing rates in the vacuum vessel and the ladle separately. The steel amount in the vacuum vessel is given by the pressure difference between vessel and atmosphere and the geometry of the vessel [5]. The steel circulation rate is calculated depending on the vessel pressure and the lift gas flow rate according to a mathematical model which is described in [7].

For verification of the dehydrogenation model the data of 30 deoxidised heats were evaluated. The data include Hydris measurement values for start and final hydrogen content as well as the content from two measurements during vacuum treatment. For each of the heats the model parameters of the dehydrogenation model, i.e. the reaction time constant T_{HV} , the additional pressure P_{ZE} and the dilution efficiency of the lift gas R_{VQ} were optimised, to minimise the difference between the measured hydrogen content and the simulated one at the time of measurement.

Figure 7 shows for two example heats the results of the dehydrogenation simulation with optimised parameters, together with the measured hydrogen content from the different Hydris measurements. As can be seen the correspondence between simulation and measurement is very good.

For verification of the denitrogenation model the data of 46 deoxidised heats were evaluated in the same way as for dehydrogenation. The data include analysed values for start and final nitrogen content as well as from at least two samples during vacuum treatment. Furthermore the nitrogen pickup from alloy material additions was recorded. The sulphur content of the evaluated heats did not vary much from heat to heat. The average value was 30 ppm with a maximum content of 70 ppm. Therefore no remarkable difference in the denitrogenation behaviour dependent on the sulphur content could be found. The denitrogenation kinetics coefficient R_N was taken from the evaluation of the tank degassing heats. The influence of oxygen could be neglected because the heats were deoxidised by aluminium addition. **Figure 8** shows for two example heats with remarkable nitrogen pickup by alloy material addition the simulated course of denitrogenation simulation based on optimised model parameters, together with the analysed nitrogen content from the different samples. The simulation error is slightly higher than for dehydrogenation, especially shortly after the material additions.

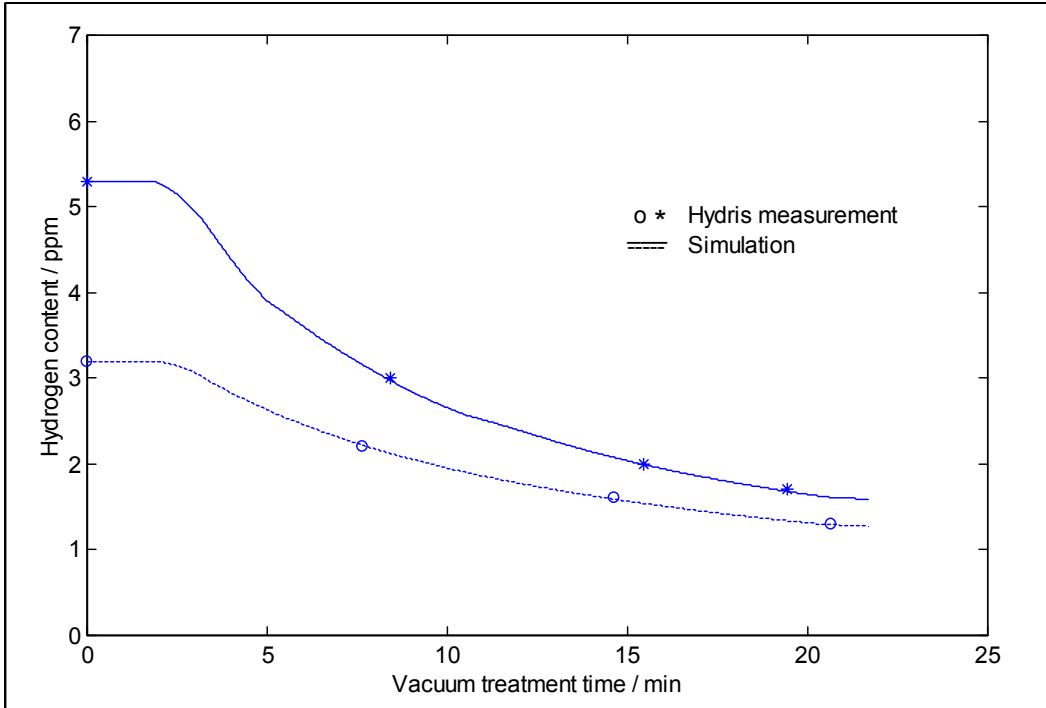


Figure 7: Simulated and measured hydrogen content for two RH example heats

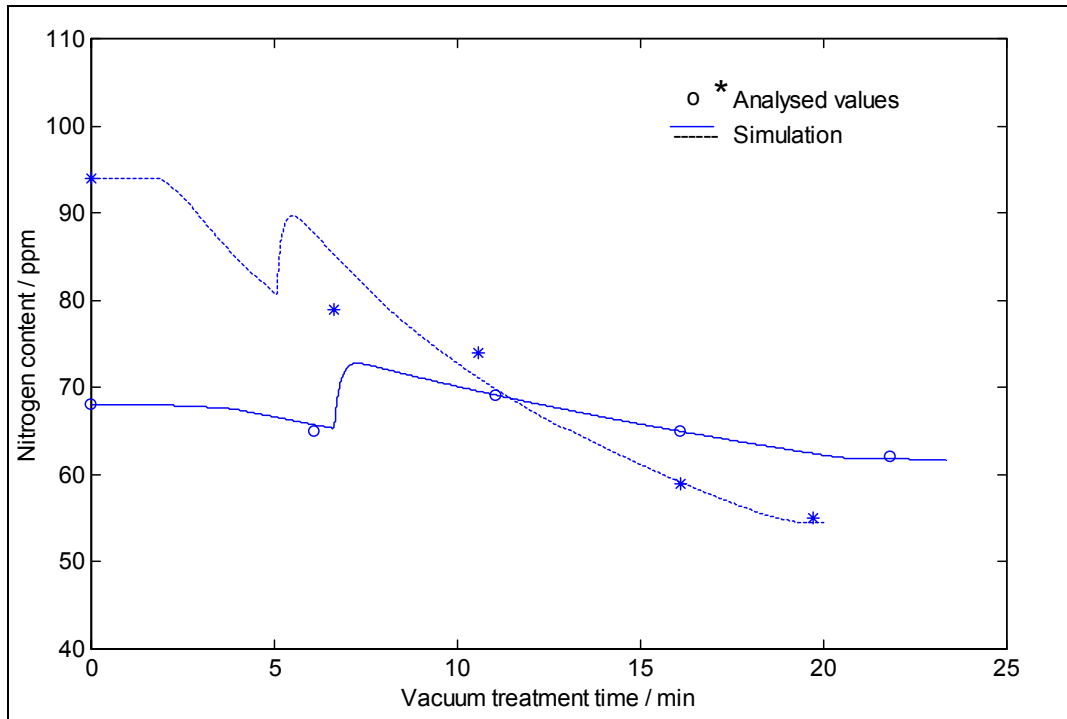


Figure 8: Simulated and measured nitrogen content for two RH example heats

From the parameter optimisation results of all dehydrogenation and denitrogenation heats, mean values for the model parameters were calculated, which are compiled in Table 3 together with the values for the tank degassing process. The accuracy of the simulation model was checked using these mean parameter values. **Figure 9** shows for all evaluated dehydrogenation heats a comparison between measured and simulated hydrogen content during RH treatment. For the final hydrogen content, the mean value of the difference between measurement and simulation is 0.00 ppm with a standard deviation of 0.20 ppm.

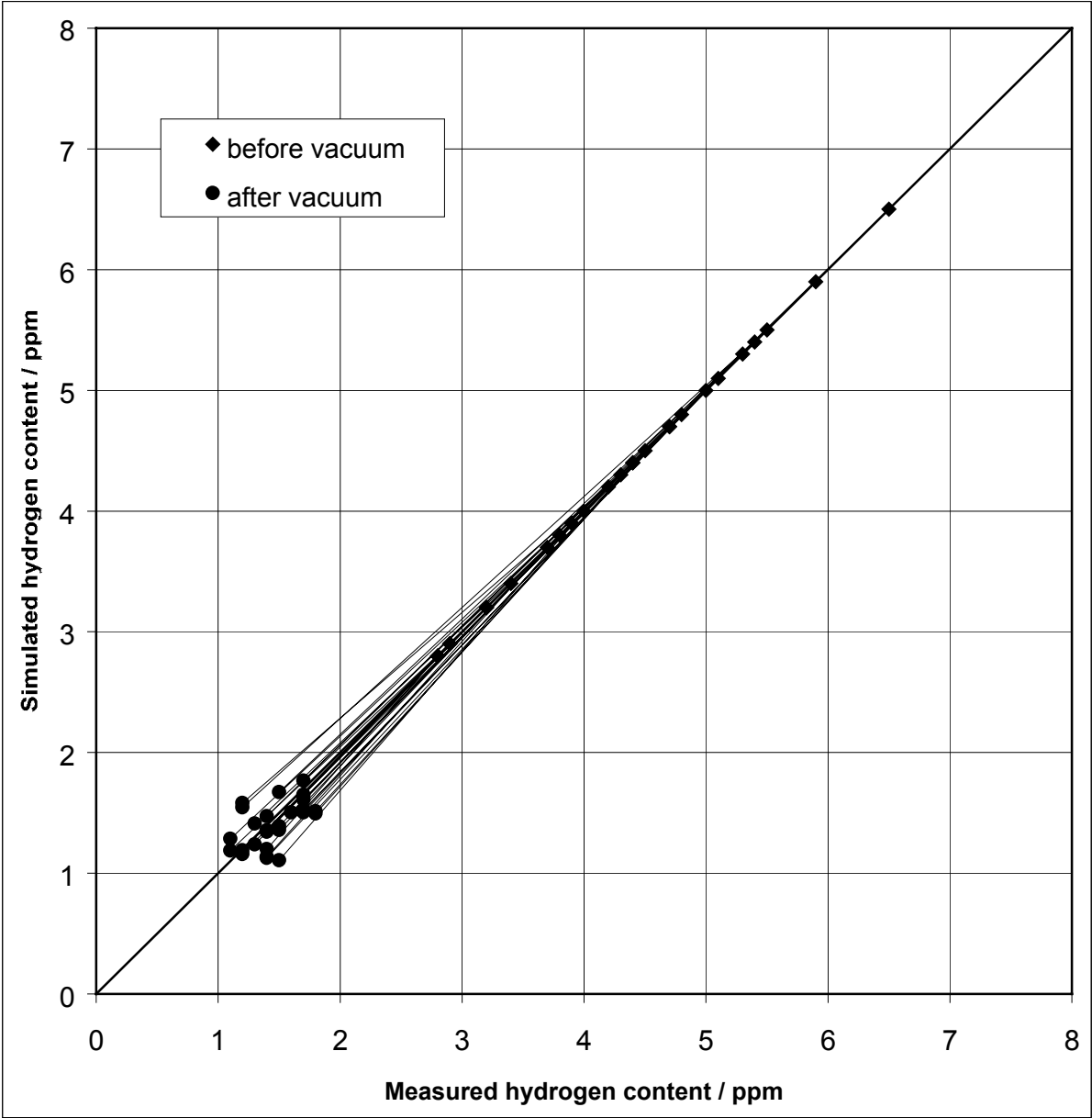


Figure 9: Simulated versus measured hydrogen content during RH treatment at Voest plant

Figure 10 shows the corresponding simulation results for the 46 denitrogenation heats. For the final nitrogen content, the mean value of the simulation error is 0.0 ppm with a standard deviation of 7.6 ppm. The simulation accuracy is included in Table 4 for comparison to the values for the tank degassing process.

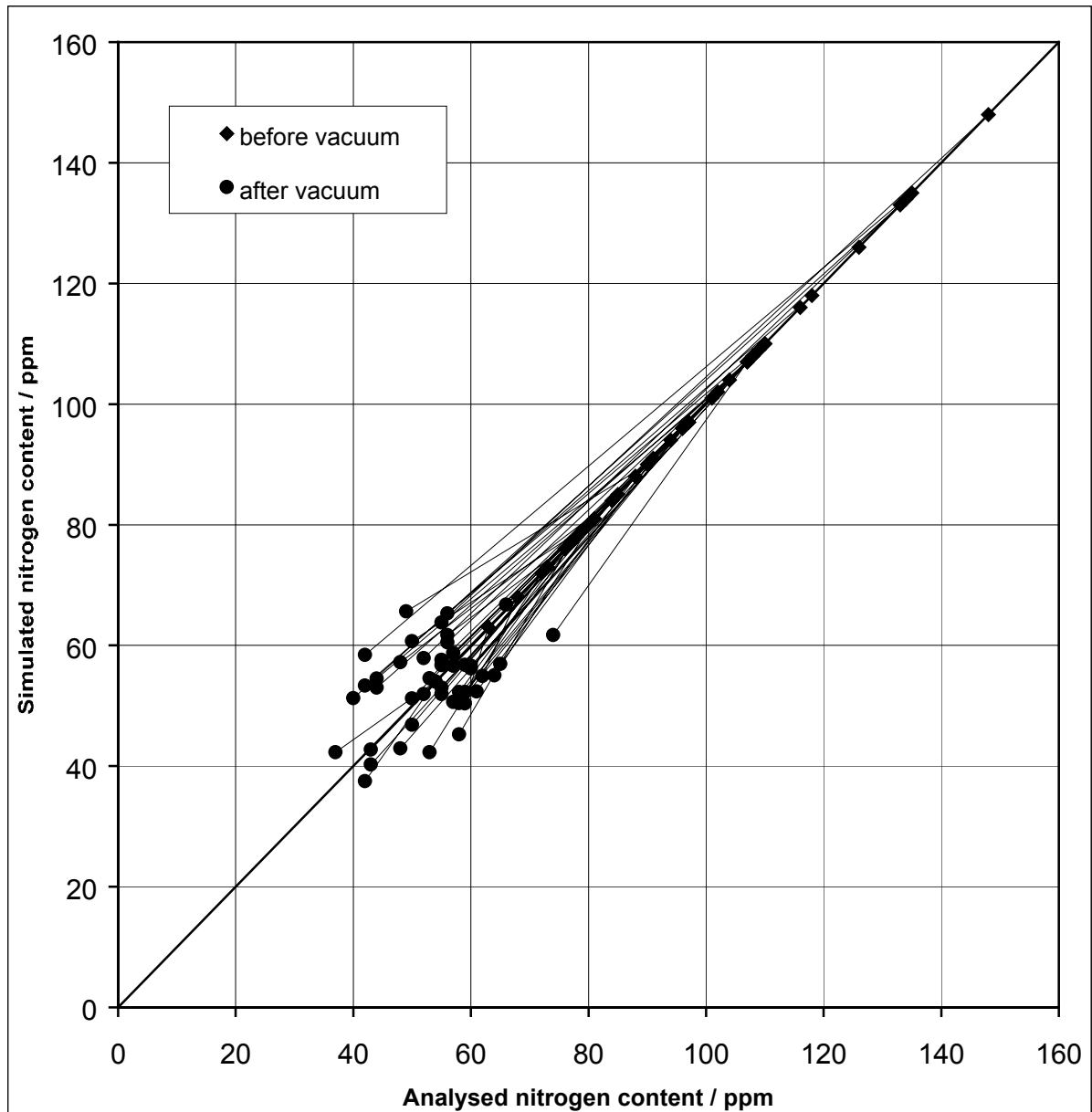


Figure 10: Simulated versus analysed nitrogen content during RH treatment at Voest plant

As can be seen from Table 3, the identified parameter value for the additional pressure P_{ZE} is with 38 mbar respectively 43 mbar much higher than the final vessel pressure during degassing. According to equ. (7) it can be expected that the additional pressure P_Z reduces the influence of the vessel pressure on the degassing efficiency. To prove this exemplary for the vacuum circulation process, the final hydrogen content was plotted against the average vessel pressure during RH treatment, see **Figure 11**. This average pressure was taken to allow a comparison of the heats, because the minimum vessel pressure could not be maintained during the complete vacuum treatment for some heats. As can be seen there is a small influence of the vessel pressure on the achievable final hydrogen content. Values below 1.5 ppm could not be reached for an average vessel pressure higher than 10 mbar. On the other hand it seems not to be necessary to operate with a vessel pressure below 1 mbar, as the same final hydrogen content can also be reached with a value of around 2 mbar.

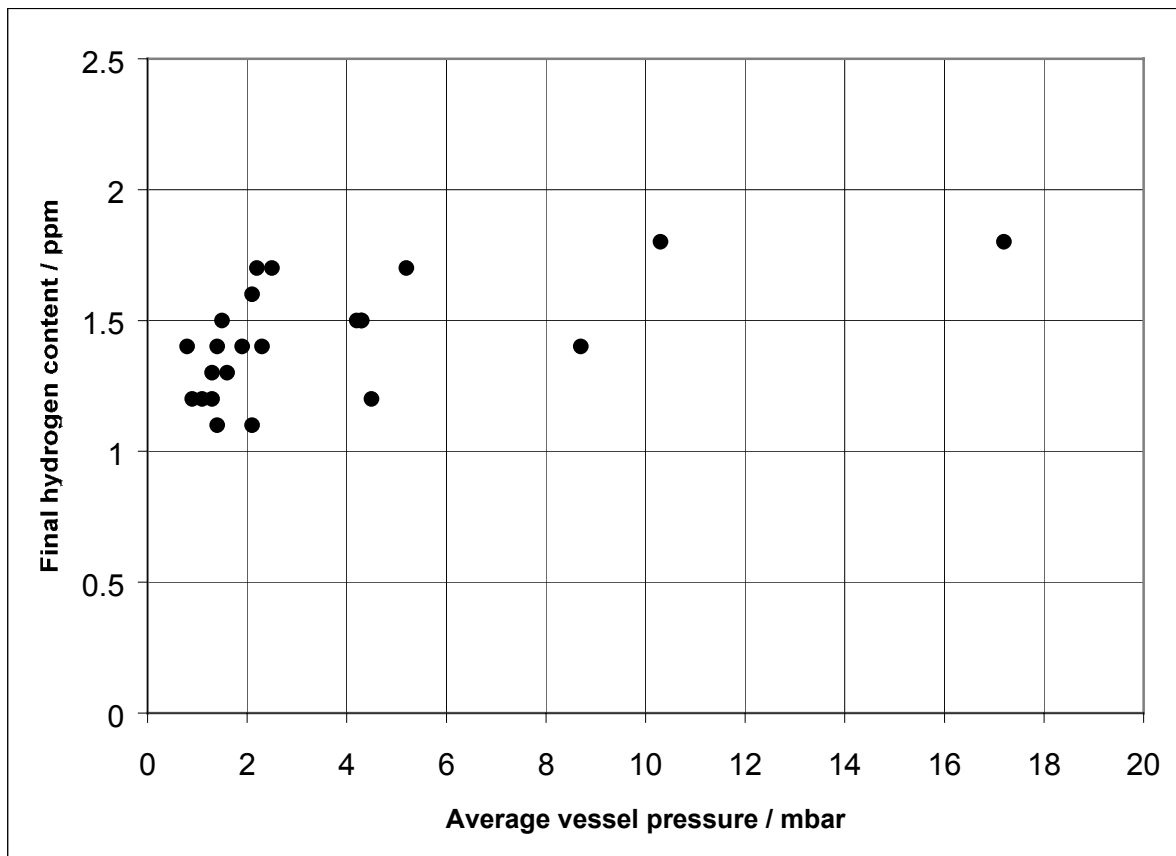


Figure 11: Dependence of the final hydrogen content on the average vessel pressure during RH treatment

Similar investigations for denitrogenation showed that, resulting from the influence of the additional pressure, there is no clear dependence of the nitrogen removal efficiency on the final vessel pressure, at least for values below 10 mbar.

5. ON-LINE APPLICATION OF THE MODEL FOR PROCESS OBSERVATION

As already stated in the introduction, the process model for dehydrogenation and denitrogenation shall be used for on-line calculation of the hydrogen and nitrogen content. For this purpose the process model was simplified, especially for the vacuum circulation process, with respect to the necessary input variables and the model equations.

The main simplification of the degassing model for the vacuum circulation process is that the element concentrations $X = H, N$ of steel in the vacuum vessel and in the ladle are not calculated separately but as one common concentration. The differential equation for this common concentration is given by equ. (13) for dehydrogenation and by equ. (20 a, b) for denitrogenation. The effective time constant T_{XRH} , which covers the influence of the reaction time constant T_{XV} and of the steel circulation through the vacuum vessel with the rate Q_M , is given by equ. (14) and equ. (19) respectively. The equilibrium content X_Q is calculated in the same way as in the complete simulation model.

The steel amounts W_V and W_L in the vacuum vessel and the ladle as well as the steel circulation rate Q_M , which are required to calculate the effective time constant T_{XRH} , change during vacuum treatment. As the vessel pressure decreases, the steel amount in the vacuum vessel increases, and at a certain pressure level the steel circulation through the vessel starts with an also increasing rate. But as after a few minutes steady-state values for W_V and Q_M are reached, a fixed value for the effective time constant T_{XRH} can be chosen. This means that a dynamic calculation of the steel amount and the circulation rate in the vacuum vessel is not required for on-line purposes.

By application of these simplifications, the degassing model for the vacuum circulation process obtains the same structure as the one for the tank degassing process. The values of the additional model parameters for the Voest RH plant are compiled in **Table 5**.

Table 5: Additional model parameter values of the simplified RH degassing model

Model parameter	Symbol	Value
Effective time constant of RH dehydrogenation	T_{HRH}	124 s
Effective time constant of RH denitrogenation	T_{NRH}	294 s
Average steel weight in the vacuum vessel	W_V	11.5 t

For on-line calculation of the hydrogen and nitrogen content of deoxidised heats the following input values are required:

- vessel pressure (cyclically measured)
- inert gas flow rate (cyclically measured)
- start hydrogen content
- start nitrogen content
- start sulphur content (for influence on denitrogenation)
- start steel weight
- material additions during degassing treatment (for nitrogen pickup)

To check the accuracy of the simplified model for the vacuum circulation process, its simulation results were compared to the ones of the complete simulation model mentioned in chapter 4. The applied model parameter values are compiled in Table 3 and 5. As can be seen from **Table 6**, by the simplification of the RH degassing model its accuracy is only slightly decreased.

Table 6: Accuracy of the complete and the simplified RH degassing model

	Simulation error of final content / ppm					
	Complete model		Simplified model		Simplified model Average start value	
	Mean value	Stand. dev.	Mean value	Stand. dev.	Mean value	Stand. dev.
Dehydrogenation	0.00	0.20	0.03	0.20	0.04	0.20
Denitrogenation	0.0	7.6	0.1	7.7	1.2	7.9

A further simplification of the degassing model with respect to the input values is possible. As can be seen from Fig. 4, 7 and 9, the final hydrogen content, which is reached after a degassing duration of about 20 minutes, is almost independent from the start content. Therefore the measurement of the start hydrogen content can be omitted without reducing the accuracy of the on-line observation significantly. For the 30 RH dehydrogenation heats, which were evaluated for model verification, the average start content is 4.2 ppm with a standard deviation of 1 ppm. As can be seen from Table 6, the simulation accuracy is nearly not changed when using this average start content instead of the individual ones. For denitrogenation at the RH plant, the simulation accuracy is slightly decreased when the average start content of 94 ppm is used, although its standard deviation is with 21 ppm in the same range as for hydrogen. The reason is that, as can be seen from Fig. 10, the scatter in the final nitrogen content is higher due to the nitrogen pickup, which occurs for some heats after alloy material addition.

At the Buderus tank degassing plant a model-based on-line calculation of the hydrogen content is already implemented. Based on the cyclically measured vessel pressure and the stirring gas flow rate as well as average start values for hydrogen (6 ppm), nitrogen (120 ppm) and sulphur (80 ppm), the final hydrogen content can be calculated with an error mean value of -0.09 ppm and an error standard deviation of 0.20 ppm. The accuracy is only slightly decreased compared to the one which was achieved with exact start values, see Table 4.

6. CONCLUSIONS

Based on the principles of thermodynamics and reaction kinetics a process model for denitrogenation and dehydrogenation was developed. The model was applied to the tank degassing and the vacuum circulation process and was verified by the comparison of simulation results to measured process data. The main process parameters were identified for three different degassing plants. The good simulation accuracy with about 0.2 ppm for hydrogen and 8 ppm for nitrogen makes it possible to use the process model for several applications:

- The simulation model can be used to improve the operation of vacuum degassing plants. For example the influence of inert gas flow rate and final vessel pressure on the necessary degassing time can be investigated with the help of simulation calculations. By this expensive plant trial campaigns can be substituted or at least prepared carefully. As for example shown for dehydrogenation within the vacuum circulation process, the minimum vessel pressure can be increased without influence on the achievable final hydrogen content. This means that the suction speed of the vacuum pumps can be reduced, which lowers the operation costs.
- A simplified version of the process model can easily be used for on-line observation of the hydrogen and the nitrogen content during degassing treatment. For this calculation it is not necessary to know the exact start contents, which means that the effort and the expense for sampling and analysis before vacuum treatment can be avoided. This is especially of interest for hydrogen with the expensive Hydris measurement or gas analysis method.
- From the cyclically calculated hydrogen and nitrogen content of a heat, the time when the aim contents are reached can be determined with a good accuracy. With this additional information of the actual process state, it is not necessary to elongate the vacuum treatment time for a safe achievement of the aim values.

Acknowledgements

The process models for denitrogenation and dehydrogenation within the vacuum tank degassing and the vacuum circulation process were developed within two different research projects of the European Coal and Steel Community (ECSC). The authors like to thank the ECSC for their financial support.

References

1. Janke, D.:
Metallurgische Grundlagen der Vakuumbehandlung von Stahlschmelzen.
Stahl und Eisen 107 (1987), No. 19, p. 867 - 874
2. Bannenberg, N.; Bergmann, B.; Gaye, H.:
Combined decrease of sulphur, nitrogen, hydrogen and total oxygen in only one secondary steelmaking operation.
Steel research 63 (1992), No. 10, p. 431 - 437
3. Szekely, J.; Martins, G. P.:
Studies in Vacuum Degassing. Part I: Fluid Mechanics of Bubble Growth at Reduced Pressure.
Transaction of the Metallurgical Society of AIME 245 (1969), p. 629 - 636
4. Köhle, S.; Kleimt, B.:
Ein betriebsnahes Modell für die Entgasung von Stahlschmelzen.
Stahl und Eisen 116 (1996), No. 5, p. 81 - 87
5. Kleimt, B.:
Entwicklung und Anwendung eines Modells für den Vakuum-Umlauf-Prozeß zur Entkohlung von Stahlschmelzen.
Fortschritt-Berichte VDI, Reihe 5, Nr. 395, VDI-Verlag Düsseldorf, 1995
6. Harada, T.; Janke, D.:
Nitrogen desorption from pure iron melts under reduced pressure.
Steel research 60 (1989), No. 8, p. 337 - 342
7. Ahrenhold, F.; Pluschkell, W.:
A New Mathematical Model of the Circulation Flow in RH Units.
Scaninject VII, Lulea 1995, p. 83 - 106.