Denitrogenation model for vacuum tank degasser

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Abstract. Nitrogen in steel is both beneficial and detrimental depending on grade of steel and its application. To get desired low nitrogen during vacuum degassing process, VD parameters namely vacuum level, argon flow rate and holding time has to optimized depending upon initial nitrogen level. In this work a mathematical model to simulate nitrogen removal in tank degasser is developed and how various VD parameters affects nitrogen removal is studied. Ladle water model studies with bottom purging have shown two distinct flow regions, namely the plume region and the outside plume region. The two regions are treated as two separate reactors exchanging mass between them and complete mixing is assumed in both the reactors. In the plume region, transfer of nitrogen to single bubble is simulated. At the gas-liquid metal interface (bubble interface) thermodynamic equilibrium is assumed and the transfer of nitrogen from bulk liquid metal in the plume region to the gas-metal interface is obtained using mass transport principles. The model predicts variation of Nitrogen content in both the reactors with time. The model is validated with industrial process and the predicted results were found to have fair agreement with the measured results.

1. Introduction
With technological advances the current steel quality has improved drastically with comparison with quality a decade ago. With emphasis on clean steel technology inclusion content and gas content are controlled to greater extent. Nitrogen acts as a detrimental and beneficial element in steel based on its nature of post processing and applications. Grades of steel which undergoes deep drawing requires lower nitrogen content. For such grades control of nitrogen starts from primary steelmaking to till caster. To get desired nitrogen one has to control incoming nitrogen through use of low nitrogen ferroalloys and controlling nitrogen pickup during the entire process. The other way is to remove it through degassing operation from the liquid steel by purging argon from bottom of the ladle through the porous plug system. As the argon bubbles rise through the plume, it picks up nitrogen gas and leaves to gases maintained at low pressure at the top. In the present work a mathematical model to predict temporal evolution of nitrogen in liquid steel during vacuum degassing for different operating parameters namely argon flow rate, vacuum level and holding time is developed.

2. Model conceptualization
Water model studies [1] [2] [3] on ladle with bottom purging have shown presence of two distinct flow regions inside the ladle, namely the plume region (mixture of liquid steel and air bubbles) and outside plume region (the recirculating region) and this is illustrated in figure 1 (a). In the model these two regions are considered as separate reactors for model formulation. In the plume region, say reactor 1, the argon bubbles are formed and they rise up in the bath. During this ascent of a bubble, transfer of nitrogen from liquid steel to bubble takes place. The liquid from the plume region flows to the reactor 2
at the top of the ladle as shown in the figure 1 (b), and vice versa at the bottom. This mass transfer of liquids results in mixing.

3. Transfer of nitrogen into a Single Bubble

Modelling transfer of species across a single bubble is taken from works of Haijuan Wang et.al. [4]. Nitrogen removal from liquid steel takes place in the following three steps.
1. Liquid phase mass transfer of nitrogen from liquid steel to the gas-liquid interface.
2. Conversion of N into N$_2$ takes place by interfacial reaction given by equation (1).

\[
N = \frac{1}{2} N_2
\]  

3. Transfer of N$_2$ into the argon bubble.

When argon is purged into liquid steel argon bubbles are produced. Argon bubble at the bottom of the ladle has zero partial pressure of nitrogen and as it travels up, the amount of nitrogen and partial pressure inside the bubble keeps on increasing. The nitrogen transfer from liquid steel to the gas-liquid steel interface is governed by mass transfer. At this interface dissolved N in liquid steel is assumed to be in equilibrium with N$_2$ in the gas phase and this assumption is fairly valid under such high steel making temperatures. The N$_2$ from the interface is transferred to the bulk gas in the bubble by convective mass transport. When the partial pressure of nitrogen inside the bubble attains equilibrium, then the transfer of nitrogen into the bubble ceases. During the travel of any particular bubble, no compositional change occurs in plume region because bubble travel time is assumed much shorter than the refining time. The rate of nitrogen transfer (moles/sec) into argon bubble is given mathematically by equation (2) and equation (3) gives equilibrium nitrogen in the bath

\[
\dot{n}_{N_2} = \frac{A_b k_N p}{100 M_{N_2}} (wt\% N^R - wt\% N^{eq}) 
\]  

\[
wt\% N^{eq} = \frac{1}{P_{N_2} f_N} (K_{eq} * f_N) 
\]  

$K_{eq}$ is the equilibrium constant for the reaction [1].
At any height of the ladle the moles of nitrogen \( (n_{N_2}) \) inside the bubble can be traced by doing a mass balance of nitrogen as given by equation (4). The molar balance for the bubble travelling a small distance \( \text{`}dh\text{`} \) is

\[
\frac{d(U_b n_{N_2})}{dh} = \dot{n}_{N_2}
\]

\( U_b \) is the velocity of bubble at any height \( \text{`}h\text{`} \) in the plume region.

The next step in the model is predicting rate of nitrogen removal in the plume region, which can be calculated from equation (5)

\[
\frac{d(\text{wt}\%N)_p}{dt} = \frac{\dot{N}_b \cdot n_{N_{2\text{top}}} \cdot 100 \cdot M_{N_2}}{m_p}
\]

The term \( n_{N_{2\text{top}}} \) is the number of moles of nitrogen inside a bubble when it escapes at the top of melt surface, \( m_p \) is the plume liquid mass and equation (6) gives number of bubbles produced per unit time \( \dot{N}_b \)

\[
\dot{N}_b = \dot{n}_{Ar} \cdot R \cdot \frac{T}{V_b \left( P_v + \rho g Z + \frac{4 \sigma}{d_b} \right)}
\]

The term \( 4\sigma/d_b \) in the above equation is the excess pressure due to surface tension of liquid steel \( (\sigma = 1.8 \text{ N/m}) \) which restricts the increase in bubble number.

4. Bubble parameters and mass transfer

Numerous cold model studies were done to study bubble dispersion modes with modified parameters. At higher gas flow rates through porous plug, a single large bubble is formed at plug exit [1][2][3]. The rising bubble disintegrates into number of small bubbles during its upward movement. Sano and Mori [5][6] found that the large bubble disintegrates into small bubbles within 12cm from the orifice and estimated average bubble diameter after disintegration and empirical relation for determining bubble size is given by equation (7)

\[
d_b = 0.091 \left( \frac{\sigma}{\rho_l} \right)^{0.5} V_s^{0.44}
\]

In this model the number of bubbles at any time is assumed to be constant and change in bubble size during a bubbles upward movement happens due to change in pressure inside the ladle with height. The increase in bubble size with respect to entrant of nitrogen into bubble is negligible. When the bubbles move upward, the bubble expands due to decrease in ferrostatic pressure and it breaks into number of bubbles. Subsequently, the ascending bubbles also coalescence by which the number of bubbles decreases [1][2]. Due to simultaneous breakage and coalescence, constant bubble population is assumed throughout the bath. Spherical capped bubbles are formed during ladle refining operation [7] and equation (8) gives the empirical relation for velocity of spherical capped bubble is [7]

\[
U_b = 1.02 \left( \frac{gd_b}{2} \right)^{0.5}
\]

The mass transfer rate depends on the mass transfer coefficient \( k_{N}^m \). Mass transfer coefficient of nitrogen, equation (9) is given by Richardson and Bradshaw is used in the model [8].
\[ k_N^m = 1.08 \left( \frac{1}{d_b} \right)^{1/4} D g^{1/4} \]  

(9)

5. Plume Parameters
As nitrogen removal takes place in plume region, plume dynamics plays crucial role in rate of denitrogenation. Empirical relations for plume parameters for a conical plume are available in works of Krishnapisharody et.al. [9] [10]. The plume cone angle varies from 15 to 20 degrees. Plume parameters namely gas fraction (\( \alpha \)) equation (10) and liquid velocity (\( U_l \)) equation (11) was derived with plume angle as 17.5 degrees in their work, which is used in the present model also

\[ \alpha = 1.84Q^{0.63}Z^{-1.57} \]  

(10)

\[ U_l = 2.57Q^{0.31}Z^{-0.28} \]  

(11)

Mass of steel in the plume region is calculated by equation (12)

\[ m_p = \frac{\rho \cdot \text{steel fraction} \cdot V_p}{1000} \]  

(12)

From the gas fraction (ratio of volume of gas in the plume region to volume of plume) in plume region, steel fraction can be calculated.

6. Mixing inside the ladle
Porous plug is used to assist mixing in the ladle for homogenising composition and temperature. This mixing is favoured by rising bubbles in the plume region. The rising bubble creates mass flow inside the ladle which makes the mixing possible. Tanks in series model approach is employed for simulating mixing in an agitated bath [11] [12]. In modelling mixing in VOD process, the vessel is divided into two well stirred tanks between which there is a constant exchange of the liquid [12]. As discussed earlier the current model was formulated by dividing the entire ladle into two well stirred reactors or tanks for simulating the mixing behaviour. Both the reactors are treated as continuously stirred reactors. This mixing leads to change in nitrogen concentration in both the reactors with time and nitrogen evolution inside plume and outside plume can be evaluated by performing a mass balance. The difference equations are given by equation (13) and equation (14).

\[ N_{OPt+dt} = \frac{m_{OPt} + m_{t}N_{Pt+dt}}{m_{OPt} + m_{t} \Delta t} \]  

(13)

\[ N_{Pt+dt_{mixing}} = \frac{m_{P}N_{Pt+dt} + m_{t}N_{OPt+dt}}{m_{P} + m_{t} \Delta t} \]  

(14)

where \( m_t \) is mass flow rate of liquid exchanged between the two reactors.

Water model study [1] shows the flow of the liquid is predominantly vertical in the plume region and the movement becomes horizontal at the top of plume region. Liquid transfer from plume region to the rest of the ladle and vice-versa happens as shown in figure 1. The mass flow rate \( m_t \) between the two reactors is given by using the equation (15)

\[ m_t = (1 - \alpha)A_c \rho U_l \]  

(15)
7. Plant process and trial
The process route at JSW Steel Limited Salem works is through Energy Optimizing Furnace-Ladle Furnace-Vacuum Degassing-Caster route. The plant produces low alloy special steel long products for automobile application. The model is developed for a 45-ton ladle. After the refining process the ladle is taken to vacuum degassing station at average temperature of 1620° C. Vacuum is obtained through steam ejectors. The liquid steel temperature is assumed to be 1600 °C and no change in temperature occurs during the degassing process. LECO oxygen nitrogen analyser is used to measure nitrogen content before and after the degassing process. In the model denitrogenation at surface is ignored. Slag is not considered in the simulation. Table 1 shows process parameters for few heats for which model validation was done.

| Case no | Holding time (mins) | Argon flow rate (Nm3/hr) | mbar | BVD Nppm | Measured value AVD Nppm |
|---------|---------------------|--------------------------|------|----------|------------------------|
| 1       | 8                   | 7                        | 0.30 | 43.0     | 36.6                   |
| 2       | 9                   | 5                        | 0.40 | 58.0     | 42.9                   |
| 3       | 9                   | 10                       | 0.40 | 82.0     | 48.1                   |
| 4       | 8                   | 8                        | 0.48 | 58.3     | 44.1                   |
| 5       | 8                   | 8                        | 0.50 | 44.3     | 38.7                   |
| 6       | 8                   | 8                        | 0.50 | 44.6     | 34.4                   |

8. Model assumptions
- The model is assumed to be isothermal and temperature of liquid steel is 1600° C. The effect of temperature drop during vacuum degassing is ignored.
- When the bubbles move upward, there is a volume expansion due to decrease in ferrostatic pressure. The volume expansion results in breakage of bubbles and more number of bubbles are generated, but simultaneously coalescence of bubbles also takes place. Due to simultaneous breakage and coalescence, the bubble population is assumed to be same throughout the bath. Similarly, for the above reason an average bubble size has been assumed.
- Composition of liquid steel inside the plume remains the same during the travel of any particular bubble.
- Slag is neglected in the simulation.
- No CO bubbles are formed due to decarburization as oxygen ppm before degassing is in the range of 10-15 ppm.
- In JSW process the average oxygen and sulphur level before degassing is 15 ppm and 120 ppm, their effect as surface effective element is ignored. This assumption is valid as after degassing process the sulphur level is 10 ppm.

9. Effect of Steel composition
The presence of other alloying elements also affects the removal of nitrogen. The activity coefficient of nitrogen is influenced by the other solutes such as C, Mn, Si, Al, P, S, Cr, Ti, V and others. When the activity coefficient of nitrogen is raised then the removal of nitrogen will be more because of the
decrease in equilibrium nitrogen level. Sulphur, phosphorus and aluminium are generally present in steel in the range 0.005-0.015, 0.005-0.015 and 0.020-0.030 respectively. Their influence on activity coefficient is insignificant. For a low alloy steel, the activity coefficient of nitrogen is approximately around 1. Since the second order interaction parameter for nitrogen on nitrogen is zero, the change in nitrogen while denitrogenation makes no change in the activity. So thermodynamically it is the partial pressure which determines the effectiveness of denitrogenation.

10. Model validation

Without validation the model cannot be accepted. The model was validated with the plant data as given in table 1. The model was developed and the governing equations are solved in MATLAB software. For the simulation diffusion coefficient for nitrogen, the equilibrium constant $K_{eq}$ is calculated from standard Gibbs energy data from MSTS [13]. Interaction parameters for nitrogen in liquid iron is taken from Sigworth and Elliot [14]. The model validation covers for different flow rates and different initial nitrogen levels to ascertain the applicability of the model for various process conditions. The inputs for the model namely, liquid steel weight, chemical composition of the liquid steel and VD parameters are taken for simulation. The evolution of nitrogen concentration is calculated using a small time step $\Delta t$ for a given mass of liquid steel. The model predicts nitrogen concentration in both the reactors (plume region and outside plume region) with time, which is shown in figure 2 for case 4. From figure 2 it can be seen that due to the mixing phenomena, the nitrogen concentration in both the reactors converges with progress in degassing time and finally almost same value is achieved. The measured and model predicted value (44.1 ppm) is same for this case. Figure 3 shows comparison between predicted and measured values for 6 heats and close agreement is seen, which shows the model is reliable in predicting the final nitrogen for a vacuum tank degassing process. The effect of vacuum parameters is also analysed in the current work which shows lower vacuum level and increased argon flow rate favours better denitrogenation, as in works of other researchers. As the current work is focussed on nitrogen prediction for given parameters the results on effect of VD parameters is ignored here.

The limitations of the model are denitrogenation on the surface layer is ignored and the model cannot be used if oxygen and sulphur contents are high enough to affect denitrogenation.
11. Conclusion

Based on thermodynamics, mass transfer coupled with bubble dynamics and mixing principles a mathematical model to simulate nitrogen removal in vacuum tank degassing process was developed. The model features nitrogen removal through single argon bubble and nitrogen composition in the plume region with time. Nitrogen evolution in rest of the ladle is captured by incorporating the mixing phenomena. Model validation with plant trials showed close agreement between model value and measured value. Lower vacuum levels and increased argon flow rate shows better denitrogenation. As the results are comparable with actual values the model can be used for predicting final nitrogen for a tank vacuum degassing process.

12. List of symbols

Variables

| Symbol | Description                              |
|--------|------------------------------------------|
| $A_b$  | Surface area of bubble (m$^2$)           |
| $A_c$  | Cross sectional area of plume (m$^2$)    |
| $d_b$  | Diameter of bubble (m)                   |
| $d_h$  | Small distance (m)                       |
| $d_t$  | Small time (sec)                         |
| $D_i$  | Diffusion coefficient of species ‘$i$’ (m$^2$/s) |
| $f_N$  | Henrian activity coefficient             |
| $g$    | Gravitational constant (m/s$^2$)         |
| $N$    | Dissolved nitrogen in liquid steel       |
| $k_m$  | Mass transfer coefficient of species ‘$i$’ (m/s) |
| $M$    | Molar mass (kg/mol)                      |
| $m$    | Mass of steel (kg)                       |
| $n$    | Moles                                    |
| $\dot{n}$ | Moles/sec                               |
| $P$    | Pressure (bar)                           |
| $P_{N_2}$ | Partial Pressure of Nitrogen (atmosphere) |
| $Q$    | Argon flow rate (m$^3$/s)                |
| $R$    | Gas constant (m$^3$ atm K$^{-1}$ mol$^{-1}$) |
| $T$    | Temperature (Kelvin)                     |
| $t$    | Time (sec)                               |
| $V$    | Volume (m$^3$)                           |
| $V_s$  | Superficial velocity (m/sec)             |
| $Z$    | Axial height of liquid steel in ladle (m) |

Figure 3. Comparison between model predicted value and plant measured value
Greek Symbols
\( \rho \) Density of liquid steel (kg/m\(^3\))
\( \alpha \) Gas fraction
\( \sigma \) Surface tension of liquid steel (N/m)

Superscript
B Bulk nitrogen concentration
eq Equilibrium

Subscript
Ar Argon
h Height
P Plume
OP Outside plume
\( v \) Vacuum pressure

13. References
[1] Anagbo P E, Brimacombe J K and Castillejos A H 1989 Canadian Metallurgical Quarterly. 28 323
[2] Anagbo P E and Brimacombe J K 1990 Metallurgical Transactions B 21 637
[3] Alexiadis A 2007 Applied Mathematical Modelling 31 1534
[4] Wang H, Viswanathan N N, Ballal N B and Seetharaman S 2010 International Journal of Chemical Reactor Engineering 8 1
[5] Sano M and Mori K 1980 Trans. ISIJ. 20 668
[6] Mori K, Sano M and Sato T 1979 Trans. ISIJ. 19 553
[7] Szekely J 1979 Fluid Flow Phenomena in Metals Processing (New York: Academy Press)
[8] Bradshaw A V and Richardson F D 1965 The Iron and Steel Institute 24.
[9] Krishnapisharody K and Irons G A 2007 Metallurgical and Materials Transactions B 38 367
[10] Krishnapisharody K and Irons G A 2007 Metallurgical and Materials Transactions B 38 377
[11] Meitz J and Oeters F 1989 Canadian Metallurgical Quarterly 28 19
[12] Krishnakumar K, Ballal N, Sinha P, Sardar M and Jha K 1999 ISIJ international. 39 419
[13] Turkdogan E T and Fruehan R J 1999 Fundamentals of iron and steelmaking The Making, Shaping, and Treating of Steel vol. 2, ed R J Fruehan (Pittsburgh: The AISE Steel Foundation)
[14] Sigworth G K and Elliott J F 1974 Metal Science 8 298
[15] Bannenbergg N, Bergmann B and Gaye H 1992 Steel Research 63 431

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