Prevent of greenhouse gas emissions in aluminum smelter by carbon nanotube (Monte Carlo simulation)

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Greenhouse gas emissions in aluminum smelter and separation this gases from hydrogen is very important. The gaseous constituents are carbon dioxide, sulphur dioxide and hydrogen fluoride, carbon tetrafluoride, di-carbon hexafluoride, silicon tetrafluoride, carbon disulphide, and hydrocarbons gaseous have been identified. Challenged by growing environmental concerns, the primary aluminium industry has undergone major changes over the last two decades to become a much more efficient industry with GHG emissions during the smelting process. The aluminium industry has been identified as a major contributor to GHG emissions and is therefore under particular scrutiny from the Intergovernmental Panel on Climate Change (IPCC), one of whose targets is to reduce these emissions by 50 to 85% by 2050. This study has been conducted to figure out the adsorption and separation of greenhouse gas emissions with hydrogen on (8,8) armchair carbon nanotubes (CNTs). Lennard-Jones potential was used for gas-gas and gas-carbon nanotube interactions and the potential parameters for the carbon-gas and carbon-carbon interactions were obtained from the Lorenz-Berthelot combining rules. My calculations have shown that adsorption between hydrogen and these gases in aluminum smelter is possible and separation between studied gases in inside and first layer of outside carbon nanotube is possible.

Keywords: “carbon nanotube, monte carlo simulation, adsorption gas”

INTRODUCTION

Greenhouse gas emissions in the production of primary aluminum come from processes such as coke calcination, anode production and consumption, lime production, and electrical generation. Process carbon dioxide emissions make up about half of total direct carbon dioxide equivalent emissions from aluminum production with the remaining greenhouse gases (GHG) emitted being perfluorinated carbon (PFC) gases. For example, the measurements of the two perfluorocarbons (PFCs) tetrafluoromethane (CF4) and hexafluoroethane (C2F6) -- emitted directly from the manufacture of primary aluminum are used in the calculation of facility specific greenhouse gas emission factors. Commercial aluminum production has been identified as the largest emitter of these two compounds. Although the annual amount of PFC emissions is not great, the impact is magnified because of the high global warming potentials (GWP) of these two gases over the lifetime of the a facility.

Fluoride emissions in the form of gaseous hydrogen fluoride and sodium and aluminium fluorides and unused cryolite as particulates, are the major undesirable fume component produced in the aluminium smelting process. Such emissions can be reduced through the use of fume control systems, operational good practice and improved technology. The gaseous fluorides generated in the process are mainly HF, CF4, C2F6 and SiF4, the major component being HF. The particulates are mainly mixtures of aluminum oxides and cryolite [1]. This paper focuses on the prevention of global warming potential (GWP) in primary aluminum production and the aim of this paper is this problem. Figure 1 and 2 show that emissions fluoride increasing by increase the production of aluminum [2].
In this work, grand canonical Monte Carlo (GCMC) method is used to study the compounds adsorption gas on carbon nanotube. Single-Walled carbon nanotubes are selected to be the adsorbent. To make a comprehensive work, the influence of temperature as well as pressures on the adsorption is also studied.

The simulation results in this work can be used to optimize the separation between hydrogen and Fluoride Gases in aluminum smelter at a given pressures and temperatures. We published an article dedicated to nanotechnology to remove toxic \( \text{H}_{2}\text{S} \) gaseous compounds from exhaust gases in primary aluminum industry [6]. Given the importance of adsorption and separation and adsorption of these gases in aluminum industry this project in the after it was defined.

SIMULATION METHOD

The Monte carlo statistical mechanical simulation were carried out in standard manner using the Metropolis sampling technique in canonical \((T, V, N)\) ensemble. In this work, all of the particles include Sulfur compounds molecules, and carbon atoms are treated as structureless spheres. Particle-Particle interactions between them are modeled with Lennard-Jones potential located at the mass-center of the particles. In this work, as in the works of many researchers, the cut and shifted Lennard-Jone (LJ) potential was used to represent the interaction between HF, CF\(_4\), C\(_2\)F\(_6\) and SiF\(_4\) compounds molecules.

\[
\phi_{ij}(r) = \begin{cases} 
\phi_{ij}(r) - \phi_{ij}(r_c) & r < r_c \\
0 & r \geq r_c
\end{cases}
\]

(1)

Where \( r \) is the interparticle distance, \( r_c \) is the cut off radius, \( \phi_{ij} \equiv S\sigma_{ij} \). \( \phi_{ij} \) is the full LJ potential, \( \phi_{ij} = 4\varepsilon_{ij}\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6} \), where \( \varepsilon_{ij} \) and \( \sigma_{ij} \) are the energy and size parameters of the fluid. They are 301.1 and 3.62nm for hydrogen sulfide also 335.4 and 4.112nm for Sulfur dioxide also 467 and 4.483 for Carbon disulfide here [5-7].

The interaction between the wall and a hydrogen sulfide molecule is calculated by the site-to-site method[8,9].

\[
U_{\text{fw}} = 4\varepsilon_{\text{fw}} \sum_{i=1}^{N_{\text{fw}}} \sum_{j=1}^{N_{\text{wall}}} \left[ \left( \frac{\sigma_{\text{fw}}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\text{fw}}}{r_{ij}} \right)^{6} \right]
\]

(2)

For example Where \( N_{\text{fw}} \) is the number of Sulfur dioxide gas molecules, \( N_{\text{carbon}} \) is the number of carbon atoms of the wall of SWNT \( \sigma_{\text{fw}} \) and \( \delta_{\text{fw}} \) are
the cross-energy and size parameters, which are obtained from the Lorentz-Berthelot (LB) combining rules. Energy and size parameters of carbon atoms are 28.0 and 0.34nm, respectively [10].

The quantity \( r_{ij} \) is the distance between a gas hydrogen sulfide molecule and an atom of the wall of SWNT.

Lorentz-Berthelot rules are used to calculate the parameters of interaction between different kinds of particles. In this calculation, all of the particles are regarded as spheres. Interaction among particles are modeled with Lennard-Jones potential acted on the mass center. The initial configuration was generated randomly (Figure1). For a fixed cell, three types of moves were used to generate a markov chain, including moving, creating, and deleting a molecule and make new configurations. The three types of moves have the same probability and each has different receiving opportunities. Configurations are accepted when they obey Metropolis Sampling scheme in proportion to \( \exp(-\Delta E/RT) \) where \( \Delta E \) is the change of total energy in the system.

To insure good thermodynamical averages, for a single isotherm point typically \( 5 \times 10^5 \) moves have been performed to equilibrate the system. For each of five hundred configuration, one configuration is selected, and names snapshot. Diagram energy of produced configuration to number of snapshot show that system reaches to the equilibrium.

The ensemble average energy of system for second half of snapshot is drawn, and initial part is discarded. Because initial part far away to the equilibrium, diagram of energy for second half, show that, the system reach to equilibrium.

The statistical error have been reported in this work. STDEW is the standard deviation of the calculated average in the simulation of eight number is 0.64% (simulation error). The dimensions of simulation cell is \((200 \times 100 \times 34.5)\) Å. We considered single-walled armchair (8, 8) nanotubes with open edge (Figure6). The number of carbon
The number of molecules gas calculated by virial equation of state and input to the GCMC calculation. The equation of state of real gases is best represented, by the series (Equation 3)

\[
P V_n = R T \left[ 1 + \frac{B(r)}{V_n^2} + \frac{C(r)}{V_n^4} + \frac{D(r)}{V_n^6} + \ldots \right]
\]

(3)

Where \(B(r)\), \(C(r)\), and \(D(r)\) are respectively termed the second, third, and fourth virial coefficients. \(P\) is the pressure, \(V_n\) is molar volume, \(T\) the absolute temperature, and \(R\) is the gas constant[11].

\[
\sigma_{ij} = \left( \sigma_{ii} + \sigma_{jj} \right) / 2
\]

\[
\epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}}
\]

Table 1. Lennard Jones potential for interaction between gas-gas and gas-carbon nanotube

<table>
<thead>
<tr>
<th>Interactions</th>
<th>(\epsilon_{ii}(K))</th>
<th>(\sigma_{ii}(nm))</th>
<th>(\epsilon_{jj}(K))</th>
<th>(\sigma_{jj}(nm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_2F_6) – carbon nanotube</td>
<td>83.12</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_2F_6 - H_2)</td>
<td>120.43</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H_2 - carbon nanotube)</td>
<td>58.62</td>
<td>3.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CO - carbon nanotube)</td>
<td>197.3</td>
<td>3.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CO_2 - carbon nanotube)</td>
<td>141.03</td>
<td>3.47</td>
<td></td>
<td></td>
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<tr>
<td>(H_2 - CO_2)</td>
<td>74.19</td>
<td>3.39</td>
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<tr>
<td>(CO - CO)</td>
<td>50.82</td>
<td>3.32</td>
<td></td>
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<tr>
<td>(CO - H_2)</td>
<td>73.67</td>
<td>3.25</td>
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<td>(H_2S - carbon nanotube)</td>
<td>92.1</td>
<td>3.31</td>
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<td>(H_2 - NO)</td>
<td>133.51</td>
<td>3.22</td>
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<td>(NO - carbon nanotube)</td>
<td>59.36</td>
<td>3.27</td>
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<tr>
<td>(NO - H_2)</td>
<td>83.11</td>
<td>3.15</td>
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<td>(SF_6 - carbon nanotube)</td>
<td>78.66</td>
<td>3.68</td>
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<tr>
<td>(SF_6 - H_2)</td>
<td>114.66</td>
<td>3.97</td>
<td></td>
<td></td>
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<tr>
<td>(HF - carbon nanotube)</td>
<td>96.46</td>
<td>3.27</td>
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<tr>
<td>(HF - H_2)</td>
<td>139.77</td>
<td>2.98</td>
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<td>(CF_4 - carbon nanotube)</td>
<td>61.47</td>
<td>3.57</td>
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<tr>
<td>(CF_4 - H_2)</td>
<td>89.06</td>
<td>3.74</td>
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<tr>
<td>(SF_6 - carbon nanotube)</td>
<td>69.62</td>
<td>3.62</td>
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<tr>
<td>(SF_6 - H_2)</td>
<td>100.87</td>
<td>3.58</td>
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Table 2. Lennard Jones potential for gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>(\epsilon_{ii}(K))</th>
<th>(\sigma_{ii}(nm))</th>
<th>(\epsilon_{jj}(K))</th>
<th>(\sigma_{jj}(nm))</th>
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</thead>
<tbody>
<tr>
<td>(C_2F_6)</td>
<td>4.38</td>
<td>245</td>
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<tr>
<td>(CO)</td>
<td>4.13</td>
<td>336</td>
<td></td>
<td></td>
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<tr>
<td>(CO_2)</td>
<td>3.64</td>
<td>195.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CO)</td>
<td>3.69</td>
<td>91.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H_2)</td>
<td>3.62</td>
<td>301.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NO)</td>
<td>3.49</td>
<td>116.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(SF_6)</td>
<td>5.12</td>
<td>222.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(HF)</td>
<td>3.14</td>
<td>330</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CF_4)</td>
<td>4.66</td>
<td>134</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(SF_6)</td>
<td>4.88</td>
<td>171.9</td>
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</tbody>
</table>

Table 3. Lennard Jones potential for interaction between hydrogen and carbon nanotube

<table>
<thead>
<tr>
<th>(H_2)</th>
<th>Carbon Nanotube</th>
<th>(\epsilon_{ii}(K))</th>
<th>(\sigma_{ii}(nm))</th>
<th>(\epsilon_{jj}(K))</th>
<th>(\sigma_{jj}(nm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.94</td>
<td>195.2</td>
<td>3.4</td>
<td>28.2</td>
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</tbody>
</table>

RESULT AND CONCLUSION

The first phase of research

Feasibility of separating and adsorption of oxide gases with hydrogen. In the first phase of research, adsorption of gas mixture of 50% oxide gases with 50% of hydrogen gas emissions in aluminum industry was investigated in pressure of 11 MPa and at temperature of 273.

Figures 9, 10 and 11 shows the distribution of composition of CO, CO\(_2\) and NO gases with hydrogen, on carbon nanotubes. Potential parameters have been extracted from Ref [7].

Considering the figure, although the number of moles of gas oxide gases and hydrogen is equal, but
the gas adsorption of oxide gases is greater than hydrogen that indicated stronger interactions between oxide gases with carbon nanotubes and according to figures, in separating, usually the diameter of nanotube, relative size of molecule and the potential of interactions are used as the most important criteria for determining the adsorption of molecules and consequently the isolation [12,13]. Since the diameter of nanotube is considered stable and is not our discussion, it seems that due to differences in relative size of molecules oxide gases and hydrogen, they are separated by a high partition coefficient. The reason for this change is that the interaction of carbon nanotube molecules and oxide gases is much more intensive than the interaction of molecules hydrogen. Therefore, the adsorption of hydrogen gas is slow.

The second phase of research
Feasibility of separating and adsorption of sulfur gases with hydrogen. In the second phase of research, adsorption of gas mixture of 50% sulfur gases with 50% of hydrogen gas emissions in aluminum industry was investigated in pressure of 11 MPa and at temperature of 273 K.

Figures (12,13,14) shows the distribution of composition of sulfur gases and hydrogen on carbon nanotubes. Potential parameters have been extracted from Ref. [14].

Fig. 12. Comparison of gas adsorption between 50 carbonyle sulfide and hydrogen (with fifty percent combination).

Generally, internal and external walls of nanotubes can adsorb constant value of a gas.

When carbon nanotubes are filled with larger molecules of sulfur gases they have less additional sites to store small molecules of hydrogen. According to Figures 12,13,14 related to chart adsorption of sulfur gases in combination with hydrogen in equal molar ratio show that, sulfur gases adsorption in nanotube is more than the adsorption of these gases. However, these gases show the greatest ability to adsorb in the first adsorption layer on the nanotube axis.

Fig. 13. Comparison of gas adsorption between carbon disulfide and hydrogen (with fifty fifty percent combination).

Adsorption of combination of these gases in the second adsorbent layer is close, so their separation seems impossible. Hydrogen sulfide maximum shows more adsorption than other gases.

In this case, sulfur gases adsorption inside the nanotubes is greater similar to oxide gases. While, the maximum peak shows more adsorption and in comparison, sulfur gases shows more adsorption than hydrogen. Out of nanotubes have irregular process of adsorption. This adsorption process is opposite. So that, where hydrogen has more adsorption sulfur gases adsorb less.

The third phase of research
Feasibility of separating and adsorption of fluoride gases and hydrogen. In the third phase of research, adsorption of gas mixture of 50% fluoride gases with 50% of hydrogen gas emissions in aluminum industry was investigated in pressure of 11 MPa and at temperature of 273.

Figures 15,16,17,18 shows the distribution of composition of sulfur gases and hydrogen, on carbon nanotubes. Potential parameters have been extracted from Ref. [15,16].
In the case of fluoride gases, hydrogen gas adsorption is less than the respective gas inside nanotubes. Adsorption process is quite irregular from second layer in comparison with investigated oxide gases and sulfur gases. This different is completely obvious in figures. The maximum adsorption peak of hydrogen in HF gas has the highest value among studied gases.

In the following (Fig. 20 and Tables 4,5), adsorption behavior of 50% hydrogen gas was investigated in combination with 50% of other gases. Assessment of corresponding charts show that silicon tetrafluoride has lowest adsorbed density in combination with hydrogen gas. Evaluation of internal and external adsorbed density show that the highest adsorbed density is related to oxide gases.
Table 4, 5. The maximum adsorption peak of hydrogen gases in inside and outside of carbon nanotube

In general, we investigated the adsorption behavior of 50% of each gas in combination with 50% of gas hydrogen. Adsorption behavior comparison of these gases show that the maximum adsorption peak is as follows.

In the following (Fig. 20 and Tables 6,7), adsorption behavior of 50% hydrogen gas was investigated in combination with 50% of other gases.

Table 6,7. The maximum adsorption peak of total gases in inside and outside of carbon nanotube

Assessment of corresponding charts show that hydrogen fluoride has highest adsorbed density in combination with hydrogen gas. Evaluation of internal and external adsorbed density show that the highest adsorbed density is related to hydrogen fluoride.

Summary of adsorption behavior of these gases show that these gases have relatively similar adsorption process in composition with hydrogen gas. The highest adsorption value (adsorption peak) on the first axis of the nanotubes is as follows.

Tables 6 and 7 show the adsorption peak of these gases in combination with hydrogen. Calculations show that, Hydrogen fluoride which is one of the most important diffused gases in aluminum industry has the highest adsorption inside and outside of nanotube. After that, hydrogen sulfide indicated the greatest adsorption ability in combination with 50% hydrogen. The exact amount of other absorbance has been given in table.

Hydrogen has the highest adsorption rate in equal combination of gases such as oxide gases inside and outside of nanotubes. Exact amount of adsorption of other gases has been given in Tables 4,5.

REFERENCES