Mathematical modeling of a Molten Carbonate Fuel Cell for CO₂ separation

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Abstract: A mathematical model of a Molten Carbonate Fuel Cell (MCFC) is shown. The model is used to simulate a CO₂ emission reduction made from the flue gas of a coal fired boiler. The MCFC is placed in the flue gas stream and separates CO₂ from the cathode side to the anode side. As a result, a mixture of CO₂ and H₂O is obtained; pure CO₂ can be obtained by water condensation. The main advantages of this solution are: additional electricity generated, reduced CO₂ emissions and higher system efficiency. The results obtained show that the use of an MCFC could reduce CO₂ emissions by 56%, which gives a relative CO₂ emission rate of 288 kg CO₂ per MWh.

Key–Words: Mathematical model, Molten Carbonate Fuel Cell, CO₂ separation, coal fired boiler

1 Introduction

The European Union has placed limits on CO₂ emissions by Member States as part of its Emission Trading Scheme. This impacts fossil fuel power plants to a significant degree as their emissions are governed by the number of emission allowances they receive from the Member State allocation. Excess CO₂ emissions have to be covered by purchasing extra allowances, which is in effect a penalty (€100/Mg). In contrast, undershooting emission limits enables the emitter to sell CO₂ allowances. The selling price of a traded allowance is estimated at €15/Mg CO₂.

Fuel cells generate electricity through electrochemical processes. There are many types of fuel cells; two of them—the Molten Carbonate Fuel Cell (MCFC) [29, 31, 32, 34] and the Solid Oxide Fuel Cell (SOFC) [14, 15] – are high temperature fuel cells. They work at temperatures ranging from 600 to 1,000°C and potentially can achieve ultra high efficiencies [3]—especially when coupled with a gas turbine [31, 34].

Hydrogen, natural gas, methanol and biogas may be used as fuels for MCFCs. On the cathode side, a mixture of oxygen and carbon dioxide is required.

An MCFC can work as a carbon dioxide separator/concentrator because the CO₂ is transported from the cathode side to the anode side through molten electrolyte (see Fig. 1). Negative ions are transferred through the molten electrolyte. Each ion is composed of one molecule of carbon dioxide, one atom of oxygen and two electrons. This means that an adequate ratio of carbon dioxide to oxygen is 2.75 (mass based) or 2.0 (mole based).

There are a variety of methods available to remove CO₂ from a fossil fuel power plant system [5, 9]. The idea of adopting a molten carbonate fuel cell to reduce CO₂ emissions was developed by Campanari [6]. In that paper it was shown that an estimated reduction of 77% in CO₂ emissions can be achieved in a steam turbine power plant.

A few years later Campanari et al. [7] investigated the possibility of separating CO₂ from combined cycles integrated with Molten Carbonate Fuel Cells. The results obtained show that CO₂ reduction can reach 80% while electrical efficiency remains virtually unchanged, with the power of the cell contributing 17% of the entire system.

Amorelli et al. [1] described an experimental investigation into the use of molten carbonate fuel cells to capture CO₂ from gas turbine exhaust gases. They obtained an emission reduction of 50%. Those exper-
iments were performed using a singular cell.

Lusardi et al. [16] investigated the application of a fuel cell system for separating CO\textsubscript{2} from thermal plant exhaust. They found that, even without CO\textsubscript{2} separation, the relative emission of carbon dioxide could be reduced to below the Kyoto Protocol limit. If a separator is used, emissions could be reduced by 68%.

The use of an MCFC as a carbon dioxide concentrator was investigated by Sugiura et al. [30]. In this work the experimental results of CO\textsubscript{2} sequestration through the use of an MCFC are given. One key conclusion from this work is that the CO\textsubscript{2} removal rate can be obtained by making calculations using electrochemical theory.

Novel methods whereby carbonates were used as an electrochemical pump in carbon dioxide separation from gases were described by Granite et al. [10]. In [20, 22, 24] consideration was given to reducing CO\textsubscript{2} emissions from a coal fired power plant through the use of a molten carbonate fuel cell and in [18, 21, 25, 26] from a gas turbine power plant and in [17, 19] – from Fossil Power Plants.

Jung-Ho Wee in [12] analyzed three fields (mobile application, transportation application and stationary application) in terms of CO\textsubscript{2} emission reduction through the use of fuel cells. Only the last of them considered the possibility of using MCFC for the separation of CO\textsubscript{2}.

Cryogenic separation CO\textsubscript{2} from combined cycles integrated with molten carbonate fuel cells was shown by Chiesa et al. [8]. The considered system affords the possibility to separate 80% CO\textsubscript{2}, while the increase in power as a result of the proposed solution is 22% with nearly unchanged efficiency (59% LHV).

In [33] Nansheng Xu et al. presented tests of a new composite – a dual phase mixed carbonation and electron conducting membrane (molten carbonate and silver). The possibility of separation of CO\textsubscript{2} from simulated flue gas was explored, yielding higher CO\textsubscript{2} and O\textsubscript{2} flux densities compared with molten metal carbonate systems.

Based on the above review of literature, a reduction of at least 50% in CO\textsubscript{2} emissions could be expected.

A typical composition of flue gas of lignite fired boiler is given in Table 1 other flue gas compositions are presented in Table 2. The ratio of CO\textsubscript{2} to oxygen is hence 4.9 (mole based). This means that the flue gas contains an insufficient quantity of oxygen to trap all of the CO\textsubscript{2}.

### Mathematical model of MCFC

The presented results are based on calculations made using an appropriate mathematical model. The governing equations of this model are presented in this section.

The equivalent electric circuit of a singular cell is shown in Fig. 2 [23].

Two types of area specific resistances are present in fuel cells: ionic resistance $r_\text{i}$ and electronic resistance $r_\text{e}$. Resistance $r_\text{load}$ is the external load resistance of the fuel cell and is varied by the operator of the MCFC.

The voltage generated by a singular cell is given by the following equation [23]:

$$E_{\text{MCFC}} = E_{\text{max}} - \eta_f \cdot i_{\text{max}} \cdot r_i - \frac{r_e}{r_\text{e}} \cdot (1 - \eta_f) + 1$$

(1)

An MCFC installed in the flue gas stream requires a large active area due to the large amount of gas and low CO\textsubscript{2} content. The $i_{\text{max}}$ and $r_\text{e}$ values were determined by analysis of experimental data [2] and determined by the researchers’ own calculations at values of 0.23–1.28 A/cm\textsuperscript{2} and 55.5 cm\textsuperscript{2}/S, respectively.
Table 2: Examplary flue gases compositions

<table>
<thead>
<tr>
<th>Component</th>
<th>Hard coal</th>
<th>Lignite</th>
<th>Oil</th>
<th>Natural Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂, vol. %</td>
<td>2.5–10</td>
<td>5</td>
<td>2–6</td>
<td>1–5</td>
</tr>
<tr>
<td>CO₂, vol. %</td>
<td>11–16</td>
<td>10–14</td>
<td>8–10</td>
<td>6–8</td>
</tr>
<tr>
<td>N₂, vol. %</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>H₂O, vol. %</td>
<td>5–10</td>
<td>16–20</td>
<td>2–6</td>
<td>0</td>
</tr>
<tr>
<td>NOₓ, vol. %</td>
<td>0.1</td>
<td>0.1</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>SO₂, ppm</td>
<td>&lt;2000</td>
<td>&lt;2600</td>
<td>&lt;1000</td>
<td>0</td>
</tr>
<tr>
<td>SO₃, ppm</td>
<td>11</td>
<td>40</td>
<td>&lt;6</td>
<td>0</td>
</tr>
<tr>
<td>HCl, ppm</td>
<td>0–250</td>
<td>300</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>HF, ppm</td>
<td>0–16</td>
<td>45</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>dust, mg/m³</td>
<td>50–150</td>
<td>50</td>
<td>0.05–0.3</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 3: Experimental and simulation data at various H₂ molar fractions (based on data provided by [2]—see Table 3)

These experimental data were used for model validation as well (see Fig. 3). In fact in [2], the exact experimental data are not given for which the E – i curves are generated. Thus, the validation process is mainly qualitative in nature.

The maximum voltage of a singular cell is given by the following equation:

$$E_{\text{max}} = \frac{RT}{4F} \ln \frac{p_{O_2,\text{cathode}}^2 \cdot p_{CO_2,\text{cathode}}}{p_{O_2,\text{anode}}^2 \cdot p_{CO_2,\text{anode}}}$$ (2)

The anode and cathode outlet partial pressures were calculated using software [11]. The calculations were based on the Peng-Robinson equation of state and minimization of the Gibbs free energy.

The ionic resistance of molten carbonate electrolytes as a function of temperature is shown in Fig. 4. This diagram contains values obtained by the researchers’ own calculations, which were based on data published by Morita et al. [27].

Table 4: Electrolytes’ material factors

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>σ₀, S/cm</th>
<th>E_{\text{act}}, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/K</td>
<td>5.653</td>
<td>37.36</td>
</tr>
<tr>
<td>Li/Na</td>
<td>15.22</td>
<td>44.02</td>
</tr>
</tbody>
</table>

The internal area specific ionic resistance can be described by the following relationship:

$$r_{i} = \delta \frac{\sigma}{\sigma_0}$$ (3)

The ionic conductivity of the electrolyte can be described by the following relationship:

$$\sigma_{i} = \sigma_0 \cdot e^{-E_{\text{act}} / RT}$$ (4)

The thickness of the Li/K electrolyte matrix was assumed at 1 mm.

Cell efficiency is defined by the following equation:
Table 3: Experimental data provided by [2]

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Flow, mol/s $\times 10^5$</th>
<th>$\text{CO}_2$, %</th>
<th>$\text{H}_2$, %</th>
<th>$\text{H}_2\text{O}$, %</th>
<th>$\text{N}_2$, %</th>
<th>$\text{O}_2$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode I</td>
<td>26.00</td>
<td>5.38</td>
<td>25.00</td>
<td>8.85</td>
<td>60.77</td>
<td>–</td>
</tr>
<tr>
<td>Cathode IA</td>
<td>154.40</td>
<td>9.26</td>
<td>–</td>
<td>–</td>
<td>80.96</td>
<td>9.78</td>
</tr>
<tr>
<td>Cathode IB</td>
<td>166.10</td>
<td>28.90</td>
<td>–</td>
<td>–</td>
<td>56.17</td>
<td>14.93</td>
</tr>
<tr>
<td>Anode II</td>
<td>42.80</td>
<td>5.61</td>
<td>85.51</td>
<td>8.88</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cathode II</td>
<td>253.50</td>
<td>9.19</td>
<td>–</td>
<td>–</td>
<td>81.03</td>
<td>9.78</td>
</tr>
</tbody>
</table>

$\eta_{MCFC} = \frac{E_{MCFC} \cdot i \cdot A}{m_{fuel} \cdot LHV_{fuel}}$ (5)

The BOX method was used for optimizing all systems [11]. The procedure is loosely based on the “Complex” method of Box [4]; the Downhill Simplex algorithm of Press et al. [28] and the BOX algorithm of Kuester and Mize [13].

This method is a sequential search technique which solves problems with non-linear objective functions, subject to non-linear inequality constraints. No derivatives are required. It handles inequality but not equality constraints. This method is not very efficient in terms of the required number of function evaluations. It generally requires a large number of iterations to converge on the solution.

The size of the MCFC installed in the flue gas stream was assumed at 55 cm$^2$ (the same as for the modeled experimental lab-stand). On the other hand the same fuel utilization ratio can be achieved with different size fuel cells. Thus, the fuel utilization factor, flue gas mass flow and fuel mass flow were taken as primary variables of the optimization process.

Additional air is added to the flue gas prior to entry into the MCFC because the quantity of oxygen is too low for total CO$_2$ sequestration (see Table 1). Additional air flow should be assumed at a value which gives a CO$_2$/O$_2$ ratio of 2.0 (mole based). But it was adopted that the value of air addition is also varied during the optimizing procedures.

Parameters to be optimized:

1. MCFC fuel mass flow
2. MCFC flue gas mass flow
3. Air mass flow added to flue gas
4. Fuel utilization factor

During the optimizing process the cell temperature was kept at a constant value of 650°C and the original composition of anode inlet gases (Anode I) was analyzed (for details see 3).

3 Results

To rate the degree of the quantity of CO$_2$ separated from flue gas, an additional factor is introduced: “CO$_2$ emission reduction factor”:

$\eta_{CO_2} = 1 - \frac{\dot{m}_{CO_2, cathode, out}}{\dot{m}_{CO_2, cathode, in}}$ (6)

In total, two objective functions were taken into consideration:

- Maximum efficiency: $\max (\eta_{MCFC})$
- Optimal variant: $\max (\eta_{opt})$

The Optimal variant was optimized for the following objective function:

$\eta_{opt} = \eta_{MCFC} \cdot \eta_{CO_2}$ (7)

Table 5 presents the results of the optimizing processes for all analyzed cases. The achievable CO$_2$ emission reduction factor depends on the optimization objective function chosen and varies in the range of 7–93%.

Even for a low inlet CO$_2$ fraction in the flue gas means that the MCFC can achieve relatively high electric efficiency, in the range of 37–52%.

The MCFC module can generate 49–460 kW of power per standard cubic meter of flue gas.

4 Discussion

The presented investigations are limited to a laboratory size MCFC as a CO$_2$ separator. It was assumed that the flue gas composition is similar to that of lignite fired boiler exhaust gas.

Important technical issues such as sulfur or dust resistances of the MCFC fell outside the remit of this paper, although they can evidently limit the application of MCFCs in lignite fired power plants. It should be noted that there is a different form of sulfur (SO$_x$) in flue gas than in fuel (H$_2$S, COS)—thus the effect of sulfur contaminants may be different in this case and...
Table 5: Main parameters of the analyzed cases

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum efficiency</th>
<th>Optimal</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCFC power per Nm³/s of flue gas, kW</td>
<td>49</td>
<td>463</td>
</tr>
<tr>
<td>Fuel cell efficiency, %</td>
<td>52</td>
<td>37</td>
</tr>
<tr>
<td>Fuel utilization factor, %</td>
<td>94</td>
<td>92</td>
</tr>
<tr>
<td>Air added to flue gas (mass based), %</td>
<td>47</td>
<td>217</td>
</tr>
<tr>
<td>CO₂ emission reduction factor, %</td>
<td>7</td>
<td>93</td>
</tr>
<tr>
<td>Cell voltage, V</td>
<td>0.69</td>
<td>0.51</td>
</tr>
</tbody>
</table>

hence it is not scientifically wise to transfer the results of sulfur dependence on the anode to the cathode.

MCFCs could be profitably used in existing power plants which have been given CO₂ limits. MCFCs could potentially decrease CO₂ emissions, leaving the power generation capacity of the system at least the same, if not greater.

5 Conclusions

Numerical simulation has been used to estimate the possible CO₂ emission reductions achievable through use of the MCFC. Three different scenarios were analyzed: maximum efficiency, maximum CO₂ emission reduction and the optimal variant. It was shown that the CO₂ emission reduction factor can reach values of up to 70%. The obtained MCFC efficiency has moderate values of around 40%.

Some technical and economic aspects of the investigations performed are discussed.

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References:


