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## Separating CO<sub>2</sub> from Flue Gases Using a Molten Carbonate Fuel Cell

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### Abstract

A Molten Carbonate Fuel Cell (MCFC) is shown to reduce CO<sub>2</sub> emissions from a Coal Fired Power Plant (CFPP). The MCFC is placed in the flue gas stream of the coal fired boiler. The main advantages of this solution are: higher total electric power generated by a hybrid system, reduced CO<sub>2</sub> emissions and higher system efficiency. The model of the MCFC is given and described. The results obtained show that use of an MCFC could reduce CO<sub>2</sub> emissions by 56%, which gives a relative CO<sub>2</sub> emission rate of 288 kg<sub>CO<sub>2</sub></sub> per MWh.

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### 1. Introduction

The European Union has placed limits on CO<sub>2</sub> 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 CO<sub>2</sub> emissions

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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 CO<sub>2</sub> allowances. The selling price of a traded allowance is estimated at €15/Mg CO<sub>2</sub>.

There are a variety of methods available to remove CO<sub>2</sub> from a fossil fuel power plant system [1, 2]. The idea of adopting a molten carbonate fuel cell to reduce CO<sub>2</sub> emissions was developed by Campanari [3]. In that paper it was shown that an estimated reduction of 77% in CO<sub>2</sub> emissions can be achieved in a steam turbine power plant.

A few years later Campanari et al. [4] investigated the possibility of separating CO<sub>2</sub> from combined cycles integrated with Molten Carbonate Fuel Cells. The results obtained show that CO<sub>2</sub> reduction can reach 80% while electrical efficiency remains virtually unchanged, with the power of the cell contributing 17% of the entire system.

Fuel cells generate electricity through electrochemical processes. There are many types of fuel cells; two of them – the Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC) – are high temperature fuel cells. They work at temperatures ranging from 600 to 1,000°C and potentially can achieve ultra high efficiencies [5] – especially when coupled with a gas turbine [6, 7]. Amorelli et al. [8] described an experimental investigation into the use of molten carbonate fuel cells to capture CO<sub>2</sub> from gas turbine exhaust gases. They obtained an emission reduction of 50%. Those experiments were performed using a singular cell.

Lusardi et al. [9] investigated the application of a fuel cell system for separating CO<sub>2</sub> from thermal plant exhaust. They found that, even without CO<sub>2</sub> 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. [10]. In this work the experimental results of CO<sub>2</sub> sequestration by use of an MCFC are given. One key conclusion from this work is that the CO<sub>2</sub> 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. [11].

In [12–14] consideration was given to reducing CO<sub>2</sub> emissions from a coal fired power plant through the use of a molten carbonate fuel cell and in [15–18] from a gas turbine power plant and in [19, 20] – from Fossil Power Plants.

Jung-Ho Wee in [21] analyzed the three fields (mobile application, transportation application and stationary application) in terms of CO<sub>2</sub> emission reduction through the use of fuel cells. Only the last of them considered the possibility of using MCFC for the separation of CO<sub>2</sub>.

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

In [23] 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<sub>2</sub> from simulated flue gas was explored, yielding higher CO<sub>2</sub> and O<sub>2</sub> flux densities compared with molten metal carbonate systems.

Based on the above review of literature, a reduction of at least 50% in CO<sub>2</sub> emissions could be expected.

Hydrogen, natural gas, methanol or 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 CO<sub>2</sub> is transported from the cathode side to the anode side through molten electrolyte.

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). A typical composition of flue gas of CFPP is

CO<sub>2</sub>/N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O is 0.15/0.79/0.06/0.005. The ratio of CO<sub>2</sub> to oxygen is hence 2.5 (mole based) and 3.43 (mass based). This means that flue gas contains an insufficient quantity of oxygen to trap all of the CO<sub>2</sub>.

## 2. Separating CO<sub>2</sub> from flue gases using a Molten Carbonate Fuel Cell

All analyzed cases were optimized with the objective function being total power generation efficiency. Nevertheless, there is room for discussion as to the choice of this as the objective function of the optimizing process. While the main task of an MCFC is to capture CO<sub>2</sub> from flue gas, it also increases total power generation efficiency due to its higher efficiency compared with that of the cycle which generates flue gas.

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.

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<sub>2</sub> sequestration (see Table 0). Additional air flow should be assumed at value which gives CO<sub>2</sub>/O<sub>2</sub> 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. The value of  $i_{max}$  in the range 0.06 A/cm<sup>2</sup> to 0.6 A/cm<sup>2</sup>
3. Heat Exchanger efficiency in the range 0 to 85%
4. Air mass flow added to flue gas

The optimizing process was carried out with the following constraint functions:

1. Maximum temperature inside the stack < 650 °C
2. Cell voltage at last cell > 0V
3. steam-to-carbon ratio > 1.4

An MCFC module equipped with four heat exchangers was analysed. The system is fed by methane with an addition of water to avoid carbon deposition. Both methane and water are pre-heated in two heat exchangers (HX-1 and HX-2) prior to insert MCFC module. Heat from the anode outlet gas is used by the heat exchangers HX-1, HX-2 and HX-4, respectively to heat up fuel, water and flue gas.

Flue gas is mixed (Mixer-2) with air and then pre-heated in two heat exchangers (HX-3 and HX-4) prior to entering the cathode side of the MCFC. Flue gas with a lower quantity of CO<sub>2</sub> leaves the cathode and is directed to the heat exchanger HX-3 for heat recovery.

To rate the degree of the quantity of CO<sub>2</sub> separated from flue gas, an additional factor is introduced: "CO<sub>2</sub> emission reduction factor":

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

In total, three objective functions were taken into consideration:

- Maximum efficiency:  $\max(\eta_{MCFC})$
- Maximum CO<sub>2</sub> emission reduction factor:  $\max(\eta_{CO_2})$
- Optimal variant:  $\max(\eta_{opt})$

The Optimal variant was optimized for the following objective function:

$$\eta_{opt} = \eta_{MCFC} \cdot \eta_{CO_2} \quad (2)$$

Table 1. Coal-Fired Boiler flue gas composition

Parameter	Maximum efficiency	Maximum CO <sub>2</sub> reduction	Optimal
MCFC power per Nm <sup>3</sup> /s of flue gas, kW	3.2	2.8	2.65
Fuel cell efficiency, %	41	39	37
Fuel utilization factor, %	86	90	88
Air added to flue gas, %	13	14	14
Fuel cell temperature, °C	648	643	650
CO <sub>2</sub> emission reduction factor, %	52	74	70
Cell voltage, V	0.50	0.40	0.44
s/c ratio	1.50	1.44	1.43
Effectiveness of HX-1, %	8	5	1
Effectiveness of HX-2, %	13	1	1
Effectiveness of HX-3, %	70	46	55
Effectiveness of HX-4, %	17	2	2

The achievable CO<sub>2</sub> emission reduction factor depends on the optimization objective function chosen and varies in the range of 50--70%.

A low inlet CO<sub>2</sub> fraction in the flue gas means that the MCFC can achieve relatively moderate electric efficiency, in the range of 37--41%.

The MCFC module can generate 2.7--3.2 kW of power per cubic meter of flue gas in normal conditions. This means that the origin power can be increased by about 50%.

The presented investigations are limited to the MCFC module as CO<sub>2</sub> separator. It was assumed that the flue gas composition is close to the coal fired boiler exhaust gas. Both outlet streams of the MCFC module (flue gas with decreased CO<sub>2</sub> content and the CO<sub>2</sub> +O<sub>2</sub> mixture) still have quite high temperatures ( $\approx 400^\circ\text{C}$ ). This heat can be utilized later on in other processes, e.g. to heat up feed water or air at boiler inlet. This will cause a power increase in the origin cycle for which the MCFC has been installed.

On the other hand, oxygen is required to burn hydrogen, carbon monoxide and methane, which remain in the anode outlet stream due to a fuel utilization factor of less than 1. Oxygen needs to be separated from air, which requires a supply of energy.

It should be borne in mind that prices of tradable CO<sub>2</sub> allowances used to be very low in the past, which afforded little opportunity to realize profits from carbon trading. Today, the average price of the allowances is around €15/Mg<sub>CO<sub>2</sub></sub> what could make the proposed solution profitable.

Important technical issues such as sulphur or dust resistances of the MCFC fell outside the remit of this paper, although they can evidently limit the application of MCFCs in coal fired power plants. It should be noted that there is a different form of sulphur (SO<sub>x</sub>) in flue gas than in fuel (H<sub>2</sub>S, COS) -- thus the effect of sulphur contaminants may be different in this case and hence it is not scientifically wise to transfer the results of sulphur dependence on the anode to the cathode.

MCFCs could be profitably used in existing power plants which have been given CO<sub>2</sub> limits. MCFCs could potentially decrease CO<sub>2</sub> emissions, leaving the power generation capacity of the system at least the same, if not greater.

### 3. Conclusions

Numerical simulation has been used to estimate the possible CO<sub>2</sub> emission reductions achievable through use of the MCFC. Three different scenarios were analyzed: maximum efficiency, maximum CO<sub>2</sub> emission

reduction and the optimal variant. It was shown that the CO<sub>2</sub> emission reduction factor can reach values of up to 70%. The obtained MCFC efficiency has moderate values around 40%.

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

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## Nomenclature

$\sigma$	electrolyte ionic conductivity, S/cm	$i$	cell number; current density, A/cm <sup>2</sup>
$\delta$	electrolyte matrix thickness, cm	$F$	Faraday’s constant, 96500 C/mol
$\eta_f$	fuel utilization factor	$E$	voltage, V
$\dot{m}$	mass flow, kg/s	$LHV$	Lower Heating Value, kJ/kg
$\dot{n}$	molar flow, mol/s	$m$	number of stacks
$\sigma_0, E_{act}$	factors depended on electrolyte material	$n$	number of cell in a stack
$A$	cell area, cm <sup>2</sup>	$p$	partial pressure, Pa
$I$	stack current, A	$r$	area specific internal resistance, $\Omega \cdot \text{cm}^2$
		$R$	universal gas constant, 8.315 J/mol/K
		$T$	absolute temperature, K