A Nuclear Energy Based Hydrogen and Power Production Plant with Hydrogen Storage

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November 22nd, Vienna, 2016
• Akkuyu Nuclear Plant: Russia – Turkey coop. Water-Water Energetic Reactor (VVER) – 2018 first reactor in use

• Sinop Nuclear Plant: Mitsubishi Heavy Industries - Japan- medium-power pressurized water reactor (PWR) (ATMEA) – 2023

• Igneada Nuclear Plant - Westinghouse Electric Company - two AP1000 and two CAP1400 - pressurized water reactor – First will be in use in China in 2017 - This plant is expected to be under management of Turkish professionals

• Now more than a 1000 students study on Nuclear Engineering within an exchange program between Russia and Turkey

• It is expected to create more than million new jobs, and thousand of establishments, as well as a technical expertise for Turkish professionals.

• Nuclear co-generation option is never discussed by the government.
OUTLINE

• Introduction and Background
• Literature Review
• Mg-Cl Cycle and its configurations
• Description of the co-generation System
• Experimental Procedures and Apparatus
• Results and Discussion
• Conclusions and Recommendations
INTRODUCTION

World primary energy demand by fuel from 1980 to 2030,
(IEA World Energy Outlook 2013)

Hydrogen production methods from various means of energy sources (Naterer et al., 2013)
Minimization of Gibbs free energy by using hybrid cycles (Source: Yan and Hino, 2011)

**Four-step Cu-Cl cycle**
(Source: Levis and Masin, 2009)

**Three-step Mg-Cl cycle**
(Source: Simpson et al., 2006)

**Hybrid Sulfur (HyS) cycle**
(Source: Yildiz and Petri, 2005)
## LITERATURE REVIEW

### Mg-Cl Cycle

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric reactions</td>
<td>Funk, 1976</td>
</tr>
<tr>
<td>Three-step configurations</td>
<td>Hesson, 1978</td>
</tr>
<tr>
<td>Reaction thermodynamics</td>
<td>Kelley, 1946; Petri et al., 2006</td>
</tr>
</tbody>
</table>

### Cycle Thermochemistry

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO chlorination reaction kinetics</td>
<td>Haag, 1977</td>
</tr>
<tr>
<td>Controlled dehydration of MgCl₂ hydrates and intermediate steps</td>
<td>Kashani-Nejad et al., 2004-2005; Kipouros and Sadoway, 2001; Ng et al., 2005;</td>
</tr>
<tr>
<td>MgCl₂ hydrolysis</td>
<td>Simpson et al., 2006</td>
</tr>
<tr>
<td>MgOHCl formation</td>
<td>Lamy, 2004</td>
</tr>
<tr>
<td>HCl capture with MgO</td>
<td>Rappold and Luft, 1999; Partanen et al., 2005</td>
</tr>
<tr>
<td>HCl electrolysis</td>
<td>Eames and Newman, 1995; Bartling and Winnick, 2003, Gooding, 2009</td>
</tr>
</tbody>
</table>

### Overall Mg-Cl Cycle Analysis

<table>
<thead>
<tr>
<th>Analysis Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy and exergy analyses</td>
<td>Balta et al., 2012</td>
</tr>
<tr>
<td>Thermodynamics of reactions</td>
<td>Ozcan and Dincer, 2014a; 2014b</td>
</tr>
<tr>
<td>Cycle configurations</td>
<td>Ozcan and Dincer, 2015</td>
</tr>
</tbody>
</table>
SYSTEM DESCRIPTIONS

• Two configurations of the three-step Mg-Cl cycle

• A novel four-step Mg-Cl cycle

• Modified four-step Mg-Cl cycle with HCl capture

• A nuclear energy based system to provide heat and work
  • Post treatment of H₂ using a Linde-Hampson liquefaction plant
# Mg-Cl Cycle Configurations

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Max. Temp. (°C)</th>
<th>Reactions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Cl-A</td>
<td>537</td>
<td><strong>H:</strong> $MgCl_2 + H_2O \rightarrow MgO + 2HCl_{(aq)}$</td>
<td>- HCl is in mixture with steam</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>C:</strong> $MgO + Cl_2 \rightarrow MgCl_2 + 1/2O_2$</td>
<td>- Hydrolysis reaction is endothermic</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>E:</strong> $2HCl_{(aq)} \rightarrow Cl_2 + H_2 (1.8 \text{ V})$</td>
<td></td>
</tr>
<tr>
<td>Mg-Cl-B</td>
<td>500</td>
<td><strong>H:</strong> $2MgCl_2 + 2H_2O \rightarrow 2MgOHCl + 2HCl_{(aq)}$</td>
<td>- Doubled stoichiometry</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>C:</strong> $2MgOHCl + Cl_2 \rightarrow 2MgCl_2 + H_2O + 1/2O_2$</td>
<td>- Chlorination reaction is endothermic</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>E:</strong> $2HCl_{(aq)} \rightarrow Cl_2 + H_2 (1.8 \text{ V})$</td>
<td></td>
</tr>
<tr>
<td>Mg-Cl-C</td>
<td>450</td>
<td><strong>H:</strong> $MgCl_2 + H_2O \rightarrow MgOHCl + HCl_{(aq)}$</td>
<td>- Half of HCl is dry form.</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>D:</strong> $MgOHCl \rightarrow MgO + HCl_{(g)}$</td>
<td>- Decomposition reaction is endothermic</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>C:</strong> $MgO + Cl_2 \rightarrow MgCl_2 + 1/2O_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>E:</strong> $2HCl_{(g)} \rightarrow Cl_2 + H_2 (1.4 - 1.8 \text{ V})$</td>
<td></td>
</tr>
</tbody>
</table>
The three-step Mg-Cl cycle

The three-step MgCl₂-MgOHCl cycle
The four-step Mg-Cl-C cycle
THE FOUR STEP Mg-Cl CYCLE WITH HCL CAPTURE

The four-step Mg-Cl-C cycle with HCl capture

The HCl capture hierarchy
Schematic of the System
EXPERIMENTAL PROCEDURES

**MgCl₂ Hydration Experimental Setup**

\[ MgCl₂ + HCl_{aq} \rightarrow MgCl₂ \cdot nH₂O \cdot mHCl + HCl_g \]

- TGA/DTA analysis
- Measurement of captured HCl
- Uncertainty assessment
- XRD analysis

**Hydrochlorination Experimental Setup**

\[ MgO + 2HCl \rightarrow MgCl₂ + H₂O \quad (-141 \text{ kJ/mole}) \quad A \]

\[ MgO + H₂O \rightarrow Mg(OH)_2 \quad (-37 \text{ kJ/mole}) \quad B \]

\[ MgO + HCl \rightarrow MgOHCℓ \quad (-105 \text{ kJ/mole}) \quad C \]
EXPERIMENTAL PROCEDURES

Precipitation-titration apparatus

- 5 mL sample of the NaCl/NaOH solution is measured in a volumetric flask
- Deionized water is added until the pH is lower than 10
- Droplets of AgNO₃ solution into the flask
- Observation of the rapid change in pH meter
- Molar amount of Cl⁻ ions are balanced with the total amount of the stock

\[
Ag^+ + Cl^- \rightarrow AgCl_s
\]
\[
AgNO_3 + NaCl \rightarrow AgCl_s + NaNO_3_{aq}
\]
RESULTS and DISCUSSION - Reactor Simulations

Hydrolysis Reaction

Decomposition Reaction

Chlorination Reaction

Anhydrous HCl Electrolysis
RESULTS and DISCUSSION - Cycle Configurations

Energy requirement comparisons of the Mg-Cl cycle configurations

Efficiency comparisons of the Mg-Cl cycle configurations
RESULTS and DISCUSSION - Experimental Results

Experimental results:

Model derived from experimental results:

\[ HCl_{cap,f} = 20.29e^{-N^{0.1766} + CM^{0.1688e^{N^{0.1766}}} + 1.433 \cdot 10^{-3} e^{(N^{0.0683} - CM^{0.1259e^{N^{0.2701}}})_T}} \]
RESULTS and DISCUSSION - Experimental Results

Sample from experiment at 250°C

Sample from experiment at 275°C

Results for the 400°C sample
RESULTS and DISCUSSION - Final Configuration

Composite curves of the final configuration

Comparison of efficiencies
RESULTS and DISCUSSION - Exergoeconomic Analysis

Exergy destruction rates of cycle components

Cost rates of exergy destruction

Plant cost rate variation
RESULTS and DISCUSSION - Optimization

Pareto front of the multi-objective optimization

Optimum decision variables

<table>
<thead>
<tr>
<th>Decision Variable</th>
<th>Unit</th>
<th>Optimum Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis Temperature</td>
<td>°C</td>
<td>251.8</td>
</tr>
<tr>
<td>Decomposition Temperature</td>
<td>°C</td>
<td>485.8</td>
</tr>
<tr>
<td>Steam/Magnesium ratio</td>
<td>-</td>
<td>8.01</td>
</tr>
<tr>
<td>Inert gas flow rate</td>
<td>kmol/s</td>
<td>1.57</td>
</tr>
</tbody>
</table>

Model for cost-exergy efficiency relation

Optimum cost and efficiency

<table>
<thead>
<tr>
<th></th>
<th>Base model</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exergy efficiency (%)</td>
<td>53</td>
<td>56.25</td>
</tr>
<tr>
<td>Plant cost rate ($/s)</td>
<td>14.54</td>
<td>12.98</td>
</tr>
</tbody>
</table>
RESULTS and DISCUSSION - System II

Effect of compression pressure on liquefaction plant

Boiler pressure effect on SRC

T-s diagram of the liquefaction plant

T-s diagram of the SRC plant

Effect of compression pressure on liquefaction plant

Boiler pressure effect on SRC
RESULTS and DISCUSSION

Efficiency comparison

Exergy destruction ratios
CONCLUSIONS

- The four-step cycle recovers half of the HCl in dry form, where the remaining HCl is still in mixture with steam.

- Further dry HCl capture is experimentally accomplished by a separation process.

- HCl capture is accomplished safely at 275°C reactor temperature at its highest level by 30.8 \(\pm\) 0.36%.

- Cost of H\(_2\) production from the modified four-step Mg-Cl cycle is $3.67/kg H\(_2\).

- Optimized plant cost rate is 10.73% lower, and plant exergy efficiency is 5.8% higher than the base case results.

- Energy and exergy efficiencies of the
  - Modified four-step Mg-Cl cycle are 44.3% and 53%.
  - The cogeneration system are 18.6%, and 31.35%.
RECOMMENDATIONS FOR FUTURE WORK

• Characteristics of chlorination of MgO particles produced from decomposition of MgOHCl

• A fluidized bed type reactor for increased HCl capture ratio

• Kinetics study for the hydrochlorination reactor

• An extensive study for a less steam requiring hydrolysis reactor

• Co-, tri-, and multi-generation plants for enhanced integrated system performances
THANK YOU FOR YOUR ATTENTION!