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Study Level Design of a Vanadium Redox Flow Battery

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To Whom It May Concern:

This report was prepared in response to a request by Dr. Robert Counce to create an economic model for the vanadium redox flow battery system. This study optimized the flow rate of the vanadium solutions in the battery with respect to the potential profit. In this study, the Douglas method of process synthesis was used. The calculations for this report were completed in Microsoft Excel.

As further outlined, there was a net annual loss of $912,977. This is largely due to the high cost of vanadium. As this type of battery becomes more common, the cost of vanadium may decrease. Moreover, although there is an annual loss, we must consider the benefit of this plant to the power grid itself. This battery helps to balance fluctuations in power demand so that power can be distributed at a more constant rate.

We recommend a more detailed evaluation of operation and labor costs. This study neglects the cost of the plant facility itself including the cost of land and facility operating costs such as lighting, heating and air conditioning, plumbing, etc. As can be seen in the manufacturing cost summary table, our calculations showed that less than one employee was required at the plant at any given time. Liability and safety issues alone would require significantly more employees, increasing the net annual loss. In our opinion, although we are currently showing a net loss, further studies should be conducted on this system in light of the potential benefits to the power grid.

Sincerely,

Morgan Baltz       Katie Lutes       Michael Wierzbicki       Akshitha Yarrabothul
Study-Level Design of a Vanadium Redox-Flow Battery

CBE 488- Group 2
April 15, 2013

Morgan Baltz
Katie Lutes
Michael Wierzbicki
Akshitha Yarrabothula

Advisors: Dr. Robert Counce
Mr. Mark Moore
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1.0 Introduction

The purpose of this study was to produce a study-level design and analysis of the Vanadium Redox-Flow Battery (VRFB). One important characteristic of the VRFB is its flexibility in design. Because the design of redox-flow batteries is scalable, they are able to be coupled with other forms of renewable energy technologies such as solar and wind energy.

A higher flow rate of the electrolyte in a VRFB provides for a higher electrical potential; however, this requires a larger and more expensive pump. In addition, a higher flow rate also leads to a greater pressure drop of the electrolyte solution through the stack. Our objective in this study is to find the optimal flow rate of the electrolyte that will lead to an optimized capital cost of operation.

The design objectives are to provide a study-level design and analysis of a 10 MW battery. Base-case information is provided in Table 1 below.

| 1. Aqueous solutions of 1M Vanadium and 5M Sulfuric acid are used. The Vanadium solution is oxidized from V^{2+} to V^{3+} and from V^{4+} to V^{5+}. |
| 2. The power capacity is 10 MW. |
| 3. Membrane cost $25/m^2. |
| 4. All costs are to be in 2013 dollars (CE Index = 575.4). |
| 5. Produced electric energy can be sold at $0.14/kW-h. |
| 6. The cost of the purchased electrical energy cost is $0.01/kW-h. |
| 7. The total cycle time is 12 hours, which includes a charge and discharge time of 6 hours each. |
| 8. The liquid rate (to half-cell or stack) is to be optimized based on capital cost of operation analyses. |
| 9. State of Charge (SOC) limits are 0.2 and 0.8. |
| 10. The temperature and pressure of the battery is assumed to be at ambient conditions. |

*Table 1. Base-case information variables*

Included in this manuscript are results of the optimization studies. More details and full examples of the calculations that were carried out can be found in the Appendix.

We thank Dr. Robert Counce and Mark Moore for providing valuable insight into the project and supporting us throughout the duration of this project.
2.0 Synthesis of Information for Process

The battery studied contains cell stacks, two storage tanks, and a power conditioning system (PCS). The reactor is composed of cells stacked such that each cell acts as a cathode for the cell on one side and as an anode for the cell on the other side. Two solutions flow from storage tanks to the reactor and exchange protons across the membranes of the cells. These membranes are made from Nafion® 115. The PCS changes the electricity from AC to DC during the charging cycle and from DC to AC during the discharge cycle.

The current state of research about VRFBs shows that they can supplement lower cost energy sources to mitigate a variable energy flow. These batteries are able to store energy during the off peak hours and supply energy during peak hours.

From the Blanc and Rufer publication, *Understanding Vanadium Redox Flow Batteries*, we have gathered reaction related information (Table 2), design information (Table 3) and cost information (Table 4). Data correlating cell voltage to current density was used to determine the theoretical voltage (Graph 1). The efficiency was calculated from Equation 1 to be 91.79%, using an extracted theoretical voltage of 1.5056 V and an open source voltage of 1.64 V.

Equation 1:

$$\eta = \frac{\text{theoretical voltage}}{\text{open source voltage}}$$

<table>
<thead>
<tr>
<th>Reaction Related Information</th>
<th>VO₂⁺ + 2H⁺ + e⁻ ↔ VO²⁺ + H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometry</td>
<td>VO²⁺ ↔ V³⁻ + e⁻</td>
</tr>
<tr>
<td>V²⁺ + VO₂⁺ + 2H⁺ ↔ VO²⁺ + V³⁻ + H₂O</td>
<td></td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Conc. Of Vanadium</td>
<td>1M</td>
</tr>
<tr>
<td>Conc. Of Sulfuric Acid</td>
<td>5M</td>
</tr>
<tr>
<td>Power Capacity</td>
<td>10 MW</td>
</tr>
<tr>
<td>Energy Capacity</td>
<td>60 MW-hr</td>
</tr>
<tr>
<td>SOC Limits</td>
<td>0.2≤SOC≤0.8</td>
</tr>
<tr>
<td>Solution Density</td>
<td>Sulfuric Acid = 1.84 g/cm³</td>
</tr>
</tbody>
</table>

*Table 2. Reaction Related Information*

<table>
<thead>
<tr>
<th>Design Details</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycles per Year</td>
<td>329</td>
</tr>
<tr>
<td>Cross Sectional Area of Cell</td>
<td>1 m²</td>
</tr>
<tr>
<td>Current Density of Current Collector</td>
<td>200 mA/cm²</td>
</tr>
<tr>
<td>Material of Construction: Tanks</td>
<td>Fiberglass</td>
</tr>
</tbody>
</table>

4
<table>
<thead>
<tr>
<th>Material of Construction: Heat Exchangers</th>
<th>High Ni Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Adjustment</td>
<td>Use heat exchanger only if change in fluid temperature &gt; 100°C</td>
</tr>
<tr>
<td>Efficiency</td>
<td>91.79%</td>
</tr>
</tbody>
</table>

*Table 3. Design Details*

<table>
<thead>
<tr>
<th>Cost Information Details</th>
<th>2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price of Output Power</td>
<td>$0.15 per kW-hr</td>
</tr>
<tr>
<td>Price of Input Power</td>
<td>$0.01 per kW -hr</td>
</tr>
<tr>
<td>Vanadium Cost</td>
<td>$14,028 per lb</td>
</tr>
<tr>
<td>Ion-exchange membrane</td>
<td>$25 per m²</td>
</tr>
<tr>
<td>Current Collectors</td>
<td>$52.51 per m²</td>
</tr>
<tr>
<td>Carbon Felt</td>
<td>$20 per m²</td>
</tr>
</tbody>
</table>

*Table 4. Design Details*

![Figure 1. Cell Voltage vs. Current Density](image)

\[ y = -0.0005x + 1.6065 \]

\[ R^2 = 0.99938 \]
3.0 Study Level Analysis

**Level 2 Analysis**

Level two economic potential evaluates the economic potential as the value of products, in this case electricity stored, minus the cost of raw goods, in this case electricity required. Total revenue from electricity is calculated in Equation 2 as $452,997 per year. Total cost of electricity is calculated in Equation 3 as $35,842 per year. Maximal profit per year is equal to $417,155.

Equation 2:

\[
Revenue = Power\ Capacity \ast \eta \ast number\ of\ cycles\ per\ year \ast price\ of\ output\ power
\]

Equation 3:

\[
Cost = \frac{Power\ Capacity}{\eta} \ast number\ of\ cycles\ per\ year \ast price\ of\ input\ power
\]
**Level 3 Analysis**

In Level 3, we combine the level 2 economic potential with considerations for power capacity costs which include the equipment cost and power supplied to both pumps and the stacks.

To determine the pump required for the system, we first had to determine the flow rates of solution in the system and the pressure drop across the reactor. In order to calculate our flow rates, we set the SOC lower limit constant at 0.2 and varied the SOC upper limit from a range of 0.25-0.8. Equation 6 was used to determine the flow rate in liters per second but this calculation depends on the calculation of the average voltage in Equation 4 and the number of cells per stack, N_{cell}, which was calculated using Equation 5.

**Equation 4:**

\[ V_{avg} = V_0 + RT \ln \left( \frac{SOC^2}{1 - SOC^2} \right) \]

**Equation 5:**

\[ N_{cell} = \frac{P}{38 \times \text{current density} \times \text{area of cell} \times V_{avg}} \]

**Equation 6:**

\[ \dot{Q} = \frac{b \times N_{cell} \times \text{current density}}{(C_{out} - C_{in}) \times F}, \text{where} \quad C_{out/in} = \frac{SOC_{upper/lower}}{[\text{Vanadium}]} \]

After a flow rate was calculated for each SOC limit, this flow rate was converted to m³/sec and used to calculate the pressure drop, using Equation 7. The efficiency of the pump was then calculated using Equation 8 and pump power was calculated using Equation 9.

**Equation 7:**

\[ \Delta P = \dot{Q}R, \text{where} \quad R \text{ (hydraulic resistance)} \]

**Equation 8:**

\[ \varepsilon = (1 - 0.12\dot{Q}^{-0.27})(1 - \mu^{0.8}) \]

**Equation 9:**

\[ P_{pump} = \frac{Q \Delta P}{\varepsilon} \]

A sample calculation of pump power is provided in the Appendix. To select and cost our pump equipment, we used the costing charts and techniques provided in Chemical Engineering Process Design and Economics by Ulrich and Vasudevan. The pump power and
cost are included in Table 5. The cost of power supplied to the pump in dollars per year
was calculated using Equation 10 and this was included in the annualized pump cost. The
annualized pump cost is shown in Table 5.

Equation 10:

\[
Cost_{pump\ power} = P_{pump} \times \text{cycle time} \times \text{cycles per year} \times \text{cost of power}
\]

<table>
<thead>
<tr>
<th>Pump Power (kW)</th>
<th>Annualized Pump Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.68</td>
<td>$3,273.95</td>
</tr>
<tr>
<td>0.79</td>
<td>$3,367.43</td>
</tr>
<tr>
<td>0.94</td>
<td>$3,462.26</td>
</tr>
<tr>
<td>1.14</td>
<td>$3,514.55</td>
</tr>
<tr>
<td>1.41</td>
<td>$3,569.78</td>
</tr>
<tr>
<td>1.80</td>
<td>$3,629.68</td>
</tr>
<tr>
<td>2.39</td>
<td>$6,766.66</td>
</tr>
<tr>
<td>3.35</td>
<td>$13,476.66</td>
</tr>
<tr>
<td>5.08</td>
<td>$14,434.40</td>
</tr>
<tr>
<td>8.71</td>
<td>$15,911.97</td>
</tr>
<tr>
<td>18.71</td>
<td>$20,755.06</td>
</tr>
<tr>
<td>70.09</td>
<td>$33,458.98</td>
</tr>
</tbody>
</table>

*Table 5. Pump power and cost values*

The next step in the level 3 economic potential calculation was including the cost of the
reactor. Reactor cost is the sum of the equipment cost of the current collectors, membranes,
and carbon-felt electrodes, all of which were provided in $/m^2 and multiplied by the
number of cells and number of stacks. The cost of the reactor was then annualized based on
the equation shown in the appendix. EP3 was then calculated according to Equation 11.
Figure 3 demonstrates the changes in our EP3 estimate with respect to flow rate (m$^3$/s):

Equation 11:

\[
EP3 = EP2 - C_{pump,annualized} - C_{reactor,annualized} - C_{pump\ power}
\]
Figure 3. EP3 Estimate

Level 4 Analysis

The Level 4 economic potential includes the cost of the energy capacity equipment, including the tanks and the vanadium. Because the electrolyte is in a 5M sulfuric acid solution, fiberglass tanks must be used to prevent corrosion. The tanks were then sized based on the amount of vanadium required, calculated in Equation 13 using value of the minimum number of moles of Vanadium required to meet the designated SOC limits calculated in Equation 12. The tank size was subsequently calculated using Equation 14 and scaled up by 10% to account for unforeseen fluctuations.

Equation 12:

\[ N_{VMin} = \left( \frac{\text{Current Density} \times \text{Area}}{F} \right) \times N_{cell} \times t_{\text{discharge}} \]

Equation 13:

\[ N_{VTot} = \frac{N_{VMin}}{\text{SOC}_{\text{upper}} - \text{SOC}_{\text{lower}}} \]

Equation 14:

\[ V_{\text{tank}} = \frac{N_{VTot}}{[\text{Vanadium}]} \]
Based on these values, two spherical fiberglass tanks of 0.5 barg were selected and the 2004 prices for these tanks were obtained from Figure 5.61 of *Chemical Engineering Process Design*. These prices were then scaled up based on the 2013 CE Index Value. The 2013 capital cost of the tanks was then annualized using Appendix Equation 1. Equation 15 was used to calculate $EP_4$. Figure 4 demonstrates the changes in the Level 4 Economic potential estimate with respect to flow rate (m$^3$/s):

Equation 15:

\[
EP_4 = EP_3 - C_{tank, \text{annualized}} - C_{vanadium,\text{annualized}}
\]

![Figure 4. Level 4 Economic Potential Estimate](image)

### 4.0 Optimization

Based on our study level analysis accounting for all fixed capital costs, we note that lower flow rates lead to lower annualized fixed capital costs. At flow rates greater than 0.0220 m$^3$/sec, we observe a significant increase in fixed capital costs, primarily contributed by rising pump costs. In all subsequent calculations, we will use the lowest flow rate of 0.0047 m$^3$/sec, corresponding to an SOC range between 0.2-0.8. The manufacturing cost summary, shown in Table 6, was produced from Table 6.1 of *Chemical Engineering Process Design*. 
<table>
<thead>
<tr>
<th>Capital</th>
<th>Annualized Cost ($/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Capital</td>
<td></td>
</tr>
<tr>
<td>Pumps</td>
<td>$6,548</td>
</tr>
<tr>
<td>Tanks</td>
<td>$608,276</td>
</tr>
<tr>
<td>Reactor</td>
<td>$34,919</td>
</tr>
<tr>
<td>Vanadium</td>
<td>$421,488</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>$1,071,231</strong></td>
</tr>
<tr>
<td>Working Capital</td>
<td>$107,123</td>
</tr>
<tr>
<td><strong>Total Capital Investment</strong></td>
<td><strong>$1,178,354</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Manufacturing Expenses</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Labor</td>
<td></td>
</tr>
<tr>
<td>Reactor (0.3 people)</td>
<td>$16,772.08</td>
</tr>
<tr>
<td>Supervisory and Clerical Labor</td>
<td>$5,031.62</td>
</tr>
<tr>
<td>Utilities</td>
<td></td>
</tr>
<tr>
<td>Electricity @ 3,131,166.79kWh @ 0.01$/kWh</td>
<td>$35,841</td>
</tr>
<tr>
<td>Maintenance and repairs (10% of fixed capital)</td>
<td>$107,123</td>
</tr>
<tr>
<td>Operating Supplies (10% of maintenance and repairs)</td>
<td>$10,712</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>$175,480</strong></td>
</tr>
</tbody>
</table>

| Indirect Manufacturing Expenses             |                           |
| Local Taxes (3%)                            | $32,136                   |
| Insurance (2%)                              | $21,424                   |
| **TOTAL**                                   | **$53,561**               |

| TOTAL MANUFACTURING EXPENSE                 | **$229,042**              |

| General Expenses                            |                           |
| Distribution                                | $22,904                   |
| Research and Development                    | $11,452                   |
| **TOTAL GENERAL EXPENSE**                   | **$34,356**               |

| Depreciation                                | 10%                       |
| **TOTAL EXPENSES**                          | **$1,548,875**            |

| Revenue from Sales                          | (10MW/yr @ $0.15/yr)      |
| **Revenue from Sales**                      | **$452,996**              |
| Net Annual Profit                           | -$1,095,878               |
| Income Taxes                                | 35%                       |
| **Net Annual Profit After Taxes**           | **-$1,278,780**           |

*Table 6. Manufacturing cost summary sheet*
Conclusion

As can be seen in Table 6, the net annual profit after taxes for this plant was a loss of $912,976. The Level 2 economic potential was equal to $417,155 and was not a function of flow rate. The Level 3 economic potential for the optimal case was equal to $375,688 and decreased as flow rate increased. This trend is due to the increase in the capital and operating cost of the pump. The Level 4 economic potential for the optimal case was equal to ($654,077) and followed the same trend as the Level 3 economic potential. Although there is an annual loss from the operation of this plant, we must consider the benefit of this plant to the power grid itself. This battery helps to balance fluctuations in power demand so that power can be distributed at a more constant rate.

Recommendations

If this project were to be carried further towards implementation, we would recommend a more detailed evaluation of operation and labor costs. This study neglects the cost of the plant facility itself including the cost of land and facility operating costs such as lighting, heating and air conditioning, plumbing, etc. As can be seen in the manufacturing cost summary table, we accounted for less than one employee at the plant. This is obviously too low. Liability and safety issues alone would require significantly more employees, reducing the net annual profit.

References

Appendix

Equation for annualized cost:

\[
C_{\text{annualized}} = C_{\text{base}} \times \frac{i(i + 1)^{lifespan}}{(i + 1)^{lifespan} - 1}
\]

Sample calculation for the optimal case:

Equation 1:

\[
\eta = \frac{\text{theoretical voltage}}{\text{open source voltage}}
\]

\[
0.918 = \frac{1.5056}{1.64}
\]

Equation 2:

\[
Revenue = \text{Power Capacity} \times \eta \times \text{number of cycles per year} \times \text{price of output power}
\]

\[
\frac{452,997}{\text{year}} = 1000kW \times 0.918 \times 329 \text{cycles/year} \times \$0.15kWh
\]

Equation 3:

\[
\text{Cost} = \frac{\text{Power Capacity}}{\eta} \times \text{number of cycles per year} \times \text{price of input power}
\]

\[
\frac{35,842}{\text{year}} = 1000kW \times 0.918 \times 329 \text{cycles/year} \times \$0.01kWh
\]

Equation 4:

\[
V_{avg} = V_0 + RT\ln\left(\frac{\text{SOC}^2}{1 - \text{SOC}^2}\right)
\]

\[
1.640 \text{volts} = 1.64 \text{volts} + 8.314 \times \frac{L}{\text{mol} \cdot K} \times 303K \times \ln\left(\frac{0.5^2}{1 - 0.5^2}\right)
\]

Equation 5:

\[
N_{cell} = \frac{P}{38 \times \text{current density} \times \text{area of cell} \times V_{avg}}
\]

\[
80.2 = \frac{10 \times 10^6 \text{Pa}}{38 \times 2000 \frac{A}{m^2} \times 1 \text{m}^2 \times 1.64 \text{volts}}
\]

Equation 6:

\[
Q = \frac{b \times N_{cell} \times \text{current density}}{(C_{out} - C_{in}) \times F}
\]
\[ 0.0047 \, \frac{m^3}{s} = 4.712 \, \frac{L}{s} = \left( \frac{1 \times 80.2 \times 2000}{0.471 \, \frac{mol}{L} - 0.118 \, \frac{mol}{L}} \right) \times 96,485.34 \, \frac{\text{Coulombs}}{mol} \]

Equation 7:
\[ \Delta P = \dot{Q}R, \text{where } R \text{ (hydraulic resistance)} \]
\[ 66,849 \, Pa = 0.0047 \, \frac{m^3}{s} \times 14,186,843 \, \frac{kg}{m^3 \times s} \]

Equation 8:
\[ \varepsilon = (1 - 0.12 \dot{Q}^{-0.27})(1 - \mu^{0.8}) \]
\[ 0.54 = \left( 1 - 0.12(0.0047 \, \frac{m^3}{s})^{-0.27} \right)(1 - 0.0267^{0.8}) \]

Equation 9:
\[ P_{\text{pump}} = \frac{Q \Delta P}{\varepsilon} \]
\[ 680 \, W = \frac{0.0047 \, \frac{m^3}{s} \times 66,849 \, Pa}{0.54} \]

Equation 10:
\[ \text{Cost}_{\text{pump, power}} = P_{\text{pump}} \times \text{cycle time} \times \text{cycles per year} \times \text{cost of power} \]
\[ \frac{$26.85}{\text{year}} = 0.68 kW \times 12 \, hr \times 329 /year \times $0.01/kwh \]

Equation 11:
\[ \text{EP3} = \text{EP2} - C_{\text{pumps, annualized}} - C_{\text{reactor, annualized}} \]
\[ $375,688/year = $417,155/year - $6,248/year - $34,919/year \]

Equation 12:
\[ N_{\text{VMin}} = \left( \frac{\text{Current Density} \times \text{Area}}{F} \right) \times N_{\text{cell}} \times \text{time}_{\text{discharge}} \]
\[ 1,365,050 \, \text{moles} = \left( \frac{2000 \, \frac{\text{A}}{m^2} \times 1 \, m^2}{96,485.34 \, \frac{\text{Coulombs}}{mol}} \right) \times 80 \, \frac{\text{cells}}{\text{stack}} \times 38 \, \text{stacks} \times 6 \, hr \times 3,600 \, \frac{\text{seconds}}{hour} \]
Equation 13:

\[ N_{VT_{otal}} = \frac{N_{V_{Min}}}{SOC_{upper} - SOC_{lower}} \]

\[ 2,275,083 \text{ moles} = \frac{1,365,050 \text{ moles}}{0.8 - 0.2} \]

Equation 14:

\[ V_{tank} = \frac{N_{VT_{otal}}}{[\text{Vanadium}]} \]

\[ 1,338,284 \text{ L} = \frac{2,275,083 \text{ moles}}{1.7 \frac{\text{moles}}{\text{L}}} \]

Equation 15:

\[ EP4 = EP3 - C_{tank, \ annualized} - C_{vanadium, \ annualized} \]

\[ -$654,077/\text{year} = $375,688 - $608,276/\text{year} - $421,488/\text{year} \]