Advanced Integrated Technologies for Treatment and Reutilization of Impaired Water in Fossil Fuel-based Power Plant Systems

Thursday April 21st, 2016

David Ogden (OHIO), Xiujuan Chen (WVU), Xingbo Liu (WVU), and Jason Trembly (OHIO)

Institute for Sustainable Energy and the Environment
Institute for Sustainable Energy and the Environment (ISEE)

Institute Facts
- Established in 2004
- Faculty: 3
- Staff: 5 (Engineers and scientists)
- Graduate Students: 12
- Undergraduate Students: 14
- Space: 14,000 ft²

Core Capabilities
- Thermocatalytic Processes
- Process Engineering & Design
- Process Modeling & Simulation

• Algae growth/conversion
• Thermocatalytic conversion

• Wastewater management
• Electrochemical conversion
• SAGD operations
• Fracturing simulation

• Coal conversion (syngas & pyrolysis)
• CO₂ utilization
• Solid oxide fuel cells

• Nutrient recovery
• Acid mine drainage
• NORM removal
• Hydrocarbon removal

Home to Two Ohio Third Frontier Technology Commercialization Centers
Project Specifics and Team

**Project Specifics**
- DOE/NETL Cooperative Agreement No. DE-FE0026315
- DOE Project Manager: Barbara Carney
- Principal Investigator: Jason Trembly

**Project Funding**
- DOE Funding: $750,000
- Cost Sharing: $187,500

**Period of Performance**
- September 1, 2015 to February 28, 2017

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**OHIO Project Team**

- **Project Management**
  - Jason Trembly (OHIO)

- **Process Development**
  - Xingbo Liu (WVU)
  - David Ogden (OHIO)
  - Wen Fan (OHIO)
  - Shyler Switzer (OHIO)

- **Process Engineering**
  - Dora Lopez (OHIO)
  - Matt Usher (AEP)
Water-Energy Constraints

Major U.S. Water Consumers

- Agriculture: 70%
- Industry: 19%
- Municipal: 11%

U.S. Water Supply

- Critical to U.S. energy/economic security
- Major constraints
  - Increasing population
  - Increasing energy production
  - Competing demands
  - Climate change
- Power generation
  - Withdraws 950-2,700 M/bbl daily
  - Consumes 45-90 M/bbl daily
  - Fresh water supply geographically dependent
    - East of Mississippi River: Surface water
    - West of Mississippi River: Ground water
  - Contributes to stress on nearly 100 U.S. watersheds

Energy Production Accounts for 80% of Industrial Use
Power Plant Water Requirements

Power Plant Makeup Water Requirements

<table>
<thead>
<tr>
<th>Unit Operation</th>
<th>Subcritical PC</th>
<th>Supercritical PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling Tower</td>
<td>-440 gal/MWh</td>
<td>385 gal/MWh</td>
</tr>
<tr>
<td>Flue Gas Desulfurizer (FGD)</td>
<td>~70 gal/MWh</td>
<td>~60 gal/MWh</td>
</tr>
<tr>
<td>Boiler Feedwater</td>
<td>~10 gal/MWh</td>
<td>~10 gal/MWh</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>~520 gal/MWh</strong></td>
<td><strong>~455 gal/MWh</strong></td>
</tr>
</tbody>
</table>

- **Advanced Cycles**
  - IGCC (Slurry fed): 310 gal/MWh
  - NGCC: 190 gal/MWh

CCS Addition Increases Water Makeup Requirements by 50-90%

1. NETL, 2009.

Cooling Tower

FGD Installation
## Power Plant Makeup Water

### Makeup Water Quality Guidelines

<table>
<thead>
<tr>
<th>Constituent</th>
<th>FGD</th>
<th>Circulation Water</th>
<th>Boiler Feedwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.0-9.0</td>
<td>6.8-7.2&lt;sup&gt;1&lt;/sup&gt;</td>
<td>9.3-9.6</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt; (mg/L)</td>
<td>300</td>
<td>147,200</td>
<td>0</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt; (mg/L)</td>
<td>100-110</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>F&lt;sup&gt;-&lt;/sup&gt; (mg/L)</td>
<td>2</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;total&lt;/sub&gt; (mg/L)</td>
<td>2</td>
<td>&lt;0.5</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt; (mg/L)</td>
<td>100-150</td>
<td>900</td>
<td>0</td>
</tr>
<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt; (mg/L)</td>
<td>30-50</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt; (mg/L)</td>
<td>75-125</td>
<td>-</td>
<td>0.003-0.005</td>
</tr>
<tr>
<td>HCO&lt;sub&gt;3&lt;/sub&gt;- (mg/L)</td>
<td>150-200</td>
<td>30-250&lt;sup&gt;1&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>Mn&lt;sup&gt;2+&lt;/sup&gt; (mg/L)</td>
<td>-</td>
<td>&lt;0.5</td>
<td>0</td>
</tr>
<tr>
<td>Al&lt;sup&gt;3+&lt;/sup&gt; (mg/L)</td>
<td>-</td>
<td>&lt;1</td>
<td>0</td>
</tr>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt; (mg/L)</td>
<td>-</td>
<td>&lt;0.1</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>NH&lt;sub&gt;4&lt;/sub&gt; (mg/L)</td>
<td>-</td>
<td>&lt;2</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt; (mg/L)</td>
<td>10-50</td>
<td>150</td>
<td>0</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>500-1,000</td>
<td>70,000</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Mg x SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>35,000-75,000</td>
<td>0</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>200-300</td>
<td>100-300</td>
<td>0</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>200-2,000</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>500-1,000</td>
<td>-</td>
<td>0.5, Max.</td>
</tr>
<tr>
<td>Hardness (mg&lt;sub&gt;CaCO3&lt;/sub&gt;/L)</td>
<td>200-300</td>
<td>500,000</td>
<td>0</td>
</tr>
<tr>
<td>Oil &amp; Grease</td>
<td>0</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>

### Makeup Water Considerations
- Water chemistry
- Volume
- Process considerations
  - Scaling
  - Corrosion
  - Biofouling
Proposed Impaired Water Treatment Process

- **Technologies**
  - UV Treatment
  - NORM Absorption (Produced water)
  - Electrochemical Removal
    - Minor constituent removal (Fe$^{2+}$/Fe$^{3+}$, Mn$^{2+}$, Ru$^{2+}$, Zn$^{2+}$, and Cu$^{2+}$)
  - Selective precipitations
    - Minor constituents (Ba$^{2+}$ and Sr$^{2+}$)
  - SCW Treatment
    - Bulk constituents
## Project Schedule and Tasks

<table>
<thead>
<tr>
<th>Task</th>
<th>Start Date</th>
<th>End Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1.0 - Project Management and Planning</td>
<td>9/1/2015</td>
<td>2/28/2017</td>
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<tr>
<td>Task 2.0 - Small Scale Impaired Water Treatment Testing</td>
<td>9/1/2015</td>
<td>2/28/2017</td>
</tr>
<tr>
<td>Sub-task 2.1 - Electrochemical Stripping of Minor Constituents</td>
<td>9/1/2015</td>
<td>2/28/2017</td>
</tr>
<tr>
<td>Sub-task 2.2 - Corrosion Resistant Coatings Testing</td>
<td>9/1/2015</td>
<td>2/28/2017</td>
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<tr>
<td>Sub-task 2.3 - Evaluation of Scalable SCW Unit for Impaired Water Treatment</td>
<td>9/1/2015</td>
<td>2/28/2017</td>
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<tr>
<td>Task 4.0 - Pilot Scale Scoping Study</td>
<td>9/1/2015</td>
<td>2/28/2017</td>
</tr>
</tbody>
</table>

### Milestone Log
- **A:** Updated project management plan
- **B:** Complete SCW Test Unit Modifications
- **C:** Kickoff meeting
- **D:** Determine preliminary electrostripping minor constituent removal efficiency
- **E:** Determine new SCW unit design major constituent removal efficiency
- **F:** Identify best suited power plant make-up water application(s)

Vertical arrows indicate interdependencies between tasks.

Q: Quarterly reports; FR: Final report due three months after project's end.
Project Objectives

Overall

• Develop a site deployable cost-effective technology for treating impaired water generated from CO₂ storage operations

Small Scale Testing

• Validate technical and commercial feasibility of new internally heated SCW treatment methodology for removal of major constituents from impaired water
• Determine effectiveness of electrochemical stripping to remove minor constituents from impaired water
• Determine effectiveness of corrosion resistant coatings to improve SS performance in high chloride content water

Process Engineering

• Identify process configurations which maximize constituent removal, optimize heat integration, and minimize water treatment costs
• Prepare scope for implementing the SCW-based impaired water treatment for a pilot scale effort
• Identify best suited power plant makeup water applications for treated water product
Preliminary Electrocoagulation Results
Electrocoagulation Process

Major steps:
1) Anodic oxidation and cathodic reduction;
2) Generation of coagulants;
3) Precipitation of pollutants on coagulants;
4) Separation by flotation with generated $\text{H}_2$. 

Electro-Coagulation Process

Major Objectives
- Maximize removal efficiency
- Kinetic assessment: minimize energy consumption while maintaining higher removal efficiency
- Assess EC process mechanism: (absorption, co-precipitation, surface complexation or electrostatic attraction)

Efficiency Considerations
- Electrode materials and arrangement
- Distance of the electrodes
- Conductivity of wastewater
- Initial pH
- Current density and EC time
Preliminary Results

- Generally, the solution pH ($pH_f$) increased at the end of EC process due to OH$^-$ generation.
- Metals ions still consuming OH$^-$. 

Note: If water electrolysis is the only favorable reaction, the bulk pH would remain constant, due to equimolar production of H$^+$ and OH$^-$. 
### Preliminary Results

**Table 1** Initial and residual metal concentration, metal removal (%), residual concentration of anode ion after Al EC and Fe EC process. Control sample (marked with red lines) was obtained after 30 min of Al EC at initial pH 4.6, electrode distance of 10mm.

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Sample 7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrode material</strong></td>
<td>Al</td>
<td>Al</td>
<td>Al</td>
<td>Al</td>
<td>Al</td>
<td>Al</td>
<td>Fe</td>
</tr>
<tr>
<td><strong>Initial concentration of Zn (mg/l)</strong></td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td><strong>Current density (mA/cm²)</strong></td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
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<td>4.1</td>
</tr>
<tr>
<td><strong>Electrodes distance (mm)</strong></td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td><strong>EC time (min)</strong></td>
<td>30</td>
<td>15</td>
<td>30</td>
<td>60</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td><strong>Concentration of NaCl (mol/l)</strong></td>
<td>0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Initial pH</strong></td>
<td>5.2</td>
<td>4.5</td>
<td>4.7</td>
<td>4.5</td>
<td>4.5</td>
<td>3.2</td>
<td>4.5</td>
</tr>
<tr>
<td><strong>Final pH</strong></td>
<td>3.8</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.3</td>
<td>4.5</td>
</tr>
<tr>
<td><strong>Residual concentration of Zn (mg/l)</strong></td>
<td>355.5</td>
<td>363.3</td>
<td>349.3</td>
<td>255.2</td>
<td>334.7</td>
<td>310.9</td>
<td>294.6</td>
</tr>
<tr>
<td><strong>Removal (%)</strong></td>
<td>29</td>
<td>27</td>
<td>31</td>
<td>49</td>
<td>33</td>
<td>38</td>
<td>41</td>
</tr>
<tr>
<td><strong>Residual concentration of Al/Fe (mg/l)</strong></td>
<td>24.4</td>
<td>6.7</td>
<td>5.4</td>
<td>2.2</td>
<td>5.5</td>
<td>43.4</td>
<td>106.5</td>
</tr>
</tbody>
</table>
## Preliminary Results

**Table 2** Metal removal (%), residual concentration of anode ion after 30 min Al EC and Fe EC process. With electrode distance of 10 mm.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Samples</th>
<th>Current density (mA/cm²)</th>
<th>pH</th>
<th>Removal (%)</th>
<th>Residual anode ions (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pH₀</td>
<td>pHᵢ</td>
</tr>
<tr>
<td>Ba²⁺-Ca²⁺-Mg²⁺-Sr²⁺</td>
<td>Sample 1</td>
<td>4.2</td>
<td>5.8</td>
<td>4.63</td>
<td></td>
</tr>
<tr>
<td>Al electrode</td>
<td>Sample 2</td>
<td>8.4</td>
<td>5.75</td>
<td>4.77</td>
<td></td>
</tr>
<tr>
<td>Ba²⁺-Ca²⁺-Mg²⁺-Sr²⁺</td>
<td>Sample 3</td>
<td>4.2</td>
<td>pH₀</td>
<td>pHᵢ</td>
<td></td>
</tr>
<tr>
<td>Fe electrode</td>
<td></td>
<td></td>
<td>5.75</td>
<td>4.46</td>
<td></td>
</tr>
</tbody>
</table>
Preliminary Results – Conclusions

1) The optimum current density for this case is not located in the range of 0.1-0.2A;
2) Acceleration of EC process is possibly unfavorable for the removal of these metal ions.
3) In this case, Fe-electrode is more efficient than Al-electrode.
4) Different removal mechanisms for Ba$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, and Sr$^{2+}$ during EC process.

Future Work – Improving Removal Efficiency

- Optimum characteristics of EC reactor.
  - $d_{a-c}$: 0.5-2 cm;
  - Conductivity: concentration of NaCl
- Key factors: $pH_{initial}$, CD, $t_{EC}$
  - $pH$=3-7; $I$= 0.05-0.2 A, 0.5-1A; $t$=0-60 min
Preliminary TDS Removal Results
Small Scale Testing: Internally Heated SCW Treatment

Goal: Determine technical and commercial feasibility of Joule-based heating for SCW treatment of brines

• Methodology
  – Utilize lab prepared and field derived brine solutions
  – Analyze products using ICP, IC, and GC/MS

• Experimental Parameters
  – Inlet temperature: 340-380 °C
  – Pressure: 22.1-25.0 MPa
  – Flow rate: 50-200 mL/min
  – Power flux
  – Impaired water composition

OHIO Prototype Internally-Heated SCW Reactor
Comparison of SCW Reactor Types

- **Reverse Flow Reactor**
  - Externally heated
  - Inlet turbulence results in mixing and critical transition
  - Flow regime prevents internal wall scaling

- **Internally Heated Reactor**
  - AC power provides heating between primary/counter electrodes, rapid heat transfer
  - Creates homogeneous salt nucleation preventing surface scaling
  - Results in significantly cooler reactor wall temperature leading to higher throughput and small footprint

- Inlet feed swirling causes sub- to supercritical transition
- Results in TDS precipitation
  - Precipitates form in the center of the reactor
  - Prevents scale formation on inner reactor wall
  - Solids accumulate and are removed from the reactor bottom

OHIO Reverse Flow SCW Reactor

OHIO Internally Heated SCW Reactor
### Prototype Overview

<table>
<thead>
<tr>
<th>Design Criteria</th>
<th>Design Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>29 MPa</td>
</tr>
<tr>
<td>Temperature</td>
<td>400 °C</td>
</tr>
<tr>
<td>Flowrate</td>
<td>10-200 mL/min</td>
</tr>
<tr>
<td>Current Supply</td>
<td>140 A (max)</td>
</tr>
<tr>
<td>Reactor Power</td>
<td>7.0 kW</td>
</tr>
</tbody>
</table>

**OHIO Prototype Brine Treatment Reactor and System P&ID**
Prototype Modifications

- Electrode Arcing and Overheating
  - Extended insulators
  - Alternative electrode materials
  - Electrode centering spacers
- Filter Plugging
  - Flow through sintered metal filters
Experimental Results: Reactor Temperature Profiles

Reactor Phenomena
1. Salt Injection
2. Inlet temp increase
3. Temperature dynamic due to inlet temp change

Reactor Temperature Profiles After Injection of 50 mL/min Brine Solution at 23 MPa and 500 W. Pseudocritical temperature is 377.5 °C.
Experimental Results (Cont.)

Experimentally determined effluent a) Na\(^+\) and b) Ca\(^{2+}\) concentrations based upon water density
Experimental Results (Cont.)

Experimentally determined effluent a) Mg²⁺ and b) Cl⁻ concentrations based upon water density
Summary

Preliminary Conclusions

1. Internally heated reactor design is capable of heating brine solution to critical condition.

2. Minimal heating occurs beyond the critical point due to precipitation of dissolved solids and resulting decrease in solution conductivity.

3. Water density is major factor controlling TDS removal level.

4. TDS removal greater than 99.5% from solutions containing greater than 100k ppm TDS.

5. Internally heated reactor design shows capability of producing water product with multiple beneficial reuse applications.

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Power Plant Makeup Water Quality Guidelines and Preliminary OHIO Water Product Results

<table>
<thead>
<tr>
<th>Constituent</th>
<th>FGD</th>
<th>Circulation Water</th>
<th>Boiler Feedwater</th>
<th>Preliminary Product Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6-9.0</td>
<td>6.8-7.2</td>
<td>9.3-9.6</td>
<td>6.2</td>
</tr>
<tr>
<td>SO_4^{2-} (mg/L)</td>
<td>300</td>
<td>147-200</td>
<td>0</td>
<td>BDL</td>
</tr>
<tr>
<td>Cl^- (mg/L)</td>
<td>100-110</td>
<td>-</td>
<td>0</td>
<td>200-850</td>
</tr>
<tr>
<td>Fe^{3+} (mg/L)</td>
<td>2</td>
<td>-</td>
<td>0</td>
<td>DNT</td>
</tr>
<tr>
<td>Ca^{2+} (mg/L)</td>
<td>100-150</td>
<td>900</td>
<td>0</td>
<td>7-38</td>
</tr>
<tr>
<td>Mg^{2+} (mg/L)</td>
<td>30-50</td>
<td>-</td>
<td>0</td>
<td>1-3.8</td>
</tr>
<tr>
<td>Na^+ (mg/L)</td>
<td>75-125</td>
<td>-</td>
<td>0.003-0.005</td>
<td>180-700</td>
</tr>
<tr>
<td>HCO_3^- (mg/L)</td>
<td>150-200</td>
<td>30-250</td>
<td>0</td>
<td>BDL</td>
</tr>
<tr>
<td>Mn^{2+} (mg/L)</td>
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<td>&lt;0.5</td>
<td>0</td>
<td>DNT</td>
</tr>
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<td>Al^{3+} (mg/L)</td>
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<td>&lt;1</td>
<td>0</td>
<td>DNT</td>
</tr>
<tr>
<td>Cu^{2+} (mg/L)</td>
<td>-</td>
<td>&lt;0.1</td>
<td>&lt;0.002</td>
<td>DNT</td>
</tr>
<tr>
<td>NH_3^- (mg/L)</td>
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<td>&lt;2</td>
<td>&lt;0.02</td>
<td>DNT</td>
</tr>
<tr>
<td>SiO_2 (mg/L)</td>
<td>10-50</td>
<td>150</td>
<td>0</td>
<td>DNT</td>
</tr>
<tr>
<td>Mg x SiO_2</td>
<td>-</td>
<td>35,000-75,000</td>
<td>0</td>
<td>DNT</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>200-300</td>
<td>100-300</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>200-2,000</td>
<td>-</td>
<td>0</td>
<td>DNT</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>500-1,000</td>
<td>-</td>
<td>0.5, Max.</td>
<td>DNT</td>
</tr>
<tr>
<td>Hardness (mg CaCO_3/L)</td>
<td>200-300</td>
<td>500,000</td>
<td>0</td>
<td>DNT</td>
</tr>
<tr>
<td>Oil &amp; Grease</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

BDL: Below detectable limit
DNT: Did not test to date
Upcoming Work

OHIO

- Continue prototype testing to evaluate TDS removal efficiency and evaluate reactor operability (Ongoing)
- Update existing techno-economic analyses using newly generated experimental data (Starting mid-May)

WVU

- Continue evaluating electrocoagulation and electrochemical stripping techniques to remove high-value trace elements (Ongoing)
- Begin evaluating corrosion resistant cladding materials for low-cost steels (Starting June)
Create for Good.

Questions: trembly@ohio.edu