Waste Heat Recovery Opportunities for Thermoelectric Generators

presented at the

2009 Thermoelectric Applications Workshop

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September 30, 2009
The Case For Thermoelectrics (TE)

- Current TE conversion efficiency usually too low to compete with dynamic technologies for stand-alone systems
  - Current TE materials:
    - Power: 8 to 15% against 25 to 45%
    - Cooling: COP is 3x lower than typical compressor
  - Advanced TE materials goals in the next 3-5 years:
    - Power: 20-30% efficiency (average ZT of 2.0)
    - Cooling: 2x to 5x increase in COP, 100x power density

- But TE technology has highly valuable attributes
  - Solid-state, highly scalable and modular
    - No moving parts, no vibrations, silent operation
    - Can outperform competition for small scale applications
  - High level of reliability and redundancy
    - Proven record of long life space and terrestrial applications

- Waste Heat Recovery is attractive application for TE
  - Thermal energy source is “free”
  - TE generator as a “bottoming/topping cycle retrofit”
  - Scalability and mass production lead to low cost $/kWh

**Power generation**

State-Of-Practice materials: $ZT_{average} \sim 0.5$
State-Of-the-Art materials: $ZT_{average} \sim 0.9$
Best SOA materials: $ZT_{peak} \sim 1.5$ to $2.0$
Waste Heat Sources
Average Power Plant Generation Efficiency

- Efficiency has not improved significantly in last 40 years for large scale power plants
Opportunities for Power Generation by Recovering Waste Heat

Wide range of heat source types and temperatures from energy intensive industrial processes

* USA data
Technologies for Waste Heat Recovery
Power Generation

• Commercial Technologies
  – Single Fluid Rankine Cycle
    • Steam cycle
    • Hydrocarbons
    • Ammonia
  – Binary/Mixed Fluid Cycle
    • Ammonia/water absorption cycle
    • Mixed-hydrocarbon cycle

• Emerging Technologies
  – Supercritical CO\textsubscript{2} Brayton Cycle
  – Thermoelectric energy conversion

• Combined Cycles

• Technology Merits
  • Conversion efficiency and effective utilization of waste heat
  • Heat transfer equipment
  • System integration and interfacing with industrial processes
  • System reliability
  • Economic values
  • Ability to integrate into combined cycles
Dynamic Power Systems Are Efficient

- Thermoelectrics cannot compete “head-on” with dynamic technologies
  - Some industrial processes are potentially attractive for TE systems
    - Medium to high grade heat
    - Limited opportunity to reuse the waste heat
    - Difficulties in effectively transporting that heat to separate energy conversion systems

Major Opportunities in Manufacturing & Energy Industries

• Large scale waste heat recovery of industrial and power generation processes
  – Benefit from higher energy costs and reduction of fossil fuel pollution to retrofit existing facilities
  – High grade waste heat sources from a variety of industrial manufacturing processes
  • For near term applications in the US alone, between 0.9 and 2.8 TWh of electricity might be produced each year for materials with average ZT values ranging from 1 to 2
  – Efficient heat exchangers, large scale production of TE materials and modules are required
  • Also need to focus on economical, low toxicity materials

![Potential High Temperature Thermoelectric Waste Heat Recovery System](image)

(Concept developed for 100 kW-class thermoelectric generators operating up to 1275 K)


<table>
<thead>
<tr>
<th>Applications Set A: low hot-side temperature, relatively clean flue gas</th>
<th>T&lt;sub&gt;source&lt;/sub&gt; (K)</th>
<th>Available Waste Heat GWh/year</th>
<th>T&lt;sub&gt;E&lt;/sub&gt; Recoverable Waste Heat GWh/year</th>
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</thead>
<tbody>
<tr>
<td>Commercial Water/Steam Boilers</td>
<td>425</td>
<td>164,010</td>
<td>n/a</td>
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<tr>
<td>Industrial Water/Steam Boilers</td>
<td>425</td>
<td>178,654</td>
<td>n/a</td>
</tr>
<tr>
<td>Ethylene Furnace</td>
<td>425</td>
<td>8,786</td>
<td>n/a</td>
</tr>
</tbody>
</table>

| Applications Set B: medium hot-side temperature, mixed flue gas quality |
|-------------------------|-----------------|-----------------------------|----------------------------------|
| Aluminum Smelting | 1230 | 1,230 | 59 |
| Aluminum Melting | 1025 | 8,376 | 410 |
| Metal Casting Iron Cupola | 850 | | |
| Steel Blast Furnace | | | |
| Lime Kiln | | | |
| Cement Kiln (with pre-heater) | 475 | 2,050 | 88 |

| Applications Set A: High hot-side temperature, mixed flue gas quality |
|-------------------------|-----------------|-----------------------------|----------------------------------|
| Cement Kiln (no pre-heater) | 1000 | 2,460 | 117 |
| Glass Oxy-fuel Furnace | 1700 | 1,406 | 59 |
| Glass Regenerative | 750 | 3,456 | 176 |

<table>
<thead>
<tr>
<th></th>
<th>T=1</th>
<th>T=2</th>
<th>T=4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>370,428</td>
<td>908</td>
<td>2,841</td>
</tr>
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</table>
TE for Vehicle Waste Heat Recovery

- Thermoelectrics in Vehicles
  - TE has unique advantages for integration
- What has been done?
  - Low efficiency Bi$_2$Te$_3$-based TE generators (TEG) demonstrations
- What is needed?
  - Increase TEG operating temperatures, $\Delta T$
  - Integrate higher ZT materials ($ZT_{ave} \sim 1.5$ to 2)
  - Develop and scale up HT TE module technology
  - Integrate with efficient heat exchangers

$\Delta T = 500$ K
Performance Goal

$ZT_{ave} \sim 3.5$

$ZT_{ave} \sim 1.3$

$ZT_{ave} \sim 0.7$

Heat Exchanger Efficiency (%)

Increase in Engine Efficiency (%)

Exhaust Pipe TE
diesel fuel

Electrical power
generator

DOE Workshop 09/30/2009

Advanced TE R&D - 9

> 10% Fuel Efficiency improvement with exhaust waste heat recovery

> 15 kW high grade waste heat
TE Materials Considerations for Large Scale Waste Heat Recovery Applications

- Cost of pure elements (see table for preliminary assessment)
  - Must take into account volume of material required for practical, efficient device design
- Future availability of pure elements
  - Te, Ge…
- Toxicity of elements
  - PbTe….
- Materials and device processing costs
  - Also, how energy intensive these processes are (“energy payback time”) is important

<table>
<thead>
<tr>
<th>Material</th>
<th>$ per kg</th>
<th>$/W</th>
<th>$/W</th>
<th>$/W</th>
</tr>
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<tbody>
<tr>
<td>Si$<em>{80}$Ge$</em>{20}$</td>
<td>630</td>
<td>10.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si$<em>{90}$Ge$</em>{2}$</td>
<td>83</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb$<em>{14}$MnSb$</em>{11}$/La$_{3-x}$Te$_4$</td>
<td>163</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg$<em>2$Si$</em>{0.6}$Sn$_{0.4}$ (n)</td>
<td>11</td>
<td>0.2</td>
<td></td>
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<tr>
<td>Skutterudites</td>
<td>12</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAGS (p)</td>
<td>631</td>
<td>4.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbTe</td>
<td>83</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$_2$Te$_3$</td>
<td>170</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Segmented$^5$</td>
<td>117</td>
<td>1.0</td>
<td></td>
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</tr>
</tbody>
</table>

1 Used 2008 USGS data (mostly)
2 For long term operation
3 Based on 300 K cold side temperature, (except for TAGS)
4 Assumed 10 W/cm$^2$ heat flux to size up amount of TE material required
5 Used Zintl/SKD/(Bi$_3$Sb)$_2$Te$_3$ and La$_3$Te$_4$/SKD/Bi$_2$Te(Se)$_3$; similar efficiency results can be achieved with PbTe-based materials
NASA’s Advanced TE Research & Technology Program

TE Materials Performance Objective

**TE conversion efficiency as a function of hot junction temperature and ZT**

- **Best experimentally demonstrated maximum ZT values ~ 1.5 to 2.0 for Bulk Materials**
- **Goal for Advanced TE Materials Integrated in Segmented Configuration for maximizing ZT over Wide ΔT**
- **Current Best TE Materials Integrated in Segmented Configuration for maximizing ZT over Wide ΔT**
- **TE Materials for RTGs Flown on NASA Missions**
- **New materials could also be used in high grade waste terrestrial applications**

**Advanced TE R&D Performance Goal**

- **ATEC (P²Ge - \(t_{id} \approx 550 \text{ K})**
- **ATEC (T²Ge - \(t_{id} \approx 560 \text{ K})**
- **Stat - PbTe/TAGS \((T_{cold} \approx 480 \text{ K})**
- **St - "RTG" Si_{1.8}Ge_{0.2} \((t_{rod} ~ 570 \text{ K})**

**\(T_{col} = \)**
Impact of Advanced high temperature materials on RTG Performance

Ultimate goal: > 15% efficient, 10 W/kg Advanced RTGs
## TE Converter Configurations

<table>
<thead>
<tr>
<th>P-leg</th>
<th>N-leg</th>
<th>Configuration</th>
<th>Program</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Te$_3$/TAGS/PbSnTe</td>
<td>Bi$_2$Te$_3$/PbTe</td>
<td>Segmented Unicouple</td>
<td>Terrestrial RTG</td>
</tr>
<tr>
<td>TAGS/PbSnTe</td>
<td>PbTe</td>
<td>Segmented Unicouple</td>
<td>SNAP-19, MMRTG</td>
</tr>
<tr>
<td>Si$<em>{0.63}$Ge$</em>{0.37}$/Si$<em>{0.8}$Ge$</em>{0.2}$</td>
<td>Si$<em>{0.63}$Ge$</em>{0.37}$/Si$<em>{0.8}$Ge$</em>{0.2}$</td>
<td>Segmented Unicouple</td>
<td>MHW-, GPHS-RTG</td>
</tr>
<tr>
<td>Bi$_2$Te$_3$/Filled Skutterudite</td>
<td>Bi$_2$Te$_3$/Skutterudite</td>
<td>Segmented Unicouple</td>
<td>Segmented TE Unicouple</td>
</tr>
<tr>
<td>Zintl</td>
<td>Nano Si$<em>{0.63}$Ge$</em>{0.37}$/Si$<em>{0.8}$Ge$</em>{0.2}$</td>
<td>Segmented Unicouple</td>
<td>ATEC-1</td>
</tr>
<tr>
<td>Filled Skutterudite/Zintl</td>
<td>Nanocomposite Filled Skutterudite/La$_{3-x}$Te$_4$</td>
<td>Segmented Unicouple</td>
<td>ATEC-2</td>
</tr>
<tr>
<td>Filled Skutterudite</td>
<td>Skutterudite</td>
<td>Multicouple</td>
<td>STMC (2005)</td>
</tr>
<tr>
<td>Si$<em>{0.8}$Ge$</em>{0.2}$</td>
<td>Si$<em>{0.8}$Ge$</em>{0.2}$</td>
<td>Multicouple</td>
<td>SP-100, MOD-RTG</td>
</tr>
</tbody>
</table>

![Diagram of TE Converter Configurations](image)

- Multicouples best suited to higher power systems
- Unicouples are simpler, lower risk devices suitable for lower power systems
- Segmenting has been preferred method to maximize ZT across large ΔT due to simpler system integration
Candidate TE Materials for HT Power Applications
Complex Low $\lambda_L$ Materials and Nanostructured High PF Compounds

High Temperature $n$-type

- Si-based Clathrates
- oxides

1273 K

~ 873 K $\Delta T$

400 K

low Temperature $n$-type

- Nano bulk III-V compounds

Low Temperature $p$-type

- Nano bulk GaAs
- Layered oxides

400 K $\Delta T$

hot $n_h$, $p_h$

cold $n_c$, $p_c$

$R_L$ V

- Nano bulk III-V compounds
- Self-assembling nanostructured Chalcogenides
Developing Efficient High Temperature TE Materials

Materials Synthesis Scale-up and Reproducibility of TE properties

Bulk Nanostructured and Bulk Nanocomposite Materials

Nanoscale features produced using high energy ball milling and self-assembling synthesis techniques

x30 reduction in lattice thermal conductivity of Si

Basic Transport Property Modeling/Analysis and Guidance to Experimental Materials Research

Tuning electrical transport in complex rare earth compounds

DOE Workshop 09/30/2009
# Maturity of Advanced Materials for High Temperature Converter Development

**Initial Selection for 1st generation ATEC RTG**

<table>
<thead>
<tr>
<th></th>
<th>Nano Bulk Si-Ge (p&amp;n)</th>
<th>14-1-11 Zintl (p)</th>
<th>La$_{3-x}$Te$_4$ (n)</th>
<th>Skutterudites (p&amp;n)</th>
<th>Other Materials (Clathrates, Ti-doped PbTe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reproducible TE properties</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Scale-up of synthesis</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Thermally stable TE properties</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Sublimation suppression possible</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Stable low resistance metallizations</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Temperature dependence of basic mechanical properties</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>

**Initial Selection of 2nd generation ATEC RTG**

**Alternate for 1st generation ATEC RTG**
Thermal/Mechanical Considerations for Development of High Temperature TE Converters

- **Critical Structural Integrity Issues**
  - Coefficient of thermal expansion mismatches within TE device stack, and between stack and large heat exchangers
  - "Bowing" of TE legs due to large DT
  - Surviving fabrication and assembly steps - and operation

Stresses during high temperature fabrication steps

Stresses back at room temperature after fabrication

Stresses when operating across large $\Delta T$
Bonded to hot and cold side heat exchangers
TE Materials Selection for Segmented Device

- Si-Ge alloys have much lower coefficient of thermal expansion (CTE) and their TE properties are not compatible with those of other candidate materials
  - Would require cascading, not practical for RTG applications
- Zintl and La$_{3-x}$Te$_4$ best high temperature materials for segmented devices
  - Excellent CTE match for both refractory rare earth compounds
  - Good TE compatibility with skutterudites, PbTe, TAGS
  - Characterization of basic high temperature mechanical properties conducted in FY09
    - With U. Mississippi collaboration
- Segmentation with skutterudites
  - Would result in couple efficiency increase from ~ 10% to more than 13%

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass Density (g/cm$^3$)</th>
<th>CTE ($10^{-6}$ K$^{-1}$)</th>
<th>Maximum $T_{hot}$ (K)</th>
<th>ZT$_{peak}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanostructured</td>
<td>Si$<em>{80}$Ge$</em>{20}$</td>
<td>2.9</td>
<td>4.1*</td>
<td>1275</td>
</tr>
<tr>
<td>La$_{3-x}$Te$_4$</td>
<td>6.7</td>
<td>18.0</td>
<td>1275</td>
<td>1.25</td>
</tr>
<tr>
<td>CoSb$_3$</td>
<td>7.6</td>
<td>12.2*</td>
<td>875</td>
<td>1.1</td>
</tr>
<tr>
<td>PbTe</td>
<td>8.3</td>
<td>~ 20</td>
<td>815</td>
<td>0.85</td>
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*N-type materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass Density (g/cm$^3$)</th>
<th>CTE ($10^{-6}$ K$^{-1}$)</th>
<th>$T_{hot}$ (K)</th>
<th>ZT$_{peak}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanostructured</td>
<td>Si$<em>{80}$Ge$</em>{20}$</td>
<td>2.9</td>
<td>4.4*</td>
<td>1275</td>
</tr>
<tr>
<td>Yb$<em>{14}$MnSb$</em>{11}$</td>
<td>8.4</td>
<td>17.5*</td>
<td>1275</td>
<td>1.45</td>
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<tr>
<td>CeFe$<em>{5}$Sb$</em>{12}$</td>
<td>7.9</td>
<td>14.5*</td>
<td>875</td>
<td>0.85</td>
</tr>
<tr>
<td>PbTe</td>
<td>8.3</td>
<td>~ 20</td>
<td>815</td>
<td>0.9</td>
</tr>
<tr>
<td>TAGS</td>
<td>6.5</td>
<td>~ 16</td>
<td>675</td>
<td>1.2</td>
</tr>
</tbody>
</table>

* Ravi et al., J. Electronic Materials, published online 28 March 2009

Near identical CTE of Zintl and La$_{3-x}$Te$_4$
Couple Configurations in Development

Zintl / NanoSiGe Couple

Zintl / $\text{La}_{3-x}\text{Te}_4$ Couple

Zintl/SKD // $\text{La}_{3-x}\text{Te}_4$/SKD Segmented Couple
Advanced TE Research & Technology Program
How far are we?

Current (FY09) System Performance Projection when using best TE materials in segmented couple configuration:

- n-type $\text{La}_{3-x}\text{Te}_4$/double filled SKD with
- p-type $\text{Yb}_{14}\text{MnSb}_{11}/\text{nanoPbTe}$

$ZT_{ave} \sim 1.15$
($\sim 15\%$ couple efficiency)
$\sim 12.5\%$ System efficiency

$ZT_{ave} \sim 1.5$ needed between $1273 \text{ K}$ and $500 \text{ K}$ to achieve $15\%$ RTG system efficiency

Computational models based on experimental data on bulk nanostructured materials predict $ZT_{ave} > 2$

- $T_{cold} = 1275 \text{ K}$

(Based on radiatively coupled vacuum operation unicouple based RTG concept)
Summary and Conclusions

• Thermoelectrics have unique advantages for integration into selected waste heat recovery applications
  – Long, proven track record of high temperature TEGs
  – Well understood technology development roadmap
• Significant opportunities available in waste heat recovery
  – Vehicle exhaust heat recovery could provide “proving grounds” as best combination of small scale TEG system with large scale application
• TE materials efficiency is critical to TEG performance:
  – x 2 to 3 increase in $ZT_{ave}$ needed, especially for low to medium grade waste heat
  – But cost, environmental friendliness and availability are also key parameters (potential issues with elements such as Ge, Te, Pb, Tl)
• Most of the technology risk lies in TE couple/module development and is a must to enable new applications
• Converter & heat exchanger designs are critical to efficient system implementation
• Demonstrated new high temperature couple based on new materials
  – Now focusing on development of segmented devices
The work presented here benefited from contributions from a number of collaborators in the past year

- California Institute of Technology
- University of California at Los Angeles
- University of California at Davis
- Boston College
- Massachusetts Institute of Technology

Part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration