The extent of surface destabilization of $\text{ZrO}_2$ - 8 wt % $\text{Y}_2\text{O}_3$ ceramic disks was determined after exposure to molten salt mixtures of sodium sulfate containing up to 15 mole\% sodium metavanadate ($\text{Na}_3\text{V}_2\text{O}_8$) at 1173 K. The ceramic surface was observed to transform from the cubic/tetragonal to monoclinic phase, concurrent with chemical changes in the molten salt layer in contact with the ceramic. Significant attack rates were observed in both pure sulfate and metavanadate-sulfate melts. The rate of attack was found to be quite sensitive to the mole fraction of vanadate in the molten salt solution and the partial pressure of sulfur trioxide ($1\times10^6$ to $1\times10^{-3}$ atm) in equilibrium with the salt melt. The observed parabolic rate of attack is interpreted to be caused by a reaction controlled by diffusion in the salt that penetrates into the porous layer formed by the destabilization. The parabolic rate constant in mixed sodium metavanadate - sodium sulfate melts was found to be proportional to the $\text{SO}_3$ partial pressure and the square of the metavanadate concentration. In-situ Raman spectroscopic measurements allowed simultaneous observations of the ceramic phases and salt chemistry during the attack process.

1 This work supported by the U.S. Dept. of Energy, Office of Basic Energy Sciences.
Table I
Exposure Environment Composition
( percent )

Initial Gas Composition  Equilibrium Composition at 1173 K

<table>
<thead>
<tr>
<th></th>
<th>O₂</th>
<th>SO₂</th>
<th>O₂</th>
<th>SO₂</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>10</td>
<td>90</td>
<td>7.7</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>0.2%</td>
<td>1</td>
<td>99</td>
<td>.76</td>
<td>.24</td>
<td></td>
</tr>
<tr>
<td>1.0%</td>
<td>0.1</td>
<td>99.9</td>
<td>7.6x10^{-2}</td>
<td>2.5x10^{-2}</td>
<td></td>
</tr>
<tr>
<td>2.0%</td>
<td>0.015</td>
<td>99.99</td>
<td>1.1x10^{-2}</td>
<td>3.7x10^{-3}</td>
<td></td>
</tr>
</tbody>
</table>

Table II
Parabolic Rate Constants
( P_{SO₃} = 2.4 \times 10^{-3} )

NaV03 Concentration  Parabolic Rate Constant
( mole percent )  ( cm²/sec )

|      | 1x10^{-11} |
|------| 1x10^{-11} |
| 0.0  | 1.7x10^{-10} |
| 0.2% | 5.4x10^{-10} |
| 1.0% | 1.5x10^{-9} |
**RAMAN EFFECT**

\[ \omega_1 - \omega_s = \omega_{\text{VIB}} \]

**Figure 1.**

**RAMAN BACKSCATTERING CONFIGURATION**

**Figure 2.**

**RAMAN ADVANTAGES**

1. **NON-PERTURBING**
2. **IN SITU**
3. **QUANTITATIVE CHEMICAL COMPOUND IDENTIFICATION**
4. **SENSITIVE TO LATTICE SYMMETRY**
5. **LATERAL RESOLUTION - 1 \( \mu \)m**
6. **DEPTH RESOLUTION - (100 \( \AA \) - 100 \( \mu \)m)**
7. **GAS ENVIRONMENT CHARACTERIZATION**
8. **SAMPLE/GAS TEMPERATURE**
9. **TEMPORAL RESOLUTION (ms - hs)**

**Figure 3.**
Experimental Procedure

- Stabilized zirconia ceramics immersed in sulfate-vanadate melts contained in platinum crucibles.
- Temperature, sulfur dioxide and sulfur trioxide content varied.
- Post-exposure analysis by electron microscopy, electron microprobe and Raman spectroscopy.
\[
\text{ZrO}_2 - 8 \text{ wt\% } \text{Y}_2\text{O}_3
\]

**Exposure:** 900°C

Pure Na\(_2\)V\(_2\)O\(_6\)

10 min.

1 hr.

Figure 6.
ZrO$_2$ - 8wt\% Y$_2$O$_3$
NaVO$_3$ 24hr 700°C

Figure 9.
ZrO$_2$ - 8 wt% Y$_2$O$_3$

Exposure: 900°C 24 hr.

2 mol% Na$_2$V$_2$O$_6$ in Na$_2$SO$_4$

Exposed in air

Exposed to 93% SO$_2$ 5% SO$_3$ 2% O$_2$

Figure 12.
Figure 13.

Figure 14.
YTTRIUM LEACHING REACTIONS

- in sulfate melts

\[ \text{Y}_2\text{O}_3 + 3 \text{ SO}_3 \rightleftharpoons 2 \text{Y}^{+3} + 3 \text{ SO}_4^{-2} \]

- in sulfate-vanadate melts

\[ \text{Y}_2\text{O}_3 + \text{V}_2\text{O}_5 \rightleftharpoons 2 \text{Y}^{+3} + 2 \text{ VO}_4^{-3} \]

Figure 19.

\[ \text{SO}_2 + 1/2 \text{ O}_2 \rightleftharpoons \text{SO}_3 \]
\[ \text{Na}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{O} + \text{SO}_3 \]

\[ a_{\text{Na}_2\text{O}} = \frac{K_2}{p_{\text{SO}_3}} a_{\text{Na}_2\text{SO}_4} \]

\[ 2 \text{NaVO}_3 \rightleftharpoons \text{Na}_2\text{O} + \text{V}_2\text{O}_5 \]

\[ a_{\text{V}_2\text{O}_5} = \frac{K_3 a_{\text{NaVO}_3}^2}{a_{\text{Na}_2\text{O}}} = \frac{K_3 p_{\text{SO}_3} a_{\text{NaVO}_3}^2}{K_2 a_{\text{Na}_2\text{SO}_4}} \]

Figure 20.
1173 K 1% SO\textsubscript{2} in O\textsubscript{2}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{zro2_15wt_percent_mgo.png}
\caption{ZrO\textsubscript{2} - 1.5 wt\% MgO}
\end{figure}

96 hr

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{zro2_8wt_percent_y2o3.png}
\caption{ZrO\textsubscript{2} - 8 wt\% Y\textsubscript{2}O\textsubscript{3}}
\end{figure}

164 hr

\textit{Figure 22.}
Summary

- Attack of zirconia ceramics is sensitive to sodium metavanadate concentration, and thus to vanadium impurity level in fuel.

- The attack is also sensitive to sulfur dioxide content of the environment.

- The attack follows parabolic kinetics and is proportional to the square root of the sulfur trioxide partial pressure.

Figure 23.