

# Fission product behavior in high-temperature water: CsI vs MoO<sub>4</sub>

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**Abstract.** Fission product behaviors of Cs, a major element released in a severe nuclear accident, still remain unclear. The question frequently addressed is whether Cs released will be in the form of Cs<sub>2</sub>MoO<sub>4</sub> or CsOH. This is a challenging issue since it has been demonstrated that the reaction between Cs<sub>2</sub>MoO<sub>4</sub> and water leading to CsOH production is thermodynamically favored. The present research aims at investigation of CsOH generation through this chemical channel. A high-temperature setup with a flow system based on the cooling system of a water-cooled nuclear reactor has been assembled. The reaction between aqueous solutions of CsI and Na<sub>2</sub>MoO<sub>4</sub> in a high-corrosion-resistant hot cell (Hastelloy) has been studied up to 80 °C in deoxygenated system. The products have been characterized using FTIR and XRD. The results have shown that there is no reaction between CsI and Na<sub>2</sub>MoO<sub>4</sub> under the experimental conditions.

## 1. Introduction

The information on severe nuclear accident source terms is of particularly importance as it is strongly required for risk assessment and emergency response. Release of radionuclides from an overheated fuel element during a severe nuclear accident starts from gaseous evolution of radionuclides within fuel. The volatile species then migrate to cladding wall and escape through damaged parts of the cladding into the containment, coolant and finally environment[1]. The release behavior of radioactive materials and the subsequent interactions among the materials themselves and with the environments are highly complicated. Despite intensive studies for many decades, nuclear scientists and engineers have not been able to understand these matters entirely. As of now, the studies of source term have focused mainly on radioactive nuclide of inert gases and iodine. However, based on the recent data available after the nuclear accidents at Chernobyl and Fukushima Daiichi, radioactive nuclide Cs-137 whose half-life is 30 years is the only species determining the long-term impacts of the accidents[2].

It is believed that the majority of Cs released would stay in the forms of CsI and CsOH. Therefore, source term studies of Cs have mostly dedicated to the behaviors of the two compounds[3-8].

The well-known Phebus experiments demonstrated that Cs would firstly react with I or Mo to form CsI and Cs<sub>2</sub>MoO<sub>4</sub>, respectively[9]. Based on thermodynamics calculations, in contact with water the latter species tends to further react with water molecules producing CsOH[10]. Unfortunately, CsOH formation through this chemical channel has not been confirmed by any laboratory studies. Therefore, investigation of Cs behaviors in contact with water under nuclear accident conditions is critical.

The present research has focused on the investigation of Cs<sub>2</sub>MoO<sub>4</sub> and CsOH formations from the reaction of CsI and MoO<sub>4</sub>-containing species (Na<sub>2</sub>MoO<sub>4</sub>) under high-temperature condition. A high-

temperature setup with a flow system has been developed, the details of which and products characterization will be discussed.

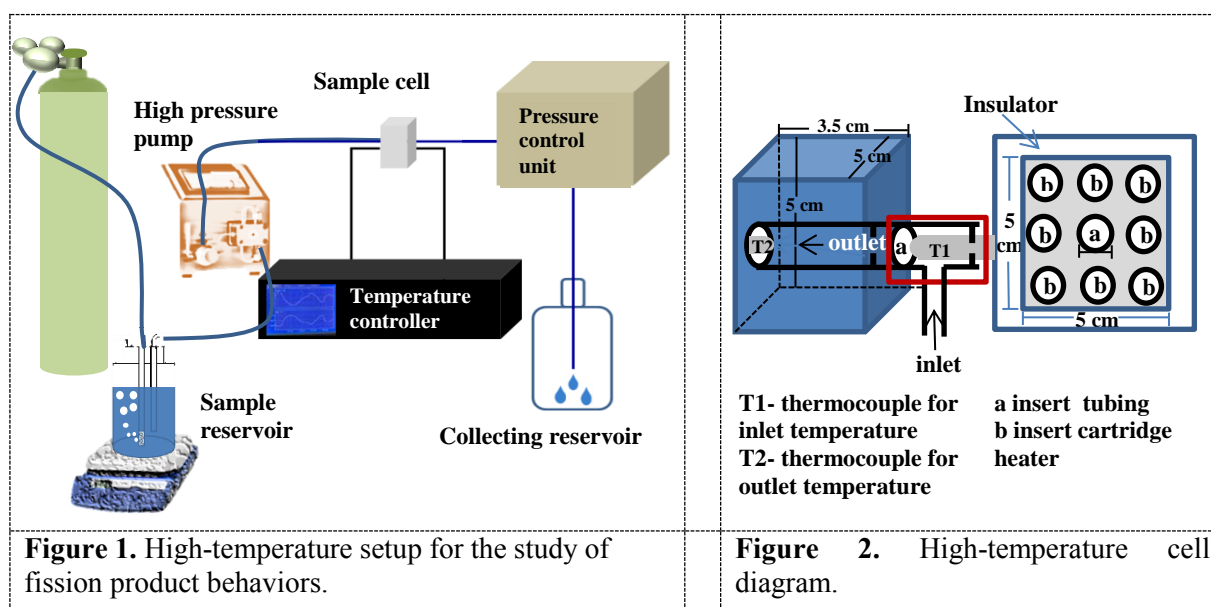
## 2. Experimental Section

### 2.1. Experimental setup

The high-temperature setup consists of a sample reservoir, a high pressure pump, a sample cell, temperature and pressure control units and a collecting reservoir as shown in Figure 1. The details for the major components are as follows.

**2.1.1. Sample reservoir and high-pressure pump.** The sample reservoir was made of high quality glass with volume scale and a custom-made cap. The cap was equipped with 3 inserts for gas inlet (purging), gas outlet (venting) and sample outlet. To minimize oxygen level, the sample solutions were purged with Ar or N<sub>2</sub>. The liquid samples from the container were pumped through stainless steel tubing to the hot cell using a high-pressure pump. The high-pressure pump used in this study was a High Performance Liquid Chromatography (HPLC) pump with dual-piston running at maximum pressure of 400 bars.

**2.1.2. High-temperature cell.** The custom-made hot cell was made of Hastelloy, a nickel based alloy with high corrosion resistant properties. The cell was insulated from the environment with calcium silicate board and coupled with a number of cartridge heaters and a pair of k-type thermocouples. To ensure all area of the sample cell was heated uniformly, 8 cartridge heaters were all inserted into the b-holes drilled and reamed on the surface of the Hastelloy bar as demonstrated in Figure 2. A Hastelloy tube with the inside diameter (ID) of 6 mm and the length of 3.5 cm was inserted into a-hole in the center of the bar making the cell volume of 3.96 ml.



**2.1.3. Temperature and pressure control units.** The voltage supplying to the heaters was controlled by a PID (Proportional-Integral-Derivative) temperature controller based on the feedback provided by the k-type thermocouples. PID controlling system is based on the combination of 3 correcting terms: proportional, integral and derivative. The proportional term ensures that the system will supply power output that minimizes the temperature difference between the setpoint and the system state, whereas the other terms are additional adjustments[11]. In order to liquefy the samples at high temperature, the

flow system needed to be pressurized. The pressure of the system was regulated by a back pressure regulator. A back pressure regulator controls the pressure of the system by closing or opening the valve in response to its spring force setting. When the inlet pressure exceeds the spring force setting, the valve opens and when the inlet pressure is lower than the spring force setting, the valve closes[12].

The flow system components were assembled. After the cartridge heaters, thermocouples and insulator were installed on the hot cell, PID parameters for temperature controlling were set up. Testing with water flow was done at flow rate 3 ml/min in a temperature range of 25 °C – 90 °C. Time taken to raise the temperature to 50 °C and 90 °C were about 5 min and 20 min, respectively (including stabilization).

## 2.2. Chemicals and experimental conditions

All chemicals were used as received without further purification. CsI (99.9%) and Na<sub>2</sub>MoO<sub>4</sub> (dihydrate, analytical grade) were purchased from Sigma-Aldrich and Merck Millipore, respectively. Deionized water (18.2 MΩ-cm resistivity) with total organic carbon < 1ppb from Thermo Scientific was used throughout the experiment.

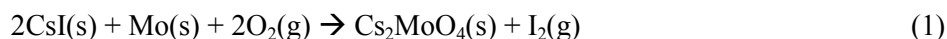
The fission product behavior study was carried out using an HPLC pump. The pump was used to deliver the mixtures of aqueous CsI and Na<sub>2</sub>MoO<sub>4</sub> (Ar or N<sub>2</sub> saturated) at different concentrations (0.1 mM – 3.0 mM) to the hot cell at flow rate 3 ml/min. The cell temperature was elevated with the maximum temperature of 80 °C at atmospheric pressure. After passing through the hot cell, the samples were then collected at the collecting reservoir. The liquid samples collected were finally evaporated at low temperature (T<50 °C) until dry before storing in a desiccator.

## 2.3. Characterization

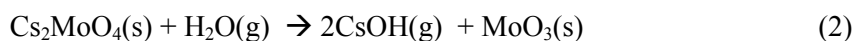
The solid left from evaporation was characterized using a Bruker TENSOR 27 Fourier Transform Infrared (FTIR) spectrometer and a Bruker D8 Advance X-ray Diffractometer (XRD) ( $\lambda = 1.54056 \text{ \AA}$ , 30 mA, 30 kV).

## 3. Results and Discussion

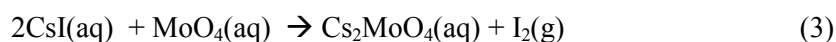
Cs<sub>2</sub>MoO<sub>4</sub> and CsOH formation is the subject of interest in our study. According to the literature, Cs<sub>2</sub>MoO<sub>4</sub> is highly stable at room temperature, whereas CsOH is particularly active when dissolving in water. Based on the elemental concentration ratio (Cs/I) and concentration of free iodine measured in a high temperature study of CsI and MoO<sub>3</sub> mixture, it was also proposed that Cs<sub>2</sub>MoO<sub>4</sub> might form via Reaction (1)[5].



Stable solid Cs<sub>2</sub>MoO<sub>4</sub> when contacts with water molecules under high temperature condition in steam can lead to CsOH production which can be explained by the following reaction[9]:



However, Reaction 2 was based on solely thermodynamics calculations without any laboratory confirmation. Our experiment therefore was designed to investigate the possibility of this important step of fission product behavior. CsI and Na<sub>2</sub>MoO<sub>4</sub> were selected as the starting compounds with the assumption that Na<sup>+</sup> ions play no role in this system. The summarized chemical mechanism designed for the Cs<sub>2</sub>MoO<sub>4</sub> formation shown in Reaction (3). After Cs<sub>2</sub>MoO<sub>4</sub> was produced, the further reaction of water with this compound as in Reaction 2 was expected in our chemical system.

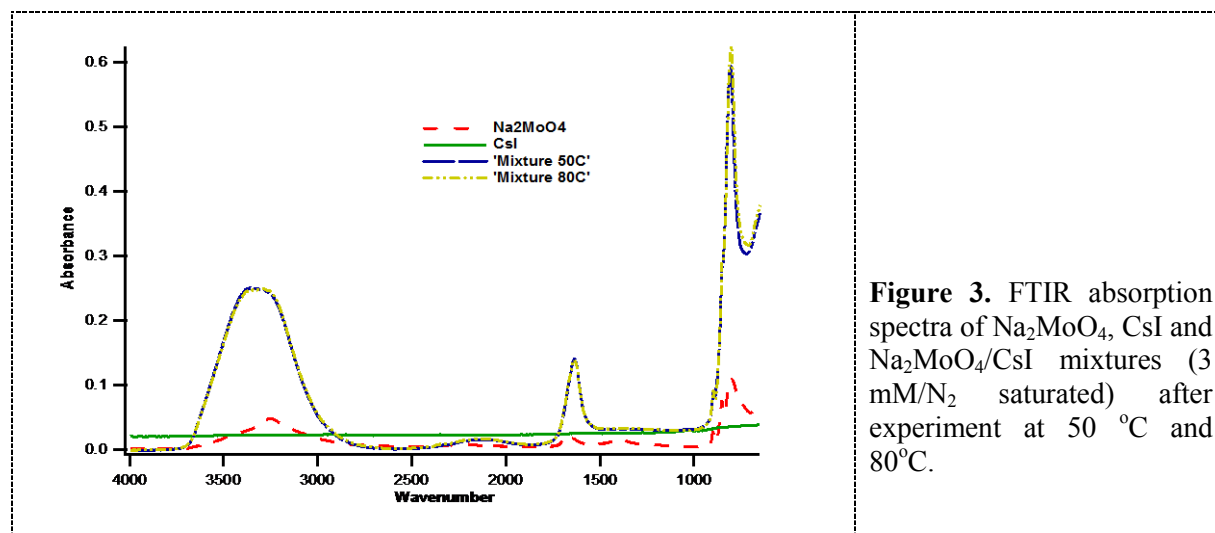


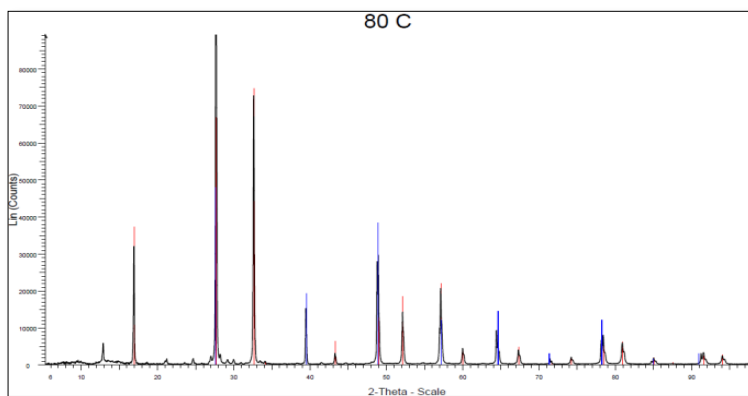
The experiments with mixtures of CsI and Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (0.1 mM – 3 mM) were performed at flow rate 3 ml/min at 25 °C - 80 °C. The flow rate was chosen to ensure that at least 1 min dwell time of the liquid sample in the hot cell was given. At the concentration range of 0.1 mM – 3 mM, both

reactants were found to dissolve completely in water resulting in homogeneous solutions with clear color. The physical appearance of the solutions remained the same even after experiment.

The liquid samples from the experiments at 50 °C and 80 °C were evaporated at low temperature ( $T < 50^\circ\text{C}$ ). Subsequently, the solid samples left from evaporation were characterized using FTIR and XRD. Figure 3. shows FTIR absorption spectra of  $\text{Na}_2\text{MoO}_4/\text{CsI}$  mixtures (3 mM/ $\text{N}_2$  saturated) after experiment at 50 °C and 80 °C in comparison with those of  $\text{Na}_2\text{MoO}_4$  and CsI reactants. It can be seen that  $\text{Na}_2\text{MoO}_4$  gives a broad peak at wavenumber around 3200 – 3400  $\text{cm}^{-1}$  and sharp peaks at 1680 and 820  $\text{cm}^{-1}$ . These IR characteristics of  $\text{Na}_2\text{MoO}_4$  are corresponding to the results previously observed[13]. On the other hand, it is obvious that there are no IR-active modes of CsI in this region. The experimental results from  $\text{Na}_2\text{MoO}_4/\text{CsI}$  mixtures at both temperatures (50 °C and 80 °C) suggest that  $\text{Na}_2\text{MoO}_4$  is still present in the post-experiment samples. Higher absorbance in the post-experiment samples stems from the fact that the solid samples left from evaporation were in slurry, thus enhancing deposition of the samples on the ZnSe single crystal of FTIR spectrometer while analyzing. In addition, the peaks at 830 and 893  $\text{cm}^{-1}$  which are corresponding to metal-oxygen stretching modes of  $\text{Cs}_2\text{MoO}_4$ [14]are not observed. There is also no observation of broad O-H stretching band around 1500 – 2200  $\text{cm}^{-1}$  of OH group from CsOH[15]. The results from further characterization by XRD at 50 °C and 80 °C are similar. The XRD pattern of the solid sample after the experiment performed at temperature 80 °C is given in Figure 4. The XRD patterns from both experiments indicate that the post-experiment samples contain CsI and  $\text{Na}_2\text{MoO}_4$  with no trace of  $\text{Cs}_2\text{MoO}_4$  and CsOH. The information revealed by XRD is in good agreement with that from the FTIR measurements.

All evidence provided by the present study strongly supports that  $\text{Cs}_2\text{MoO}_4$  and CsOH productions from Reactions (3) and (2) do not occur at temperatures up to 80 °C. This information confirms that when CsI and molybdenum oxide together leaking into the region at this range of temperature both compounds still remain in the original forms.





**Figure 4.** XRD pattern of the solid sample from the experiment performed at temperature 80 °C (N<sub>2</sub>-saturated).

#### 4. Conclusion

A high-temperature high-pressure setup for investigation of fission product behavior has been designed and assembled. The flow system was composed of a reactant reservoir, an HPLC pump, a hot cell and a collecting reservoir. The preliminary experiments on fission production behaviors of CsI and MoO<sub>4</sub> were performed at temperatures up to 80 °C at atmospheric pressure. The samples from 50 °C and 80 °C were characterized using FTIR and XRD. The results from both techniques indicate that under the experimental conditions CsI and MoO<sub>4</sub> remain in their original forms.

#### References

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