Numerical simulation of the interaction of uranium hexafluoride with methane and oxygen in turbulent flame

P A Popov¹, V A Talalov², D S Pashkevich³, P S Kambur², V V Kapustin², A R Zimin² and Yu I Alekseev³

¹ Ioffe Institute, Saint-Petersburg, Russia
² Peter the Great St. Petersburg Polytechnic University, Saint Petersburg, Russia
³ New Chemical Products LLC, Saint Petersburg, Russia

E-mail: pavel.popov@mail.ioffe.ru

Abstract. Model of the uranium hexafluoride conversion in a methane-oxygen turbulent diffusion flame is presented. Model of the weighted sum of grey gases was used to calculate the absorption coefficient of mixture of uranium dioxide particles and carbon dioxide. Radiation heat transfer model was calibrated using available experimental data. A good agreement was obtained between the simulation results and experimental data.

1. Introduction

Uranium hexafluoride is a uranium enrichment process by-product in the production cycle of nuclear fuel. Currently, up to 2 million tons of $UF_6$ are accumulated in the world, including up to 1 million tons in Russia. This compound is volatile, prone to hydrolysis, belongs to hazard class 1 and poses a threat to the environment. One of the promising methods of uranium hexafluoride utilization is a conversion in combustion mode with hydrogen-containing fuel and oxygen. The products of reaction are hydrogen fluoride and uranium oxides [1], for example:

$UF_6 (gas) + 3H_2(gas) + O_2(gas) \rightarrow UO_2(solid) + 6HF(gas) + 583kJ$  \hspace{1cm} (1)

$UF_6 (gas) + 1.5CH_4(gas) + 2.5O_2(gas) \rightarrow UO_2(solid) + 6HF(gas) + 1.5CO_2(gas) + 1054kJ$  \hspace{1cm} (2)

The adiabatic temperature of the products of these reactions is $T_1 = 2540K$ and $T_2 = 3280K$. Resulting hydrogen fluoride can be used in the nuclear fuel cycle to produce natural uranium fluorides. Uranium dioxide is convenient for long-term storage, since very low vapor pressure in a wide temperature range, and also it does not dissolve in water.

Physical experiments, especially on pilot-scale facilities are very expensive and complex research method. Therefore, it is advisable to use numerical simulation of processes (1) or (2). This paper describes the model of uranium hexafluoride conversion in a methane-oxygen turbulent diffusion flame (2), where only essential thermophysical and hydrodynamic processes are taken into account.

2. Experimental facility

Processes (1) and (2) were experimentally investigated in a pilot-scale experimental facility with a “tunnel burner” type reactor. It was shown that the main reaction products are hydrogen fluoride and uranium oxides [2]. The reactor is a vertical pipe with inner radius of 71 mm and length of 2650 mm. The channels for injecting reagents are axially located on the reactor’s upper flange. The radius of the
axial channel is 2 mm, the inner radius of the annular channel is 3 mm, and the outer 4 mm. Hydrogen-containing fuel was injected through the axial channel, oxygen and uranium hexafluoride were injected through the circular channel. The opposite end of the reactor is connected to a heat exchanger for cooling the gaseous reaction products and to a collector of solid particles of uranium dioxide. Thermocouples are installed inside the reactor close to and at some distance from the flame. The outer surface of the reactor is cooled by water. The heat transfer coefficient from water to the outer wall was significantly higher than the heat transfer coefficient from gas flow to the inner wall of the reactor. This made it possible to maintain a constant temperature of the reactor wall.

Methane is the most commercially available hydrogen-containing fuel, so the process (2) is considered further. Table 1 shows the mass and mole flow rate of reagents for one of the experiments.

| Reagent | Mass flow rate, kg/s | Mole flow rate, mole/s | Mole ratio |
|---------|----------------------|------------------------|------------|
| UF₆     | 3.0 \cdot 10^{-3}    | 8.5 \cdot 10^{-3}      | 1          |
| CH₄     | 2.2 \cdot 10^{-4}    | 1.4 \cdot 10^{-2}      | 1.61       |
| O₂      | 8.0 \cdot 10^{-4}    | 2.5 \cdot 10^{-2}      | 2.93       |

3. Mathematical model
A detailed simulation of thermophysical and chemical processes in the flame (2) is impossible due to the lack of details of reaction kinetics. Therefore, it considers only a global chemical mechanism. In the model, all reagents and reaction products are considered as gaseous. The turbulent flow of the mixture is modeled using the k – ω SST model. Turbulent diffusion combustion is simulated using the eddy dissipation model [3], where the reaction rate is limited only by the turbulent diffusion of unmixed reagents, and the chemical reaction itself occurs “instantly”. It is also assumed that water vapor generated in flame interacts with uranium hexafluoride to form uranium dioxide and hydrogen fluoride. This assumption follows from the comparison of experimental results and thermodynamic calculations [1, 2].

Since there is an excess of oxygen in the reagent mixture, the model does not take into account the possibility of soot formation. The thermal effect of the reaction is calculated using the formation enthalpies and heat capacity value of each of the reactants and reaction products [4]. The density of all components except the uranium dioxide is calculated by the equation of state of ideal gas. It is assumed that the solid particles of uranium dioxide are homogeneous and their density is constant \( \rho_{UO₂} = 10500 \text{ kg/m}^3 \). The mixture density is calculated as the sum of the densities of all components with their weight coefficient equal to their mass fraction. The heat capacity depends on the temperature [4]. The coefficients of molecular thermal conductivity and diffusion are considered negligible compared to turbulent.

Radiation heat transfer is calculated using the discrete ordinates method. The absorption coefficient of the mixture is calculated using a weighted sum of gray gas model [5]. Since it is assumed that water vapor instantly reacts with uranium hexafluoride, its effect on radiation heat transfer is not considered. Also, the absorption of radiation by uranium hexafluoride is not taken into account, since it is negligible at temperatures \( T \approx 2000 \text{ K} \) [6]. Only the contribution of carbon dioxide and particles of uranium dioxide is taken into account. The model assumes that the absorption and emission of radiation by uranium dioxide particles occurs in the same way as soot particles. Since their average volume concentration \( n_{UO₂} \approx 5 \cdot 10^{-5} \) exceeds the typical values of the soot concentration in the hydrocarbon flame \( n_{soot} \approx 10^{-7} \div 10^{-5} \), and their emissivity is less, the empirical constant in the local absorption coefficient \( k_{s,j} = f_{α} k_{fus,i} \) [5] requires adjustment for matching the calculated temperature fields and those measured in the experiment.

From the experiment it is known that the minimum diameter of the solid particles formed in the reaction is \( \approx 1 \mu m \) [2]. This allows us to consider their temperature equal to the local gas temperature, and the relative velocity equal to zero. Larger particles are probably formed as a result of collisions in the circulation region inside the reactor and in the collector outside the reactor. The particle
temperature in the circulation zone is lower and their contribution to the heat transfer by radiation is significantly reduced.

Table 2 shows the corresponding boundary conditions for the simulation. The Reynolds number calculated from the methane flow parameters is \( Re = 6000 \), which corresponds to a turbulent flow formed directly at the axial channel exit [7]. The simulation was performed in ANSYS FLUENT.

**Table 2.** Boundary conditions.

| Component         | Experiment | Simulation |
|-------------------|------------|------------|
| Axial channel     | \( V_x = 31.6 \text{ m/s}, V_r = 0, T = 353 \text{ K}, Y_{CH_4} = 1 \) | \( V_x = 0, V_r = 0, T = 353 \text{ K}, \varepsilon = 0.8 \) |
| Circular channel  | \( V_x = 44.3 \text{ m/s}, V_r = 0, T = 353 \text{ K}, Y_{O_2} = 0.21, Y_{UF_6} = 0.79 \) | |

Since the geometry of the reactor has axial symmetry, the simulation is carried out in a two-dimensional axisymmetric formulation. The length of the investigated initial section of the reactor is 1200 \( mm \). The number of cells in the longitudinal direction \( N_x = 1000 \), in the radial direction \( N_r = 800 \) with concentrating to the reagent channels. The minimum cell size is \( \Delta x = 1.5 \cdot 10^{-4} \text{ m} \) and \( \Delta r = 2.5 \cdot 10^{-5} \text{ m} \). The near-wall cell size was selected based on the condition \( y^+ \approx 1 \).

4. Results

Table 3 shows the mole ratio of the mixture components at the reactor outlet obtained in experiment and in simulation. The presence of \( CH_4 \) and \( O_2 \) in the products and the absence of \( H_2O \) is a result of chosen chemical reaction model. Good agreement is observed for the remaining components of the mixture.

**Table 3.** Mole ratio of the mixture components at the reactor outlet.

| Component | Experiment | Simulation |
|-----------|------------|------------|
| \( UF_6 \) | 0          | 0          |
| \( CH_4 \) | 0          | 0.112      |
| \( O_2 \)  | 0.08       | 0.443      |
| \( UO_2 \) | 0.74 \( UO_2 \) + 0.21 \( UO_2 \text{St} \) | 0.995 |
| \( HF \)   | 5.8        | 5.97       |
| \( CO_2 \) | 1.6        | 1.49       |
| \( H_2O \) | 0.3        | –          |

Original model of the weighted sum of grey gases are suitable to calculate the absorption coefficient of soot particles, but in this model it is used to calculate the absorption coefficient of uranium dioxide particles. Therefore, a series of additional calculations was carried out with different coefficients \( \alpha \) to determine the energy loss of the flow due to radiation (Table 4). Good agreement between the temperatures obtained in the experiment and calculation is observed at \( \alpha \approx 0.001 - 0.1 \).

**Table 4.** Effect of radiation energy loss by uranium dioxide particles due to on the flow temperature.

| Point coordinates | \( \alpha = 0.001 \) | \( \alpha = 0.01 \) | \( \alpha = 0.1 \) | \( \alpha = 1 \) | Experiment |
|-------------------|----------------------|----------------------|----------------------|----------------------|------------|
| \( x = 55 \text{ mm} \) \( r = 40 \text{ mm} \) | 871 \text{ K} | 849 \text{ K} | 813 \text{ K} | 716 \text{ K} | 823 – 1043 \text{ K} |
| \( x = 55 \text{ mm} \) \( r = 70 \text{ mm} \) | 440 \text{ K} | 436 \text{ K} | 431 \text{ K} | 421 \text{ K} | 463 \text{ K} |
| \( x = 1100 \text{ mm} \) \( r = 10 \text{ mm} \) | 566 \text{ K} | 557 \text{ K} | 499 \text{ K} | 420 \text{ K} | 523 – 593 \text{ K} |
| \( x = 1100 \text{ mm} \) \( r = 20 \text{ mm} \) | 570 \text{ K} | 560 \text{ K} | 501 \text{ K} | 419 \text{ K} | 523 – 593 \text{ K} |

Table 5 shows the volume averaged emissivity and the absorption coefficient of the components for various values of \( \alpha \). In [8], for a wide spectral range, the value \( \varepsilon_{UO_2} = 0.82 \) is recommended at
temperature $T = 1000 \, K$. Thus, the agreement of the temperatures in simulation and measured in the experiment, as well as the emissivity correlation confirms the correctness of the used assumptions. The following results were obtained at $\alpha = 0.1$.

| Parameter | $\alpha = 0.001$ | $\alpha = 0.01$ | $\alpha = 0.1$ | $\alpha = 1$ |
|-----------|------------------|------------------|----------------|---------------|
| $\varepsilon_{CO_2}$ | 0.06 | 0.06 | 0.06 | 0.06 |
| $\varepsilon_{UO_2}$ | 0.10 | 0.10 | 0.59 | 0.99 |
| $\varepsilon_{mix}$ | 0.06 | 0.08 | 0.18 | 0.70 |
| $k_{CO_2}$ $1/m$ | 0.51 | 0.51 | 0.50 | 0.49 |
| $k_{UO_2}$ $1/m$ | 0.08 | 0.80 | 7.10 | 44.83 |
| $k_{mix}$ $1/m$ | 0.52 | 0.61 | 1.53 | 9.39 |

Table 5. The volume averaged emissivity and the mixture components absorption coefficient for various values of $\alpha$.

Figure 1 shows the calculated stationary fields of temperature, absorption coefficient, velocity magnitude and stream function. It can be seen that the flame length and the jet flow region approximately equal 0.4 m. Here is also the boundary of the circulation flow region, which stabilizes the flame and in which, apparently, there is an active interaction of solid particles with each other with the formation of clusters. The maximum temperature of the reaction products $T = 2294 \, K$ is close to the results of a thermodynamic calculation $T = 2082 \, K$ [1].

Figure 2 shows the distribution of the total and radiation heat flux to the inner surface of the reactor. It can be seen that the main heating occurs in the flame area. The average total heat flux is $q_w \approx 16 \, kW/m^2$. A close value $q_w \approx 17 - 22 \, kW/m^2$ was obtained in the experiment on the recorded water temperature difference and mass flow rate in the cooling system.
5. Conclusion

The simplified model of the uranium hexafluoride conversion in a methane-oxygen turbulent diffusion flame is presented. The model of the weighted sum of grey gases was used to calculate the absorption coefficient of uranium dioxide particles and it was calibrated using available experimental data. The calculated volume averaged absorption coefficient of uranium dioxide close to the published data. Good agreement of calculated and measured temperature in the flame region and at the outlet of the reactor was obtained, as well as the heat flux to the inner wall of the reactor.

Acknowledgement

This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation No. 05.608.21.0277, project identification number RFMEFI60819X0277.

References

[1] Pashkevich D S, Zimin A R, Kapustin V V and Petrov V B 2020 J. Eng. Thermophys. (in press)
[2] Pashkevich D S, Alekseev Yu I, Muhortov D A, Kambur P S, Petrov V B, Bazhenov D A, Zimin A R and Kapustin V V 2020 J. Eng. Thermophys. (in press)
[3] Magnussen B F and Hjertager B H 1977 Proc. of the Comb. Inst. vol 16(1) p 719
[4] Glushko V P and Gurvich L V 1979 Thermodynamic properties of individual substances (Moscow: Nauka) p 560
[5] Cassol F, Brittes R, Franca F H R and Ezekoye O A 2014 Int. J. Heat Mass Transf. 79 796–806
[6] Lappo G B and Lomakin B N 1996 High Temp. 34 (4) 525–9
[7] Lemanov V V, Terekhov V I, Sharov K A and Shumeiko A A 2013 Tech. Phys. Lett. 39 421–3
[8] Fink J K 2000 J. Nucl. Mater. 279 (1) 1–18

Figure 2. Distribution of the total (black curve) and radiation heat flux (red curve) to the inner wall of the reactor.