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Mathematical Modelling of MNUP-Fuel Production by the Carbothermic Synthesis Process for Fast Neutron Reactors

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The studying of the obtaining nitride fuel technology by the carbothermic synthesis is a result of this work. The developed model of the carbothermic synthesis furnace for mixed nitride uranium-plutonium fuel obtaining allows getting the most important parameters of the facility, such as the composition of the gas atmosphere, pressure, temperature and composition of furnace feed and obtained products. In MATLAB, the numerical modelling of the carbothermic synthesis process was used. This model allows user to monitor the effect of construction parameters of the furnace and control system parameters.

1. Introduction

Work, presented in this paper, were made as a part of project “Breakthrough”. State Atomic Energy Corporation “Rosatom” is a creator of it. One of the project goals is a nuclear fuel cycle closure. This goal could be reached by using fast nuclear reactors with mixed nitride uranium-plutonium fuel (MNUP-fuel). Steps of the fuel cycle are production, enrichment, burning and regeneration (Vilnina et al., 2017). Major goal of this work is to improve effectiveness of MNUP-fuel production. Sub-goals are theory analysis of carbothermal synthesis, mathematical and computer models creation, analysis of this models and automatic control system (ACS) algorithms creation. Carbothermal synthesis (CTS) is one of the major steps in MNUP-fuel production. This is a chemical process, which is a high-temperature calcination of a uranium and plutonium oxide powder mixture with carbon under nitrogen. According to the uranium and plutonium mononitride synthesis technology is envisaged to produce fuel blocks in the moulds to ensure close contact between reagents. Fuel blocks having the cylinder shape with a height of 0.3-0.5 cm and a diameter of 1.8 - 2 cm are heated till 1,650 °C (the working temperature). The heating process is carried out in an argon atmosphere, then the furnace feed is soaked in a nitrogen atmosphere for 22 hours at the working temperature. After that, a nitrogen-hydrogen mixture replaces the current atmosphere and again the furnace feed is soaked at the working temperature for 24 hours. The final stage of synthesis is the obtained products cooling in the argon atmosphere.
The facility for the CTS process is an industrial furnace for the uranium and plutonium nitride synthesis. The furnace, gas-filled electric resistance furnace, is a chamber box with a hermetic horizontal reaction zone. Size of the furnace depends on amount of the furnace feed. There is temperature and pressure ACS for atmosphere in the reaction zone of the furnace. The atmosphere in the furnace is changed, refreshed and cleaned by the gas supply system. Every zone of the CTS facility is isolated for the purpose of having different atmospheres.
The CTS process can be described by the lumped reaction (Bardelle and Warren, 1992):

$$UO_2+PuO_2+2C+N_2= UN+PuN+2CO_2 \quad (1)$$

However, this reaction does not describe chemical reaction in all ways. There are undescribed intermediate and accessory substances of the reaction in fuel blocks and the atmosphere during the synthesis. These substances in atmosphere assume as pollution and they are filtered. Concentration of these substances in fuel blocks are less than one percent so this value is neglected.
There are papers about CTS process and its features like studies of synthesis parameters (Muromura, 1982), investigations of process variables (Lindemer et al., 2015), technology investigations (Yasufumi et al., 1982).

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However, there is lack of information about CTS and furnace models, researches of this subject can improve synthesis effectiveness. Synthesis effectiveness means high quality of the final product and lowest possible energy consumption.

2. Mathematical model

2.1 Foundation of the model

There are demands for mathematical model; the model should describe dynamic of chemical processes and influences of the synthesis parameters. Major synthesis parameters are temperature and atmospheric composition. Defined parameters depend on different parameters of furnace, such as size of the reaction zone; structure of ACS; effectiveness of gas supply system; size of heat exchange surface area and others. Thus, the model should describe influences of the major and minor synthesis parameters on the synthesis results. Quality of synthesis result is a number of transformed elements in the fuel block (Koning et al., 2014).
There are several simplifications and limitations for the model; which are connected with special aspects of the CTS process and the CTS facility:

- Mathematical description includes perfect mixing model for the atmosphere in the reaction zone; which means the same conditions in every part of the atmosphere (concentration, temperature, pressure, etc.)
- Mathematical description includes equilibrium distribution model for chemical elements in fuel blocks
- Mathematical description neglects intermediate and accessory substances of the reaction as was mentioned before
- Mathematical description neglects heat exchange processes with the environment because of multi-layer construction of the furnace
- Reaction zone of the furnace is described as isolated system because of a pressure-proof construction
- Mathematical description includes thermal uniformity for fuel blocks; reasons for that are small size of blocks and long duration of the synthesis

There are some problems with the identification of CTS process as object of automatic control. Major problem is a lack of exploited CTS facilities, which does not allow getting any experimental data about CTS process. Other problems are complexity and lack of knowledge of CTS process. In view of the above, the mathematical model of CTS process is based on:

- Program of CTS technology, which contains set of requirements for getting high quality synthesis result; these requirements are temperature modes, atmosphere parameters, time of synthesis and others
- Known physical principles of the process
- ACS algorithms for temperature and pressure of atmosphere in the furnace

2.2 Structure of the model

A structural diagram of the model is shown in Figure 1. This diagram contains a basic logic of model calculations; also, it has lists of inputs and outputs.

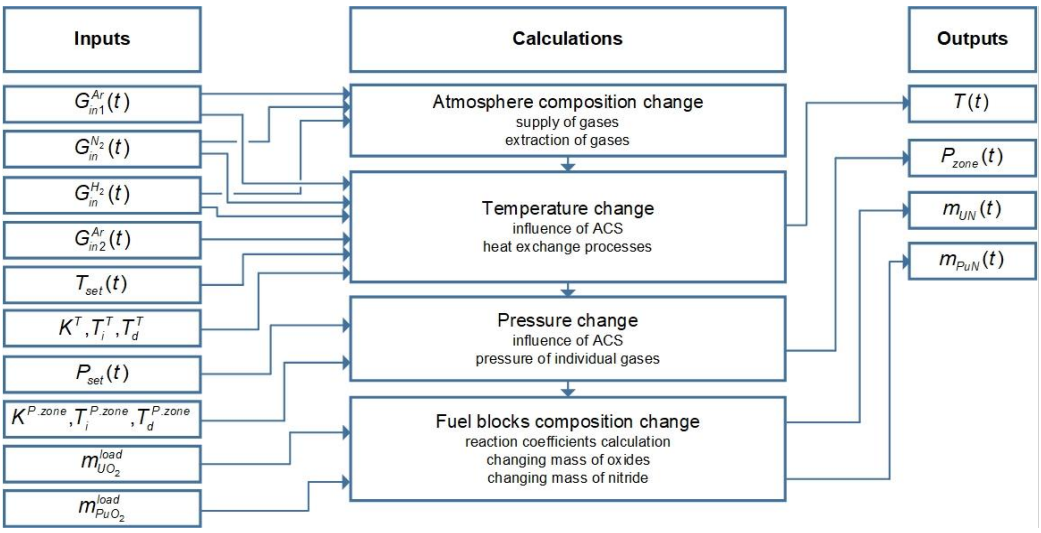


Figure 1: Structural diagram of the CTS furnace model

Model inputs are: $G_{in1}^{Ar}(t)$ – mass flow of argon into the reaction zone; $G_{in2}^{Ar}(t)$ – mass flow of argon into the subzone; $G_{in}^{N_2}(t)$ –mass flow of nitrogen into the reaction zone; $G_{in}^{H_2}(t)$ – mass flow of hydrogen into the reaction zone; $T_{set}(t)$ –set point temperature in the reaction zone for the ACS; K^T, T_i^T, T_d^T – parameters for temperature PID-controller for the ACS; $P_{set}(t)$ – set point pressure in the reaction zone for the ACS; $K^{P.zone}, T_i^{P.zone}, T_d^{P.zone}$ – parameters for pressure PID-controller for the ACS; $m_{UO_2}^{load}$ – total weight of uranium dioxide sent to synthesis; $m_{PuO_2}^{load}$ – total weight of plutonium dioxide sent to synthesis.

Model outputs are $T(t)$ – the furnace atmosphere temperature, $P_{zone}(t)$ – the furnace atmosphere pressure, $m_{UN}(t)$ – synthesized mass of uranium nitride, $m_{PuN}(t)$ – synthesized mass of plutonium nitride.

Thus, an operating mode of the furnace is determined by the number of loaded elements, the mass flow of gases and the ACS parameters. The dynamics of outputs describe the efficiency of the ACS work and synthesis process. Calculations have the following order: the atmosphere composition change due to supply and extraction of gases; temperature change due to heat exchange processes and an influence of ACS; pressure change due to influence of individual gases and an influence of ACS; fuel blocks composition change due to dynamic of the reaction.

The grouping of equations by logical blocks helps to understand steps of calculating and influencing of parameters and input data on these steps.

A complete system of equations for CTS process model contains 23 equations. In this paper, it is impossible to consider them all. Further, in the text only a few of the most important will be described.

A temperature in the reaction zone is calculated by the following equation (2):

$$\frac{dT(t)}{dt} = \frac{W(t) - \alpha \cdot S \cdot (T(t) - T_{\text{cool}}) - (C_{Ar} \cdot (G_{in1}^{Ar}(t) + G_{in2}^{Ar}(t)) + C_{N_2} \cdot G_{in}^{N_2}(t) + C_{H_2} \cdot G_{in}^{H_2}(t)) \cdot (T(t) - T_{\text{gas}})}{C_{\text{zone}} \cdot m_{\text{zone}} + C_{\text{mater}} \cdot m_{mater} + CM_{blocks}(t) + C_{atm.subzone} \cdot m_{\text{atm.subzone}}(t) + CM_{\text{atm.zone}}(t)} \quad (2)$$

In this equation, $T(t)$ – temperature in the reaction zone; α – coefficient of thermal conductivity of the furnace walls; S – surface size of the heat exchange between the furnace and the cooling system; T_{cool} – temperature of the water in the cooling system; T_{gas} – temperature of supply gases; $C_{N_2}, C_{Ar}, C_{H_2}, C_{\text{zone}}, C_{\text{mater}}, C_{atm.subzone}$ – thermal capacities of nitrogen, argon, hydrogen and materials of the furnace; $m_{\text{zone}}, m_{mater}, m_{\text{atm.subzone}}(t)$ – masses of the furnace materials; $CM_{blocks}(t)$ – sum of multiplication of masses and thermal capacities of fuel blocks elements; $CM_{\text{atm.zone}}(t)$ – sum of multiplication of masses and thermal capacities of atmospheric gases.

In the numerator, sources of heat exchange are presented. The first summand represents a power of a heating element, the second summand represents the heat exchange between the reaction zone and the cooling system, the third summand represents the heat exchange between the reaction zone and cool supply gases. The denominator contains objects of the heat exchange process: gases, elements of fuel blocks and reaction zone materials.

The temperature control system in CTS furnace is similar to the one mentioned in list of references (Wei and Weipeng, 2017).

Changes in fuel blocks composition are described by following Eq(3)-(6):

$$T_{reac}(T(t), G_{in}^{N_2}(t)) \cdot \frac{dm_{UO_2}(t)}{dt} + m_{UO_2}(t) = 1 \quad (3)$$

$$T_{reac}(T(t), G_{in}^{N_2}(t)) \cdot \frac{dm_{PuO_2}(t)}{dt} + m_{PuO_2}(t) = 1 \quad (4)$$

$$m_{UN}(t) = \frac{M_{UN}}{M_{UO_2}} \cdot (m_{UO_2}^{load} - m_{UO_2}(t)) \quad (5)$$

$$m_{PuN}(t) = \frac{M_{PuN}}{M_{PuO_2}} \cdot (m_{PuO_2}^{\text{load}} - m_{PuO_2}(t)) \quad (6)$$

In this equations, $T_{reac}(T(t),G_{in}^{N_2}(t))$ – reaction coefficient, which depends on the mass flow rate of nitrogen and the temperature of fuel blocks; $m_{UO_2}(t), m_{PuO_2}(t)$ – masses of uranium dioxide and plutonium dioxide in fuel blocks, respectively; $M_{UN}, M_{UO_2}, M_{PuN}, M_{PuO_2}$ – molal masses of uranium nitride, uranium dioxide, plutonium nitride and plutonium dioxide, respectively; $m_{UN}(t), m_{PuN}(t)$ – masses of synthesized uranium nitride and plutonium nitride, respectively; $m_{UO_2}^{load}, m_{PuO_2}^{load}$ – masses of initial load of uranium dioxide and plutonium dioxide in fuel blocks, respectively.

Equations of chemical transformation dynamic in the CTS process were obtained by approximating the model created by Zababakhin All-Russian Scientific Research Institute of Technical Physics (former VNIIP). The change in the mass of oxides in fuel blocks is represented by differential equations of first order. This means exponential trends in the mass of oxides during synthesis. The change in the mass of nitrides depends on amount of reacted oxides.

The rest of the equations of the model are:

- Two PID controllers for pressure and temperature in the reaction zone, tuned by Hiroi and Terauchi rule (O'Dwyer, 2009)
- Gases mixture pressure calculations (Averill and Eldredge, 2012)
- Individual gases concentrations and mass flow exchanges (Averill and Eldredge, 2012)

3. Simulation experiment

A computer model is the next step in the work. It serves for analysis and visualization of calculation results. The computer model was created by means of MATLAB environment. Differential equations were presented in computer model as recurrence relations, which were transformed by Z-transformation. In the computer model, the approach with lumped parameters is used; early mentioned the perfect mixing model for atmosphere and the thermal uniformity model for fuel blocks already mean same parameters of the process in any point of the reaction zone at any given time of synthesis. A minor advantage of this approach is shorter calculation time of the model.

After creating the computer model, the next step is a simulation experiment. Simulation experiment is an approach of studying physical processes by mathematical modeling. Script of the experiment contains:

- Supplying nitrogen
- Switching on the heating element and heating the reaction zone to 1,650 °C
- First calcination of fuel blocks within 22 hours
- Changing the atmosphere to nitrogen-hydrogen mixture
- Second calcination of fuel blocks within 24 hours
- Shutting down the furnace

Parameters and inputs of the experiment were chosen from standard conditions of the synthesis, which are the same as in a real CTS furnace. Some of these parameters are the size of the furnace, the temperature of gases, materials of the furnace and others. The modeling duration is 165,000 seconds or 46 hours, as it is for a real CTS furnace. Results of the modeling are depicted in Figures 2-6.

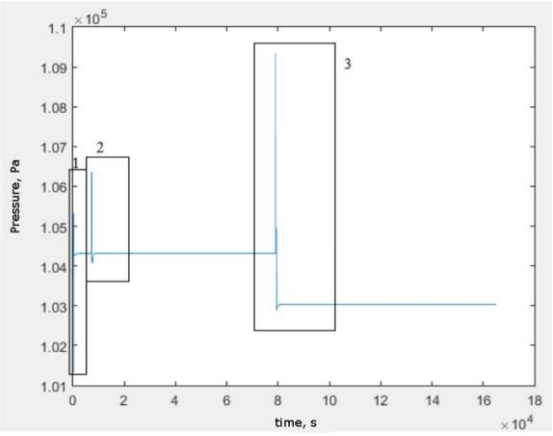
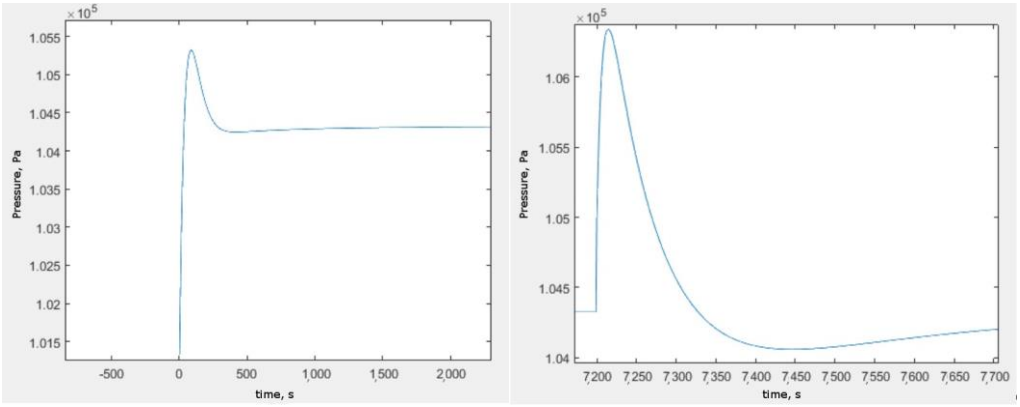


Figure 2: The pressure trend in the reaction zone during synthesis

The pressure changes in the reaction zone due to the ACS influence are depicted in Figure 2. There are several pieces that are worth considering. Pieces 1 and 2 are depicted in Figure 3.



(a) (b)

Figure 3: Piece 1 (a) and Piece 2 (b) of the pressure trend

Figure 3a shows the pressure response on the heating in the reaction zone. There is 500 Pa overcorrection due to ACS reaction. Piece 2 is presented in Figure 3b. It shows the pressure response on the atmosphere changing (from argon to nitrogen). There is 2,000 Pa overcorrection due to the ACS reaction. The pressure is stabilized after the complete change in the atmosphere. Piece 3 is not depicted because of the same overcorrection nature as in piece 2.
Changes in the composition of fuel blocks are shown in Figures 4 and 5.

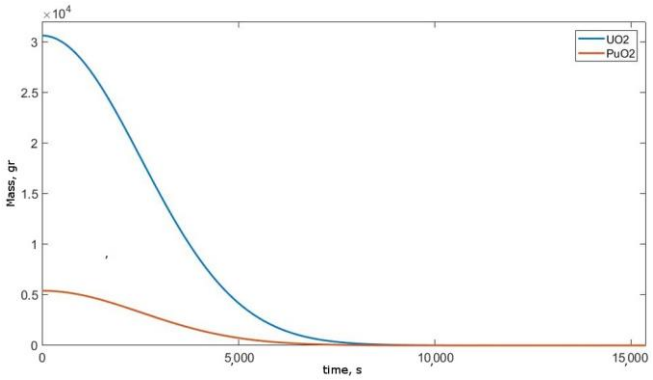


Figure 4: Trends oxides mass in the fuel blocks during synthesis

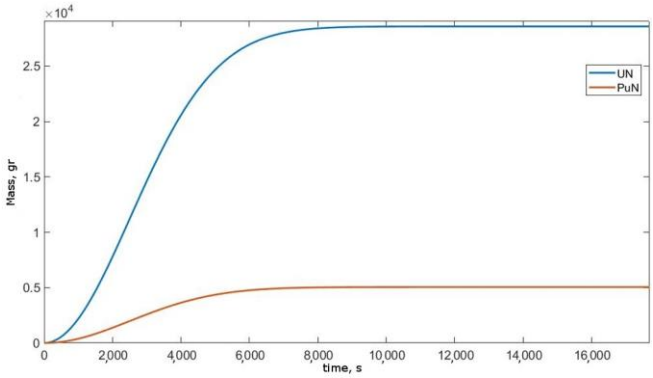


Figure 5: Trends nitrides mass in the fuel blocks during synthesis

Figure 4 shows an exponential decrease in masses of oxides during first 1,000 seconds of synthesis. On the other hand, Figure 5 shows exponential increase of nitrides masses during same period (Butt, Jaques, 2009). The Figures 4 and 5 show that reagents and reaction products are not equal. This is due to undescribed intermediate and accessory substances (Greenhalgh, 1973) of the reaction, as was mentioned before. Figures 4, 5 also show high rate of the synthesis processes, but the CTS technology program requires 46 hours of synthesis to achieve required fuel blocks parameters.

The final step in creating any computer model is experimental verification. However, as was mentioned before, there is a lack of exploited CTS facilities; that fact it does not allow getting any experimental data about CTS process. Therefore, it is impossible to make a proper validation of the model. As for the nearest plans, model will be upgraded by comparing experimental data of real CTS facility and results of the model calculations. This will allow greater accuracy of calculations for further the model uses.

4. Conclusions

The studying of problems and difficulties of CTS process model creation is the result of this paper. The basic physical principles of the CTS process were studied. Foundation, structure, equations, simplifications and limitations of the model were examined. In MATLAB, the numerical modeling of the CTS synthesis process was used. Simulation experiments approved working capacity of the model.

The model of CTS process allows user to analyze influence of the furnace major parameters on results of the synthesis. The model is used for:

- Synthesis of the furnace ACS
- Analysis of working capacity and robustness of different control algorithms
- Learning, as a part of computer trainer for CTS facility staff
- Analysis of technological processes optimization

Further plans for the model are experimental validation and an increase in the accuracy of calculations.

References

Averill B., Eldredge P., 2012, Principles of general chemistry, Creative Commons, Mountain View, California, U.S.A., 1154.

Bardelle P., Warren D., 1992, Mechanism and kinetics of the uranium-plutonium mononitride synthesis, Journal of Nuclear Materials, 188, 36-42.

Butt D.P., Jaques B., 2009, Synthesis and optimization of the sintering kinetics of actinide nitrides, Technical Report, Boise State University, Boise, Idaho, U.S.A., 33-35.

Greenhalgh W.O., 1973, Kinetic measurements for the carbothermal synthesis of UN, PuN, and (U,Pu)N, Journal of the American Ceramic Society, 56, 553-557.

Koning R.J.M., Livens F., Dacheaux N., 2014, Synthesis and characterization of advanced nuclear fuels, Master Thesis, Complutense University of Madrid, Madrid, Spain, 19-21.

Lindemer T.B., Silva C.M., Henry J.J., McMurray J.W., Voit S.L., 2015, Carbothermic syntesis of ~820-μm UN kernels: investigation of process variables, Technical Report, Oak Ridge, 44.

Muromura T., 1982, Carbothermic synthesis of high purity plutonium nitride from plutonium oxide, Journal of Nuclear Science and Technology, 19, 638-645.

O'Dwyer A., 2009, Handbook of PI and PID controller tuning rules, Imperial College Press, London, UK, 170.

Vilnina A.V., Efremov E.V., Pletnev A.O., Chursin Y.A., Barkov D.E., Kabrysheva O.P, 2017, Automatic control system of the evaporator in the technology of spent nuclear fuel processing, Chemical Engineering Transactions, 61, 1441.

Wei Z., Weipeng N., 2017, Research on interactive design of temperature control system for magnesium alloy melting furnace based on PLC, Chemical Engineering Transactions, 59, 265-269.

Yasufumi S., Yasuo A., Tatsuo S., 1982, Carbothermic synthesis of plutonium mononitride from the dioxide, Journal of Nuclear Materials, 115, 331-333.