CHEMICAL ENGINEERING TRANSACTIONS

VOL. 57, 2017

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza, Serafim Bakalis

ISBN 978-88-95608- 48-8; **ISSN** 2283-9216

Mathematical Modeling of the Thermal Denitration of Actinides in a Microwave Oven

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The experimental research in general is needed in order to develop an efficient control system for a process. However, the high radioactivity of the spent nuclear fuel limits the possibility of direct experiments, because it is necessary to ensure a high level people and equipment security. The only way to avoid this situation is to implement a virtual experiment on denitration of nitrates actinides. The mathematical model of the process is necessary for implementation the virtual experiment. This article is devoted on the development of a mathematical model of the thermal denitration of nitrates actinides in a microwave oven.

1. Introduction

Nowadays, the enterprise of the fuel industry could produce great damages to the environment like the release of CO_2 into the atmosphere. In this regard, the aim of reduce CO_2 emissions is gaining more attention and, consequently, the number of publications on this topic is growing every year. For instance, lithium orthosilicate-based pellets were developed and characterized as potential regenerable high-temperature CO_2 sorbents (Puccini et al. 2016). Molina et al. (2015) studied an alternative way to absorb CO_2 in ammonia aqueous solution with a membrane contactor in order to improve the capture processes and to intensify the gas-liquid transfer. Another example comes from the work of Bassani et al. (2016) in which CO_2 emissions is reduced by means of an oxi-reduction reaction with H_2S taking advantage of a novel technology, called AG2S^{TM}.

Nuclear energy is one of the main energy sources in the future and the number of nuclear plants are increasing all over the world (Taylor, 2004). However, the disposal of extinguish nuclear fuel remains a pressing issue. Therefore, the development of novel technologies, that are able to reuse the spent nuclear fuel, is necessary. Toumanov et al. (1991) describe some of these techniques that are being developed from the 80s to the present. One of these (Oshima et al. (1989)) studied the methods for obtaining MOX fuel using microwave energy. Another authors (Imai et al. (2011)) investigate the electric power absorption of the solid Pu/U mixed nitrate medium in a cylindrical oven cavity. Therefore, it is important to underline the fact that one of the principal stages for reprocessing spent nuclear fuel is to obtain actinide oxides by using thermal denitration of actinide nitrate in a microwave oven. Unfortunately, the high radioactivity of the spent nuclear fuel limits the possibility of direct experiments because it is necessary to ensure a high level of protection of the researchers and also to those working close to the area near the experimental apparatus. Thus, the aim of this work is to develop a mathematical model of the thermal denitration of nitrates actinides in a microwave oven in order to implement a virtual experiment avoiding the actual experimental procedure.

2. Description of the process

In this section is presented the description of the global process starting from the difference between the conventional process using a resistance furnace and the novel using microwave oven. In the novel process, heating takes place simultaneously over the entire volume, providing a higher heating rate with activation of chemical reactions by microwave. However, the violation of the required temperature or residence time of thermal denitration, may lead to product formation that are refractory to the action of the microwave field. This can be avoided by pre-calculating the optimum temperature and residence time of microwave oven denitration. The technological scheme of the thermal denitration process is shown in Figure 1.

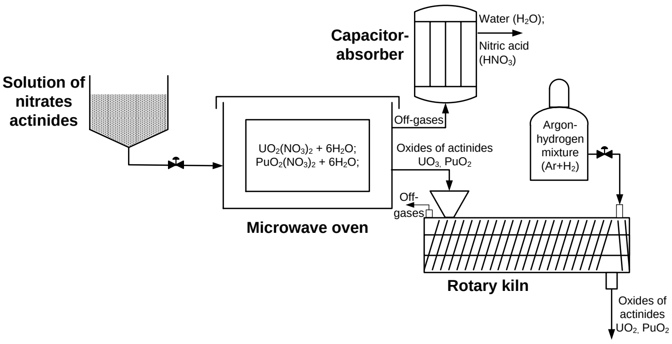


Figure 1: The technological scheme of the thermal denitration process

The process flow diagram includes the tank for preparation of feed solution, microwave oven, rotary kiln to convert the oxides actinides, such as UO_3 to UO_2, balloon with mixture of argon-hydrogen and capacitor-absorber. The preparation of feed solution, carried out in the tank, consists in a mixture, diluted with water, of uranium-plutonium ligature and the uranyl nitrate solution. Then, the solution is sent to the microwave oven in which the thermal denitration generates a mixture of off-gases and actinide oxides. The off-gases are treated using the capacitor-absorber and the actinide oxides are reduced in a rotary kiln to obtain a uranium dioxide (UO_2) from uranium trioxide (UO_3). In this work, only the processes that take place in the microwave oven are considered. The first stage, that takes place at 120 °C, consist in the evaporation of free water and nitric acid according to the following chemical reactions (1) that lead to crystal hydrate uranyl nitrate formation:

$$\begin{aligned} &UO_2(NO_3)_2(liq) + 6H_2O\ (liq) = UO_2(NO_3)_2{\cdot}6H_2O\ (liq);\\ &PuO_2(NO_3)_2(liq) + 6H_2O\ (liq) = PuO_2(NO_3)_2{\cdot}6H_2O\ (liq);\\ &H_2O\ (liq) = H_2O\ (gas);\\ &HNO_3(liq) = HNO_3\ (gas); \end{aligned} \tag{1}$$

As mentioned before, the control of temperature and residence time is crucial for this stage. Then, in second stage of the process, which is carried out at 350 °C, occurs the decomposition of crystalline hydrate uranyl nitrate on components. The stage process takes place according to the following chemical reactions:

$$\begin{aligned} &UO_2(NO_3)_2{\cdot}6H_2O\ (liq) = UO_3(sol) + 2NO_2(gas) + 0.5O_2(gas) + 6\ H_2O(gas);\\ &Pu(NO_3)_4{\cdot}5H_2O\ (liq) = PuO_2(sol) + 4NO_2(gas) + O_2(gas) + 5\ H_2O(gas); \end{aligned} \tag{2}$$

After this brief introduction of the process, a conceptual model of the process is presented in order to develop the mathematical model of the denitration process. The conceptual model, shown in Figure 2, describes the relationship between the input and output variables.

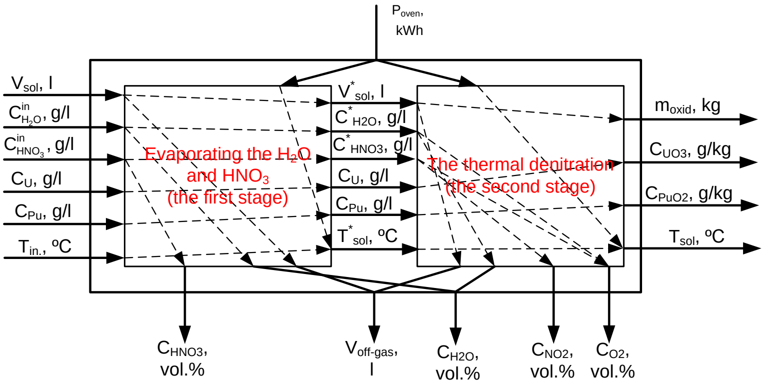


Figure 2: The conceptual model of the thermal denitration process in a microwave oven

The input variables of the model are the volume of feed solution (V_{sol}), the concentrations of the components in the feed solution ($C^{in}_{H_2O}$, $C^{in}_{HNO_3}$, C_U, C_{Pu}), and the power of the microwave oven (P_{oven}). The output variables are the mass of the produced oxides (m_{oxid}), the volume of the formed mixture off-gas ($V_{off\text{-}gas}$), the concentrations of components in the mixture off-gas mixture (C_{H2O}, C_{HNO3}, C_{NO2}, C_{O2}) and in the solid products (C_{UO3}, C_{PuO2}) and the temperature of the solution (T_{sol}) in the microwave oven. The mathematical model includes both stages of the process. So, it is necessary to define also the output variables of the first stage. These variables are the volume of solution (V^*_{sol}), the concentrations of the components in the solution (C^*_{H2O}, C^*_{HNO3}, C_U, C_{Pu}), and the temperature of solution (T^*_{sol}) in the microwave oven. These variables are at the same time the input variables of the second stage.

3. Mathematical model

In order to maintain optimal temperature of the thermal denitration in the microwave oven is necessary to control the residence time of the process. The optimal residence time for thermal denitration is defined as follows:

$$t = \sum_{i=1}^{2} t^i_{stage} \tag{3}$$

In Eq.(3), t^i_{stage} is the time required for each stage of the thermal denitration. Time for each stage is defined as follows:

$$t^i_{stage} = t_{\text{heat}} + t_{\text{reaction.}} \tag{4}$$

where t_{heat} is time necessary to heat the solution up to the operating temperature and t_{reaction} is related to the chemical reactions rate at operating temperature. These variables are defined as follows:

$$\begin{aligned} t_{\text{heat}} &= \frac{V_{sol} \cdot \rho_{sol} \cdot c_{sol} \cdot \left(T_{proc.} - T_{in.}\right)}{0.24 \cdot P_{oven}} \\ t_{\text{reaction.}} &= \frac{1}{k_{T_{proc}}} \end{aligned} \tag{5}$$

where ρ_{sol} is the density of the feed solution, c_{sol} is the specific heat of feed solution, 0.24 is thermal equivalent of work; T_{in} is the initial temperature of the feed solution, T_{proc} is the temperature of the feed solution in the microwave oven during the denitration process, $k_{T_{proc}}$ is the rate constant of the chemical reactions of denitration process. The variation of the feed solution temperature in the microwave oven is evaluated using the expression presented by Didenko (2003). Temperature of the feed solution is defined as follows:

$$\frac{dT^*_{sol}}{dt} = \frac{\eta \cdot P_{oven} + \left(\gamma_{eff} - 1\right) \cdot \sigma \cdot S \cdot {T^*_{sol}}^4}{V_{sol} \cdot \rho_{sol} \cdot c_{sol}} \tag{6}$$

where S is the area of heated surface, σ is the Stefan-Boltzmann constant, η is the coefficient of transmission of microwave power to the heating solution, γ_{eff} is effective coefficient of the reflection of power. It is important to underline the fact that the the solution is heated uniformly over the entire volume in microwave ovens and, as a result the chemical reactions takes place uniformly. Thus, the developed mathematical model is a lumped-parameters model. At the first stage of the process, Dalton law determines the evaporation of water and nitric acid. The system of differential equations describing the material balance of the processes occurring at the first stage is as follows:

$$\begin{cases} \frac{dV_{off-gas}}{dt} = V^1_{H_2O} + V_{HNO_3} \\ \frac{dV^*_{sol}}{dt} = V_{sol} - V_{off-gas} \\ \frac{dV^1_{H_2O}}{dt} = V_m \cdot C \cdot S \cdot \frac{\left(P^{H_2O}_{Par} - P^{H_2O}_S\right)}{M_{H_2O} \cdot P_0} \\ \frac{dV_{HNO_3}}{dt} = V_m \cdot C \cdot S \cdot \frac{\left(P^{HNO_3}_{Par} - P^{HNO_3}_S\right)}{M_{HNO_3} \cdot P_0} \\ \frac{dC^*_{H_2O}}{dt} = \frac{1}{V^*_{sol}} \cdot \left(C^{in}_{H_2O} \cdot V_{sol} - \frac{V^1_{H_2O} \cdot M_{H_2O}}{V_m}\right) \\ \frac{dC^*_{HNO_3}}{dt} = \frac{1}{V^*_{sol}} \cdot \left(C^{in}_{HNO_3} \cdot V_{sol} - \frac{V_{HNO_3} \cdot M_{HNO_3}}{V_m}\right) \\ \frac{dC_{H_2O}}{dt} = \frac{V^1_{H_2O}}{V_{off-gas}} \cdot 100 \\ \frac{dC_{HNO_3}}{dt} = \frac{V_{HNO_3}}{V_{off-gas}} \cdot 100 \end{cases} \tag{7}$$

where V^*_{sol} is volume of the feed solution that remains after the first stage, $m^*_{H_2O}$ and $m^*_{HNO_3}$ are mass of water and nitric acid, which remain in solution after the first stage (g), $V^1_{H_2O}$ and V_{HNO3} are volume of water and nitric acid after the evaporation process, M_k is the molar mass of the *k*-th component, V_m is molar volume of an ideal gas, *C* is a coefficient in order to take into account of the blowing air speed and density (C = $0.95 \cdot 10^{-4}$ (g/(m^2·h) because is not blowing), P_0 is the barometric pressure of the atmosphere; P^k_S is the pressure of steam at a temperature of evaporating liquid, P^k_{Par} is partial pressure of *k*-th component vapor.

The dependence of water and nitric acid vapor pressure on temperature was obtained by analysis of experimental data by means of a regression model by using *cftool* tool included in MatLab. The dependences obtained are as follows:

$$\begin{aligned} P^{H_2O}_S &= 12.47 \cdot e^{0.04143 \cdot T^*_{sol}} \\ P^{HNO_3}_S &= 1.757 \cdot e^{0.01586 \cdot T^*_{sol}} \end{aligned} \tag{8}$$

where T^*_{sol} is the temperature of the solution in a microwave oven at the first stage.

At the end of the first stage of the process is formed a crystals of hydrate uranyl nitrate that have to be sent at the second stage of the process. In this stage, microwave oven power is increased in order to rise up the temperature of the solution. As a result, the exothermic chemical reactions, reported in equation (2), take place. This stage is described by a system of differential equations of material balance and equation of heat balance:

$$\begin{cases} \frac{dm_{oxid}}{dt} = m_{UO_3} + m_{PuO_2} = k_U \cdot V^*_{sol} \cdot C_U \cdot C^*_{H_2O} \cdot C^*_{HNO_3} + k_{Pu} \cdot V^*_{sol} \cdot C_{Pu} \cdot C^*_{H_2O} \cdot C^*_{HNO_3} \\ \frac{dC_j}{dt} = \frac{k_i \cdot V^*_{sol} \cdot C_i \cdot C^*_{H_2O} \cdot C^*_{HNO_3}}{m_{oxid}}, \ (j = UO_3, PuO_2; \ i = U, Pu) \\ \frac{dV_{off-gas}}{dt} = V_{H_2O} + V_{HNO_3} + V_{NO_2} + V_{O_2} \\ \frac{dV_{NO_2}}{dt} = \frac{V_m \cdot V^*_{sol} \cdot C^*_{H_2O} \cdot C^*_{HNO_3}}{M_{NO_2}} \cdot \left(2 \cdot k_U \cdot C_U + 4 \cdot k_{Pu} \cdot C_{Pu}\right) \\ \frac{dV_{O_2}}{dt} = \frac{V_m \cdot V^*_{sol} \cdot C^*_{H_2O} \cdot C^*_{HNO_3}}{M_{O_2}} \cdot \left(0.5 \cdot k_U \cdot C_U + k_{Pu} \cdot C_{Pu}\right) \\ \frac{dV_{H_2O}}{dt} = \frac{V_m \cdot V^*_{sol} \cdot C^*_{H_2O} \cdot C^*_{HNO_3}}{M_{HO_2}} \cdot \left(6 \cdot k_U \cdot C_U + 5 \cdot k_{Pu} \cdot C_{Pu}\right) + V^1_{H_2O} \\ \frac{dC_k}{dt} = \frac{V_k}{V_{off-gas}} \cdot 100, \ \left(k = \ H_2O, \ NO_2, \ O_2\right) \\ \frac{dT_{chem}}{dt} = \frac{V^*_{sol}}{m^*_{sol} \cdot c^*_{sol}} \cdot \left(\Delta H_U \cdot k_U \cdot C_U \cdot C^*_{H_2O} \cdot C^*_{HNO_3} + \Delta H_{Pu} \cdot k_{Pu} \cdot C_{Pu} \cdot C^*_{H_2O} \cdot C^*_{HNO_3} \right) \end{cases} \tag{9}$$

where m_{oxid} is the mass of actinide oxides, k_i is the rate constant of the *i*-th chemical reaction, which depends on the temperature according to the Arrhenius law, V_{H2O}, V_{HNO3}, V_{NO2}, V_{O2} are volume of water, nitric acid, nitrogen oxide and oxygen generated as a result chemical reactions, M_k is the molar mass of the *k*-th component, ΔH_i is enthalpy of the *i*-th chemical reaction.

Due to the fact that the reactions are exothermic, the equation that allows to calculate the change of the solution temperature in the second stage, has the following form:

$$\frac{dT_{sol}}{dt} = \frac{\eta \cdot P_{oven} + \left(\gamma_{eff} - 1\right) \cdot \sigma \cdot S \cdot T_{sol}{}^{4}}{V_{sol}^{*} \cdot \rho_{sol}^{*} \cdot c_{sol}^{*}} + \frac{V_{sol}^{*}}{m_{sol}^{*} \cdot c_{sol}^{*}} \cdot \left(\Delta H_1 \cdot k_U \cdot C_U \cdot C_{H_2O}^{*} \cdot C_{HNO_3}^{*} + \Delta H_2 \cdot k_{Pu} \cdot C_{Pu} \cdot C_{H_2O}^{*} \cdot C_{HNO_3}^{*}\right) \tag{10}$$

4. Results and discussions

The developed mathematical model of the denitration process was implemented in MatLab package using following input values: V_{sol} = 3.5 l, $C_{H_2O}^{in}$ = 340 g/l, $C_{HNO_3}^{in}$ = 210 g/l, C_U = 150 g/l, C_{Pu} = 90 g/l, T_{in} = 25 °C, P_{oven} = 5 kWh.

First of all, was calculated the necessary time for the process. The duration of the first stage of the process is 1.6 hours and of the second stage is 3.6 h. The result variation of the solution temperature in the microwave oven is shown in Figure 3.

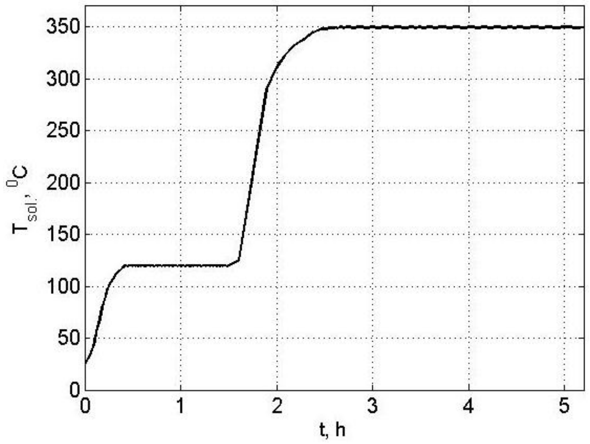
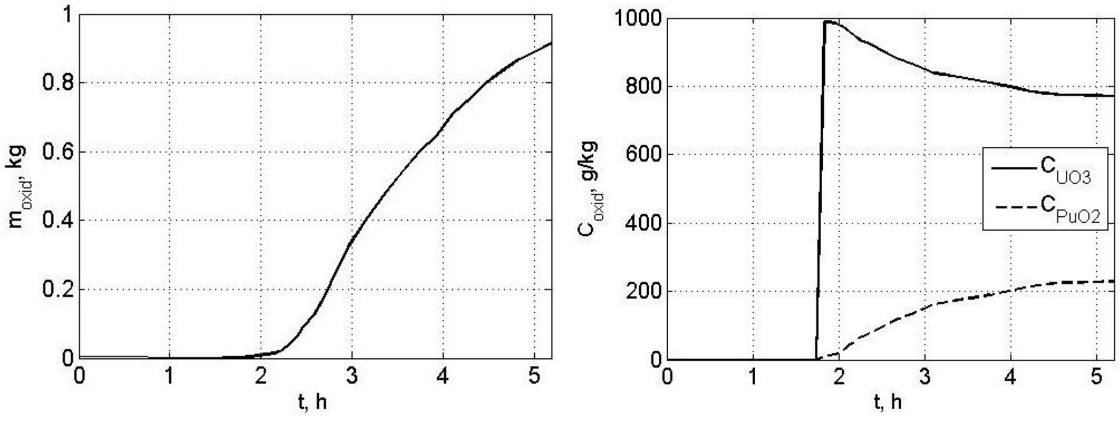
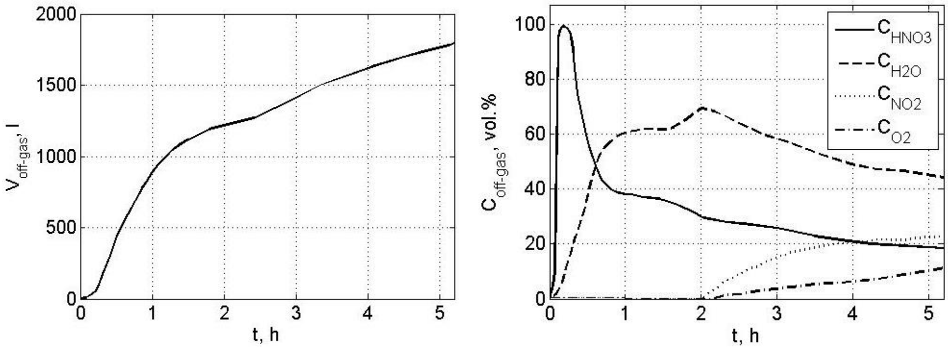


Figure 3: Changing of the solution temperature in the microwave oven during thermal denitration

In order to maintain the solution temperature at the desired level, the power of the microwave oven is modify during the process. As reported in Figure 3, at time 1.6 h the solution temperature increases since the second stage of denitration process (300 – 350 °C). The results of simulations are shown in Figure 4.



Changing of the mass and concentrations actinide oxides during the thermal denitration



Changing of the volume and concentrations mixture of off-gas during the thermal denitration

Figure 4: The modelling results

As shown in Figure 4, the formation of oxides actinides begins at time of 2 h, when the temperature of the solution in the microwave oven reaches 300°C and when the chemical processes, described in equations (2), are activated. Initially there is the formation of uranium trioxide (UO_3), and then of plutonium dioxide (PuO_2). This is due to the different concentrations of uranium and plutonium in the feed solution, as well as because of the different values of the rate constants of chemical reactions.

In addition, Figure 4 reports the change of volume and concentrations of the off-gas. As seen from the graphs, the evaporation of water and nitric acid occurs in the first stage of the process. Nitric acid starts to evaporate before, since its boiling point is 80 °C. The formation of nitric acid is terminated at the second stage of the process. But begins formation nitrogen dioxide and oxygen according to the chemical reactions (2). Thus, the concentration of nitric acid and water is rather reduced in the off-gas

5. Conclusions

This article is devoted to the development of a mathematical model of a thermal denitration of actinides nitrates in a microwave oven. The conceptual model has been developed as a result of analysis of the process. The paper presents a mathematical model that allows to calculate the optimal time of the denitration process, as well as the variations of the solution temperature. The developed system based on differential equations, allow to estimate productivity of the denitration method. The modeling results will be compared to experimental data in the near future. At present, experimental apparatus is develops. In the future, it is planned to use this model in order to optimize the process and to develop an efficient control system for the microwave oven.

Acknowledgments

This work was funded as a part of the project 8.3079.2017/ПЧ of the Federal government-sponsored program «Science».

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