Progress in Nuclear Energy 88 (2016) 240–244

Contents lists available at ScienceDirect

Progress in Nuclear Energy

journal homepage: www.elsevier.com/locate/pnucene

Drying kinetics of thorium oxalate: Experimental investigation and modeling

Sadegh Beigi [a], Mohammad Amin Sobati [a], Amir Charkhi [b, *]

[a] School of Chemical Engineering, Iran University of Science and Technology (IUST), Tehran, Iran
[b] Nuclear Fuel Cycle Research School, Nuclear Science and Technology Research Institute, P.O. Box 11365-8486, Tehran, Iran

ARTICLE INFO

Article history:
Received 23 August 2015
Received in revised form
28 December 2015
Accepted 8 January 2016
Available online 28 January 2016

Keywords:
Drying kinetics
Thorium oxalate
Modeling
Moisture diffusivity

ABSTRACT

In the present study, the drying behavior of thorium oxalate in the temperatures range of 353–393 K was studied to determine drying kinetics and effective moisture diffusivity. Thirteen widely used semi-theoretical thin-layer drying models with temperature-dependent constants were selected to describe the drying kinetics. The results revealed that all examined models were acceptable, but Balbay and Sahin model was the best for describing drying kinetics of thorium oxalate. Moreover, the effective moisture diffusivity in the temperature range of 353–393 K varied from 3.68×10^{-9} to 5.47×10^{-9} m^2/s. In addition, the drying activation energy was found to be 11.21 kJ/mol.

1. Introduction

Thorium oxide (ThO_2) is the main compound of thorium fuel cycle that is used as nuclear fuel in light-water, heavy-water, and liquid-metal fast-breeder reactors. Thorium fuels have several important advantages in comparison with uranium fuels. These advantages are long term availability due to the high amount of thorium resources in the earth crust, better chemical and thermal properties of ThO_2 in comparison with UO_2, and low amount of plutonium and long-lived minor actinide production (Keni, 1991; Lee et al., 1991; Raje and Reddy, 2010). Besides, utilization of thorium in thoria-urania fuels can reduce uranium consumption and diversify the nuclear energy resources for a long-term energy program (Anthonysamy and Rao, 2013; Mukerjee et al., 2013).

Two different methods have been proposed for the production of ThO_2 powder from purified thorium nitrate solutions (Hart et al., 1979; Hart, 1979) including direct and indirect process. In the direct process, denitration of thorium nitrate solution leads directly to produce the ThO_2. In the indirect process, thorium is removed from solution through precipitation of different thorium compounds such as thorium oxalate, thorium formate, and thorium hydroxide. Among these compounds, precipitation of thorium oxalate has been widely applied in commercial scale (Mukerjee et al., 2013). The thorium oxalate precipitate is normally produced by the reaction of thorium nitrate with oxalic acid solution (Mukerjee et al., 2013):

$$Th(NO_3)_4 + 2H_2C_2O_4 + 6H_2O \rightarrow Th(C_2O_4)_2.6H_2O + 4HNO_3 \quad (1)$$

After the precipitation step, ThO_2 powder is produced by calcination of the thorium oxalate precipitate (Hart et al., 1979). The main common processing steps before calcination are filtration and drying of thorium oxalate (Belle and Berman, 1984). After the filtration step, the thorium oxalate filter cake should be dried to reduce its moisture content below 10% in order to avoid spattering and agglomeration during the calcination step (Young et al., 1980).

Deep knowledge regarding drying kinetic is necessary to design a suitable thorium oxalate dryer (Mujumdar, 2006). According to our survey, there is no report available on the drying kinetics of thorium oxalate in the open literature. Therefore, the main aim of the present work was to study the drying kinetics of thorium oxalate. In the present study a two-steps strategy was followed:

(1) Data on drying kinetics of thorium oxalate were obtained, experimentally.
(2) It was tried to model drying kinetics of thorium oxalate and calculate effective moisture diffusivity. It should be noted that thin layer drying kinetics can be categorized in several

* Corresponding author.
E-mail address: acharkhi@aeoi.org.ir (A. Charkhi).

http://dx.doi.org/10.1016/j.pnucene.2016.01.007
0149-1970/

categories including empirical models, semi-empirical models, and theoretical models (McMinn, 2006; Perea-Flores et al., 2012; Sander et al., 2010; Tahmasebi et al., 2014; Wiktor et al., 2013). In the empirical models, the mass transfer resistance inside the particles is neglected and the variation of average particle moisture with time is considered (Magalhaes and Pinho, 2008). In semi-empirical models, it is assumed that the moisture in the particle surface reaches in equilibrium with the surrounding air, immediately (Akpinar, 2006; Balbay and Sahin, 2012; Panchariya et al., 2002).

2. Materials and methods

2.1. Thorium oxalate preparation

The thorium oxalate precipitate was prepared by addition of oxalic acid solution (1 mol/L) to thorium nitrate solution (1 mol/L) while stirring in the reaction temperature of 10 °C and digest temperature of 75 °C for 4 h. The formed precipitate was filtered and washed three times with distilled water. The materials including thorium nitrate (99.9%) and oxalic acid (99.8%) was obtained from J.T. Baker Chemicals Co., and Merck Co., respectively.

2.2. Drying process method

In the beginning, 10 g of 20 wt% thorium oxalate slurry was filtered by Buchner funnel that connected to the vacuum pump. The filtration time was 5 min. Then, the thin layer of filter cake with 2 mm thickness was placed in the crystallizing dish with 0.00283 m^2 area. Afterwards, this crystallizing dish was weighted and put in the oven. The temperature was controlled by adjusting the air flow in the oven convection channel. Drying experiments were conducted at different five temperatures (i.e., 80, 90, 100 and 110, 120 °C).

In each experimental run, the solid sample weight loss was measured every 2 min. The experimental run was terminated when the sample weight became constant between two measurements. Afterwards, the crystallizing dish was put in the oven at 120 °C for 24 h in order to find the sample dry weight. It is important to note that for each data point, the experimental runs were repeated three times and the average value was reported. Then, the solid moisture ratio (MR) was calculated as follows:

$$MR = \frac{X - X_{eq}}{X_0 - X_{eq}} \tag{2}$$

Where, MR, X, X_0, and X_{eq} are the moisture ratio, the solid moisture content at time t (kg water/kg dry matter), the initial solid moisture content (kg water/kg dry matter), and equilibrium solid moisture content (kg water/kg dry matter), respectively. It is important to note that X_{eq} was assumed to be zero because the value of equilibrium moisture content was small in comparison with X and X_0 (Yaldyz and Ertekyn, 2001; Dadalı, 2007). The variation of MR with drying time was considered according to the obtained experimental data.

3. Mathematical modeling on drying kinetics

3.1. Modeling of drying kinetics

Different kinetic models have been proposed to relate moisture ratio with time. The experimental data obtained under isothermal conditions were fitted with thirteen models listed in Table 1.

In order to take into account the effect of temperature on the drying kinetics, an Arrhenius relationship is considered between k constant and temperature:

$$k = k_0.\exp(-E/RT) \tag{3}$$

Several statistical criteria, including coefficient of determination (R^2), root mean square error (RMSE), and Chi-square (χ^2) were applied to evaluate the fitting quality of different models obtained under different conditions:

$$R^2 = 1 - \frac{\sum_{i=0}^{N}\left(M_{exp,i} - M_{pre,i}\right)^2}{\sum_{i=0}^{N}\left(M_{exp,i} - \overline{M}_{exp,i}\right)^2} \tag{4}$$

$$E_{RMS} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(M_{exp,i} - M_{pre,i}\right)^2\right]^{1/2} \tag{5}$$

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(M_{exp,i} - M_{pre,i}\right)^2}{N - Z} \tag{6}$$

Where$M_{pre,i}$, $M_{exp,i}$, N, and z are predicted moisture ratio, experimental moisture ratio, number of experimental data, and the number of constants in the drying model, respectively.

Higher values of coefficient of determination and lower values of the root mean square error, and chi-square are preferred for the fitted models (Magalhaes and Pinho, 2008; Zhang et al., 2014).

Table 1
The proposed Mathematical thin-layer drying models.

No.	Model name	Model equation	Ref.
1	Lewis	$MR = exp(-kt)$	(Lewis, 1921)
2	Henderson and Pabis	$MR = a.exp(-kt)$	(Henderson and Pabis, 1961)
3	Page	$MR = exp(-kt^n)$	(Page, 1949)
4	First modified Page	$MR = exp(-(kt)^n)$	(Overhults et al., 1973)
5	Logarithmic	$MR = a.exp(-kt)+b$	(Yagcioglu et al., 1999)
6	Midilli and Kucuk	$MR = a.exp(-kt^n)+bt$	(Midilli et al., 2002)
7	Balbay and Sahin	$MR = (1-a)exp(-kt^n)+b$	(Balbay and Sahin, 2012)
8	Two term	$MR = aexp(-kt)+bexp(-k_1t)$	(Basunia and Abe, 2001)
9	Two term exponential	$MR = a.exp(-kt)+ (1-a).exp(-k.a.t)$	(Kaleta et al., 2013)
10	Diffusion approach	$MR = a.exp(-kt)+ (1-a).exp(-kbt)$	(Kassem, 1998)
11	Verma et al.	$MR = aexp(-kt)+(1-a)exp(-k_1t)$	(Verma et al., 1985)
12	Simplified Fick's diffusion (SFFD) equation	$MR = a.exp\left(-k\left(\frac{t}{L^2}\right)\right)$	(Diammante and Munro, 1991)
13	Second modified Page	$MR = \exp\left(-k\left(\frac{t}{L^2}\right)^n\right)$	(Diammante and Munro, 1991)