Modeling of the Actinide Oxides Reduction Process in the Rotary Kiln

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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 he only way to avoid this situation is to implement a virtual experiment on the recovery process of actinide oxide in the rotary kiln. This article is devoted to the development of a mathematical model of the process that generates actinide oxides in a rotary kiln.

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. Zarogiannis et al. (2016) described a systematic approach proposed for the preliminary screening of binary amine mixtures as a CO_2 capture candidates. Peirce et al. (2015) studied the improvement of Carbon Capture and Storage processes (CCS) due to biocatalyst stability at the typical operating conditions (high temperature, alkaline pH, high salt concentration). Another example comes from the work of Bassani et al. (2016) in which CO_2 emissions is reduced (not stored as in the previous case) by means of an oxi-reduction reaction with H2S 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. Oshima et al. (1982) and Koisumi et al. (1983) describe research aimed at the use of microwave energy for denitration of nitrate solutions of uranium and plutonium. One of the stages for reprocessing spent nuclear fuel is the calcination of actinide oxides in a rotary kiln. 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 equipment and of the researchers. Therefore need develop mathematical model of the process in order to implement a virtual experiment avoiding the actual experimental procedure. For these reasons, the aim of this study is to develop a mathematical model of the process related to obtain a mixture of actinide oxides in the rotary kiln. This model will be use in future study for setting an optimal control system for rotary kiln.

2. Description of the process

Toumanov et al. (1991) presents the technological scheme of the thermal denitration process of actinide nitrate in a microwave oven. This technological scheme includes the tank for preparation of feed solution, the microwave oven, the rotary kiln for the recovery of actinide oxides of UO_3 and UO_2, a balloon with a mixture of argon-hydrogen and the capacitor-absorber. In this paper, only the processes occurring in the rotary kiln are

considered. The rotary kiln has a screw conveyor with a constant step on which the mixture of oxides is moved. Argon-hydrogen mixture is supplied into the rotary kiln in a countercurrent configuration. Moreover, in order to maintain the temperature of about 700 °C, the rotary kiln is equipped with a tubular electric heating elements. When the inlet kiln temperature reach 650 ºC, the chemical reactions of uranium dioxide (UO_2) formation occurs. The process follows this chemical reaction:

$$UO_3(sol) + H_2(gas) = UO_2(sol) + H_2O(gas) \tag{1}$$

As mention before, it is necessary to maintain the temperature in the kiln at a certain level in order to have a stable chemical process. In addition, it is necessary to regulate the rotation speed of the screw to reach the optimum residence time of the process. After this brief introduction of the process, a conceptual model of the process is presented in order to develop the mathematical model. The conceptual model, shown in Figure 1.
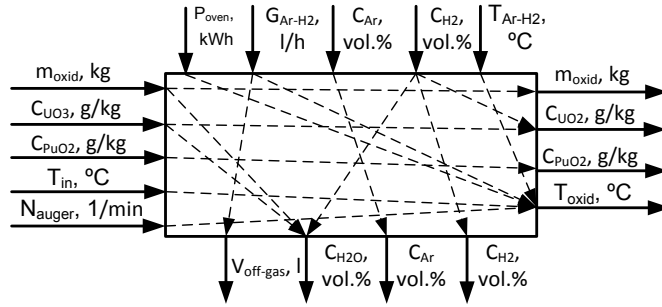

Figure 1: A conceptual model of recovery process of the oxides of actinides

The input variables are the mass of the oxide mixture (m_{oxid}), the concentration of oxides in the mixture (C_{UO3}, C_{UO2}, C_{PuO2}), the initial temperature of the mixture (T_{in}), the electric power used by heating tube (P_{oven}), the number of the revolutions of the screw conveyor (N_{auger}), the volumetric flow rate (G_{Ar-H2}) and the temperature (T_{Ar-H2}) of the hydrogen-argon mixture and the concentration of argon (C_{Ar}) and hydrogen (C_{H2}). The output variables are mass of produced oxides (m_{oxid}), the volume of the off-gas ($V_{off-gas}$), the concentration of components (C_{Ar}, C_{H2}, C_{H2O}) and oxides (C_{UO3}, C_{UO2}, C_{PuO2}) in the off-gas and the oxides temperature in the rotary kiln (T_{oxid}).

3. Mathematical model

In order to evaluate the speed of rotation of the screw conveyor it is necessary to calculate the time for reducing oxides in the rotary kiln. The required time is calculated following this expression:

$$t = t_{heat} + t_{reaction.} \tag{2}$$

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:

$$t_{heat} = c_{oxid} \cdot m_{oxid} \cdot (T_{proc.} - T_{in.}) \cdot (0.24 \cdot P_{oven})^{-1}$$
$$t_{reaction.} = k_{T_{proc}}^{-1} \tag{3}$$

where, c_{oxid} is the heat capacity of oxides actinides mixture, 0.24 is the thermal equivalent of work, T_{proc} is the operating temperature of the recovery process of oxides in the rotary kiln, $k_{T_{proc}}$ is the rate constant of chemical reduction reaction. The rotational speed of the screw conveyor is evalueted according to the expression:

$$N_{auger} = l_{oven} \cdot (t \cdot \Delta l_{auger})^{-1} \tag{4}$$

where, l_{oven} is the length of the rotary kiln, Δl_{auger} is the step of blades on screw conveyor. During one rotation of the screw auger, the mixture of oxides moves in the kiln by an amount equal to the step blades (Δl_{auger}).
The oxides are moved into the kiln by means of a use of a screw auger. Based on the design features of kiln, it is supposed that an ideal mixing of actinide oxides loaded occurs in the interval Δl_{auger} and so the rotary kiln was divided into 40 cells of width 25 mm. The principle of the rotary kiln partitioning is shown in Figure 2.
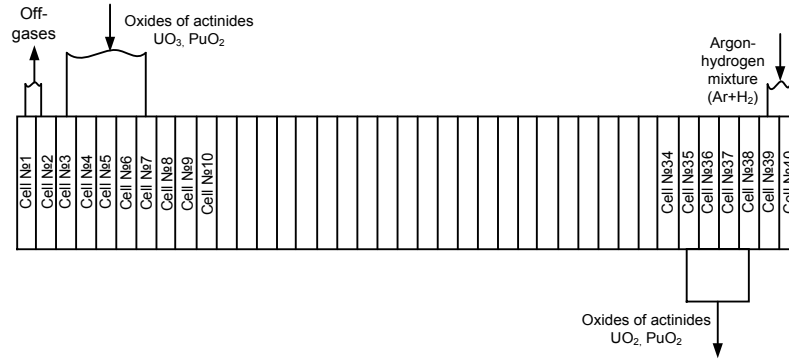
Figure 2: Cell model of the rotary kiln

The diameter of the loading neck is 100 mm. the feed loading is carried out in the cells 4-6 and partially in the cells 3 and 7 (Figure 2). Unloading of the obtained oxides occurs from cells 35 and 36, since the auger has blades in the opposite direction of cells 37 and 38. Therefore, the obtained oxides do not enter into the cells 37-40. Each cell has a different contact area with the neck of the kiln and so the distribution of loading and unloading oxides is not evenly in the cells. The distribution of oxides mass in the cells is determined according to the following expression:

$$m_{oxid}^i = \left(\frac{S_i}{S_{neck}} \right) \cdot m_{oxid} \qquad (5)$$

where, S_i is area of crossing neck with the i-th cell, S_{neck} is area of the neck, m_{oxid} is mass of actinides oxides entering the kiln, m_{oxid}^i is mass of actinides oxides entering the i-th cell. S_i is defined as an area of a circle segments. The weight of cells is calculated by correlating the areas S_i and S_{neck}. The distribution of oxides mass, which is loaded into the kiln, is in accordance with these weights. The system of differential equations that describe the distribution of mass of the actinides oxides along the length kiln is reported below:

$$
\begin{cases}
\dfrac{dm_{oxid}^i}{dt} = \dfrac{\left(m_{UO_3}^{i-1} + m_{PuO_2}^{i-1} + m_{UO_2}^{i-1} \right) - \left(m_{UO_3}^i + m_{PuO_2}^i + m_{UO_2}^i \right)}{2 \cdot T_{auger}} \\[2mm]
\dfrac{dC_k^i}{dt} = \dfrac{m_k^i}{m_{oxid}^i}, \quad \left(k = UO_3, PuO_2, UO_2 \right) \\[2mm]
\dfrac{dm_{UO_3}^i}{dt} = \dfrac{\left(C_{UO_3}^{i-1} \cdot m_{oxid}^{i-1} - C_{UO_3}^i \cdot m_{oxid}^i \right)}{2 \cdot T_{auger}} - k_{T_{proc}} \cdot m_{UO_3}^i \cdot m_{H_2}^i \\[2mm]
\dfrac{dm_{UO_2}^i}{dt} = \dfrac{\left(C_{UO_2}^{i-1} \cdot m_{oxid}^{i-1} - C_{UO_2}^i \cdot m_{oxid}^i \right)}{2 \cdot T_{auger}} + k_{T_{proc}} \cdot m_{UO_3}^i \cdot m_{H_2}^i \\[2mm]
\dfrac{dm_{PuO_2}^i}{dt} = \dfrac{\left(C_{PuO_2}^{i-1} \cdot m_{oxid}^{i-1} - C_{PuO_2}^i \cdot m_{oxid}^i \right)}{2 \cdot T_{auger}} \\[2mm]
\dfrac{dV_{Ar}^i}{dt} = C_{Ar}^i \cdot G_{Ar-H_2} \\[2mm]
\dfrac{dV_{off-gas}^i}{dt} = V_{Ar}^i + \dfrac{m_{H_2}^i \cdot V_m}{M_{H_2}} + \dfrac{m_{H_2O}^i \cdot V_m}{M_{H_2O}} \\[2mm]
\dfrac{dC_{Ar}^i}{dt} = \dfrac{V_{Ar}^i}{V_{off-gas}^i} \cdot 100 \\[2mm]
\dfrac{dC_{H_2}^i}{dt} = \left(\dfrac{\left(m_{H_2}^i \cdot V_m \right)}{M_{H_2} \cdot V_{off-gas}^i} \right) \cdot 100 \\[2mm]
\dfrac{dC_{H_2O}^i}{dt} = \left(\dfrac{\left(m_{H_2O}^i \cdot V_m \right)}{M_{H_2O} \cdot V_{off-gas}^i} \right) \cdot 100 \\[2mm]
\dfrac{dm_{H_2}^i}{dt} = \left(\dfrac{M_{H_2} \cdot \left(C_{H_2}^{i-1} \cdot G_{Ar-H_2} - C_{H_2}^i \cdot G_{Ar-H_2} \right)}{V_m} \right) \cdot \left(\dfrac{V_{cell}}{G_{Ar-H_2}} \right)^{-1} - k_{T_{proc}} \cdot m_{UO_3}^i \cdot m_{H_2}^i \\[2mm]
\dfrac{dm_{H_2O}^i}{dt} = \left(m_{H_2O}^{i-1} - m_{H_2O}^i \right) \cdot \left(\dfrac{V_{cell}}{G_{Ar-H_2}} \right)^{-1} + k_{T_{proc}} \cdot m_{UO_3}^i \cdot m_{H_2}^i
\end{cases}
\qquad (6)
$$

where, m_{oxid}^{j} is mass of mixture of oxides actinides in the *i*-th cell, m_k^i is the mass of the *k*-th component in the *i*-th cell, $k_{T_{proc}}$ is the rate constant of chemical reaction, which depends on temperature according to the Arrhenius equation, V_{Ar}^i is the volume of argon in *i*-th cell, V_m is the molar volume of an ideal gas, M_k is the molar mass of the *k*-th component, V_{cell} is the volume of cell, which is calculated according to the following formula:

$$V_{cell} = \left(S_{oven} - S_{auger} \right) \cdot \Delta l_{auger} \tag{7}$$

where S_{oven} is sectional area of the rotary kiln, S_{auger} is area of the screw, located in the rotary kiln. T_{auger} is the time constant of screw conveyor (s). The dependence between the time constant the screw rotation speed was obtained experimentally and is represented by this following relation:

$$T_{auger} = \frac{60}{\left(4 \cdot N_{auger} \right)} \tag{8}$$

The developed mathematical model, based on a cell model, allows to evaluate the temperature change in a rotary kiln with a countercurrent heat exchange between the gas and the particulate material. This model is also based on the theory of Markov chains (Mizonov et al. (2002)). The process conditions are described by vectors *m*, *T*, *Q*. These vectors represent the distribution in the cells, i.e. along the kiln, respectively of mass, temperature, and heat. Thus, the obtained system of equations (from (9) to (14)) of model is:

$$Q_{oxid}^i = T_{oxid}^i \cdot m_{oxid}^i \cdot c_{oxid}^i \tag{9}$$

$$Q_{gas}^i = T_{gas}^i \cdot m_{gas}^i \cdot c_{gas}^i \tag{10}$$

$$\Delta Q^i = \alpha^i \cdot S \cdot \left(T_{oxid}^i - T_{gas}^i \right) \cdot \Delta t \tag{11}$$

where c_{oxid} and c_{gas} are the heat capacity of oxides and argon-hydrogen mixture (J/(kg·K)); α is the heat transfer coefficient, S is the surface of heat exchange in the cell.

$$Q_{oxid}^{i+1} = Q_{oxid}^i - \Delta Q^i + Q_{EHT}^i \tag{12}$$

$$Q_{gas}^{i+1} = Q_{gas}^i + \Delta Q^i \tag{13}$$

In Eq.(12), Q_{EHT} is the quantity of heat transmitted to oxides from the tubular heating elements in the rotary kiln (J).

$$T_{oxid}^{i+1} = \frac{Q_{oxid}^{i+1}}{\left(c_{oxid}^{i+1} \cdot m_{oxid}^{i+1} \right)} \quad \text{and} \quad T_{gas}^{i+1} = \frac{Q_{gas}^{i+1}}{\left(c_{gas}^{i+1} \cdot m_{gas}^{i+1} \right)} \tag{14}$$

4. Results and discussions

The mathematical model presented before, was implemented in MatLab. The simulation was carried out with the following parameters and input variables: P_{oven} = 20 kWh, G_{Ar-H2} = 2500 l/h, C_{Ar} = 90 vol %, C_{H2} = 10 vol.%, T_{Ar-H2} = 25 ºC, m_{oxid} = 2200 g, C_{UO3} = 760 g/kg, C_{PuO2} = 240 g/kg, T_{in} = 100 ºC, S_{oven} = 0.23 m^2, S_{auger} = 0.13 m^2.

The first result, obtained from equations (2)-(4), is that the recovery process of uranium trioxide takes 1.8 h. Therefore, the screw rotation speed should not exceed N_{auger} = 0.1 min^{-1}. Then, the distribution of the oxides mass along the kiln, the variation of oxides temperature and of argon-hydrogen mixture over the kiln length were calculated. The results are shown in Figure 3.
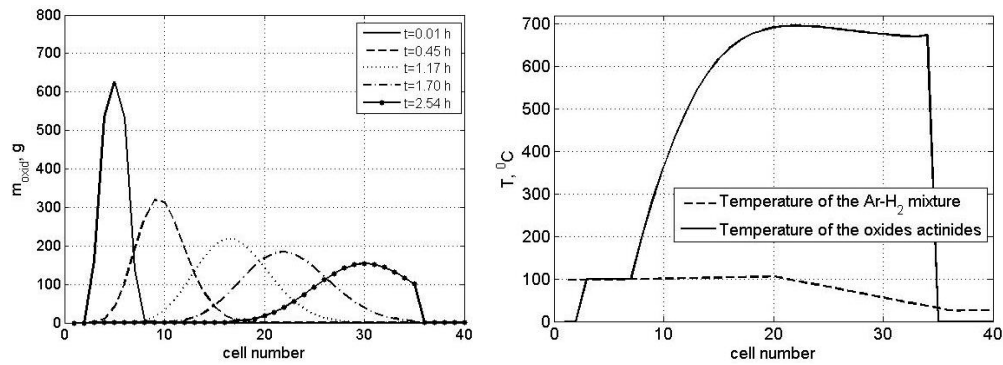
Figure 3: The modelling results

As seen from the simulation results (Figure 3), the oxide mixture moves along the rotary kiln by means of screw conveyor. At the same time, oxides are heated up to 700 °C and the heat exchange takes place with the argon-hydrogen mixture that enters the kiln. The variations in the composition of oxides mixture and of the off-gas are due to the chemical reactions (1). As a result, the progress of the chemical process is obtained and is shown in Figure 4.
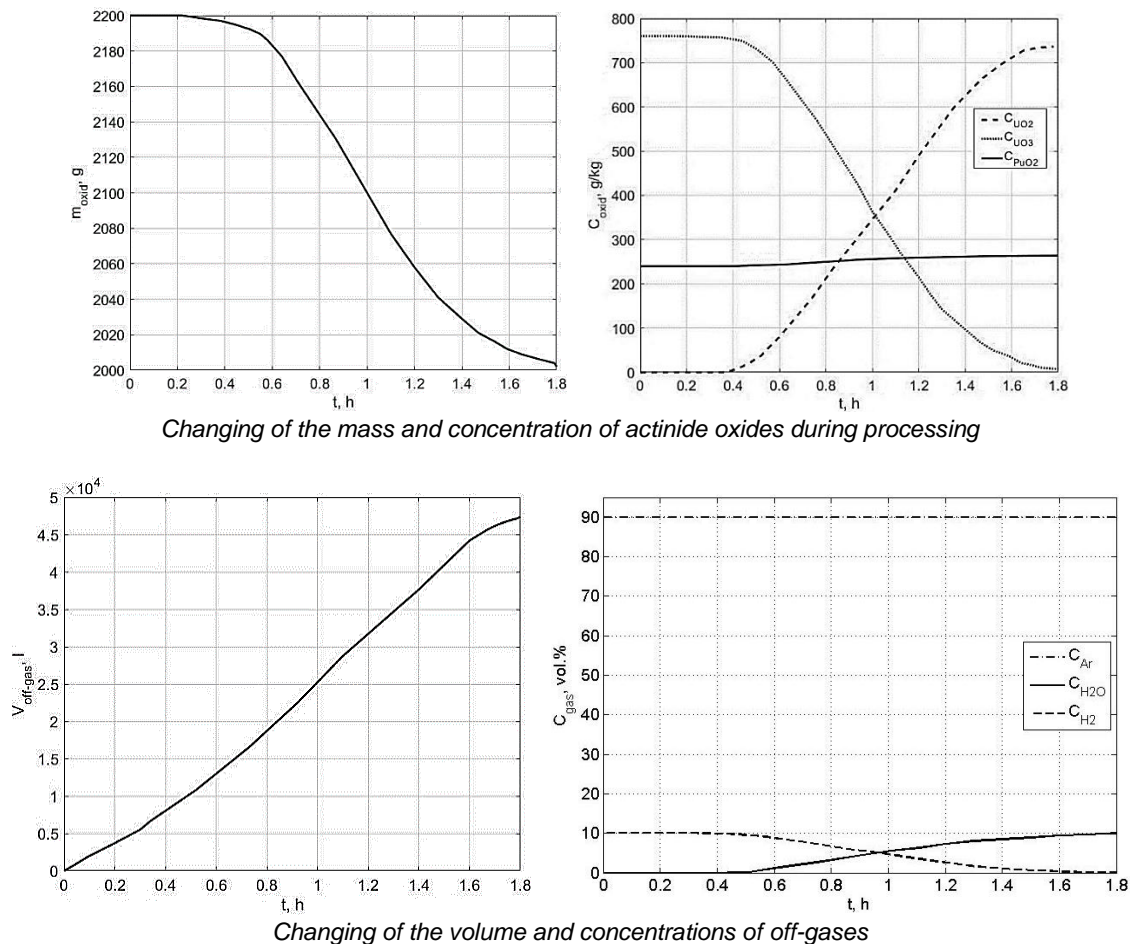

Changing of the mass and concentration of actinide oxides during processing

Changing of the volume and concentrations of off-gases

Figure 4: The modelling results

Figure 4 shows that the mass of the oxides is decreased during heat treatment in the rotary kiln. Furthermore, the concentrations of plutonium dioxide (PuO_2) are increased and uranium trioxide (UO_3) is converted to uranium dioxide (UO_2). The interaction between hydrogen (H_2) and oxygen (O_2) generates water, which

comes out with the off-gases. The concentration of argon (Ar) in the off-gases is decreased. The obtained actinide oxides start to be unloaded from the kiln after 1.8 h (Figure 5).
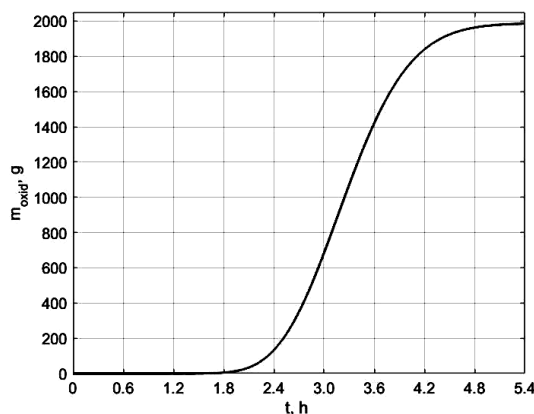

Figure 5: Mass of the actinide oxides at the outlet of the rotary kiln

As seen from the transition process (Figure 5), the unloading of the oxides takes more than 3.5 h, if N_{auger} = 0.1 min^{-1}. In the future, it is necessary to develop a control system for rotary kiln, which will reduce the time of unloading of actinide oxides from the kiln.

5. Conclusions

This paper presents the results of a development of mathematical model related to the process for obtaining uranium dioxide from uranium trioxide in a rotary kiln. The mathematical model is based on a cell model and describes both the material balance and the heat balance which lead to the evaluation of the oxides temperature variation in the rotary kiln. The obtained simulation results show that it is necessary to develop a robust control system for rotary kiln. The development of a control system should allow to reduce the time of unloading of actinide oxides from the kiln.

Acknowledgments

References

Bassani A., Pirola C., Maggio E., Pettinau A., Frau C., Bozzano G., Manenti F., 2016, Acid Gas to Syngas (AG2S™) technology applied to solid fuel gasification: Cutting H_2S and CO_2 emissions by improving syngas production, Applied Energy, 184, 1284-1291.

Koisumi M., Ohtsuka K., Isagava H., 1983, Development of the Process of the Co-Conversion of Pu-U Nitrate Mixed Solution to Mixed Oxide Powder Using a Microwave Heating Method, Nucl. Technology, 61(1), 55-70.

Mizonov V., Berthiaux H., Zhukov V., 2002, Application of the Theory of Markovian Chains to Processes Analysis and Simulation. Ecole des Mines d'Albi, 61.

Oshima H., Tamura T., Koizumi M., 1982, Process to Produce Starting Material for Fuel fabrication. Outline of the Co-Conversion Facility of Pu-U Nitrate Solution to the Mixed Oxide Powder Using a Microwave Heating Method, Trans. Amer. Nucl. Soc., 40, 48-50.

Peirce S., Russo M.E., De Luca V., Capasso C., Rossi M., Olivieri G., Salatino P., Marzocchella A., 2015, Immobilization of Carbonic Anhydrase for Biomimetic CO_2 Capture in a Slurry Absorber as Cross-Linked Enzyme Aggregates (CLEA), Chemical Engineering Transactions, 43, 259-264.

Taylor J.J., 2004, The Nuclear Power Bargain, Issue Science and Technology, 20(3), 41-47.

Toumanov I.N., Sigailo A.V., 1991, Plasma Synthesis of Disperse Oxide Materials from Disintegrated Solutions, Materials Science and Engineering, A140, 539-548.

Zarogiannis T., Papadopoulos A.I., Seferlis P., 2016, Systematic selection of amine mixtures as post-combustion CO_2 capture solvent candidates, Journal of Cleaner Production, 136, 159-175.