Selected Applications for Rotary Tube Furnaces in Rare Earth and Thorium/Uranium Processing

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The present article describes the basic approaches to Rare Earth Elements (REE) as well as UO_2/ThO_2 processing and reflects the implementation of the involved technological necessities for selected heat treatment steps during REE and UO_2/ThO_2 production.

Introduction

Recent developments in innovative technologies like electromobility or generation of renewable energies have increased the demand for Rare Earth Elements (REE). Moreover, shortages in uranium-based nuclear fuels have led to increasing demand for uranium oxide (UO_2). This leads to a global necessity for exploring novel REE as well as uranium deposits, and consecutively, the necessity to design and commission custom-tailored thermoprocessing equipment for REE and UO_2/ThO_2 processing.
The present article describes the basic approaches to REE as well as UO_2/ThO_2 processing and reflects the implementation of the involved technological necessities for selected heat treatment steps during REE and UO_2/ThO_2 production.

REE mineral processing

One of the most abundant REE containing minerals is monazite, a mineral mixture of lanthanide and thorium phosphates (Ce, Ln, Th)PO_4, $Th_3(PO_4)_4$. Depending on the particular location, REE contents may vary and attain values of up to 60 mass-%, while U_3O_8 as well as ThO_2 may attain values of up to 1 and 10 mass-%, respectively. A typical composition of monazite ore from India is given as an example in Tab. 1.

Tab. 1 Typical composition of Indian monazite [mass-%] [1]

RE_2O_3	P_2O_5	ThO_2	CaO	U_3O_8	Fe_2O_3	PbO	MgO	Al_2O_3	Balance
59	27	9	0,5	0,35	0,2	0,18	0,1	0,1	3

Biggest monazite reservoirs worldwide include deposits in Australia, India, Brasil, USA, China and Korea, where the Bayan Obo reservoir in China is considered as the biggest industrial reservoir worldwide [2]. Besides yielding REE, monazite ores also constitute feasible sources for uranium and thorium which are used as raw materials for fuel in nuclear power plants [1].
Typically, the as-mined monazite ore is first crushed to sub-millimetre size and then digested chemically, i.e. by using caustic soda or sulfuric acid. Prior to acid treatment, the raw material needs to be dried to remove physically and chemically bonded water as well as other volatile species, e.g. fluoride minerals which may be present in the raw material as well.
Upon digestion in concentrated H_2SO_4 up to concentrations of 93 mass-%, REE respectively thorium phosphates are transformed in to the corresponding sulfates:

$$2\ RE(PO_4) + 3\ H_2SO_4 \rightarrow RE_2(SO_4)_3 + 2\ H_2PO_4$$

$$Th_3(PO_4)_4 + 6\ H_2SO_4 \rightarrow 3\ Th(SO_4)_2 + 4\ H_2PO_4$$

where temperatures up to 200 °C at dwell times up to 4 h need to be applied. For sufficient solubility, an acid : ore ratio of up to 2,5 may be applied [3]. Further processing to yield REE as well as thorium and uranium includes sulfate solution in water and selective extraction by precipitation, transformation of REE and Th/U sulfates into oxalates which are then calcined to the corresponding RE and/or thorium and uranium oxides (Fig. 1 [4]).

Fig. 1 RE oxides obtained after calcination: clockwise direction starting with black: Pr, Ce, La, Nd, Sm, and Gd [5]

Rotary tube furnaces

Rotary tube furnaces have gained considerable interest for a vast variety of processing methods of particulate matter, like powders, chopped fibers and many more [6]. As they yield a continuous process, batch inconsistencies are reduced and – moreover – the energy consumption is greatly reduced.
The basic principle of a rotary tube furnace is based on rotation-assisted material movement through an inclined tube (Fig. 2).
Material movement in a rotating tube can be distinguished in seven subspecies, assuming water-like flow behavior of the treated material (Tab. 2).

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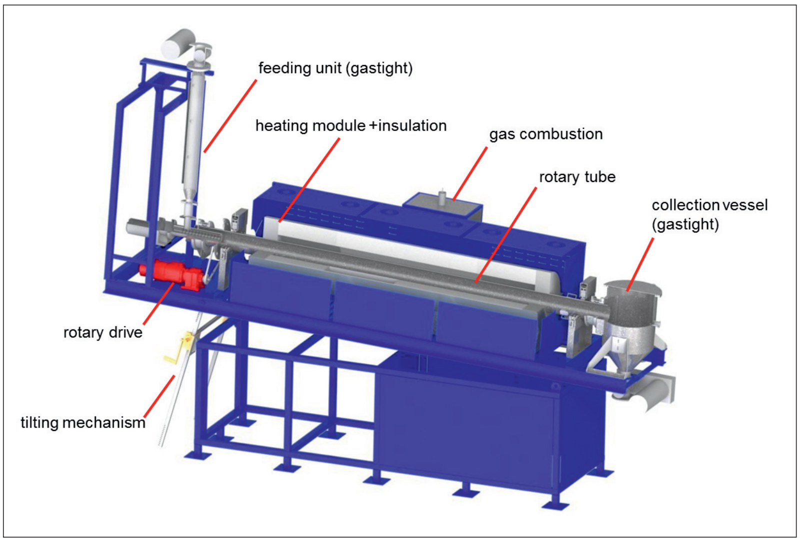


Fig. 2 Sketch of a gastight rotary tube furnace for uranium oxide processing

1. Pure sliding: the friction between tube wall and bulk good is minor, such that the material stands in the furnace tube with timely constant angle without movement and stirring.
2. Weaving: an increased number of revolutions makes a consecutive change between adhesion and slide friction with the tube wall, stirring will still not take place. Hence, the first two conditions do not have big practical meaning.
3. Periodic plunging: at transition from phase 2 to 3 it can be observed that stirring on the surface and lateral face of the bulk good occurs. The surface of the material is marked through two levels standing on each other with a stub angle.
4. Rolling up: this angle enlarges with increasing number of revolutions so that finally one single level composes on whose surface a material transport happens which also here will be continued on the lower side.
5. Sloping: the top edge of the bulk good continues to increase with number of revolutions and continues to round off through the sliding down. The stirring gets more intensive.
6. Plunging: a big turnover occurs over the whole cross section area which is able to hackle the bulk cargo. This type of transport appears often when it is worked with installations in the tube.
7. Centrifugation: the typical centrifuge process at which the whole material adheres on the outside can only be observed with sufficiently high adhesion between furnace wall and bulk good. This is an undesired condition. However this can be often transferred to condition 6 through an additionally installed deflector.

The residence time can be varied steplessly over the number of revolutions and setting angle. The number of revolutions for the tube is typically in the range of 1–10 min^{-1}. The tilting angle can be adjusted in case of smaller furnaces manually over rotary cranks between 0–10° inclination, at big rotary tube furnaces over hydraulics in the range 0–3°.

The dwell time t_0 and output m(t) can be calculated according to the following formulas:

$$t_0 = \frac{L}{n \cdot \pi \cdot D \cdot \frac{\sin\alpha}{\sin\beta}}$$

$$m(t) = \frac{\pi \cdot D^2 \cdot \varphi \cdot L \cdot \rho}{4 \cdot t_0}$$

with D being the tube diameter, L the tube length, φ the volumetric filling degree, ρ the bulk density, n the revolutions per minute and β and α being bulk and furnace decline angle, respectively.

Geometric considerations yield that in case of given dwell time the output increases proportionally to the square of the diameter and linear with the tube length. The tube surface, through which the needed energy is introduced, increases linear in both cases. This leads to typical rotary tube furnace configurations with a diameter : length ratio D/L between 1 : 5 to 1 : 12.

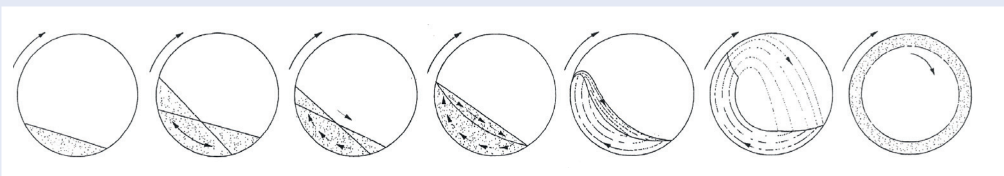
If the bulk density, desired output and the necessary dwell time are known, the geometry of the tube in the dwell zone can be calculated as follows:

$$V_{tube} = \frac{m(t) \cdot t_0 \cdot 100}{\rho \cdot \varphi\,[\%]}$$

With

$$q = \frac{D}{L}$$

Tab. 2 Material movement in a rotating tube

Form	Sliding	Cascading	Cataract				
Type	1	2	3	4	5	6	7
Appearance							
Process	Sliding		Mixing			Comminution	Centrifuging
Application	None		Rotary tube furnaces and reactors, drying and cooling drums, ball mills			Drum mixer	None

the solution of the equation for rotary tube diameter or length becomes:

$$L_{tube} = \frac{1}{q} \; x \; \sqrt[3]{\frac{V}{\pi}}$$

$$D_{tube} = \sqrt[3]{\frac{V}{\pi}}$$

Application 1: monazite ore digestion

Up until recently, the monazite digestion process was carried out batch-wise in rigid vessels, where agitation was conducted by stirring. It may be easily imagined that, in this case, batch processing is prone to failure and batch inconsistencies and may consume considerable amounts of energy as well as reactants. Rotary tube furnaces constitute feasible equipment for REE processing. Besides ore drying, the sulphuric acid digestion may be realized in rotary tube furnaces as well once all parameters are known and dimensions according to the given equations are calculated (Tab. 3).

To account for the highly corrosive environment containg sulphuric and phosphoric acid, special corrosion resistant stainless steels, like, e.g. X1NiCrMoCu32-28-7, need to be applied for material-facing parts, especially at elevated treatment temperatures. To attain sufficient mixing/tumbling of the raw material, paddles may be installed at the inner tube surface.

Continuous sulphatisation in a rotary tube furnace also greatly reduces the consumption of H_2SO_4 which may only be applied at a ratio of 1 : 1 with respect to the treated amount of monazite. Fig. 3 shows the rotary tube furnaces for monazite drying as well as digestion.

Application 2: oxides processing for nuclear fuels

As the digested monazite ore also contains considerable amounts of thorium and uranium, both can be obtained by applying feasible extraction methods to yield nuclear pure uranium and thorium compounds [4]. These can then be used as raw material for the nuclear fuel production cycle which yields enriched uranium oxide, UO_2 [7]. As last step of the nuclear fuel cycle, U_3O_8 needs to be reduced to UO_2 which is con-

Tab. 3 Summary of process conditions and resulting furnace geometries for monazite ore drying and digestion

Process	Drying	Sulphatisation/Digestion
Production rate [kg/h]	2500	1000
Addition of H_2SO_4 [kg/h]	–	600–1000
Treatment time [h]	6	4
Overall humidity [mass-%]	40	–
Bulk density at inlet [g/cm³]	1,3–1,8	1,45
Furnace atmosphere	Air + H_2O + H_2SO_4	Air + H_2SO_4
Process temperature [°C]	20–450	450–550
Tube diameter [mm]	1400	1800
Heated length [mm]	10 800	10 800
Heating power [kW]	1500	600

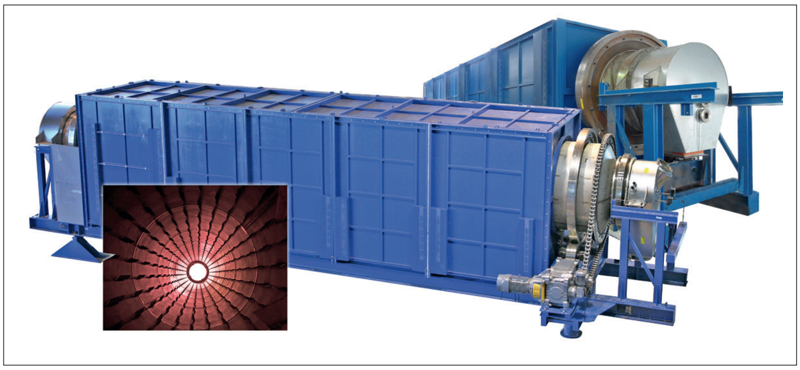


Fig. 3 **Rotary tube furnaces for monazite drying (FDHK-5-1400/10800/450, front) and digestion (FDHK-5-1800/10800/550, back); insert: paddles installed at the rotary tube interior to enhance material tumbling during processing**

Fig. 4 **FDHK-3-140/2200/1100 rotary tube furnace for uranium oxide reduction: view of hot zone of the furnace tube**

sidered as the most stable uranium oxide phase, hence its usage as raw material for nuclear fuel [8]:

$$2\ H_2 + U_3O_8 \rightarrow 3\ UO_2 + H_2O$$

This process involves treatment in pure hydrogen atmosphere at temperatures up to 1000 °C and, as the raw material is already powdery, it can be carried out by using a rotary tube furnace. Used equipment must, however, be designed such that operational safety is given at all times. For instance, complete gastightness of the furnace is a must to prevent air ingress. Also, exhaust gas must be combusted in a controlled way to prevent hydrogen accumulation in the plant.

Fig. 2 gives an overview of the implemented design features in a rotary tube furnace. Both requirements – application temperature and gas tightness – as well as the necessary long-term stability yield nickel chromium alloys, e.g. alloy 601, as the best solution for the rotary tube material in this application.

Fig. 4 shows an example of a hydrogen-gastight rotary tube furnace designed for uranium oxide calcination.

Conclusions

An overview of REE and UO_2/ThO_2 processing was given and the necessity for thermoprocessing equipment was discussed for selected processing steps. Moreover, the working principle of rotary tube furnaces as well as their feasibility in selected heat treatment steps was described.

Design requirements as well as their technological implementations in equipment used for REE as well as UO_2/ThO_2 processing were presented.

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