The Research and Development Of Thorium Fuel for CANDU-6 Reactors in Baotou

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中核集团 CNNC

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General Introduction

China North Nuclear Fuel Corporation (CNNFC) has developed and produced many kinds of Uranium based fuels for research and test reactor and power reactor.

Existing lines：

- CANDU-6 nuclear fuel element production line;
- AFA 3G nuclear fuel element production line.

Lines under construction：

- AP1000 nuclear fuel element production line;
- High temperature gas cooled reactor nuclear fuel element production line.

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General Introduction

After 50 years of construction and development, CNNFC has established a complete system for nuclear fuel element research and production:

- **Specialized nuclear fuel research center;**
- **Advanced process equipment for chemical engineering, metallurgy, pressure processing, machining, welding, physical and chemical analysis, non-destructive testing, radiation protection, and so on;**
- **Enterprise technology center, Institute of metallurgy, and Physical and chemical inspection center.**

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General Introduction

Thorium resources:

- 286,000 tons in China;
- Ranked second in the would;
- More than 220,000 tons in Baotou;
- About 80% of national proven reserves.

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General Introduction

R&D work for thorium utilization in CNNFC:

- **Late in the 20 century, some basic research works;**
- **2007, started again to research and develop the Thorium based fuel;**
- **2008.07, CNNFC and Baotou Science and Technology Bureau signed a contract to develop the thorium based fuel elements for heavy water reactor;**
- **2009.06, The application on building up the research and engineering centre for thorium fuel at CNNFC passed the evaluation organized by Inner Mongolia science and technology Bureau;**
- **2009.07, CNNFC, TQNPC, NPIC and AECL signed Advanced CANDU Fuel Development and Demonstration Phase 2 Agreement (Thorium Fuel). CNNFC is responsible to develop, fabricate and supply two ThO_2 bundles.**

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General Introduction

The Quartet agreement:

- **Phase I: Running the test on CANDU-6 thorium dioxide based fuel manufacture; the organization of laboratory will be formed; the test line of fuel manufacture at the laboratory will be completed by the end of 2010.**
- **Phase II: To develop the commercial manufacture technology for Th-based fuels; to conduct research for manufacture technology of Th-based fuels for different reactors gradually; to build up a research and fabrication centre for Th-based fuels in China.**

Powder preparation

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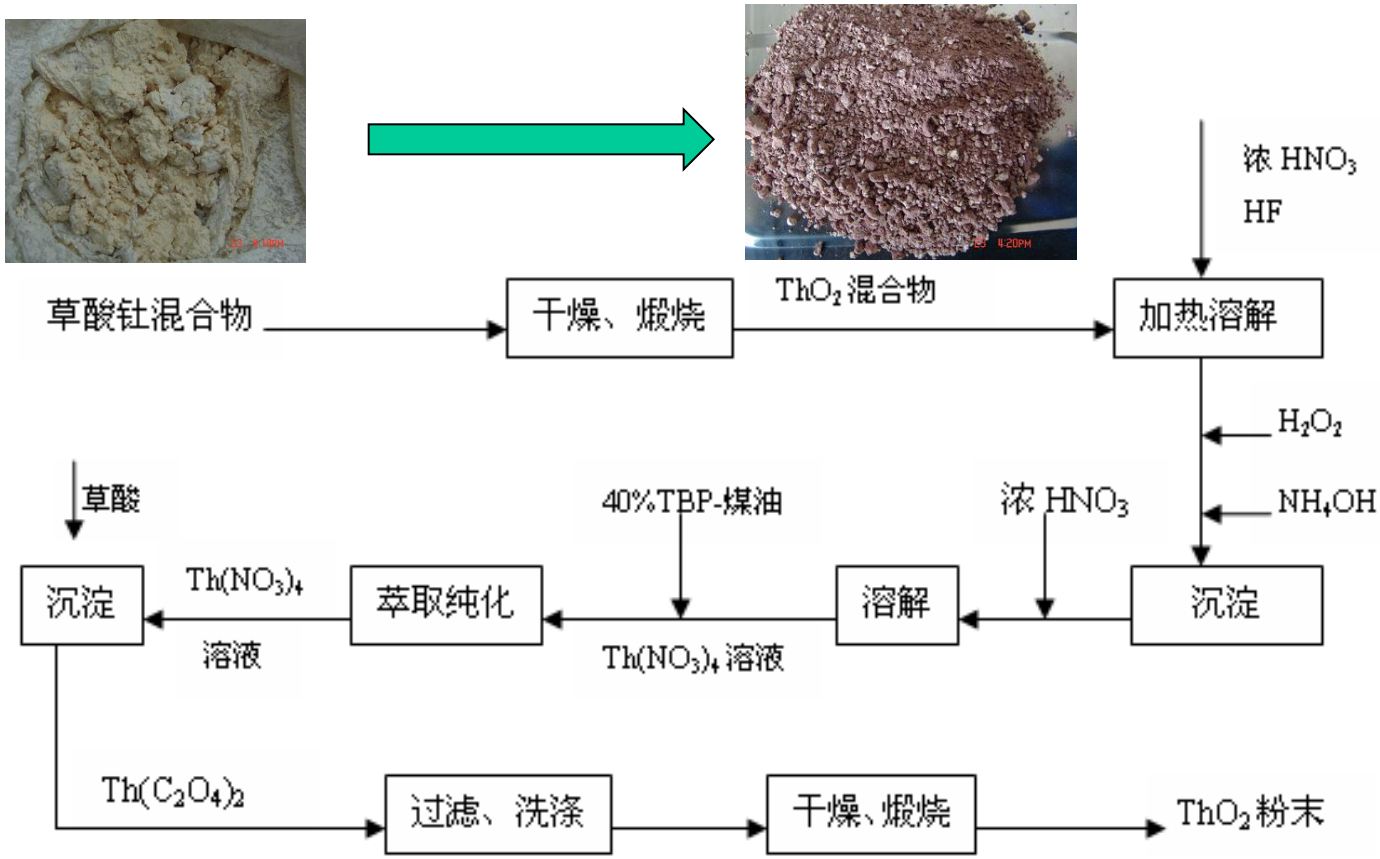

Process route of thorium dioxide powder fabrication

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Powder preparation

1. Calcination process of raw materials;
2. Dissolution process of ThO_2;
3. Precipitation process of thorium oxalate;
4. Extraction and purification process;
5. Oxalate precipitation process ;
6. Calcination process of thorium oxalate.

Powder preparation

1. Calcination process of raw materials

- Calcination temperature: Dissolution rate increases with temperature; but if temperatures too high, ThO_2 powder will agglomerate, and dissolution rate decrease. Studies have shown that 600℃ is the suitable for dissolution.

600℃

700℃

- Holding time: With holding time increasing, thorium oxalate decomposes completely, and dissolution rate of ThO_2 powder increases. But if the time increases further, dissolution rate could not grow. It is shown that 600℃/3h is suitable for dissolution.

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2. Dissolution process of ThO_2

- Under the same conditions, concentrated nitric acid content increases, the solubility of ThO_2 powder is enhanced; and when dissolution temperature and time increase, solubility changes similarly。

- Optimum process conditions:
  content of concentrated nitric acid;
  dissolution temperature;
  dissolution time;
  hydrofluoric acid content.

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3. Precipitation process of thorium oxalate

- Using thorium nitrate solution as raw liquid, PH value of aqueous solution is adjusted by ammonia.
- This process can remove RE impurity effectively (about half of RE content).

4. Extraction-purification process

- The single-stage extraction-purification experiment of thorium nitrate was carried out. The third phase was well controlled during extraction, and the cerium was separated with thorium.

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5. Oxalate precipitation process

- The solution treated by extraction-stripping process should be precipitated by oxalate in order to achieve the purpose of further purification
- In the process, the influence of deposition temperature on precipitation is most important. Studies show that when the temperature is between 50~90℃, sedimentation and purification will go well.

6. Calcination process of thorium oxalate

- Thorium oxalate should go through calcination to change into ThO_2. Up to now, the optimum calcination parameters have been determined.

ThO_2 powder
Nuclear grade

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Present situation of technology

- The purity of ThO_2 powder can be larger than 99.9%;
- Th $(NO_3)_4$ extraction solution should be extracted by 5% TBP-kerosene used for extraction, in order to achieve separation of U and Th;
- ThO_2 powder preparation pilot has been carried out, and the powder can meet the specification requirements;
- In the calcination stage, introducing grinding and N_2 protection steps can be effective in removing water of crystallization.

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Pellet Fabrication

1. Granulation process of ThO_2 powder;

2. Forming process of ThO_2 green pellets;

3. Sintering process of ThO_2 pellets.

Pellet Fabrication

1. Granulation process of ThO_2 powder

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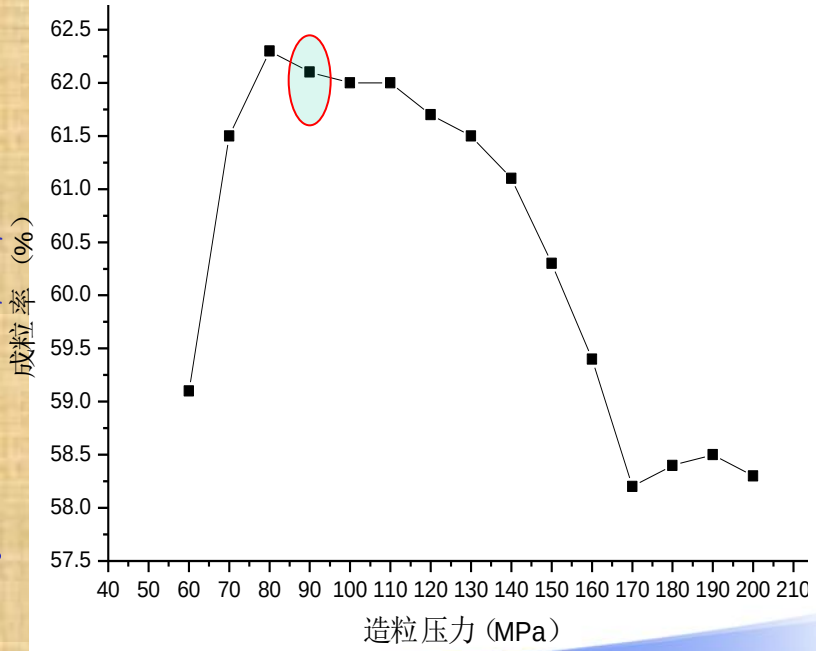
- Thorium dioxide powder should be granulated to improve the particle density and mobility.
- Granulation process includes preloading cake, crushing and screening.

- The granulation rate increases rapidly with pressure increasing, but as the pressure increased further, there is a certain degree of drop.
- Based on the results, select 85Mpa as the pressure for granulation.



Pellet Fabrication

2. Forming process of ThO_2 green pellets

- After granulation, cold forming of green pellets could be conducted.
- ThO_2 green pellets are fabricated by the traditional molding process. The lubricant is zinc stearate mixed with carbon tetrachloride.
- During the molding process, bi-directional pressing was used to improve the uniformity of green pellets, and can also reduce grinding amount of sintered samples.

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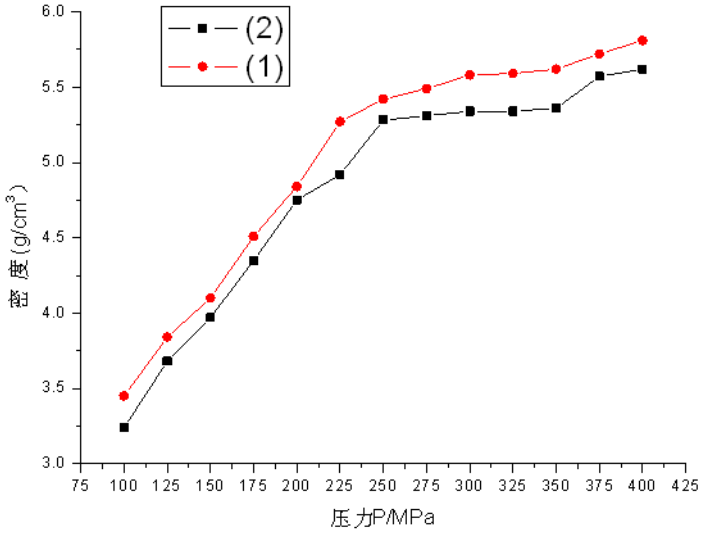
Pellet Fabrication

2. Forming process of ThO_2 green pellets

- The most important parameters which affects the green density is forming pressure.
- The green density increases with pressure rising. When the molding pressure is 250MPa, the magnitude of the increase of green density decreases.



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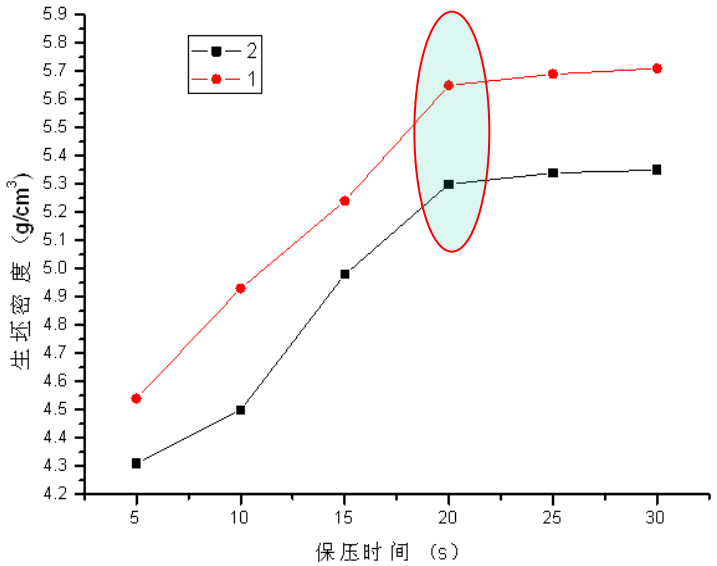
Pellet Fabrication

2. Forming process of ThO_2 green pellets

- In addition to forming pressure, holding time is also the important factor to the green density.
- The forming pressure was selected 300MPa in order to investigate the effect of holding time on green density.

- Green densities were extended as the dwell time increases, and when holding time rising to 20s, the growth rate reduced. That is, holding 20 seconds is enough to obtain higher green density.



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3. Sintering process of ThO_2 pellets

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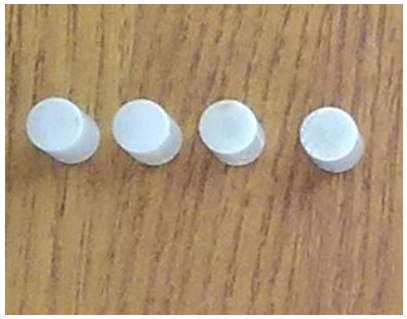
3.1 Crucible materials:

- Graphite crucibles, lined with molybdenum and tungsten respectively
- Alumina crucibles, lined with ThO_2 powder

Experimental results:

- Graphite crucibles --- surface of samples darkens
- Alumina crucibles --- surface smooth, translucent



Graphite crucibles

Alumina crucibles

Pellet Fabrication

3. Sintering process of ThO_2 pellets

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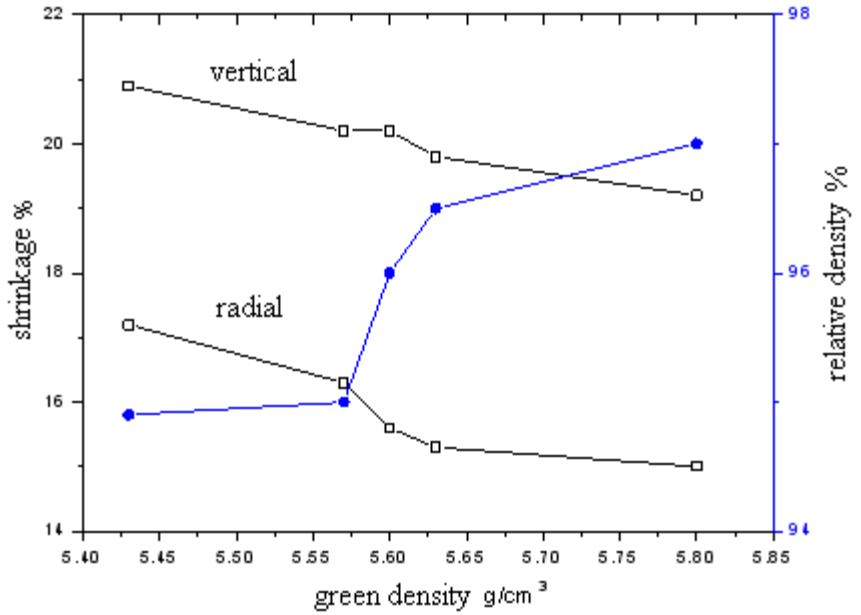
3.2 Effect of green density: (base for mould design)

•As the green density increases, there is a greater degree of increase in the densities of samples, and the radial shrinkage and vertical shrinkage decrease.(1750℃)



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3. Sintering process of ThO_2 pellets

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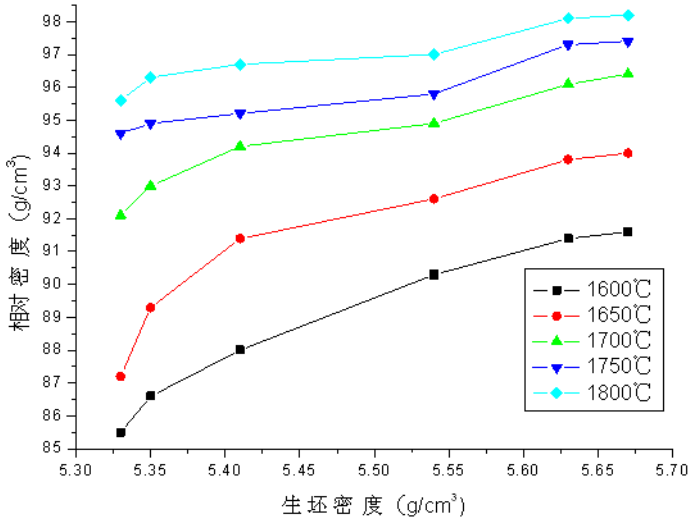
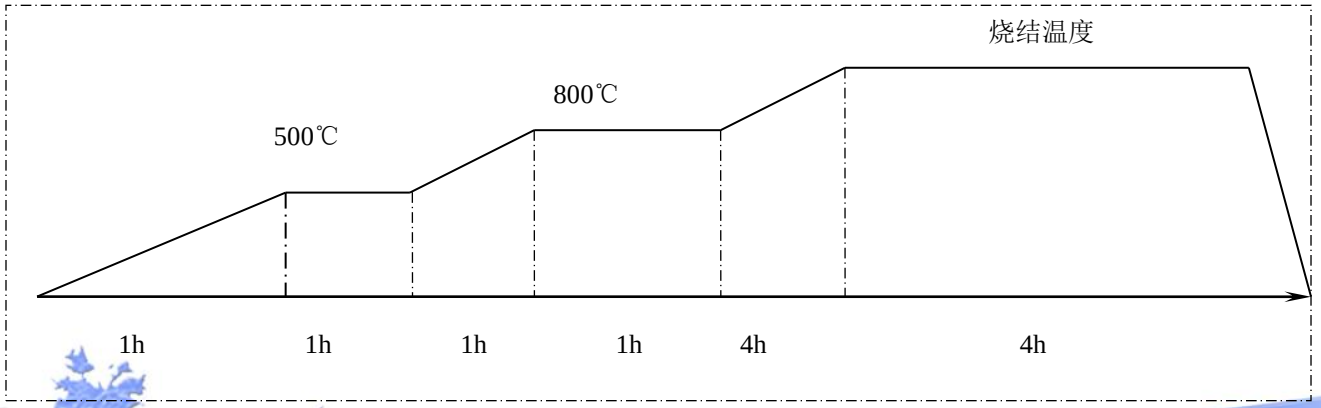
3.3 Effect of sintering temperatures:
- 5 green densities
- Sintered at five temperatures respectively for 4h





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3. Sintering process of ThO_2 pellets

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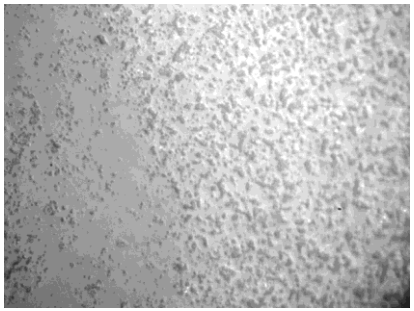
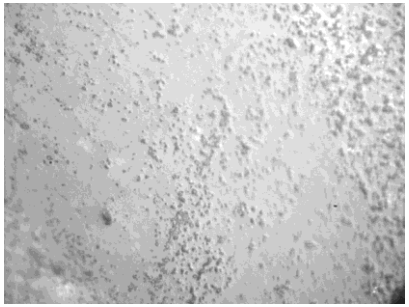
- Following figures are the pore morphology of sintered pellets.
- As sintering temperatures increase, the size of pores grows down, and pores distribute more uniformly.



1600℃（91.6%）



1700℃（96.5%）

1800℃（98.5%）

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3. Sintering process of ThO_2 pellets

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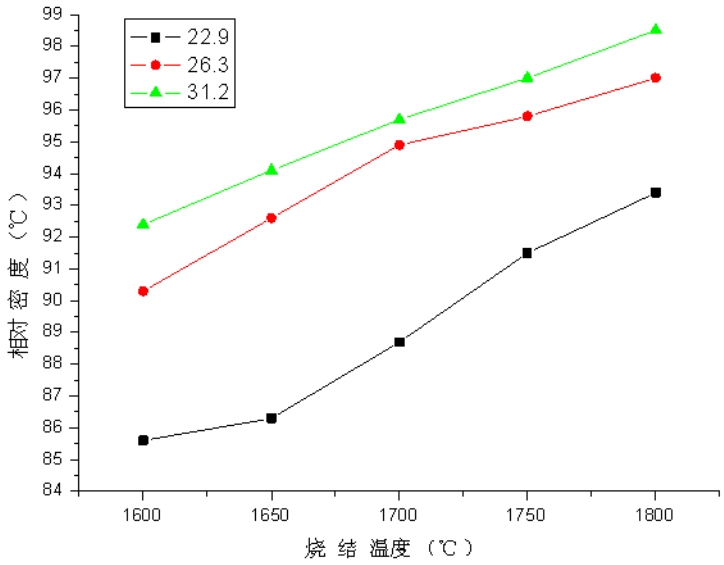
3.4 Effect of powder surface area:

- 3 kinds of powder: 22.926.3m^2/g, 26.326.3m^2/g, 31.226.3m^2/g
- Surface area greater, relative densities of sintered pellets higher



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3. Sintering process of ThO_2 pellets

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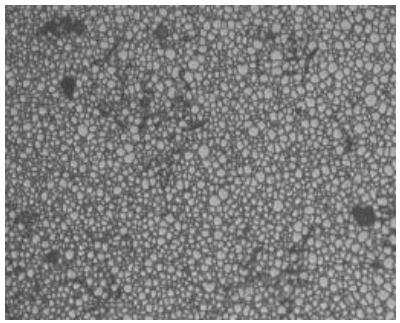
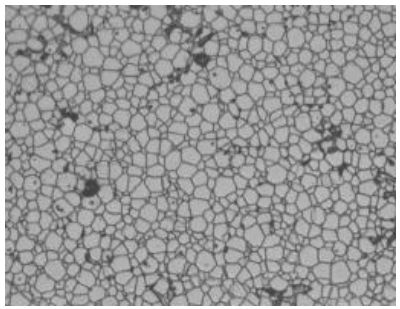
Grain size:(1750℃/4h)

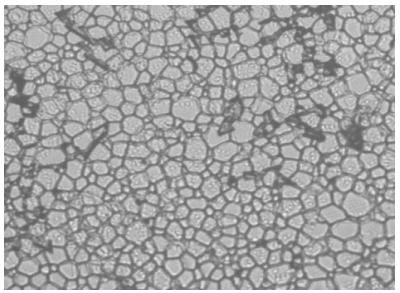
- Left --- Average size 2 μ m
- Middle --- 4μm~20μm
- Right --- Average size 15 μ m



22.926m^2/g



26.326m^2/g



31.226m^2/g

Phys.-chem. analysis

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·In 2008, to establish twelve methods of chemical analysis on forty-eight elements, such as Inductively Coupled Plasma-Mass Spectrometer（ICP-MS), Inductively Coupled Plasma-Atomic Emissio Spectrometer (ICP-AES), Atomic Absorption Spectrometer (AAS), Spectrophotometry, Noble Gas Melt Infrared Absorption, Volumetry, Pyrohydrolysis Selective Electrode, and so on.

·By the end of 2010, established and optimized methods of physical and chemical analysis for ThO_2 pellets.

Radiation protection

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2008, to get a lot of information about radiation protection of Thorium，including：

- Thorium Radiation Characters
- Toxicology and Environmental Behaviors
- Elementary method of radiation protection
- Means for emergency and first aid to person
- Started to set up the methods how to monitor and calculate the personal exposure dose，environment impact and disposing of thorium waste during thorium based fuel manufacture process.

By the end of 2010, establishment and optimization of methods for radiation protection.

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- Thorium chemical test line of CNNFC has been equipped with drying and calcination system, dissolution/filter system, extraction-purification system and wastewater treatment system. Using it, we can carry out small-scale chemical experiments, and has the ability to conduct medium-scale chemical experiments and production.
- Thorium pellets test line is equipped with mixing system, powder granulating system, pressing system and pellet sintering system. ThO_2 powder, purity greater than 99.9%, and thorium dioxide pellets, relative density greater than 95%T.D., have been manufactured.

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- The appropriate methods for physical and chemical analysis have been established related to ThO_2 powder and pellets; and radiation protection has been monitored and studied.
- Two lines above not only can carry out process tests, but also have certain production capacity. Combining the fabrication capacity for fuel elements of power or research reactors, our company already has a certain capacity for large-scale production of thorium fuels.
- In addition, the relatively complete nuclear fuel research and production system in our company, can provide a technology platform for research and development of thorium fuels. So, we sincerely hope to carry out extensive exchanges and cooperation at home and abroad, in order to make some substantial progress in the field of thorium resources utilization.

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Thank you!