HTR FUEL MANUFACTURING EXPERIENCE

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1. Introduction

The development of the HTR line promises the availability of a number of technologies which can be used in many areas of energy supply. In addition to efficient electric power generation the exploitation of HTR heat is aimed at the creation of new energy media which may be used as substitutes for oil and natural gas depending on requirements. In particular, domestic coal resources are to be used to cover the demand for clean and easily applicable energy media /1, 2/.

Special characteristics of the exploitation of nuclear energy in high-temperature reactors include the enconomical uranium consumption and the lower pollution of the environment by waste heat. Increased siting flexibility combined with the potential of remote heat transport expand the possibilities of HTR applications /3/.

The beginning of high-temperature reactor development in the Federal Republic of Germany goes back to 1957. The first HTR project was the AVR, a 15 MW_e experimental power plant which has now passed 15 years of successful operation. The last years it operated at elevated coolant outlet temperatures of approximately at 950 °C.

The follow-up project, the THTR-300, a 300 MW_e reactor is now loaded with fuel elements in Schmehausen and expected to go into power service in 1985. More informations are given in the presentation: Operational Requirements of Spherical HTR Fuel Elements and their Performance.

The significant characteristic of these reactor types is the selection of a spherical fuel element which allows continuous loading under power generation.
The main goal for the development of spherical fuel elements for high temperature gas cooled reactors is to provide a single fuel element which can be used in plant with different purposes like electricity generation, steam generation for chemical reactions, coal liquefaction, production of natural gas. The predominant property of the fuel elements is its low fission product release during operation.

It is the aim of this presentation to describe some features of our HTR fuel manufacturing experience. In general different fuel cycles and/or fuel management strategies afford separate development lines for the most suited fuel. Let me concentrate here only on the thorium/uranium fuel cycle with high enriched uranium.

2. Kernel Fabrication Technology

2.1 Overview

The increasing quality and performance requirements for coated fuel particles have favored the wet chemical processes over dry agglomeration processes. Wet chemical processes are flexible in producing kernels of different size and chemical composition with high throughput and yield, good spherical shape, and narrow size distribution. The chemical processes used to produce kernels have in common that aqueous solutions containing uranium and/or thorium nitrate are transformed into droplets by means of vibrating nozzles. The droplets preconsolidate by internal or external gelation. The kernels are then washed, dried, calcined, and sintered to produce uranium and/or thorium oxide kernels.
The quality of the kernels produced must satisfy several requirements not only so that they can be processed further, but mainly for reasons of good irradiation behaviour of the complete coated fuel particles. These are mainly:

- high density
- narrow diameter range
- almost theoretical sphericity

2.2 The fabrication process

At present for all HTR fuel produced in Germany the gel-precipitation process is adopted /4/. With only a slight change in the composition of the feed solution, this process can be employed to produce all types of reactor fissile and fertile materials in current use. The gel-pricipitation process for $(Th,U)O_2$-kernels is characterized by the following steps:

Uranyl nitrate solution is mixed with thorium nitrate solution and additives. This feed solution is passed through nozzles developing jets of liquid in air which form uniform droplets under the influence of an electromagnetic vibration system. The droplets are solidified by a reaction with NH_3 gas and are collected in NH_4OH solution. Then the spherical particles are washed with water to remove NH_4NO_3 and dehydrated with isopropanol. Drying takes place to remove the isopropanol. The dried particles are calcined in air at medium temperatures whereby the thorium oxide hydrate is dehydrated, and the ammonium diuranate thermally decomposed. The kernels are then sintered in an H_2 atmosphere to $(Th,U)O_2$ mixed oxide of nearlytheoretical density. The kernels are screened, and shape separated on vibrating plates removing small amounts of misshaped kernels, and finally divided on a representative basis into coating batches. The present throughput of our HEU Kernel line is matched to the requirements of THTR. However scale up for advanced LEU-fuel is foreseen.

To date, about 10 t of $(Th,U)O_2$ kernels have been produced in a mixture ratio of $ThO_2:UO_2$ ranging between 4:1 and 40:1, and with diameters required by current specification. In addition, about 2 t of ThO_2 kernels were fabricated.

3. Manufacture of Coating

3.1 General aspects

Coatings of the fuel kernels have to retain the heavy metals and the fission products within the coated particles. These coatings are deposited by pyrolytic decomposition of hydrocarbon gas and silane vapor in fluidized beds. The noncontinuous batchwise fluidized bed process is used for all coatings.

The reference coating design is the so-called Triso LTI coating. It consists of a buffer layer, an inner and an outer dense isotropic LTI layer, and a sandwiched SiC layer deposited from CH_3SiCl_3. The SiC layer is an excellent diffusion barrier for solid fission products. Low defect rate during manufacture and good irradiation performance are the main requirements for the whole coating.

3.2 The coating process

Fuel kernels are coated using the fluidized bed procedure.
The particles to be coated are located in the cone of a vertical graphite tube, into which the gas for pyrolysis together with an inert carrier gas is introduced by means of a nozzle system. The fluidized bed furnace is heated by an electric resistance heater /5/.

3.2.1 Pyrocarbon coatings

Because of the anisotropic dimensional changes of pyrocarbon under irradiation, only isotropic pyrocarbon with a random distribution of the crystallites is suitable for coated fuel particles. This type of pyrocarbon can be obtained by pyrolysis of methane, propene or propene-acetylene mixtures. The requirements of sufficient high apparent carbon density and low optical anisotropy can be met by maintaining definite coating conditions. Methane-derived coatings require very high deposition temperatures and sufficient high methane concentration in the pyrolysis gas.
If the coating is deposited by propene or propene/ethine pyrolysis, the deposition temperature can be reduced significantly.
The pyrocarbon coating of HTGR fuel particles consists always of at least two layers. The inner layer adjacent to the fuel kernel is highly porous, providing the particle with empty volume for fuel kernel swelling and gaseous fission product reception. The outer layer forms a pressure vessel and fission product diffusion barrier.

3.2.2 Silicon carbide coatings

Another coating material of increasing importance is silicon carbide.
The main advantage of this material are the very low diffusion coefficients of some long living fission products (e.g. ^{90}Sr, ^{134}Cs, ^{137}Cs). Usually,

the silicon carbide is deposited as an interlayer between two highly dense pyrocarbon layers ("TRISO particles"). Silicon carbide coatings are obtained by pyrolysis of methyltrichlorsilane in a hydrogen atmosphere:

$$CH_3SiCl_3 \longrightarrow SiC + 3\ HCl.$$

Similar to the pyrocarbon deposition process the mechanism of SiC formation is a very complicated chemical reaction. The hydrogen concentration in the pyrolysis gas as well as the CH_3SiCl_3 concentration and the deposition temperature controls the density, microstructure and chemical composition of the silicon carbide coating.

For large scale silicon carbide coatings the deposition temperature has to be in a range similar to the pyrocarbon coating.
Currently the coating facility is designed for coating batches of about 10 kg heavy metal. All coating layers are applied without a shutdown phase between different layers. Requirements concerning coatinhg defects due to fabrication and operation are met with the fabrication technology used at present.

3.3 Quality control

Coated particle fuel is inspected to prove that quality is in compliance with the fuel product specificatio. Kernel and coating properties generally have a Gaussian distribution. This is also true for composite batches if the process is in control. Therefore the quality inspection is done on composites. Random samples that are split from the parent composite batches are used for the different controls to prove that tolerance limits for single values, confidence interval limits for mean values, or confidence interval limits for attributes are met with the required statistical criterion.

4. Fuel Element Fabrication

4.1 General remarks

The main goal of the present development of HTR fuel is to provide an element which can be used in power plants for different purposes. Due to advanced demands, this fuel elements must ensure a significantly lower fission product release than the well-proven THTR fuel element. Thus, extremely low fractions of heavymetal contamination and defect coated particles are required. This goal is independent of the choice of the reference fuel cycle.

4.2 The fabrication process

The fuel element fabrication presently seems to be the most critical step regarding the fracture of coated particles during fabrication. It starts with the "overcoating" of the particles: hereby, the coated particles are covered by a thin layer of resinated graphite powder, usually called pressing powder. Those overcoated particles together with further pressing powder are pressed to form the fueled center of the element. A fuel free shell of pressing powder is then pressed around the fuel zone. To obtain low anisotropy, all pressing steps are carried out in silicon rubber dies, equivalent to a quasi-isostatic forming procedure. This standard pressing process takes place at room temperature, i.e.below the melting point of the resin binder, and requires a pressure in the range of 10^3-10^4 bar. Then the fuel elements are heat treated to coke the binder material and to remove volatile impurities. Finally lathing to obtain the correct diameter is done.

Design requirements as:

- narrow bandwidth in diameter
- sufficient high matrix density
- high mechanical strength
- good irradiation performance
- low fission product release during operation

can be met with current fabrication technology.

The centre goal of work for the fuel element production is to guarantee a low number of failed particles during manufacture ($< 50 \times 10^{-6}$). One important factor to reduce particle failure during manufacture is the quality of the applied overcoating. A homogeneous overcoating with pressing powder excludes during moulding any direct contact between adjacent particles.

Having identified this production step as a very sensitive one the work concentrated on strict classification of coated and overcoated particles as well as improvement of the overcoating itself.

Effort in the classification step is geared towards thorough separation of all oddshaped particles. A special shape separator was installed. The present status shows an improvement of one order of magnitude even at high heavy metal loadings which might be required for future reactors.

5. Conclusions

Fuel cycle, design and irradiation performance requirements impose restraints on the fabrication processes. Both kernel and coating fabrication processes are flexible enough to adapt to the needs of the various existing and proposed high temperature gas-cooled reactors. Extensive experience has demonstrated that fuel kernels with excellent sphericity and uniformity can be produced by wet chemical processes. Similarly experience has shown that the various multilayer coatings can be produced to fully meet design and specification requirements. In a comprehensive qualification program for fuel elements the low failure fraction of coated fuel particles, optimal matrix behavior and the required fission product retention of integral fuel elements was successfully demonstrated.

6. References

1. P. Engelmann et al.
KFA Report Jül 1612 (1979)

2. H.J.Neef, I. Weissbrodt
Coal Gasification with Heat from HTR
Nucl. Eng. Des. 54 (1979), 157

3. Fassbender et al.
Proc. Conf. "Gas cooled Reactors Today"
BNES London 1982

4. M.Kadner, J.Baier
Production of Fuel Kernels for HTR Fuel Elements
Kernt. 18 (1976), 413

5. H.Huschka, P.Vygen
Coated Fuel Particles
Nucl. Techn. 35 (1977), 238

6. H.J.Becker, W. Heit
Fabrication of Spherical HTR Fuel Elements
Trans. ENS Conf. "Nuclear Power-Option for the World"
Hamburg 1979

7. W. Heit, W. Rind, W. Burck
HTR-Elemente, Stand bei Herstellung und Erprobung
Jahrest. KTG, Mannheim 1982 S. 497