

PERSPECTIVE OF THORIUM RESEARCH AND BORON CARBIDE COATING OF URANIA-GADOLINIA FUEL IN TURKEY*

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Abstract. Turkey has thorium resources amounting to about 380,000 tonnes as observed until today. Thorium content in complex ore reserves is roughly 0.2% in average. An extensive survey including determination of tenor for complex ore is expected to be undertaken till the end of year 2000. Other main constituents are composed of rare earth elements including yttria (^{203}Y). These constituents and regional thorium contents are tabulated and mapped in this presentation in detail. The research and development (R&D) institutions in Turkey consider R&D studies on thorium fuel technology as a key element for future reactor technologies. Recently, some other R&D investigations on advanced fuel production were undertaken at the Middle East Technical University (Ankara) in collaboration with the Turkish Atomic Energy Authority. As an example; pure UO_2 and urania-gadolinia (5% and 10% gadolinia) fuels were then coated with boron carbide by chemical vapor deposition (CVD). Boron carbide was produced from the reaction of carbon tetrachloride and boron trichloride under excess hydrogen in a thermal CVD furnace at $1000^\circ\text{C} - 1175^\circ\text{C}$. The morphology and the thickness of the coating and preliminary burnup calculations have been investigated.

1. INTRODUCTION

In the 21st century, the conventional fission energy issue may not be practical to solve the global energy problem. Not only severe global environmental problems, but also economical energy supply, poverty and desertification of the world will not be inevitable.

However, the future nuclear energy technology will undertake the main global difficulties in the medium and long terms in the next 21st century. Therefore, increase in energy demand in the next century will lead to a considerable increase in nuclear energy contribution when climate change problems are considered [1].

In order to solve these global energy and environmental problems, a new philosophy is required. One of this philosophy can be thorium utilisation, as thorium is more abundant and widely localized resource in the world. In addition, thorium molten salt technology has main benefits, such as utilisation of fissile materials; ^{233}U , ^{235}U and plutonium, and this utilisation is achieved without reactor-core design modifications [2]. Additionally, molten salt reactors carry some advantages in terms of cost and safety.

On the other hand, fluid fuel reactors possess attractive waste facilities due to continuous processing and immediate separation of the residual fuel from waste, and simple waste handling applications.

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There are three possible general fuel types to burn plutonium in light water reactors (LWR):

- i) uranium-based mixed oxides (U,Pu)O₂, (MOX);
- ii) thorium-based mixed oxides (Th,Pu)O₂ and
- iii) inert matrix fuels (IMF).

In these types of fuels, PuO₂ is dispersed in a neutron transparent ceramic carrier [3] (such as yttria, Y₂O₃, zirconia, ZrO₂ etc.). Plutonium oxide is diluted in inert ceramic oxides and/or thoria. The (Th,Pu)O₂ fuel contributes to increase the Pu consumption with respect to (U,Pu)O₂ fuel in terms of lack of uranium. Furthermore, the (Th,Pu)O₂ fuels exhibit good capability under irradiation conditions and they have high stability which enable us to produce a ²³³U having high gamma activity in burnt fuel.

2. THORIA FUEL STUDIES

Recovery of thorium from the ore and production of thoria fuel powder were carried out in the past, including sol-gel with oxalate precipitation [4] and calcination of thorium oxalate to obtain thoria fuel. Mixed thoria-uranium fuel pellets are prepared by mechanical blending in various proportions. In the above study [4], more than 90% theoretical pellet density is obtained. Sintering kinetics of prepared pellets is investigated at a high sintering temperature.

The survey on the thorium and rare earth element deposits and tenor determining studies is expected to be speeded up when sufficient financial support is provided. Therefore the exact amount of thorium and rare earth elements are not yet to be determined. But recent determination of thorium oxide reserves is about 380,000 tonnes in Eskisehir estate. Thorium and uranium reserve distribution in Turkey is mapped in Figure 1.

Reserve determination survey exhibited a various thorium and rare earth element contents according to the different deposit regions. While some ore deposits seem to be rentable to operate thorium ores, in contrast, some deposits do not seem to be rentable to operate ores. However, it seems to be rentable in case of operation in both thorium and rare earth elements ore together.

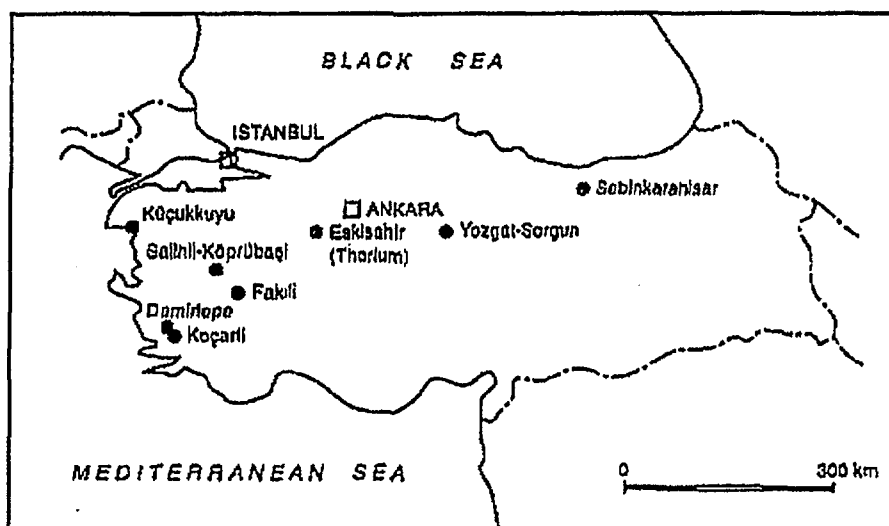


Figure 1. Thorium and uranium deposits and occurrences in Turkey.

Rare earth contents in thorium deposits are about 3% in a cumulative average. Yttria content in determined in rare earth deposits is considerably a high amount. Some deposits in Eskisehir have reached to 8-9% rare earth element tenor and 0.12-0.02% thoria content. In China, rare earth element and thoria content have reached to 7% and 0.035% respectively. Thorium and rare earth element contents in examined ore samples are tabulated [5,6] in Tables I and II.

Table I. Elemental Concentrations of Ore Samples.

Element	KTS-1	KTS-2	KTS-3	KTS-4
Na(g/kg)	-	7.2	7.8	8.3
Fe(g/kg)	26.7	96.5	26.0	18.8
Sr(g/kg)	-	2.50	1.3	18.8
Y(g/kg)	-	-	-	42.3
Ba(g/kg)	111	132	36	145
La(g/kg)	3.84	9.42	4.35	12.5
Ce(g/kg)	15.3	13.6	4.8	12.0
Nd(g/kg)	14.8	3.4	1.3	2.5
Sm(g/kg)	3.00	0.63	0.15	0.35
Th(g/kg)	5.3	2.9	2.9	1.5
Sc(mg/kg)	18.0	14.6	10.6	8.4
Cr(mg/kg)	500	39.1	30.1	168
Co(mg/kg)	25.8	1.8	1.4	1.0
Zn(mg/kg)	-	-	360	210
As(mg/kg)	200	-	160	-
Zr(mg/kg)	143	87	94	104
Nb(mg/kg)	3.0	1.2	1.6	7.0
Sb(mg/kg)	5.6	2.9	3.8	10.7
Cs(mg/kg)	10.3	1.0	1.8	5.0
Eu(mg/kg)	370	71.1	27.4	41.3
Gd(mg/kg)	540	420	520	150
Tb(mg/kg)	54	12.5	8.2	11.3
Yb(mg/kg)	62.6	28.4	21.9	37.4
Lu(mg/kg)	-	-	36.2	-
Hf(mg/kg)	4.2	10.6	30.1	4.4
U (mg/kg)	9.4	181	8.0	8.61

As seen from the Tables I and II, thorium content does not seem to be rantable by itself except rare earth elements. Thoria deposit ores almost include all the following rare earth elements in various contents. Since the importance and usage of rare earth elements are continuously increasing, more research should be carried out for both rare earth elements and thorium estimation in Turkey.

Reserve determination survey is not over, it is expected that the amount of thoria and rare earth elements would increase more as survey studies sustain at these regions.

Table II. Elemental Concentrations of Ore Samples.

Element D(Dolamitte-2	Dolamitte-4	K. Hoyuklu	K. Devebagirtan
Na(g/kg)	-	16.0	-	-
Fe(g/kg)	4.30	5.18	2.69	3.19
Sr(g/kg)	-	1.55	2.34	-
Ba(g/kg)	0.44	0.45	109	72.6
La(g/kg)	5.0	-	10.3	12.4
Ce(g/kg)	6.2	5.0	21.3	22.0
Nd(g/kg)	-	-	3.9	-
Gd(g/kg)	1.13	0.41	0.19	0.41
Th(g/kg)	11.5	4.0	2.4	3.0
Sc(mg/kg)	35.2	32.2	14.0	42.5
Cr(mg/kg)	27.7	82.8	74.4	66.6
Co(mg/kg)	27.2	22.2	5.3	4.6
Zn(mg/kg)	210	-	200	320
As(mg/kg)	-	-	-	6.66
Y (mg/kg)	-	-	840	-
Zr(mg/kg)	144	165	97	95
Nb(mg/kg)	6.08	4.20	1.05	1.27
Mo(mg/kg)	-	-	46.7	-
Sb(mg/kg)	20.5	23.8	11.4	4.0
Cs(mg/kg)	11.5	4.8	9.2	8.4
Eu(mg/kg)	20.6	11.8	46.0	67.8
Tb(mg/kg)	17.4	6.6	8.0	18.5
Yb(mg/kg)	69.0	50.6	19.2	28.7
Lu(mg/kg)	-	-	2.15	-
Hf(mg/kg)	4.22	3.37	1.38	9.71
Ta(mg/kg)	1.0	0.95	-	1.46
U (mg/kg)	-	996	24	45

3. BORON CARBIDE COATING OF URANIA-GADOLINIA FUEL

Controlling a nuclear reactor with strong neutron absorbers causes flux depressions at certain locations, therefore fluctuation of power production, and inefficient burning of fuel is inevitable. However, the new generation control rods are made of weak neutron absorbers. In this case, the excessive reactivity is compensated with the amount of burnable absorbers used in fuels. Thus, burnable absorber consumption and build up of fission products minimise the need for the control rods.

Recently longer operating fuel cycles and more efficient fuel management have been proposed to utilize some form of burnable absorbers for power distribution and reactivity control. For this aim, suitable burnable absorbers can be Gd, Er, Ho or B. Gadolinium is being used as a burnable absorber in the commercial reactors. In recent studies, erbium, Er, seems to be used as the best compromise, in spite of a fairly large residual absorption among the effective burnable absorbers [7].

Burnable absorbers in nuclear fuel are commonly used in current nuclear reactor design. Since they are a part of the fuel rod, separate handling of the absorbers used in fuels can be classified in two categories : burnable absorber mixed with fuel (gadolinium oxide mixed

with fuel), and burnable absorber coated with fuel (zirconium diboride, ZrB_2 , and boron nitride, BN). ZrB_2 coated gadolinium oxide fuels are commercially available.

There are many advantageous of gadolinia on soluble absorbers: first, Gd has higher thermal cross section than boron ; this contributes to the significant control of the reactivity at the very beginning of the cycle when fuel is very fresh. In addition, it does not cause residual reactivity at the EOC. Secondly, boric acid changes the properties of the moderator (water) such as thermal conductivity, pH, corrosivity, density. Thirdly, the cooling system creates additional waste, ion exchange resin and necessitates additional storage and disposal. Lithium formed due to the reaction of $^{10}B(n, ^7L)He$, must be removed in the ion exchanger.

However, the use of excessive amount of gadolinia creates some problems. The thermal conductivity of the fuel decreases as gadolinium content increases. Gadolinia retards sintering and so results in higher porosity. In addition to the above, it causes solid solution formation in the fuel.

Another method of using burnable absorber is to coat the fuel pellets with a thin layer of burnable absorbers. In this method the fuel is coated with ZrB_2 and boron nitride [8]. Boron has a low neutron absorption cross section compared to the gadolinium. Therefore boron does not totally burn out when it is mixed with the fuel and introduces residual negative reactivity at EOC.

However, as a burnable absorber exists on the surface of the fuel, it interacts with the thermalized neutrons on their return from the moderator before the fuel does. As the thermal neutrons are partially absorbed by burnabl absorber on the fuel surface the spectrum becomes hardened. So burning of boron is achieved at high rate while sufficiently hardened neutrons go inside the fuel. This naturally increases the conversion efficiency of ^{238}U into ^{239}Pu .

The fabrication technology of ZrB_2 . is quite complicated and the dissolution of unburned ZrB_2 creates solubility problems. On the other hand, boron nitride coating of the fuel is relatively a new technique and more advantageous than ZrB_2 coating. However, the BN coating has a disadvantageous since reaction with $^{14}N(n,p)$ results in undesired radioactive ^{15}N on the surface of the fuel.

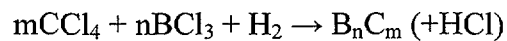
In this study, a new approach is applied during the coating of the fuel pellets with burnable absorbers. This is boron carbide coating of the fuel by chemical vapor deposition technique. Some difficulties and solubility problems in ZrB_2 coating technology and also radioactive neutron reaction with nitrogen in BN coating have however eliminated by coating fuel pellets through B_4C .

3.1. Experiment

In this experiment, UO_2 and UO_2 - ^{203}Gd nuclear fuels are obtained by sol-gel technique, and then these fuels are pelletised and sintered. After that pellets are coated with boron carbide in a thin layer (about 5 μm thickness) through chemical vapor deposition [9].

The B_4C films prepared in this experiments are formed by reacting BCl_3 and CCl_4 under excess H_2 , at temperatures of 1000°C, 1100°C and 1175°C at 1 atm in a CVD tube furnace. BCl_3 and CCL_4 are carried by argon and hydrogen respectively into reaction medium. CVD

tube furnace used in this experiment is shown in Figure 2. The general overall reaction to form B₄C is the following:



This reaction gives homogeneous boron-carbon compounds with rhombohedral structure and a carbon ratio of 9-20% (B₁₀C-B₄C). The electrical and thermal conductivities were found to change with the carbon content.

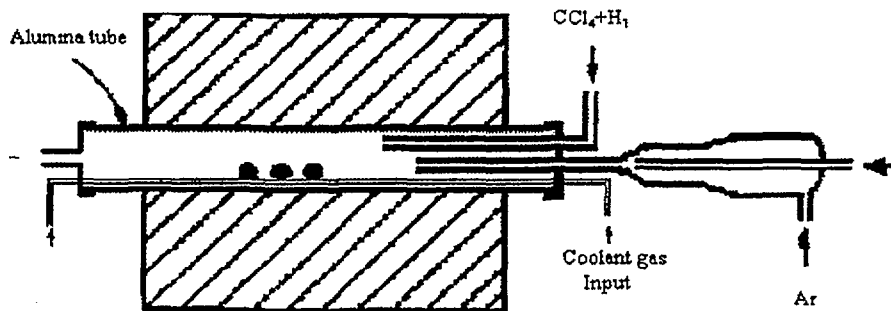


Figure 2. Thermal CVD tube furnace.

As substrate, silica plates were also used besides three nuclear fuels. CCl₄ was kept warm at 76 °C and its vapor was carried to the reaction medium by H₂ gas. BCl₃ kept in a steel tube was fed to the reactor with Ar gas through a nozzle. The ratio of BCl₃/CCl₄ was kept between 4-9 throughout the experiment.

4. PRELIMINARY NEUTRONIC CALCULATIONS OF THE COATED FUEL

The preliminary neutronic calculations performed by WIMS-D/4 have been mainly based on k_{eff} and burnup. Fresh fuels are replaced near the center of reactor vessel to decrease neutron exposure to the vessel and thus to increase the reactor vessel life in in-core fuel management. In this case, fresh fuels result in power peaks in the reactor core. Burnable absorbers, like gadolinium oxide, have been added natural or slightly enriched fresh fuels to remove these power peaks.

In this study, standard and slightly enriched standard fuels are assumed to be coated with boron carbide and used in PWR. Boron carbide coated fuel is examined in comparison with boron nitride coated fuels due to its superiorities [9].

A standard PWR has been assumed with 17X17 fuel bundles. There is a neutron detector or neutron source tube together with 24 blank tubes for control rods in the center of the bundle. The remaining 240 fuel rods consist of 4% enriched UO₂, and 24 fuel rods consist of 4% enriched UO₂ or B₄C coated 4% enriched UO₂. These are symmetrically situated in the fuel bundle.

Three different unit fuel cells are used in this computation: a standard fuel with no burnable absorber, fuel containing burnable absorber gadolinia and also boron carbide coated fuel.

Burnup versus k_{∞} data for boron carbide and boron nitride coated fuel is shown in Figure 3. B₄C coating is more effective in terms of k_{∞} increase in comparison to BN coating owing to the higher boron content in B₄C compound.

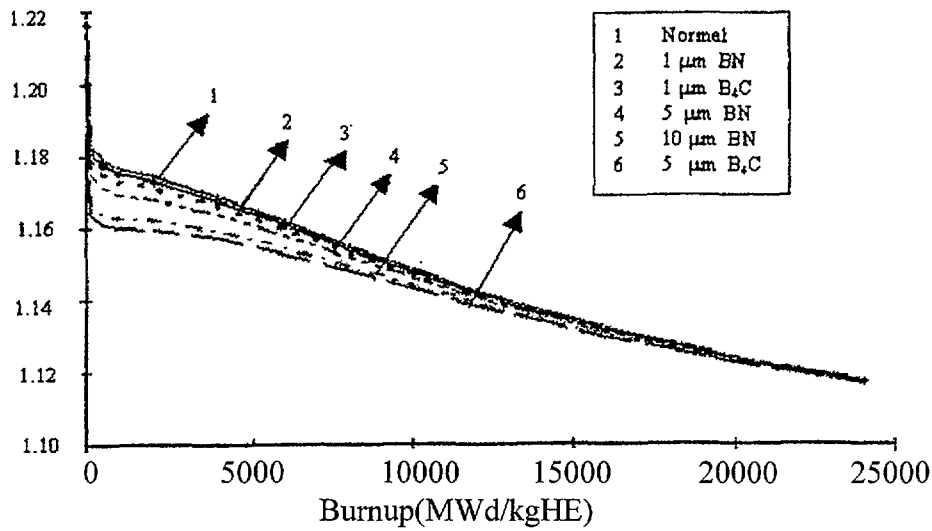


Figure 3. Comparing k -infinity.

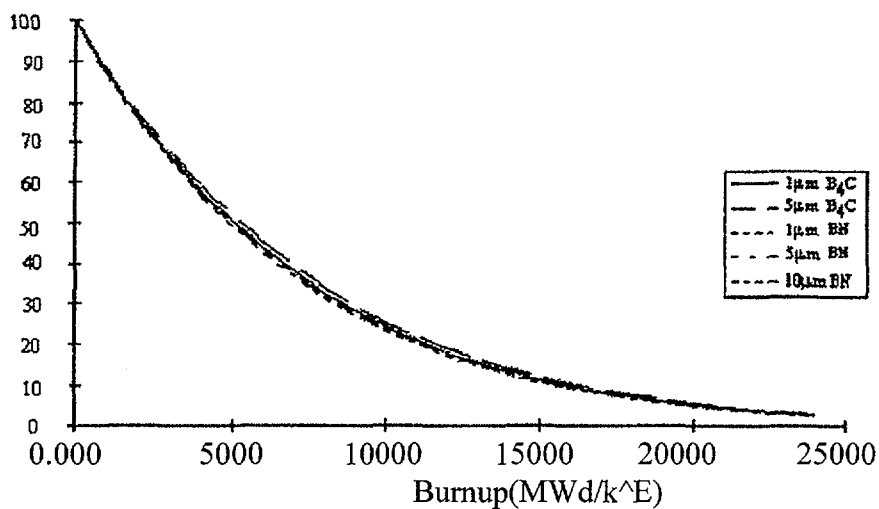


Figure 4. Comparison of burnable poison.

Burnable poison and burnup curves are almost same and overlapped in both B₄C and BN cases given in Figure 4.

Burnup and amounts of fissile ²³⁹Pu and ²⁴¹Pu produced during burning are given in Figure 5. As seen from the Figure 5, the curves are overlapped in both boron carbide and boron nitride coated cases. Thus B₄C coating and BN coating are comparable due to fissile Pu-production.

B₄C and BN coated fuel bundles are examined in terms of power distributions and compared in 5 μm coating thickness. Power peak values for B₄C and BN coating is almost constant at the order of 1.05 value.

B₄C coating yields the same k_{∞} effect as BN coating even with smaller thicknesses due to the high amount of boron content in B₄C. Therefore B₄C coating compared to BN coating is more effective and superior in terms of neutronic perspective especially in k_{eff} case.

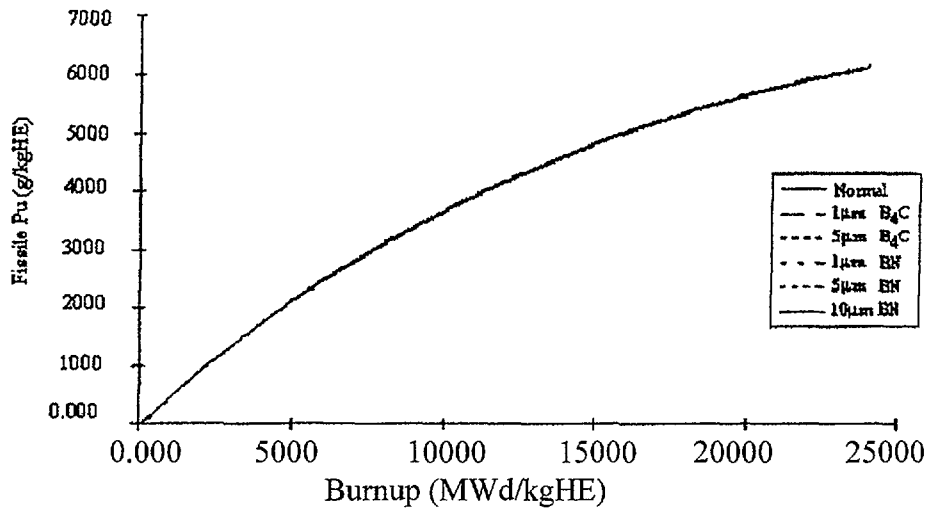


Figure 5. Comparison of fissile plutonium.

5. CONCLUSIONS

Thorium deposits

1. Thorium survey studies together with rare earth elements have not been finished until today. This survey should be finished as soon as possible, as Turkey has considerable amounts of thorium deposits.
2. At the present time thorium and rare earth deposits seem to be rentable due to co-operation of them. Especially yttria (Y_2O_3) between rare earth deposits is to be considered.

B₄C coating

1. Homogeneous and thermodynamically stable B₄C compound was successfully coated on pure urania and urania-gadolinia fuel.
2. Boron carbide coats were formed in layered, particle and rod shaped on the fuel experiments.
3. Coated B₄C compound did not penetrate and interact with the fuel but it only well-adhered on the fuel surfaces.
4. B₄C coating thicknesses were mostly 5 µm however 12 µm thicknesses were rarely observed.
5. B₄C concentration was decreased almost in a negligible amount in any step after burnup at 24000 MW·d/kgHE (MW·d/kg Heavy Element).
6. B₄C coating compared to the BN coating is more effective and superior at the same coating thickness in terms of neutronic perspective. Power peak values both B₄C and BN coating cases are almost constant at the magnitude of 1.05 value.
7. ZrB₂ coating is quite complicated and also there are some solubility problems in the fuel processing management. On the other hand, the BN coating has disadvantage since reaction with $^{14}N(n,p)$ results in an undesired radioactive ^{15}N reaction on the fuel surfaces. However, B₄C coating of the fuel has mostly eliminated such the above problems due to the coating of the pellets with ZrB₂ and BN.

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