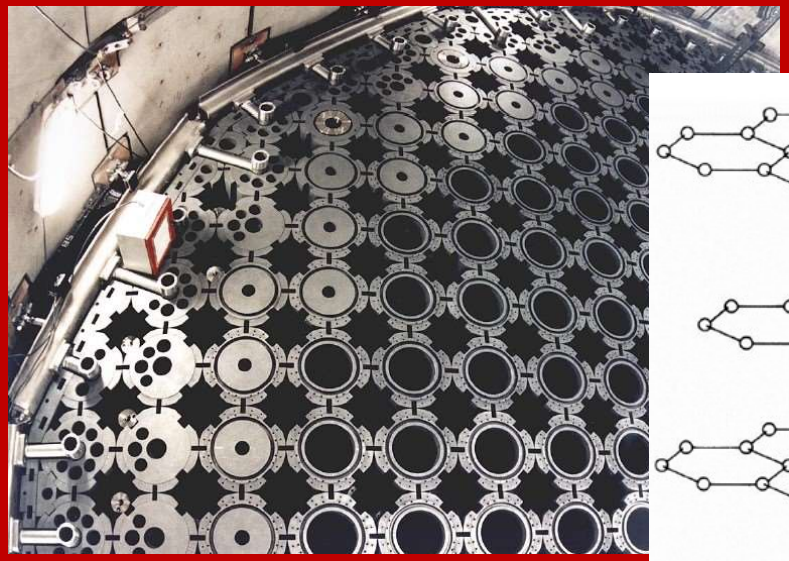
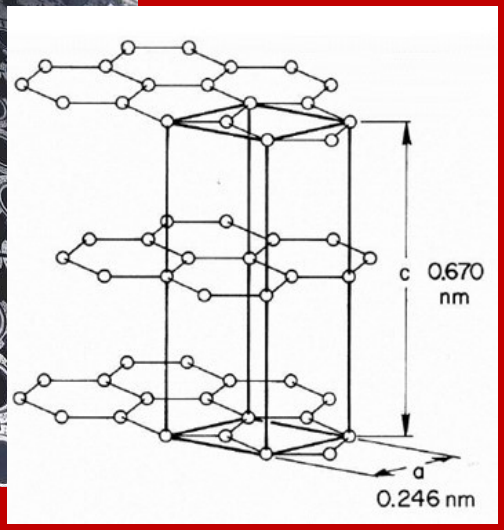
Managing Radioactive Graphite





Why graphite?

Graphite is used as a neutron moderator, reflector, radiation shield, and structural support.

It is used to slow fast neutrons into thermal neutrons which are more likely to propagate a nuclear chain reaction with U-235.

Control rods are used to control the rate of the chain reaction.

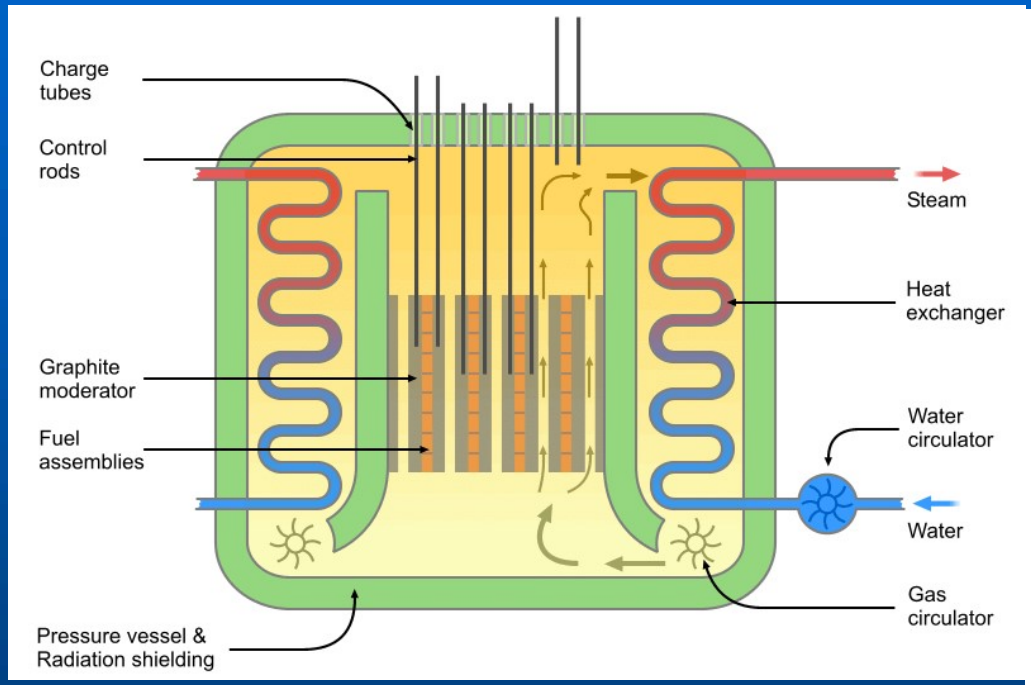
Neutron moderators

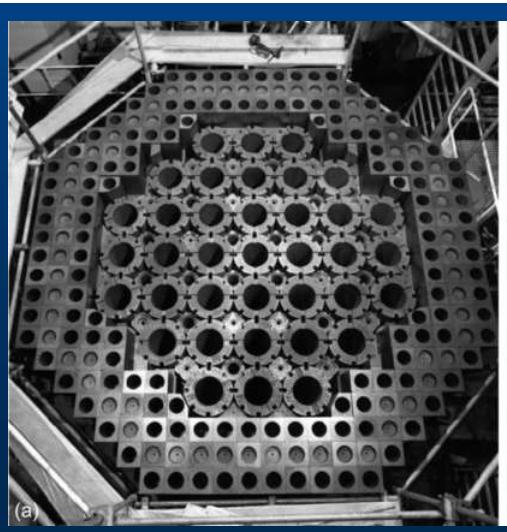
Water is used as the moderator in 75% of the world's reactors.

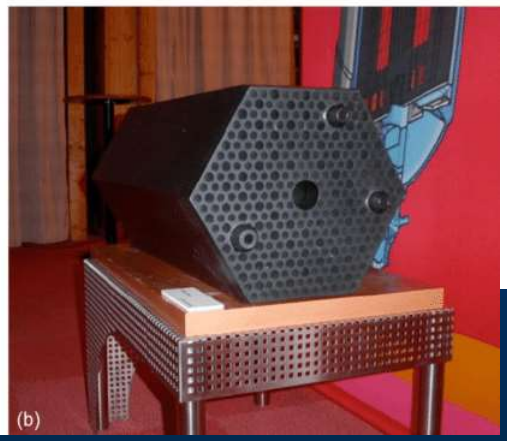
Graphite is used in about 20% to the world's reactors as a neutron moderator.

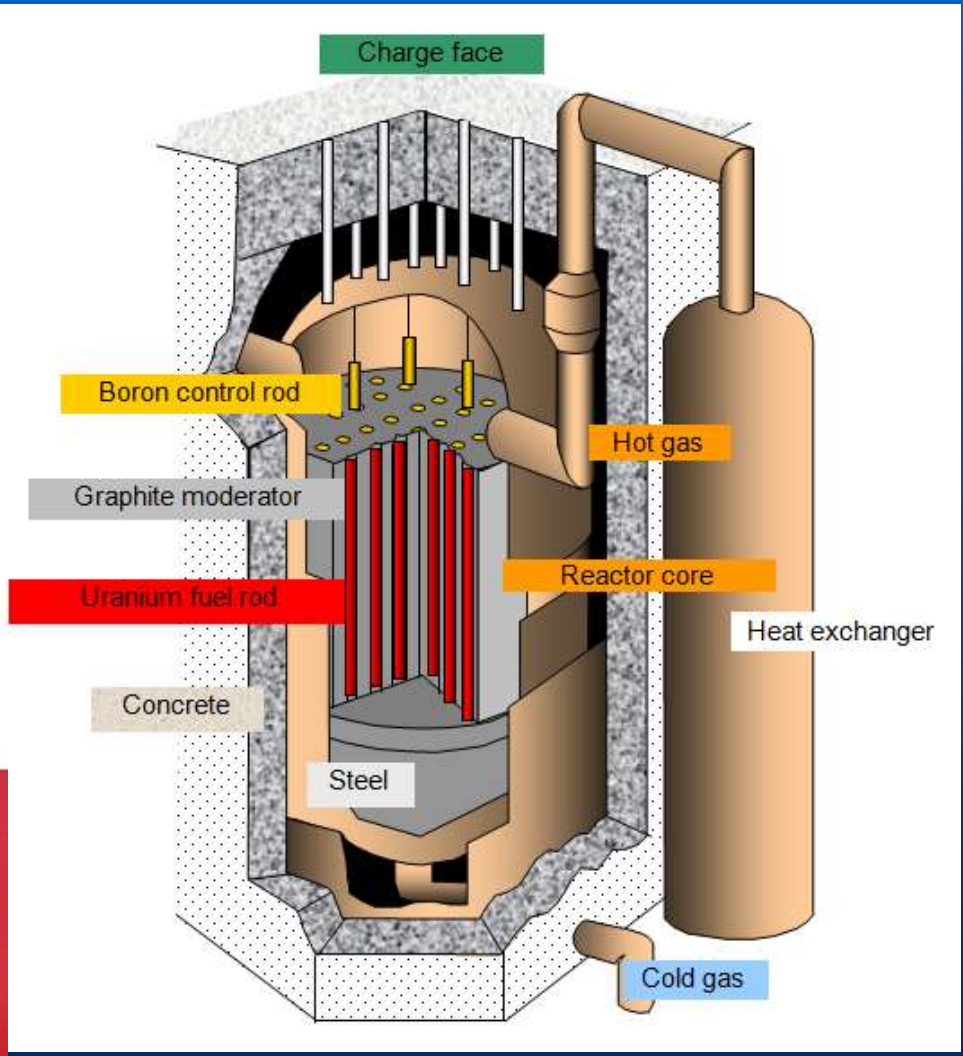
Heavy water (D_2O) is used in 5% of the reactors.

Graphite Moderators in Use

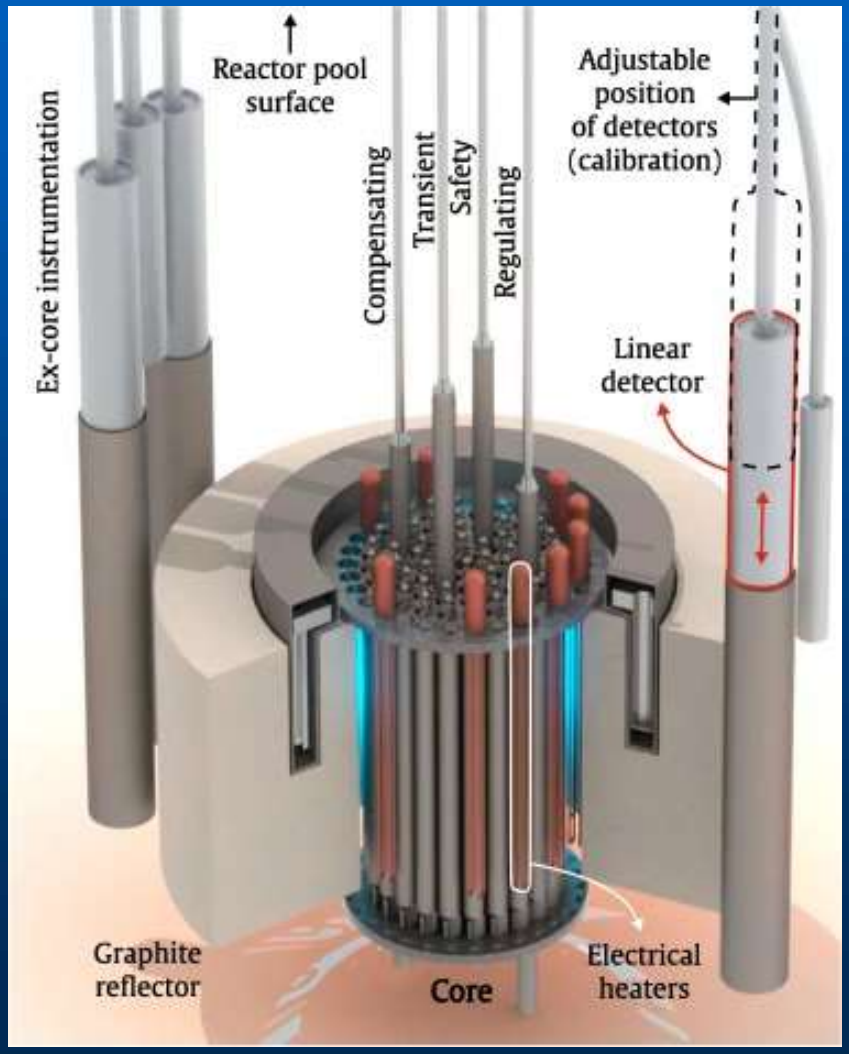






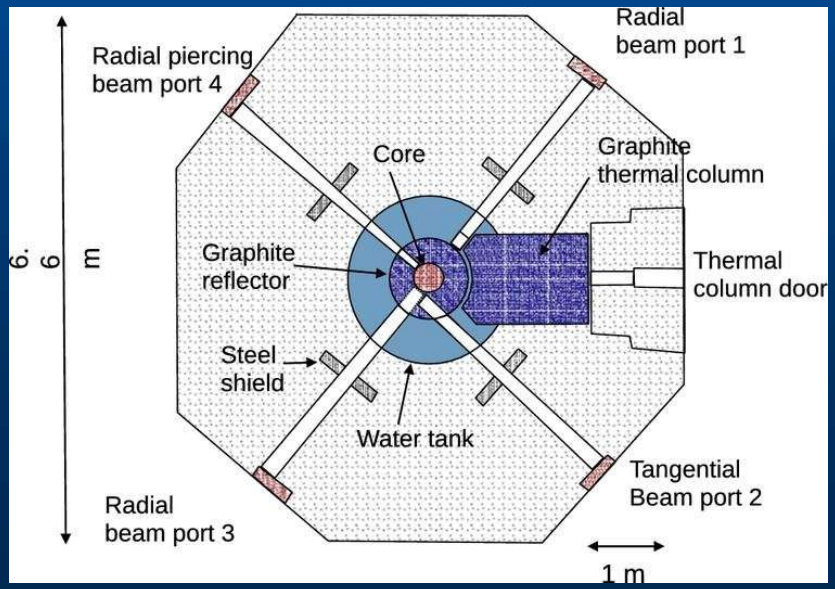


Graphite reflectors are used to reduce neutron leakage and as a radiation shield.



Graphite thermal columns

A thermal column is a graphite-filled horizontal penetration through the biological shield which provides neutrons in the thermal energy range (about 0.025 eV) for irradiation experiments.



How is nuclear-grade graphite made?

What is graphite? Crystalline carbon. Pencils are made of natural or synthetic graphite mixed with kaolin (clay). Natural graphite is mostly carbon that occurs in metamorphic rocks as a result of the chemical reduction of carbon compounds.

How is nuclear-grade graphite made?

Nuclear graphite is more complicated.

It is made from a mixture of coal or petroleum coke and binders that are heated, then treated with petroleum pitch and heated again to produce nuclear graphite.

How is nuclear-grade graphite made?

Petroleum coke is a carbon-rich by-product from oil refining. Petroleum pitch is residue from heat treatment and distillation of petroleum fractions.

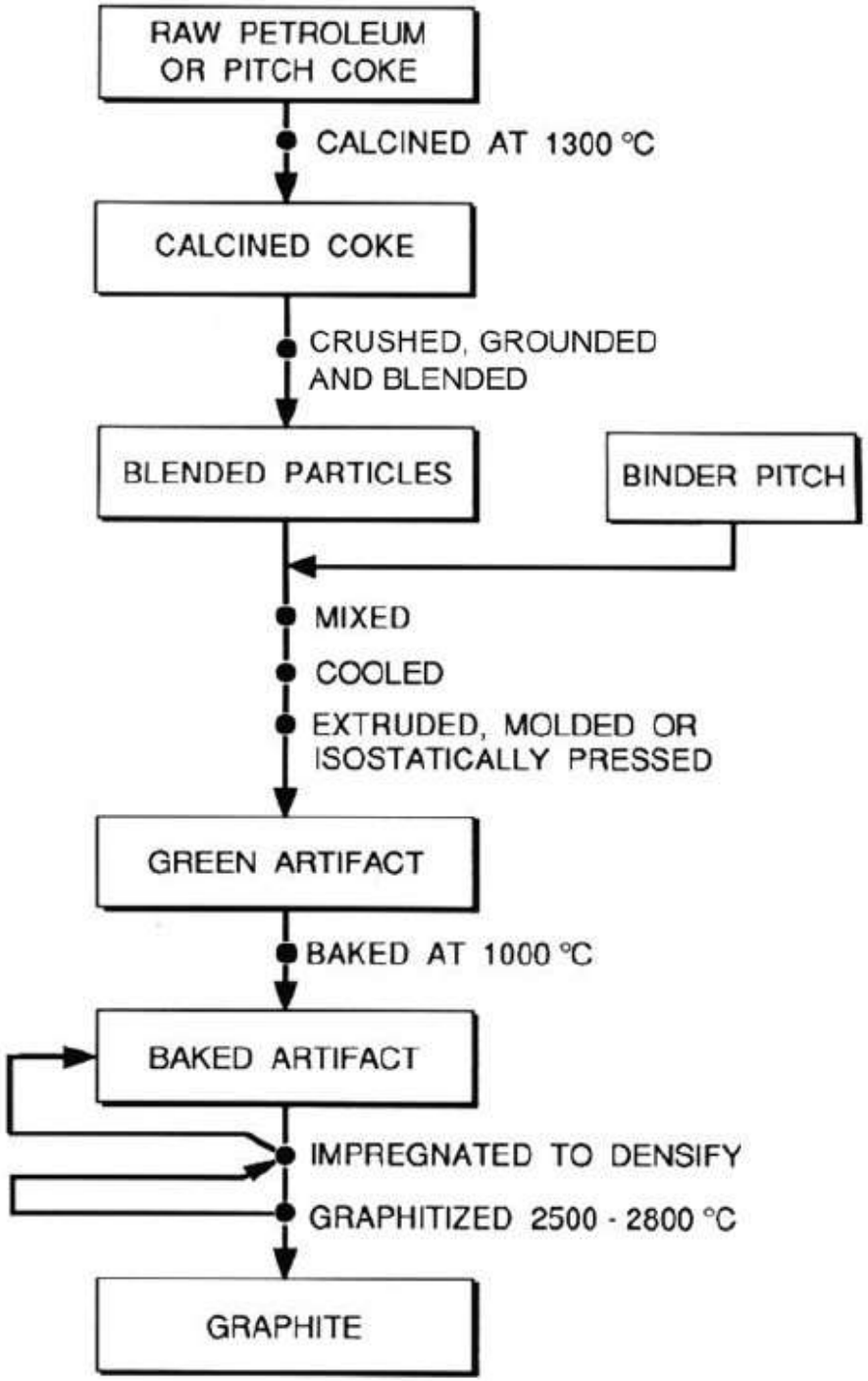
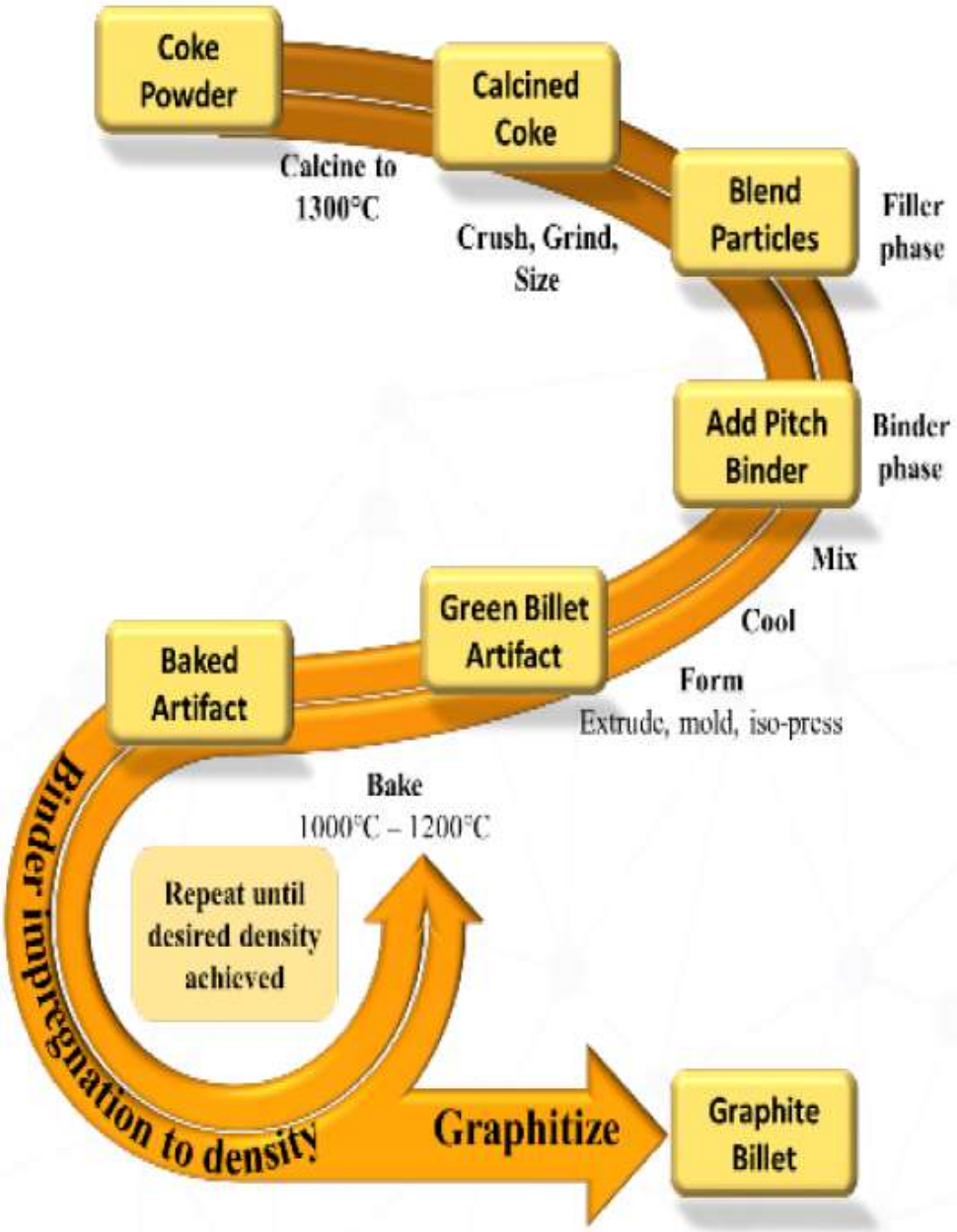


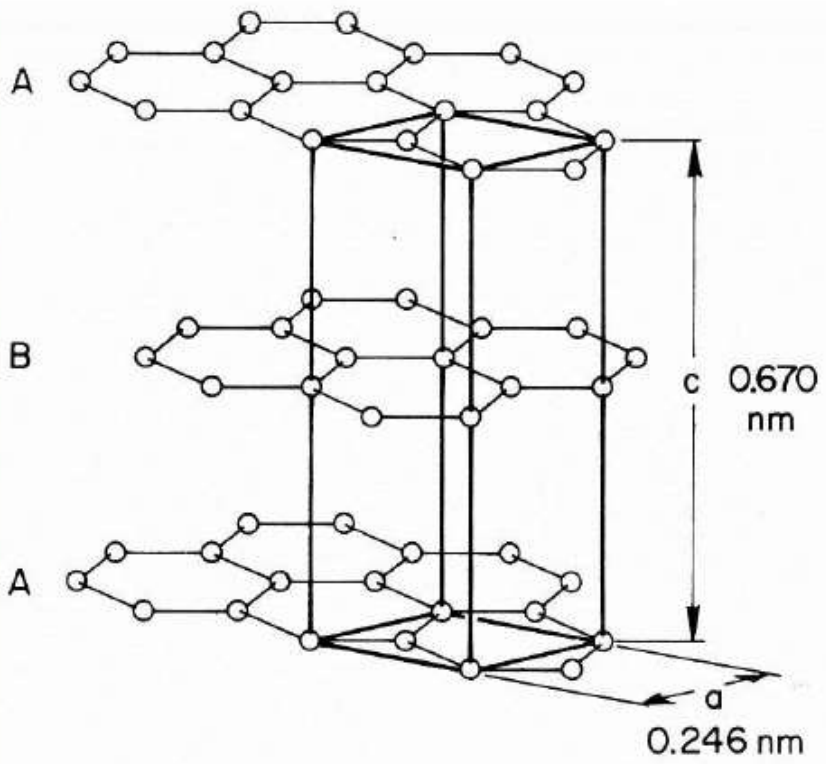
Fig. 1. The process steps in the manufacture of nuclear graphite.[3]

Graphite Manufacture



- All graphite grades **are proprietary**. Only limited/general fabrication data is known
- Unique manufacturing processes for graphite must be understood to appreciate graphite behavior
  - Graphite is a porous material (15-20%) - ***By design***!
  - Porosity provides thermal and irradiation stability
- Graphite is manufactured from calcined coke and a pitch binder.
  - Multiple pitch impregnations to increase density
- Green forming technique influences the final microstructure
  - Desire isotropic (or near isotropic) material response
- Properties and performance of graphite are significantly influenced by both raw materials and processing
  - Nuclear graphite undergoes further purification steps

Graphite Crystal Structure



- Carbon atoms in a hexagonal structure
- Covalent (strong) bonding in basal plane
- Van der Waals (weak) bonding between the planes
- ABAB stacking sequence
- Bond anisotropy and crystal perfection impart unique combination of properties
- In-plane conductor
- Cross-plane insulator

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Partial Chemical Composition of Petroleum Coke

Component	Concentration
Carbon (%)	80 to 95
Hydrogen (%)	3.0 to 4.5
Nitrogen (%)	0.1 to 0.5
Sulfur (%)	0.2 to 6.0
Boron (mg/kg)	0.1 to 15
Cobalt (mg/kg)	10 to 16
Iron (mg/kg)	50 to 5,000
Manganese (mg/kg)	2 to 100
Molybdenum (mg/kg)	10 to 20
Nickel (mg/kg)	10 to 500

Partial Composition of Radioactive Graphite

Radionuclide	Range as pCi/g
^{3}H	25.4 to 6 x 10^{6}
^{133}Ba	2.51 to 5,946
^{14}C	0.08 to 6 x 10^{6}
^{36}Cl	121 to 9,189
^{60}Co	0.005 to 270,000

Partial Composition of Radioactive Graphite

Radionuclide	Range as pCi/g
^{134}Cs	0.92 to 11,081
^{137}Cs	2.62
^{152}Eu	0.02 to 17.2
^{154}Eu	0.34 to 25,946
^{155}Eu	7.49 to 5,405
^{55}Fe	5.1×10^5

i-Graphite

Fuks et al. (2020)

98% of irradiated graphite (called i-graphite) is a low-level radioactive waste. About 95% of the radioactivity is from C-14. May be close to upper limit for Class C waste.

~ 50 Tbq/ton of C-14 and ^{3}H (1.35×10^{9} pCi/g).

~ 0.5 TBq/ton of Cl-36 (1.35×10^{7} pCi/g)

Long-Term Radionuclides

C-14 and Cl-36 are the most significant, long-term hazards in irradiated graphite, because of their long-lives (5,730 and 301,000 years), and because Cl is mobile (Metcalf and Tzeleppi, 2019).

There are 250,000 tonnes of irradiated graphite worldwide (excluding China) that will require eventual disposal.

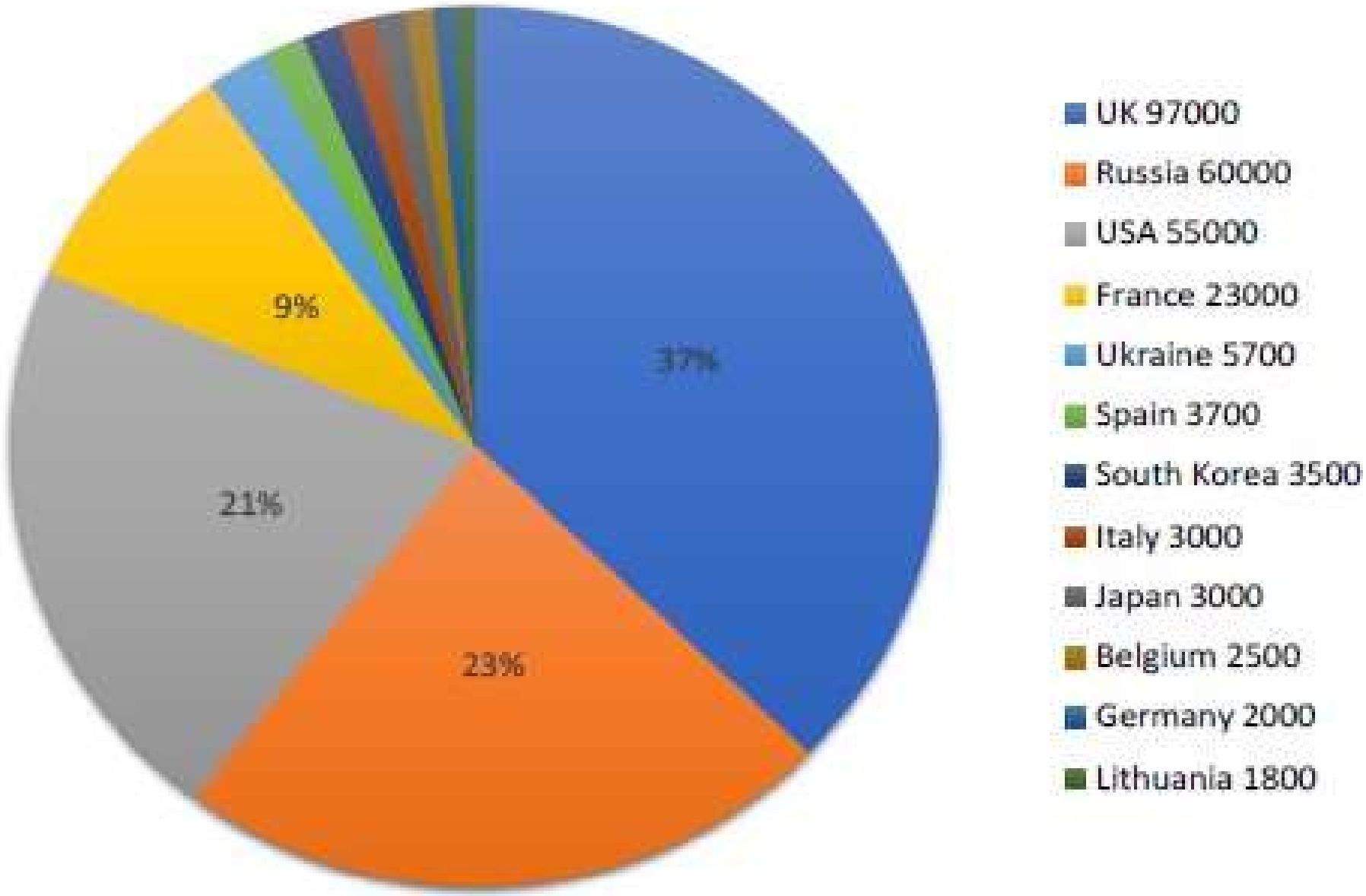


Figure 1. World inventory of irradiated graphite waste (tonnes), not including China (based on data from [1]).

Radioactive graphite is an Intermediate-Level Waste in the UK

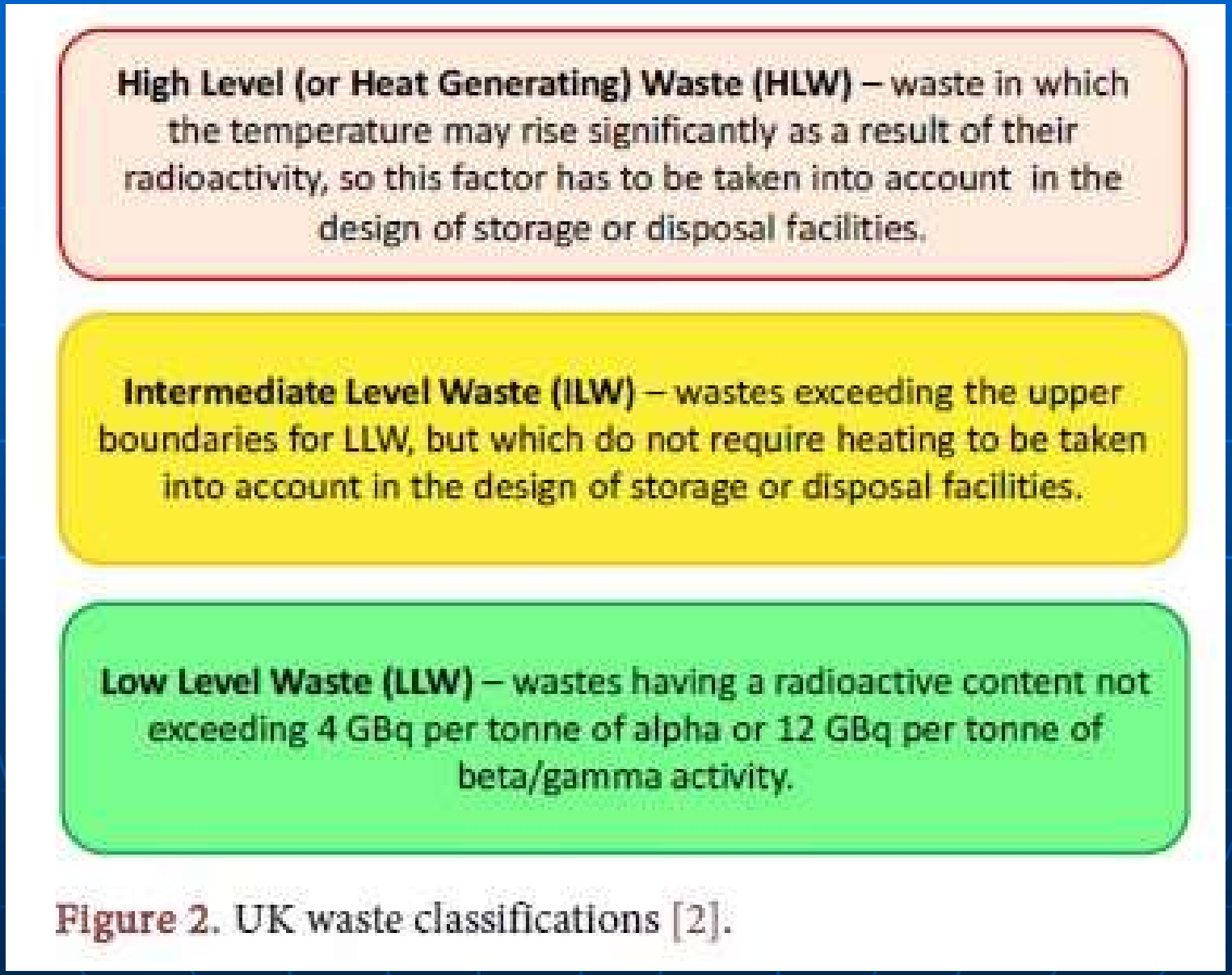


Figure 2. UK waste classifications [2].

Carbon 14

Radioactive graphite is mostly carbon, but the C is not the major source of C-14. Most of it forms as an activation product from nitrogen in the graphite:

$$^{14}N + {}^{1}\eta \rightarrow {}^{14}C + {}^{1}H$$

C-14 decays by beta minus:

$$^{14}C \rightarrow {}^{14}N + e^{-} + \text{anti-neutrino}$$

Half-life of 5,730 years.

Carbon 14

C-14 can form from C-13 which occurs in graphite in trace amounts:

$$^{13}C + {}^{1}\eta \rightarrow {}^{14}C + \gamma$$

C-14 can form from C-12 in the graphite:

$$^{12}C + 2{}^{1}\eta \rightarrow \text{C-14} + 2\gamma$$

Chlorine-36

Cl-36 forms by neutron activation of Cl-35 impurities in the graphite.

$$^{35}Cl + \eta \rightarrow {}^{36}Cl + \gamma$$

Cl-36 decays as:

$$^{36}Cl \rightarrow {}^{36}Ar + \beta^- \ (98\%)$$

$$\rightarrow {}^{36}S + \beta^+ \ (2\%)$$

Half-life of 301,000 years

Leaching Studies

The major concern: the potential for radionuclides to leach from radioactive wastes and migrate from the disposal site in groundwater.

Graphite wastes are usually land-disposed. Leaching or extraction studies are conducted to gain information about the solubility of radionuclides in waste graphite.

NUCLEAR GRAPHITE WASTE

Nuclear graphite waste in France

- 9 UNGG reactors (graphite moderated, fueled with natural uranium, CO_2 cooled)
- 23000 t of irradiated graphite => 100 000 m^3 of conditioned waste in cementitious packages
- Nuclear graphite are classified as "Long Life Waste – Low Level" (^{14}C, ^{36}Cl ..)
- 81% of the graphite still in reactor waiting for dismantling

The disposal behavior of the radionuclides is one of the main issues when considering graphite waste long-term management scenarios

Disposal studies

A "leaching test" program in accordance with EDF, ANDRA and CEA was initiated in 2008

- Objective : **characterize ^{36}Cl source term** (leaching rate) on irradiated graphite.

^{36}Cl is the main radionuclide which can contribute to the long term radiological impact of graphite in disposal due to his long lifetime, high mobility and solubility

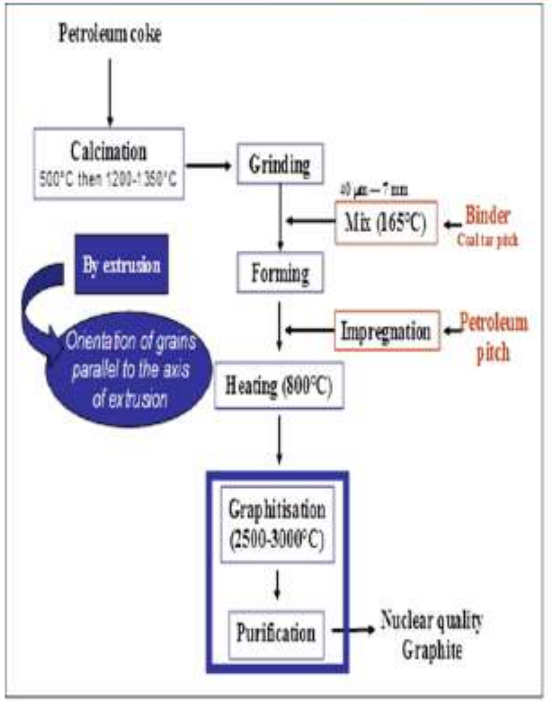
- Methodologies : CEA develop leaching procedure optimized for ^{36}Cl measurement (similar to AIEA standards) with those followed specifications:
  1. Sampling times are defined to focus on diffusion mechanism and water uptake
  2. Analytical methodology was optimized to measure the ^{36}Cl

IRRADIATED GRAPHITE ORIGIN OF CHLORINE 36

Origin of natural chlorine in nuclear graphite

- As an impurity in the basic materials used for the manufacture (Coke, Coal tar pitch, cleaning agents(NaF, MgF_2..),…)
- Brought by air pollution (end of the manufacture, during storage)
- Present at low level in the coolant gas (Air, CO_2)

Cl in nuclear graphite are around 5 to 40 ppm



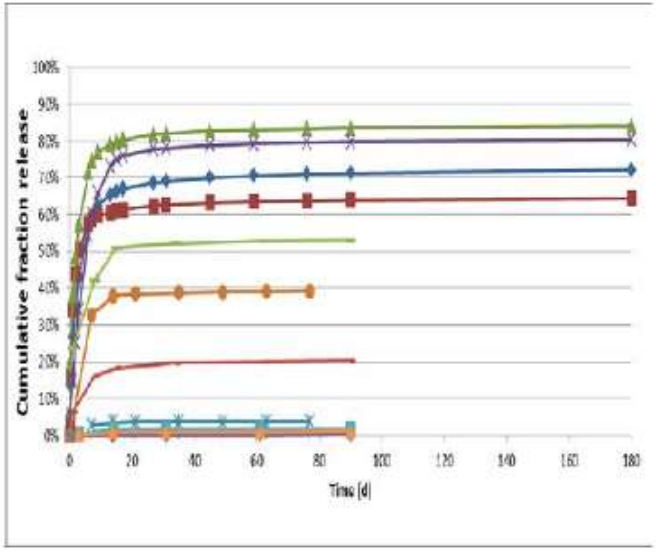
Origin of ^{36}Cl (long live radionuclide 3.10^5y, β^-)

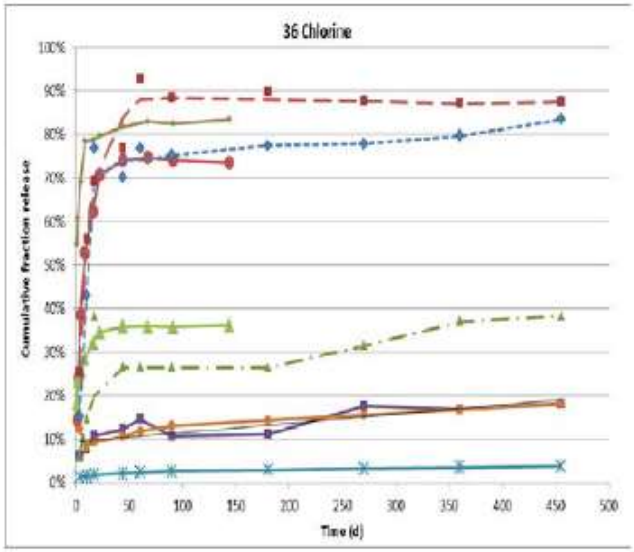
- Production
  - Direct activation of ^{35}Cl (77,5%) 44 barns
  - Direct activation of ^{39}K (93,25%) 0,004 barns
  - Indirect activation of ^{34}S (4,2%) 0,34 barns

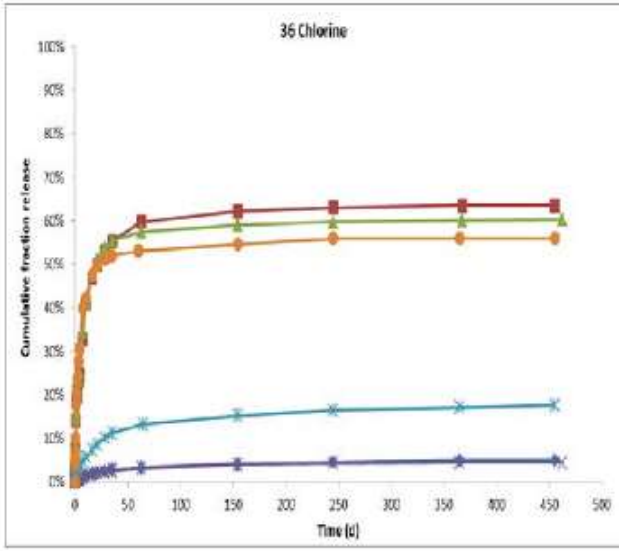
=>$^{35}Cl(n,g)^{36}Cl$ is the predominant reaction for the formation of ^{36}Cl in irradiated graphite but with nuclear recoil ^{36}Cl location should be different from ^{35}Cl initial position (atoms are 'displaced', some maybe re-form covalent bonds =>different speciation of ^{36}Cl and ^{35}Cl)
=> ^{36}Cl activity in French i-graphite is very low but with a huge variability (1-10^3 Bq/g) and a specific analytical procedure must be used (with low detection limit)

CHLORINE 36 LEACHING DATA

- **Overall leaching tests (^{36}Cl)**
  - High variability of the leaching rate (from few % to 90%)
  - ^{36}Cl is release in liquid phase in two stages
    1. With a very quick release kinetics (called "labile fraction")
    2. Slow release kinetics (called "non labile fraction")
  - No release in the contact gas phase (Air, N_2, Ar)
- **Others common points**
  - Water uptake kinetics are fast in irradiated graphite samples (70 % of the open porosity is filled within a few days)







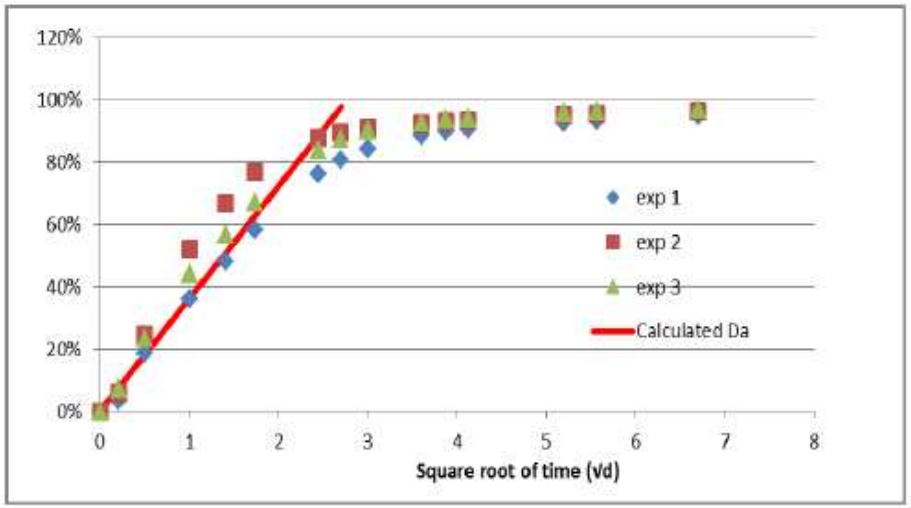
Chlorine 36 cumulative fractional release as a function of time for irradiated graphite samples. Tests performed with pure water or lime water under air or inert atmosphere

INTERPRETATION

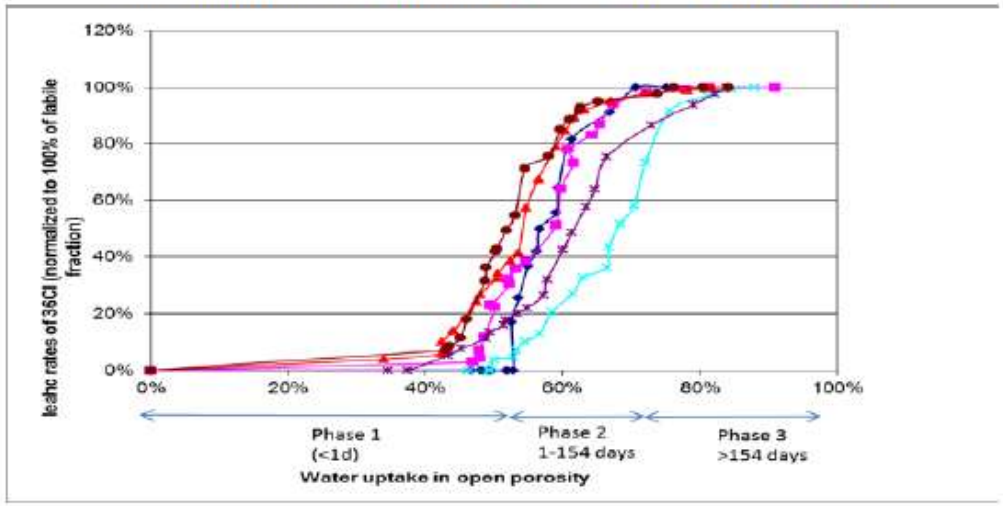
Chlorine 36 labile fraction

- The release kinetics of labile ^{36}Cl can be described by a diffusion model of dissolved Chlorine (Cl^-) through the graphite porosity
- Chlorine 36 release is not limited by water up-take
- Low impact of leaching parameters (water chemistry, pH, temperature)

Comparison of ^{36}Cl release with a diffusion model
The overall release is normalized to 100% of ^{36}Cl labile fraction



Correlation between 36Cl labile fraction leach rate and water uptake in graphite open porosity
The overall release is normalized to 100% of ^{36}Cl labile fraction



Diffusion calculations are performed by adjusting the value of the diffusion coefficients to reproduce the experimental data of the leaching tests according to Equation

$$F = 2.\frac{S}{V}.\sqrt{\frac{D_a.t}{\pi}}$$

F: Leached fraction
S: Geometric area subject to leaching
V: Geometric volume of sample
t: Time
Da: Apparent diffusion coefficient

Coke	Mean Da ($m^2.s^{-1}$)	Mean De ($m^2.s^{-1}$)
« Spécial »	3.10^{-11}	6.10^{-12}
« Lockport »	9.10^{-12}	2.10^{-13}
« Lima »	3.10^{-12}	$6,5.10^{-13}$

CONCLUSIONS

- Leaching tests demonstrate :
  - Two forms / localization of ^{36}Cl in irradiated graphite
    - One labile form, controlled by a diffusion process through graphite porosity
    - A second stage showing slow release kinetics (non-labile fraction)
  - ^{36}Cl leaching rate depends on i-graphite operating temperature
    - Low leaching rate => Irradiated at high temperature
    - High leaching rate => Irradiated at low temperature

- Perspectives of work
  - Study the correlation of the variability of leaching rate with graphite structural evolution
  - Influence of the coke/reactor /other graphite waste need to be clarified
  - Study the non labile fraction (speciation / localization)

- Perspectives for disposal
  - To get a better understanding of the underlying mechanisms which govern chlorine 36 release in order to increase confidence in the demonstration of long term safety
  - To assess long term chlorine 36 release rate to improve the source term model and therefore the safety assessment

Graphite from a Magnox Reactor (UK)

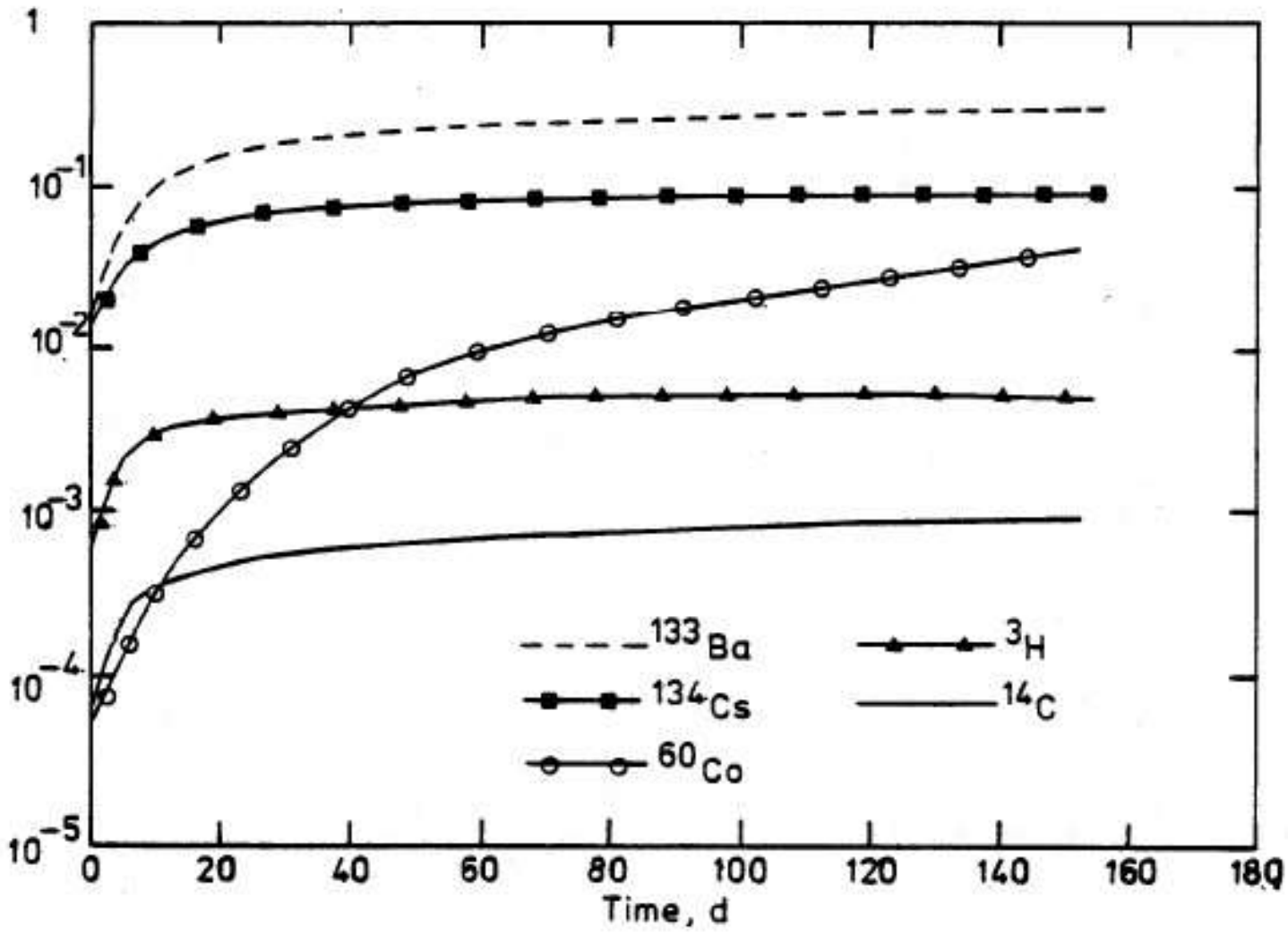


Figure A-2
Cumulative Fraction of Activity Leached in Demineralised Water (1 bar, 25°C)

Graphite from a Magnox Reactor (UK)

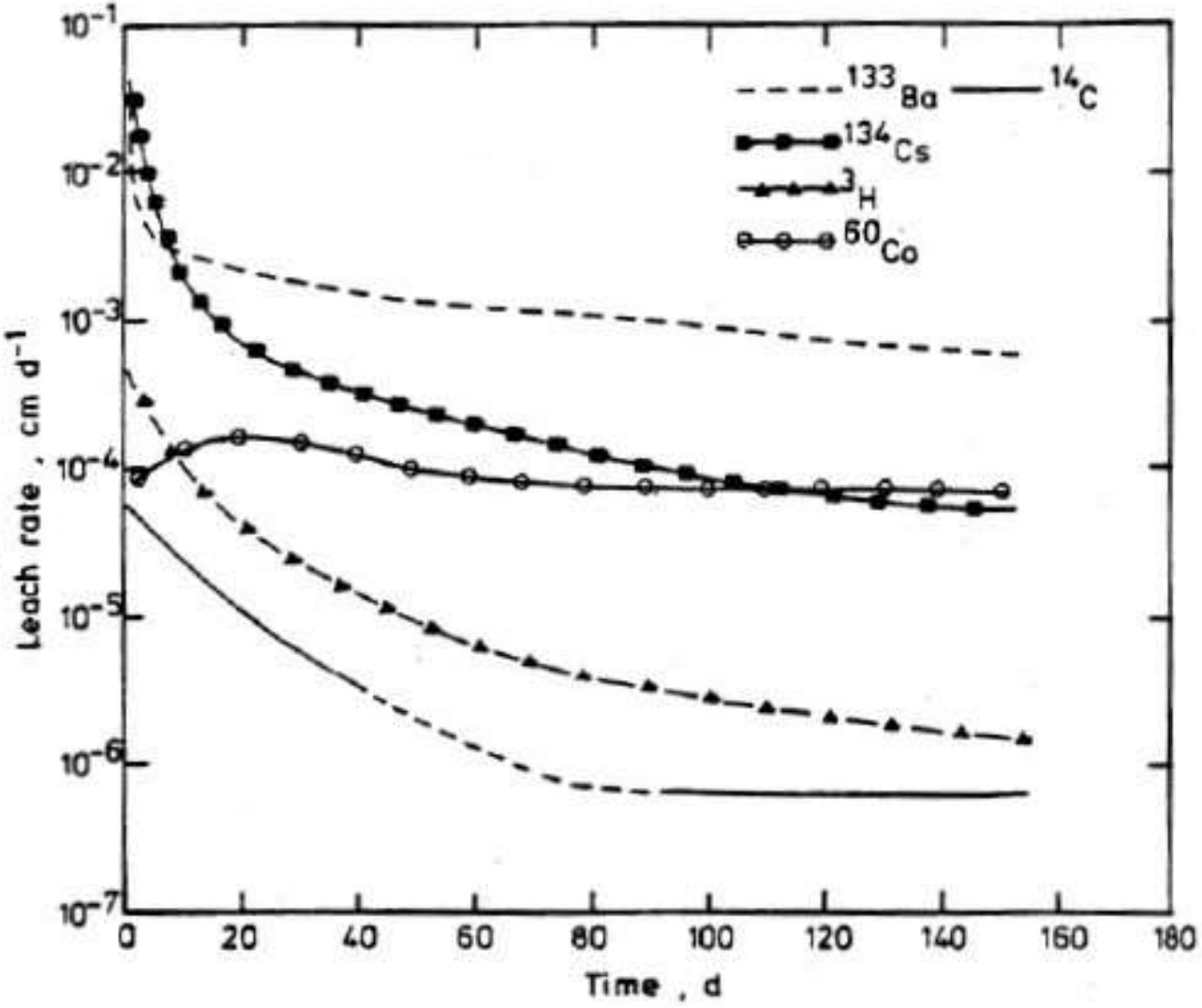


Figure A-5
Leach-Rate Curves in Simulated Ground Water (1 bar, 25°C)

Disposal of i-Graphite

Has been studied more in Europe than the U.S. because of greater volumes and fewer disposal options.

Proposed treatments prior to disposal of i-graphite:

SAFSTOR (most commonly used)

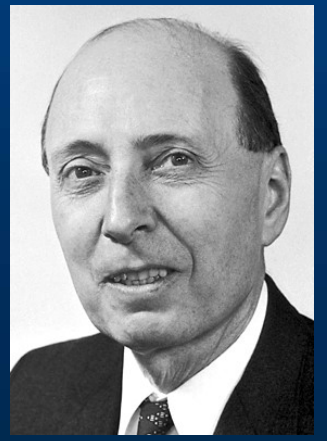
Break down then mix pieces with cement.

Incineration then manage the ash by blending it with cement.

Wigner Effect

The Wigner Effect is a type of stored energy in graphite when neutrons have enough kinetic energy to displace atoms in the graphite lattice. This stored energy can be released from the graphite later as heat which may complicate disposal. May cause fires (The Windscale Fire).

Discovered by Hungarian-American theoretical physicist Eugene Wigner.



Future Graphite Disposal

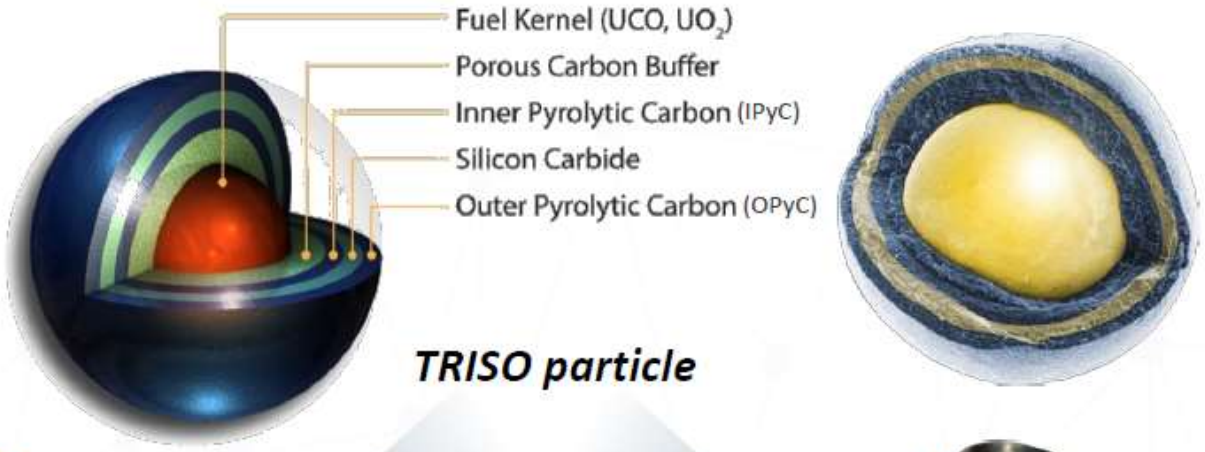
Uranium kernels encased in layers of carbon.

TRISO Fuel (TRIstructural ISOtropic).

https://www.youtube.com/watch?v=zHIjaZJ-AzA (3:15)

ART
ADVANCED REACTOR TECHNOLOGIES

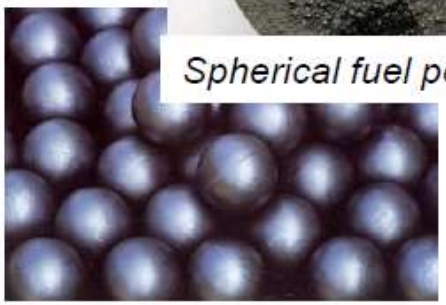
Tristructural Isotropic (TRISO) Coated Particle Fuel



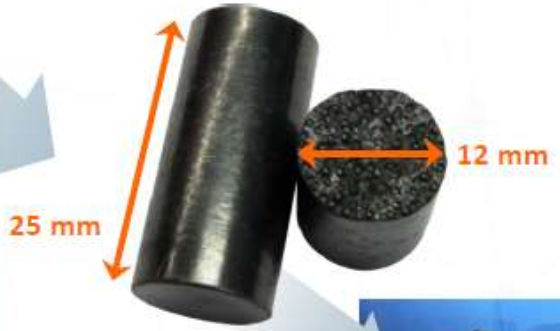
TRISO particle

60 mm

Spherical fuel pebbles



Particle design provides excellent fission product retention in the fuel and is at the heart of the safety basis for high temperature gas reactors



Cylindrical fuel compacts

Prismatic graphite blocks

Future Graphite Disposal

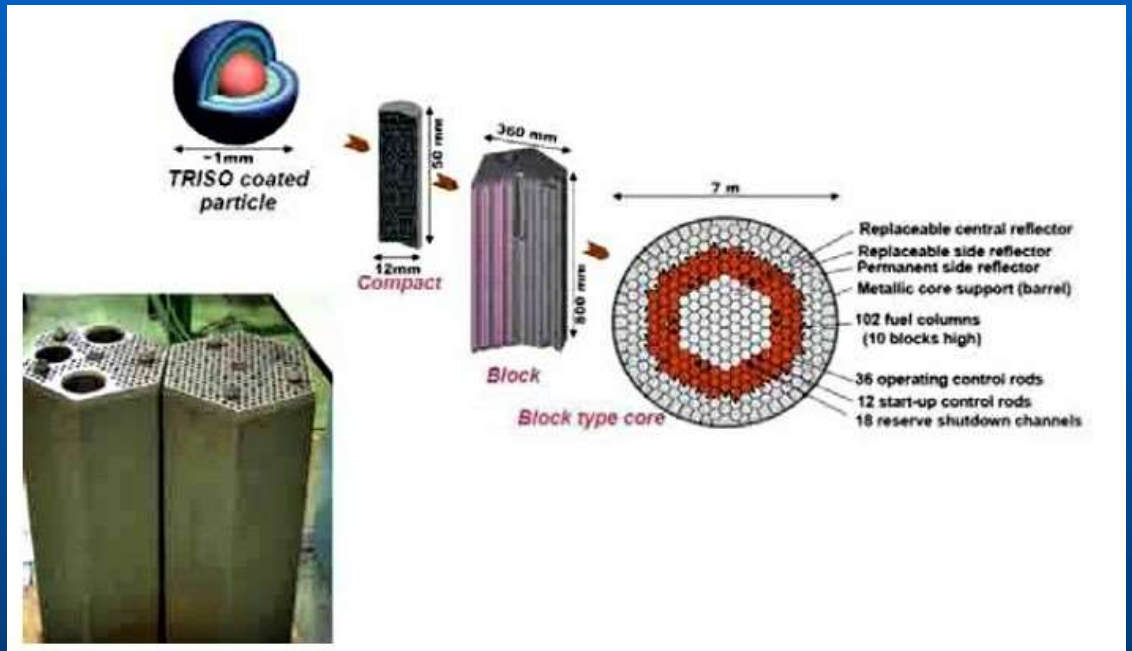
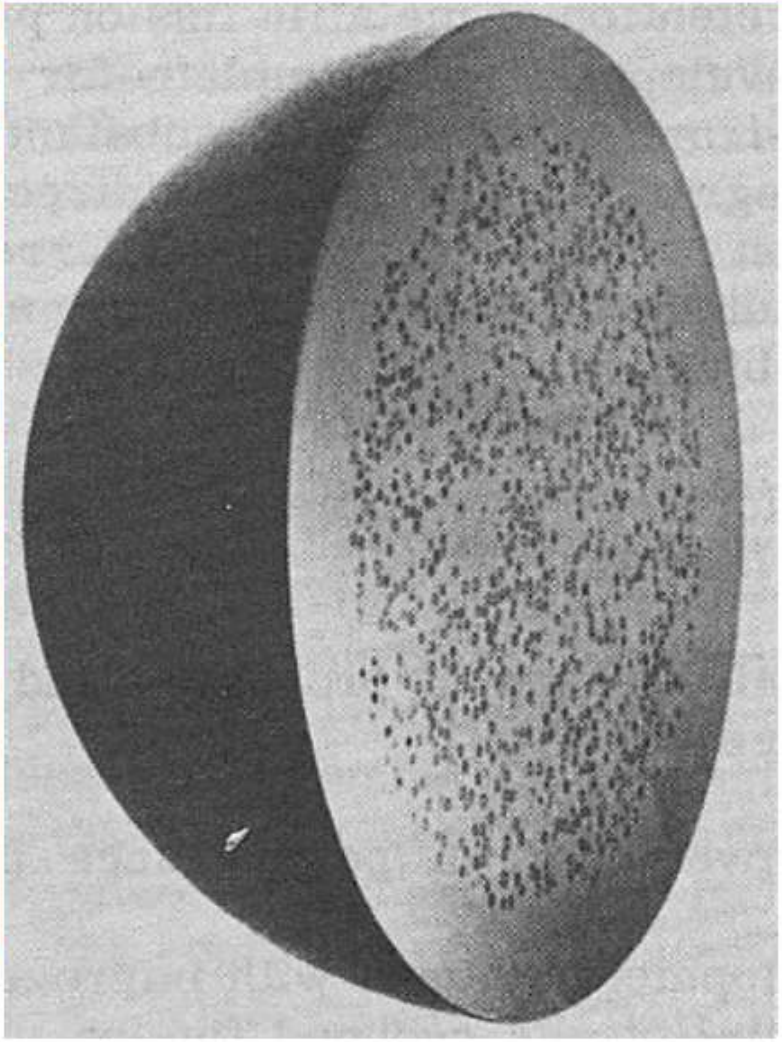


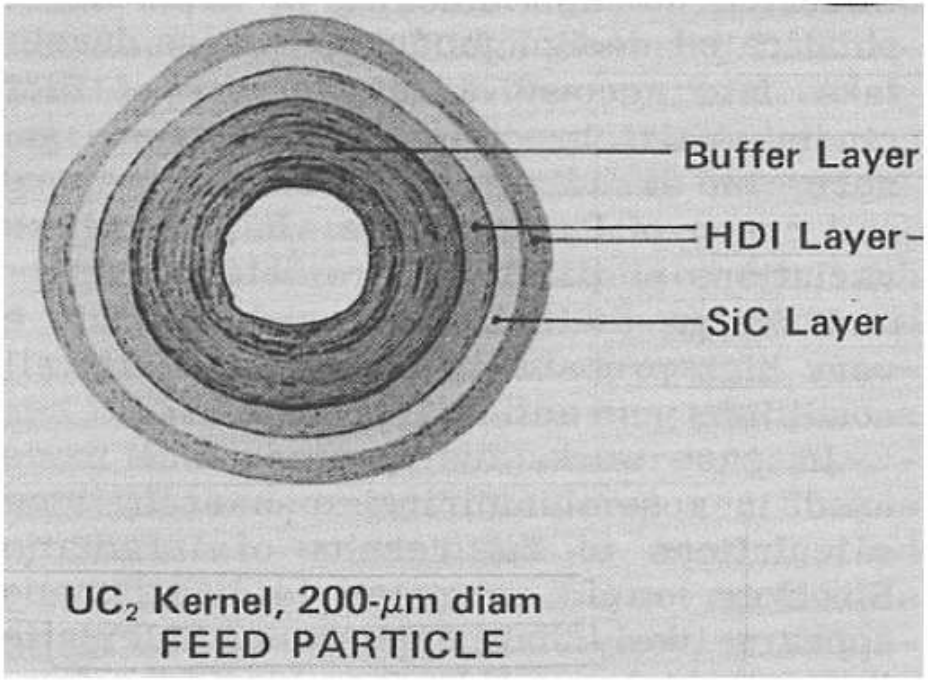
FIG. 3. Fuel element designs for the prismatic core concepts. Both pebble and block HTR core concepts employ the fuel particle as the basic fuel-containing unit.

FIG. 4. Japanese fuel element, fuel rods, compacts and particle.

The Pebble Type HTR Utilizes Ceramic Coated Particle Fuel



The TRISO fuel particles are combined into a graphite (carbon) fuel ball (pebble) 6 cm in diameter



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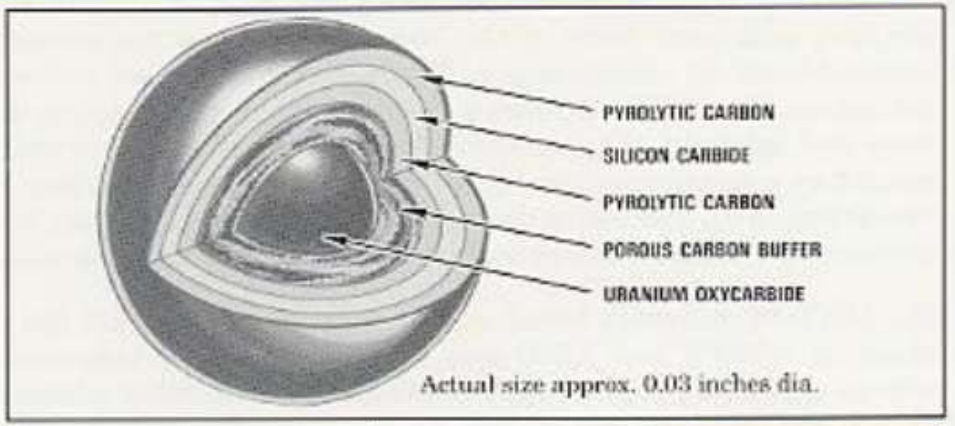
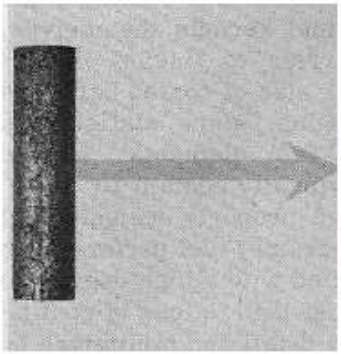
ASME Code for Graphite

The GT-MHR Utilizes Ceramic Coated Particle Fuel

The TRISO fuel particles are formed into 12 mm diameter graphite (carbon) fuel sticks and inserted into graphite fuel blocks





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Future Graphite Disposal

Processing Advanced Reactor Fuels

- **TRISO Fuel**
  - It is challenging to destroy the outer coatings of TRISO particles to access the uranium
  - Historically, a grinding, burning, and leaching approach was developed, but burning the graphite releases C-14
  - Besides the carbon coating of the particles, there is a very large mass of contaminated graphite in the compacts, prisms, or pebbles that will require disposal
  - Methods that need developed are:
    - Separating TRISO particles from the graphite material
    - Accessing the uranium inside the TRISO particle
      - SRNL molten nitrate salt
      - Electrochemical method
      - Sonication
      - Others ?

Questions?