NE 795: Advanced Reactor Materials

Fall 2023

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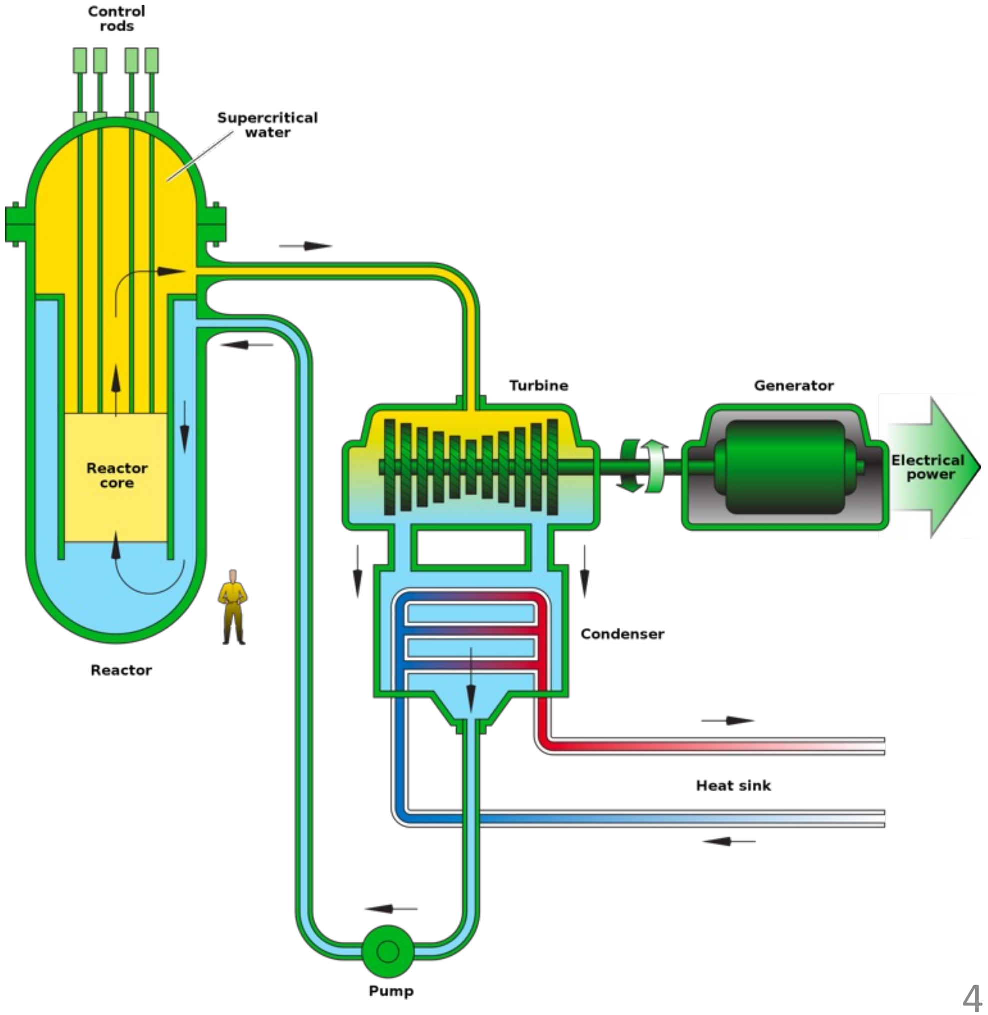
Housekeeping

- Last exam on Thursday
- Complete the class eval poll
- Complete my poll also for a +5 on exam:
  - https://docs.google.com/forms/d/1t09SuKXjy14ONIIMwl9JbGAfjAnQe30bZCRzleXsFJI/edit
- Will send this out to everyone after class

SUPERCRITICAL WATER COOLED REACTORS

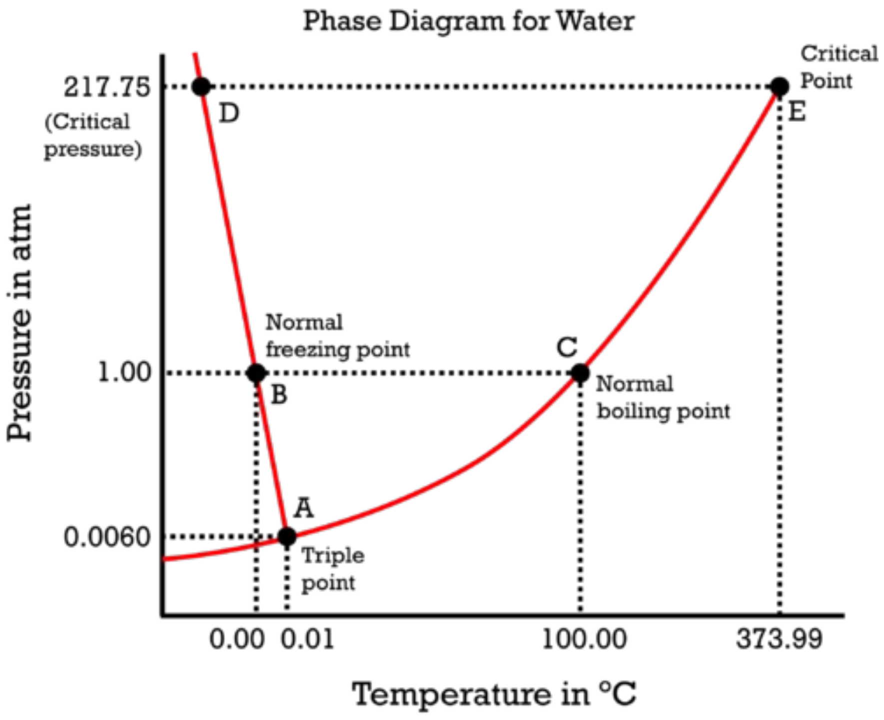
Supercritical Water Reactor (SCWR)

- Similar to a traditional light water reactor, but operates at a supercritical pressure
- Water heated in the core becomes a supercritical fluid, which can directly be used in a steam turbine
- Removes the added step of a heat exchanger, increasing the efficiency of the reactor system



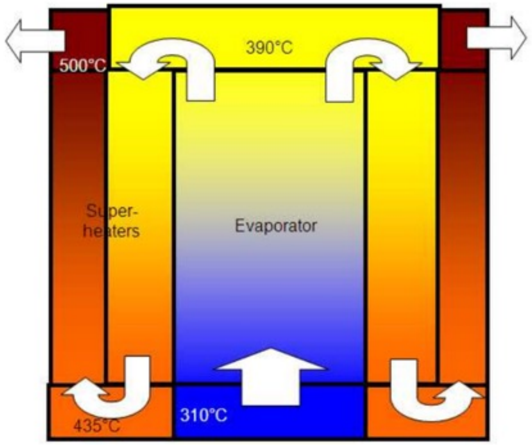
Supercritical water

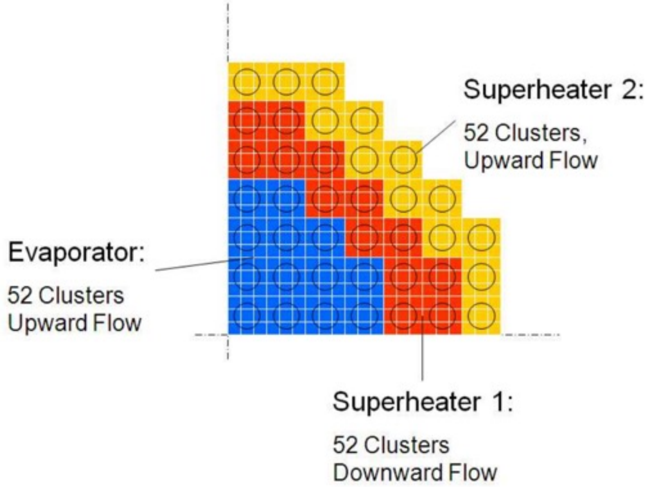
- A supercritical fluid is a substance with a temperature and pressure above its critical point
- At such a point, distinct solid and liquid phases do not exist
- Critical point of water is 22 MPa and 647 K
- Density is highly variable, based on temperature and pressure:
  - 0.78 g/cc @ 25 MPa and 280 C
  - 0.09 g/cc @ 25 MPa and 500 C
  - these are reasonable inlet/outlet temperatures for SCWR coolant



Comparison to LWR

- SCWR
  - coolant in: 280 C
  - coolant out: 600 C
  - outlet specific enthalpy: 3150 kJ/kg
  - three pass coolant
  - coolant pressure: 25 MPa
- LWR
  - coolant in: 275 C
  - coolant out: 315 C
  - outlet specific enthalpy: 200 kJ/kg
  - one pass coolant
  - coolant pressure: 15 MPa





Features

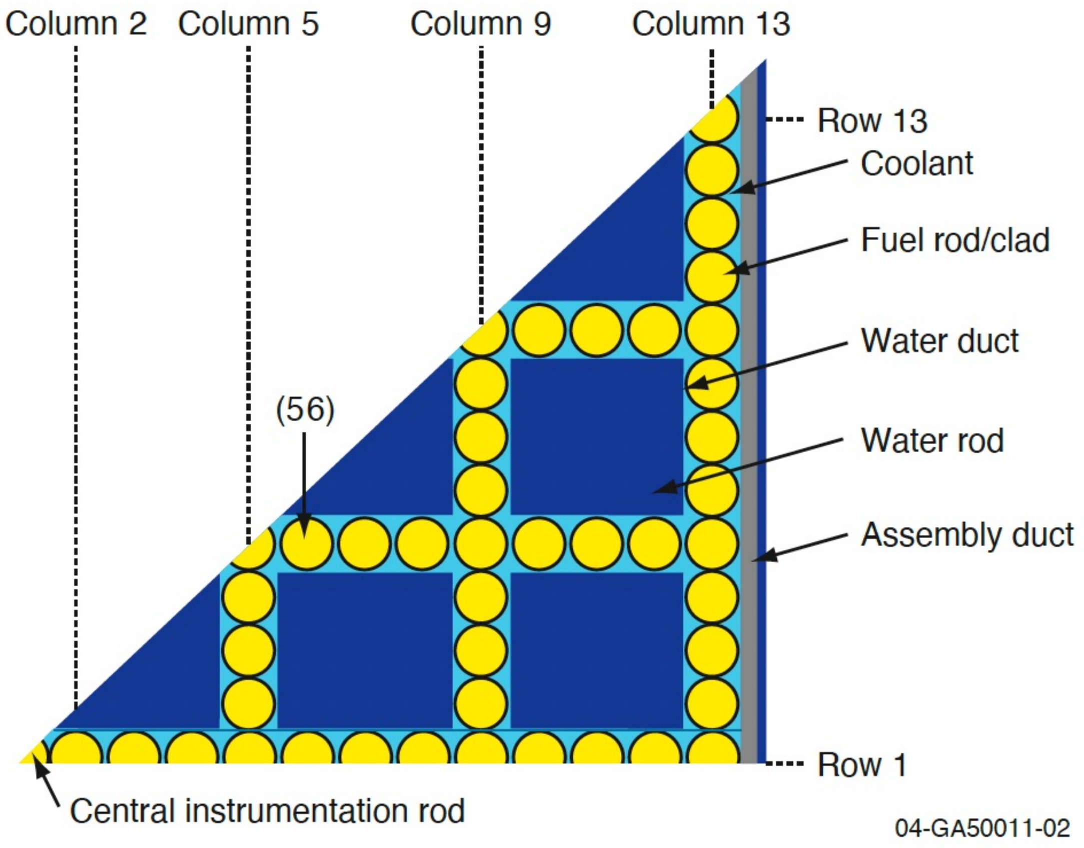
- Supercritical water has excellent heat transfer properties allowing a high power density, a small core, and a small containment structure
- The use of a supercritical Rankine cycle with its typically higher temperatures improves efficiency (would be ~45 % versus ~33 % of current PWR/BWRs)
- This higher efficiency would lead to better fuel economy and a lighter fuel load, lessening residual (decay) heat
- SCWR is typically designed as a direct-cycle, whereby steam or hot supercritical water from the core is used directly in a steam turbine with no intermediate heat exchangers, etc
- SCWRs can operate as a fast breeder, or utilize heavy water and the thorium fuel cycle
- Disadvantages include operating at very high temperatures and pressures, increasing material challenges
- The economic advantage of a direct cycle is a downside with regard to safety, in that a cladding breach means your turbine and generators are directly exposed to radioactivity
- Corrosion in SCW is a challenge

SCW geometry

- There is experience in SCW cycles in the fossil fuel industry, however they are able to use thick-walled geometries that are not feasible in nuclear designs

Fuel rod outer diameter = 12 mm
Clad wall thickness = 0.4–0.6 mm

Water rod outer diameter = 40 mm (square)
Water rod wall thickness = 0.4 mm



1/8 assembly model SCWR core

Corrosion

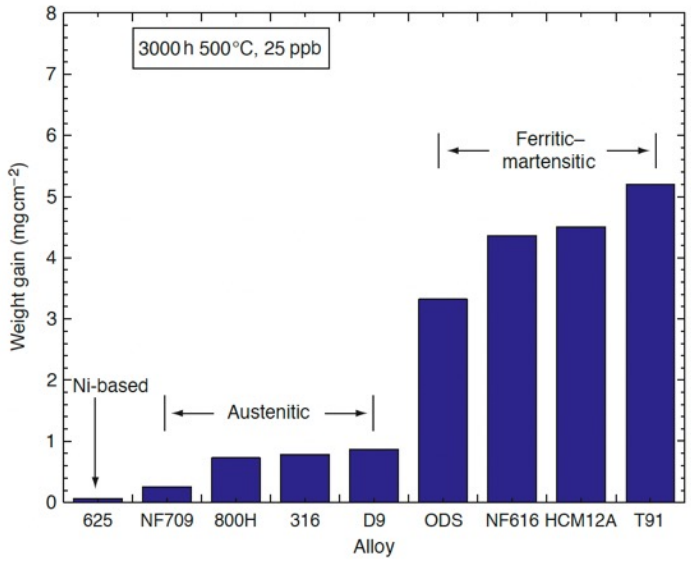
- These very thin-walled components provide little margin for corrosion in an SCWR core, where the consequences of failure are significant
- Oxide films and deposition of corrosion products from out-of-core components can lead to overheating (and failure) and changes in reactivity

- SCW corrosion studies have included F/M steels, austenitic steels, Ni alloys, Zr alloys and Ti alloys

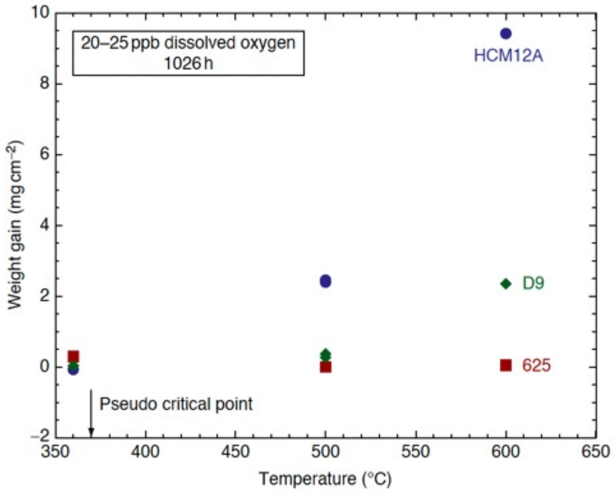
Alloy class	*Alloy*	*Temp. (°C)*	*Water chemistry*	*Exposure time (h)*
Austenitic stainless steel	304, 304L, 316, 316L, 316 + Zr, 310, 310S, 310 + Zr, 347H, Sanicro28, D9, 800H, AL6XN, Carpenter 20C B3, Nitronic-50, PNC1520, alloy 1.4970	290–650	Deaerated (<10 ppb) to 8000 ppb dissolved oxygen	100–3000
Nickel-based	600, 625, 690, 718, 825, C22, B2, C276, MAT21, MC	290–600	Deaerated (<10 ppb) to 8000 ppb dissolved oxygen, <0.1 mS cm^{-1}	100–3000
Ferritic–martensitic	T91, T91a, T91b, HCM12A (T122), HCM12, HT-9 (12Cr–1Mo–1WVNb), NF616 (T92), MA956, 2.25Cr–1Mo (T11), P2	290–650	Deaerated (<10 ppb) to 8000 ppb dissolved oxygen, <0.1 mS cm^{-1}	100–3000
Oxide dispersion strengthened	9Cr, 12Cr, F/M, 316, Inconel, Hastelloy G-30, 19Cr, 14Cr–4Al, 16Cr–4Al, 19Cr–4Al, 22Cr–4Al	360–600	25 ppb	200–3000
Zirconium-based	Zr, Zr–Nb, Zr–Fe–Cr, Zr–Cr–Fe, Zr–Cu–Mo, Zr-2, Zr-4	400–500	Deaerated (<10 ppb dissolved oxygen), <0.1 mS cm^{-1}	<2880
Titanium-based	Ti–3Al–2.5V, Ti–6Al–4V, Ti–15Mo–5Zr–3Al, Ti–15V–3Al–3Sn–3Cr	290–550	8000 ppb dissolved oxygen, 0.1 mS cm^{-1}	500

Alloy Classes

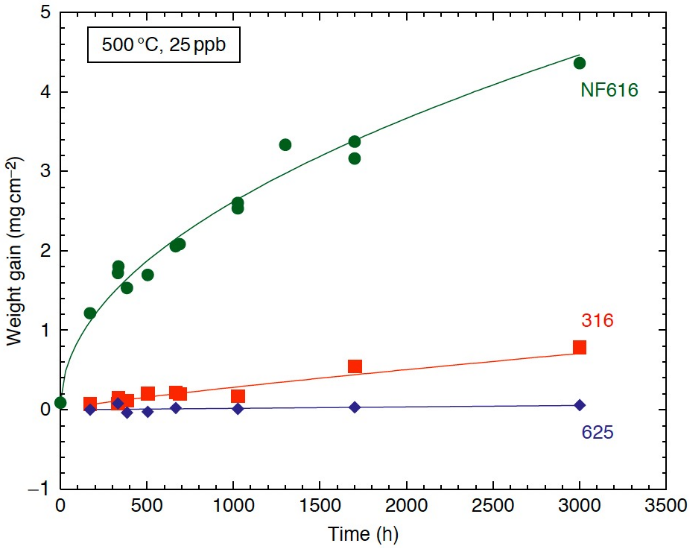
- Corrosion is strongly dependent upon the alloy class
- Oxidation is most rapid for F/M steels and slowest for Ni alloys
- Temperature has a very strong effect on corrosion



Dissolved O content 25 ppb



HCM12A = F/M
D9 = aust.
625 = Ni



NF616 = F/M
316 = aust.
625 = Ni

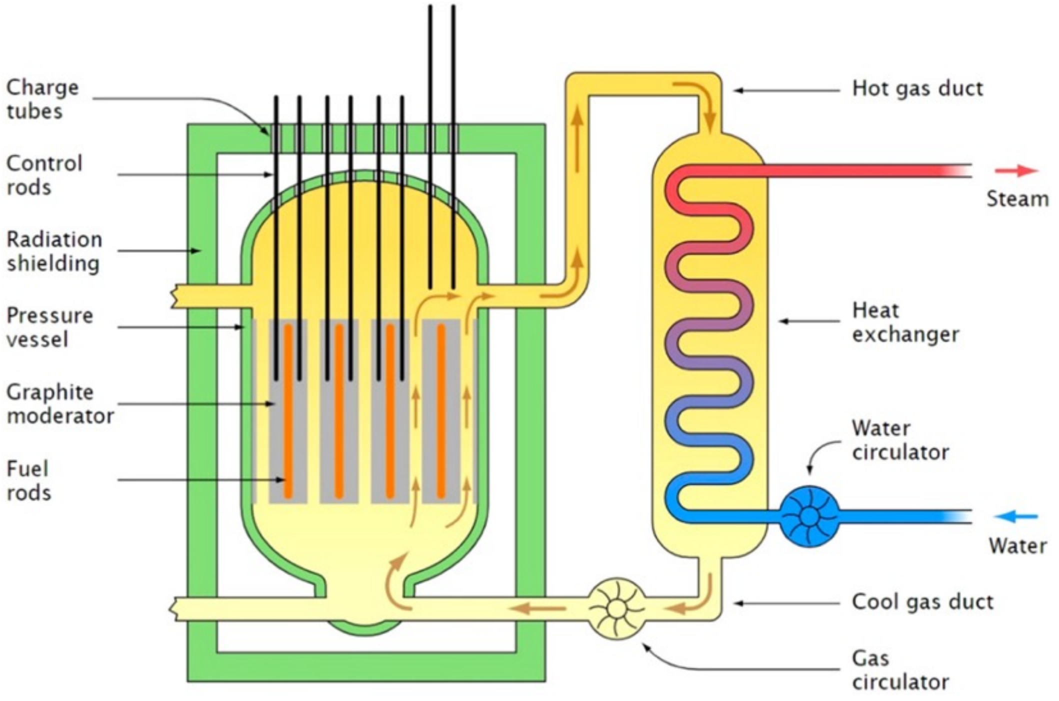
Stress Corrosion Cracking

- Austenitic stainless steels and nickel-based alloys exhibit susceptibility to IGSCC in pure SCW over the temperature range of 400–650C
- IGSCC decreases with temperature, but overall fracture increases with temperature
- Small additions of HCl or H2SO4 increase susceptibility to IGSCC in austenitic alloys
- Ni based alloys are more susceptible to SCC than austenitic steels
- Higher Cr content in Ni alloys seems to reduce the extent of SCC
- F/M alloys are generally resistant to SCC (HT-9 is an exception)
- Irradiation strongly exacerbates SCC, but the effect decreases with increasing temperature

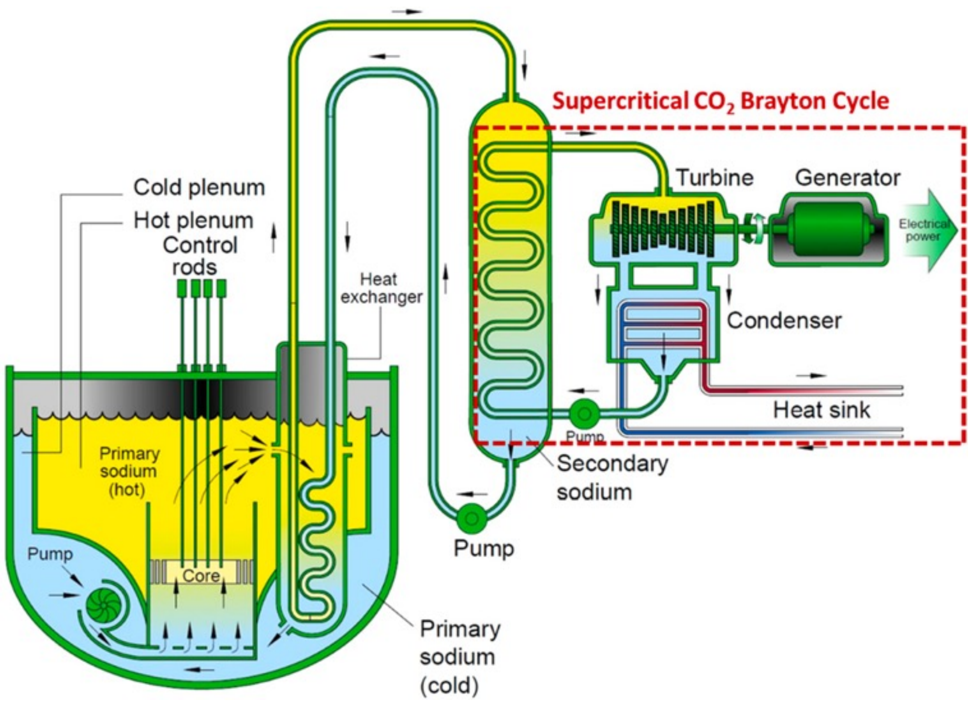
CO2 CORROSION IN REACTORS

CO2 Applications

- Magnox CO2-cooled reactor



- Tertiary cycle with supercritical CO2



CO2 Usage

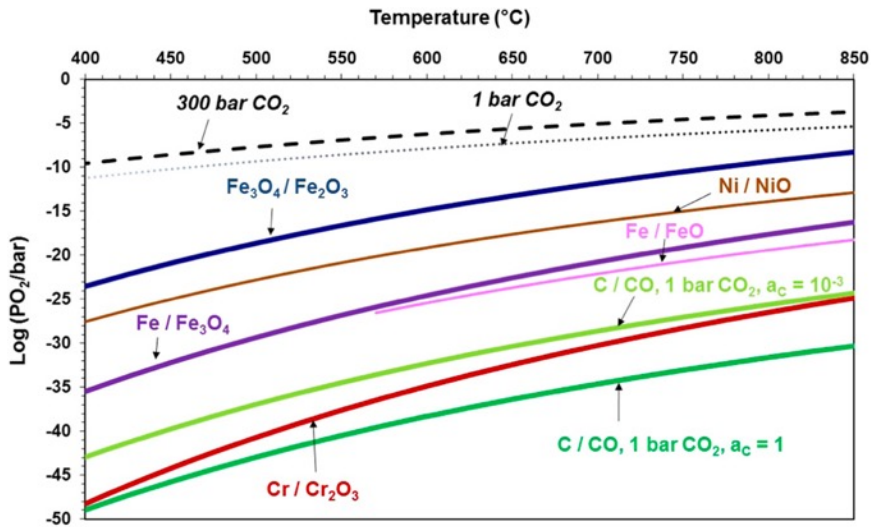
- Remove concerns for interaction of liquid metal coolants with water/steam while achieving similar efficiencies
- CO2 can serve as primary coolant in gas cooled reactor systems
- Fe-Cr steels are considered as the primary structural components in contact with CO2 gas
- Corrosion resistance is of primary concern, especially for parts at high temperatures and with expected long lifetimes
- Unlike conditions encountered in SCWRs, corrosion in pure sCO2 is not electrochemical in nature but is instead characteristic of a gas-phase oxidation process

CO2 Corrosion

- Exposure of structural alloys to CO2 results in the formation of a metal oxide layer on the surface
- Oxidation comes from partial pressure of oxygen in the CO2 decomposition reaction:

$$CO_2 = CO + \frac{1}{2}O_2$$

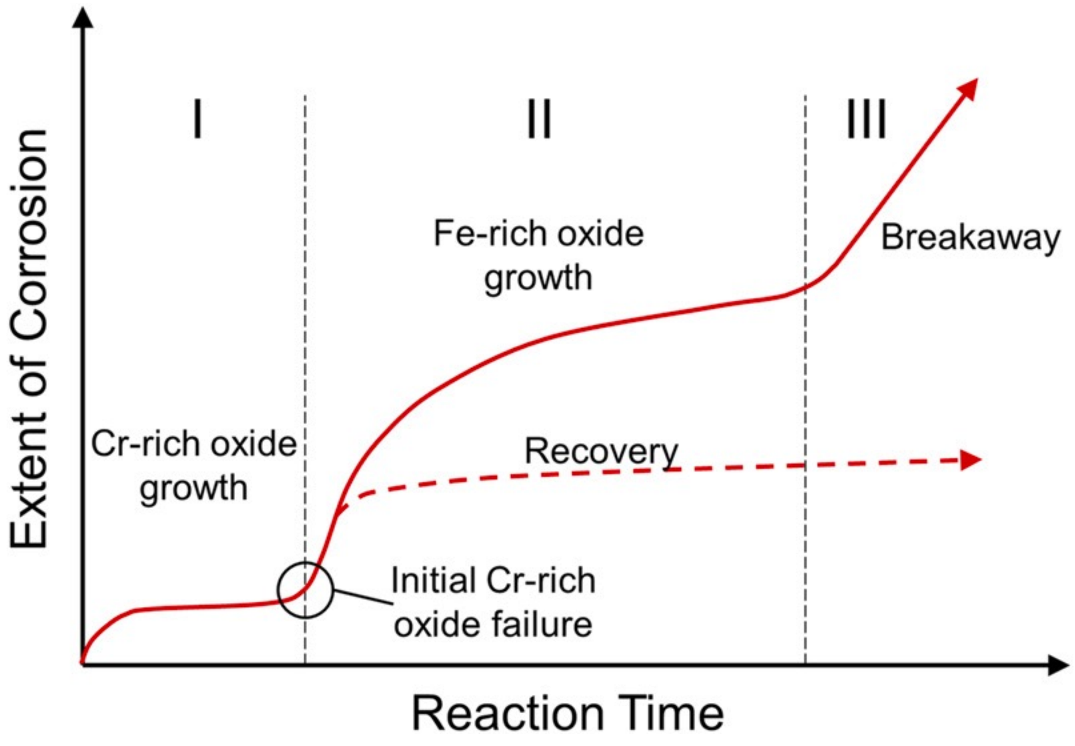
- Even at very low oxygen PP, metal oxides will still want to form



- Typically, steady-state parabolic growth kinetics are achieved, with the rate-limiting step of diffusion through the oxide layer

Three-regime corrosion

- For steels with enough Cr, a thin Cr-rich oxide scale forms during the early stages of exposure
- If the steel does not contain enough Cr or if the previously formed Cr-rich oxide scale growth is disrupted, an Fe-rich oxide scale is formed
- The growth rate of Fe-rich oxides is significantly faster than Cr-rich oxides, leading to higher oxidation rates
- Third regime is linear kinetics and labeled breakaway swelling



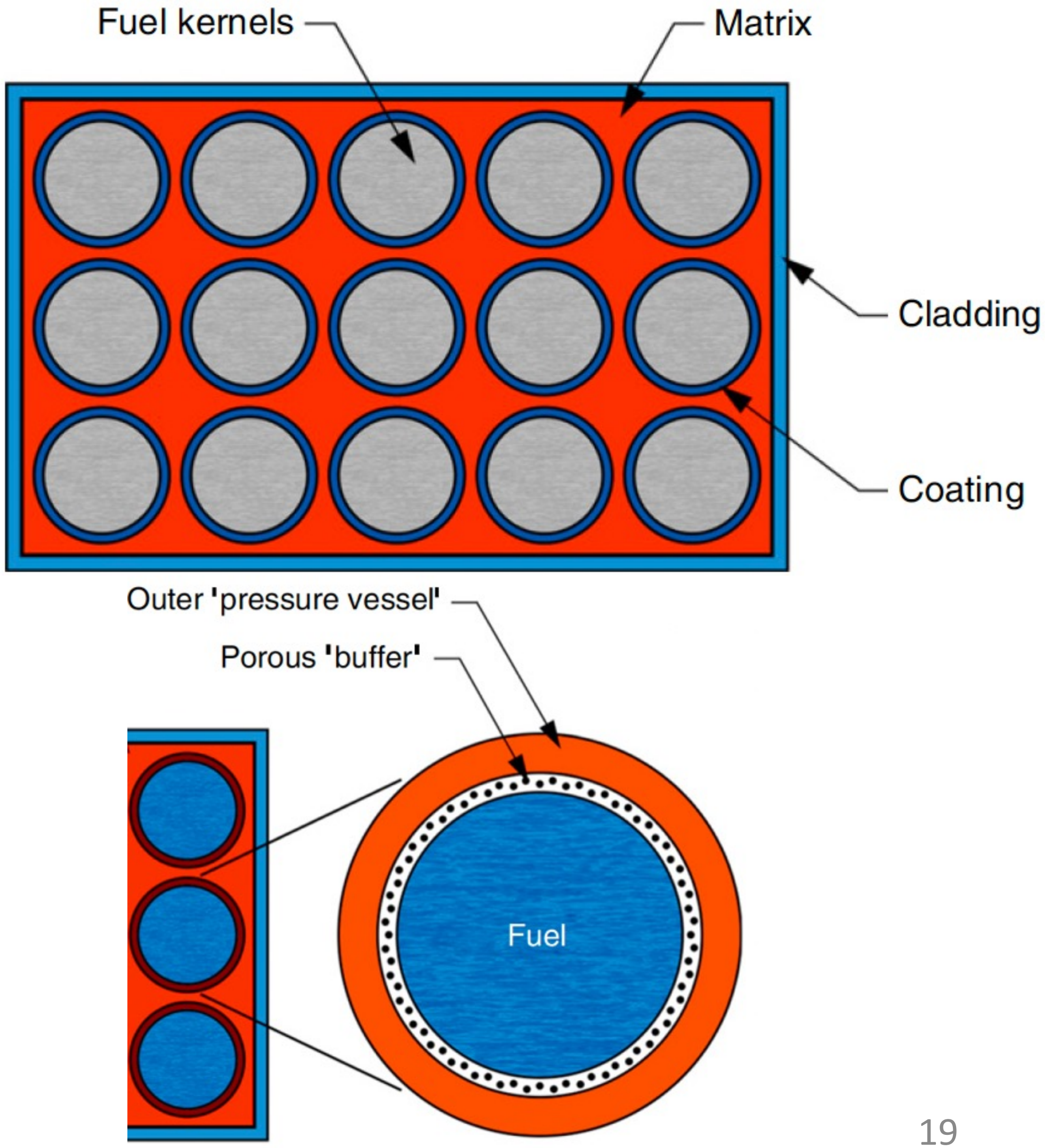
COMPOSITE FUELS

Composite Fuels

- Composite fuels consist of a fissile phase dispersed in an inert, nonfuel matrix
- These types of fuels have been used since the 1950s in high-temperature and high-power density applications
- Composite fuels are typically distinguished into two types: Cermet and Cercer
- Cermet: ceramic fuel particles dispersed in a metallic matrix
- Cercer: ceramic fuel particles in a ceramic matrix
- 47 different fuel matrix combinations have been experimentally explored
- Composite fuels have potential as high burnup fuels to either transmute transuranic elements, or to replace conventional UO2 fuel pellets

Composite Fuels

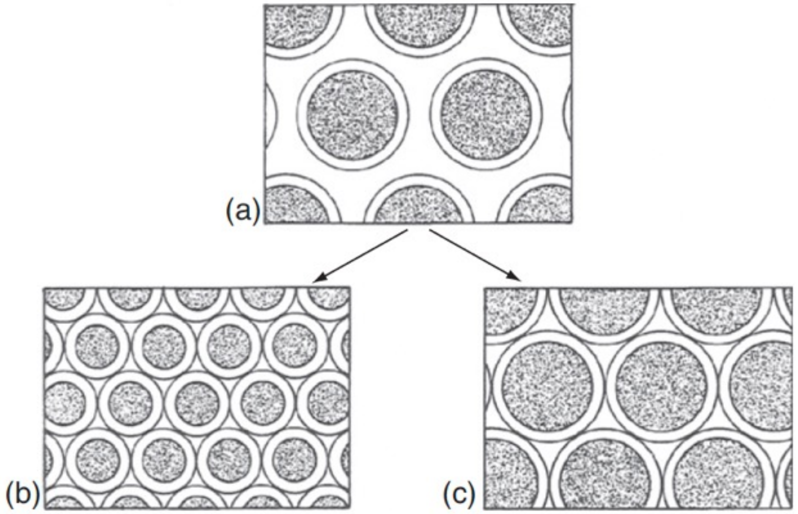
- The most complete experimental work focused on UO2 particles dispersed in stainless steel
- The primary feature that distinguishes composite fuels from the pellet-in-cladding fuel types is the localization of fuel material within an inert matrix
- Fuel particles can be individually clad within the matrix material by an individual coating



Cermet Fuel

- The performance of the Cermet fuel depends on the ability of the matrix to retain strength and ductility during irradiation
- The strength of the matrix must be sufficient to resist cracking from stresses due to solid fission products and fission gas swelling
- The major source of matrix degradation is the fission fragments ejected from the fuel

- The distance between (or density) of fuel particles must be sufficient such that the damage region around a given particle does not overlap with an adjacent particle



Cercer Fuel

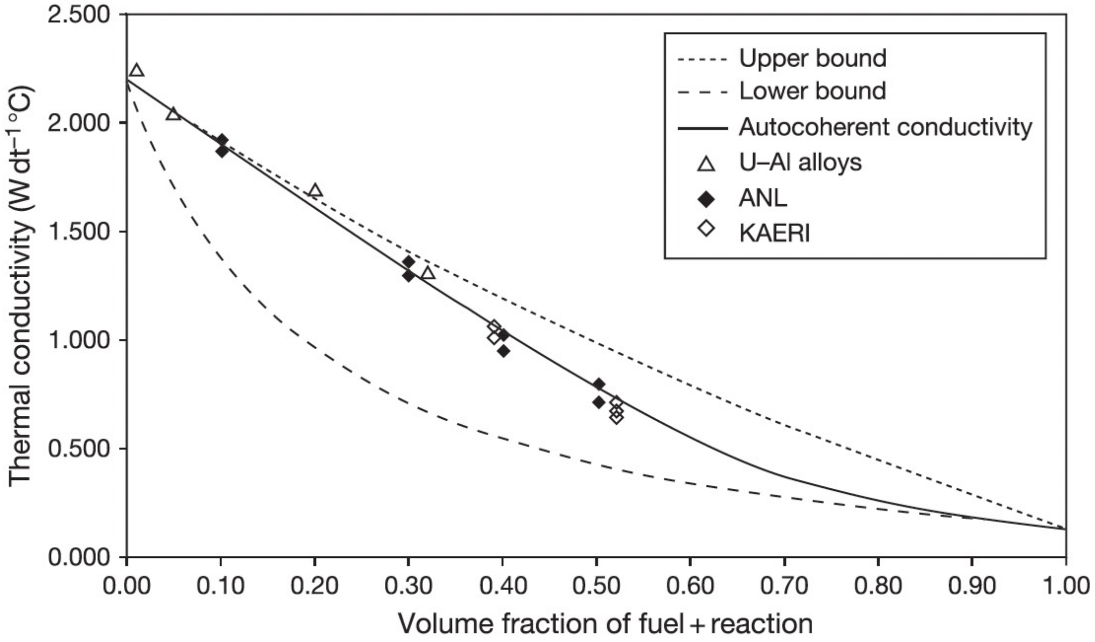
- The typical failure mode in cercer fuels is fuel particle swelling that leads to a tensile stress in the matrix, followed by matrix cracking
- Models have been constructed to predict failure taken from thermal expansion in duplex ceramics

- Increasing the interparticle distance, decreasing the particle size, decreasing fuel swelling and thermal expansion, etc., reduce the probability of fracture of the matrix

$$\left[\frac{\beta R_p(\beta+2)}{\pi(\beta+1)}\right]^{1/2}\left[\left(\frac{1}{(\beta+1)^2}+6\frac{\sqrt{2}}{\pi}V_p\right)c_4\right] > K_{IC}$$

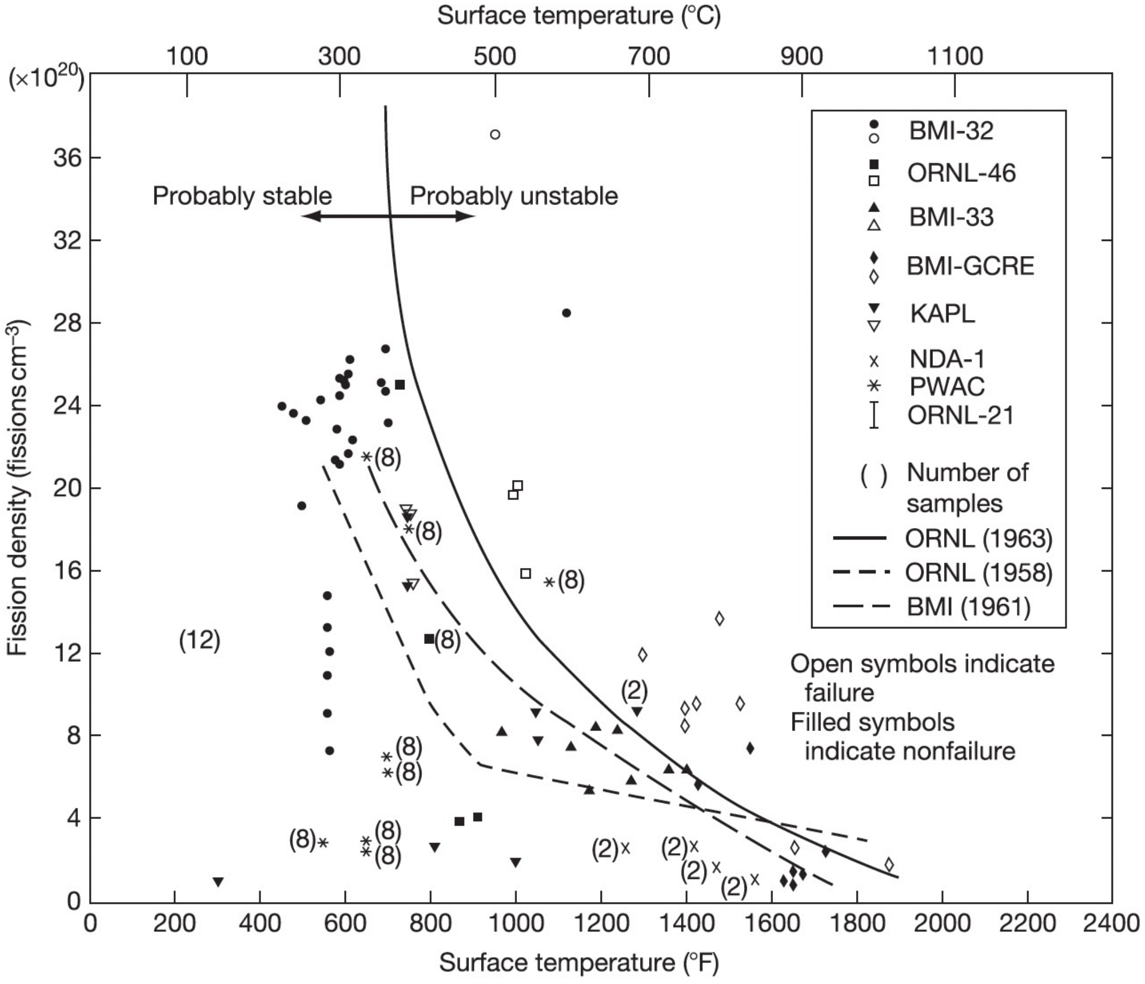
Composite Thermal Conductivity

- The behavior of composite fuels can be heavily influenced by fuel operating temperature, and thermal conductivity is of primary importance in the irradiation behavior of these fuels
- Fuel particle size, shape, orientation, and distribution, and matrix porosity and the thermal conductivities of the fuel and matrix species are the key properties of interest



Irradiation Behavior

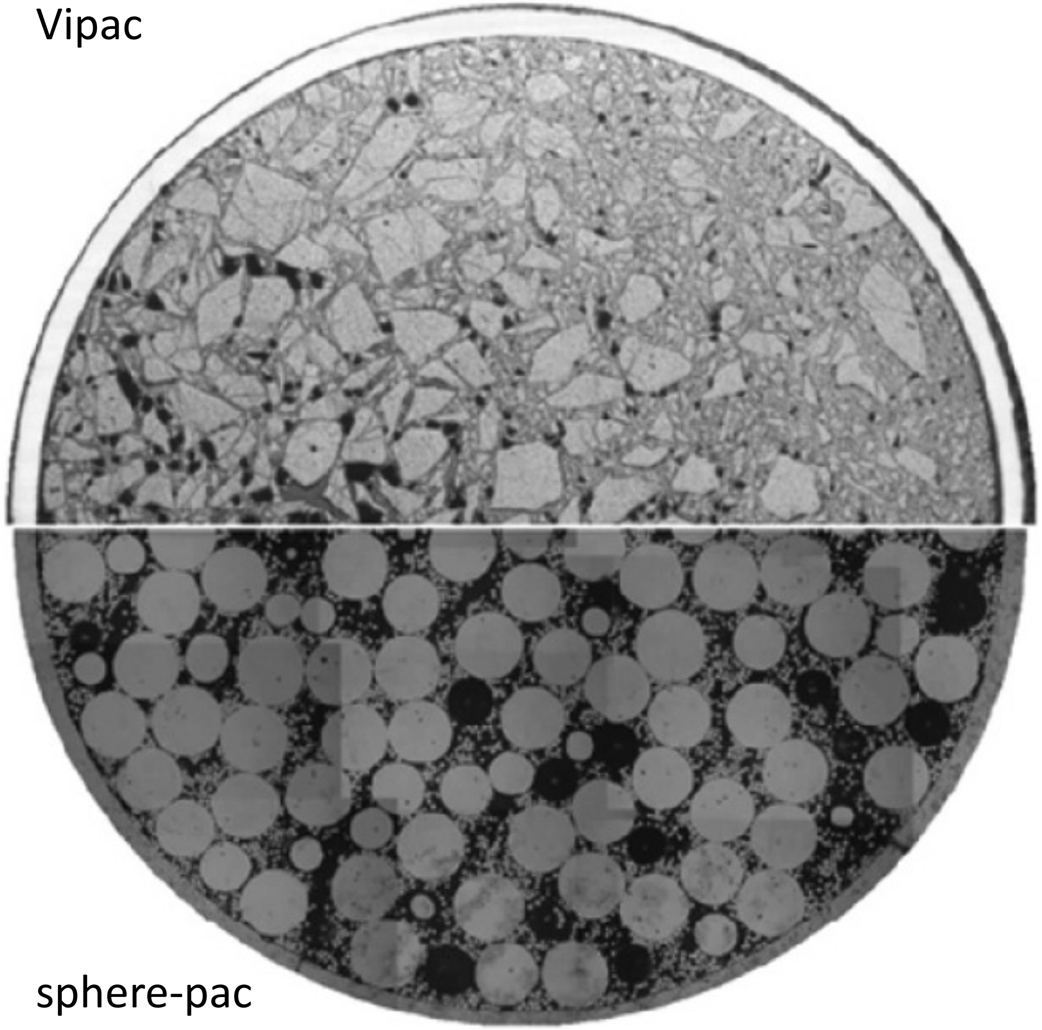
- Most irradiation information is on UO2 dispersed in stainless steel
- Full-size 20vol% plate-type elements reached 65 at% burnup at surface temperatures of 315–427C with no blistering or cracking
- There are bounding limits on fission density (+ loading) and surface temperature
- Higher matrix loadings are possible, but are restricted to low (<15%) burnups



PARTICLE FUELS

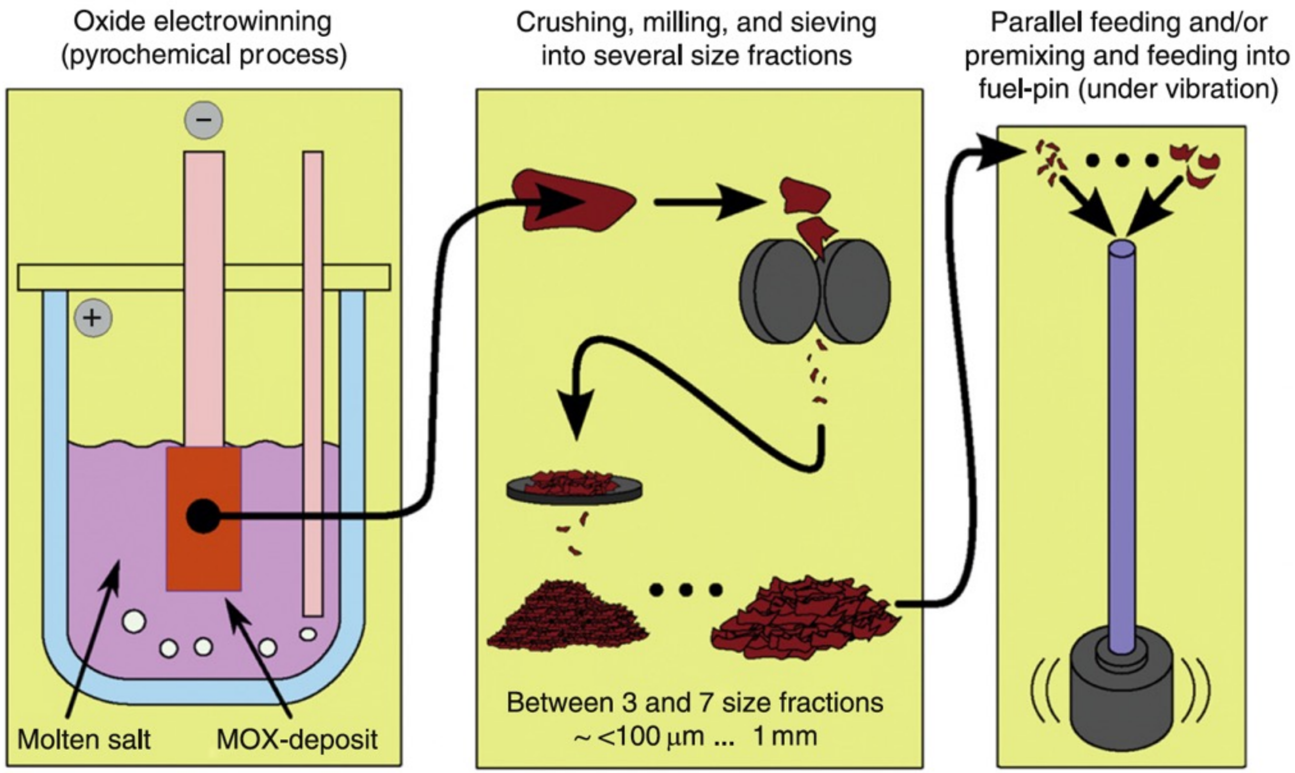
Particle Fuels

- When the fissile isotopes are coming from spent fuel that is chemically separated (reprocessed), particle fuel with its direct filling of fuel particles into the fuel pin offers several advantages
- Two major types of particle fuel are sphere-pac and Vipac



Vipac

- The usage of randomly shaped (angular shards) particles as nuclear fuel component filled in a cladding goes back to the 1950s
- Reprocessing of fuel from the BOR-60 reactor was pursued to developed fuel for the BN-600 reactor – MOX fueled fast reactors
- These particles are fed into the cladding under vibration
- Vibration packing = Vipac



Sphere-Pac

- Sphere-pac fuel is also composed of particles which are directly filled into a fuel pin
- However, particles are shaped into spheres to generate a more predictable arrangement of particles in the fuel pin
- Sphere-pac is used in conjunction with the PUREX process, combined with follow-up processes such as actinide extraction
- A fully aqueous method offers excellent distribution of the fissile material in the matrix and the formation of solid solution in the ceramic
- This also eliminates the need for mechanical devices, reduces powder generation, and thus minimizes contamination

Particle Fuels

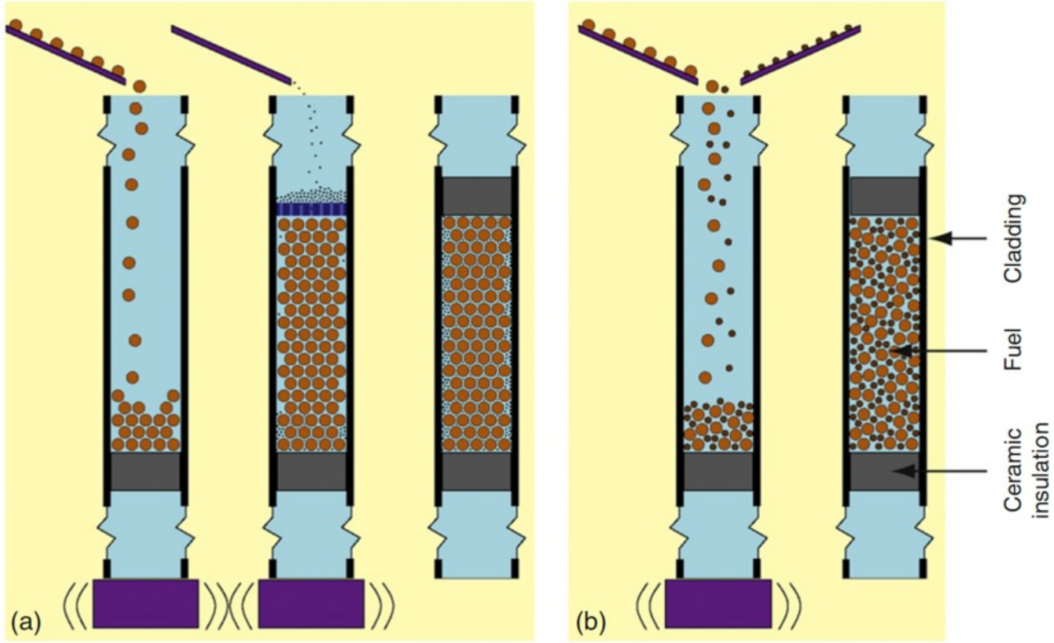
- This modified geometry of fuel will present important changes in the fuel properties as a unit
- The thermal conductivity is reduced, which increases the centerline temperature, and can lead to restructuring
- The fuel is softer because of the void space, reducing FCMI
- Significantly higher fission gas release, due to the prevalence of free surfaces
- In the case of a cladding breach, this increased fuel surface area provides greater opportunity for coolant reaction with the fuel
- At fuel startup, fuel particles are not bonded, and in case of early life cladding breach, potential loss of fuel particles

Macrostructure Changes

- The macrostructure of the fuel changes with operation
- The high temperature will lead to sintering and restructuring into different zones (as in MOX fuel)
- Similar four zone restructuring will occur, but with different zones
- 1: central void; 2: highly dense fuel similar to a pellet; 3: sintered microstructure with retained porosity; 4: original particle macrostructure
- As the structure of the fuel changes, the properties change dramatically with radius and time

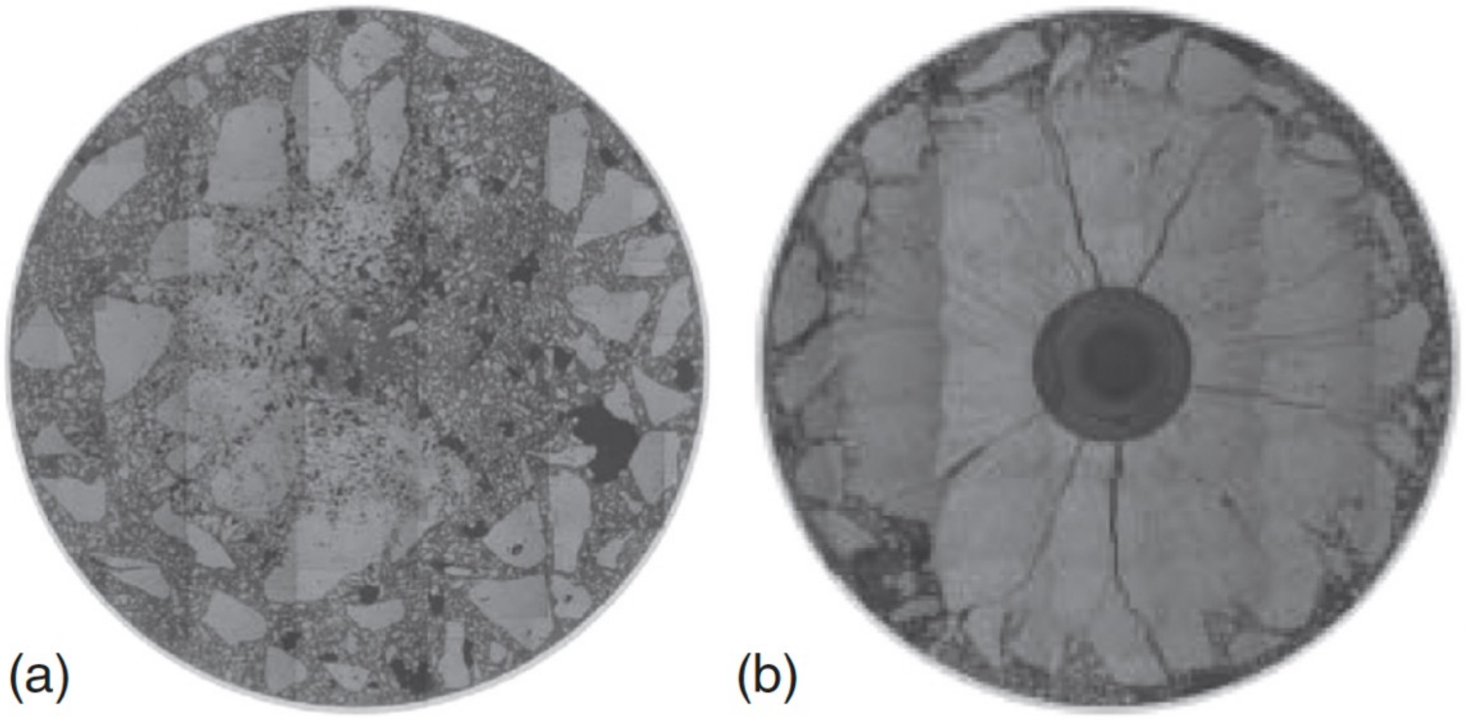
Sphere-Pac Concepts

- While the sphere-pac concept is more complex than vipac, it offers additional flexibility
- Particle sizes and particle distributions can be included
- Spherical particles offer low friction resistance during the filling procedure
- Sphere-pac can thus reach up to 90% smear density
- Infiltration filling allows for tailoring of small particles to serve specific purposes, such as an oxygen getter, a low reactivity with cladding, etc.



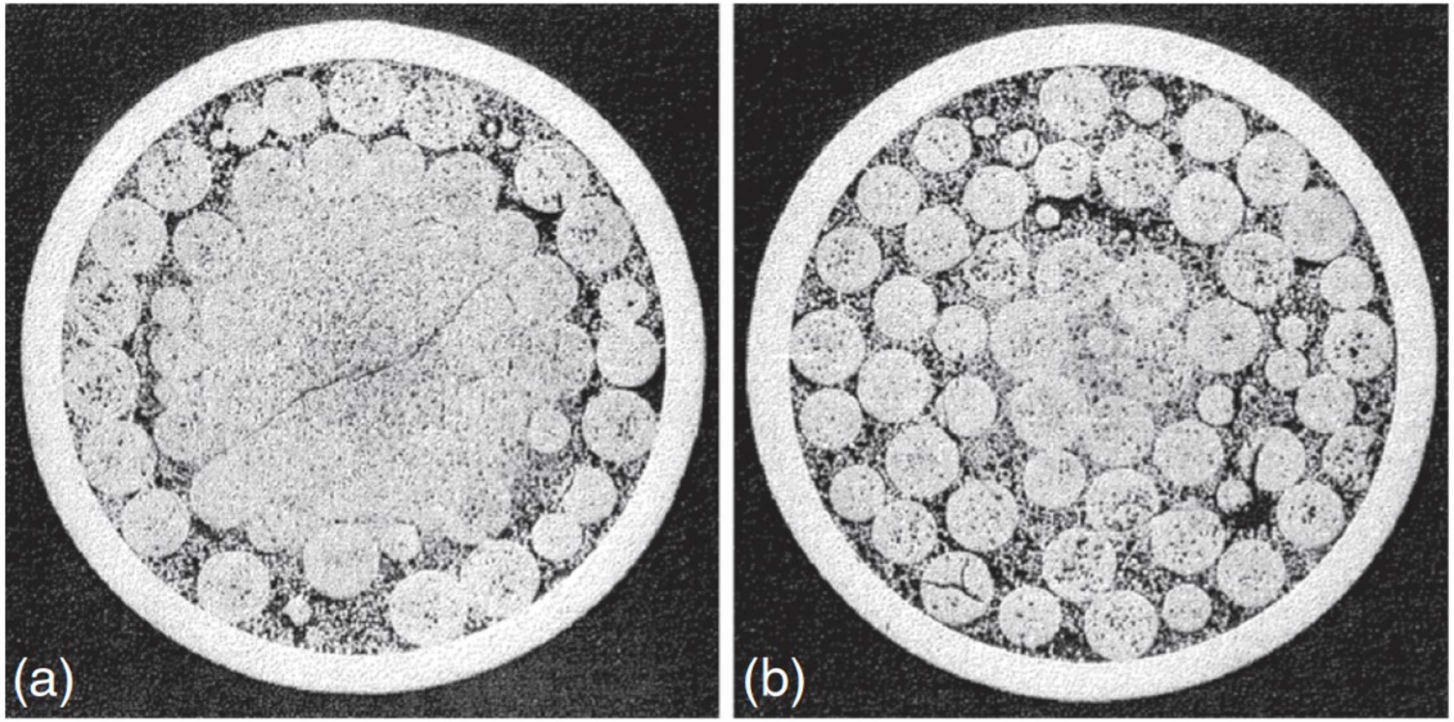
Vipac Irradiations

- Japanese irradiations (FUJI Project), with MOX fuel 20% Pu
- Vipac fuel after initial sintering test irradiated up to 487 W/cm after 36h
- a) Restructuring test with ramping up to 502 W/cm for 36h and b) holding at 502 W/cm for 96h



Sphere-Pac Irradiations

- Dounreay fast reactor – UPu-C fuels
- a) 62 kW/m, 7.3% FIMA, 458C
- b) 49 kW/m, 5.7% FIMA, 320C



Overview

- Particle fuels are a realistic option for fast reactor systems
- Fast reactors allow for efficient burning of actinides
- Nominal fast reactor fuel pins are designed for fission gas release, and thus the larger gas release, compared to UO2, is not detrimental
- Other fuel bases, other than oxides, can easily be deployed
- FCMI is greatly reduced due to the inherent space allowing for swelling of the particles
- LWR application is limited

WASTE GLASSES

Waste Forms

- Fission products (FPs) and minor actinides (MAs) produced during fuel irradiation in the reactor only represent about 5% of the weight of used nuclear fuel, but about 98% of its radioactivity
- When fuel is reprocessed, the FPs and MAs end up in concentrated solutions (High Level Waste – HLW) temporarily stored in tanks
- Long term (>100 year) storage requires a different path, with initial targets on glass or glass-ceramics to immobilize FPs
- The first attempts at the CEA in 1957 targeted crystals of mica-phlogopite: M2Mg6(AlSi3)2O20F4
- Twenty years later, borosilicate glass had appeared as the standard choice for the HLW matrix

Glasses

- Some liquid phase materials have a high viscosity near the melting point, and such materials tend to crystallize slowly
- If a cooling rate is faster than the crystallization rate, the material will rigidify into a “vitreous state”, in which no periodic crystal structure is present
- Glass has an absence of order in the distribution of elementary structural units at scales larger than 10–30 Å
- Glass is in a metastable state, but is not unstable because the energy barrier to bring it to its more stable crystallized state is generally significant due to the high viscosity
- Glass is a non porous, impermeable, isotropic, non cleavable, elastic, solid with a fragile rupture behavior
- Glass is a material which transitions continuously and reversibly from liquid to solid state with temperature

Waste Glasses

- Vitrification consists of making a new material where the waste components are contained at the atomic scale within the matrix and can only be released by destruction of the network bonds
- One major requirement is then that the selected matrix be able to incorporate all of the waste stream components in its structure
- By using the flexibility brought about by the disordered and relatively loose structure of a glass, it is possible to design glass compositions able to integrate a very wide range of elements within their structure, and which are tolerant to compositional variations in the waste stream

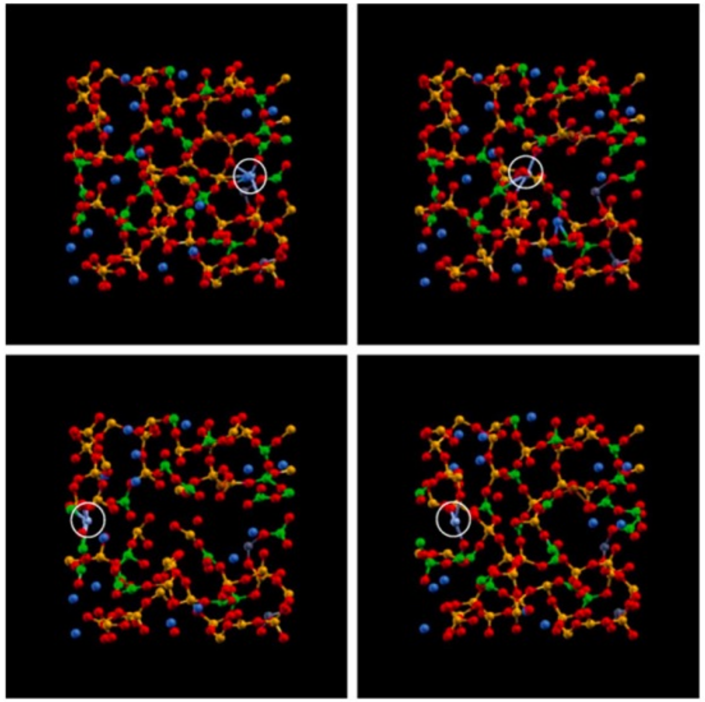
Behavior of Waste Glasses

- The main phenomena that could alter glass containment properties over the long term are heat (for HLW only), radiation damage, and alteration by water
- Heat can potentially induce the glass to reach a point beyond the glass transition temperature
- However, in nuclear glasses the diffusion is sufficiently slow (high viscosity) to make crystallization incredibly difficult
- In the R7T7 glass, a period of several millions of years are required for the three main phases to be completely crystallized at any temperature below 600C

Radiation Damage

- Alpha decay is the main cause of radiation damage, where a radioactive nuclide emits an alpha particle (He atom) and a recoil nucleus, generating damage cascades
- Due to the effect of alpha decay the glass density decreases slightly, and its mechanical properties improve, especially fracture toughness

- MD simulations have been performed that show the capacity of glasses to restore its structure following a cascade event



Waste Glass Summary

- Vitrification is the world reference solution to the containment of HLW
- Glasses can easily incorporate all known fission product species
- Glasses will not undergo crystallization due to decay heat
- Glasses self-heal irradiation damage
- Glasses are reasonably resistant to long-term exposure to sea water

QUESTIONS?