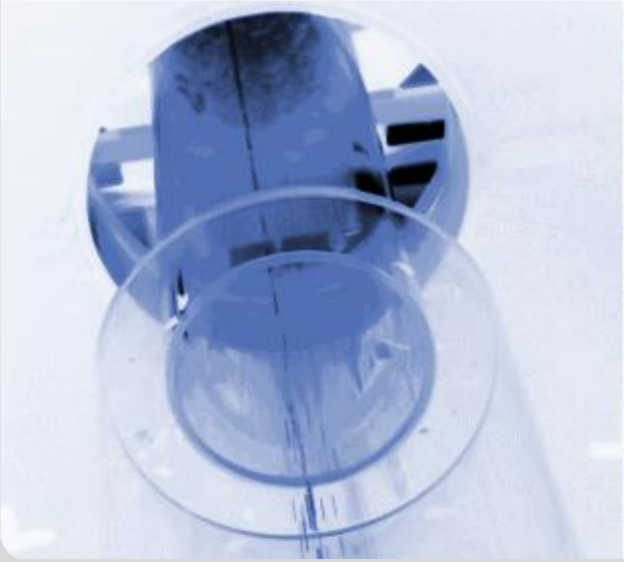
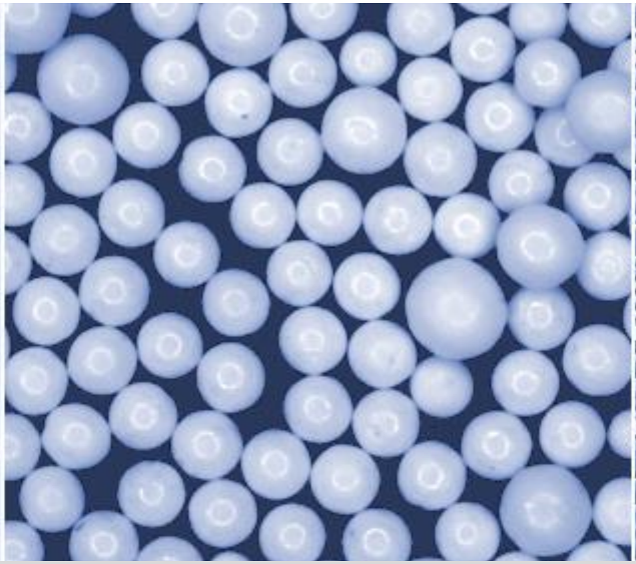
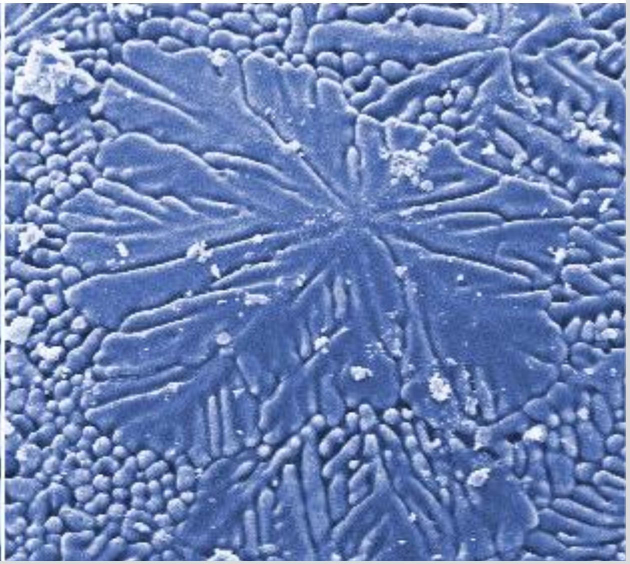
Tritium breeder materials

M.H.H. Kolb

INSTITUTE FOR APPLIED MATERIALS - MATERIAL PROCESS TECHNOLOGY







D-T Fusion Power Plants

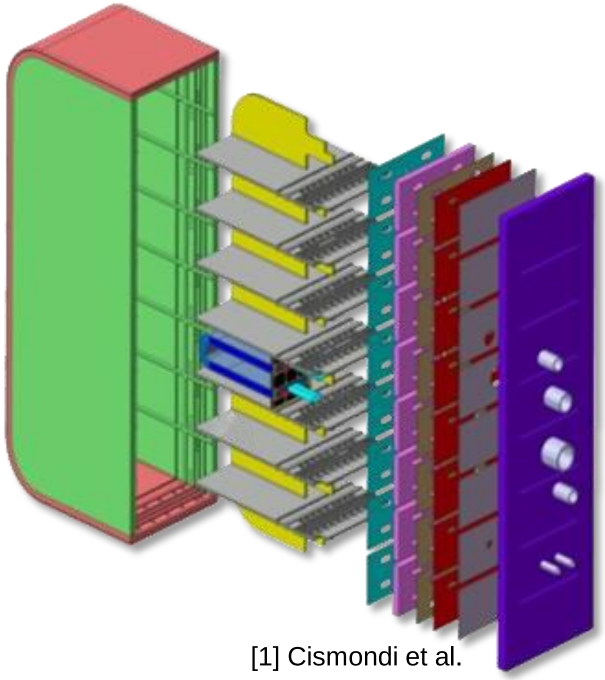
Plasma: $^{2}H + {}^{3}H \rightarrow {}^{4}He + n \quad + 17.6\ MeV$

Blanket: $^{6}Li + n \rightarrow {}^{4}He + {}^{3}H + 4.8\ MeV$

tritium self-sufficiency

- Properties of lithium
  - Melting point: ~180 °C
  - Readily reacts with:
    - Oxygen
    - Nitrogen
    - Hydrogen
    - Carbon dioxide
    - Water
    - …

EU He cooled pebble bed TBM



[1] Cismondi et al.

- How can lithium be put into the blanket?

Lithium in fusion blankets

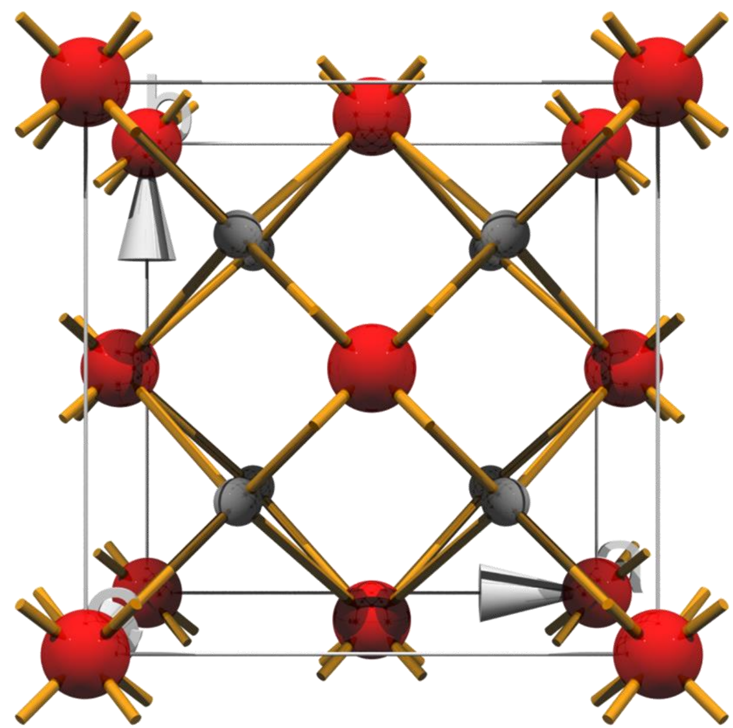
Plasma: $^{2}H + {}^{3}H \rightarrow {}^{4}He + n \quad + 17.6\ MeV$

Blanket: $^{6}Li + n \rightarrow {}^{4}He + {}^{3}H \quad + 4.8\ MeV$

tritium self-sufficiency

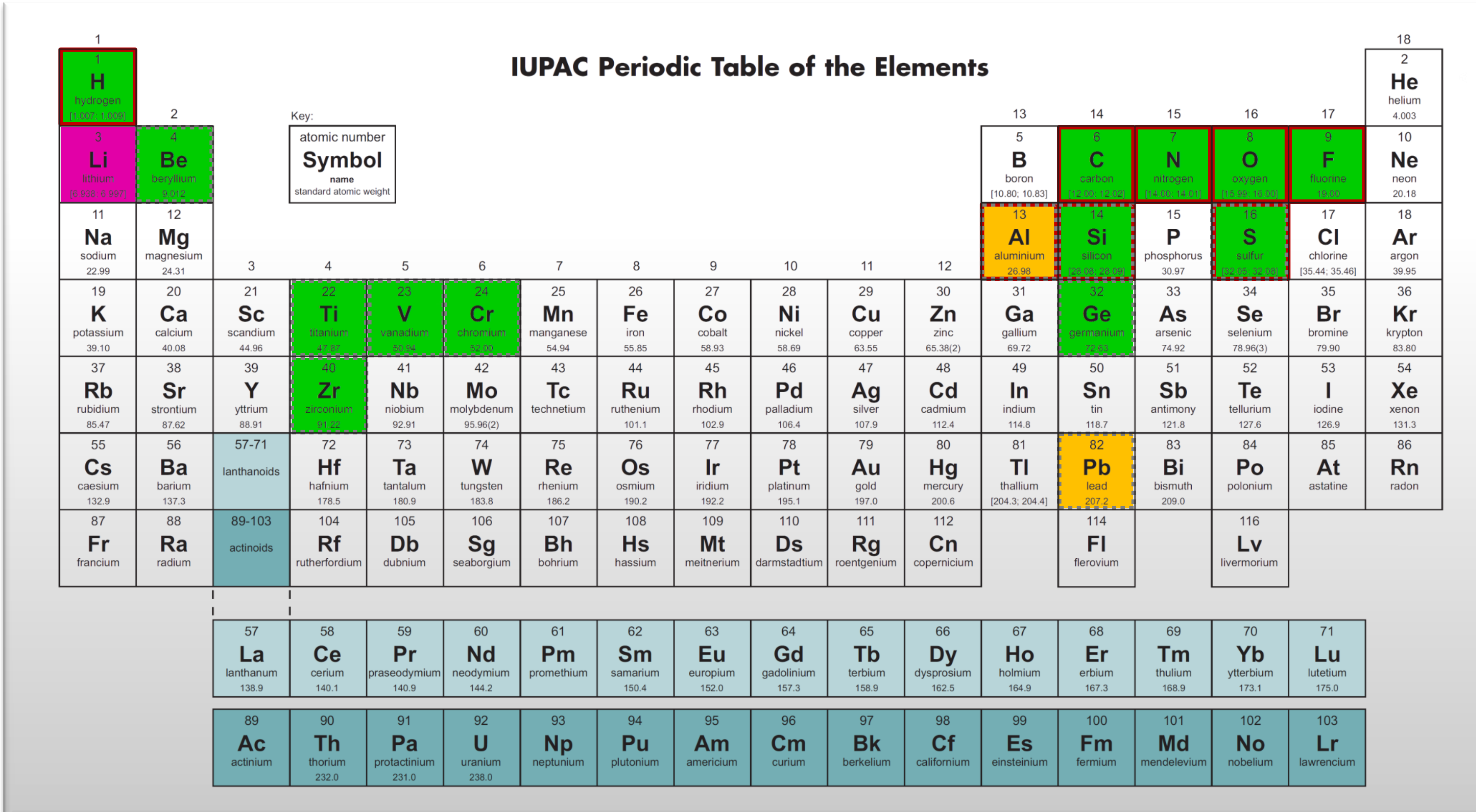
Surrounding lithium with other atoms

- Liquid system
  - Lithium is still quite mobile and reactive
  - Possible magnetohydrodynamic effects
  - Examples:
    - Lithium-Lead
    - Lithium-Beryllium-Fluorine (FLiBe)
- Solid system
  - Reactivity can be reduced to a minimum
  - Ceramic or intermetallic compounds
  - “Low” complexity

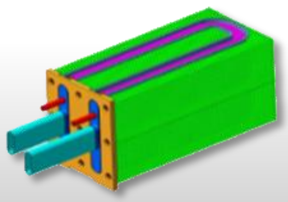


Possible elements for lithium compounds

KIT Karlsruhe Institute of Technology



Lithium compounds as solid breeders



- **Tritium breeder** pebbles
- **beryllium** pebbles

Requirements for solid breeders

- Operability	
- Produce enough tritium (TBR ≥ 1.1)	High Li-density & low T-trapping
- Reliability	
- Neutron irradiation	
- High temperatures within the blanket	High melting point and/or thermal conductivity
- Mechanical stress	Reasonable resilience
- Safety	
- Compatibility with structural material	Little interdiffusion
- Cost-efficiency	
- Fabrication & Recycling	As easy as possible

Lithium compounds as solid breeders

- Reference class solid breeder materials
  - Li_4SiO_4
  - Li_2TiO_3

- Well investigated solid breeder materials

Li_2O	Very high lithium density	Swelling, sintering & creep
$LiAlO_2$	Excellent mechanical strength	Activation & lithium density
Li_2ZrO_3	Tritium retention	Lithium density
Li_2SiO_3	Good properties in general	Lithium density

- Potential solid breeder materials

Li_8PbO_6	To be determined	To be determined
$Li_2Be_2O_3$	To be determined	To be determined
$Li_{22}Si_5$	To be determined	To be determined

[2-4] Hoshino et al.; Palermo et al.; Knitter et al.

Solid breeder concepts for ITER

Lithium Orthosilicate Li_4SiO_4

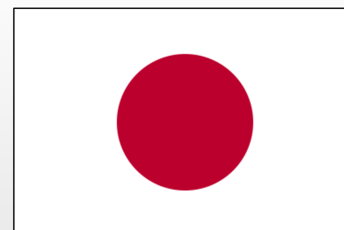
+ Li_2TiO_3 as back-up

Melt-spraying

Melt-spraying

Slurry dropping

Lithium Metatitanate Li_2TiO_3



Sol-Gel

Extrusion+Spheronization

[5] Knitter et al.

Contents

- Fabrication techniques for solid breeder pebbles
  - European Union
  - Japan
  - Korea
- Mechanical and thermal properties of solid breeder pebbles & pebble beds
  - Weibull distribution
  - DEM modeling
  - Pebble bed experiments
- Neutron irradiation of breeder materials
  - Thermo-mechanics
  - Tritium release

Pebble fabrication by melt-spraying

- EU reference fabrication process for lithium orthosilicate

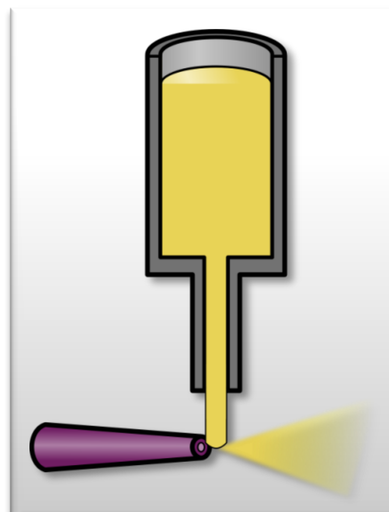
Raw materials
- LiOH
- SiO_2
- Blending

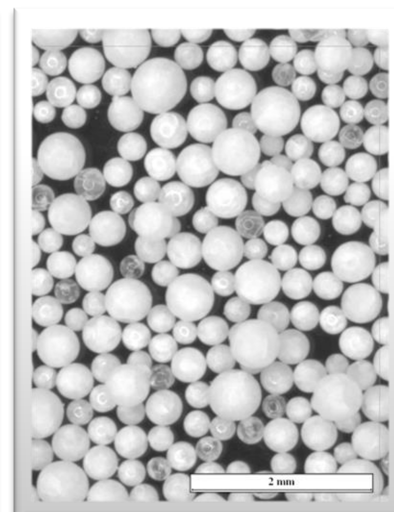
Synthesis & melting
- 1450 °C
- Platinum-Crucible

Droplet generation
- Melt-Spraying
- Air jet:
- 1.8 bar
- 100°C

- Pre-industrial scale at Schott AG, Mainz
- Batch process, 1.5 kg/batch
- Yearly capacity: 300 kg

- Slightly substoichiometric
  - 2.5 wt.% excess of silica
  - 2-phase material

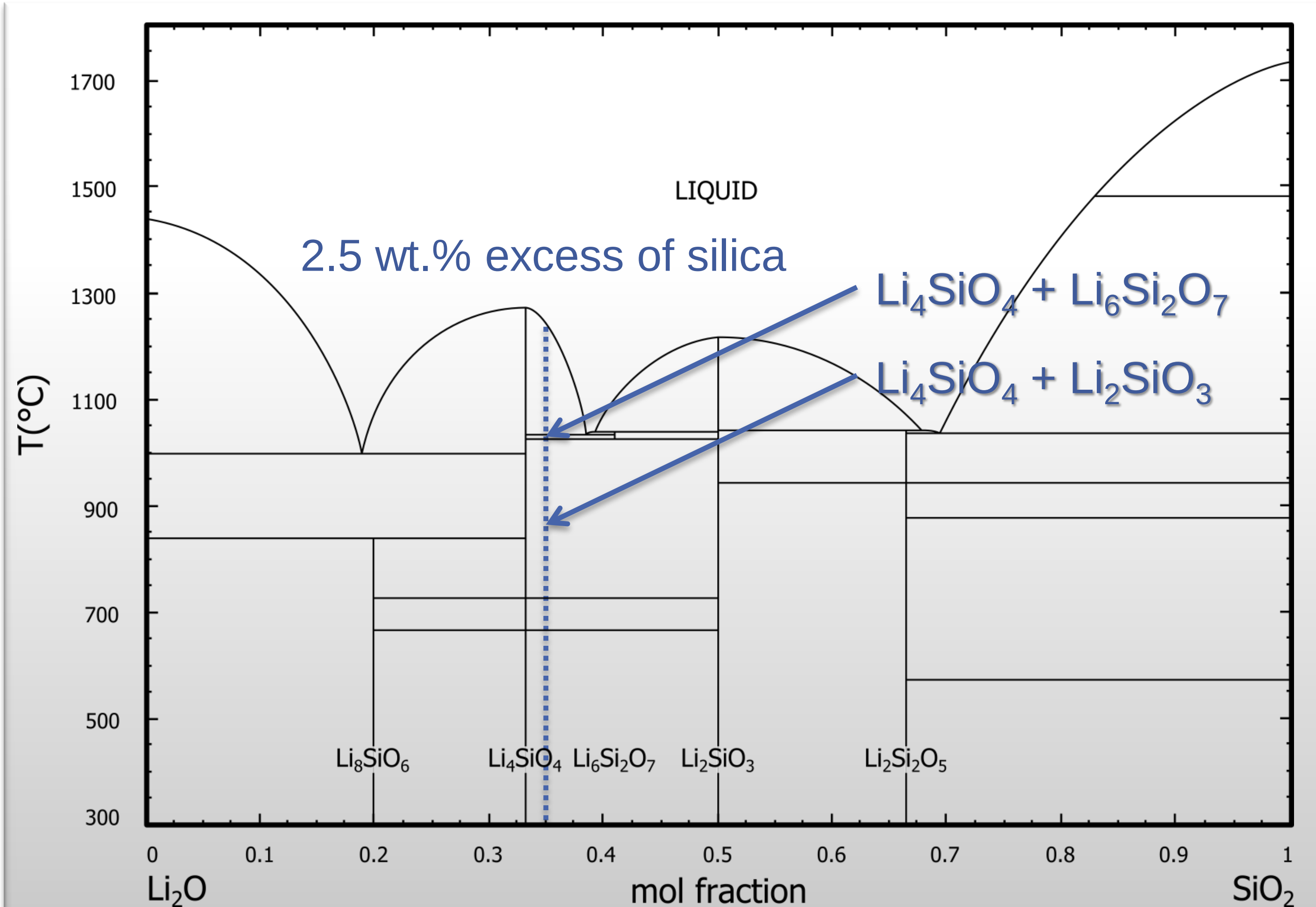




[6,7] Pannhorst et al.; Kolb et al.

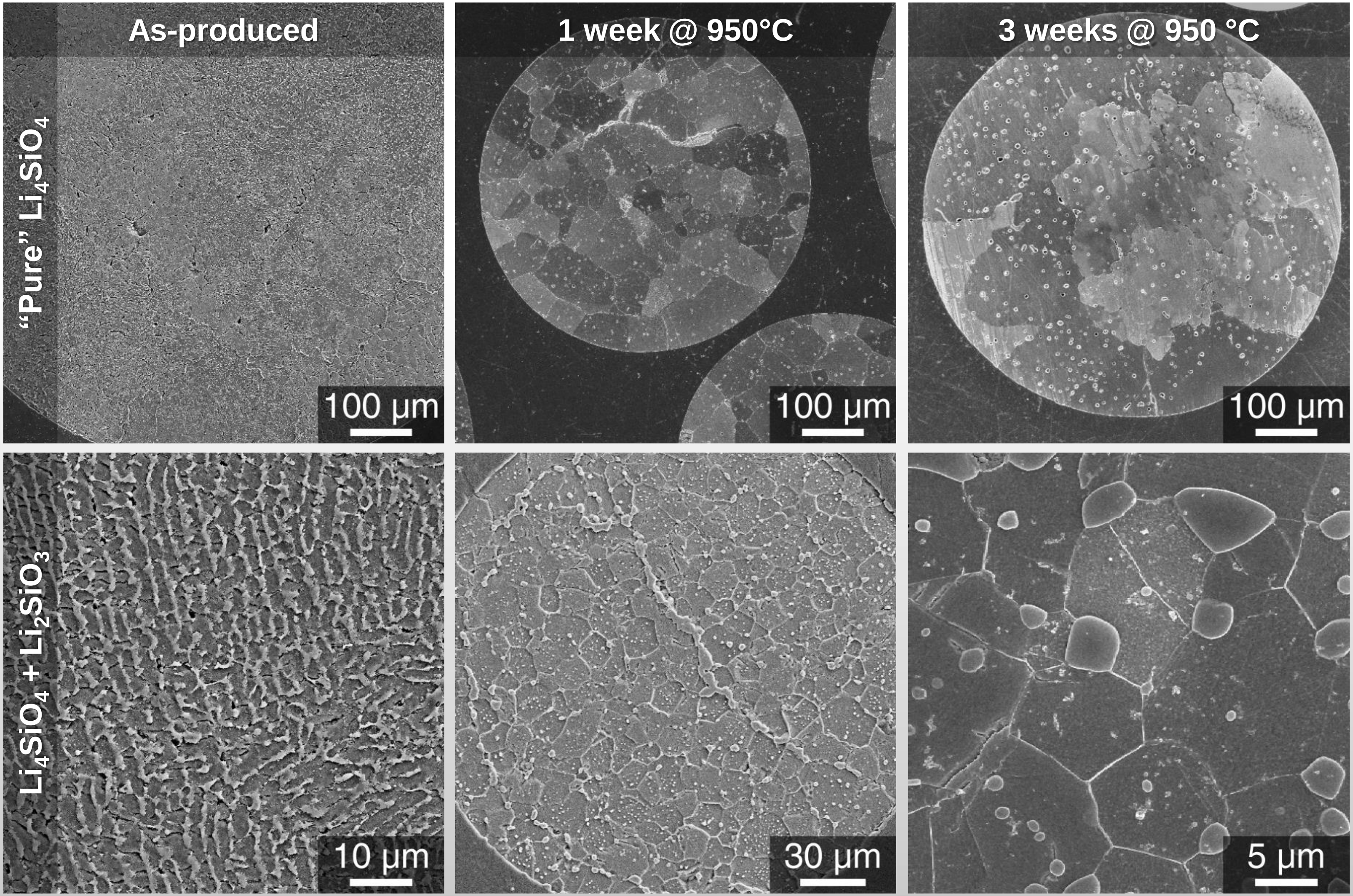
Fabrication of Li_4SiO_4 pebbles

- Phase equilibria in the system Li_2O-SiO_2



[8] Claus et al.

Pebble fabrication by melt-spraying



Pebble fabrication by slurry dropping

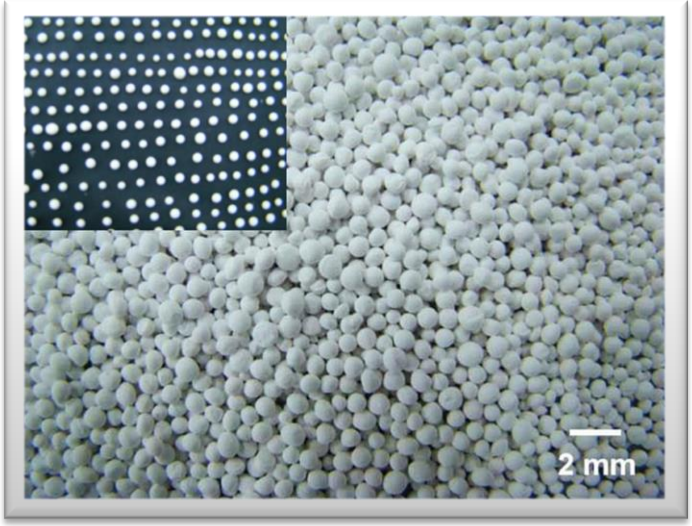
Karlsruhe Institute of Technology

- Korean reference fabrication process for lithium orthosilicate

Raw materials	Powder synthesis	Shaping	Sintering
$LiNO_3$ SiO_2 Dissolution in dilute HNO_3	Addition of PVA Drying Grinding Calcination at 900 °C	Addition of water to form a slurry Dropping of single droplets on a hydrophobic cloth Drying Rolling in a cylindrical jar	1050 °C

- Laboratory-scale
- Continuous fabrication possible?
- Yearly capacity: 250 kg

- Stoichiometric Li_4SiO_4 is aimed for
  - "Single" phase material
  - Minor impurities of a glassy phase



[5] Knitter et al.

Pebble fabrication by extrusion & spheronization

EU reference fabrication process for lithium metatitanate

Raw materials
- Li_2CO_3
- TiO_2
- Blending

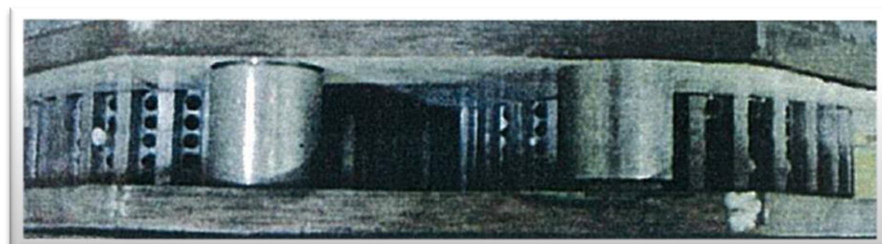
Powder synthesis
- 700 °C
- 3 hours
- Li_2TiO_3

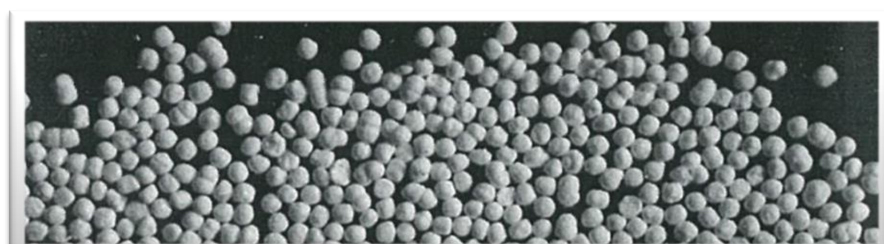
Plastic shaping
- Plasticization
- Extrusion
- Cutting
- Spheronization

Sintering
- Air
- 1050 °C
- Properties can be varied easily

- Pre-industrial scale at CTI
- Continuous fabrication possible
- Yearly capacity: 150 kg

- Slightly substoichiometric
  - Li/Ti-fraction: 1.9
  - Single phase material





[9] Lulewicz et al.

Pebble fabrication by a sol-gel method

Japanese reference fabrication process for lithium metatitanate

Gel formation
- $LiOH \cdot H_2O$
- H_2TiO_3
- $Li/Ti \geq 2.0$
- Blending for 48 hours

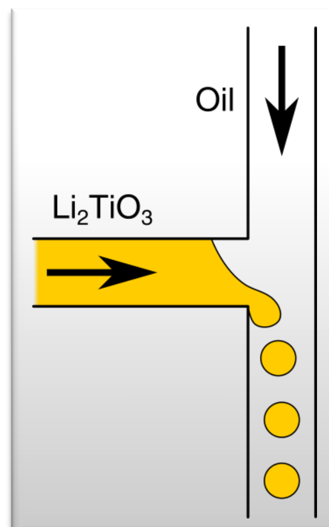
Powder synthesis
- Drying
- Calcination at 600 °C
- Sintering at 1100 °C in N_2

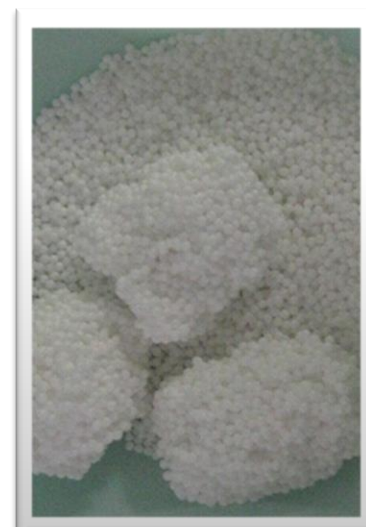
Shaping
- Mixing with binder, formation of slurry
- Cutting with emulsion method

Sintering
- Calcination at 600 °C
- Sintering at 1100 °C in He/H_2

- Laboratory scale at JAEA
- Continuous fabrication possible
- Yearly capacity: 100 kg

- Slightly hyperstoichiometric
  - Li/Ti-fraction typically 2.15
  - Single phase material

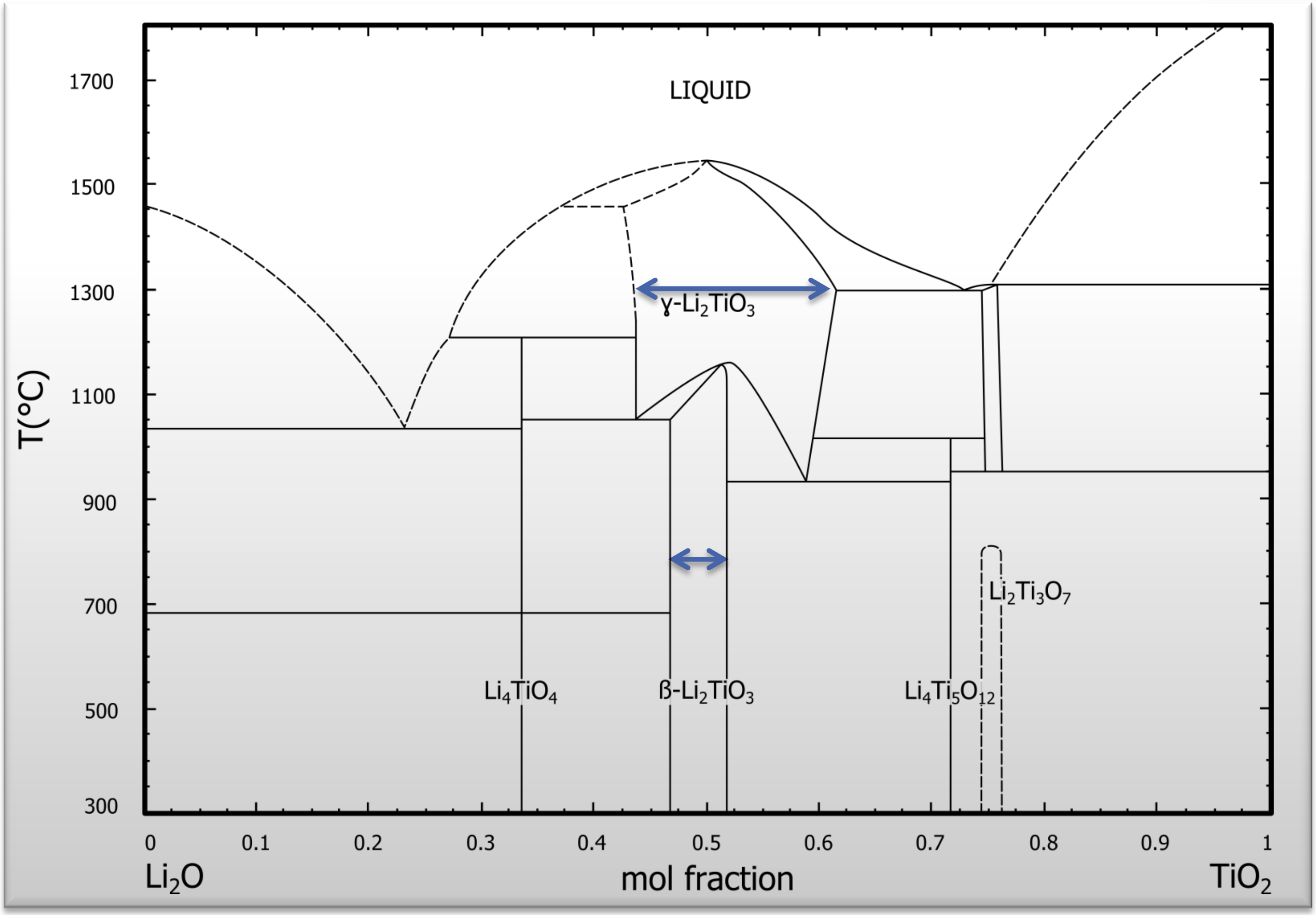




[5,10] Knitter et al.; Hoshino et al.

Fabrication of Li_2TiO_3 pebbles

- Phase equilibria in the system Li_2O-TiO_2

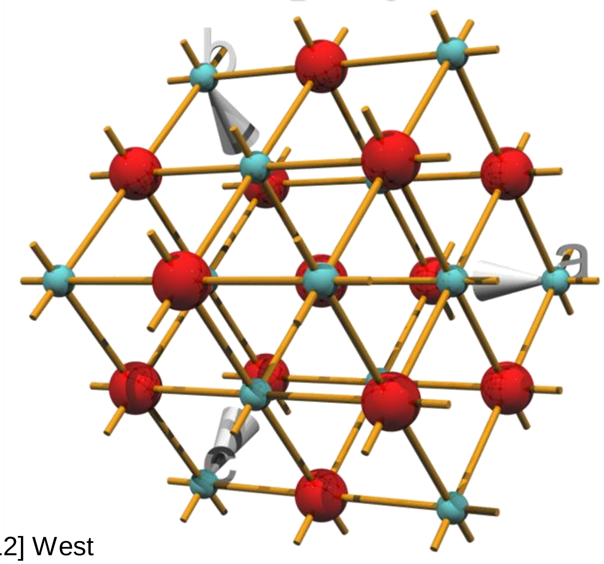


[11] Mergos et al.

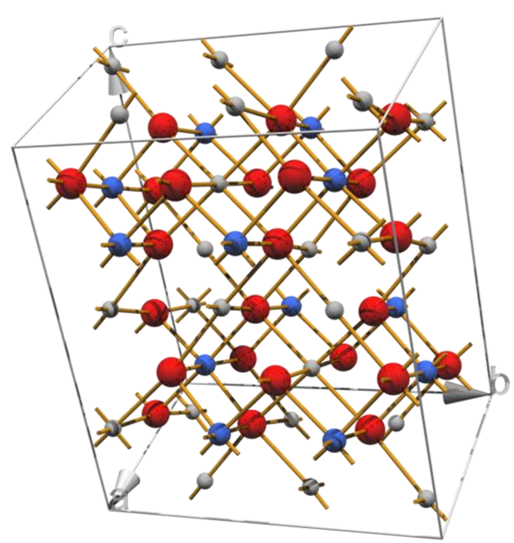
Fabrication of Li_2TiO_3 pebbles

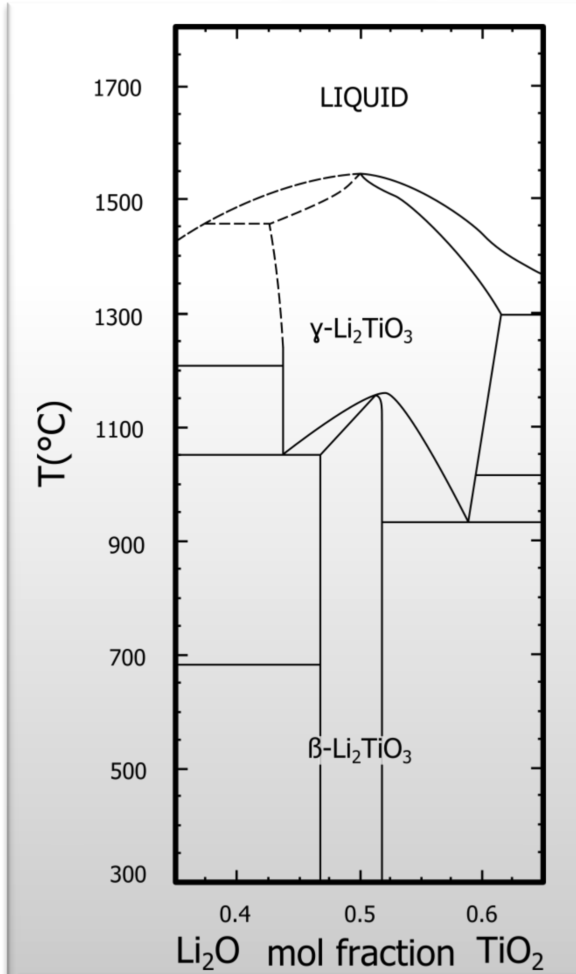
- Large homogeneity range of Li_2TiO_3
  - Li^+ and Ti^{4+} are of similar size
  - Part of the Li^+ ions occupy the same Wykoff positions as Ti^{4+} or as in γ-Li_2TiO_3 the same lattice site
  - $4Li^+ \rightleftharpoons Ti^{4+}$

γ-Li_2TiO_3



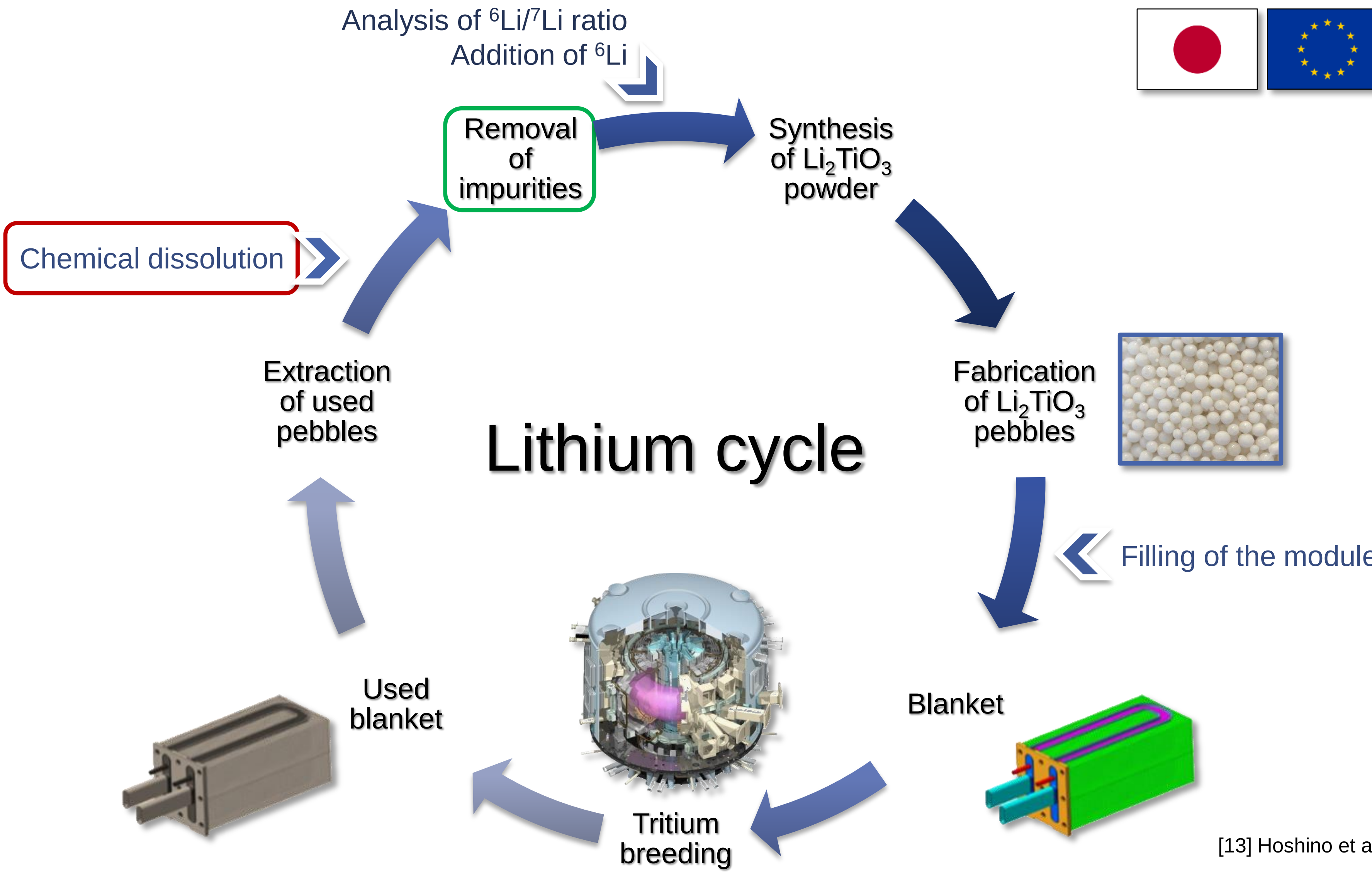
ß-Li_2TiO_3





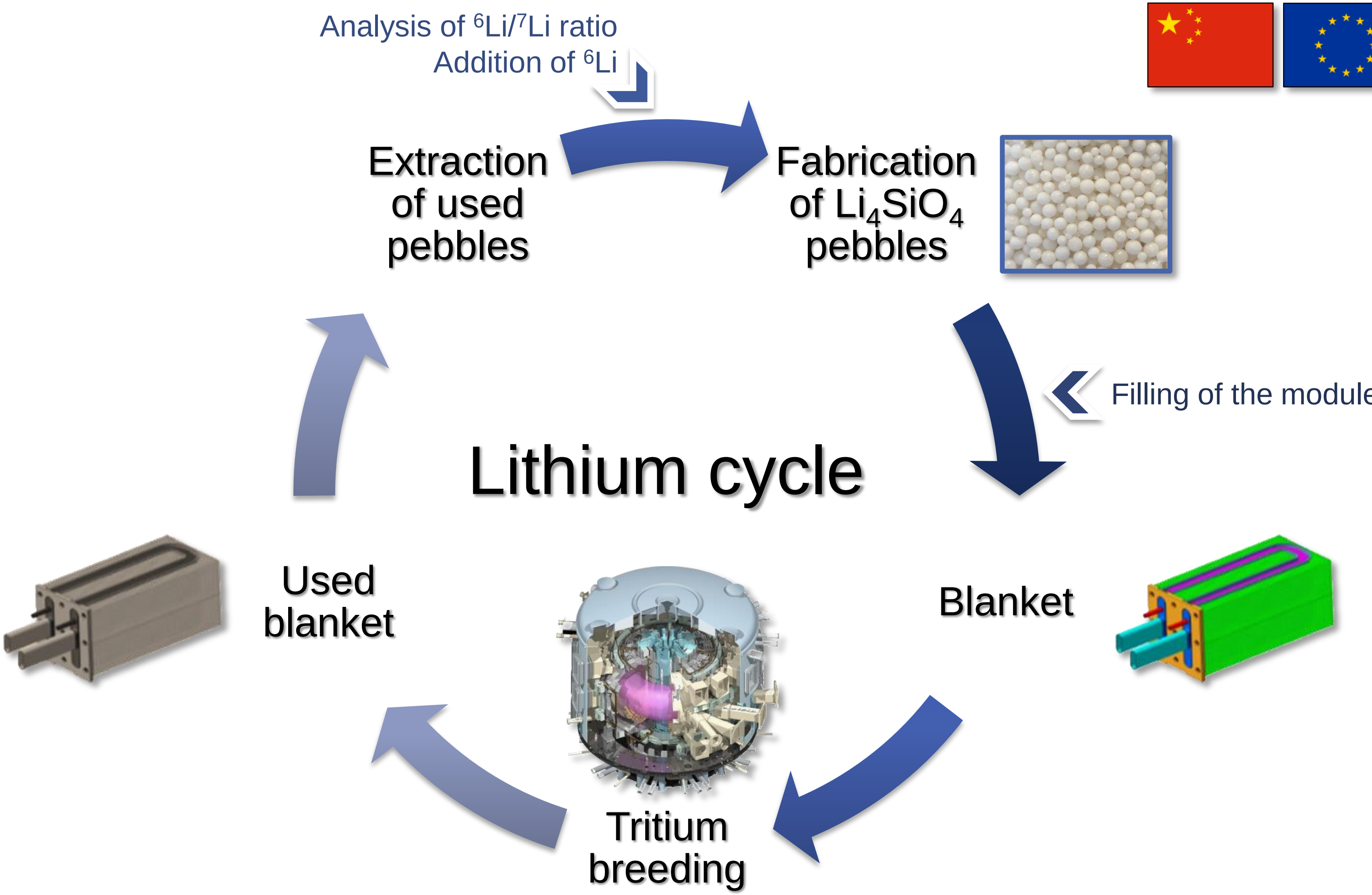
[12] West

Wet-chemical reprocessing



[13] Hoshino et al.

Melt-based reprocessing



Solid breeders in comparison

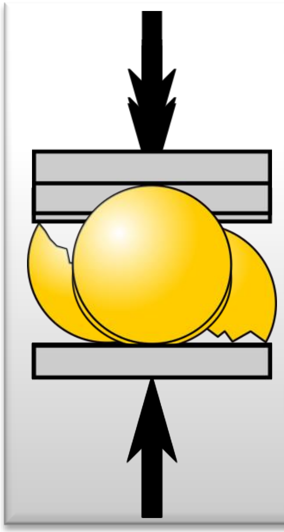
ITER partner	China	EU	India	Japan	Korea
Material	Li_4SiO_4	Li_4SiO_4	Li_2TiO_3	Li_2TiO_3	Li_4SiO_4
Stoichiometry	sub	sub	exact	hyper	exact
Pebble size / mm	0.80 – 1.00	0.25 – 0.63	1.00 – 1.25	1.18	0.90 – 1.10
Pebble density / %	94	95	90	89	77
Open porosity / % Closed porosity / %	<4 <1.5	<1 <5	6-9 2-5	n.a.	11 12
Pebble bed density / %	60.5	61.0	60.0	64.0	48.0
Max. pebble bed temperature / °C	900	930	900	900	900
Crushload / N	7.0	7.0 ± 1.5	n.a.	n.a.	15 – 35

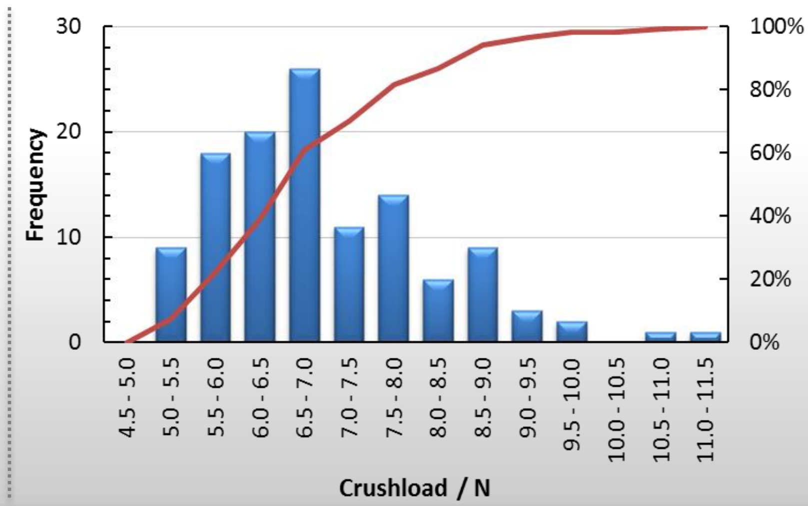
[5, 14-16] Knitter et al.; Feng et al.; Knitter et al.; Park et al.

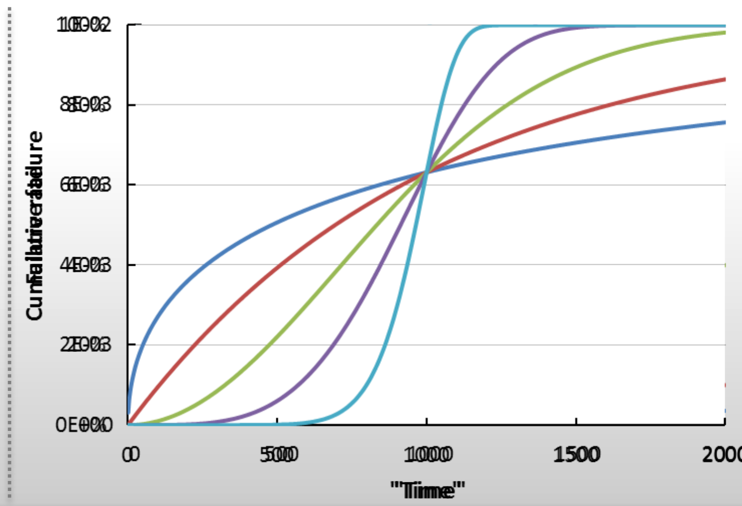
Mechanical characterization

Weibull distribution

- Life distribution model: $L(x) = e^{-H(x)}$
- Cumulative hazard function: $H(x) = \left(\frac{x}{\alpha}\right)^{\gamma}$
- (Non-constant) failure rate: $h(x) = \frac{\gamma}{\alpha}\left(\frac{x}{\alpha}\right)^{\gamma-1}$
- Cum. distribution function of failure: $F(x) = 1 - e^{-\left(\frac{x}{\alpha}\right)^{\gamma}}$
  - α: Characteristic Life, ɣ: Shape factor





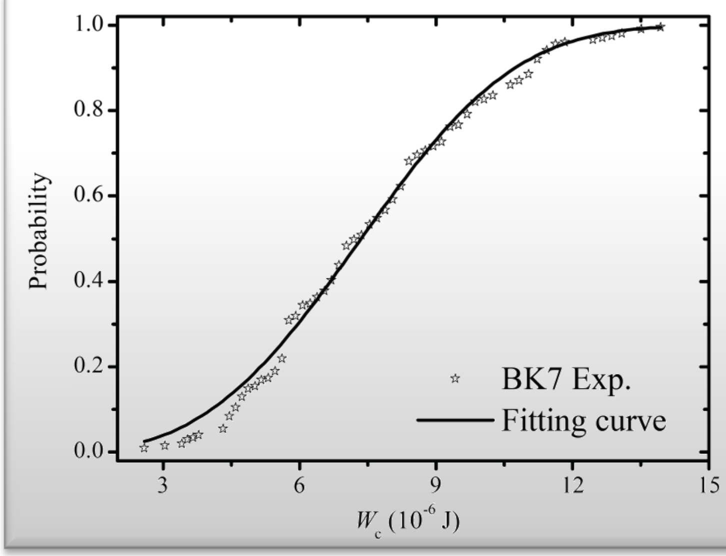


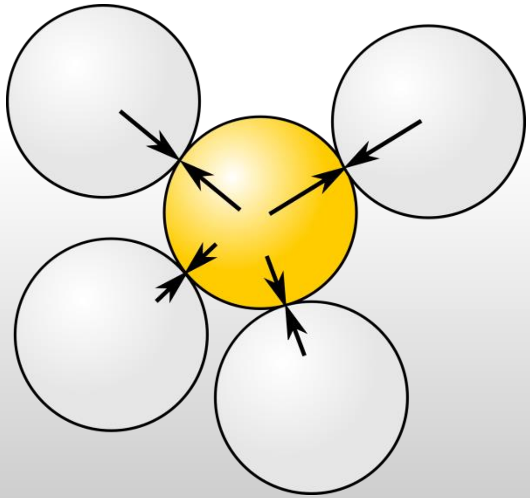
Mechanical characterization

- Describing the failure of brittle materials
  - Cum. distribution function of failure (function of stored elastic energy W_c):

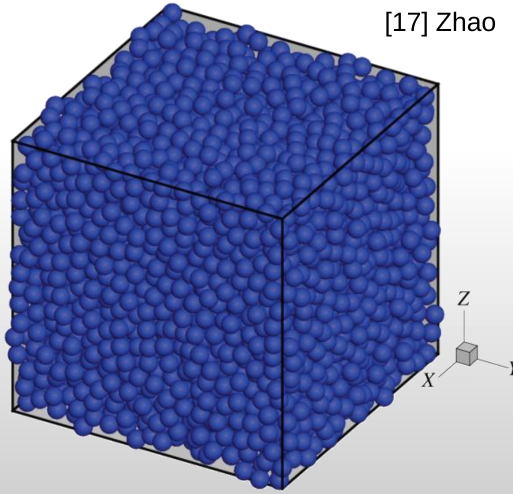
$$F(W_c) = 1 - e^{-\left(\frac{W_c}{W_{Mat}}\right)^m} \longrightarrow F(W_c) = 1 - e^{-(12116 W_c)^{3.17}}$$

    - Many experimental limitations can be overcome
      - Defect orientation, effect of plate materials, high stress gradients
    - Works well in complicated stress states
    - Offers the possibility to model pebble beds (*discrete element method*, DEM)





[17] Zhao



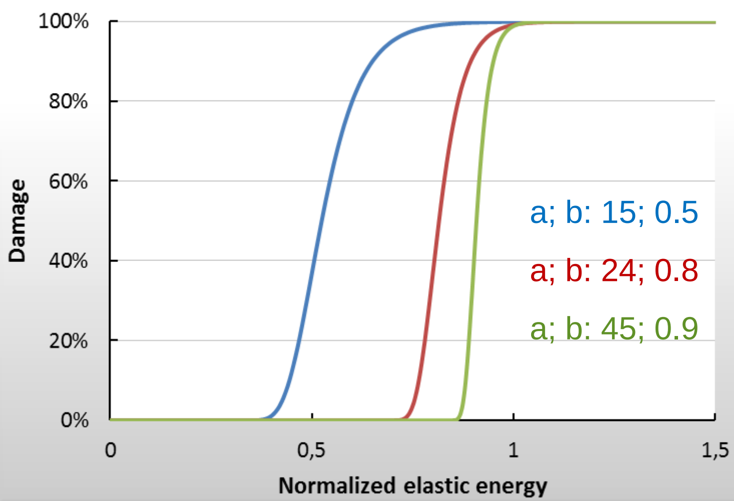
Random assembly of 5000 pebbles

DEM modeling of pebble beds

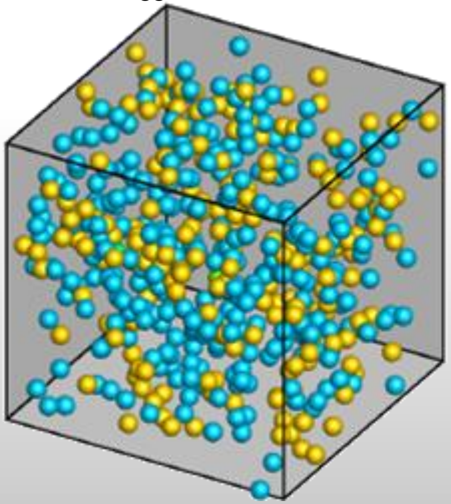
- Describing the failure of brittle pebbles in pebble beds
  - Damage criterion: $D\left(\frac{W}{W_c}\right) = \exp\left(-\exp\left(-a\left(\frac{W}{W_c} - b\right)\right)\right)$
    - Lowering of Young's modulus $E = (1 - D)E_0$
    - Fragments are not taken into account
  - No localization of damage

D: 0 0.25 0.5 0.75 1

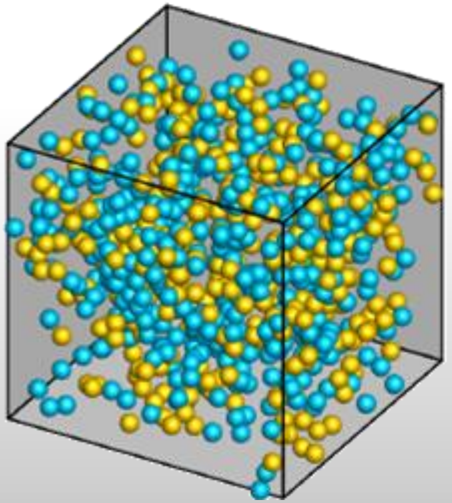
[18] Annabattula et al.



$\varepsilon_{33} = 1.65\%$



$\varepsilon_{33} = 3.00\%$

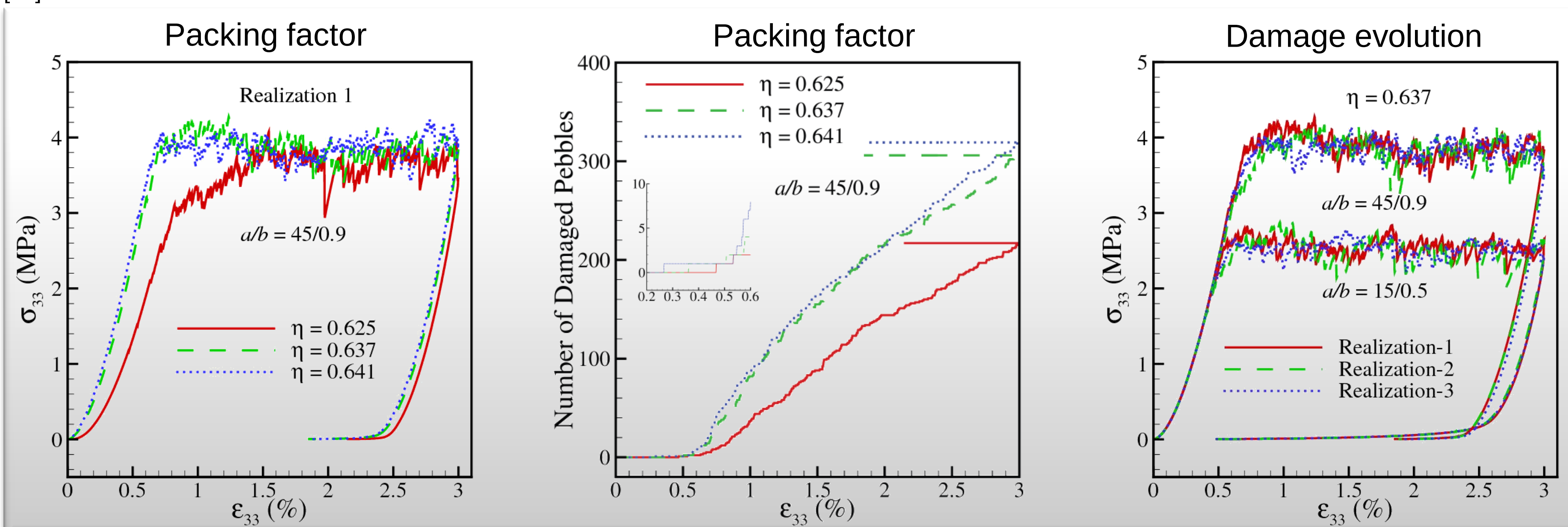


DEM modeling of pebble beds

Pebble bed response

- Saturation at critical stress followed by creep-like behavior
  - Continuous failing of pebbles
- More gradual damage evolution leads to lower critical stress
- Significantly lower residual stress for more gradual damage evolution
- Critical stress does not depend on the density of the pebble bed packing

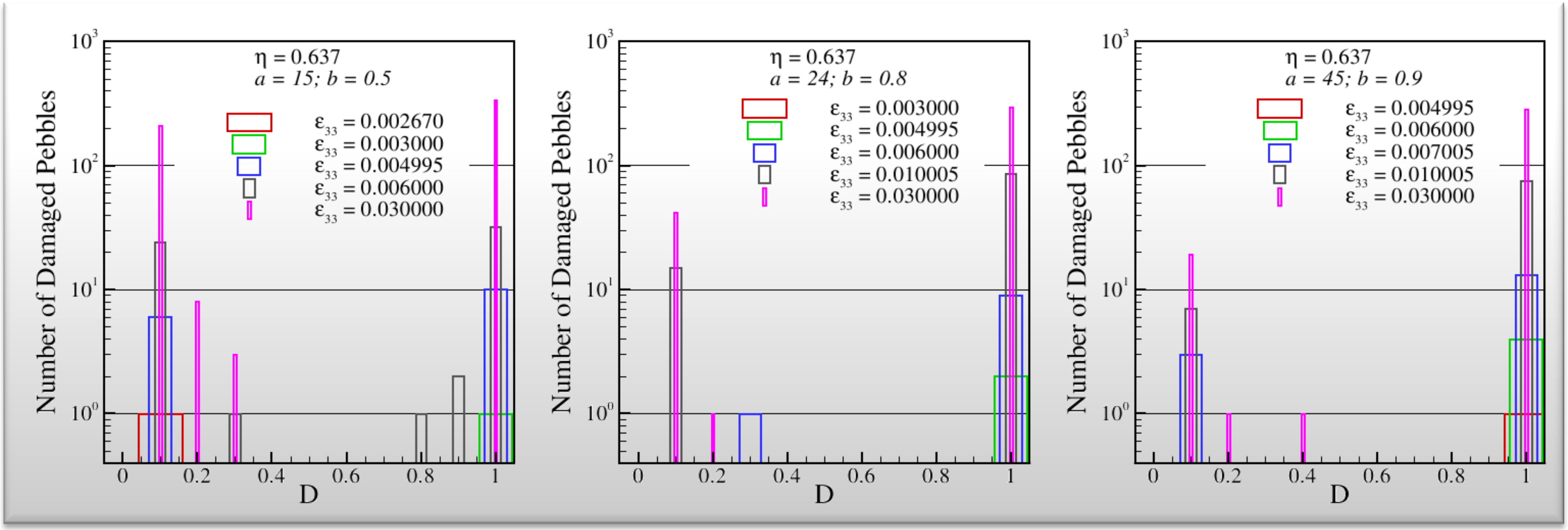
[18] Annabattula et al.



DEM modeling of pebble beds

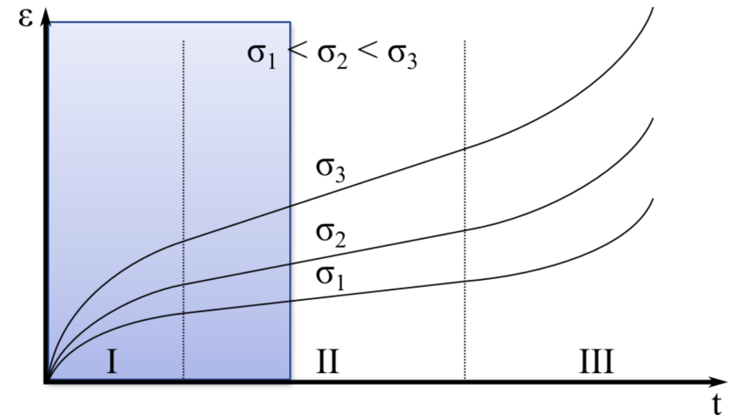
- Damage analysis of pebble beds
  - Total number of “completely” damaged pebbles ($D = 1$) is independent of the damage evolution
  - At about 0.2% of “completely” failed pebbles, the critical stress is reached
  - Gradual damage evolution of the pebbles leads to a significantly higher number of “partly” damaged pebbles

[18] Annabattula et al.

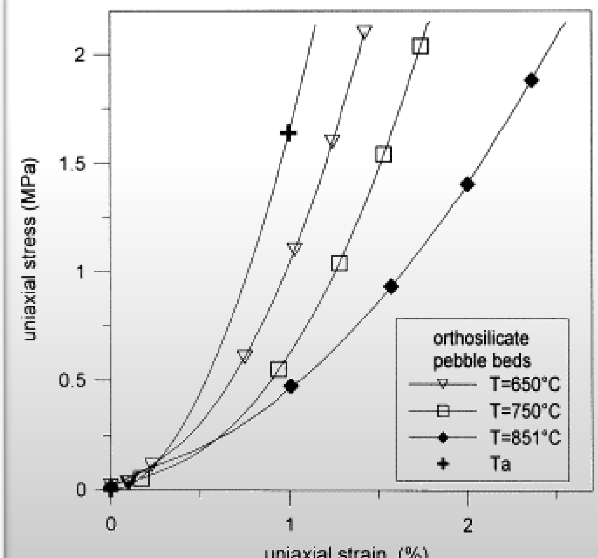


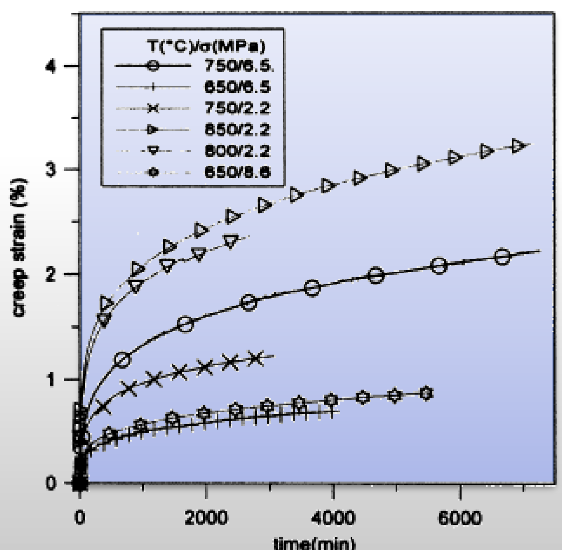
Characterization of pebble beds

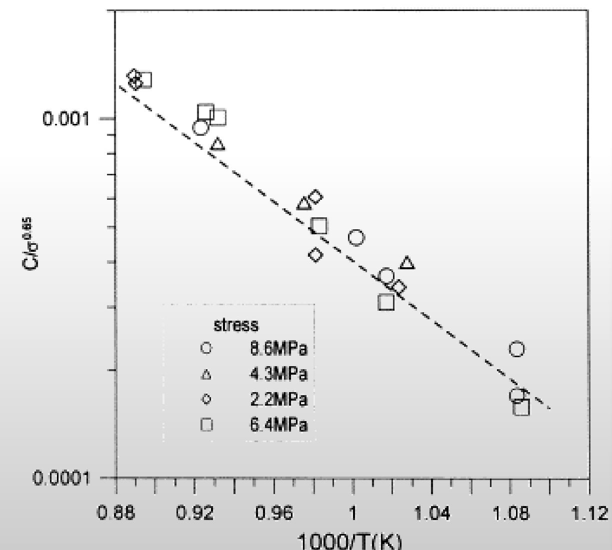
- Thermal creep
  - Negligible below 600 °C (Li_4SiO_4)
  - Power law description: $\varepsilon_c = Ae^{\left(-\frac{B}{T}\right)}\sigma^n t^m$
    - Relations to the behavior of individual pebbles can be drawn
    - Temperature, stress and time dependence
    - Parameters are only valid for one grade



[19] Reimann et al.





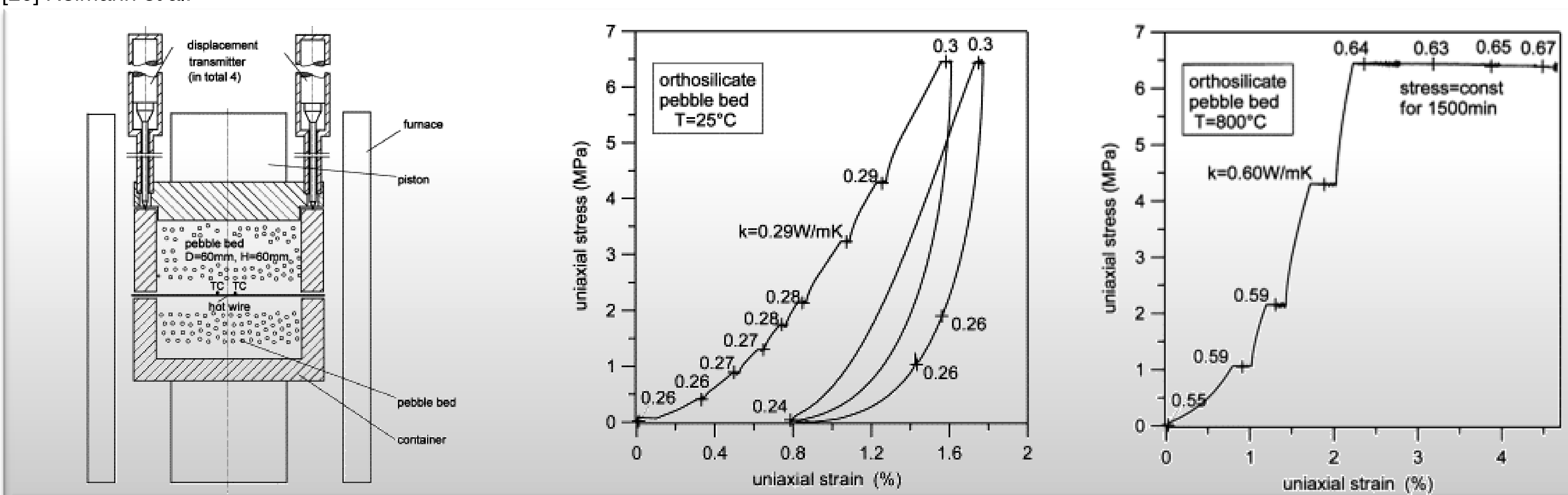


Characterization of pebble beds

Thermo-mechanical behavior

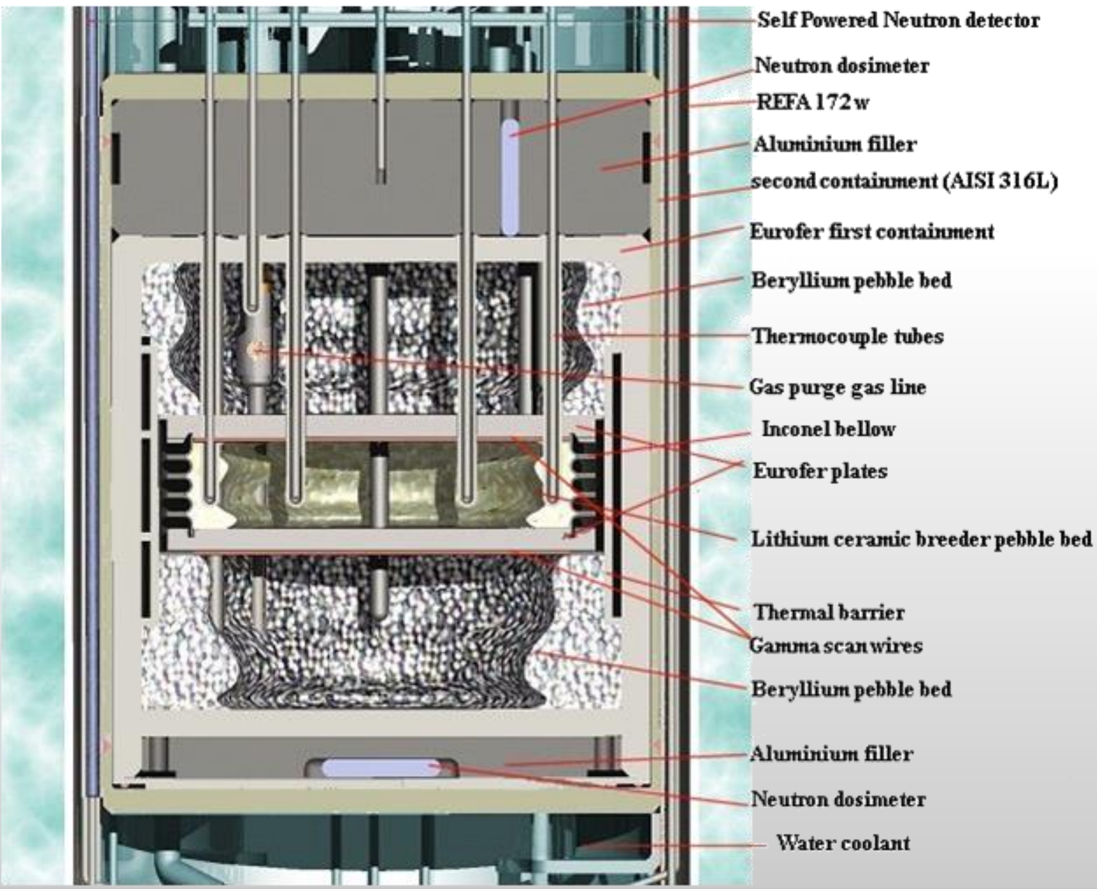
- Thermal conductivity increases with strain and temperature
  - Consolidation of the pebble bed with increasing strain
  - Increased contact area between the pebbles
    - Elastic leveling of the pebble caps
    - Considerable creep at elevated temperatures
- Gas atmosphere has a major effect on the thermal conductivity

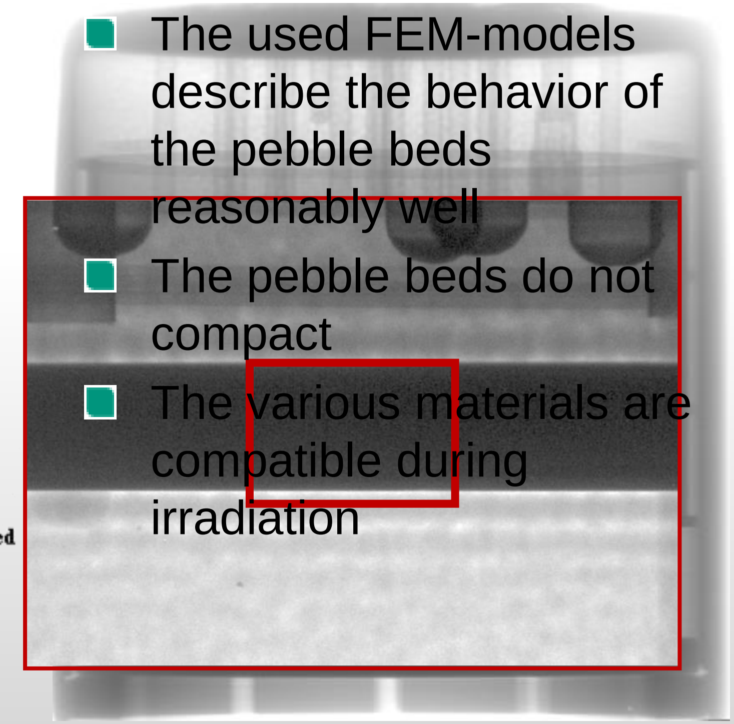
[20] Reimann et al.



Neutron irradiation of breeder materials

- Thermo-mechanics of pebble beds during irradiation
  - DEMO (2000) relevant power densities: 20-26 W/cm³





- The used FEM-models describe the behavior of the pebble beds reasonably well
- The pebble beds do not compact
- The various materials are compatible during irradiation

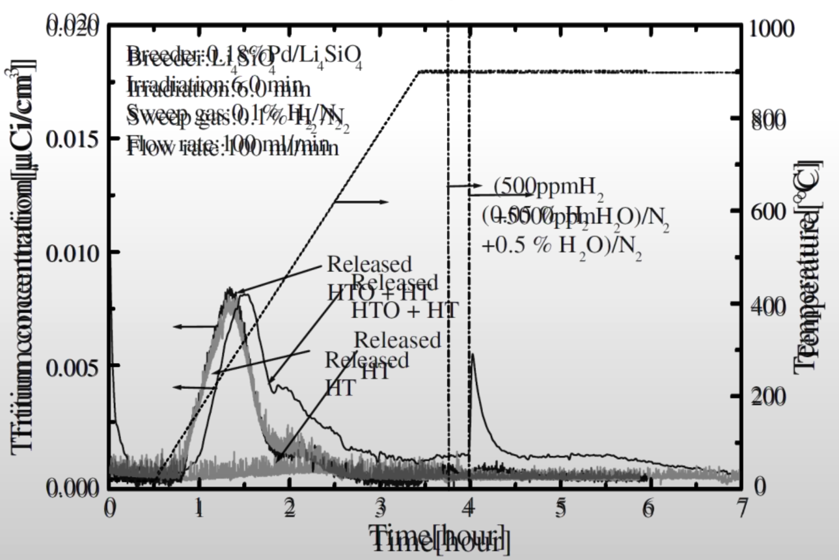
[21] van Til et al.

Neutron irradiation of breeder materials

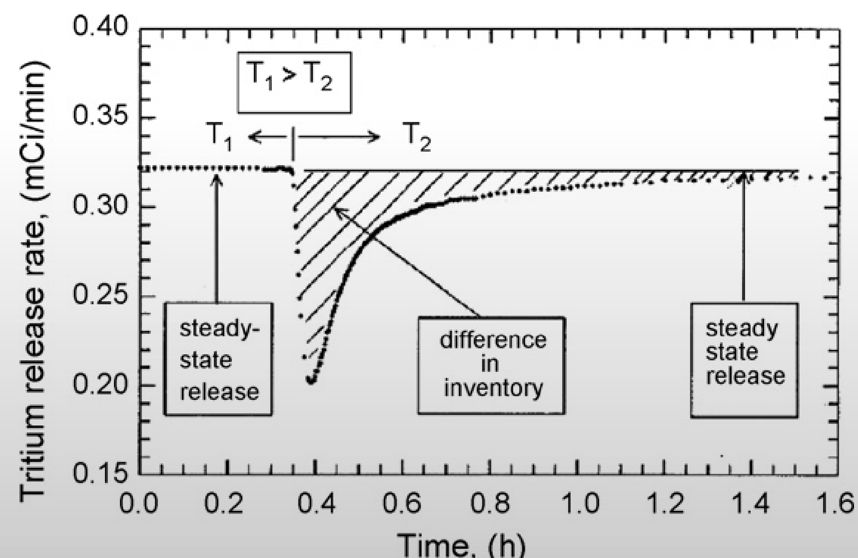
Tritium release experiments

- Residence time: $\tau = \frac{V}{q}$; V: Capacity of the system; q: Flow through the system
- Tritium inventory of a pebble: $I = \int_{V_{pebble}} \dot{m}(r) \times \tau\big(T(r)\big) dV$
- In-pile experiments show steady-state release: $G = R$
- Temperature programmed desorption (TPD) for out-of-pile experiments

Out-of-pile



In-pile



[22,23] Munakata et al.; Peeters et al.

Summary

- Fabrication of solid breeder pebbles
  - Lithium orthosilicate and lithium metatitanate are the reference class solid breeder materials
  - The ITER partners use different approaches to fabricate breeder pebbles
  - Reprocessing depends on the fabrication process
- Modeling of pebble beds
  - DEM models are an important tool to study pebble beds in detail
  - Pebble beds withstand 0.2 % of failed pebbles until they show creep-like behavior
- Neutron irradiation
  - Tritium residence time is an important design value
  - Out-of-pile and in-pile experiments deliver complementary results

Thank you for listening

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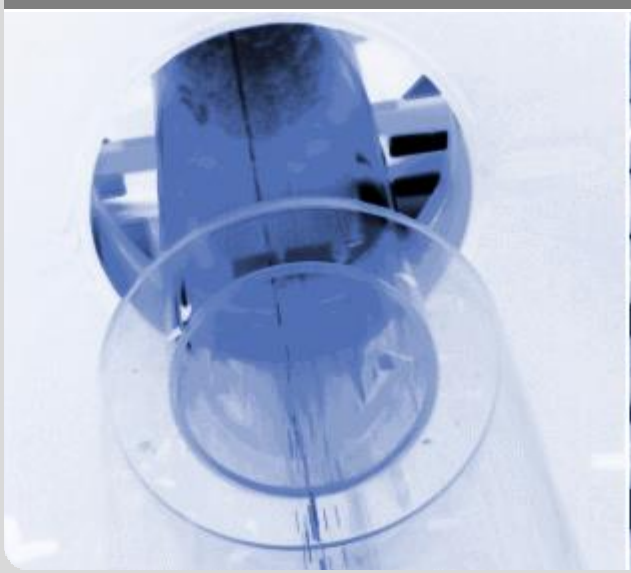
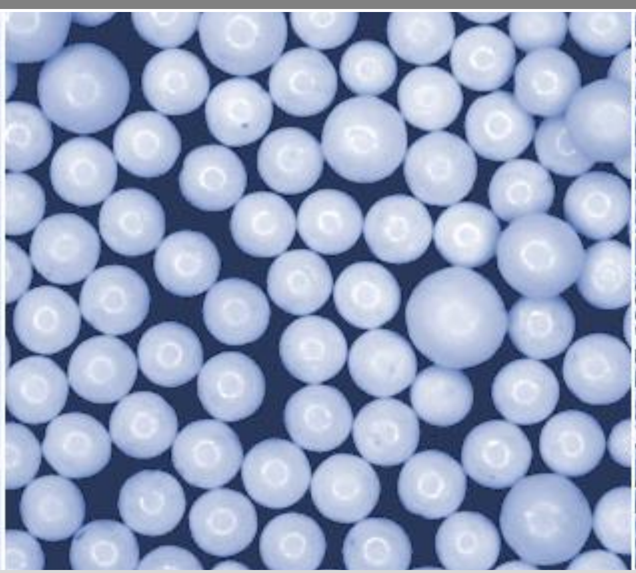
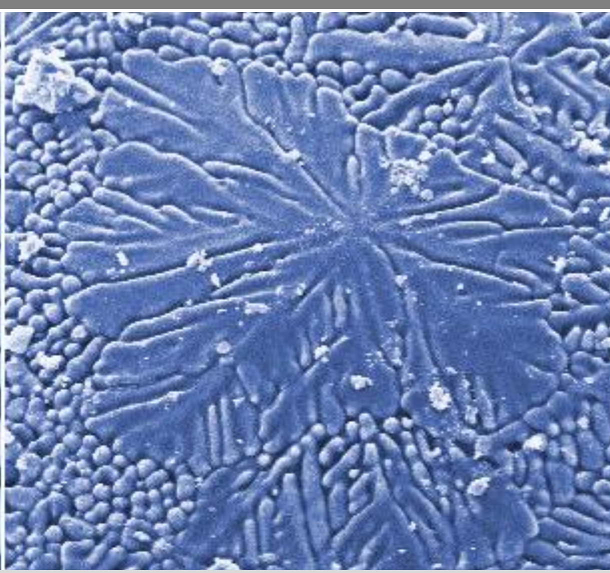

References

- [1] Cismondi et al. (2009) Fusion Engineering and Design 84 (2-6) , pp. 607-612
- [2] Hoshino et al. (2013) Fusion Engineering and Design, http://dx.doi.org/10.1016/j.fusengdes.2013.05.013
- [3] Palermo et al. (2012) Fusion Engineering and Design 87 (2) , pp. 195-199
- [4] Knitter et al. (2012) Journal of Nuclear Materials 420 (1-3) , pp. 268-272
- [5] Knitter et al. (2013) Journal of Nuclear Materials, http://dx.doi.org/10.1016/j.jnucmat.2013.02.060
- [6] Pannhorst et al. (1998), Proc. 20th SOFT, CEA, pp. 1441–1444
- [7] Kolb et al. (2011) Fusion Engineering and Design 86 (9-11) , pp. 2148-2151
- [8] Claus et al. (1996) Journal of Nuclear Materials 230 (1) , pp. 8-11
- [9] Lulewicz et al. (2002) Journal of Nuclear Materials 307-311 (1 SUPPL.) , pp. 803-806
- [10] Hoshino et al. (2012) Fusion Engineering and Design 87 (5-6) , pp. 486-492
- [11] Mergos et al. (2009) Materials Characterization 60 (8) , pp. 848-857

References

- [12] West (1981) Journal of Materials Science 16 (7) , pp. 2023-2025
- [13] Hoshino et al. (2009) Journal of Nuclear Materials 386-388 (C) , pp. 1107-1110
- [14] Feng et al. (2012) Fusion Engineering and Design 87 (5-6) , pp. 753-756
- [15] Knitter et al. (2007) Journal of Nuclear Materials 361 (1) , pp. 104-111
- [16] Park et al. (2011) Presentation at CBBI-16, Portland, Oregon http://www.fusion.ucla.edu/cbbi/cbbi16/
- [17] Zhao (2010) PhD thesis, Karlsruhe Institute of Technology, http://digbib.ubka.uni-karlsruhe.de/volltexte/1000021237
- [18] Annabattula et al. (2011) Presentation at CBBI-16, Portland, Oregon http://www.fusion.ucla.edu/cbbi/cbbi16/
- [19] Reimann et al. (2001) Fusion Engineering and Design 58-59 , pp. 647-651
- [20] Reimann et al. (2002) Fusion Engineering and Design 61-62 , pp. 345-351
- [21] van Til et al. (2012) Fusion Engineering and Design 87 (5-6) , pp. 885-889
- [22] Munakata et al. (2009) Journal of Nuclear Materials 386-388 (C) , pp. 1091-1094
- [23] Peeters et al. (2007) Fusion Engineering and Design 82 (15-24) , pp. 2318-2325