High k Sourcing & the Supply Chain for Hafnium and Zirconium

CMC Conference 2017
Critical Materials for Semiconductor Device Manufacturing
May 11 - 12, 2017 | Richardson, TX

Resourcing tomorrow's technology

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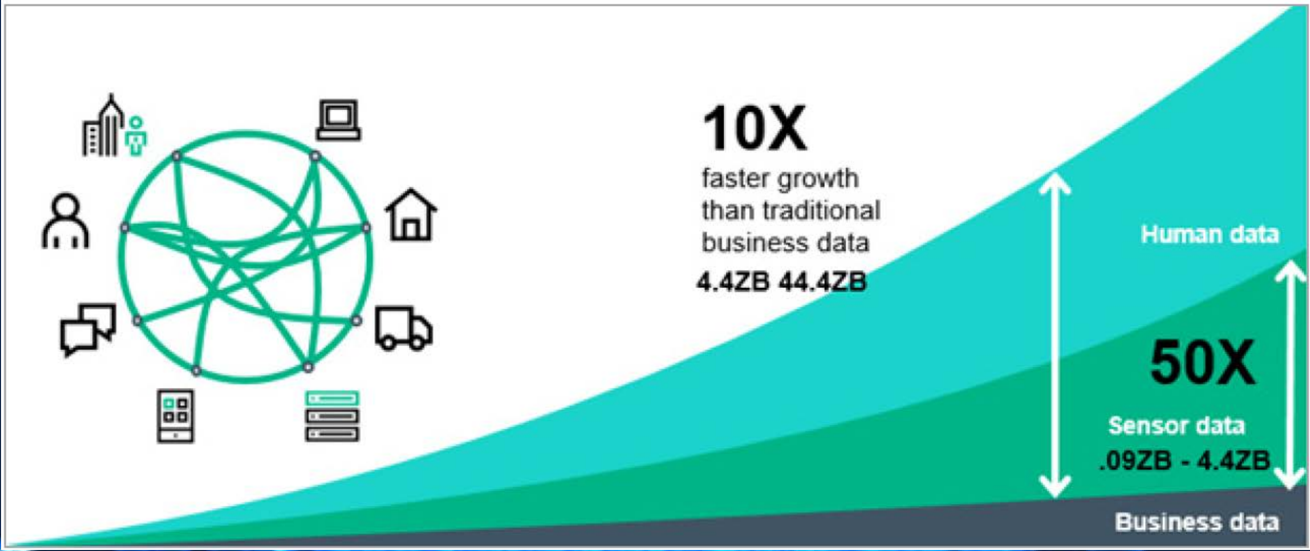
Technology

- Rapid pace of technological change
- Increasing connectivity & ubiquity
- Data growth
- New innovations



Source: Hewlett Packard Enterprise

Collection of Big Data by Sensors & Actuators

"Australian Strategic Materials & Alkane can supply up to 19 critical elements"

Connecting people and processes ubiquitously for Smart Systems and IoT

- Machine Vision / Optical Ambient Light
- Acoustic / Sound / Vibration
- Flow
- Position / Presence / Proximity
- Force / Load / Strain / Torque / Pressure
- Leaks / Levels
- Motion / Velocity / Displacement
- Electric / Magnetic
- Chemical / Gas
- Temperature
- Acceleration / Tilt
- Humidity / Moisture

Lanthanum
Cerium
Praseodymium
Neodymium
Samarium
Europium
Gadolinium
Terbium
Dysprosium
Erbium
Ytterbium
Lutetium

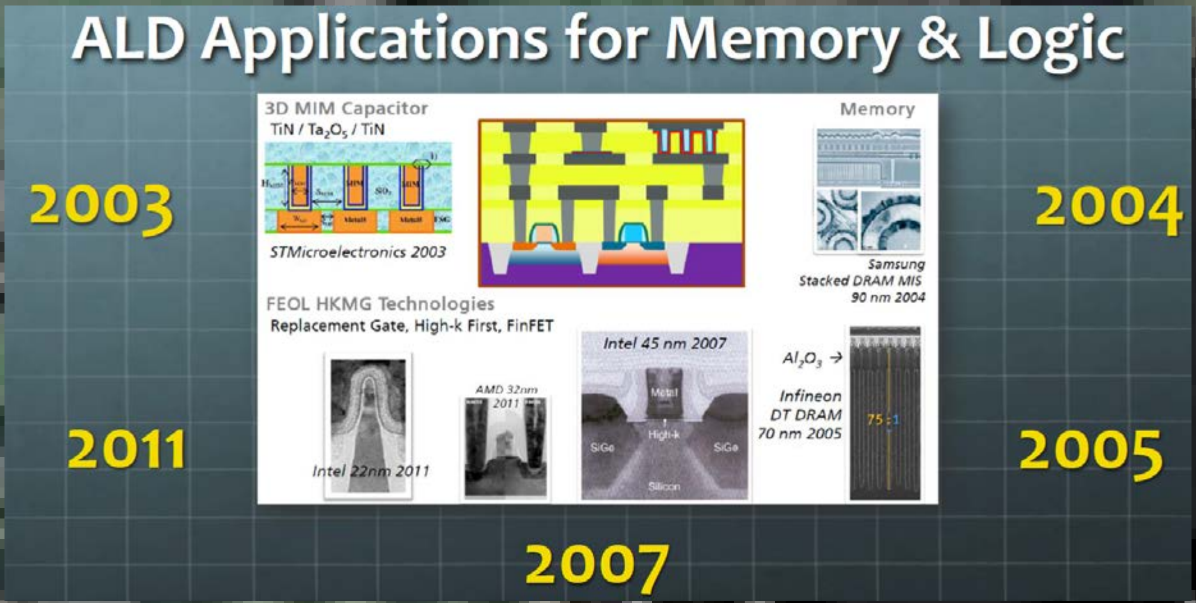
Gold
Silver
Tantalum

Hafnium
Yttrium
Zirconium
Niobium

Hafnium: The ideal memory material

First use of HfO_2

- DRAM Memory (by Samsung 90 nm 2003/2004):
  - Transition from HfO_2 to ZrO_2 took place at 65 nm
- High-k & Metal Gate (Intel; 45 nm, 2007):
  - HfO_2 is still in use



Source: Techchet CA LLC

Hafnium: The ideal memory material

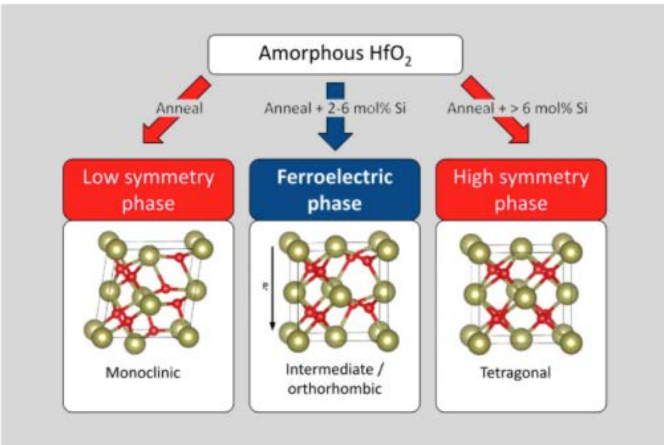


Fig. 1: Transformation of amorphous hafnium oxide into its known crystalline states and into the newly discovered ferroelectric phase

Important material parameters for memory applications:	Characteristics of ferroelectric HfO_2:	Expected limits of the material:
Temperature stability	-190°C to +200°C (published)	-270°C to +450°C (phase transition at ~450°C)
Endurance	> 10^9 cycles (published)	> 10^{15} cycles (like classical ferroelectrics)
Data retention	> 1000 h at 125°C (published)	> 10y at 175°C
Switching speed	10 ns – range (published)	< 1 ns – range (limited only by circuit RC-delay)
Switching energy	Minimum (field effect)	Minimum (field effect)
Radiation hardness	TBD	> 5 Mrad (Ferroelectricity)

Fig. 2: Memory properties of ferroelectric hafnium oxide as derived from experiments and expected material limits.

Source: ferroelectric-memory.com

FMC The Ferroelectric Memory Company

Home | Technology | Target applications | About

Ferroelectric hafnium oxide

FE-HfO_2: The ideal memory material

FMC's memory technology is based on a fundamental material discovery, i.e. the discovery of ferroelectric properties in hafnium oxide. During the days in which HfO_2 was researched as a DRAM capacitor dielectric, it was found that a previously unexpected crystal phase can be stabilized by doping and thermal treatment of the material. Within that crystal phase (an orthorhombic, non-centrosymmetric phase, see Fig. 1), the oxygen atoms of HfO_2 can reside in two stable positions, shifting either up or down according to the polarity of an externally applied electric field. Therefore and depending on the position of the oxygen atoms, a permanent electric dipole is created that can either point upwards or downwards in this way enabling the storage of two binary states. Hence, it is a bulk memory effect that can be controlled by application of an electric field only.

Due to the fact that the ferroelectric effect was so unexpected, the material was researched heavily during the last years in order to proof its potential as a memory material. The results of this research are given in Fig. 2. It has already been demonstrated that the material shows extreme temperature stability as well as endurance, retention and switching speed characteristics similar to classical ferroelectrics. However now with a ferroelectric material that is 100% CMOS compatible.

Source: ferroelectric-memory.com

What is hafnium?

- A shiny, silvery metal that resists corrosion and can be drawn into wires.
- Discovered in 1923 by George Charles de Hevesy and Dirk Coster
- The name is derived from the Latin name for Copenhagen, 'Hafnia'

- In its natural state it is always bound up with zirconium compounds, from which it needs to be extracted using advanced metallurgical processing.

http://www.rsc.org/periodic-table/element/72/hafnium

Properties of hafnium

Melting point: 2233°C, 4051°F, 2506 K
Boiling Point: 4600°C
Density (g cm^{-3}) : 13.3
Key isotopes: ^{177}Hf, ^{178}Hf, ^{180}Hf
Electron configuration: [Xe] $4f^{14}5d^{2}6s^{2}$

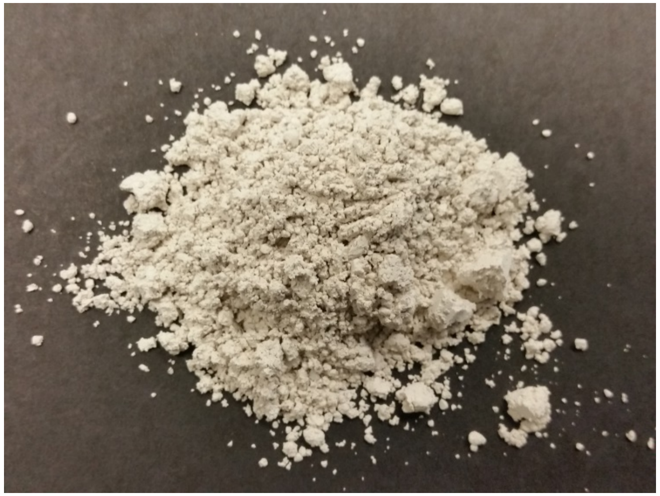
- High thermal neutron absorption cross section **(~600 times zirconia)**
- High stability & strength at high temperatures in metallic & compound form
- High dielectric constant
- Thermoelectric material
- High-index/low optical absorption properties
- The main source of hafnium is as a by-product from producing **nuclear grade hafnium free zirconium metal**

Hafnium traded as

Hafnium metal in 'crystal form'

Source: http://www.periodictable.com/Items/072.5/index.html

Hafnium oxide (HfO_2)

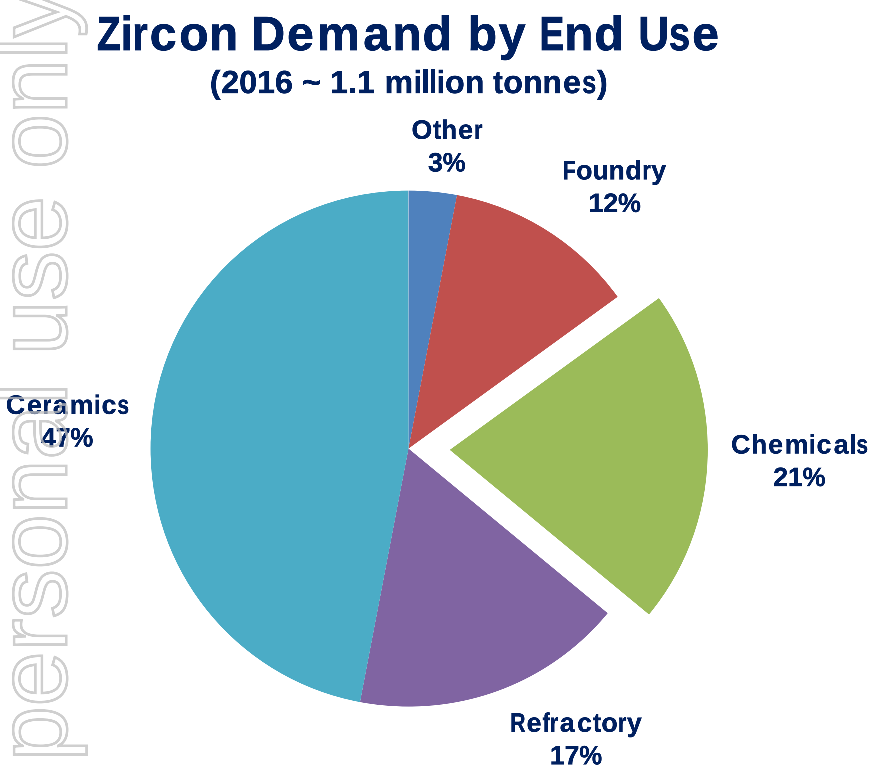


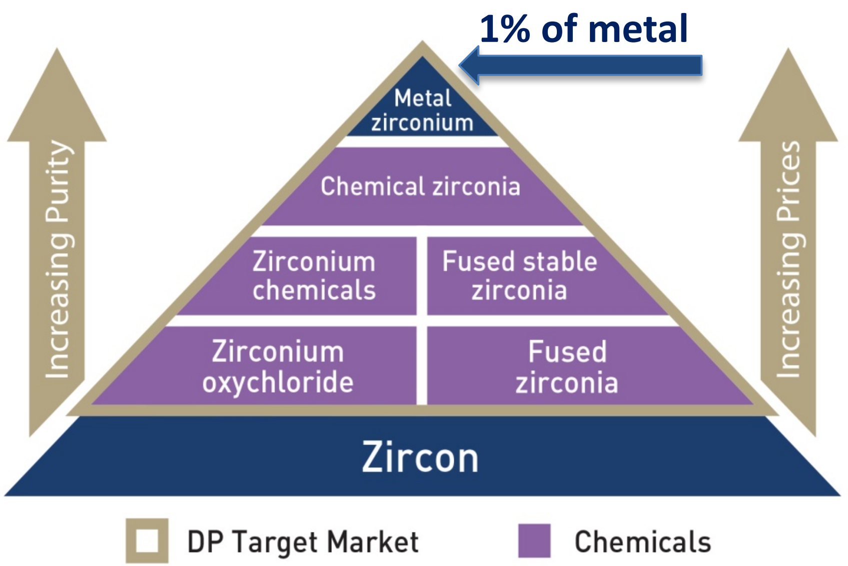
Source: Alkane Dubbo Project

Hafnium tetrachloride ($HfCl_4$)

Source: http://onyxmet.com/?route=product/product&product_id=795

Zirconium Industry: hafnium source





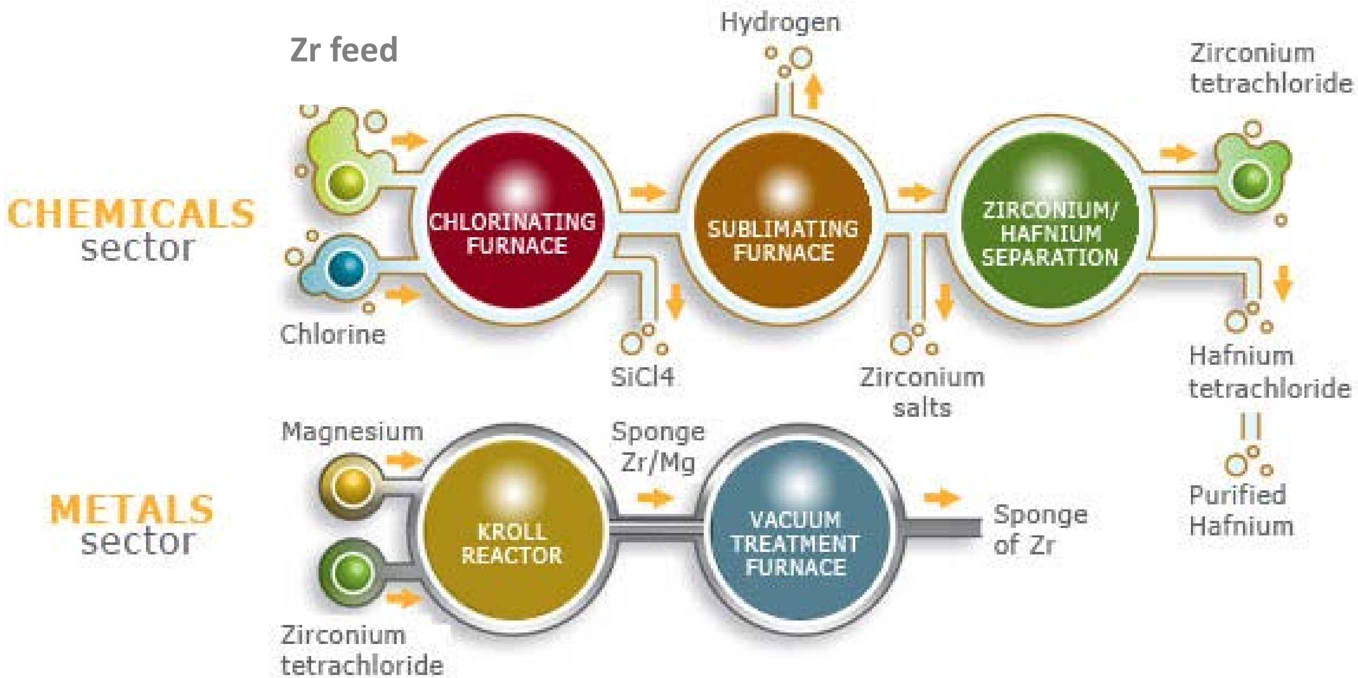
- Global market US$2-3B
- 2017 producer zircon inventories low
- Demand increasing/supply constrained
- CAGR anticipated at 3-5% pa for zirconium chemicals

- China dominates downstream zirconium industry (Supply 75+%)
- Zirconium metal 5-6,000 tpa
- Nuclear zirconium metal 3,500 tpa

60 tpa Hafnium

Source: TCMS and Industry Sources

Zr-Hf separation process



Zr:Hf

50:1

1,000t : 20t HfO_2

17t Hf metal

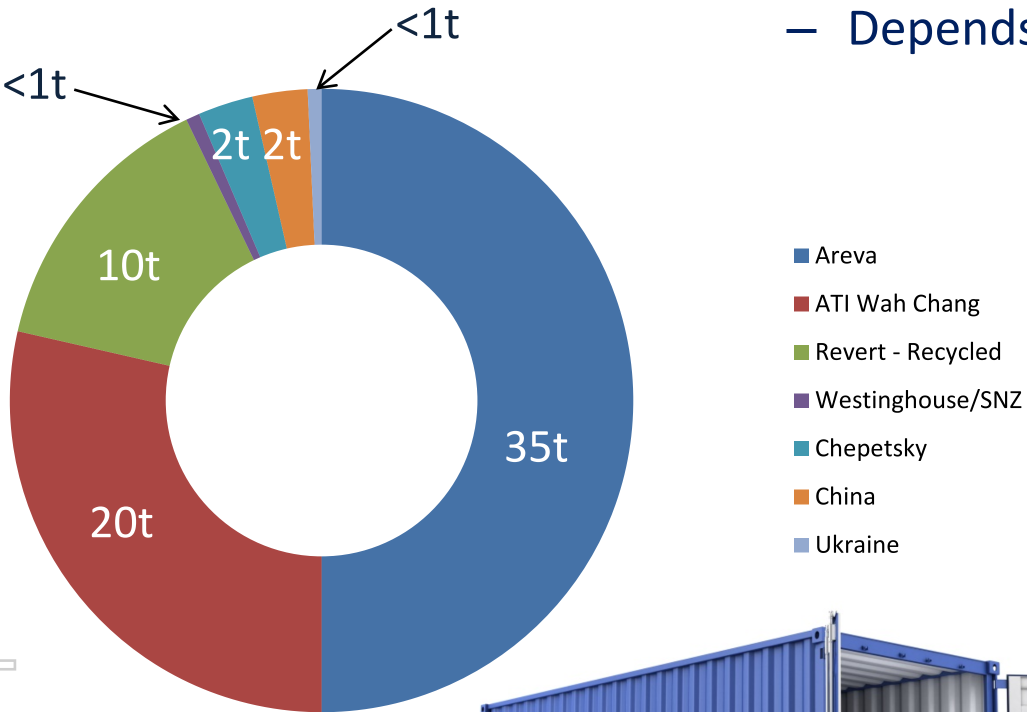
Source: http://www.areva.com/EN/operations-913/jarrie-production-of-zirconium-sponge.html

- Main source of hafnium is the Nuclear industry, where it must be removed from zirconium to produce hafnium free zirconium
- Main application is neutron-transparent fuel assemblies
- **Most Hafnium supply is Nuclear industry dependent**

Current world supply

2016 Hafnium supply

Estimated 70 tonnes

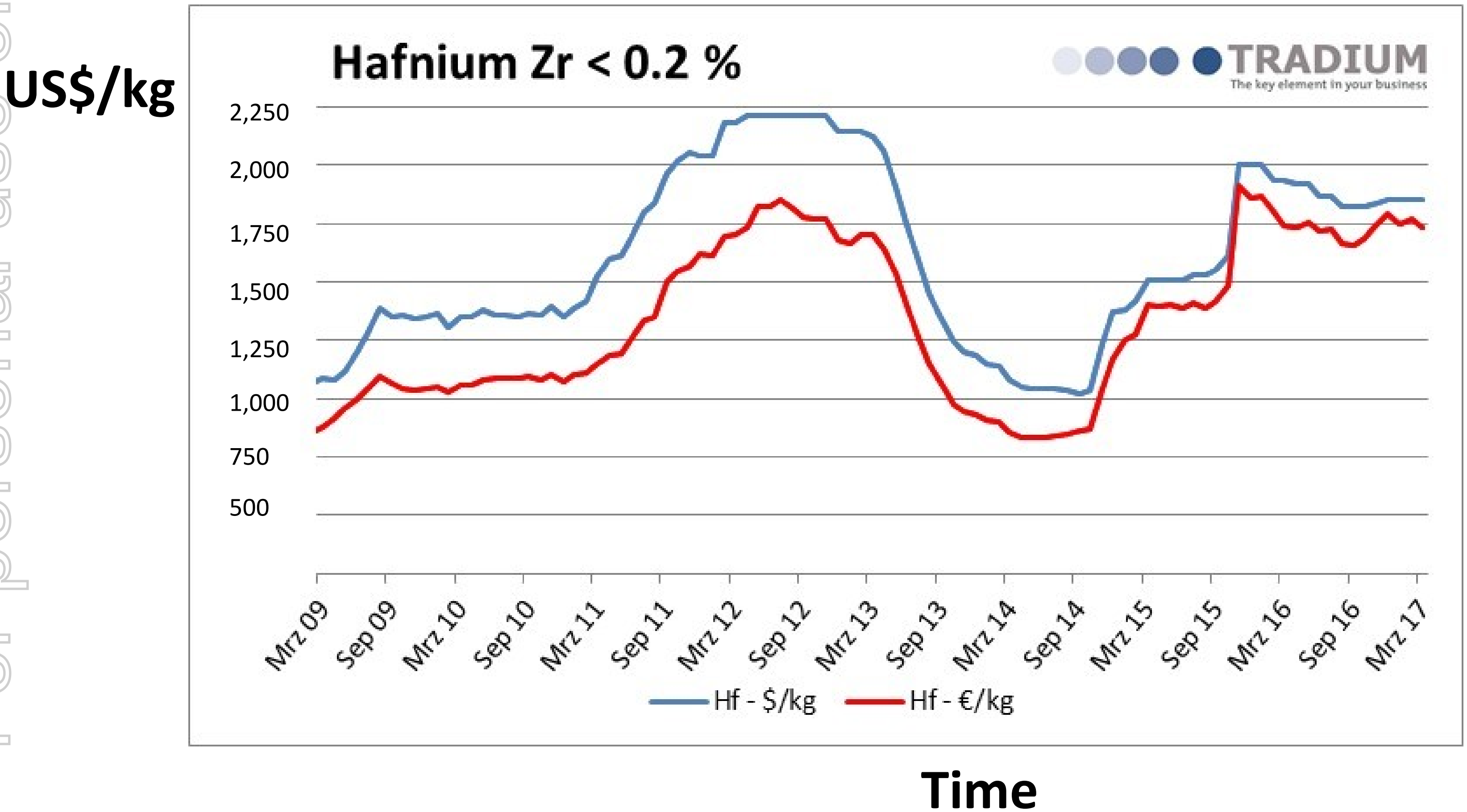


- **By-product from zirconium metal purification**
  - Depends on nuclear industry
- **Prices escalating through demand by aerospace industries 2014 into 2015**
- **3 western companies produce – hafnium (metal) from HfO_2**
  - ATI (US)
  - Westinghouse (US)
  - Areva (France)
- **Total world supply fits in a 40 foot shipping container**

Source: Roskill ASM Internal report (draft)

Historical hafnium pricing

Hafnium Pricing (2009 – 2017)



Chinese zirconium metal capacities

Company	Industrial Grade tpa	Nuclear Grade tpa	Nuclear Grade Expansion Plans by 2020 tpa
State Nuclear WEC	-	1,500	2,500
Guangdong Orient	600	150	1,000
Jinan H-Technology	0	0	400
Others	1,400	100	300
Total	2,000	1,750	4,200
Hafnium supply	**0**	**30**	**70**

- Chinese zirconium metal production ~1,500 tpa - 2014 (mostly industrial grade)
- China's strategy is to be self-sufficient in nuclear power plants
- Maximise value adding across supply chain (same as for rare earths)
- **China will require all hafnium for its own industry**

China's Zirconium Industry Challenges

1. Zirconium chemicals

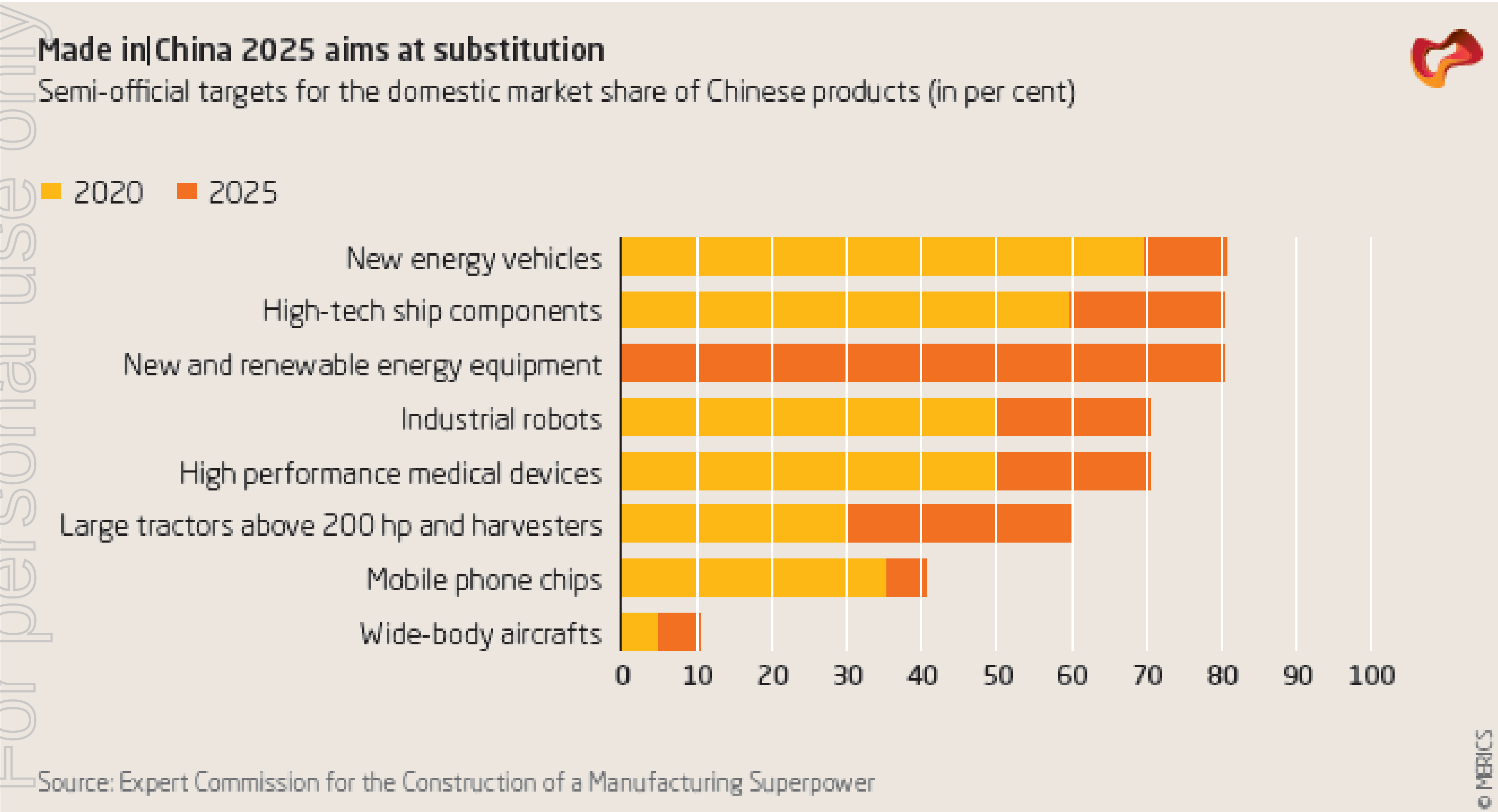
- Dealing with U+Th waste residues for ZOC production
  - ZOC production of 210,000 tpa requires 130,000 tpa zircon
    - **Contains 65 tpa of U+Th**
    - Where does it go now and in the future?
- Occupational health and safety issues for workers
- Environmental compliance is becoming increasingly difficult
- **1/3rd of Chinese ZOC industry shut down in April 2017**

2. Fused zirconia

- Regulations require <500 ppm U+Th for USA or Japan
  - China and exports elsewhere?
- Chinese Fused zirconia production of 45,000 tpa requires 70,000 t of zircon with U+Th <300 ppm to obtain U+Th <500 ppm
- Where will premium zircon come from?

Source: TCMS and Industry Sources

China: Critical Supply Issues to 2025



Source: European Chamber of Commerce, China

China Manufacturing 2025: A warning

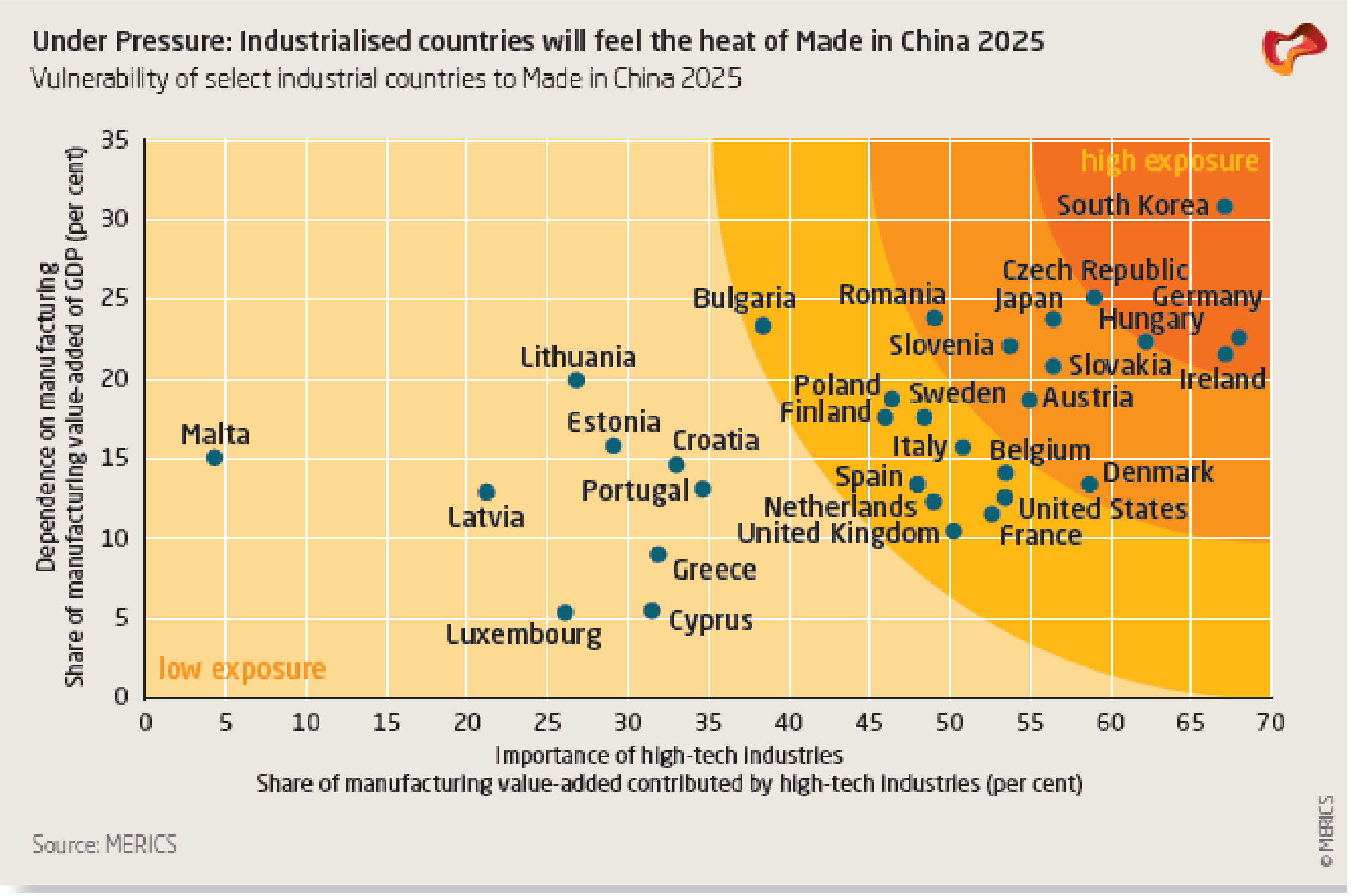
Ambitious goals: 10 advanced industries & technologies

- US$100Bs of support: subsidies, funds, and "other"
- Move away from low value, and polluting industries to manufacturing for high value markets
- Avoid the middle income trap: being squeezed between developed and developing countries
- Race to get rich before growing old: 400 million ageing baby boomers
- **Targeting 70-80% domestic supply: large scale import substitution**

Factory of the world (2015)

- 90%+of world's mobile phones
- 80%+ of world's air-conditioners
- 80%+ of world's computers
- 60% of world's colour TV sets
- Half of the world's steel
- 50%+ of world's refrigerators
- 41% of world's ships
- 28% of world's automobiles
- 24% of world's power, &
- **20% of global manufacturing**

China: Critical Supply Issues to 2025



Source: European Chamber of Commerce, China

China: Critical Supply Issues to 2025

1. **China Manufacturing 2025 is targeting 70-80% domestic supply by 2005 for key high value markets**
   - Critical supply risk for rare earths as China supplies 90+ % of world supply
   - High growth rates for magnets will reduce supply for export- China will need to be a net importer
2. **China's rare earth industry is US$3-4 billion, with a US$30-40 billion environmental clean up legacy**
   - Rare earth prices will need to double in order to pay environment clean up costs over 10 years
3. **With 40-50% of all rare earths coming from illegal mining: Western companies need to become accountable**

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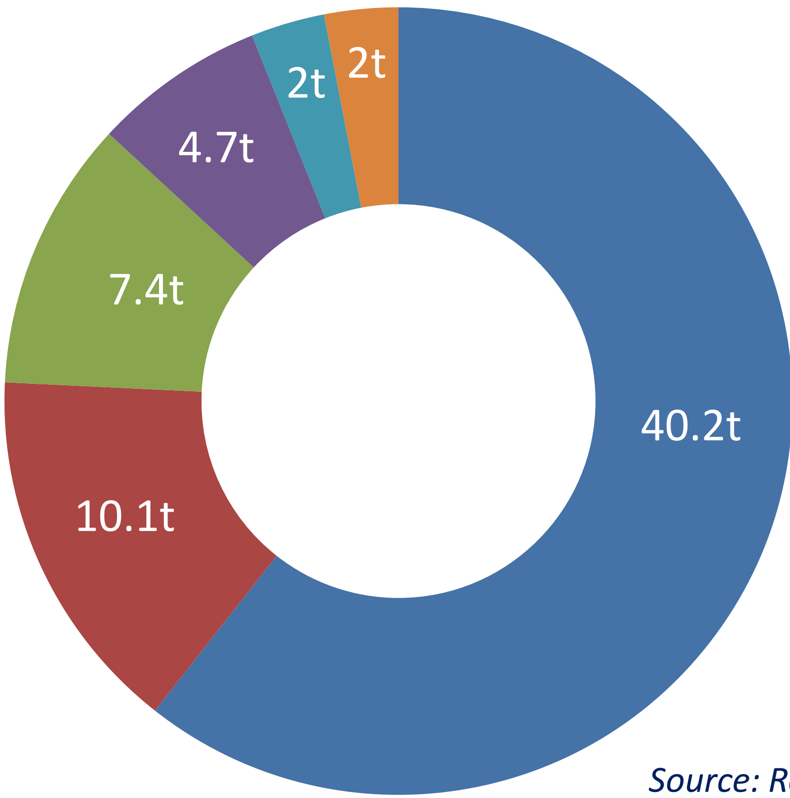
Current global demand

2016 Hafnium demand

Estimated 67 tonnes



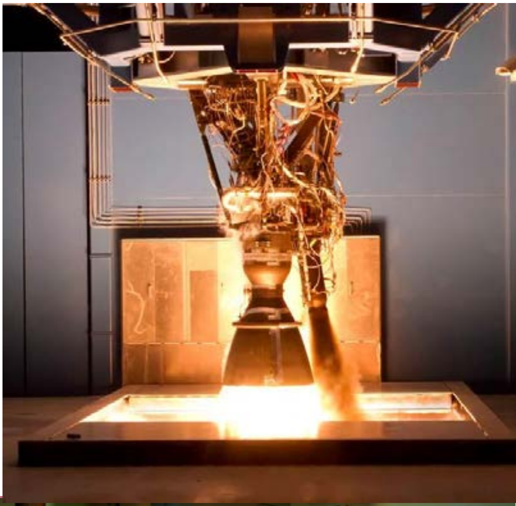
Major markets
(global output by weight):

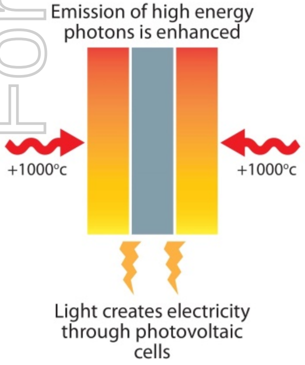
- Superalloy (60%)
- Plasma cutting tips (15%)
- Nuclear control rod (11%)
- Catalyst precursor (7%)
- Semiconductors (3%)
- Oxide for Optical (3%)

Source: Roskill ASM Internal Report (draft)

Other potential hafnium demand

1. **Reusable spacecraft**
   - **Hafnium offers extreme heat and creep resistance**
   - SpaceX uses C103 -10% hafnium & 90% niobium metals
   - Blue Origin, NASA, European Space Agency
   - U.K. Space agency, Russia/China/India/other
2. **Thermoelectric generators**
3. **High temperature refractories**
4. **Hafnium carbide cutting tools**
5. **HfO_2 nanoparticles in radiation oncology**
6. **Radiative cooling**





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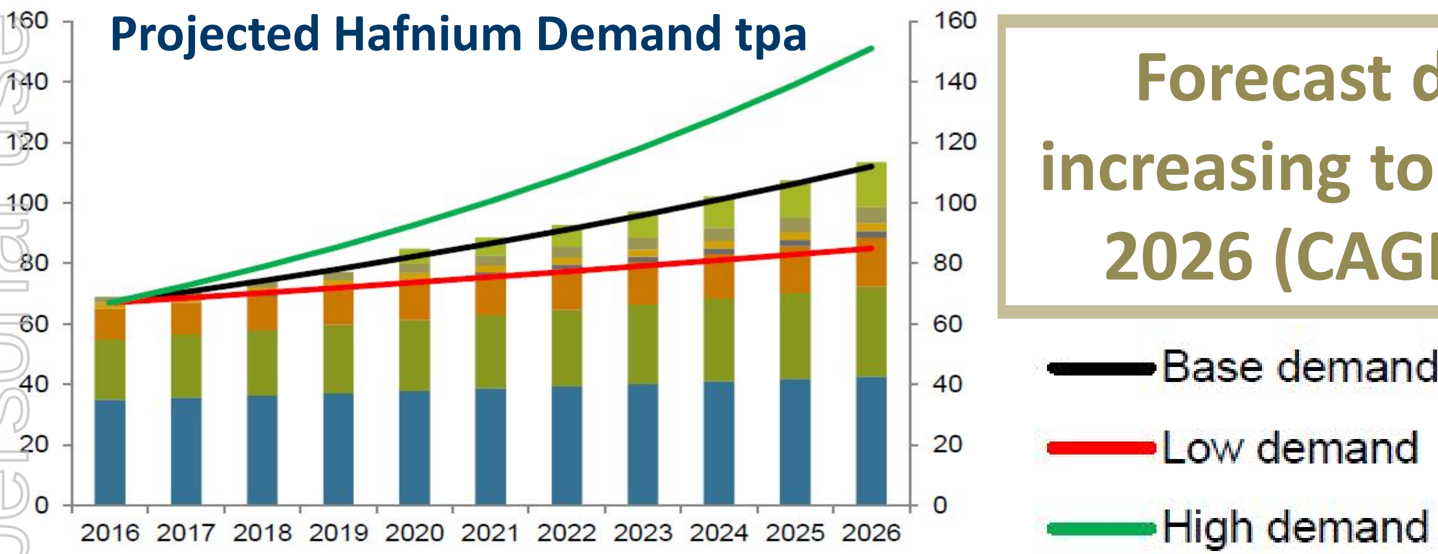
Hafnium Demand outlook 2016 - 2026

Depends on existing producers + expanded Russia/China supply

- Not sufficient for base-case demand growth - Will impact price or substitution endeavours	-Constrained or abundant: If supply is more abundant demand may emerge from new sectors



Forecast demand increasing to 152tpa by 2026 (CAGR +5.3%)

*Source: Roskill ASM Internal Report (draft) CAGR min 2.4%pa low supply constrained to max 8.5%pa high supply unconstrained *5.3% base supply expanded*

Alkane's Dubbo Project the only supply option not tied to Nuclear industry and Chinese zirconium industry

Dubbo Project

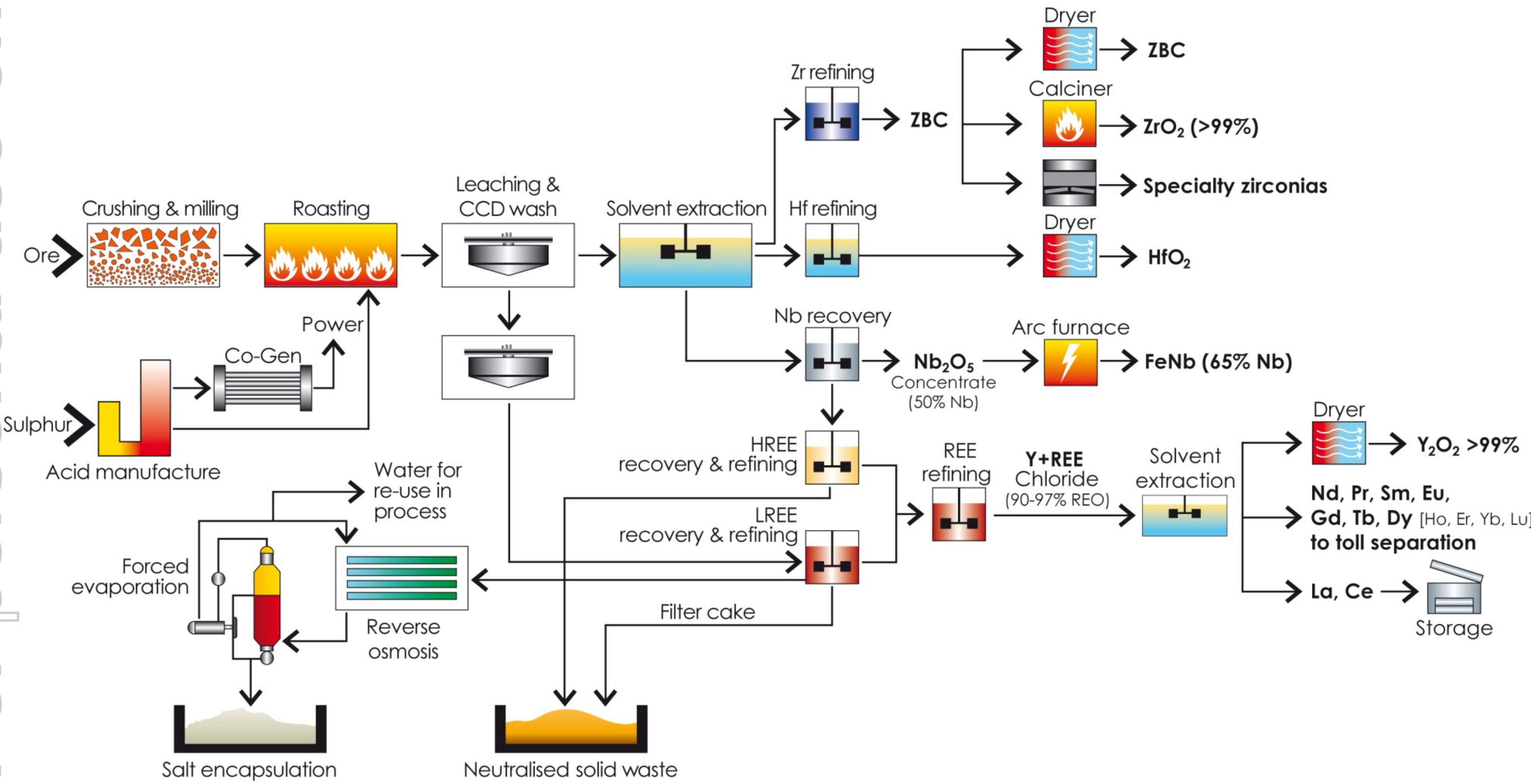
- Large polymetallic resource - zirconium, hafnium, niobium (tantalum), yttrium and rare earths
- Defined resource supports 80+ years at 1 m tpa
- Pilot Plant at ANSTO has operated since 2008
- All State & Federal environment approved
- Outotec Finnish technology & engineering solutions company to present a fixed price EPC
- Sumitomo Mitsui Banking Corporation financial advisors
- Modular design option (halves CAPEX costs and output) for lower risk
- Dubbo infrastructure – roads, rail, power, gas, light engineering, people (pop~45,000)

DUBBO PROJECT IS CONSTRUCTION READY

A new Hf supply – Dubbo Project

- Hafnium concentrate has been successfully produced on the hafnium pilot plant at ANSTO from the zirconium refining circuit
- **Orebody contains ~450 ppm hafnium oxide**
  - 1 million tpa production rate x 450 ppm = **450 tpa**
  - **50% recovery: ~200 tpa of hafnium oxide (95% HfO_2)**
  - **Initial start up output of 50 tpa**
- Potential to increase hafnium supply as
- Independent of zircon and nuclear industry
- Sustainable and traceable supply
- Urban mining to recycle end of life materials

Separation Process



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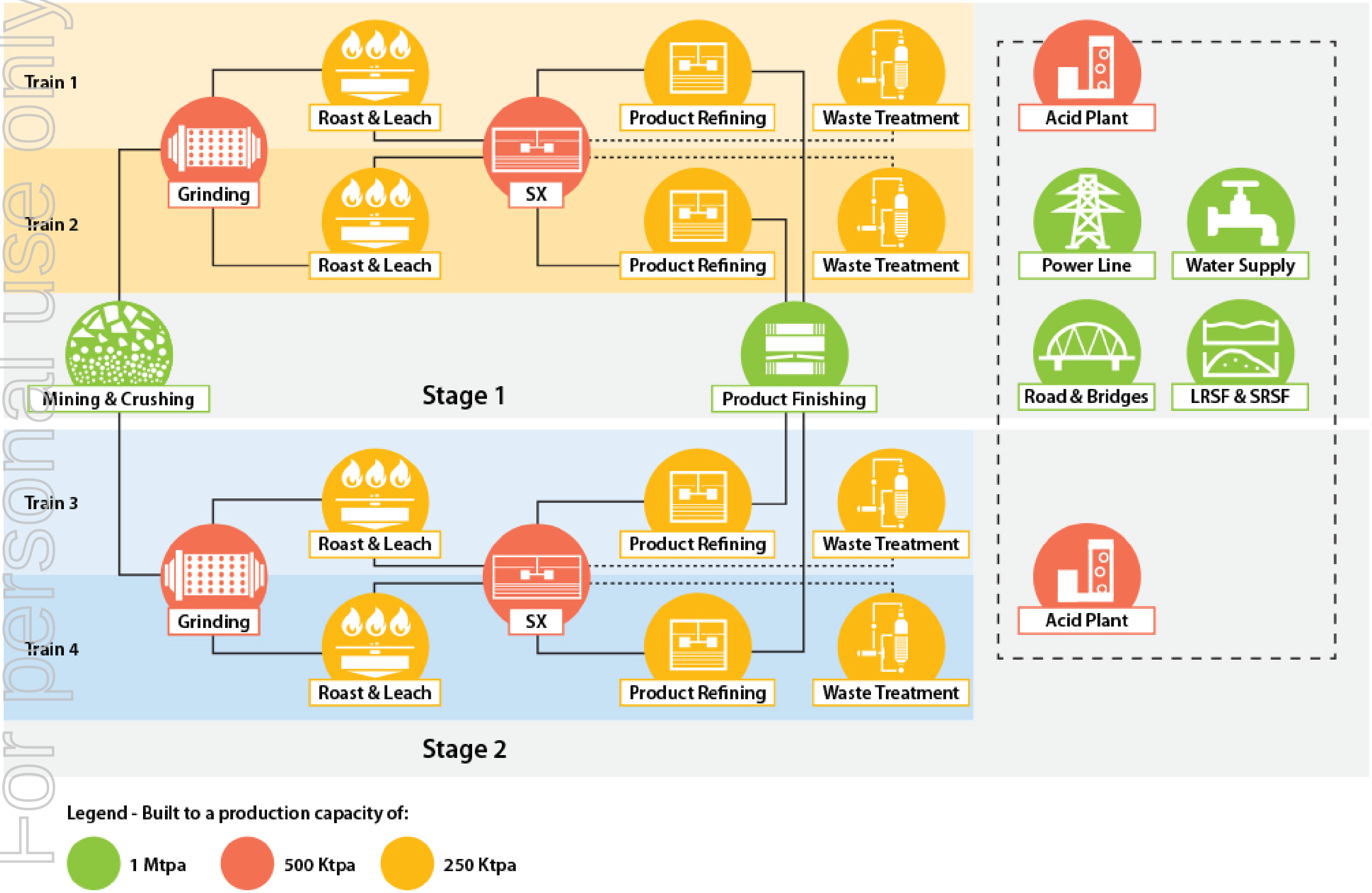
Modular Design



Construction 2017 - 2019

Estimated cost US$480M

Construction 2022 - 2023

Estimated cost US$360M

Estimated total Cost US$840M

Product Output

Dubbo Project Process Plant

Product	Grade	Output
Rare earth chemical concentrate	95% REO	6,664 tpa (REO units)
Zirconium as ZBC (carbonate) & zirconia	99% ZrO_2	16,374 tpa (ZrO_2 units)
Hafnium as HfO_2 concentrate	HfO_2 conc	50 tpa * (Hf units)
Niobium as ferro-niobium	65% Nb	1,967 tpa (Nb units)

Total output approximately 25,200 tpa of all products

Tonnage based upon recoveries developed from mass balances of the demonstration pilot plant.

*** Start up output: 200tpa potential depending upon market demand**

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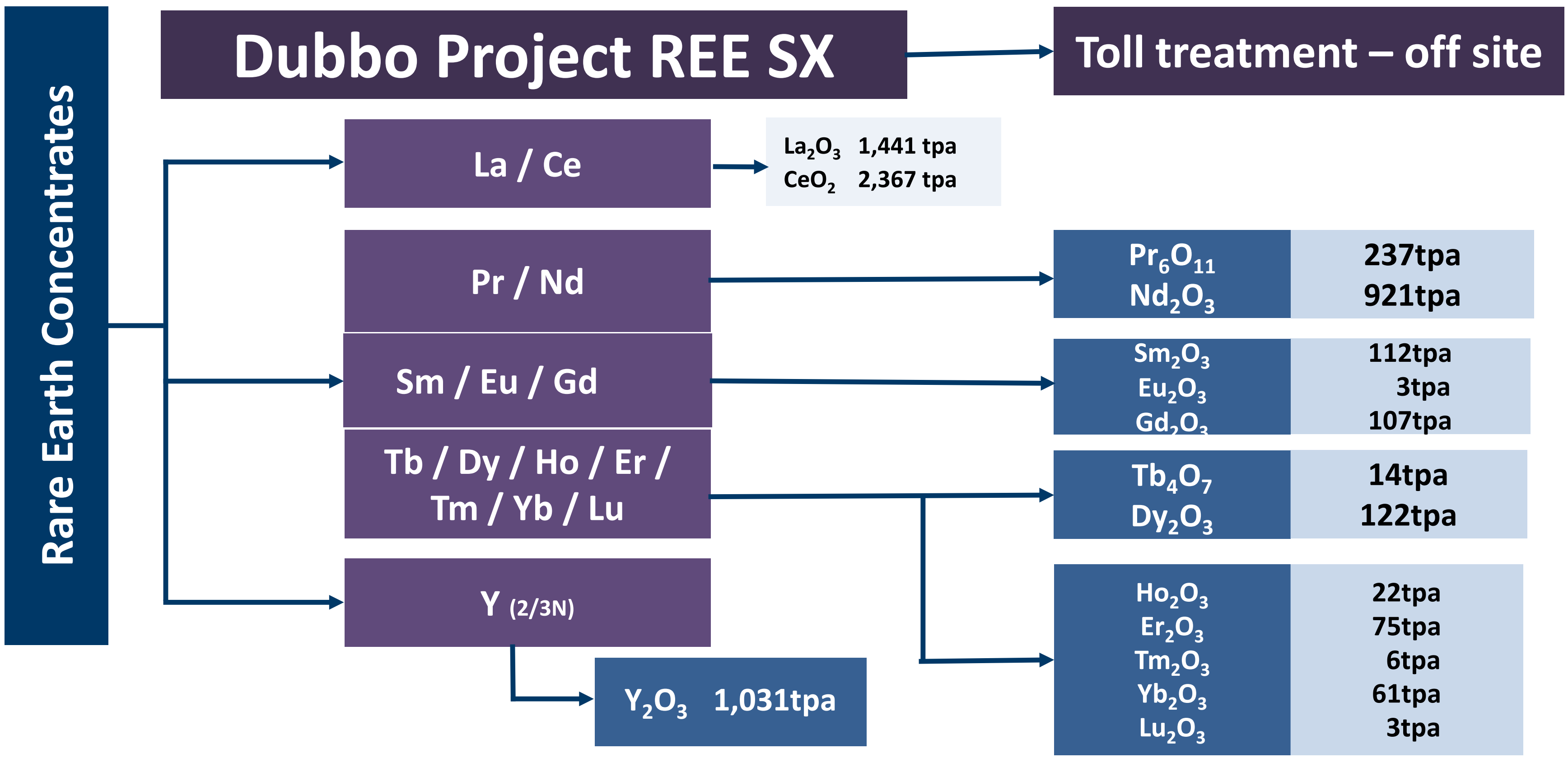
Rare Earth Output



Tonnage based upon recoveries developed from mass balances of demonstration pilot plant, & preliminary solvent extraction stages on site at the DP. Total saleable RE products from site ~1,030 tpa and off site ~ 1,675 tpa.

Conclusions

Ideal Hafnium Supply Scenario?

- ✓ Independent of nuclear fuel industry
- ✓ Independent of Zircon
- ✓ Independent of Chinese zirconium industry
- ✓ Sustainable and traceable supply
- ✓ Urban mining to recycle end of life materials
- ✓ Complementary other technology metals
- ✓ Low sovereign risk

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Competent Person

Unless otherwise stated, the information in this presentation that relates to mineral exploration, mineral resources and ore reserves is based on information compiled by Mr D I Chalmers, FAusIMM, FAIG, (director of the Company) who has sufficient experience which is relevant to the style of mineralisation and type of deposit under consideration and to the activity which he is undertaking to qualify as Competent Person as defined in the 2012 Edition of the Australasian Code for Reporting of Exploration Results, Mineral Resources and Ore Reserves. Ian Chalmers consents to the inclusion in the presentation of the matters based on his information in the form and context in which it appears.

Dubbo Project Resources & Reserves

Dubbo Project – Mineral Resources

Toongi Deposit	Tonnage (Mt)	ZrO_2 (%)	HfO_2 (%)	Nb_2O_5 (%)	Ta_2O_5 (%)	Y_2O_3 (%)	REO (%)
Measured	35.70	1.96	0.04	0.46	0.03	0.14	0.75
Inferred	37.50	1.96	0.04	0.46	0.03	0.14	0.75
Total	73.20	1.96	0.04	0.46	0.03	0.14	0.75

These Mineral Resources are based upon information compiled by Mr Terry Ransted MAusIMM (Alkane Chief Geologist) who is a competent person as defined in the 2012 Edition of the Australasian Code for Reporting of Exploration Results, Mineral Resources and Ore Reserves. Terry Ransted consents to the inclusion in the report of the matters based on his information in the form and context in which it appears. The full details of methodology were given in the 2004 Annual Report.

Dubbo Project – Ore Reserves

Toongi Deposit	Tonnage (Mt)	ZrO_2 (%)	HfO_2 (%)	Nb_2O_5 (%)	Ta_2O_5 (%)	Y_2O_3 (%)	REO (%)
Proved	8.07	1.91	0.04	0.46	0.03	0.14	0.75
Probable	27.86	1.93	0.04	0.46	0.03	0.14	0.74
Total	35.93	1.93	0.04	0.46	0.03	0.14	0.74

These Ore Reserves are based upon information compiled by Mr Terry Ransted MAusIMM (Alkane Chief Geologist) who is a competent person as defined in the 2012 Edition of the Australasian Code for Reporting of Exploration Results, Mineral Resources and Ore Reserves. The reserves were calculated at a1.5% combined ZrO_2+Nb_2O_5+Y_2O_3+REO cut off using costs and revenues defined in the notes in ASX Announcement of 16 November 2011. Terry Ransted consents to the inclusion in the report of the matters based on his information in the form and context in which it appears.

Note: ASX announcements 16 November 2011, 11 April 2013, 30 October 2013 and 27 August 2015 - the Company confirms that all material assumptions and technical parameters underpinning the estimated Mineral Resources and Ore Reserves, and production targets and the forecast financial information as disclosed continue to apply and have not materially changed.