Development of Technologies and Management Options for Irradiated Graphite and Carbonaceus Waste

AtomEco 2013 (Moscow)

05 November 2013 | **Werner von Lensa, Corrado Rizzato, Natalia A. Girke,**
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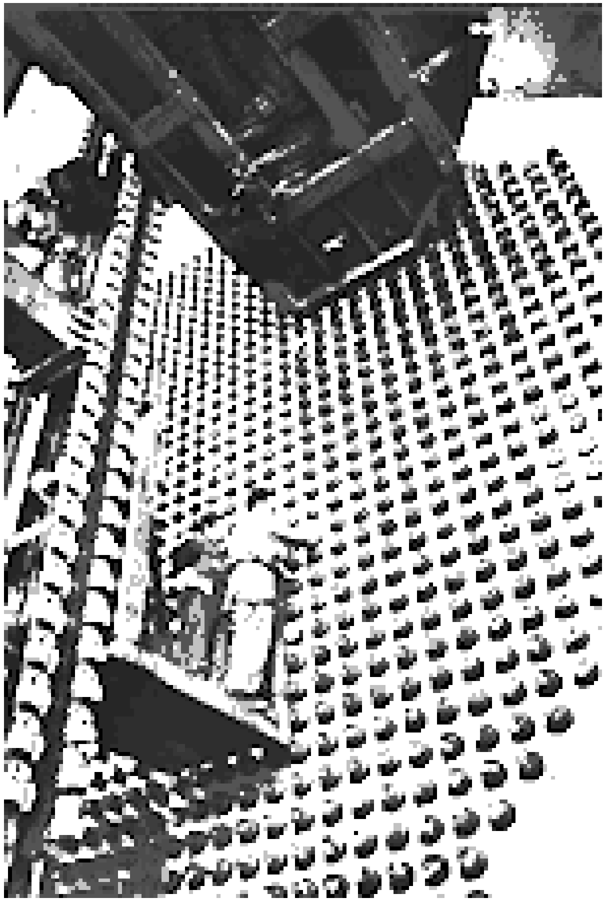
Reactor Graphite - Dimension of the Problem

- **About 250.000 Mg already accumulated, worldwide**

- **Origin from different reactor types & retrieval option**
- (MAGNOX, UNGG, AGR, HTR, RBMK, MTR, TRIGA etc.)
- **Types and grades with various impurities**
- **Individual irradiation „history“ and contamination sources**
- **Varying content of long-lived radioisotopes**
- (**Radiocarbon ^{14}C** plus ^{36}Cl, ^{3}H, ^{129}I, ^{99}Tc, ^{79}Se, ^{135}Cs etc.)



Source: PKS

- **Significant amounts of Radiocarbon ^{14}C (5730 y half-life)**

- **From $^{14}N(n,p)^{14}C$ *(approx. 90%, 1,81 barn)***
  Nitrogen as nitrides and N_2 absorbed in graphite matrix
- **From ^{13}C *(1,1%; 0,0009 barn)* and ^{17}O *(0,037%, 0,235 barn)***

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Reactor Graphite – German Situation

More than 1.000 Mg of graphite (including carbon bricks)

Operating and decommissioned reactors

→ **Power Reactor** THTR

→ **Research Reactors** **AVR,** DIDO, MERLIN, TRIGA-MHH, FRF, RFR, FRM, BER etc.

AVR - Specific inventory of components in Bq/g [1]				
	Graphite (65Mg)	Carbon bricks [2] (158 Mg)	Steam generator (42,5 Mg)	Thermal shield (141,5 Mg)
C-14	7,1	1,8 E+06	4,2 E+01	6,2 E+01
H-3	5,5	1,8 E+07	6,4 E+04	9,2 E+04
Co-60	8,0	8,2 E+05	2,8 E+04	3,9 E+04
Cl-36	2,3	3,7 E+02	-	-
Cs-137	1,0	2,0 E+04	7,0 E+05	3,0 E+03
Sr-90	1,0	5,0 E+04	7,1 E+05	1,0 E+03

Source: PKS

Current disposal option in mine KONRAD

KONRAD

LAW/MAW
former iron ore mine
licensed,
operating ≥ 2018

Source : www.deutschland.de/aufeinenblick/deutschlandkarte

Gorleben

HAW
former salt mine
projected

ERAM

LAW/MAW
former salt mine
closed

Asse

LAW/MAW
former salt mine
test repository
closed

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Activity limits for C-14 in mine KONRAD

Volume repository „KONRAD“: 303.000 cbm

Total C-14 activity permitted: 4 E+14 Bq

Average activity per cbm: 1,32 E+09 Bq/cbm

Typical volume of „Konrad-Container“ (Typ V): ca. 10 cbm

average load of typical waste container: 1,32 E+10 Bq

Source: Ironwork Bassum

In addition limits from 3 safety analyses have to be considered:
⇒Most restrictive ^{14}C limits for internal operation

C-14 (condition)	Limited activity* [Bq / Container]
non specified	1,8 E+08 – 2,0 E+08
volatile fraction (> 1 % and ≤ 10 %)	1,8 E+09 – 2,0 E+09
low volatile fraction (≤ 1 %)	1,8 E+10 – 2,0 E+10

*depending on thightness of waste package

For optimum usage most of ^{14}C should be on hand as ≤ 1 % volatile

What does that "*de facto*" mean ?

- How many containers do we need to dispose 4E+14 Bq of C-14 ???

C-14 (condition)	Limited activity [Bq/container]	Hypothethical waste containers for 4 E+14 Bq	
non specified	1,8 E+08	2.222.000	⇨ 70 x Volume KONRAD
volatile (> 1 % **and** ≤ 10 %)	1,8 E+09	222.000	⇨ 7 x Volume KONRAD
volatile (≤ 1 %)	1,8 E+10	22.000	⇨ 0,7 x Volume KONRAD

For disposal of ^{14}C waste KONRAD can only be used effectively

if condition of ^{14}C meets the requirement: low volatile fraction ≤ 1%

CARBODisp:

Disposal of Irradiated Graphite in Mine KONRAD

Aim: Development of concepts and methods for the final disposal of irradiated graphite in KONRAD (or other possible German repositories)

Funded by BMBF, 2010-2014, Budget ~ 1. Mio. Euro

Objectives

- Bond type of ^{14}C in i-graphite and release form
- Release factors, rates and paths
- Release rates from conditioned waste packages under various storages and handling conditions

Scientific cooperation with MEPhI (Moscow)

Supported by the Russian-German committee of Rosatom and BMWi

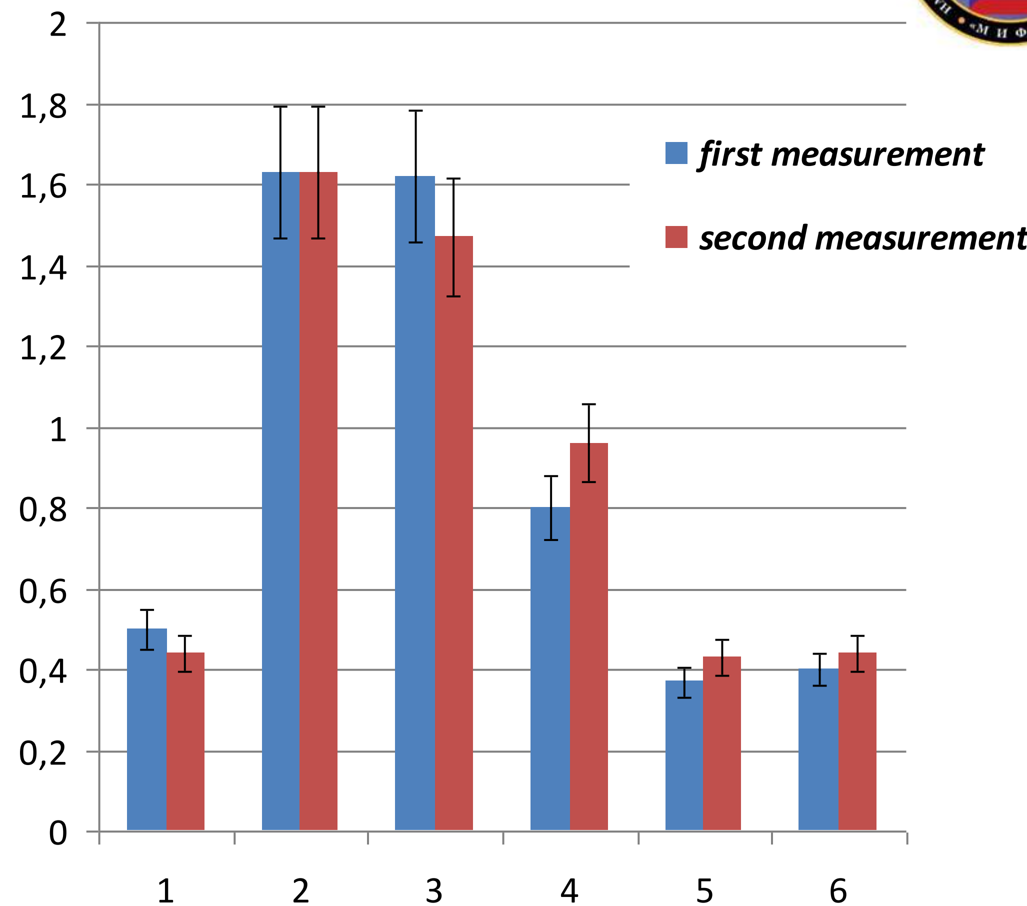
A. Bushuev, V. Zubarev, E. Petrova et al.

Comparative measurements on C-14 release (MEPhI)

Graphite from air cooled reactor

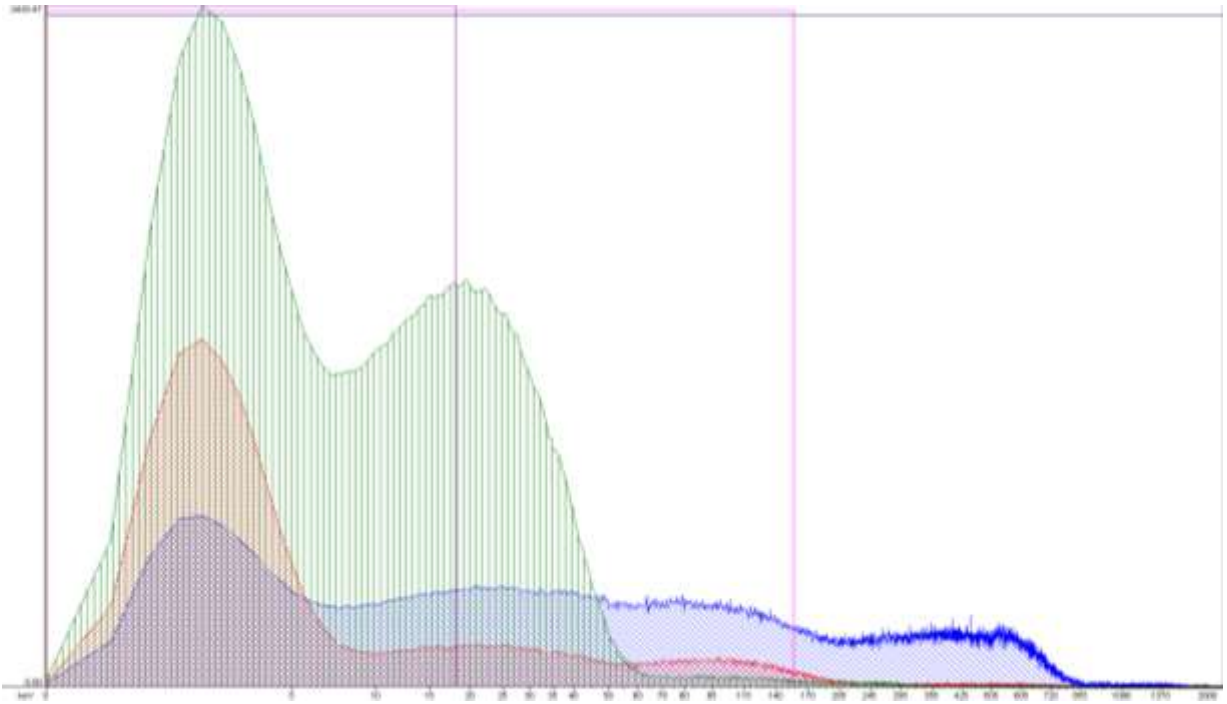
Storage approx. 9-10 years (NPT), only quantitative, no systematical analysis

Sample Nr.	Data	C-14 [10^6 Bq/g]
1	2001	0,50
	2009	0,44
2	1999	1,63
	2010	1,63
3	1999	1,62
	2010	1,47
4	1999	0,80
	2010	0,96
5	2001	0,37
	2010	0,43
6	2001	0,40
	2010	0,44



No changes observed within the accuracy of the method

Releases under different Storage Conditions



Releases under basic pH?

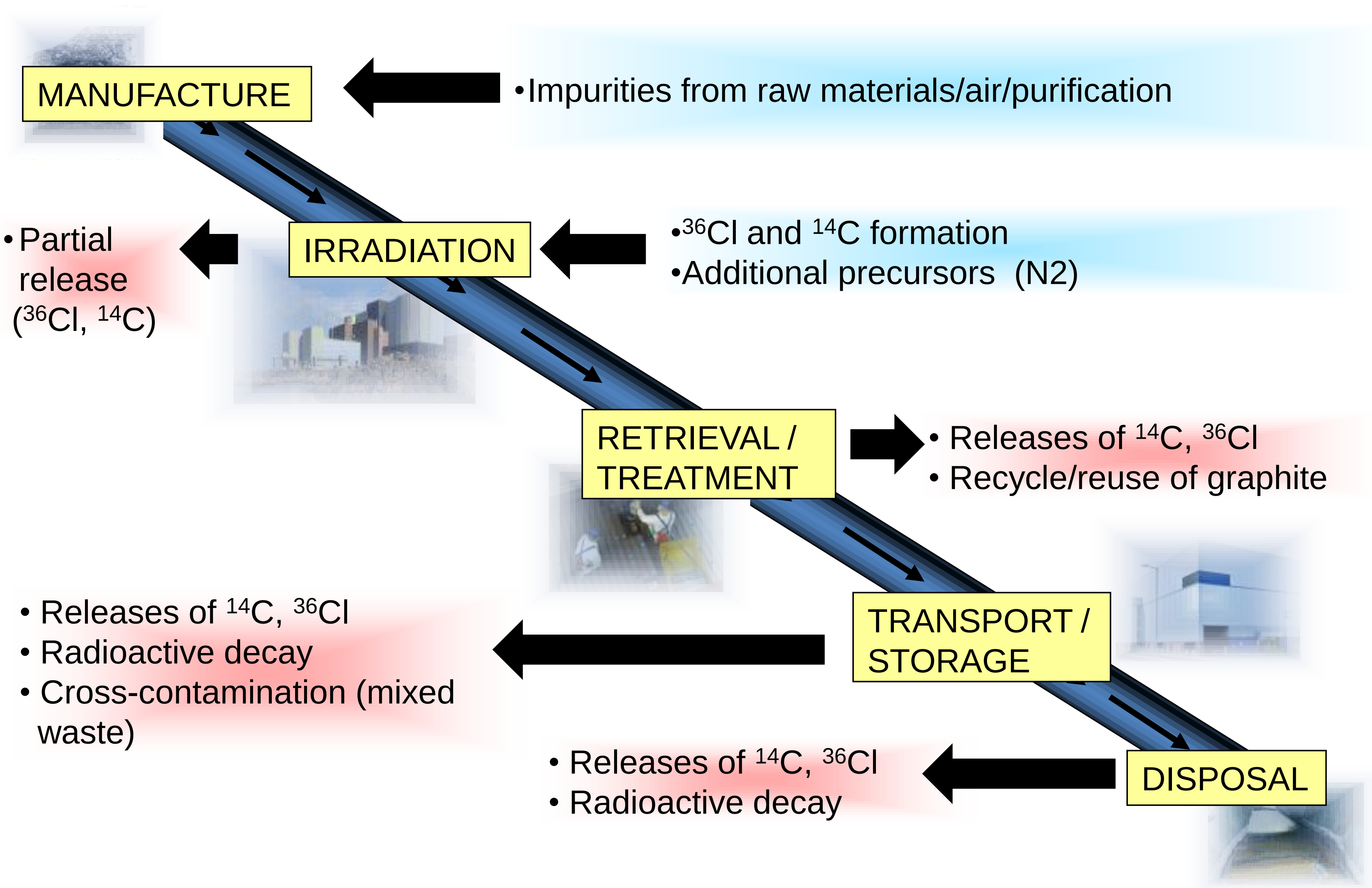
Releases under moist air?

Release of C-14	Relative Fractional release [%]	Time [y]
Air	0,0018	1.56
Moist Air	0,07629	1.56
Packed in PE	0,00730	0.94

What is the impact of the storage conditions?

And sample form ?
(block, powder, pellet)

Nuclear Graphite: Influencing Variables



CARBOWASTE:

Treatment and Disposal of Irradiated Nuclear Graphite and other Carbonaceous Waste

Coordinated by JÜLICH FORSCHUNGSZENTRUM **Dr. Werner von Lensa**

Objectives:

1. Retrieval and Segregation
2. Characterization and Modelling
3. Treatment Options
4. Re-use and Recycle
5. Disposal Behaviour

- **Development of „Best Practices“**
- **Providing a „Toolbox“ of sustainable and economic options for decommissioning and management of i-graphite**

Carbowaste: Facts and Partners

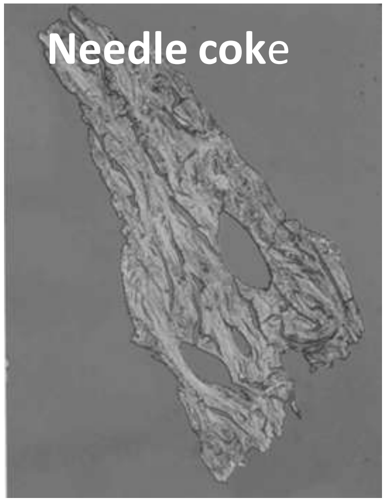
- **Start:** **April 2008**
- **Duration:** **60 Months (48)**
- **Total Budget:** **~ 11 Mio. EURO**
- **EU-Funding:** **6 Mio. EUR**

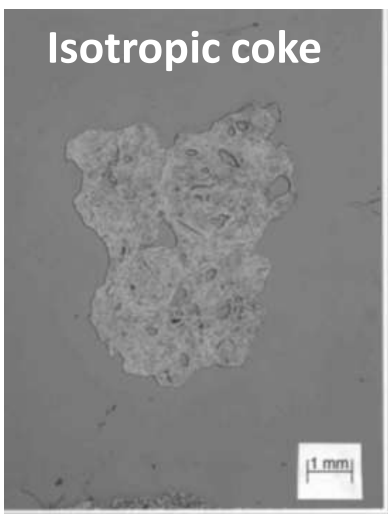
31 Partners, 10 EU Countries & RSA

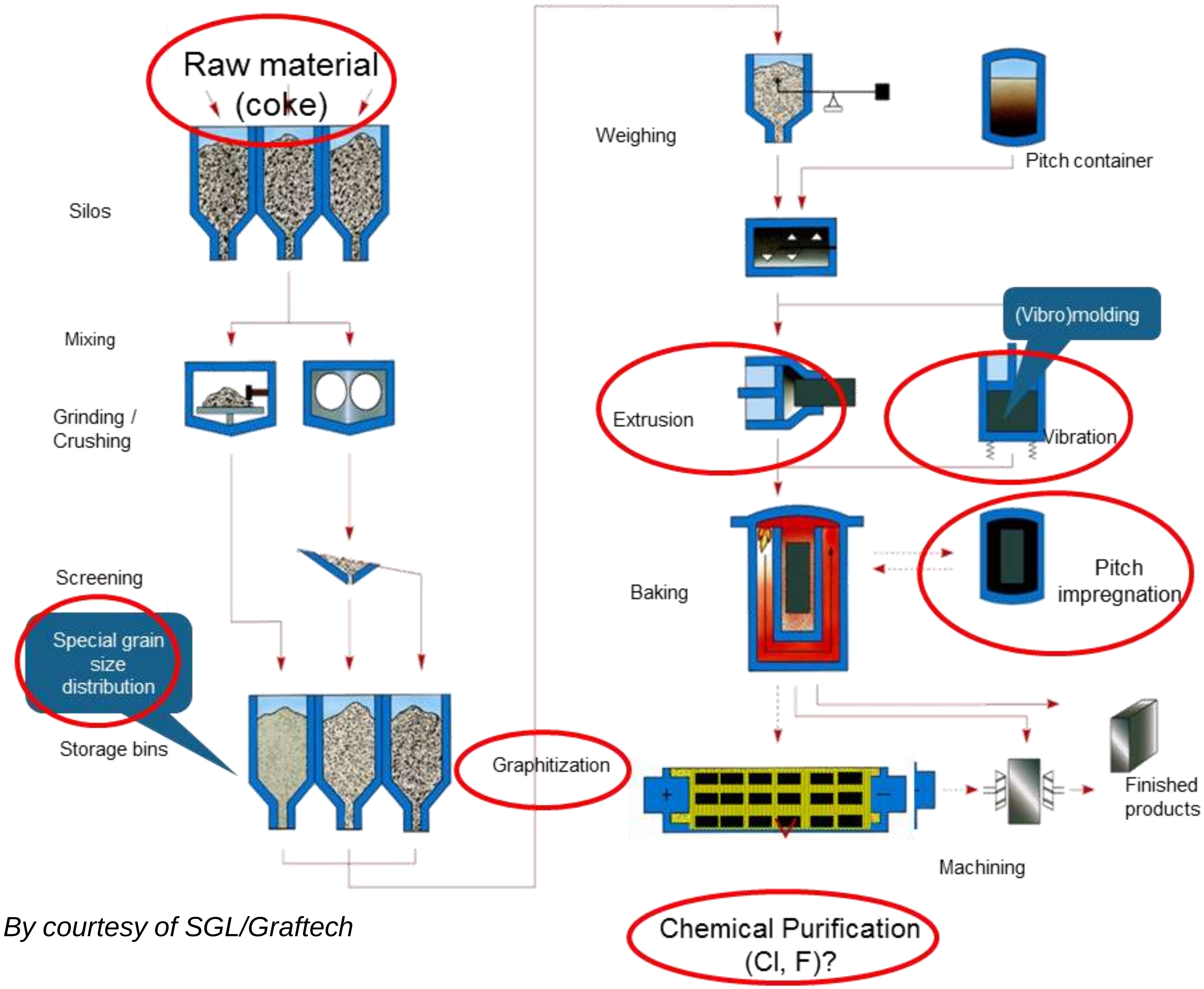
- **nuclear industries** (AMEC NNC, AREVA NP, Doosan Babcock, PBMR)
- **waste management companies** (Bradtec, Studsvik, Hyder, FNAG)
- **utilities** (EDF, Sogin, (EPRI))
- **graphite manufacturers** (GrafTech, SGL-Carbon)
- **waste management authorities** (ANDRA, NDA, ENRESA)
- **research** (CEA, CIEMAT, ENEA, FI, FZJ, INR, JRC, LEI, UK NNL, NRG, SCK•CEN, NECSA)
- **universities** (EMN, CNRS-ENS, IPNL, The University of Manchester)
- **Co-sponsors** (ANDRA, EDF, HSE, NDA etc.)

Manufacture of Nuclear Graphite

Several influencing variables even in virgin material



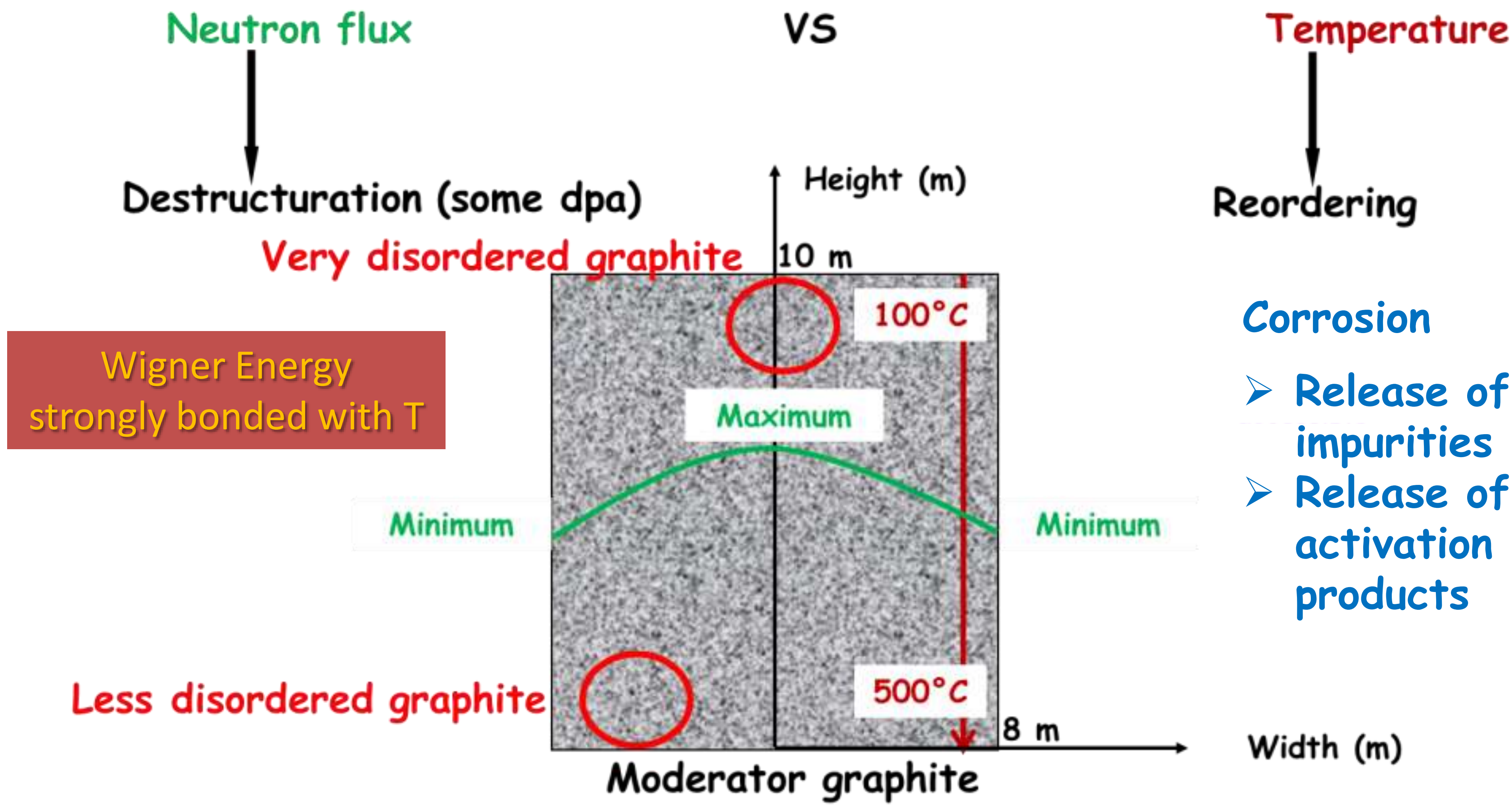




By courtesy of SGL/Graftech

Different graphite grades result in different i-graphite characteristics

Impact of Operational Conditions?



Corrosion

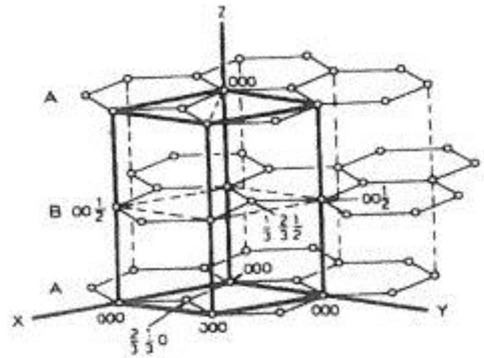
- Release of impurities
- Release of activation products

⇒ **i-graphite characteristics even differ within the same reactor !**

Structural Heterogeneity

Nuclear graphite is an heterogeneous material very far from mono-crystalline graphite:
high porosity, polycristalline material with well graphitized and amorphous zones

More a graphitized carbon/carbon composite !



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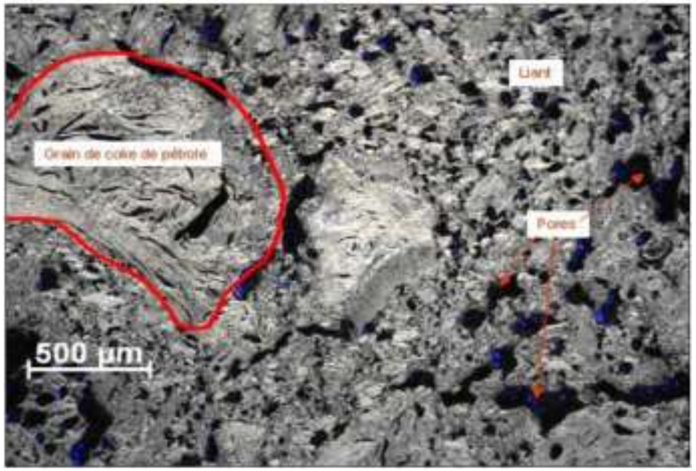
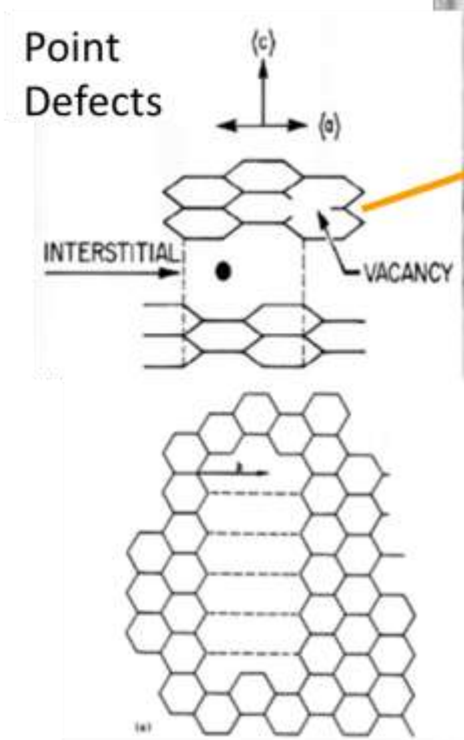


⇒ Characterization of its multiscale organisation
<u>not trivial</u> !

Irradiation-Induced Structural Changes

HRTEM characterisation of defects and dislocation damage in neutron irradiated graphite



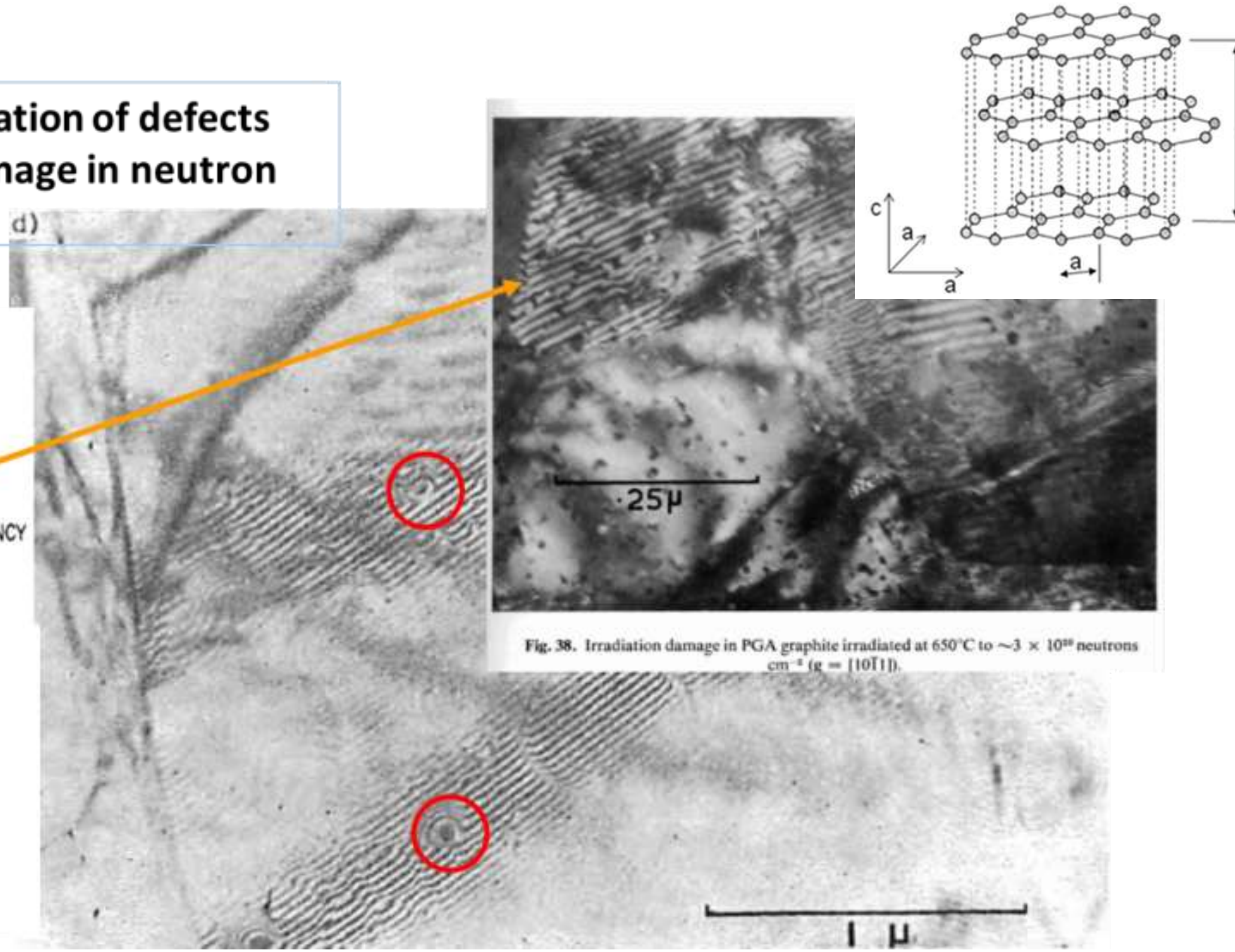


Fig. 38. Irradiation damage in PGA graphite irradiated at 650°C to ~3 × 10^{20} neutrons cm^{-2} ($g = [10\bar{1}1]$).

Treatment Options

❑ Purpose:

- Selective removal of (volatile) radionuclides / Decontamination
- Improving the dispoal behaviour
- Closing the Graphite/C-14-cycle (Recycling)

❑ Options:

- Thermal Treatments
  - High/Low Temperature Gas Oxidation (O2) (FZJ)
  - Low Temperature-Pressure Gas Oxidation (O2) (FZJ)*
  - Steam Reforming (Studsvik)
  - Thermal Reaction of reloaded reactants (FZJ)
- Chemical Treatments
  - Wet Oxidation (Ciemat, ENEA, INR)
  - Acid solution treatment (Subatech)

❑ Conditioning:

- Pore Sealing with glas (Impermeable Glas Matrix)
- Pore Closing with Silicone
- Embedding in Geopolymere

Carbon-14 Release by Thermal Treatment

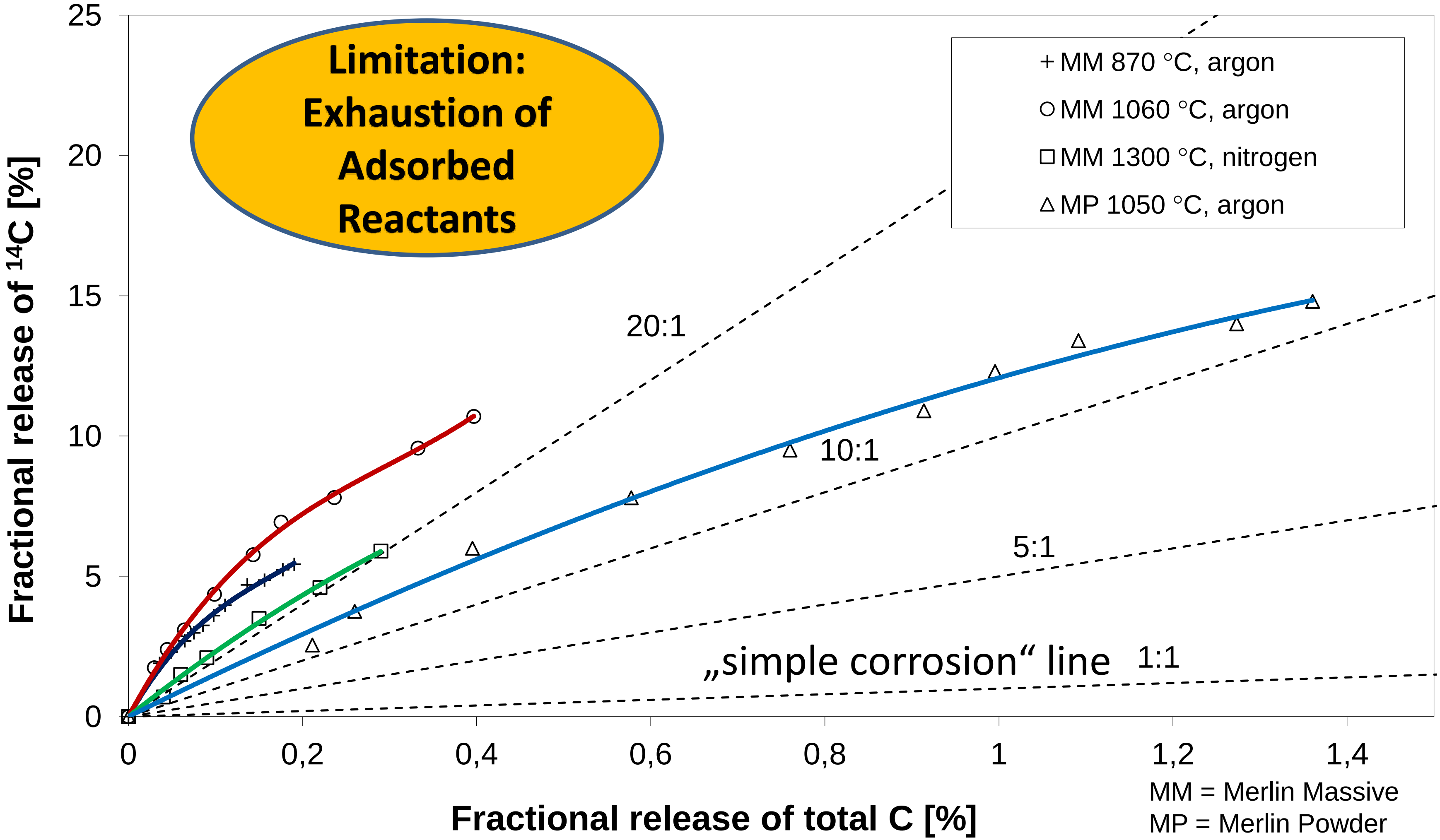
Treatment	Sample [No.]	Heating Temperature [°C]	C-14 Content [Bq/g]	Release C-14 [%]
I – to 1.500°C under vaccum	1	NPT (start)	7.44E+05	11
		1500	6.44E+05	
		1500	6.74E+05	
	2	NPT	9.91E+05	4
		1500	1.01E+06	
		1500	8.99E+05	
	3	NPT (start)	9.62E+05	(-1)
		1500	1.06E+06	
		1500	8.83E+05	
II – to 2.200 °C under argon	4	NPT (start)	1.34E+06	5
		2200	1.30E+06	
		2200	1.25E+06	
	5	NPT (start)	1.28E+06	5
		2200	1.20E+06	
		2200	1.24E+06	
	6	NPT (start)	1.17E+06	(-2)
		2200	1.17E+06	
		2200	1.21E+06	

accuracy: +/- 10 %

No significant release has been observed within the precision of the method.
More Systematic investigations are necessary for better understanding.

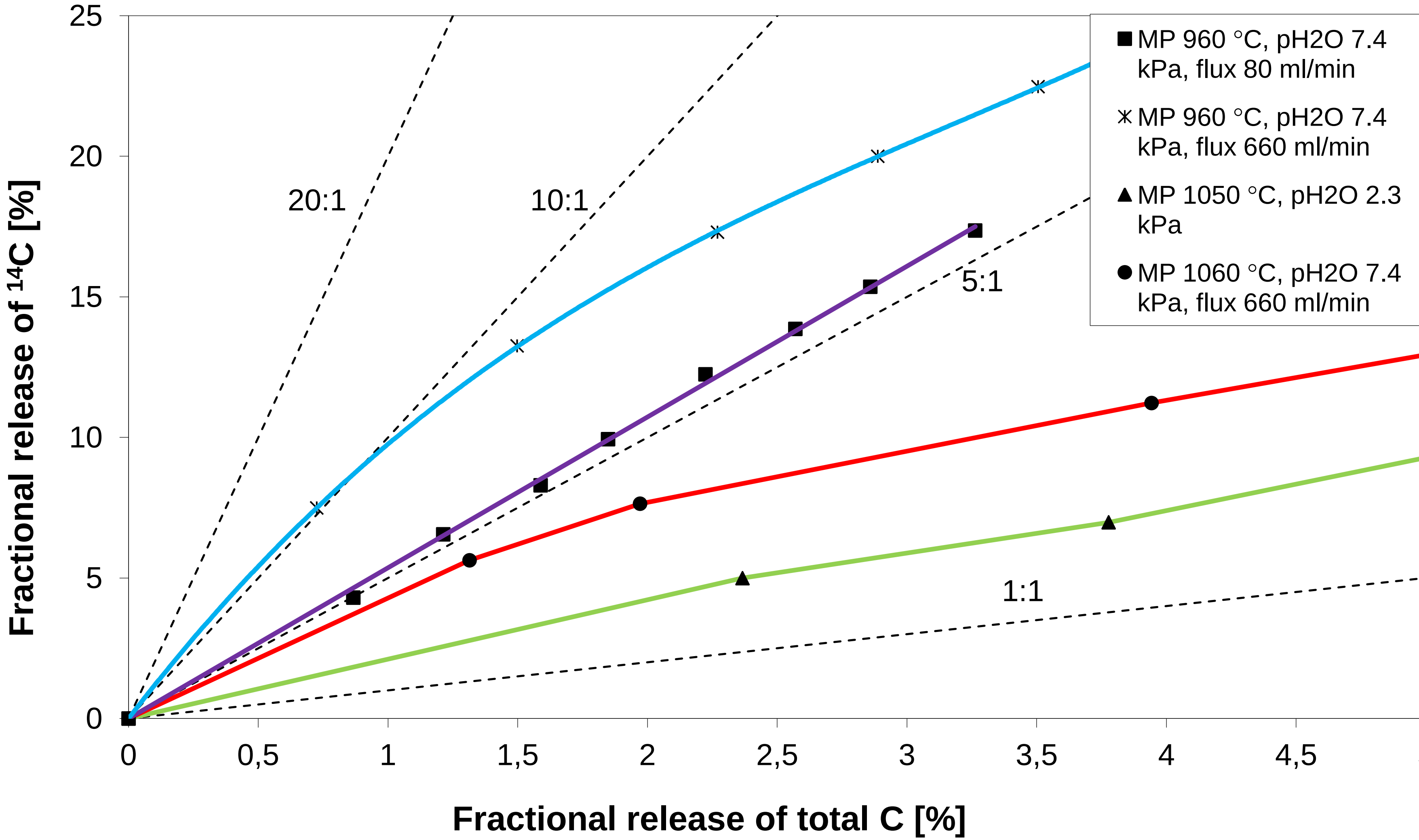
Carbon-14 Release by Thermal Treatment (inert)

- Oxidants already adsorbed on the graphitic matrix (soon exhausted)
- Inert Atmosphere with low amount of impurities (up to 20 ppm O_2)*



*Depending on the experimental equipment implied

Carbon-14 Removal by Thermal Treatment (steam)

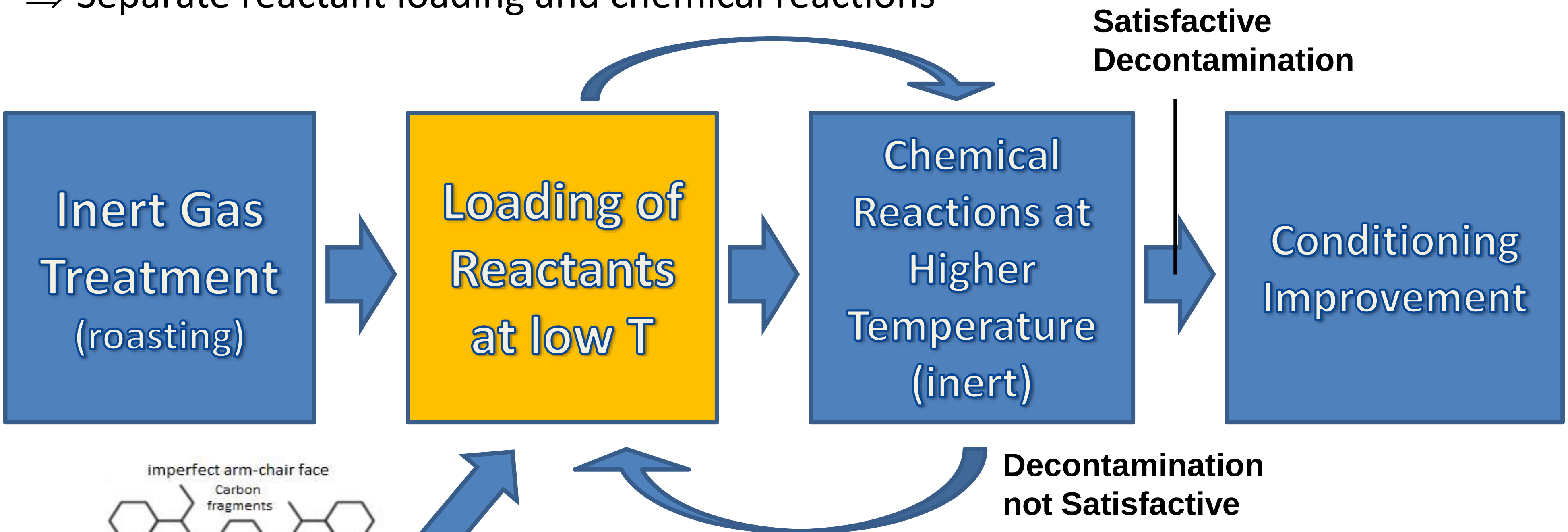


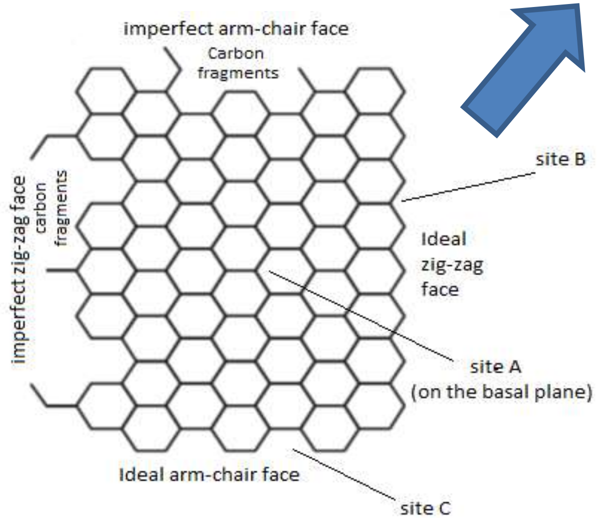
Effective on Removal but HIGH mass losses compare to the previous case

New Approach

- C-14 removal is a local effect: removed by oxidation
- Continuous provision of reactants is not efficient (temperature vs reaction rate)

⇒ Separate reactant loading and chemical reactions





Chemisorption at active sites

Patent applied recently

Conclusions

The CARBOWASTE Project:

- ***Revealed*** that the relevant RN exist in different chemical forms & locations
- ***Explored*** the existance of mobile & stable / less mobile fractions of RN
- ***Provided*** a much better understanding of RN behaviour in i-graphite
- ***Offers*** a ‚Tool Box' for i-graphite management strategies on MCDA basis
- ***Showed*** the impact of ‚Manufacture and Operation Histories' on i-graphite
- ***I-graphite*** disposability is supported by the generated performance assessment data
- **Treatment/decontamination** have been demonstrated as viable options

Created a basis for innovative i-graphite management options

→ **CarboSOLUTIONS**


Thanks for Your Attention
X
Z

Additional Slides

JÜLICH FORSCHUNGSZENTRUM

CarboSOLUTIONS
Implementing i-graphite Waste Management

- **Innovative waste management SOLUTIONS on**
  - Irradiated-graphite (i-graphite) &
  - other carbonaceous waste (e.g. backed carbon, pyrocarbon)

- **Multi-scale investigations on i-graphite characteristics**
  - Systematic correlation of influencing parameters (Temp., Atm. etc)
  - Predictive models for radionuclide releases

- **Demonstration of "Best Practices" in Retrieval of i-graphite from reactor core,**
  - Treatment / purification options,
  - Storage, Conditioning and Disposal,
  - Recycling of i-graphite for future V/HTR, MSR & Fusion reactors

- **Synergies across near & medium-term decommissioning projects**

⇒ High Relevance within FP8