Imperial College London

BCURA B73 Research Contract

"The Selection of Low Cost Sorbents & Process Conditions for Mercury Capture from Flue Gases"

Imperial College London
Department of Chemical Engineering
London SW7 2AZ

Prof D R Dugwell, Prof R Kandiyoti, Dr A George, Mr H R Seneviratne

Imperial College London

MERCURY EMISSIONS REGULATIONS

- **Mercury is a cumulative poison - causes kidney and brain damage**

- **USA – Clean Air Mercury Rule (CAMR)**
  cap & reduce mercury emissions from coal-fired power plants (2005)
  - 1st phase cap of 38 tpy effective in 2010
  - 2nd phase cap of 15 tpy effective in 2018

- **Emission limits proposed by the US EPA (2005) – based on gross energy output**
  - Bituminous units: 9.5 kg/TWh [had the highest limits]

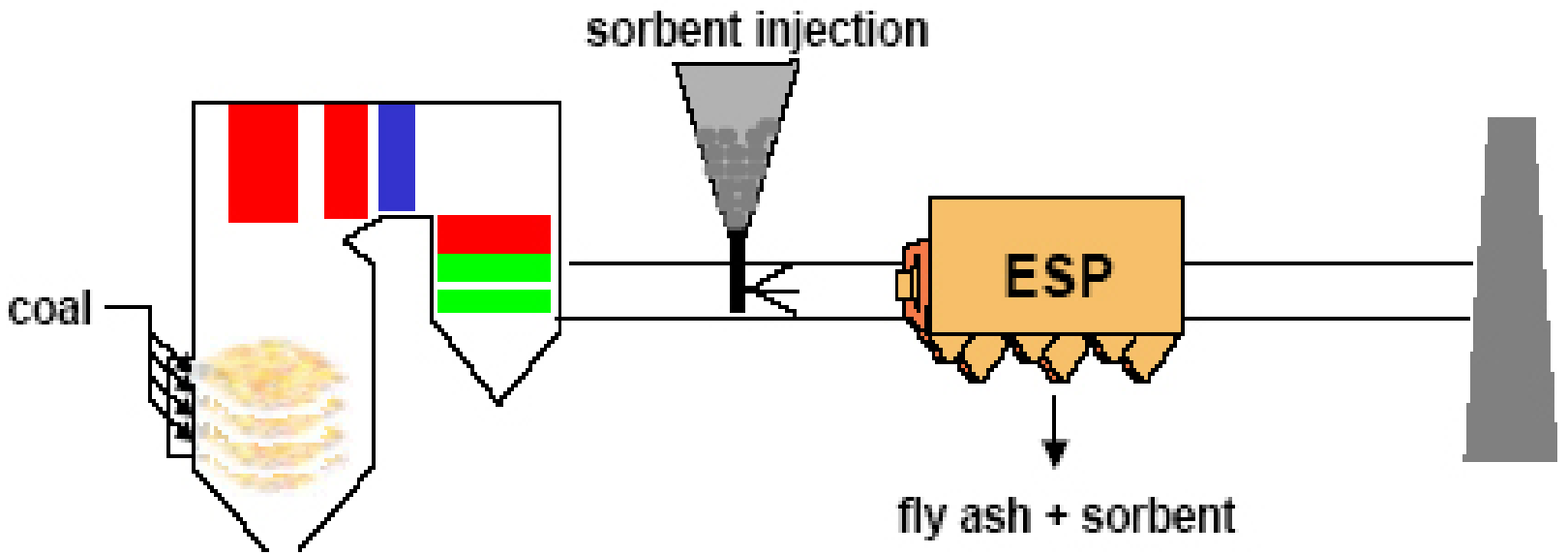
- **Canada Wide Standard**
  - Bituminous units: 3 kg/TWh

- **UK - No specific regulations yet for coal-fired power plants, however mercury emissions from the plants will be monitored**

Imperial College London

POSSIBLE COST EFFECTIVE METHOD OF MERCURY CAPTURE

- Based around current emission control systems
- Possible method
  - inject sorbent before particulate control device



Imperial College London

PRINCIPAL ACTIVITIES

- Identification and sourcing of suitable sorbents
- Characterisation of promising sorbents
  - SEM
  - BET
  - TGA
- Hg retention capability
  - Adsorption temperature
  - flue gas composition [e.g. HCl and SO_2]
  - Hg speciation
- Measurement of leaching stability of Hg from spent sorbent

Imperial College London

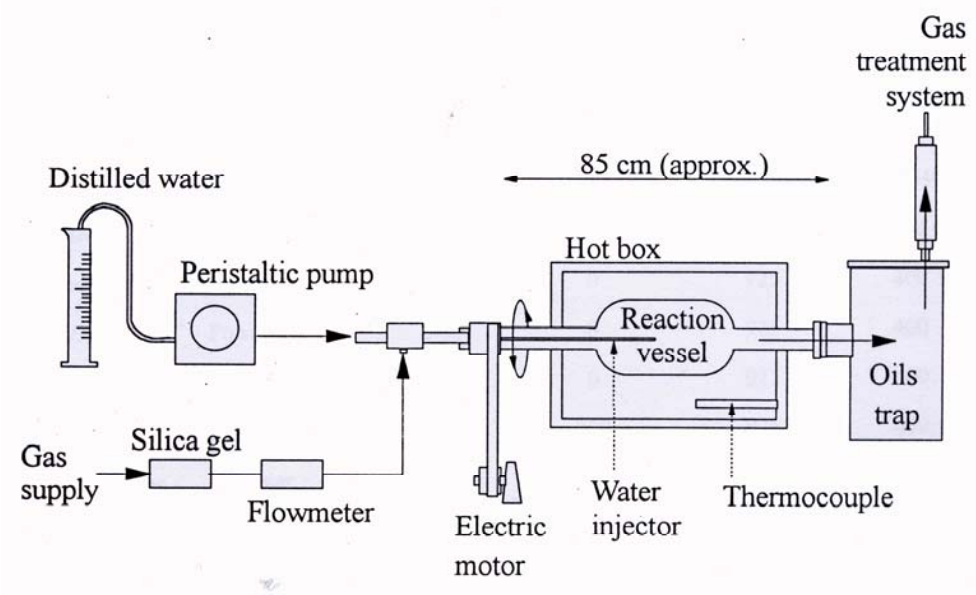
SORBENTS TESTED

- **Commercial sorbents**
  - Norit Darco Hg™
  - Norit Darco Hg-LH™
- **Scrap tyre rubber**
  - Tyre rubber charcoal
  - Tyre rubber activated carbon –steam activation
  - Tyre rubber activated carbon – Bromine impregnation
- **Sewage sludge**
  - Sewage sludge charcoal
  - Sewage sludge AC – bromine impregnation
- **Coal fly ash – UK power plants (8 ashes)**

Imperial College London

MAKING SORBENTS FROM SCRAP TYRE & SEWAGE SLUDGE

- **Char from scrap tyre pyrolysis**
  - **Pyrolysis temperature = 700^{0}C**
- **Activated Carbon from scrap tyre**
  - **Activation temperature = 925^{0}C**
- **Char from DEMAD sewage sludge**
  - **Pyrolysis temperature = 600^{0}C**



- **Bromine impregnated activated carbon from scrap tyre rubber and sewage sludge**
  - **Pyrolysis temperature = 600^{0}C**
- **Particle size between 38 – 75 μm**

Imperial College London

BET SURFACE AREA & MICROPORE VOLUME

Sorbent	BET surface area (m^2/g)	Micropore volume (mm^3/g)
Norit Darco Hg™	**660**	**169**
Norit Darco Hg-LH™	335	61
Fly ash	1 - 15	0.2 - 2
Tyre charcoal	76	1
Tyre AC -steam	249	67
Tyre AC -bromine	97	3
Sewage sludge charcoal	53	10
Sewage sludge AC -bromine	**700**	**147**

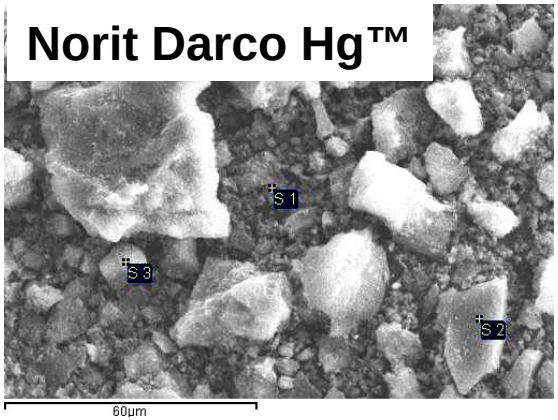
Imperial College London

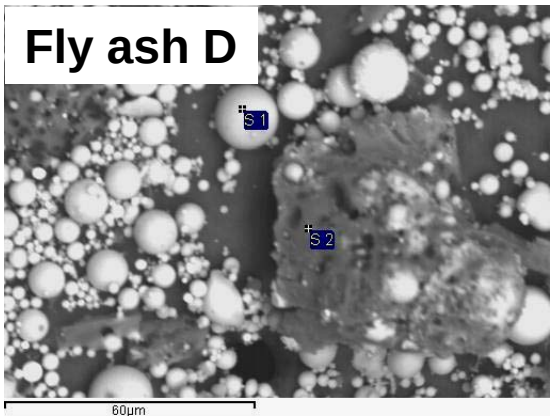
ASH AND ELEMENTAL ANALYSIS

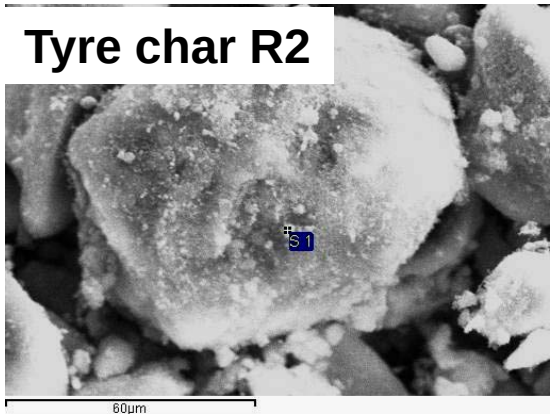
Sorbent	Ash	C	N	O	H	S	Cl	Br
Norit Darco Hg™	10	77	0.6	4	0.2	0.4	0.03	<100 ppm
Norit Darco Hg-LH™	27	58	0.4	6	0.3	1.1	0.03	**3.05**
Fly ash D	92	7	0.2	<0.1	<0.05	0.3	0.02	<100 ppm
Tyre charcoal	13	83	0.3	<0.1	0.3	3	0.03	510 ppm
Tyre AC – steam	13	83	0.4	<0.1	0.1	3	0.01	NA[a]
Tyre AC – bromine	4	90	0.3	3.0	0.2	0.8	0.01	**1.08**
Sewage sludge charcoal	71	23	2.5	<0.1	0.7	1.0	0.06	0.01
Sewage sludge -bromine	32	47	4.6	7.8	0.9	1.9	0.01	**2.09**

Imperial College London

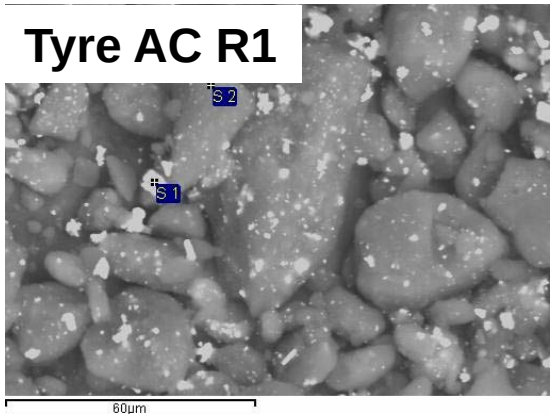
SEM / EDX ANALYSIS OF SORBENTS

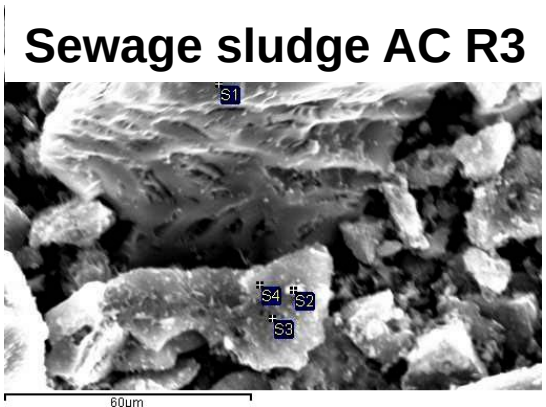






- Inorganic species in fly ash agglomerated into spherical globules
- Wurtzite (ZnS) in sorbents from scrap tyre rubber – not part of the carbon matrix
- Bromine presence on the impregnated PAC confirmed





Imperial College London

SIMULATED FLUE GAS

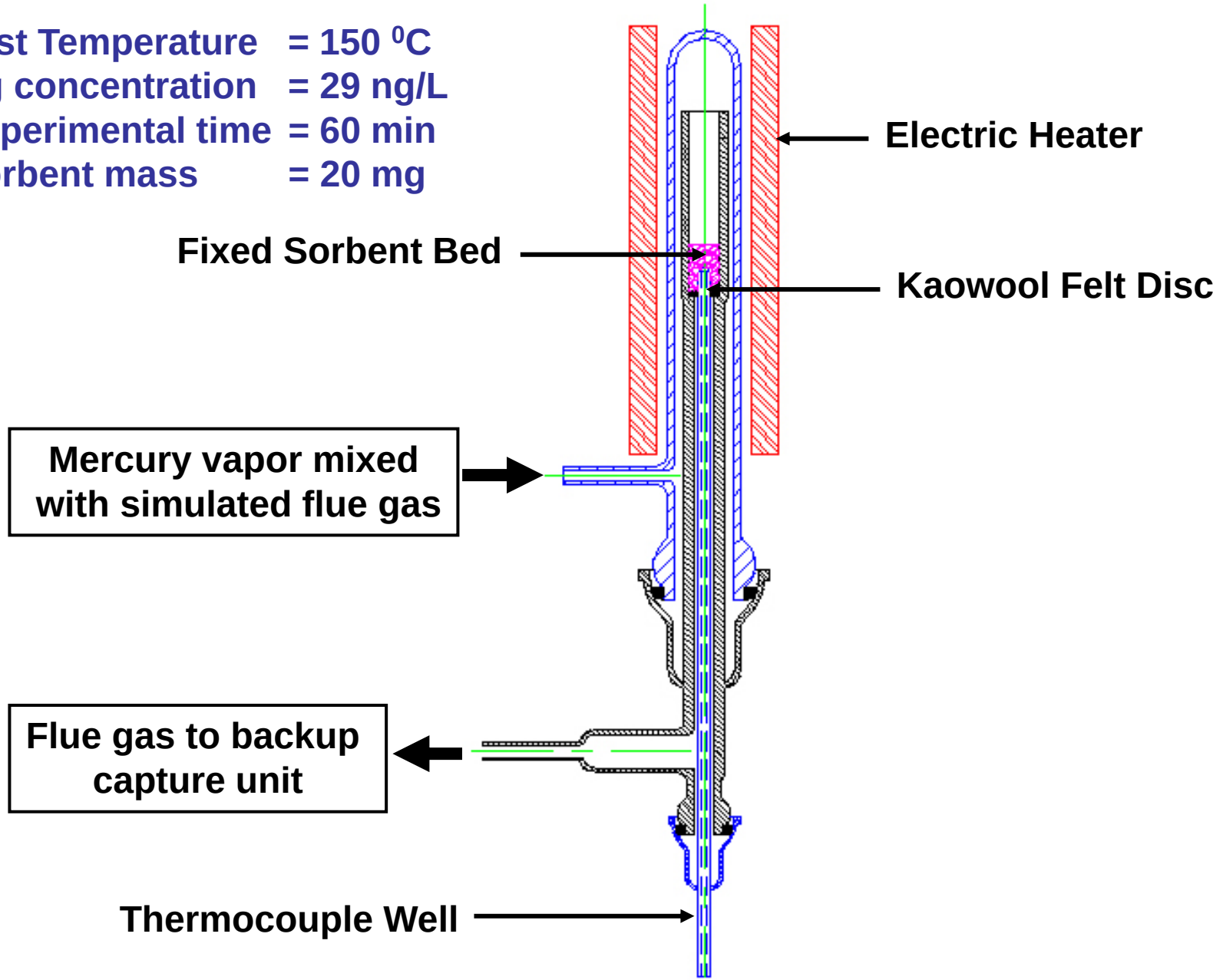
Harworth coal

Constituent	Concentration	Volume flow rate (at NTP) [ml/min]
Hg^0	3.5 ppb_v	$1.3x10^{-7}$
O_2	6%	2
CO_2	12%	5
SO_2	1800 ppm_v	$7x10^{-2}$
HCl	200 ppm_v	$7x10^{-3}$
H_2O	7%	2.5
NO	490 ppm_v	$2x10^{-2}$
NO_2	17 ppm_v	$6x10^{-4}$
N_2	75%	28 mL/min
Total	100%	37

Imperial College London

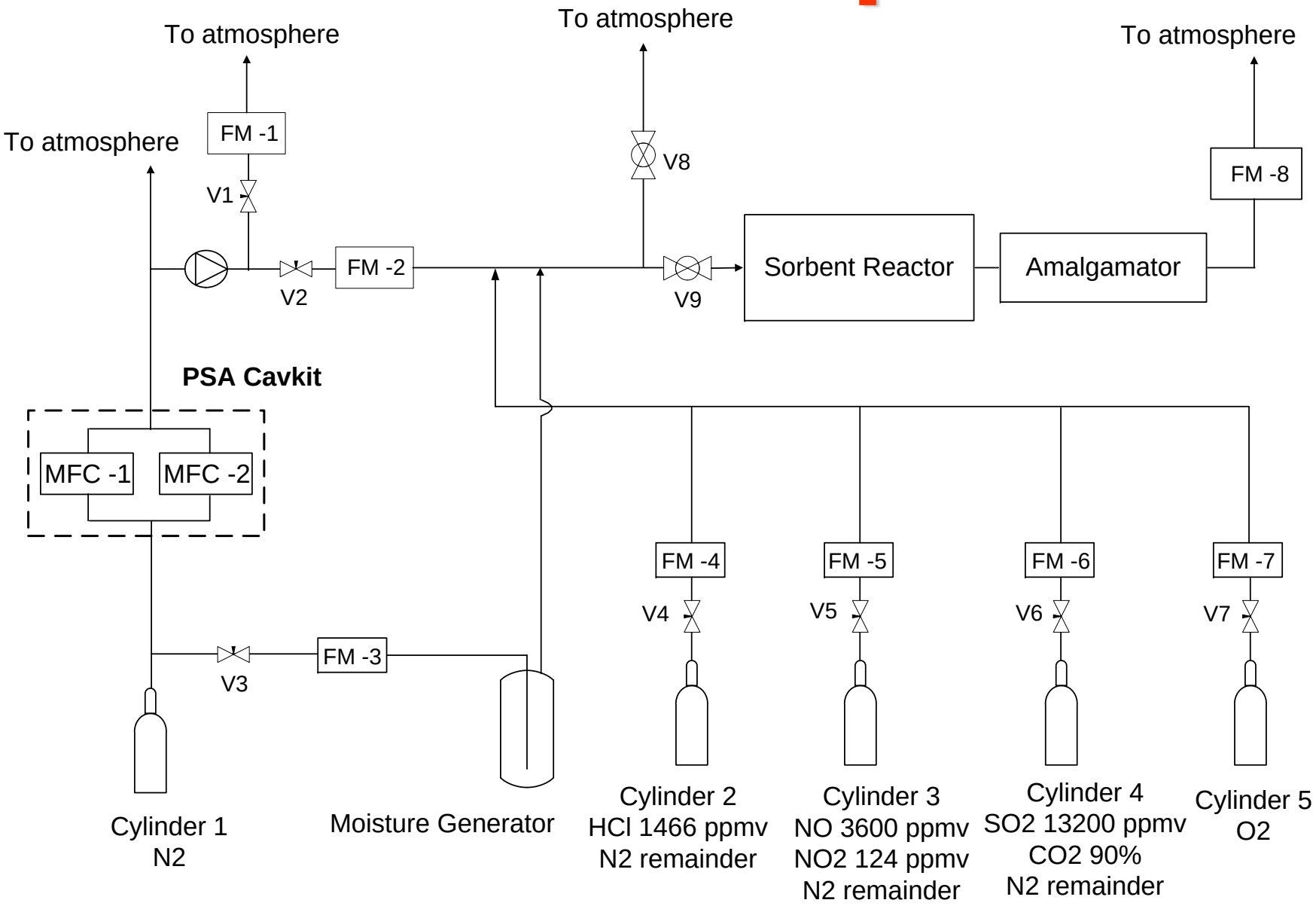
LOW TEMPERATURE HG CAPTURE REACTOR

Test Temperature = 150 ^{0}C
Hg concentration = 29 ng/L
Experimental time = 60 min
Sorbent mass = 20 mg



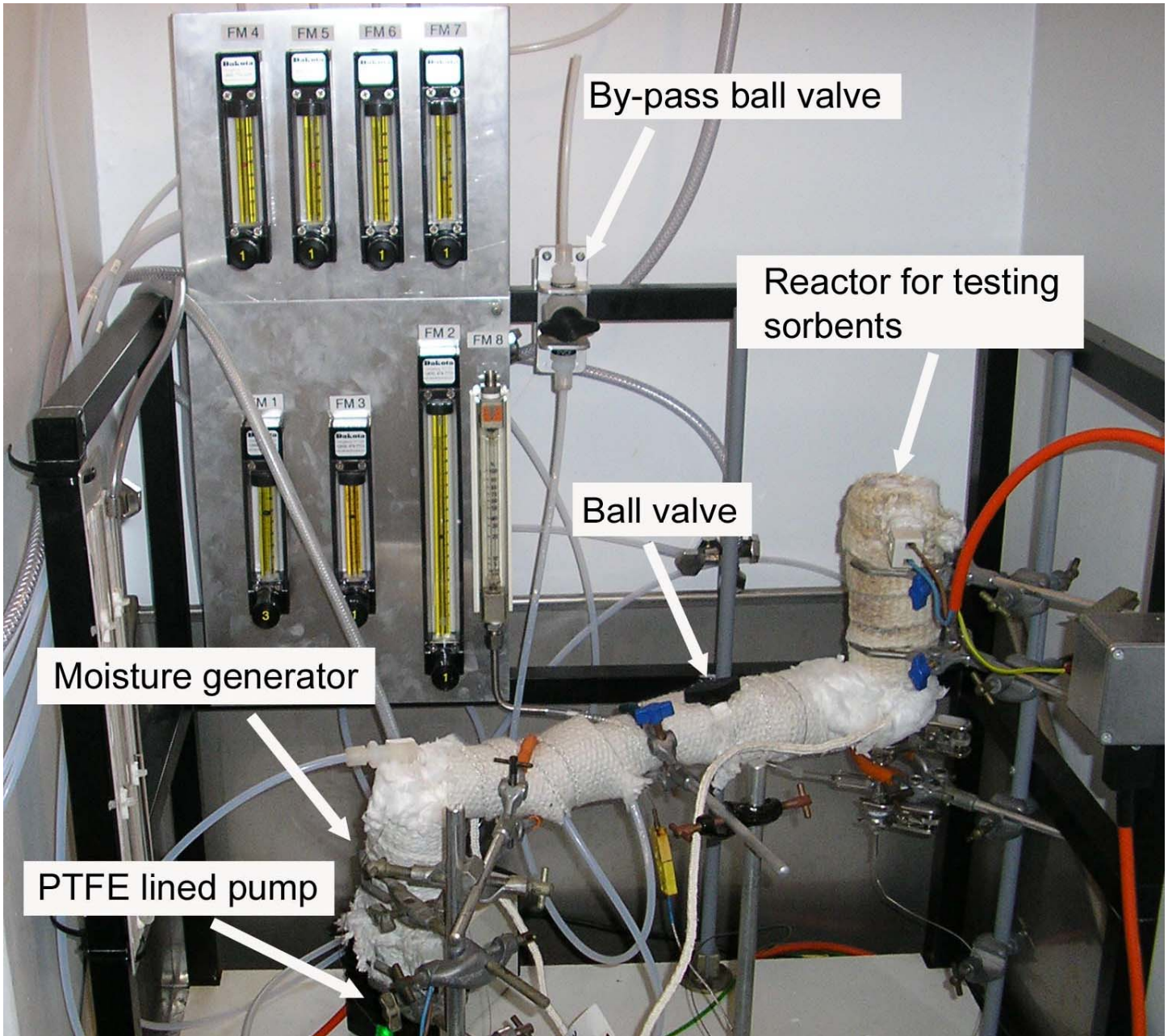
Imperial College London

EXPERIMENTAL SCHEME [Gas scheme -6]



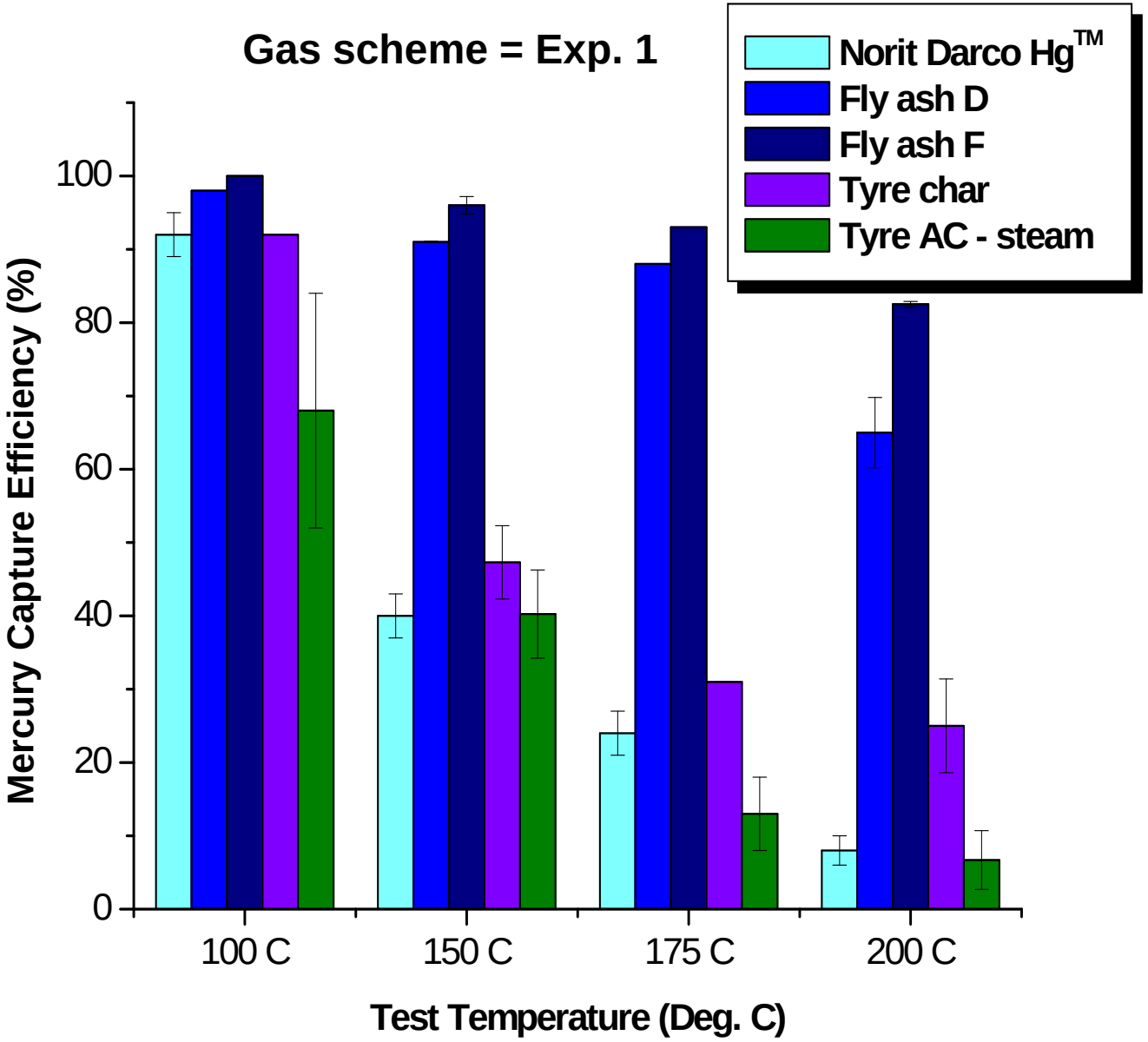
Imperial College London

BENCH SCALE SORBENT TESTING SYSTEM



Imperial College London

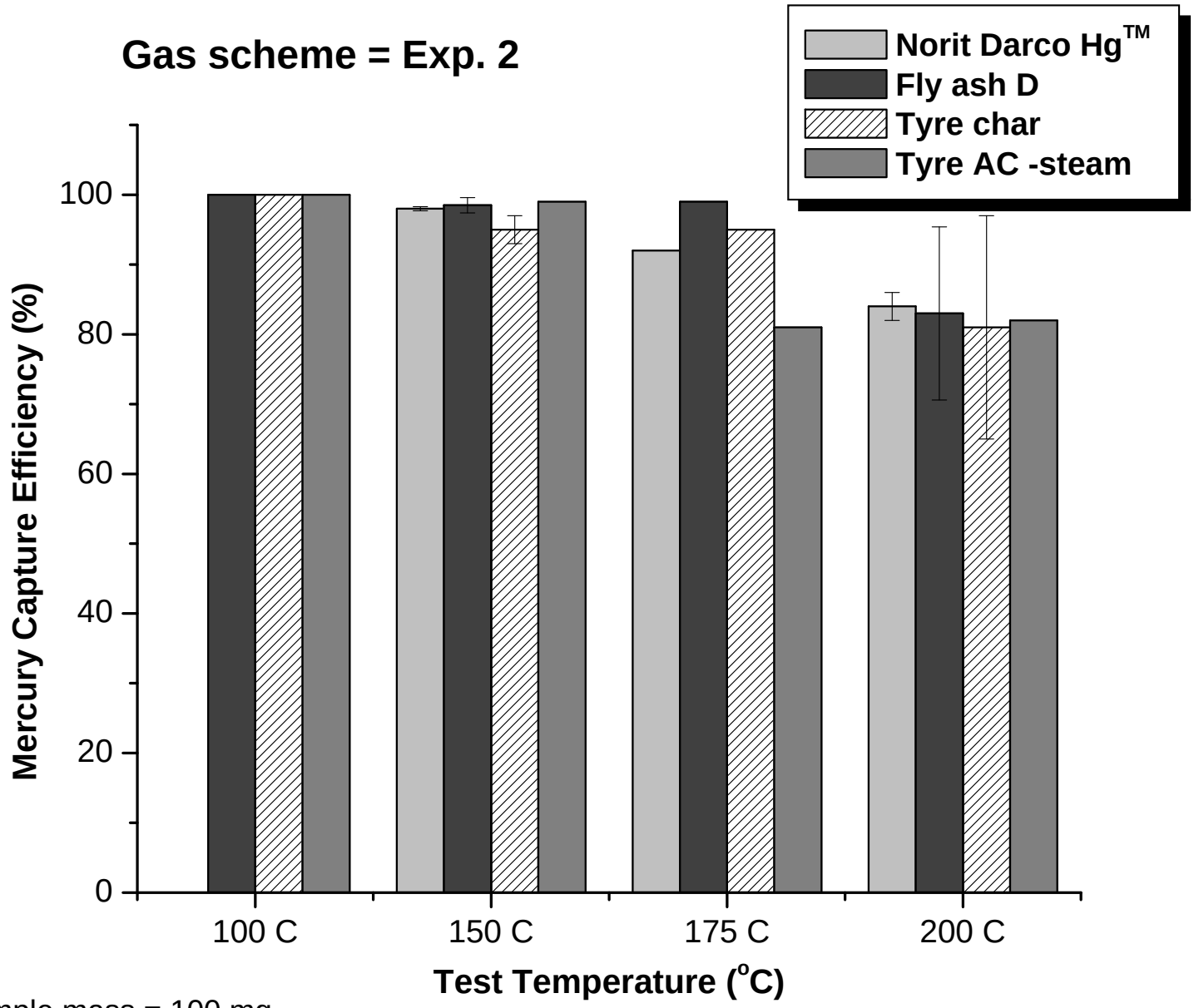
HG CAPTURE – TEMPERATURE



Sample mass = 100 mg Hold time = 60 min

Imperial College London

HG CAPTURE – TEMPERATURE

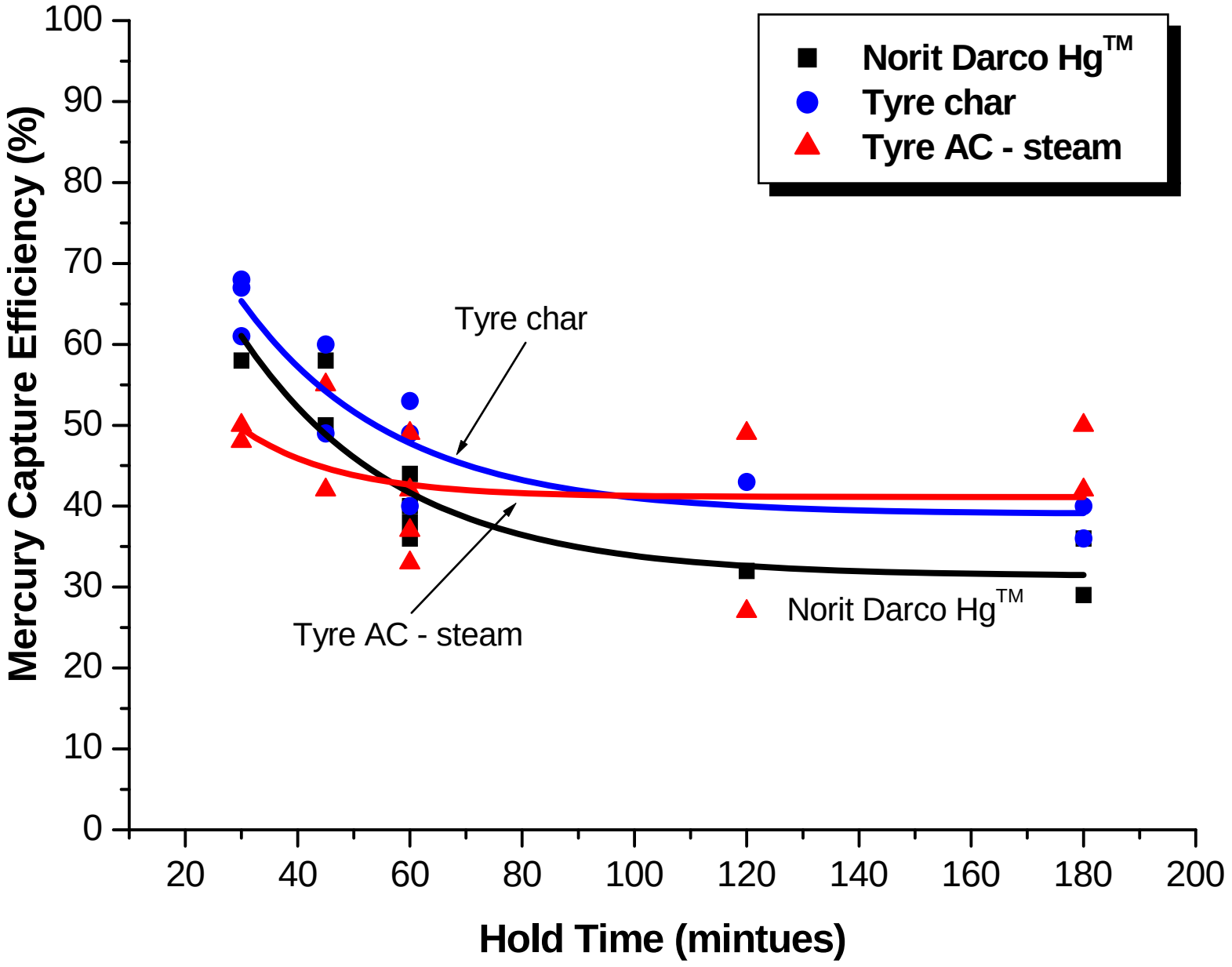


Sample mass = 100 mg

Norit Darco Hg™ - test duration = 60 min. All other sorbents - test duration = 30 min.

Imperial College London

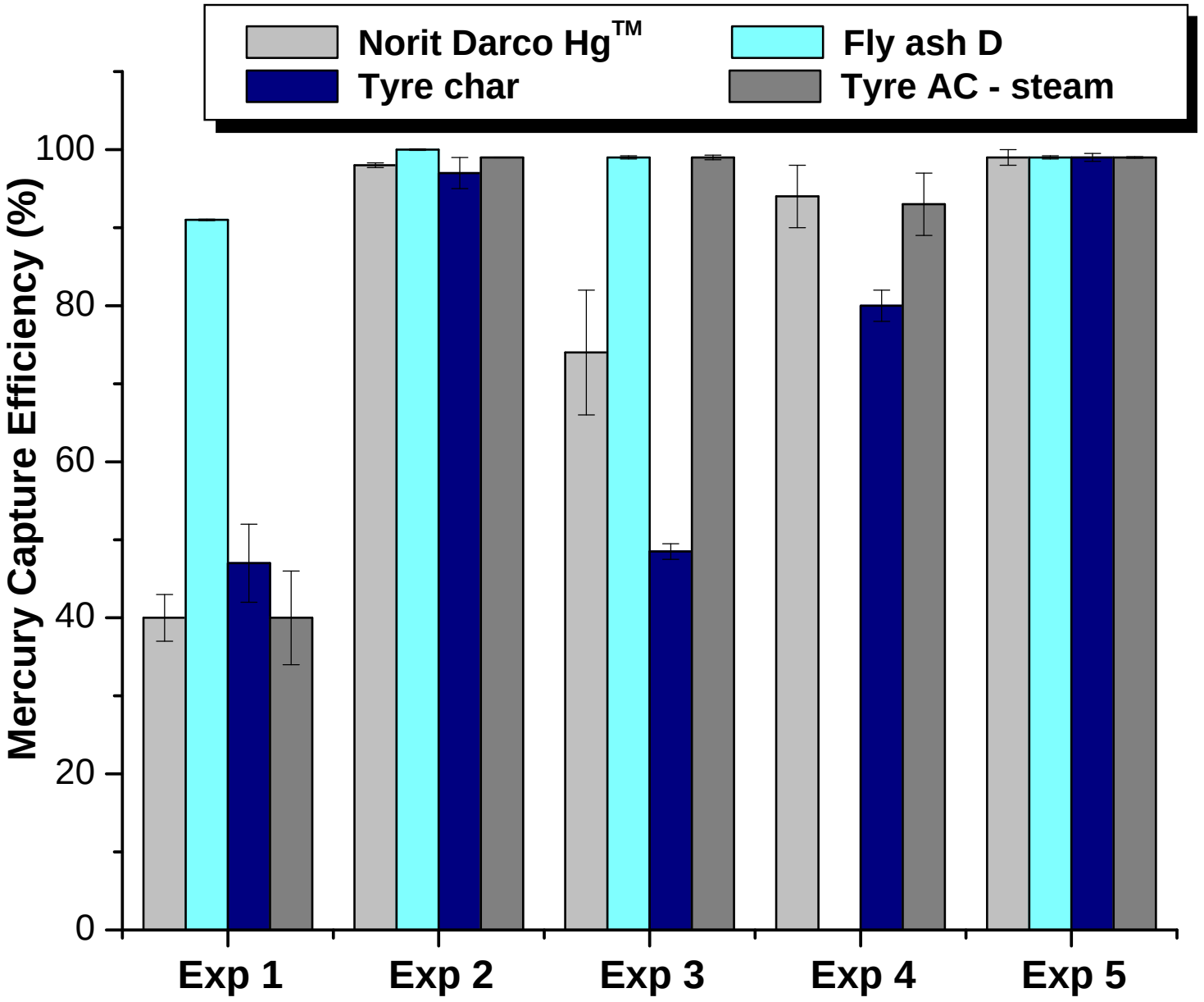
HG CAPTURE – WITH SCHEME -1



Note - sample mass = 100 mg Test Temperature = 150°C

Imperial College London

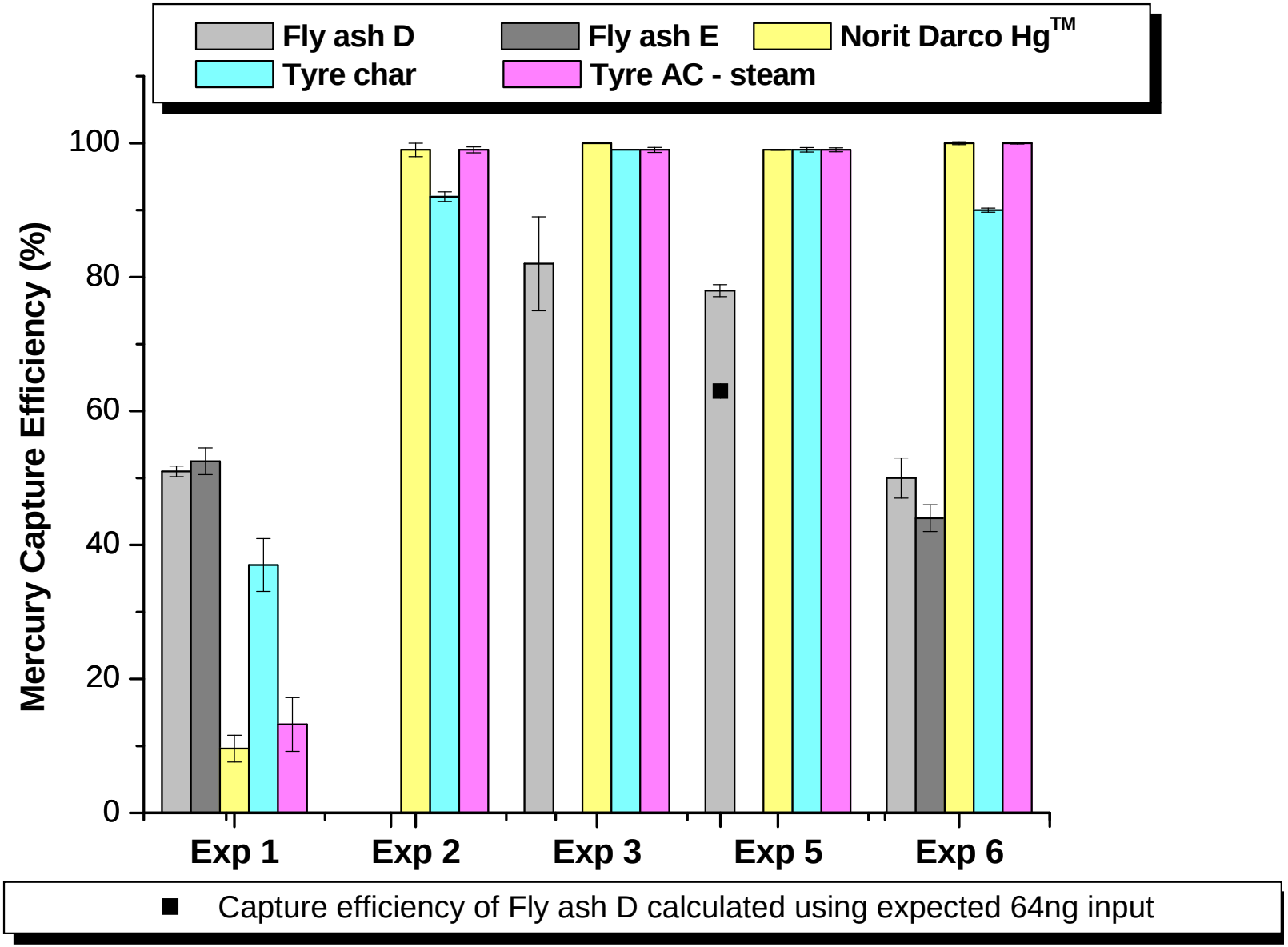
HG CAPTURE – EXP. 1 TO EXP. 5



Note - Fly ash D was not tested with gas scheme Exp.4

Imperial College London

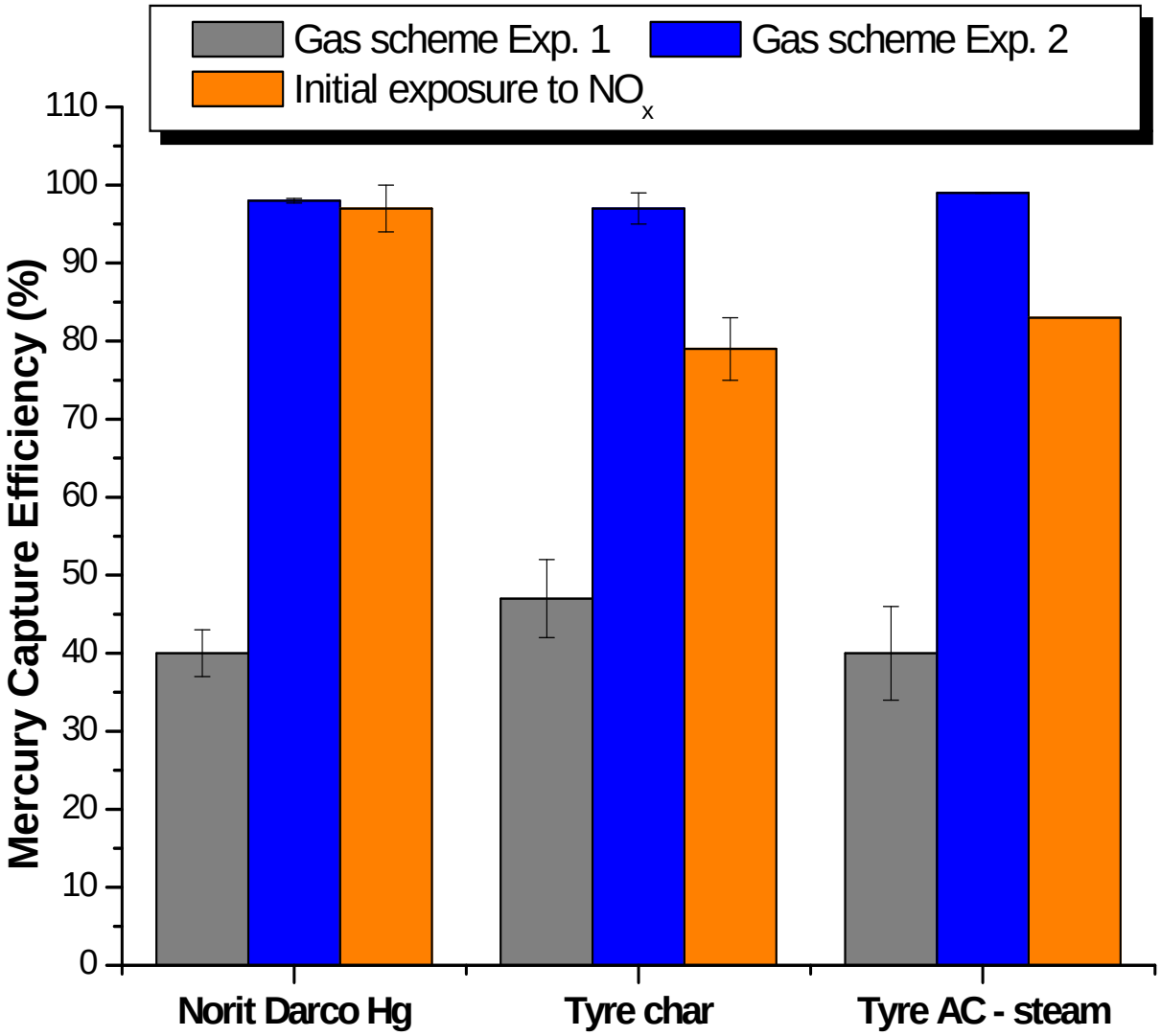
HG CAPTURE – EXP. 1 TO EXP. 6



Note - sample mass = 20 mg

Imperial College London

HG CAPTURE – INITIAL EXPOSURE TO NO_x

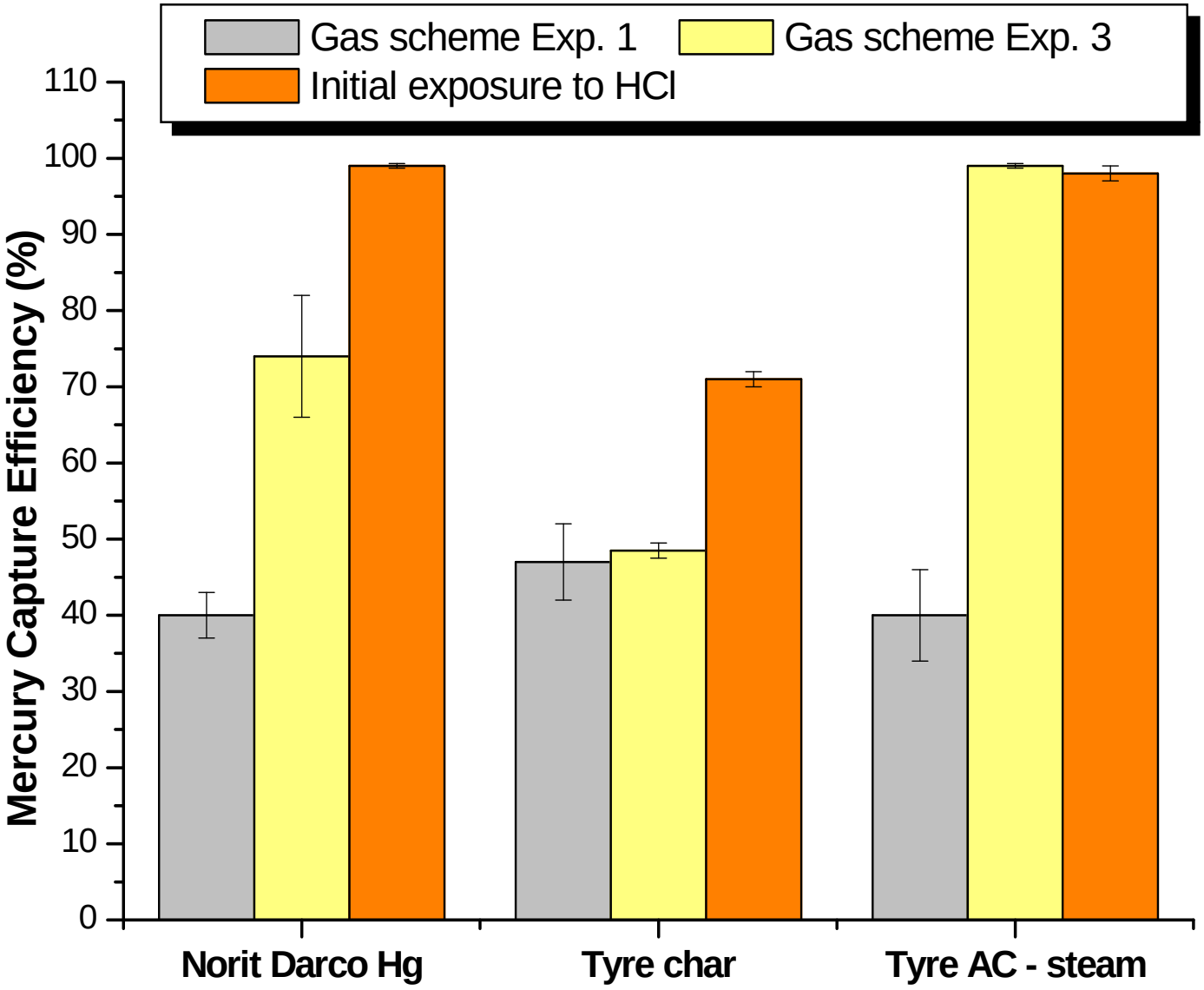


Sample mass = 100 mg
Hold time = 60 min.

Test temperature = 150°C

Imperial College London

HG CAPTURE – INITIAL EXPOSURE TO HCL

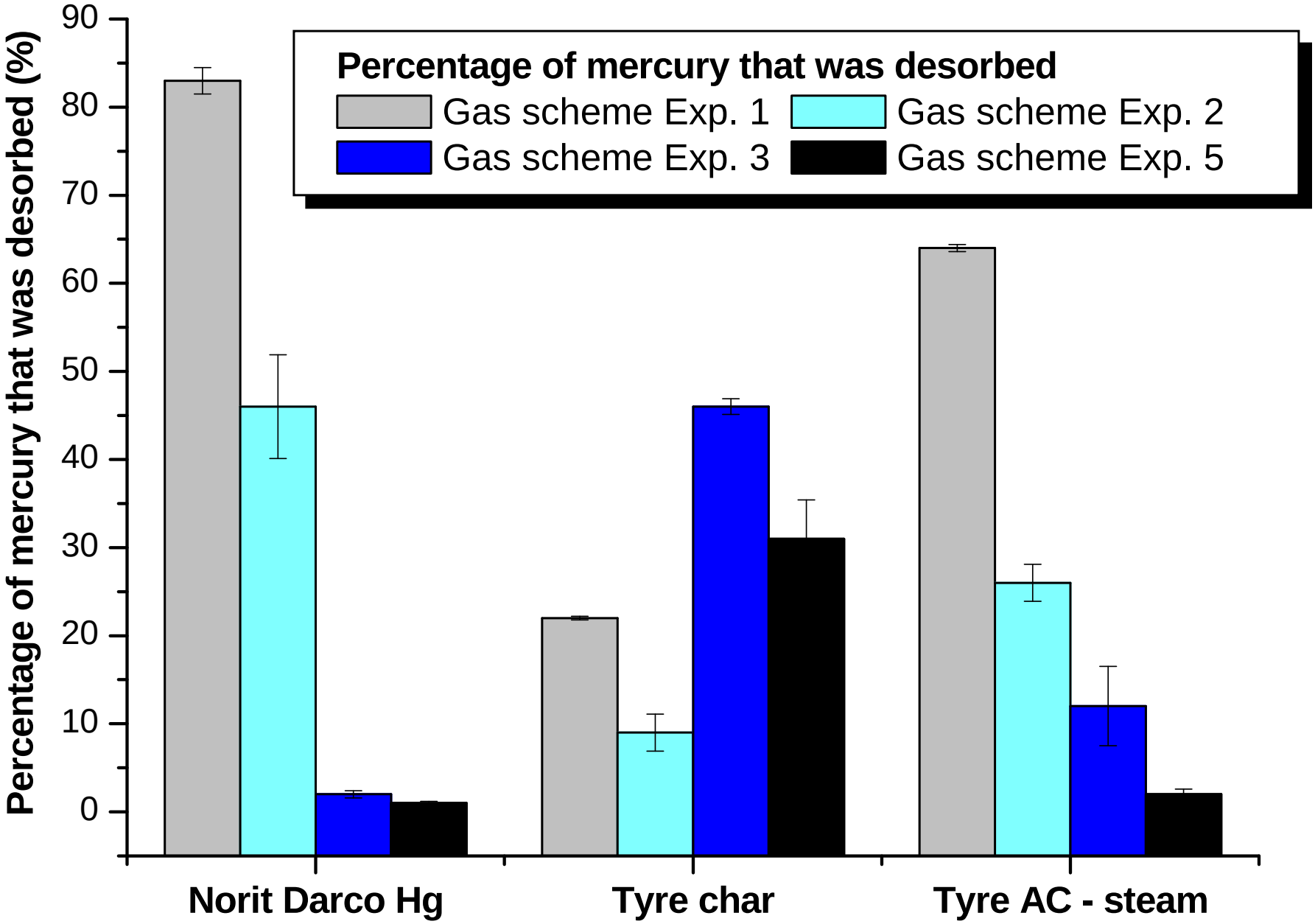


Sample mass = 100 mg
Hold time = 60 min.

Test temperature = 150°C

Imperial College London

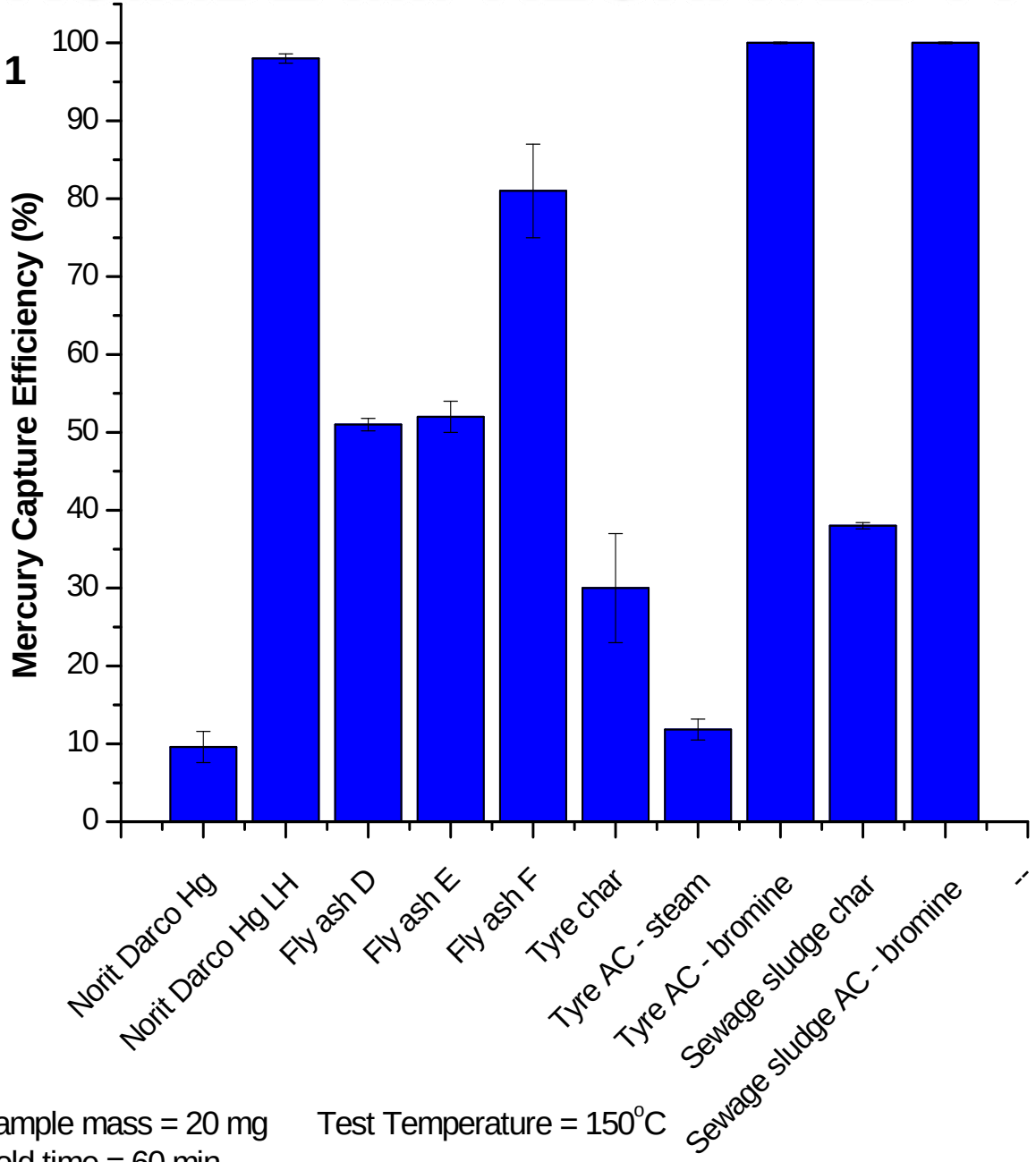
THERMAL DESORPTION TESTS



Imperial College London

BROMIDE IMPREGNATED PAC

Gas scheme = Exp. 1

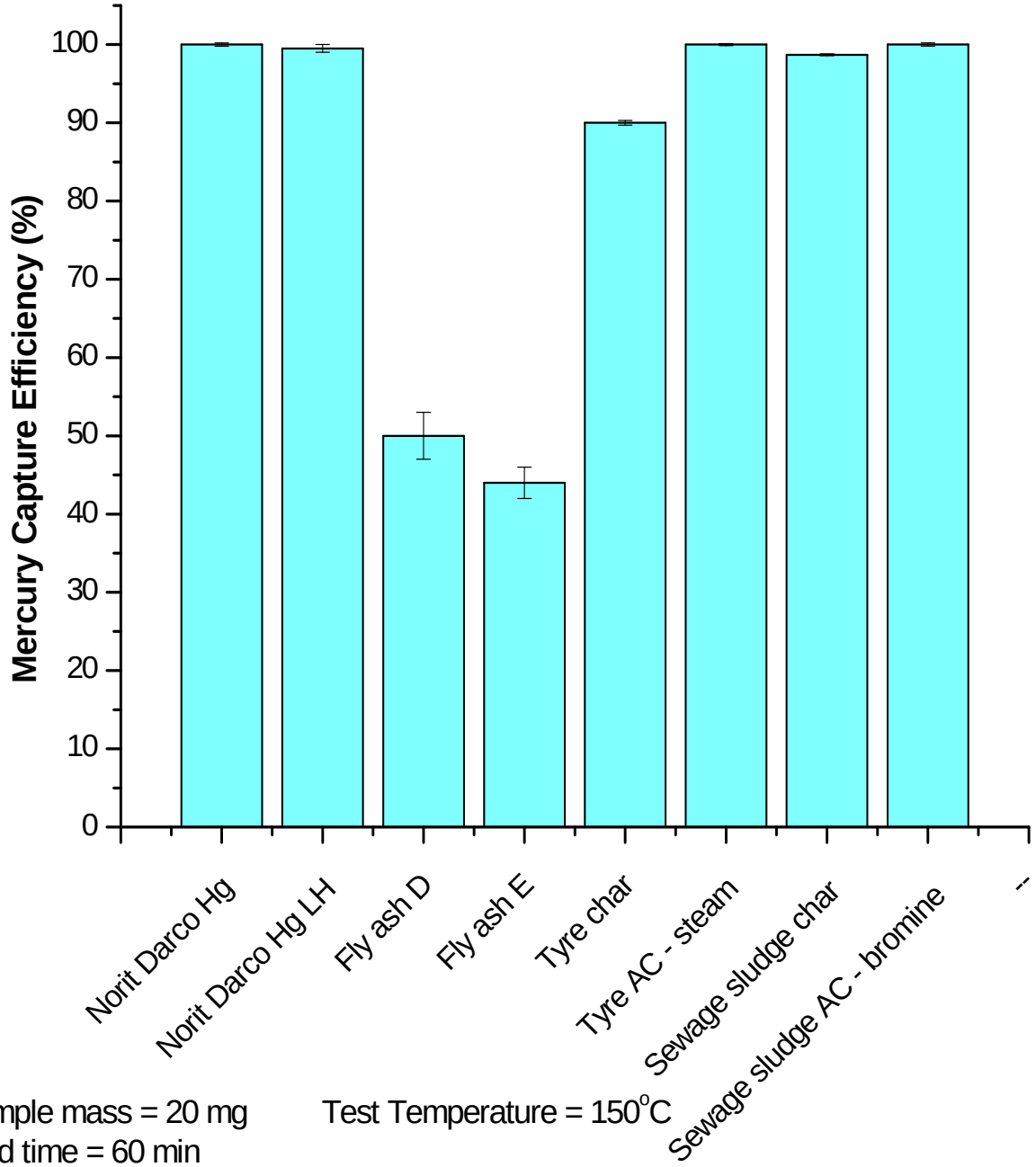


Sample mass = 20 mg Test Temperature = 150°C
Hold time = 60 min

Imperial College London

BROMIDE IMPREGNATED PAC

Gas scheme = Exp. 6

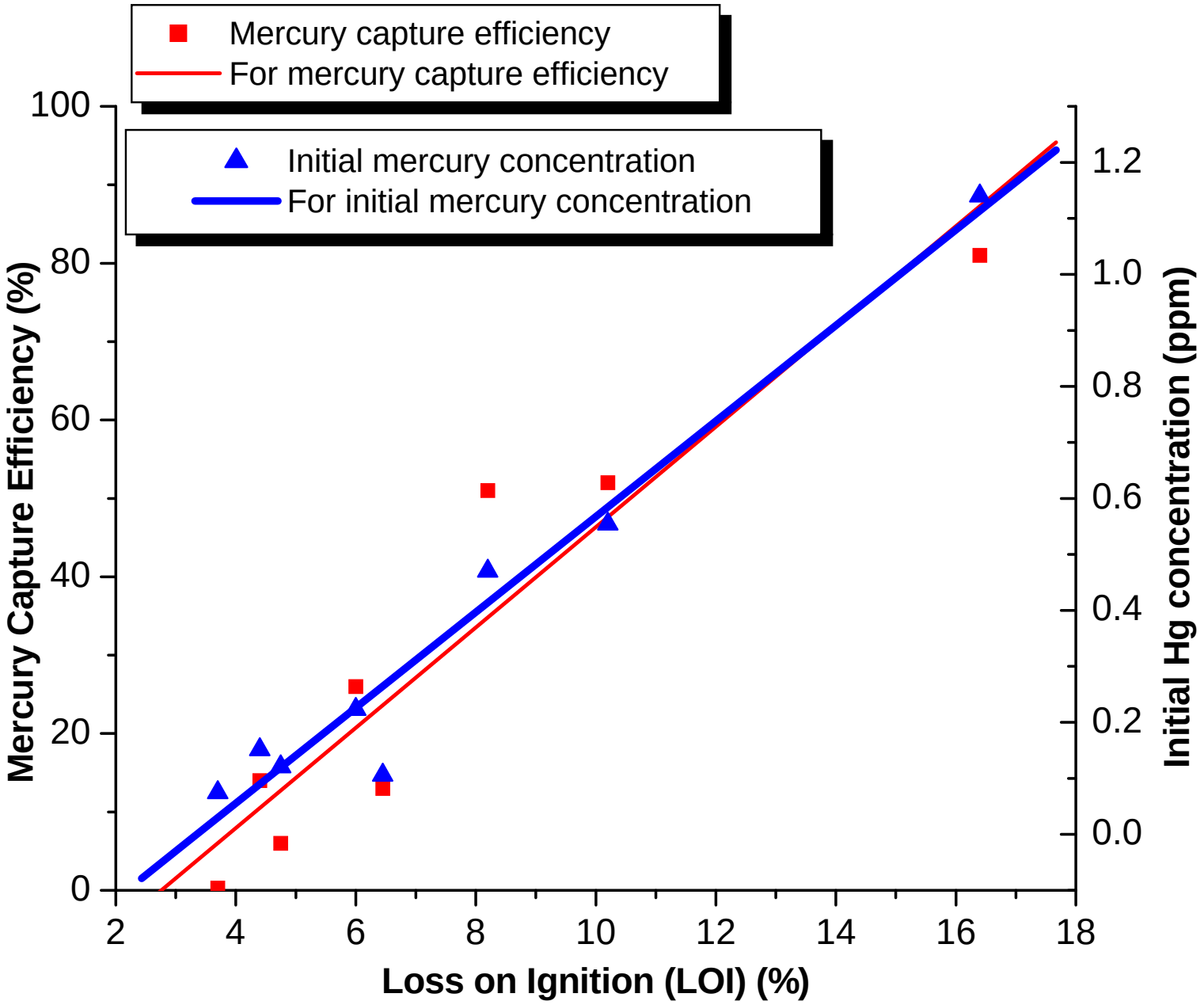


Sample mass = 20 mg
Hold time = 60 min

Test Temperature = 150°C

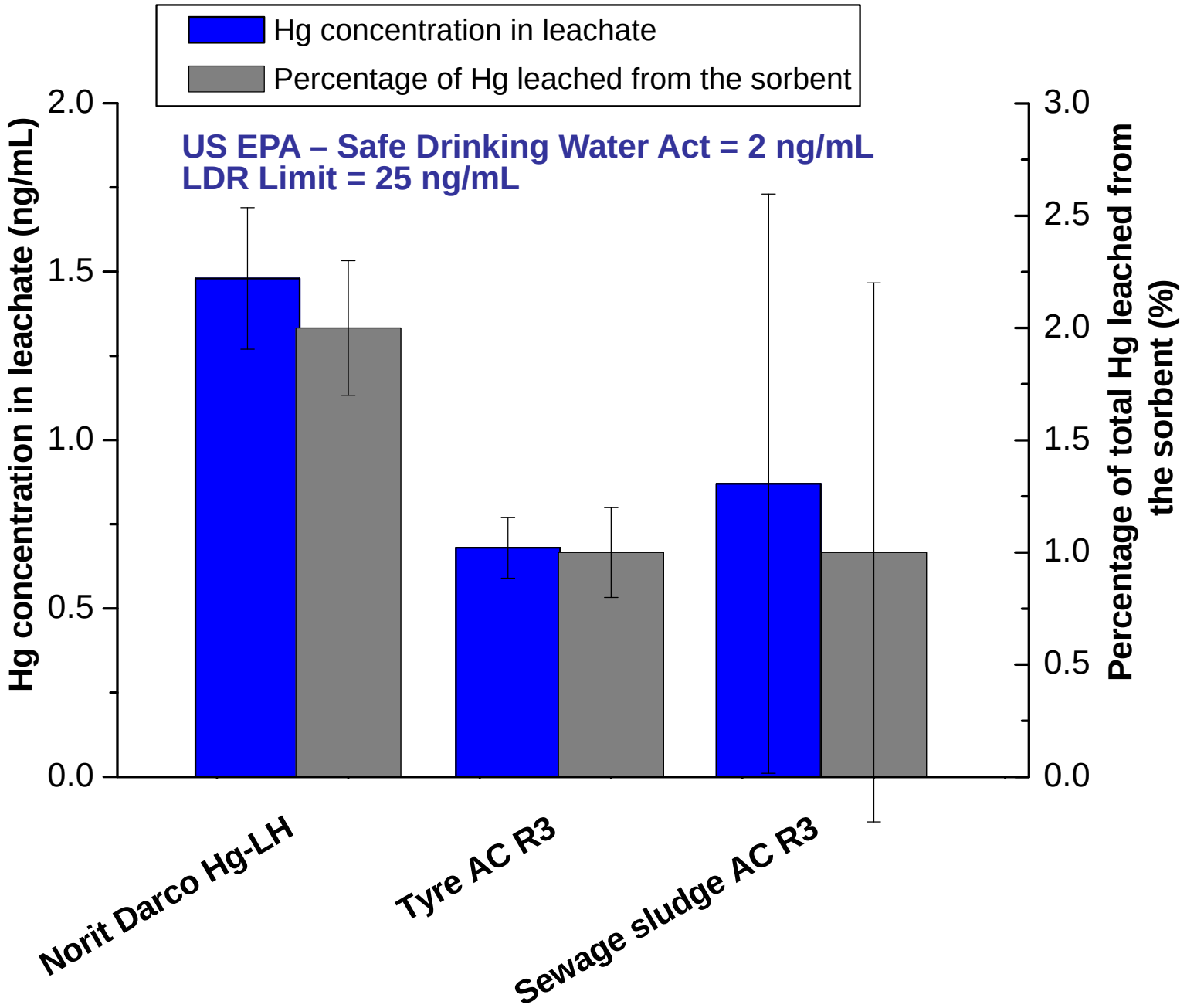
Imperial College London

FLY ASH FROM UK PLANTS



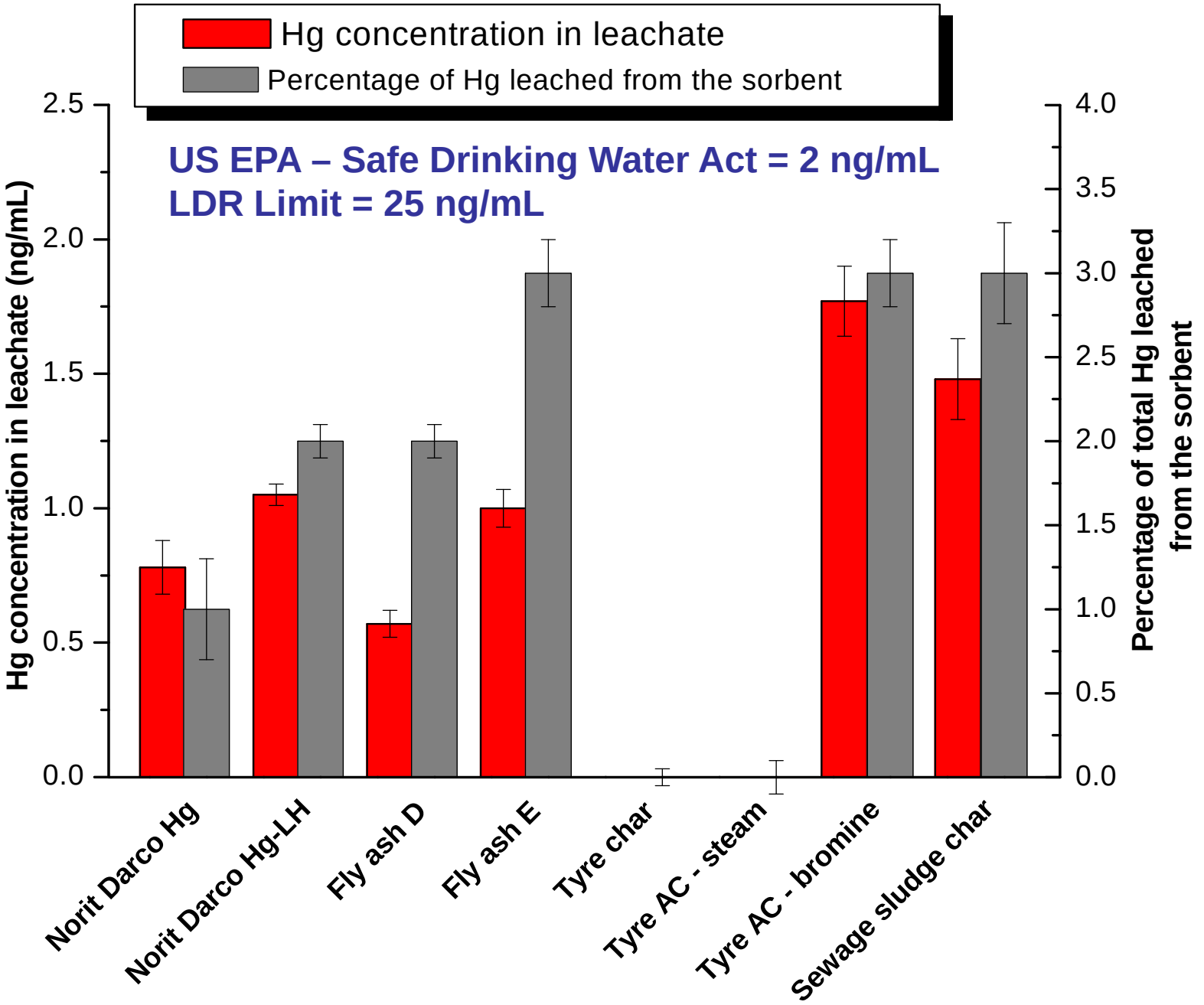
Imperial College London

LEACHING TESTS – EXP. 1



Imperial College London

LEACHING TESTS – EXP. 5



Imperial College London

CONCLUSIONS

- Brominated sorbents ~ 100% effective when gas scheme – Exp. 1 is used.
  - **Needed less than 5% the mass of Norit Darco Hg™**
- Sorbents without Br impregnation (except the fly ash)
  - **Efficiency increased with NOX or HCl**
- Tests with Exp. 1: Physically adsorbed - steam PAC
  Chemical bond – Tyre pyrolysis char
- Test with Exp. 5 – Strong chemical bond
  probably due to HCl
- Hg capture on fly ash related to LOI
  - **LOI >17% needed to equal Br impregnated sorbents**
- TCLP leaching test showed very little mercury is leached
  - **Hg conc. in leachate < EPA safe limit for drinking water**

Imperial College London

CONCLUSIONS

- Norit Darco Hg™ substitute
  - **Steam activated PAC from scrap tyre rubber**
- Norit Darco Hg-LH™ substitute
  - **Bromide impregnated PAC from scrap tyre rubber**

Imperial College London

RECOMMENDATIONS FOR FUTURE WORK

- Test with SO_3
  - Might consume active sites which would have adsorbed mercury
- Entrained flow reactor
  - Difficult to correlate bench scale fixed bed results with full-scale field tests
  - Entrained flow reactor results in USA have had better correlations with full-scale tests

Imperial College London

THANK YOU FOR LISTENING

Acknowledgment

I would like to express my sincere thanks to BCURA for funding this project and P S Analytical for providing the Mercury generator and helping in analysing the bromine impregnated sorbents.

Special thanks to the BCURA Project Officer, Dr D Fitzgerald, and also to Dr W. Quick and Dr S Weatherstone for their help and encouragement throughout the project