Advanced 13
Energy System
and Green Technology

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Contents

1) Future Energy & Environmental Issues

2) Coal Utilization Technologies

3) Biomass/Waste Utilization Technologies

4) Countermeasures for Environmental Pollution

5) What do we have to do in the near future?

Life Period of Fossil Fuels

How long can we use the fossil fuels?

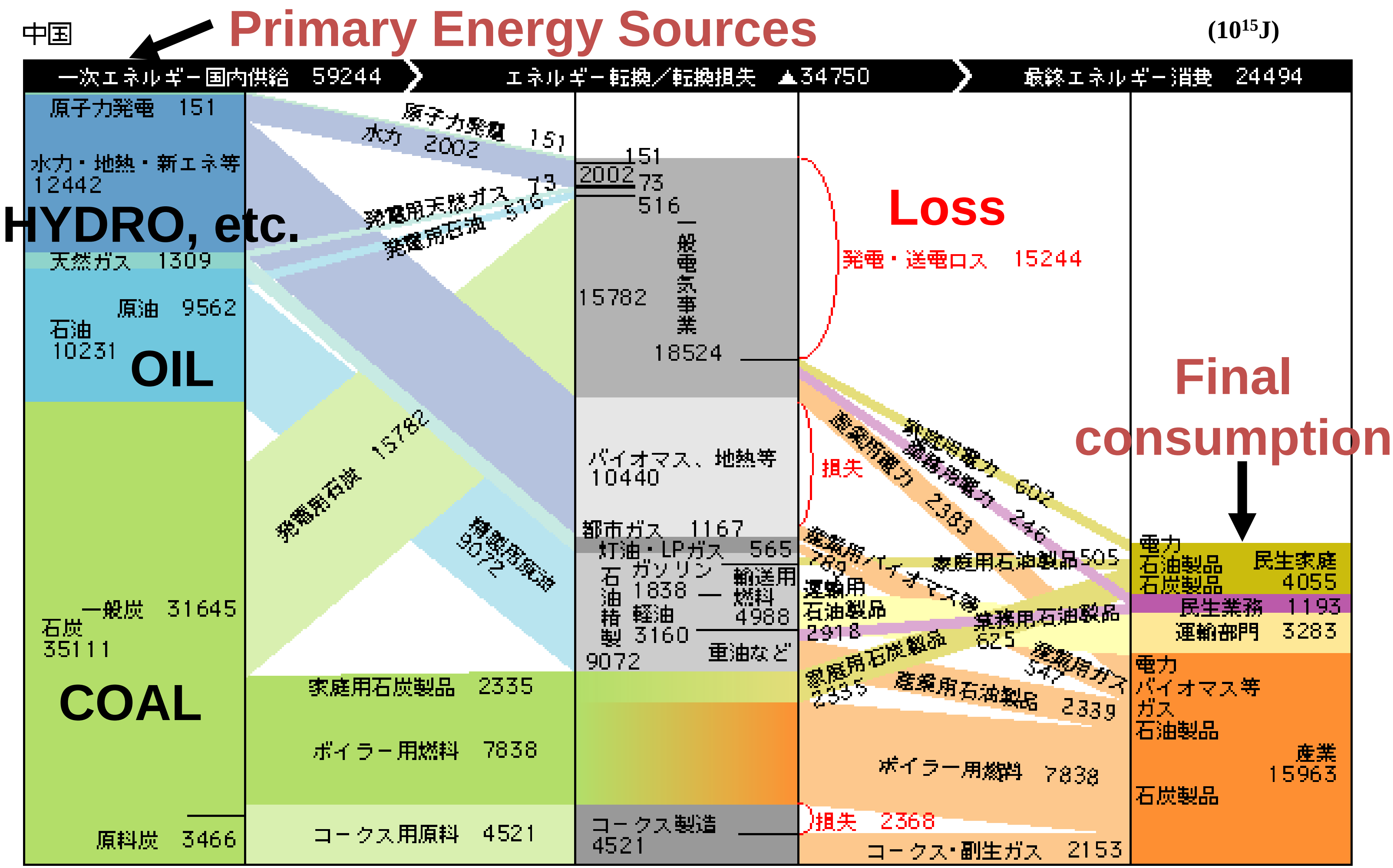
Primary fossil fuels	Life period
Oil	40.6 years
Natural gas	61 years
Coal	204 years
Uran	61.1 years

http://www.enecho.meti.go.jp/hokoku/

Life Period of metals

Gold ・・・・・・	20 years	Aluminum ・・・	211 years
Silver ・・・・・・	19 years	Iron ・・・・・・	151 years
Copper ・・・・・	31 years	Nickel ・・・・・	45 years
Diamond ・・・・	17 years	Lead ・・・・・・	25 years
Platinum ・・・・	218 years	Zinc ・・・・・・	20 years
		Herium ・・・・	>74 years

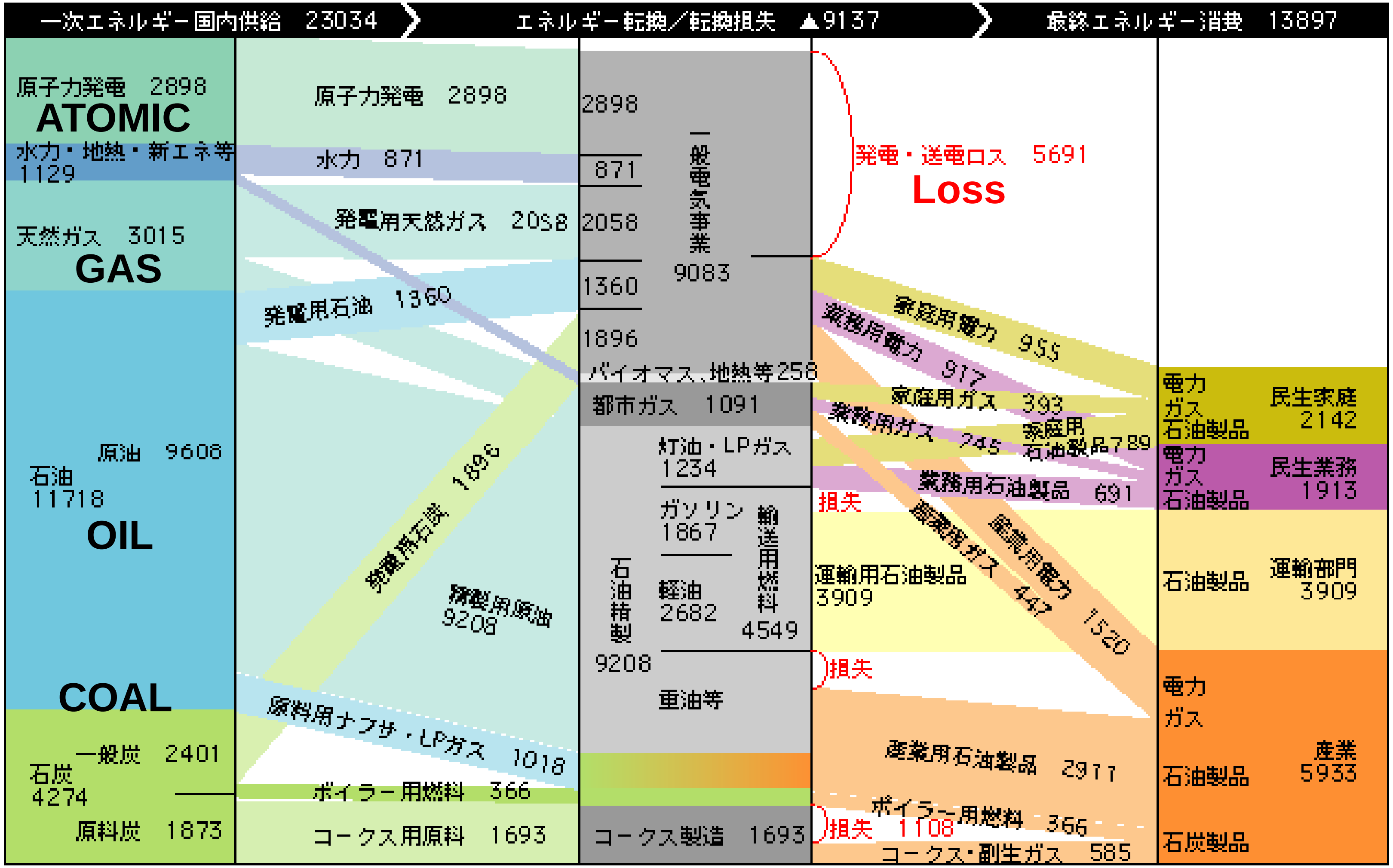
http://home.hiroshima-u.ac.jp/er/A_Japan_Sea/A3.PDF



Energy Balance in China（2000年）

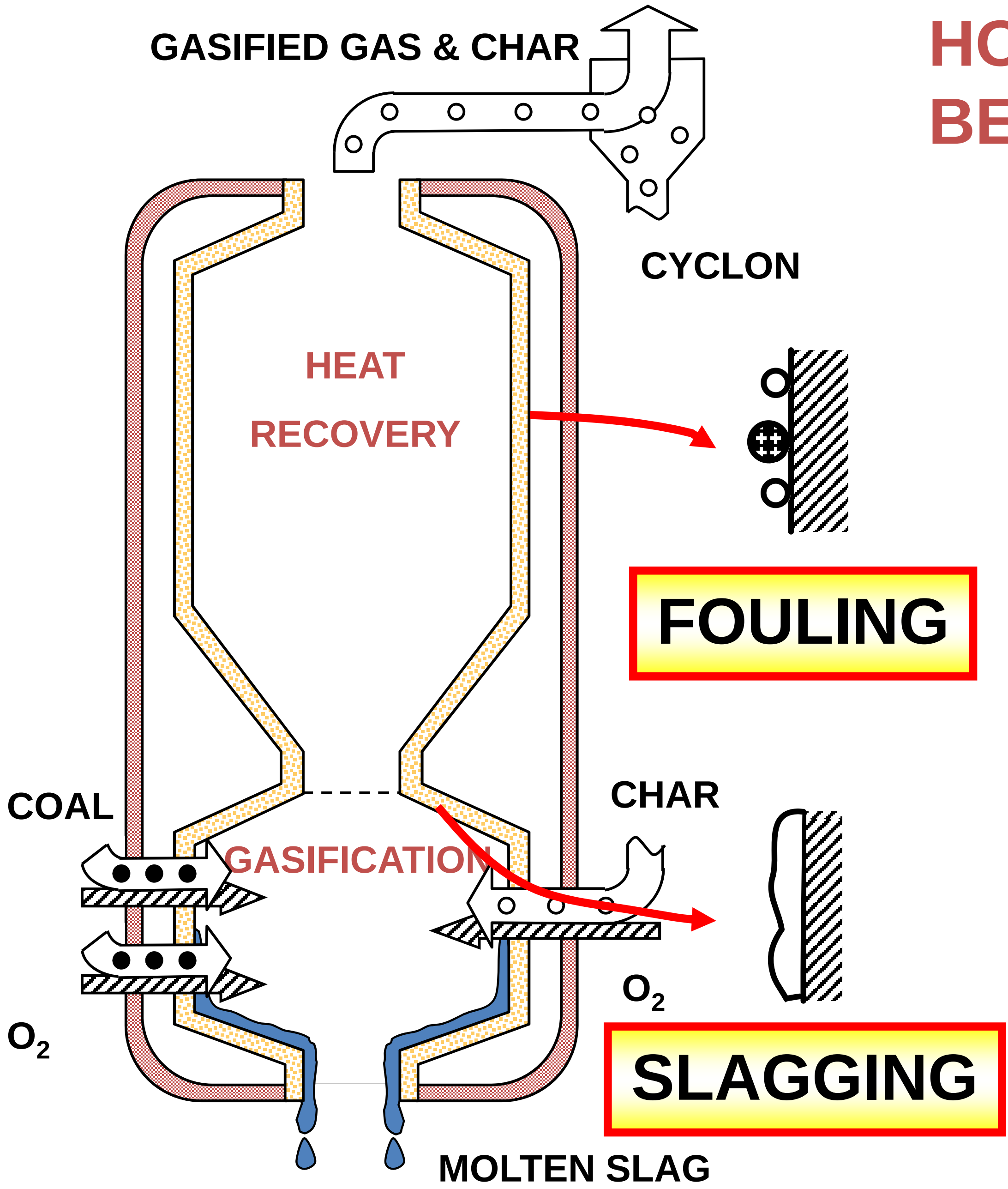
資料：IEA「Energy Statistics of OECD countries 1999－2000」2002 Edition（アメリカ、カナダ、ドイツ、イギリス、フランス、日本）
IEA「Energy Statistics of non OECD countries 1999－2000」2002 Edition（中国、インド）

日本 （10^{15}J）



Energy Balance in Japan（2000年）

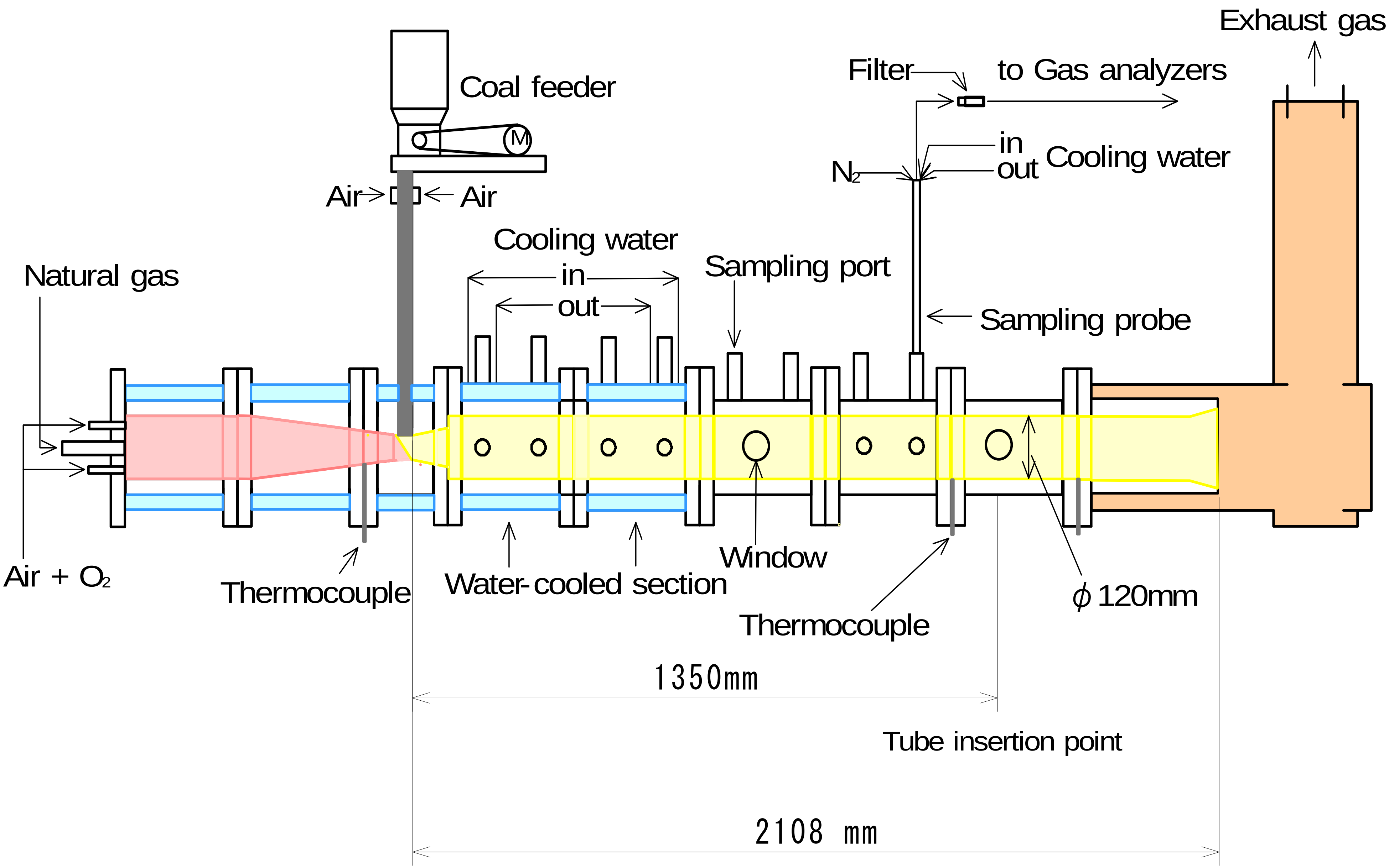
1) Coal Utilization Technologies



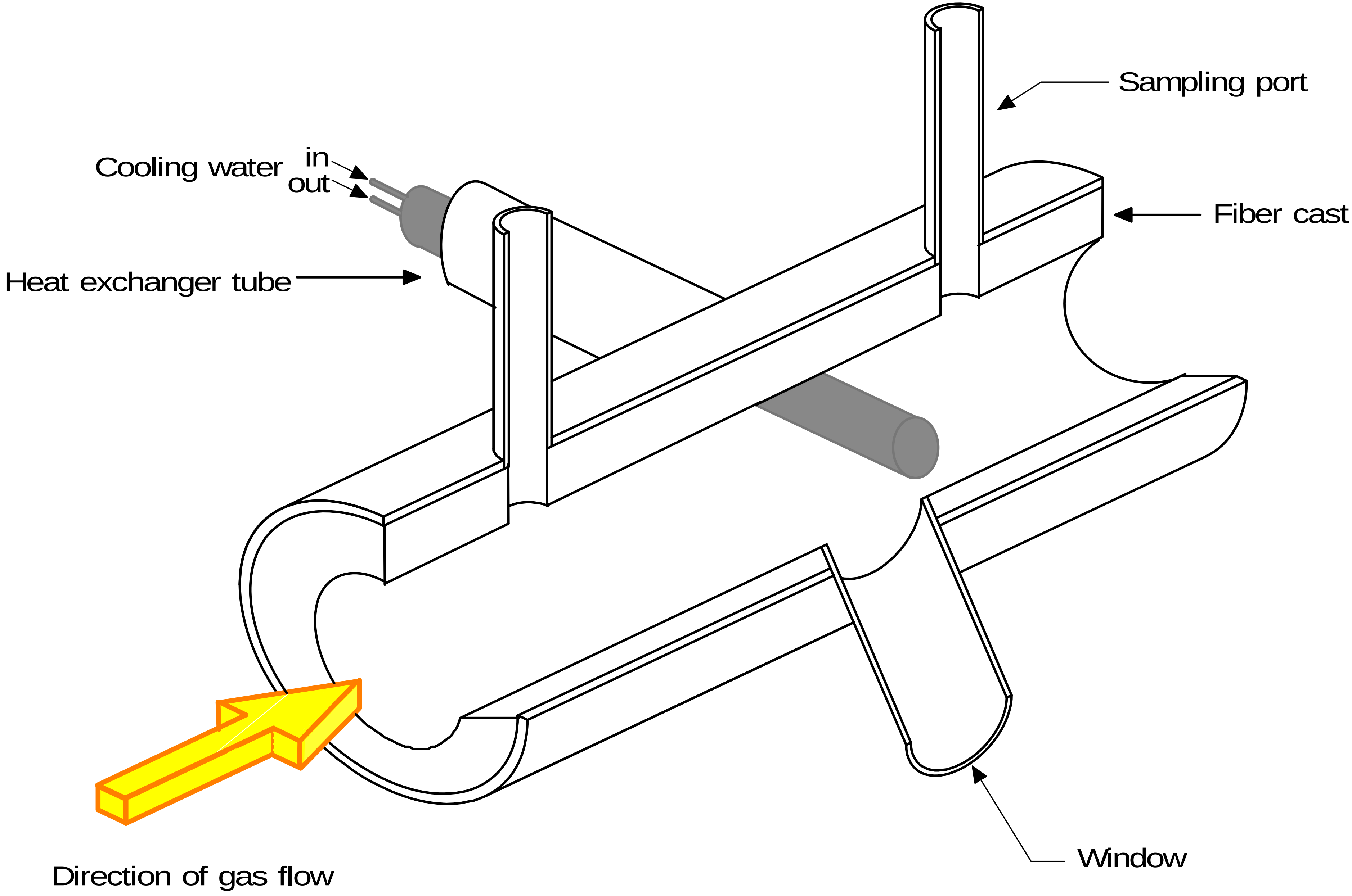
HOW SHOULD THE GASIFIER BE CONTROLLED STEADILY?

- **DEPOSITION MECHANISMS**
- **EFFECT OF COAL TYPE**
- **ASH FORMATION PATH**

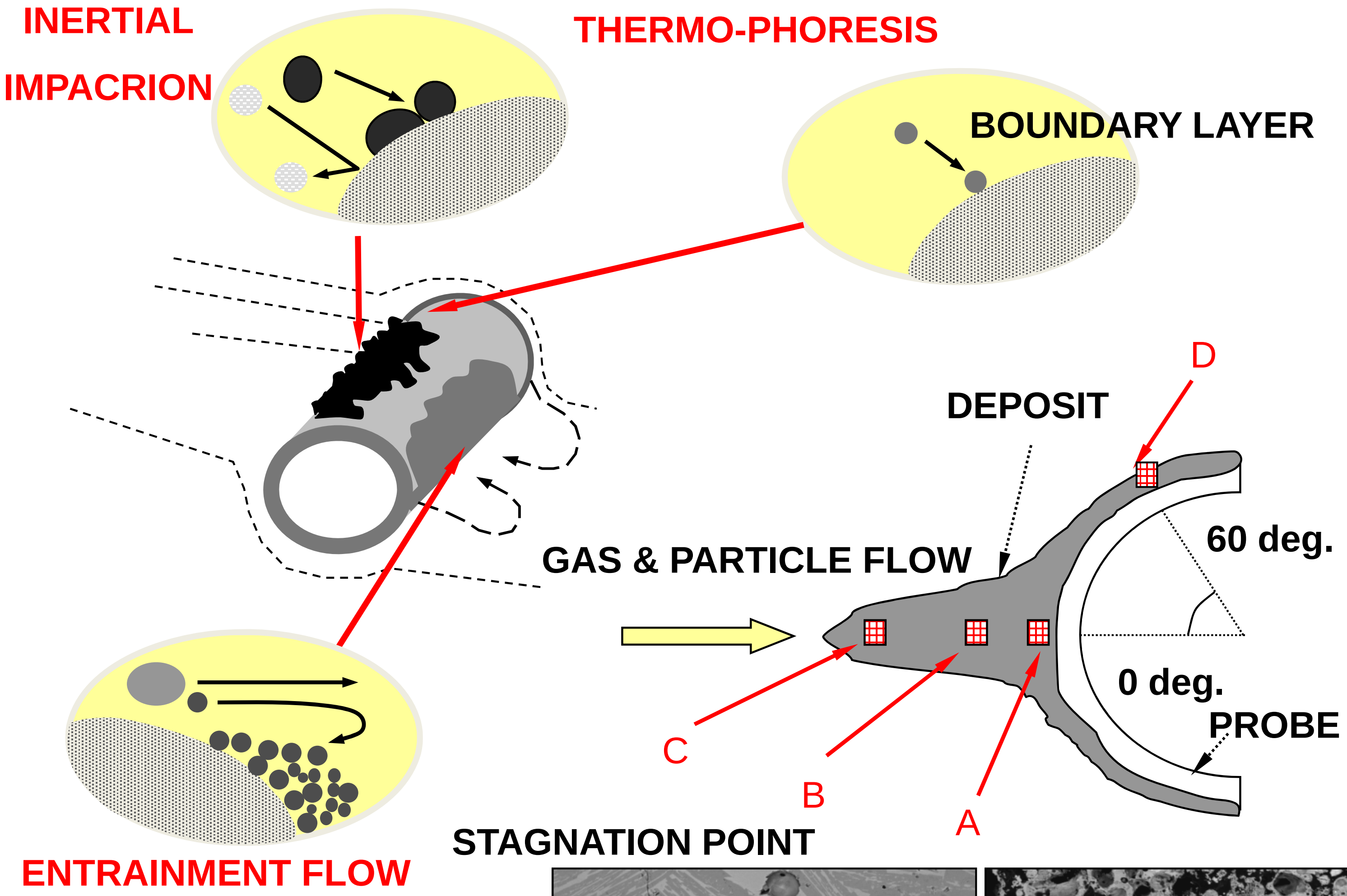
SCHEMATIC DIAGRAM OF HORIZONTAL PULVERIZED COAL REACTOR

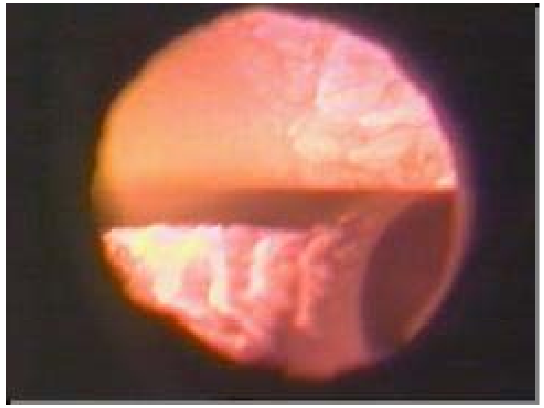


SECTION OF ASH DEPOSITION

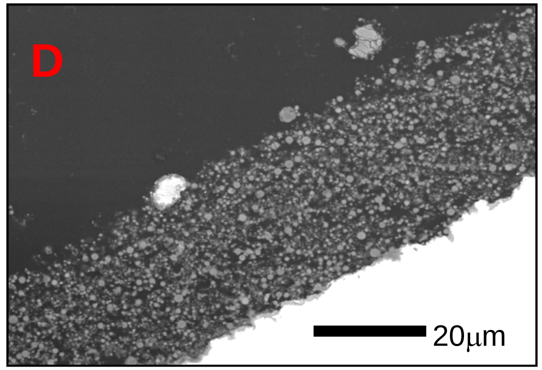


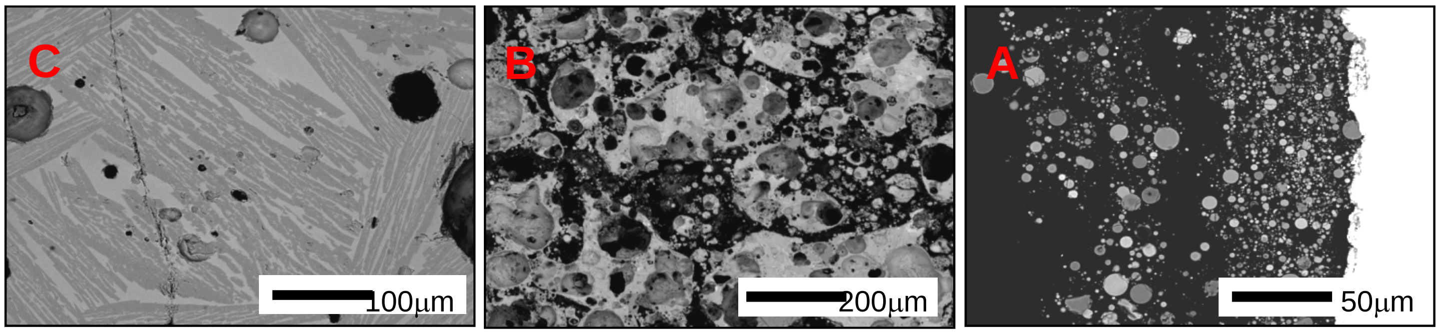
SECTION OF ASH DEPOSITION





60 deg. FROM STAG. POINT

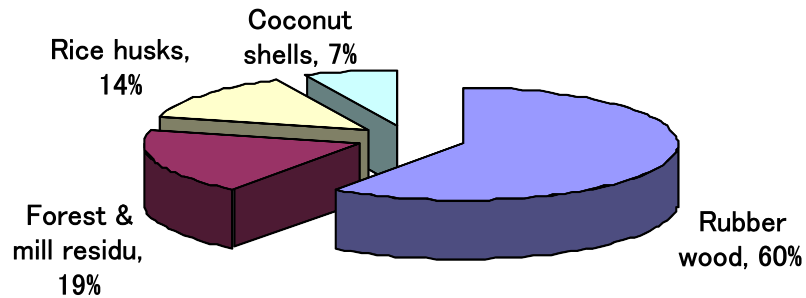




Low-grade Coal

High moisture content
High ash content (>20%)
Low heating value (<20MJ/kg)
High fuel ratio (>5)
High S and N content (>2%)

Biomass



39.7 million ton

Renewable
Much inventory
Easy reservation
Fuel exchangable
Carbon neutral

Co-combustion

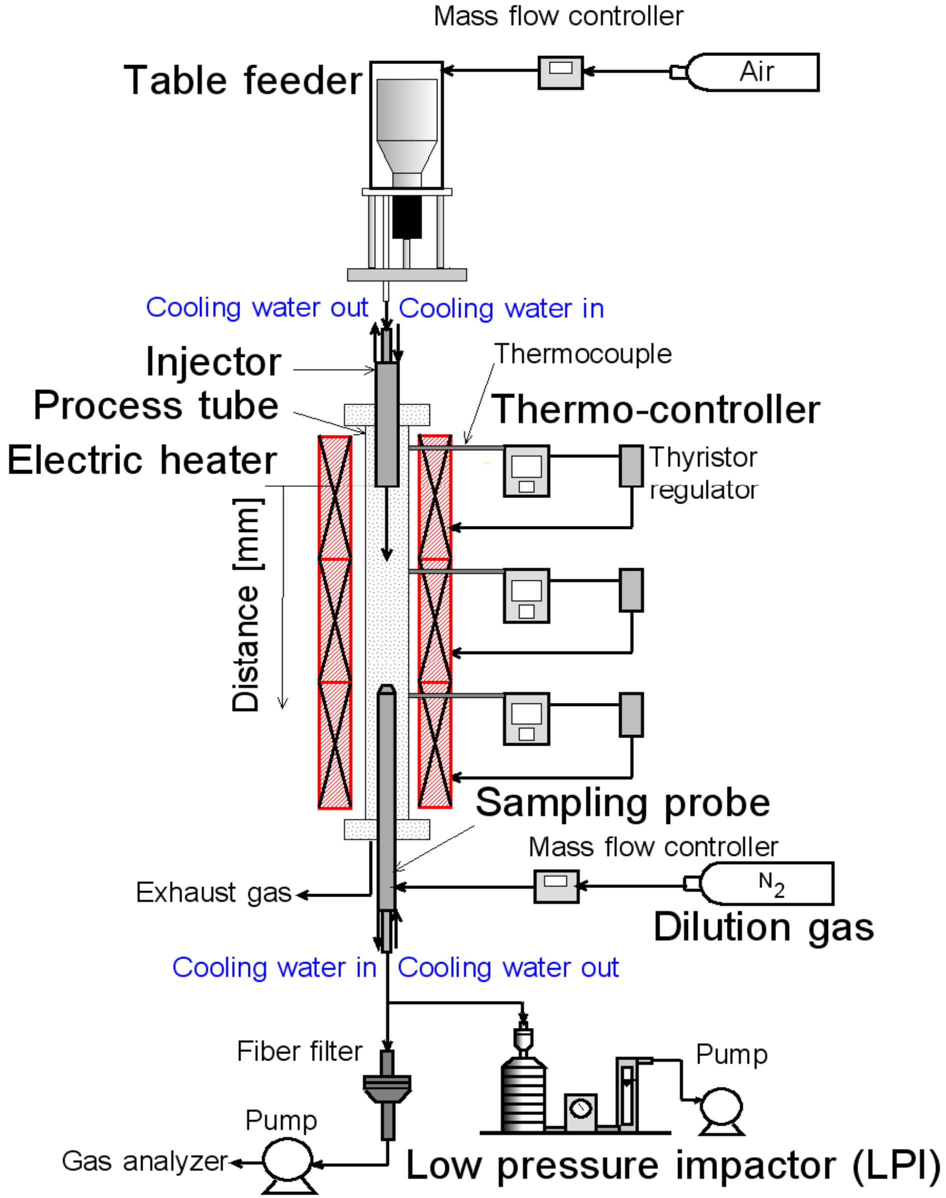
High fuel ratio = FC/VM

To develop effective utilization of low-grade coal and biomass, using co-combustion with biomass.

Research contents:

- Combustion behavior for biomass, coal and co-fuel (DTF: Electrically heated drop tube furnace)
- NOx behavior (Experimental)
- Kinetic simulation of NOx behavior (CHEMKIN)

Experimental setup and condition



Experimental condition

Sample	SH coal	Biomass	SH + Biomass
Furnace temperature [K]	1073		
Stoichiometric ratio [-]	1.2		
Flow rate [l/min]	4.31	4.29	4.35
Lower heating value [kW]	0.23	0.22	0.23

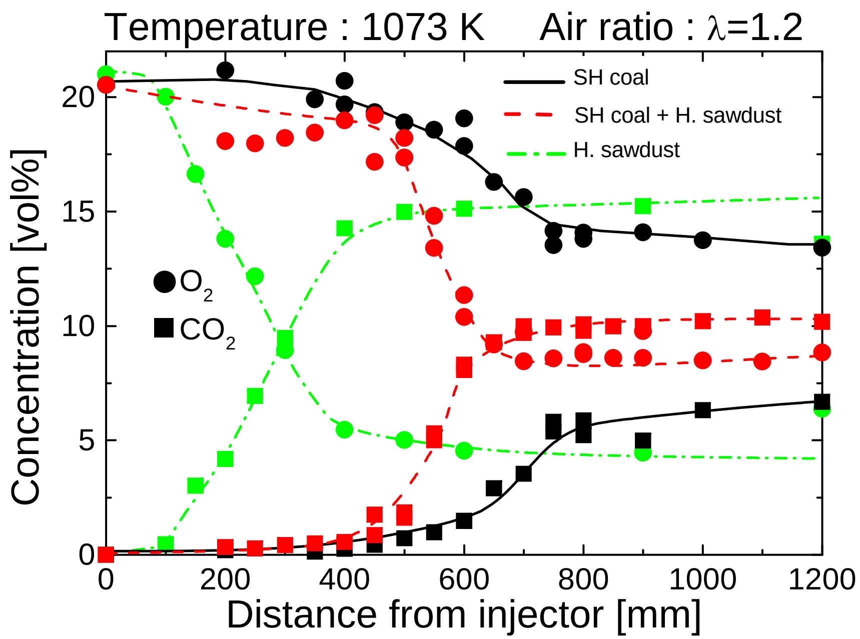
SH coal : Biomass = 1:1 (wt%)

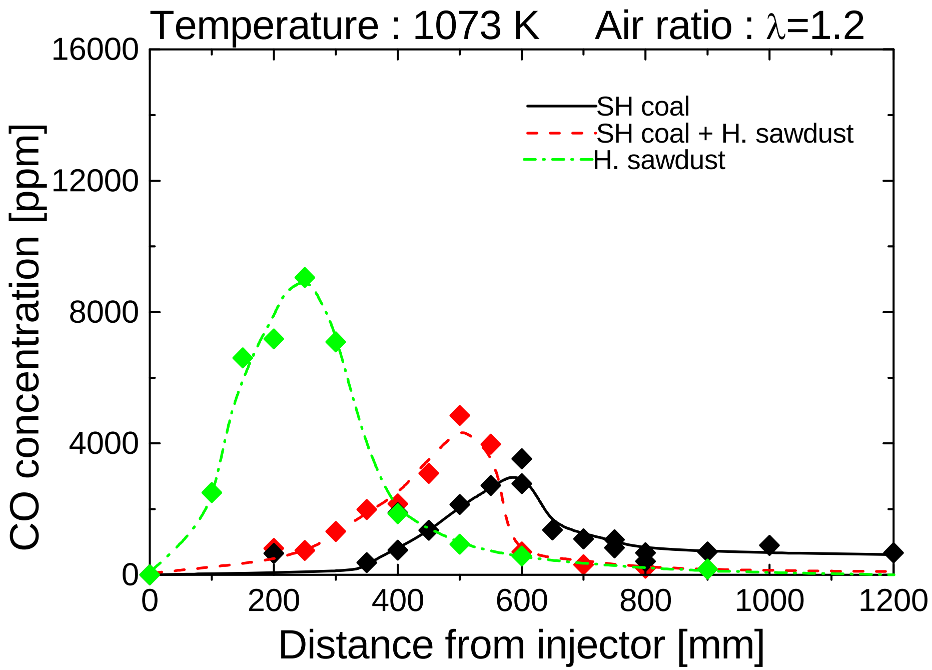
Gas composition detected:

O_2, CO_2, CO, NO and N_2O

Experimental setup

Co-combustion behavior of coal with biomass



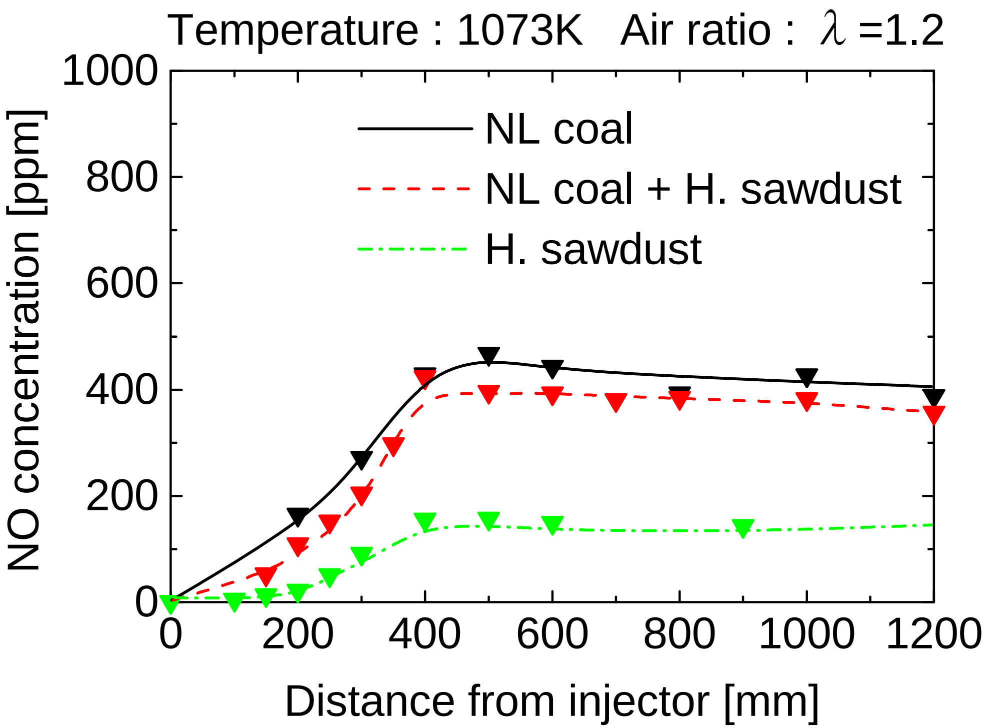


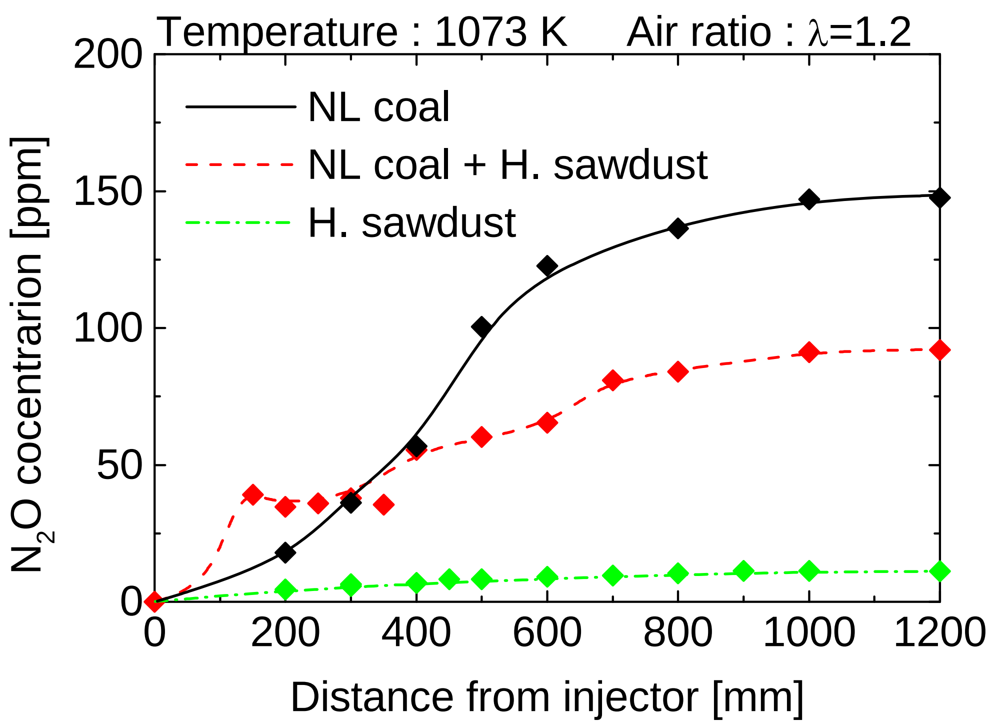
O_2, CO_2

CO

Profiles of CO_2, O_2 and CO concentrations along the furnace axis during combustion

NO and N_2O formation (NL Coal)





NO

N_2O

Heterogeneous reactions scheme

Formation:

$NCO + NO \rightarrow N_2O$

$NO + \text{char-C} \rightarrow CN + O$

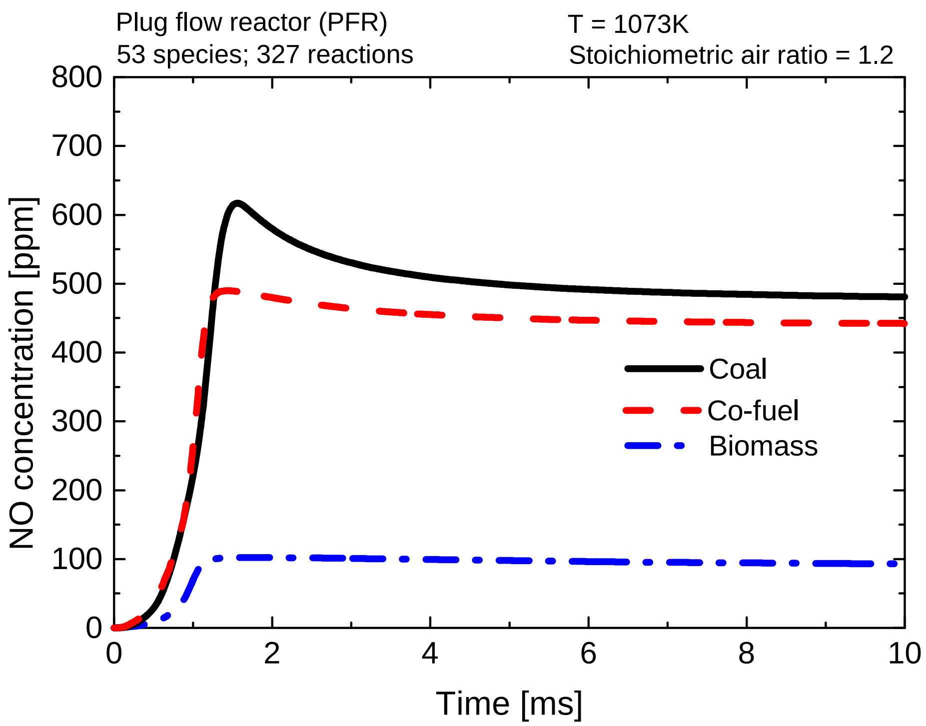
$CN + OH \rightarrow NCO + H$

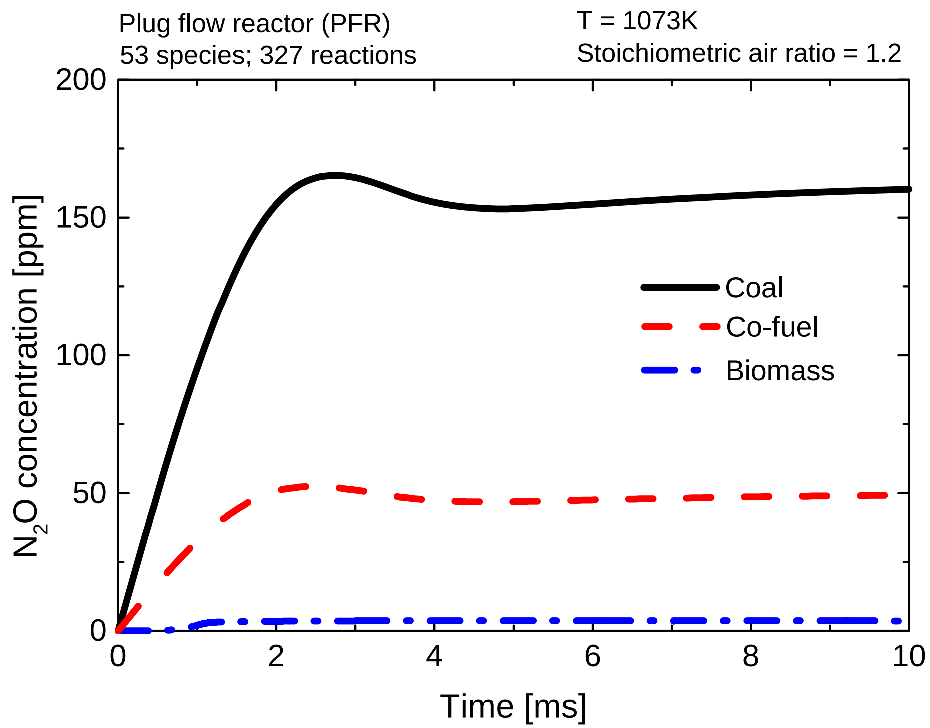
$NCO + NO \rightarrow N_2O$

Destruction:

$N_2O + \text{char-C} \rightarrow N_2 + CO$

Simulation results for NOx

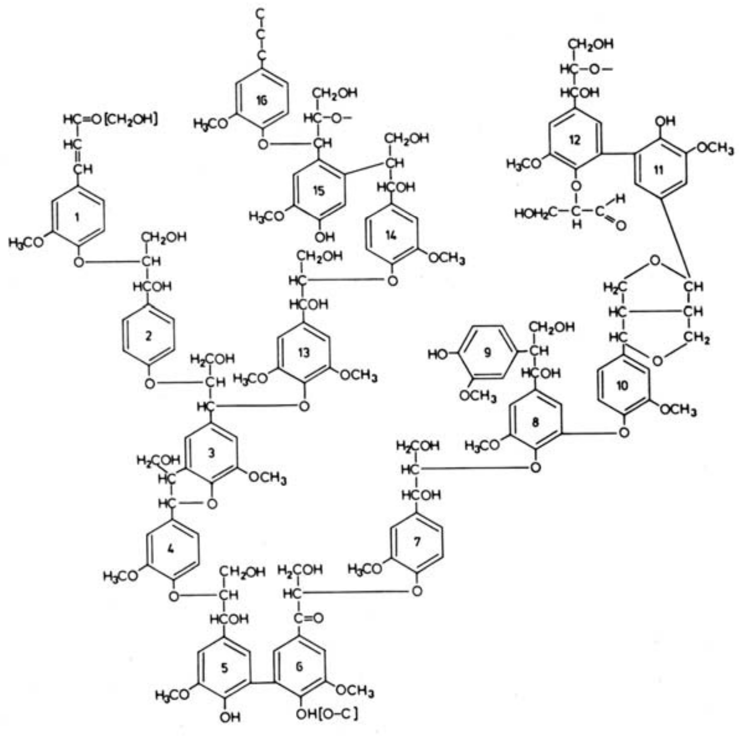




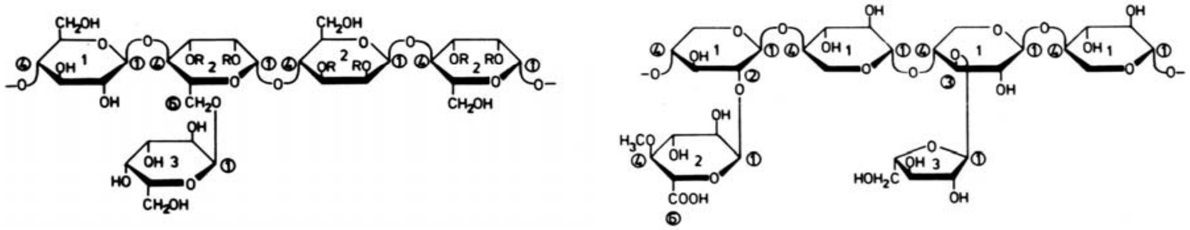
NO

N_2O

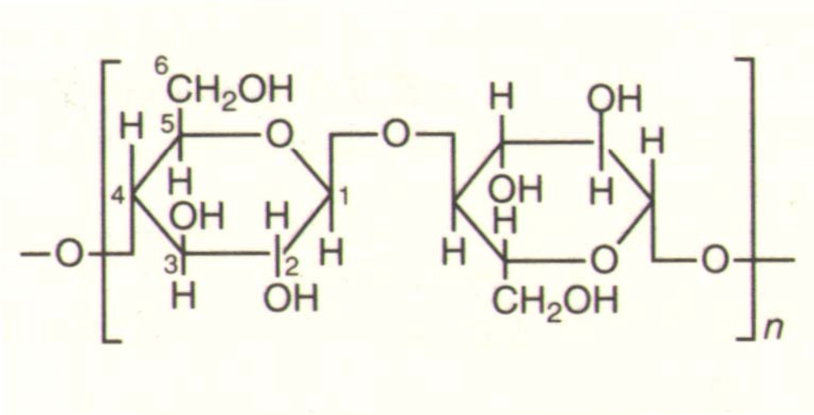
Biomass components（cellulose, hemicellulose, and lignin）



Lignin

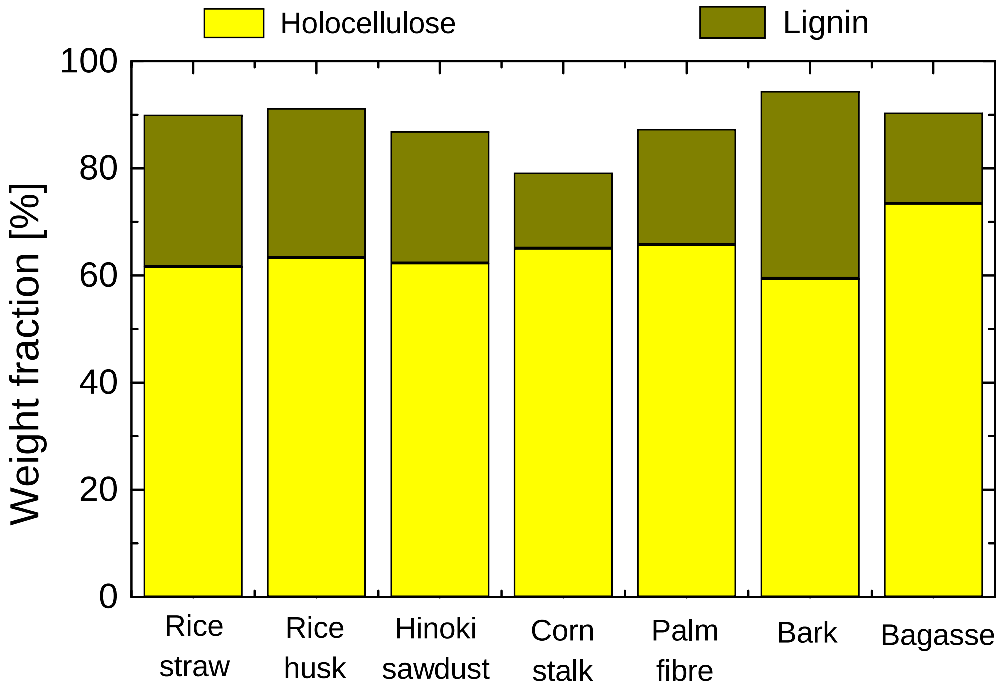


Hemicellulose

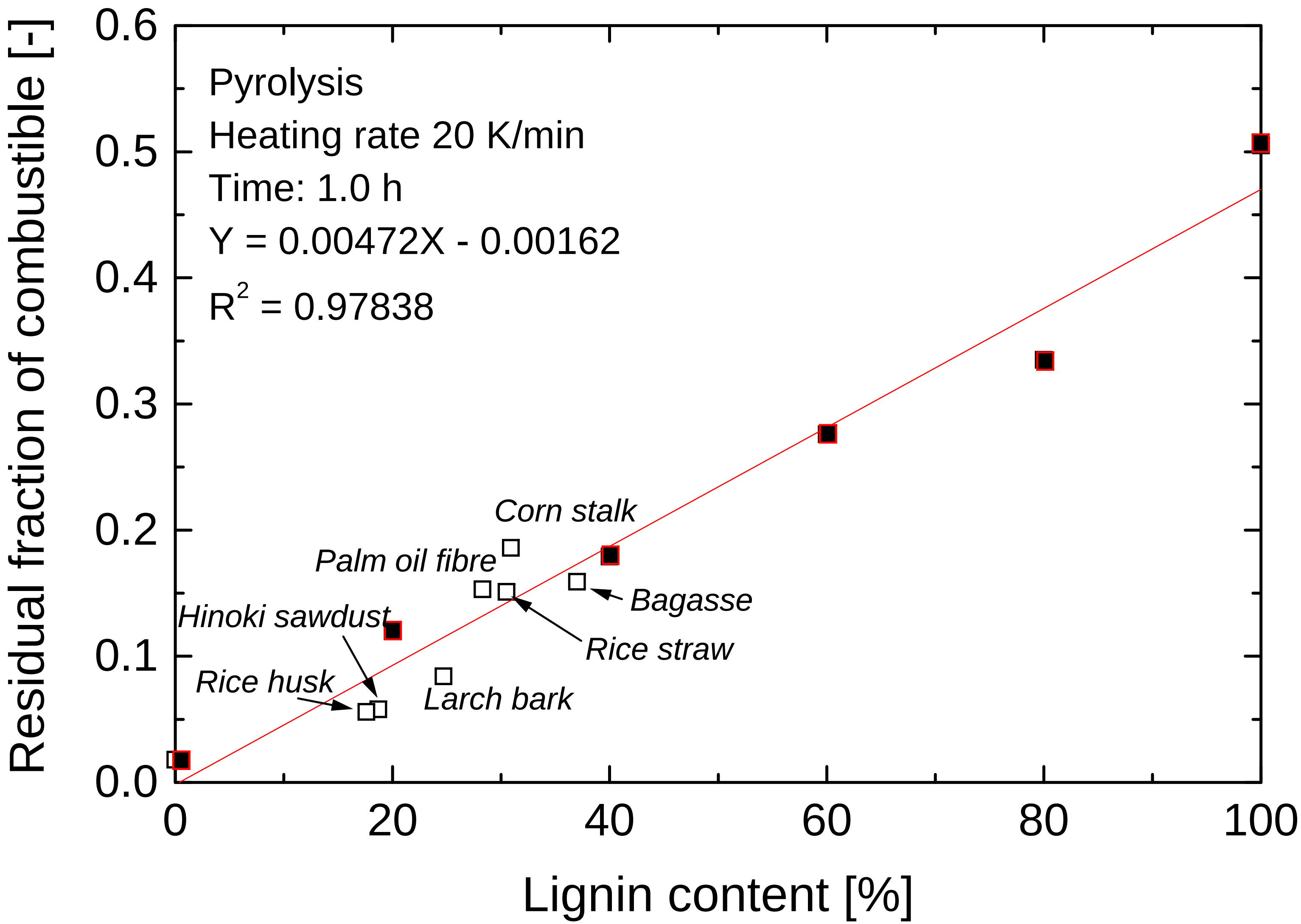


Cellulose ($C_6H_{10}O_5$)

Cellulose and lignin content in several biomasses

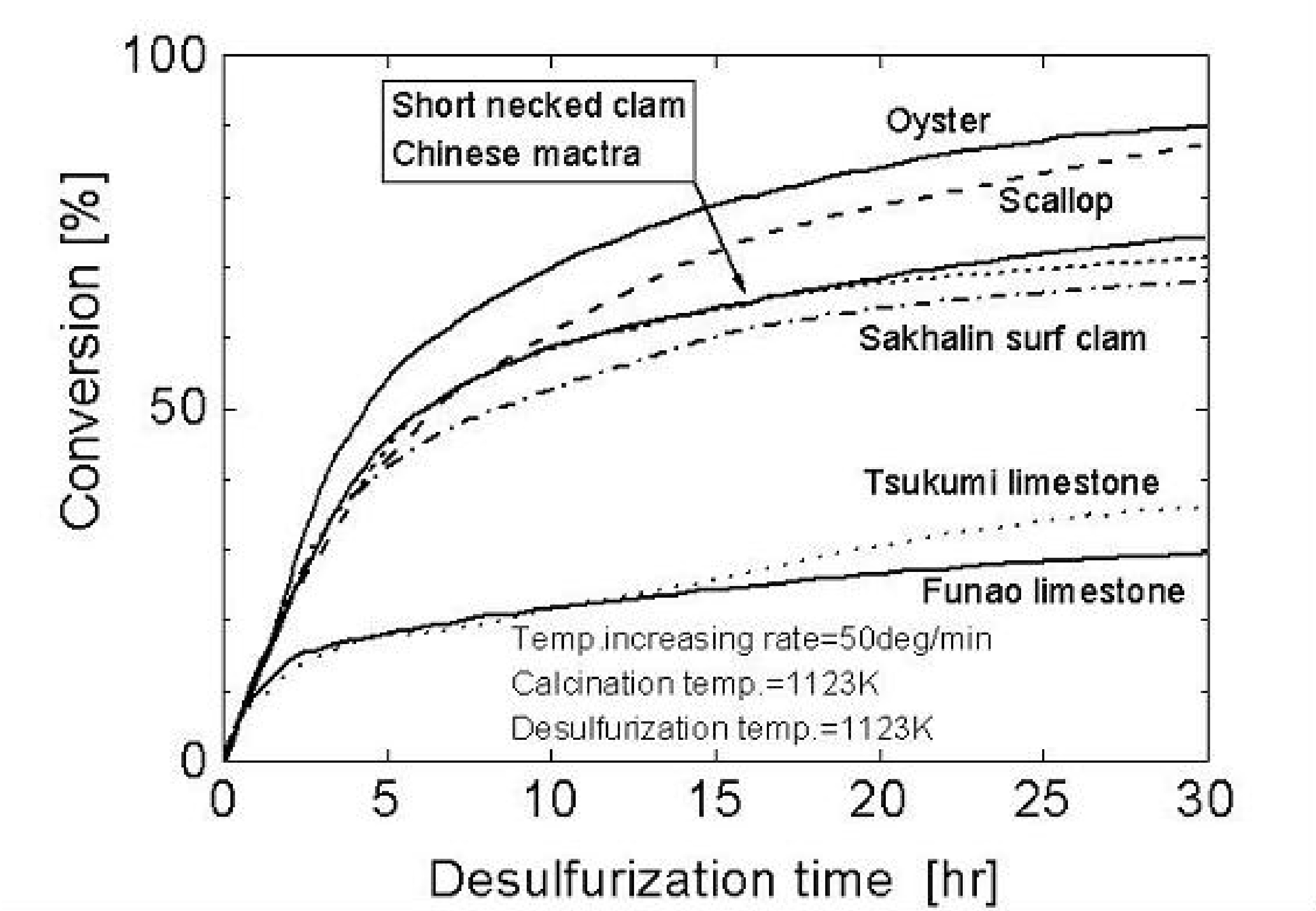


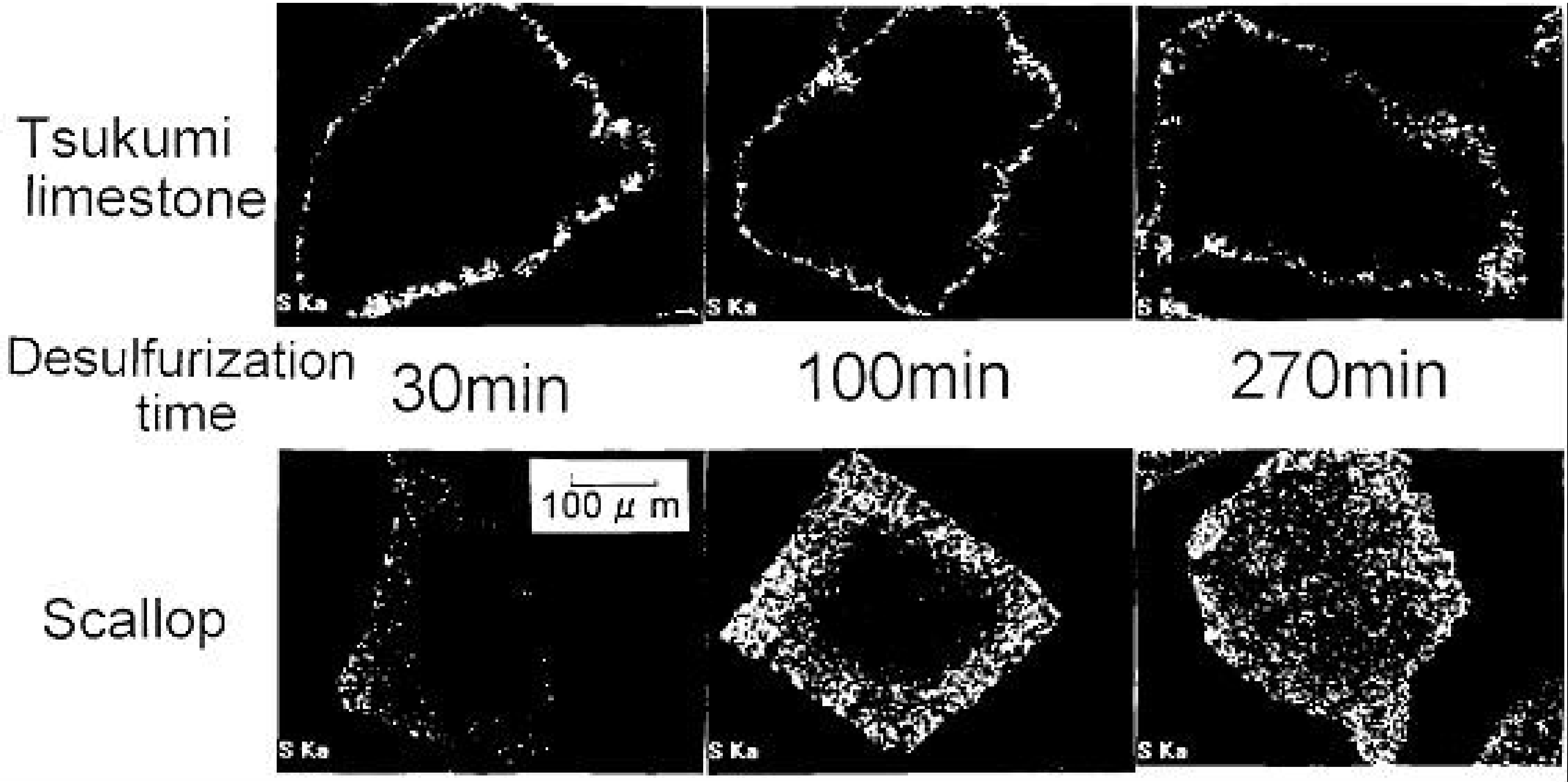
Effect of cellulose and lignin content on residual fraction of combustible during biomasses pyrolysis



Pyrolysis

Waste Utilization De-SOx by Wasted Seashell





Cross-section of particle
White region: S

Surface area & Pore size

	Shell			Limestone	
	Scallop	Oyster	Short-necked clam	Tsukumi	Funao
Raw material ($CaCO_3$) [m^2/g]	0.19	2.17	2.58	0.21	0.11
After calcination (CaO) [m^2/g]	0.59	1.61	0.82	15.5	15.7
Raw material ($CaCO_3$) [μm]	0.38	0.13	0.02	0.70	0.54
Pore size After calcinations (CaO) [μm]	0.40	1.47	1.63	0.07	0.05

4) Countermeasures for Environmental Pollution

Sources and emission amounts of trace elements [kt/y] (Nriagu, 1990)

	As	Cd	Cr	Co	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Tl	V	Zn
Human activities																
Energy production	2.2	0.8	12.7	-	8.0	2.3	12.1	-	42.0	12.7	1.3	3.9	3.3	1.1	84.0	16.8
Mining	0.1			·	0.4		0.6	·	0.8	2.6	0.1	0.2				0.5
Smelting & refining	12.3	5.4		·	23.2	0.1	2.6	·	4.0	46.5	1.4	2.2	1.1		0.1	72.0
Manufacturing	2.0	0.6	17.0	·	2.0		14.7	·	4.5	15.7				4.0	0.7	33.4
Commercial	2.0			·				·		4.5						3.3
Waste incineration	0.3	0.8	0.8	-	1.6	1.2	8.3	-	0.4	2.4	0.7	0.1	0.8		1.2	5.9
Transport										248.0						
Total	18.9	7.6	30.5	·	35.3	3.5	38.2	·	51.6	332.3	3.5	6.3	5.1	5.1	86.0	131.8
Natural																
Wind-borne dustS	2.6	0.2	27.0	4.1	8.0	0.1	221.0	1.3	11.0	3.9	0.8	0.2	·	·	16.0	19.0
Sea salt spray	1.7	0.1	0.1	0.1	3.6	0.0	0.9	0.2	1.3	1.4	0.6	0.6	·	·	3.1	0.4
Volcanic activity	3.8	0.8	15.0	1.0	9.4	1.0	42.0	0.4	14.0	3.3	0.7	1.0	-	-	5.6	9.6
Forest fire	0.2	0.1	0.1	0.3	3.8	0.0	23.0	0.6	2.3	1.9	0.2	0.3	·	·	1.8	7.6
Biogenic sources	3.9	0.2	1.1	0.7	3.3	1.4	30.0	0.5	0.7	1.7	0.3	8.4	·	·	1.2	8.1
Total	12.2	1.4	43.3	6.1	28.1	2.5	316.9	3.0	29.3	12.2	2.6	10.3	·	·	27.7	44.7
Overall total	31.1	9.0	73.8	·	63.4	6.0	355.1	·	80.9	344.5	6.1	16.6	·	·	113.7	176.5

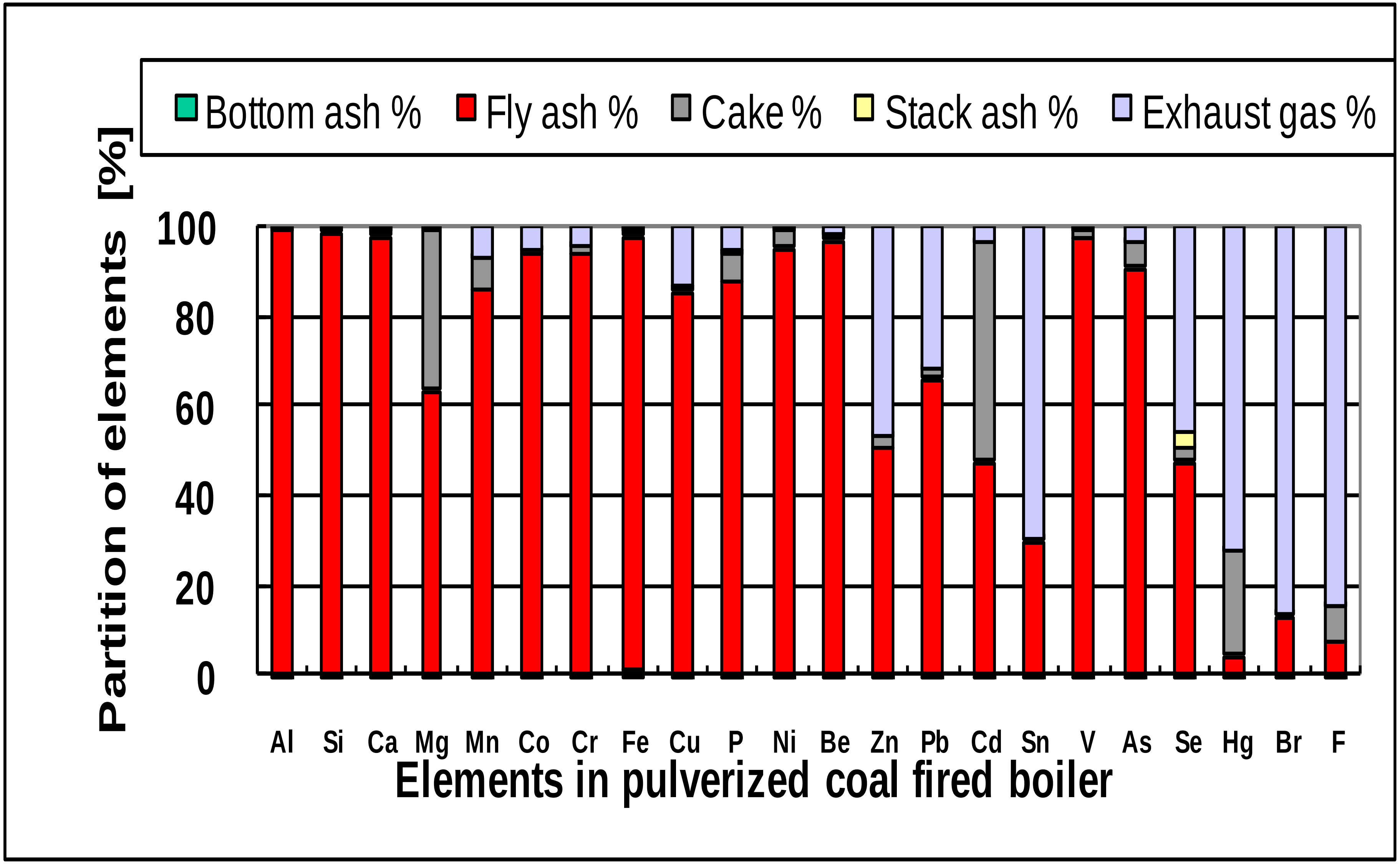
*energy production includes coal, oil, and gas
S includes industrial sources of dust

Health Effect

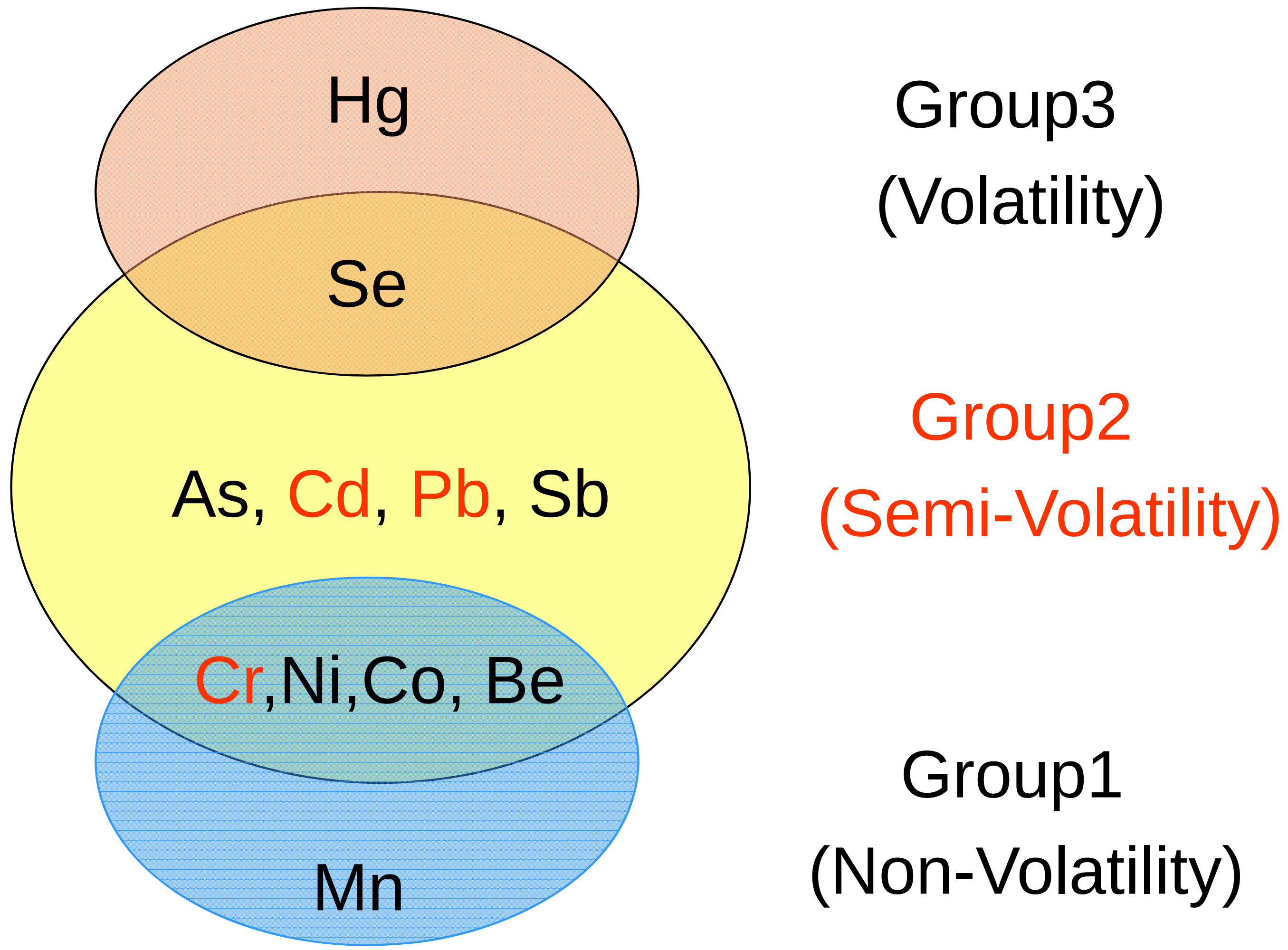
Health effect depens on type of compounds of the metals.

Elements	Adverse effect (at high levels)
Hg	Damage the brain, kidneys, and developing fetus
Se	Cause brittle hair, deformed nails, and loss of feeling and control in the arms and legs
As	Inorganic arsenic can cause death
Cd	Damages the lungs, cause kidney disease, and irritate the digestive tract
Pb	Damage the nervous system, kidneys, and reproductive system
Sb	Irritate the eyes and lungs, cause problems with the lungs, heart, and stomach
Cr	Chromium (VI) damages the nose and cause cancer
Ni	Skin is sensitive to nickel. Developing lung and nasal sinus cancers
Co	Harm the lungs
Mn	Cause damage to the brain, liver, kidneys, and the developing fetus
Be	Lung damage , highly sensitive

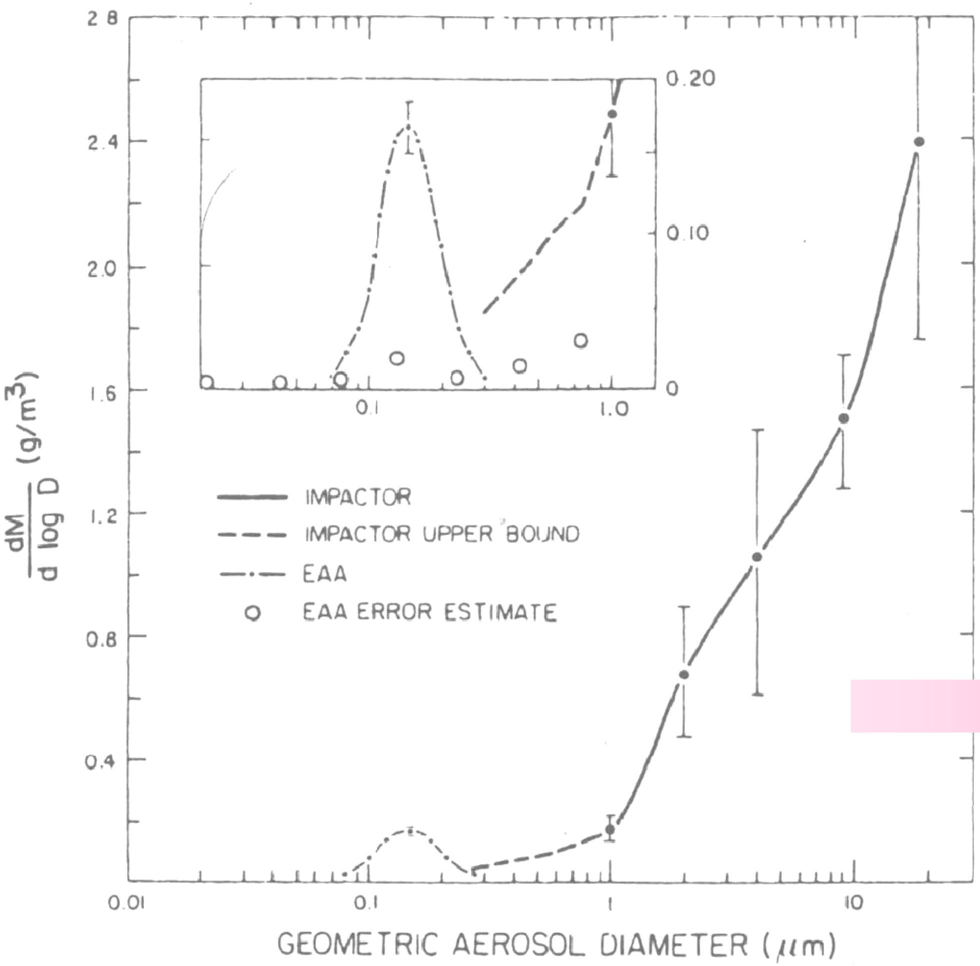
Elements Emission in Plant



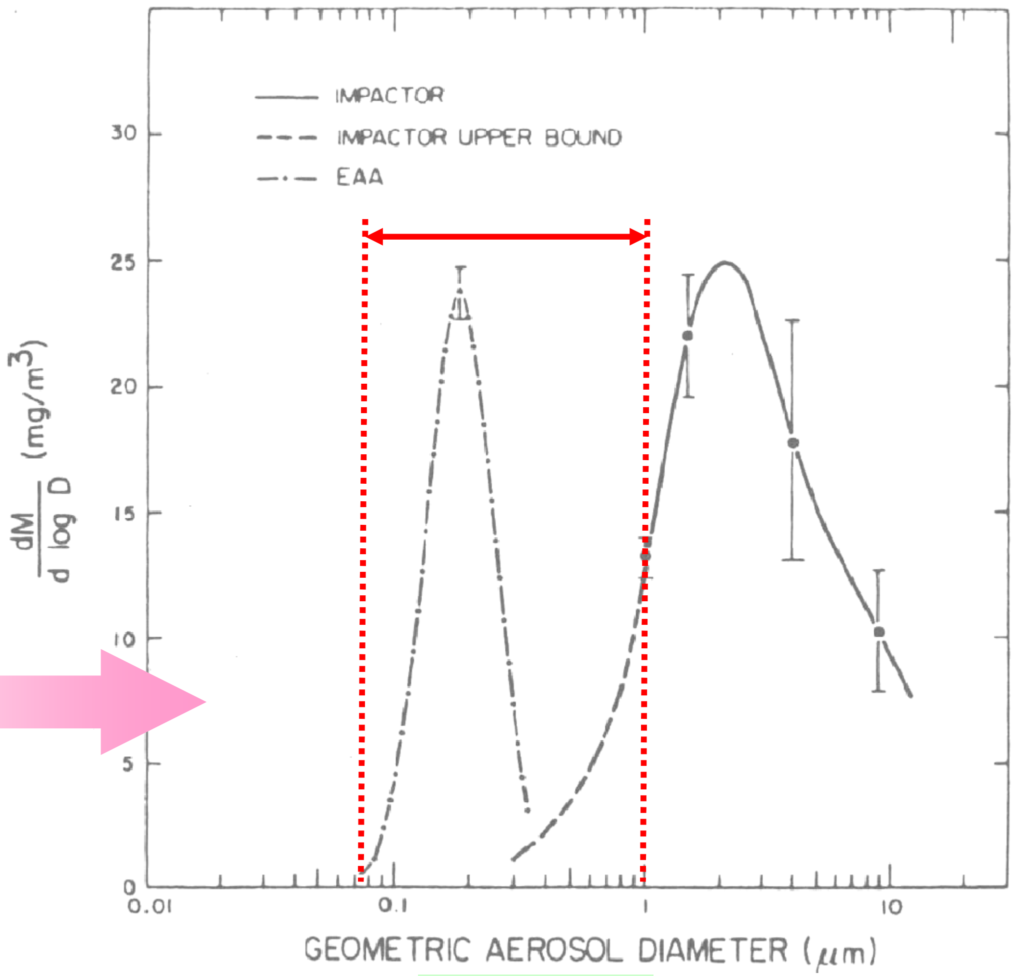
Classification of Trace Metals



Particulate sizes before and after a dust collector



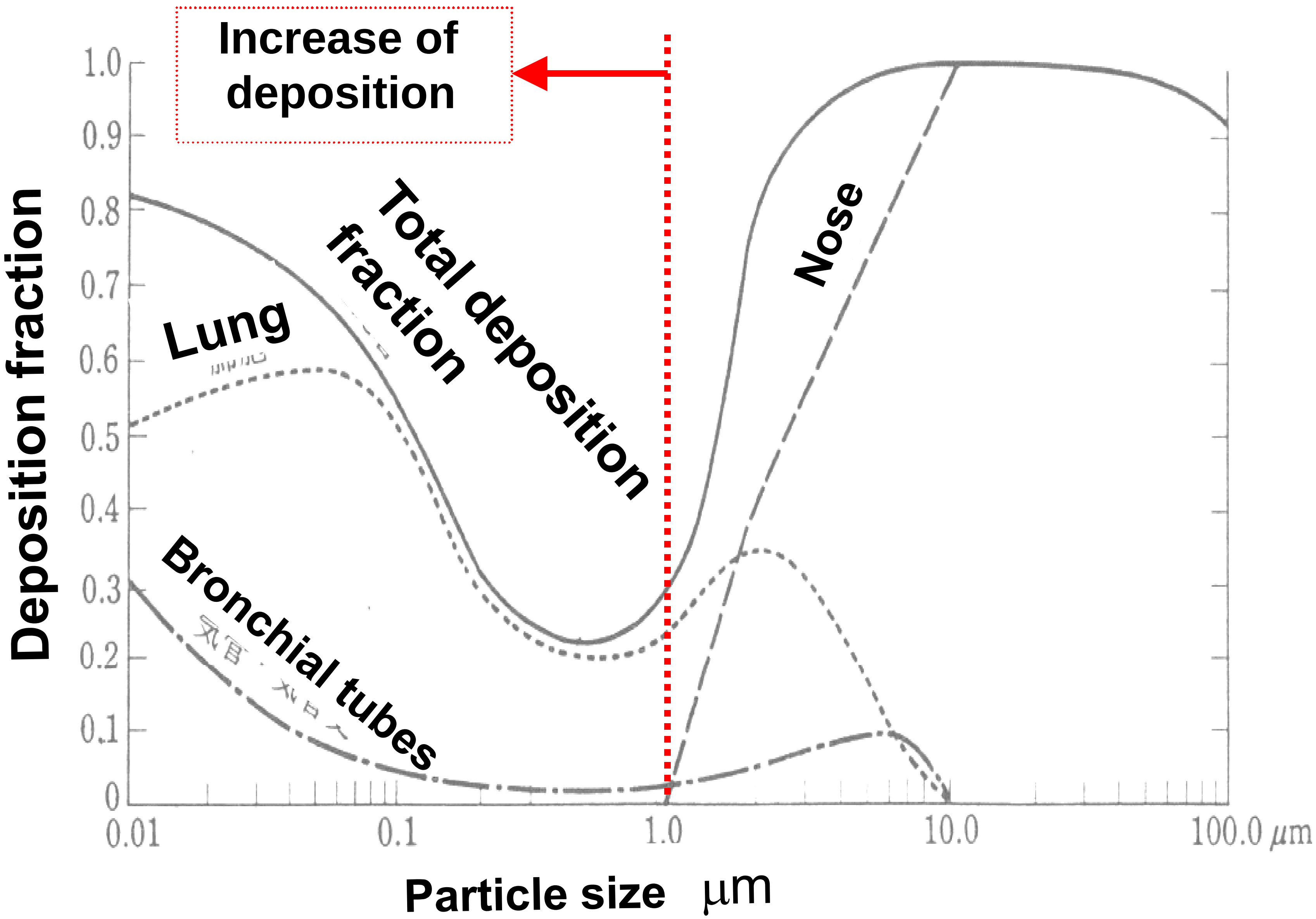
Before



After

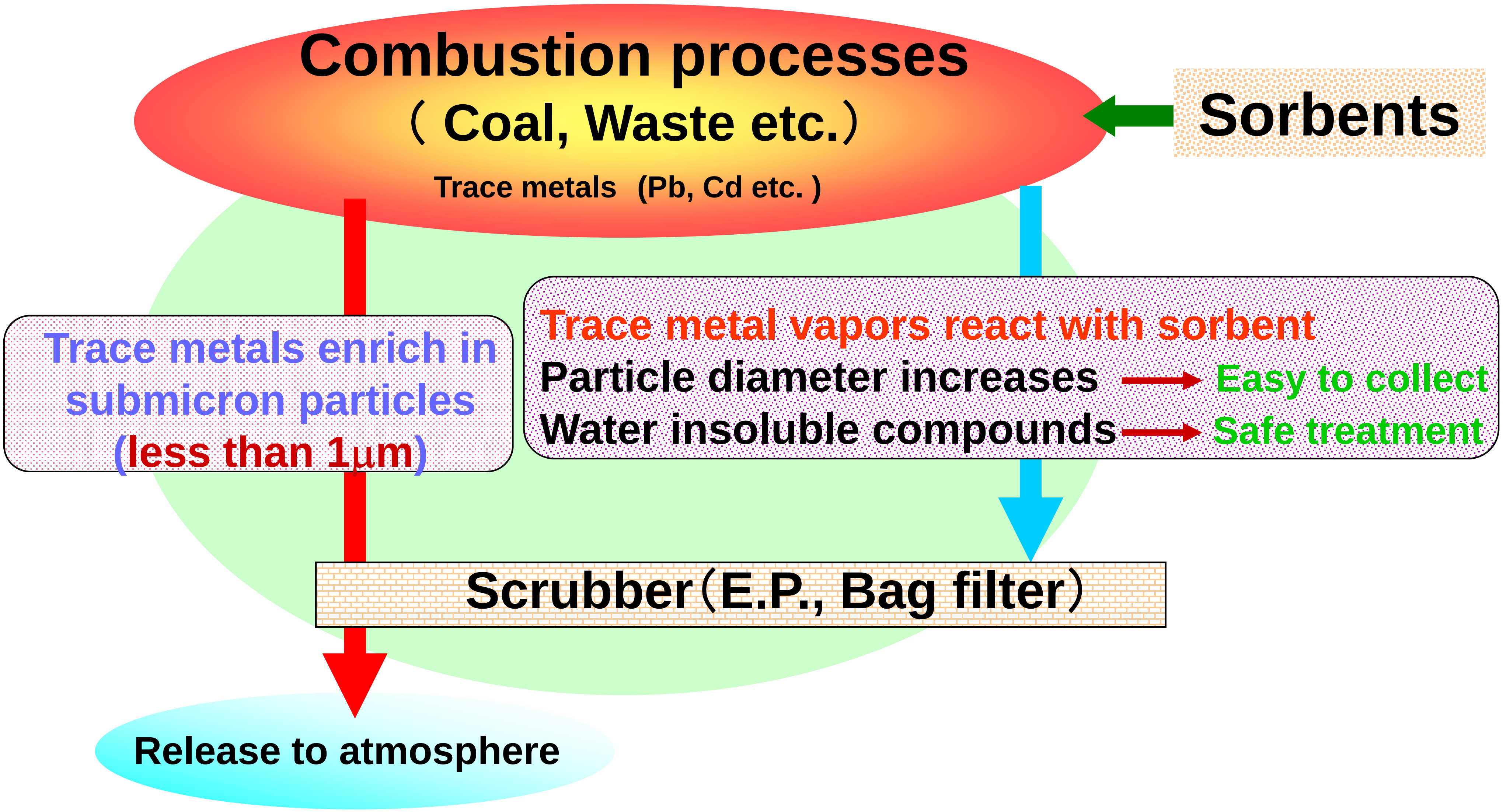
Reference：Markowski, G. R., *et. al., Environmental Science & Technology* (1980)

Deposition of particulate to respiratory organs

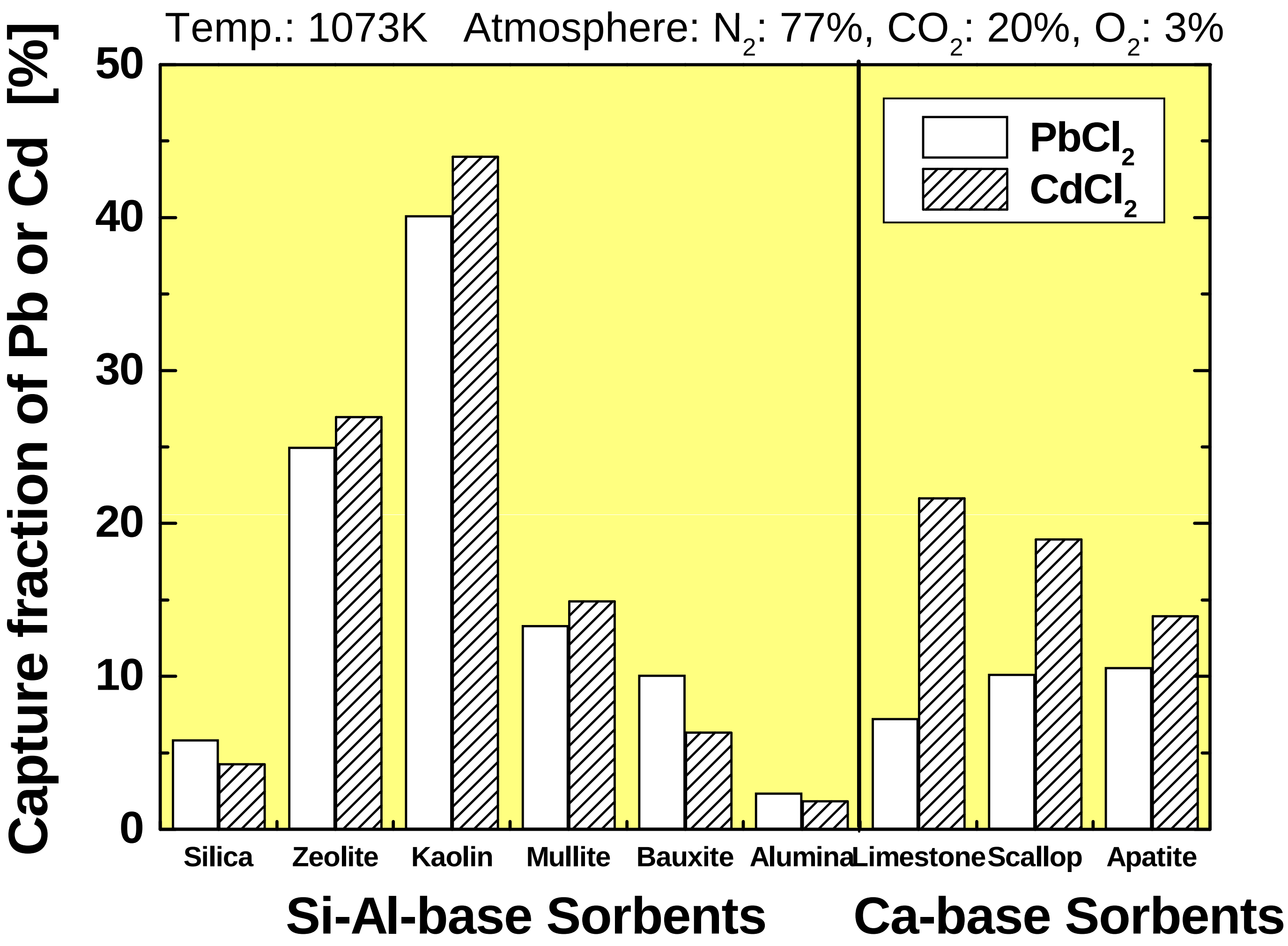


Emission of PM2.5 will be regulated.

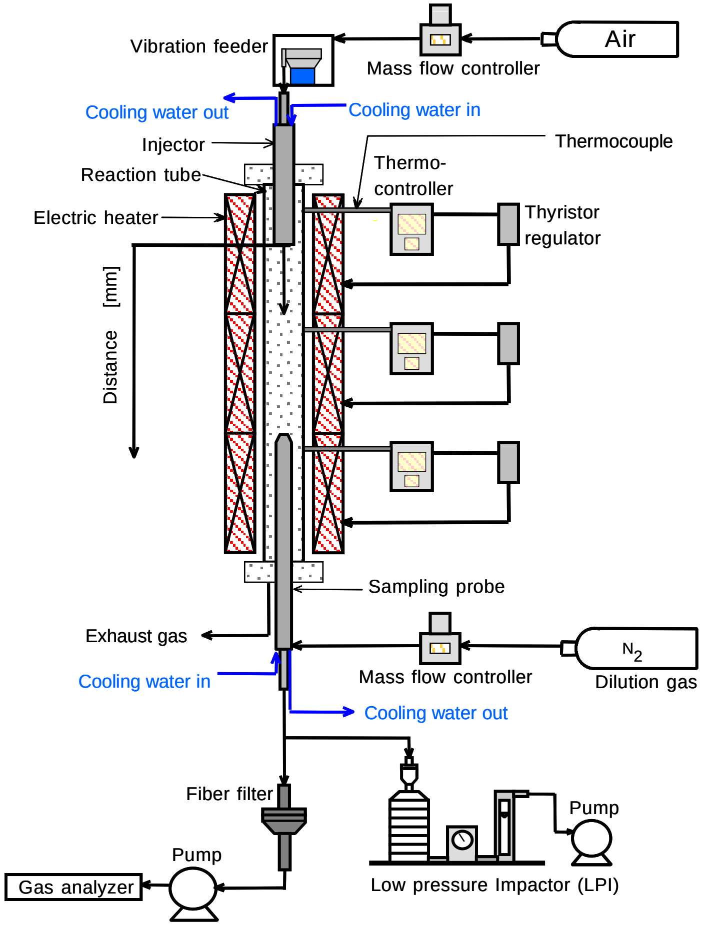
Objectives


Combustion processes
(Coal, Waste etc.)
Trace metals (Pb, Cd etc.)
Sorbents
Trace metals enrich in submicron particles
(less than 1μm)
Trace metal vapors react with sorbent
Particle diameter increases
Easy to collect
Water insoluble compounds
Safe treatment
Scrubber(E.P., Bag filter)
Release to atmosphere

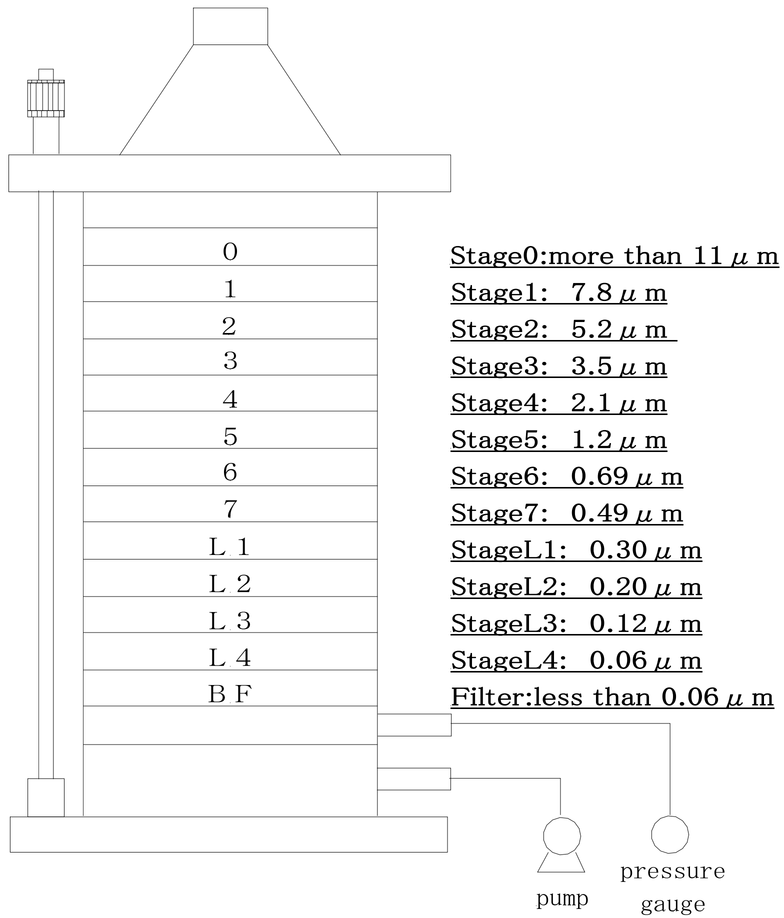
Results: Capture Efficiency



Downflow Furnace and LPI



Drop tube furnace

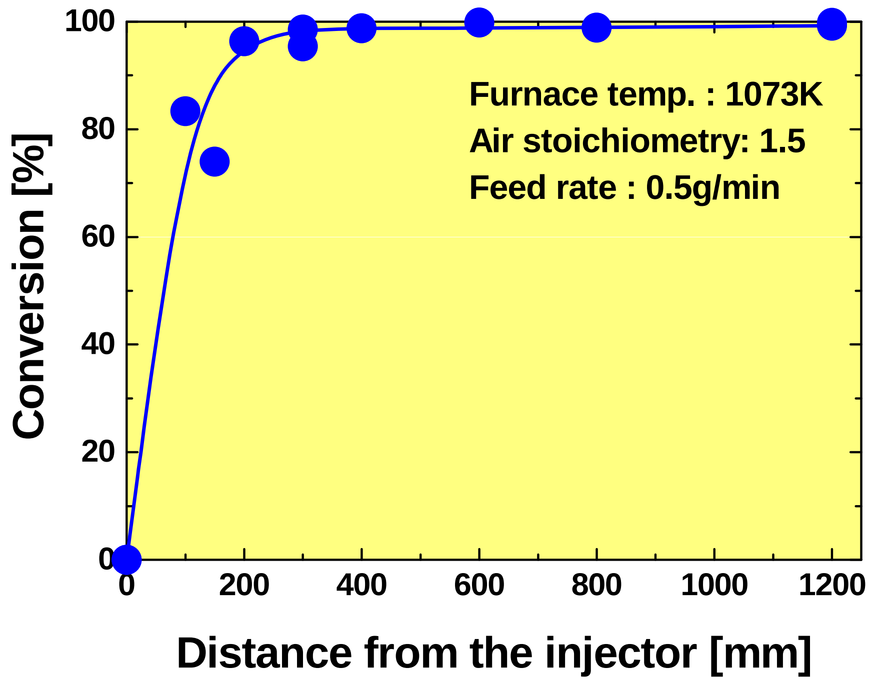


Low pressure impactor (LPI)

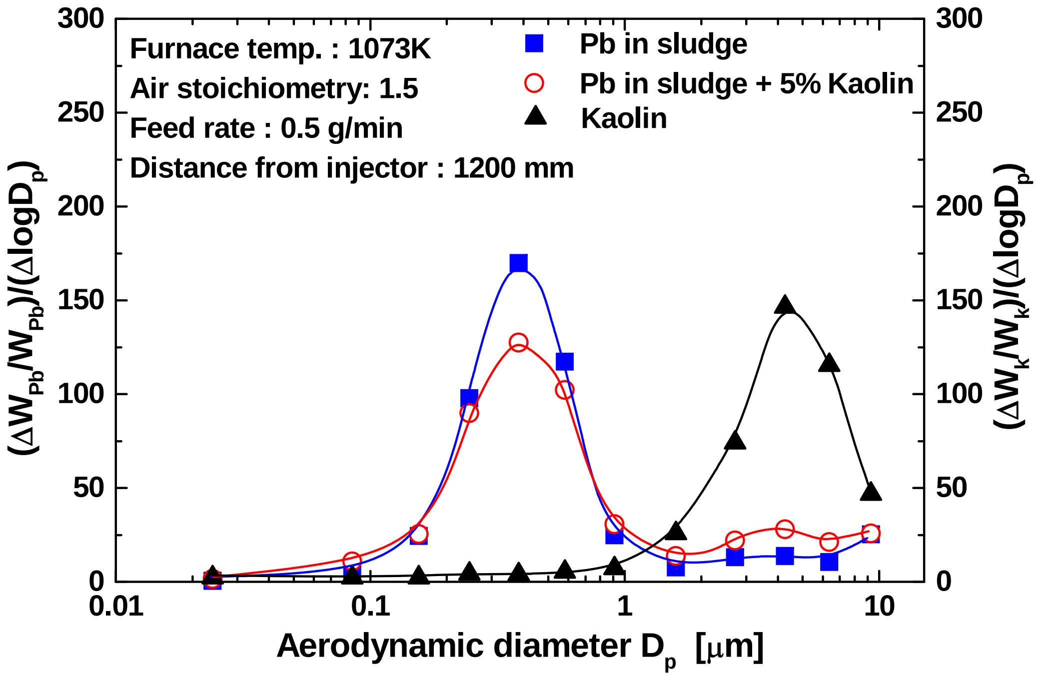
Properties of Sludge & Experimental Conditions

		Sludge
Proximate analysis [mass%,dry]	VM	59.7
	FC	9.1
	Ash	19.8
Ultimate Analysis [mass%,d.a.f]	C	44.96
	H	6.92
	N	6.17
	O	29.43
	S	1.08
	Cl	0.12
Ash Composition [mass%,oxide]	Al_2O_3	26.38
	CaO	2.75
	Na_2O	0.97
	SiO_2	21.96
Trace metals [mg/kg sludge]	Cd	1.7
	Cr	122.2
	Pb	52.0

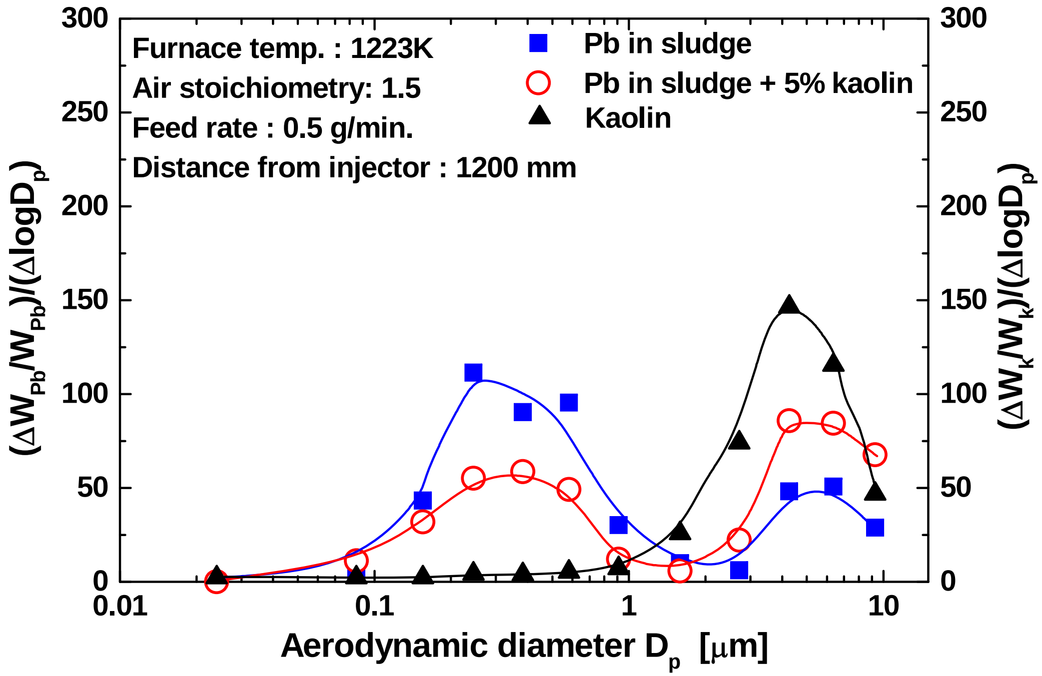
Furnace temperature [K]	1073,1148 1223
Air stoichiometry	1.5
Feed rate [g/min.]	0.5
Sorbent addition	5% of sludge
Kaolin/(Na+K+Pb+Cd)	2.37



Particle Size Distribution of Pb



1073K

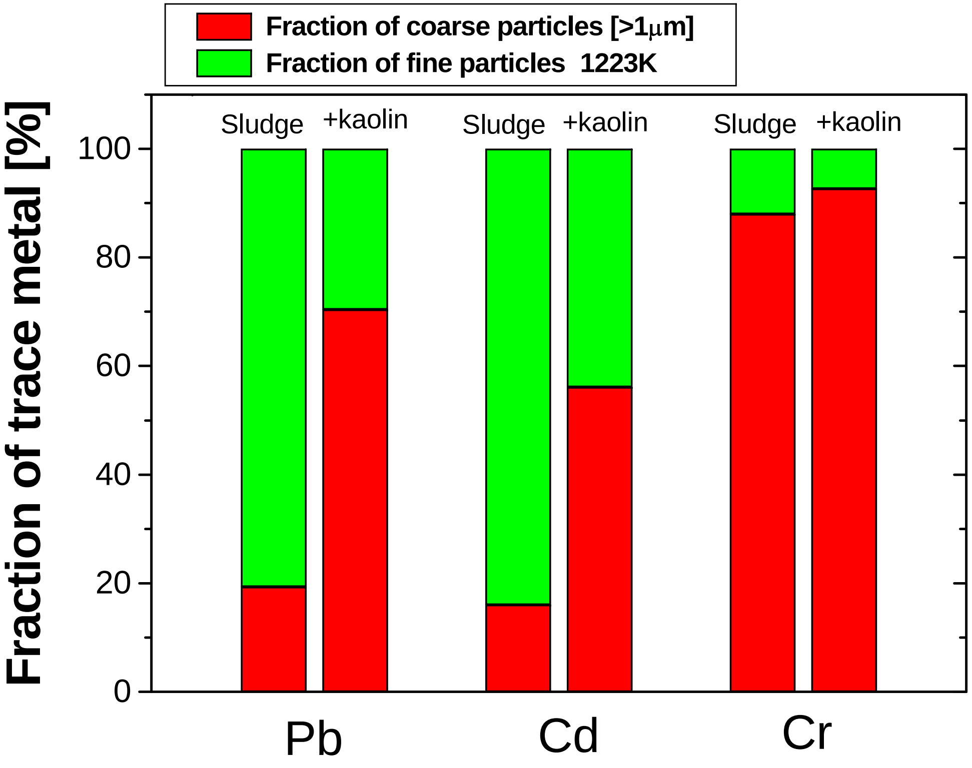


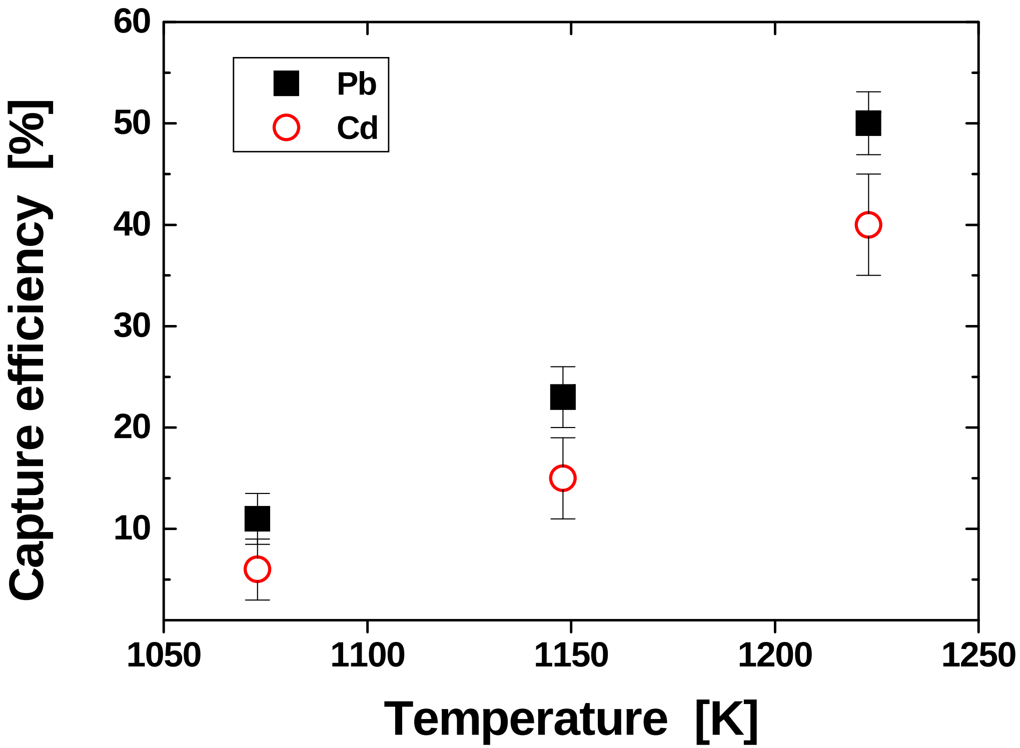
1223K

Capture Efficiency

$$\left(\frac{(W_{>1\,\mu m})_{kaolin\ \ adding} - (W_{>1\,\mu m})_{Sludge}}{W_{Total}}\right) \times 100\ \%$$

W: trace metals mass

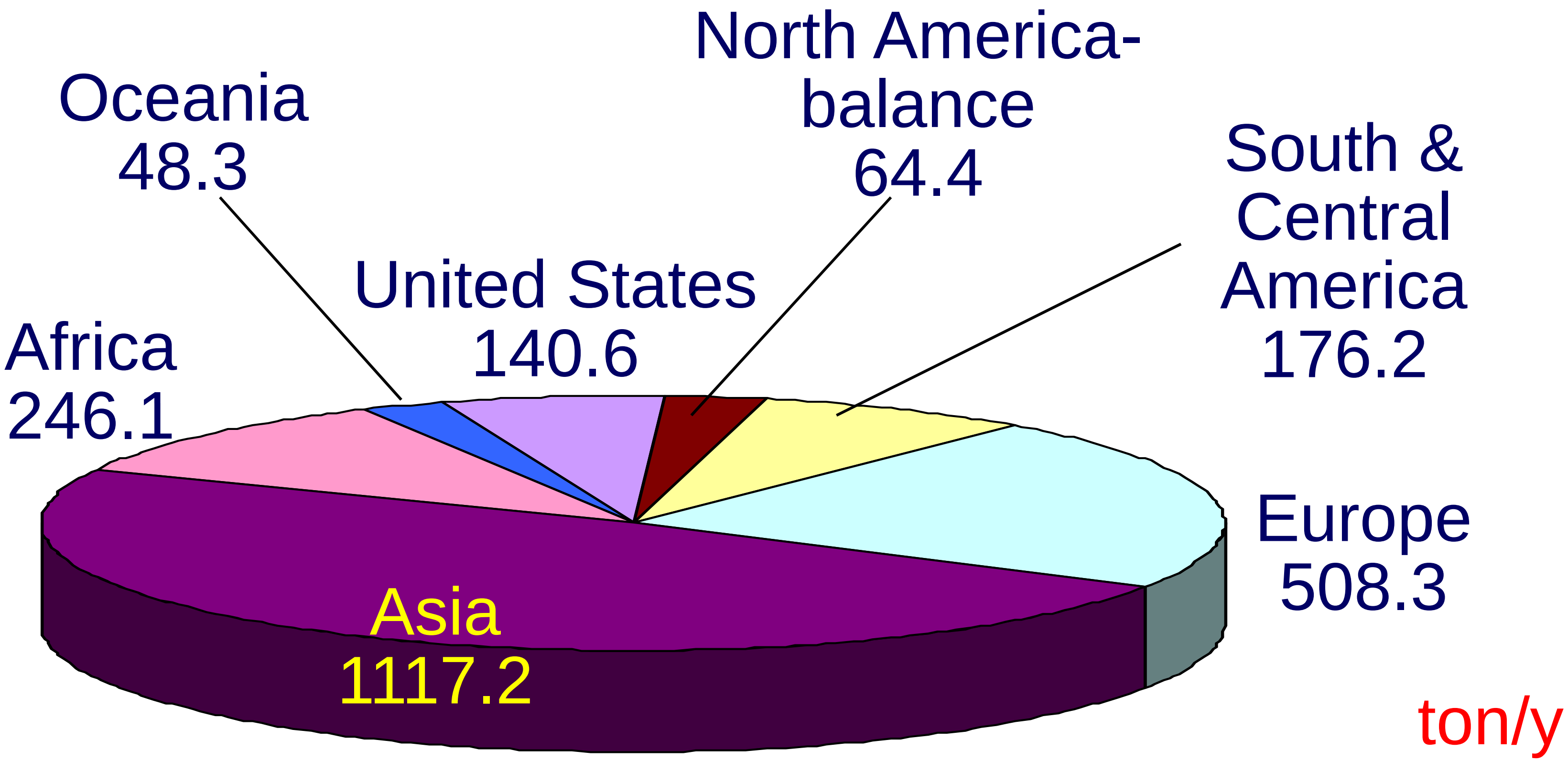




At 1223K

At 1073-1223K

Artificial Mercury Emission [EPRI]

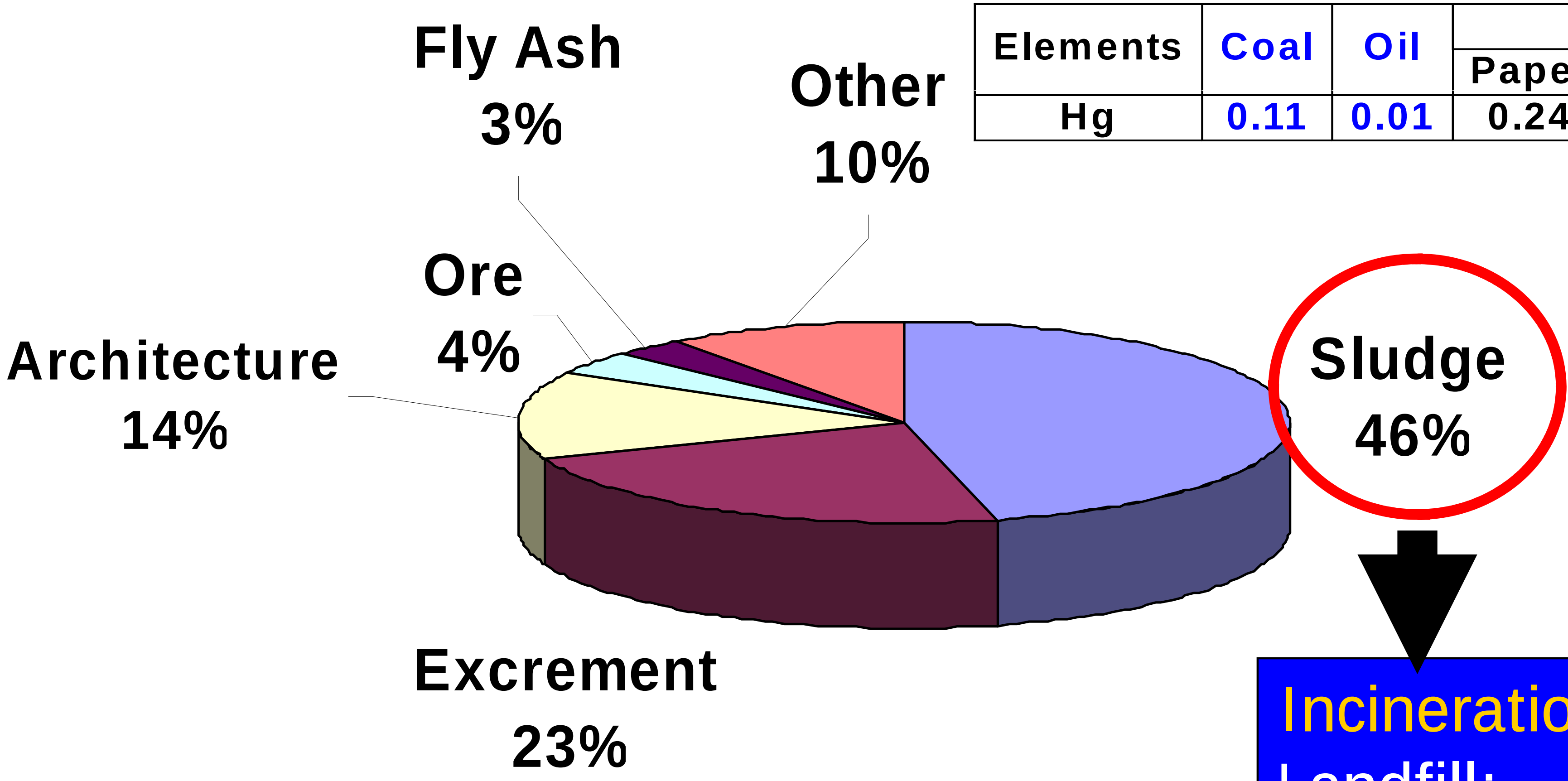


(Fossil fuel combustion and waste incineration)

Situation: Wastes in Japan

Elements	Coal	Oil	Sludge	
			Paper	Municipal
Hg	0.11	0.01	0.24	3.28

[mg / kg fuel]

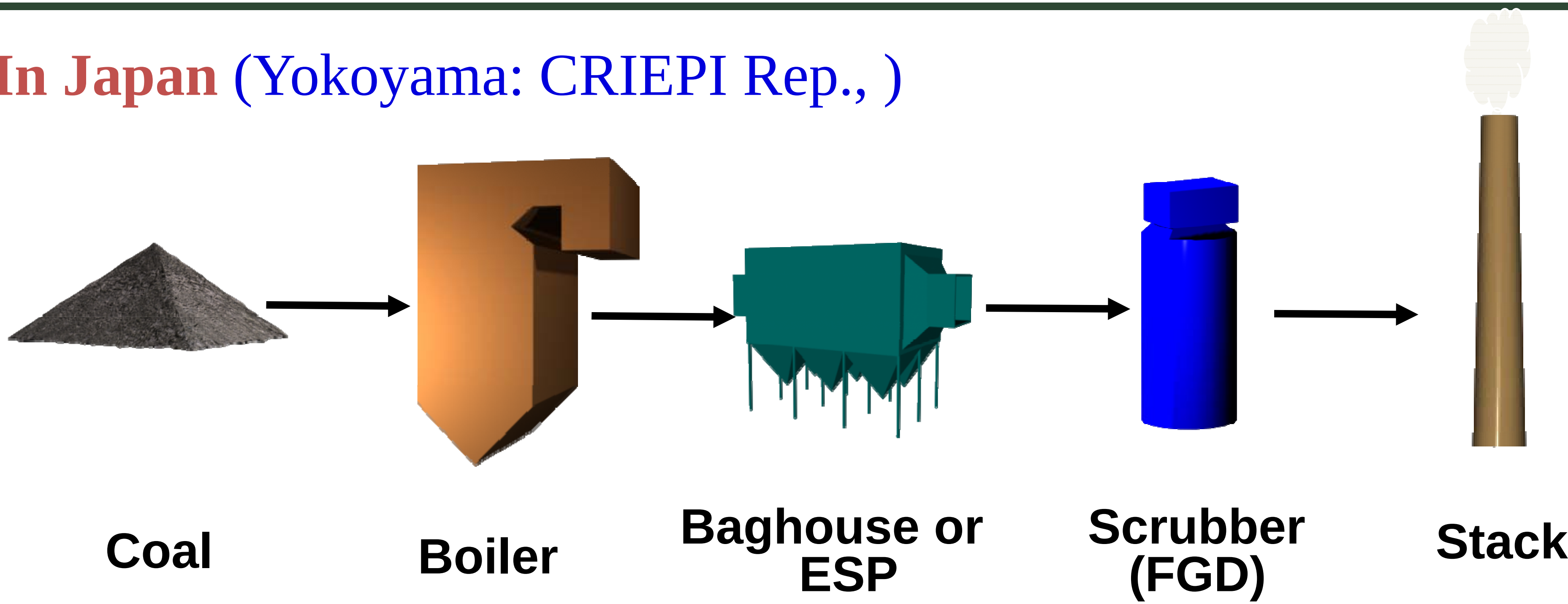


Percent of Wastes
(Environment Report, 2001)

Incineration: 78%
Landfill: 15%
Recycle: 7%
(total: 193.2 million ton/Year)

Mercury emission in pulverized coal fired boiler

In Japan (Yokoyama: CRIEPI Rep.,)



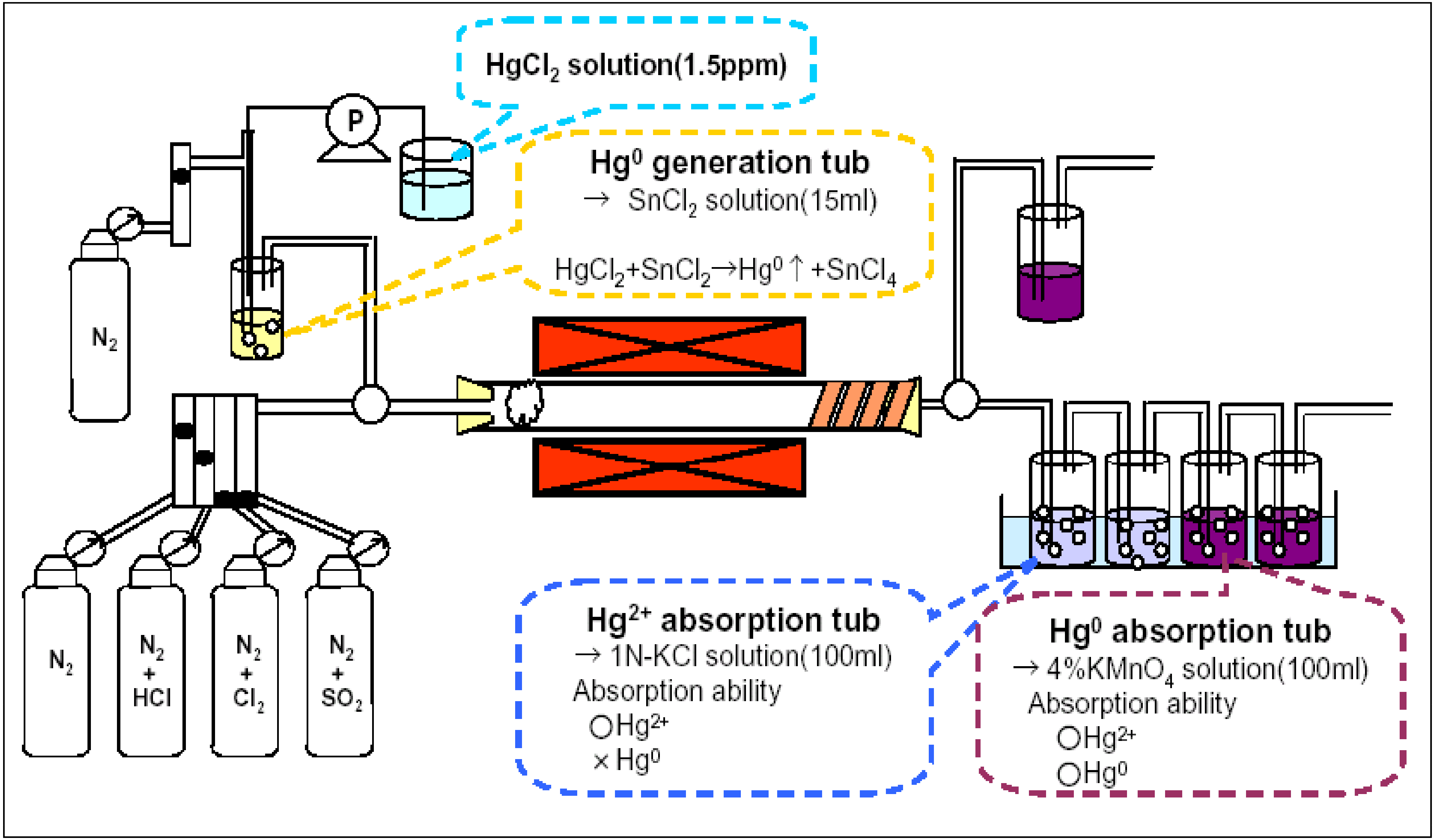
100%	**=**	**0.1% (Hg^{2+})**	**+ 33.3% (Hg^{2+})**	**+ 36.0% (Hg^{2+})**	**+ 30.6% (Hg)**

Objective

✧ Hg Emission

✧ Hg ⟶ Hg^{2+}

Experimental Apparatus for Hg Homogeneous Reactions



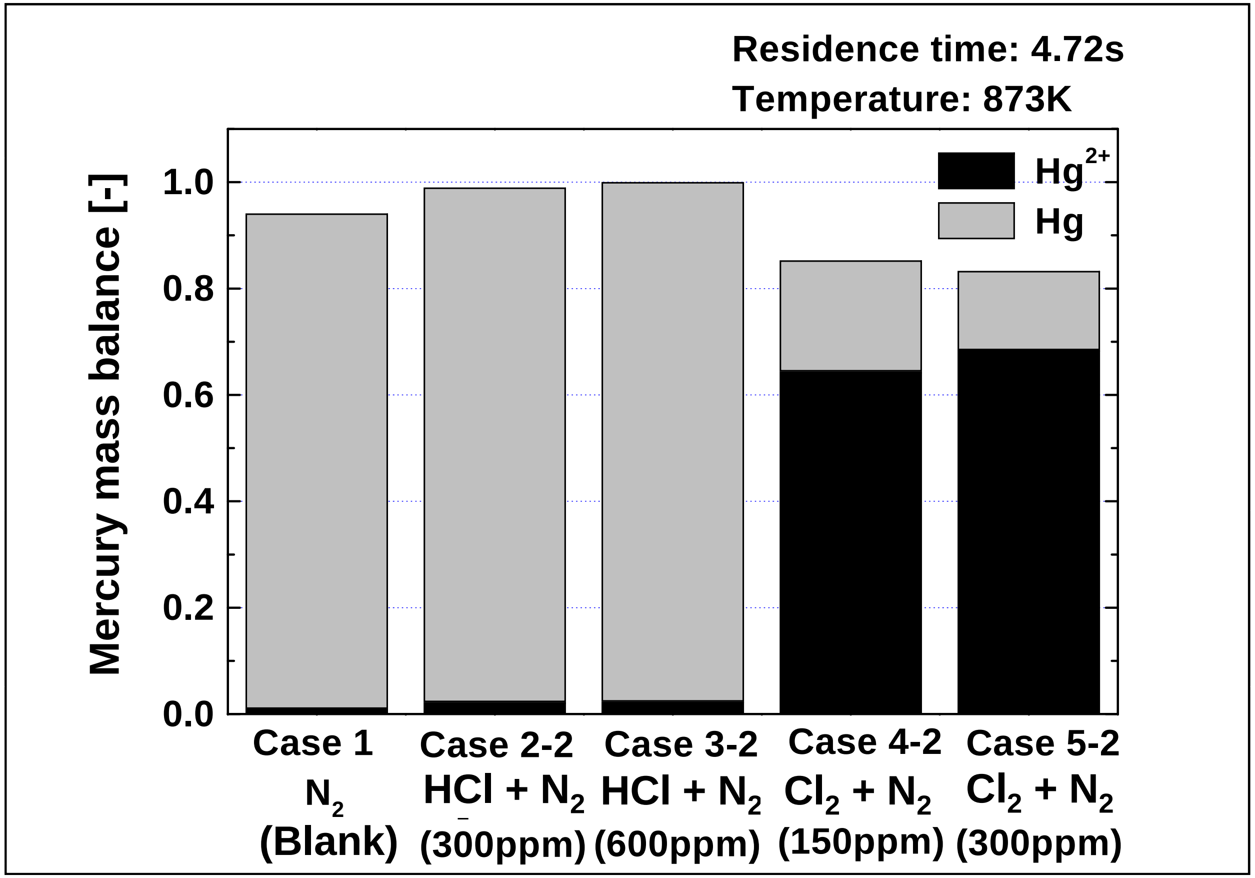
Experimental Conditions

$HgCl_2$ solution concentration [ppm]	1.5
$HgCl_2$ solution flow rate [ml/min]	0.5
N_2 for Hg transportation [l/min]	0.5
Temperature [K]	873
Ribbon heater temperature [K]	423
Experimental time [min]	20
Total atmosphere flow rate [l/min]	1.5
Residence time [sec]	4.72

Reaction Atmospheres

		Hg^0	HCl	Cl_2	H_2O	N_2
Atmosphere composition [mole fraction]	Case 1	3.74×10^{-9}	–	–	5.40×10^{-4}	balance
	Case 2-2	3.74×10^{-9}	3.00×10^{-4}	–	5.40×10^{-4}	balance
	Case 3-2	3.74×10^{-9}	6.00×10^{-4}	–	5.40×10^{-4}	balance
	Case 4-2	3.74×10^{-9}	–	1.50×10^{-4}	5.40×10^{-4}	balance
	Case 5-2	3.74×10^{-9}	–	3.00×10^{-4}	5.40×10^{-4}	balance

Results of Hg Oxidation



Oxidation fraction $HCl + N_2$: < 3% $Cl_2 + N_2$: > 60%

Oxidation Ability $Cl_2 >> HCl$

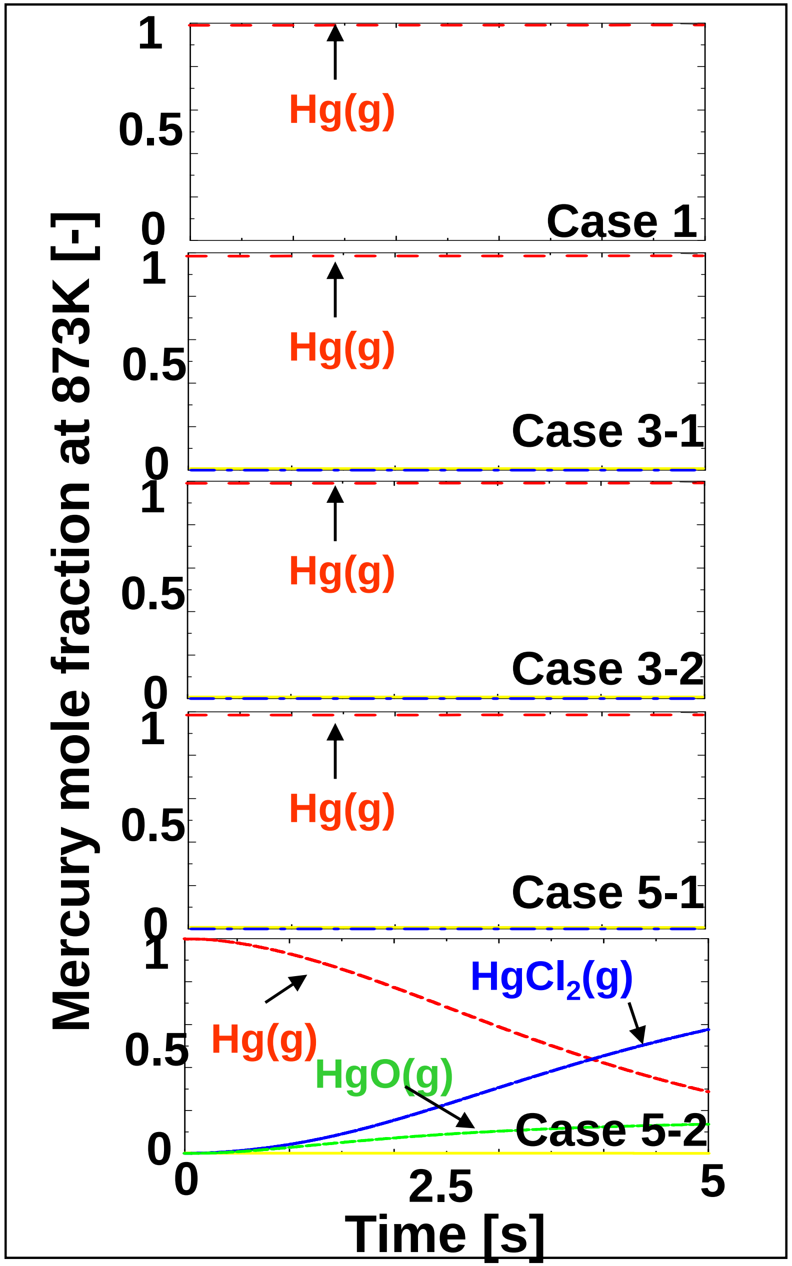
Elementary Reaction Kinetics

Simulation Conditions

	Hg	HCl	Cl_2	H_2O	N_2
Case 1	3.74×10^{-9}	-	-	5.40×10^{-4}	balance
Case 3-1	3.74×10^{-9}	6.00×10^{-4}	-	-	balance
Case 3-2	3.74×10^{-9}	6.00×10^{-4}	-	5.40×10^{-4}	balance
Case 5-1	3.74×10^{-9}	-	3.00×10^{-4}	-	balance
Case 5-2	3.74×10^{-9}	-	3.00×10^{-4}	5.40×10^{-4}	balance

Elemental Reactions

Reaction	A (cm^3/mol-sec)	n	E(cal/mol)	Reference
1. $Hg+Cl+M \leftrightarrows HgCl+M$	9.49×10^{14}	0.5	0	Niksa
2. $Hg+Cl_2 \leftrightarrows HgCl+Cl$	2.30×10^{12}	0	1599	Helbel
3. $Hg+HOCl \leftrightarrows HgCl+OH$	1.43×10^{13}	0	12790	Helbel
4. $Hg+HCl \leftrightarrows HgCl+H$	2.20×10^{8}	0	1756	Gaspar
5. $HgCl+Cl_2 \leftrightarrows HgCl_2+Cl$	1.48×10^{12}	0	37250	Helbel
6. $HgCl+HCl \leftrightarrows HgCl_2+H$	4.94×10^{14}	0	21500	Widmer
7. $HgCl+Cl+M \leftrightarrows HgCl_2+M$	1.16×10^{14}	0.5	0	Niksa
8. $HgCl+HOCl \leftrightarrows HgCl_2+OH$	4.27×10^{13}	0	1000	Widmer
9. $Hg+ClO \leftrightarrows HgO+Cl$	1.38×10^{12}	0	8320	Xu
10. $Hg+ClO_2 \leftrightarrows HgO+ClO$	1.87×10^{7}	0	51270	Xu
11. $Hg+O_3 \leftrightarrows HgO+O_2$	7.02×10^{14}	0	42190	Xu
12. $Hg+N_2O \leftrightarrows HgO+N_2$	5.08×10^{12}	0	59810	Xu
13. $HgO+HCl \leftrightarrows HgCl+OH$	9.63×10^{4}	0	8920	Xu
14. $HgO+HOCl \leftrightarrows HgCl+HO_2$	4.11×10^{13}	0	60470	Xu



$H_2O + N_2$(Case 1)
⇒ $Hg^0(g)$

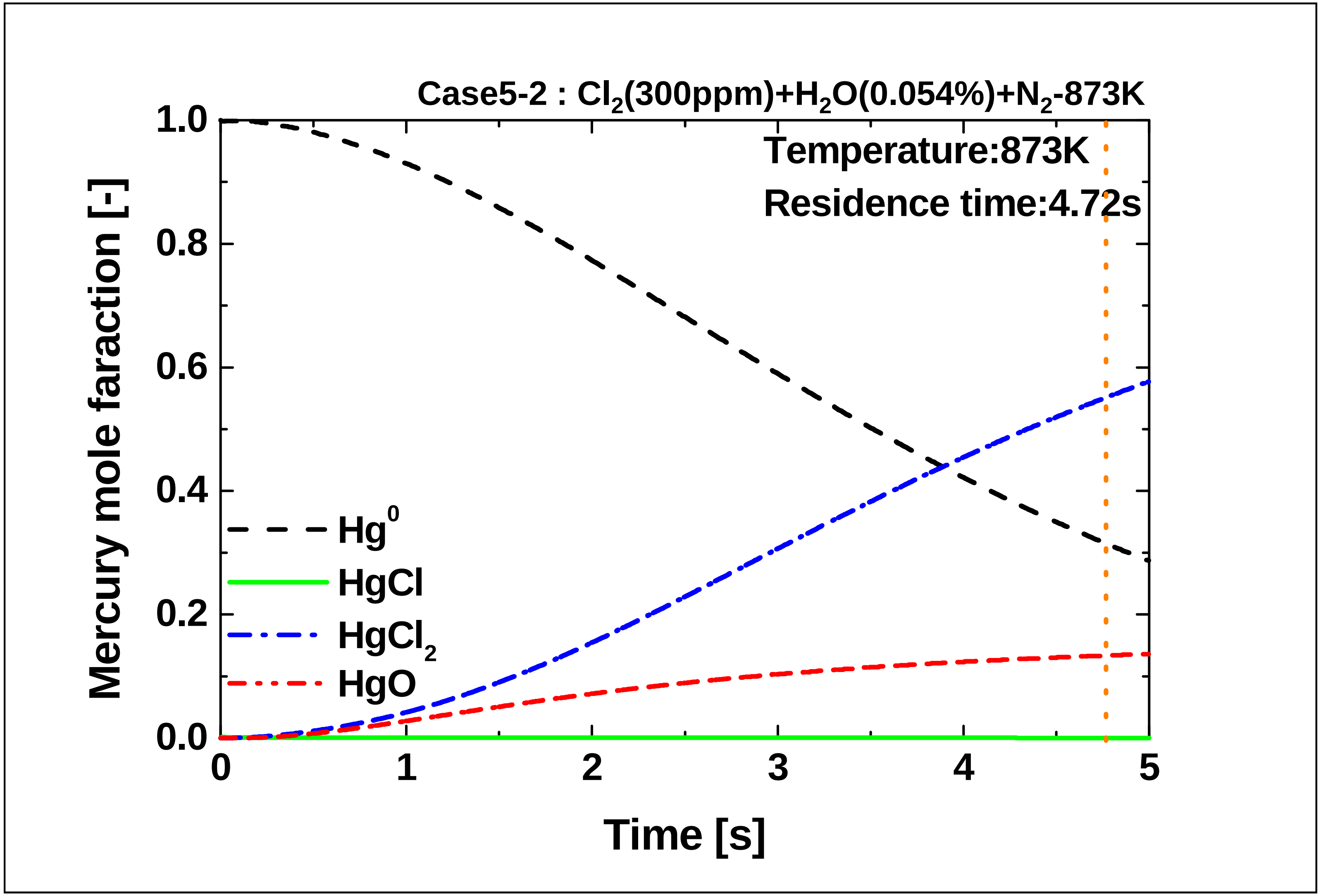
$HCl + N_2$(Case 3-1)
⇒ $Hg^0(g)$

$HCl + H_2O + N_2$(Case 3-2)
⇒ $Hg^0(g)$

$Cl_2 + N_2$(Case 5-1)
⇒ $Hg^0(g)$

$Cl_2 + H_2O + N_2$(Case 5-2)
⇒ $HgCl_2(g)$, $HgO(g)$, $Hg^0(g)$

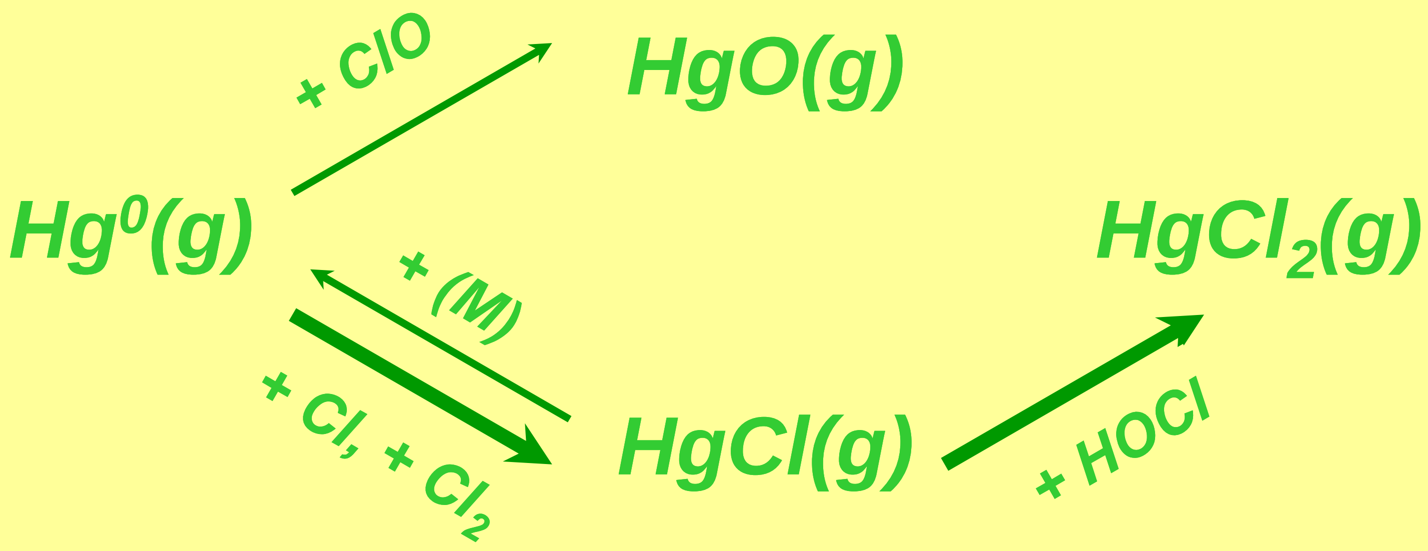
Example of Simulation Result



Oxidized Mercury: $HgCl_2$(<60%), HgO(>10%)

Oxidization Fraction: 70% ⇔ Experimental: 60%

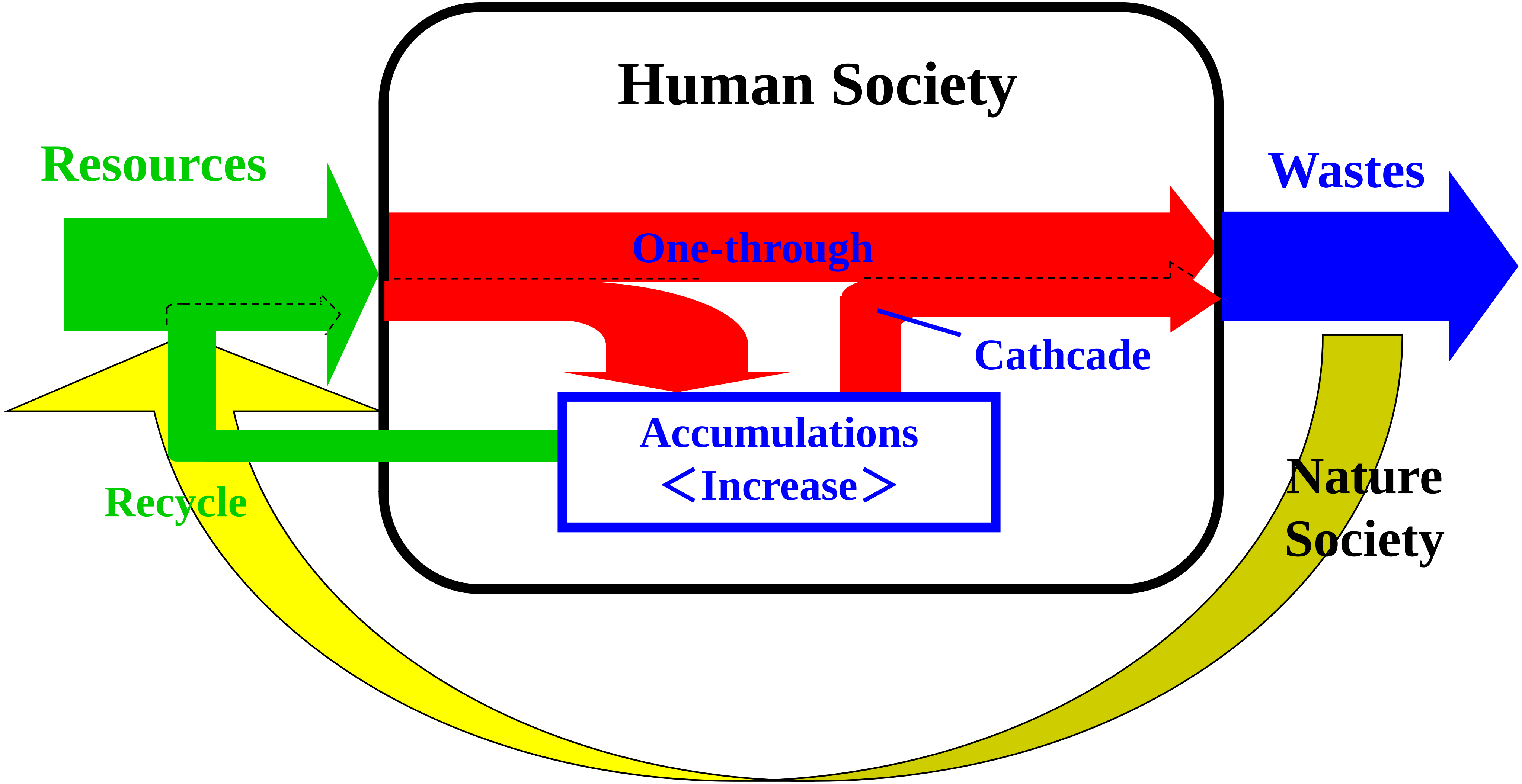
Reaction Scheme



At 873 K

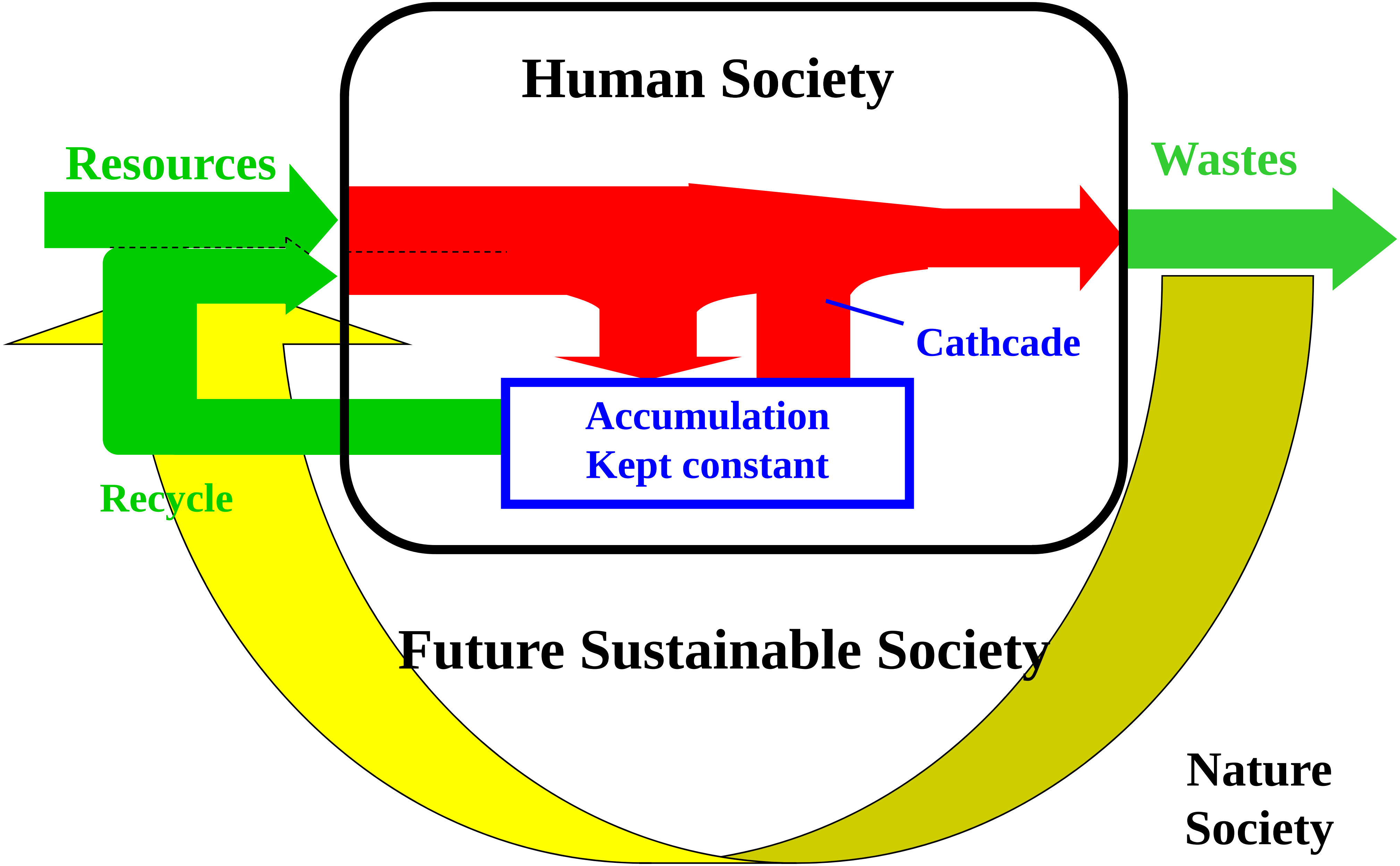
5) What do we have to do in the near future?

Present Society



Degradation of grand cycle

Revival of Grand Cycle



Earth Calendar

Earth was born before 4.6 billion years(46億年)

Time when Earth was born: at 0:00 on January 1st
Present: at 24:00 on December 31st

Middle of February (40億年前) : Life was born
End of June (24億年前) : O_2 was produced(Photosynthesis)
November 23rd (４億６千年前) : Plants & Insects were appeared on the ground
December 14th (２億年前) : Dinosaurs were born
December 26th (6,500年前) : End of Dinosaurs period
Evening in December 26th (5,500年前) : Primates(霊長類) were born

Evening in December 30（600万年前）：
Original of human was born

December 31st

23:59 Chinese Civilization

23:59:40 Egyptian Civilization

23:59:59 1867 (The Meiji Resroration)