GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA, INDUSTRIA Y COMPETITIVIDAD
Ciemat
Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

ASSESS OF BIOMASS CO-FIRING UNDER OXY-FUEL CONDITIONS ON HG SPECIATION AND ASH DEPOSIT FORMATION

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IEA CLEAN COAL CENTRE

The eighth international conference on Clean Coal Technologies

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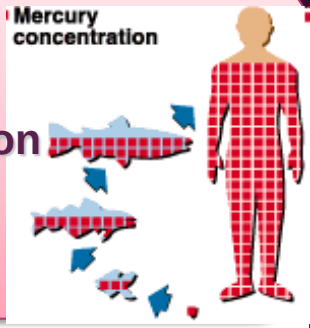
ENVIRONMENTAL CONCERNS

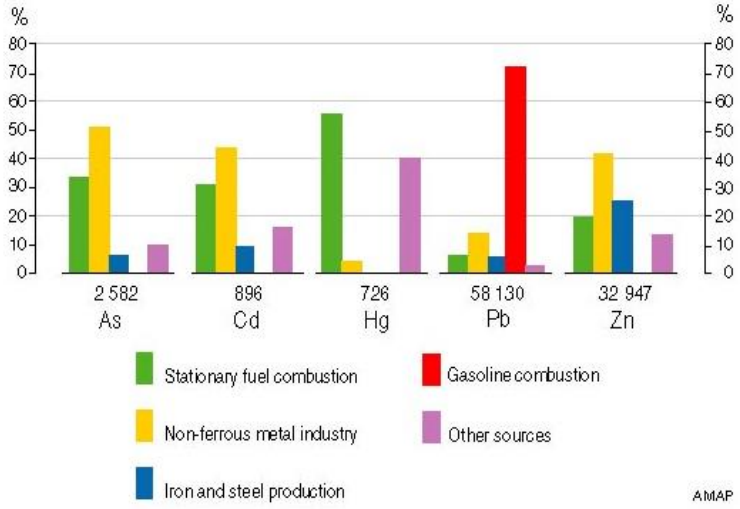
COAL-FIRED POWER STATIONS

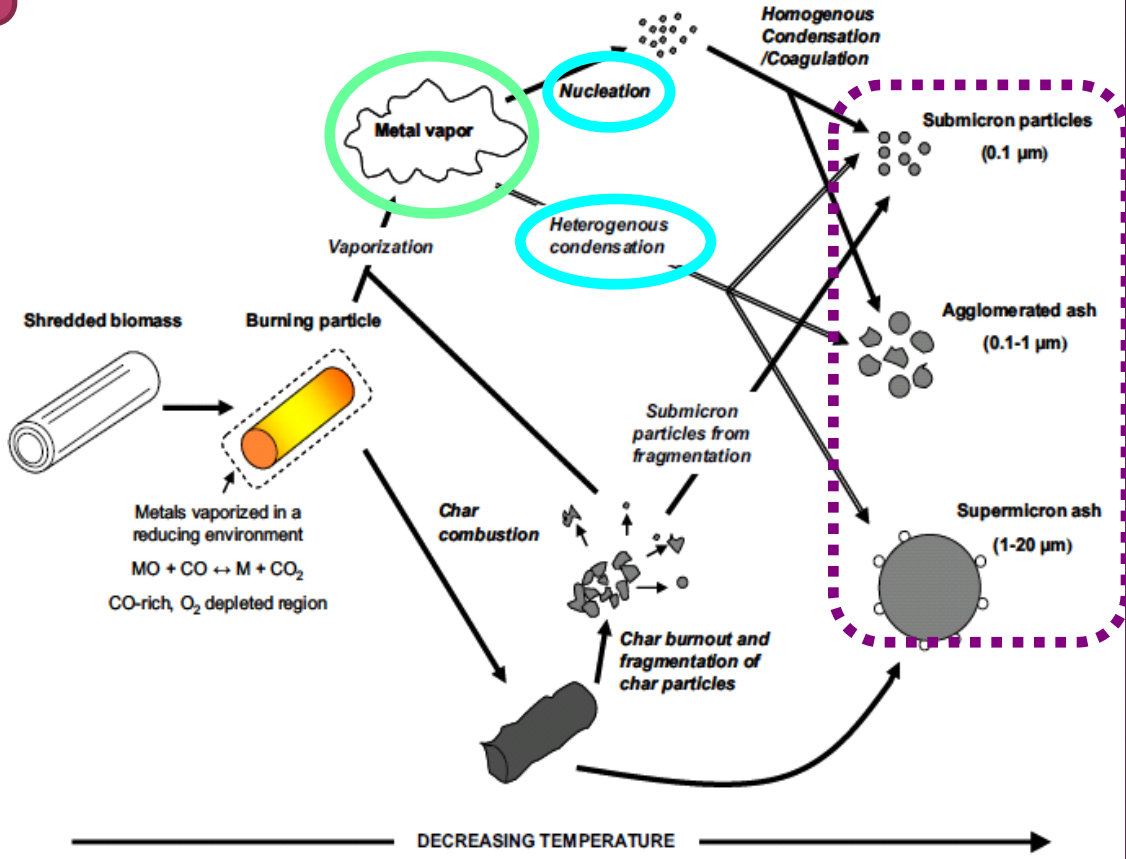
ANTHROPOGENIC TES EMISSIONS

- **Volatility**
- **Persistence** → **Bioaccumulation**
- **Toxicity** → **Health impacts**



Atmospheric emissions of TEs selected in Europe (tons/ year).



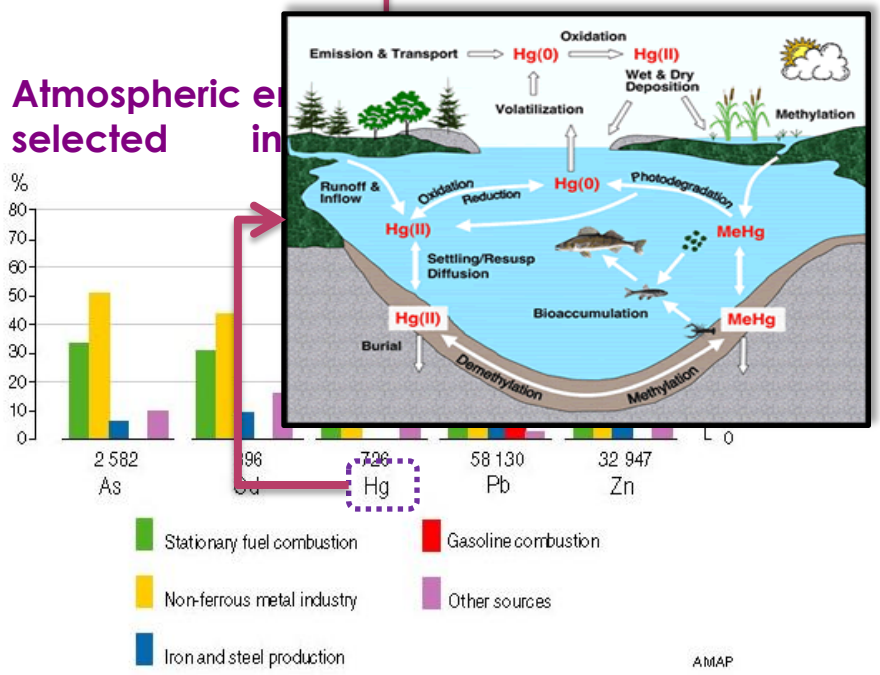


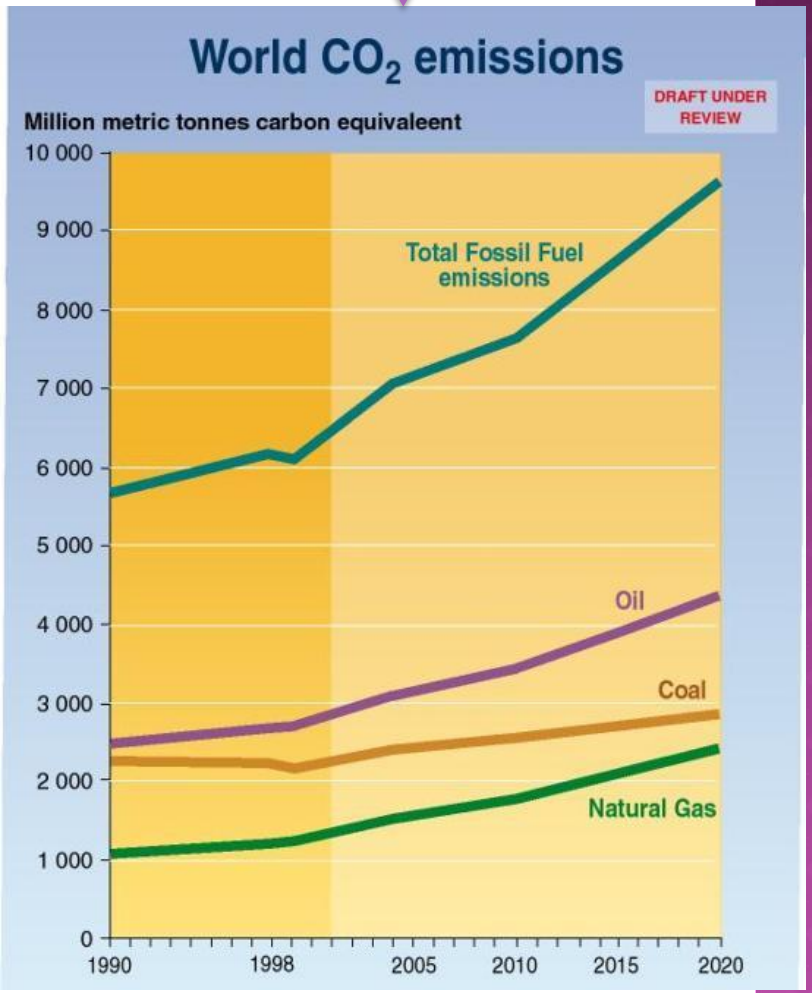
ENVIRONMENTAL CONCERNS

COAL-FIRED POWER STATIONS → **CO_2 EMISSIONS**

ANTHROPOGENIC TES EMISSIONS

Atmospheric e
selected in





❑ CURRENT CO_2 CAPTURE APPROACHES

- ✓ Post-Combustion Capture.
- ✓ Pre-Combustion Capture
- ➢ **Oxy-fuel Combustion CO_2 Capture Systems**

➢The system uses oxygen rather than air for the combustion of coal

➢Combustion produces flue gas that is mainly water vapor and CO_2

➢Flue gas has a relatively high CO_2 concentration (greater than 80% by volume)

➢**CO_2 is separated** from the water vapor by cooling and compressing the flue gas

- **Biomass** fuel is renewable and CO_2-neutral.
- **Combination of oxy-fuel combustion with biomass** fuels:
  - Become a CO_2 sink for power plants
  - Ignition; Excess of heat control

Lower NO_x and SO_x emissions

TMs?

Ash deposition, corrosion?

Objectives

Evaluate the effect of **biomass addition** in **oxy-fuel combustion** processes on:

- Hg fate and speciation.
- Ash quality (fouling and corrosion processes)

Scope of work

- Modellization of *Hg speciation in gas and solid phase,* in fluidized bed combustion (FBC), under different atmosphere compositions (O_2 /N_2 and O_2+ CO_2 mixtures), and for different fuel compositions.
- Experimental tests at the **BFB reactor**:
  - *Hg partitioning* in the different out-coming streams
  - *Hg speciation in flue gas.*

  → during coal/biomass cofiring, under different oxy-atmospheres.

- Analysis of the influence of oxy-fuel combustion on *ash quality and deposits* formation processes, in comparison to a conventional combustion process.

❑ Fuels Analysis.

Samples	Puertollano Coal (Pu)	Thistle (Th)
Proximate analysis (% as received basis)		
Moisture	4.0	5.5
Ash	33.5	5.0
Volatile matter	24.5	74.5
Ultimate analysis (% dry basis)		
C	49	44
H	3.8	6.2
N	1.0	0.70
S	**0.71**	0.19
O	12	42
Cl	0.070	**1.3**
Calorific value (MJ/kg)		
HHV, w.b.	18.91	16.75
HHV, d.b.	19.70	17.73
LHV, w.b.	17.95	15.28
Ash analysis (g/ Kg, as received)		
Na	0.70	**6.0**
K	4.2	**8.7**
Ca	4.6	9.2
Mg	2.5	2.1
Al	41	0.70
Fe	26	0.60
Si	98	0.030
Trace metals (µg/g)		

Fuels selection

Attending:

- Sulphur
- Alkaline compounds
- Hg content

Milestone DMA-80 Direct Mercury Analyzer

- Thermal decomposition.
- Catalytic conversion.
- Amalgamation.
- Atomic absorption spectrophotometry

❑Thermodynamical Equilibrium Calculations.

*HSC Chemistry 6.1: Minimizing Gibbs free energy

Schema of the equilibrium reactor.

Fuel composition (analysis)

✓C, H, O, N, S, Cl.

✓Si, Al, Ca, Fe, Mg, Na, K.

✓TEs

❑ Combustion atmospheres:

✓ Air: 21%O_2/79%N_2.
✓ Oxy-firing: 21% O_2/ 79% CO_2.
✓ Oxy-firing: 30% O_2/ 70% CO_2.
✓ Oxy-firing:: 40% O_2/ 60% CO_2.

❑ T= 200- 1200ºC, special attention,

➢800- 900º C, FB reactor

➢300- 400ºC, operation temperature at particulate control devices.

Equilibrium Reactor

T

P

Gas phase

Condensed phases

- Amount
- Composition

MATRIX FOR MERCURY THEORETICAL STUDIES

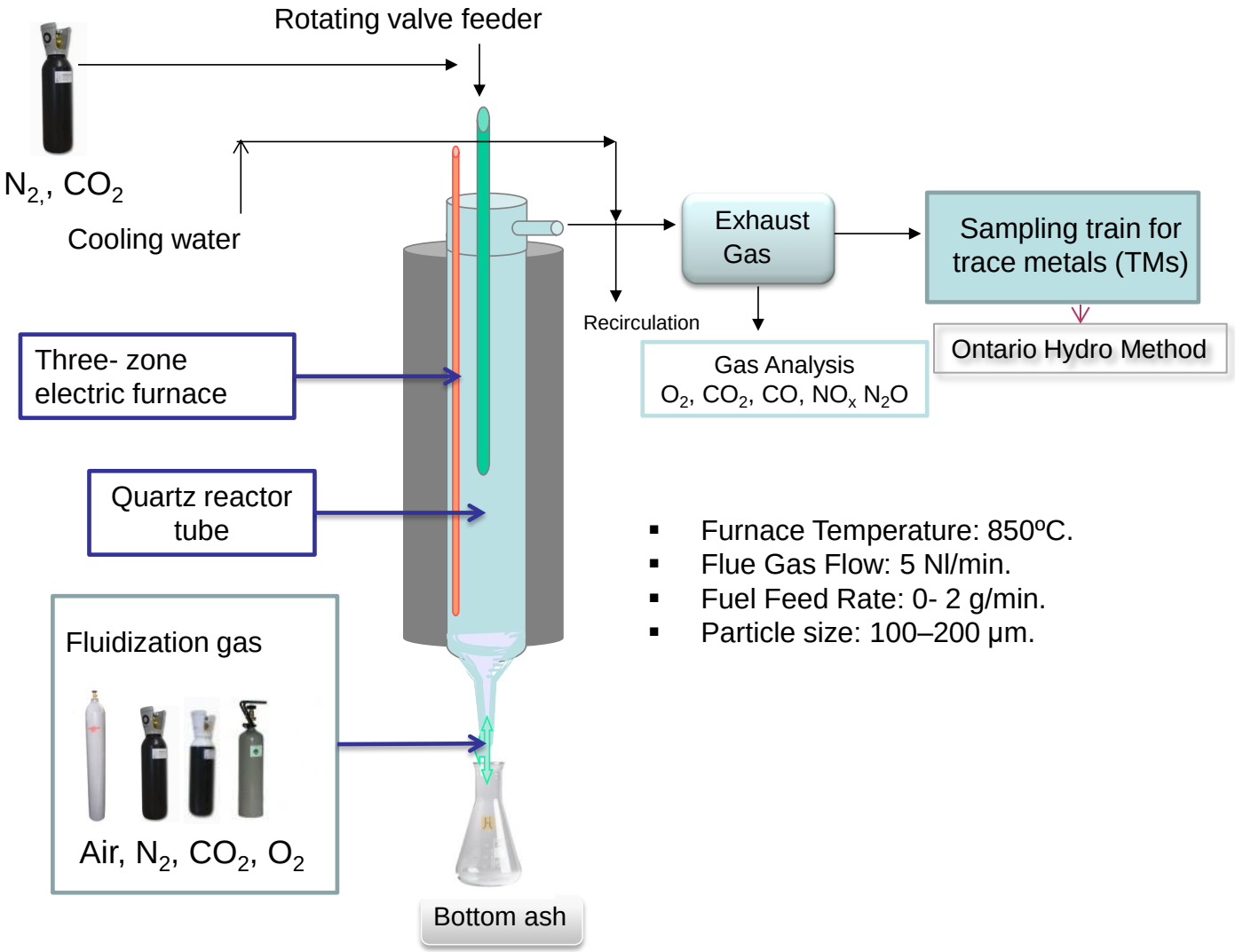
	21%O_2/79%N_2	30%O_2/ 70% CO_2	40%O_2/ 60% CO_2
100% Puertollano Coal	PU-AIR	PU-OX30	PU-OX40
75/25% Coal/Thistle	PU75TH25-AIR	PU75TH25- OX30	PU75TH25- OX40
50/50% Coal/Thistle	PU50TH50-AIR	PU50TH50- OX30	PU50TH50- OX40
25/75% Coal/Thistle	PU25TH75-AIR	PU25TH75- OX30	PU25TH75- OX40
100% Thistle	TH-AIR	TH-OX30	TH-OX40

Oxy-fuel combustion effects on corrosive compounds formation.

- 1blend selected: 60/40 wt.% Puertollano coal/ thistle.

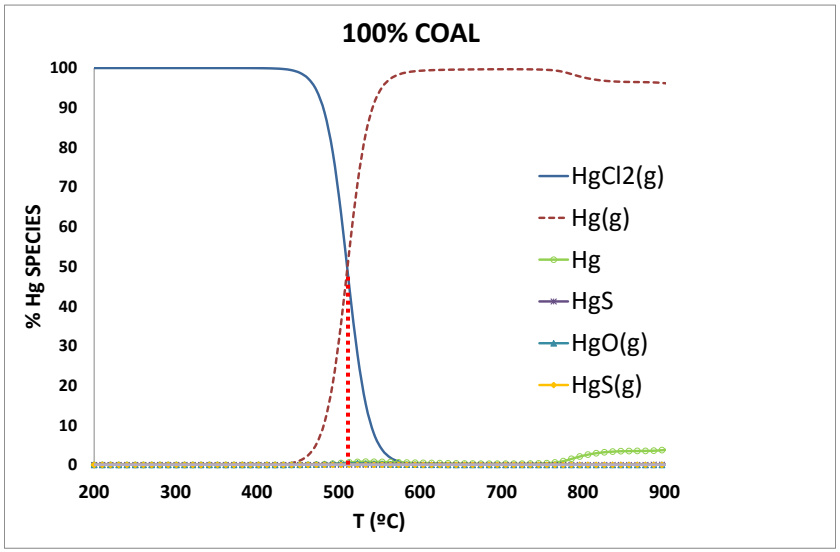
❑ Utility boiler and gas analysis

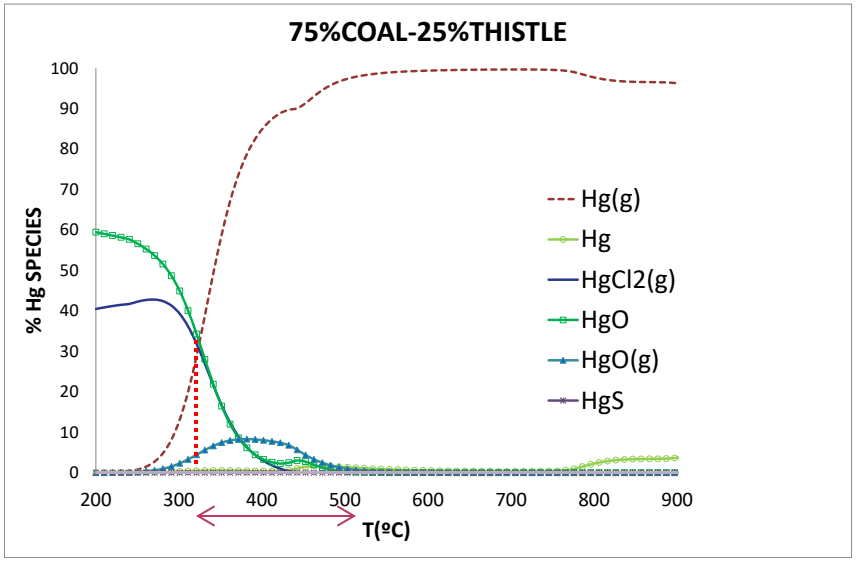
➢ **CIEMAT- LAB-SCALE FLUIDIZED BED REACTOR FOR OXY- FUEL COMBUSTION.**



- Furnace Temperature: 850ºC.
- Flue Gas Flow: 5 Nl/min.
- Fuel Feed Rate: 0- 2 g/min.
- Particle size: 100–200 µm.

❑ Effect of biomass addition in a conventional combustion process on Hg speciation by thermodynamic equilibrium calculations.

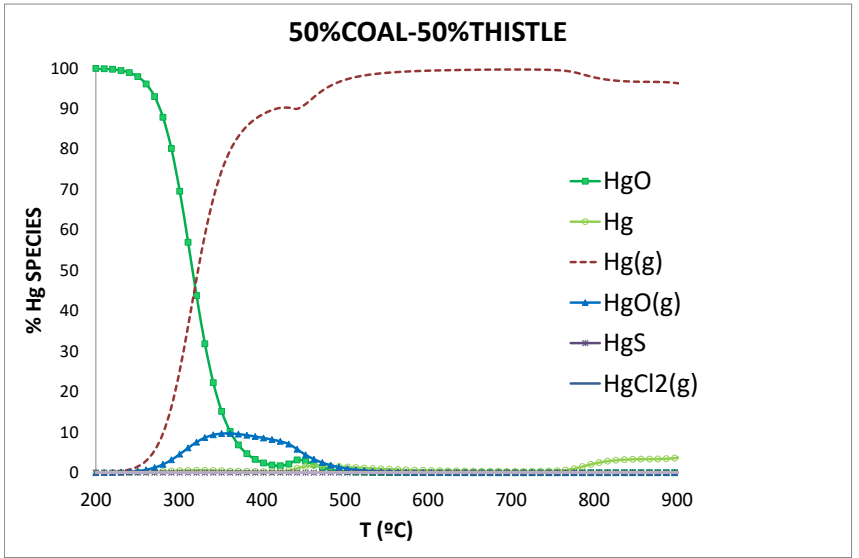




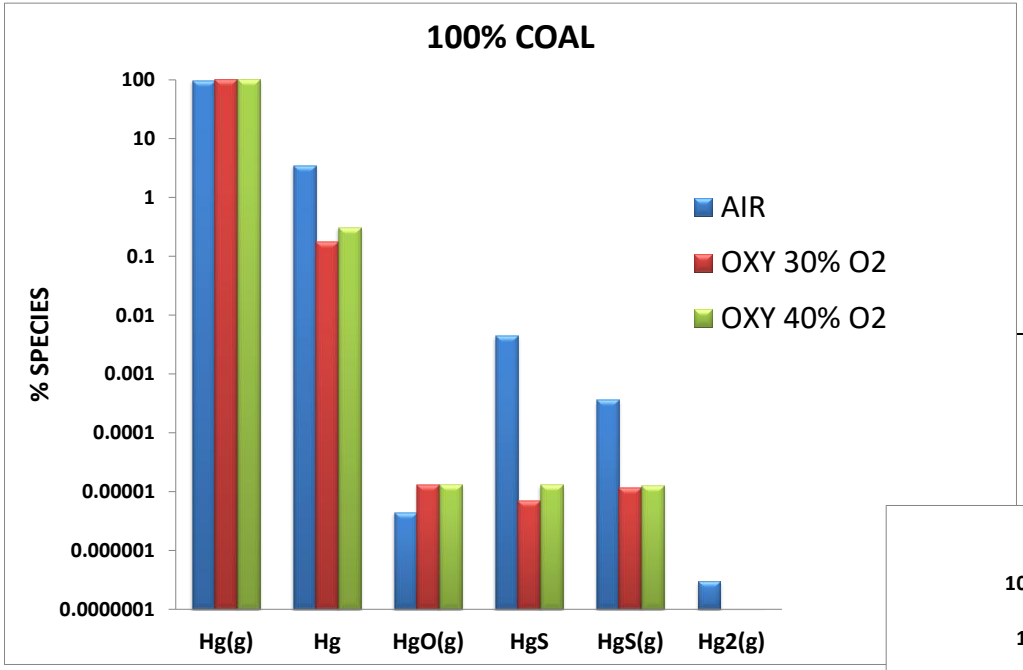
- ✓ A 25wt% biomass addition involves:
  - ➢ Thermal range for Hg°(g) increases→ major volatilization
  - ➢ Oxidation as HgO is favoured vs $HgCl_2(g)$.

- ✓ A 50 wt% biomass addition involves:
  - ➢ Hg condensation as HgO at low temperatutres (T<400ºC).

- ✓ No differences for major biomass percentages



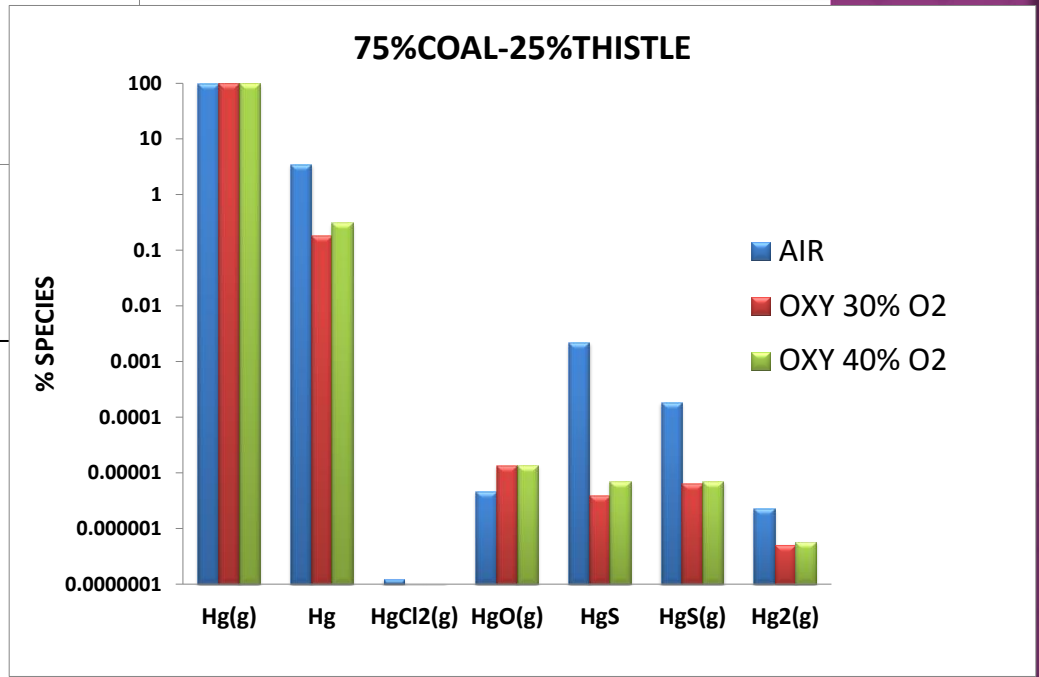
❑ Mercury speciation in the oxy-firing reactor (T=850ºC) at different combustion atmospheres.



OX-FIRING VS AIR-FIRING

- ✓ Increase in HgO(g) formation
- ✓ Decrease in concentration of: Hg, Hg_2(g), HgS, HgS(g),
- ✓ No changes in Hg^o(g).

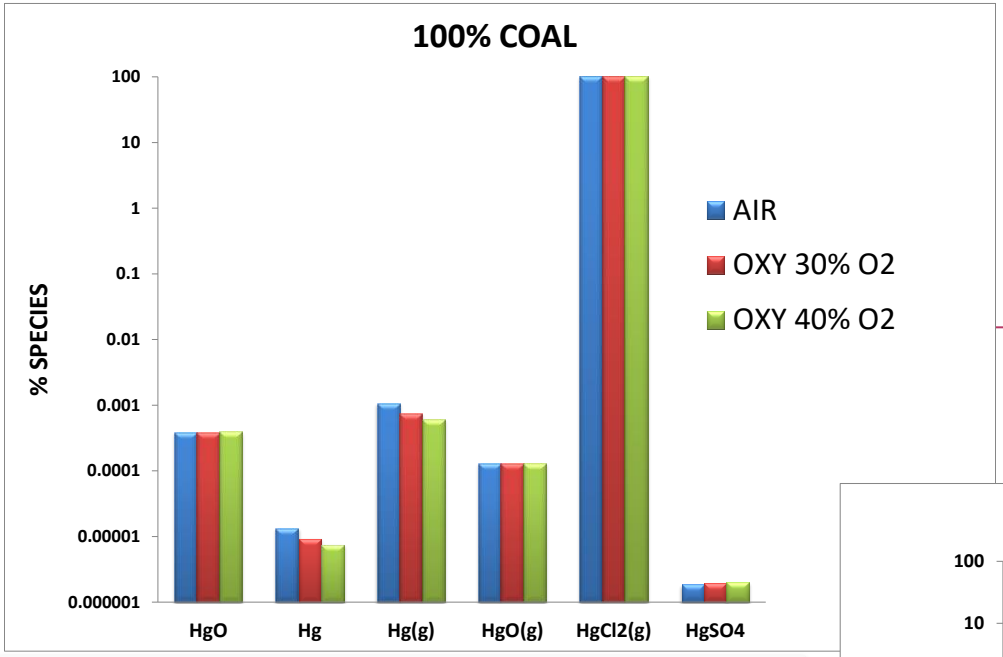
➢ Hg condensation/ capture within the reactor (850ºC) is reduced in oxy-firing vs air combustion



OX-FIRING VS AIR-FIRING

- ✓ With a 25wt% biomass addition:
  - ➢ Same tendency than coal.
  - ➢ Some HgCl2(g) detected in air, which decreases in the oxy-atmospheres
- ✓ No significant differences for major biomass percentages

❑ Hg speciation prediction within the pollution control devices (T<350ºC), at different combustion atmospheres.



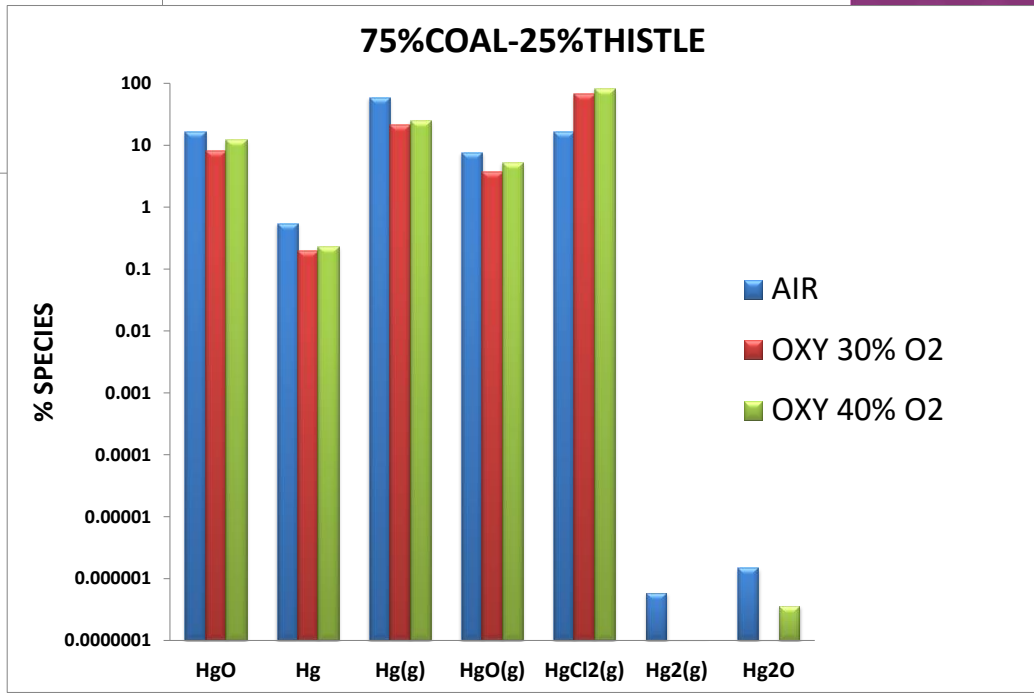
OX-FIRING VS AIR-FIRING

- ✓ Decrease volatilization as $Hg^o(g)$.
- ✓ Little increase in sulphates formation.
- ✓ No significant cahnges in the main form $HgCl_{2(}g)$

OX-FIRING VS AIR-FIRING

- ✓ With a 25wt% biomass addition:
- ✓ Oxy-fuel combustion exert major influence in speciation.

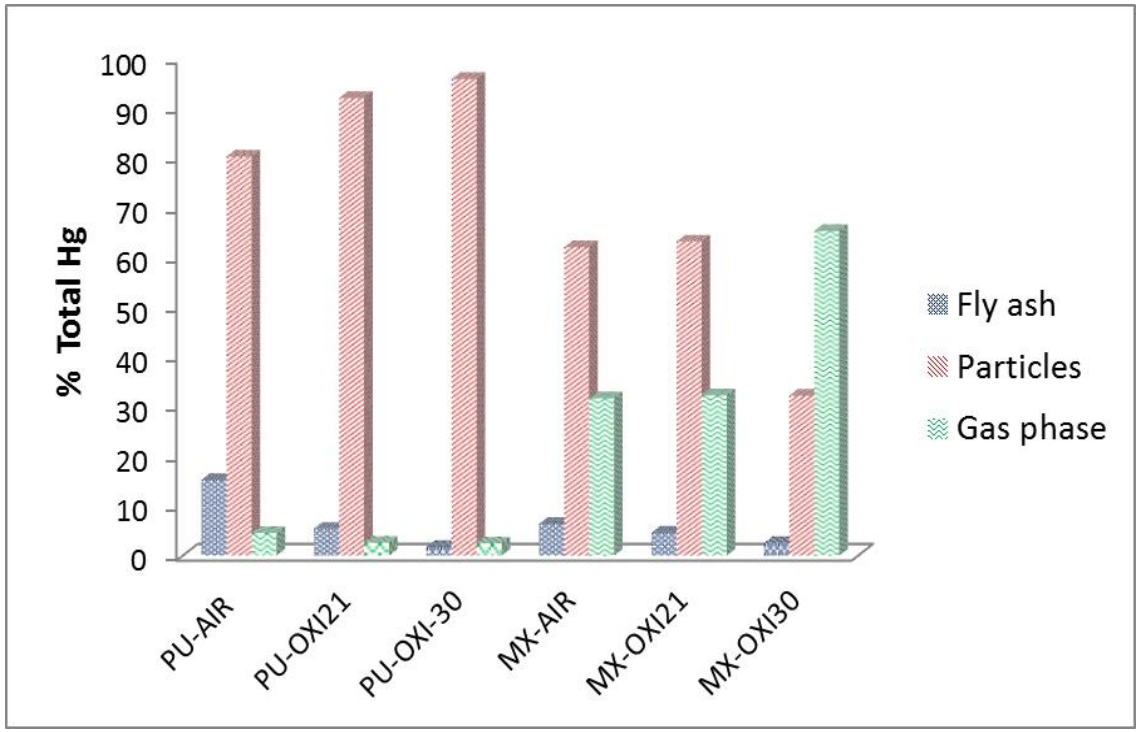
- ➢ Promotes Hg oxidation: $HgCl_2(g)$, secondly as oxides.
- ➢ Emissions as Hg(g) are reduced.



❑ Hg behaviour during the experimental tests of fluidized bed combustion and oxyfiring of coal and coal-biomass mixtures.

COMBUSTION ATMOSPHERE			
FUEL	21%O_2/79%N_2	21% O2/ 79% CO2	30% O_2/ 70% CO_2
100% Coal	PU-AIR	PU-OXI21	PU-OXI30
75/25%Coal/ /thistle mixture	MX-AIR	MX- OXI21	MX- OXI30

✓ HG MAIN ROUTES IN THE COMBUSTION PLANT.



OX-FIRING VS AIR-FIRING:

➢ **Coal case.**

- ✓ Increase retention in particles.
- ✓ Less enrichment in fly ash.
- ✓ Hg emissions reduction.

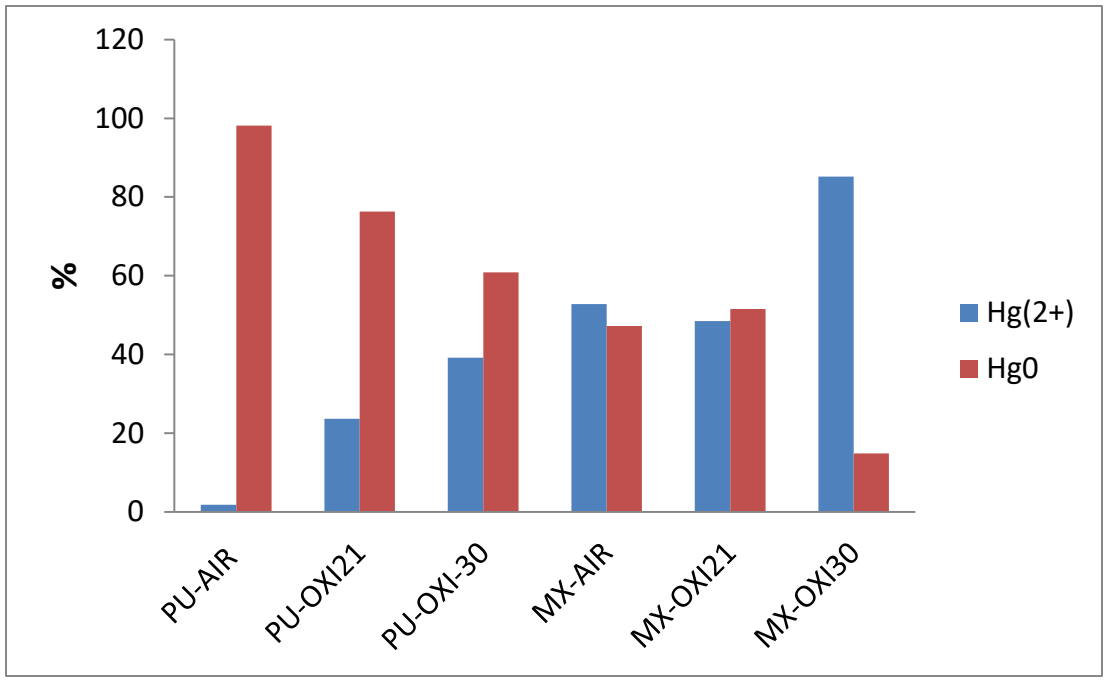
Oxy-coal combustion enhances Hg capture in particles

➢ **Cofiring case**

- ✓ Also decrease in fly ash RE.
- ✓ Major differences for a 30% v/v O_2:
  - ✓ Increase flue gas (Fg) emissions

Speciation in Fg phase

✓ HG SPECIATION IN THE GAS PHASE, DURING THE OXYFIRING TESTS OF COAL AND COAL-THISTLE BLEND, DETERMINED THROUGH ONTARIO HYDRO METHOD.



OX-FIRING VS AIR-FIRING:

➢ **Coal case.**

- ✓ Decrease in the dominant form $Hg^{o}(g)$
- ✓ Oxidation in Fg phase enhanced
- ✓ For 30% v/v O_2, $Hg^{o}/Hg^{2+}>1$

↓

Oxy-coal combustion enhances Hg *oxidation* and capture in Fg *particles*

➢ **Cofiring case**

- ✓ Air-firing: $Hg^{o}/Hg^{2+}\sim1$
- ✓ Oxy-firing:
  - ✓ Main differences for O_2>30% v/v
  - ✓ Remarkable increase in Hg oxidation.

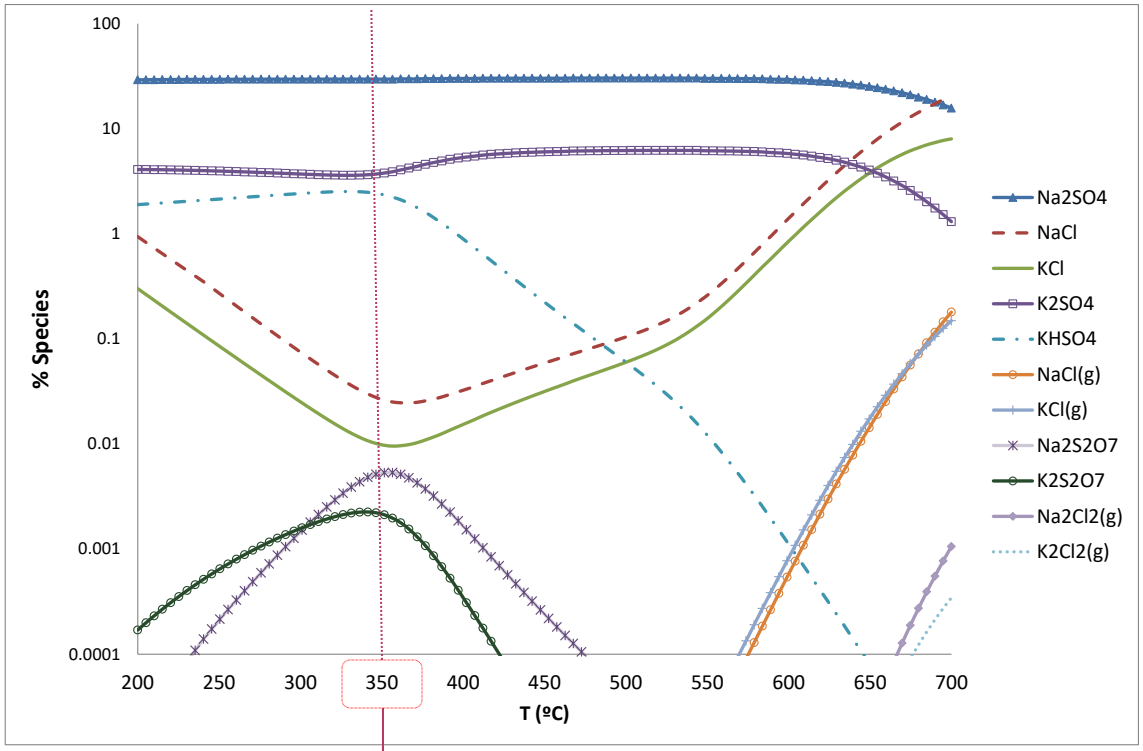
→

Biomass in oxy-firing, enhances Hg *volatilization* but also its *oxidation* in Fg phase, for high O_2 concentration.

❑ Oxy-fuel combustion effects on corrosive compounds formation.

✓ DEPOSITS FORMATION DURING CONVENTIONAL COMBUSTION, AT DIFFERENT TEMPERATURES.

Fuel mixture: 60/40 wt% Puertollano coal/ thistle.



- ✓ At T>350ºC chlorides formation favored,
  - ✓ NaCl, KCl
  - ✓ NaCl (g), KCl(g, Na2Cl2(g), K2Cl2(g)

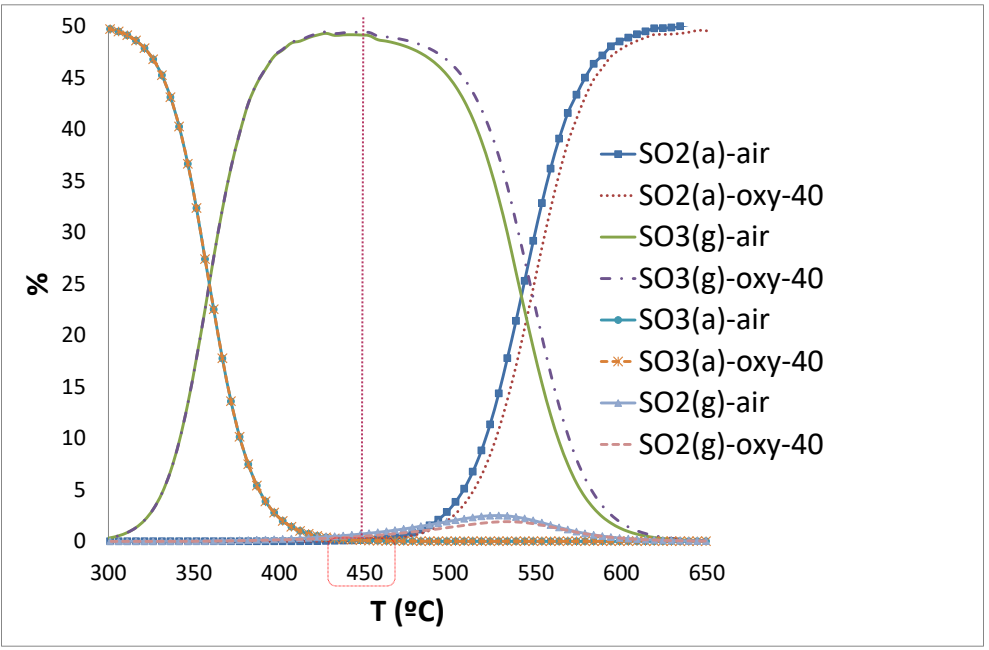
- ✓ At T<350ºC , prevail sulphur-interactions,
  - ✓ Na_2SO_4,
  - ✓ K_2SO_4 , $KHSO_4$
  - ✓ Na_2S_2O7 y $K_2S_2O_7$,

→ $(Na,K)_2SO_4 + SO_3 \leftrightarrow (Na,K)_2S_2O_7$

→ SO_3 vs SO_2 at 350ºC ⟶ What happens in oxy-conditions?

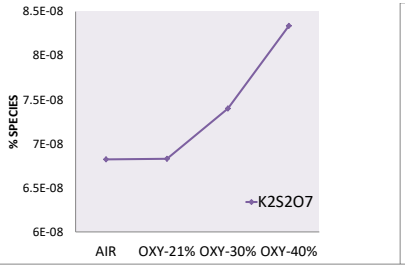
✓ OXY-FIRING EFFECT ON SULPHUR COMPOUNDS FORMATION.

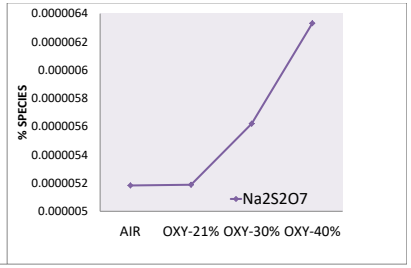
SO_X PARTITIONING :AIR VS 40%O_2/60%CO_2 V/V.

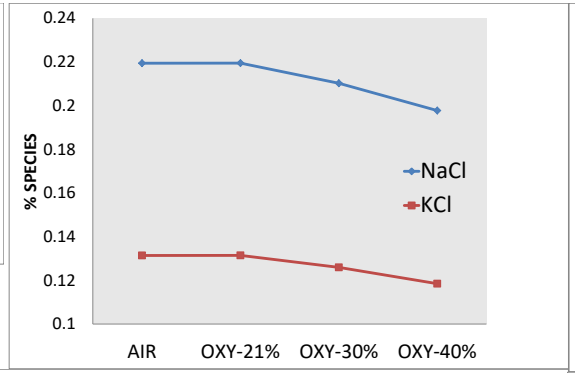


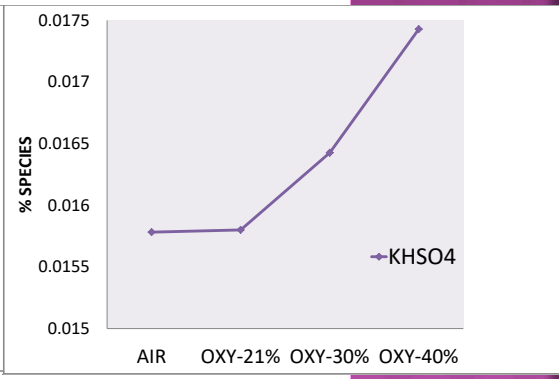
- ✓ Main changes at 450-600ºC:
  - ✓ SO_3(g) transition to SO_2(g) at higher T in oxy-conditions:
- ✓ Sulphates-to-chlorides transition temperature increases

Effect on deposits formation, at 540ºC.

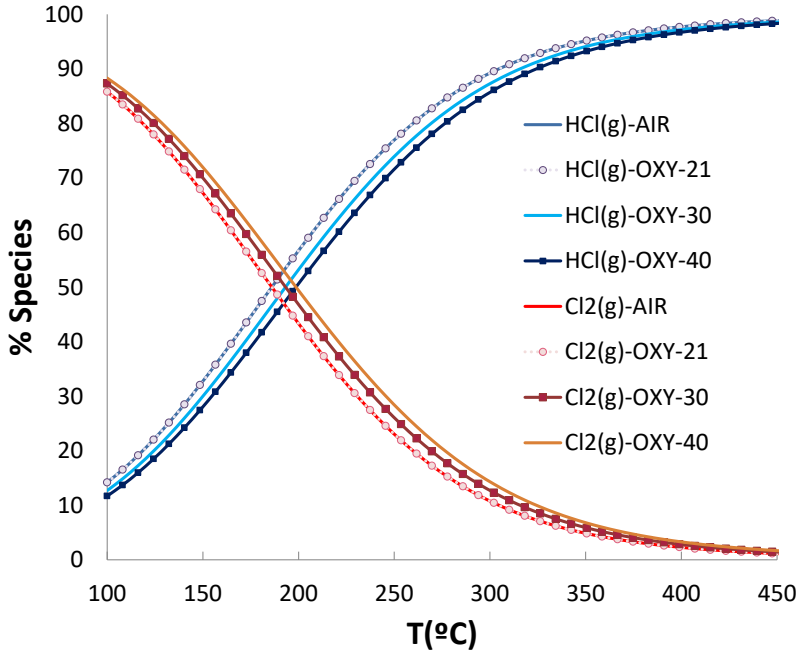








✓ OXY-FUEL COMBUSTION EFFECT ON CHLORIDE COMPOUNDS FORMATION.

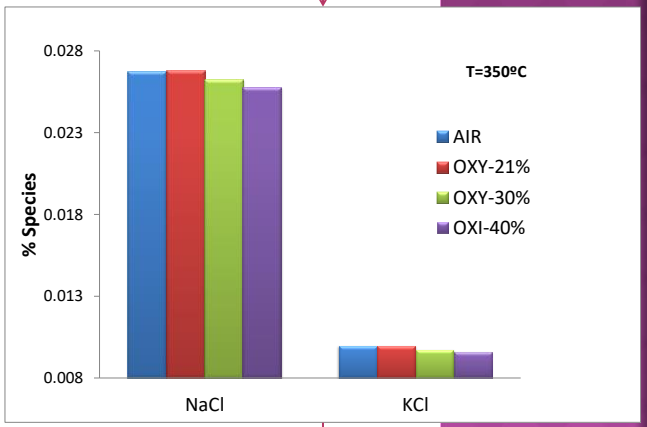


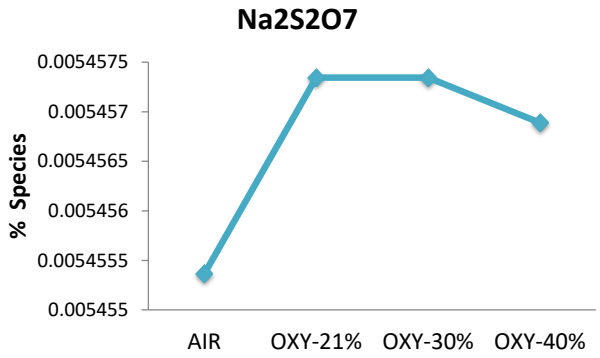
- ✓ Air vs Oxy-21: No differences
- ✓ Differences for O_2>30% v/v at T<400ºC
  - ✓ Reduction in HCl(g) concentration
  - ✓ Cl2(g) increases:

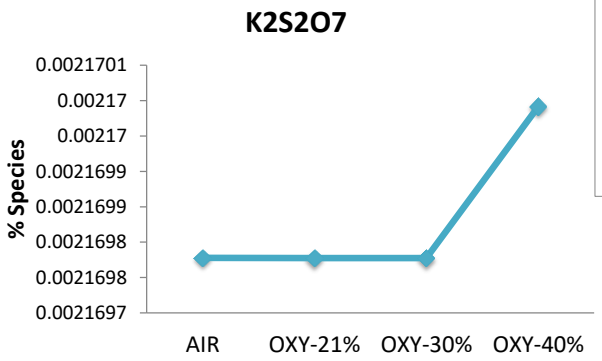
$$2K(Na)Cl + CO_2 + 0.5O2 = K(Na)_2CO_3 + Cl_2$$

$$Ca(Mg)Cl_2 + CO_2 + 0.5O_2 = Ca(Mg)CO_3 + Cl_2$$

At a reference T =350ºC, effects on deposits







Main Conclusions

- Oxy-fuel combustion effects on Hg fate vs Air-firing (coal case):
  - ✓ At high T (850ºC), Hg capture is reduced (sulphides, oxides, condensed Hg).
  - ✓ At low T (<350ºC):
    - ✓ Less enrichment in fly ashes.
    - ✓ Enhances Hgº oxidation and capture in Fg particles
    - ✓ Major Hg sulphates formation.

- Inclusion of biomass, involves:
  - In *conventional combustion* of coal:
    - ✓ Major volatilization as Hgº.
    - ✓ At low T (<400ºC), HgO favored vs $HgCl_2$(g): Effect increase with biomass %.
  - In *oxy-coal* combustion,
    - ➢ Also less enrichment in fly ashes.
    - ➢ at high T (850ºC), increases Hg volatilization but also its oxidation in Fg phase, for high O_2% (30%v/v).
    - ➢ at low T (<350ºC), oxy-fuel combustion exert major influence on Hg speciation than with coal:
      - ➢ Enhances Hg oxidation (mainly $HgCl_2$ (g), secondly as oxides)
      - ➢ Hg(g) emissions are reduced.

- Oxy-firing effects on deposits formation
  - ➢ Tends to decrease deposition phenomena as chlorides while sulphates compounds are favoured, at low concentrations→ Attention on $KHSO_4$ and pyrosulphates.

FUTURE WORK

GENERA (Ref. ENE2014-52359-C3-1-R)

- *Oxy-firing effects on corrosion:*
  - *Validate with experimental research*:
    - Pilot FBC plant, 5 KWth, modified for oxyfuel combustion.
    - Tests at bench scale, quartz reactor.

Thank you for your attention.

ACKNOWLEDGMENTS

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DEPARTMENT OF ENERGY

Energy Valorization of Fuels and Wastes.