# Effect of Co-firing on Alkali Sulfate Formation during Oxy-combustion

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# Oxy-combustor facility

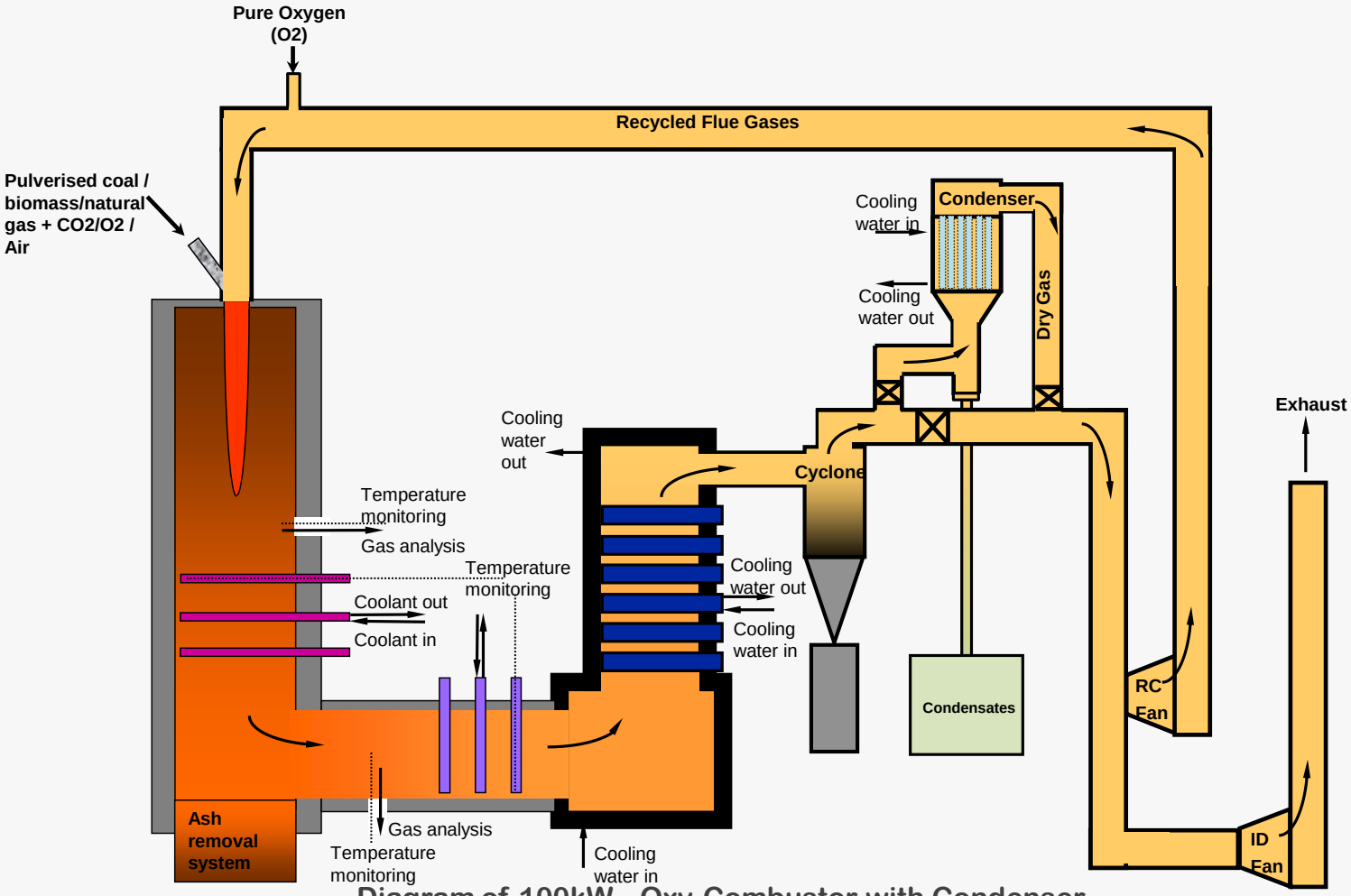


Diagram of 100kW$_{th}$ Oxy-Combustor with Condenser

# Retrofitting Process
## LATEST MODIFICATIONS

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## CONDENSER

*New calibration model needed for the FTIR (Higher concentrations of $CO_2$ expected)*

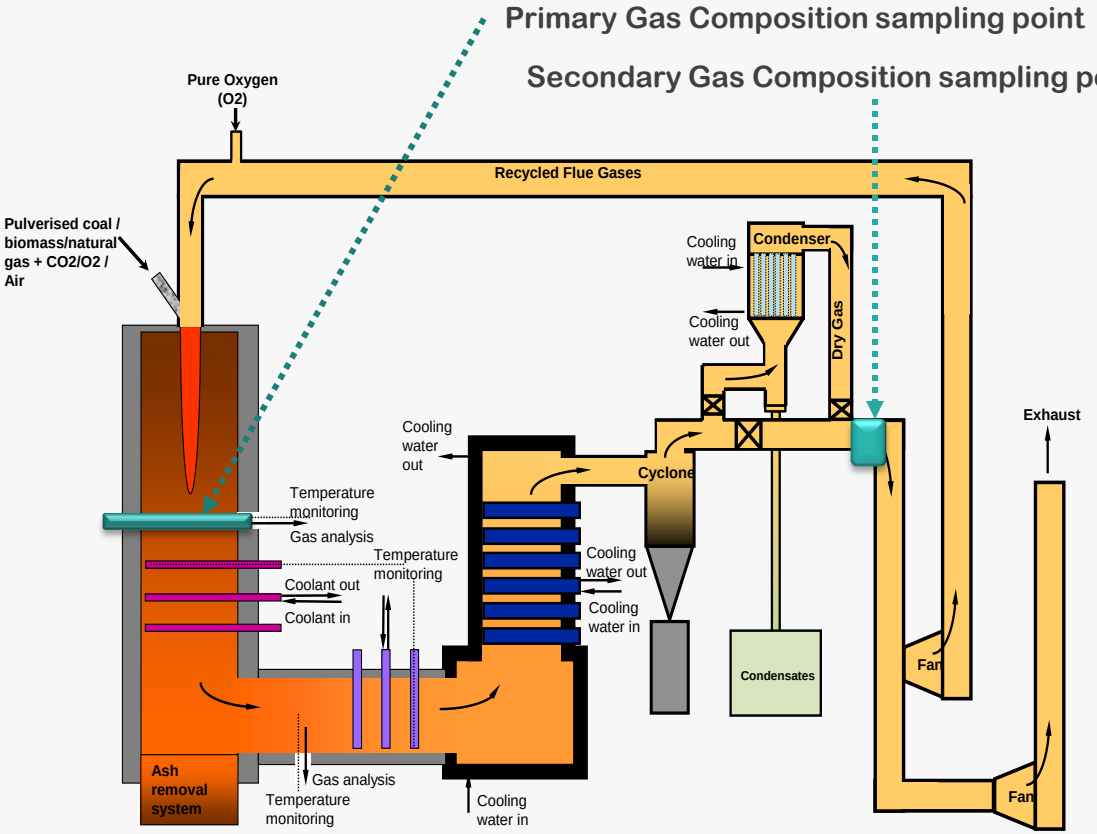
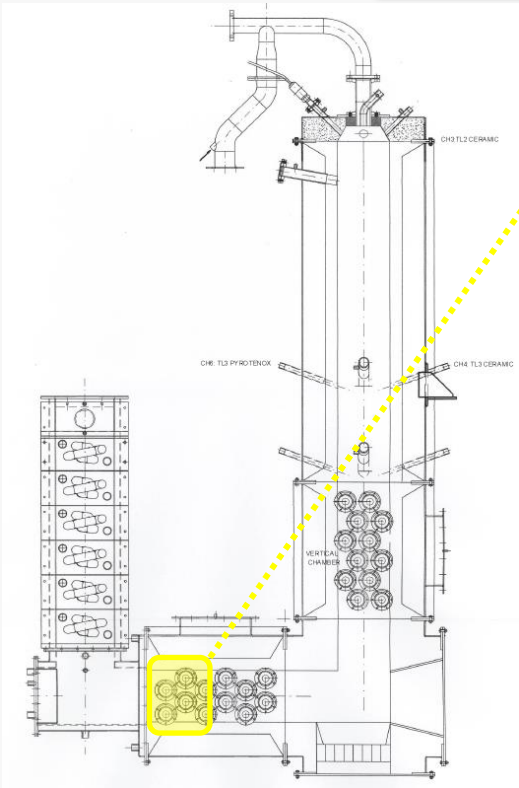



Diagram of 100kWth Oxy-Combustor with Condenser

# Oxy-combustor facility
## NEW MEASUREMENTS

### $SO_3$ AND SULFATES MEASUREMENT
### (Controlled Condensation Method)



Location of the sampling point

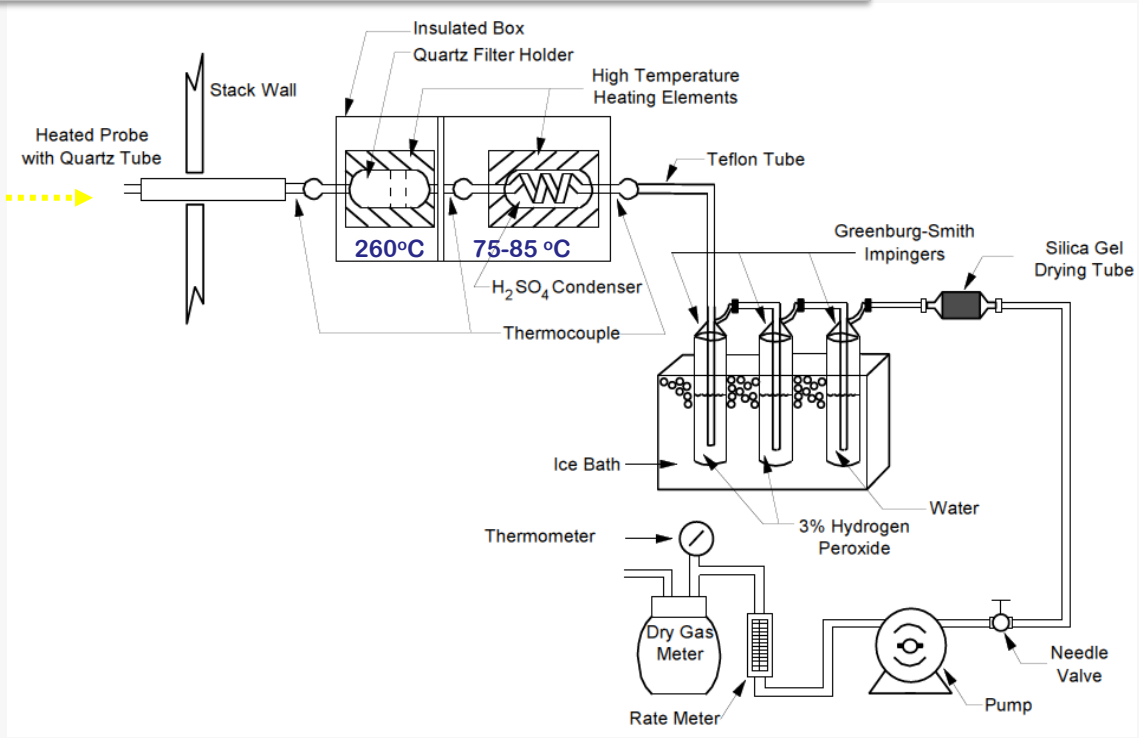



Diagram for SOx sampling train proposed in EPA Method 8A

*Modification of procedure suggested by EPA Method 8A applied*

# Retrofitting Process
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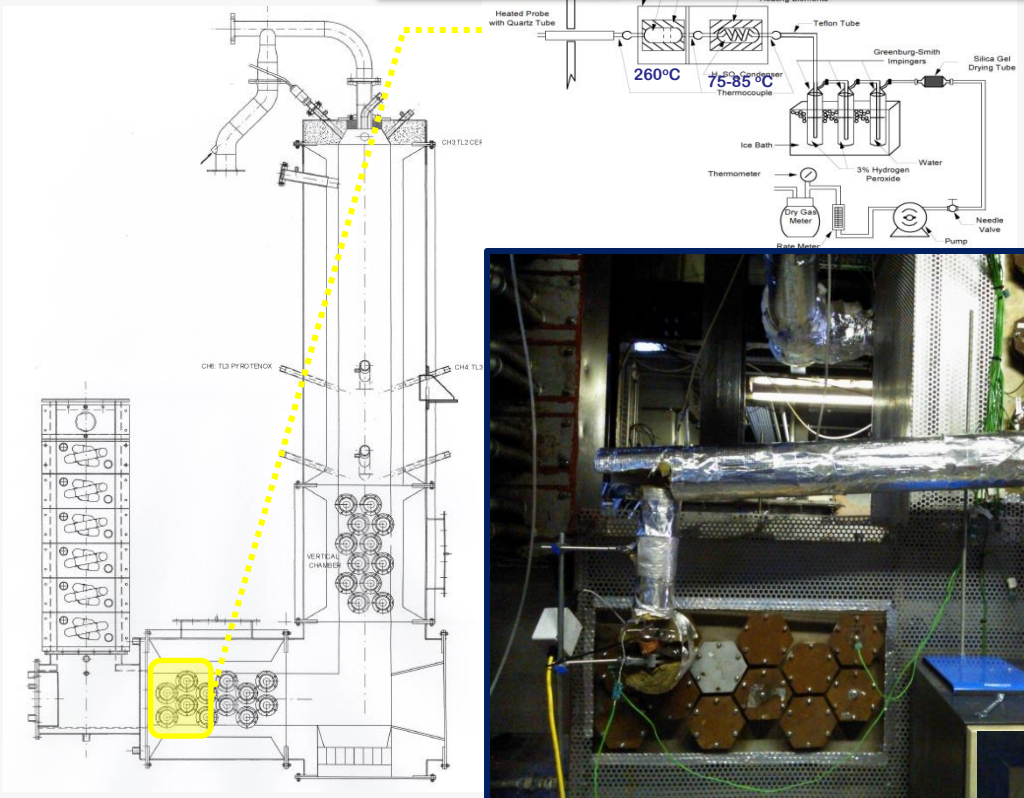


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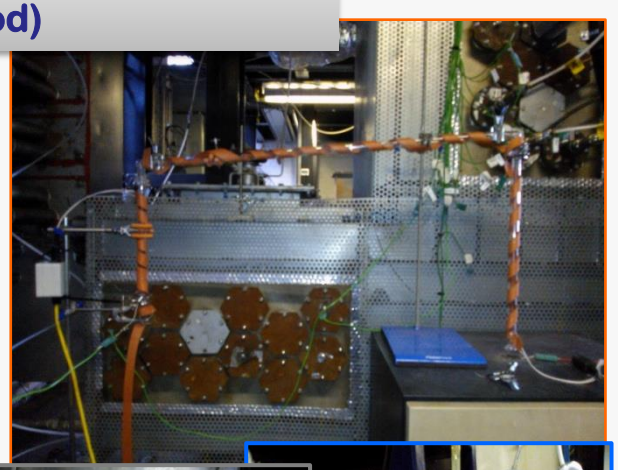

# Experimental conditions

- Type of fuel: El Cerrejon Coal 13.5kg/h
  75% El Cerrejon -25% CCP 15kg/h
  50% El Cerrejon -50% CCP 16.7kg/h
  Cereal co –product 22kg/h
- Percentage of Recycled Flue Gas :60-65%
- Types of Recycled Flue Gas
  - Wet- Hot Recirculation (After Particle Removal )
  - Dry – Cool Recirculation (After Particle, Condenser)
- Oxygen Injection
  - Primary $O_2$ (Fuel carrier draught): Not Used
  - Secondary $O_2$: 34-38% in gas supplied

# Experimental conditions
## FUEL ANALYSIS

| | El Cerrejon coal | Cereal co-product |
|---|---|---|
| Proximate analysis (% (wt) as received) | | |
| Moisture | 5.80 | 8.10 |
| Volatile matter | 34.80 | 70.80 |
| Ash | 8.60 | 4.20 |
| Calorific value, (MJ/kg) | | |
| Gross calorific value | 27.85 | 17.61 |
| Net calorific value | 27.12 | 16.34 |
| Ultimate analysis (% (wt) as received) | | |
| Carbon | 69.2 | 43.30 |
| Hydrogen | 4.40 | 5.80 |
| Nitrogen | 1.42 | 2.70 |
| Chlorine | 0.02 | 0.17 |
| Sulfur | 0.58 | 0.16 |
| Oxygen | 9.98 | 35.57 |
| Ash analysis (% (wt)) | | |
| $SiO_2$ | 60.69 | 44.36 |
| $Al_2O_3$ | 22.01 | 2.79 |
| $Fe_2O_3$ | 7.43 | 2.47 |
| $TiO_2$ | 0.92 | 0.12 |
| CaO | 2.27 | 7.78 |
| MgO | 2.90 | 3.96 |
| $Na_2O$ | 1.06 | 0.36 |
| $K_2O$ | 2.32 | 24.72 |
| $Mn_3O_4$ | 0.06 | 0.10 |
| $P_2O_5$ | 0.21 | 12.04 |
| $SO_3$ | - | - |
| BaO | 0.11 | 0.05 |

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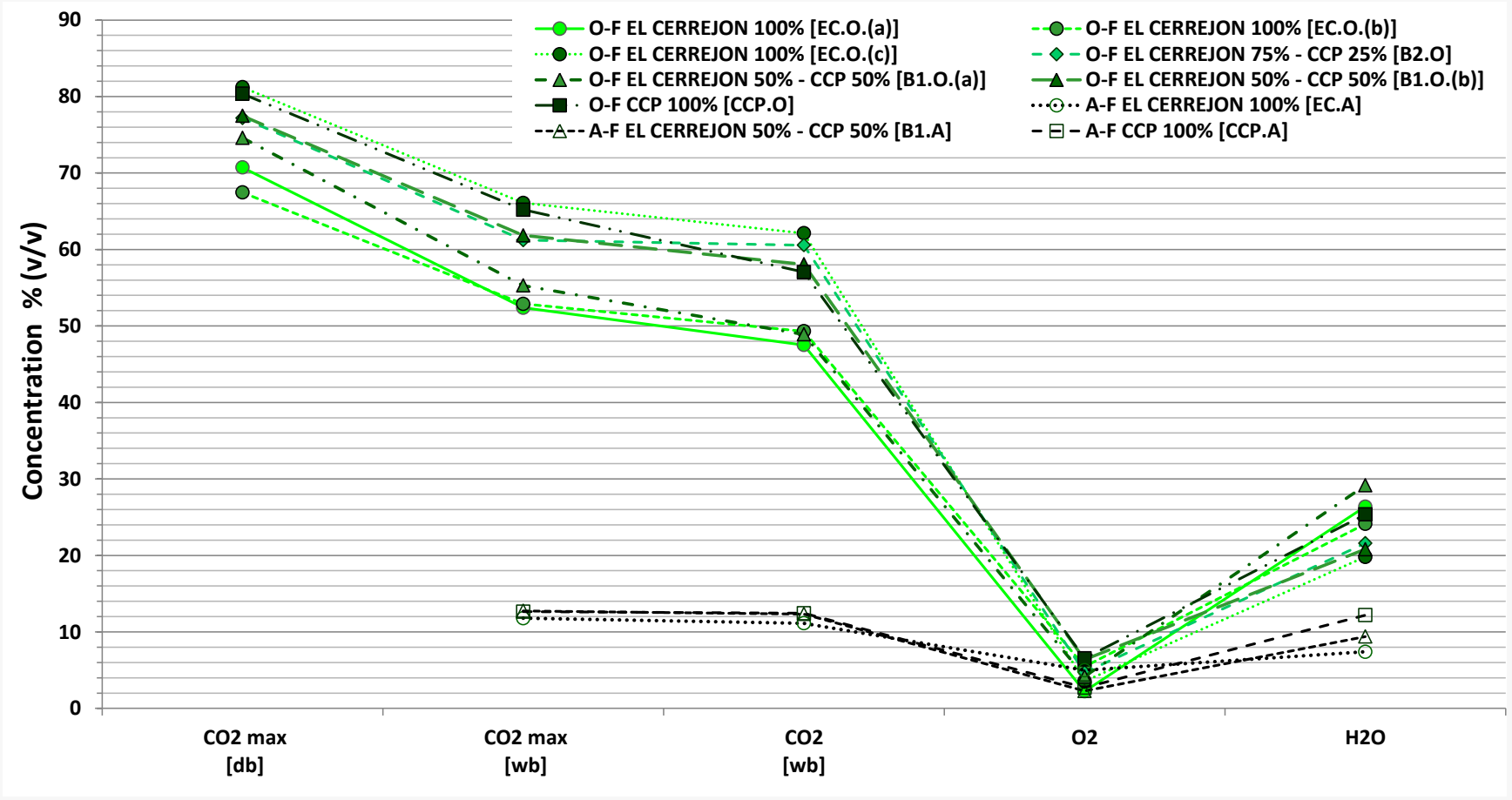
# Experimental Results
## GAS COMPOSITION

- Maximum $CO_2$ : 57-62% wet basis [80-81% (d. b.)]
- $H_2O$ ~ 20-29% (v/v)
- $O_2$~ 4.3% (v/v)



# Experimental Results
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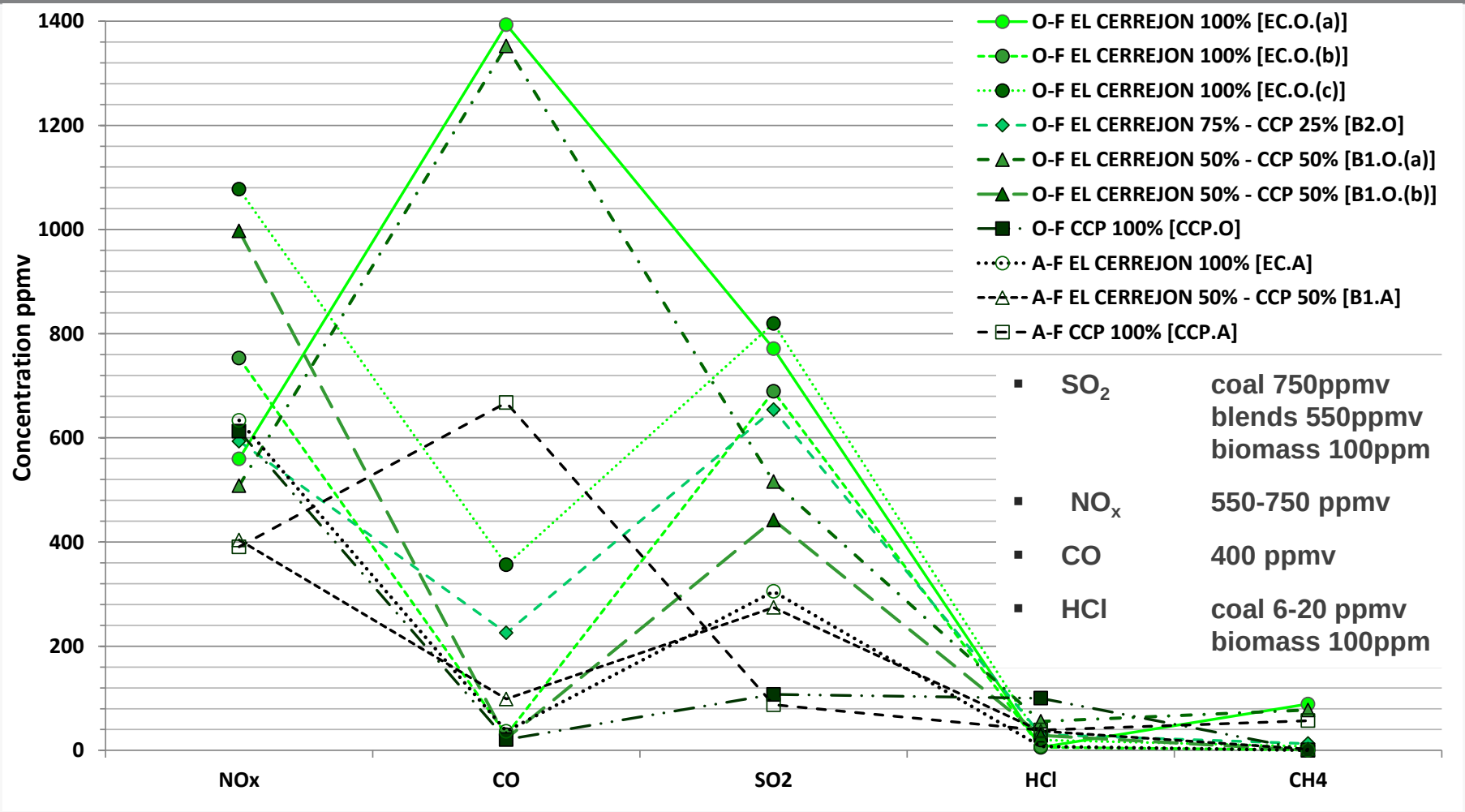

# Experimental Results
## SO3 & SULFATES

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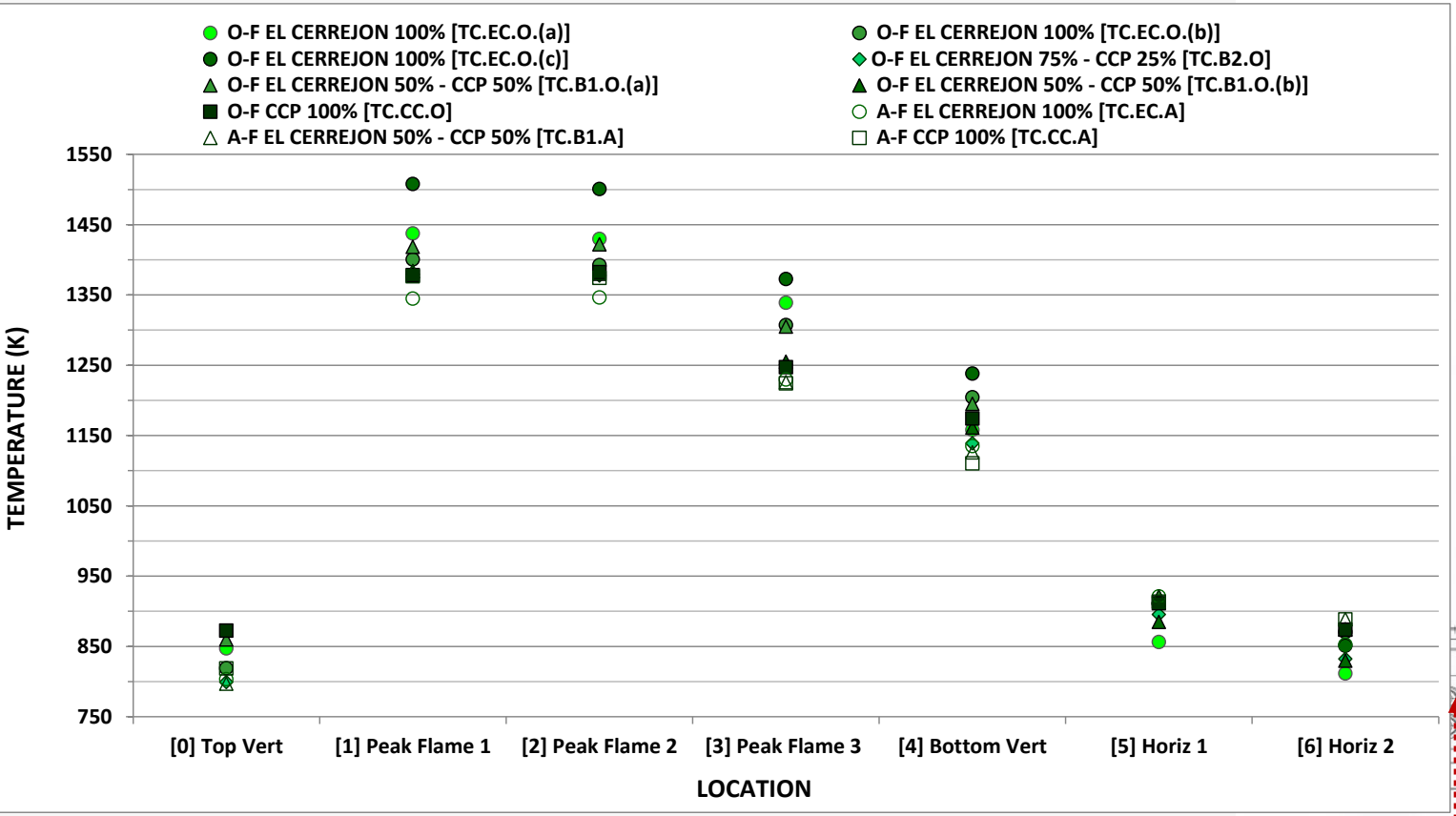
| | $SO_2$_FTIR (ppmv) | $SO_2$_CCM (ppmv) | $(SO_3+SO_4^{2-})$_CCM (ppmv) | $(SO_3+SO_4^{2-})/SO_2$ (%) |
|---|---|---|---|---|
| Air-firing El Cerrejon | 305.2 | 83.5 | 3.0 | 3.6 |
| Air-firing 50%EC-50%CCP | 274.3 | 245.8 | 16.6 | 6.7 |
| Air-firing CCP | 87.6 | 98.9 | 20.8 | 21.0 |
| Oxy-firing El Cerrejon | 819.6 | 566.8 | 16.9 | 3.0 |
| Oxy-firing 75%EC-25%CCP | 654.3 | 525.2 | 13.8 | 2.6 |
| Oxy-firing 50%EC-50%CCP | 442.2 | 231.4 | 29.5 | 12.7 |

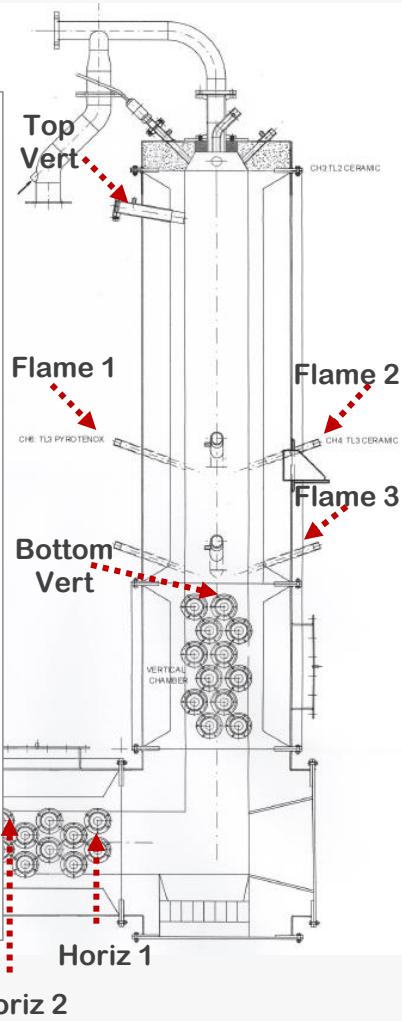
**Effect of fuel**: $SO_3+SO_4^{2-}$ levels rising as the share of CCP increases

- Alkalis reaction with $SO_3$ to generate sulfates
- $SO_2$ to $SO_3$ promoted by alkalis

**Effect of firing mode**: $SO_3+SO_4^{2-}$ levels in oxy-firing higher than in air-firing

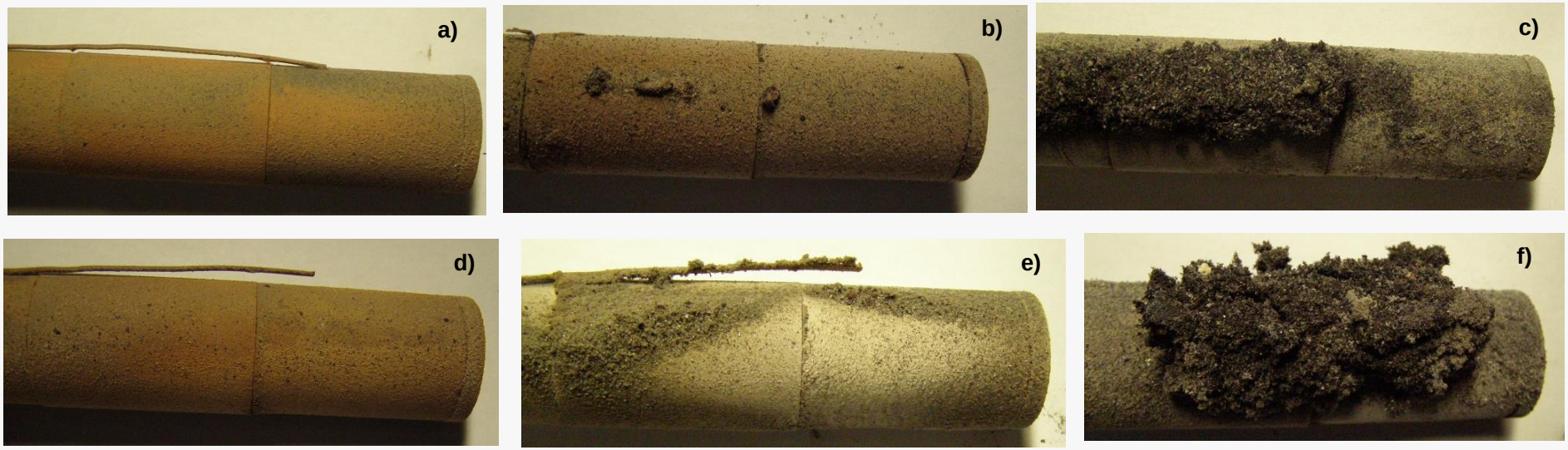
# Experimental Results
## TEMPERATURES



# Experimental Results
## ASH DEPOSITS

***The structure of the deposit is more fibrous and porous using 100% CCP than when oxy-firing 100% El Cerrejon coal or the coal-biomass blends. No significant difference in the aspect of the deposits can be observed comparing the cases under oxy and air-firing conditions.***

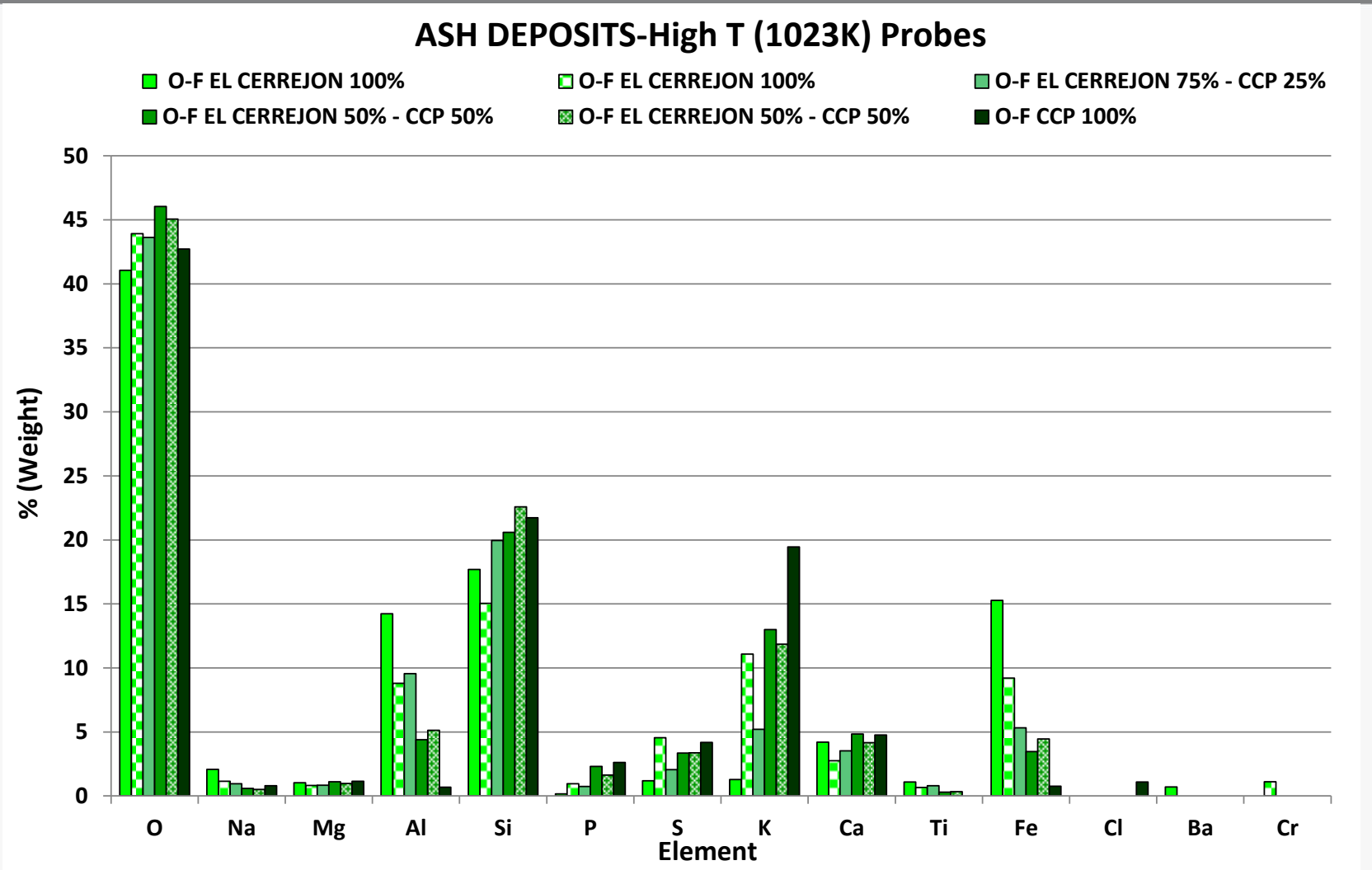



a) Air- firing El Cerrejon b) Air-firing 50%EC-50%CCP c) Air-firing CCP
d) Oxy- firing El Cerrejon e) Oxy-firing 50%EC-50%CCP f) Oxy-firing CCP

# Experimental Results

## ASH DEPOSITS

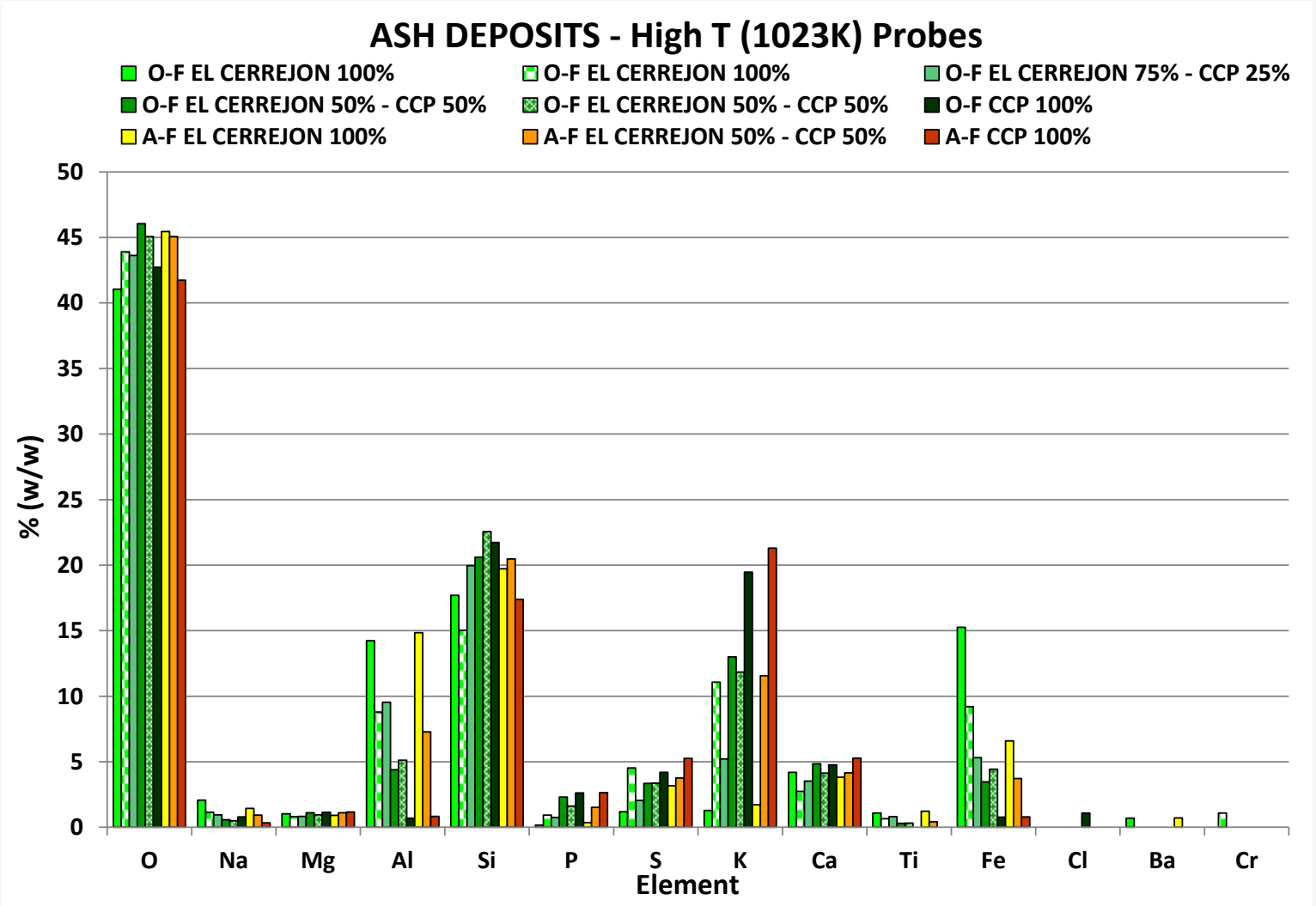
## Oxy-firing: coal .vs. biomass



# Experimental Results

## ASH DEPOSITS

## Oxy-firing .vs. air-firing

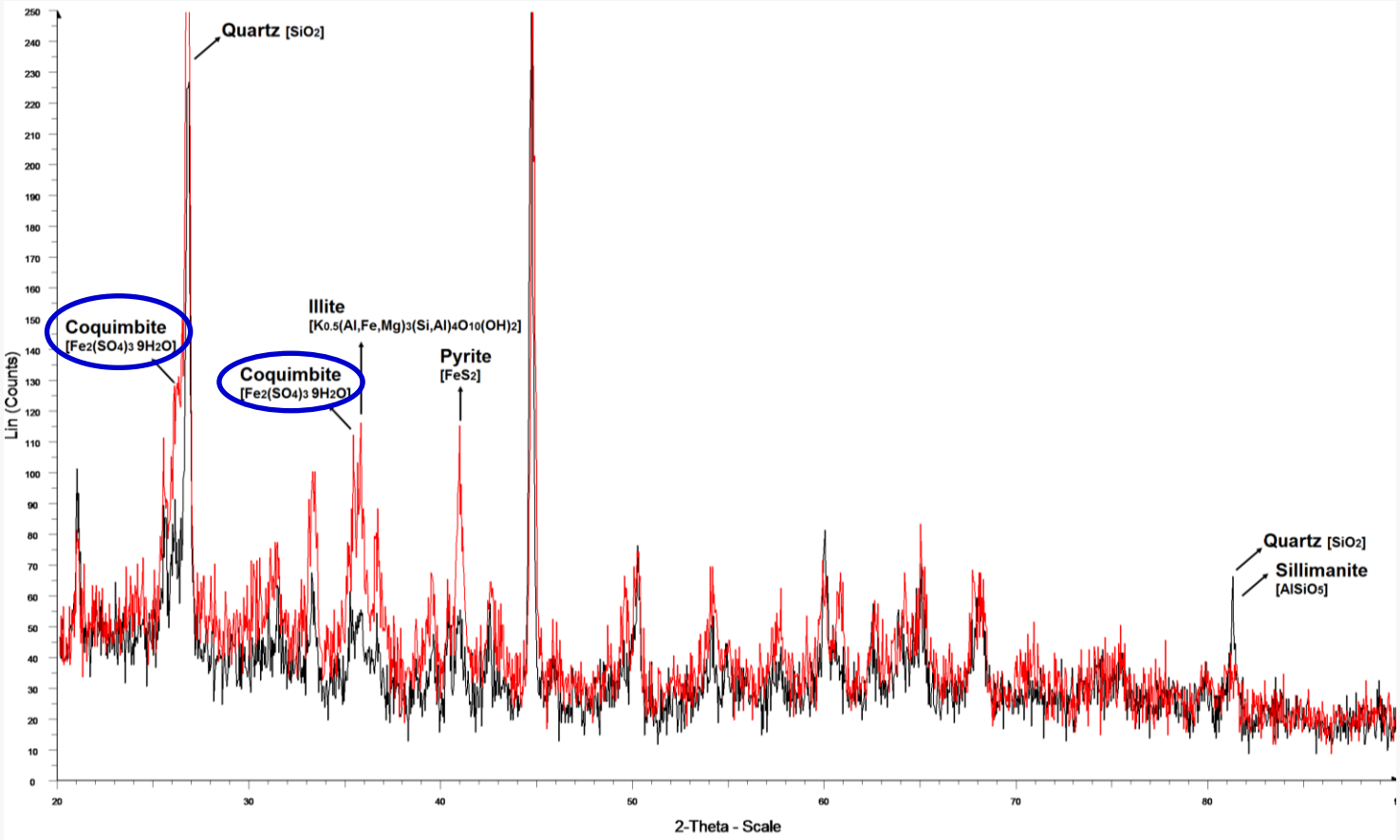


# Experimental Results

## ASH DEPOSITS - XRD Results

## Air vs. Oxy

## Coal



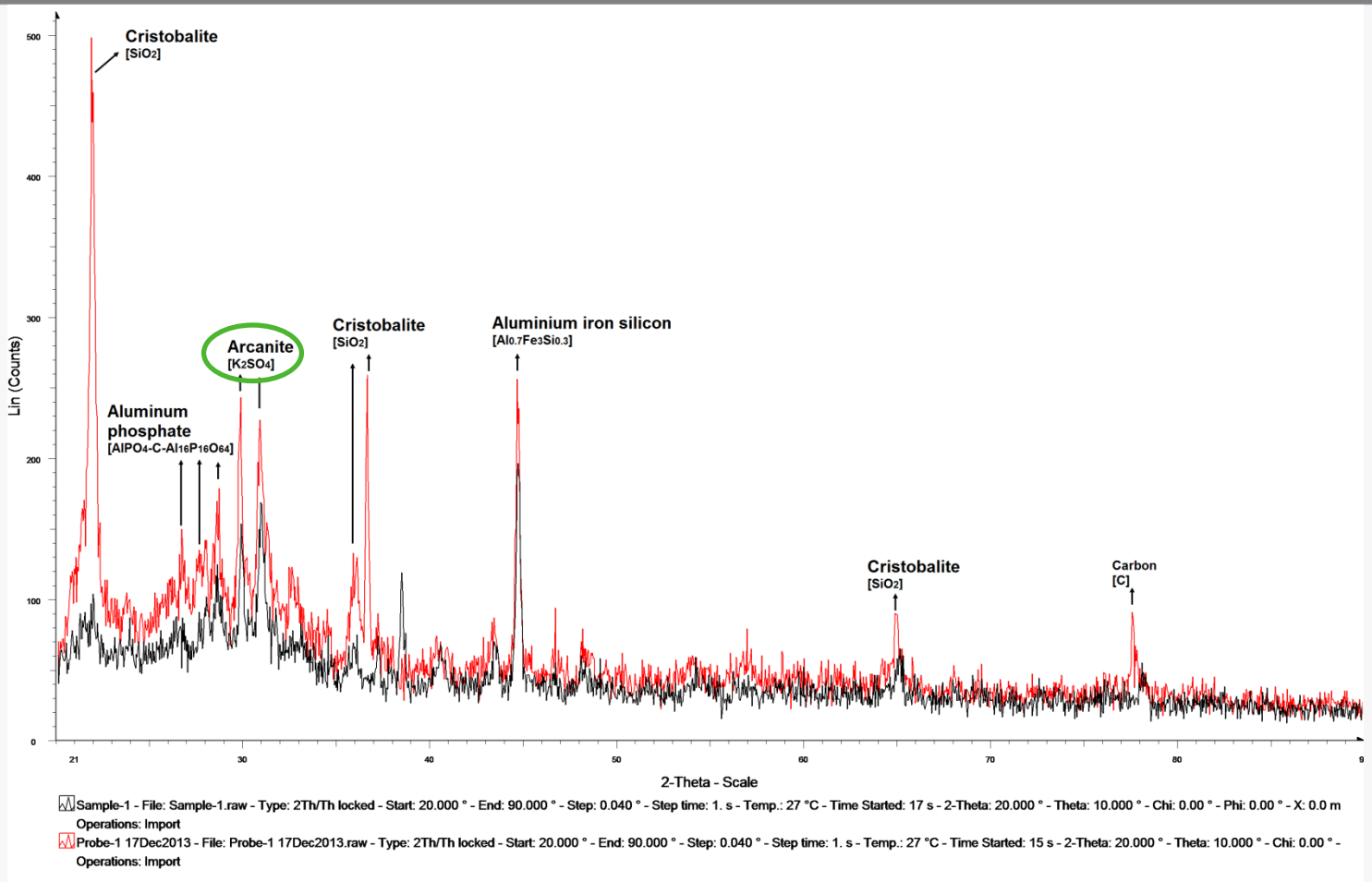

**XRD charts_ El Cerrejon coal ashes collected at 700°C; air-firing test (black spectrum) against oxy-firing test (red spectrum)**

# Experimental Results

## ASH DEPOSITS - XRD Results

## Air vs. Oxy

## Biomass

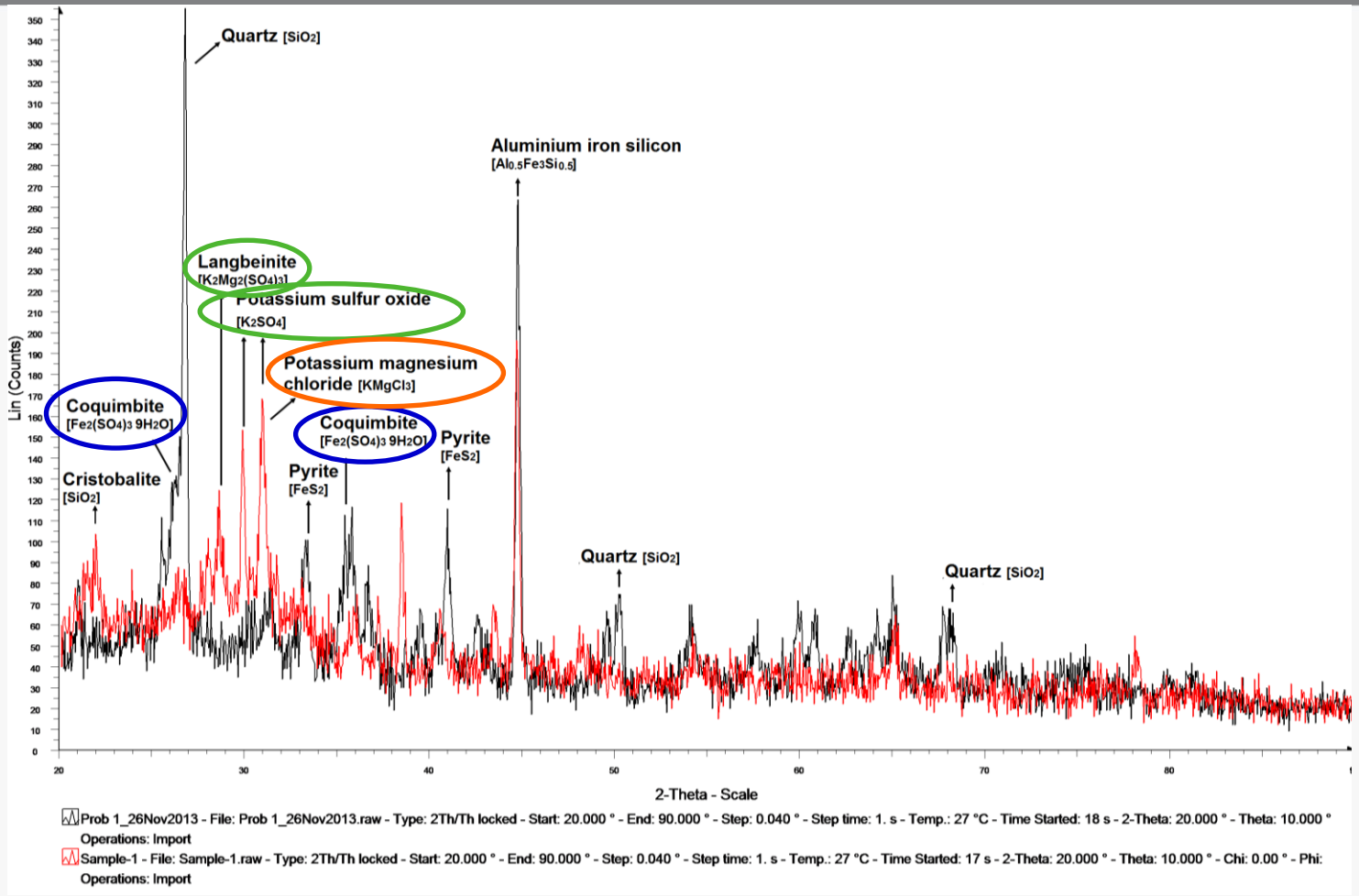



**XRD charts _ 100% CCP ashes collected at 660°C; air-firing test (red spectrum) against oxy-firing test (black spectrum)**

# Experimental Results

## ASH DEPOSITS - XRD Results

### Coal vs. Biomass




**XRD charts _ Oxy-firing ashes collected at 700°C; coal test (black spectrum) against biomass test (red spectrum)**

# Key findings- Experimental

- Gas composition
  - $CO_2$ >80% (db) for pure coal and pure biomass
  - $H_2O$ 20-29%, even with dry recycle
  - $NO_x$ 550-750ppmv
  - $SO_2$ 100-750ppmv
  - HCl 8-100ppmv
  - $SO_3+SO_4^{2-}$ 14-30ppmv

***Clear increase in $(SO_3+SO_4^{2-})/SO_2$ ratio when ↑%CCP***

- Ash deposits
  - Markedly fibrous and cohesive for high shares of CCP
  - Similar S levels for pure coal and biomass ($K_2SO_4$ generation)
  - Chloride only observed in ash deposits from pure CCP

# Future challenges

- **Use of other fuels:**
  - *Coal with higher S levels: effect on $SO_x$ generation*
  - *Biomass with higher Na contents: effect on ash deposits characteristics*

- **Further investigation on $SO_3/SO_2$ ratios using high shares of biomass**
  *Applying identical procedure to EPA-Method 8A (avoiding sulfates interferences)*

# Effect of Co-firing on Alkali Sulfate Formation during Oxy-combustion

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## Thanks for your attention

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