Imperial College London

Coal mineral transformations under oxy-fuel combustion conditions

BCURA project B81

Fraser Wigley
Imperial College London

Aim and Objectives

The **aim** is to explore the impact of oxy-fuel combustion conditions on the transformations of coal minerals.

The **objectives** of this project are:

- to investigate the changes in mineral transformations and interactions under oxy-fuel gas conditions through laboratory experiments and the characterisation of combustor samples,
- to explore the origin for these changes through thermodynamic calculations, and
- to predict the impact of oxy-fuel combustion on ash properties and deposition behaviour.

Typical coal ash contents and chemistries

	UK	Aust.	UK	Russia	S Afr.	C Am.	Indo.
Ash	17.7	17.0	15.0	12.6	12.1	9.6	1.0
SiO_2	52.3	75.7	47.8	60.1	54.1	60.3	37.3
Al_2O_3	24.7	17.3	26.8	24.0	33.5	21.5	16.1
Fe_2O_3	12.0	3.7	16.6	6.0	3.1	8.7	32.3
CaO	2.6	0.9	1.3	4.1	4.1	2.3	8.5
MgO	1.9	0.6	1.1	1.1	1.3	2.1	3.4
K_2O	3.6	0.7	3.5	3.0	0.7	2.5	1.1
Na_2O	1.9	0.3	1.7	0.4	0.1	1.1	0.7
TiO_2	1.1	0.8	1.1	1.2	1.7	1.1	0.7

Major coal minerals

Clays:

- Kaolinite $Al_4Si_4O_{18}H_8$
- 'Illite' $(K,Na,Ca,Mg,Fe,Al,Si)_{14}O_{24}H_4$

Quartz SiO_2

Pyrite FeS_2

Carbonates: Siderite $FeCO_3$, Calcite $CaCO_3$ and Ankerite $Ca(Fe,Mg,Mn)(CO_3)_2$

Others: Rutile TiO_2 and Apatite $Ca_5(PO_4)_3OH$

Organically-bound: K^+, Na^+, Ca^{2+} and Mg^{2+}

Mineral transformations on combustion

Clays dehydrate and melt to form rounded/spherical aluminosilicate glass particles. Mullite crystallises.

Quartz partially melts and may dissolve in aluminosilicate particles.

Pyrite loses S and gains O, through a liquid stage, to form spherical iron oxide particles.

Carbonates lose CO_2, with remaining component partially transferring to aluminosilicate particles.

Others lose volatile components and form oxides.

NB mineral-mineral associations, and volatilisation.

Coal ash deposition

In a power station, most coal ash particles leave the boiler with the flue gas and are separated out by electrostatic precipitators.

Some ash particles impinge on walls or super-heaters and are retained, forming deposits that cause ‘slagging’ in the boiler or ‘fouling’ in the convective pass.

A certain level of deposition is anticipated. Boilers are equipped with soot-blowers (steam lances) to remove excess deposit.

Operational problems can occur when deposits reduce heat removal through boiler walls, or cause damage when falling.

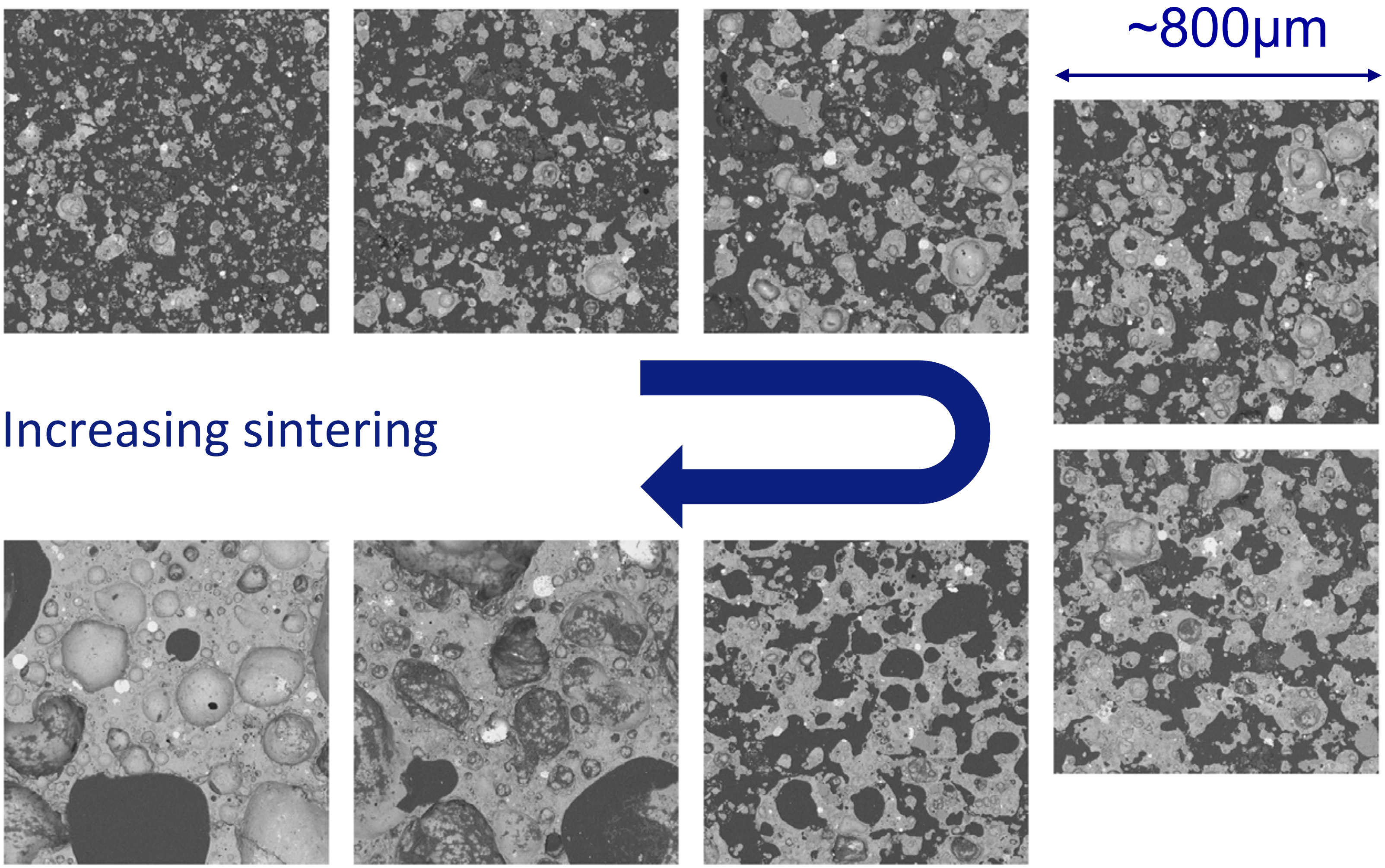
Variation in deposit microstructure

As either coal deposition propensity or substrate temperature increases, ash deposit microstructures show:

- fewer isolated ash particles
- more necks between adjacent ash particles
- greater evidence of particle coalescence
- larger clumps of particles
- reduced porosity and higher deposit density
- a higher proportion of matrix material
- a lower abundance of quartz grains

leading to denser deposits that are more difficult to remove and grow thicker, reducing heat transfer from the boiler.

Cross-sections through ash deposits



Why worry about ash behaviour in oxy-coal firing?

Prof. Terry Wall and colleagues reviewed research on oxy-fuel combustion in 2005 and concluded that "no studies have been found that assess its possible impact on deposit formation and structure". They identified "ash related issues" as requiring further attention.

A 2005 presentation on the current state of oxy-fuel knowledge by the IEA Greenhouse Gas R&D Programme stated that "issues regarding slagging and fouling should be elucidated" and further information is "still necessary regarding the composition of ash, size distribution, ash morphology, slagging and fouling propensity etc."

Oxy-coal combustion – Consequences for ash 1

Combustion of pulverised coal in a mixture of oxygen and recycled flue gas, to produce a flue gas rich in CO_2.

Higher CO_2 partial pressures may affect the transformations of coal minerals, particularly carbonates such as calcite $CaCO_3$ and siderite $FeCO_3$. These minerals are important sources of Ca and Fe, which reduce the viscosities of aluminosilicate liquids – changing the 'stickiness' of the coal ash particles and rate of sintering of the deposits.

Ash deposition in the boiler, and the saleability of ash, may be affected.

Dissociation of calcite, $CaCO_3 \rightarrow CaO + CO_2$

DTA (heating at 3°C/min) shows that calcite dissociates at:

- 600-700°C in air
- 900-960°C in pure CO_2

Calcite reconstitutes at 1000-950°C on cooling in pure CO_2.

Siderite $FeCO_3$ dissociates at ~530°C.

Equilibrium thermodynamic calculations suggest that Na, K, Ca, Mg and Fe will tend to form sulphates, rather than carbonates, on cooling in flue gas.

Kinetics and inhomogeneity dominate the transformations of coal minerals during combustion.

Oxy-coal combustion – Consequences for ash 2

Some fly ash is currently sold for use as a partial cement replacement, and for other civil engineering uses. Fly ash that cannot be sold incurs transport costs and landfill tax.

Condensed gypsum $CaSO_4.2H_2O$ on the ash particle surfaces has a retarding effect on the setting of cement, but this effect is negligible in commercial cements.

Although the literature is ambiguous, condensed calcite $CaCO_3$ on the ash particle surfaces probably accelerates the initial setting slightly but has no effect on final strength. A significant impact here could be a real show-stopper!

OxyCoal-UK: Phase 1 – Project Participants

Lead company

Doosan Babcock Energy Limited

University Participants

Imperial College London

University of Nottingham

Industrial Participants

Air Products plc

BP Alternative Energy International Limited

E.ON UK plc

RWE npower plc

Sponsors / Sponsor Participants

Scottish and Southern Energy plc

ScottishPower Energy Wholesale

EDF Energy plc

Drax Power Limited

DONG Energy Generation A/S

Government Support

Department of Business, Enterprise and Regulatory Reform

Technology Strategy Board

Engineering and Physical Sciences Research Council

CTF deposits for characterisation

CTF deposit samples were acquired under the following conditions:

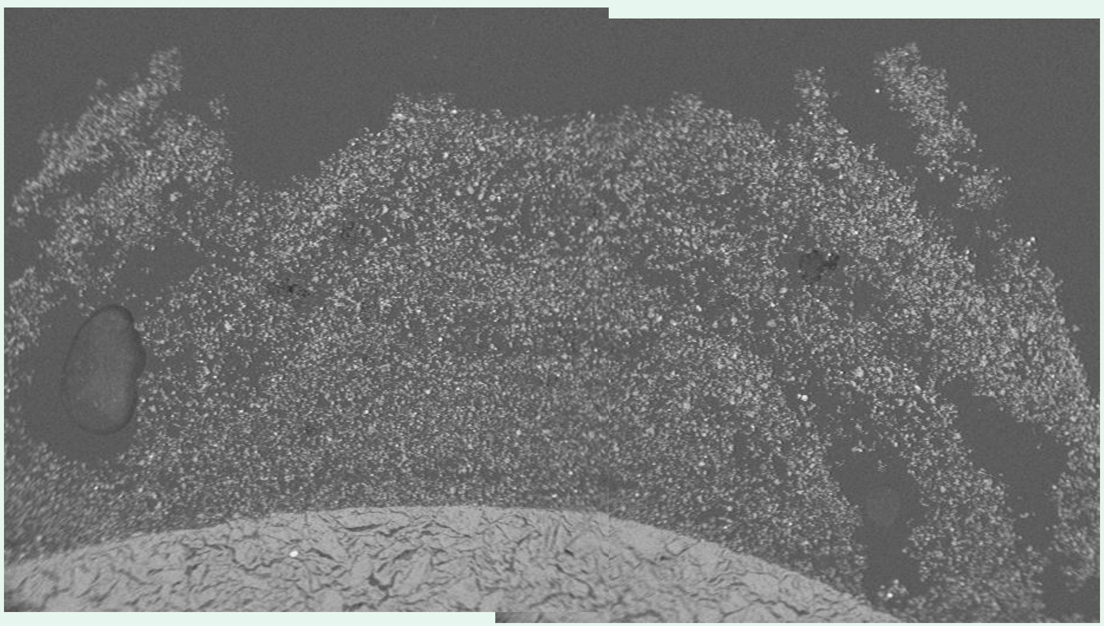
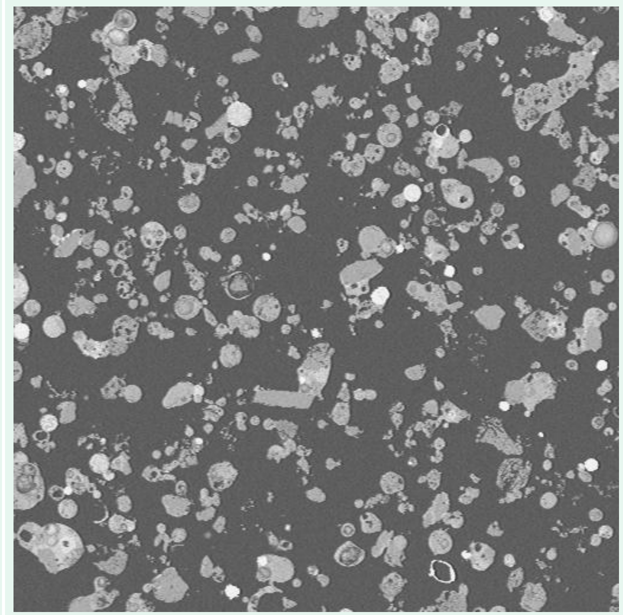
- Two firing modes (air-firing & oxy-firing)
- Three levels of enriched O_2 in the combustion gas (21, 24 & 26 %) for the oxy-fired samples
- Two levels of excess O_2 in the flue gas (2 & 4%)
- Two levels of air staging (0% & 15% OFA)
- Two deposition locations (722 & 726)

With an extra two pairs of deposits collected at higher levels of excess O_2, 36 deposits are available for analysis.

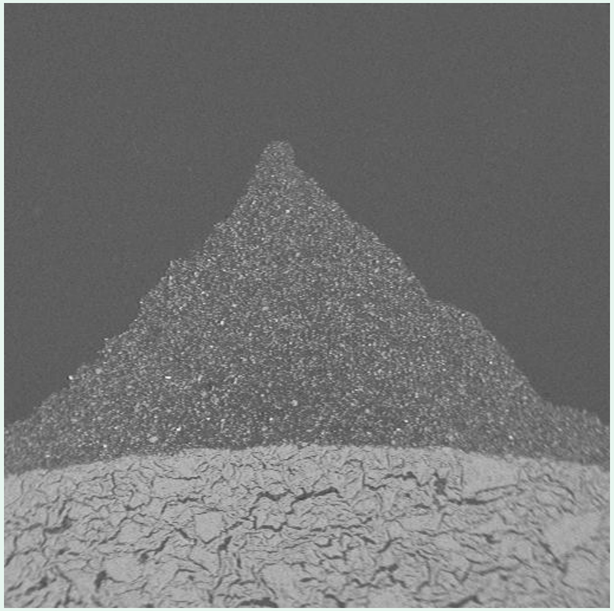
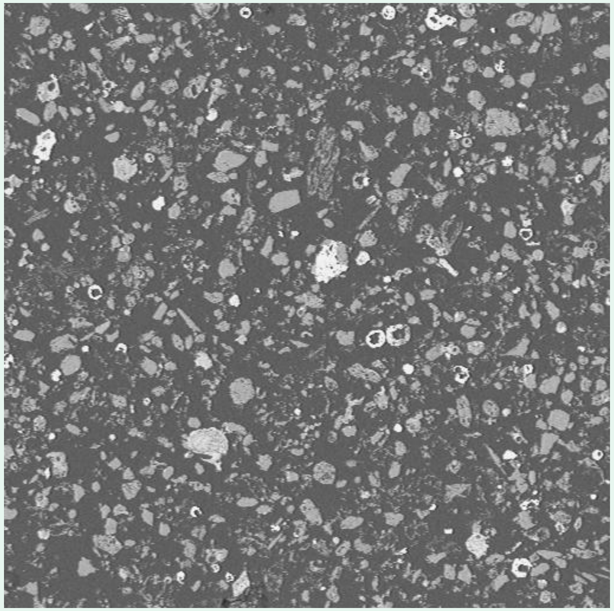
Photographs of El Cerrejon CTF deposits (15% OFA, 2% Excess O_2)

Air-fired	Oxy-fired 21%	Oxy-fired 24%	Oxy-fired 26%
			

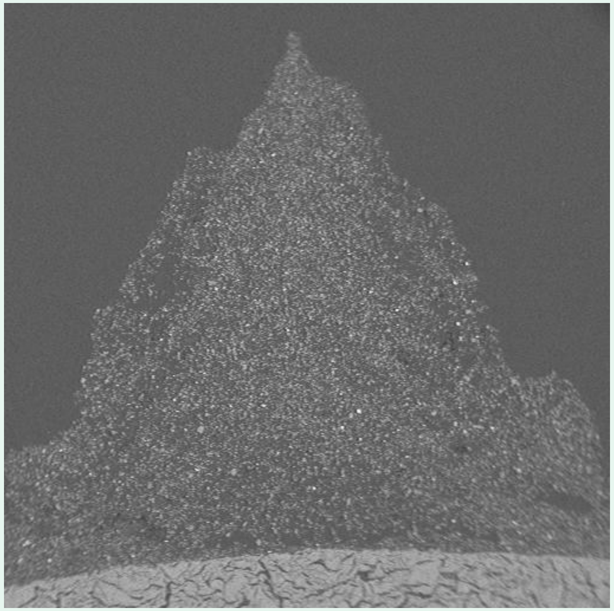
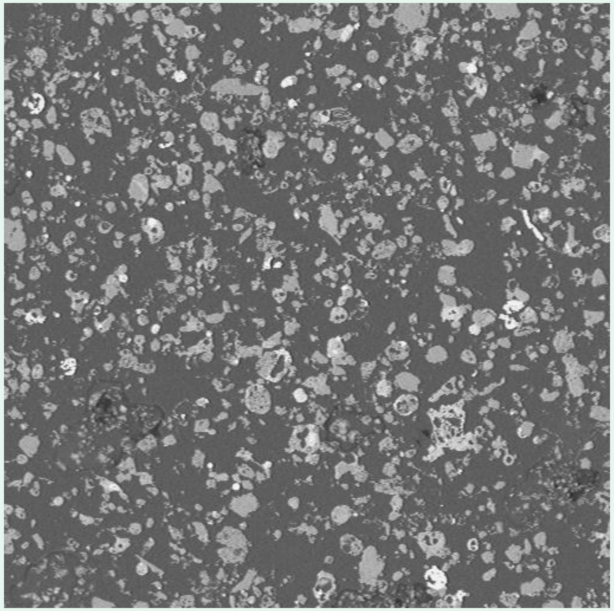
Air-fired

Low magnification Image side length ~8mm	Higher magnification Image side length ~800µm
	

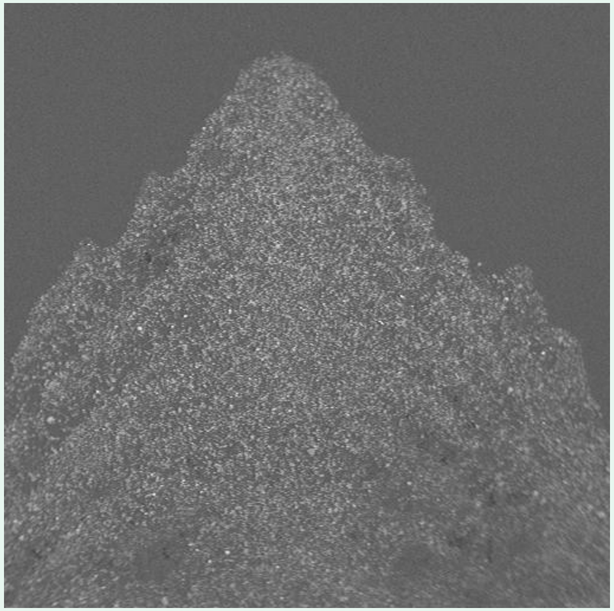
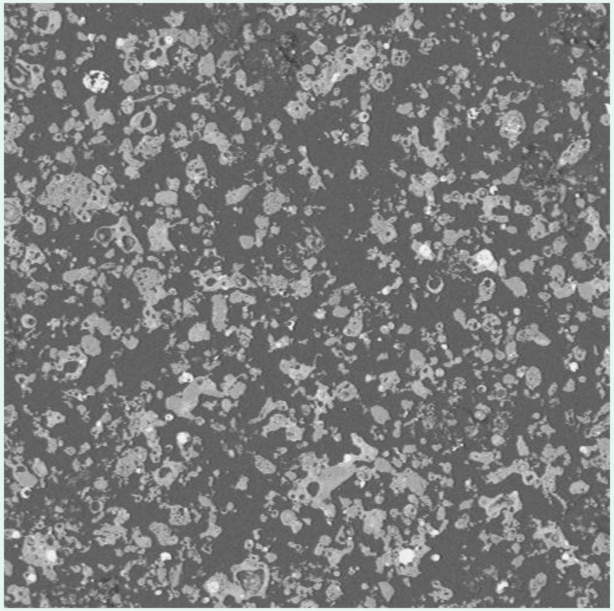
Oxy-fired, 21% O_2 enriched

Low magnification Image side length ~8mm	Higher magnification Image side length ~800µm
	

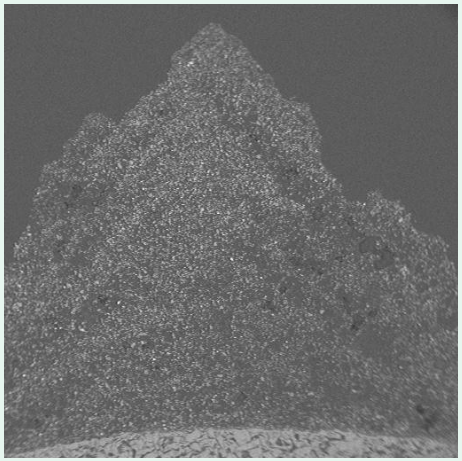
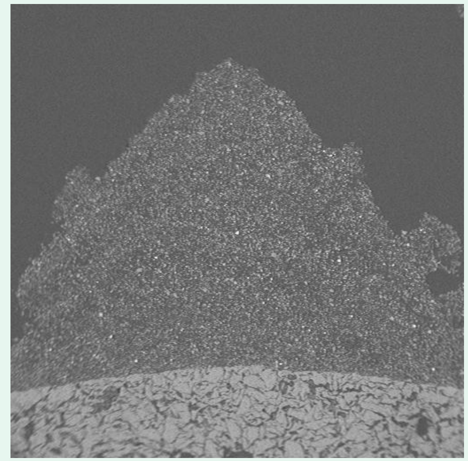
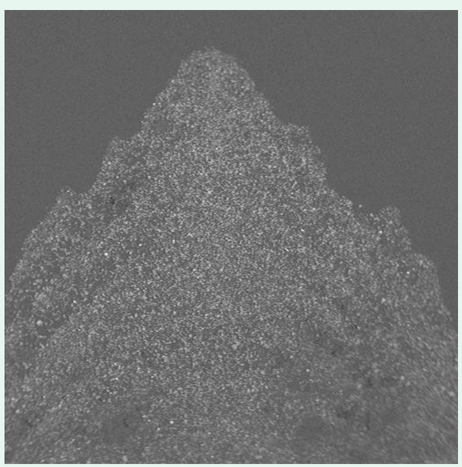
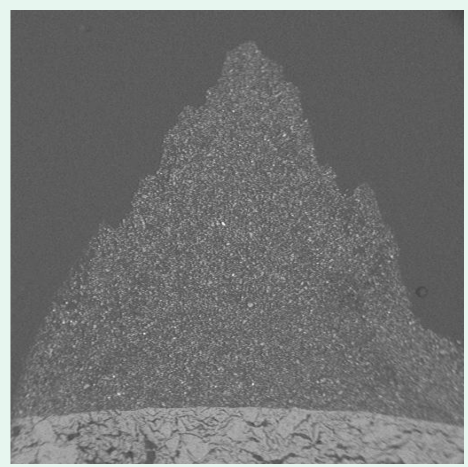
Oxy-fired, 24% O_2 enriched

Low magnification Image side length ~8mm	Higher magnification Image side length ~800µm
	

Oxy-fired, 26% O_2 enriched

Low magnification Image side length ~8mm	Higher magnification Image side length ~800µm
	

Cross-sections through CTF deposits Oxyfired 26% O_2 Low magnification

	2% Excess O_2	4% Excess O_2
0% OFA		
15% OFA		

CTF deposit macrostructures – Summary

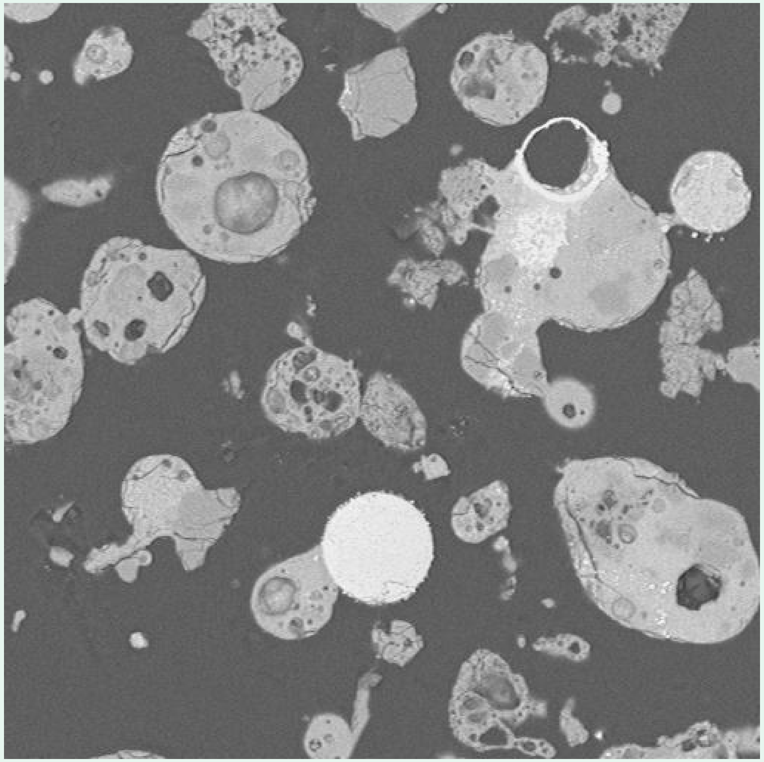
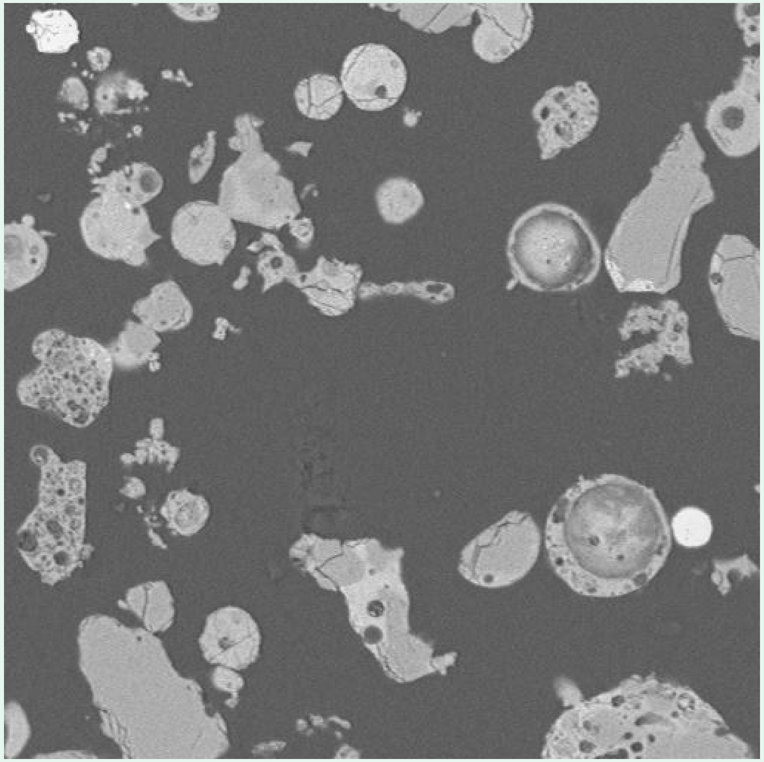
Compared to air-fired deposits, oxy-fired deposits were:

- Smaller
- More friable (weaker)
- Different shape (wedge)
- More densely packed

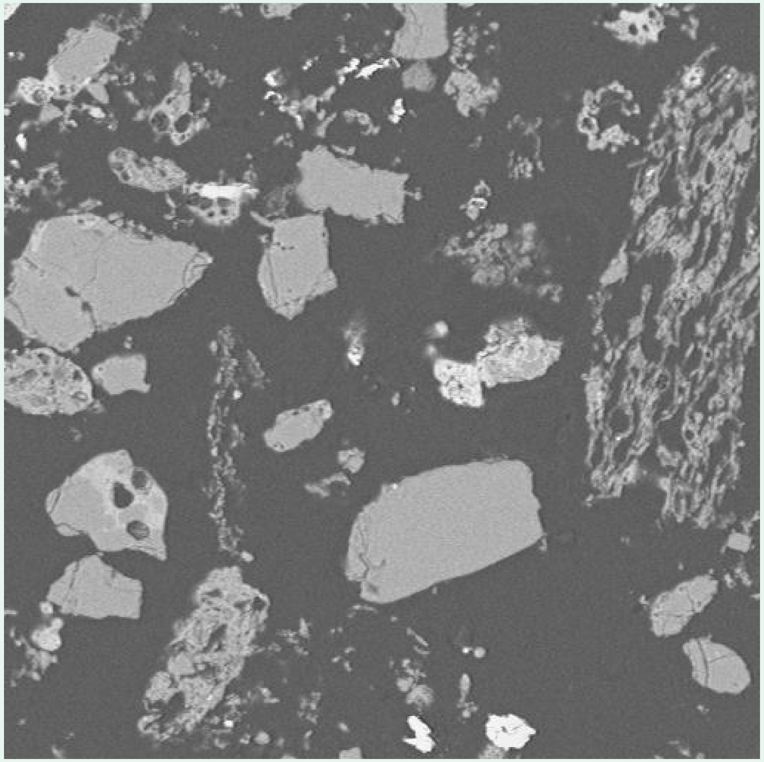
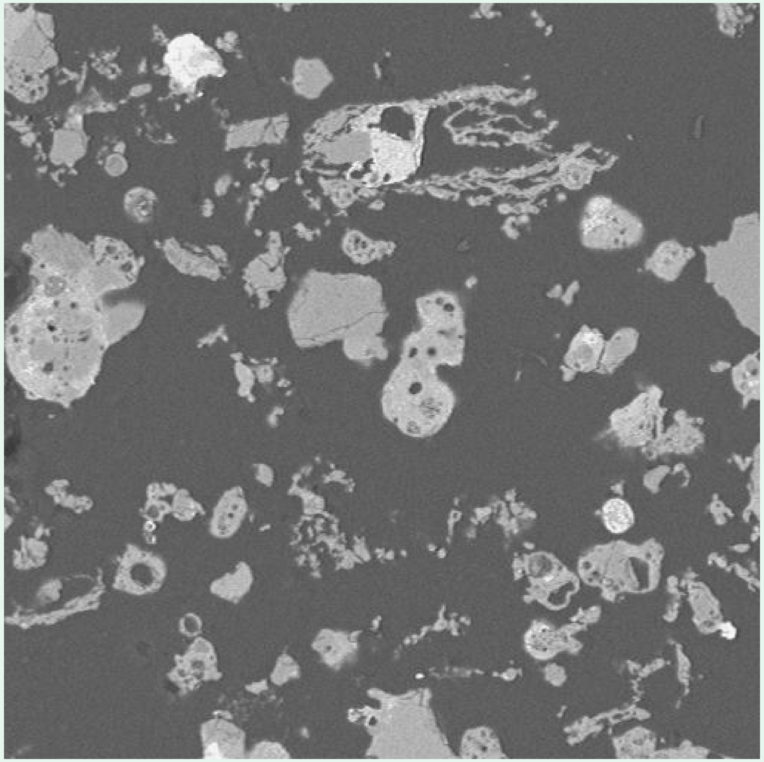
Oxy-fired deposits became larger as the level of O_2 enrichment increased.

Deposit macrostructure was not significantly affected by the level of excess oxygen or the proportion of over-fire air.

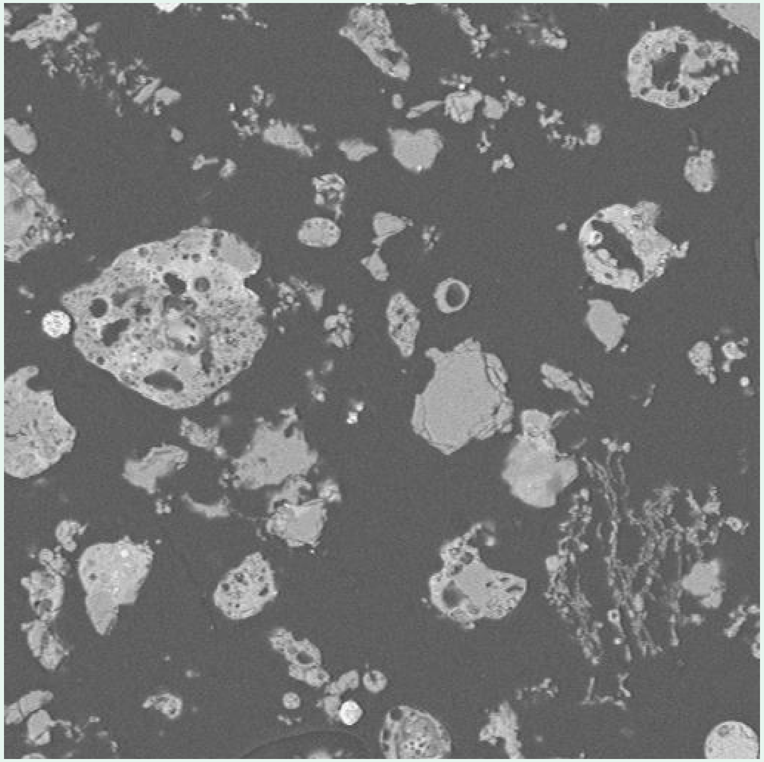
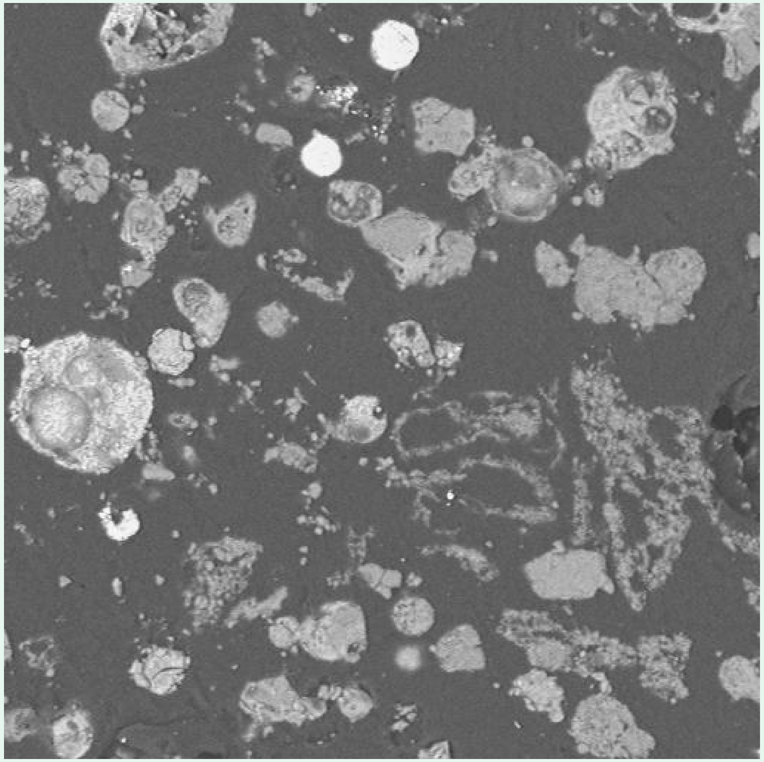
Cross-sections through air-fired deposits

15% OFA, 2% Excess O_2	15% OFA, 4% Excess O_2
	

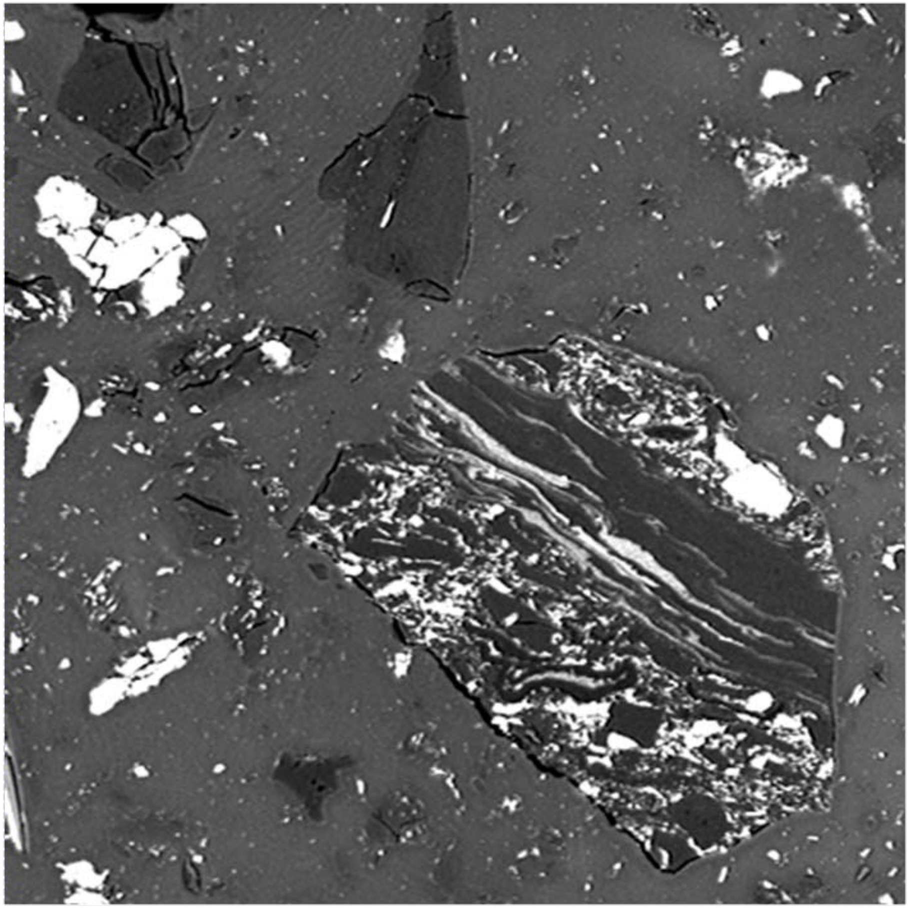
Cross-sections through oxy-fired deposits 1

21% O_2 enriched	24% O_2 enriched
	

Cross-sections through oxy-fired deposits 2

24% O_2 enriched	26% O_2 enriched
	

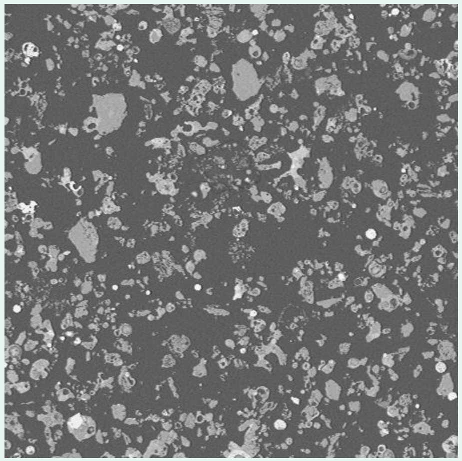
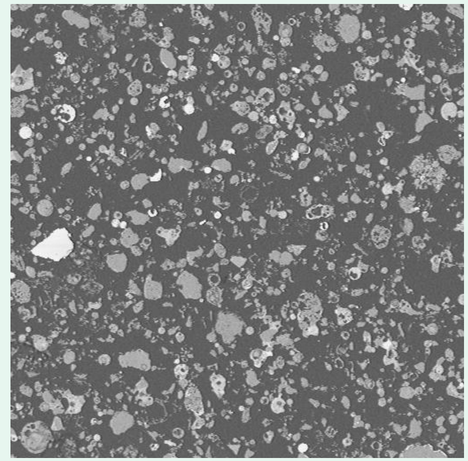
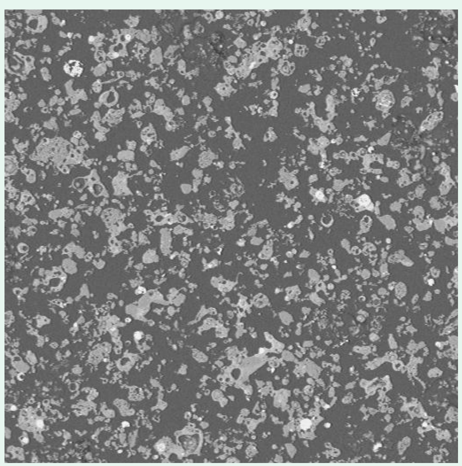
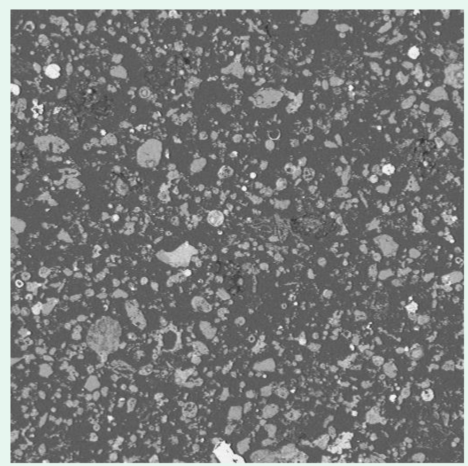
Interlayered macerals and clay in a coal particle



Back-scattered electron image of a larger coal particle containing organic macerals (darker) interlayered with clay and quartz (white) in a resin matrix (lighter).

Image side ~100 μm

Cross-sections through CTF deposits
Oxy-fired 26% O_2 Higher magnification

	2% Excess O_2	4% Excess O_2
0% OFA		
15% OFA		

CTF deposit microstructures – Summary

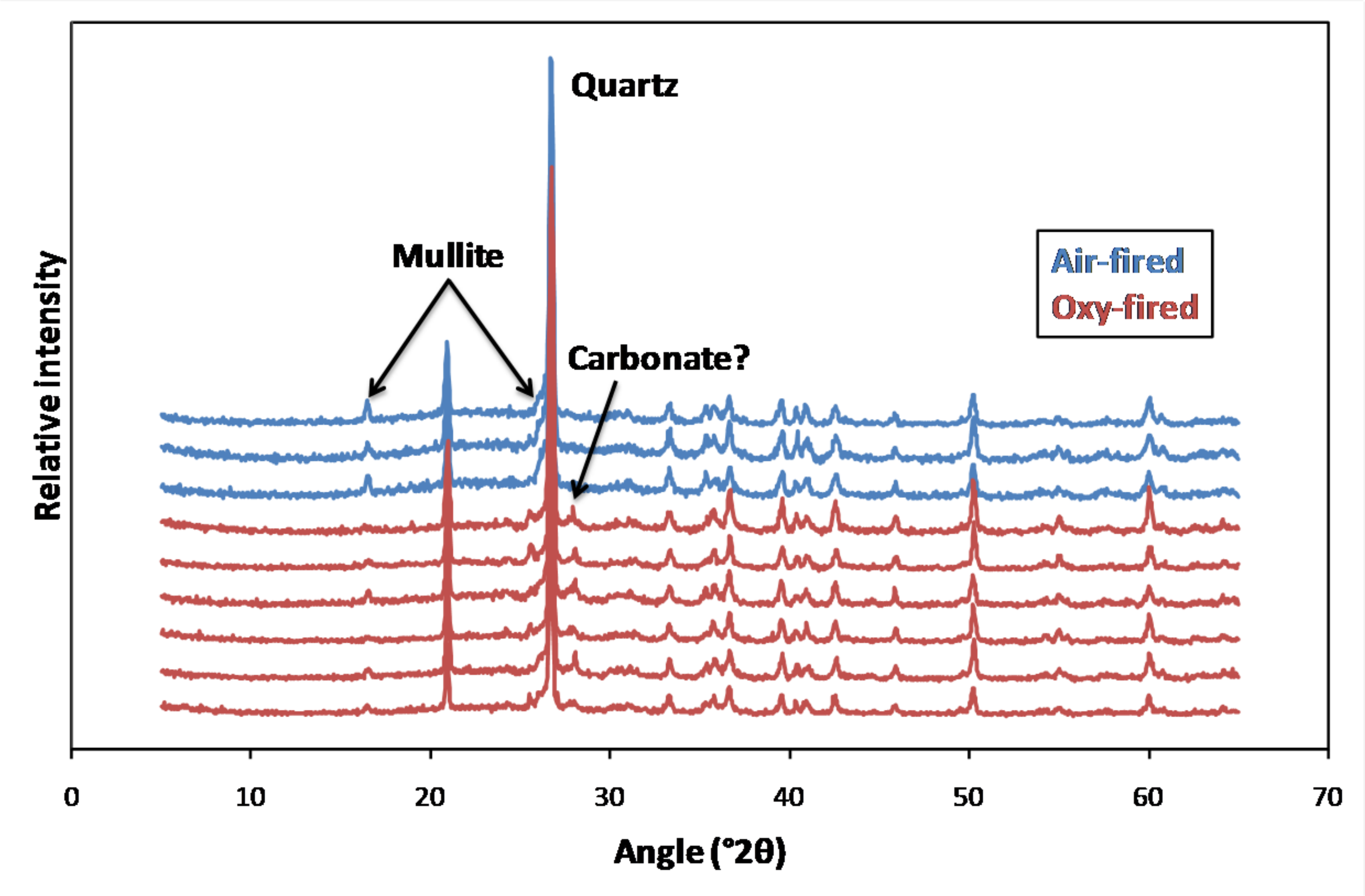
Compared to air-fired deposits, oxy-fired deposits:

- Had similar particle size
- Were less well sintered
- Contained particles that were less rounded
- Were richer in clay-derived particles that were not fully fused

Oxy-fired deposits showed no significant changes in microstructure as the level of O_2 enrichment increased.

Deposit microstructure was not significantly affected by the level of excess oxygen or the proportion of over-fire air.

Crystalline phases in CTF deposits, by XRD



CTF deposit phases - Summary

The phases identified in oxy-fired deposits are generally the same as those found in air-fired deposits; coal minerals have shown the same transformations on combustion.

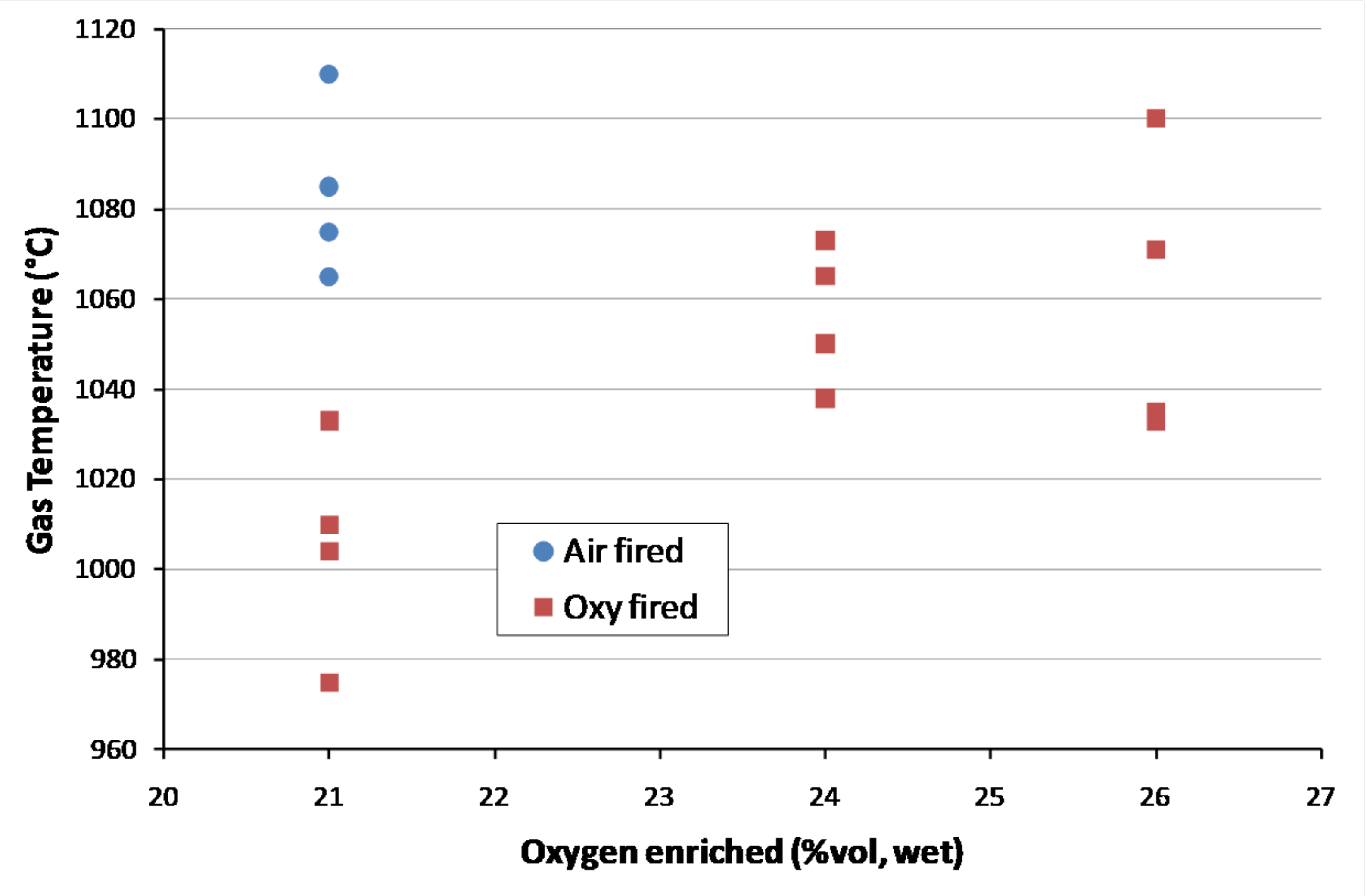
Mullite and glass are less abundant (compared to quartz) in the oxy-fired deposits than in the air-fired deposits.

The lower level of mineral transformation is a consequence of lower flame temperatures.

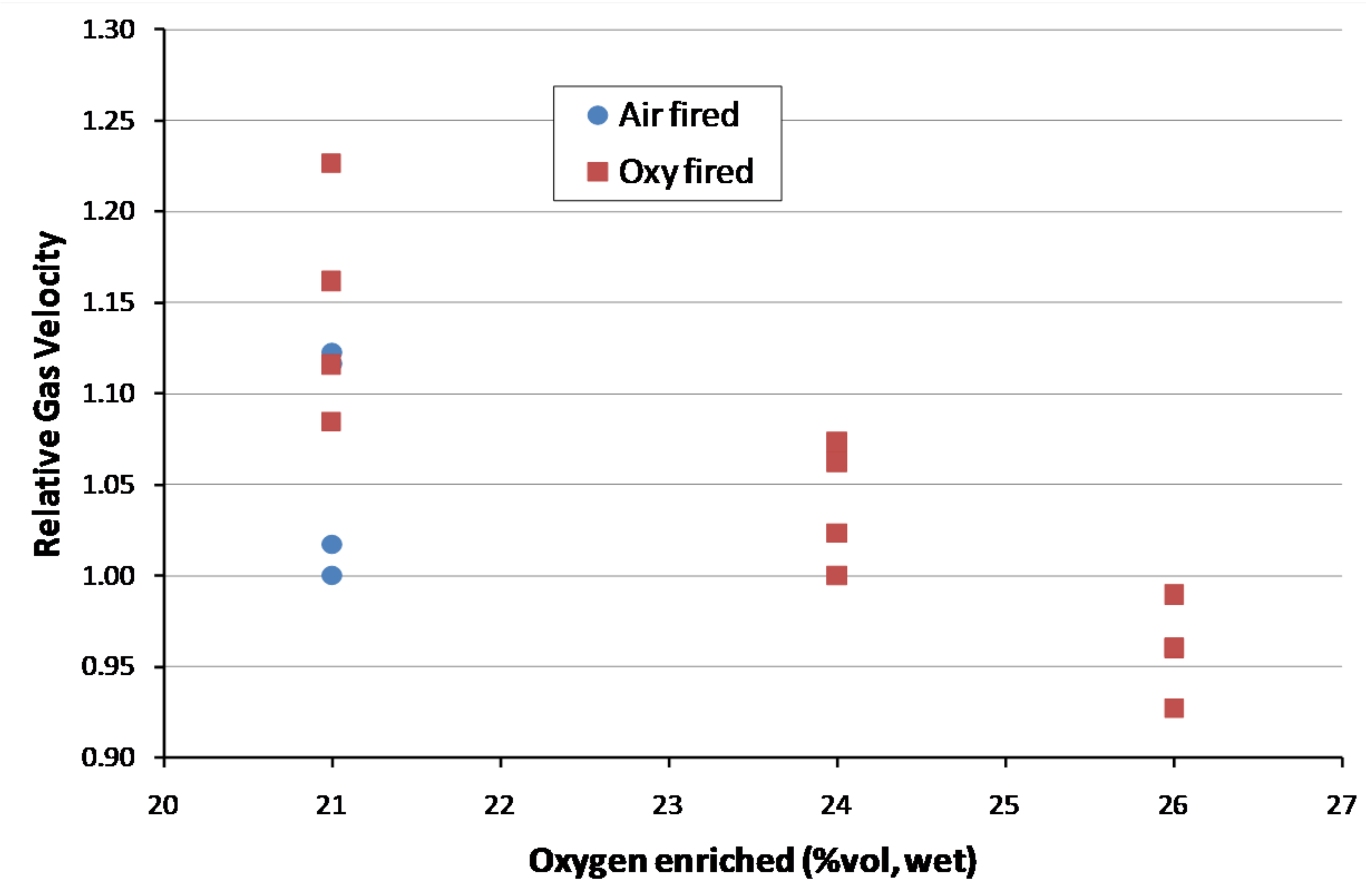
Carbonates may be present in the oxy-fired deposits, which might suggest that they have persisted through the flame.

The two major phases in the XRD spectra (quartz and glass) are not in thermodynamic equilibrium.

Gas temperatures for CTF deposits



Relative gas velocities for CTF El Cerrejon deposits



Recent results from IVD, University of Stuttgart

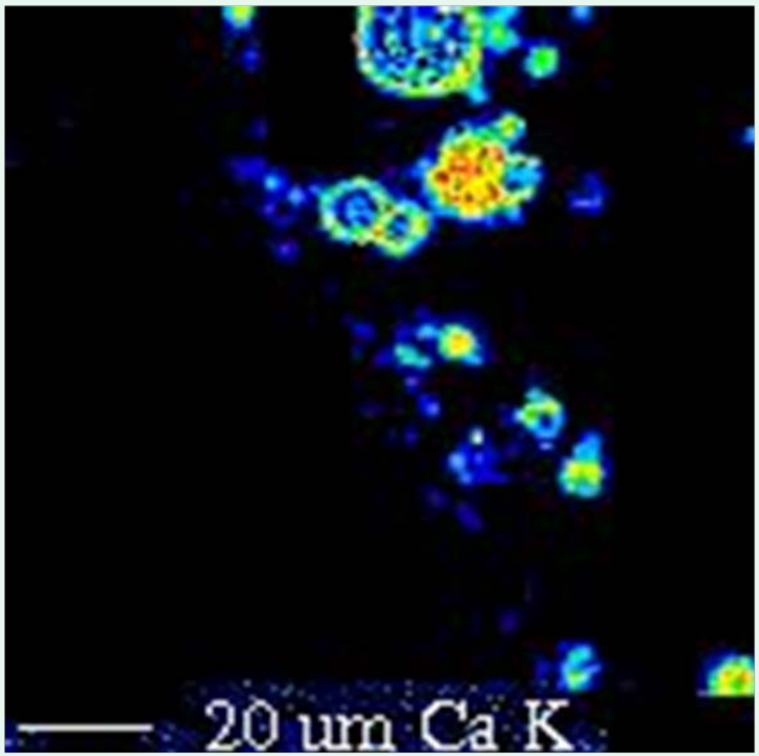
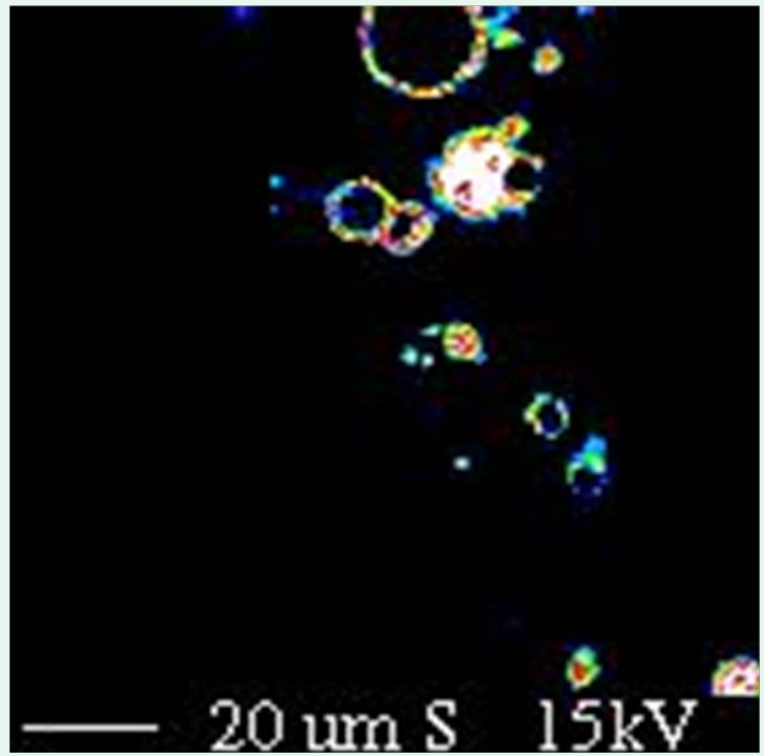
Dr Jörg Maier and group have:

- Produced samples of fly ashes and deposits on a 0.5MW rig under oxy-firing conditions
- Characterised the distribution of elements in ash particles cooled to below 850°C

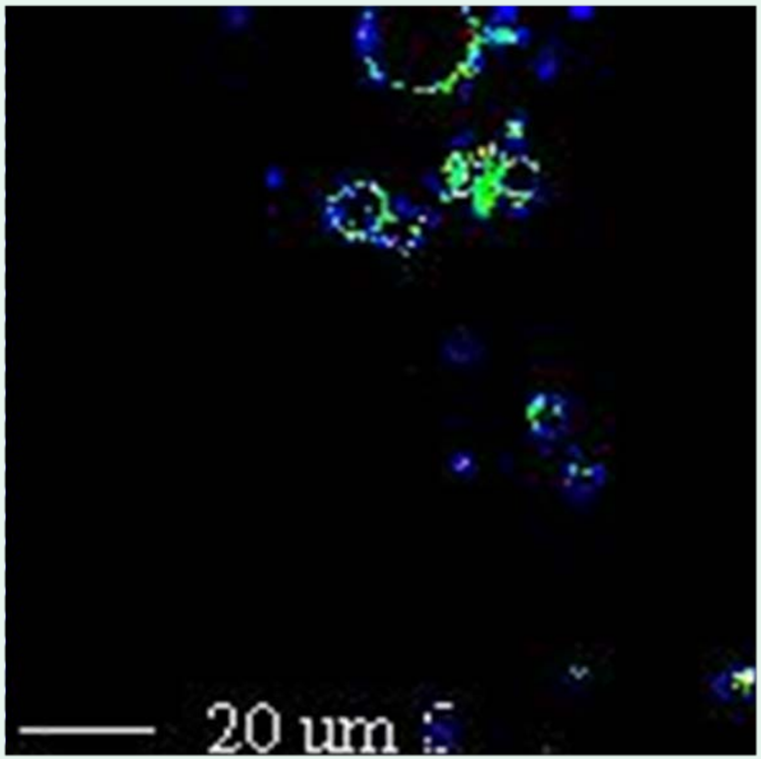
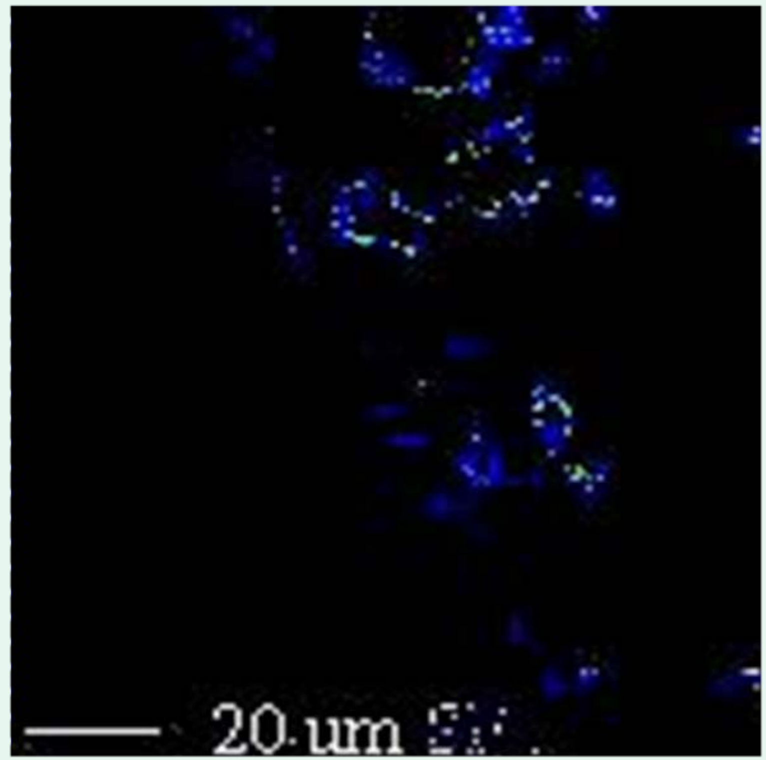
Dr Maier concludes:

- "Indications that, beside sulfatization, carbonization on the particle surface of deposits occurs under Oxyfuel conditions"
- "Impact of carbonization on fouling and corrosion in the convective section of the boiler needs further testing"

Ca and S on the surface of fine fly ash particles

Distribution of Ca Image side length ~100µm	Distribution of S Image side length ~100µm
	

Associations of Ca with S and with C

Association of Ca with S Image side length ~100µm	Association of Ca with C Image side length ~100µm
	

Provisional overall conclusions from one coal

For oxy-firing, compared to air-firing:

- Coal minerals showed the same transformations, but to a lesser extent because of lower flame temperatures
- Deposits were smaller and showed less sintering, because lower flame temperatures and gas temperatures meant that the ash particles were less 'sticky'
- Deposit structures were affected by different gas velocities and densities
- Deposits appeared to become more like air-fired deposits as the level of oxygen enrichment increases
- Carbonates may have persisted, and formed on cooling

Future Work

Acquire and characterise oxy-fired ashes and deposits from more coals.

Focus on the oxy-firing combustion conditions that are likely to be used at full scale.

Start laboratory investigation of the thermal dissociation and reconstitution of carbonate minerals.

Acknowledgements

- Colleagues on the OxyCoal-UK project and at Imperial
- Funding from BCURA, BERR and EPSRC (views are solely those of the author)