

Investigating the Effect of Coal Mineral Matter on Blast Furnace Coal Injection

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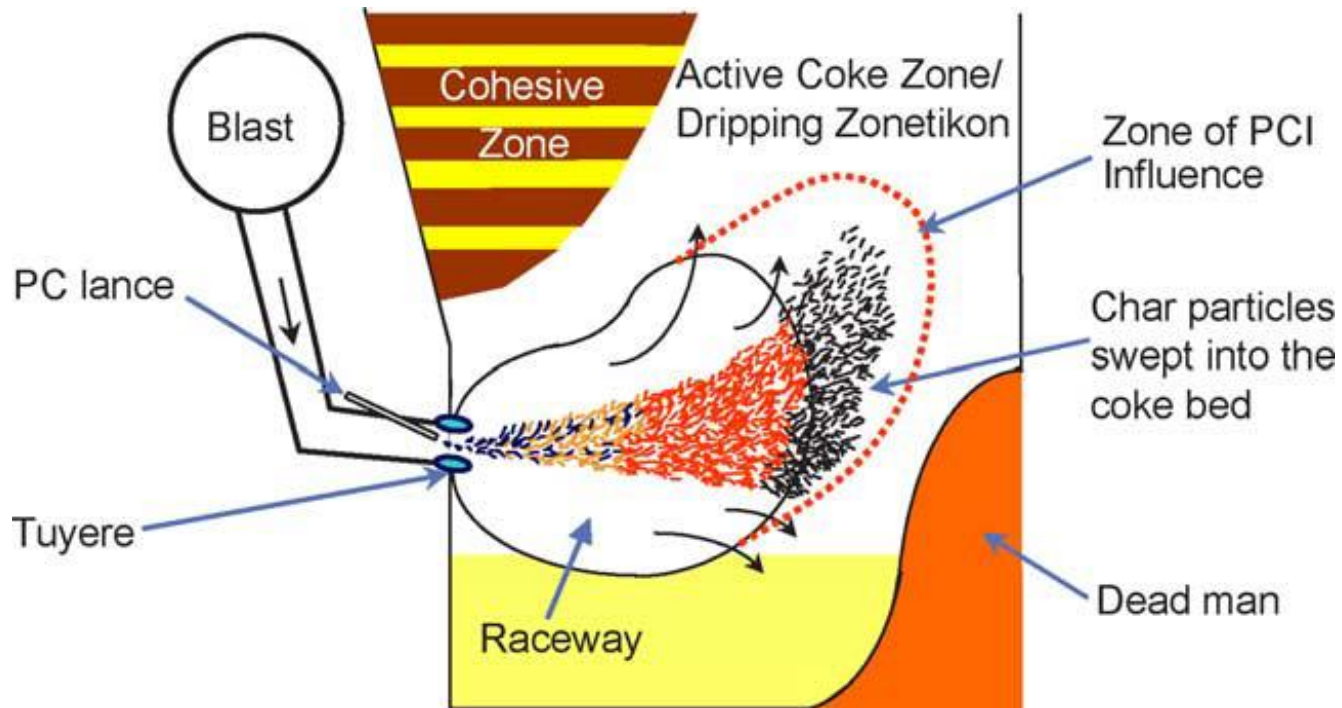
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Sponsored by Tata Steel IJmuiden

Industrial Supervisor: Stefan Born



Introduction



Raceway. Figure taken from (Mathieson et al. 2005)

- Coal is injected with hot oxygen enriched air at the bottom of the blast furnace via the **tuyeres**.
- This creates a void known as the **raceway**.
- The coal contains **mineral matter** which is made up of numerous elements.
- These elements have different properties in the blast furnace.
- They have effects within the raceway, the blast furnace as a whole, and for the slag chemistry.

Research Summary

- To use a Drop-Tube Furnace (DTF) to prepare chars and ashes under a range of conditions.
- To analyse the ash mineralogy and chemistry using a range of techniques.
- To investigate physical and chemical properties of the ash with respect to the injection, combustion, burden interaction and slag chemistry.

Hard, high melting point minerals

May cause wear in the coal injection zone.

Ash fusion temperature

Could determine whether ash is caught in the bird's nest or travels up the furnace as a dust.

Better understanding of the ash changes can allow us to determine which minerals may:

- Volatilise
- Stick in the back of the raceway.
- Go up the stack
- Cycle through the furnace
- End up in the slag

Experimental Procedure

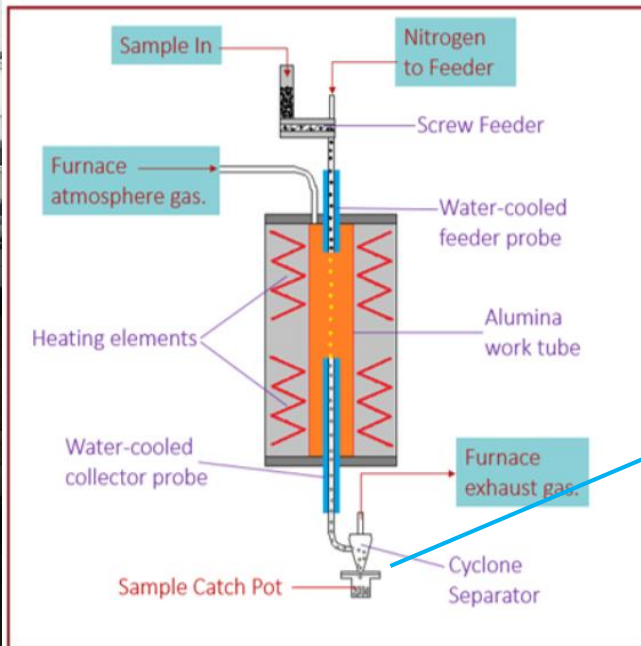


Low Volatile injection coal

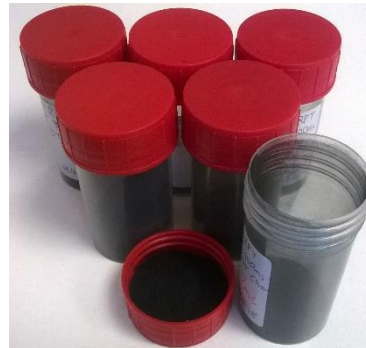
- Pulverised particle size.
- 100% <300 μm 50% <75 μm .
- Volatiles: 8.5%. Ash: 10.4%

Drop Tube Furnace (DTF)

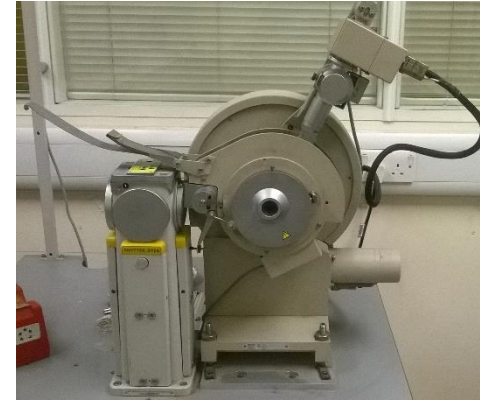
- High heating rates 10^4 - 10^5 K/s
- Temperature up to 1300°C
- Choice of feed gases: air, nitrogen, CO₂
- Sample feed 30 g/hr
- Residence times ranging from 35-700 ms



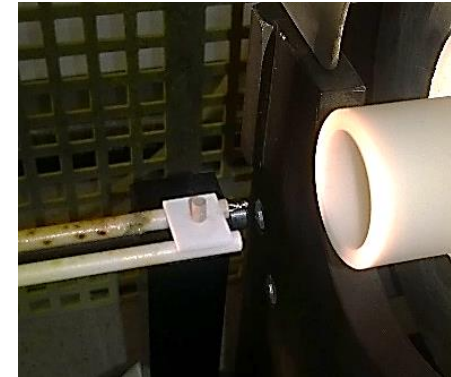
Char from DTF



X-ray Diffraction (XRD) Mineral Analysis



Ash Fusion Testing To determine ash melting temperature.



X-ray Fluorescence Elemental Analysis

Ash



Furnace Ashing at 815°C BS ISO 1171:2010 Determination of Ash



Testing Conditions

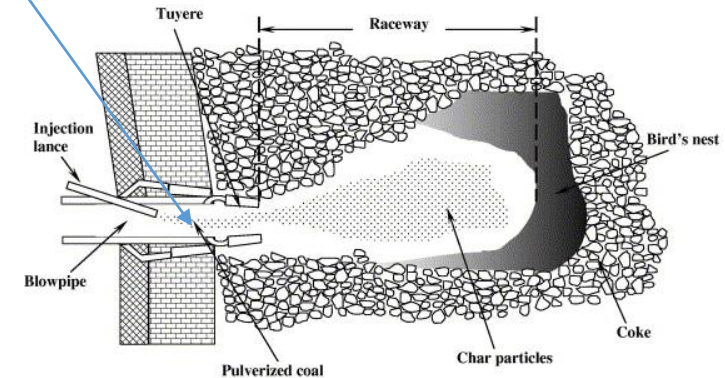
- The DTF reaction conditions are shown in the table below.
- Aiming to investigate the effect of temperature, residence time and gas environment.

| Temperature | Residence Time | Gas Environment |
|-------------|----------------|-----------------|
| 1100°C | 100ms | Air |
| 1100°C | 350ms | Air |
| 1300°C | 100ms | Air |
| 1300°C | 350ms | Air |
| 1100°C | 100ms | Nitrogen |
| 1100°C | 350ms | Nitrogen |
| 1300°C | 100ms | Nitrogen |
| 1300°C | 350ms | Nitrogen |
| 1100°C | 100ms | CO ₂ |
| 1100°C | 350ms | CO ₂ |
| 1300°C | 100ms | CO ₂ |
| 1300°C | 350ms | CO ₂ |

Combustion occurs in the raceway in the presence of O₂ enriched air. High particle temperatures reached.

A nitrogen atmosphere will be cooler than in air, due to absence of combustion.

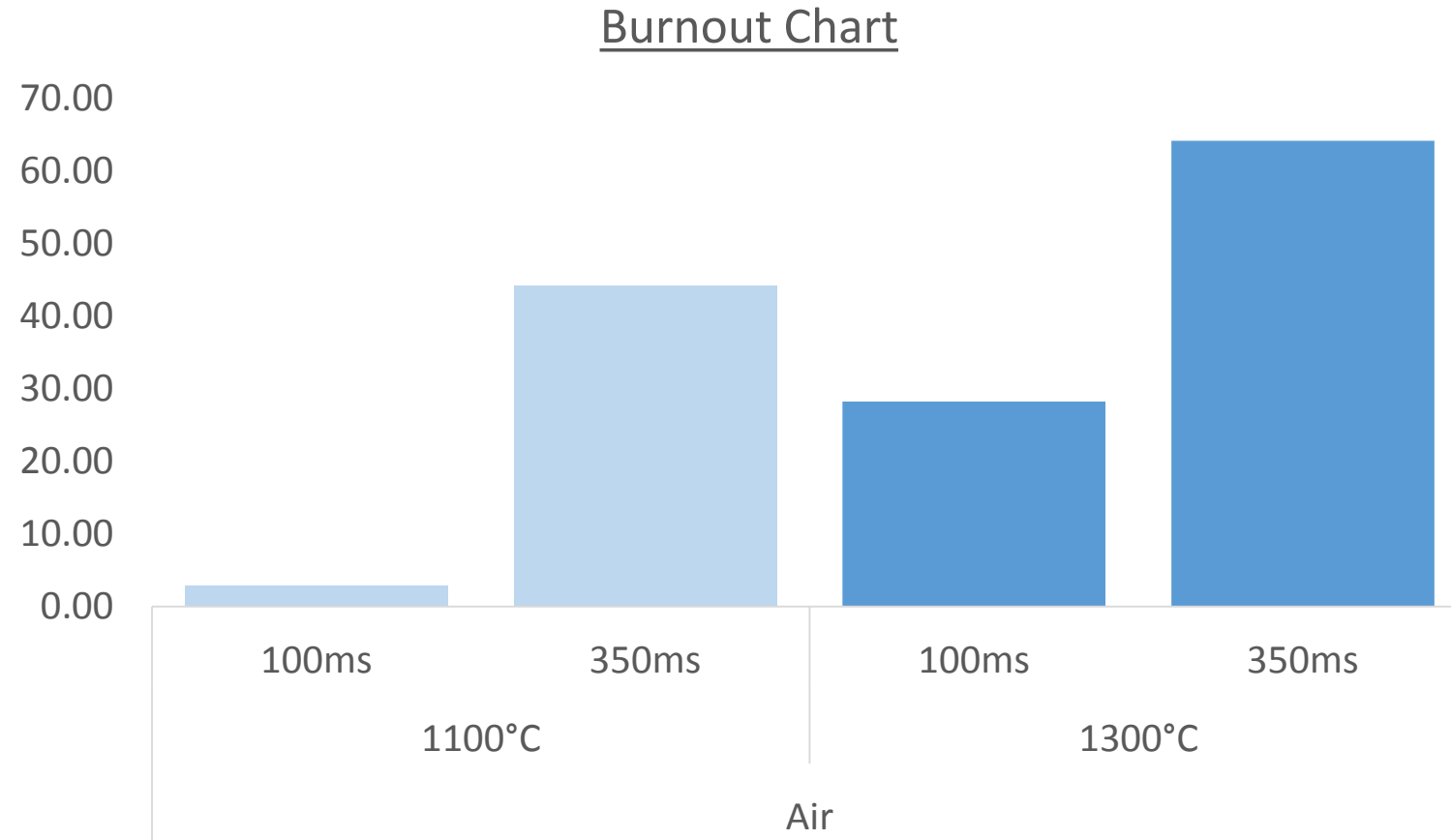
CO₂ is used to investigate what might happen in a reducing environment where $C + CO_2 \leftrightarrow 2CO$.



Raceway. Figure taken from (Chen et al. 2007)

- Minerals present in the ashes were semi-quantitatively analysed (using XRD diffractograms).
- Ash melting temperature was determined for each of the reaction conditions.

DTF Coal Combustion



- The sample in 1300°C Air burns out to a greater extent than the 1100°C sample.
- The samples in the non-oxidising gases do not combust.
- DTF allows us to compare injection coal reactivity.

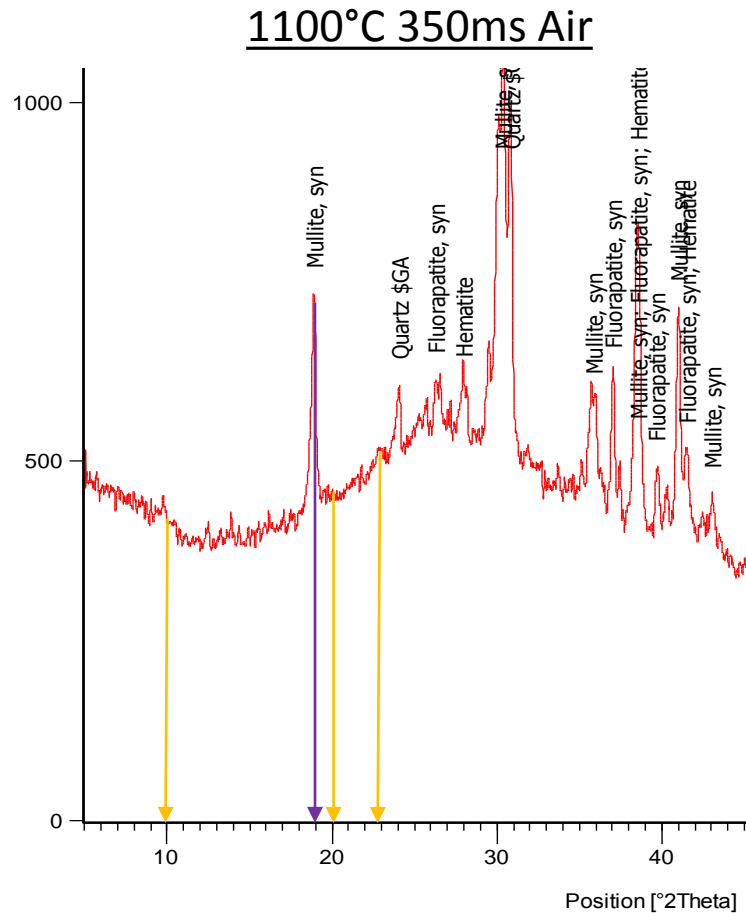
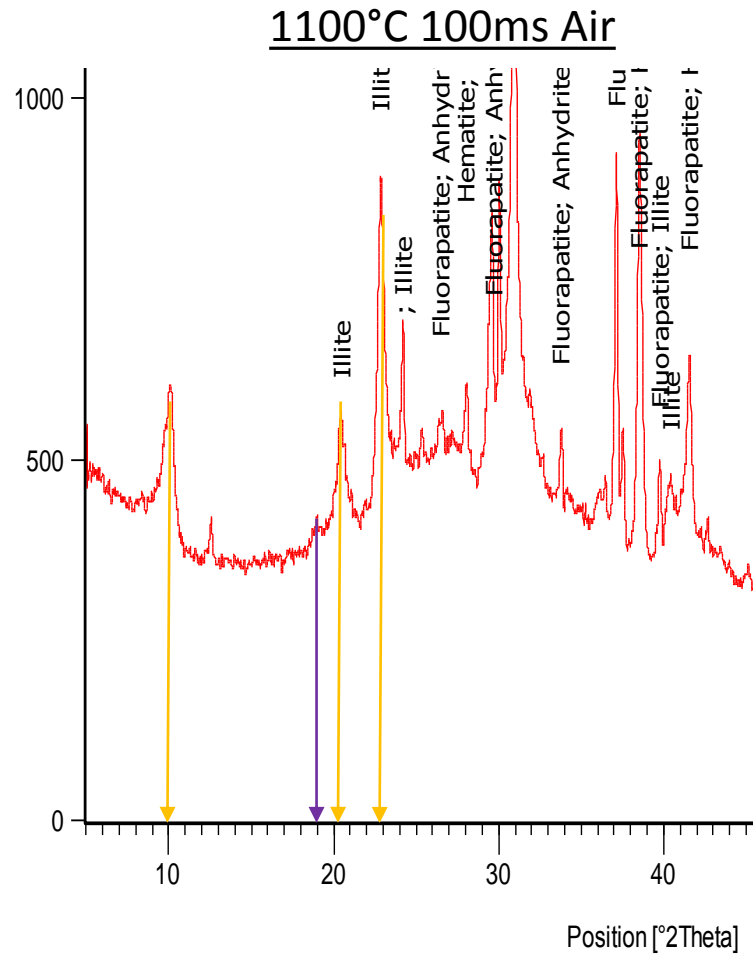
Typical Coal Minerals

- Typical coal minerals are described on the left table.
- The resultant elements and potential effects are described on the right.

| Mineral Type | Common Example |
|-------------------|--|
| Silicate (Quartz) | SiO ₂ |
| Clays | Al ₂ Si ₂ O ₅ (OH) ₄ , (Na,Ca) _{0.33} (Al,Mg) ₂ (Si ₄ O ₁₀), KAl ₂ (AlSi ₃ O ₁₀)(F,OH) ₂ |
| Carbonates | CaCO ₃ , CaFe(CO ₃) ₂ |
| Sulphates | CaSO ₄ |
| Sulphides | FeS ₂ |
| Phosphates | Ca ₅ (PO ₄) ₃ F |
| Metal oxides | Fe ₂ O ₃ , TiO ₂ |

| Element | Effect on Ash Melting Temperature | Effect in the raceway | Effect in the furnace |
|------------|-----------------------------------|------------------------------|--|
| Silicon | Increase | Possible silica vaporisation | Enters slag. |
| Aluminium | Increase | | Enters slag. |
| Iron | Decrease | Catalytic | |
| Magnesium | Decrease | | Enters slag. |
| Calcium | Decrease | Catalytic | Enters slag. |
| Sodium | Decrease | Catalytic | Cycling and accumulation. Coke degradation |
| Potassium | Marginal Effect | Catalytic | Cycling and accumulation. Coke degradation |
| Sulphur | Decrease | | Enters slag and hot metal |
| Titanium | Increase | None | Healing effect on refractory lining |
| Phosphorus | | | 90-100% Enters hot metal. |

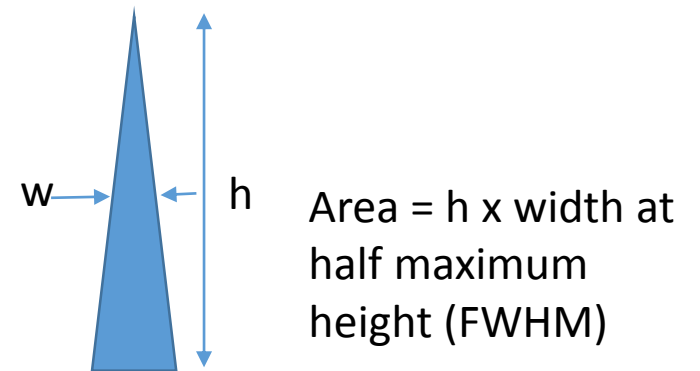
XRD Diffractogram Analysis



With increasing residence time, the following occurs:

- The structure of the clays are destroyed.
- Mullite forms.
- There are other changes also.

We can semi-quantify the percentage of a mineral phase by measuring the **area** of its main peak. But we need to identify all of the minerals present.



Therefore given sufficient temperature and time this hard mineral forms.

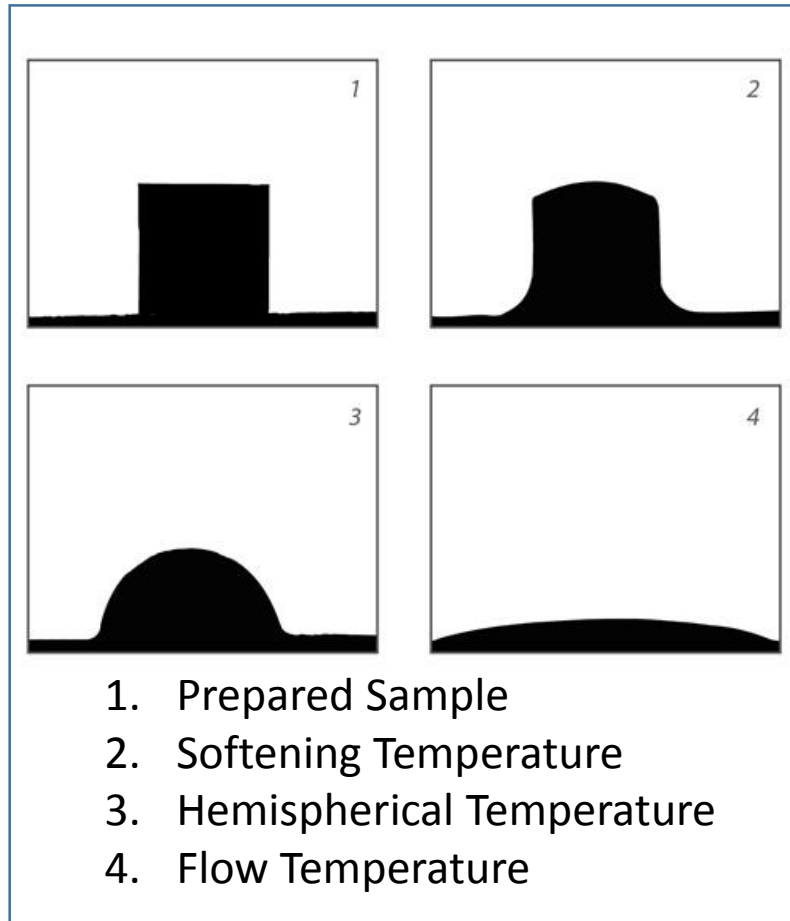
X-Ray Diffraction Mineral Identification and Quantification

| Temperature | Residence Time | Gas Environment | % Quartz (SiO ₂) | % Hematite (Fe ₂ O ₃) | % Fluorapatite [Ca ₅ (PO ₄) ₃ F] | % Clay Al ₂ Si ₂ O ₅ (OH) ₄ | % Anhydrite (CaSO ₄) | % Mullite (3Al ₂ O ₃ .2SiO ₂) |
|-------------|----------------|-----------------|------------------------------|--|--|---|----------------------------------|---|
| 1100°C | 100ms | Air | 33.5 | 13.2 | 14.6 | 19.8 | 13.9 | 4.9 |
| 1100°C | 350ms | Air | 29.8 | 25.0 | 7.8 | 8.3 | 2.2 | 26.8 |
| 1300°C | 100ms | Air | 34.5 | 24.2 | 8.3 | 3.6 | 6.2 | 23.2 |
| 1300°C | 350ms | Air | 28.2 | 30.1 | 6.0 | 2.8 | 8.3 | 24.6 |
| 1100°C | 100ms | Nitrogen | 36.9 | 7.9 | 11.8 | 36.3 | 7.1 | 0.0 |
| 1100°C | 350ms | Nitrogen | 31.7 | 10.9 | 16.2 | 32.7 | 8.4 | 0.0 |
| 1300°C | 100ms | Nitrogen | 32.1 | 12.1 | 14.3 | 26.1 | 15.4 | 0.0 |
| 1300°C | 350ms | Nitrogen | 35.3 | 23.1 | 19.1 | 3.3 | 4.2 | 15.0 |
| 1100°C | 100ms | CO ₂ | 34.5 | 11.5 | 13.8 | 31.8 | 8.4 | 0.0 |
| 1100°C | 350ms | CO ₂ | 35.6 | 9.0 | 15.6 | 35.5 | 4.3 | 0.0 |
| 1300°C | 100ms | CO ₂ | 39.6 | 14.3 | 16.7 | 23.9 | 5.5 | 0.0 |
| 1300°C | 350ms | CO ₂ | 27.4 | 18.3 | 18.4 | 10.7 | 13.9 | 11.3 |

- As temperature and residence time increases, the proportion of clay decreases.
- Mullite forms in air but there is more at 1300°C than 1100°C
- Mullite only forms in N₂ and CO₂ at 1300°C 350ms.
- Therefore, the formation of mullite is temperature dependent.

Ash Fusion Tests (AFT)

- Ash fusion tests (AFTs) were carried out on a Misura Heating Microscope at Materials Processing Institute (MPI).



- Prepared Sample
- Softening Temperature
- Hemispherical Temperature
- Flow Temperature

Ideal Ash Fusion Test



Heating Microscope
Misura 3.32
www.expertsystemsolutions.com
tech@expertsystemsolutions.com



| | | | |
|---------------------|--------------------------|--------------------------|---------------|
| Code: | 003575 | Test type: | Single sample |
| Description: | Celtic coal ash 815C rpt | Min. temperature: | 500 °C |
| Date: | 01/02/2017 | Max. temperature: | 1326 °C |

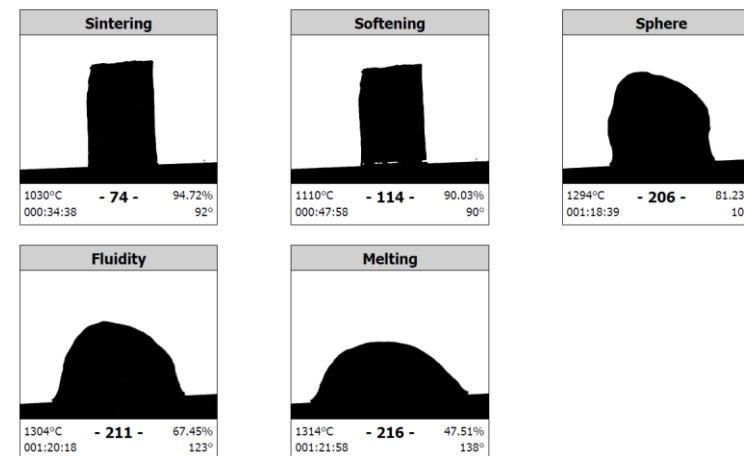
| Thermal cycle | | | |
|---------------|------|---------|--------|
| | Rise | Temp | Stasis |
| 1 | 50.0 | 900 °C | 0.0 |
| 2 | 6.0 | 1500 °C | 0.0 |
| 3 | | | |
| 4 | | | |
| 5 | | | |
| 6 | | | |
| 7 | | | |
| 8 | | | |

| Typical values | |
|----------------|-------------|
| Shape | Temperature |
| Sintering | 1030 °C |
| Softening | 1110 °C |
| Sphere | 1294 °C |
| Fluidity | 1304 °C |
| Melting | 1314 °C |

| Test duration | |
|-----------------------|-----------|
| Total | 001:23:59 |
| From 1st click | 001:18:55 |

| Breaks | | | |
|--------|-------|---------|--------|
| | Start | Interv. | End |
| 1 | 500°C | 50°C | 900°C |
| 2 | | 2°C | 1300°C |
| 3 | | 2°C | 1500°C |

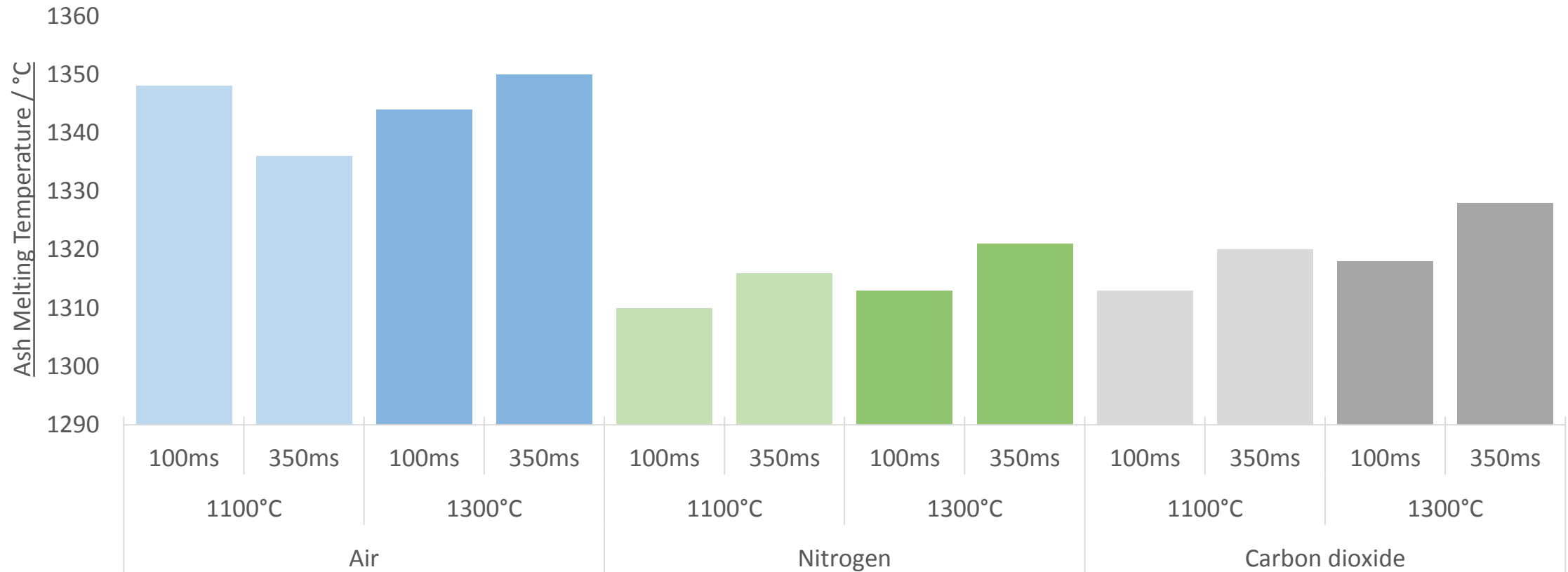
| Thickness | |
|---------------|--|
| MISURA | |



Example of a real Ash Fusion Test

Ash Melting Temperature

The Effect of DTF Gas Environment, Temperature and Residence Time on Ash Melting Temperature



- In almost all cases, the melting temperatures increase with residence time.
- The highest ash melting temperatures are from the chars that reacted in the DTF in air.
- Therefore, ash melting temperature is dependent on the DTF reaction temperature.

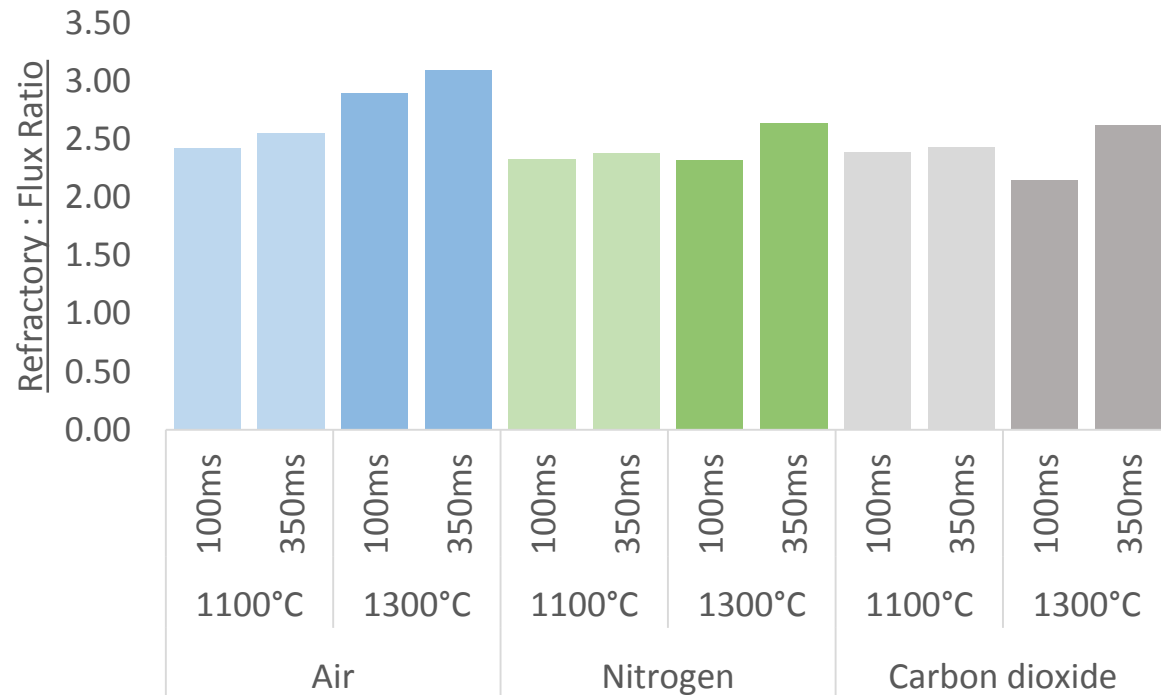
What is causing the increase in ash melting temperature?

| Temperature | Residence Time | Gas Environment | % Mullite | Ash Melting Temperature / °C |
|-------------|------------------|-----------------|-----------|------------------------------|
| 1100°C | Furnace Coal Ash | Air | 29.3 | 1308 |
| 1100°C | 100ms | Air | 4.9 | 1348 |
| 1100°C | 350ms | Air | 26.8 | 1336 |

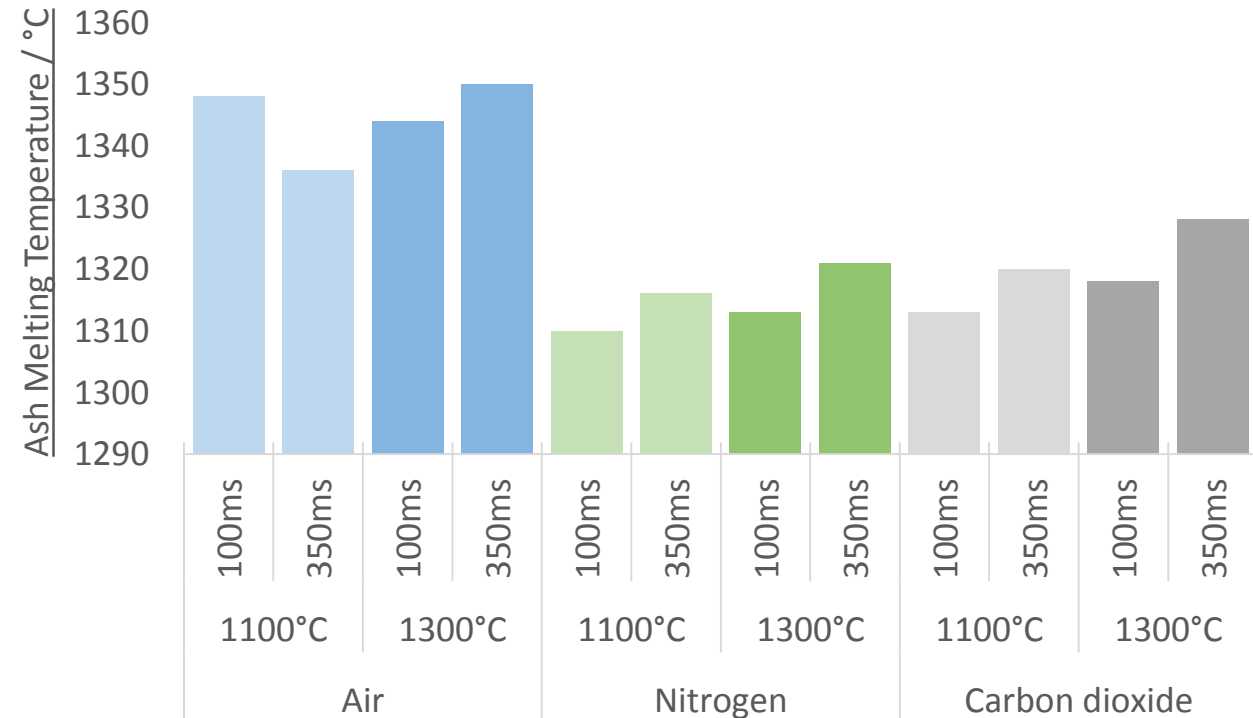
- Mullite formation?

- Changes in the acidity, basicity, fluxing agents in the ash?

Element Oxide Ratio of Si; Al; Ti to Fe; Ca; S



Ash Melting Temperature



Key points

- Mullite may cause wear in the coal injection zone of the blast furnace.
- The softening behaviour could determine whether ash is caught in the bird's nest or travels up the furnace as a dust.
- Elemental analysis shows changes that affect the properties of the ash and thus could affect its behaviour in the furnace.
- Recirculating elements such as K and Na can be studied.

Future Work

- Investigate the abrasivity / hardness of different coal ashes.
- Investigate the effect of ashes on coal / coke gasification.
- Look at the sulphur related changes that occur in the ash.