COAL MINERAL MATTER TRANSFORMATIONS UNDER OXYFUEL COMBUSTION: EFFECT OVER SLAGGING.

M.C. Mayoral, J.M. Andrés, M.T. Izquierdo, B. Rubio, C.R. Ruiz

Instituto de Carboquímica, CSIC. C/Miguel Luesma, 4. 50018 Zaragoza (Spain)
Email: mayoral@icb.csic.es

Abstract.
The main objective of this work is to simulate the impact of oxyfuel combustion over mineral matter in coal particles, in order to determine the influence of high flame temperature and high heating rates over the thermal history of the particles. These combustion conditions will be found in generation plants with oxyfuel technology for CO$_2$ capture. In this way, the effect of oxyfuel combustion over slagging and high temperature corrosion, both important operational problems, will be determined.

The novel approach to the issue consists of the simulation of realistic combustion parameters such as particle fast heating rate and high temperatures. The minerals are projected through a flame spray gun, flying along the flame and impacting onto metallic surfaces of selected composition for fireside waterwall construction. Particle velocity and temperature are continuously recorded. Flame adiabatic temperature and final composition can be calculated from initial comburant composition (O$_2$, N$_2$, CO$_2$ mixtures). In this way high temperatures (form 1500 to 2000ºC) can be conferred to particle in milliseconds, before impacting on selected surfaces.

The characterization of cross sections of deposits will be performed with SEM-EDX, and analyzed with image software. In this way, the quantification of deposit mechanical characteristics and corrosion penetration will be correlated with flame (T, O$_2$/CO$_2$) and particle (granulometry, velocity, temperature) parameters, as a function of coupon composition (% Cr, % Ni, alloys, CoNiCrAlY coatings).

Introduction.
The evolution of coal mineral matter in oxyfuel combustion and its incidence in slagging, fouling and corrosion is one of the operational issues not solved in the theoretical studies. In new oxyfuel designs, with high oxygen contents, higher flame temperatures are expected, and fusion and vaporisation of otherwise solid species can happen. On the other hand, for conventional boilers refurbishment with CO$_2$ recycle, the influence of CO$_2$ rich flue gas should be studied as a comparison with air combustion in mineral matter evolution.

In the Instituto de Carboquímica (CSIC, Spain), the previous experience in coal slagging and materials corrosion is reoriented to study the effect of oxyfuel combustion in coal mineral matter. Public funding from Spanish Science and Technology Ministry and from Europe’s Research Fund for Coal and Steel was obtained for those studies. Three different scenarios are considered in these projects in terms of materials selection and temperature ranges: conventional subcritical boilers with CO$_2$ recycle, where ferritic steels can withstand waterwall temperatures, supercritical boilers with higher grade austenitic parts, and high-T oxyfuel combustors, where special alloys are needed.

Among all the mineral constituents of coal, pyrite is known to be the major responsible of waterwall slagging, due to the formation of a low melting point monosulphide which upon impact, not only grows as an adhesive deposit but is also a sulphidizing agent favouring corrosion.
Thermal behaviour of pyrite by differential scanning calorimetry (DSC) with simultaneous thermogravimetry.

This instrumental technique allows the simultaneous measurement of changes in weigh and enthalpy along thermal treatment for a certain atmosphere. In this way, phenomena such as decomposition, oxidation, melting and calcinations can be monitored and the heat flow calculated as a function of temperature and gas atmosphere. These data can be used to predict the slagging potential of coal mineral matter of isolated minerals and their combinations. Thermogravimetric studies were performed over different granulometry of pure pyrite to determine the influence of gaseous environment in its melting point and final composition. The first important finding was that pyrrhotite experienced an earlier fusion in CO\textsubscript{2} than in Ar and N\textsubscript{2} environments: pyrite once transformed in pyrrhotite, melts at 994\textdegree C in CO\textsubscript{2}, whereas the melting point is 1080\textdegree C in Ar, as it can be seen in the next figure.

![Figure 1. Comparison of the thermal behaviour of pyrite in Ar and CO\textsubscript{2} atmospheres.](image1)

XRD and elemental sulphur composition were performed on final samples. The results indicate that meanwhile pure pyrrhotite is found at 1050\textdegree C in Ar, there is a presence of magnetite (Fe\textsubscript{3}O\textsubscript{4}) when heated to 975\textdegree C in CO\textsubscript{2}. The conclusion obtained is that transformation in CO\textsubscript{2} involved partial oxidation to magnetite, producing the euthectic compound whose melting point is lower than the pure pyrrhotite. The results were confirmed by elemental analysis, where elemental presence of sulphur inversely correlates with the oxide percentage.

Experimental set up.

A new experimental setup has been used in this kind of experimentation to speed up the studies of corrosion processes induced by the transformation of coal mineral matter. The thermal projection gun Metco 5P-II is able to produce high speed flames from H\textsubscript{2}/CO\textsubscript{2} and CO\textsubscript{2}/O\textsubscript{2} and air mixtures, with high flame temperatures. Adiabatic flame temperatures have been calculated with specific software. This gun was adapted to project mineral matter powder or fine ground minerals onto metallic surfaces. The temperature of solid projected throughout the flame

![Figure 2. Flame spray gun](image2)
was measured with the Accuraspray system, which takes into account visible emissions of particles as dark bodies in two wavelengths. Gas composition after combustion was calculated with specific software. Coupon temperatures were measured with contact thermocouples. Chemical composition of deposit surfaces were measured by X-ray diffraction. SEM-EDX was used to study cross sections of deposits.

**Main findings.**

1. Different mixtures H\textsubscript{2}-O\textsubscript{2}/CO\textsubscript{2} and H\textsubscript{2}/air were selected to ensure different gas compositions for the same adiabatic flame temperature, to compare deposition composition of deposits as a function of flue gas and deposition temperature.

   For all cases, the fast decomposition of pyrite to pyrrhotite happens in the first milliseconds in the high T plume. The particles fly as pyrrhotite and impact on the coupon, where the deposits oxidises as a function of coupon temperature. In the case of stoichiometric oxygen, no Fe\textsubscript{2}O\textsubscript{3} is obtained at coupon T=500°C, and the deposits remains as pyrrhotite partially oxidised to magnetite. At higher temperatures, the deposits tend to oxidise, mainly in air flames.

   ![Figure 3. Surface melted pyrrhotite](image)

   **Table 1. XRD composition of deposits.**

<table>
<thead>
<tr>
<th>Coupon T</th>
<th>% presence</th>
<th>CO\textsubscript{2} flame (5% O\textsubscript{2} excess)</th>
<th>Air flame (5% O\textsubscript{2} excess)</th>
<th>CO\textsubscript{2} flame (O\textsubscript{2} stoi.)</th>
<th>Air flame (O\textsubscript{2} stoi.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 °C</td>
<td>Pirrhottite</td>
<td>97</td>
<td>99</td>
<td>72</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>Magnetite</td>
<td>13</td>
<td>19</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>500 °C</td>
<td>Pirrhottite</td>
<td>47</td>
<td>51</td>
<td>51</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>Hematite</td>
<td>47</td>
<td>51</td>
<td>31.5</td>
<td>31.5</td>
</tr>
<tr>
<td></td>
<td>Magnetite</td>
<td>11</td>
<td>11</td>
<td>68.5</td>
<td>68.5</td>
</tr>
<tr>
<td>600°C</td>
<td>Pirrhottite</td>
<td>87</td>
<td>99</td>
<td>72</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>HEMATITE</td>
<td>87</td>
<td>99</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Magnetite</td>
<td>13</td>
<td>19</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>700°C</td>
<td>Pirrhottite</td>
<td>87</td>
<td>99</td>
<td>72</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>HEMATITE</td>
<td>87</td>
<td>99</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Magnetite</td>
<td>13</td>
<td>19</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2. Aging. Deposits of T\textsubscript{coupon}=600° and 700°C were aged in a muffle furnace for 72 hours at deposition temperature to simulate long residence times of deposits over metallic surfaces. Surface analysis of samples and SEM observation confirmed a complete oxidation to hematite for both conditions.

   ![Figure 4. Cross section of aged pyrrhotite](image)

3. Fine minerals projection. Finely ground calcite, alumina and kaolinite were projected through different flames to study thermal evolution. Projection over metallic coupons was not obtained provided these minerals have high melting points; the transformed powders were recovered by an air filtration system from the outlet gases. A mixture 50% weigh of pyrite with kaolinite was projected. Coupon temperatures ranged from 400°C to 557°C. In all the cases studied, only pyrite projection was achieved: surface XRD composition varied from pyrrhotite to hematite with the complete absence of mullite nor unconverted kaolinite. These
results indicate that low surface temperatures, the melted pyrrhotite cools down and the deposit is not adhesive enough to produce a mixed deposit.

(4) Highly alloyed materials for USC parts. In order to explore the corrosion effect of flame composition and coupon temperature over different materials, the following steels and alloys have been selected: 347, 304H, I800HT, I617 and I690. Three of them are iron based steels with similar chromium composition and variable Ni presence, and two Ni alloys, one Cr-Fe balanced and one Cr-Co-Mo balanced. These highly alloyed materials combine high temperature and creep resistance and they can be found in material selections to design ultra supercritical boiler parts and heaters or reheaters. Projection of pyrite \( T_{	ext{coupon}} = 700^\circ C \) were performed. XRD confirmed hematite composition of deposits in all cases. Cross sectional SEM observation of deposits after muffle aging showed small differences of behaviour of the selected materials under the two conditions studied, just a slight oxidation areas in the Fe rich steels when air projection and small sulphidation points in CO\(_2\) deposits. Further studies with a broader temperature range and longer aging times are under development.

![Figure 5 (a) Aged pyrrhotite over In617 projected in air and (b) in CO\(_2\).](image)

(5) New materials selection. At the present moment of the project, new materials are selected, including high ferritic steels, with chromium content from 8 to 11%, with other metals as Co or W. Temperatures ranging from 455 to 595\(^\circ\)C for waterwall materials will be studied in variable gas flames, from air to 40%O\(_2\)/CO\(_2\), to study oxycombustion effect over deposition.

References
- IEA Greenhouse Gas R&D Programme, [www.co2captureandstorage.info](http://www.co2captureandstorage.info)
- EPRI, Materials and Chemistry Report, Junio 2006

Acknowledgements
The authors want to express their gratitude to the Spanish Ministry of Science and Innovation for the financial support of the work, project ENE2007-66329, to the Diputación General de Aragón, for the project PM040/2006, and to the Research Fund for Coal and Steel, RFCR-CT-2007-00009.