

# ***IMAGING GAS TRANSPORT AND REACTIVITY EFFECTS IN METALLURGICAL COKE USING XENON***

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- **Summary:** The strength and reactivity of metallurgical coke determines its desirability for use in a blast furnace. Previous work showed reactivity is affected by both gas transport limitations and the selective reactivity of different coke components. In this study we use xenon gas as a contrast agent to gain insight into gas transport in coke samples before and after reaction in a furnace.

## **1. INTRODUCTION**

The rate and extent to which coke reacts with carbon dioxide (CO<sub>2</sub>) at high temperature determines its suitability for use in a blast furnace. Different cokes react at different rates. Coke has a complex structure that includes both carbon that is highly macroporous and highly ordered ('reactives') and carbon that is poorly ordered but has very few large pores ('inerts'). These different components themselves react at very different rates with carbon dioxide. Until recently it has been difficult to separate the contribution of these components to total reactivity – information that is vital to be able to predict the reactivity of coke. In recent work we found unreacted coke contains many nanopores that are inaccessible to gas. Structural changes in coke following reaction with CO<sub>2</sub> showed effects due to gas transport limitations as well as selective reactivity of different coke components [1].

We have used K-edge subtraction to observe the transport of xenon gas in coke before and after reaction with CO<sub>2</sub>. K-edge subtraction is a synchrotron imaging technique which utilises pairs of images (or tomographic scans) acquired at x-ray energies immediately above and below the xenon absorption edge at 34.5keV. The x-ray attenuation of xenon at 35keV is much higher than at 34keV whereas that of other components changes very little. Subtraction of a 34keV image from the 35keV one results in a synthetic image of the xenon distribution alone. This technique has previously been used to study porosity in coal and other geomaterials[2].

## **2. EXPERIMENTAL METHOD**

Samples of six types of coke were placed in sealable tubes for tomographic imaging at the Imaging and Medical Beamline at the Australian Synchrotron. For the initial experiment the samples were first imaged at 35keV x-ray energy with only air in the tubes. Following this the tubes were pressurized with xenon to approximately 7 atm. The samples were then imaged twice in rapid succession at 34keV and then 35keV. This process was repeated for all the samples multiple times over the remaining time of the two day experiment. Each pair of images could be used for K-edge subtraction as outlined above. The sequential sets of scans allow xenon transport in these samples over the time of the experiment to be observed.

Following these initial scans the samples were heated to 1100 °C in a N<sub>2</sub> atmosphere, then changed over to 100% CO<sub>2</sub> at 1100 °C in thermogravimetric analyser, at CSIRO Clayton, to approximately 20 to 25% weight loss. The samples were then returned to the synchrotron for a final set of imaging experiments including one scan at 35keV in air and a pair of scans at 34keV and 35keV while pressurized with xenon.

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The pairs of 34keV and 35keV 3D scans resulting from the synchrotron experiment were registered in 3D using the Avizo software package and then subtracted to produce a 3D image of the xenon distribution. Successive scans from the same sample were aligned to that changes over time could be observed. Scans of the same sample acquired before and after reaction could only be aligned approximately due to mass loss and shrinkage of the reacted specimens.

### 3. RESULTS

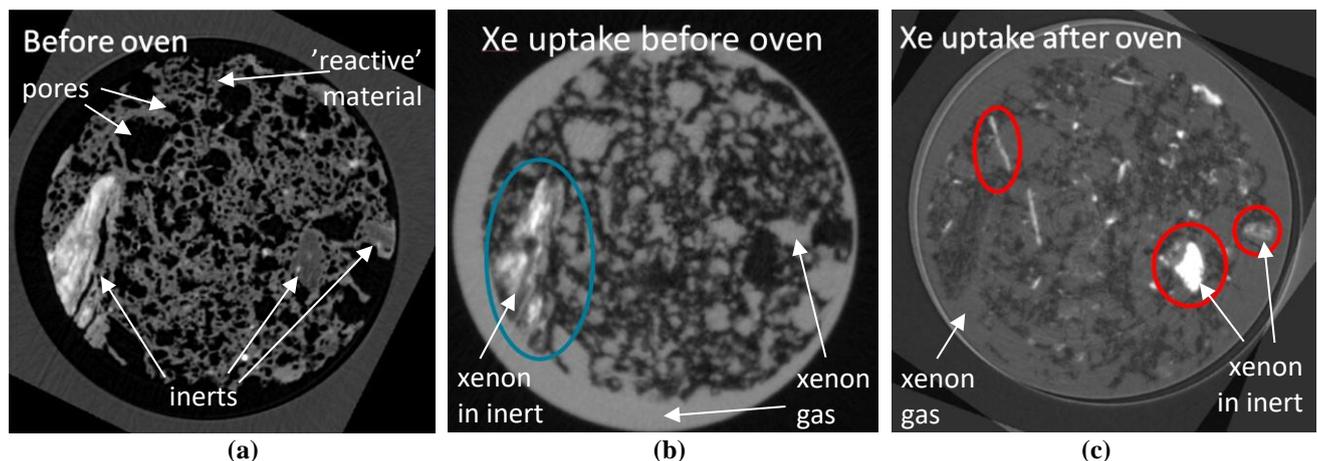
Surprisingly very little xenon was taken up in these samples prior to reaction in either the reactivities or inerts despite its rapid diffusion through the mesoscopic pore structure. This is in stark contrast to coal where earlier studies showed that xenon adsorbed and diffused readily into the bulk from any exposed surface. A small amount of xenon appears to have been taken up into the fused component of the coke almost instantaneously but this did not increase further over time. A very limited subset of inerts took up a larger concentration of xenon which did increase observably during the first two-day experiment.

Following reaction the response to Xenon addition was quite different. The samples had lost significant mass (around 25% on average) and this was seen in a thinning of the walls of the porous fused component and an overall shrinkage and distortion of the samples compared to their appearance before reaction. Xenon uptake in the fused material was still limited but non-zero; however, many of these inerts had also lost significant mass during reaction and xenon uptake in many of the inerts was greatly enhanced following reaction. However, a few inerts that had taken up xenon prior to reaction took up much less after reaction.

These results emphasize the importance of the inerts component in mediating reactivity and surface area in these materials; once reaction begins they can rapidly become activated and change their gas transport behavior. This, together with parallel studies of nanoscale pore behavior can be used to improve prediction of coke properties.

### References

- [1] See ACARP funded studies: C24053, C21056, C24060, reports available from <https://www.acarp.com.au>
- [2] Mayo, S. et al. *Dynamic micro-CT study of gas uptake in coal using Xe, Kr and CO<sub>2</sub>*. *Fuel*, 2018, **212**, 140– 150, DOI: 10.1016/j.fuel.2017.10.041



**Figure 1:** Three similar tomographic sections of the same sample sitting inside an 8mm bore tube, showing (a) the sample in air prior to reaction in the oven; (b) the xenon distribution prior to reaction, including the xenon gas inside the tube and in the coke pores; and (c) the xenon distribution after reaction (with a lower concentration of gas in the tube). The large inert which is bright due to mineral content in image (a) takes up significant xenon as highlighted in blue in (b) whereas other inerts take up little or none. After reaction in the oven, as shown in (c), a range of other inerts now take up xenon readily (some are highlighted in red) but xenon is no longer taken up in the large inert.

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