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Joint Coal Board Health and Safety Trust

Project 19811
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"Chemical and Physical Characterisation of Coal Dust"

Final Report + Future Work
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Report Outline

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1. Analytical Capabilities Developed at UNSW

Objectives

The key objectives of this project was to develop techniques for the chemical characterisation of the surface and bulk composition of freshly cleaved coal and coal dust particles, associated sample handling procedures and the correlation of this information with other coal properties. These objectives have been realised through the development of analytical capabilities at UNSW for studying the chemical species present on the surface of coal. This surface chemical approach provides more biologically relevant information (eg. possible surface dust-toxicity relationships) than more conventional coal analysis techniques such as electron microscopy / X-ray analysis techniques.

Surface Chemical Analysis Capabilities

1. Mapping the distribution of chemical species on individual particles using time-of-flight secondary ion mass spectrometry (TOFSIMS).

Benefits

- allows molecular/chemical species and, potentially, surfactacts present on the surface of the particles to be identified.
- shows differences between the surface chemistry of freshly cleaved particles and aged particles which may be the key to understanding particle toxicity.

Future

- currently developing automated image analysis to assist in rapid partcle identification of mineral and maceral species through chemical surface maps. This will add significantly to the usefulness and accessibility of mineralogical information in the TOFSIMS image data.
- Professor Geoff Taylor, Department of Earth Sciences, School of Mines, UNSW is providing image processing software used in satellite remote sensing images (Landsat). We are presently modifying this for the analysis of TOFSIMS images of coal surfaces and particles. Integration of this software with the existing equipment will allow chemical associations to be extracted from TOFSIMS images of particle surfaces. Further development of the system will allow automated identification and mineral and organic phases on the surface.

2. Small spot analysis with complete chemical composition spectrum using laser ionisation mass analysis (LIMA).

Benefits

- Rapid particle identification
- Both bulk and surface characterisation can be carried out quickly

Future

- Development of more precise computer controlled sample manipulation
- Fluorescence microscopy to rapidly identify maceral and mineral species prior to chemical analysis.

3. Quantitative compositional analysis of coal surfaces using X-ray photoelectron spectroscopy (XPS)

Benefits

- Allows quantitative compositional analysis of samples
- Correlation between XPS quantitative and TOFSIMS qualitative chemical analysis and thus the most complete picture avaliable of the surface composition.

Future

- Improved (x100) XPS imaging capability - 1 μm spatial resolution with the delivery of new ($1 million) instrumentation in June 1995 (Fisons VG ESCALAB 220iXL).
- Application and subsequent modification of newly developed methodologies for coal surface chemistry

2. Work in Progress

Sample investigation and preparation

A range of coals have been investigated during the development of analytical capabilities, predominantly from NSW seams. Mounting and polishing techniques for have been developed. Coals and other mineral reference materials used include:

Coal Samples	
Greta seam, Aberdare Colliery	Moura seam, Bowen Basin, Qld
Katoomba seam, Clarence Colliery	Dartbrook seam
Lithgow seam, Baal Bone Colliery	Pennsylvania coals, USA
Upper Liddell seam, Howick Colliery	Australian Standard Coals
Whybrow seam, Saxonvale Colliery	ASCRM - 012 A,B,C,D
Young Wallsend seam, Newstan Colliery	ASCRM - 013 - 04

Mineral Reference Materials	
Calcite	Montmorillonite
Pyrite	Quartz

Detailed studies have been undertaken on Upper Liddell, Whybrow and Young Wallsend coals using a series of analytical techniques in combination. The minerals occurring in Whybrow coal have been investigated using XPS (quantitative surface chemical information), LIMA (mass spectra from discrete points) and routine coal analysis methods such as proximate analysis and X-ray diffraction.

The work had two purposes:

- to provide a comprehensive picture of mineral occurence in Whybrow coal
- optimise experimental techniques.

LIMA was used for rapid "fingerprinting" of mineral inclusions in coal surfaces. This work is the subject of a manuscript prepared for the international journal *Fuel.*

Young Wallsend and Whybrow coals have been examined in detail with TOFSIMS imaging . Methods developed allow associations between

- elemental species
- chemical species
- large molecular clusters

These can be analysed on individual dust particles and freshly cleaved coal surfaces.

It is the chemical species on the surface of mineral particles in coal which are reported to be related to biological reactions within body tissue (eg. possible lung disease).

We have developed the ability to characterise these species in freshly produced coal dusts provides a unique opportunity to pursue this interaction. To this end TOFSIMS images have been correlated with compositional information obtained from XPS and LIMA. This work was the subject of a poster paper at the *4th Symposium on Respirable Dust in the Mineral Industries* in Pittsburgh from November 8 - 10, 1994. The study was also reported in more detail in the *Applied Occupational Health and Hygiene Journal.* (Published in the US).

A study has been carried out using TOFSIMS and XPS to investigate the occurence of nitrogen species in Young Wallsend coal. An ammonium illite species was identified suing TOFSIMS chemical imaging and XPS chemical state analysis in combination. This is the first report ammonium (NH_4^+) species in a bituminous coal and may have important implications in coal cleaning processes and utilisation. This work is the subject of a manuscript prepared for the *International Journal of Coal Geology.*

Collaboration

The rapid development of the combined surface analytical techniques and the application of these with a variety of coal samples has stimulated both national and international interest. As a result we have developed some collaborations outlined below

CSIRO Division of Coal and Energy Technology

A collaboration has been initiated with Dr Alan Buckley of CSIRO Division of Coal and Energy Technology, North Ryde. A study has been commenced using the analytical techniques developed for this project to investigate the organic components in coal. In particular, TOFSIMS imaging is being used to show the spatial association between a series of larger organic cluster molecules and thereby determine the nature of the organic material in theparent coal.

Pennsylvania State University, USA

The collaboration with Professor Alan Davis' group in the Coal and Organic Petrology Laboratories, Pennsylvania State University, USA has continued and resulted in a joint experimental study of the effect of ultraviolet irradiation on the types of chemical bonds and molecular structures present on the surface of coal. The results of this study will be presented to a meeting of the American Chemical Society in the second half of 1995. Dr Paul Pigram visited Professor Davis' group immediately prior to the *4th Symposium on Respirable Dust in the Mineral Industries*, in Pittsburgh.

Department of Applied Geology, UNSW

The collaboration with Professor Ward of the Department of Applied Geology, UNSW has continued and resulted in the preparation of the manuscript for the international journal *Fuel*. In addition, assistance has been obtained with X-ray diffraction analysis of powdered coals for the identication of crystalline mineral species in the coal samples under investigation.

School of Mines, Fuel Technology, UNSW

Collaborations have been initiated with Professor Geoff Taylor regarding computerised image analysis of TOFSIMS data as discussed above. Professor Geoff Sergeant has provided proximate analyses of coal samples for comparison with coal compositions deduced using XPS.

Conference

3. *4th Symposium on Respirable Dust in the Mineral Industries*

Dr Paul Pigram attended the *4th Symposium on Respirable Dust in the Mineral Industries* in Pittsburgh from November 8 - 10, 1994, hosted by The Generic Mineral Technology Center for Respirable Dust. A poster paper detailing coal dust research at the University of New South

Wales was presented at the Symposium. A manuscript dealing with the Joint Coal Board research in more detail was prepared and submitted for publication in the Symposium proceedings and the *Allied Occupational Heath and Hygiene Journal.*. The abstract for the poster and manuscript presentations is shown below.

Characterisation of the surface chemistry of the mineral constituents of coal dusts using *in situ* analytical techniques: TOFSIMS, LIMA, XPS

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Abstract The surface chemistry of coal dust in the environment is a product of a number of factors including coal composition, the modes of occurrence of mineral constituents, dust generation mechanisms and subsequent chemically and physically induced changes to the dust surface. Surface analytical techniques such as time-of-flight secondary ion mass spectrometry (TOFSIMS), laser ionisation mass analysis (LIMA) and X-ray photoelectron spectroscopy (XPS), in combination, can be used to characterise chemically dust surfaces as generated, without any additional sample treatments.

The chemical reactivity of freshly cleaved coal surfaces is much greater than similar weathered surfaces. The chemical differences can readily be seen using the *in situ* vacuum surface techniques noted above. Qualitative ion images from TOFSIMS indicate the spatial distribution ($\leq 1\ \mu m$) and association of chemical species on the outermost surface of individual coal dust particles. This information can be correlated with surface mass spectral data generated via laser ablation (LIMA) at discrete points ($\sim 2\ \mu m$ in diameter) on the surface and quantitative elemental and chemical images produced by XPS with a spatial resolution of better than $500\ \mu m$. These complementary techniques allow surface composition and reactivity to be studied from both an elemental and chemical perspective.

A series of Australian coals from the Hunter region of New South Wales were analysed. TOFSIMS indicated the spatial association of Al^+ and Si^+ atomic ions with SiO^+ and $SiOH^+$ molecular ions on the surface of kaolinite mineral species distributed in coal dust; similar associations were observed for strontium compounds on freshly cleaved coal surfaces. The interfacial chemistry of silica particles occluded in vitrinite was investigated using LIMA. A thin organic phase at the interface, similar to liptinite, was shown to contain a significant concentration of sulfur. XPS imaging was used to show spatial associations of elements in kaolinite particles. Quantitative XPS compositional analysis of coal surfaces was correlated with TOFSIMS mass spectra showing the chemical relationships between the organic structures and mineral species.

4. Other Benefits of Joint Coal Board Sponsored Research

The surface science research sponsored by the Joint Coal Board at UNSW has a range of other applications in the minerals industry and for research and development in Australia generally.

Coal industry

TOFSIMS chemical mapping is very useful for identifying the chemical species on the surface of coal particles. This information has direct application in the coal processing area in optimising and understanding coal flotation. Similarly, TOFSIMS can be used to examine any mineral flotation system to optimise recovery and efficiency.

Biomedical research

TOFSIMS at UNSW is being used to study surfactants and proteins on human contact lenses. Experience in this area can be transferred to the proposed study of surfactants on coal and silica.

5. Proposal for Future Work

Interaction between silica surfaces and human tissue and industrial surfactants

The aims outlined in the current project have essentially been realised with the development of a series of new analytical methods for studying chemical species on the surfaces of cleaved coal and coal dusts. During the course of this work and particularly as a result of the UNSW group's participation in the "4th Symposium on Respirable Dust in the Mineral Industries" a number of new research directions have been developed which take advantage of the expertise in coal characterisation.

One of the most significant research directions considered is the investigation of the underlying chemical cause of dust toxicity, in particular, coal dust and silica dust. The analytical capabilities developed at UNSW are well suited to investigating the interaction between silica surfaces and human lung and industrial surfactants.

This proposal seeks to build on the work funded by the Joint Coal Board and addresses critical issues in lung disease in the mining industry. A unique opportunity has been created by the work in progress to bring a new analytical approach to this area. This approach has not , to our knowledge, been employed anywhere else in the world. The objectives of this research are outlined below:

Objectives and issues to be addressed

1 Investigate the fundamental interaction between freshly cleaved silica and human lung surfactant. How is this interaction different from the low toxicity interaction of the lung with clay surfaces? Why is freshly cleaved silica more toxic than aged silica?

2. Investigate the interaction at the silica surface between human lung surfactant and industrial surfactants used in dust suppression processes in mining. Does the presence of industrial surfactants modify the lung response to inhaled silica dust?

3. Investigate the importance of the mode of occurrence and crystal structure of inhaled silica in the interaction with surfactants. Is crystalline silica the only toxic phase of silica present in the mine environment?

The Symposium provided an opportunity to make contact with a research group from the US National Institute of Occupational Safety and Health (NIOSH) based in Morgantown West Virginia and Cincinnati Ohio which is studying the interaction of freshly cleaved silica with animal lung tissue. This group is using secondary electron microscopy techniques and X-ray analysis to investigate silica surfaces. These techniques lack the surface sensitivity of the analytical techniques available at UNSW. However, the NIOSH group believes surface coatings on the silica particles play an important role in toxicity. Freshly cleaved silica is the most dangerous type; particles lightly covered with clay are <u>much</u> less toxic.

Opportunities exist for collaboration between UNSW and the NIOSH group. Two studies which will be of benefit are:

(a) prepare silica powder samples in several ways (eg. fresh, air aged, boiled) and expose/treat with lung surfactant.

Compare surfactant/silica and surfactant/clay interactions

(b) prepare silica plates with model surfaces representing powder surfaces. Investigate surfactant wettabilities

UNSW TOFSIMS chemical mapping can show chemical differences between fresh silica, aged silica and coated silica. This may allow the coated part of fresh cleaved silica surfaces to be identified. The US research approach (NIOSH) can only show the <u>elemental</u> species present.

UNSW TOFSIMS chemical/molecular mapping can be used to identify large complex molecules on surfaces such as human lung surfactant (phospholipid) and industrial surfactacts. TOFSIMS can be used to discriminate between these surfactants by showing differences in chemical structure. From June 1995, new, enhanced XPS equipment will also allow rapid imaging of elemental states with a spatial resolution less than 1 μm.

The UNSW group also has well established expertise in studying the surface chemistry of silica and glasses. Methods have been developed in other projects for determining the composition of the outermost layer of silica surfaces and for modifying the surface in a controlled way. Analytical capabilities include the surface spectroscopies using for the current study as well as equipment for measuring surface wettability

The UNSW groups established links to geology groups will also be advantageous for identifying and obtaining silica materials to be used as model systems for silica species found in coal. A comparison will be undertaken between the surface chemistry of crystalline (quartz) and non-crystalline (opalised minerals) forms of silica and the associated interactions with surfactants. This is a key aspect of identifying the triggering factors underlying toxic response.

Collaborations with researchers with interests in the area of the pathology of silicosis and coal workers' pneumoconiosis (CWP) must be developed. The logical starting point for these collaborations is through the Joint Coal Board and the medical research/advisory officers employed by the Board. There are several collaborations possible pathology research groups at UNSW. It would also seem logical to approach the Dust Diseases Board (NSW) and the Royal College of Pathologists of Australasia for assistance in this area.

Costings

The present programme of research was originally scheduled for two years and has been extended a further year without requiring additional financial support. During this time a significant amount of experience has been developed in the handling and characterization of dust particles. It is proposed to continue this work as outlined above.

Note that with the installation of a further XPS instrument in the laboratory this year (supported at a cost of $1.1 million by Department of Industry, Science and Technology) we have not requested any significant equipment in the next few years. Note also that we imply a committment of three years for the student but not necessarily for the postdoctoral researcher.

Staffing

1. full time postdoctoral position $39,000 + 30% on costs = $50,700

2. PhD student (background in the biological /chemical sciences)
$18,000 = $18,000

Total over 1 years	$68,700
3 years	$206,100

Equipment /

We presently have a spare $30,000 pumping stack for attaching to the vacuum preparation system purchased as part of the present grant. We would like to build a transfer system to increase through put of samples. Also we would like to develop a system for cleaving samples in vacuum to investigate the pure uncontaminated surfaces of the dust.

1. Vacuum Transfer System. $8,500
2. Sample cleaver $9,000

Total over 3 years $17,500

Operating expenses

1. Operating expenses (TOFSIMS/XPS) Total over 1 years $15,000
3 years $45,000
2. Information Dissemination Total over 3 years $6,000

Travel

1. Within Australia @$2,500/annum
Overseas @ 6,000/annum Total over 1 years $8,500
3 years $25,500

Overall TOTAL (year 1)	$111,700
(year 2)	$94,200
(year 3)	$94, 200

Assessment of the Surface Bioavailability of Quartz Particles in Australian Coal Mine Dusts

Summary

The following outlines some very recent results concerning the characterization of particulates identified within the surface of respirable coal dust and is in addition to the previous work reported for project 19811.
We initially outline the main problems which have been identified with respect to quartz toxicity.
In the subsequent technical overview we summarize the existing state of play concerning laboratory methods for surface characterization of coal dust.
Clear limitations with previous studies have resulted in no definitive relationship between toxicity and composition of dust surfaces being established.
Very recent experimental results have suggested that a much clearer definition may be possible

1. Introduction

The pneumoconiosis risk caused by the inhalation of respirable coal dust depends not only on the accumulative dust exposure but also on the specific harmfulness of some particular mineral species. It has been understood for some time that the quartz contained in respirable coal dust has high toxicity while minerals other than silica, such as carbonates or silicates, have little or no toxicity in comparison. The toxicity and pathogenic interactions of quartz grains have as a result been the focus of a number of studies over the last 30 years.

It is significant however that despite the large body of information that has been amassed the origin of the quartz harmfulness is still uncertain. We believe that much of this is due to the limitations on characterization of the materials until very recently.

If the important biological property of harmful silica dust were known, an advanced hygiene standard on respirable dust could be established, which would clearly be very of significant benefit to number of industries and in particular the mining industries. To achieve this aim, it is necessary to develop a routine analytical testing method to evaluate the harmfulness of different respirable coal mine dusts based on the physical, chemical and mineralogical characterization of quartz grains contained in coal or coal dust. In other word to access the state of the art technology being made available in other areas (eg. for the characterization of semiconductors in microelectronics) to the more comprehensive study of surface composition of minute quartz particulates within relatively larger (but still micron size) individual coal dust particles.

2. Studies of quartz in coal

Previous studies have indicated that the harmfulness of a respirable coal mine dust has no significant relation to its total quartz content. It has been realised that it is free (or pure) quartz surface rather than its bulk content that plays a critical role in determining the toxicity of quartz grains.
One of the critical factors on quartz surfaces which may induce cytotoxicity is silanol radical (-SiOH) concentration. If the surfaces of quartz particles are contaminated by impurities, such as clays, carbonates and coal organic matter, the toxicity of quartz can be inhibited. However, this surface contamination layer has no long term protective effect as the removal of some of impurities in the biological environment results in recovery of the toxicity of quartz.

In order to evaluate the toxicity of a coal dust, a study of the quartz bioavailability, not only in raw coal dust but also its development in bio-environment, is of a great importance. Wallace et al. (USA) found (1995) that the bioavailability of silica-assayed particles in coals increases with the increasing of coal rank, supporting the hypothesis that quartz-containing particles are intergrown with clay and other minerals as well as with coal organic substance, more so in lower rank coal than in high rank coals. This shows a remarkable correlation with the fact that workers in high rank coal mines had a higher incidence of pneumoconiosis than those miners who worked in low rank coals at equal accumulative dust exposures.

In summary, to assess the surface bioavailability and hence the pneumoconiosis risk of a coal mine dust and correlate its toxicological data with physico-chemistry parameters, thorough and detailed investigations of the quartz surface of coal mine dust are necessary. This will involve identifying both inorganic and organic substances which could be present on the quartz surface as contaminants, impurities and occlusion layers. The characterization should be comprehensive in that it isolates not only elemental and chemical components but also The relative distribution of these species both across and profiled into the surface and near surface of the particle.

3. Surface studies

Kriegseis et al (German,1982, 1987) demonstrated, using Xray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), that low toxicity quartz particles have high surface concentrations of aluminium and other elements (Ca, K, and C) and that the uncontaminated SiO_2 surface is responsible for the pathogenic behaviour of quratz in respirable dust.Tourmann and Kaufmann (German, 1994), by means of Laser ionization mass analysis (LIMA) analyses of individual coal dust particles established that the incidence of pure quartz particles represents cytotoxic factor of quartz-containing respirable coal dust.

The occurrence of a clay layer on quartz surfaces has also been examined by Wallace et al. (1990,1994), via Scanning electron microscope (SEM-EDX) of individual quartz particles.

From the surface analysis point of view, all the techniques mentioned have their intrinsic weaknesses. In the case of analysing respirable coal mineral dust, the Auger sensitivity for Al or Si is quite low (20-30 times lower than that for O). Another problem with the application of AES for analysis of insulating mineral particles is charging effect which results poor reproducibility. Using SEM-EDX by reducing electron beam energy to 5 keV limits the detection of a range of significant elements. LIMA is suitable for identification of bulk composition of individual dust particles but not for surface characterisation, because the its analysis depth is in the order of a half of micrometer.

4. Recent developments in the present research programme

We have been carrying out a fundamental study of the surface characterisation of coal and coal dust. Development of a methodology for the surface and near surface analysis of individual mineral particles has been focussed on quartz and utilized innovations in the area of imaging surface mass spectroscopic analysis (TOF SIMS). Recent results obtained from samples of a NSW bituminous coal, indicated that many elements, including Li, Na, Mg, Al, K, Ca, Ti, Fe, Cu, Pb and etc, may occur on the surfaces of quartz grains. These elements have different distributions both across and through a ultra thin layer surrounding the quartz inclusions. For example, Li is concentrated in the inner layer close to the true quartz surface characterised by -SiOH radicals. While other elements are normally occur in the outer surface layer. In addition we have just reported (Lamb and Wood, J. Surf. Int Analysis 1995) the first quantitative study of -SiOH radicals on quartz surfaces.This and other detailed information concerning near surface composition by far the most comprehensive reported to date and will have significant implications for assessing bioavailability.

In this work, a more powerful surface analytical technique, time of flight secondary ion mass spectrometry (TOFSIMS), has been used. The technique has significant advantages:

- ability to analysis of all elements including H;
- high detection sensitivity, up to parts per million order for some elements;
- ability to characterise molecular structure by analysing cluster or fragment ions;
- very sensitive to surface, sub monolayer when used in a static mode;
- mapping of every elemental and molecular peak;
- depth profiling of every elemental and molecular peak from a small area (10-20 μm in cross) through a thin surface layer with vertical resolution of the order of 10 nm.

In addition the latest surface analysis techniques, such as imaging-XPS, scanning-AES, as well as LIMA are also available in this laboratory. We have recently taken delivery of the highest resolution XPS instrument available in the southern hemisphere which was purchased ($ 1 million) through support from both government and industry.

5. Sample collection

The sample collection used in this project is intended to cover different coal ranks, ie. brown coal, sub-bituminous, bituminous, and anthracite, taken from eastern Australia. Two kinds of samples are needed:

a. Coal mine dusts from the work places

b. Coal samples from the seams where the coal mine dust samples are collected

6. Experiment details

- The emphasis is analysis of individual mineral particles using TOFSIMS to reveal the occurrence model of quartz grains in coal and coal mine dust.
- To access individual quartz particles easily, methods will be developed for separation of quartz from the realtively massive amounts of coal mine dust without modifying the surface properties.
- Low temperature ashing (100-150 C, in oxygen plasma) may be one of processes to concentrate minerals in coal dust.
- XRD will be used for mineralogy analysis.
- TOFSIMS will be also used for assessment the level of trace amount elements associated with quartz.
- XPS as the most convenient surface analytical technique has a potential to be used for development of a routine test procedure for characterisation of harmful components in respirable coal mine dust.

7. Some of the questions to be addressed

- Is coal mine dust different with mother coal in mineral content ?
- How do quartz particles occur in different rank coal ?
- What is the surface composition on quartz particles in different rank coal ?
- Trace amount elements associated with quartz in coal mine dust.
- The chemical and biochemical stability of the surface layer on quartz particles of different rank coal.
- Surface concentration of silanol (-SiOH) of quartz particles in coal mine dust.

- Depth profiles of various mineral elements and molecular clusters through the surface layer of quartz particles in coal mine dust

8. Primary Aims

a. Accumulation of bioavailability data of Australian coal mine dusts

b. Development of a routine analysis procedure for assessing harmfulness of coal mine dusts

c. Initiate a study of the quartz surface modified in biological environments