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SURFACE ANALYSIS OF PARTICULATE EMISSIONS
BEFORE AND AFTER ATMOSPHERIC AGING

by
Geoffrey Stephen Henshaw

A thesis submitted to
the University of Auckland
in fulfilment of the
requirements for the degree of
Doctor of Philosophy in Chemistry.

Auckland

The reactions and transformations of atmospheric primary particles have been studied using the surface analysis techniques of X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Scanning Electron Microscopy (SEM) and Secondary Ion Mass Spectrometry (SIMS).

Particles emitted from a steel mill were studied at their point of emission, during transport through the atmosphere and after deposition. The mill was located in a coastal region removed from other major industrial particle sources which made the identification of the mill particulate emissions possible in ambient samples. The mill utilizes indigenous titanomagnetite ironsand and coal as the raw materials. There is evidence of the surface enrichment of volatile trace elements such as Zn, S, Na, K and P from the raw materials in the particulate emissions.

Particle samples were collected from sites within the mill which represented different stages in the iron-making process, including the rotary kilns, electric melting furnaces and the vanadium recovery plant. This established an inventory of particulate emissions.

Mill sourced particles were then identified and studied in air samples collected downwind of the mill on silver-coated nucleopore filters. AES and SIMS depth profiling studies indicated the mill particles became surface enriched in sea salt components such as S, predominately as sulfate, Cl⁻ and Na⁺ after atmospheric aging. This was attributed to their coagulation with
the marine derived ambient aerosol. SIMS ion imaging and mass spectral analysis suggested a characteristic "fingerprint" of the mill emissions could be distinguished in the ambient aerosol up to 8 km downwind of the mill.

An experimental rig was constructed to model the interaction between the mill particles and the natural marine aerosol. A bubble nebuliser was developed to produce an artificial sea salt aerosol which was reacted with a metal powder in the fluidised bed of the rig. The metal powder was then aged under controlled relative humidity (RH) conditions. It was shown that an iron powder, after reaction and aging at 75 % RH, developed an aqueous surface layer which quickly led to electrochemical corrosion, dissolution and oxidation of the particle surface.

Evidence of this corrosion of metal particles occurring in the environment was found in a SEM-EDX study of the mill particles deposited on pine needles downwind of the mill. It was argued that these reactions would increase the bio-availability of the particle components. A model which incorporated these observations was developed to describe the morphogenesis of atmospheric primary particles during aging in the New Zealand environment.

XPS was used to study ambient aerosols deposited on both botanical and artificial passive sampling surfaces. Plant leaves were shown to be excellent collectors of particulate material and were suited to analysis by XPS. Site differences in the atmospheric aerosol load and composition were detected on vine leaves located on a hill side (high NaCl) and at a roadside (high sulfate and silicates) in a rural area. Zn and Fe species were detected by XPS on pine needles up to 2 km downwind of the steel mill.
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I would also like to thank NZ Steel Ltd for their financial support and the staff in Technical Services, particularly Jeremy Batchelor, for their co-operation and interest in this work.

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<td>$A$</td>
<td>Isotope abundance</td>
<td></td>
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<tr>
<td>$C$</td>
<td>Slip correction factor for particle velocity</td>
<td></td>
</tr>
<tr>
<td>$d$</td>
<td>Overlayer thickness</td>
<td>$\text{Å}$</td>
</tr>
<tr>
<td>$D$</td>
<td>Particle diameter</td>
<td>$\mu\text{m}$</td>
</tr>
<tr>
<td>$D'$</td>
<td>Fick's diffusion co-efficient</td>
<td></td>
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<td>$D_0$</td>
<td>Critical diameter for growth through homogeneous nucleation</td>
<td>$\mu\text{m}$</td>
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<td>$D_a$</td>
<td>Aerodynamic diameter</td>
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<td>$E_b$</td>
<td>Binding energy</td>
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<td>$E_k$</td>
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<tr>
<td>$h\nu$</td>
<td>Photon energy</td>
<td>$\text{eV}$</td>
</tr>
<tr>
<td>$I$</td>
<td>Intensity</td>
<td>counts per sec (cps)</td>
</tr>
<tr>
<td>$j$</td>
<td>Total angular momentum quantum number</td>
<td></td>
</tr>
<tr>
<td>$J$</td>
<td>Flux of particles</td>
<td>$\text{cm}^2\text{s}^{-1}$</td>
</tr>
<tr>
<td>$l$</td>
<td>Particle mean free path through the air</td>
<td>$\mu\text{m}$</td>
</tr>
<tr>
<td>$m$</td>
<td>Atomic mass</td>
<td>$\text{amu}$</td>
</tr>
<tr>
<td>$N_a$</td>
<td>Number concentration</td>
<td>$\text{cm}^{-3}$</td>
</tr>
<tr>
<td>$r$</td>
<td>Uptake resistance</td>
<td>$\text{s.cm}^{-1}$</td>
</tr>
<tr>
<td>$s$</td>
<td>Spin orbital quantum number</td>
<td></td>
</tr>
<tr>
<td>$z$</td>
<td>Atomic charge</td>
<td></td>
</tr>
</tbody>
</table>
GREEK

α Auger parameter eV
η Gas viscosity m.l⁻¹.s⁻¹
λ Inelastic mean free path of an electron through a solid Å
ρ Density g.cm⁻¹
t Atmospheric residence time day
φ Spectrometer work function eV

ABBREVIATIONS

AES Auger Electron Spectroscopy
FWHM Full Width Half Maximum
LAMMA Laser Microprobe Mass Analysis
RH Relative Humidity
RSF Relative Sensitivity Factor
SEM-EDX Scanning Electron Microscopy with Energy Dispersive X-ray analysis.
SIMS Secondary Ion Mass Spectroscopy
XPS X-ray Photoelectron Spectroscopy
UHV Ultra High Vacuum