CHAPTER 2

EXPERIMENTAL METHODS

IN

Aspects of solid-state chemistry of fly ash and ultramarine pigments

2. EXPERIMENTAL METHODS

2.1. Chemicals

Sphere-Fill (Pty) Ltd size-classified the fly ash that it obtained from the Lethabo power station. The different size fractions were obtained by pneumatic control within cyclones at the power plant, a process described as air 'classification'.[1] Class F (low calcium carbonate content)[1], fly ash samples were used in the experiments. The fly ash particles were of similar size: in the range of 1 μm to 12 μm, with an average diameter of less than 5 μm. This size distribution was determined with a laser particle size analyser at Sphere-Fill (Pty) Ltd.

Sulphur [sulphur powder CP, Labchem (Pty) Ltd], carbon [charcoal-activated extra pure, Merck] and sodium carbonate [BDH AnalR] were used as starting reagents.

2.2. Infrared Spectroscopy

A Bruker IFS 113V Fourier transform infrared spectrometer was used to scan the infrared transmittance through a KBr [Uvasol, potassium bromide, Merck] pellet 64 times at a resolution of 2 cm^{-1} under vacuum. This was the minimum resolution suggested by Russel[2] for investigating minerals. The pellets were prepared with approximately 2 mg of sample and 100 mg of KBr. The averaged spectrum was background-corrected using a pure KBr pellet run under similar conditions. The spectra were analysed with OpusNT v 2.0[3] and PeakFit[4] software, as well as dedicated self-developed software written in Delphi4[5] (Appendix A1).

2.3. Raman Spectroscopy

Laser Raman spectra were collected at room temperature using a Dilor XY Raman microprobe with a resolution of 3 cm^{-1}. Radiation at 514.5 nm from an Ar^{+} Coherent Innova 300 laser was used to excite the samples. The laser power was set at 100 mW. The recording time was set at between 30 s and 180 s, with two accumulations per spectrum segment. An Olympus Mplan 100X objective on an

Olympus BH2 microscope was used to focus on the sample. The Raman spectra were analysed using Labspec v 2.04[6] software and normalised to an intensity of 1 with the self-developed software (Appendix A1).

2.4. X-Ray Diffraction[7]

The X-ray diffraction (XRD) analyses were performed using a CuK_α (0.15418 nm) source (40 kV, 40 mA) from a Siemens D-501, with a graphite secondary monochromator and a scintillation counter detector.[7] The powdered sample was placed on a flat plastic plate, which was rotated at 30 r/min.[7] The scans were performed at 25 ºC in 2θ steps of 0.04°, with a 2 s recording time for each step.[7] Where accurate 2θ values were required, Si was added as internal 2θ standard.[7]

2.5. X-Ray Fluorescence[8]

An ARL 9400XP+ wavelength-dispersive XRF spectrometer with a Rh source was used for the X-ray fluorescence analyses of the samples.[8] The XRF spectrometer was calibrated with certified reference materials.[8] The NBSGSC fundamental parameter program was used for matrix correction of major elements, as well as Cl, Co, Cr, V, Sc and S. The Rh Compton peak ratio method was used for the other trace elements.[8] Samples were dried and fired at 1 000 ºC to determine the percentage loss on ignition; for the fly ash samples, this was less than 2 %.[8] Major element analyses were carried out on fused beads, following the standard method used in the XRD and XRF laboratory of the University of Pretoria,[8] as adapted from Bennett and Oliver.[9] A pre-fired sample of 1 g and 6 g of lithium tetraborate flux was mixed in a 5 % Au/Pt crucible and fused at 1 000 ºC in a muffle furnace, with occasional swirling.[8] The glass disk was poured into a preheated Pt/Au mould and the bottom surface was analysed.[8] The trace element analyses were done on pressed powder pellets, using an adaptation of the method described by Watson,[10] with a saturated Mowiol 40-88 solution as binder.[8]

2.6. Scanning Electron Microscopy

Samples for scanning electron microscopy (SEM) were prepared by placing the powder samples on conductive carbon tape, which was in turn fixed to an aluminium plate. The samples were coated with gold to prevent charge build-up. The samples for energy dispersive analyses were coated for 30 seconds. A JEOL JSM 840 (JEOL, Tokyo, Japan) was used for imaging, and a JEOL JSM 5800 LV Noran Voyager 4 Image Analysis System (JEOL, Tokyo, Japan) for energy dispersive analyses.[11]

2.7. pH Measurement

The pH of 10 g suspensions of fly ash in 200 ml of water were determined using a Precisa pH 900 instrument with glass electrode, filled with KCl solution.

2.8. Drawdown Test

A drawdown test is a colour-matching test used in the pigment industry. The pigment being evaluated was prepared in a standardised formulation. This formulation was applied to a sampling board which also had on it standard pigments. The colours were compared by eye to evaluate the colour-strength and purity of the pigment being tested.[12] A representative from Rolfes Colour Pigments International (Pty) Ltd conducted these tests on the prepared ultramarine samples.

2.9. Molecular Modelling

HyperChem[13] was used to perform the computations on a Compaq Pressario 1200 notebook with Celeron 850 MHz processor and 128 MB RAM.

A disadvantage inherent in all the computations was that the data obtained were related to gas phase molecules in vacuum at 0 K. No interaction between molecules within a crystal was taken into account. Therefore disparities between computed and observed quantities could be large.

Geometry optimisations were performed by means of the Fletcher-Reeves conjugate gradient method with a convergence limit of less than $3x10^{-3}$ kcal/Åmol. The self-consistent field convergence limit was set at $1x10^{-8}$. The maximum number of iterations allowed before convergence was 50.

2.9.1. Semi-empirical ZINDO/1 Modelling Scheme

ZINDO/1 is a semi-empirical method based on a modified version of the **I**ntermediate **N**eglect of **D**ifferential **O**verlap (**INDO**) method.[14] The overlap weighting factors were set to 1 for both sigma-sigma and pi-pi interactions, as required for geometry optimisation.[14]

Semi-empirical and *ab initio* methods took into account both molecular geometry and the electron distribution and the results from HyperChem[13] were interpreted in terms of the **L**inear **C**ombination of **A**tomic **O**rbitals (**LCAO**) - **M**olecular **O**rbital (**MO**) theory.[14] These molecular orbitals were assumed to describe the motion of the electrons in molecules and the shapes of molecular orbitals to determine the reactivity of bonds in the molecule. [14]

Using molecular orbitals HyperChem calculated the potential energy as a basis for geometry optimisation and the calculation of force constants, vibrational modes, charge and spin density, atomic charges, dipole moments and electrostatic charges. The electronic spectrum could also be calculated when configuration interaction was taken into account.[14] Because quantum mechanical computations dealt explicitly with the electrons, it was necessary to specify the charge and spin multiplicity of the molecules.[14] When a singlet state was considered the computation was usually done with **R**estricted **H**artree-**F**ock (**RHF**) wave functions.[14] In the restricted Hartree-Fock method it was assumed that all electrons were paired and that each pair occupied the same spatial molecular orbital.[14] For higher multiplicity computations the **U**nrestricted **H**artree-**F**ock (**UHF**) wave functions that distinguish between spin states were used.[14] Alpha electrons would then be in the highest occupied molecular orbital, because they were assigned first and then the remaining electrons to beta positions.[14] The excess of alpha electrons was calculated based on the number of

electrons in the neutral atoms and the number of electrons lost or won due to the charge and on the specified multiplicity.[14]

HyperChem applied the *aufbau* principle when assigning electrons to molecular orbitals[14] and the highest occupied molecular orbital and lowest unoccupied molecular orbital of the molecules under consideration, were thereby determined. Self-consistency was sometimes difficult to obtain, especially when degenerate states were involved.[14] To avoid the problem HyperChem was run with a convergence accelerator, the **D**irect **I**nversion in the **I**terative **S**ubspace (**DIIS**) method, although the computational effort was increased.[14]

Several molecular properties could be plotted in HyperChem. A useful property was the total charge density. The total charge density was the probability of finding an electron at a point in space, which could be used to determine the bonding characteristics within a molecule.[15] Individual molecular orbitals could be represented on a grid in space. This was the key to deductions made regarding the reactivity of molecules; the so-called frontier orbital approach of Woodward and Hoffmann. [16-21]

2.9.2. *Ab Initio* - 6-311G** Modelling Scheme

The **M**øller-**P**lesset **second**-order perturbation, **MP2**, correlation energy[22] compensated for some of the assumptions made during the Hartree-Fock computations and was used to correct the calculated energy.[14] The MP2 energy correction was only done at the energy minimum in a single point computation. This differed from its application in more advanced software packages. The *ab initio* computations in HyperChem expanded the molecular orbitals into a linear combination of atomic orbitals, without any further approximation. Several different basis sets to describe the atomic orbitals existed.[14] The 6-311G** implied a triple valence basis set with polarisation functions.[14] The computations were performed at the self-consistent Hartree-Fock level of theory extended by MP2 energy correction. The initial guess of the molecular orbital coefficients was taken from the eigenvectors of the core Hamiltonian. The two-electron integral buffers were 3 200 words (double precision) long and the two-electron integrals used a cut-off of 1×10^{-10}. The regular

integral format was used. No extra orbitals were added to the basis set, and five d-orbitals were used in the basis set.

2.9.3. Vibrational Analyses

The vibrational analysis and infrared spectroscopic data were obtained from the numerical Hessian matrix of second derivatives of the total energy with respect to the nuclear positions, and a normal coordinate analysis, based on mass-weighted coordinates.[14] The analysis was based on data obtained from quantum mechanical computations, but it remained classical.[14] The calculation of vibrational frequencies was described by Matsuura and Yoshida.[23] *Ab initio* determined vibrational frequencies were usually larger than observed frequencies, and needed scaling.[23,24] The scale factor depended on the basis set and the level of theory used. The recommended scale factor for HF/6-311G** is 0.9051.[24] The scale factor was based on 1 066 experimental frequencies from 122 molecules. The molecules consisted mainly of carbon and hydrogen atoms. Krossing and Passmore,[25] however, suggested scale factors larger than unity be used, when considering sulphur clusters. Brabson and others,[26] suggested a scale factor of 0.87, based on experimental data for S_3 and a self-consistent field method. This scale factor was used in this work.

2.9.4. Configuration Interaction and Electronic Transitions

HyperChem supported Configuration Interaction (CI) only in the restricted Hartree-Fock mode. The configuration interaction computations led to the energies of the ground state and singly excited states, which were then used to calculate the electronic spectrum.[14] HyperChem could, therefore, only compute an electronic spectrum for molecules with a singlet spin state.[14] Configuration interaction was performed in one of two ways, either as a singly excited state or as a microstate. The electrons are allowed to exchange from a limited number of occupied to a limited number of unoccupied electronic states. Configuration interaction is used to obtain a more accurate set of states by taking appropriate linear combinations of these microstates or singly excited states.[14]

Only the stable minima were characterised according to their electronic and vibrational spectra. Electronic spectra were computed for the structures with a spin multiplicity of one, using the configuration interaction approach.[14] This could only be done with the Restricted Hartree-Fock methodology and a singly excited state. For the S_4 species, 8 occupied and 16 unoccupied orbitals were involved to give 257 configurations. This number of configurations was deemed sufficient to ensure that no degenerate orbitals were left out of the computation. For S_3, 6 occupied and 13 unoccupied orbitals were involved to give 157 configurations. For S_2O, 8 occupied and 10 unoccupied orbitals were involved to give 161 configurations. The number of configurations chosen influenced the results. Sometimes negative excitation energies were computed. These negative excitation energies occurred when the unrestricted Hartree-Fock energy was lower than the restricted Hartree-Fock energy, the so-called triplet instabilities.[27] This inversion in energy indicated that the extra computational effort involved in the unrestricted Hartree-Fock computations was worthwhile for some structures.

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