

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

by

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## ABSTRACT

Ultramarine pigments are aluminosilicate-based and contain sulphur-based chromophores. Several samples from two batches of fine fly ash, a predominantly aluminosilicate waste product of coal combustion, were used successfully to synthesise ultramarine blue. This was confirmed by infrared, Raman and X-ray diffraction results. Fly ash had the advantage of being amorphous, whereas the traditional starting reagent, kaolin, needed to be heat-treated before the ultramarine synthesis to weaken its structure. A comparison of the scanning electron micrographs of fly ash, fly ash treated at 1 000 °C, fly ash reacted with sodium carbonate at 860 °C and the ultramarine products showed that sulphur had a structure-directing effect.

The sulphur clusters found in ultramarine pigments were studied by Self-Consistent-Field Hartree-Fock theory extended by Møller-Plesset second order perturbation theory at the minimum energy with the 6-311G\*\* basis set to determine the relative stability of  $S_2$ ,  $S_2^-$ ,  $S_2^{2-}$ , and  $S_3$ ,  $S_3^-$ ,  $S_3^{2-}$ . The singly charged species were the most stable in both sets, supporting the hypothesis that the exothermic transition from green to blue ultramarine was the transformation of the doubly charged species to the singly charged species. The open,  $C_{2v}$ , isomer was most stable for the  $S_3^-$  molecule - the blue ultramarine chromophore. The  $S_4$  molecule was a likely chromophore in ultramarine red. A Woodward-Hoffmann analysis supported the concerted formation of the puckered square  $S_4$ , pyramidal  $S_4$ , and gauche  $S_4$  chain isomers. Other possible species for the red chromophore were  $S_4^-$ ,  $S_3$ ,  $S_3Cl$ ,  $S_3Cl^-$ ,  $S_2Cl$ ,  $S_2O$ , and  $S_2O^-$ . On the basis of their calculated vibrational spectra most of the species could be discounted as possible red chromophores. The best candidate chromophore was the *cis*  $S_4$  chain based on the computed electronic spectrum.

## SAMEVATTING

Ultramarine pigmente is aluminosilikaat gebaseer en bevat swael-gebaseerde chromofore. Verskeie monsters, geneem uit twee lotte fyn stofas, 'n hoofsaaklik aluminosilikaat afvalproduk van steenkoolverbranding, is suksesvol gebruik om ultramarine blou te sintetiseer. Die resultaat is deur infrarooi, Raman en X-straal diffraksie resultate bevestig. Die tradisionele uitgangstof, kaolin, moet eers hittebehandeling ondergaan voordat die kaolin in die sintese van ultramarine gebruik kan word. Stofas is egter reeds amorf en het dus nie vooraf hittebehandeling nodig nie. 'n Vergelyking tussen die mikrofoto van stofas, stofas behandel teen 1 000 °C, stofas gereageer met natrium karbonaat teen 860 °C en die ultramarine produkte het getoon dat swael 'n struktuurrigtende effek het.

Self-Konsistente-Veld Hartree-Fock teorie en Møller-Plesset tweede orde steuringsteorie met die 6-311G\*\* basisstel is gebruik om die relatiewe stabiliteite van  $S_2$ ,  $S_2^-$ ,  $S_2^{2-}$ , en  $S_3$ ,  $S_3^-$ ,  $S_3^{2-}$ , wat in ultramarine pigmente voorkom, te bepaal. Die enkelgelaai spesie was die stabielste in beide stelsel, ter ondersteuning van die hipotese dat die eksotermiese oorgang vanaf die groen tot die blou ultramarine spesie die omskakeling vanaf die dubbelgelaai spesie na die enkelgelaai spesie is. Die oop,  $C_{2v}$ , isomeer, is die stabielste  $S_3^-$  molekule - die blou chromofoor in ultramarine. Die geslote,  $D_{3h}$ , geometrie word as 'n oorgangsfase beskou. 'n Woodward-Hoffmann-ontleding het die meervoudige vorming van die gebuigde vierkantige  $S_4$ , piramidale  $S_4$ , en gauche  $S_4$  ketting isomere ondersteun. Ander moontlike rooi chromofore was  $S_4^-$ ,  $S_3$ ,  $S_3Cl$ ,  $S_3Cl^-$ ,  $S_2Cl$ ,  $S_2O$ , en  $S_2O^-$ . Op grond van hul berekende vibrasie spektra kan meeste van die spesies as moontlike rooi chromofore uitgeskakel word. Op grond van die berekende elektroniese spektrum was die *cis*  $S_4$  ketting die beste kandidaat.

**Psalm 37:3-5:**

Trust in the LORD and do good;  
dwell in the land and enjoy safe  
pasture.

Delight yourself in the LORD  
and he will give you the desires of  
your heart.

Commit your way to the LORD;  
trust in him and he will do this.<sup>1</sup>

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<sup>1</sup> *The Youthwalk Devotional Bible*, New International Version, Zondervan Publishing House, Grand Rapids, Michigan, p. 568, 1992.

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**Table of Contents**

|                                                                              |       |
|------------------------------------------------------------------------------|-------|
| ACKNOWLEDGEMENTS                                                             | ii    |
| ABSTRACT                                                                     | iv    |
| SAMEVATTING                                                                  | v     |
| PSALM                                                                        | vi    |
| LIST OF FIGURES                                                              | xi    |
| LIST OF TABLES                                                               | xiii  |
| LIST OF EQUATIONS                                                            | xiv   |
| NOMENCLATURE AS USED BY THE AUTHOR                                           | xv    |
| PREFACE                                                                      | xvii  |
| PUBLICATIONS AND CONFERENCE PROCEEDINGS                                      | xviii |
| 0. INTRODUCTION: THE EVOLUTION OF THIS RESEARCH PROJECT                      | 1     |
| 0.1. The Original Objectives                                                 | 2     |
| 0.2. Limitations of Current Techniques and the Development of New Techniques | 5     |
| 0.3. Synthetic Methods                                                       | 6     |
| 0.3.1. Mass Measurements during Synthesis                                    | 6     |
| 0.3.2. Temperature for Synthesis                                             | 6     |
| 0.3.3. Time for Synthesis                                                    | 7     |
| 0.3.4. Crucibles for Synthesis                                               | 7     |
| 0.3.4.1. Metal Crucibles                                                     | 7     |
| 0.3.4.2. Ceramic Crucibles                                                   | 8     |
| 0.3.5. Furnace Technology                                                    | 8     |
| 0.3.5.1. Muffle Furnaces                                                     | 8     |
| 0.3.5.2. Tube Furnaces                                                       | 10    |
| 0.3.6. Scrubbers                                                             | 10    |
| 0.3.7. Thermocouples                                                         | 10    |
| 0.4. Aims of this Research                                                   | 10    |
| 0.5. Format of the Thesis                                                    | 11    |

|        |                                                      |    |
|--------|------------------------------------------------------|----|
| 1.     | LITERATURE REVIEW OF FLY ASH                         | 13 |
| 1.1.   | Introduction                                         | 14 |
| 1.2.   | Need for Research into Fly Ash                       | 16 |
| 1.3.   | Characteristics of Fly Ash                           | 17 |
| 1.4.   | Past Applications of Fly Ash                         | 24 |
| 1.5.   | Potential Uses of Fly Ash                            | 29 |
| 1.6.   | Conclusion                                           | 29 |
| 2.     | EXPERIMENTAL METHODS                                 | 38 |
| 2.1.   | Chemicals                                            | 39 |
| 2.2.   | Infrared Spectroscopy                                | 39 |
| 2.3.   | Raman Spectroscopy                                   | 39 |
| 2.4.   | X-Ray Diffraction                                    | 40 |
| 2.5.   | X-Ray Fluorescence                                   | 40 |
| 2.6.   | Scanning Electron Microscopy                         | 41 |
| 2.7.   | pH Measurement                                       | 41 |
| 2.8.   | Drawdown Test                                        | 41 |
| 2.9.   | Molecular Modelling                                  | 41 |
| 2.9.1. | Semi-empirical ZINDO/1 Modelling Scheme              | 42 |
| 2.9.2. | <i>Ab Initio</i> - 6-311G** Modelling Scheme         | 43 |
| 2.9.3. | Vibrational Analyses                                 | 44 |
| 2.9.4. | Configuration Interaction and Electronic Transitions | 44 |
| 3.     | SYNTHESIS OF ULTRAMARINE BLUE FROM FLY ASH           | 47 |
| 3.1.   | Introduction                                         | 48 |
| 3.2.   | Experimental                                         | 49 |
| 3.2.1. | Synthesis                                            | 49 |
| 3.2.2. | Kinetic Experiment                                   | 50 |
| 3.3.   | Results and Discussion                               | 54 |
| 3.4.   | Conclusions                                          | 62 |

|        |                                                                    |     |
|--------|--------------------------------------------------------------------|-----|
| 4.     | THE ROLE SULPHUR PLAYS IN THE FORMATION OF<br>ULTRAMARINE BLUE     | 64  |
| 4.1.   | Introduction                                                       | 65  |
| 4.2.   | Synthesis                                                          | 68  |
| 4.3.   | Results                                                            | 68  |
| 4.4.   | Discussion                                                         | 72  |
| 4.5.   | Conclusion                                                         | 74  |
| 5.     | MODELLING SULPHUR CLUSTERS IN ULTRAMARINE                          | 77  |
| 5.1.   | Introduction                                                       | 78  |
| 5.2.   | Experimental Data                                                  | 80  |
| 5.3.   | Molecular Modelling                                                | 82  |
| 5.4.   | Results                                                            | 83  |
| 5.5.   | Discussion                                                         | 88  |
| 5.6.   | Conclusion                                                         | 90  |
| 6.     | AN <i>AB INITIO</i> STUDY OF THE RED CHROMOPHORE IN<br>ULTRAMARINE | 93  |
| 6.1.   | Introduction                                                       | 94  |
| 6.2.   | Experimental Data                                                  | 95  |
| 6.3.   | Molecular Modelling                                                | 97  |
| 6.4.   | Results                                                            | 97  |
| 6.4.1. | Modelling the Cavities in the Ultramarine Structure                | 111 |
| 6.5.   | Discussion                                                         | 112 |
| 6.6.   | Conclusion                                                         | 115 |

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|          |                                                                                         |     |
|----------|-----------------------------------------------------------------------------------------|-----|
| 7.       | SUGGESTIONS FOR FURTHER INVESTIGATION                                                   | 118 |
| 7.1.     | The Spectroscopy of Silicates                                                           | 119 |
| 7.2.     | Ultramarine Blue                                                                        | 119 |
| 7.2.1.   | Industrial Process for the Synthesis of Ultramarine Blue                                | 119 |
| 7.2.1.1. | Laboratory Preparation and Optimisation                                                 | 120 |
| 7.2.1.2. | Scaling Up                                                                              | 121 |
| 7.2.2.   | Kinetics                                                                                | 121 |
| 7.2.3.   | The Crystal Structure of Ultramarine Pigments                                           | 122 |
| 7.3.     | Treating Fly Ash with Surfactants                                                       | 123 |
| 7.3.1.   | Anionic Surfactants                                                                     | 123 |
| 7.3.2.   | Cationic Surfactant                                                                     | 123 |
| 7.4.     | Adding Colour to Fly Ash                                                                | 126 |
| 7.4.1.   | Alkali Metals                                                                           | 126 |
| 7.4.2.   | Alkaline-earth Metals                                                                   | 126 |
| 7.4.3.   | Main Group Elements                                                                     | 127 |
| 7.4.4.   | Transition Metals                                                                       | 127 |
| 7.5.     | Artificial Neural Networks                                                              | 128 |
| 7.6.     | Molecular Mechanics                                                                     | 129 |
| 7.7.     | Density Functional Theory                                                               | 130 |
| APPENDIX |                                                                                         |     |
| A.       | Programs                                                                                | A2  |
| A.1.     | Spectral Manipulations Program                                                          | A2  |
| A.2.     | Volume Calculation Program                                                              | A11 |
| B.       | Raw Data                                                                                | A15 |
| B.1.     | Ultramarine Blue Kinetic Peak Fitting Data                                              | A15 |
| C.       | Raw Data for the Calculation of the Truncated Octahedron Volume<br>in Sodalite Crystals | A16 |
| D.       | Posters                                                                                 | A17 |
| E.       | Beneficiaries                                                                           | A26 |
| F.       | Published Articles                                                                      | A27 |

---

## LIST OF FIGURES

|       |                                                                                                                                                                                                                                                                                                  |     |
|-------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 0-1.  | Samples of fly ash and fly ash treated at 1 000 °C, indicating the colour of fly ash and heat treated fly ash                                                                                                                                                                                    | 2   |
| 0-2.  | The original objectives and information relating to the research project in 1999                                                                                                                                                                                                                 | 3   |
| 0-3.  | The spherical microscopic structure of fly ash as observed by scanning electron microscopy                                                                                                                                                                                                       | 3   |
| 0-4.  | The results of the project as in 2000                                                                                                                                                                                                                                                            | 4   |
| 0-5.  | Objectives resulting from previous work as in 2001                                                                                                                                                                                                                                               | 5   |
| 0-6.  | Damage to a nickel crucible due to reaction with oxygen (top two) and sulphur dioxide (bottom)                                                                                                                                                                                                   | 9   |
| 0-7.  | Damage to a zirconia crucible due to phase changes                                                                                                                                                                                                                                               | 9   |
| 0-8.  | Coloration of alumina crucibles due to cobalt (blue), vanadium (yellow) and iron (red) salts                                                                                                                                                                                                     | 9   |
| 0-9.  | Cracking of alumina crucibles due to acid washing                                                                                                                                                                                                                                                | 9   |
| 0-10. | Muffle furnace                                                                                                                                                                                                                                                                                   | 9   |
| 1-1.  | The predominantly spherical microscopic structure of fly ash                                                                                                                                                                                                                                     | 19  |
| 1-2.  | The mineralogy of fly ash                                                                                                                                                                                                                                                                        | 21  |
| 1-3.  | Infrared spectrum of fly ash                                                                                                                                                                                                                                                                     | 23  |
| 3-1.  | Flow diagram of the production of ultramarine blue                                                                                                                                                                                                                                               | 52  |
| 3-2.  | X-ray diffraction patterns of washed (bottom) and unwashed (top) ultramarine products identified as ultramarine blue, ultramarine red and Lazurite, and Na <sub>2</sub> SO <sub>4</sub>                                                                                                          | 53  |
| 3-3.  | Agglomerated layered pigment cake formed during the synthesis of ultramarine blue, using fly ash as a starting reagent                                                                                                                                                                           | 55  |
| 3-4.  | Infrared spectrum of the ultramarine blue product obtained from this process between 400 cm <sup>-1</sup> and 2 500 cm <sup>-1</sup> ; the band at 583 cm <sup>-1</sup> was assigned to $\nu_3$ of S <sub>3</sub> <sup>-</sup>                                                                   | 56  |
| 3-5.  | Raman spectra of the ultramarine species obtained (bottom) and an industrial ultramarine blue sample (top)                                                                                                                                                                                       | 57  |
| 3-6.  | Plot of the ratio, R, between the concentration of the S <sub>2</sub> <sup>-</sup> species and the concentration of the S <sub>3</sub> <sup>-</sup> species, against time and plot of the second-order rate law for the conversion of S <sub>2</sub> <sup>-</sup> to S <sub>3</sub> <sup>-</sup> | 60  |
| 3-7.  | Drawdowns of two sets of ultramarine products from this research and a commercial standard                                                                                                                                                                                                       | 61  |
| 3-8.  | Plastic samples prepared with ultramarine products from this research and a commercial standard as pigments                                                                                                                                                                                      | 61  |
| 4-1.  | POV-Ray images of AM1 force field generated $\beta$ -cages                                                                                                                                                                                                                                       | 66  |
| 4-2.  | X-ray diffraction patterns of a) fly ash, b) fly ash treated at 1 000 °C, c) fly ash treated with sodium carbonate at 860 °C, d) ultramarine product                                                                                                                                             | 69  |
| 4-3.  | The predominantly spherical microscopic structure of fly ash was intact after treatment at 1 000 °C                                                                                                                                                                                              | 70  |
| 4-4.  | The microscopic structure of fly ash treated with sodium carbonate at 860 °C was characterised by needle shapes crystals growing from the spherically shaped particles                                                                                                                           | 71  |
| 4-5.  | The microscopic structure of the ultramarine product showing that the spherical shape of the fly ash particles was lost and that the regular shape of zeolite-type material was formed                                                                                                           | 72  |
| 5-1.  | S <sub>3</sub> , S <sub>2</sub> O and SOS species                                                                                                                                                                                                                                                | 78  |
| 5-2.  | Possible S <sub>4</sub> isomers                                                                                                                                                                                                                                                                  | 81  |
| 5-3.  | Highest occupied and lowest unoccupied molecular orbitals of S <sub>2</sub> <sup>-</sup>                                                                                                                                                                                                         | 86  |
| 5-4.  | Molecular orbital diagram of S <sup>+</sup> (ZINDO/1 and 6-311G** LUMO) and S <sub>3</sub> <sup>-</sup> (ZINDO/1 and 6-311G** $\alpha$ and $\beta$ HOMO)                                                                                                                                         | 87  |
| 5-5.  | Charge distribution in S <sub>3</sub> <sup>-</sup> and branched chain S <sub>4</sub> at thrice (3d), twice (2d) and at its normal distance (1d)                                                                                                                                                  | 88  |
| 6-1.  | S <sub>3</sub> Cl and S <sub>2</sub> Cl isomers                                                                                                                                                                                                                                                  | 96  |
| 6-2.  | Total charge density plot of the double triangle S <sub>4</sub> isomer                                                                                                                                                                                                                           | 102 |
| 7-1.  | Broken alumina crucible used for the synthesis of ultramarine blue                                                                                                                                                                                                                               | 121 |
| 7-2.  | Ultramarine blue crystal structure                                                                                                                                                                                                                                                               | 122 |
| 7-3.  | Synperonic A9, Tamol NN 8906, stearic acid/NaOH, and sulphonated naphthalene formaldehyde used to suspend fly ash in water, after 5 minutes of settling time                                                                                                                                     | 124 |

|      |                                                                                                                                                                                                                |     |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 7-4. | Hypermer CG6 (successful), Empicol LZ/D, Morez, and stearic acid used to suspend fly ash in water, after 5 minutes of settling time                                                                            | 124 |
| 7-5. | Octadecyltrimethylammoniumbromide (successful), Synperonic A4 (successful), Synperonic A7, sulphonated naphthalene formaldehyde sodium salt used to suspend fly ash in water, after 5 minutes of settling time | 125 |
| 7-6. | Synperonic A4 (successful), Hypermer CG6 (successful), and sulphonated naphthalene formaldehyde sodium salt used to suspend fly ash in water, after 5 minutes of settling time                                 | 125 |
| 7-7. | Periodic table of experiments and colours obtained. Grey indicates elements that were not tested, and the coloured cells indicates the colour obtained with the aid of the element                             | 126 |
| 7-8. | Fly ash reacted with cobalt salt and 15 mass % $\text{NH}_4\text{VO}_3$                                                                                                                                        | 127 |

## LIST OF TABLES

|       |                                                                                                                        |     |
|-------|------------------------------------------------------------------------------------------------------------------------|-----|
| 1-1.  | Eskom statistics regarding coal consumption and ash production                                                         | 15  |
| 1-2.  | Environmental implications of using 1 kW of power                                                                      | 15  |
| 1-3.  | X-ray diffraction mineralogy of fly ash                                                                                | 20  |
| 1-4.  | XRF determined composition of fly ash and kaolin                                                                       | 22  |
| 1-5.  | Applications in which fly ash acts as an additive                                                                      | 26  |
| 1-6.  | Applications in which fly ash acts as a metal and metal oxide source                                                   | 27  |
| 1-7.  | Applications in which fly ash acts as an adsorbent                                                                     | 27  |
| 1-8.  | Applications in which fly ash acts as starting material for zeolite synthesis                                          | 28  |
| 3-1.  | Raw mix compositions for ultramarine production                                                                        | 53  |
| 3-2.  | Assignments of Raman bands for ultramarine products                                                                    | 57  |
| 4-1.  | EDX-Data for the samples in the step-wise study of the formation of ultramarine blue                                   | 69  |
| 5-1.  | Experimental characteristics of $S_3$ , $S_3^{2-}$ , and $S_3^{2-}$                                                    | 82  |
| 5-2.  | Bond lengths (Å) and angles (°) for $S_2$ and $S_3$ species                                                            | 84  |
| 5-3.  | Relative energy (kJ/mol) results for $S_2$                                                                             | 84  |
| 5-4.  | Relative Energy (kJ/mol) for $S_3$                                                                                     | 85  |
| 5-5.  | Vibrational frequencies in $cm^{-1}$ of $S_2$ $\sigma$ stretching vibration                                            | 85  |
| 5-6.  | Vibrational frequencies in $cm^{-1}$ of open $S_3$                                                                     | 85  |
| 5-7.  | Vibrational frequencies in $cm^{-1}$ of closed $S_3$                                                                   | 86  |
| 5-8.  | Vibrational frequencies in $cm^{-1}$ of negatively charged open $S_3$                                                  | 86  |
| 6-1.  | Experimental characteristics of $S_4$                                                                                  | 97  |
| 6-2.  | Bond lengths (Å) and bond angles (°) for the geometry of open and closed $S_3$                                         | 98  |
| 6-3.  | Vibrational frequencies in $cm^{-1}$ of open $S_3$                                                                     | 99  |
| 6-4.  | Vibrational frequencies in $cm^{-1}$ of closed $S_3$                                                                   | 99  |
| 6-5.  | Electronic spectrum of several suspected chromophores in ultramarine red                                               | 100 |
| 6-6.  | Bond lengths (Å) and bond angles (°) for $S_4$                                                                         | 101 |
| 6-7.  | Relative energy (kJ/mol) results of modelling $S_4$                                                                    | 102 |
| 6-8.  | Vibrational frequencies in $cm^{-1}$ of puckered ring $S_4$                                                            | 103 |
| 6-9.  | Vibrational frequencies in $cm^{-1}$ of singlet cis $S_4$                                                              | 104 |
| 6-10. | Vibrational frequencies in $cm^{-1}$ of singlet branched chain $S_4$                                                   | 104 |
| 6-11. | Vibrational frequencies in $cm^{-1}$ of trans $S_4$                                                                    | 104 |
| 6-12. | Vibrational frequencies in $cm^{-1}$ of bent exocyclic $S_4$                                                           | 104 |
| 6-13. | Vibrational frequencies in $cm^{-1}$ of triplet gauche $S_4$                                                           | 105 |
| 6-14. | Relative energy results of modelling the triplet state of $S_4$                                                        | 106 |
| 6-15. | Bond lengths (Å) and bond angles (°) of $S_4^-$                                                                        | 106 |
| 6-16. | Relative energy results of modelling $S_4^-$                                                                           | 107 |
| 6-17. | Bond lengths (Å) and bond angles (°) of SOS, $S_2O$ , $S_3Cl$ , and $S_2Cl$                                            | 108 |
| 6-18. | Relative energy results of modelling $S_2O$ , SOS, $S_3Cl$ , and $S_3Cl^-$                                             | 109 |
| 6-19. | Vibrational frequencies in $cm^{-1}$ of branched $S_3Cl$                                                               | 109 |
| 6-20. | Vibrational frequencies in $cm^{-1}$ of singlet gauche $S_3Cl^-$                                                       | 110 |
| 6-21. | Vibrational frequencies in $cm^{-1}$ of $S_2Cl$                                                                        | 110 |
| 6-22. | Vibrational frequencies in $cm^{-1}$ of $S_2O$                                                                         | 110 |
| 6-23. | Vibrational frequencies in $cm^{-1}$ of singlet SOS                                                                    | 111 |
| 6-24. | Volume (Å <sup>3</sup> ) of the modelled species                                                                       | 112 |
| 6-25. | Approximations of the volume (Å <sup>3</sup> ) of the cavities in sodalite structures                                  | 113 |
| 7-1.  | Ranges for the parameters describing standard peaks to be found in the infrared spectra of fly ash and its derivatives | 129 |

## LIST OF EQUATIONS

|     |                                                |     |
|-----|------------------------------------------------|-----|
| 3-1 | Reaction for the formation of ultramarine blue | 58  |
| 3-2 | Reaction for the formation of ultramarine blue | 58  |
| 3-3 | Reaction for the formation of ultramarine blue | 58  |
| 3-4 | Second order rate law                          | 60  |
| 5-1 | Formation of $S^+$                             | 90  |
| 6-1 | Crystal cavity volume calculation              | 111 |

## NOMENCLATURE AS USED BY THE AUTHOR

|                |                                                                                                           |
|----------------|-----------------------------------------------------------------------------------------------------------|
| Compute        | Perform a calculation to obtain information on a molecular system.                                        |
| Calculate      | Mathematically determine a descriptive value.                                                             |
| Calcine        | Heat a substance to an elevated temperature to facilitate a reaction, for example decomposition reaction. |
| Sinter         | Heat a chemical species in order to facilitate crystallisation or particle growth.                        |
| Filler         | Substance used to make up volume in a polymeric product.                                                  |
| Pigment        | Non-soluble substance that imparts colour to its matrix.                                                  |
| Chromophore    | Chemical species responsible for colour.                                                                  |
| Ceramic        | Inorganic non-metallic compounds that can withstand high temperatures.                                    |
| Band           | Theoretically predicted or experimentally observed absorption in a spectrum.                              |
| Peak           | Mathematically assigned band, which is described by its position, intensity, width and shape.             |
| $\nu$          | Stretch                                                                                                   |
| $\delta$       | Deformation                                                                                               |
| as (subscript) | Antisymmetric                                                                                             |
| s (subscript)  | Symmetric                                                                                                 |
| (IR)           | Infrared active                                                                                           |
| (R)            | Raman active                                                                                              |
| (IR/R)         | Infrared and Raman active                                                                                 |
| (0)            | Infrared and Raman inactive                                                                               |
| Fa             | Fly ash                                                                                                   |
| Fa1000         | Fly ash reacted at 1 000 °C                                                                               |
| Fa860          | Fly ash reacted at 860 °C                                                                                 |
| FaNa           | Fly ash reacted with sodium carbonate                                                                     |

|                       |                                                                                                                                                                                                                                           |
|-----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Aluminosilicate       | A chemical species in which silica and alumina tetrahedra are linked together to form species similar to those found in silicates. Aluminium silicate is sometimes substituted for aluminosilicate but is not used by the current author. |
| Crystalline           | Used to indicate that a chemical species has long-range structure.                                                                                                                                                                        |
| Amorphous             | Used to indicate that a chemical species does not have long-range structure. This does, however, not preclude the existence of short-range structure.                                                                                     |
| Ring size             | The ring size in aluminosilicates is the number of tetrahedra that make up the ring, not the number of atoms in the ring.                                                                                                                 |
| Microscopic structure | The shape of a particle as observed with a microscope, using either an optical or an electron microscope.                                                                                                                                 |
| Structure             | The sub microscopic structure, that is the relative positions of atoms within chemical species.                                                                                                                                           |

## PREFACE

To most young researchers the thought of embarking on a research project with the aim of getting a PhD is daunting. This is, however, all too often based on unreliable data as to what is expected of a PhD graduate. Phillips and Pugh<sup>2</sup> feel that a PhD graduate should become a fully professional researcher, described as follows (quoted from ref 2):

- First, at the most basic level it means that you have something to say that your peers want to listen to.
- Second, in order to do this you must have a command of what is happening in your subject so that you can evaluate the worth of what others are doing.
- Third, you must have the astuteness to discover where you can make a useful contribution.
- Fourth, you must have mastery of appropriate techniques that are currently being used, and also be aware of their limitations.
- Fifth, you must be able to communicate your results effectively in the professional arena.
- Sixth, all this must be carried out in an international context; your professional peer group is worldwide. (It always was, of course, but the rate of diffusion is infinitely faster than it used to be.) You must be aware of what is being discovered, argued about, written and published by your academic community across the world.<sup>2</sup>

The acceptance of this thesis signifies that the above-mentioned criteria were met.

Several style and format references<sup>3,4</sup> are available to aid the young researcher. Literature review articles are of great help in starting to map one's path through a research topic. Patent literature is available and opens new avenues of thought. Computer searches of the available literature often yield overwhelming amounts of hits, possibly all important. Searching *The Chemical Abstracts* hard copies seems tedious, but is worth the effort.

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2 E.M. Phillips, D.S. Pugh, *How to get a PhD*, Second edition, Open University Press, Buckingham, 1994.

3 Style Manual Committee, Council of Biology Editors, *Scientific Style and Format, The CBE Manual for Authors, Editors, and Publishers*, Sixth edition, Cambridge University Press, Cambridge, 1994.

4 M. O'Connor, *Writing successfully in Science*, First edition, HarperCollinsAcademic, London, 1991.

## PUBLICATIONS AND CONFERENCE PROCEEDINGS

### A. PUBLISHED ARTICLES

1. Landman AA, De Waal D, **Orbital Symmetry in Sulphur Pigments**, *Crystal Engineering*, 4, pp 159-169, 2001.
2. Landman AA, De Waal D, **Fly Ash as a Potential Starting Reagent for the Synthesis of Ultramarine Blue**, *Materials Research Bulletin*, 39, pp 655-667, 2004.

### B. RE-SUBMITTED ARTICLES

Landman AA, De Waal D, **Modelling Sulphur Clusters for an Understanding of Ultramarine**, *South African Journal of Chemistry*.

### C. SUBMITTED ARTICLE

Landman AA, De Waal D, **The Nature of the Chromophore in Ultramarine Red: An *Ab Initio* study**, *Journal of Computational Materials*.

### D. ARTICLES PREPARED FOR SUBMISSION

1. Landman AA, De Waal D, **A quick reference to fly ash as a valuable resource with many applications, and many more to be developed**, *South African Journal of Chemistry*.
2. Landman AA, De Waal D, **A Scanning Electron Microscope Study of Changes in the Microscopic Structure during the formation of Ultramarine Blue, and the Role Sulphur Plays**, *Materials Research Bulletin*.

## E. NATIONAL CONFERENCE CONTRIBUTIONS

### E.1. INVITED PAPERS

1. Landman AA, De Waal D, **Skepping van pigmente met Vliegasspektrum**, *Akademie vir Wetenskap en Kuns Jong Chemikus*, Bloemfontein, 21 September 1999.
2. Landman AA, De Waal D, **Infrared investigation into the reactions of aluminosilicates**, *Young Spectroscopists Symposium of the South African Spectroscopic Society*, Johannesburg, 26 September 2001.
3. Landman AA, De Waal D, **Modelling ultramarine sulphur chromophores**, 4 July 2002, *SACI2002, 36th Convention of the South African Chemical Institute*, Port Elizabeth, 1-5 July 2002, p s30

### E.2. POSTERS

1. Landman AA, De Waal D, **Interpreting Infrared Spectra of Silicates**, *proc SACI2000*, Potchefstroom, 26 September 2000, p 138.
2. Landman AA, De Waal D, **Using The Microscope To Elucidate Sub Microscopic Changes During The Formation Of Ultramarine Pigments**, Johannesburg, December 2001, *proc Microscopic Society of Southern Africa*, 31, p 37, 2001.
3. Landman AA, Boeyens JCA, De Waal D, **The Nature of the Ultramarine Red Chromophore**, *7th Annual Materials Modelling Meeting*, University of the North, Polokwane, 2003.
4. Landman AA, De Waal D, **Vanadium in the Mullite Structure**, *SACI Inorganic '03*, Roode Vallei Country Lodge, Pretoria, 2003.

## F. INTERNATIONAL CONFERENCE CONTRIBUTIONS

### F.1. POSTERS

1. Landman AA, De Waal D, **Symmetry in Pigmentary Chromophores**, *Proc INDABA III*, Skukuza, 8 August 2000.

2. Landman AA, De Waal D, **Vanadium electrons in Pigmentary Chromophores**, *Proc INDABA III*, Skukuza, 9 August 2000.
3. De Waal D, Landman AA, Kruger RA, van Schalkwyk J, **Using Raman Spectroscopy to verify pigment identity**, *Proc Seventeenth International Conference on Raman Spectroscopy (ICORS 2000)*, Beijing, China, August 2000.
4. Landman AA, De Waal D, **Vibrational Spectroscopy of Vanadia in Silicates**, *Proc Colloquium Spectroscopicum Internationale (CSI) XXXII*, Pretoria, p P8-9, 10 July 2001.
5. Landman AA, De Waal D, **The Benefits of Deconvoluting Vibrational Spectra of Pigments Based on Aluminosilicates**, *The First International Conference on Advanced Vibrational Spectroscopy ICAVS-1*, Turku, p P5.44, 19 - 24 August 2001.

## CHAPTER 0

# INTRODUCTION: THE EVOLUTION OF THIS RESEARCH PROJECT

IN

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



## 0. INTRODUCTION: THE EVOLUTION OF THIS RESEARCH PROJECT

### 0.1. The Original Objectives

Fly ash is an industrial waste resulting from burning coal in the production of electricity. Sphere-Fill, which sources fly ash from the Lethabo Power Station in the Northern Free State, aims to extend the market of this by-product. Cosmetic changes, for example changing the trade name to Plasfill, size separation and packaging was, however, not enough. The grey colour (Figure 0-1), familiar from the cinders of a barbeque, was detrimental to the marketing of fly ash as a filler for plastics. Fillers were used to make up volume, thereby using less of the expensive polymer, to impart strength and/or colour to the plastics, performing a functional role. The inherent grey colour of fly ash was strong enough to mask the effects of pigments in plastics. Changing the colour of fly ash to make it more marketable was, therefore, the original aim of the project in 1999 (Figure 0-2). The spherical form of fly ash formed the basis of its marketability (Figure 0-3).

The amorphous aluminosilicate nature of fly ash made it difficult to characterise, but versatile. Solid-state chemistry could theoretically be used to change the colour of fly ash in order to make fly ash a valuable marketable product. This process, however, needed to be supported by scientific method. Vibrational spectroscopy was chosen to monitor the process and add scientific value to the syntheses. The search for answers regarding fly ash and its reactions resulted in extending the technique of vibrational spectroscopy to an even more useful tool.

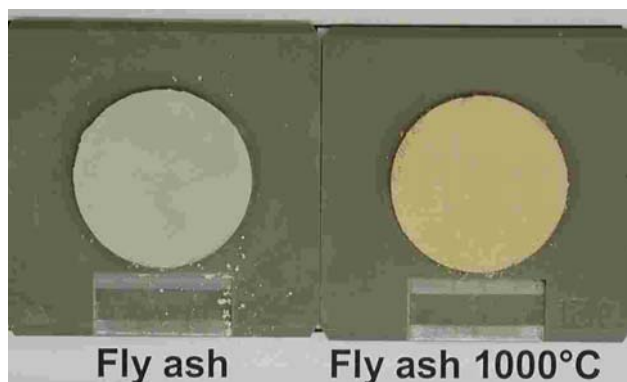


**Figure 0-1: Samples of fly ash and fly ash treated at 1000 °C, indicating the colour of fly ash and heat treated fly ash**

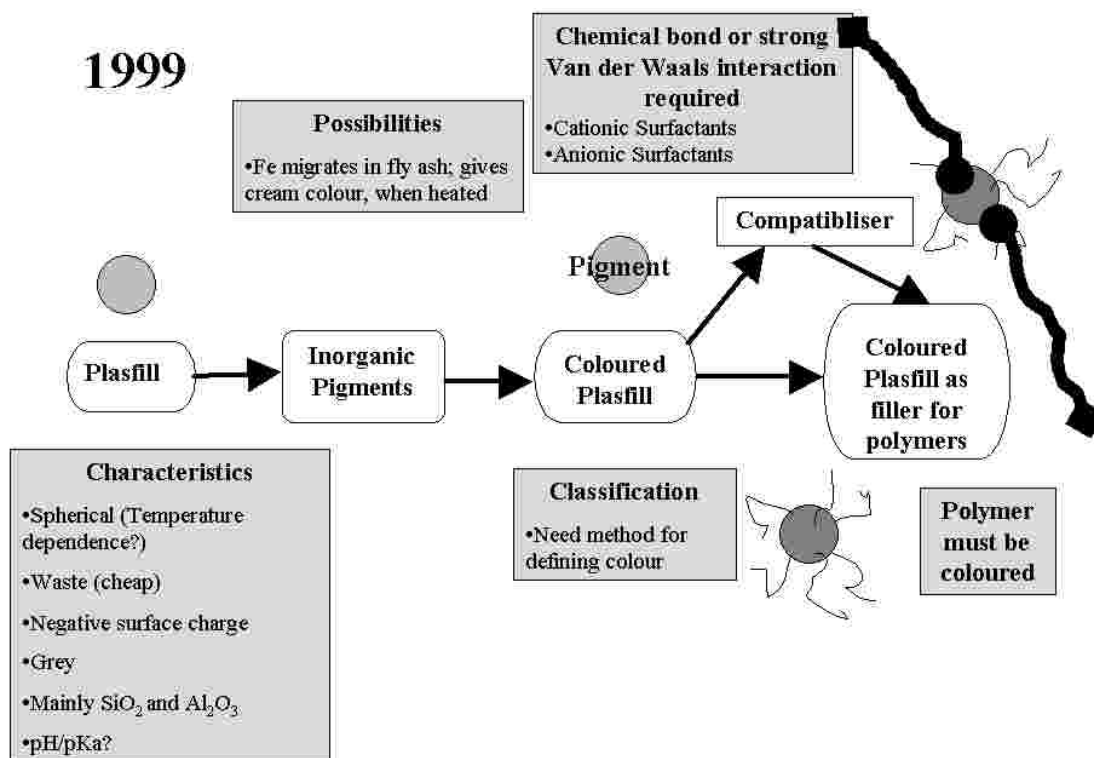


**Figure 0-2: The original objectives and information relating to the research project in 1999**

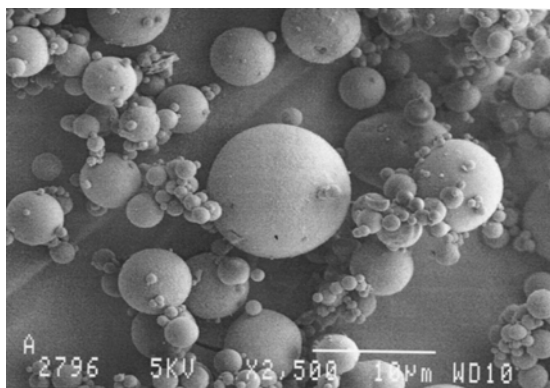


**Figure 0-3: The spherical microscopic structure of fly ash as observed by scanning electron microscopy**

During the first part of the research it was clear that wet chemistry was not adequate to realise the original goals. Therefore, solid-state chemistry was chosen as research methodology. Treating fly ash at 1 000 °C led to a cream colour (Figure 0-1). Transition metals seemed most likely to solve the colour problem. Unfortunately the transition metals did not deliver, except cobalt and vanadium. Cobalt reacted at 1 000 °C to yield a blue pigment, at an unfortunate high loading. Vanadium, on the

other hand yielded interesting results. Ammonium metavanadate was expected to decompose to  $V_2O_5$ , a brown crystalline powder. A yellow colour was, however, observed in the presence of fly ash. The interaction between vanadium species and fly ash was not reported in this thesis, but left for later publication, after the refinement of the ideas.

The other interesting and valuable element turned out to be sulphur. Sulphur together with an aluminosilicate starting reagent led to the commercial artificial pigments, Ultramarine Blue, Green and Red. Theoretical studies into proposed structures for the chromophores proved beneficial (Figure 0-4 and Figure 0-5). The kinetics of the reactions involved posed research opportunities (Chapter 3). Spectroscopic models for the characterisation of aluminosilicates were initiated (Figure 0-4 and Figure 0-5).

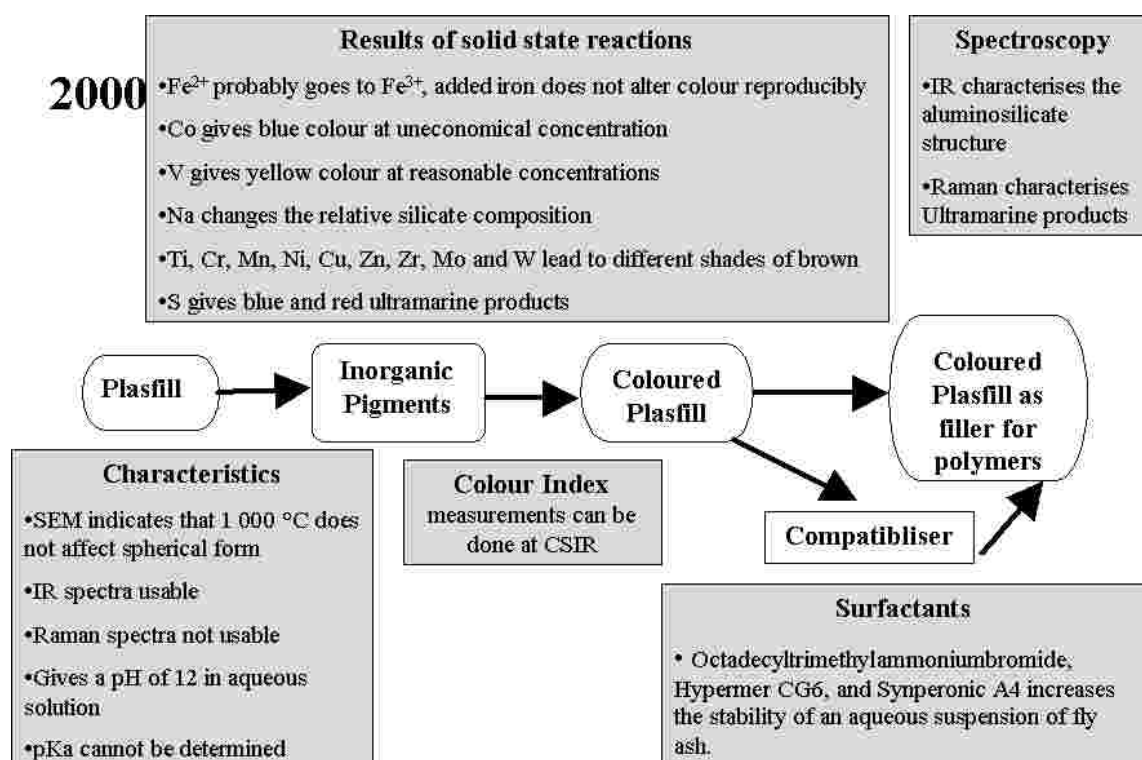
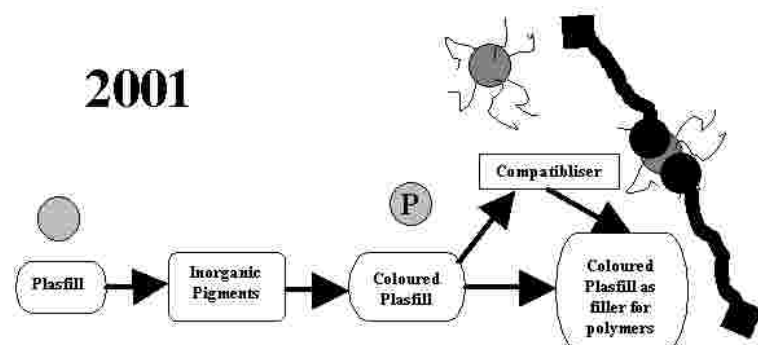


**Figure 0-4: The results of the project as in 2000**



|                           |                                                                                                                                                                               |
|---------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Ultramarine-Raman</b>  | <ul style="list-style-type: none"> <li>•Kinetic study</li> <li>•Structural elucidation</li> </ul>                                                                             |
| <b>Vanadium-Raman/IR</b>  | <ul style="list-style-type: none"> <li>•Chemical species responsible for the yellow colour</li> <li>•Extent of vanadium content</li> </ul>                                    |
| <b>Aluminosilicate IR</b> | <ul style="list-style-type: none"> <li>•Structural classification of aluminosilicates</li> <li>•Elucidation of structural change</li> <li>•Cement quality analysis</li> </ul> |

**Figure 0-5: Objectives resulting from previous work as in 2001**

## 0.2. Limitations of Current Techniques and the Development of New Techniques

This project focused on high temperature work of solid materials. The materials were generally amorphous, meaning that the structure did not extend far enough to be characterised by single crystal X-ray diffraction data. This did, however, not mean that the materials had no structure. Therefore, the current project emphasised the use of infrared spectroscopy (and Raman) to characterise amorphous material as material composed of smaller components that had structure. These were augmented by X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM) (Figure 0-3).

The reactions were performed at an appropriate temperature for an appropriate time, followed by analysis by the aforementioned spectroscopic methods. This was necessary because the result of a solid-state reaction was unsure. The product might or might not be of an already characterised structure (XRD) furthermore its composition was affected by the volatilities of its constituents (XRF).

Raman spectroscopy did not yield good vibrational spectra of aluminosilicates. The broad features of the infrared spectra could not be interpreted in a straightforward manner.

### **0.3. Synthetic Methods**

Some general comments regarding useful experimental techniques are made here, and therefore necessitate a change in tense. In solid-state chemistry the solid reagents can be reacted directly at high temperatures. Grinding is essential to ensure that the particles of the different chemical species are in contact with one another, because reactions occur at these contact points. Co-precipitating chemical species are often beneficial, because a more homogeneous starting mixture of finer particles is obtained. These characteristics lead to lower reaction temperatures and shorter times for the reactions to go to completion. Often the solvent is evaporated to simulate co-precipitation. In all cases the presence of a low melting salt is useful, because this often reduces the temperature at which reactions occur and also promotes homogeneity, by proper mixing of the reagents within the melt. This process is commonly known as fluxing. Fluxing agents are often removed by washing the sample in hot water and filtration. Washing samples with acetone before drying leads to quick drying with less agglomeration.

#### **0.3.1. Mass Measurements during Synthesis**

Unlike wet chemistry, solid-state chemical products can often not be separated from each other, therefore careful mass measurements are essential in order to obtain the proper stoichiometry. The role of good planning and a well kept lab book, which includes sample names and dates, cannot be emphasised enough.

#### **0.3.2. Temperature for Synthesis**

Not only is the temperature at which the reaction occurs important, but also the rate at which the temperature is reached, the so-called ramping rate. Some reactions need to be heated slowly at the same rate as the furnace. For example the loss of crystal water from nitrates might influence the reaction by acting as a temporary solvent, in a positive sense, or forcing the solids out of the crucible, in a negative

sense. Other samples need to be heated quickly in a pre-heated furnace. Pre-treating the reactant mixture at temperatures ranging from 70 to 200 °C and milling the dehydrated reactants is often beneficial.

### **0.3.3. Time for Synthesis**

Although solid-state reactions only occur where contact exists between the particles, most solid-state reactions occur at a reasonable rate. Most reactions in this study were performed for 24 hours to ensure good crystallinity for good spectroscopy and to be sure that the reactions were complete. Optimising is required.

### **0.3.4. Crucibles for Synthesis**

Solid-state reactions are performed in crucibles. Crucibles can be either metallic/alloy or ceramic. The choice of crucible is dependent on the chemical environment during the reaction and the temperature used. When fast heating of the sample is required, metallic crucibles are essential, due to their low specific heat capacity and high thermal conductivity.

#### **0.3.4.1. Metal Crucibles**

Although metals often have melting points above the desired reaction temperatures one should bear in mind that the metal might react with oxygen or with product gases in the furnace. For example, nickel melts at 1 453 °C but reacts with oxygen in the atmosphere at a low 600 °C to form the black oxide. The black colour indicates that an insufficient amount of oxygen has reacted to meet the stoichiometric requirements. With further reaction these black crucibles become green (Figure 0-6). Furthermore, sulphur reacts with nickel to form various sulphates and sulphides, which destroys the crucible completely (Figure 0-6). Platinum crucibles are cleaned by melting  $\text{Na}_2\text{CO}_3$  below 900 °C in the crucible to act as a flux. The  $\text{Na}_2\text{CO}_3$  is then reacted with concentrated HCl while boiling. Platinum crucibles have limited resistance to sodium carbonate at temperatures higher than 900 °C and this should be kept in mind when planning experiments.

#### 0.3.4.2. Ceramic Crucibles

Ceramic crucibles are most often used. When deciding on a crucible one should bear the reaction temperature in mind and ensure that the crucible material can withstand such temperatures and does not undergo phase changes. For example  $\text{ZrO}_2$  undergoes a phase change at 950 °C, from a monoclinic to a tetragonal phase.<sup>1</sup> The phase transition of  $\text{ZrO}_2$  is associated with a 3-5 % change in volume,<sup>1</sup> which results in cracking of the ceramic crucible when the furnace temperature is kept constant in this temperature region (Figure 0-7). Tetragonal stabilisation of  $\text{ZrO}_2$  is possible,<sup>1</sup> producing high quality crucibles. The pores in ceramic crucibles are often the source of reactive sites. One should check to see that the ions of the reactants do not diffuse into the crucible itself, leading to coloured crucibles and loss of reactants. This is the case for reactions involving cobalt, vanadium and iron salts (Figure 0-8). Washing ceramic crucibles in acid, without properly drying the crucible at 100 to 200 °C for approximately 48 hours, can lead to cracking of the crucible (Figure 0-9). Crucibles can be marked with a pencil or by painting on them with a dilute solution of an iron or cobalt salt.<sup>2</sup>

#### 0.3.5. Furnace Technology

Thermal energy is supplied to the reactions within furnaces, which can be electrically heated via heating element coils or by a gas flame. Muffle furnaces and tube furnaces are mostly electrically heated.

##### 0.3.5.1. Muffle Furnaces

In a muffle furnace (**Figure 0-10**) the reaction takes place within an enclosed chamber, surrounded by the heating elements. Muffle furnaces are ideal for obtaining large amounts of product under oxidizing atmosphere conditions. Within a muffle furnace the temperature varies depending on the position in the furnace. Furthermore, the position of the thermocouple determines the volume in the furnace, which has a known temperature.



Figure 0-6: Damage to a nickel crucible due to reaction with oxygen (top two) and sulphur dioxide (bottom)

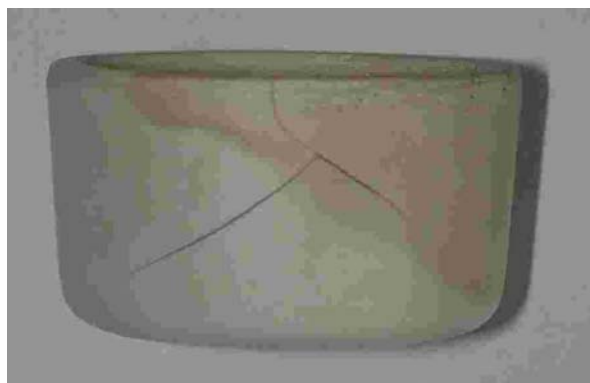


Figure 0-7: Damage to a zirconia crucible due to phase changes



Figure 0-8: Colouration of alumina crucibles due to cobalt (blue), vanadium (yellow) and iron (red) salts



Figure 0-9: Cracking of alumina crucibles due to acid washing

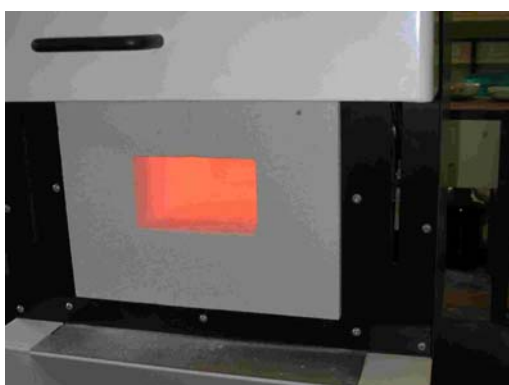


Figure 0-10: Muffle furnace

#### **0.3.5.2. Tube Furnaces**

Tube furnaces consist of a tube of suitable material, often alumina or quartz, around which the heating elements have been coiled and then protected by insulating material. Tube furnaces are more versatile than muffle furnaces in respect to the reaction conditions, because an inert or reducing gas might be passed through the open tube. Tube furnaces are, however, limited to small sample sizes.

#### **0.3.6. Scrubbers**

When a salt decomposes to an oxide species a gas is often released. These gases are often environmentally undesirable. The release of these gases into the environment is prevented by the use of a scrubber. Pretorius<sup>1</sup> bubbled the SO<sub>2</sub> resulting from the thermal decomposition of Zr(SO<sub>4</sub>)<sub>2</sub> through an ammonia solution forming (NH<sub>4</sub>)SO<sub>3</sub>, a useful fertiliser. In this way the process is made environmentally friendly and a useful by-product is formed, a procedure employed by SASOL.

#### **0.3.7. Thermocouples**

Thermocouples come in different shapes and sizes. The most important characteristic is the working range of the thermocouple and whether the thermocouple can resist the conditions within the furnace. Ceramic coatings increase the chemical resistance of the thermocouples.

### **0.4. Aims of this Research**

Neither the solid-state chemistry nor the vibrational analysis of fly ash has received much attention in literature.<sup>3-6</sup> This study aimed to aid in the understanding of the solid state chemistry of fly ash, and the methods of characterisation of fly ash and the reactions of fly ash, in order to facilitate the future application of fly ash as a valuable resource of aluminosilicate starting material.

### **0.5. Format of the Thesis**

This thesis was compiled from articles written for different scientific journals indicated as a footnote to the title of the chapter. The reference method of the South African Journal of Chemistry was used throughout the thesis. The words "and others" and not "et al" were used to indicate that more than three authors contributed to the cited reference. An extensive appendix to this thesis is available on request. The benefits to several beneficiaries were discussed in Appendix E.

## REFERENCES

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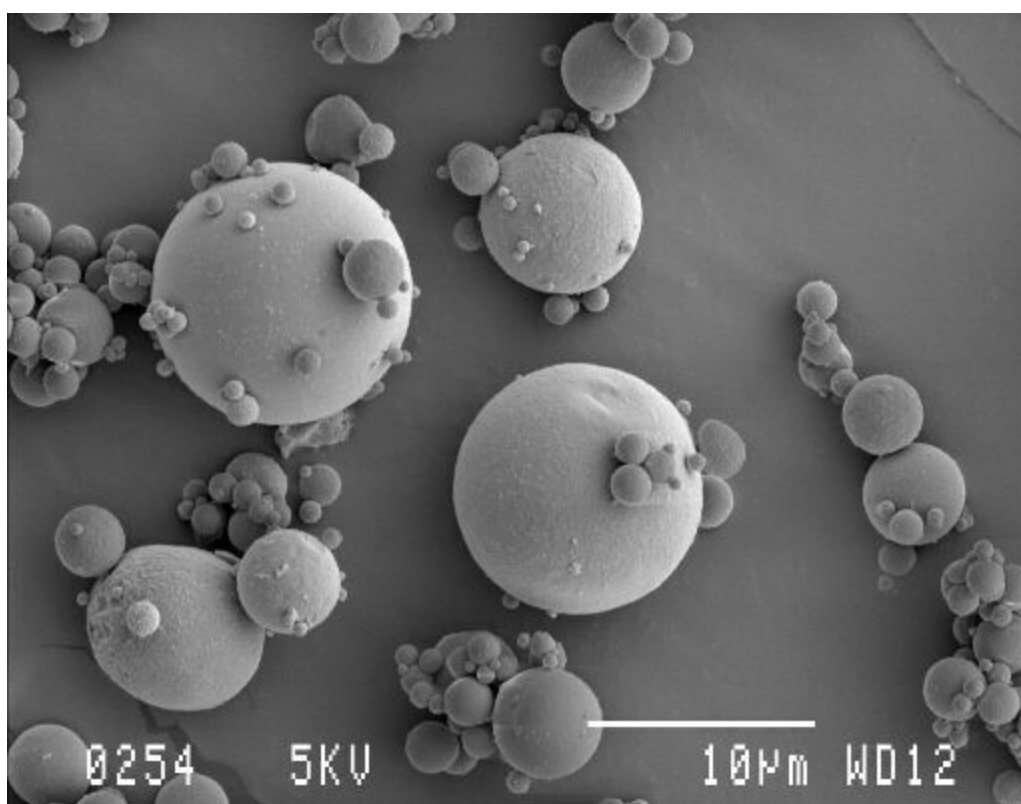
- 1 G. Pretorius, *Applied Solid State Chemistry of Zircon (ZrSiO<sub>4</sub>) and Zirconia (ZrO<sub>2</sub>)*, PhD thesis, led by A.M. Heyns, Institute for Applied Materials, University of Pretoria, Pretoria, Republic of South Africa, pp. 9, 14, 37-56, 81, 1995.
- 2 M.L. Nichols, C.W. Morse, *Laboratory Manual of Introductory Quantitative Analysis*, Ithaca, New York, p. 8, 1952.
- 3 C-S. Ho, S-M. Shih, *The Canadian Journal of Chemical Engineering*, 1993, **71**, 934-939.
- 4 R.K. Vempati, A. Rao, T.R. Hess, D.L. Cocke, H.V. Lauer Jr, *Cem. Concr. Res.*, 1994, **24**(6), 1153-1164.
- 5 M.Y.A. Mollah, S. Promreuk, R. Schennach, D.L. Cocke, R. Guler, *Fuel*, 1999, **78**, 1277-1282.
- 6 M.Y.A. Mollah, T.R. Hess, D.L. Cocke, *Cem. Concr. Res.*, 1994, **24**(1), 109-118.

# **CHAPTER 1**

## **LITERATURE REVIEW OF FLY ASH**

IN

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



## 1. LITERATURE REVIEW OF FLY ASH

### 1.1. Introduction

Kruger reports that the US Congress has classified fly ash as the sixth most abundant resource in the United States of America.<sup>1</sup> Israel could sell good-quality fly ash, based on imported South African coal, at \$20 per tonne in 1999.<sup>2</sup> Yet, few chemists in South Africa see fly ash as a field worthy of study. What follows aims to highlight the opportunities within the field of fly ash research.

Fly ash is a predominantly inorganic residue obtained from the flue gases of furnaces at pulverised coal power plants. When coal is burnt in pulverized coal boilers, the minerals, entrained in the coal, are thermally transformed into chemical species that are reactive or could be chemically activated, for example by the addition of calcium hydroxide.<sup>3</sup> The finely divided glass phase, the predominant phase in fly ash, reacts as a pozzolan, defined by Manz as "...a siliceous and aluminous material that in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties."<sup>4</sup>

Eskom, a major power utility in the Republic of South Africa, is a major producer of fly ash. South African fly ash for use as a cement extender is processed and marketed by Ash Resources (Pty) Ltd.<sup>5</sup>

Worldwide, the cement industry has almost reached its maximum consumption level of fly ash, so too its use as landfill. Sphere-Fill (Pty) Ltd, which sources fly ash from the Lethabo (a Tswana word, which means "good living" or "happiness"<sup>6</sup>) Power Station in the Northern Free State of the Republic of South Africa, aims to extend the market for this by-product.

The coal in the Republic of South Africa is high in ash content; therefore, the use of fly ash is an environmentally important issue. Eskom produced approximately 27 megatonnes of fly ash in 2001 of which only 1.2 megatonnes were sold

(Table 1-1). Emission control legislation has led to an increasing amount of fly ash in a recovered form (Table 1-2).<sup>7</sup>

**Table 1-1: Eskom statistics regarding coal consumption and ash production<sup>8</sup>**

| Item                                                             | 2001   | 2000   | 1999   | 1998   | 1997   |
|------------------------------------------------------------------|--------|--------|--------|--------|--------|
| Total electricity sold, GWh                                      | 181511 | 178193 | 173412 | 171457 | 172550 |
| Total electricity for Eskom system (Stations and purchased), GWh | 198790 | 194601 | 188475 | 185583 | 187850 |
| Total produced by Eskom stations, GWh (net)                      | 189590 | 189307 | 181818 | 183093 | 187811 |
| Total available for distribution, GWh                            | 196613 | 191123 | 184968 | 182284 | 184339 |
| Coal burnt, kt                                                   | 94136  | 92289  | 88470  | 87225  | 90169  |
| Average ash content, %                                           | 28.8   | 28.6   | 28.5   | 29.1   | 28.4   |
| Particulate emissions, kt                                        | 59.64  | 66.08  | 67.08  | 65.21  | 83.43  |
| Ash produced, Mt                                                 | 26.5   | 24.6   | 24.3   | 24.7   | 23.7   |
| Ash sold, Mt                                                     | 1.2    | 1.1    | 1.1    | 1.2    | 1.1    |

**Table 1-2: Environmental implications of using 1 kW of power<sup>8</sup>**

| Grams per 1 kW of power | 2001 | 2000 | 1999 | 1998 | 1997 | 1992 |
|-------------------------|------|------|------|------|------|------|
| Coal burnt              | 500  | 500  | 500  | 500  | 500  | 500  |
| Ash produced            | 140  | 130  | 134  | 135  | 126  | —    |
| Ash emitted             | 0.3  | 0.4  | 0.4  | 0.4  | 0.4  | 1.0  |

Sphere-Fill (Pty) Ltd markets several size fractions of fly ash. Super-Pozz is a fine fraction of fly ash with a 90 % top cut passing of 11  $\mu\text{m}$  and a 99 % top cut passing of 25  $\mu\text{m}$ .<sup>9</sup> The material safety data sheet reports the specific gravity as 2.25, the melting point as 1 350 °C and that Super-Pozz is not classified as a hazardous material.<sup>10</sup> Pozzfill is a coarser grade fly ash, varying in size between 40 and 150  $\mu\text{m}$ .<sup>11</sup> A finer fraction of fly ash is marketed as Plasfill, with a size less than 12  $\mu\text{m}$ .

Much of the research into fly ash focuses on the measurement of trace concentrations, and the effects of leaching, by X-ray fluorescence, atomic absorption, inductively coupled plasma-optical emission spectroscopy, gas chromatography - mass spectroscopy and laser ionisation mass spectroscopy. Another field of study is the surface adsorbed dioxins and other pollutant chemicals. These were not treated in this review.

Fly ash can be classified as either cementitious or pozzolanic. The cementitious fly ash is labelled as Class C, with  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  making up at least 50 mass percent.<sup>11,12</sup> In pozzolanic fly ash, Class F,  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  makes up more than 70 mass percent of the composition of the fly ash.<sup>11,12</sup>

There are two primary sources of fly ash: fly ash from a pulverised coal power plant and fly ash from a municipal waste incineration plant.<sup>13</sup> This review focuses on class F fly ash from a pulverised coal power plant.

## 1.2. Need for Research into Fly Ash

In 2000, the *Journal of Hazardous Materials* published a special issue on fly ash, its characterization and uses.<sup>14</sup> The following comment is made in the preface to that special issue:

Of the hundreds of millions of metric tons of fly ash that are produced annually on a worldwide basis, only a small portion e.g., 20% to 40% of the fly ash is re-used for productive purposes, such as an additive or stabilizer in cement. The remaining amount of fly ash produced annually must either be disposed in controlled landfills or waste containment facilities, or stockpiled for future use or disposal. As a result of the cost associated with disposing these vast quantities of fly ash, a significant economical incentive exists for developing new and innovative, yet environmentally safe, applications for the utilization of coal fly ash.<sup>14</sup>

In an article discussing the beneficiation of fly ash, Kruger<sup>11</sup> urges researchers

... to a better understanding of the fundamental characteristics of ash; for example, to what degree do surface characteristics control the reactivity, and what beneficiation techniques are applicable to maximize a particular characteristic? Can fly ash be

beneficiated to enrich it as a pre-concentration step for the recovery of gallium? Is a particular fraction more suited to producing slow-release fertilizers? How can beneficiation play a role in selecting a portion of fly ash more appropriate to geopolymerization? Knowledge of the needs in the market-place and the symbiotic relation between research and product development is paramount in creating these new opportunities for fly ash.<sup>11</sup>

Scheetz and Earle<sup>12</sup> comment on the use of fly ash in America. Only 27.4 % of the ash produced in 1996 was used in non-landfill applications (confirmed by Hower and others<sup>7</sup>). Scheetz and Earle<sup>12</sup> challenge researchers with the following remark:

...[Fly ash] was imparted with an excess energy, either chemical or stored surface energy, which can be utilized to participate in chemical reactions, if properly activated. The challenge for the scientific community is to exploit these resources, as low tech materials, to solve large-volume societal-environmental needs.<sup>12</sup>

Malhotra and others<sup>15</sup> report on the use of fly ash in America in 2002. They estimate that only 30 % of the fly ash produced is used. Two thirds is used in the concrete industry, which has reached a maximum consumption figure. Malhotra and others<sup>15</sup> challenge researchers to find low cost but high volume applications of fly ash, and to convert ashes into value- added products.<sup>15</sup>

Foner and others<sup>2</sup> emphasize the role of developing new applications of fly ash in 1999, by pointing out that Israel would produce 1.3 megatonnes of coal ash per annum by 2001 and that only 0.6 megatonnes could be used by the cement industry.<sup>2</sup> Nathan and others<sup>16</sup> estimated the figures as 1.2 megatonnes and 0.8 megatonnes respectively by 2000.

In the United Kingdom approximately 50 % of the fly ash produced is used,<sup>17</sup> and in India only 6 %.<sup>18</sup>

### **1.3. Characteristics of Fly Ash**

Fly ash is a diverse substance. The characteristics of fly ash differ depending on the source of the coal used in the power plant and the method of combustion.<sup>3,12,19</sup> Cenospheres, hollow spherical particles as part of fly ash, are believed to be formed

by the expansion of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  gas, evolved from minerals within the coal being burnt.<sup>20</sup> The predominant forces are, however, the pressure and surface tension on the melts,<sup>20</sup> as well as gravity. The predominantly spherical microscopic structure of fine fly ash is related to the equilibrium of the forces on the molten inorganic particle as it is forced up the furnace or smoke stack against gravity. The molten inorganic particles cool down rapidly, maintaining their equilibrium shape. A similar situation is found in spherical drops of water falling from a faucet.

Because cenospheres are hollow, they have a low bulk density. The percentage cenospheres increase with the ash content in the coal, and decrease with the concentration of  $\text{Fe}_2\text{O}_3$ .<sup>21</sup> This indicates that  $\text{Fe}_2\text{O}_3$  is concentrated in the higher density fraction of fly ash,<sup>21</sup> which is to be expected from the high density of  $\text{Fe}_2\text{O}_3$  ( $5.25 \text{ g/cm}^3$ )<sup>22</sup> and  $\text{Fe}_3\text{O}_4$  ( $5.17 \text{ g/cm}^3$ ).<sup>22</sup> The iron species should not contribute significantly to the infrared spectra.<sup>21</sup>

The inorganic material entrained over years in the coal melt during the combustion of coal in the furnace, and with some, but limited, fusing of the molten particles.<sup>19</sup> Some of the vaporized low boiling elements, for example alkali metal salts, coalesce to form submicron particles.<sup>19</sup> Some of the vaporised compounds, most notably the polynuclear aromatic hydrocarbons and polycyclic aromatic hydrocarbons, adsorb onto the surface of the fly ash particles.<sup>19</sup> The surface of fly ash particles is, therefore, commonly enriched in carbon, potassium, sodium, calcium and magnesium.<sup>19</sup>

Fly ash has, as mentioned before, a characteristic spherical microscopic structure (Figure 1-1). This microscopic structure is, in fact, so beautiful that a scanning electron microscope photograph of fly ash was published on the cover of Science magazine, 7 May 1976, vol 192, no 4239; and again on 19 December 1980, vol 210, no 4476.

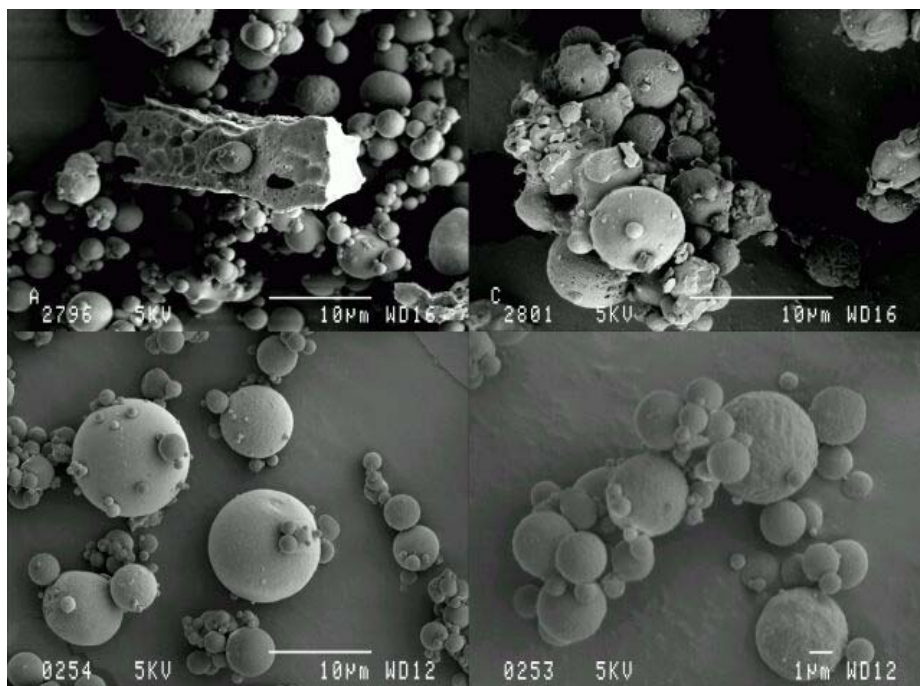


**Figure 1-1: The predominantly spherical microscopic structure of fly ash**

Fly ash can be approximated as an aluminosilicate and can be used like other minerals. The amorphous aluminosilicate nature of fly ash makes the chemical structure of fly ash difficult to characterise, but also very versatile, since the glassy phase reacts first before the crystalline phase, and also goes into solution first.

X-ray diffraction is mainly used to describe the mineralogy of fly ash. The mineralogy of fly ash is closely related to the minerals entrained in the coal and several different minerals have been identified as part of fly ash (Table 1-3). The main phases are glass, mullite, quartz, magnetite, haematite<sup>19,23</sup> and anhydrite. Methods of quantifying these minerals, and therefore the glass content, have been developed.<sup>47</sup> The samples analysed, showed similar mineralogy (Figure 1-2). The mullite present in fly ash forms by the decomposition of kaolinite<sup>62</sup> which is entrained in the coal.

**Table 1-3: X-ray diffraction mineralogy of fly ash**

|                                                                                   |                                                                       |
|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| Glass <sup>2,3,7,24-52</sup>                                                      | Quartz <sup>2,3,7,16,24-34,36-72</sup>                                |
| Mullite <sup>2,3,16,24,27-55,60,61,64-74</sup>                                    | Sillimanite <sup>38,67,68</sup>                                       |
| Haematite <sup>3,16,24,26,28-32,34,37-39,44, 46,47,55,60-62, 66,70,71,73,75</sup> | Magnetite <sup>3, 16,24,27-30,32-34,38,39,44-47,55,62, 66,71,76</sup> |
| Anhydrite <sup>2,26,29-31,39,47,60,63,77</sup>                                    | Plagioclase <sup>3,26,52,63</sup>                                     |
| Gehlenite <sup>26,34,63</sup>                                                     | Calcite <sup>2,3,26,28,39,44,52,63,71</sup>                           |
| Cristobalite <sup>3,28,45,46,52</sup>                                             | Anorthite <sup>66,70,72</sup>                                         |
| Lime <sup>2,3,26,28,29,31,39,16,62,63</sup>                                       | Alkali Feldspars <sup>3,16,26,28,30,37,39,52,55,63</sup>              |
| Bassanite <sup>26,63</sup>                                                        | Gypsum <sup>3,26,39,62,63,75</sup>                                    |
| Mica <sup>3,26,39,63</sup>                                                        | Amorphous Al-Fe silicates <sup>16</sup>                               |
| Amorphous Ca-Al-Fe silicates <sup>16</sup>                                        | Melilite <sup>3,31</sup>                                              |
| Merwinite <sup>31</sup>                                                           | Brown millerite <sup>31,63</sup>                                      |
| Enstatite <sup>70,72</sup>                                                        | Sodalite <sup>31</sup>                                                |
| Illite <sup>65</sup>                                                              | Kianite <sup>55</sup>                                                 |
| Calcium Silicate <sup>44</sup>                                                    | Unburnt coal <sup>26,27,39,63</sup>                                   |

The magnetite referred to in Table 1-3 should be classified as ferrite, due to the different rates of substitution of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  by other ions, for example vanadium, chromium, manganese, cobalt, nickel and zinc.<sup>42,71</sup> Spinels containing mainly iron, and some chromium and nickel impart magnetic properties to approximately 39 % of the particles (more so in the finer fractions).<sup>78</sup> This leads to the concentration of these elements in these fractions, and makes fly ash a valuable "ore" for these elements.

Although fly ash contains many potentially toxic trace elements (Table 1-4), leaching tests have shown that these are stable within the aluminosilicate matrix.<sup>27,79,80</sup> Accordingly fly ash is not classified as a hazardous waste in America.<sup>27</sup> The only element that might pose a problem is hexavalent chromium.<sup>2</sup> The Ministry of the

Environment of Israel, however, considers the use of fly ash as landfill potentially harmful, and forbids its use as landfill,<sup>2</sup> possibly in reaction to the greater leaching test results of Nathan and others<sup>16</sup> for arsenic, selenium and chromium. The leaching behaviour is influenced by several factors;<sup>79,81</sup> therefore results can be expected to vary for fly ash samples from different sources.

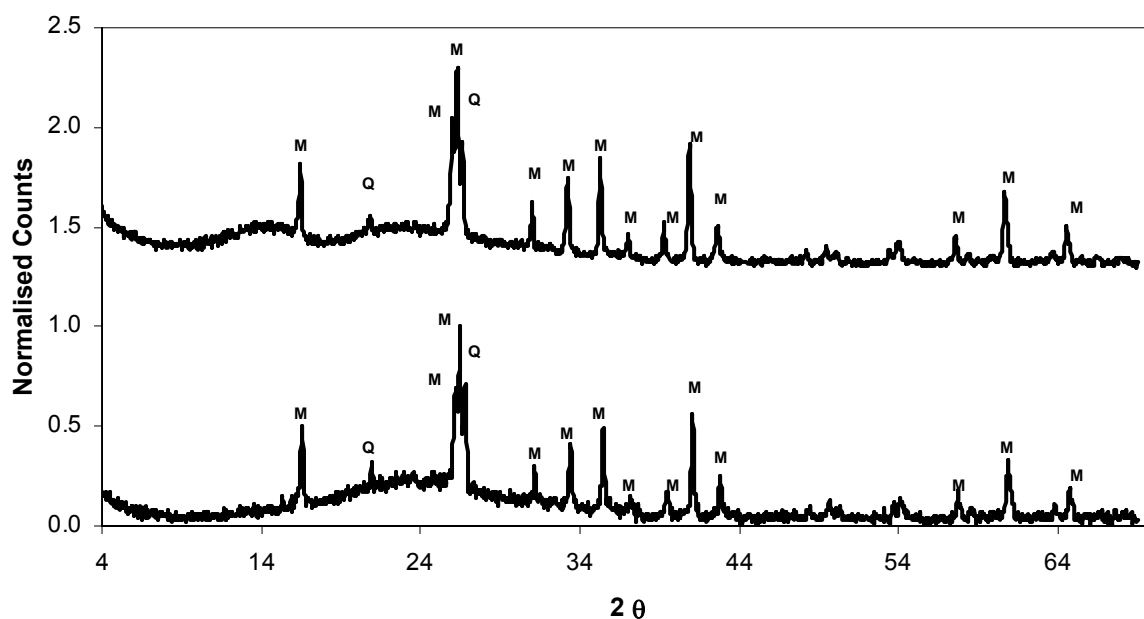


**Figure 1-2: The mineralogy of fly ash; M: mullite, Q: quartz**

Several atomic force microscopy studies on fly ash have been done.<sup>45,46,82,83</sup> Fine fly ash has a spherical microscopic structure (Figure 1-1). Not all particles are spherical (Figure 1-1). The size distribution can also be assessed by investigation of the micrographs. The present micrographs are similar to those in literature.<sup>19,20,24,26,33,35,38,39,46,50,53,54,72,75-77, 83-108</sup> Quantitative work by energy dispersive X-ray analyses indicates the heterogeneous nature of the fly ash particles.<sup>19,20,40,53,54,71, 83,96,100-105</sup>

The infrared spectra of fly ash have also been reported<sup>41,45,46,53,54,104,109</sup> but these results differ from the infrared spectra for fly ash used in our studies (Figure 1-3). Mollah and others<sup>46</sup> assign the bands in their spectra. The band at  $1080\text{ cm}^{-1}$  is assigned to the antisymmetric stretching vibration of Si-O-Si and the band at

792  $\text{cm}^{-1}$  to the corresponding symmetric vibration.<sup>46</sup> The band at 1135  $\text{cm}^{-1}$  is tentatively assigned to the antisymmetric stretching vibration of Si-O-Al and the band at 700  $\text{cm}^{-1}$  to the symmetric Si-O-Al stretching vibration.<sup>46</sup> The band at 481  $\text{cm}^{-1}$  is assigned to the O-Si-O bending vibration.<sup>46</sup> The shoulder at 950  $\text{cm}^{-1}$  is assigned to a non-bridging oxygen ion band, Si-O-Na.<sup>46</sup> The bands at 800 and 481  $\text{cm}^{-1}$  are assigned to the presence of cristobalite, and the band at 700  $\text{cm}^{-1}$  to the presence of mullite.<sup>46</sup>

**Table 1-4: XRF determined composition of fly ash and Kaolin**

| Compound                       | Mass (g/100g) <sup>a</sup> |                     | Compound                       | Mass (g/100g) <sup>a</sup> |                     |
|--------------------------------|----------------------------|---------------------|--------------------------------|----------------------------|---------------------|
|                                | Fly ash                    | Kaolin <sup>b</sup> |                                | Fly ash                    | Kaolin <sup>b</sup> |
| SiO <sub>2</sub>               | 50.9(7)                    | 45.53(9)            | MnO                            | 0.038(8)                   |                     |
| Al <sub>2</sub> O <sub>3</sub> | 37.1(6)                    | 37.3(2)             | ZnO                            | 0.024(4)                   | 0.0035(3)           |
| CaO                            | 4.5(3)                     | 0.0331(5)           | La <sub>2</sub> O <sub>3</sub> | 0.018 <sup>d</sup>         |                     |
| Fe <sub>2</sub> O <sub>3</sub> | 3.0(2)                     | 0.647(3)            | NiO                            | 0.017(4)                   | 0.0014(6)           |
| TiO <sub>2</sub>               | 1.8(1)                     | 0.852(3)            | As <sub>2</sub> O <sub>3</sub> | 0.016 <sup>d</sup>         | 0.0009(7)           |
| MgO                            | 0.8(3)                     | 0.286(3)            | PbO                            | 0.015(2)                   | 0.0108(2)           |
| K <sub>2</sub> O               | 0.62(4)                    | 0.949(4)            | Y <sub>2</sub> O <sub>3</sub>  | 0.014(5)                   | 0.00573(8)          |
| P <sub>2</sub> O <sub>5</sub>  | 0.48(4)                    | 0.1519(5)           | CeO <sub>2</sub>               | 0.012(9)                   |                     |
| SO <sub>3</sub>                | 0.2(2) <sup>c</sup>        | 0.0198(5)           | Ga <sub>2</sub> O <sub>3</sub> | 0.012(3)                   | 0.0110(2)           |
| SrO                            | 0.15(2)                    | 0.01944(6)          | CuO                            | 0.010(3)                   | 0.0008(5)           |
| BaO                            | 0.11(5)                    |                     | Rb <sub>2</sub> O              | 0.01 <sup>d</sup>          | 0.0192(2)           |
| Na <sub>2</sub> O              | 0.058(9)                   | 0.049(3)            | Nb <sub>2</sub> O <sub>5</sub> | 0.007(2)                   | 0.0095(6)           |
| ZrO <sub>2</sub>               | 0.055(9)                   | 0.00470(9)          | Sc <sub>2</sub> O <sub>3</sub> | 0.006 <sup>d</sup>         | 0.0043(2)           |
| Cr <sub>2</sub> O <sub>3</sub> | 0.052(5)                   | 0.0074(6)           | Ag <sub>2</sub> O              | 0.005 <sup>d</sup>         |                     |
| V <sub>2</sub> O <sub>5</sub>  | 0.039(8)                   | 0.0195(3)           | MoO <sub>3</sub>               | 0.0005(2)                  | 0.0002(2)           |

- The data represents the average of four XRF analyses on fly ash and fly ash treated at 1 000 °C with the standard deviation indicated in brackets, that is 50.9(7) implies 50.9 ± 0.7 g/100g sample.
- The data represents the average of four XRF analyses on Kaolin, content found in Kaolin but not in fly ash is omitted, for example uranium.
- The uncertainty in the value of SO<sub>3</sub> is related to the heat treatment of the samples and the analysis method.
- The compound occurred only once in the set of four repeat analyses.

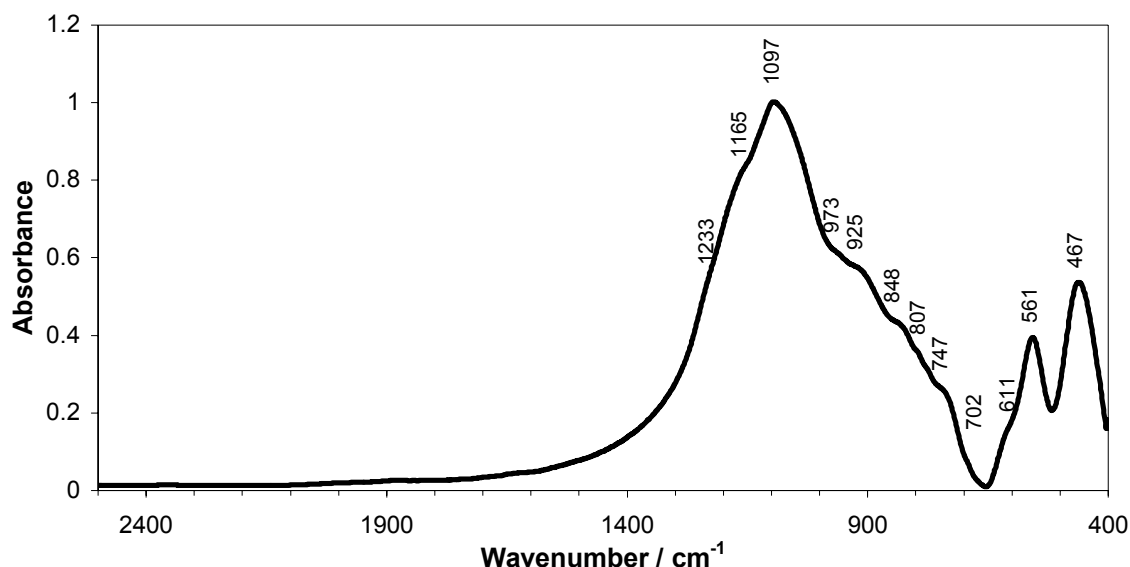


**Figure 1-3: Infrared spectrum of fly ash**

The pH of a suspension of 10 g of fly ash in 200 ml of water is  $11.473 \pm 0.009$  after 10 minutes of agitation. After treating the fly ash at  $1\,000\text{ }^{\circ}\text{C}$ , the pH under similar conditions only reaches  $8.28 \pm 0.03$ , a statistically different pH, even at the 99.99 % confidence level. This possibly indicates that some of the alkali and alkaline-earth salts on the surface of the particles decomposed to their respective oxides, and were not free to go into solution. Ding and others<sup>74</sup> identify  $\text{Ca}^{2+}$ ,  $\text{K}^{+}$  and  $\text{Na}^{+}$  as the soluble constituents of fly ash and find that a suspension of fly ash in water gives a pH of 12.2, in agreement with the present study as well as the work of Foner and others.<sup>2</sup> Bayat<sup>31</sup> observes similar trends in pH development over time, to a maximum of approximately 12.5, although some fly ash samples gave peak values as low as 9.7 and 10.4. Bayat<sup>31</sup> further determines, through leaching experiments, that sodium and potassium are almost entirely in their free ionic states, whereas calcium and magnesium are only predominantly in their free ionic states. Hydroxides and sulphates are also common in the fly ash suspensions.<sup>31</sup>

Further investigation needs to be done on the characterisation of fly ash, since the validity of any result regarding fly ash for one batch would need to be tested for other batches. Furthermore, fly ash can be studied in its different fractions. Fly ash can be

separated based on particle size, magnetic characteristics, and density. The order of these fractionation steps can be swapped around, possibly yielding different results.<sup>45</sup>

#### **1.4. Past Applications of Fly Ash**

Many patents are claimed for the use and beneficiation of fly ash. The classification of fly ash is not discussed, and is reviewed by Kruger.<sup>11</sup> The most important use of fly ash is in the cement industry, where the presence of fly ash adds strength to concrete. The minerals in South African fly ash are not hydraulic, that is the minerals do not add strength to cement.<sup>110</sup> The glass phase is believed to react with lime released from cement while the cement is curing.<sup>110</sup> This pozzolanic reaction adds strength to the cement.<sup>110</sup> In general fly ash reduces the water consumption of cement, increases the setting time, reduces the heat of hydration and adds long-term strength to cement products, for example concrete.<sup>3</sup> The unreactivity of the mineral or crystalline phases in fly ash is also evident during zeolite formation.<sup>24,73,77</sup> The unreactivity of the crystalline material in fly ash in terms of cement strength development does not mean that these parts of the fly ash particles are unreactive in all situations, nor does it imply that these minerals prevent the glassy phases from reacting.

Different applications of fly ash are tabulated below (Tables 1-5 to 1-8). The focus is on the period January 1980 to August 2003. In compiling the list of applications, applications regarding cement and concrete have largely been ignored, as well as non-coal based fly ash, for example municipal solid waste incineration ash. Helmuth<sup>19</sup> and Wesche<sup>23</sup> review the use of fly ash in cement, giving background on the characteristics of fly ash. Solid stabilisation of waste products has not been included either.<sup>111</sup>

Fly ash is used as cement extender, or filler in the manufacture of building material such as panels and boards (Table 1-5), and is also added to gypsum boards.

Fly ash retains water, which makes it a good soil amender. Boron and selenium enrichment seems to be the most detrimental aspect of fly ash amended soils. In these applications, fly ash is often mixed with sewage sludge (Table 1-5). The

possibility exists that the high levels of boron and selenium originate from the sewage sludge rather than from the fly ash. An extension of these soil amendment applications is the formation of artificial reefs.<sup>80,112,113</sup>

Polymers are expensive chemical species. To make up volume without using unnecessary amounts of polymer other inexpensive materials are added, known as fillers. Functional fillers are fillers that add extra quality to the final plastic, for example colour, fire retardancy, or UV stability. Fly ash has the potential to be a good functional filler (Table 1-5), due to its spherical microscopic structure (Figure 1-1). Cu-coated cenosphere particles are used in conducting polymers for EMI-shielding applications.<sup>105</sup>

The mullite and quartz in the non-magnetic fraction of fly ash could be a valuable resource in the ceramics industry (Table 1-5). The use of fly ash in frictional or brake material for the automotive industry is a high technology application of the hardness of fly ash.<sup>15</sup> Some transition metals are concentrated in the magnetic fraction of fly ash and can, therefore, be extracted from this concentrated matrix (Table 1-6).<sup>102</sup> Minerals essential to humans and animals can also be recovered from fly ash.<sup>114</sup> Ferrospheres exist in fly ash<sup>84</sup> and have found direct use as part of copier toner.<sup>115-118</sup>

Fly ash is used as an adsorbent for organic wastes (Table 1-7). Whether this adsorbent nature of fly ash can be ascribed to the porous nature of the silicates or to the activated carbon particles embedded on the surface of the fly ash particle is still a matter for debate. To remove  $\text{SO}_x$  from gas streams, fly ash is usually mixed with  $\text{Ca}(\text{OH})_2$  (Table 1-7). Fly ash is also used for the removal of heavy metals from aqueous samples (Table 1-7). This property of fly ash is dramatically enhanced by the formation of zeolites from fly ash (Table 1-8). The zeolites formed from fly ash (Table 1-8) cover a substantial range of the known structures for zeolites, and have been reviewed by Querol and others.<sup>119</sup> Smith,<sup>120</sup> Suib,<sup>121</sup> and Cundy and Cox<sup>122</sup> review the structure of these, and other, zeolites. Mullite is the least reactive component in fly ash during the formation of zeolites,<sup>24,73,77</sup> while the glass phase reacts first. Hollman and others<sup>86</sup> emphasize that the formation of the zeolite takes place on the surface of the fly ash particles. This leads to an impure product. In a

two-step synthesis, designed to separate the silica-rich leached fraction from the fly ash, 85 g of pure zeolite can be produced from 1 kg of fly ash.<sup>86</sup>

**Table 1-5: Applications in which fly ash acts as an additive**

| Building Industry                                              |                                                                  |
|----------------------------------------------------------------|------------------------------------------------------------------|
| Cement and Concrete <sup>1,2,4,11,12,17,19,23,31,123-126</sup> | Grout <sup>11,12,17,127</sup>                                    |
| Roof Tiles <sup>12,128-131</sup>                               | Roads <sup>123,125,132</sup>                                     |
| Bricks <sup>11,12,30,1,123-125,131,133-135</sup>               | Patches on Roads <sup>12,133,136,137</sup>                       |
| Panels and boards <sup>2,12,131,133,138-144</sup>              | Binder <sup>17</sup>                                             |
| Soil Beneficiation <sup>1,30,31,44,124,125,132,145-163</sup>   |                                                                  |
| Sewage treatment <sup>164,165</sup>                            | Landfill <sup>12,124,133,166-168</sup>                           |
| Soil stabilization <sup>169-171</sup>                          | Sludge stabilization <sup>172-174</sup>                          |
| Soil stabilization for roads <sup>175</sup>                    | Coagulation and sludge conditioning agents <sup>97,172,176</sup> |
| Fertiliser or composting <sup>30,49,177-181</sup>              |                                                                  |
| Filler Material <sup>182-184</sup>                             |                                                                  |
| Foams <sup>11</sup>                                            | Polyisocyanurate or polyurethane foam <sup>185,186</sup>         |
| Phenolic resole foam <sup>187</sup>                            | Polyester-polyurethane hybrid resin foams <sup>188</sup>         |
| Polyurethane foam <sup>189</sup>                               | Polymers <sup>11,133,190</sup>                                   |
| Polypropylene <sup>191,192</sup>                               | PVC <sup>193</sup>                                               |
| Epoxy resin <sup>105,194</sup>                                 | Polyester <sup>195</sup>                                         |
| Resins <sup>11</sup>                                           | Rigid shaped articles based on fly ash and resin <sup>196</sup>  |
| Polyurethane <sup>197</sup>                                    | Fibreglass <sup>11,198</sup>                                     |
| Mineral foam <sup>199</sup>                                    | Fibre reinforced fly ash <sup>107,200</sup>                      |
| Insulating Material <sup>125</sup>                             |                                                                  |
| High temperature <sup>11</sup>                                 | Low temperature applications. <sup>2,201,202,203</sup>           |
| Ceramic Material <sup>11,18,30,69,108,132,133,204-207</sup>    |                                                                  |
| Mineral wool <sup>124,133,208</sup>                            | Coated cellular glass pellet <sup>209</sup>                      |
| Glass-ceramics <sup>70,72,124,133,210-212</sup>                | Glass <sup>213</sup>                                             |

**Table 1-6: Applications in which fly ash acts as a metal and metal oxide source**  
1,31,133,214

|                                                   |                                  |
|---------------------------------------------------|----------------------------------|
| Iron <sup>34,53,97,215-226</sup>                  | Gallium <sup>215,227-230</sup>   |
| Germanium <sup>228,229</sup>                      | Lead and Zinc <sup>231</sup>     |
| Antimony <sup>232</sup>                           | Chromium <sup>232,233</sup>      |
| Vanadium <sup>227,232,234</sup>                   | Molybdenum <sup>232,234</sup>    |
| Aluminium <sup>53,75,97,215,222-226,234-238</sup> | Boron <sup>234,239</sup>         |
| Uranium <sup>31,222</sup>                         | Silica <sup>215,97,223-226</sup> |
| Selenium <sup>234</sup>                           | Titanium <sup>234,222,226</sup>  |
| Thorium <sup>222</sup>                            | Cobalt <sup>234</sup>            |

**Table 1-7: Applications in which fly ash acts as an adsorbent**

| Adsorbent for Organic wastes <sup>173</sup>                     |                                                       |
|-----------------------------------------------------------------|-------------------------------------------------------|
| Chlorophenols <sup>240</sup>                                    | Phenol <sup>241,242</sup>                             |
| o-xylene <sup>243</sup>                                         | Toluene <sup>244</sup>                                |
| Oil and tar <sup>242</sup>                                      |                                                       |
| Adsorbent for Inorganic Wastes <sup>12,31,170,173,245,246</sup> |                                                       |
| SO <sub>x</sub> <sup>41,50,53,65,89-94,98,247-255</sup>         | NO <sub>x</sub> <sup>250,252,253</sup>                |
| Nitrates <sup>256</sup>                                         | Phosphate <sup>67,68,256-258</sup>                    |
| Cadmium <sup>24,28,77,145,259-261</sup>                         | Lead <sup>28,43,77,256</sup>                          |
| Selenium <sup>262,263</sup>                                     | Mercury <sup>264-266</sup>                            |
| Radium <sup>267</sup>                                           | Barium <sup>24,28,77</sup>                            |
| Strontium <sup>61</sup>                                         | Copper <sup>24,28,77,88,246,256,259,261,268,269</sup> |
| Zinc <sup>24,28,77,86,269</sup>                                 | Cobalt <sup>24,270</sup>                              |
| Chromium <sup>246,259,271</sup>                                 | Caesium <sup>64,272</sup>                             |
| Nickel <sup>24,28,77,86,259,269,273</sup>                       | Iron <sup>28,274</sup>                                |
| Fluoride <sup>275</sup>                                         | Ammonia <sup>28,36,86,88</sup>                        |

Fly ash is used to aid in the oxidation of  $\text{Na}_2\text{S}$ <sup>276</sup> and organic material<sup>277</sup> in wastewater, and of  $\text{H}_2\text{S}$  and ethanethiol in gas streams.<sup>278</sup> This catalytic effect can also be used in other areas of chemistry, such as catalyst support, for example in the selective catalytic reduction of  $\text{NO}$ .<sup>279</sup> Fly ash is used as carbon monoxide disproportionating catalyst, useful in the production of hydrogen and methane,<sup>280</sup> and for hydrocracking.<sup>281</sup>

Fly ash is composited with aluminium,<sup>103,282,283</sup> tin,<sup>282</sup> zinc,<sup>282</sup> and sulphur,<sup>284</sup> by melting the elements in the presence of the fly ash. A less high technology and a malodorous application is the manufacture of cat litter.<sup>285</sup>

**Table 1-8: Applications in which fly ash acts as starting material for zeolite synthesis**<sup>145</sup>

|                                                           |                                                   |
|-----------------------------------------------------------|---------------------------------------------------|
| Zeolite Na-P1 <sup>2,24,28,43,77,86,95</sup>              | Zeolite P <sup>24,36,37,48,61,64</sup>            |
| Zeolite P1 <sup>87</sup>                                  | Phillipsite <sup>2,28,77,37</sup>                 |
| Zeolite K-G, ZK19 and Linde A <sup>24</sup>               | MCM41 <sup>286</sup>                              |
| Merlinoite and nosean <sup>77</sup>                       | K-Chabazite <sup>28,287</sup>                     |
| Hydroxy-cancrinite, perialite and Kalsilite <sup>28</sup> | Zeolite F Linde <sup>28,37</sup>                  |
| Na-Chabazite <sup>60,287</sup>                            | Herschelite and tobermorite <sup>28</sup>         |
| Nepheline hydrate <sup>29,37</sup>                        | Zeolite A <sup>24,28,36,60,64,86,95,270,288</sup> |
| Faujasite <sup>28,36,48,64</sup>                          | Analcime <sup>28,29,37,77</sup>                   |
| Gmelinite <sup>29</sup>                                   | Sodalite and cancrinite <sup>53</sup>             |
| Hydroxy-sodalite <sup>28,37,43,48,60,86,95</sup>          | Zeolite Y <sup>48,88</sup>                        |
| Zeolite X <sup>48,60,73,86,270,288</sup>                  | Zeolite J and M <sup>287</sup>                    |
| Zeolite R <sup>60</sup>                                   | Geopolymers <sup>51,53,54,109,289-291</sup>       |

### 1.5. Potential Uses of Fly Ash

The amorphous aluminosilicate nature of fly ash makes fly ash a possible starting point for many industrial reactions, such as the synthesis of ultramarine blue (Chapter 3).<sup>292</sup>

Repeated harvesting of foodstuff depletes the trace elements in soil. Although the use of fly ash as soil amendment has been studied, the full-scale application of this technology has not been implemented. In future, farmers might use fly ash, rather than lime, to enrich their soil. The trace elements in fly ash might be used to replace the trace elements in the soil, and to increase the mineral content of the foodstuff.

Fly ash can be considered a valuable resource and needs to be studied, in order to facilitate the application of fly ash to new and innovative areas of economic interest. This review aimed to act as a stepping-stone for the prospective researcher into the rewarding field of fly ash.

### 1.6. Conclusion

Several non-cement applications of fly ash were reported briefly, for example as filler in plastics. The characteristics of fly ash were also discussed, with the goal of challenging the scientific community to study and evaluate further potential uses of fly ash.

## REFERENCES

- 1 R.A. Kruger, *South African Journal of Science*, 1986, **82**, 177.
- 2 H.A. Foner, T.L. Robl, J.C. Hower, U.M. Graham, *Fuel*, 1999, **78**, 215-223.
- 3 S.V. Vassilev, C.G. Vassileva, *Fuel Processing Technology*, 1996, **47**, 261-280.
- 4 O.E. Manz, *Fuel*, 1999, **78**, 133-136.
- 5 J.E. Kruger, *An Overview*, in: Guides on the use of South African fly ash as a cement extender Guide 1, J.E. Kruger (ed), The South African Coal Ash Association (SACAA), Cresta, p. 2, 01 July 1998.
- 6 Eskom - Lethabo Visitor Centre, Eskom, [http://www.eskom.co.za/education/visit/lathabo/Lethabo\\_body.htm](http://www.eskom.co.za/education/visit/lathabo/Lethabo_body.htm), 2002, downloaded 17 December 2002 - 15:30.
- 7 J.C. Hower, T.L. Robl, G.A. Thomas, *Fuel*, 1999, **78**, 701-712.
- 8 *Statistics*, Eskom, <http://www.eskom.co.za/Enviro%20data%202002/report01/stats.htm>, 2002, downloaded 9 September 2002 - 16:00.

- 9 *Product Specifications*, Sphere-Fill, <http://www.superpozz.com/product.shtml>, 2002, downloaded 10 September 2002 - 9h36.
- 10 *Safety Data Sheet*, Sphere-Fill, <http://www.superpozz.com/contact1.html>, 2002, downloaded 10 September 2002 - 9h50.
- 11 R.A. Kruger, *Fuel*, 1997, **76** (8), 777-779.
- 12 B.E. Scheetz, R. Earle, *Current Opinion in Solid State & Material Science*, 1998, **3**, 510-520.
- 13 S.V. Vassilev, C. Braekman-Danheux, P. Laurent, *Fuel Processing Technology*, 1999, **59**, 95-134.
- 14 C.D. Shackelford, *Journal of Hazardous Materials*, 2000, **76**, vii-viii.
- 15 V.M. Malhotra, P.S. Valimbe, M.A Wright, *Fuel*, 2002, **81**, 235-244.
- 16 Y. Nathan, M. Dvorachek, I. Pelly, U. Mimran, *Fuel*, 1999, **78**, 205-213.
- 17 M.J. McCarthy, R.K. Dhir, *Fuel*, 1999, **78**, 121-132.
- 18 L.N. Satapathy, *Ceramics International*, 2000, **26**, 39-45.
- 19 R. Helmuth, *Fly Ash in Cement and Concrete*, Portland Cement Association, Skokie, 1987, pp 36-61.
- 20 G.L. Fisher, D.P.Y. Chang, M. Brummer, *Science*, 1976, **192** (4239), 553-555.
- 21 S. Ghosal, S.A. Self, *Fuel*, 1995, **74** (4), 522-529.
- 22 *CRC Handbook of Chemistry and Physics*, D.R. Lide (Ed), CRC Press LCC, Boca Raton, 1998-1999, 79th edition, p 4-141.
- 23 J.L. Alonso, K. Wesche, *Characterization of Fly Ash*, in: Fly Ash in Concrete - Properties and Performance, K. Wesche (Ed), First edition, E & FN Spon, London, 1991, p. 8.
- 24 P. Catalfamo, F. Corigliano, P. Primerano, S. Di Pasquale, *J. Chem. Soc. Faraday Trans.*, 1993, **89** (1), 171-175.
- 25 G. Steenbruggen, G.G. Hollman, *J. Geochem. Explor.*, 1998, **62**, 305-309.
- 26 V. Sakorafa, K. Michailidis, F. Burragato, *Fuel*, 1996, **75** (4), 419-423.
- 27 J.C. Hower, J.D. Robertson, G.A. Thomas, A.S. Wong, U.M. Graham, R.F. Rathbone, T.L. Robl, *Fuel*, 1996, **75** (4), 403-411.
- 28 X. Querol, J.C. Umana, F. Plana, A. Alastuey, A. Lopez-Soler, A. Medinaceli, A. Valero, M.J. Domingo, E. Garcia-Rojo, *Fuel*, 2001, **80**, 857-865.
- 29 X. Querol, A. Lopez-Soler, *Fuel*, 1997, **76** (8), 793-799.
- 30 I. Queralt, X. Querol, A. Lopez-Soler, F. Plana, *Fuel*, 1997, **76** (8), 787-791.
- 31 O. Bayat, *Fuel*, 1998, **77** (9/10), 1059-1066.
- 32 S. Gomes, M. François, *Cem. Concr. Res.*, 2000, **30**, 175-181.
- 33 E.V. Sokol, N.V. Maksimova, N.I. Volkova, E.N. Nigmatulina, A.E. Frenkel, *Fuel Processing Technology*, 2000, **67**, 35-52.
- 34 S. Prakash, J.K. Mohanty, B. Das, R. Venugopal, *Minerals Engineering*, 2001, **14** (1), 123-126.
- 35 Y. Fang, Y. Chen, M.R. Silsbee, D.M. Roy, *Mater. Lett.*, 1996, **27**, 155-159.
- 36 W-H. Shih, H-L. Chang, *Mater. Lett.*, 1996, **28**, 263-268.
- 37 H. Höller, U. Wirsching, *Fortschr. Miner.*, 1985, **63** (1), 21-43.
- 38 K. Tazaki, W.S. Fyfe, K.C. Sahu, M. Powell, *Fuel*, 1989, **68**, 727-734.
- 39 S.V. Vassilev, *Fuel*, 1992, **71**, 625-633.
- 40 A.R. Ramsden, M. Shibaoka, *Atmospheric Environment*, 1982, **16** (9), 2191-2206.
- 41 C-S. Ho, S-M. Shih, *Can. J. Chem. Eng.*, 1993, **71**, 934-939.
- 42 L.D. Hulett, A.J. Weinberger, *Environ. Sci. Technol.*, 1980, **14** (8), 965-970.
- 43 C.D. Woolard, K. Petrus, M. Van der Horst, *Water SA*, 2000, **26** (4), 531-536.
- 44 B. Indraratna, P. Nulalaya, N. Kuganenthira, *Quarterly Journal of Engineering Geology*, 1991, **24**, 275-290.
- 45 R.K. Vempati, A. Rao, T.R. Hess, D.L. Cocke, H.V. Lauer Jr, *Cem. Concr. Res.*, 1994, **24** (6), 1153-1164.
- 46 M.Y.A. Mollah, S. Promreuk, R. Schennach, D.L. Cocke, R. Guler, *Fuel*, 1999, **78**, 1277-1282.
- 47 M. van Roode, E. Douglas, R.T. Hemmings, *Cem. Concr. Res.*, 1987, **17**, 183-197.
- 48 H. Tanaka, S. Matsumura, S. Furusawa, R. Hino, *J. Mater. Sci. Lett.*, 2003, **22**, 323-325.
- 49 J.G. Yoo, Y.M. Jo, *J. Air & Waste Manage. Assoc.*, 2003, **53**, 77 - 83.

- 50 R-B. Lin, S-M. Shih, *Powder Technology*, 2003, **131**, 212-222.
- 51 H. Xu, J.S.J. Van Deventer, *Minerals Engineering*, 2002, **15**, 1131–1139.
- 52 S.V. Vassilev, R. Menendez, *Fuel*, 2004, **83**, 585-603.
- 53 W.K.W. Lee, J.S.J. van Deventer, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2002, **211**, 49-66.
- 54 W.K.W. Lee, J.S.J. van Deventer, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2002, **211**, 115-126.
- 55 J.F.C. Alcalá, R.M. Dávila, R.L. Quintero, *Trans. Iron Steel Inst. Jpn.*, 1987, **27**, 531-538.
- 56 D. Havlíček, R. Pribil, B. Kratochvíl, *Atmospheric Environment*, 1989, **23** (3), 701-706.
- 57 C.C. Hinckley, G.V. Smith, H. Twardowska, M. Saporoschenko, R.H. Shiley, R.A. Griffen, *Fuel*, 1980, **59**, 161-165.
- 58 J. Fernández, J. Renedo, A. Garea, J. Viguri, J.A. Irabien, *Powder Technology*, 1997, **94**, 133-139.
- 59 M. Park, C.L. Choi, W.T. Lim, M.C. Kim, J. Choi, N.H. Heo, *Microporous and Mesoporous Materials*, 2000, **37**, 81-89.
- 60 C. Poole, H. Prijatama, N.M. Rice, *Minerals Engineering*, 2000, **13** (8-9), 831-842.
- 61 W. Ma, P.W. Brown, S. Komarneni, *J. Mater. Res.*, 1998, **13** (1), 3-7.
- 62 S.C. White, E.D. Case, *J. Mater. Sci.*, 1990, **25**, 5215-5219.
- 63 A. Filippidis, A. Georgakopoulus, *Fuel*, 1992, **71**, 373-376.
- 64 H-L. Chang, W-H. Shih, *Ind. Eng. Chem. Res.*, 1998, **37** (1), 71-78.
- 65 R.A. Diffenbach, M.J. Hilterman, E.A. Frommell, H.B. Booher, S.W. Hedges, *Thermochim. Acta*, 1991, **189**, 1-24.
- 66 N.V. Russel, F. Wigley, J. Williamson, *Fuel*, 2002, **81**, 673-681.
- 67 N.M. Agyeia, C.A. Strydom, J.H. Potgieter, *Cem. Concr. Res.*, 2000, **30**, 823-826.
- 68 N.M. Agyeia, C.A. Strydom, J.H. Potgieter, *Cem. Concr. Res.*, 2002, **32**, 1889-1897.
- 69 N.N. Sampathkumar, A.M. Umarji, B.K. Chandrasekhar, *Mat. Res. Bull.*, 1995, **30** (9), 1107-1114.
- 70 M. Erol, A. Genç, M.L. Öveçoğlu, E. Yücelen, S. Küçükbayrak, Y. Taptik, *Journal of the European Ceramic Society*, 2000, **20**, 2209-2214.
- 71 U. Kukier, C.F. Ishak, *Environmental Pollution*, 2003, **123**, 255–266.
- 72 M. Erol, U. Demirler, S. Küçükbayrak, A. Ersoy-Meriçboyu, M.L. Öveçoğlu, *Journal of the European Ceramic Society*, 2003, **23**, 757-763.
- 73 N. Shigemoto, H. Hayashi, K. Miyaura, *J. Mater. Sci.*, 1993, **28**, 4781-4786.
- 74 M. Ding, M. Guesebroek, H.A. van der Sloot, *J. Geochem. Explor.*, 1998, **62**, 319-323.
- 75 K. Felker, F. Seeley, Z. Egan, D. Kelmers, *Chemtech*, 1982, **12** (2), 123-128.
- 76 S. Gomes, M. François, M. Abdelmoula, P.H. Refait, C. Pellissier, O. Evrard, *Cem. Concr. Res.*, 1999, **29**, 1705-1711.
- 77 X. Querol, A. Alastuey, J.L. Fernandez-Turiel, A. Lopez-Soler, *Fuel*, 1995, **74** (8), 1226-1231.
- 78 J.C. Hower, R.F. Rathbone, J.D. Robertson, G. Peterson, A.S. Trimble, *Fuel*, 1999, **78**, 197-203.
- 79 F. Ariese, K. Swart, R. Morabito, C. Brunori, S. Balzamo, J. Slobodnik, E. Korenková, P. Janox, M. Wildnerova, J. Hlavay, K. Polyák, P. Fodor, H. Muntau, *Intern. J. Environ. Anal. Chem.*, 2002, **82**(11-12), 751-770.
- 80 N. Kress, M. Tom, E. Spanier, *ICES Journal of Marine Science*, 2002, **59**, S231–S237.
- 81 J. Yan, I. Neretnieks, *The Science of the Total Environment*, 1995, **172**, 95-118.
- 82 C.M. Demanet, *Applied surface science*, 1995, **89**, 97-101.
- 83 S.R. Mishra, S. Kumar, A. Wagh, J.Y. Rho, T. Gheyi, *Mater. Lett.*, 2003, **57**, 2417-2424.
- 84 L. Cañadas, L. Salvador, C. Cortés, *Fuel*, 1990, **69**, 690-695.
- 85 E.V. Sokol, V.M. Kalugin, E.N. Nigmatulina, N.I. Volkova, A.E. Frenkel, N.V. Maksimova, *Fuel*, 2002, **81**, 867-876.
- 86 G.G. Hollman, G. Steenbruggen, M. Janssen-Jurkovicova, *Fuel*, 1999, **78**, 1225-1230.
- 87 M. Park, C.L. Choi, W.T. Lim, M.C. Kim, J. Choi, N.H. Heo, *Microporous and Mesoporous Materials*, 2000, **37**, 91-98.
- 88 S. Rayalu, S.U. Meshram, M.Z. Hasan, *Journal of Hazardous Materials*, 2000, **B77**, 123-131.

- 
- 89 J.C. Martínez, J.F. Izquierdo, F. Cunill, J. Tejero, J. Querol, *Ind. Eng. Chem. Res.*, 1991, **30** (9), 2143-2147.
  - 90 C-S. Ho, S-M. Shih, *Ind. Eng. Chem. Res.*, 1992, **31** (4), 1130-1135.
  - 91 J.F. Sanders, T.C. Keener, J. Wang, *Ind. Eng. Chem. Res.*, 1995, **34** (1), 302-307.
  - 92 H. Tsudhiai, T. Ishizuka, T. Ueno, H. Hattori, H. Kita, *Ind. Eng. Chem. Res.*, 1995, **34** (4), 1404-1411.
  - 93 T. Ishizuka, H. Tsudhiai, T. Murayama, T. Tanaka, H. Hattori, *Ind. Eng. Chem. Res.*, 2000, **39** (5), 1390-1396.
  - 94 A. Al-Shawabkeh, H. Matsuda, M. Hasatani, *Journal of Chemical Engineering of Japan*, 1995, **28** (1), 53-58.
  - 95 M.W. Grutzeck, D.D. Siemer, *J. Am. Ceram. Soc.*, 1997, **80** (9), 2449-2453.
  - 96 A. Hazrati, J.T. Schrodtt, *Surf. Interface Anal.*, 1988, **13**, 142-148.
  - 97 J.W. Smith, J. Condra, *J. Envir. Enrg.*, ASCE, 1983, **109**, 1168-1180.
  - 98 A. Al-Shawabkeh, H. Matsuda, M. Hasatani, *Can. J. Chem. Eng.*, 1995, **73**, 678-685.
  - 99 S.J. Rothenberg, P. Dennee, P. Holloway, *Appl. Spectrosc.*, 1980, **34** (5), 549-555.
  - 100 H. Yokozawa, T. Kikuchi, K.F. Ando, K. Hoshino, *Anal. Chim. Acta*, 1987, **195**, 73-80.
  - 101 K. Mukai, T. Kikuchi, K. Furuya, *Mikrochim. Acta*, 1988, **1988 III**, 41-56.
  - 102 L.D. Hulet Jr, A.J. Weinberger, K.J. Northcutt, M. Ferguson, *Science*, 1980, **210** (4476), 1356-1358.
  - 103 R.Q. Guo, P.K. Rohatgi, *Metall. Mater. Trans. B*, 1998, **29B**, 519-525.
  - 104 M.Y.A. Mollah, T.R. Hess, D.L. Cocke, *Cem. Concr. Res.*, 1994, **24** (1), 109-118.
  - 105 S. Shukla, S. Seal, Z. Rahaman, K. Scammon, *Mater. Lett.*, 2002, **57**, 151-156.
  - 106 S.M. Kulkarni, Kishore, *J. Mater. Sci.*, 2002, **37**, 4321-4326.
  - 107 S.R. Kaniraj, V. Gayathri, *Geotextiles and Geomembranes*, 2003, **21**, 123-149.
  - 108 E. Benavidez, C. Grasselli, N. Quaranta, *Ceramics International*, 2003, **29**, 61-68.
  - 109 J.G.S. van Jaarsveld, J.S.J. van Deventer, G.C. Lukey, *Mater. Lett.*, 2003, **57**, 1272-1280.
  - 110 J.E. Kruger, *Pozzolanic and hydration reactions involving fly ash, Guides on the use of South African fly ash as a cement extender Guide 3*, J.E. Kruger (ed), The South African Coal Ash Association (SACAA), Cresta, p. 1, May 1999.
  - 111 J.H. Potgieter, S.S. Potgieter, M. Loubser, E. Kearsley, C.A. Strydom, *Journal of Chemical Technology and Biotechnology*, 2002, **77** (3), 311-314.
  - 112 W.H. Gehrmann III, C.E. Anderson, S.M. Ray, W.B. Baker Jr, *Artificial reefs manufactured from coal combustion by-products*, final patent no. 5,199,377, USA, 06 April 1993.
  - 113 T.A. Wilding, M.D.J. Sayer, *ICES Journal of Marine Science*, 2002, **59**, S250-S257.
  - 114 A.M. Vognsen, H. Boisen, *Element-rich composition*, final patent no. 4,442,215, USA, 10 April 1984.
  - 115 R.G. Aldrich, G.H. Earl, D.W. Trunko, *Process for making ferrite spherical particulate toner core from raw fly ash*, final patent no. 4,698,289, USA, 06 October 1987.
  - 116 R.J. Hagenbach, *Carrier and developer compositions generated from fly ash particle*, final patent no. 4,894,305, USA, 16 January 1990.
  - 117 R.G. Aldrich, G.H. Earl, D.W. Trunko, *Ferrite toner carrier core composition derived from fly ash*, final patent no. 4,592,988, USA, 03 June 1986.
  - 118 R.J. Hagenbach, *Carrier and developer compositions generated from fly ash particle*, final patent no. 5,087,545, USA, 11 February 1992.
  - 119 X. Querol, N. Moreno, J.C. Umaña, A. Alastuey, E. Hernández, *International Journal of Coal Geology*, 2002, **50**, 413-423.
  - 120 J.V. Smith, *Chem. Rev.*, 1988, **88** (1), 149-182.
  - 121 S.L. Suib, *Chem. Rev.*, 1993, **93** (2), 803-826.
  - 122 C.S. Cundy, P.A. Cox, *Chem. Rev.*, 2003, **103**, 663-701.
  - 123 K. Kautz, *Fortschr. Miner.*, 1984, **62** (1), 51-72.
  - 124 E.J. DeGuire, S.H. Risbud, *J. Mater. Sci.*, 1984, **19**, 1760-1766.
  - 125 G.S. Ghuman, M.P. Menon, K. Chandra, J. James, D.C. Adriano, K.S. Sajwan, *Water, Air, and Soil Pollution*, 1994, **72**, 285-295.
  - 126 K.S. Rebeiz, A.P. Craft, *Journal of Energy Engineering- ASCE*, 2002, **128**(3), 62-73.
  - 127 D.A. Smetana, R.J. Lenczewski, A.L. Wilson, *Pumpable backfill grout*, final patent no. 5,294,255, USA, 15 March 1994.
-

- 
- 128 C.W. Pike, *Method of making asphaltic roofing material containing class F fly ash filler*, final patent no. 5,565,239, USA, 15 October 1996.
  - 129 B.J. Morrison, *Roofing and similar materials*, final patent no. 4,745,032, USA, 17 May 1988.
  - 130 P.J. Clearly, *Roofing composition and structure*, final patent no. 4,331,726, USA, 25 May 1982.
  - 131 W.M. Strabala, *Structural products manufactured from fly ash*, final patent no. 5,534,058, USA, 09 July 1996.
  - 132 E. Vazquez, *Fly Ash in Road Construction*, in: Fly Ash in Concrete - Properties and Performance, K. Wesche (Ed), First edition, E & FN Spon, London, 1991, pp. 174-175.
  - 133 L. Barbieri, I. Lancellotti, T. Manfredini, I. Queralto, J. Ma. Rincon, M. Romero, *Fuel*, 1999, **78**, 271-276.
  - 134 J. Bijen, *Bricks and Blocks*, in: Fly Ash in Concrete - Properties and Performance, K. Wesche (Ed), First edition, E & FN Spon, London, 1991, p. 169.
  - 135 J.C. Howlett, *Process for forming solid aggregates including shaped articles*, final patent no. 5,718,857, USA, 17 February 1998.
  - 136 T.W. Evans, *Method of repairing potholes in road surfaces by filling them with fly ash hardened in water*, final patent no. 4,431,335, USA, 14 February 1984.
  - 137 E. Weill, G.A. Crenson, *Cement based patching composition for asphalt pavement*, final patent no. 5,244,304, USA, 14 September 1993.
  - 138 J. Bijen, *Lightweight Aggregates*, in: Fly Ash in Concrete - Properties and Performance, K. Wesche (Ed), First edition, E & FN Spon, London, 1991, pp. 172-174.
  - 139 W.M. Strabala, *Fly ash composites and methods for making same*, final patent no. 6,200,379, USA, 13 March 2001.
  - 140 R.B. Bruce, R.A. Kuntze, *Sag-resistant gypsum board containing coal fly ash and method for making same*, final patent no. 4,403,006, USA, 06 September 1983.
  - 141 S. Matsuura, Y. Arai, S. Aoki, S. Ando, *Process for producing a fire-resistant, light-weight construction board*, final patent no. 4,586,958 and 4,812,169, USA.
  - 142 H. Kawai, *Method of manufacturing a wood-cement board*, final patent no. 5,863,477, USA, 26 January 1999.
  - 143 H. Kawai, *Wood-cement board product*, final patent no. 6,001,169, USA, 14 December 1999.
  - 144 T.E. Clear, *Cementitious structural building panel*, final patent no. 6,079,175, USA, 27 June 2000.
  - 145 C-F. Lin, S-S. Lo, H-Y. Lin, Y. Lee, *Journal of Hazardous Materials*, 1998, **60**, 217-226.
  - 146 R. Sikka, B.D. Kansal, *Bioresource Technology*, 1995, **51**, 199-203.
  - 147 R.J. Wright, E.E. Codling, S.F. Wright, *Chemosphere*, 1998, **36** (6), 1463-1474.
  - 148 S.N. Singh, K. Kulshreshtha, K.J. Ahmad, *Ecological Engineering*, 1997, **9**, 203-208.
  - 149 J.W.C. Wong, D.C. Su, *Bioresource Technology*, 1997, **59**, 97-102.
  - 150 J.W.C. Wong, D.C. Su, *Bioresource Technology*, 1997, **59**, 57-62.
  - 151 M. Fang, J.W.C. Wong, K.K. Ma, M.H. Wong, *Bioresource Technology*, 1999, **67**, 19-24.
  - 152 N.W. Menzies, R.L. Aitken, *Scientia Horticulturae*, 1996, **67**, 87-99.
  - 153 M.R. Khan, M.W. Khan, *Environmental Pollution*, 1996, **92** (2), 105-111.
  - 154 S. Sharma, M.H. Fulekar, C.P. Jayalakshmi, *Critical reviews in environmental control*, 1989, **19** (3), 251-275.
  - 155 P.J.A. Shaw, *Journal of Applied Ecology*, 1992, **29**, 728-736.
  - 156 J.L. Fail Jr, *Plant and Soil*, 1987, **101**, 149-150.
  - 157 J.S.C. Mbagwu, *Plant and Soil*, 1983, **74**, 75-81.
  - 158 M.H. Wong, J.W.C. Wong, *Environ. Pollut. Ser. A.*, 1986, **40**, 127-144.
  - 159 D.A. Toll, M.F. Arthur, *The Science of the Total Environment*, 1983, **31**, 243-261.
  - 160 M. Ghodrati, J.T. Sims, B.L. Vasilas, *Water, Air, and Soil Pollution*, 1995, **81**, 349-361.
  - 161 M.P. Menon, K.S. Sajwan, G.S. Ghuman, J. James, K. Chandra, B. Bacon, *Water, Air, and Soil Pollution*, 1993, **69**, 209-216.
  - 162 G. Petruzzelli, L. Lubrano, S. Cervelli, *Water, Air, and Soil Pollution*, 1987, **32**, 389-395.
  - 163 H. Veeresh, S. Tripathy, D. Chaudhuri, B. Ghosh, B. Hart, M. Powell, *Environmental Geology*, 2003, **43**(5), 513-520.
-

- 164 G.O. Schumacher, L. Weber, M. Nowicki, A. Dunbar, J.M. Douglas, *Method of treating municipal sewage sludge and product produced thereby*, final patent no. 5,143,481, USA, 01 September 1992.
- 165 E.R. Markham, J.T. Markham, E.G. Markham, *Organic base fertilizer from municipal sewage sludge*, final patent no. 5,252,116, USA, 12 October 1993.
- 166 W. Chesner, *Process for waste injection into landfills for waste management, landfill reclamation, enhanced biodegradation and enhanced methane gas generation and recovery*, final patent no. 5,139,365, USA, 18 August 1992.
- 167 D.L. Hansen, *Pozzolanic mixture for stabilizing landfill leachate*, final patent no. 4,917,733, USA, 17 April 1990.
- 168 C.L. Smith, J.J. Juzwiak, *Synthetic aggregate and landfill method*, final patent no. 5,211,750, USA, 18 May 1993.
- 169 G. Cain, J.D. Teague, P.J. Wright, *Stabilization of earth subsurface layers*, final patent no. 4,084,381, USA, 18 April 1978.
- 170 L.B. Spangle, S.E. Coleman, *Method for underground support and removal of hazardous ions in ground waters*, final patent no. 4,741,834, USA, 03 May 1988.
- 171 T. Punshon, D.C. Adriano, J.T. Weber, *The Science of the Total Environment*, 2002, **296**, 209-225.
- 172 C.L. Smith, W.C. Webster, *Process for treating aqueous chemical waste sludges and compositions produced thereby*, final patent no. RE 29,783, USA, 26 September 1978.
- 173 R.M. Gleizes, *Coal ashes used for treating various media and facilities for using same*, final patent no. 6,015,498, USA, 18 January 2000.
- 174 S. Lim, W. Jeon, J. Lee, K. Lee, N. Kim, *Wat. Res.*, 2002, **36**, 4177-4184.
- 175 B.C. Young, A.L. Harris, *Soil stabilizing method and apparatus*, final patent no. 4,990,025, USA, 05 February 1991.
- 176 H.H. Wardell, *Waste water clarification*, final patent no. 4,882,070, USA, 21 November 1989.
- 177 H. Segawa, K. Akizuki, *Apparatus for producing potassium silicate fertilizer*, final patent no. 4,293,523, USA, 06 October 1981.
- 178 S. Kamo, T. Watanabe, K. Nakayama, *Process for producing granular basic phosphate fertilizer*, final patent no. 4,248,617, USA, 03 February 1981.
- 179 R.F. Stockel, *Coal ash fertilizer compositions*, final patent no. 4,469,503, USA, 04 September 1984.
- 180 Y.B. Lee, H.S. Ha, K.D. Lee, K. Do Park, Y.S. Cho, P.J. Kim, *Soil Sci. Plant Nutr.*, 2003, **49**(1), 69-76.
- 181 S. Gaiind, A.C. Gaur, *Bioresource Technology*, 2003, **87**, 125-127.
- 182 R.W. Styron, K.S. Abiodun, *Method of making a mineral filler from fly ash*, final patent no. 6,139,960, USA, 31 October 2000.
- 183 D.J. Najvar, B.G. Pope, N.R. Loeffler, *Fly ash reactive filler for dehydrating and bonding aqueous polymeric compositions*, final patent no. 4,714,722, USA, 22 December 1987.
- 184 R.W. Styron, K.S. Abiodun, *Method of making mineral filler and pozzolan product from fly ash*, final patent no. 6,242,098, USA, 05 June 2001.
- 185 S.J. Glorioso, J.H. Burgess, *Extruded polymer foam with filler particles and method*, final patent no. 5,723,506 and RE37,095, USA.
- 186 W.G. Stobby, *Rigid polyurethane modified polyisocyanurate containing fly ash as an inorganic filler*, final patent no. 4,661,533, USA, 28 April 1987.
- 187 A. Albertelli, L.M. Hohmann, A.N. Curtis, *Foamed plastic materials*, final patent no. 4,843,103 and 4,595,710, USA.
- 188 J.N. Mushovic, *Cured unsaturated polyester-polyurethane hybrid highly filled resin foam*, final patent no. 5,302,634, USA, 12 April 1994.
- 189 E.L. Clay, J.L. Baker, *Natural sandwich of filled polyurethane foam*, final patent no. 4,164,526, USA, 14 August 1979.
- 190 V.K. Srivastava, *Engng. Fracture Mech.*, 1992, **43** (6), 1093-1096.
- 191 B.M. Sole, A. Ball, *Tribology International*, 1996, **29** (6), 457-465.
- 192 P.A. Järvelä, P.K. Järvelä, *J. Mater. Sci.*, 1996, **31**, 3853-3860.
- 193 F. Yang, V. Hlavacek, *Powder Technology*, 1999, **103**, 182-188.

- 
- 194 V.K. Srivastava, P.S. Shembekar, *J. Mater. Sci.*, 1990, **25**, 3513-3516.
  - 195 N. Chand, *J. Mater. Sci. Lett.*, 1988, **7**, 36-38.
  - 196 J.G. Smillie, *Shaped rigid articles containing fly ash and resin*, final patent no. 4,352,856, USA, 05 October 1982.
  - 197 R.C. Jenkins, *Carpet backing precoat, laminate coats, and foam coats prepared from polyurethane formulations including fly ash*, final patent no. 6,096,401, USA, 01 August 2000.
  - 198 Y. Ahluwalia, *Coated structural articles*, final patent no. 5,965,257, USA, 12 October 1999.
  - 199 C.N. Ferguson, *Foam composition and process*, final patent no. 4,328,034, USA, 04 May 1982.
  - 200 A. Boominathan, S. Hari, *Soil Dynamics and Earthquake Engineering*, 2002, **22**, 1027–1033.
  - 201 R. Bloembergen, J.A. Verhave, *Flame retardant thermally insulating material*, final patent no. 4,425,440, USA, 10 January 1984.
  - 202 H. Sperber, *Method for insulating a cavity*, final patent no. 5,389,167, USA, 14 February 1995.
  - 203 H. Sperber, *Method for insulating a cavity*, final patent no. 5,393,794, USA, 28 February 1995.
  - 204 Y.M. Jo, R.B. Hutchison, J.A. Raper, *Powder Technology*, 1997, **91**, 55-62.
  - 205 S. Kumar, K.K. Singh, P. Ramachandrarao, *J. Mater. Sci. Lett.*, 2000, **19**, 1263-1265.
  - 206 I.G. Talmy, D.A. Haught, C.A. Martin, *Ash-based ceramic materials*, final patent no. 5,521,132, USA, 28 May 1996.
  - 207 J.T. Golitz, J.F. Mainieri, B.H. Bennett, R.D. Moore, A.M. Paxton, *Ceramic products, of glass, fly ash and clay and methods of making the same*, final patent no. 5,583,079, USA, 10 December 1996.
  - 208 G.J. Monaghan, *High quality mineral wool*, final patent no. 4,504,544, USA, 12 March 1985.
  - 209 E. Tseng, M. Bassin, *Ash coated cellular glass pellet*, final patent no. 4,143,202, USA, 06 March 1979.
  - 210 L. Barbieri, A.M. Ferrari, I. Lancellotti, C. Leonelli, J.M. Rincón, M. Romero, *J. Am. Ceram. Soc.*, 2000, **83** (10), 2515-2520.
  - 211 R.E. Byrne, *Production of amber glass*, final patent no. 4,065,281, USA, 27 December 1977.
  - 212 H. Hojaji, P.B. de Macedo, T.A. Litovitz, *Method for making foam glass from diatomaceous earth and fly ash*, final patent no. 4,430,108, USA, 07 February 1984.
  - 213 J. Sheng, B.X. Huang, J. Zhang, H. Zhang, J. Sheng, S. Yu, M. Zhang, *Fuel*, 2003, **82**, 181-185.
  - 214 J. Shabtai, G. Fleminger, J. Fleming, *Extraction of metal oxides from coal fly ash by microorganisms and a new microorganism useful therefor*, final patent no. 5,231,018, USA, 27 July 1993.
  - 215 Z. Fang, H.D. Gesser, *Hydrometallurgy*, 1996, **41**, 187-200.
  - 216 T.M. Gilliam, R.M. Canon, B.Z. Egan, A.D. Kelmers, F.G. Seely, J.S. Watson, *Resources and Conservation*, 1982, **9**, 155-168.
  - 217 M.S. Dobbins, G. Burnet, *Resources and Conservation*, 1982, **9**, 231-242.
  - 218 R.G. Aldrich, *Separation of high grade magnetite from fly ash*, final patent no. RE31,540, USA, 20 March 1984.
  - 219 R.G. Aldrich, *Separation of high grade magnetite from fly ash*, final patent no. 4,319,988, USA, 16 March 1982.
  - 220 J.W. Brown, *Process for recovering magnetite from fly ash*, final patent no. 4,191,336, USA, 04 March 1980.
  - 221 M.S. Dobbins, M.J. Murtha, *Recovery of iron oxide from coal fly ash*, final patent no. 4,386,057, USA, 31 May 1983.
  - 222 W.J. McDowell, F.G. Seeley, *Recovery of aluminum and other metal values from fly ash*, final patent no. 4,254,777, USA, 24 February 1981.
  - 223 J.J. Russ, J.S. Russ, R.T. Heagy, *Process for recovering mineral values from fly ash*, final patent no. 4,130,627, USA, 19 December 1978.
-

- 
- 224 J.J. Russ, J.W. Smith, *Method for separating and recovering silica, aluminum and iron from fly ash, mineral ores and mine tailings*, final patent no. 4,539,187, USA, 03 September 1985.
- 225 J.E. Reynolds, A.R. Williams, *Process for recovering aluminum and other metal values from fly ash*, final patent no. 4,159,310, USA, 26 June 1979.
- 226 W.E. Dunn Jr, *Two stage chlorination process for aluminum value containing source*, final patent no. 4,355,007, USA, 19 October 1982.
- 227 I. Tsuboi, S. Kasai, E. Kunugita, I. Komasaawa, *Journal of Chemical Engineering of Japan*, 1991, **24** (1), 15-20.
- 228 B. Lisowyj, D. Hitchcock, H. Epstein, *Direct fuel-fired furnace arrangement for the recovery of gallium and germanium from coal fly ash*, final patent no. 4,643,110, USA, 17 February 1987.
- 229 B. Lisowyj, D. Hitchcock, H. Epstein, *Process for the recovery of gallium and germanium from coal fly ash*, final patent no. 4,678,647, USA, 07 July 1987.
- 230 B. Lisowyj, D.C. Hitchcock, *Beneficiation of gallium in fly ash*, final patent no. 4,686,031, USA, 11 August 1987.
- 231 S. Santen, B. Johansson, *Treatment of fly ash*, final patent no. 6,155,965, USA.
- 232 C. Kersch, M.J.E. Van Roosmalen, M.J.E. Roosmalen, G.F. Woerlee, G.J. Witkamp, *Ind. Eng. Chem. Res.*, 2000, **39** (12), 4670-4672.
- 233 G.P. Dasmahapatra, T.K. Pal, B Bhattacharya, *Sep. Sci. Technol.*, 1996, **31** (20), 2843-2853.
- 234 R. Fass, J. Geva, Z.P. Shalita, M.D. White, J.C. Fleming, *Bioleaching method for the extraction of metals from coal fly ash using thiobacillus*, final patent no. 5,278,069, USA, 11 January 1994.
- 235 M.J. Murtha, *Process for the recovery of alumina from fly ash*, final patent no. 4,397,822, USA, 09 August 1983.
- 236 W.J. McDowell, F.G. Seeley, *Salt-soda sinter process for recovering aluminum from fly ash*, final patent no. 4,254,088, USA, 03 March 1981.
- 237 M. Boybay, T. Demirel, *Process for preparing cryolite from fly ash*, final patent no. 4,362,703, USA, 07 December 1982.
- 238 A.E. Torma, *Process for the recovery of alumina from fly ash and production of cement constituents*, final patent no. 4,242,313, USA, 30 December 1980.
- 239 I. Tsuboi, E. Kunugita, I. Komasaawa, *Journal of Chemical Engineering of Japan*, 1990, **23** (4), 480-485.
- 240 P-C. Kao, J-H. Tzeng, T-L. Huang, *Journal of Hazardous Materials*, 2000, **76**, 237-249.
- 241 T. Viraraghavan, F.D. Alfaro, *Journal of Hazardous Materials*, 1998, **57**, 59-70.
- 242 B. Zinke, *Method for absorbing organic pollutants*, final patent no. 5,769,777, USA, 23 June 1998.
- 243 K. Banerjee, P.N. Cheremisinoff, S.L. Cheng, *Wat. Res.*, 1997, **31** (2), 249-261.
- 244 A. Peloso, M. Rovatti, G. Ferraiolo, *Resources and Conservation*, 1983, **10**, 211-220.
- 245 J. Bijen, *Waste Neutralization and Stabilization*, in: Fly Ash in Concrete - Properties and Performance, K. Wesche (Ed), First, E & FN Spon, London, 1991, pp. 177-178.
- 246 S. Babel, T. A. Kurniawan, *Journal of Hazardous Materials*, 2003, **B97**, 219-243.
- 247 A. Garea, M.I. Ortiz, J.R. Viguri, M.J. Renedo, J. Fernandez, J.A. Irabien, *Thermochimica Acta*, 1996, **286**, 173-185.
- 248 A. Garea, I. Fernández, J.R. Viguri, M.I. Ortiz, J. Fernandez, M.J. Renedo, J.A. Irabien, *Chemical Engineering Journal*, 1997, **66**, 171-179.
- 249 A. Garea, J.R. Viguri, A. Irabien, *Chemical Engineering Science*, 1997, **52** (5), 715-732.
- 250 H. Tsudhiai, T. Ishizuka, H. Nakamura, T. Ueno, H. Hattori, *Ind. Eng. Chem. Res.*, 1996, **35** (3), 851-855.
- 251 A.P. Simko, *Process for removing sulfur dioxide in a wet scrubber*, final patent no. 4,164,547, USA, 14 August 1979.
- 252 N.C. Samish, *Removal of SO<sub>x</sub> and NO<sub>x</sub> gases from flue gas by absorption using an absorbent*, final patent no. 4,980,138, USA, 25 December 1990.
- 253 R.G. Hooper, *Method for SO<sub>x</sub>/NO<sub>x</sub> pollution control*, final patent no. 5,002,741, USA, 26 March 1991.
-

- 254 L. Zhang, A. Sato, Y. Ninomiya, E. Sasaoka, *Fuel*, 2003, **82**, 255-266.
- 255 M.J. Renedo, J. Fernández, *Fuel*, 2004, **83**, 525-532.
- 256 G. Gupta, N. Torres, *Journal of Hazardous Materials*, 1998, **57**, 243-248.
- 257 A. Demirbaş, *Cem. Concr. Res.*, 2003, **33**, 935.
- 258 N.M. Agyeia, C.A. Strydom, J.H. Potgieter, *Cem. Concr. Res.*, 2003, **33**, 937.
- 259 B. Bayat, *Journal of Hazardous Materials*, 2002, **B95**, 275-290.
- 260 S. Chatterjee, R.K. Asthana, A.K. Tripathi, S.P. Singh, *Process Biochemistry*, 1996, **31** (5), 457-462.
- 261 J. Ayala, F. Blanco, P. García, P. Rodriguez, J. Sancho, *Fuel*, 1998, **77** (11), 1147-1154.
- 262 D.J. Hassett, K.E. Eylands, *Fuel*, 1997, **76** (8), 807-809.
- 263 R. Renk, *Selenium adsorption process*, final patent no. 4,971,702, USA, 20 November 1990.
- 264 A.K. Sen, A.K. De, *Wat. Res.*, 1987, **21** (8), 885-888.
- 265 H.C. Hsi, M.J. Rood, M. Rostam-Abadi, S.G. Chen, R. Chang, *J. Envir. Enrg.*, ASCE, 2002, **128**(11), 1080-1089.
- 266 G.E. Dunham, R.A. DeWall, C.L. Senior, *Fuel Processing Technology*, 2003, **82**, 197-213.
- 267 F.M. Scheitlin, *Removal of radium from acidic solutions containing same by adsorption on coal fly ash*, final patent no. 4,431,609, USA, 14 February 1984.
- 268 K.K. Panday, G. Prasad, V.N. Singh, *Wat. Res.*, 1985, **19** (7), 869-873.
- 269 B. Bayat, *Journal of Hazardous Materials*, 2002, **B95**, 251-273.
- 270 H-L. Chang, W-H. Shih, *Ind. Eng. Chem. Res.*, 2000, **39** (11), 4185-4191.
- 271 G.S. Gupta, G. Prasad, K.K. Panday, V.N. Singh, *Water, Air, and Soil Pollution*, 1988, **37**, 13-24.
- 272 G.S. Gupta, G. Prasad, V.N. Singh, *Wat. Res.*, 1990, **24** (1), 45-50.
- 273 P. Ricou-Hoeffler, V. Héquet, I. Lécuyer, P. Le Cloirec, *Wat. Sci. Tech.*, 2000, **42** (5-6), 79-84.
- 274 M. Ding, M. Guesbroek, H.A. van der Sloot, *J. Geochem. Explor.*, 1998, **62**, 319-323.
- 275 A.K. Chaturvedi, K.P. Pathak, V.N. Singh, *Water, Air, and Soil Pollution*, 1990, **49**, 51-61.
- 276 D. Mallik, S.K. Chaudhuri, *Wat. Res.*, 1999, **33** (2), 585-590.
- 277 S.K. Chaudhuri, B. Sur, *J. Envir. Enrg.*, ASCE, 2000, **126** (7), 583-594.
- 278 J.R. Kastner, K.C. Das, N.D. Melear, *Journal of Hazardous Materials*, 2002, **B95**, 81-90.
- 279 X. Xuan, C. Yue, *Fuel*, 2003, **82**, 575-579.
- 280 D.R. Corbin, L.J. Velenyi, M.A. Pepera, S.R. Dolhyj, *Activation of fly ash*, final patent no. 4,607,021, USA, 19 August 1986.
- 281 C.P. Khulbe, R. Ranganathan, B.B. Pruden, *Hydrocracking of heavy oils/fly ash slurries*, final patent no. 4,299,685, USA, 10 November 1981.
- 282 R.B. Pond Sr, *Metal composites with fly ash incorporated therein and a process for producing the same*, final patent no. 4,888,054, USA, 19 December 1989.
- 283 N. Sobczak, J. Sobczak, J. Morgiel, L. Stobierski, *Materials Chemistry and Physics*, 2003, **81**, 296-300.
- 284 E.J. Schwoegler, *Compositions of sulfur and fly ash and shaped articles produced therefrom*, final patent no. 4,134,775, USA, 16 January 1979.
- 285 R.F. Stockel, *Animal litter composition*, final patent no. 4,129,094, USA, 12 December 1978.
- 286 H-L. Chang, W-H. Shih *Ind. Eng. Chem. Res.*, 1999, **38** (3), 973-977.
- 287 H. Höller, U. Wirsching, *Fortschr. Miner.*, 1985, **63** (1), 21-43.
- 288 N. Shigemoto, S. Sugiyama, H. Hayashi, K. Miyaura, *J. Mater. Sci.*, 1995, **30**, 5777-5783.
- 289 J.C. Swanepoel, C.A. Strydom, *Applied Geochemistry*, 2002, **17** (8), 1143-1148.
- 290 J.G.S. Van Jaarsveld, J.S.J. Van Deventer, *Ind. Eng. Chem. Res.*, 1996, **38** (10), 3932-3941.
- 291 J.G.S. van Jaarsveld, J.S.J. van Deventer, G.C. Lukey, *Chemical Engineering Journal*, 2002, **89**, 63-73.
- 292 A.A. Landman, D. De Waal, *Materials Research Bulletin*, 2004, **39**, 655-667.

## 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'.<sup>1</sup> Class F (low calcium carbonate content)<sup>1</sup>, fly ash samples were used in the experiments. The fly ash particles were of similar size: in the range of 1  $\mu\text{m}$  to 12  $\mu\text{m}$ , with an average diameter of less than 5  $\mu\text{m}$ . 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  $\text{cm}^{-1}$  under vacuum. This was the minimum resolution suggested by Russel<sup>2</sup> 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<sup>3</sup> and PeakFit<sup>4</sup> software, as well as dedicated self-developed software written in Delphi<sup>4</sup> (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  $\text{cm}^{-1}$ . Radiation at 514.5 nm from an Ar<sup>+</sup> 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<sup>6</sup> software and normalised to an intensity of 1 with the self-developed software (Appendix A1).

## **2.4. X-Ray Diffraction<sup>7</sup>**

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

## **2.5. X-Ray Fluorescence<sup>8</sup>**

An ARL 9400XP+ wavelength-dispersive XRF spectrometer with a Rh source was used for the X-ray fluorescence analyses of the samples.<sup>8</sup> The XRF spectrometer was calibrated with certified reference materials.<sup>8</sup> 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.<sup>8</sup> Samples were dried and fired at 1 000 °C to determine the percentage loss on ignition; for the fly ash samples, this was less than 2 %.<sup>8</sup> 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,<sup>8</sup> as adapted from Bennett and Oliver.<sup>9</sup> 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 °C in a muffle furnace, with occasional swirling.<sup>8</sup> The glass disk was poured into a preheated Pt/Au mould and the bottom surface was analysed.<sup>8</sup> The trace element analyses were done on pressed powder pellets, using an adaptation of the method described by Watson,<sup>10</sup> with a saturated Mowiol 40-88 solution as binder.<sup>8</sup>

## **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.<sup>11</sup>

## **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.<sup>12</sup> A representative from Rolfes Colour Pigments International (Pty) Ltd conducted these tests on the prepared ultramarine samples.

## **2.9. Molecular Modelling**

HyperChem<sup>13</sup> 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  $3 \times 10^{-3}$  kcal/Åmol. The self-consistent field convergence limit was set at  $1 \times 10^{-8}$ . 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 Intermediate Neglect of Differential Overlap (INDO) method.<sup>14</sup> The overlap weighting factors were set to 1 for both sigma-sigma and pi-pi interactions, as required for geometry optimisation.<sup>14</sup>

Semi-empirical and *ab initio* methods took into account both molecular geometry and the electron distribution and the results from HyperChem<sup>13</sup> were interpreted in terms of the Linear Combination of Atomic Orbitals (LCAO) - Molecular Orbital (MO) theory.<sup>14</sup> 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.<sup>14</sup>

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.<sup>14</sup> Because quantum mechanical computations dealt explicitly with the electrons, it was necessary to specify the charge and spin multiplicity of the molecules.<sup>14</sup> When a singlet state was considered the computation was usually done with Restricted Hartree-Fock (RHF) wave functions.<sup>14</sup> In the restricted Hartree-Fock method it was assumed that all electrons were paired and that each pair occupied the same spatial molecular orbital.<sup>14</sup> For higher multiplicity computations the Unrestricted Hartree-Fock (UHF) wave functions that distinguish between spin states were used.<sup>14</sup> Alpha electrons would then be in the highest occupied molecular orbital, because they were assigned first and then the remaining electrons to beta positions.<sup>14</sup> 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.<sup>14</sup>

HyperChem applied the *aufbau* principle when assigning electrons to molecular orbitals<sup>14</sup> 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.<sup>14</sup> 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.<sup>14</sup>

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.<sup>15</sup> 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.<sup>16-21</sup>

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

The **M**øller-**P**lesset **second**-order perturbation, **MP2**, correlation energy<sup>22</sup> compensated for some of the assumptions made during the Hartree-Fock computations and was used to correct the calculated energy.<sup>14</sup> 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.<sup>14</sup> The 6-311G\*\* implied a triple valence basis set with polarisation functions.<sup>14</sup> 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  $1 \times 10^{-10}$ . 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.<sup>14</sup> The analysis was based on data obtained from quantum mechanical computations, but it remained classical.<sup>14</sup> The calculation of vibrational frequencies was described by Matsuura and Yoshida.<sup>23</sup> *Ab initio* determined vibrational frequencies were usually larger than observed frequencies, and needed scaling.<sup>23,24</sup> 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.<sup>24</sup> 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,<sup>25</sup> however, suggested scale factors larger than unity be used, when considering sulphur clusters. Brabson and others,<sup>26</sup> suggested a scale factor of 0.87, based on experimental data for S<sub>3</sub> 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.<sup>14</sup> HyperChem could, therefore, only compute an electronic spectrum for molecules with a singlet spin state.<sup>14</sup> 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.<sup>14</sup>

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.<sup>14</sup> 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.<sup>27</sup> This inversion in energy indicated that the extra computational effort involved in the unrestricted Hartree-Fock computations was worthwhile for some structures.

## REFERENCES

- 1 R.A. Kruger, *Fuel*, 1997, **76**, 777-779.
- 2 J.D. Russel, *Instrumentation and Techniques*, in: *The infrared spectra of minerals*, VC Farmer (Ed), Mineralogical Society, London, 1974, pp. 11-26.
- 3 OPUS, Version 3.1, distributed by Bruker Optik GmbH, Ettlingen, Germany, 2000.
- 4 PeakFit, Version 4.06, distributed by AISN Software Inc., Mapleton, 1995.
- 5 Borland Delphi Professional, Version 4.0 (Build 5.104) Update Pack 2, distributed by Inprise Corporation, 1998.
- 6 Labspec, Version 2.04, distributed by DILOR SA & Université de Reims, France, 1997.
- 7 S. Verryin, Details of the XRD procedure used at the University of Pretoria XRD laboratory, Personal Written Communication, University of Pretoria, Pretoria, 2002.
- 8 M. Loubser, Typed report on XRF analyses, mloubser@postino.up.ac.za, Pretoria, 20 June 2002.
- 9 H. Bennett, G. Oliver, *XRF Analysis of Ceramics, Minerals and Applied Materials*, John Wiley & Son, Chichester, 1992, p. 67.
- 10 J.S. Watson, *X-Ray Spectrometry*, 1996, **25**, 173-174.
- 11 A.N. Hall, A.J. Botha, C. Van der Merwe, The instrumentation and sample preparation for SEM, Verbal communication, University of Pretoria, Pretoria, 2002.
- 12 T.V. Whittington, *Paint Testing*, in: *Paint Handbook*, G.E. Weismantel (Ed), McGraw-Hill Book Company, New York, 1981, pp. (2-5) to (2-6).
- 13 HyperChem, ver. 6.03 for Windows, distributed by HyperCube Inc, 2000.
- 14 HyperChem Computational Chemistry, HyperCube Inc, Canada, 1996, p. 32-35, 37, 41-42, 44-45, 47-48, 234, 251, 294, 331-336.
- 15 R.B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**(9), 2046-2048.
- 16 R.B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**(9), 2046-2048.
- 17 R.B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**(11), 2511-2513.
- 18 R.B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**(2), 395-397.
- 19 R. Hoffmann, *Account Chem. Res.*, 1971, **4**(1), 1-9.
- 20 K. Fukui, *Tetrahedron Letters*, 1965, **28**, 2427-2432.

- 21 K. Fukui *Tetrahedron Letters*, 1965, **24**, 2009-2015.
- 22 C. Møller, M.S. Plesset, *Phys. Rev.*, 1934, **46**, 618-622.
- 23 H. Matsuura, H. Yoshida, *Calculation of Vibrational Frequencies by Hartree-Fock-based and Density Functional Theory*, in: *Handbook of Vibrational Spectroscopy*, J.M. Chalmers and P.R. Griffiths (eds), vol 3, John Wiley & Sons Ltd., New York, 2002, pp. 2012-2028.
- 24 A.P. Scott, L. Radom, *J. Phys. Chem.*, 1996, **100**(41), 16502-16513.
- 25 I. Krossing, J. Passmore, *Inorg. Chem.*, 1999, **38**, 5203-5211.
- 26 G.D. Brabson, Z. Mielke, L. Andrews, *J. Phys. Chem.*, 1991, **95**(1), 79-86.
- 27 J. Miller, in e-mail communication regarding Negative electronic transition energy with Andreas A Landman, support@hyper.com, 17 February 2003.

## CHAPTER 3

# SYNTHESIS OF ULTRAMARINE BLUE FROM FLY ASH

IN

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



### 3. SYNTHESIS OF ULTRAMARINE BLUE FROM FLY ASH

#### 3.1. Introduction

Ultramarine pigments come in different shades and colours, they are green, blue, greenish blue, reddish blue, violet, pink and red.<sup>1-8</sup> The sulphur content of these pigments was lower in the violet and red species than in the blue species. In 1828, JB Guimet in France and Christian Gmelin in Germany developed processes for the industrial production of ultramarine products.<sup>1,9</sup> Several ideal stoichiometries for ultramarine blue were reported: for example  $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_x$  ( $x$  between 1 and 4),<sup>4,10</sup>  $\text{Na}_{6.9}\text{Al}_{5.6}\text{Si}_{6.4}\text{O}_{24}\text{S}_{4.2}$ ,<sup>1</sup>  $\text{Na}_{6.3}[\text{Al}_{4.79}\text{Si}_{7.21}\text{O}_{24}]\text{S}_{3.74}$ <sup>6</sup> and  $\text{Na}_{7.5}[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_{4.5}$ .<sup>7</sup> Kaolin was the traditional starting reagent in the synthesis of industrial ultramarine blue (Figure 3-1).<sup>1,11-16</sup> The ratio of Si to Al in kaolin is 1.16. The samples of fly ash used in this study also had a Si to Al ratio of 1.16 (Table 1-4). This ratio determined the amount of sulphur that could be incorporated into the structure.<sup>1</sup> In ultramarine pigments, sodium ions acted as counter-ions for both aluminium ions and polysulphide species. When fewer aluminium ions were present in the aluminosilicate framework, more sodium ions were free to act as counter-ions for the polysulphide species. More polysulphide molecules could, therefore, be incorporated into the structure. This led to a stronger colour.

Ultramarine was useful in the production of plastics, paints and powder coatings, printing inks, paper and paper coatings, rubber and thermoplastic elastomers, latex products, detergents, cosmetics and soaps, artists' colours, toys and educational equipment, leather finishes, powder markers, roofing granules, synthetic fibres, theatrical paints and blue mattes, cattle salt licks and as a white enhancer.<sup>1</sup>  $\text{S}_3^{2-}$ , the blue species, and  $\text{S}_2^{2-}$ , the yellow species,<sup>2,5,17</sup> were stable in the aluminosilicate framework,<sup>18, 19</sup> and the quality of the synthesized pigment depended on the quality of the aluminosilicate framework, in other words the framework should be defect-free.<sup>20</sup>

The present industrial process (Figure 3-1) involved the activation of kaolin, also known as Chinese clay, at approximately 700 °C, after which it was reacted with a source of sodium, sulphur and a reducing agent (Table 3-1).<sup>1,11,19</sup> Tarling and

others<sup>21</sup> emphasized that the ratio of the furnace to the sample volume should be close to 1 in order to maintain a concentrated sulphurous environment. Sulphur was lost from the surface of the reagent mix due to over-oxidation. This loss led to a non-pigmentary outer perimeter, 10 to 20 mm thick, which was usually discarded.

### **3.2. Experimental**

#### **3.2.1. Synthesis**

The traditional procedure for synthesizing ultramarine blue from kaolin began with clay activation, followed by the blending of raw materials, reductive heating, oxidative heating, and purification and refinement. The lefthand side of Figure 3-1 represents a traditional synthesis.<sup>1</sup> The procedure used for synthesizing ultramarine blue from fly ash differed from the traditional in that there was no clay activation involved – this step was redundant because fly ash was largely amorphous. The intermediate steps (blending of raw materials, reductive heating and oxidative heating) were the same. The last step was also different, but only because the scale of the synthesis differed. An industrial-scale version of the fly ash-based ultramarine blue synthesis would have the same final steps since the same products would be formed.

The process of synthesizing ultramarine blue using fly ash commenced with mixing sulphur (30 %), fly ash (36 %), carbon (4 %) and sodium carbonate (30 %) as starting reagents (Figure 3-1, Table 3-1) in a coffee mill to ensure optimal mixing of the reagents. The fly ash and sodium carbonate were mixed first, then the sulphur was mixed into the combined fly ash and sodium carbonate. Finally, the finely divided activated carbon was added. Because sulphur and carbon were two of the three ingredients of gunpowder, the carbon was added only after the sulphur had been mixed with the largely inert fly ash. The reagent mix was packed into an alumina crucible (height 50 mm, inner diameter 45 mm) with a ceramic tile lid. The crucible was filled to approximately 95 % capacity to minimize the amount of oxygen entrapped in the crucible, in accordance with the observations by Tarling and others.<sup>21</sup> The filled crucible with its lid was placed into a muffle furnace, preheated to 750 °C. It was found that the synthesis was not successful if the crucible and furnace were allowed to heat simultaneously from room temperature to the desired

temperature. The carbon monoxide atmosphere reduced the elemental sulphur ( $S_8$ ) at 750 °C. The time allowed for the reduction step was between 24 and 36 hours. After the reduction step, which yielded a green product, the crucible was opened to the air atmosphere of the muffle furnace, without any effort to establish a sulphur dioxide atmosphere, at 300 - 400 °C. The ultramarine green was now allowed to oxidize over a 48-hour period to form the desired ultramarine blue. The ultramarine product was milled in a coffee grinder and in an agate mortar. The fine powdery pigment was washed with boiling water to remove excess  $Na_2SO_4$ . X-ray diffraction analysis revealed the importance of washing (Figure 3-2). The water-filtered product was then dried at 100 °C.

### **3.2.2. Kinetic Experiment**

The oxidation of ultramarine green to ultramarine blue was followed by reacting 2 g portions of ultramarine green at 1 000 °C in a 5 % Au/Pt crucible in a muffle furnace for 10, 30, 60 and 90 minutes. The reacted samples were allowed to cool and later studied by Raman spectroscopy.



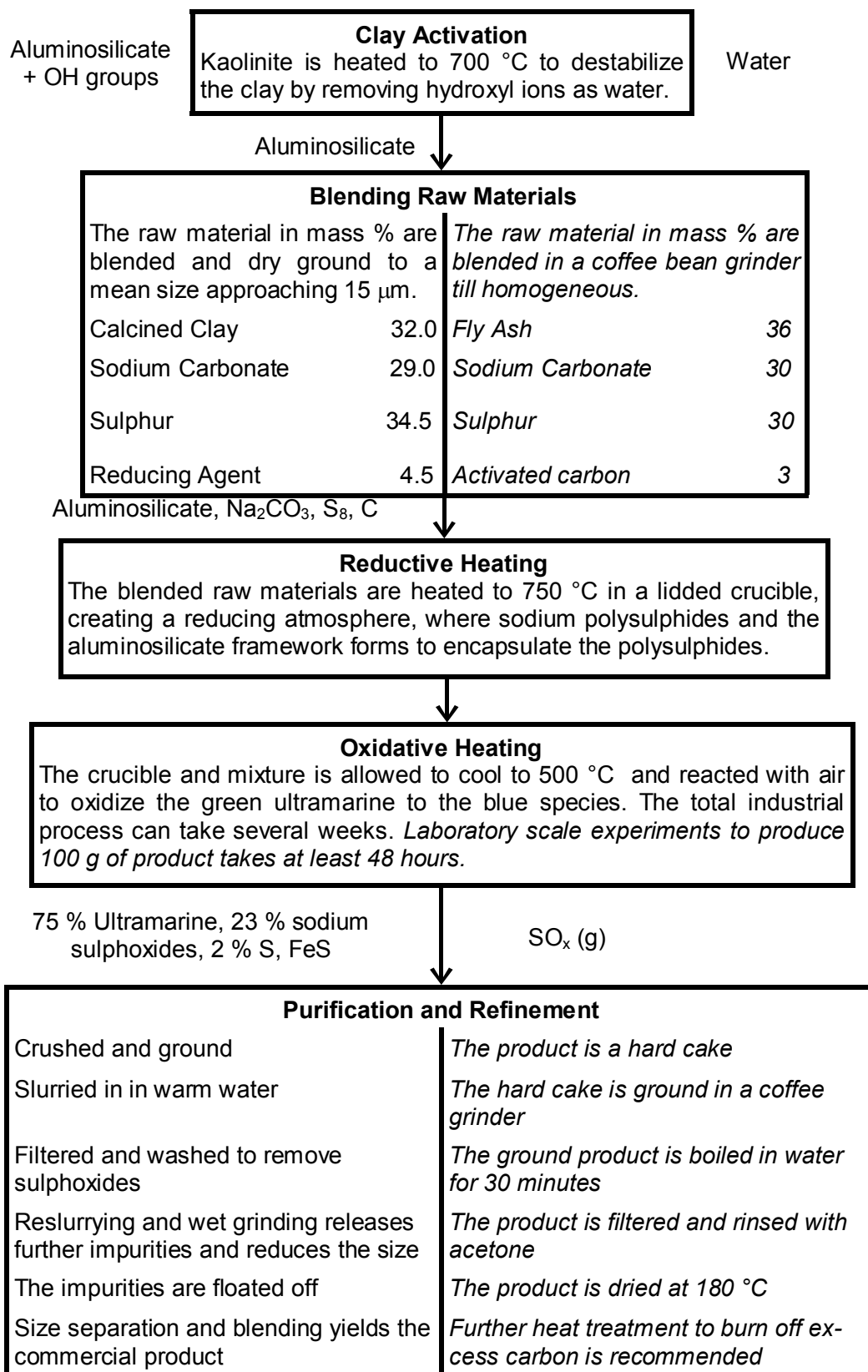


**Figure 3-1: Flow diagram of the production of ultramarine blue; the left-hand side represents the industrial process, described by Cork,<sup>1</sup> and the right-hand side represents the reported process**

**Table 3-1: Raw mix compositions for ultramarine production<sup>a</sup>**

|                             | Current work | ref 11 | ref 11 | ref 11 | ref 12 | ref 13 | ref 14,15 |
|-----------------------------|--------------|--------|--------|--------|--------|--------|-----------|
| Kaolin                      |              |        |        |        | 37     | 31     | 34        |
| Dried china clay            |              | 30     | 43     |        |        |        |           |
| Calcined china clay         |              |        |        | 34     |        |        |           |
| Diatomite                   |              | 7      | 11     | 5      |        |        | 5         |
| Fly ash                     | 36           |        |        |        |        |        |           |
| Sodium sulphite             |              |        |        |        |        | 24     |           |
| Soda ash                    | 30           | 28     | 41     | 31     | 37     |        | 31        |
| Caustic soda                |              |        | 0.4    |        |        |        |           |
| Reducing agent (e.g. resin) |              |        |        |        |        | 4      |           |
| Charcoal                    | 4            |        |        |        | 4      |        |           |
| Rosin                       |              | 4      | 5      | 2      |        |        | 2         |
| Sulphur                     | 30           | 31     |        | 28     | 22     | 41     | 28        |

a. Numbers indicate parts per mass and have been normalised to add up to 100

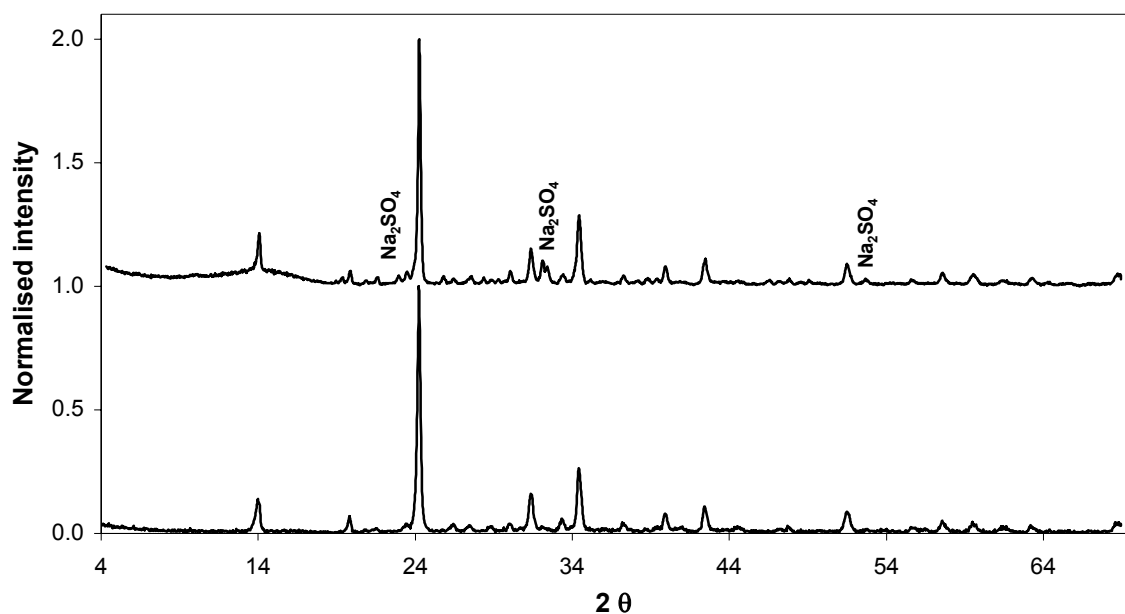


**Figure 3-2: X-ray diffraction patterns of washed (bottom) and unwashed (top) ultramarine products identified as ultramarine blue, ultramarine red and Lazurite, and  $\text{Na}_2\text{SO}_4$**

### 3.3. Results and Discussion

X-ray fluorescence analysis indicated that, as far as the toxic trace elements were concerned, Lethabo fly ash was not significantly less environmentally friendly than kaolin (Table 1-4). The fly ash used contained more iron than kaolin. Iron in the aluminosilicate was known to be detrimental to the successful production of ultramarine,<sup>22,23</sup> and this should be taken into account when the process is applied on a larger scale.

The reaction was repeated several times, with an 80 % success rate. When water vapour was allowed to come into contact with the reagents, the synthesis was unsuccessful. As described above, the heating method also played an important role. Changes in the composition, viscosity and heat capacity of the sulphur melt and vapour<sup>16,24,25</sup> were probably responsible for the increased reactivity of the fly ash during the formation of the ultramarine pigments. The fact that these pigments formed only when the reactant mixture was added to a preheated furnace could be ascribed to the nature of sulphur.<sup>16,24,25</sup> The ultramarine blue laboratory synthesis resulted in an agglomerated pigment cake. The caking coincided with an increase in the volume of the reagents, which sometimes caused the ceramic tile lid to become cemented to the crucible. At other times, the ceramic tile lid broke and the reduction process was not completed. The agglomerated pigment cake had a distinctive layered appearance (Figure 3-3) and the top part of the cake was grey due to the loss of dopant caused by excessive firing time. The agglomeration necessitated grinding, which influenced the colour strength.

The X-ray diffraction patterns of the products (Figure 3-2) compare well with the X-ray diffraction patterns<sup>26</sup> of ultramarine blue and ultramarine red, as well as lazurite, the naturally-occurring archetype. Sodium sulphate was also present in the unwashed samples, as can be seen from the X-ray diffraction patterns (Figure 3-2). The X-ray diffraction patterns for different ultramarine species were similar.<sup>19</sup>

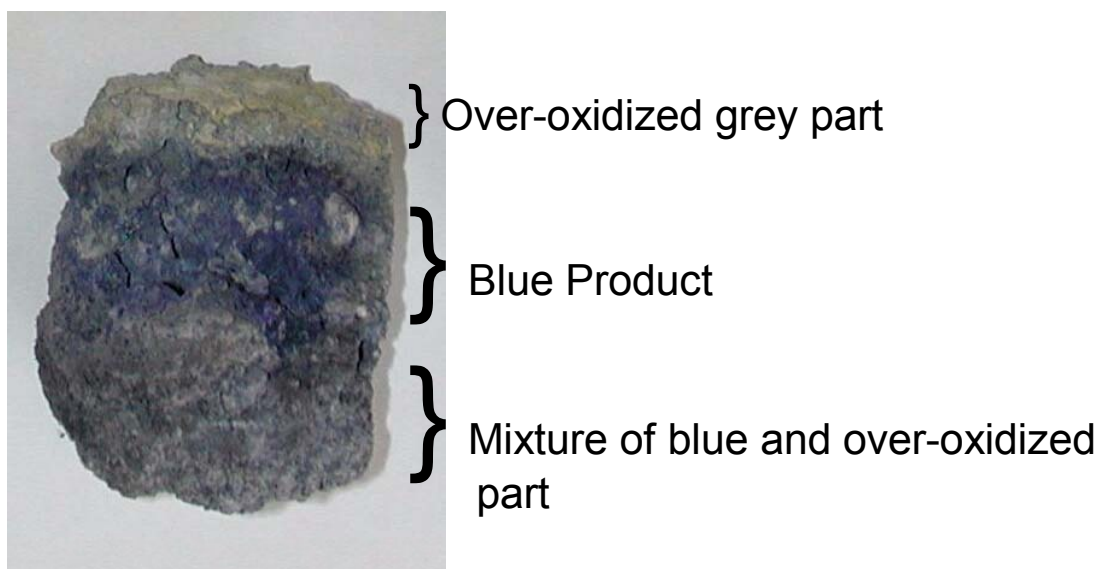


**Figure 3-3: Agglomerated layered pigment cake formed during the synthesis of ultramarine blue, using fly ash as a starting reagent**

The infrared spectra showed the aluminosilicate framework of this pigment, but the bands related to the chromophore species were obscured (Figure 3-4). Clark and

Cobbold<sup>2</sup> obtained the infrared spectrum of ultramarine blue in a Nujol mull and observed a strong band at  $582\text{ cm}^{-1}$ , assigned to  $\nu_3$  of  $\text{S}_3^{2-}$ , and a weak band at  $547\text{ cm}^{-1}$ , assigned to  $\nu_1$ .<sup>2</sup> These bands were visible in the infrared spectrum of ultramarine blue reported by Afremow and Vandenberg,<sup>27</sup> but only the  $582\text{ cm}^{-1}$  band was visible in the current infrared spectra (Figure 3-4), which accorded with the literature.<sup>4,28</sup> The spectrum, however, was undoubtedly that of ultramarine blue, which confirmed the identity of the product.

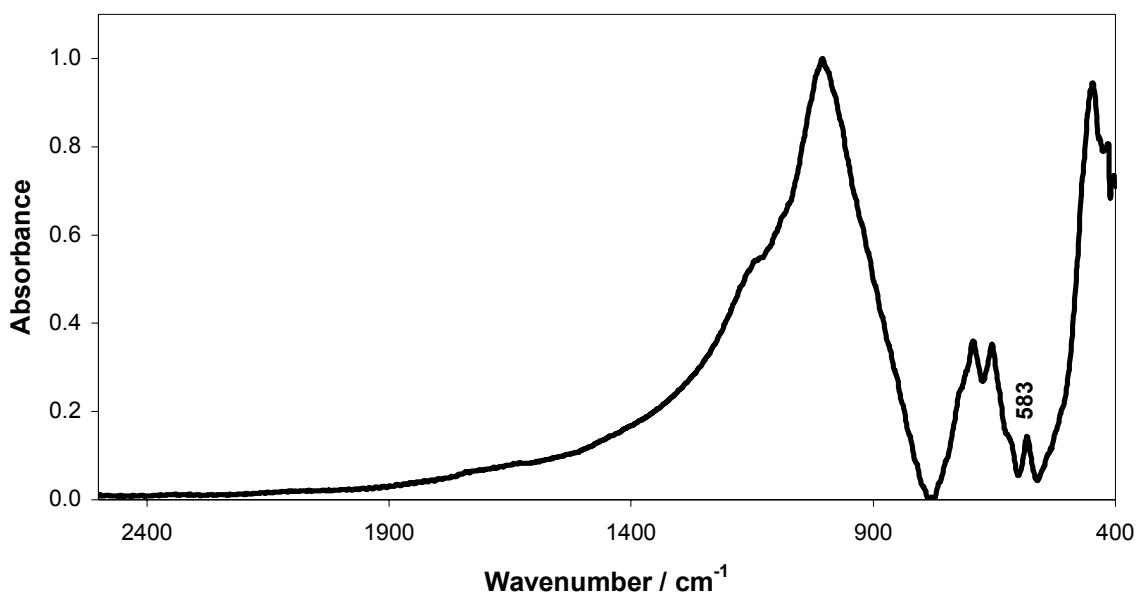


**Figure 3-4: Infrared spectrum of the ultramarine blue product obtained from this process between  $2\ 500\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$ ; the band at  $583\text{ cm}^{-1}$  was assigned to  $\nu_3$  of  $\text{S}_3^{2-}$ .**

The observed Raman spectra of the prepared ultramarine blue and industrial product were compared (Figure 3-5). It was found that the spectra of the prepared product corresponded to those presented in the literature.<sup>4,5,16</sup> The assignments of the observed bands were known from the literature (Table 3-2).<sup>4,16,29</sup>

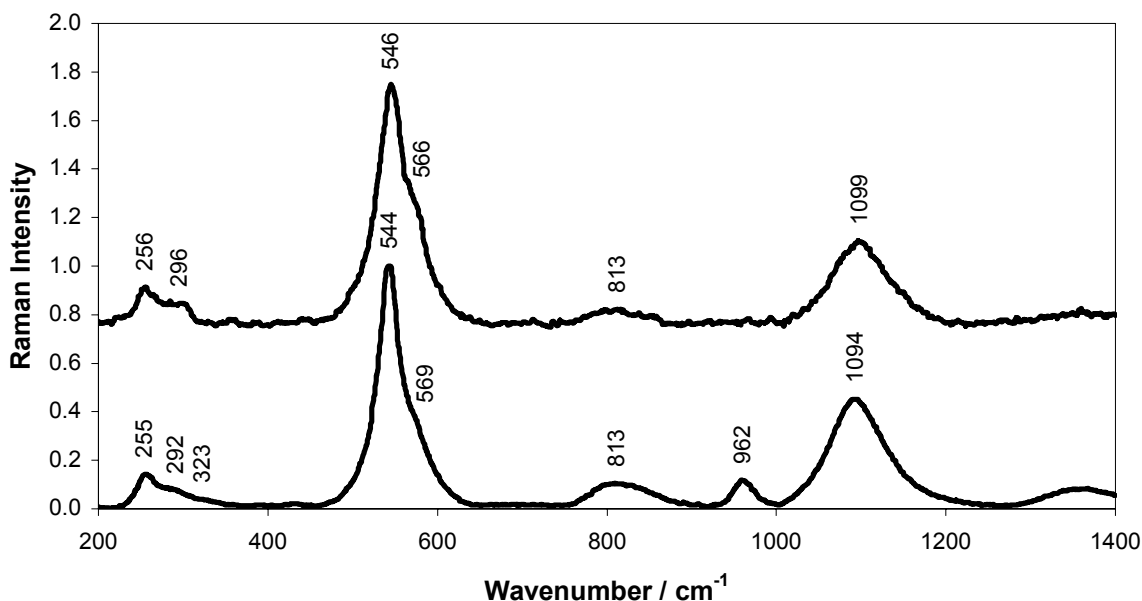


**Figure 3-5: Raman spectra of the ultramarine species obtained (bottom) and an industrial ultramarine blue sample (top)**

**Table 3-2: Assignments of Raman bands for ultramarine products<sup>a</sup>**

| Lazurite                                | Ultramarine Red | Industrial Ultramarine Blue | Ultramarine Blue         | Assignment <sup>b</sup>                                                                |
|-----------------------------------------|-----------------|-----------------------------|--------------------------|----------------------------------------------------------------------------------------|
| 258w b <sup>c</sup><br>Obs <sup>e</sup> | 216w b          | 255w b<br>293sh             | 257w b<br>287sh<br>323sh | -<br>S <sub>3</sub> <sup>-</sup> Bending <sup>d</sup><br>-                             |
| 548st s<br>Obs <sup>e</sup>             | 461w b          | 545st s<br>568sh            | 543st s<br>573sh         | -<br>S <sub>3</sub> <sup>-</sup> Symmetric stretch<br>S <sub>2</sub> <sup>-</sup><br>- |
| 822w b                                  | 626w b          | 813w b                      | 804w b                   | -                                                                                      |
| 1096m b                                 | 994st s         | 1097m b                     | 967w b<br>1092m b        | Si-O<br>S <sub>3</sub> <sup>-</sup> Overtone                                           |

a. The following notation is used to describe the intensity and general shape of the peaks:  
w – weak, m – medium, st – strong, b – broad, sh – shoulder, s – sharp

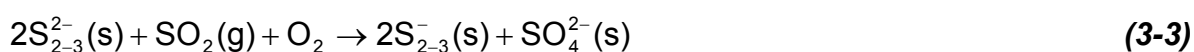
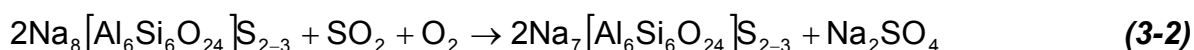
b. From references 4 and 29

c. The description given differs from those in the cited reference, so as to have the same notation as the rest of the data

d. In accordance with the plausible assignment by Chivers and Drummond<sup>17</sup>

e. The corresponding bands were observable, but were not assigned in reference 29

Ultramarine blue was synthesized in two steps (Equation 3-1): a reduction step, followed by an oxidation step. However, the nature of these steps was disputed. Some authors endorsed Equation 3-1,<sup>2,5,17,30</sup> whereas others promote the questionable existence of divalent species as in Equation 3-2<sup>11,32,31</sup> and Equation 3-3.<sup>1,32</sup>



Beardsley and Whiting<sup>11</sup> described the production of ultramarine blue and mentioned that oxygen was originally used as oxidizing agent; these authors introduced the use of SO<sub>2</sub> in the synthesis of ultramarine blue. For the current synthesis any sulphur dioxide formed during the oxidation of ultramarine green was vented from the furnace, as evidenced by the smell. The evolved SO<sub>2</sub> should be treated in an environmentally friendly way. Nevertheless a blue oxidation product was observed. Oxygen was probably responsible for the oxidation process, without the help of external SO<sub>2</sub>. Gorshtein's mechanism<sup>32,31</sup> was based on the slow participation of oxygen in the transformation from the green to the blue species. The present evidence suggested that it was possible that external SO<sub>2</sub> did not play a role in the reaction.

Gorshtein<sup>32,31</sup> (Equation 3-2 and 3-3) successfully explained the formation of Na<sub>2</sub>SO<sub>4</sub> and the role of SO<sub>2</sub>, noted by Tarling and others,<sup>21</sup> and Gobeltz and others.<sup>18</sup> However, this explanation was premised on the basis of the questionable identification of both S<sub>3</sub><sup>2-</sup> and S<sub>2</sub><sup>2-</sup> as the species responsible for the yellow chromophore, and of both S<sub>3</sub><sup>2-</sup> and S<sub>2</sub><sup>2-</sup> for the blue chromophore. These assignments were questionable in the light of the evidence that S<sub>3</sub><sup>2-</sup> was responsible for the blue colour, and S<sub>2</sub><sup>2-</sup> for the yellow colour.<sup>2,5,17</sup> No spectroscopic evidence of the divalent species was recorded in the literature, nor in the current observed spectra. Molecular modelling results, however, support this hypothesis (Chapter 5). Weller and others,<sup>33</sup>

who synthesized ultramarine from thiocyanate sodalites, concluded that a colourless polysulphide sodalite was the initial product at high temperatures. They maintained that this initial product underwent a secondary in-cage reaction, producing the coloured polysulphide radical anions *in situ* when heated in SO<sub>2</sub> at about 500 °C. The presence of a doubly charged species might be supported by the formation of a noselite-like (nosean) phase, which implied that divalent anions are present, with only half the cages occupied.<sup>33</sup> The high ratio of sulphur atoms to unpaired electrons in the ultramarine green species found by Hofmann and others<sup>6</sup> supported the possibility of the existence of divalent non-radical sulphide species in the green ultramarine pigments. The validity of these results is, however, questionable.<sup>34</sup>

Gobeltz-Hautecoeur and others<sup>34</sup> suggested that the intermediate sulphur species was S<sub>2</sub><sup>2-</sup>. S<sub>2</sub><sup>2-</sup> would not be observable by infrared spectroscopy, nor by electron paramagnetic resonance spectroscopy. Therefore, S<sub>2</sub><sup>2-</sup> was favoured above S<sub>3</sub><sup>2-</sup> and S<sub>2</sub><sup>2-</sup> to be the intermediate species. Köhler and others<sup>35</sup> were able to synthesize ultramarine yellow from the thiocyanide derivative of sodalite. They confirmed that the yellow chromophore is S<sub>2</sub><sup>•-</sup> and that the oxidation of ultramarine yellow leads to the formation of ultramarine green, with the simultaneous formation of S<sub>3</sub><sup>•-</sup>. The evidence supports the formation of S<sub>3</sub><sup>•-</sup> from S<sub>2</sub><sup>•-</sup> rather than from S<sub>3</sub><sup>2-</sup>.

For the kinetic study the band at 545 cm<sup>-1</sup> and the shoulder at 580 cm<sup>-1</sup> in the Raman spectra of the heated ultramarine green were fitted with Gaussian-Lorentzian peaks and the intensity ratio of these two fitted peaks was used to estimate the relative concentrations of the S<sub>3</sub><sup>•-</sup> species and the S<sub>2</sub><sup>•-</sup> species (Table 3-2). Because the concentrations of the individual species were not known<sup>34</sup> no direct kinetic study could be done on the reactions with the current data. The pseudo-kinetic analysis did, however, lead to a mathematical description of the generally observed trend that the ratio of S<sub>3</sub><sup>•-</sup> to S<sub>2</sub><sup>•-</sup> increased as the green ultramarine species changed to the blue species.<sup>2,5,18,30</sup> A plot of Equation 3-4 indicated that the transformation from S<sub>2</sub><sup>•-</sup> to S<sub>3</sub><sup>•-</sup> was pseudo-second order relative to the ratio of the concentration of the S<sub>2</sub><sup>•-</sup> species and the concentration of the S<sub>3</sub><sup>•-</sup> species (Appendix B1, Figure 3-6), with a rate constant, *k*, of 0.060 ± 0.002 min<sup>-1</sup>. The second-order kinetics might indicate that two S<sub>2</sub><sup>•-</sup> molecules were needed to react with each other for S<sub>3</sub><sup>•-</sup> to form.

$$\frac{1}{R} - \frac{1}{R_0} = kt \quad (3-4)$$

where  $R$  is the ratio of the peaks in question and  $R_0$  is the ratio of the peaks at time 0.<sup>36</sup>

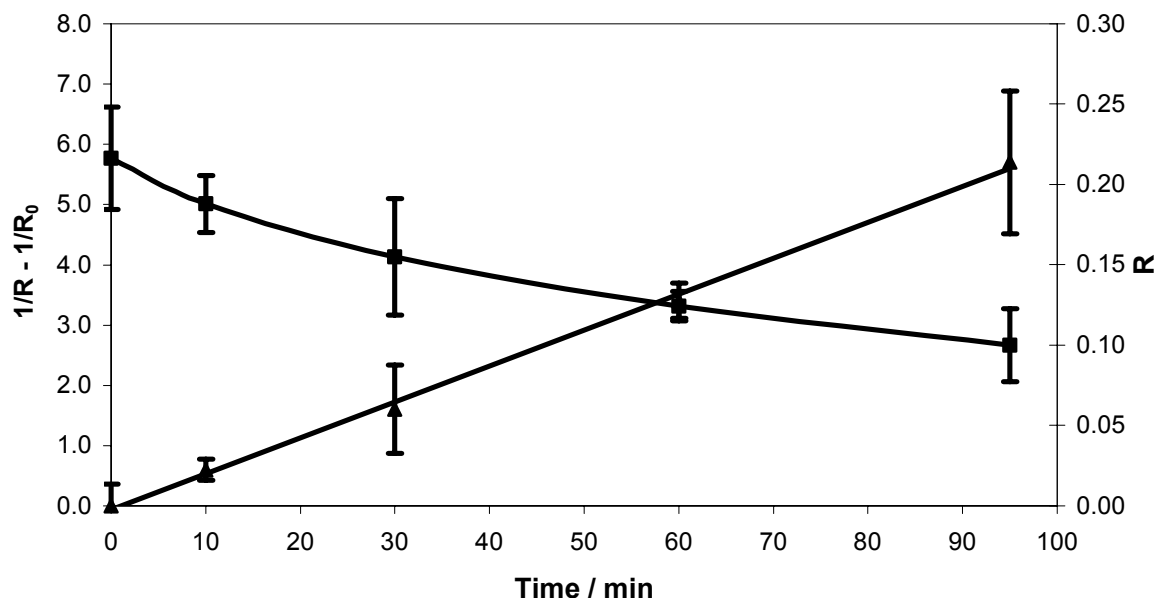


**Figure 3-6: Plot of the ratio,  $R$ , between the concentration of the  $S_2^{\bullet}$  species and the concentration of the  $S_3^{\bullet}$  species, against time (right axis, ■); plot of the second-order rate law for the conversion of  $S_2^{\bullet}$  to  $S_3^{\bullet}$  (left axis, ▲)**

The synthesized blue pigment was dark blue. A drawdown test (Figure 3-7) indicated that the pigment contained some black contaminants. These contaminants were not visible in the pigment because of the dark colour of the ultramarine blue pigment. The black contaminants were made visible by the drawdown test, because the black contaminants and the ultramarine blue had different colour strengths. The drawdown test further indicated that the current ultramarine blue product was of weaker colour strength than the industrial pigment. The prepared pigments were also tested within plastic samples (Figure 3-8).

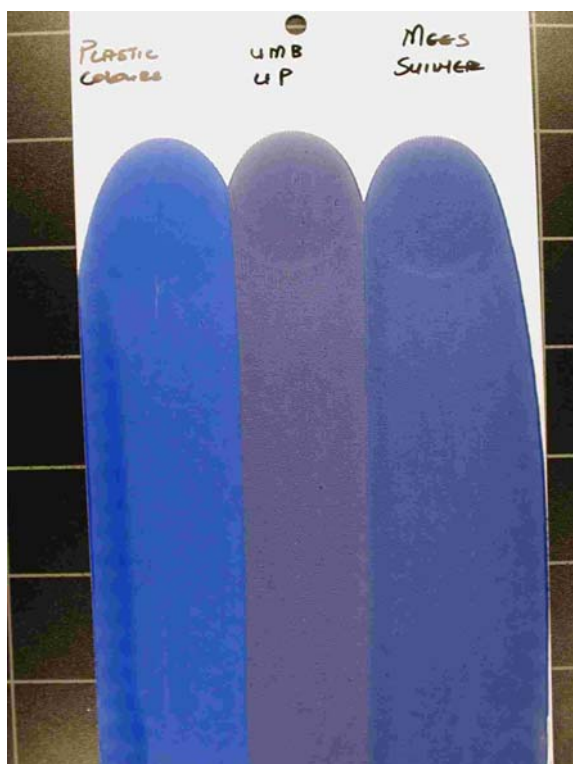


**Figure 3-7: Drawdowns of two sets of ultramarine products from this research and a commercial standard**



**Figure 3-8: Plastic samples prepared with ultramarine products from this research and a commercial standard as pigments**

According to Cork,<sup>1</sup> the mean particle size of a commercial product ranged from 0.7 to 5.0  $\mu\text{m}$ . This was considerably smaller than the particle size of the current ultramarine product. The weaker colour strength of the product could be due to its larger particle size and the related higher crystallinity. This higher crystallinity was demonstrated by the higher Raman intensities of the current product compared with those of the commercial pigment. A further improvement in the product quality could possibly be obtained by discarding the white or grey over-oxidized parts before milling. The use of fly ash as starting reagent for the synthesis of ultramarine blue would be beneficial to the environment because less fly ash would end up as landfill. Since only one size fraction of fly ash was used to synthesize the ultramarine blue product, other size fractions need to be tested and evaluated. The non-magnetic fraction of fly ash could also be tested (for a further discussion on future possibilities see Chapter 7).

### 3.4. Conclusions

The traditional starting reagent for the synthesis of ultramarine blue, namely kaolin, had to be heated before the synthesis to weaken the structure of the kaolin. Two batches of fine fly ash were successfully used to synthesize ultramarine blue. Infrared, Raman and X-ray diffraction results confirmed the formation of the product. Fly ash had the advantage over kaolin of being amorphous. The results further showed that the transition from the green ultramarine species to the blue species coincided with an increase in the ratio of the amount of  $\text{S}_3^{\cdot-}$  species relative to the amount of  $\text{S}_2^{\cdot-}$  species.

### REFERENCES

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- 1 W.B. Cork, *Ultramarine pigments*, in: *Industrial Inorganic Pigments*, G. Buxbaum (Ed.), VCH, Weinheim, 1993, pp. 124-132.
  - 2 R.J.H. Clark, D.G. Cobbold, *Inorg. Chem.*, 1978, **17**(11), 3169-3174.
  - 3 H. He, T.L. Barr, J. Klinowski, *J. Phys. Chem.*, 1994, **98**(33), 8124-8127.
  - 4 K-H. Schwarz, U. Hofmann, *Z. anorg. allg. Chem.*, 1970, **378**(8), 152-159.
  - 5 R.J.H. Clark, T.J. Dines, M. Kurmoo, *Inorg. Chem.*, 1983, **22**(7), 2766-2772.
  - 6 U. Hofmann, E. Herzenstiel, E. Schonemann, K-H. Schwarz, *Z. anorg. allg. Chem.*, 1969, **367**, 119-129.
  - 7 U. Hofmann, E. Herzenstiel, *Z. anorg. allg. Chem.*, 1964, **329**, 102-109.
  - 8 J. Klinowski, S.W. Carr, S.E. Tarling, P. Barnes, *Nature*, 1987, **330**, 56-58.
  - 9 S.E. Tarling, P. Barnes, J. Klinowski, *Acta Cryst.*, 1988, **B44**, 128-135.
  - 10 J.S. Prener, R. Ward, *J. Amer. Chem. Soc.*, 1950, **72**, 2780-2781.
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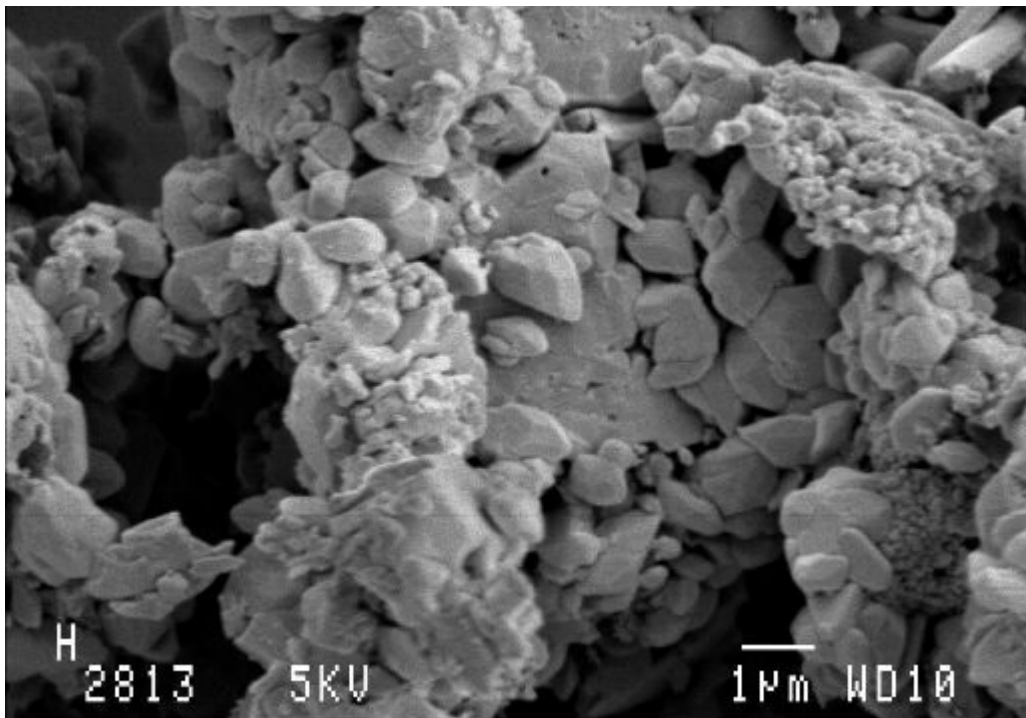
- 11 A.P. Beardsley, S.H. Whiting, *Manufacture of Ultramarine*, final patent no. 2 441 950, 2 441 951, 2 441 952, United States.
- 12 R.G. Woodbridge, *J. Chem. Ed.*, 1949, **26**, 552.
- 13 A. Guillochin, *Process for the manufacture of Ultramarine*, final patent no. 1 400 431, United States, 13 December 1921.
- 14 W.J. Kruppa, G.J. Marlowe, *Manufacture of Ultramarine*, final patent no. 2 700 618, United States, 25 January 1955.
- 15 R.B. Van Order, R.F. Reeves, *Manufacture of Ultramarine*, final patent no. 2 723 917, United States, 15 November 1955.
- 16 D.G. Booth, S.E. Dann, M.T. Weller, *Dyes and Pigments*, 2003, **58**, 73-82.
- 17 T. Chivers, I. Drummond, *Chem. Soc. Rev.*, 1973, **2**(16), 233-248 and *Inorg. Chem.*, 1972, **11**(10), 2525-2527.
- 18 N. Gobeltz, A. Demortier, J.P. Liliour, C. Duhayon, *J. Chem. Soc., Faraday Trans.*, 1998, **94**(15), 2257-2260.
- 19 F.M. Jaeger, *Trans. Faraday Soc.*, 1929, **25**, 320-345.
- 20 V.A. Berezin, *Journal of Applied Chemistry of the USSR*, 1981, **54**(4), 750-751.
- 21 S.E. Tarling, P. Barnes, A.L. Mackay, *J. Appl. Cryst.*, 1984, **17**, 96-99.
- 22 C.A. Kumins, *Process for making Ultramarine*, final patent no. 2 544 694, United States, 13 March 1951.
- 23 E.F. Kur, F. Wilkinson, *Improvements in the manufacture of Silicious Ultramarine colours*, final patent no. 209 961, Great Britain, 24 January 1924.
- 24 N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Second edition, Butterworth-Heinemann, Oxford, pp. 652-661, 1997.
- 25 B. Meyer, *Chem. Rev.*, 1976, **76**(3), 367-387.
- 26 JCPDS-ICCD (2000) - Joint Committee on Powder Diffraction Standards - International Centre for Diffraction Data. Entry No. 36 - 0796, 02-0338(N), 77-1702(C).
- 27 L.C. Afremow, J.T. Vandeberg, *J. Paint Technol.*, 1966, **38**(495), 169-202.
- 28 S. Kowalak, M. Strózyk, *J. Chem. Soc., Faraday Trans.*, 1996, **92**(9), 1639-1642.
- 29 I.M. Bell, R.J.H. Clark, P.J. Gibbs, *Spectrochimica Acta Part A*, 1997, **53**, 2159-2179.
- 30 D.M. Gruen, R.L. McBeth, A.J. Zielen, *J. Amer. Chem. Soc.*, 1971, **93**(24), 6691-6693.
- 31 A.E. Gorshtein, *The Canadian Journal of Chemical Engineering*, 1992, **70**, 960-965.
- 32 A.E. Gorshtein, *Journal of Applied Chemistry of the USSR*, 1985, **58**(7), 1468-1473.
- 33 M.T. Weller, G. Wong, C.L. Adamson, S.M. Dodd, J.J.B. Roe, *J. Chem. Soc., Dalton Trans.*, **1990**, 593-597.
- 34 N. Gobeltz-Hautecoeur, A. Domortier, B. Lede, J.P. Lelieur, C. Duhayon, *Inorg. Chem.*, 2002, **41**(11), 2848-2854.
- 35 P. Köhler, G. Winter, F. Seel, K-P. Klös, *Z. Naturforsch.*, 1987, **42b**, 663-665.
- 36 P.W. Atkins, *Physical Chemistry*, Sixth Edition, Oxford University Press, Oxford, 1998, p. 769.

## CHAPTER 4

# THE ROLE SULPHUR PLAYS IN THE FORMATION OF ULTRAMARINE BLUE

IN

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



## 4. THE ROLE SULPHUR PLAYS IN THE FORMATION OF ULTRAMARINE BLUE

### 4.1. Introduction

Ultramarine Blue, a strong blue pigment, could be described, in a simplified way, as a zeolite-type structure that occluded a polysulphide anion radical,  $S_2^{\cdot-}$  and  $S_3^{\cdot-}$ , thereby stabilising the radical. The  $S_3^{\cdot-}$  and  $S_2^{\cdot-}$  were stable in the aluminosilicate framework,<sup>1</sup> and the quality of the synthesised pigment depended on the quality, that is defect-free, aluminosilicate framework.<sup>2</sup> The main building block of this aluminosilicate framework was the  $\beta$ -cage, consisting of twelve alumina or silica tetrahedra linked to each other to form six- and four-membered rings of tetrahedra in a cage formation (Figure 4-1). According to Deer, Howie and Zussman<sup>3</sup> the sodalite group consisted of sodalite,  $Na_8[Al_6Si_6O_{24}]Cl_2$ ; Nosean,  $Na_8[Al_6Si_6O_{24}]SO_4$ ; and Haüyne,  $(Na,Ca)_{4-8}[Al_6Si_6O_{24}](SO_4,S)_{1-2}$ . Based on powder X-ray diffraction results Jaeger<sup>4</sup> concluded that there was a fixed aluminosilicate periodic framework for the ultramarine species and that the other components, for example sodium and sulphur were wandering, statistically distributed atoms. X-ray diffraction patterns, therefore, were dependent on the fixed framework structure. They were not greatly influenced by the wandering constituents. This explained why so many different ultramarine species yielded similar X-ray diffraction patterns (Section 3-3).<sup>4</sup> This fixed framework was cubic, and closer to nosean than to sodalite,<sup>4</sup> a notion supported by the work of Weller and others.<sup>5</sup>

Ultramarine species had similar properties to zeolites, for example the sodium cation could be exchanged for several other cations, for example Ag, K, Rb, Cs, Li, Mg, Ca, Sr, Ba, Tl, and Pb.<sup>4</sup> The selenium and tellurium ultramarine analogs were also known.<sup>4,6-8</sup>

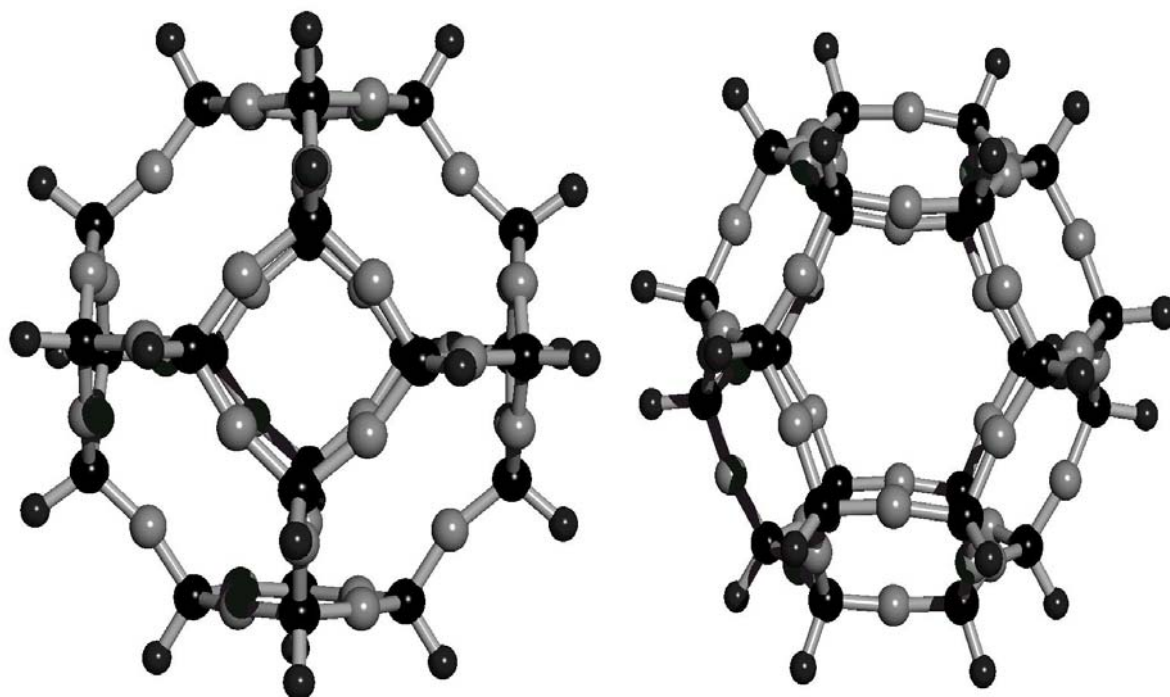


**Figure 4-1: POV-Ray<sup>9</sup> images of AM1 force field<sup>10</sup>-generated  $\beta$ -cages**

The industrial process for the manufacture of ultramarine blue<sup>4,11-13</sup> involved the activation of kaolinite, also known as Chinese clay, at approximately 700 °C. The activation destabilizes the clay by removing the adsorbed water and the hydroxyl groups. The activated clay was mixed with a sodium salt (usually sodium carbonate or sodium sulphate) and sulphur, in the form of elemental sulphur, sodium sulphide or sodium polysulphides. A carbon-based reducing agent, for example coal, rosin, or colophony was added. The raw materials were intimately mixed and milled to a desired fineness. This was placed in a crucible of low permeability, to ensure that the reagents were not in contact with the reaction gases in the furnace. The crucible was placed in a furnace. A crucible with a diameter of 22 cm delivered the best results. Individual crucibles allow the consistent heating of the reagent mix. The product depends on the thermal energy added to the reagents. Overheating and underheating led to a heterogeneous product. The filled crucibles were heated to a temperature of approximately 750 °C and maintained at that temperature for 8 to 48 hours. This concluded the reduction phase of the ultramarine blue synthesis. The product at this stage was known as primary ultramarine blue and had a green colour - ultramarine green. The furnace and contents were then allowed to cool

slowly. Air was allowed into the furnace. The green primary ultramarine was oxidized to the desired blue ultramarine blue. This slow cooling and oxidation could take place over several weeks. Alternatively, this second step could be performed in a different open crucible at an optimal temperature of between 400 and 550 °C. The oxidising step involved the loss of between one seventh and one eighth of the sodium atoms. Some sodium sulphate is formed in the process. The final product contained approximately 10 % combined sulphur.<sup>4,11-13</sup>

An over-oxidized reaction mix had a white or greyish colour. The problem of over-oxidizing the exterior of the reaction cake and under-oxidising the interior of the reaction cake led to many alterations in the method of manufacturing ultramarine blue.<sup>12</sup> Gessler and Kumins<sup>14</sup> suggested that the simultaneous synthesis of the zeolite-type aluminosilicate framework and formation of the chromophore species was detrimental to both the oxidation and reduction steps in the ultramarine blue synthesis, because the result was "hard, fused masses". They<sup>14</sup> stated that "[a]t this high temperature of formation of the zeolite the structure is compacted and less susceptible to the entrance of the rather large polysulphide linkage into the crystal lattice. The polysulphide formation is an equilibrium reaction and excess sulfur is required for the formation of the desirable higher polysulfides, Na<sub>2</sub>S<sub>3</sub>, Na<sub>2</sub>S<sub>4</sub> etc. Under the high temperature conditions of the operation required for the reduction of sodium carbonate and/or sodium sulfate, these higher content polysulphides may not form, due to loss of sulfur by volatilization."<sup>14</sup> Gessler and Kumins<sup>14</sup> first synthesized the zeolite species by wet precipitation at 60 °C, and then incorporated the sulphur species into the zeolite framework at high temperature, preferably between 750 °C and 850 °C, with the exclusion of air and preferably in the presence of hydrogen sulphide gas. They<sup>14</sup> also believed that the polysulphides could be formed *in situ* by the incorporation of monosulphide into the zeolite crystal lattice. This monosulphide reacted with additional sulphur, and so incrementally incorporated the polysulphide chain into the structure.<sup>14</sup> Gobeltz-Hautecoeur and others<sup>15</sup> supported the monosulphide hypothesis, based on electron paramagnetic resonance and Raman spectroscopic evidence.

The relative formation of the aluminosilicate framework and the formation of the chromophores were studied in the current work. Scanning electron microscopy allowed one to look at the microscopic structure of the solid particles. Changes in microscopic structure of starting reagents indicated reaction progress.

Reinen and Lindner<sup>16</sup> reviewed the state of knowledge on ultramarine pigments. They<sup>16</sup> were of the opinion that the sulphur "radicals have to be generated simultaneously with the formation of the zeolitic cages in the synthesis procedure, because the latter are impermeable for the colour centres."<sup>16</sup> In my opinion, this statement was unjustified, and was researched in literature.

## **4.2. Synthesis**

Fly ash was heated to 1 000 °C (Fa1000), and kept at this temperature for twenty-four hours. This was done to establish the effect of heating on the microscopic structure of fly ash (Fa).

Fly ash (4 g) and sodium carbonate (4 g) (FaNa50) were intimately mixed in an agate mortar, and reacted in an alumina crucible at 860 °C, for twenty-four hours. This was followed by the slow cooling of the products, to ensure maximum crystallinity. The effect of sodium carbonate on the microscopic structure of fly ash could thereby be determined. Ultramarine blue (UMB) was successfully synthesized from fly ash, as described in Chapter 3.

## **4.3. Results**

Fly ash had a predominantly spherical microscopic structure (Figure 1-1). The micrographs were similar to those in literature.<sup>17,18-50</sup> Quantitative work by energy dispersive X-ray analysis evidenced the heterogeneous nature of the fly ash particles<sup>17,41-50</sup> (Table 4-1). Ferrospheres, particles rich in iron, existed in fly ash. This was a prime example of the heterogeneous nature of fly ash (Sample Fa II in Table 4-1).<sup>24</sup> Energy dispersive analysis data (Table 4-1) indicated that the sodium carbonate reacted with the fly ash in the intended ratios. The data for UMB III in Table 4-1 were collected on a regularly shaped crystal and indicated that the

compositions were reconcilable with the composition of ultramarine blue, and was not a sodium sulphate crystal.

**Table 4-1: EDX-Data for the samples in the step-wise study of the formation of ultramarine blue<sup>a</sup>**

|    | Fa<br>I | Fa <sup>b</sup><br>II | Fa1000<br>I | Fa1000<br>II | FaNa50<br>I | FaNa50<br>II | UMB<br>I | UMB<br>II | UMB<br>III | UMB2<br>I | UMB2<br>II |
|----|---------|-----------------------|-------------|--------------|-------------|--------------|----------|-----------|------------|-----------|------------|
| Na | 0.4(2)  | 0.4(3)                | 0.31(8)     | 0            | 31.5(4)     | 30.1(3)      | 20.6(3)  | 26.4(3)   | 17.9(3)    | 15.5(3)   | 12.0(3)    |
| Al | 31.0(4) | 16.8(5)               | 36.6(4)     | 30.9(5)      | 21.0(4)     | 21.3(3)      | 20.5(4)  | 14.0(3)   | 21.0(3)    | 19.0(3)   | 18.9(3)    |
| Si | 51.5(6) | 18.8(5)               | 53.4(5)     | 50.4(7)      | 32.4(5)     | 35.6(3)      | 30.0(5)  | 18.3(3)   | 33.0(4)    | 28.3(4)   | 27.7(4)    |
| S  | 0       | 0                     | 0           | 0            | 0           | 0            | 22.1(5)  | 34.7(4)   | 24.5(4)    | 31.1(4)   | 29.6(5)    |

- a. The data represent the element mass % determined by fitting the X-ray dispersion spectrum and the uncertainty in the measurement, that is 15.9(7) implies  $15.9 \pm 0.7$  mass %. Fa connotes fly ash, Fa1000 connotes Fa treated at 1 000 °C, FaNa 50 connotes Fly Ash treated with sodium carbonate at 860 °C, UMB and UMB2 represent two different sets of ultramarine products.

- b. The particle was rich in iron, see text.

The X-ray diffraction pattern of fly ash was characterised by a large amorphous halo, indicating that fly ash consisted predominantly of a glassy phase. The crystalline material in fly ash was characterised as mullite with some quartz being present<sup>17,51</sup> (Figure 4-2a). Some anorthite was also present.<sup>52</sup>

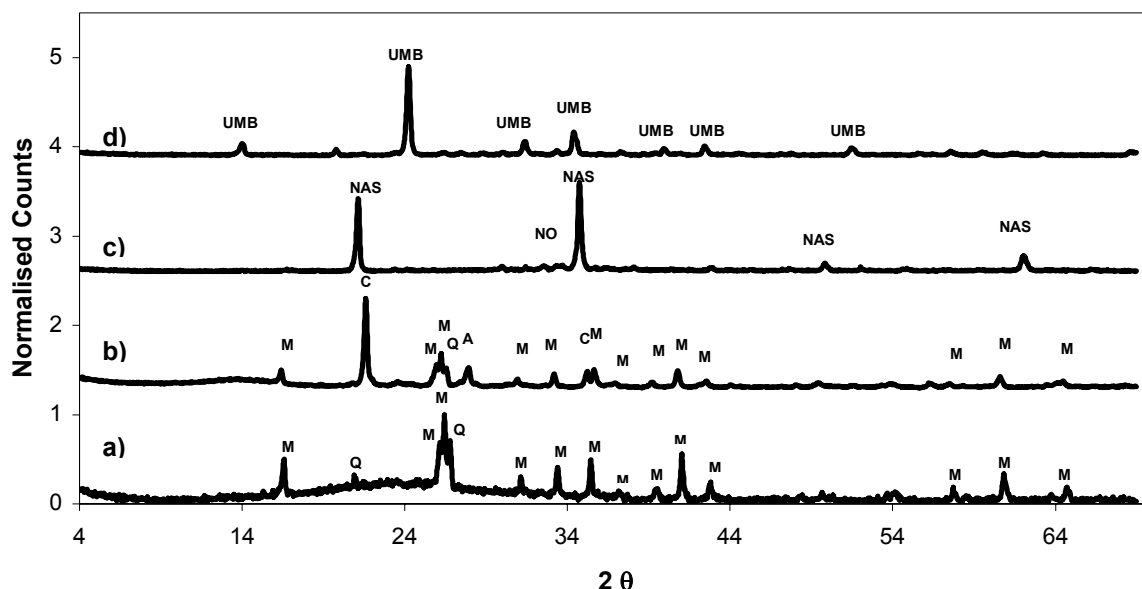


**Figure 4-2: X-ray diffraction patterns of a) fly ash, b) fly ash treated at 1 000 °C, c) fly ash treated with sodium carbonate at 860 °C, d) ultramarine product; A: anorthite, C: cristobalite, M: mullite, Q: quartz, UMB: ultramarine product**

Upon heating fly ash, the scanning electron micrographs changed only slightly<sup>28,29</sup> (Figure 4-3). The X-ray diffraction patterns indicated the formation of some cristobalite (Figure 4-2b).<sup>29</sup>

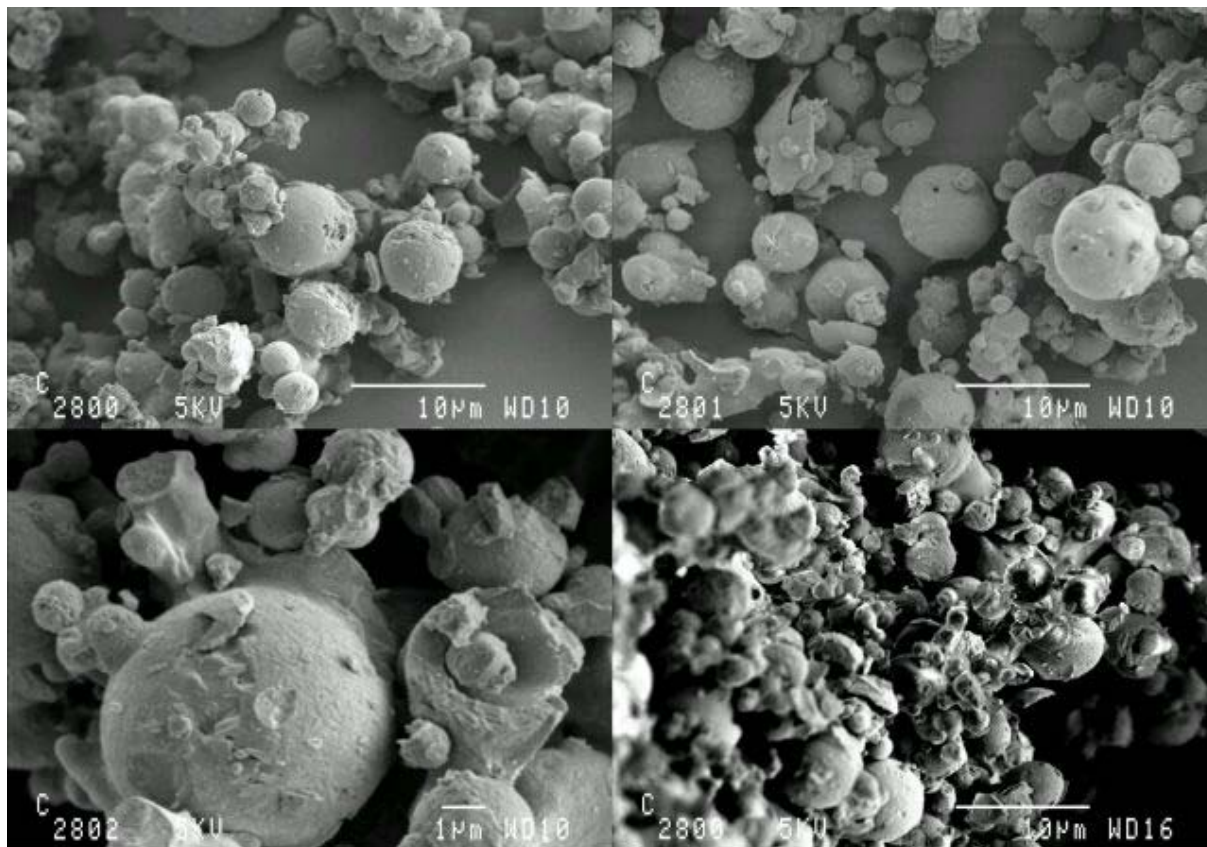


**Figure 4-3: The predominantly spherical microscopic structure of fly ash was intact after treatment at 1 000 °C**

Scanning electron microscopy indicated that the reaction between fly ash and sodium carbonate did not change the microscopic structure of fly ash significantly (Figure 4-4). However, some melted species were present. Needles observed on the spherical particles indicated the formation of sodium rich aluminosilicates (Figure 4-4). However, these needles were only visible in the secondary electron images and not in the backscattered images. Therefore, no quantitation could be done, to establish experimentally the nature of these needles (Figure 4-4). Fly ash hydrothermally treated with sodium hydroxide also showed the needles, and evidenced the formation of zeolite Na-P1 according to Woolard and others.<sup>53</sup> These needles probably formed because the glass phase reacted first, and the crystalline phases only reacted later. The crystalline particles of the fly ash did not react and

formed spherical templates for the crystal growth. The glass-mullite-quartz structure of fly ash changed to a sodium aluminosilicate described as  $(\text{Na}_2\text{O})_{0.33}\text{NaAlSiO}_4$  structure (Figure 4-2c).

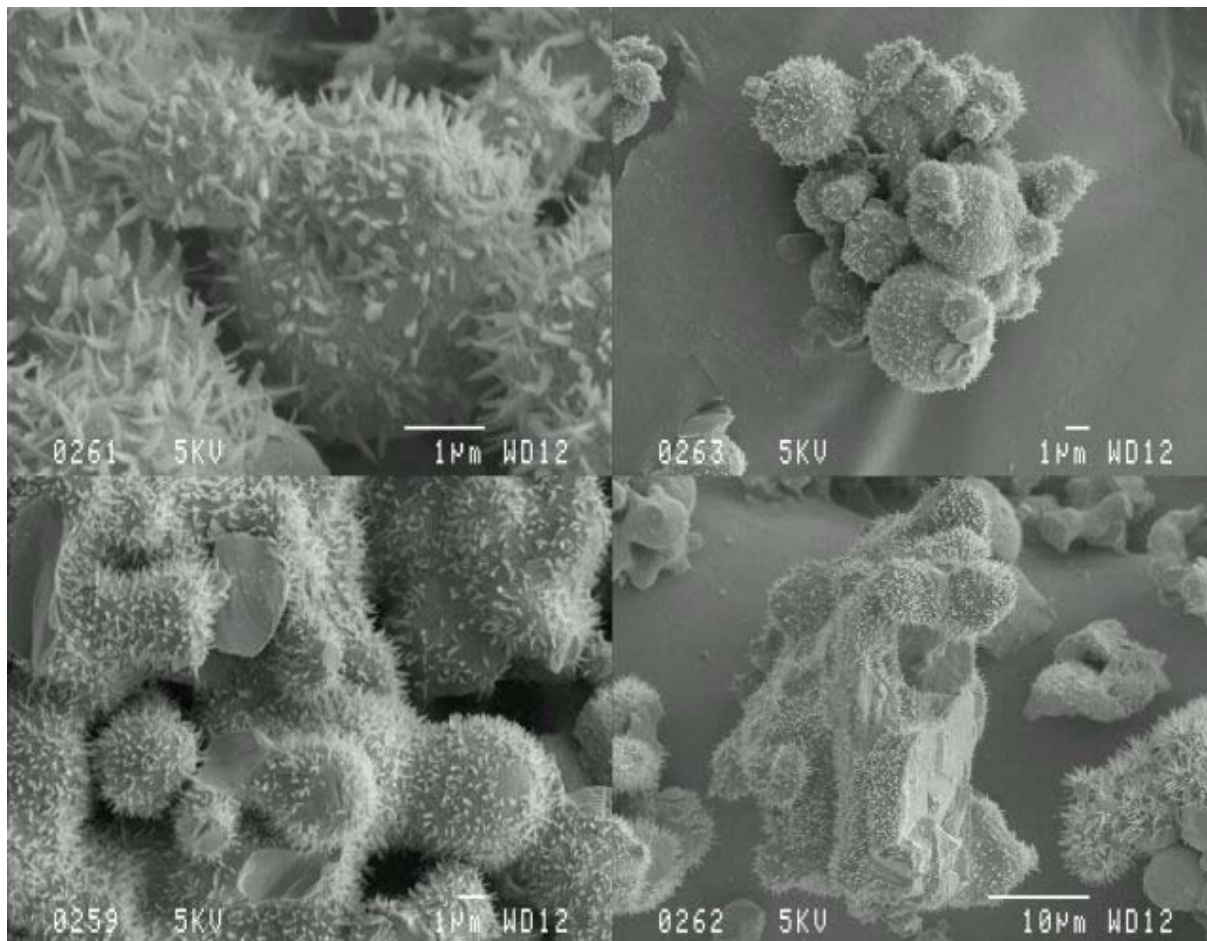


**Figure 4-4: The microscopic structure of fly ash treated with sodium carbonate at 860 °C was characterised by needle shapes crystals growing from the spherically shaped particles**

When sulphur was added to the mix, the microscopic structure changed (Figure 4-5), and ultramarine blue was produced (Figure 4-2d).

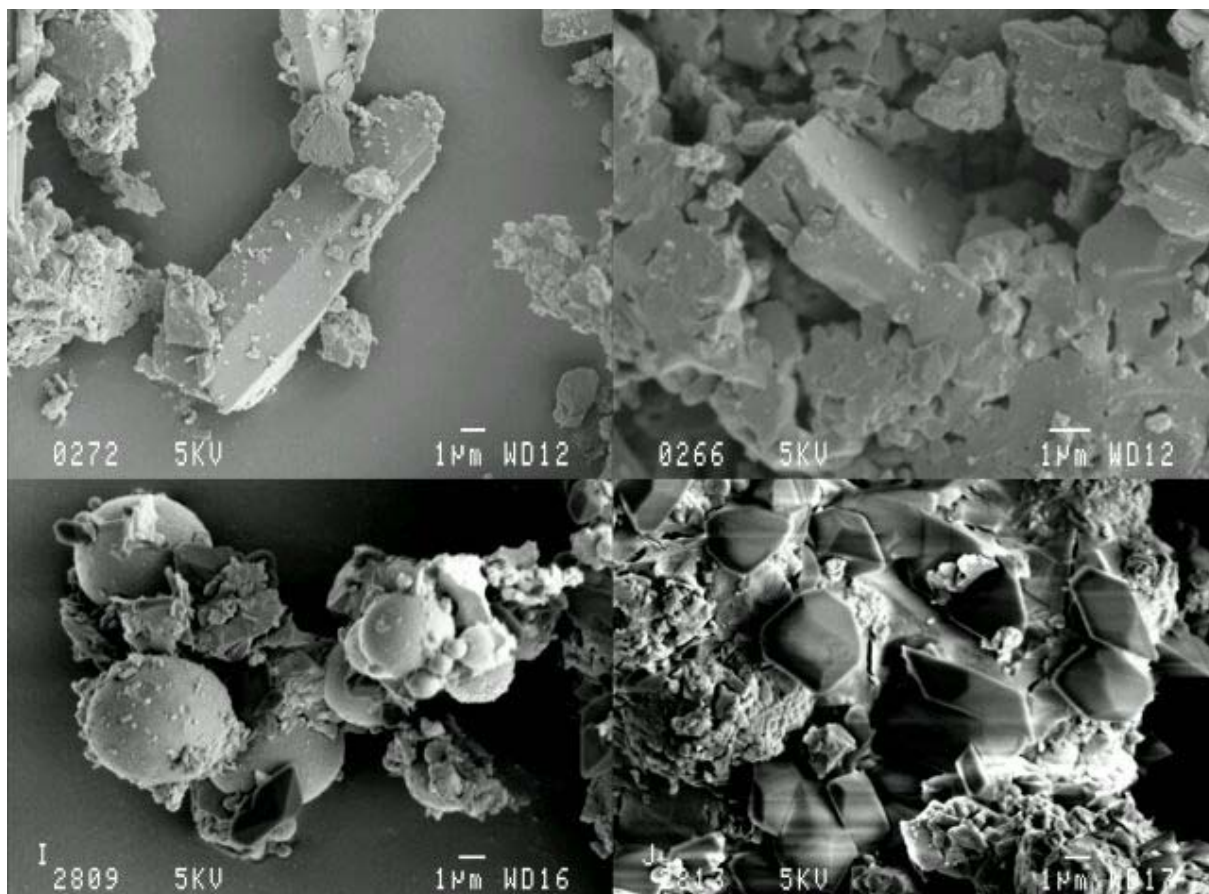


**Figure 4-5: The microscopic structure of the ultramarine product showing that the spherical shape of the fly ash particles was lost and that the regular shape of zeolite-type material was formed**

#### 4.4. Discussion

The composition of sulphur in the liquid and vapour phase was very complex. Sulphur melted at a temperature of between 106 and 133 °C.<sup>54,55,56</sup> Sulphur polymerised at approximately 159 °C.<sup>54-56</sup> The boiling point was accepted to be 444.6 °C.<sup>54-56</sup> As the temperature rose, the composition of the sulphur liquid and vapour changed, and the smaller molecular mass allotropes increased their contribution to the composition.<sup>57</sup> The characteristics of sulphur at high temperature might have had an influence on the aluminosilicate structure that formed at high temperature.

Zeolites formed from fly ash had scanning electron micrographs that were similar to those observed for the synthesized ultramarine species.<sup>31,53,58,59</sup> This zeolite microscopic structure was not observed when fly ash was heated or reacted with sodium carbonate. The conclusion was that the sulphur had a structure-directing

effect on the aluminosilicate building blocks provided by the fly ash. This implied that the three-dimensional structure,  $\beta$ -cages (Figure 4-1), did not only stabilize the polysulphide, but was formed by the sulphur. This might be related to a fluxing effect in the molten polysulphides. On the other hand, the polysulphides might direct the structure of sodium counterions and the accompanying aluminosilicate framework in such a way as to stabilize the radical species. Kowalak and Pawłowska<sup>60</sup> stated that when zeolites A, X, and Y impregnated with sulphur radical precursors were heated to above 700 °C, the zeolite structures were transformed to the sodalite structure.<sup>60</sup> They<sup>60</sup> believed that the sulphur had a structure-directing effect.<sup>60</sup> Gorshtein<sup>61</sup> promoted the formation of the aluminosilicate framework around the polysulphide species. The same structure-directing effect was observed in the case of fly ash and sulphur.

Returning to the issue of whether sulphur species could enter the aluminosilicate framework after the framework was formed, the following evidence to the contrary was offered. McLaughlan and Marshall<sup>62</sup> hydrothermally synthesised sulphur-doped sodalite crystals, by adding the sulphur to the sodalite cage after the formation of the cage. They<sup>62</sup> claimed that  $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$  was less successful in imparting colour to the sodalite crystals. The addition of  $\text{Na}_2\text{S}_4$  led to a blue product, when concentrated.<sup>62</sup> Prener and Ward<sup>63</sup> showed that the polysulphide could be added to the sodalite structure after the  $\beta$ -cages were formed.<sup>63</sup> Gobeltz and others,<sup>1</sup> and Jaeger<sup>4</sup> also observed this trend. Gobeltz and others<sup>1</sup> emphasized that the polysulphides not only entered the sodalite structure before the oxidation process while the sodalite structure was formed, in accordance with results by Tarling and others,<sup>64</sup> but also after the formation of the sodalite structure.<sup>1</sup> Treating hydroxysodalite with ammonium polysulphide,  $(\text{NH}_4)_2\text{S}_6$  led to the formation of ultramarine blue type products.<sup>64</sup> This demonstrates that the chromophore could be incorporated into the sodalite structure after the formation of the aluminosilicate framework. Reacting zeolite X and Y with ammonium polysulphide did not lead to a stable blue colour at room temperature.<sup>60</sup> This showed that the specific aluminosilicate structure needed to be available to stabilize the sulphur radicals. The incorporation of the ultramarine chromophore into an already formed zeolitic aluminosilicate framework was supported by the work of Gessler and Kumins.<sup>14</sup> A softer ultramarine product was

produced when the clay was calcined to remove constitutional water and then treated in a solution of 10 % NaOH or 10 % LiOH.<sup>65</sup> The resulting aluminosilicate was washed free of excess hydroxides and was found to have ion exchange properties.<sup>65</sup> This new aluminosilicate was then used in the place of the clay and some of the sodium species in the usual raw mix. If the above evidence was taken into account<sup>60</sup> this new aluminosilicate probably had a structure close to the desired zeolite-type structure. This was a further indication that the chromophores can be incorporated into the aluminosilicate framework after the framework was formed.

#### 4.5. Conclusion

A comparison of the scanning electron micrographs of fly ash, fly ash treated at 1 000 °C, fly ash reacted with sodium carbonate at 860 °C and the ultramarine products formed from fly ash showed that sulphur was responsible for the formation of the specific zeolite-type aluminosilicate framework observed in ultramarine pigments. Sulphur, therefore, had a structure directing effect. Literature reports that the sulphur was only incorporated into the ultramarine structure during the formation of ultramarine blue were refuted by other literature references.

## REFERENCES

- 1 N. Gobeltz, A. Demortier, J.P. Lillieur, C. Duhayon, *J. Chem. Soc., Faraday Trans.*, 1998, **94**(15), 2257-2260.
- 2 V.A. Berezin, *Journal of Applied Chemistry of the USSR*, 1981, **54**(4), 750-751.
- 3 W.A. Deer, R.A. Howie, J. Zussman, *An Introduction to the Rock-Forming Minerals*, Fifteenth impression, Longman Group Ltd., Harlow, 1985, pp. 375-379.
- 4 F.M. Jaeger, *Trans. Faraday Soc.*, 1929, **25**, 320-345.
- 5 M.T. Weller, G. Wong, C.L. Adamson, S.M. Dodd, J.J.B. Roe, *J. Chem. Soc. Dalton Trans.*, 1990, 593-597.
- 6 H. Schlaich, G-G. Lindner, J. Feldmann, E.O. Göbel, D. Reinen, *Inorg. Chem.*, 2000, **39**, 2740-2746.
- 7 G-G. Lindner, D. Reinen, *Z. anorg. allg. Chem.*, 1994, **620**, 1321-1328.
- 8 G-G. Lindner, K. Witke, H. Schlaich, D. Reinen, *Inorganica Chimica Acta*, 1996, **252**, 39-45.
- 9 *Persistence of Vision Raytracer*, ver. 3.1g.watcom.win32 [Pentium II optimized], distributed by Persistence of Vision Development Team, Indianapolis, USA (1999).
- 10 *HyperChem*, ver. 6.03 for Windows, distributed by HyperCube Inc. (2000).
- 11 W.B. Cork, *Ultramarine pigments*, in: *Industrial Inorganic Pigments*, G. Buxbaum (Ed), VCH, Weinheim, 1993, pp. 124-132.
- 12 A.P. Beardsley, S.H. Whiting, *Manufacture of Ultramarine*, final patent no., 2 441 950, 2 441 951, 2 441 952, United States.
- 13 D.G. Booth, S.E. Dann, M.T. Weller, *Dyes and Pigments*, 2003, **58**, 73-82.
- 14 A.E. Gessler, C.A. Kumins, *Process for making Ultramarine*, final patent no. 2 535 057, United States, 26 December 1950.

- 15 N. Gobeltz-Hautecoeur, A. Domortier, B. Lede, J.P. Lelieur, C. Duhayon, *Inorg. Chem.*, 2002, **41**(11), 2848-2854.
- 16 D. Reinen, G-G., Lindner, *Chem. Soc. Rev.*, 1999, **28**, 75-84.
- 17 R. Helmuth, *Fly Ash in Cement and Concrete*, Portland Cement Association, Skokie, 1987.
- 18 K. Tazaki, W.S. Fyfe, K.C. Sahu, M. Powell, *Fuel*, 1989, **68**, 727-734.
- 19 L. Cañadas, L. Salvador, C. Cortés, *Fuel*, 1990, **69**, 690-695.
- 20 S.V. Vassilev, *Fuel*, 1992, **71**, 625-633.
- 21 S. Gomes, M. François, M. Abdelmoula, P.H. Refait, C. Pellissier, O. Evrard, *Cem. Conc. Res.*, 1999, **29**, 1705-1711.
- 22 E.V. Sokol, N.V. Maksimova, N.I. Volkova, E.N. Nigmatulina, A.E. Frenkel, *Fuel Processing Technology*, 2000, **67**, 35-52.
- 23 G. Steenbruggen, G.G. Hollman, *J. Geochem. Explor.*, 1998, **62**, 305-309.
- 24 E.V. Sokol, V.M. Kalugin, E.N. Nigmatulina, N.I. Volkova, A.E. Frenkel, N.V. Maksimova, *Fuel*, 2002, **81**, 867-876.
- 25 V. Sakorafa, K. Michailidis, F. Burrigato, *Fuel*, 1996, **75**(4), 419-423.
- 26 G.G. Hollman, G. Steenbruggen, M. Janssen-Jurkovicova, *Fuel*, 1999, **78**, 1225-1230.
- 27 X. Querol, A. Alastuey, J.L. Fernandez-Turiel, A. Lopez-Soler, *Fuel*, 1995, **74**(8), 1226-1231.
- 28 Y. Fang, Y. Chen, M.R. Silsbee, D.M. Roy, *Mat. Lett.*, 1996, **27**, 155-159.
- 29 M.Y.A. Mollah, S. Promreuk, R. Schennach, D.L. Cocke, R. Guler, *Fuel*, 2002, **78**, 867-876.
- 30 M. Park, C.L. Choi, W.T. Lim, M.C. Kim, J. Choi, N.H. Heo, *Microporous and Mesoporous Materials*, 2000, **37**, 91-98.
- 31 S. Rayalu, S.U. Meshram, M.Z. Hasan, *Journal of Hazardous Materials*, 2000, **B77**, 123-131.
- 32 J.C. Martínez, J.F. Izquierdo, F. Cunill, J. Tejero, J. Querol, *Ind. Eng Chem. Res.*, 1991, **30**(9), 2143-2147.
- 33 C-S. Ho, S.-M. Shih, *Ind. Eng Chem. Res.*, 1992, **31**(4), 1130-1135.
- 34 J.F. Sanders, T.C. Keener, J. Wang, *Ind. Eng Chem. Res.*, 1995, **34**(1), 302-307.
- 35 H. Tsudhiai, T. Ishizuka, T. Ueno, H. Hattori, H. Kita, *Ind. Eng Chem. Res.*, 1995, **34**(4), 1404-1411.
- 36 T. Ishizuka, H. Tsudhiai, T. Murayama, T. Tanaka, H. Hattori, *Ind. Eng Chem. Res.*, 2000, **39**(5), 1390-1396.
- 37 A. Al-Shawabkeh, H. Matsuda, M. Hasatani, *Journal of Chemical Engineering of Japan*, 1995, **28**(1), 53-58.
- 38 M.W. Grutzeck, D.D. Siemer, *J. Am. Ceram. Soc.*, 1997, **80**(9), 2449-2453.
- 39 J.W. Smith, J. Condra, *J. Envir. Enrg.*, ASCE, 1983, **109**, 1168-1180.
- 40 A. Al-Shawabkeh, H. Matsuda, M. Hasatani, *Can. J. Chem. Eng.*, 1995, **73**, 678-685.
- 41 S.J. Rothenberg, P. Denee, P. Holloway, *Appl. Spectrosc.*, 1980, **34**(5), 549-555.
- 42 K. Felker, F. Seeley, Z. Egan, D. Kelmers, *Chemtech*, 1982, **12**(2), 123-128.
- 43 A. Hazrati, J.T. Schrodtt, *Surf. Interface Anal.*, 1988, **13**, 142-148.
- 44 H. Yokozawa, T. Kikuchi, K.F. Ando, K. Hoshino, *Anal. Chim. Acta*, 1987, **195**, 73-80.
- 45 K. Mukai, T. Kikuchi, K. Furuya, *Mikrochim. Acta*, 1988, **1988 III**, 41-56.
- 46 J.F.C. Alcalá, R.M. Dávila, R.L. Quintero, *Trans. Iron Steel Inst. Jpn.*, 1987, **27**, 531-538.
- 47 L.D. Hulett Jr., A.J. Weinberger, K.J. Northcutt, M. Ferguson, *Science*, 1980, **210**(4476), 1356-1358.
- 48 G.L. Fisher, D.P.Y. Chang, M. Brummer, *Science*, 1976, **192**(4239), 553-555.
- 49 R.Q. Guo, P.K. Rohatgi, *Metall. Mater. Trans. B*, 1998, **29B**, 519-525.
- 50 A.R. Ramsden, M. Shibaoka, *Atmospheric Environment*, 1982, **16**(9), 2191-2206.
- 51 J.L. Alonso, K. Wesche, *Fly Ash in Concrete*, First edition, E & FN Spon, London, 1991.
- 52 N.V. Russel, F. Wigley, J. Williamson, *Fuel*, 2002, **81**, 673-681.
- 53 C.D. Woolard, K. Petrus, M. Van der Horst, *Water SA*, 2000, **26**(4), 531-536.
- 54 N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Second, Butterworth-Heinemann, Oxford, 1997, pp. 652-661.
- 55 B. Meyer, *Chem. Rev.*, 1976, **76**(3), 367-387.
- 56 T. Chivers, I. Drummond, *Chem. Soc. Rev.*, 1973, **2**, 233-248.
- 57 H. Rau, T.R.N. Kutty, J.R.F. Guedes de Carvalho, *J. Chem. Thermodynamics*, 1973, **5**, 833-844.
- 58 H-L. Chang, W-H. Shih, *Ind. Eng Chem. Res.*, 1998, **37**(1), 71-78.
- 59 M.W. Grutzeck, D.D. Siemer, *J. Am. Ceram. Soc.*, 1997, **80**(9), 2449-2453.

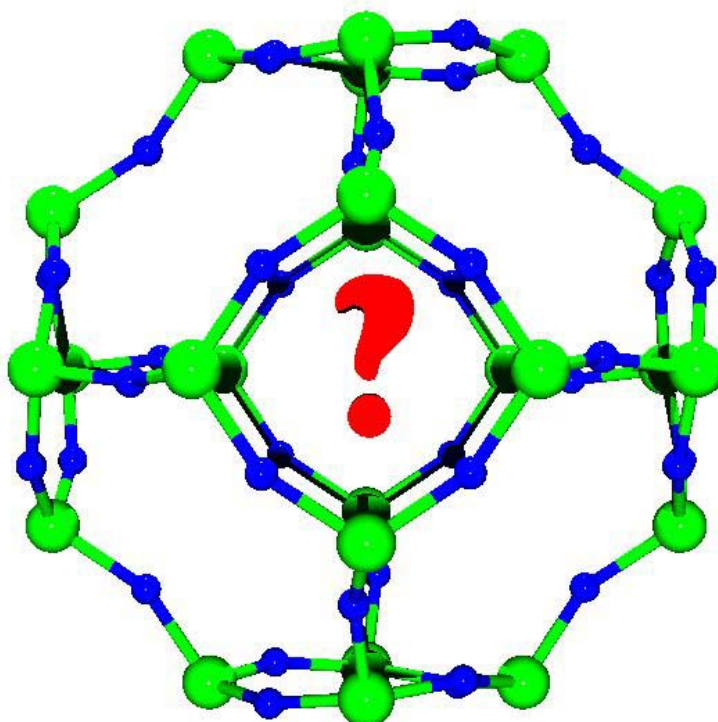
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- 60 S. Kowalak, M. Pawłowska, M. Miluška, M. Stróżyk, J. Kania, W. Przystajko, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1995, **101**, 179-185.
- 61 A.E. Gorshtein, *Journal of Applied Chemistry of the USSR*, 1985, **58**(7), 1468-1473.
- 62 S.D. McLaughlan, D.J. Marshall, *J. Phys. Chem.*, 1970, **74**(6), 1359-1363.
- 63 J.S. Prener, R. Ward, *J. Amer. Chem. Soc.*, 1950, **72**, 2780-2781.
- 64 S.E. Tarling, P. Barnes, A.L. Mackay, *J. Appl. Cryst.*, 1984, **17**, 96-99.
- 65 C.A Kumins, *Process for making ultramarine pigment*, final patent no. 2 544 695, United States, 13 March 1951.

## Chapter 5

# MODELLING SULPHUR CLUSTERS IN ULTRAMARINE

in

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



## 5. MODELLING SULPHUR CLUSTERS IN ULTRAMARINE

### 5.1. Introduction

Ultramarine pigments come in green, blue, greenish blue, reddish blue, violet, pink and red variants.<sup>1-7</sup> Several chromophores are present in the aluminosilicate zeolite-type framework of the ultramarine species.  $S_2^{\cdot-}$  is the yellow chromophore<sup>2,5,8-10</sup> in ultramarine and  $S_3^{\cdot-}$  (Figure 5-1) is the blue chromophore.<sup>2,5,8,9</sup> Ultramarine green is an ultramarine species in which the yellow and blue chromophores are present in such a ratio as to allow the green colour to be observed.

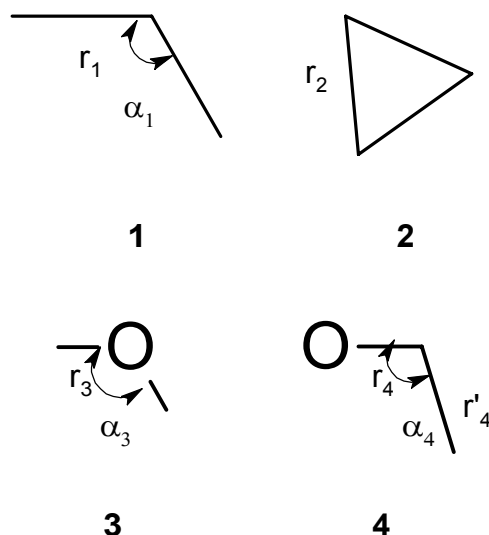


**Figure 5-1:  $S_3$ ,  $S_2O$  and  $SOS$  species: (1) Open  $S_3$  ( $C_{2v}$ ), (2) Closed  $S_3$  ( $D_{3h}$ ), (3)  $SOS$  ( $C_{2v}$ ), (4)  $S_2O$  ( $C_s$ )**

As mentioned in Chapter 3 ultramarine blue is synthesised in two steps, a reduction step followed by an oxidation step.<sup>1,2,5,8,9,11-14</sup> The nature of these steps is, however, disputed. Some authors suggested Equation 4-1,<sup>2,5,8,9</sup> whereas others supported the existence of doubly charged species according to Equations 4-2 and 4-3.<sup>1,11-13</sup> The oxidation of ultramarine green to ultramarine blue is related to an increasing  $S_3^{\cdot-}/S_2^{\cdot-}$  ratio (Chapter 3),<sup>2,5,8,9,14</sup> in support of Equation 4-1. Beardsley and Whiting<sup>12</sup> described the formation of ultramarine blue with oxygen as oxidising agent and introduced the use of  $SO_2$  in the production thereof.<sup>12</sup> Gorshtein<sup>11,13</sup> (Equations 4-2 and 4-3) successfully explained the formation of  $Na_2SO_4$  and the role

of  $\text{SO}_2$ , noted by Tarling and others<sup>15</sup> and Gobelitz and others.<sup>8</sup> This explanation was based on the identification of  $\text{S}_3^{2-}$  and  $\text{S}_2^{2-}$  as the yellow, and  $\text{S}_3^{\cdot-}$  and  $\text{S}_2^{\cdot-}$  as the blue chromophores. Other evidence identified  $\text{S}_3^{\cdot-}$  as responsible for the blue colour and  $\text{S}_2^{\cdot-}$  for yellow.<sup>2,5,8,9,16</sup> No spectroscopic evidence of the doubly charged species was available in the literature (Chapter 4).<sup>14</sup> Köhler and others<sup>10</sup> synthesized ultramarine yellow from the thiocyanide derivative of sodalite. They<sup>10</sup> confirmed that the yellow chromophore was  $\text{S}_2^{\cdot-}$  and that oxidation led to the formation of ultramarine green, with the simultaneous formation of  $\text{S}_3^{\cdot-}$ .<sup>10</sup> The evidence supported the formation of  $\text{S}_3^{\cdot-}$  from  $\text{S}_2^{\cdot-}$  rather than from  $\text{S}_3^{2-}$ . On the other hand, Weller and others,<sup>17</sup> presented evidence that of a doubly charged species was involved, as described on pages 58 and 59. The high ratio of sulphur atoms to unpaired electrons found by Hofmann and others<sup>6</sup> in the ultramarine green pigment supported the possible existence of doubly charged non-radical sulphide species. This conclusion was not generally accepted.<sup>18</sup>

The ultramarine red chromophore had been identified as an isomer of the  $\text{S}_4$  molecule (Figure 5-2).<sup>1,2,5,19</sup> The  $\text{S}_4$  molecule could possibly form from  $\text{S}_3^{\cdot-}$  and  $\text{S}^{++}$  in a concerted reaction.<sup>20</sup> The feasibility of single-step concerted reactions could be evaluated by examining the phase symmetry of the molecular orbitals, by the methods of Fukui<sup>21,22</sup> and of Woodward and Hoffmann.<sup>23-26</sup> The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were assumed to feature in reactions to form new bonds. For a reaction to take place the HOMO (LUMO) of the attacked species and the LUMO (HOMO) of the attacking species must have had the same phase symmetry. This condition allowed regions of the same phase in the molecular orbitals to overlap and to form new bonding and anti-bonding molecular orbitals provided favourable overlap occurred. Sannigrahi and Grein<sup>27</sup> used the Woodward-Hoffmann methodology to show that the formation of  $\text{S}_4^{2+}$  from  $\text{S}_2^+$  was not allowed.

The molecular orbitals of  $\text{S}^{++}$ ,  $\text{S}_2^{\cdot-}$ , and  $\text{S}_3^{\cdot-}$  were computed in this work in order to use a Woodward-Hoffmann analysis to evaluate the feasibility of the formation of some of the  $\text{S}_4$  isomers.  $\text{S}_2$ ,  $\text{S}_2^{2-}$ ,  $\text{S}_3$ , and  $\text{S}_3^{2-}$  were also modelled in an effort to find the most stable sulphur species. These results might confirm that green ultramarine yielded blue ultramarine by the formation of  $\text{S}_2^{\cdot-}$ ,  $\text{S}_3^{\cdot-}$  from  $\text{S}_2^{2-}$ ,  $\text{S}_3^{2-}$ .<sup>11-13</sup>

## 5.2. Experimental data

Naudé<sup>28,29</sup> studied the rotational substructure of the vibrational spectrum of  $S_2$  and determined the bond length to be 1.893 Å. Based on the absorption band fine structure between 160 and 190 nm Maeder and Miescher<sup>30</sup> calculated a vibrational frequency of  $724\text{ cm}^{-1}$ , for  $S_2$ .  $S_2^{\cdot-}$  had a Raman band at  $590\text{ cm}^{-1}$ ,<sup>2,5</sup> and  $S_2^{2-}$  a band at  $451\text{ cm}^{-1}$ .<sup>31</sup>

Hopkins and others<sup>32</sup> observed the  $S_3$  molecule as part of an electric discharge reaction and observed Raman bands at 585, 490, and  $650\text{ cm}^{-1}$ . Brabson and others<sup>33</sup> recorded the infrared spectrum of  $S_3$  in a solid argon matrix (Table 5-1). They concluded that the structure of  $S_3$  was the  $C_{2v}$  open geometry, with an angle of  $116 \pm 2^\circ$ .<sup>33</sup> Lenain and others<sup>34</sup> studied the Raman spectra of  $S_3$  and also concluded that the  $C_{2v}$  isomer was the observed species (Table 5-1). Clark and Cobbold<sup>2</sup> observed both the Raman and infrared bands for  $S_3^{\cdot-}$  (Table 5-1). Janz and others<sup>31,35,36</sup> studied several polysulphides. For  $BaS_3$  the  $S_3^{2-}$  structure was said to be  $C_{2v}$  with vibrational modes at 227/238 (R), 458 (R,IR), and  $476\text{ cm}^{-1}$  (R,IR).<sup>35</sup> For  $K_2S_3$  the same interpretation held, with the stretching modes accidentally degenerate: 238 (R) and  $466\text{ cm}^{-1}$  (R,IR).<sup>36</sup>

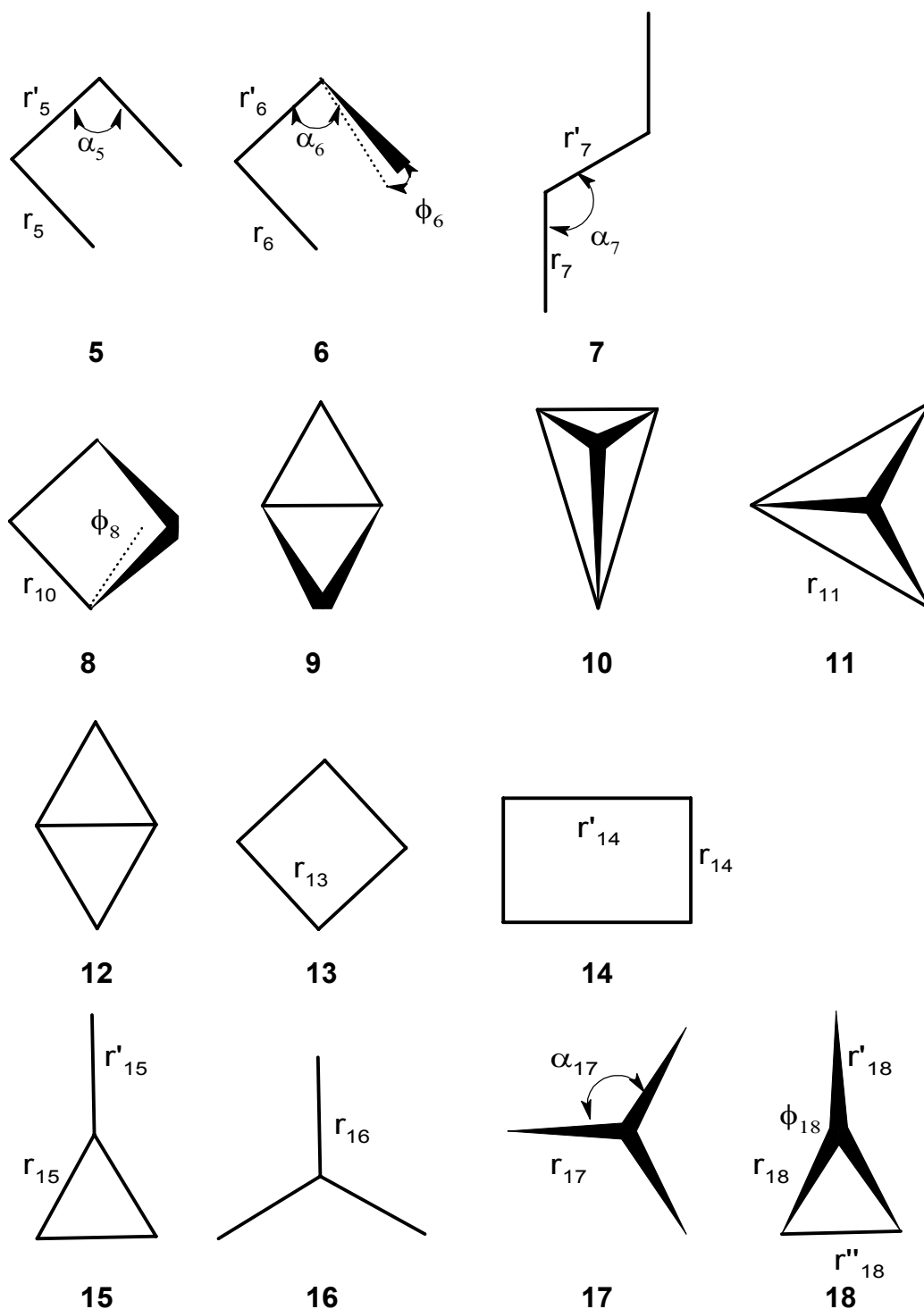


**Figure 5-2: Isomers of  $S_4$ : (5) Cis Chain ( $C_{2v}$ ), (6) Gauche Chain ( $C_2$ ), (7) Trans Chain ( $C_{2h}$ ), (8) Puckered Ring ( $D_{2d}$ ), (9) Butterfly ( $D_{2d}$ ), (10) Tetrahedral (Geometry optimised) ( $D_{2d}$ ), (11) Tetrahedral ( $T_d$ ), (12) Double Triangle ( $D_{4h}$ ), (13) Square Planar ( $D_{4h}$ ), (14) Rectangle ( $D_{2h}$ ), (15) Exocyclic ( $C_{2v}$ ), (16) Branched Chain ( $D_{3h}$ ), (17) Pyramidal ( $C_s$ ), (18) Bent exocyclic ( $C_s$ )**

**Table 5-1: Experimental characteristics of  $S_3$ ,  $S_3^{\cdot-}$ , and  $S_3^{2-}$** 

|                | Reference | Assignment              | Infrared<br>$\text{cm}^{-1}$ | Raman<br>$\text{cm}^{-1}$ |
|----------------|-----------|-------------------------|------------------------------|---------------------------|
| $S_3$          | [32]      | $\nu_1$                 |                              | 585                       |
|                |           | $\nu_2$ ?               | 495 or 310                   | 490                       |
|                |           | $\nu_3$                 |                              | 650                       |
|                | [33]      | $\nu_1$                 |                              | 583                       |
|                | [33,35]   | $\nu_2$                 | 680                          |                           |
|                |           | Vibrational progression |                              |                           |
|                | [33,37]   |                         | 340                          |                           |
|                |           |                         | 450                          |                           |
|                | [34]      | $\nu_1$                 |                              | 575                       |
|                |           | $\nu_2$                 |                              | 256                       |
|                |           | $\nu_3$                 |                              | 656                       |
| $S_3^{\cdot-}$ | [2,5]     | $\nu_1$                 |                              | 548                       |
|                | [2]       | $\nu_3$                 | 582                          |                           |
|                | [2]       | $\nu_1$                 | 547                          |                           |
|                | [38]      | $\nu_2$                 |                              | 232                       |
| $S_3^{2-}$     | [35]      | $\nu_1$ or $\nu_3$      | 457                          | 458                       |
|                |           | $\nu_2$                 |                              | 227/238                   |
|                |           | $\nu_1$ or $\nu_3$      | 476                          | 476                       |
|                | [36]      | $\nu_1$ and $\nu_3$     |                              | 466                       |
|                |           | $\nu_2$                 |                              | 238                       |

### 5.3. Molecular Modelling

When doing molecular modelling the objectives need to be clear. In the work on sulphur compounds the shape of the molecular orbitals was important because it dictated the reactivity of the species under consideration and was used in the Woodward-Hofmann analyses. The energies were also important as an estimate of the relative stability of the ionic states of  $S_2$  and  $S_3$ . A potential energy surface specified the classical potential energy as a function of molecular structure.<sup>39</sup> This concept was useful for the comparison of the possible geometrical isomers. The potential energy surface was inspected for  $S_2$ ,  $S_2^{\cdot-}$ ,  $S_2^{2-}$ ,  $S_3$ ,  $S_3^{\cdot-}$ , and  $S_3^{2-}$  in an effort to find the most favourable oxidation states of these species, and to obtain the molecular orbitals for use in a Woodward Hoffmann analysis.

## 5.4. Results

The geometry optimisation gave reasonable results, compared to literature values (Table 5-2). As the charge on the  $S_2$  species became more negative the bond distance increased (Table 5-2). The geometry of the closed  $S_3^{\cdot-}$  isomer did not optimise to the desired  $D_{3h}$  symmetry and the bond length was therefore set to the average of the values found in the literature (Table 5-2). The geometry of the closed  $S_3^{2-}$  isomer optimised to unrealistically long bond lengths, and the bond distance was set to 2.24 Å.<sup>40</sup> The nature of this optimisation anomaly was not investigated.

The singly charged anions of both  $S_2$  and  $S_3$  were found to be the most stable states relative to the neutral and doubly charged states (Tables 5-3 and 5-4). The reaction that transformed ultramarine green to blue was exothermic.<sup>12</sup> The calculated results supported the proposal that this reaction involved the transition from  $S_2^{2-}$ ,  $S_3^{2-}$  to  $S_2^{\cdot-}$ ,  $S_3^{\cdot-}$ .<sup>1,11-13</sup> The computational results at the SCF UHF with the 6-311G\*\* basis set and MP2 extension at the minimum energy indicated that the open,  $C_{2v}$ , structure was the most stable isomer for the  $S_3^{\cdot-}$  molecule (Table 5-4). In fact, at this level, the closed,  $D_{3h}$ ,  $S_3^{\cdot-}$  geometry was shown to be a transition state. Since the  $S_3^{\cdot-}$  molecule was the blue chromophore in ultramarine blue,<sup>1,2,5,8,9</sup> the geometry of this important stable radical polysulphide was calculated. This geometry could now be used in modelling the ultramarine pigment itself,<sup>41</sup> and could assist in crystallographic interpretation.<sup>15</sup> The calculated vibrational frequencies for  $S_2$ ,  $S_2^{\cdot-}$ , and  $S_2^{2-}$  were in good agreement with the experimental values (Table 5-5). For  $S_2^{2-}$  the unscaled frequencies fit best (Table 5-5). The vibrational frequency decreased with an increase in the negative charge on the  $S_2$  molecule as expected from the reverse trend in the bond distances (Table 5-2). After applying the scale factor of 0.87 to calculated frequencies (Table 5-6) of the open  $S_3$  isomer, they corresponded well with experimental values (Tables 5-1 and 5-6). The scaled vibrational frequencies of the closed,  $D_{3h}$ ,  $S_3$  isomer (Table 5-7) agreed with the experimental values as well. The calculated vibrational frequencies of  $S_3^{\cdot-}$  were less accurate (Table 5-8). The antisymmetric stretching frequency was underestimated. Again no scaling was needed as discussed in the conclusion. For  $S_3^{2-}$ , the vibrational frequencies were close to the experimental values without scaling (Table 5-8).

**Table 5-2: Bond lengths (Å) and angles (°) for  $S_2$  and  $S_3$  species**

| Structure name        | Symmetry       | Structural parameter <sup>a</sup> | This work   | Average from literature <sup>b</sup> | References       |
|-----------------------|----------------|-----------------------------------|-------------|--------------------------------------|------------------|
| $S_2$                 | $D_{\infty h}$ | $r$                               | 1.88        | 1.91(2)                              | [42-44]          |
| $S_2^{\cdot-}$        | $D_{\infty h}$ | $r$                               | 2.01        | 2.12(8)                              | [42,45]          |
| $S_2^{2-}$            | $D_{\infty h}$ | $r$                               | 2.21 (2.80) |                                      |                  |
| Singlet open $S_3$    | $C_{2v}$       | $r_1$                             | 1.90        | 1.98(2)                              | [40,43,44,46-51] |
|                       |                | $\alpha_1$                        | 117         | 116.6(7)                             | "                |
| Singlet closed $S_3$  | $D_{3h}$       | $r_2$                             | 2.08        | 2.12(2)                              | "                |
| $^3A_2$ open $S_3$    | $C_{2v}$       | $r_1$                             | 1.99        | 2.00(4)                              | [43,47]          |
|                       |                | $\alpha_1$                        | 93          | 93(2)                                | "                |
| Open $S_3^{\cdot-}$   | $C_{2v}$       | $r_1$                             | 2.00        | 2.02(3)                              | [40,45,51]       |
|                       |                | $\alpha_1$                        | 115         | 113(2)                               | "                |
| Closed $S_3^{\cdot-}$ | $D_{3h}$       | $r_2$                             | 2.24        | 2.241(5)                             | [40,51]          |
| Open $S_3^{2-}$       | $C_{2v}$       | $r_1$                             | 2.13        | 2.08(8)                              | [40,45]          |
|                       |                | $\alpha_1$                        | 113         | 109(6)                               | "                |
| Closed $S_3^{2-}$     | $D_{3h}$       | $r_2$                             | 2.24        | 2.244                                | [40]             |

a. As defined in Figure 5-1

b. The value given is the average from several literature values, the number in brackets denotes one standard deviation of the mean

**Table 5-3: Relative energy (kJ/mol) results for  $S_2^a$** 

| Structure name     | This work          |
|--------------------|--------------------|
| $S_2$ singlet      | 146                |
| $S_2$ triplet      | 113                |
| $S_2^{\cdot-}$     | 0                  |
| $S_2^{2-}$ singlet | 427                |
| $S_2^{2-}$ triplet | 632 i <sup>b</sup> |

a. The energy of the most stable isomer was set equal to zero and the other energies are reported relative to this most stable state

b. i indicates that the species has an imaginary frequency

**Table 5-4: Relative energy (kJ/mol) results for  $S_3^a$** 

| Structure number | Structure name            | This work          |
|------------------|---------------------------|--------------------|
| 1                | Open $S_3$ Singlet        | 197                |
| 2                | Closed $S_3$ Singlet      | 234                |
| 1                | Open $S_3$ Triplet        | 297                |
| 2                | Closed $S_3$ Triplet      | 473 i <sup>b</sup> |
| 1                | Open $S_3^-$              | 0                  |
| 2                | Closed $S_3^-$            | 192 i              |
| 2                | Closed $S_3^{2-}$ Singlet | 720 i              |
| 1                | Open $S_3^{2-}$ Singlet   | 331                |
| 2                | Closed $S_3^{2-}$ Triplet | 682 i              |
| 1                | Open $S_3^{2-}$ Triplet   | 577 i              |

a. The energy of the most stable isomer was set equal to zero and the other energies are reported relative to this most stable state

b. i indicates that the species has an imaginary frequency

**Table 5-5: Vibrational frequencies in  $cm^{-1}$  of  $S_2$  stretching vibration**

|                         | This work              | Scaled values | Experimental | References | Ratio of experimental and this work |
|-------------------------|------------------------|---------------|--------------|------------|-------------------------------------|
| Singlet (triplet) $S_2$ | 791 (790) <sup>a</sup> | 687           | 724          | [30]       | 0.92                                |
| Doublet $S_2^{-}$       | 615                    | 535           | 590          | [2][5]     | 0.96                                |
| Singlet $S_2^{2-}$      | 426                    | 371           | 451          | [31]       | 1.06                                |

a. Value in brackets is for the triplet state

**Table 5-6: Vibrational frequencies in  $cm^{-1}$  of open  $S_3$  (1)**

| Mode    | Description           | Symmetry | This work           | Scaled values <sup>a</sup> | Experimental values <sup>34</sup> | Spectroscopic activity <sup>b</sup> | Ratio of experimental and this work |
|---------|-----------------------|----------|---------------------|----------------------------|-----------------------------------|-------------------------------------|-------------------------------------|
| $\nu_1$ | Symmetric stretch     | $a_1$    | 654<br>(627)<br>294 | 569                        | 575                               | R, IR                               | 0.88 (0.92)                         |
| $\nu_2$ | Bending               | $a_1$    | (211) <sup>c</sup>  | 256                        | 256                               | R, IR                               | 0.87 (1.21)                         |
| $\nu_3$ | Antisymmetric stretch | $b_2$    | 737<br>(490)        | 641                        | 656                               | R, IR                               | 0.89 (1.34)                         |

a. Scaled with a scale factor of 0.87<sup>33</sup>

b. R: Raman active, IR: Infrared active

c. Values in brackets are for the triplet state

**Table 5-7: Vibrational frequencies in  $\text{cm}^{-1}$  of closed  $\text{S}_3$  (2)**

| Mode    | Description           | Symmetry | This work | Scaled values <sup>a</sup> | Experimental values                                     | Spectroscopic activity <sup>b</sup> | Ratio of experimental and this work |
|---------|-----------------------|----------|-----------|----------------------------|---------------------------------------------------------|-------------------------------------|-------------------------------------|
| $\nu_1$ | Symmetric Deformation | $a_1'$   | 662       | 576                        | 583, <sup>33</sup> 585, <sup>32</sup> 575 <sup>34</sup> | R                                   | 0.88, 0.88, 0.87                    |
| $\nu_2$ | Stretch               | $e'$     | 500       | 435                        | 450, <sup>33,37</sup> 490 <sup>32</sup>                 | R, IR                               | 0.90, 0.98                          |

a. Scaled with a scale factor of 0.87<sup>33</sup>

b. R: Raman active, IR: Infrared active

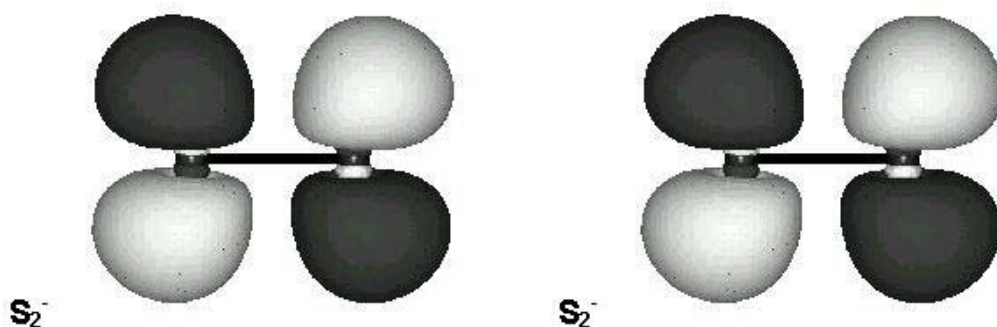
**Table 5-8: Vibrational frequencies in  $\text{cm}^{-1}$  of negatively charged open  $\text{S}_3$  (1)**

| Mode    | Description           | Symmetry | Doublet $\text{S}_3^{2-}$ | Experimental values for $\text{S}_3^{2-}$ | Singlet open $\text{S}_3^{2-}$ | Experimental <sup>35</sup> values for $\text{S}_3^{2-}$ | Spectroscopic activity <sup>a</sup> |
|---------|-----------------------|----------|---------------------------|-------------------------------------------|--------------------------------|---------------------------------------------------------|-------------------------------------|
| $\nu_1$ | Symmetric Stretch     | $a_1$    | 558                       | 548 <sup>2</sup> (0.98)                   | 459                            | 458 (1.00)                                              | R, IR                               |
| $\nu_2$ | Bending               | $a_1$    | 250                       | 232 <sup>38</sup> (0.93)                  | 202                            | 227 (1.12) / 238 (1.18)                                 | R, IR                               |
| $\nu_3$ | Antisymmetric Stretch | $b_2$    | 449                       | 582 <sup>2</sup> (1.30)                   | 496                            | 476                                                     | R, IR                               |

a. R: Raman active, IR: Infrared active

b. Values in brackets represent the ratio between the experimental frequency and the calculated frequency

Molecular modelling of the polysulphide species was done in order to obtain a molecular orbital picture of  $\text{S}_2^{2-}$  (Figure 5-3), and  $\text{S}^{2+}$  and  $\text{S}_3^{2-}$  (Figure 5-4). HyperChem<sup>52</sup> was used to model the  $\text{S}_2^{2-}$  and  $\text{S}_3^{2-}$  structures by the ZINDO/1 semi-empirical method, and self-consistent-field unrestricted Hartree-Fock simulation using a 6-311G\*\* *ab initio* basis set extended by MP2 correlation energy. The ZINDO/1 results confirmed the character of the highest occupied molecular orbital for both open ( $b_1$ ) and closed ( $a_2'$ )  $\text{S}_3^{2-}$  of a previous pictorial model<sup>20</sup> and the work of Koch and others<sup>40</sup> (Figure 5-4).

**Figure 5-3: Highest occupied (left) and lowest unoccupied (right) molecular orbital of  $\text{S}_2^{2-}$**

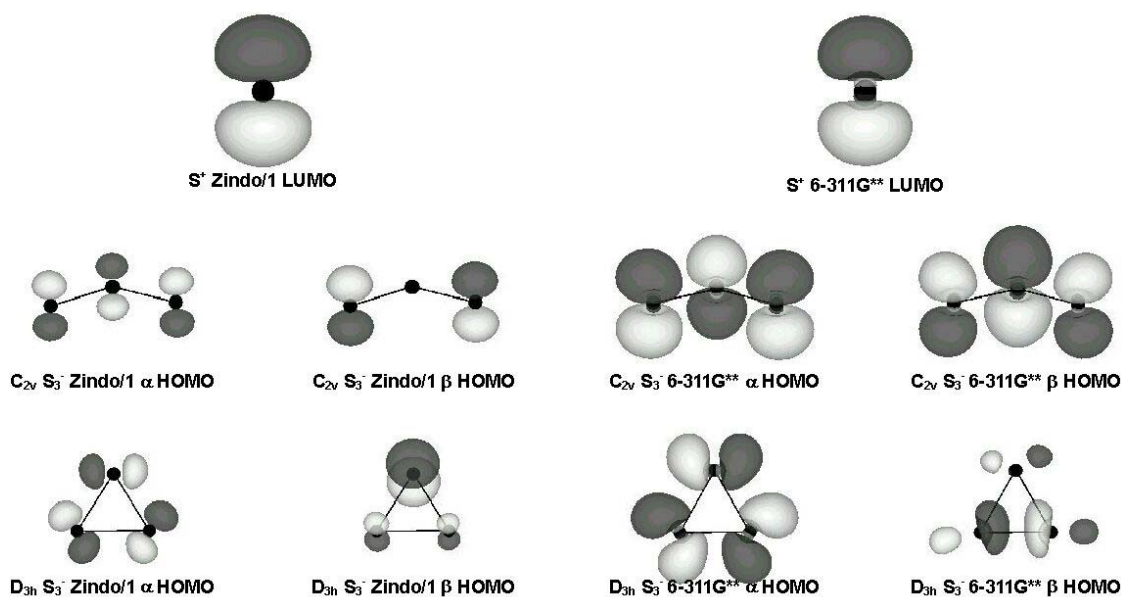


**Figure 5-4: Molecular orbital diagram of  $S^{+}$  (ZINDO/1 and 6-311G\*\* LUMO) and  $S_3^{-}$  (ZINDO/1 and 6-311G\*\*  $\alpha$  and  $\beta$  HOMO)**

It was assumed that  $S^{+}$  (Figure 5-4) attacked the  $S_3$  (Figure 5-4) species in a concerted reaction to form  $S_4$  (Figure 5-2). This was tested by means of the frontier orbital symmetry theory of Woodward and Hoffmann.<sup>23-25</sup> The HOMO of  $S_3^{-}$  (Figure 5-4) was placed near the LUMO of  $S^{+}$  (Figure 5-4) in such a way as to ensure that lobes of the same phase overlapped to form  $\sigma$ -orbitals. The charge distribution on the sulphur atoms of the  $C_{2v} S_3^{-}$  isomer indicated that the central sulphur atom was positively charged (Figure 5-5), therefore attack of  $S^{+}$  was unlikely to occur on this atom. To test whether the electrostatic charges would be detrimental to this form of attack the distance between the fourth sulphur atom and the central sulphur atom, in the branched chain isomer, was increased (Figure 5-5), with the result that the original electrostatic charge distribution was induced in the  $C_{2v} S_3^{-}$  moiety. Electrostatics did therefore not preclude the attack of  $S^{+}$  on the central sulphur of the open,  $C_{2v} S_3^{-}$  isomer.

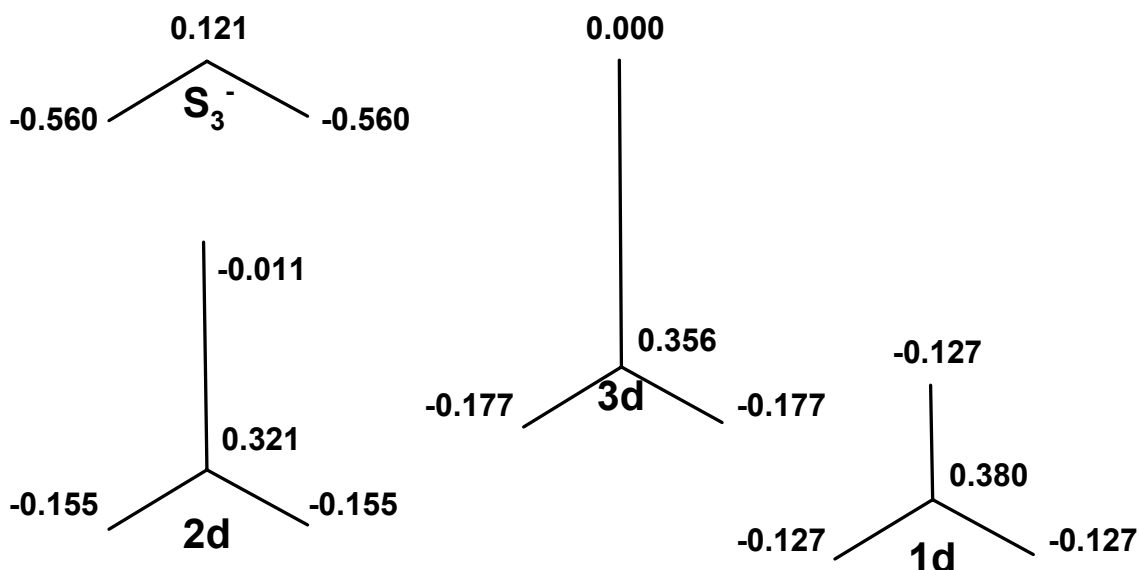


**Figure 5-5: Charge distribution in  $S_3^-$  and branched chain  $S_4$  at thrice (3d), twice (2d) and at its normal distance (1d), showing that the positive charge on the central sulphur atom in  $S_3^-$  is not necessarily a problem in the formation of branched chain  $S_4$  from  $S_3^-$  and  $S^{+}$**

A Woodward-Hoffmann analysis at the ZINDO/1 level showed that the puckered  $S_4$  ring, pyramidal branched chain  $S_4$ , gauche  $S_4$  chain and bent exocyclic  $S_4$  isomers were possible products of the concerted reaction of  $S^{+}$  and  $S_3^-$ . At the 6-311G\*\* level of theory, the highest occupied molecular orbital of the closed,  $D_{3h}$ ,  $S_3^-$  isomer precluded the formation of the bent exocyclic  $S_4$  isomer. The symmetry of the  $S_2^-$  highest occupied and lowest unoccupied molecular orbital (Figure 5-3), furthermore, predicted that the closed,  $D_{3h}$ ,  $S_3^-$  isomer could not be formed in a concerted way from  $S_2^-$ .

## 5.5. Discussion

*Ab initio* results should not be accepted at face value because of the approximations made during the analysis. Strictly speaking, *ab initio* computations are only relevant to gas phase molecules in vacuum at 0 K. The environment created by the sodium counterions and the aluminosilicate framework was not taken into account. The structure of the aluminosilicate framework did ensure that the sulphur chromophores

acted independently as molecules and did not form part of an extended sulphur-based "molecule".

The calculated vibrational frequency of  $S_2$  at  $793\text{ cm}^{-1}$ , scaled (0.87) to  $690\text{ cm}^{-1}$ , was in reasonable agreement with the experimental value of  $724\text{ cm}^{-1}$  (Table 5-5). The bond length of  $1.88\text{ Å}$  was in close agreement with the experimental  $1.893\text{ Å}$ .<sup>28,29</sup> Heinemann and others<sup>42</sup> calculated the vibrational frequency of  $S_2^*$  to be  $582\text{ cm}^{-1}$ , close to the experimental value (Table 5-5). The current value was not far from the expected value (Table 5-5). Heinemann and others<sup>42</sup> calculated that the triplet  $S_2$  molecule was less energetic than the  $S_2^*$  molecule. The current results confirmed this.

Rau and others<sup>53</sup> suggested that sulphur allotrope tautomers with an energy difference less than  $33\text{ kJ/mol}$  contributed appreciably to the vapour composition of that particular species at temperatures between  $823$  and  $1\,273\text{ K}$ , the so-called tautomeric occurrence\*. This was suggested on the basis of the work of Pauling,<sup>54</sup> who mentioned the estimate of tautomeric occurrence at  $41\text{ kJ/mol}$ . Taking into account the reliability of the computed values, sulphur allotropic isomers with an energy difference of less than  $41\text{ kJ/mol}$  relative to the most stable isomer, in this work, should be present in appreciable amounts.

The bond angle calculated for the open  $S_3$  isomer was  $117^\circ$ , within the experimental range.<sup>33</sup> The question of whether the open,  $C_{2v}$ ,<sup>40,43,47,48,50,51</sup> or closed,  $D_{3h}$ ,<sup>42,50,51,55,56</sup>  $S_3$  isomer was the more stable seemed to be an open question, since several methods gave contradictory results, depending on the methodology applied to the problem. The open,  $C_{2v}$ ,  $S_3$  isomer was calculated to be the most stable in this work. The computed closed,  $D_{3h}$ ,  $S_3$  isomer had an energy only  $38\text{ kJ/mol}$  higher than the open isomer, therefore both these isomers should be observable (Table 5-4) and probably were (Table 5-6 and Table 5-7).

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\* The term tautomer is used to describe a geometric isomer in the cited reference. The term tautomeric occurrence therefore implies the possible presence of different geometric isomers.

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From literature it seemed as though the open,  $C_{2v}$ ,<sup>40,49</sup>  $S_3^{-\bullet}$  isomer was deemed to be more stable than the closed,  $D_{3h}$ , isomer. This was confirmed in the current work. The scale factor of 0.87, suggested by Brabson and others,<sup>33</sup> worked well for the neutral sulphur molecules (Tables 5-5, 5-6 and 5-7), but failed for the ionised species (Tables 5-5 and 5-8). A scaling factor closer to or larger than 1.00 seemed more appropriate.

The assumption that the  $S_4$  molecules were formed by concerted reactions of  $S_3^{-\bullet}$  and  $S^{+\bullet}$  was theoretically useful, although the existence of the  $S^{+\bullet}$  was unlikely. Berkowitz and Chupka<sup>57</sup> studied the dissociation of  $S_2$  and determined the dissociation energy to be  $423 \pm 1$  kJ/mol from the photoionization threshold of  $14.74 \pm 0.01$  eV for Equation 5-1. The existence of  $S^{+\bullet}$ , therefore, seemed plausible.



Based on the fact that the tetrahedral geometry had an open-shell electronic configuration, Salahub and others<sup>49</sup> ruled out the tetrahedral geometry as the ground state of  $S_4$  by  $X\alpha$ -scattered wave calculations. Landman and De Waal also reached this conclusion based on Woodward-Hoffmann selection rules,<sup>20</sup> and it was verified in the current work.

## 5.6. Conclusion

At the SCF UHF level of theory with 6-311G\*\* as basis set and a MP2 energy correction the open,  $C_{2v}$ , structure was found to be the most stable isomer for the  $S_3^{-\bullet}$  molecule, which was the blue chromophore in ultramarine. The closed,  $D_{3h}$ , geometry was calculated to be a transition state (Table 5-4). For both  $S_2$  and  $S_3$  the singly charged anions were calculated to be the most stable state, in relation to the neutral and doubly charged states (Table 5-3, Table 5-4). In light of the evidence that the reaction transforming the ultramarine green to the desirable ultramarine blue was exothermic,<sup>12</sup> the current results supported the proposal that this reaction involved the transition from  $S_2^{2-}$ ,  $S_3^{2-}$  to  $S_2^{-\bullet}$ ,  $S_3^{-\bullet}$ .<sup>1,11-13</sup>

Woodward-Hoffmann orbital analyses based on ZINDO/1 suggested that the product of a concerted reaction between  $S_3^{\cdot-}$  and  $S^{\cdot+}$  was either the puckered  $S_4$  ring, pyramidal  $S_4$ , gauche chain  $S_4$  or bent exocyclic  $S_4$  structure. At the 6-311G\*\* level the formation of the bent exocyclic  $S_4$  isomer was excluded.

The symmetry of the  $S_2^{\cdot-}$  orbitals (Figure 5-3), did not favour the formation of  $D_{3h}$   $S_3^{\cdot-}$  species from  $S_2^{\cdot-}$  in a concerted way.

## REFERENCES

- 1 W.B. Cork, *Ultramarine pigments*, in: *Industrial Inorganic Pigments*, G. Buxbaum (ed), 1993, pp. 124-132.
- 2 R.J.H. Clark, D.G. Cobbold, *Inorg. Chem.*, 1978, **17**(11), 3169-3174.
- 3 H. He, T.L. Barr, J. Klinowski, *J. Phys. Chem.*, 1994, **98**(33), 8124-8127.
- 4 K.-H. Schwarz, U. Hofmann, *Z. anorg. allg. Chem.*, 1970, **378**, 152-159.
- 5 R.J.H. Clark, T.J. Dines, M. Kurmoo, *Inorg. Chem.*, 1983, **22**, 2766-2772.
- 6 U. Hofmann, E. Herzenstiel, E. Schonemann, K-H. Schwarz, *Z. anorg. allg. chem.*, 1969, **367**, 119-129.
- 7 J. Klinowski, S.W. Carr, S.E. Tarling, P. Barnes, *Nature*, 1987, **330**, 56-58.
- 8 N. Gobeltz, A. Demortier, N. Gobeltz, A. Demortier, J.P. Lillieur, C. Duhayon, *J. Chem. Soc., Faraday Trans.*, 1998, **94**(15), 2257-2260.
- 9 D.M. Gruen, R.L. McBeth, A.J. Zielen, *J. Amer. Chem. Soc.*, 1971, **93**(24) 6691-6693.
- 10 P. Köhler, G. Winter, F. Seel, K-P. Klös, *Z. Naturforsch.*, 1987, **42b** 663-665.
- 11 A.E. Gorshtein, *Journal of Applied Chemistry of the USSR*, 1985, **58**(7), 1468-1473.
- 12 A.P. Beardsley, S.H. Whiting, *Manufacture of ultramarine*, final patent no. 2 441 950, 2 441 951, 2 441 952, United States.
- 13 A.E. Gorshtein, *The Canadian Journal of Chemical Engineering*, 1992, **70**, 960-965.
- 14 A.A. Landman, D. de Waal, *Materials Research Bulletin*, 2004, **39**, 655-667.
- 15 S.E. Tarling, P. Barnes, A.L. Mackay, *J. Appl. Cryst.*, 1984, **17** 96-99.
- 16 T. Chivers, I. Drummond, *Chem. Soc. Rev.*, 1973, **2**(16) 233-248.
- 17 M.T. Weller, G. Wong, C.L. Adamson, S.M. Dodd, J.J.B. Roe, *J. Chem. Soc. Dalton Trans.*, 1990, 593-597.
- 18 N. Gobeltz-Hautecoeur, A. Domortier, B. Lede, J.P. Lelieur, C. Duhayon, *Inorg. Chem.*, 2002, **41**(11), 2848-2854.
- 19 F. Seel, H-J. Güttler, A.B. Wicowski, B. Wolf, *Z. Naturforsch.*, 1979, **34b**, 1671-1677.
- 20 A.A. Landman, D. De Waal, *Crystal Engineering*, 2001, **4**, 159-169.
- 21 K. Fukui, *Tetrahedron Letters*, 1965, **28**, 2427-2432.
- 22 K. Fukui *Tetrahedron Letters*, 1965, **24**, 2009-2015.
- 23 R.B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**(9), 2046-2048.
- 24 R.B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**(11), 2511-2513.
- 25 R.B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**(2), 395-397.
- 26 R. Hoffmann, *Account Chem. Res.*, 1971, **4**(1), 1-9.
- 27 M. Sannigrahi, F. Grein, *Can. J. Chem.*, 1994, **72**, 298-303.
- 28 S.M. Naudé, *Nature*, 1945, **155**(3936), 426-427.
- 29 S.M. Naudé, *South African Journal of Science*, 1945, **41**, 128-151.
- 30 R. Maeder, E. Miescher, *Nature*, 1948, **161**(4089), 393.
- 31 G.J. Janz, J.R. Downey Jr, E. Roduner, G.J. Wasilczyk, J.W. Coutts, A. Eluard, *Inorg. Chem.*, 1976, **15**(8), 1759-1763.
- 32 A.G. Hopkins, S.-Y. Tang, C.W. Brown, *J. Am. Chem. Soc.*, 1973, **95**(11), 3486-3494.
- 33 G.D. Brabson, Z. Mielke, L. Andrews, *J. Phys. Chem.*, 1991, **95**(1), 79-86.
- 34 P. Lenain, E. Picquenard, J.L. Lesne, J. Corset, *J. Mol. Struct.*, 1986, **142**, 355-358.
- 35 G.J. Janz, E. Roduner, J.W. Coutts, J.R. Downey Jr, *Inorg. Chem.*, 1976, **15**(8), 1751-1754

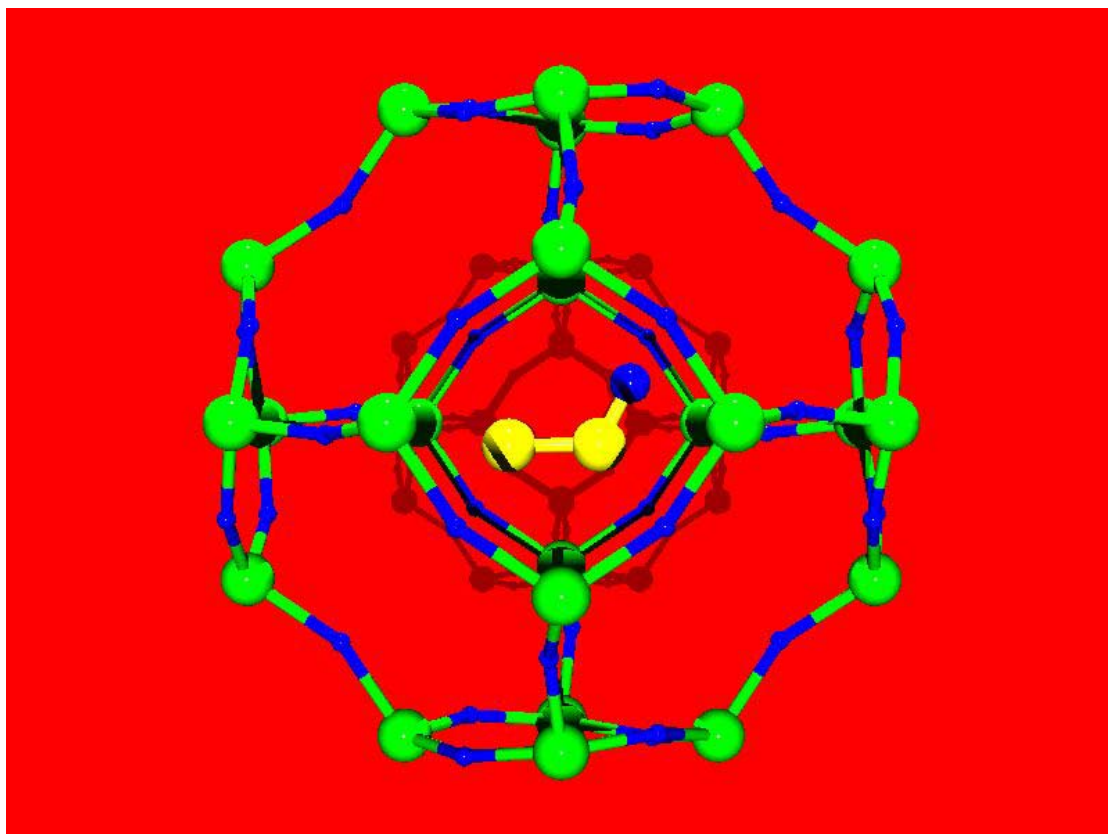
- 36 G.J. Janz, J.W. Coutts, J.R. Downey Jr, E. Roduner, *Inorg. Chem.*, 1976, **15**(8), 1755-1759  
37 P. Hassanzadeh, L. Andrews, *J. Phys. Chem.*, 1992, **96**(16), 6579-6585.  
38 T. Chivers, I. Drummond, *Inorg. Chem.*, 1972, **11**(10) 2525-2527.  
39 *HyperChem Computational Chemistry*, HyperCube Inc, Canada, 1996, p. 158.  
40 W. Koch, J. Natterer, C. Heinemann, *J. Chem. Phys.*, 1995, **102**(15), 6159-6167.  
41 M.C. Gordillo, C.P. Herrero, *J. Phys. Chem.*, 1993, **97**(31), 8310-8315.  
42 C. Heinemann, W. Koch, G-G. Lindner, D. Reinen, *Phys. Rev. A*, 1995, **52**(2), 1024-1038.  
43 D. Hohl, R.O. Jones, R. Car, M. Parrinello, *J. Chem. Phys.*, 1988, **89**(11), 6823-6835.  
44 B. Meyer, K. Spitzer, *J. Phys. Chem.*, 1972, **76**(16), 2274-2279.  
45 F.A. Cotton, J.B. Harmon, R.M. Hedges, *J. Am. Chem. Soc.*, 1976, **98**(6), 1417-1424.  
46 W.G. Laidlaw, M. Trsic, *Chem. Phys.*, 1979, **36**, 323-325.  
47 K. Raghavachari, C.M. Rohlfing, J.S. Binkley, *J. Chem. Phys.*, 1990, **93**(8), 5862-5873.  
48 M. Morin, A.E. Foti, D.R. Salahub, *Can. J. Chem.*, 1985, **63**, 1982-1987.  
49 D.R. Salahub, A.E. Foti, V.H. Smith, Jr, *J. Am. Chem. Soc.*, 1978, **100**(25), 7847-7858.  
50 J.E. Rice, R.D. Amos, N.C. Handy, T.J. Lee, H.F. Schaefer III, *J. Chem. Phys.*, 1986, **85**(2), 963-968.  
51 V.G. Zakrzewski, W. von Niessen, *Theor. Chim. Acta*, 1994, **88**, 75-96.  
52 *HyperChem*, ver. 6.03 for Windows, distributed by HyperCube Inc, 2000.  
53 H. Rau, T.R.N. Kutty, J.R.F. Guedes de Carvalho, *J. Chem. Thermodynamics*, 1973, **5**, 833-844.  
54 L. Pauling, *Proc. Nat. Acad. Sci. USA*, 1949, **35**(9), 495-499.  
55 K. Jug, R. Iffert, *J. Mol. Struct. (Theochem)*, 1989, **186**, 347-359.  
56 W. Von Niessen, P. Tomasello, *J. Chem. Phys.*, 1987, **87**(9), 5333-5337.  
57 J. Berkowitz, W.A. Chupka, *J. Chem. Phys.*, 1969, **50**(10), 4245-4250.

## CHAPTER 6

# **AN *AB INITIO* STUDY OF THE RED CHROMOPHORE IN ULTRAMARINE**

IN

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



## 6. AN *AB INITIO* STUDY OF THE RED CHROMOPHORE IN ULTRAMARINE

### 6.1. Introduction

During the synthesis of ultramarine blue a green intermediate product was obtained. This green species was the result of a yellow chromophore ( $S_2^{2-}$ ) and a blue chromophore ( $S_3^{2-}$ ) present in the zeolite structure.<sup>1-3</sup> Wieckowski and others<sup>4</sup> reported that "[u]ltramarine green can be oxidised to ultramarine blue and ultramarine red, in which sulphur is in a less negative oxidation state than in the blue ultramarine." Violet ultramarine pigments were synthesised from ultramarine blue by reaction with ammonium chloride at approximately 240 °C in the presence of air.<sup>1</sup> A pink product was produced from the violet species by reaction with hydrogen chloride gas at 140 °C.<sup>1</sup> Species containing chloride might, therefore be considered as possible red chromophores in ultramarine. Ultramarine red could be obtained by treating ultramarine violet at 130 - 150 °C with nitric acid vapour. Dilute nitric acid yielded a deeper red colour.<sup>5,6</sup>

Based on the production of  $SO_2$  and  $S_6O_6^{2-}$  when the pigment was dissolved in acids, Hoffmann and others<sup>7</sup> suggested  $S_2O$  to be the chromophore in ultramarine red. Schwarz and Hofmann<sup>8</sup> supported this, based on an average oxidation state of between 1.25 and 1.37 for sulphur in the ultramarine red pigment. The average oxidation state was determined by the sulphur  $K_\alpha$  X-ray fluorescence line. Tang and Brown<sup>9</sup> observed the Raman vibrational frequencies of  $S_2O$  in an Argon matrix at 20 K at 382, 673, and 1 157  $cm^{-1}$ . Clark and Cobbold<sup>2</sup> assigned Raman bands at 352, 653.5, 674, and 1 024  $cm^{-1}$  to the red chromophore. The 1 024  $cm^{-1}$  band was assumed to be a combination of the 352 and 674  $cm^{-1}$  band. Clark and Cobbold<sup>2</sup> concluded that the red chromophore could not be  $S_2O$  and suggested that  $S_4$  was the red chromophore, based on the absorption band for  $S_4$  observed by Meyer and others.<sup>10</sup> Seel and others<sup>11</sup> concluded that the red chromophore was  $S_4$ , based on the size of the cages in the sodalite framework, the number of alkali metal atoms present in the ultramarine red pigment, and the mobility of the suspect species.

To elucidate the nature of the red chromophore the species  $S_3$  (1,2),  $SOS$  (3),  $SOS^-$ ,  $S_2O$  (4),  $S_2O^-$ ,  $S_4$ ,  $S_4^-$ ,  $S_3Cl$ ,  $S_3Cl^-$ , and  $S_2Cl$ <sup>1,2,7,8,11</sup> were examined by molecular

modelling. This set included both open (1),  $C_{2v}$ , and closed (2),  $D_{3h}$ ,  $S_3$  (Figure 5-1), the  $S_4$  isomers with structures of (5) *cis* chain ( $C_{2v}$ ), (6) *gauche* chain ( $C_2$ ), (7) *trans* chain ( $C_{2h}$ ), (8) puckered ring ( $D_{2d}$ ), (9) butterfly ( $D_{2d}$ ), (10) tetrahedral (geometry optimised) ( $D_{2d}$ ), (11) tetrahedral (non geometry optimised) ( $T_d$ ), (12) double triangle ( $D_{4h}$ ), (13) square planar ( $D_{4h}$ ), (14) rectangle ( $D_{2h}$ ), (15) exocyclic ( $C_{2v}$ ), (16) branched chain ( $D_{3h}$ ), (17) pyramidal ( $C_s$ ), (18) bent exocyclic ( $C_s$ ) (Figure 5-2), including the negative ions of these species, *gauche* (19), *cis*, (20) *trans* (21), and branched chain (22)  $S_3Cl$  isomers and their negative ions, as well as  $S_2Cl$  (23) (Figure 6-1).

## 6.2. Experimental data

Experimental data were required as a benchmark for comparison with the modelling studies. Electron paramagnetic resonance showed that the red chromophore was less paramagnetic than the chromophores in ultramarine blue,<sup>7,12</sup> but this was questioned.<sup>13</sup> An electronic absorption band for the ultramarine red occurred at 520 nm.<sup>2,3,7,8,11</sup> Vibrational modes were observed in both infrared ( $1\,210\text{ cm}^{-1}$ )<sup>8</sup> and Raman ( $352, 654, 674$ , and  $1\,024\text{ cm}^{-1}$ )<sup>2,3</sup> spectra.

Phillips and others<sup>14</sup> found that  $S_2O$  had only one transition in the 230 - 600 nm region between 280 and 340 nm, and was colourless. The infrared spectrum of  $S_2O$  contained stretching frequencies at  $679$  and  $1\,165\text{ cm}^{-1}$ <sup>15,16</sup> and a bending vibration at  $388\text{ cm}^{-1}$ .<sup>16</sup> Hopkins and others<sup>17</sup> found infrared absorptions for  $S_2O$  at  $1\,165$ , or  $1\,125\text{ cm}^{-1}$  depending on the matrix in which the spectra were obtained.

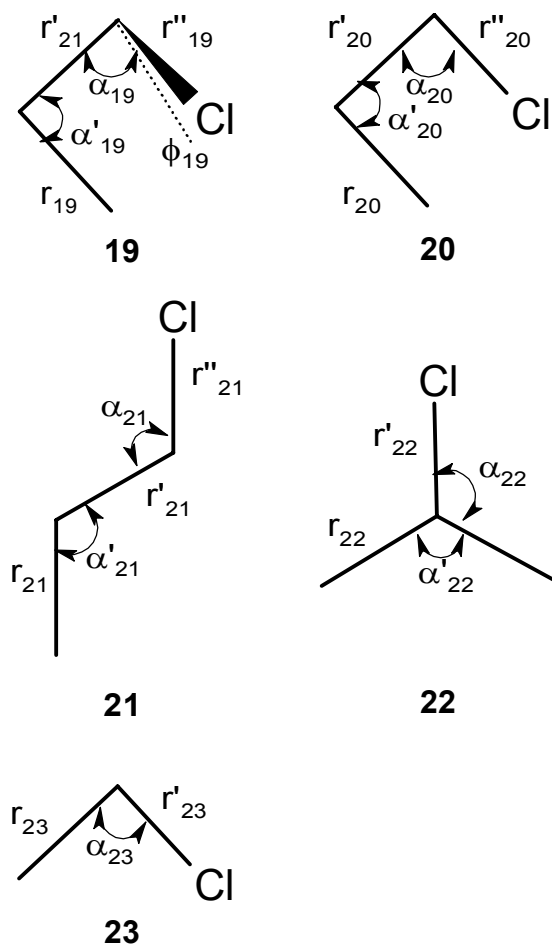


**Figure 6-1:  $S_3Cl$  and  $S_2Cl$  isomers: (19) *Gauche* ( $C_1$ ), (20) *cis* ( $C_s$ ), (21) *trans* ( $C_s$ ), (22) *branched chain* ( $C_s$ ), (23)  $S_2Cl$  ( $C_s$ )**

The neutral  $S_4$  species had an absorption band at 520 nm.<sup>18-21</sup>  $S_4$  had been studied in the vapour phase<sup>18-20,22,23</sup> and in the frozen<sup>10,19,21</sup> state. The results were interpreted in terms of different isomers (Figure 5-2), such as *cis* chain,<sup>18,21</sup> bent exocyclic,<sup>18,22</sup> *gauche* chain,<sup>20</sup> *trans* chain,<sup>20-23</sup> branched chain,<sup>20</sup> puckered ring,<sup>10</sup> or planar ring<sup>10</sup> (Table 6-1).

Brabson and others concluded from the infrared spectrum of  $S_3$  in a solid argon matrix,<sup>21</sup> that the structure of  $S_3$  was the  $C_{2v}$  open geometry, with an angle of  $116 \pm 2^\circ$ . They observed an electronic absorption between 350 and 440 nm with vibrational progressions of 340 and 450  $\text{cm}^{-1}$ , in addition to an infrared band at 680  $\text{cm}^{-1}$  and a Raman vibrational band at 583  $\text{cm}^{-1}$ . Other researchers also observed the vibrational progressions in the electronic spectrum<sup>18,19</sup> and the Raman

spectra.<sup>9</sup> Lenain and others<sup>24</sup> studied the Raman spectra of  $S_3$  and concluded that the  $C_{2v}$  isomer was the observed species, with an absorption maximum at 395 nm and observed Raman bands at 575, 256, and  $656\text{ cm}^{-1}$ .

**Table 6-1: Experimental Characteristics of  $S_4$**

| Reference       | Suggested Structure                                         | Assignment                                     | Infrared<br>$\text{cm}^{-1}$           | Raman<br>$\text{cm}^{-1}$ | UV/Vis<br>nm   |
|-----------------|-------------------------------------------------------------|------------------------------------------------|----------------------------------------|---------------------------|----------------|
| [17]            | None                                                        |                                                |                                        | 668,688<br>601<br>440     |                |
| [22]            | <i>Trans</i>                                                | $\nu_s$<br>$\nu_c$<br>$\delta_s$               |                                        | 678<br>575<br>303         | 530            |
| [18,21]         | <i>Cis</i> and/or <i>trans</i> , or bent exocyclic          | $\nu_{as}$<br>$\delta_{as}$<br>$\tau$          | 662                                    |                           | 518            |
| [22]            | Bent exocyclic                                              | $\nu_{\text{exo ring}}$<br>$\nu_s$<br>$\nu'_s$ |                                        | 635<br>575<br>400         | 560-660        |
| [18,21]<br>[10] | <i>Cis</i> and/or <i>trans</i> , or bent exocyclic<br>Chain |                                                | 642<br>668<br>483<br>320<br>270<br>647 |                           | 560-660<br>530 |
| [19]            | Puckered or planar ring                                     |                                                |                                        |                           |                |
| [23]            | <i>Trans</i>                                                | $\delta_s$<br>$\nu_c$<br>$\nu_s$               |                                        | 303<br>575<br>680         | 530            |

### 6.3. Molecular Modelling

The potential energy surface was inspected for different  $S_4$ ,  $S_4^-$ ,  $S_3$ ,  $S_3\text{Cl}$ , and  $S_3\text{Cl}^-$  isomers in an effort to find the most favourable isomer of each species.

### 6.4. Results

For  $S_3$ , the open (1),  $C_{2v}$ , isomer was calculated to be the most stable, after geometry optimisation (Table 6-2). The calculated vibrational frequencies of the open and closed  $S_3$  isomers discounted both of them as possible chromophores in ultramarine

red (Table 6-3 and Table 6-4), since no infrared vibration is expected above  $1\,200\text{ cm}^{-1}$ . Furthermore, the calculated high frequency bands,  $654$  and  $737\text{ cm}^{-1}$ , were too far apart from each other, to be assigned to the observed bands at  $654$  and  $674\text{ cm}^{-1}$ .<sup>2,3</sup> Neither  $S_3$  isomer had calculated electronic transitions in the expected region (Table 6-5).

The geometries of the  $S_4$  isomers (Figure 5-2) were optimised (Table 6-6). Some isomers were found to be less likely to be observed than others. Diradicals were expected for the chain structures, therefore multiplicities of both 1 and 3 were evaluated for all  $S_4$  species. The *cis* chain (5) geometry optimised to the *gauche* chain (6), which was surprising, in light of the relative energy results (Table 6-7). The butterfly (9) and tetrahedron structures (10,11) optimised to the puckered ring (8) geometry. The double triangle (12) was quantum mechanically equivalent to the square planar (13) structure, indicated by the total charge density plot (Figure 6-2). The exocyclic (15) structure did not yield a proper geometry, but rather seemed to dissociate into two  $S_2$  molecules. Furthermore, the pyramidal branched chain (17) optimised to a structure with an unreasonable charge density distribution. Suitable geometric parameters were chosen for these isomers to reflect the similarity to the other structures that did optimise (Table 6-6).

**Table 6-2: Bond lengths (Å) and bond angles (°)<sup>a</sup> for the geometry of open and closed  $S_3$**

|                                      | Singlet Open $S_3$<br>$C_{2v}$ |            | Singlet<br>Closed $S_3$<br>$D_{3h}$ | $^3B_2$ Open $S_3$<br>$C_{2v}$ |            | $^3A_2$ Open $S_3$<br>$C_{2v}$ |            |
|--------------------------------------|--------------------------------|------------|-------------------------------------|--------------------------------|------------|--------------------------------|------------|
|                                      | $r_3$                          | $\alpha_3$ | $r_4$                               | $r_3$                          | $\alpha_3$ | $r_3$                          | $\alpha_3$ |
| This work                            | 1.90                           | 117        | 2.08                                |                                |            | 1.99                           | 93         |
| Average from literature <sup>b</sup> | 1.98(2)                        | 116.6(7)   | 2.12(2)                             | 2.017                          | 106.8      | 2.00(4)                        | 93(2)      |
| Reference                            | [25-33]                        |            |                                     | [29]                           |            | [26,29]                        |            |

a. The parameters are defined in Figure 5-1

b. The value given is the average from several literature values, the number in brackets denotes one standard deviation of the mean

**Table 6-3: Vibrational frequencies in  $\text{cm}^{-1}$  of open  $S_3$  (1)**

| Mode    | Description           | Symmetry | Rice <sup>32</sup> | Raghavachari<br>MP2/6-31G* <sup>29</sup> | Raghavachari<br>HF/3-21G* <sup>29</sup> | This Work | Spectroscopic<br>Activity <sup>a</sup> |
|---------|-----------------------|----------|--------------------|------------------------------------------|-----------------------------------------|-----------|----------------------------------------|
| $\nu_1$ | Symmetric stretch     | $a_1$    | 668                | 577                                      | 680 (645)                               | 654 (627) | R, IR                                  |
| $\nu_2$ | Bending               | $a_1$    | 287                | 263                                      | 300 (229) <sup>b</sup>                  | 294 (211) | R, IR                                  |
| $\nu_3$ | Antisymmetric stretch | $b_2$    | 769                | 758                                      | 783 (530)                               | 737 (490) | R, IR                                  |

a. R: Raman active, IR: Infrared active

b. Values in brackets are for the triplet state

**Table 6-4: Vibrational frequencies in  $\text{cm}^{-1}$  of closed  $S_3$  (2)**

| Mode    | Description           | Symmetry | Rice <sup>32</sup> | Raghavachari<br>HF/3-21G* <sup>29</sup> | This Work | Spectroscopic<br>Activity <sup>a</sup> |
|---------|-----------------------|----------|--------------------|-----------------------------------------|-----------|----------------------------------------|
| $\nu_1$ | Symmetric deformation | $a_1'$   | 677                | 651                                     | 662       | R                                      |
| $\nu_2$ | Stretch               | $e'$     | 508                | 504                                     | 500       | R, IR                                  |

a. R: Raman active, IR: Infrared active

**Table 6-5: Electronic spectrum of several suspected chromophores in ultramarine red<sup>a</sup>**

| Transition                  | Position<br>nm | Oscillator<br>Strength | Transition                          | Position<br>nm | Oscillator<br>Strength |
|-----------------------------|----------------|------------------------|-------------------------------------|----------------|------------------------|
| <b>S<sub>3</sub> closed</b> |                |                        | <b>S<sub>4</sub> branched</b>       |                |                        |
| 1                           | 462            | 0.00                   | 1                                   | 762            | 0.00                   |
| 2                           | 462            | 0.00                   | 2                                   | 762            | 0.00                   |
| <b>S<sub>3</sub> open</b>   |                |                        | 3                                   | 708            | 0.00                   |
| 1                           | 2862           | 0.00                   | 4                                   | 592            | 0.00                   |
| 2                           | 1003           | 0.00                   | 5                                   | 401            | 0.00                   |
| 3                           | 793            | 0.00                   | 6                                   | 401            | 0.00                   |
| 4                           | 645            | 0.00                   | <b>S<sub>4</sub> cis</b>            |                |                        |
| 5                           | 731            | 0.00                   | 1                                   | -1428          | 0.00                   |
| <b>S<sub>2</sub>O</b>       |                |                        | 2                                   | 1165           | 0.00                   |
| 1                           | 667            | 0.00                   | 3                                   | 983            | 0.00                   |
| 2                           | 575            | 0.00                   | 4                                   | 837            | 0.00                   |
| 3                           | 415            | 0.00                   | 5                                   | 731            | 0.00                   |
| 4                           | 408            | 0.00                   | 6                                   | 697            | 0.00                   |
| <b>SOS</b>                  |                |                        | 7                                   | 499            | 0.34                   |
| 1                           | 602            | 0.00                   | <b>S<sub>4</sub> bent exocyclic</b> |                |                        |
| 2                           | 433            | 0.00                   | 1                                   | 484            | 0.00                   |
| 3                           | 433            | 0.00                   | <b>S<sub>4</sub> puckered ring</b>  |                |                        |
| <b>S<sub>4</sub> trans</b>  |                |                        | 1                                   | 556            | 0.00                   |
| 1                           | -1595          | 0.00                   | 2                                   | 556            | 0.00                   |
| 2                           | 1072           | 0.00                   | 3                                   | 441            | 0.00                   |
| 3                           | 784            | 0.00                   | 4                                   | 420            | 0.01                   |
|                             |                |                        | 5                                   | 420            | 0.01                   |

a. Not all computed transitions are reported

**Table 6-6: Bond lengths (Å) and bond angles (°)<sup>a</sup> for S<sub>4</sub>**

| Structure Number | Structure Name                       | Symmetry        | Structural Parameter     | This Work | Average from literature <sup>b</sup> | References       |
|------------------|--------------------------------------|-----------------|--------------------------|-----------|--------------------------------------|------------------|
| 5                | Singlet <i>cis</i> S <sub>4</sub>    | C <sub>2v</sub> | <i>r</i> <sub>5</sub>    | 2.04      | 1.95(2)                              | [28,29,31,33-36] |
|                  |                                      |                 | <i>r'</i> <sub>5</sub>   | 2.04      | 2.01(2)                              |                  |
|                  |                                      |                 | $\alpha_5$               | 110       | 109(2)                               |                  |
| 6                | Singlet <i>gauche</i> S <sub>4</sub> | C <sub>2</sub>  | <i>r</i> <sub>6</sub>    | 2.04      | 1.99(2)                              | [28,34,36]       |
|                  |                                      |                 | <i>r'</i> <sub>6</sub>   | 2.02      | 2.11(3)                              |                  |
|                  |                                      |                 | $\alpha_6$               | 92        | 105(1)                               |                  |
|                  |                                      |                 | $\phi_6$                 | 99        | 71(12)                               |                  |
| 7                | Singlet <i>trans</i> S <sub>4</sub>  | C <sub>2h</sub> | <i>r</i> <sub>7</sub>    | 1.93      | 1.95(2)                              | [26,29,33-36]    |
|                  |                                      |                 | <i>r'</i> <sub>7</sub>   | 1.97      | 2.01(3)                              |                  |
|                  |                                      |                 | $\alpha_7$               | 110       | 109(1)                               |                  |
| 8                | Puckered ring S <sub>4</sub>         | D <sub>2d</sub> | <i>r</i> <sub>8</sub>    | 2.11      | 2.10(3)                              | [26,29,33-36]    |
|                  |                                      |                 | $\phi_8$                 | 30 (86)   | 33(8) {86.6(5)}                      |                  |
| 11               | Tetrahedral S <sub>4</sub>           | T <sub>d</sub>  | <i>r</i> <sub>11</sub>   | 2.31      | 2.02(3)                              | [28,31]          |
| 13               | Square planar S <sub>4</sub>         | D <sub>4h</sub> | <i>r</i> <sub>13</sub>   | 2.12      | 2.12(5)                              | [28]             |
| 14               | Rectangular planar S <sub>4</sub>    | D <sub>2h</sub> | <i>r</i> <sub>14</sub>   | 2.00      | 1.89(2)                              | [26,29,33-36]    |
|                  |                                      |                 | <i>r'</i> <sub>14</sub>  | 2.50      | 2.538(8)                             |                  |
| 15               | Exocyclic S <sub>4</sub>             | C <sub>2v</sub> | <i>r</i> <sub>15</sub>   | 2.08      |                                      |                  |
|                  |                                      |                 | <i>r'</i> <sub>15</sub>  | 2.08      |                                      |                  |
| 16               | Branched chain S <sub>4</sub>        | D <sub>3h</sub> | <i>r</i> <sub>16</sub>   | 1.91      | 1.95(3)                              | [28,29,31,33-36] |
| 17               | Pyramidal S <sub>4</sub>             | C <sub>s</sub>  | <i>r</i> <sub>17</sub>   | 2.04      | 1.995(5)                             | [33,34]          |
|                  |                                      |                 | $\phi_{17}$              | 97        | 99(1)                                |                  |
| 18               | Bent exocyclic S <sub>4</sub>        | C <sub>s</sub>  | <i>r</i> <sub>18</sub>   | 2.10      | 2.11(2)                              | [33-36]          |
|                  |                                      |                 | <i>r'</i> <sub>18</sub>  | 1.95      | 1.95(2)                              |                  |
|                  |                                      |                 | <i>r''</i> <sub>18</sub> | 2.09      | 2.09(2)                              |                  |
|                  |                                      |                 | $\phi_{18}$              | 105       | 115(3)                               |                  |
| 5                | Triplet <i>cis</i> S <sub>4</sub>    | C <sub>2v</sub> | <i>r</i> <sub>5</sub>    | 2.04      | 2.01(5)                              | [34, 36]         |
|                  |                                      |                 | <i>r'</i> <sub>5</sub>   | 2.04      | 2.22(4)                              |                  |
|                  |                                      |                 | $\alpha_5$               | 110       | 107.8(6)                             |                  |
| 6                | Triplet <i>gauche</i> S <sub>4</sub> | C <sub>2</sub>  | <i>r</i> <sub>6</sub>    | 2.04      | 2.04(5)                              | [29,33,34,36]    |
|                  |                                      |                 | <i>r'</i> <sub>6</sub>   | 2.02      | 2.11(4)                              |                  |
|                  |                                      |                 | $\alpha_6$               | 92        | 105.7(8)                             |                  |
|                  |                                      |                 | $\phi_6$                 | 99        | 88(5)                                |                  |
| 7                | Triplet <i>trans</i> S <sub>4</sub>  | C <sub>2h</sub> | <i>r</i> <sub>7</sub>    | 1.93      | 2.03(3)                              | [34,35]          |
|                  |                                      |                 | <i>r'</i> <sub>7</sub>   | 1.97      | 2.16(3)                              |                  |
|                  |                                      |                 | $\alpha_7$               | 110       | 101.6(6)                             |                  |

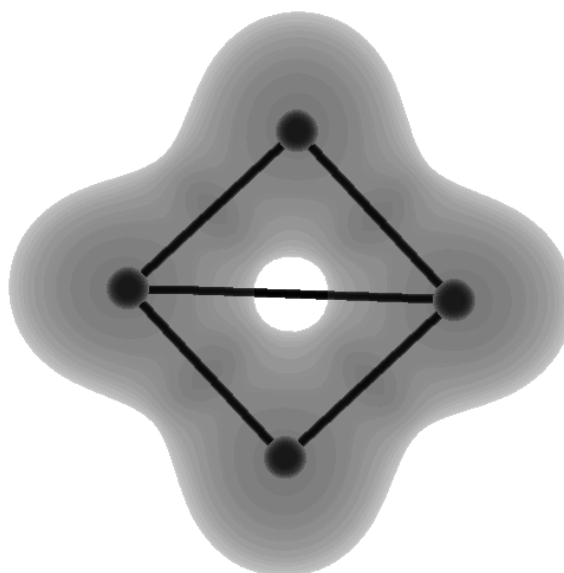
a. The parameters are defined in Figure 5-2

b. The value given is the average from several literature values, the number in brackets denotes one standard deviation of the mean

**Table 6-7: Relative Energy (kJ/mol) results of modelling  $S_4^a$** 

| Structure Number | Spin Multiplicity | Structure Name |                        |
|------------------|-------------------|----------------|------------------------|
| 5                | Singlet           | <i>Cis</i>     | 0                      |
| 6                | Singlet           | <i>Gauche</i>  | 176 (2i <sup>b</sup> ) |
| 7                | Singlet           | <i>Trans</i>   | 29                     |
| 8                | Singlet           | Puckered ring  | 84                     |
| 11               | Singlet           | Tetrahedral    | 649 (3i)               |
| 13               | Singlet           | Square planar  | 117 (i)                |
| 14               | Singlet           | Rectangular    | 272 (i)                |
| 15               | Singlet           | Exocyclic      | 377 (3i)               |
| 16               | Singlet           | Branched chain | 100                    |
| 17               | Singlet           | Pyramidal      | 318 (i)                |
| 18               | Singlet           | Bent exocyclic | 88                     |
| 5                | Triplet           | <i>Cis</i>     | 96 (i)                 |
| 6                | Triplet           | <i>Gauche</i>  | 134                    |
| 7                | Triplet           | <i>Trans</i>   | 213 (i)                |

- a. The energy of the most stable isomer was set equal to zero and the other energies are reported relative to this most stable state  
 b. i indicates that the species has an imaginary frequency

**Figure 6-2: Total charge density plot of the double triangle  $S_4$  isomer (12)**

Based on the presence of negative computed infrared frequencies the tetrahedral (11), square planar (13), rectangular (14), gauche (singlet, 6), exocyclic (15), and pyramidal (17)  $S_4$  isomers could be assigned to transition states. The gauche (6) conformer was a stable minimum in the triplet state. Only six of the proposed twelve  $S_4$  isomers (Figure 5-2) were found to be stable minima by the *ab initio* vibrational analysis, with the 6-311G\*\* basis set at the self-consistent field unrestricted Hartree-Fock level of theory and MP2 correlation energy. The following order of stability for the  $S_4$  isomers was observed (Table 6-7):

*cis* chain (5) > *trans* chain (7) > puckered ring (8) > bent exocyclic (18) > branched chain (16) > gauche chain (triplet, 6).

Apart from the puckered ring (8) (Table 6-8) and *cis* (5)  $S_4$  (Table 6-9) isomers, the stable  $S_4$  isomers all had one vibrational frequency large enough to be considered as the equivalent of the observed Raman bands, but none had two of these high energy vibrations (Tables 6-8 to 6-13). None reached the observed  $1\,210\text{ cm}^{-1}$  of the infrared spectrum.<sup>8</sup>

A Lewis diagram of a four membered chain of sulphur atoms ( $\cdot\ddot{S}:\ddot{S}:\ddot{S}:\ddot{S}\cdot$ ) was sufficient to indicate the diradical nature of the chain.<sup>7,8</sup> Rings, however, were expected to have fully paired electrons.<sup>7,19,28</sup> Despite this *cis* (5)  $S_4$  was the best candidate for the red chromophore, based on a calculated electronic transition at 499 nm (Table 6-5)

**Table 6-8: Vibrational frequencies in  $\text{cm}^{-1}$  of puckered ring  $S_4$  (8)**

| Mode    | Description      | Symmetry | Frequency | Spectroscopic Activity <sup>a</sup> |
|---------|------------------|----------|-----------|-------------------------------------|
| $\nu_1$ | Ring stretch     | $a_1$    | 563       | R                                   |
| $\nu_2$ | Pucker           | $a_1$    | 192       | R                                   |
| $\nu_3$ | Ring deformation | $b_1$    | 532       | R                                   |
| $\nu_4$ | Ring deformation | $b_2$    | 361       | R, IR                               |
| $\nu_5$ | Ring deformation | e        | 509       | R, IR                               |

a. R: Raman active, IR: Infrared active

**Table 6-9: Vibrational frequencies in  $\text{cm}^{-1}$  of singlet cis  $S_4$  (5)**

| Mode    | Description               | Symmetry | Frequency | Spectroscopic Activity <sup>a</sup> |
|---------|---------------------------|----------|-----------|-------------------------------------|
| $\nu_1$ | Central stretch           | $a_1$    | 502       | R, IR                               |
| $\nu_2$ | Symmetric stretch         | $a_1$    | 459       | R, IR                               |
| $\nu_3$ | Symmetric deformation     | $a_1$    | 151       | R, IR                               |
| $\nu_4$ | Torsion                   | $a_2$    | 244       | R                                   |
| $\nu_5$ | Antisymmetric stretch     | $b_2$    | 391       | R, IR                               |
| $\nu_6$ | Antisymmetric deformation | $b_2$    | 322       | R, IR                               |

a. R: Raman active, IR: Infrared active

**Table 6-10: Vibrational frequencies in  $\text{cm}^{-1}$  of singlet branched chain  $S_4$  (16)**

| Mode    | Description           | Symmetry | Frequency | Spectroscopic Activity <sup>a</sup> |
|---------|-----------------------|----------|-----------|-------------------------------------|
| $\nu_1$ | Symmetric stretch     | $a_1'$   | 500       | R                                   |
| $\nu_2$ | Out-of-plane          | $a_2''$  | 282       | IR                                  |
| $\nu_3$ | Antisymmetric stretch | $e'$     | 700       | R, IR                               |
| $\nu_4$ | Symmetric deformation | $e'$     | 272       | R, IR                               |

a. R: Raman active, IR: Infrared active

**Table 6-11: Vibrational frequencies in  $\text{cm}^{-1}$  of trans  $S_4$  (7)**

| Mode    | Description               | Symmetry | Frequency | Spectroscopic Activity <sup>a</sup> |
|---------|---------------------------|----------|-----------|-------------------------------------|
| $\nu_1$ | Symmetric stretch         | $a_g$    | 661       | R                                   |
| $\nu_2$ | Central stretch           | $a_g$    | 596       | R                                   |
| $\nu_3$ | Symmetric deformation     | $a_g$    | 269       | R                                   |
| $\nu_4$ | Torsion                   | $a_u$    | 90        | IR                                  |
| $\nu_5$ | Antisymmetric stretch     | $b_u$    | 557       | IR                                  |
| $\nu_6$ | Antisymmetric deformation | $b_u$    | 160       | IR                                  |

a. R: Raman active, IR: Infrared active

**Table 6-12: Vibrational frequencies in  $\text{cm}^{-1}$  of bent exocyclic  $S_4$  (18)**

| Mode    | Description           | Symmetry | Frequency | Spectroscopic Activity <sup>a</sup> |
|---------|-----------------------|----------|-----------|-------------------------------------|
| $\nu_1$ | Basal stretch         | $a'$     | 622       | R, IR                               |
| $\nu_2$ | Exocyclic stretch     | $a'$     | 563       | R, IR                               |
| $\nu_3$ | Symmetric stretch     | $a'$     | 463       | R, IR                               |
| $\nu_4$ | Wagging               | $a'$     | 245       | R, IR                               |
| $\nu_5$ | Antisymmetric stretch | $a''$    | 427       | R, IR                               |
| $\nu_6$ | Twist                 | $a''$    | 200       | R, IR                               |

a. R: Raman active, IR: Infrared active

**Table 6-13: Vibrational frequencies in  $\text{cm}^{-1}$  of triplet gauche  $\text{S}_4$  (6)**

| Mode    | Description           | Symmetry | Frequency | Spectroscopic Activity <sup>a</sup> |
|---------|-----------------------|----------|-----------|-------------------------------------|
| $\nu_1$ | Central stretch       | a        | 605       | R, IR                               |
| $\nu_2$ | Symmetric stretch     | a        | 508       | R, IR                               |
| $\nu_3$ | Symmetric bend        | a        | 269       | R, IR                               |
| $\nu_4$ | Torsion               | a        | 64        | R, IR                               |
| $\nu_5$ | Antisymmetric stretch | b        | 520       | R, IR                               |
| $\nu_6$ | Antisymmetric bend    | b        | 288       | R, IR                               |

a. R: Raman active, IR: Infrared active

Apart from the gauche  $\text{S}_4$  (6) triplet state, none of the other triplet state  $\text{S}_4$  isomers turned out to be stable minima (Table 6-14). The geometries were not re-optimised for the  $\text{S}_4^-$  isomers. The  $\text{S}_4$  geometries were used (Table 6-15), and these compare well with other data.<sup>33</sup> None of the  $\text{S}_4^-$  isomers (Table 6-16) were characterised as stable minima. This observation implied that  $\text{S}_4^-$  was not supported by *ab initio* computation to be a suitable chromophore in ultramarine red.

After geometry optimisation (Table 6-17), the gauche chain was found to be the most stable isomer for  $\text{S}_3\text{Cl}$  (19, Table 6-18). The branched (22) chain had a substantially higher energy, but was a stable<sup>♦</sup> minimum (Table 6-18). For  $\text{S}_3\text{Cl}^-$ , only the branched chain was a stable minimum (Table 6-18).  $\text{S}_2\text{Cl}$  (23) turned out to be a stable minimum as well. None of the species containing chlorine had computed vibrational frequencies (Tables 6-19 to 6-21) in the region of the observed<sup>2,3</sup>  $654\text{ cm}^{-1}$ , or the  $674\text{ cm}^{-1}$  bands in the Raman spectra of ultramarine red. These species were therefore not suitable candidates as the chromophore in ultramarine red.

<sup>♦</sup> A stable minimum denotes a local or global minimum on the energy surface being inspected and does not include transition states, which are characterised by imaginary minima.

**Table 6-14: Relative energy results of modelling the triplet state of  $S_4^a$** 

| Structure Number | Structure Name                   | Relative Energy kJ/mol |
|------------------|----------------------------------|------------------------|
| 6                | Triplet puckered ring $S_4$      | 121 (2i <sup>b</sup> ) |
| 9                | Triplet tetrahedral $S_4$        | 485 (3i)               |
| 13               | Triplet square planar $S_4$      | 13 (2i)                |
| 14               | Triplet rectangular planar $S_4$ | 0 (4i)                 |
| 15               | Triplet exocyclic $S_4$          | 326 (2i)               |
| 16               | Triplet branched chain $S_4$     | 146 (3i)               |
| 17               | Triplet pyramidal $S_4$          | 142 (i)                |
| 18               | Triplet bent exocyclic $S_4$     | 167 (2i)               |

- a. The energy of the most stable isomer was set equal to zero and the other energies are reported relative to this most stable state  
b. i indicates that the species has an imaginary frequency

**Table 6-15: Bond lengths (Å) and bond angles (°)<sup>a</sup> of  $S_4^-$** 

| Structure Number | Structure Name             | Symmetry | Structural Parameter | Zakrzewski HF/6-31+G <sup>*33</sup> | This Work |
|------------------|----------------------------|----------|----------------------|-------------------------------------|-----------|
| 5                | <i>Cis</i> $S_4^-$         | $C_{2v}$ | $r_5$                | 1.952                               | 2.04      |
|                  |                            |          | $r'_5$               | 2.056                               | 2.04      |
|                  |                            |          | $\alpha_5$           | 114.28                              | 110       |
| 7                | <i>Trans</i> $S_4^-$       | $C_{2h}$ | $r_7$                | 2.016                               | 1.93      |
|                  |                            |          | $r'_7$               | 2.022                               | 1.97      |
|                  |                            |          | $\alpha_7$           | 107.51                              | 110       |
| 14               | Rectangular planar $S_4^-$ | $D_{2h}$ | $r_{14}$             | 1.927                               | 2.00      |
|                  |                            |          | $r'_{14}$            | 2.665                               | 2.50      |
| 16               | Branched chain $S_4^-$     | $D_{3h}$ | $r_{16}$             | 1.990                               | 1.91      |
| 17               | Pyramidal $S_4^-$          | $C_s$    | $r_{17}$             | 2.176                               | 2.04      |
|                  |                            |          | $\phi_{17}$          | 110.93                              | 97        |
| 18               | Bent exocyclic $S_4^-$     | $C_s$    | $r_{18}$             | 2.054                               | 2.10      |
|                  |                            |          | $r'_{18}$            | 2.022                               | 1.95      |
|                  |                            |          | $r''_{18}$           | 2.794                               | 2.09      |
|                  |                            |          | $\phi_{18}$          | 112.87                              | 105       |

- a. The parameters are defined in Figure 5-2

**Table 6-16: Relative Energy results of modelling  $S_4^-$** 

| Structure Number | Structure Name             | Relative Energy kJ/mol <sup>a</sup> | Zakrzewski HF/6-31+G* <sup>b 33</sup> |
|------------------|----------------------------|-------------------------------------|---------------------------------------|
| 5                | <i>Cis</i> $S_4^-$         | 243 (2i)                            |                                       |
| 6                | <i>Gauche</i> $S_4^-$      | 84 (i)                              | ND                                    |
| 7                | <i>Trans</i> $S_4^-$       | 0 (2i)                              |                                       |
| 8                | Puckered square $S_4^-$    | 167 (2i)                            | ND                                    |
| 11               | Tetrahedral $S_4^-$        | 715 (4i)                            | ND                                    |
| 13               | Square planar $S_4^-$      | 163 (3i)                            | ND                                    |
| 14               | Rectangular planar $S_4^-$ | 92 (3i)                             | i                                     |
| 15               | Exocyclic $S_4^-$          | 393 (4i)                            | ND                                    |
| 16               | Branched chain $S_4^-$     | 79 (i)                              | i                                     |
| 17               | Pyramidal $S_4^-$          | 96 (2i)                             | i                                     |
| 18               | Bent Exocyclic $S_4^-$     | 188 (3i)                            | i                                     |

- a. i indicates that the structure has at least one imaginary frequency
- b. The relative energies are not provided in the cited reference, but the result of the vibrational analysis is included

**Table 6-17: Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) of SOS,  $\text{S}_2\text{O}$ ,  $\text{S}_3\text{Cl}$ , and  $\text{S}_2\text{Cl}$** 

| Structure Number | Structure Name                 | Symmetry        | Structural Parameter <sup>a</sup> | This Work |
|------------------|--------------------------------|-----------------|-----------------------------------|-----------|
| 3                | SOS                            | $\text{C}_{2v}$ | $r_3$                             | 1.68      |
|                  |                                |                 | $\alpha_3$                        | 74        |
| 4                | $\text{S}_2\text{O}$           | $\text{C}_s$    | $r'_4$                            | 1.87      |
|                  |                                |                 | $r_4$                             | 1.43      |
|                  |                                |                 | $\alpha_4$                        | 117       |
| 19               | Gauche $\text{S}_3\text{Cl}$   | $\text{C}_1$    | $r_{19}$                          | 2.00      |
|                  |                                |                 | $r'_{19}$                         | 2.05      |
|                  |                                |                 | $r''_{19}$                        | 2.04      |
|                  |                                |                 | $\alpha_{19}$                     | 104       |
|                  |                                |                 | $\alpha'_{19}$                    | 108       |
|                  |                                |                 | $\phi_{19}$                       | 84        |
|                  |                                |                 |                                   |           |
| 20               | Cis $\text{S}_3\text{Cl}$      | $\text{C}_s$    | $r_{20}$                          | 2.00      |
|                  |                                |                 | $r'_{20}$                         | 2.05      |
|                  |                                |                 | $r''_{20}$                        | 2.04      |
|                  |                                |                 | $\alpha_{20}$                     | 104       |
|                  |                                |                 | $\alpha'_{20}$                    | 108       |
| 21               | Trans $\text{S}_3\text{Cl}$    | $\text{C}_s$    | $r_{21}$                          | 2.00      |
|                  |                                |                 | $r'_{21}$                         | 2.05      |
|                  |                                |                 | $r''_{21}$                        | 2.04      |
|                  |                                |                 | $\alpha_{21}$                     | 104       |
|                  |                                |                 | $\alpha'_{21}$                    | 108       |
| 22               | Branched $\text{S}_3\text{Cl}$ | $\text{C}_s$    | $r_{22}$                          | 2.04      |
|                  |                                |                 | $r'_{22}$                         | 2.01      |
|                  |                                |                 | $\alpha_{22}$                     | 92        |
|                  |                                |                 | $\alpha'_{22}$                    | 92        |
| 23               | $\text{S}_2\text{Cl}$          | $\text{C}_s$    | $r_{23}$                          | 1.95      |
|                  |                                |                 | $r'_{23}$                         | 2.05      |
|                  |                                |                 | $\alpha_{23}$                     | 108       |

a. The parameters are defined in Figures 5-1 and 6-1

**Table 6-18: Relative energy results of modelling S<sub>2</sub>O, SOS, S<sub>3</sub>Cl, and S<sub>3</sub>Cl<sup>-</sup>**

| Structure Number | Structure Name                                      | Relative Energy kJ/mol <sup>a</sup> |
|------------------|-----------------------------------------------------|-------------------------------------|
| 3                | SOS singlet                                         | 256                                 |
| 4                | S <sub>2</sub> O singlet                            | 69                                  |
| 3                | SOS triplet                                         | 526 (i <sup>b</sup> )               |
| 4                | S <sub>2</sub> O triplet                            | 313                                 |
| 3                | SOS <sup>-</sup>                                    | 313 (i)                             |
| 4                | S <sub>2</sub> O <sup>-</sup>                       | 0                                   |
| 19               | Gauche S <sub>3</sub> Cl                            | 0                                   |
| 20               | <i>Cis</i> S <sub>3</sub> Cl                        | 180 (3i)                            |
| 21               | <i>Trans</i> S <sub>3</sub> Cl                      | 29 (i)                              |
| 22               | Branched S <sub>3</sub> Cl                          | 163                                 |
| 19               | Singlet gauche S <sub>3</sub> Cl <sup>-</sup>       | -151 (i)                            |
| 20               | Singlet <i>cis</i> S <sub>3</sub> Cl <sup>-</sup>   | -79 (i)                             |
| 21               | Singlet <i>trans</i> S <sub>3</sub> Cl <sup>-</sup> | -100 (i)                            |
| 22               | Singlet branched S <sub>3</sub> Cl <sup>-</sup>     | 0                                   |
| 19               | Triplet gauche S <sub>3</sub> Cl <sup>-</sup>       | 59 (2i)                             |
| 20               | Triplet <i>cis</i> S <sub>3</sub> Cl <sup>-</sup>   | 29 (2i)                             |
| 21               | Triplet <i>trans</i> S <sub>3</sub> Cl <sup>-</sup> | 33 (3i)                             |
| 22               | Triplet branched S <sub>3</sub> Cl <sup>-</sup>     | 184 (2i)                            |

a. The energy of the most stable isomer was set equal to zero for each subgroup and the other energies are reported relative to this most stable state for that subgroup

b. i indicates that the species has an imaginary frequency

**Table 6-19: Vibrational frequencies in cm<sup>-1</sup> of branched S<sub>3</sub>Cl (22)**

| Mode           | Description               | Symmetry | Doublet S <sub>3</sub> Cl | Singlet S <sub>3</sub> Cl <sup>-</sup> | Spectroscopic Activity <sup>a</sup> |
|----------------|---------------------------|----------|---------------------------|----------------------------------------|-------------------------------------|
| v <sub>1</sub> | S-S(-S) symmetric stretch | a''      | 524                       | 479                                    | R, IR                               |
| v <sub>2</sub> | S-Cl stretch              | a'       | 562                       | 556                                    | R, IR                               |
| v <sub>3</sub> | S-S-S bending             | a'       | 37                        | 259                                    | R, IR                               |
| v <sub>4</sub> | Symmetric deformation     | a'       | 293                       | 292                                    | R, IR                               |
| v <sub>5</sub> | Antisymmetric deformation | a''      | 409                       | 459                                    | R, IR                               |
| v <sub>6</sub> | S-S-Cl bending            | a''      | 238                       | 237                                    | R, IR                               |

a. R: Raman active, IR: Infrared active

**Table 6-20: Vibrational frequencies in  $\text{cm}^{-1}$  of singlet gauche  $\text{S}_3\text{Cl}^-$  (19)**

| Mode    | Description                        | Symmetry | Frequency | Spectroscopic Activity <sup>a</sup> |
|---------|------------------------------------|----------|-----------|-------------------------------------|
| $\nu_1$ | S-S and S-Cl antisymmetric stretch | a        | 558       | R, IR                               |
| $\nu_2$ | S-S and S-Cl symmetric stretch     | a        | 549       | R, IR                               |
| $\nu_3$ | Central stretch                    | a        | 518       | R, IR                               |
| $\nu_4$ | Antisymmetric bend                 | a        | 257       | R, IR                               |
| $\nu_5$ | Symmetric bend                     | a        | 196       | R, IR                               |
| $\nu_6$ | Torsion                            | a        | 64        | R, IR                               |

a. R: Raman active, IR: Infrared active

**Table 6-21: Vibrational frequencies in  $\text{cm}^{-1}$  of  $\text{S}_2\text{Cl}^-$  (23)**

| Mode    | Description  | Symmetry | Frequency | Spectroscopic Activity <sup>a</sup> |
|---------|--------------|----------|-----------|-------------------------------------|
| $\nu_1$ | S-S stretch  | $a'$     | 578       | R, IR                               |
| $\nu_2$ | S-Cl stretch | $a'$     | 530       | R, IR                               |
| $\nu_3$ | Bending      | $a'$     | 241       | R, IR                               |

a. R: Raman active, IR: Infrared active

The experimental geometry for  $\text{S}_2\text{O}^-$  was determined from the microwave spectrum to be  $r(\text{S-O}) = 1.46 \text{ \AA}$ ,  $r(\text{S-S}) = 1.88 \text{ \AA}$  and the S-S-O angle to be  $118^\circ$ ,<sup>37</sup> which compared well with the currently determined geometry ( $1.43 \text{ \AA}$ ,  $1.87 \text{ \AA}$ ,  $117^\circ$ ) (Table 6-17).  $\text{S}_2\text{O}^-$  was determined to be the most stable  $\text{S}_2\text{O}$  structure (Table 6-18) with vibrational frequencies larger than expected (Table 6-22). The calculated vibrational bands for  $\text{S}_2\text{O}$  (Table 6-22) were scaled by a factor of 0.87 as suggested by Brabson and others.<sup>21</sup> This procedure yielded vibrational transitions at 382, 666, and  $1\,180 \text{ cm}^{-1}$ , in close agreement with three of the four observed bands for the ultramarine red chromophore.  $\text{S}_2\text{O}$  was, however, predicted to be colourless (Table 6-5), and was observed to be colourless.<sup>11,14</sup> The SOS possibility was also negated by its vibrational frequencies (Table 6-23).

**Table 6-22: Vibrational frequencies in  $\text{cm}^{-1}$  of  $\text{S}_2\text{O}^-$  (4)**

| Mode    | Description | Symmetry | Doublet $\text{S}_2\text{O}^-$ | Singlet $\text{S}_2\text{O}$ | Triplet $\text{S}_2\text{O}$ | Spectroscopic Activity <sup>a</sup> |
|---------|-------------|----------|--------------------------------|------------------------------|------------------------------|-------------------------------------|
| $\nu_1$ | S-O stretch | $a'$     | 1401                           | 1357                         | 1342                         | R, IR                               |
| $\nu_2$ | S-S stretch | $a'$     | 796                            | 766                          | 742                          | R, IR                               |
| $\nu_3$ | Bending     | $a'$     | 344                            | 440                          | 154                          | R, IR                               |

a. R: Raman active, IR: Infrared active

**Table 6-23: Vibrational frequencies in  $\text{cm}^{-1}$  of singlet SOS (3)**

| Mode    | Description           | Symmetry | Frequency | Spectroscopic Activity <sup>a</sup> |
|---------|-----------------------|----------|-----------|-------------------------------------|
| $\nu_3$ | Bending               | $a_1$    | 592       | R, IR                               |
| $\nu_2$ | Antisymmetric stretch | $b_2$    | 657       | R, IR                               |
| $\nu_1$ | Symmetric stretch     | $a_1$    | 907       | R, IR                               |

a. R: Raman active, IR: Infrared active

#### 6.4.1. Modelling the Cavities in the Ultramarine Structure

The volumes of the cavities of the  $\beta$ -cage of ultramarine blue,<sup>38</sup> and several sodalite structures, which also contain  $\beta$ -cages,<sup>39-43</sup> were calculated using the method and atomic-ionic radii of Gavezzotti,<sup>44</sup> Bondi<sup>45</sup> and Shannon.<sup>46</sup> The details of the computer algorithm can be found in Appendix A2. The volumes of the sulphur species considered (Table 6-24) were smaller than the volumes of the cavities in the sodalite structure (Table 6-25). The volumes of the cavities were calculated taking the counter ions into account, and represent the maximum volume available to the chromophore. The small percentage difference for the volumes calculated by the HyperChem Quantitative Structure-Activity Relationships (QSAR) and the current method indicated the reliability of the current method (Tables 6-24 and 6-25). The volume of the crystal cavity was approximated as a truncated octahedron in the crystal structure, by Equation 6-1:

$$V = \frac{2}{9} [4a^2b + 3a^2c - 2b^3] \quad (6-1)$$

with

$V$ : volume of the truncated octahedron as an approximation of the available volume in sodalite structures, assuming that the octahedron was formed by two regular square pyramids and that the truncation was done by subtracting a smaller regular square pyramid from the octahedron.

$a$ : distance between two tetrahedral atoms on opposite sides of the six-membered tetrahedral ring, the size of the base of the original octahedron.

$b$ : distance between two tetrahedral atoms on opposite sides of the four-membered tetrahedral ring, the size of the base of the subtracted octahedron.

$c$ : distance between the base plane of the original octahedron and the base plane of the subtracted octahedron.

**Table 6-24: Volume ( $\text{\AA}^3$ ) of the modelled species**

| Structure Number | Molecule             | QSAR <sup>a</sup> | This Work | Difference % QSAR |
|------------------|----------------------|-------------------|-----------|-------------------|
| 1                | Open $S_3$           | 61.300            | 61.00     | 0.5               |
| 2                | Closed $S_3$         | 59.485            | 59.21     | 0.5               |
| 3                | SOS                  | 47.633            | 47.42     | 0.4               |
| 4                | $S_2O$               | 47.299            | 47.07     | 0.5               |
| 5                | <i>Cis</i> $S_4$     | 80.363            | 79.99     | 0.5               |
| 6                | Gauche $S_4$         | 79.717            | 80.12     | -0.5              |
| 7                | <i>Trans</i> $S_4$   | 78.433            | 78.10     | 0.4               |
| 9                | Puckered ring $S_4$  | 78.433            | 76.47     | 2.5               |
| 10               | Tetrahedral $S_4$    | 77.733            | 77.54     | 0.3               |
| 13               | Square $S_4$         | 77.122            | 76.74     | 0.5               |
| 14               | Rectangular $S_4$    | 79.751            | 79.39     | 0.5               |
| 15               | Exocyclic $S_4$      | 78.034            | 77.68     | 0.4               |
| 16               | Branched $S_4$       | 77.556            | 77.19     | 0.5               |
| 17               | Pyramidal $S_4$      | 80.302            | 79.98     | 0.4               |
| 18               | Bent exocyclic $S_4$ | 77.229            | 76.99     | 0.3               |
| 19               | Gauche $S_3Cl$       | 79.271            | 78.99     | 0.4               |
| 20               | <i>Cis</i> $S_3Cl$   | 78.886            | 78.50     | 0.5               |
| 21               | <i>Trans</i> $S_3Cl$ | 79.263            | 78.90     | 0.5               |
| 22               | Branched $S_3Cl$     | 78.416            | 78.08     | 0.4               |
| 23               | $S_2Cl$              | 60.293            | 60.04     | 0.4               |

a. QSAR: Quantitative Structure-Activity Relationships in HyperChem<sup>47</sup>

## 6.5. Discussion

The optimised geometries for the different isomers of  $S_3$  (1,2) fell within the range of previously determined geometrical parameters (Table 6-2).<sup>25-33</sup> The calculated vibrational frequencies were similar to those of previous studies.<sup>29,32</sup> The question of whether the open,  $C_{2v}$ ,<sup>25,26,29,30,32,33</sup> or closed,  $D_{3h}$ ,<sup>32,33,35,48,49</sup>  $S_3$  isomer was the more stable seemed to be an open one, since, depending on the methodology applied to the problem, several methods gave contradictory results. The open (1),  $C_{2v}$ ,  $S_3$  isomer was calculated to be the most stable isomer in this work. The fact that the closed (2),  $D_{3h}$ ,  $S_3$  isomer had an energy only 42 kJ/mol higher than the open isomer, suggested that both these isomers should be observable at approximately 723 K.<sup>50,51</sup>

**Table 6-25: Approximations of the volumes ( $\text{\AA}^3$ ) of the cavities in sodalite structures**

|                               | Ref  | This Work    |                              |               | QSAR    | Difference (%) | Crystal Structure <sup>a</sup> |
|-------------------------------|------|--------------|------------------------------|---------------|---------|----------------|--------------------------------|
|                               |      | Total volume | Volume occupied by the atoms | Cavity volume |         |                |                                |
| AM1 Cage Si <sup>b</sup>      |      | 1014.21      | 840.83                       | 184.00        | 844.92  | 0.5            | 231.1                          |
| AM1 Cage Al <sup>c</sup>      |      | 1324.59      | 1196.76                      | 139.12        | 1202.56 | 0.5            | 231.1                          |
| Modified Tarling <sup>d</sup> | [38] | 1323.17      | 1208.37                      | 126.07        | 1215.15 | 0.6            | 215.8                          |
| Nielsen                       | [39] | 1195.83      | 1060.83                      | 146.20        | 1066.07 | 0.5            | 227.4                          |
| Nielsen                       | [39] | 1181.91      | 1053.60                      | 139.44        | 1059.15 | 0.5            | 221.6                          |
| Nielsen                       | [39] | 1172.18      | 1048.84                      | 134.40        | 1054.21 | 0.5            | 217.5                          |
| Felsche                       | [42] | 1169.25      | 1045.47                      | 135.27        | 1050.48 | 0.5            | 213.1                          |
| Löns                          | [43] | 1168.57      | 1047.87                      | 131.82        | 1053.15 | 0.5            | 217.0                          |
| Werner                        | [41] | 1117.95      | 1017.64                      | 110.60        | 1022.89 | 0.5            | 198.9                          |
| Werner                        | [41] | 1136.75      | 1028.52                      | 118.79        | 1033.36 | 0.5            | 205.2                          |
| Werner                        | [41] | 1150.24      | 1036.56                      | 124.43        | 1041.56 | 0.5            | 209.8                          |
| Werner                        | [41] | 1171.47      | 1048.66                      | 133.86        | 1054.32 | 0.5            | 217.1                          |
| Mead                          | [40] | 1195.68      | 1059.83                      | 147.24        | 1066.04 | 0.6            | 226.5                          |
| Mead                          | [40] | 1199.59      | 1061.47                      | 149.53        | 1066.79 | 0.5            | 228.4                          |
| Mead                          | [40] | 1196.62      | 1060.02                      | 148.05        | 1065.80 | 0.5            | 226.6                          |
| Mead                          | [40] | 1203.93      | 1063.55                      | 151.85        | 1068.64 | 0.5            | 230.0                          |

- The volume of the cavity in the crystal structure was approximated as a truncated octahedron, Equation 6-1.
- The AM1 semi-empirical method of HyperChem was used to model the cage structure, where all the tetrahedral atoms were silicon atoms.
- The same structure as b, but the silicon atoms were replaced by aluminium atoms.
- The structure of Tarling and others,<sup>38</sup> was modified so that all the tetrahedral atoms were the larger aluminium atoms.

The bond angles of the gauche  $S_4$  chain (6) were determined to be smaller than the angles presented in the literature, whereas the dihedral angle was determined to be larger<sup>28,34,36</sup> (Table 6-6). The angle made by the external sulphur-sulphur bond with the ring for the bent exocyclic (18) isomer was determined to be smaller than in the literature,<sup>29,33-35</sup> but comparable with the value determined by Kao<sup>36</sup> (Table 6-6). The other geometries of the other isomers compared well with those determined in the literature<sup>26,28,29,33-36</sup> (Table 6-6). The correspondence between the geometries (Table 6-6) was also reflected in the agreement of the vibrational frequencies (Tables 6-9 to 6-12).<sup>21,34</sup> Again the gauche chain parameters deviated most from the literature values.<sup>29,34</sup> The exocyclic stretching frequency of the bent exocyclic isomer was affected by the different geometries (Table 6-13).<sup>22,34</sup> The slightly longer bond distances in the currently calculated geometry of the *cis* (5) chain was reflected in a large difference in the calculated stretching frequencies (Table 6-9).<sup>29,34</sup>

Several  $S_4$  isomers had in the past been calculated to be the most stable isomer, they were *cis* (5) chain,<sup>29,31,33,34,52</sup> puckered ring (8),<sup>35,52</sup> branched chain (16),<sup>28</sup> gauche chain (Triplet, 6),<sup>36</sup> and rectangular (14) (Table 6-7).<sup>26,29</sup> The disparity in relative energy results for  $S_4$  (Table 6-7) could be related to the slightly different geometries considered (Table 6-6). The rectangular (14)  $S_4$  isomer could not be considered as a stable minimum, because the current analysis showed it to be a transition state. Other researchers confirmed this conclusion.<sup>29,33,34</sup>

According to the computed energy of the *cis* (5) and *trans* (7) chain  $S_4$  species (Table 6-7), both species were expected to be present in the vapour phase, since the energy difference between these species was only 29 kJ/mol, compared to the 42 kJ/mol estimated for species that contribute to the occurrence of  $S_4$  species at 673 to 1 173 K.<sup>50,51</sup> The simultaneous occurrence was supported by experimental conjecture.<sup>18,21</sup>

The application of only a single determinant unduly favours triplet states.<sup>36</sup> Unfortunately no configuration interaction was allowed for the triplet state in the current investigation. This limitation did not seem to be a problem in the current computations, since most of the triplet states were transition states. The gauche chain triplet was a stable minimum, but was not considered as the most stable structure. A higher level of theory might refute this conclusion.

The lack of a stable tetrahedral state (11) was predicted by the concerted reaction approach of Landman and De Waal (Appendix F).<sup>53</sup> Only the *trans* (7), *cis* (5), branched (16), gauche chain (6), puckered ring (8) and bent exocyclic (18) isomers for  $S_4$ , stood the test of the vibrational analysis. The last three corresponded to structures that withstood the Woodward-Hoffmann analysis, although with the 6-311G\*\* basis set the bent exocyclic structure was ruled out (Chapter 5). The *trans* (7) and *cis* (5) chains were conformers of the Woodward-Hoffmann allowed gauche chain (6), whereas the branched chain (16) was the more stable conformer of the Woodward-Hoffmann allowed pyramidal structure (17).

Wong and Steudel<sup>54</sup> used several quantum mechanical methods and concluded that *cis* (5)  $S_4$  had a visible absorption at 527/525 nm in close agreement with the observed value of 520-530 nm<sup>18-21</sup> (Table 6-1), and the current calculated value of 490 nm (Table 6-5).

## 6.6. Conclusion

The relative volumes of the suspected chromophore species and the cavities available in the  $\beta$ -cages of the aluminosilicate framework, taking the counter ions into account, did not exclude any of the species from being a possible chromophore.

On vibrational spectroscopic grounds the  $S_4$  isomers did not correspond too well with the chromophore in ultramarine red. Due to the diradical nature of sulphur chains,<sup>8,7</sup> the linear chain isomers of  $S_4$  were not regarded as acceptable chromophores, since the chromophore was known to be diamagnetic.<sup>7,12</sup> However, the *cis* (5)  $S_4$  chain ( $C_{2v}$ ) had a calculated electronic transition at 499 nm (Table 6-5), which made it the only possible red chromophore, based on electronic transition, which was the primary consideration.

In *ab initio* computations the  $S_4^-$  isomers did not represent stable minima (Table 6-16) and were therefore not predicted to be suitable chromophores in ultramarine red.

None of the chlorine containing species (19-23) had computed vibrational frequencies (Tables 6-19 to 6-21) in the region of the observed<sup>2,3</sup> Raman bands of ultramarine red, and were not regarded as viable options for the ultramarine red chromophore. The current vibrational analysis of the open (1) and closed (2)  $S_3$  isomers and  $SOS$  (3) and  $S_2O$  (4) discounted them as possible chromophores in ultramarine red (Tables 6-3, 6-4, 6-22 and 6-23).

The scaled calculated vibrational frequencies for  $S_2O$  (4) were 382, 666, and 1 180  $cm^{-1}$ . These values were in close agreement with the observed bands for the ultramarine red chromophore. On these grounds  $S_2O$  was a likely chromophore in ultramarine red as suggested before.<sup>8</sup> However,  $S_2O$  is a colourless gas.<sup>14</sup> Since the

aluminosilicate framework was more likely to influence vibrational, rather than electronic spectra, the *cis* S<sub>4</sub> species, with a computed electronic transition at 499 nm, was still the best candidate as red chromophore.

## REFERENCES

- 1 W.B. Cork, *Ultramarine pigments*, in: *Industrial Inorganic Pigments*, G Buxbaum (ed), 1993, p. 124-132.
- 2 R.J.H. Clark, D.G. Cobbold, *Inorg. Chem.*, 1978, **17**(11), 3169-3174.
- 3 R.J.H. Clark, T.J. Dines, M. Kurmoo, *Inorg. Chem.*, 1983, **22**, 2766-2772.
- 4 A.B. Wieckowski, W. Wojtowicz, J. Sliwa-Niesciór, *Magn. Reson. Chem.*, 1999, **37**, 150-153.
- 5 J. Zeltner, *Verfahren zur Herstellung einer rothen Ultramarinfarbe*, final patent no. 1, German, 29 November 1877.
- 6 R. Faust, G. Knaus, U. Siemelung, *World Records in Chemistry*, translated by W.E. Russey, First, Wiley-VCH, Weinheim, 1991, p. 182.
- 7 U. Hofmann, E. Herzenstiel, E. Schonemann, K-H. Schwarz, *Z. anorg. allg. chem.*, 1969, **367**, 119-129.
- 8 K-H. Schwarz, U. Hofmann, *Z. anorg. allg. Chem.*, 1970, **378**, 152-159.
- 9 S-Y. Tang, C.W. Brown, *Inorg. Chem.*, 1975, **14**(11), 2856-2858.
- 10 B. Meyer, T. Stroyer-Hansen, *J. Phys. Chem.*, 1972, **76**(26), 3968-3969.
- 11 F. Seel, H-J. Güttler, A.B. Wiecowski, B. Wolf, *Z. Naturforsch.*, 1979, **34b**, 1671-1677.
- 12 J. Klinowski, S.W. Carr, S.E. Tarling, P. Barnes, *Nature*, 1987, **330**, 56-58.
- 13 N. Gobeltz-Hautecoeur, A. Domortier, B. Lede, J.P. Lelieur, C. Duhayon, *Inorg. Chem.*, 2002, **41**(11), 2848-2854.
- 14 L.F. Phillips, J.J. Smith, B. Meyer, *J. Mol. Spectrosc.*, 1969, **29**, 230-234.
- 15 A.V. Jones, *J. Chem. Phys.*, 1950, **18**(9), 1263-1268.
- 16 U. Blukis, R.J. Myers, *J. Phys. Chem.*, 1965, **69**(4), 1154-1156.
- 17 A.G. Hopkins, S-Y. Tang, C.W. Brown, *J. Am. Chem. Soc.*, 1973, **95**(11), 3486-3494.
- 18 P. Hassanzadeh, L. Andrews, *J. Phys. Chem.*, 1992, **96**(16), 6579-6585.
- 19 B. Meyer, T. Stroyer-Hansen, T.V. Oommen, *J. Mol. Spectrosc.*, 1972, **42**, 335-343.
- 20 B. Meyer, M. Gouterman, D. Jensen, T.V. Oommen, K. Spitzer, T. Stroyer-Hansen, *The Spectrum of Sulfur and its Allotropes*, In: *Sulfur Trands, Advances in Chemistry series*, vol. 110, American Chemical Society, Washington, 1971, p. 53-71.
- 21 G.D. Brabson, Z. Mielke, L. Andrews, *J. Phys. Chem.*, 1991, **95**(1), 79-86.
- 22 M.S. Boumedien, J. Corset, E. Picquenard, *J. Raman Spectrosc.*, 1999, **30**, 463-472.
- 23 E. Picquenard, M.S. Boumedien, J. Corset, *J. Mol. Struct.*, 1993, **293**, 63-66.
- 24 P. Lenain, E. Picquenard, J.L. Lesne, J. Corset, *J. Mol. Struct.*, 1986, **142**, 355-358.
- 25 W. Koch, J. Natterer, C. Heinemann, *J. Chem. Phys.*, 1995, **102**(15), 6159-6167.
- 26 D. Hohl, R.O. Jones, R. Car, M. Parrinello, *J. Chem. Phys.*, 1988, **89**(11), 6823-6835.
- 27 W.G. Laidlaw, M. Trsic, *Chem. Phys.*, 1979, **36**, 323-325.
- 28 B. Meyer, K. Spitzer, *J. Phys. Chem.*, 1972, **76**(16), 2274-2279.
- 29 K. Raghavachari, C.M. Rohlifing, J.S. Binkley, *J. Chem. Phys.*, 1990, **93**(8), 5862-5873.
- 30 M. Morin, A.E. Foti, D.R. Salahub, *Can. J. Chem.*, 1985, **63**, 1982-1987.
- 31 D.R. Salahub, A.E. Foti, V.H. Smith, Jr, *J. Am. Chem. Soc.*, 1978, **100**(25), 7847-7858.
- 32 J.E. Rice, R.D. Amos, N.C. Handy, T.J. Lee, H.F. Schaefer III, *J. Chem. Phys.*, 1986, **85**(2), 963-968.
- 33 V.G. Zakrzewski, W. von Niessen, *Theor. Chim. Acta*, 1994, **88**, 75-96.
- 34 G.E. Quelch, H.F. Schaefer III, C.J. Marsden, *J. Am. Chem. Soc.*, 1990, **112**(24), 8719-8733.
- 35 K. Jug, R. Iffert, *J. Mol. Struct. (Theochem)*, 1989, **186**, 347-359.
- 36 J. Kao, *Inorg. Chem.*, 1977, **16**(8), 2085-2089.
- 37 D.J. Meschi, R.J. Myers, *J. Mol. Spectrosc.*, 1959, **3**, 405-416.
- 38 S.E. Tarling, P. Barnes, J. Klinowski, *Acta Cryst.*, 1988, **B44**, 128-135.
- 39 N.Chr. Nielsen, H. Bildsoe, H.J. Jakobsen, P. Norby, *Zeolites*, 1991, **11**, 622-632.
- 40 P.J. Mead, M.T. Weller, *Zeolites*, 1995, **15**, 561-568.
- 41 S. Werner, S. Barth, R. Jordan, H. Schulz, *Z. Kristallogr.*, 1996, **211**, 158-162.

- 
- 42 J. Flesche, S. Luger, P. Fischer, *Acta Cryst.*, 1987, **C43**, 809-811.  
43 J. Lons, H. Schulz, *Acta Cryst.*, 1967, **23**, 434-436.  
44 A. Gavezotti, *J. Am. Chem. Soc.*, 1983, **105** (16), 5220.  
45 A. Bondi, *J. Phys. Chem.*, 1964, **68** (3), 441-451.  
46 R.D. Shannon, *Acta Cryst.*, 1976, **A32**, 751-767.  
47 *HyperChem*, ver. 6.03 for Windows, distributed by HyperCube Inc, 2000.  
48 W. Von Niessen, P. Tomasello, *J. Chem. Phys.*, 1987, **87**(9), 5333-5337.  
49 C. Heinemann, W. Koch, G-G. Lindner, D. Reinen, *Phys. Rev. A*, **52**(2), 1024-1038, (1995).  
50 H. Rau, T.R.N. Kutty, J.R.F. Guedes de Carvalho, *J. Chem. Thermodynamics*, 1973, **5**, 833-844.  
51 L. Pauling, *Proc. Nat. Acad. Sci. USA*, 1949, **35**(9), 495-499.  
52 W. Von Niessen, *J. Chem. Phys.*, 1991, **95**(11), 8301-8308.  
53 A.A. Landman, D. De Waal, *Crystal Engineering*, 2001, **4**, 159-169.  
54 M.W. Wong, R. Steudal, *Chem. Phys Lett.*, 2003, **379**, 162-169.

# **CHAPTER 7**

## **SUGGESTIONS FOR FURTHER INVESTIGATION**

IN

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



## 7. SUGGESTIONS FOR FURTHER INVESTIGATION

Most of the suggestions in this section are supported by preliminary studies and results. These are routes not taken in the final assembly of this report on PhD research.

### 7.1. The Spectroscopy of Silicates

Two-dimensional spectroscopy, peak fitting and cluster analysis can aid in the understanding of the convoluted infrared spectra of aluminosilicates. This would facilitate the further elucidation of the solid-state chemistry of fly ash and its potential uses.

### 7.2. Ultramarine Blue

The successful synthesis of ultramarine blue was reported (Chapter 3). The reactivity and chemical potential of fly ash could be estimated by several experiments related to the spectroscopic methods established in this work, thereby estimating the feasibility of using fly ash in different reactions for the synthesis of other chemical species.

#### 7.2.1. Industrial Process for the Synthesis of Ultramarine Blue

The large-scale production of ultramarine blue was a time- and energy-intensive process, and great care needed to be taken to ensure the success of the reaction.<sup>1</sup> Pretorius<sup>2</sup> explained that an ideal recipe for the preparation of pigment material should have had the following properties:

- homogeneous pigment cake, same pigment colour and strength throughout the pigment cake
- firing time is independent of the crucible depth, cannot over-calcine the pigment, or in the case of ultramarine cannot over-oxidise the pigment
- minimum dopant for maximum colour
- water dispersible pigment cake
- fine pigment particles
- no excess starting reagents.

Harden<sup>3</sup> promoted a greater understanding of ceramic pigments in order to facilitate the design of pigments for specific applications, taking into account both technical and economical aspects. These considerations were important in the optimising of any pigment synthesis process.

#### **7.2.1.1. Laboratory Preparation and Optimisation**

The temperature and time needed for the formation of ultramarine pigments still need to be optimised. The composition was not optimised, because this was deemed to be close to optimum. Some changes were, however, made to the literature reaction mix. On the basis of the reaction mechanism one can predict the theoretical maximum amount of sulphur that can be accommodated by the fly ash aluminosilicate matrix. This amount is increased to compensate for the amount lost during the synthesis procedures. Adding other sources of silica, for example glass cullet, to increase the silica content of the final pigment could be addressed as well. Sodium sulphate instead of sodium carbonate can be tested. Different grades of fly ash can be tested to see whether fly ash can be used as it is produced in the power plant furnace or whether one is restricted to the fine PlasFill 5 fraction. The effect of the iron content on the formation of the ultramarine product can be tested. Possibly magnetic separation techniques would need to be applied to the fly ash raw material to ensure that the iron concentrations are limited to an acceptable level. The effect of milling between the reduction and oxidation step needs to be established.

The soluble polysulphides contained in the primary ultramarine can be leached out, but this was not financially viable in 1945.<sup>4</sup> These polysulphides form insoluble crystals once precipitated, and can in future be studied by single crystal crystallography. The products obtained from the leached primary ultramarine blue are of comparable strength with the unleached primary ultramarine blue, and the polysulphides can be used as starting reagents for the following runs.<sup>5,6</sup> Studying crystals from the wash water of the ultramarine blue synthesis before and after the oxidation step can give insight into intermediate chemical species. These species need to be precipitated in a clean beaker in pure water, because the product was found not to redissolve to obtain recrystallised pure crystals.

### 7.2.1.2. Scaling Up

When scaling up one would obviously need to do things on a larger scale. Larger scale would include a larger time frame, maybe in the order of weeks or only a couple of days, depending on the process implemented. The proposed use of briquettes<sup>4</sup> and the use of milder oxidizing agents, like sulphur dioxide<sup>4</sup> and water in air<sup>7</sup> can be studied. Hydrothermal methods<sup>8,9</sup> can solve most of the environmental problems related to the pyrogenic process. Better crucibles with lids that seal-in the carbon monoxide and sulphur vapours to ensure that the sulphur and carbon monoxide stay in contact with each other to ensure the formation of the desired chromophore species need to be designed with strength in mind. The ultramarine pigment cake expands and often breaks the crucible (Figure 7-1).

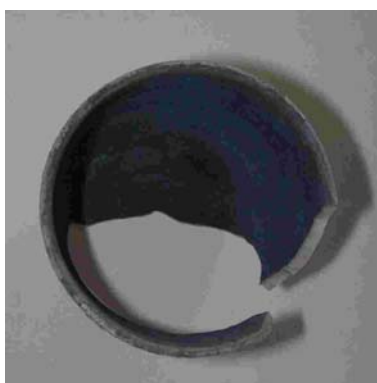


**Figure 7-1: Broken alumina crucible used for the synthesis of ultramarine blue**

### 7.2.2. Kinetics

Preliminary reported results turn out to be a bit optimistic (Chapter 3). The kinetics of solid-state reactions are often faster than expected and ultramarine is no exception. The experimental procedure is to synthesise the ultramarine product until the reduction step has proceeded to a certain degree, stopping at the green stage. This green product is then oxidised at a chosen temperature and the reaction followed by Raman spectroscopy. The relative peak intensities/areas of the  $S_2^-$  and  $S_3^-$  are then used as an indication of the progress of the reaction.<sup>10</sup> The problem here is that the reaction, after milling the intermediate, seems to take place at room temperature as

well. This might have important economic consequences. However, it makes following the reaction more difficult, but not impossible.

### 7.2.3. The Crystal Structure of Ultramarine Pigments

Jaeger<sup>11</sup> stated that the true symmetry of ultramarines was in doubt, but that the ultramarines had a cubic structure, like those of the sodalite group of minerals.<sup>11</sup> The X-ray powder patterns of different ultramarines, containing different relative amounts of silicon and sulphur, were similar, regardless of the colour of the ultramarines.<sup>11</sup> Jaeger<sup>11</sup> concluded that there was a fixed periodic framework for the ultramarine species and that the other components, for example sodium and sulphur were wandering, statistically distributed atoms, thereby explaining why so many different ultramarines gave similar X-ray diffraction patterns. This fixed framework was closer to nosean than to sodalite, supported by the work of Weller and others.<sup>12</sup>

Choosing not to assign specific positions for the sulphur atoms for the  $S_3^-$  group in ultramarine blue, Tarling and others<sup>13</sup> were able to refine X-ray powder diffraction data to obtain a possible structure for Ultramarine (Figure 7-2), presumed to be related to Sodalite. The data was, however, very uncertain, with excessively large thermal parameters for the sulphur atoms.<sup>13</sup> Furthermore, the sulphur - sulphur bond distances were in the order of 1 Å, a situation that was unacceptable to Gordillo and Herrero.<sup>14</sup> This question could be studied by electron diffraction.

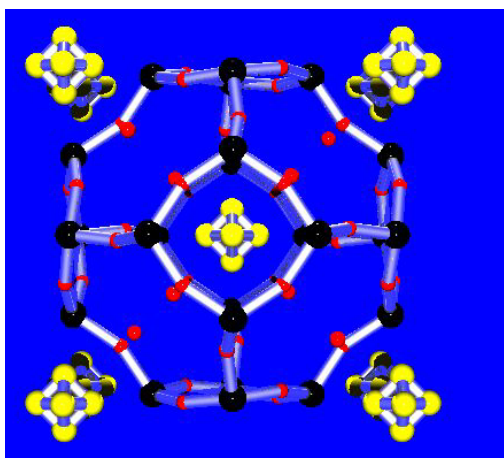


**Figure 7-2: Ultramarine blue crystal structure suggested by Tarling and others<sup>13</sup>**

### **7.3. Treating Fly Ash with Surfactants**

In order to incorporate the hard inorganic fly ash particles into plastics a surfactant needs to be added to facilitate an interaction between these chemical species. No tests were run on polymers, but the effect of different surfactants on the stability of suspensions of fly ash in water were tested. 5 g of fly ash was added to water containing similar volumes of surfactants. The fly ash in water was shaken up for 1 minute to form the suspension. After 5 minutes of settling time, the degree of suspension loss was assessed (Figures 7-3 to 7-6). Both anionic and cationic surfactants can be studied further. Large non-ionic surfactants can be tested as well.

#### **7.3.1. Anionic Surfactants**

Synperonic A4, Synperonic A7, Synperonic A9, Hypermer CG6, Empicol LZ/D, Morez, Tamol NN 8906, stearic acid, stearic acid/NaOH, sulphonated naphthalene formaldehyde and sulphonated naphthalene formaldehyde sodium salt were tested as anionic surfactants. Synperonic A7, Empicol LZ/D, and stearic acid did not stabilise the suspension, whereas Synperonic A4 and Hypermer CG6 gave the best results (Figure 7-6).

#### **7.3.2. Cationic Surfactant**

Octadecyltrimethylammonium bromide was tested as a cationic surfactant and did stabilise the fly ash suspension to some extent (Figure 7-5).



**Figure 7-3: Synperonic A9, Tamol NN 8906, stearic acid/NaOH, and sulphonated naphthalene formaldehyde used to suspend fly ash in water, after 5 minutes of settling time**



**Figure 7-4: Hypermer CG6 (successful), Empicol LZ/D, Morez, and stearic acid used to suspend fly ash in water, after 5 minutes of settling time**



**Figure 7-5: Octadecyltrimethylammonium bromide (successful), Synperonic A4 (successful), Synperonic A7, sulphonated naphthalene formaldehyde sodium salt used to suspend fly ash in water, after 5 minutes of settling time**

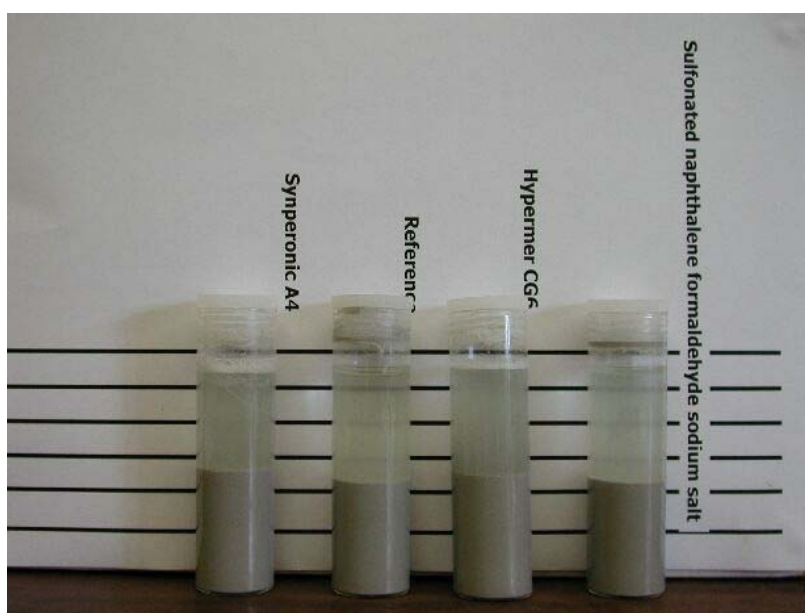


**Figure 7-6: Synperonic A4 (successful), Hypermer CG6 (successful), and sulphonated naphthalene formaldehyde sodium salt used to suspend fly ash in water, after 5 minutes of settling time**



### 7.4.3. Main Group Elements

Phosphorus (di-ammonium hydrogen phosphate - GR/ACS Merck; Iron(III)phosphate - Aldrich Chemical Company, Inc.), tin ( $\text{SnSO}_4$  - Merck) and lead (lead dioxide - Extra Pure Reagent, Kanto Chemical Co., Inc.) were also reacted with fly ash, with minimal success. Incorporating lead into fly ash led to small coloured particles within the sample, some particles were pink, some green, but most of them the familiar brown of a failed reaction.

### 7.4.4. Transition Metals

Transition metals seemed the best domain to dig out an answer to the colour problem. Unfortunately the transition metals did not deliver, except cobalt and vanadium. Cobalt carbonate reacted at 1 000 °C to yield a blue pigment (Figure 7-8), at an unfortunately high loading of 10 % m/m.  $\text{NH}_4\text{VO}_3$  reacted with fly ash to yield a yellow pigment (Figure 7-8) and will be discussed in a future publication. Titanium (titanium dioxide - Analysed Reagent, SAARCHEM Pty Ltd), chromium (sodium dichromate crystals - Merck), manganese (potassium permanganate CP - SAARCHEM Pty Ltd), Iron (Ferric Citrate CP - SAARCHEM Pty Ltd), Nickel (nickel(II)-carbonat - Riedel-De Haën AG Seelze-Hannover), copper (kupfer(II)-nitrat-3-hydrat - Riedel-De Haën AG Seelze-Hannover), zirconium (zirconia sand and  $\text{ZrSO}_4$ ), and tungsten (sodium tungstate Analar - Hopkin & Williams Ltd) were tested. In most cases a brown coloured product was obtained. Iron showed some promise, but the reddish colour was heterogeneously scattered throughout the powdered sample.



**Figure 7-8: Fly Ash reacted with cobalt salt (left) and with 15 mass %  $\text{NH}_4\text{VO}_3$  (right)**

### 7.5. Artificial Neural Networks

Peak fitting will be discussed in a further publication, but another related topic is worth mentioning. Artificial neural networks are versatile aids in data interpretation, and can be used to perform tasks where conventional computer programs fail.<sup>15</sup> A neural network could be designed and trained to perform spectroscopic functions, for instance baseline determination and peak fitting of predefined valuable peaks.

The baselines of several samples were determined with the PeakFit<sup>16</sup> program. These were statistically analysed and ranges for the different parameters that define a cubic polynomial were determined. In order for the baseline to resemble the original, three significant digits are required.

A set of assignable peaks was chosen. The ranges for the parameters that define the peaks were established (Table 7-1). Artificial infrared spectra can be generated from these parameters to train a neural network to give the peak fitting parameters as output. The peak fitting-neural network methodology can be applied to other regions of the infrared spectra, for example to study the water and OH content of cements.

**Table 7-1: Ranges for the parameters describing standard peaks to be found in the infrared spectra of fly ash and its derivatives**

| Peak designator         |     | Intensity (Absorbance) | Position (cm <sup>-1</sup> ) | Width (cm <sup>-1</sup> ) | Fraction Gaussian |
|-------------------------|-----|------------------------|------------------------------|---------------------------|-------------------|
| Decimal places Required |     | 3                      | 1                            | 1                         | 2                 |
| <b>430</b>              | Min | 0.047                  | 416.1                        | 9.2                       | 0.00              |
|                         | Max | 0.524                  | 444.0                        | 87.2                      | 1.00              |
| <b>472</b>              | Min | 0.320                  | 462.8                        | 24.3                      | 0.00              |
|                         | Max | 0.784                  | 481.7                        | 71.3                      | 1.00              |
| <b>507</b>              | Min | 0.089                  | 498.2                        | 19.7                      | 0.13              |
|                         | Max | 0.507                  | 517.8                        | 50.2                      | 1.00              |
| <b>566</b>              | Min | 0.022                  | 555.0                        | 9.1                       | 0.16              |
|                         | Max | 0.491                  | 577.9                        | 72.1                      | 1.00              |
| <b>617</b>              | Min | 0.008                  | 611.6                        | 14.7                      | 0.00              |
|                         | Max | 0.264                  | 623.4                        | 39.8                      | 1.00              |
| <b>685</b>              | Min | 0.000                  | 677.4                        | 0.0                       | 0.00              |
|                         | Max | 0.322                  | 693.9                        | 55.7                      | 1.00              |
| <b>725</b>              | Min | 0.085                  | 708.7                        | 24.7                      | 0.21              |
|                         | Max | 0.355                  | 742.0                        | 73.7                      | 1.00              |
| <b>831</b>              | Min | 0.042                  | 815.7                        | 40.2                      | 0.44              |
|                         | Max | 0.373                  | 847.5                        | 99.0                      | 1.00              |
| <b>890</b>              | Min | 0.128                  | 872.4                        | 62.6                      | 0.20              |
|                         | Max | 0.611                  | 907.5                        | 126.9                     | 1.00              |
| <b>981</b>              | Min | 0.245                  | 963.3                        | 111.4                     | 0.55              |
|                         | Max | 1.139                  | 999.4                        | 187.3                     | 1.00              |
| <b>1092</b>             | Min | 0.326                  | 1076.5                       | 79.7                      | 0.00              |
|                         | Max | 0.966                  | 1107.3                       | 177.3                     | 1.00              |
| <b>1164</b>             | Min | 0.065                  | 1142.5                       | 48.1                      | 0.00              |
|                         | Max | 0.548                  | 1184.7                       | 147.7                     | 1.00              |
| <b>1438</b>             | Min | 0.040                  | 1417.5                       | 20.8                      | 0.07              |
|                         | Max | 0.166                  | 1457.9                       | 394.1                     | 1.00              |

## 7.6. Molecular Mechanics

There is no known force field for vanadium-containing species. Based on crystal structural data and spectroscopic data a force field for such interactions can be developed, using programs such as MOME97<sup>17</sup> or PEFF<sup>18</sup> to develop a force field with parameters for vanadium. An example of such an endeavour is the work of JJP Stewart<sup>19</sup> in the development of the PM3 semi-empirical method.

Another project is to model the interaction of polymers with aluminosilicates. Molecular mechanics can be used to model calcium silicates, aluminosilicates and polymers separately, therefore modelling the interaction of aluminosilicate species with polymers is not too far off. The ability to do such modelling would prove valuable to the composites industry. A probable solution to this problem is mixed quantum/classical models as described in the HyperChem Computational guide.<sup>20</sup>

### 7.7. Density Functional Theory

The **Amsterdam Density Functional**<sup>21,22,23</sup> program can be used to calculate geometries, energies, infrared spectra<sup>24,25</sup> and Raman scattering.<sup>26</sup> The **Electron Paramagnetic Resonance (EPR)**<sup>27,28</sup> and **Electron Spin Resonance (ESR)** spectra<sup>29,30</sup> can also be calculated. Aluminosilicate, vanadia and sulphur species can be studied to enhance our understanding of these systems.

## REFERENCES

- 1 W.B. Cork, *Ultramarine pigments*, in: *Industrial Inorganic Pigments*, G Buxbaum (ed), 1993, p. 124-132.
- 2 G. Pretorius, *Applied solid state Chemistry of Zircon (ZrSiO<sub>4</sub>) and Zirconia (ZrO<sub>2</sub>)*, PhD-Thesis, led by A.M. Heyns, Institute for Applied Materials, University of Pretoria, Pretoria, Republic of South Africa, p. 99, 1995.
- 3 P.M. Harden, *The solid state Chemistry of some Titania- and Tin Pigments*, PhD, led by A.M. Heyns, Institute for Applied Materials, University of Pretoria, Pretoria, Republic of South Africa, p. 4, 1998
- 4 A.P. Beardsley, S.H. Whiting, *Production of Ultramarine*, 2 441 950, 2 441 951, United States.
- 5 E.F. Kur, F. Wilkinson, *Improvement in the Manufacture of Ultramarine*, 198 212, Great Britain, 31 May, 1923.
- 6 E.F. Kur, F. Wilkinson, *Improvements in the Manufacture of Silicious Ultramarine Colours*, 209 961, Great Britain, 24 January, 1924.
- 7 R.B. Van Order, R.F. Reeves, *Manufacture of Ultramarine*, 2 723 917, United States, 15 November, 1955.
- 8 R.B. Van Order, R.H. Hill, *Manufacture of Ultramarine*, 2 806 802, United States, 17 September, 1957.
- 9 *Ultramarine - Manufacture Recipes*, Webexhibits, <http://webexhibits.org/pigments/indiv/recipe/ultramarine.html>, 21 January 2003, downloaded 21 January 2003 - 11:15.
- 10 R.J.H. Clark, T.J. Dines, M. Kurmoo, *Inorg. Chem.*, 1983, **22**, 2766-2772.
- 11 F.M. Jaeger, *Trans. Faraday Soc.*, 1929, **25**, 320-345.
- 12 M.T. Weller, G. Wong, C.L. Adamson, S.M. Dodd, J.J.B. Roe, *J. Chem. Soc. Dalton Trans.*, 1990, 593-597.
- 13 S.E. Tarling, P. Barnes, J. Klinowski, *Acta Cryst.*, 1988, **B44**, 128-135.
- 14 M.C. Gordillo, C.P. Herrero, *J. Phys. Chem.*, 1993, **97**(31), 8310-8315.
- 15 H.M. Cartwright, *Applications of Artificial Intelligence in Chemistry*, Oxford University Press, Oxford, pp. 13-38, 1993.
- 16 *PeakFit*, Version 4.06, AISN Software Inc., Mapleton, 1995.

- 17 P. Comba, T.W. Hambley, *Molecular Modeling of Inorganic Compounds*, Second edition, Wiley-VCH, Weinheim, 2001.
- 18 J.L.M. Dillen, *J. Comp. Chem.*, 1992, **13**(3), 257-267.
- 19 J.J.P. Stewart, *J. Comp. Chem.*, 1989, **10**(2), 209-220.
- 20 *HyperChem, Computational Chemistry*, HyperCube Inc., Canada, p. 246, 1996.
- 21 G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931-967.
- 22 C. Fonseca Guerra, J.G. Snijders, G. te Velde, E.J. Baerends, *Theor. Chem. Acc.*, 1998, **22**, 391.
- 23 *ADF2002.01*, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>, 2002.
- 24 L. Fan, T. Ziegler, *J. Chem. Phys.*, 1992, **96**(12), 9005-9012.
- 25 L. Fan, T. Ziegler, *J. Phys. Chem.*, 1992, **96**(17), 6937-6941.
- 26 S.J.A. van Gisbergen, J.G. Snijders, E.J. Baerends, *Chem. Phys. Lett.*, 1996, **259**, 599-604.
- 27 G. Schreckenbach, T. Ziegler, *J. Phys. Chem.*, 1997, **101**(18), 3388-3399.
- 28 S. Patchkovskii, T. Ziegler, *J. Phys. Chem.*, **105**(22), 5490-5497.
- 29 E. Van Lenthe, A. Van der Avoird, P.E.S. Wormer, *J. Chem. Phys.*, 1998, **108**(12), 4783-4796.
- 30 E. Van Lenthe, P.E.S. Wormer, A. Van der Avoird, *J. Chem. Phys.*, 1997, **107**(7), 2488-2498.

## **APPENDIX**

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

## A.PROGRAMS

### A1. SPECTRAL MANIPULATIONS PROGRAM

**Spectral Analysis**

This Programme analyses spectra in the way you want to, just click the desired check boxes for the desired outcome

The following input files are required: Wavenumber.dat Intensity.prn Baseline.dat

The following files will contain the output: outwavenumber.dat outintensity.prn areaoutput.dat

The following files are necessary for the program to work: temp1.dat temp2.dat

Only one operation can be performed at a time to apply the procedures sequentially one should transfer the output data to the input files

How many spectra are to be analysed?

☐ Use specified maximum wavenumber in stead of file limits

☐ Normalise spectra so that the intensity is between 0 and 1

☐ Normalise the intensity to another value

☐ Normalise the area to the specified area

☐ Perform baseline correction

☐ Perform baseline correction and intensity normalisation (between 0 and specified value)

☐ Perform baseline correction and area normalisation to the specified area

☐ Calculate the standard relative areas

☐ Calculate the relative area in the user defined regions

☐ Region 1

☐ Region 2

☐ Region 3

☐ Region 4

☐ Region 5

☐ Region 6

Calculate the ratio of region  to

Status of the calculation

**unit Spectra\_an;**

**{This program incorporates previous programs and allows the user to manipulate spectra in several ways and calculate relative areas as defined by the user.}**  
**interface**

**{The area is calculated by the trapezoidal Rule as described in**  
**R Ellis, D Gulick, Calculus With Analytical Geometry, 5th edition, Saunders College**  
**Publishing, Fort Worth, 1994, pp 470-471}**

**uses**

Windows, Messages, SysUtils, Classes, Graphics, Controls, Forms, Dialogs,  
 StdCtrls, Buttons, ExtCtrls, math;

**type**

TForm1 = class(TForm)  
 CloseButton: TBitBtn;  
 Bevel1: TBevel;  
 intro\_Label: TLabel;  
 infiles\_Label: TLabel;

wavenumber\_Label: TLabel;  
 intensity\_Label: TLabel;  
 baseline\_Label: TLabel;  
 outfiles\_Label: TLabel;  
 outwavenumber\_Label: TLabel;

---

```

outintensity_Label: TLabel;
added_programmes_Label: TLabel;
temp1_Label: TLabel;
temp2_Label: TLabel;
sequential_Label: TLabel;
CalculateButton: TButton;
endbox: TEdit;
areaout_Label: TLabel;
Norm_int_radio: TRadioButton;
numberofspectrainput: TEdit;
Normarea_radio: TRadioButton;
Norm_area_input: TEdit;
Base_corr_radio: TRadioButton;
base_int_corr_radio: TRadioButton;
base_area_corr_radio: TRadioButton;
norm_area_input2: TEdit;
standard_area_calc_radio: TRadioButton;
costum_area_calc_radio: TRadioButton;
region1_CheckBox: TCheckBox;
region1begin: TEdit;
region1end: TEdit;
region2_CheckBox: TCheckBox;
region2begin: TEdit;
region2end: TEdit;
region3_CheckBox: TCheckBox;
region3begin: TEdit;
region3end: TEdit;
region4_CheckBox: TCheckBox;
region4begin: TEdit;
region4end: TEdit;
region5_CheckBox: TCheckBox;
region5begin: TEdit;
region5end: TEdit;
region6_CheckBox: TCheckBox;
region6begin: TEdit;
region6end: TEdit;
calc_ratio_Label: TLabel;
numeratorregion: TEdit;
ratio_to_Label: TLabel;
ratiodenominator: TEdit;
MaximumvalueCheckBox: TCheckBox;
maxwaveinput: TEdit;
othermaxint_radio: TRadioButton;
input_maxint: TEdit;
input_maxint2: TEdit;
procedure CalculateButtonClick(Sender:
TObject);
end;

```

**var**

```

Form1: TForm1;
datasize, topratioarea, bottomratioarea: integer;
maximumwavelength, maxintensity: real;
total, normarea, topratioareareal, bottomratioareareal: real;
intensityarray, basearray, areaarray: array of array of real;
totalint, flag, areaarraydimension: integer;
I, J, A, B, err, temp: integer;
interval: array[0..11] of integer;
wavearray, minarray, maxarray: array of real;
namearray: array of string;
textfile, textfile2: text;
region1min, region1max, region2min, region2max: real;
region3min, region3max, region4min, region4max: real;
region5min, region5max, region6min, region6max: real;
inputerror: boolean;
inputused: array[1..6] of boolean;

```

**implementation**

```

{$R *.DFM}

```

**Procedure wavenumbers\_size\_maximumset; {Determine the number of data points that the user is interested in}**

**var**

```

x: integer;
wavenumber: real;
begin
  assignfile (textfile,'wavenumber.dat');
  reset(textfile);
  x:= 0;
  readln(textfile,wavenumber);
  x:= x + 1;
  while ((wavenumber < maximumwavelength) and not(eof(textfile))) do
    begin
      readln(textfile,wavenumber);
      x:= x + 1;
    end;
  if wavenumber > maximumwavelength
  then datasize:= x-2

```

---

```

        else datasize:= x-1;
        closefile(textfile);
    end;
Procedure wavenumbers_size_fileset; {Determine the number of data points that the file supplies}
var
    x: integer;                                wavenumber: real;
begin
    assignfile (textfile,'wavenumber.dat');
    reset(textfile);
    x:= 0;
    readln(textfile,wavenumber);
    x:= x + 1;
    while not(eof(textfile)) do
        begin
            readln(textfile,wavenumber);
            x:= x + 1;
        end;
    datasize:= x;
    closefile(textfile);
end;
Procedure initialise_arrays; {Specify the size of the arrays}
begin
    setlength(intensityarray, totalint, datasize);
    setlength(wavearray, datasize);
    setlength(minarray, totalint);
    setlength(areaarray, totalint, areaarraydimension);
    setlength(maxarray, totalint);
    setlength(namearray, totalint);
end;
Procedure assign_wavenumbers; {Assign values to the wavenumber array}
var
    x: integer;
begin
    assignfile (textfile,'wavenumber.dat');
    reset(textfile);
    for x:= 0 to (datasize-1) do
        begin
            readln(textfile,wavearray[x]);
        end;
    closefile(textfile);
end;
Procedure intensities; {Input the absorbance values}
var
    x, y, position: integer;                    tempstring: string;
begin
    assignfile (textfile,'outintensity.prn');
    reset(textfile);
    readln(textfile, tempstring);
    for x:= 0 to (totalint-2) do
        begin
            position:= pos(' ',tempstring);
            if position = 1
            then position:= pos(' ',copy(tempstring,2,1000000));
            namearray[x]:= copy(tempstring, 1, position);
            delete(tempstring,1,position);
        end;
    namearray[totalint-1]:= tempstring;
    for x:= 0 to (datasize-1) do
        begin

```

```

        for y:= 0 to (totalint - 1) do
            begin
                read(textfile,intensityarray[y,x]);
            end;
        end;
        closefile(textfile);
    end;
Procedure baseline; {Input Baseline parameters}
var
    x, y: integer;                                tempstring: string;
begin
    assignfile (textfile,'baseline.dat');
    reset(textfile);
    readln(textfile, tempstring);
    for x:= 0 to 3 do
        begin
            for y:= 0 to (totalint - 1) do
                begin
                    read(textfile,basearray[y,x]);
                end;
            end;
        end;
        closefile(textfile);
    end;
Procedure find_min; {Find minimum absorbance}
var x, y: integer;
begin
    for x:= 0 to (totalint -1) do
        begin
            minarray[x]:= intensityarray[x,0];
            for y:= 1 to (datasize-1) do
                begin
                    minarray[x]:= min(minarray[x],intensityarray[x,y]);
                end;
            end;
        end;
    end;
Procedure find_max; {Find maximum absorbance}
var x, y: integer;
begin
    for x:= 0 to (totalint -1) do
        begin
            maxarray[x]:= intensityarray[x,0];
            for y:= 1 to (datasize-1) do
                begin
                    maxarray[x]:= max(maxarray[x],intensityarray[x,y]);
                end;
            end;
        end;
    end;
Procedure normalise_intensity; {Change intensities so that all absorbance values are between 0 and 1}
var x, y: integer;
begin
    for x:= 0 to (totalint - 1) do
        begin
            for y:= 0 to (datasize-1) do
                begin
                    intensityarray[x,y]:= (intensityarray[x,y]-minarray[x])/(maxarray[x]-minarray[x])*maxintensity;
                end;
            end;
        end;
    end;
end;

```

---

**procedure calculate\_total\_area; {Calculate the current total area}****var** x, y: integer;**begin**

for x:= 0 to (totalint -1) do

begin

areaarray[x,0]:= 0;

for y:= 0 to (datasize - 2) do

begin

areaarray[x,0]:= areaarray[x,0] - 0.5\*(wavearray[y]-

wavearray[y+1])\*(intensityarray[x,y]+intensityarray[x,y+1]-2\*minarray[x]);

end;

end;

**end;****Procedure normalise\_area; {Insure that the minimum absorbance is 0 and that the total area equals the desired normarea}****var** x, y: integer;**begin**

for x:= 0 to (totalint - 1) do

begin

for y:= 0 to (datasize-1) do

begin

intensityarray[x,y]:= normarea\*((intensityarray[x,y]-minarray[x])/(areaarray[x,0]));

end;

end;

**end;****Procedure baseline\_correction; {Subtract the baseline}****var**

x, y: integer;

**begin**

for x:= 0 to (totalint-1) do

begin

for y:= 0 to (datasize-1) do

begin

intensityarray[x,y]:= intensityarray[x,y] -

basearray[x,0]\*(wavearray[y]\*wavearray[y]\*wavearray[y]) -

basearray[x,1]\*(wavearray[y]\*wavearray[y]) - basearray[x,2]\*wavearray[y] - basearray[x,3];

end;

end;

**end;****Procedure determine\_intervals; {The starting wavenumbers for the six regions are defined}****var** x: integer;**begin**

flag:= 0;

For x:= 0 to (datasize-1) do

begin

if (wavearray[x] &gt;= region1min) and (flag = 0)

then

begin

interval[flag]:= x;

flag:= flag + 1;

end;

if (wavearray[x] &gt;= region1max) and (flag = 1)

then

begin

interval[flag]:= x;

flag:= flag + 1;

end;

if (wavearray[x] &gt;= region2min) and (flag = 2)

then

begin

interval[flag]:= x;

flag:= flag + 1;

end;

if (wavearray[x] &gt;= region2max) and (flag = 3)

then

begin

interval[flag]:= x;

flag:= flag + 1;

end;

if (wavearray[x] &gt;= region3min) and (flag = 4)

then

begin

interval[flag]:= x;

flag:= flag + 1;

end;

if (wavearray[x] &gt;= region3max) and (flag = 5)

then

```

begin
    interval[flag]:= x;
    flag:= flag + 1;
end;
if (wavearray[x] >= region4min) and (flag = 6)
then
    begin
        interval[flag]:= x;
        flag:= flag + 1;
    end;
if (wavearray[x] >= region4max) and (flag = 7)
then
    begin
        interval[flag]:= x;
        flag:= flag + 1;
    end;
if (wavearray[x] >= region5min) and (flag = 8)
then
    begin
        interval[flag]:= x;
        flag:= flag + 1;
    end;
end;
end;
if (wavearray[x] >= region5max) and (flag = 9)
then
    begin
        interval[flag]:= x;
        flag:= flag + 1;
    end;
if (wavearray[x] >= region6min) and (flag = 10)
then
    begin
        interval[flag]:= x;
        flag:= flag + 1;
    end;
if (wavearray[x] >= region6max) and (flag = 11)
then
    begin
        interval[flag]:= x;
        flag:= flag + 1;
    end;
end;
end;

```

end;

**Procedure write\_output; {Export the intensity normalised spectra}**

**var** x, y, z: integer;

**begin**

Assignfile (textfile, 'outintensity.prn');

Assignfile (textfile2, 'outwavenumber.dat');

rewrite(textfile);

rewrite(textfile2);

for z:= 0 to (totalint -1) do

begin

write(textfile, namearray[z]);

write(textfile, ' ');

end;

writeln(textfile);

for x:= 0 to (datasize-1) do

end;

**Procedure Mean Frequency; {Calculate the mean frequency}**

**var**

x, y, flag: integer;

area: real;

**begin**

for x:= 0 to (totalint-1) do

begin

flag:= 0;

y:= 0;

area:= 0;

while flag = 0 do

begin

area:= area - 0.5\*(wavearray[y]-

wavearray[y+1])\*(intensityarray[x,y]+intensityarray[x,y+1]-2\*minarray[x]);

if (area > (0.5\*areaarray[x,0]))

then

begin

areaarray[x,8]:= wavearray[y];

flag:= flag +1;

end;

y:= y + 1;

end;

end;

**begin**

for y:= 0 to (totalint-1) do

begin

write(textfile, intensityarray[y,x]);

write(textfile, ' ');

end;

writeln(textfile);

writeln(textfile2, wavearray[x]);

end;

closefile(textfile);

closefile(textfile2);

---

```

end;
procedure relative_areas; {Calculate the relative area in each region}
var x, y, n: integer;
begin
  for x:= 0 to (totalint - 1) do
    begin
      n:= 0;
      while n <= 11 do
        begin
          y:= interval[n];
          while y <= interval[n+1] do
            begin
              areaarray[x,round((n/2)+1)]:= areaarray[x,round((n/2)+1)]-0.5*(wavearray[y]-
wavearray[y+1])*(intensityarray[x,y]+intensityarray[x,y+1] - 2*minarray[x]);
              y:= y + 1;
            end;
            areaarray[x,round((n/2)+1)]:= areaarray[x,round((n/2)+1)]/areaarray[x,0]*100;
            n:= n + 2;
          end;
          areaarray[x,7]:= areaarray[x,topratioarea]/areaarray[x,bottomratioarea]; {ratio}
        end;
      end;
    end;
  end;
Procedure write_relative_area_output; {Export the Area, ratio and mean frequency data}
var x, y: integer;
begin
  Assignfile (textfile,'areaoutput.dat');
  rewrite(textfile);
  writeln(textfile, 'Name Total Region1 Region2 Region3 Region4 Region5 Region6 Ratio Mean
Frequency');
  for x:= 0 to (totalint - 1) do
    begin
      write(textfile, areaarray[x,y]);
      write(textfile, ' ');
    end;
    write(textfile, namearray[x]);
    write(textfile, ' ');
    writeln(textfile,"
");
    for y:= 0 to 8 do
      begin
        write(textfile, areaarray[x,y]);
        write(textfile, ' ');
      end;
      writeln(textfile,"
");
    end;
  end;
  closefile(textfile);
end;
procedure TForm1.CalculateButtonClick(Sender: TObject);
begin
  inputerror:= false;
  {Obtain the dimensions of the arrays based on wavenumber}
  if MaximumvalueCheckBox.Checked
  then
    begin
      val (maxwaveinput.text, maximumwavelength,err);
      wavenumbers_size_maximumset;
    end;
  if standard_area_calc_radio.Checked
  then
    begin
      maximumwavelength:= 2500;
      wavenumbers_size_maximumset;
      {define interval regions}
    end;
  if not(MaximumvalueCheckBox.Checked or standard_area_calc_radio.Checked)
  then wavenumbers_size_fileset;
  {Obtain the dimensions of the arrays based on number of spectra}
  Val (numberofspectrainput.text,total,err);
  totalint:= round(total);
  {Obtain the dimensions of the arrays based on whether the areaarray is used to normalise the
area or do a region analysis}

```

---

---

```

if (costum_area_calc_radio.Checked or standard_area_calc_radio.Checked)
then areaarraydimension:= 9
else areaarraydimension:= 1;
{Input intensities into initialised arrays}
initialise_arrays;
assign_wavenumbers;
fix_minus_intensity;
{Normalise intensity to 1}
if Norm_int_radio.Checked
then
begin
maxintensity:= 1;
find_min;
{Normalise intensity to another value}
if othermaxint_radio.Checked
then
begin
val
(input_maxint.text,maxintensity,err);
find_min;
{Area normalisation}
if normarea_radio.Checked
then
begin
val
(Norm_area_input.text,normarea,err);
find_min;
{Baseline correction and area normalisation}
if base_area_corr_radio.Checked
then
begin
fix_minus_base;
get_rid_of_extra_spaces_base;
setlength (basearray, totalint, 4);
baseline;
baseline_correction;

val
(Norm_area_input2.text,normarea,err);
find_min;
find_max;
calculate_total_area;
normalise_area;
write_output;
endbox.text:= 'Done';
end;

baseline;
baseline_correction;
write_output;
endbox.text:= 'Done';
end;

val
(input_maxint2.text,maxintensity,err);
find_min;
find_max;
normalise_intensity;
write_output;
endbox.text:= 'Done';
end;

region2max:= 800;
region3min:= 801;
region3max:= 1000;
region4min:= 1001;
region4max:= 1300;
region5min:= 1301;

```

---

```

        region5max:= 1700;
        region6min:= 1701;
        region6max:= 2498;
        topratioarea:= 2;
        bottomratioarea:= 1;
        determine_intervals;
        find_min;
{Calculate user defined area ratios}
        if costum_area_calc_radio.Checked
            then
                begin
                    if region1_CheckBox.Checked
                    then
                        begin
                            val (region1begin.text, region1min, err);
                            val (region1end.text, region1max, err);
                            if (region1min >= region1max)
                                or (region1min < wavearray[0])
                                or (region1max > wavearray[datasize-1])
                                then inputerror:= true;
                            inputused[1]:= true;
                        end
                    else
                        begin
                            region1min:= wavearray[1];
                            region1max:= wavearray[0];
                            inputused[1]:= false;
                        end;
                    if region2_CheckBox.Checked
                    then
                        begin
                            val (region2begin.text, region2min, err);
                            val (region2end.text, region2max, err);
                            if (region2min >= region2max)
                                or (region2min < wavearray[0])
                                or (region2max > wavearray[datasize-1])
                                then inputerror:= true;
                            inputused[2]:= true;
                        end
                    else
                        begin
                            region2min:= wavearray[1];
                            region2max:= wavearray[0];
                            inputused[2]:= false;
                        end;
                    if region3_CheckBox.Checked
                    then
                        begin
                            val (region3begin.text, region3min, err);
                            val (region3end.text, region3max, err);
                            if (region3min >= region3max)
                                or (region3min < wavearray[0])
                                or (region3max > wavearray[datasize-1])
                                then inputerror:= true;
                            inputused[3]:= true;
                        end
                    else
                        begin
                            region3min:= wavearray[1];
                            region3max:= wavearray[0];
                            calculate_total_area;
                            relative_areas;
                            Mean Frequency;
                            write_relative_area_output;
                            endbox.text:= 'Done';
                        end;
                    inputused[3]:= false;
                end;
                if region4_CheckBox.Checked
                then
                    begin
                        val (region4begin.text, region4min, err);
                        val (region4end.text, region4max, err);
                        if (region4min >= region4max)
                            or (region4min < wavearray[0])
                            or (region4max > wavearray[datasize-1])
                            then inputerror:= true;
                        inputused[4]:= true;
                    end
                else
                    begin
                        region4min:= wavearray[1];
                        region4max:= wavearray[0];
                        inputused[4]:= false;
                    end;
                if region5_CheckBox.Checked
                then
                    begin
                        val (region5begin.text, region5min, err);
                        val (region5end.text, region5max, err);
                        if (region5min >= region5max)
                            or (region5min < wavearray[0])
                            or (region5max > wavearray[datasize-1])
                            then inputerror:= true;
                        inputused[5]:= true;
                    end
                else
                    begin
                        region5min:= wavearray[1];
                        region5max:= wavearray[0];
                        inputused[5]:= false;
                    end;
                if region6_CheckBox.Checked
                then
                    begin
                        val (region6begin.text, region6min, err);
                        val (region6end.text, region6max, err);
                        if (region6min >= region6max)
                            or (region6min < wavearray[0])
                            or (region6max > wavearray[datasize-1])
                            then inputerror:= true;
                        inputused[6]:= true;
                    end
                else
                    begin

```

```

region6min:= wavearray[1];
region6max:= wavearray[0];
inputused[6]:= false;
end;
val (numeratorregion.text, topratioareareal,
err);
val (ratiodenominator.text,
bottomratioareareal, err);
topratioarea:= round(topratioareareal);
bottomratioarea:=
round(bottomratioareareal);
if not(inputused[topratioarea] and
inputused[bottomratioarea])
then inputerror:= true;
end;
end;
end.

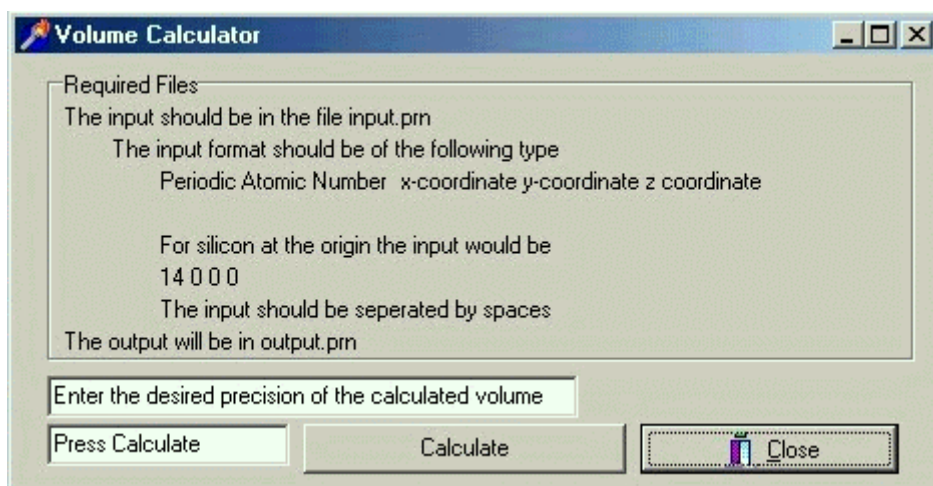
```

```

if not(inputerror)
then
begin
determine_intervals;
find_min;
calculate_total_area;
relative_areas;
Mean Frequency;
write_relative_area_output;
endbox.text:= 'Done';
end
else endbox.text:= 'There is an error in the
input';

```

## A2. VOLUME CALCULATION PROGRAM



{This program uses the Cartesian coordinates and atomic numbers of the input file to calculate the volume based on the method of A Gavezzotti, J. Am. Chem. Soc. 105, 5220-5225, 1983

The atomic radii are taken from Gavezzotti, R.D. Shannon, Acta Cryst. A32, 751-767, 1976  
A Bondi, J. Phys. Chem. 68(3), 441-451, 1964}

unit Vol\_calc;

uses

Windows, Messages, SysUtils, Classes, Graphics, Controls, Forms, Dialogs, StdCtrls, Buttons, Math;

type

TForm1 = class(TForm)  
CloseBitBtn: TBitBtn;  
Calculate\_button: TButton;  
files\_GroupBox: TGroupBox;  
input\_Label: TLabel;  
format\_Label: TLabel;  
description\_Label: TLabel;  
example\_Label: TLabel;

end;

var

more\_Label: TLabel;  
output\_Label: TLabel;  
user\_comm: TEdit;  
example\_Label2: TLabel;  
inout2\_Label: TLabel;  
Presicion: TEdit;  
procedure Calculate\_buttonClick(Sender: TObject);

---

```

Form1: TForm1;
coordinate_array: array of array of real;
in_atom_array: array of array of array of real;
VDWrad, Atom_rad: array of real;
number_of_atoms, err, number_pointsx, number_pointsy, number_pointsz: integer;
volume_total, volume_incr, startx, starty, startz: real;
volume_atoms, volume_cavity, endx, endy, endz: real;
flag_inside_atom, flag_in_cavity: boolean;
implementation
{$R *.DFM}
procedure input_vdwrاد;
var
    textfile: text;
    x: integer;
{Reads the van der Waals radii into the array}
begin;
    assignfile (textfile, 'vdw_rad.txt');
    reset(textfile);
    setlength(VDWrad, 103);
    for x:= 0 to 102 do
        begin
            readln(textfile);
            readln(textfile,VDWrad[x]);
        end;
    end;
procedure input_from_file;
var
    textfile: text;
    x, y: integer;
    atomnumber_real: real;
{Reads in the data from the input file: input.prn}
begin;
    assignfile (textfile,'input.prn');
    reset(textfile);
{First determine the number of atoms}
    x:= 0;
    while not(eof(textfile)) do
        begin
            readln(textfile);
            x:= x + 1;
        end;
    number_of_atoms:= x-1;
    reset(textfile);
{Initialise the dinamic arrays}
    setlength(coordinate_array, (number_of_atoms+1), 3);
    setlength(Atom_rad, (number_of_atoms+1));
{Read the values into the appropriate arrays}
    for x:= 0 to number_of_atoms do
        begin
            read(textfile,atomnumber_real);
            Atom_rad[x]:= VDWrad[round(atomnumber_real)-1];
            for y:= 0 to 2 do
                begin
                    read(textfile,coordinate_array[x,y]);
                end;
            readln(textfile);
        end;
    closefile(textfile);
end;
procedure coordinate_system;
var
    x: integer;
    maxrad: real;
{Determines the dimensions of the volume to be searched}
begin;

```

---

---

```

startx:= 0;
starty:= 0;
startz:= 0;
endx:= 0;
for x:= 0 to number_of_atoms do
  begin
    endx:= max(endx,coordinate_array[x,0]);
    endy:= max(endy,coordinate_array[x,1]);
    endz:= max(endz,coordinate_array[x,2]);
    startx:= min(startx,coordinate_array[x,0]);
    starty:= min(starty,coordinate_array[x,1]);
    startz:= min(startz,coordinate_array[x,2]);
    maxrad:= max(maxrad,atom_rad[x]);
  end;
{ensure that the molecule is in the correct octant of 3D space}
for x:= 0 to number_of_atoms do
  begin
    coordinate_array[x,0]:= coordinate_array[x,0] + abs(startx) + 1.1*maxrad;
    coordinate_array[x,1]:= coordinate_array[x,1] + abs(starty) + 1.1*maxrad;
    coordinate_array[x,2]:= coordinate_array[x,2] + abs(startz) + 1.1*maxrad;
  end;
  number_pointsx:= trunc((2*1.1*maxrad + endx - startx)/volume_incr) + 1;
  number_pointsy:= trunc((2*1.1*maxrad + endy - starty)/volume_incr) + 1;
  number_pointsz:= trunc((2*1.1*maxrad + endz - startz)/volume_incr) + 1;
  setlength(in_atom_array, number_pointsx+1, number_pointsy+1, number_pointsz+1);
end;
Procedure initialise_in_atom_array;
var
  x, y, z:integer;
begin
  for x:= 0 to number_pointsx do
    begin
      for y:= 0 to number_pointsy do
        begin
          for z:= 0 to number_pointsz do
            begin
              in_atom_array[x,y,z]:= 0;
            end;
          end;
        end;
      end;
    end;
  end;
end;
procedure calculate_volume;
var
  a, x, y, z, molendz:integer;
  posx, posy, posz, centerx, centery, centerz, sum_total, sum_cavity, sum_atoms : real;
  flag_inside_mol, flag_inside_wall: boolean;
begin;
  initialise_in_atom_array;
  for x:= 0 to number_pointsx do
    begin
      posx:= x*volume_incr;
      for y:= 0 to number_pointsy do
        begin
          posy:= y*volume_incr;
          for z:= 0 to number_pointsz do
            begin
              posz:= z*volume_incr;
              flag_inside_atom:= false;
              a:= 0;
              while ((a <= number_of_atoms) and not(flag_inside_atom)) do

```

---

---

```

        begin
            centerx:= posx - coordinate_array[a,0];
            centery:= posy - coordinate_array[a,1];
            centerz:= posz - coordinate_array[a,2];
            flag_inside_atom:= (((centerx*centerx)+(centery*centery)+(centerz*centerz))
<= (Atom_rad[a]*Atom_rad[a]));
            if flag_inside_atom
                then in_atom_array[x,y,z]:= 1;
                a:= a +1;
            end;
        end;
    end;
end;
sum_total:= 0;
sum_atoms:= 0;
sum_cavity:= 0;
for x:= 0 to number_pointsx do
    begin
        for y:= 0 to number_pointsy do
            begin
                flag_inside_mol:= false;
                flag_inside_wall:= false;
                molendz:= number_pointsz;
                z:= number_pointsz;
                while z >= 0 do
                    begin
                        if (in_atom_array[x,y,z] = 1)
                            then
                                begin
                                    molendz:= z;
                                    z:= 0;
                                end;
                                z:= z -1;
                            end;
                        for z:= 1 to molendz do
                            begin
                                sum_atoms:= sum_atoms + in_atom_array[x,y,z];
                                if (in_atom_array[x,y,z] = 1)
                                    then
                                        begin
                                            flag_inside_mol:= true;
                                            flag_inside_wall:= true;
                                        end;
                                if flag_inside_mol and not (in_atom_array[x,y,z] = in_atom_array[x,y,(z-1)])
                                    then flag_inside_wall:= false;
                                if flag_inside_mol and not(flag_inside_wall)
                                    then sum_cavity:= sum_cavity + 1;
                                if flag_inside_mol
                                    then sum_total:= sum_total + 1;
                            end;
                        end;
                    end;
                end;
            end;
        end;
        volume_incr:= Power(volume_incr,3);
        volume_total:= sum_total*volume_incr;
        volume_cavity:= sum_cavity*volume_incr;
        volume_atoms:= sum_atoms*volume_incr;
    end;
end;
procedure output;
var
    x, y, z:integer;
    textfile: text;
{The results are saved in the file output.prn}

```

---

```

begin
  assignfile (textfile,'output.prn');
  rewrite(textfile);
  write(textfile, 'Total volume: ');
  writeln(textfile,volume_total);
  write(textfile, 'Volume occupied by the
atoms: ');
end;
procedure TForm1.Calculate_buttonClick(Sender: TObject);
begin;
  input_vdwrads;
  input_from_file;
  Val(Precision.text,volume_incr,err);
  coordinate_system;
  calculate_volume;
  output;
  user_comm.text:= 'Done';
end;
end.

```

## B.RAW DATA

### B1. ULTRAMARINE BLUE KINETIC PEAK FITTING DATA

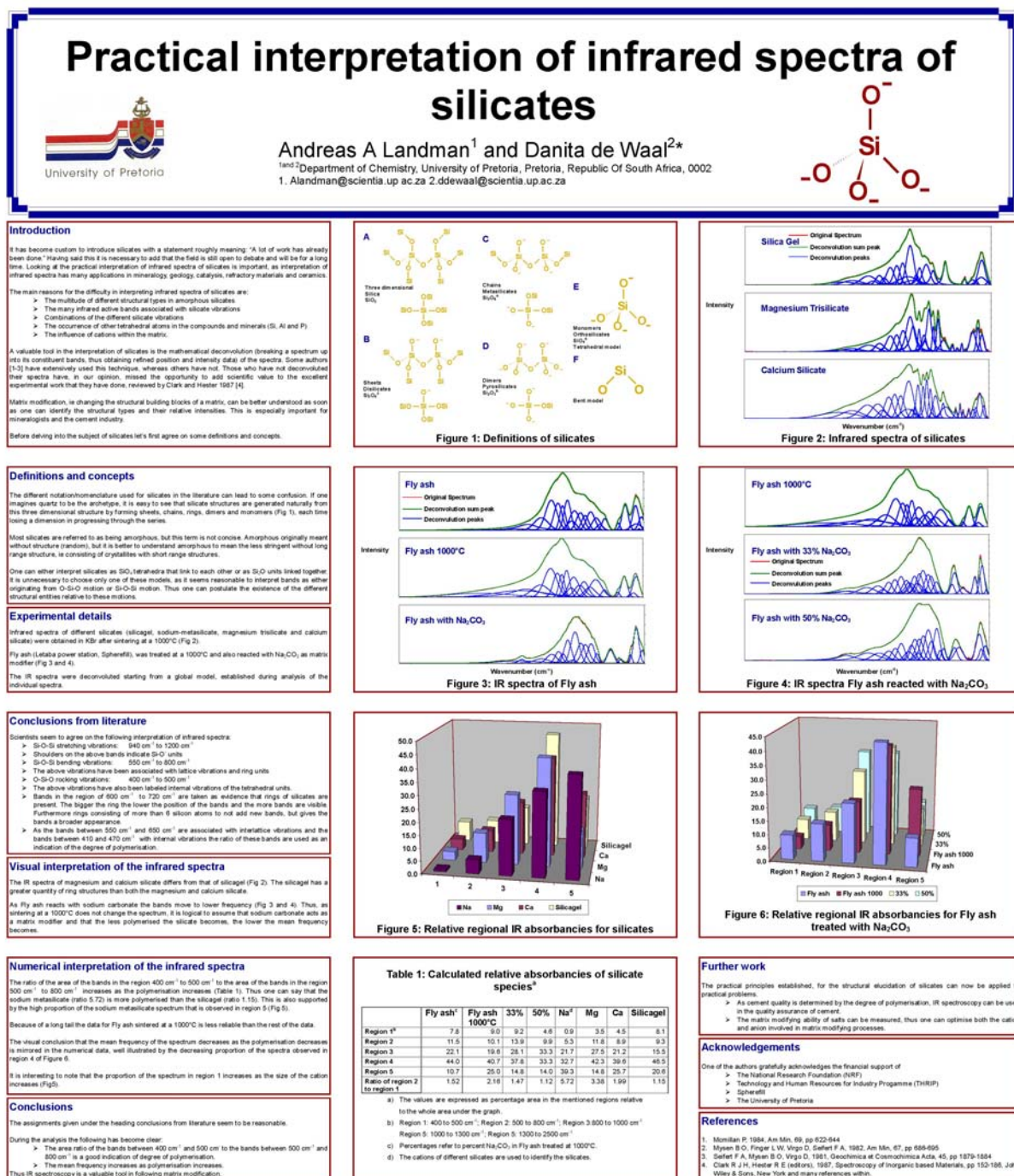
| Spectrum | Peak 1  | Peak 1 Int | Peak 2  | Peak 2 Int | Ratio | Ave Ratio | Uncertainty |
|----------|---------|------------|---------|------------|-------|-----------|-------------|
| umbl10   | 542.725 | 3456.36    | 578.986 | 670.653    | 0.2   | 0.19      | 0.02        |
| umbl102  | 540.069 | 2283.56    | 574.995 | 958.82     | 0.4   |           |             |
| umbl103  | 543.762 | 1183.07    | 578.865 | 215.091    | 0.2   |           |             |
| umbl104  | 541.757 | 1197.34    | 576.442 | 463.313    | 0.4   | 0.3       | 0.1         |
| umbl301  | 546.424 | 193.663    | 585.666 | 21.9575    | 0.1   | 0.15      | 0.04        |
| umbl302  | 545.009 | 705.423    | 582.165 | 81.9958    | 0.1   |           |             |
| umbl303  | 544.169 | 1854.61    | 580.265 | 287.992    | 0.2   |           |             |
| umbl304  | 542.403 | 4272.75    | 578.351 | 857.254    | 0.2   |           |             |
| umbl305  | 543.625 | 1178.56    | 579.748 | 222.864    | 0.2   |           |             |
| umbl60   | 544.527 | 2808.5     | 582.919 | 347.586    | 0.1   | 0.12      | 0.01        |
| umbl602  | 545.156 | 2785.09    | 583.421 | 314.326    | 0.1   |           |             |
| umbl603  | 544.237 | 4318.1     | 581.031 | 578.612    | 0.1   |           |             |
| umbl604  | 544.215 | 6725.48    | 581.998 | 851.471    | 0.1   |           |             |
| umbl95   | 545.967 | 759.234    | 578.029 | 69.1982    | 0.1   | 0.10      | 0.02        |
| umbl953  | 546.469 | 1253.29    | 583.098 | 93.691     | 0.1   |           |             |
| umbl954  | 545.479 | 1483.57    | 582.583 | 157.149    | 0.1   |           |             |
| umbl955  | 544.44  | 4829.83    | 578.315 | 617.86     | 0.1   |           |             |
| Umblack  | 543.982 | 1506.58    | 579.563 | 263.521    | 0.2   | 0.22      | 0.03        |
| Umblack2 | 543.945 | 3788.4     | 577.968 | 900.849    | 0.2   |           |             |
| Umblack3 | 543.943 | 11462.2    | 578.36  | 2456.75    | 0.2   |           |             |
| Umblack4 | 542.649 | 3574.16    | 579.635 | 853.635    | 0.2   |           |             |

## C.RAW DATA FOR THE CALCULATION OF THE TRUNCATED OCTAHEDRON VOLUME IN SODALITE CRYSTALS

| Authors  | Large Base<br>Å | Small Base<br>Å | Diagonal Height<br>Å | Height<br>Å | Volume<br>Å <sup>3</sup> |
|----------|-----------------|-----------------|----------------------|-------------|--------------------------|
| Werner1  | 6.273           | 4.435           | 4.959                | 3.841       | 217.1                    |
| Werner2  | 6.202           | 4.386           | 4.903                | 3.797       | 209.8                    |
| Werner3  | 6.156           | 4.353           | 4.867                | 3.770       | 205.2                    |
| Werner4  | 6.092           | 4.308           | 4.816                | 3.730       | 198.9                    |
| Flesche  | 6.234           | 4.408           | 4.928                | 3.817       | 213.1                    |
| Nilesen1 | 6.276           | 4.438           | 4.962                | 3.844       | 217.5                    |
| Nilesen2 | 6.316           | 4.466           | 4.993                | 3.867       | 221.6                    |
| Nilesen3 | 6.370           | 4.505           | 5.036                | 3.900       | 227.4                    |
| Mead1    | 6.362           | 4.498           | 5.029                | 3.895       | 226.5                    |
| Mead2    | 6.380           | 4.511           | 5.043                | 3.906       | 228.4                    |
| Mead3    | 6.363           | 4.500           | 5.030                | 3.896       | 226.6                    |
| Mead4    | 6.394           | 4.522           | 5.056                | 3.916       | 230.0                    |
| Lons     | 6.272           | 4.435           | 4.958                | 3.840       | 217.0                    |

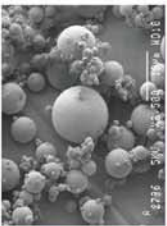
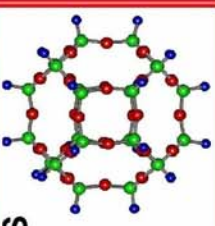
## D.POSTERS

Landman AA, De Waal D, *Interpreting Infrared Spectra of Silicates*, proc SAC12000, 26 September 2000, p 138.



Landman AA, De Waal, *Using The Microscope To Elucidate Sub Microscopic Changes During The Formation Of Ultramarine Pigments*, December 2001, proc Microscopic Society of Southern Africa, 31, p 37, 2001.

## USING THE MICROSCOPE TO ELUCIDATE SUB MICROSCOPIC CHANGES DURING THE FORMATION OF ULTRAMARINE PIGMENTS

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### Fly ash

Fly ash is formed when fossil fuels are burned in power stations. During the burning and cooling of the coal, the forces on the particles cause them to agglomerate, resulting in the characteristic spherical shape of fly ash.

As with any analytical technique, sampling is important. Thus it would be important to ensure that the particles are representative of the whole.

The near constant morphology of fly ash particles are hollow and contain smaller fly ash particles. This should make it easy to assess changes in the fly ash matrix.

### Fly ash treated at 860°C with 50% (m/m) Na<sub>2</sub>CO<sub>3</sub>

Heating fly ash with sodium carbonate is expected to lead to the formation of sodium aluminosilicates. The Na<sub>2</sub>CO<sub>3</sub> addition to the aluminosilicate matrix composition by increasing the less polymerised (monomeric) species Agglomeration and the presence of a matrix is expected. The second stage of the synthesis, but not the final Na<sub>2</sub>CO<sub>3</sub> seems to be crystallites on the surface of what seems to be mixed spherical particles.

### Fly ash treated at 1000°C

The grey colour of fly ash is due to the presence of iron. Fly ash at 1000°C in an alumina crucible in a muffle furnace, leads to an improved morphology of fly ash particles. Although some particles do break up, resulting in sharp edges, the grinding also needed to break up the agglomerated particles and may thus not be representative of the whole.

Agglomeration still persists despite the grinding step. This might be due to cement-like interactions between adjacent aluminosilicate particles, caused by, amongst others, the presence of sodium and calcium ions.

### Fly ash treated at 1000°C

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### Reactions involved in Ultramarine chemistry

The chemistry involved in the synthesis of ultramarine pigments has been discussed extensively. The above reaction has found widespread support, after several other aluminosilicate structures that encapsulate the polyphosphate radicals in the sodalite structure. This is, however, contrary to earlier work [5]. Goetz et al. concluded that the encapsulation of the polyphosphate species and the formation of the β-cage takes place [6]. Kowalski and Strzyska studied the reaction of sodalite, X and Y zeolites, polyphosphates and showed that these reactions lead to the transformation of the structure into the sodalite structure, whereas normal calcination does not [7].

### The Colour of Chemistry

The grey colour of fly ash is not very different from the colour of ultramarine. The cream colour of fly ash treated at 1000°C is due to the presence of residual carbon. Carbon is the result of the residual presence of heavy metal impurities, eg Cu, be assigned to the iron present in fly ash, but to a lesser degree.

The green colour of fly ash treated with sodium carbonate at 860°C is due to the presence of iron. This colour is also believed to originate from the predominant presence of iron, the time the iron is reduced to Fe<sup>2+</sup>, in addition to other polyphosphate oxidation state. Fe<sup>2+</sup> is, however, species. These species are stabilised within the colour structure, which is the colour structure within aluminosilicate pigments.

### What is so special about the β-cages?

The chromophore (polyphosphate) in the ultramarine pigments would ordinarily not be stable at room temperature but are stabilised inside sodalite-type cages (β-cages), which consist of alumina and silica tetrahedra that link to each other to encapsulate both the polyphosphate species and alumina [8]. The β-cages link to each other to form a ceramic type compound with characteristic morphology.

Although hydrogen (blue holes) are shown in the aluminosilicate structures these building blocks to generate three dimensional structures. The polyphosphate building blocks to generate three dimensional structures.

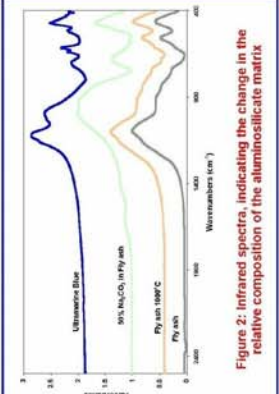
### What does all this tell us?

Heating fly ash does not significantly affect the matrix composition, nor does it have a large influence on the morphology of the particles. The addition of sodium carbonate to fly ash leads to a major morphology change towards a less polymerised state. The addition of sulphur seems to be the key ingredient in the morphology change. The infrared spectrum of ultramarine blue (Fig 2) indicates that some three dimensional polyphosphate structure is present in the system. The introduction of β-cages leads to a three-dimensional network.

### Why does sulphur play such an important role?

Sulphur melts at 115.2°C and boils at 444.6°C [9]. In the endothermic reaction the melt might persist for longer under the sulphur vapour pressure. This melt might act as a solvent, thus allowing the energy for the reactions needed in the formation of the ultramarine blue. The addition of sulphur to the Na<sub>2</sub>CO<sub>3</sub> fly ash system leads to negatively charged polyphosphates from. These species are mostly neutral radicals. These reactive radicals might then form the sodalite structure into an appropriate coordination sphere. This sphere of coordination might then form the aluminosilicate matrix. The addition of sulphur to the Na<sub>2</sub>CO<sub>3</sub> fly ash system leads to the polyphosphate building blocks to generate three dimensional structures.

### Figure 1: Infrared spectra, indicating the change in the relative composition of the aluminosilicate matrix



### Acknowledgements

1. NRS for financial support.
2. University of Pretoria, for the facilities.
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4. Spilveit, for supplying the fly ash. Spilveit substitutes fly ash from the Lelthabo Power station and does research in order to utilize fly ash as a waste resource.
5. Dr V.H. Ebrahim, for help with the HyperChem modelling.

### References

1. N.J. Greenwood, A. Earnshaw, Chemistry of the Elements, second ed., Butterworth-Heinemann, Oxford (1997).
2. R.H. Clark, L.J. Dineen, M. Kumari, *inorg. Chem.* **22**, pp 2766-2772 (1983).
3. R.H. Clark, D.J. O'Connell, *Inorg. Chem.* **17**, pp 333-337 (1978).
4. K.H. Jørgensen, *Trans. Faraday Soc.* **25**, pp 310-325 (1929).
5. F.M. Jørgensen, *Trans. Faraday Soc.* **25**, pp 310-325 (1929).
6. N. Goetz, A. Demortier, J.P. Lallemand, C. Duquenois, *J. Chem. Soc. Faraday Trans. 2* **84**(15), pp 2257-2260 (1988).
7. S. Fiksdal, *Trans. Faraday Soc.* **80**(3), pp 435-442 (1984).
8. D.S. Lide (editor), CRC Handbook of Chemistry and Physics, 76th ed., CRC Press, Boca Raton (1996).



# The Nature of the Ultramarine **Red** Chromophore

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University of Pretoria



University of Pretoria

| Reference                                                                                         | Infrared<br>cm <sup>-1</sup> | Raman<br>cm <sup>-1</sup> | UV<br>nm         |
|---------------------------------------------------------------------------------------------------|------------------------------|---------------------------|------------------|
| U. Holzmann, E. Herzogel and others., <i>Z. anorg. allg. Chem.</i> , <b>367</b> , 119-120 (1969). |                              | 520                       | 520              |
| F. Seel, H.-J. Güttler and others., <i>Z. Naturforsch.</i> , <b>34b</b> , 1675-1677 (1979).       |                              | 520                       | 520              |
| K.-H. Schwarz, U. Holzmann, <i>Z. anorg. allg. Chem.</i> , <b>378</b> , 152-159 (1970).           | 1210                         | 520                       | 520              |
| R.J.H. Clark, D.G. Cobbold, <i>inorg. Chem.</i> , <b>17</b> (11), 3189-3174 (1978).               |                              | 362                       | 520              |
| R.J.H. Clark, T.J. Dees, M. Kumos, <i>Inorg. Chem.</i> , <b>22</b> , 2766-2772 (1983).            |                              | 654<br>674<br>1024        |                  |
| U. Holzmann, E. Herzogel and others., <i>Z. anorg. allg. Chem.</i> , <b>367</b> , 119-120 (1969). |                              |                           | Low permeability |

HyperChem6 was used for the computations on a Compaq Presario 1200 Celeron 850 MHz 128 MB RAM, with the 6-311G\*\* ab initio basis set at the Hartree-Fock level extended by MP2 correlation energy.

The molecular orbitals of 5', and 5'', were determined in order to use a Woodward-Hoffmann analysis to evaluate the feasibility of some of the S<sub>2</sub> isomers.

Ab initio determined vibrational frequencies are usually larger than observed frequencies, and need scaling. A scaling factor of 0.87 was used.

Only six of the proposed  $S_{\text{isomers}}$  (Figure 1) survive the ab initio analysis. The order of stability for the  $S_{\text{isomers}}$  is shown in (Table 2).

$S_{\text{isomers}}$  = *trans chain* > *puckered ring* > *bent exocyclic* > *planar branched chain* > *gauche chain* (triple).

The last two correspond to the structures that withstood the Woodward-Hoffmann analysis (Figure 2). The bent exocyclic structure is not allowed. The *trans* and *chain* are conformers of the allowed *gauche chain* whereas the branched chain is the more stable conformer of the pyramidal structure.

None of the other triplel state  $S_{\text{isomers}}$  turned out to be true minima (Table 2), nor any of the  $S_{\text{isomers}}$  (Table 2).

For  $S_{\text{isomers}}$  the *gauche chain* and *planar branched chain* were found to be stable structures (Table 2). For  $S_{\text{isomers}}$  only the *branched chain* is a true minimum (Table 2).  $S_{\text{isomers}}$  turns out to be a good minimum as well (Table 2).

The open,  $C_{2v}$ ,  $S_{\text{isomer}}$  is established as the most stable. The closed,  $D_{2h}$ ,  $S_{\text{isomer}}$  has an energy only 9 kcal/mol higher than the open isomer (Table 2).

$S_{\text{isomers}}$ ,  $S_{\text{isomers}}$  and  $S_{\text{isomers}}$  are found to be true minima (Table 2).

### Electronic Spectra

As part from the puckered ring and the  $\text{C}_2$  isomer, the stable  $\text{S}_6$  isomers all have one vibrational frequency large enough to be considered as the equivalent of the observed Raman bands (Table 1), but none has two of these high energy vibrations (Table 4 - 7). None reach the observed 1210  $\text{cm}^{-1}$  (Table 1) of the infrared spectrum.

None of the chlorine containing species has computed vibrational frequencies (Table 8 - 11) in the region of the observed 654  $\text{cm}^{-1}$ , or the 674  $\text{cm}^{-1}$  bands in the Raman spectra of ultramarine red (Table 1).

The current vibrational analysis of the open and closed  $\text{S}_6$  isomers discounts both of them as possible chromophores in ultramarine red (Table 12,13).

The SOS possibility is also negated by its vibrational analysis (Table 14).

The calculated vibrational bands for  $\text{S}_6\text{O}$  (Table 15) could be corrected by multiplying by 0.87, which yields vibrational transitions at 362, 605, and 1180  $\text{cm}^{-1}$ . These values are in close agreement with those of the four observed bands for the ultramarine red chromophore (Table 1). Therefore, it is possible that the 654  $\text{cm}^{-1}$  of Clark and Cobbold is not a band that should be associated with the red chromophore.

The vibrational frequencies of  $\text{S}_6\text{O}$  species also fit the experimental values.

Figure 1: Isomers studied as possible chromophore in ultramarine red

**Concerted Reaction Hypothesis for the formation of  $S_4$**

In order to test the feasibility of different structures, the proposed structures of  $S_4$  (Figure 1) are taken as target structures in a Woodward-Hoffmann analysis. The objective is to analyze the frontier molecular orbitals of  $S_4$  and  $S^2$  in such a way that the target molecular structure can be formed, if possible. The highest occupied molecular orbital of  $S_4$  (Figure 1) is placed near the lowest unoccupied molecular orbital of  $S^2$  (Figure 2) in such a way as to ensure that lobes of the same phase overlap to form  $\sigma$ -orbitals.

The puckered square  $S_4$ , pyramidal branched chain  $S_4$ , and gauche  $S_4$  chain structures are reasonable structures for the 6-311G\*\* level.

| Structure Name               | Acidolite | Structure Name      | Acidolite | Structure Name       | Acidolite |
|------------------------------|-----------|---------------------|-----------|----------------------|-----------|
| Singlet Glauche S            | 42 (23)   | Singlet S           | 42        | Cn Glauche S         | 58 (20)   |
| Singlet Branch S             | 7         | Opent S             | 8         | Trunk S              | 0 (3)     |
| Singlet Punctured Square S   | 104 (30)  | Singlet S, Square   | 67 (9)    | Punctured Square S   | 42 (2)    |
| Singlet Tetrahed S           | 28 (8)    | S.S. Triplet        | 8 (3)     | Tetrahed S           | 171 (44)  |
| Singlet Square planer S      | 66 (30)   | S.S. Triplet        | 125 (7)   | Square planer S      | 26 (3)    |
| Singlet Rectangular planer S | 10 (2)    | S.S. Triplet        | 125 (7)   | Rectangular planer S | 33 (30)   |
| Singlet Eicosahed S          | 10 (2)    | S.S. Triplet        | 125 (7)   | Eicosahed S          | 34 (4)    |
| Singlet Pyramidal Chain S    | 18        | DOZ                 | 54 (8.9)  | Pyramidal Chain S    | 19 (3)    |
| Singlet Pyramidal S          | 78 (8)    | DOZ                 | 54 (8.9)  | Pyramidal S          | 28 (20)   |
| Singlet Branch S, Square S   | 23 (6)    | Branch S, S         | 43 (39)   | Branch S, Square S   | 45 (3)    |
| Triplet S                    | 30        | Tri S               | 7 (1)     | Tri S                | 45 (3)    |
| Triplet Tetrahed S           | 61 (6)    | Branch S, S         | 43 (39)   | Tri S                | 45 (3)    |
| Triplet Punctured Square S   | 149 (30)  | Singlet Glauche S-C | -38 (1)   | Tri S                | 45 (3)    |
| Triplet Tetrahed S           | 149 (30)  | Singlet Glauche S-C | -18 (1)   | Tri S                | 45 (3)    |
| Triplet Square planer S      | 38 (2)    | Singlet Glauche S-C | -24 (3)   | Tri S                | 45 (3)    |
| Triplet Rectangular planer S | 33 (14)   | Singlet Glauche S-C | -36 (3)   | Tri S                | 45 (3)    |
| Triplet Eicosahed S          | 111 (2)   | Triplet Glauche S-C | 52 (3)    | Tri S                | 45 (3)    |
| Triplet Branch S, Chain S    | 89 (3)    | Triplet S-C         | 7 (3)     | Tri S                | 45 (3)    |
| Triplet Pyramidal S          | 67 (6)    | Triplet Tri S       | 9 (3)     | Tri S                | 45 (3)    |

A Lewis diagram of a four-membered chain of sulphur atoms is sufficient to indicate the radical nature of the chain, and therefore, the linear chain isomers of  $S_4$  are not regarded as acceptable chromophores. Ring structures are expected to have fairly paired electrons. The tropezoidal chain, and subjoined ring  $S_4$  isomers, are not favourable vibrational frequencies, and can therefore not act as the chromophore in uraniamine red although there might be a suitable electronic transition for these species (Table 3). None of the  $S_4$  isomers is supported by ab initio computations to be a stable species (Table 2).

The  $S_2$  isomers do not have favourable vibrational data, although the paramagnetic character and electronic spectrum (Table 3) potentially fits the experimental observations (Table 1).

The  $S_2O$  could not be evaluated relative to its electronic spectrum, but the vibrational spectrum does not support  $S_2O$  as a suitable candidate for the chromophore in uraniamine red.  $S_2O$  is also expected to be paramagnetic.

The scaled calculated vibrational bands for  $S_2O$  is 362, 666, and 1150  $cm^{-1}$  (Table 16). These values are in close agreement with the observed Raman bands at 352, and 654874  $cm^{-1}$  and the observed infrared band at 1210  $cm^{-1}$ . Therefore,  $S_2O$  could have an electronic transition (Table 3) at 520  $nm$  (Table 1). Therefore,  $S_2O$  is most likely the chromophore in uraniamine red. This validates the conclusion of Schwarz and Hofmann.

| Table 4: Chain isomers of $S_4$        |                        |                      |          |                      |          |
|----------------------------------------|------------------------|----------------------|----------|----------------------|----------|
| Mode                                   | Description            | Straight Chain $S_4$ |          | Branched Chain $S_4$ |          |
|                                        |                        | Symmetry             | Position | Symmetry             | Position |
| v                                      | Symmetric stretch      | a <sub>g</sub>       | 991      | a <sub>g</sub>       | 608      |
|                                        | Central stretch        | a <sub>g</sub>       | 598      | a <sub>g</sub>       | 461      |
|                                        | Asymmetric stretch     | e <sub>g</sub>       | 662      | e <sub>g</sub>       | 522      |
|                                        | Symmetric Deformation  | a <sub>g</sub>       | 289      | a <sub>g</sub>       | 289      |
|                                        | Torsion                | a <sub>g</sub>       | 90       | a <sub>g</sub>       | 244      |
|                                        | Asymmetric Deformation | e <sub>g</sub>       | 180      | e <sub>g</sub>       | 244      |
| v                                      | Asymmetric Deformation | a <sub>g</sub>       | 522      | a <sub>g</sub>       | 591      |
|                                        | Asymmetric Deformation | e <sub>g</sub>       | 522      | e <sub>g</sub>       | 591      |
| Table 5: Bent cyclic $S_4$             |                        |                      |          |                      |          |
| Mode                                   | Description            | Symmetry             |          | Position             |          |
|                                        |                        | Symmetry             | Position | Symmetry             | Position |
| v                                      | Linear stretch         | a <sub>g</sub>       | 563      | a <sub>g</sub>       | 563      |
|                                        | Bent stretch           | e <sub>g</sub>       | 422      | e <sub>g</sub>       | 252      |
|                                        | Symmetric Deformation  | a <sub>g</sub>       | 687      | a <sub>g</sub>       | 770      |
|                                        | Wagging                | e <sub>g</sub>       | 245      | e <sub>g</sub>       | 272      |
|                                        | Asymmetric stretch     | e <sub>g</sub>       | 361      | e <sub>g</sub>       | 361      |
|                                        | Torsion                | a <sub>g</sub>       | 200      | a <sub>g</sub>       | 282      |
| Table 6: Puckered Square $S_4$         |                        |                      |          |                      |          |
| Mode                                   | Description            | Symmetry             |          | Position             |          |
|                                        |                        | Symmetry             | Position | Symmetry             | Position |
| v                                      | Ring stretch           | a <sub>g</sub>       | 563      | a <sub>g</sub>       | 568      |
|                                        | Puckered stretch       | e <sub>g</sub>       | 361      | e <sub>g</sub>       | 257      |
|                                        | Ring Deformation       | e <sub>g</sub>       | 532      | e <sub>g</sub>       | 549      |
|                                        | Ring Deformation       | e <sub>g</sub>       | 361      | e <sub>g</sub>       | 549      |
|                                        | Ring Deformation       | a <sub>g</sub>       | 532      | a <sub>g</sub>       | 549      |
|                                        | Ring Deformation       | e <sub>g</sub>       | 361      | e <sub>g</sub>       | 549      |
| Table 7: Straight Branched Chain $S_5$ |                        |                      |          |                      |          |
| Mode                                   | Description            | Symmetry             |          | Position             |          |
|                                        |                        | Symmetry             | Position | Symmetry             | Position |
| v                                      | Symmetric stretch      | a <sub>g</sub>       | 608      | a <sub>g</sub>       | 522      |
|                                        | Central stretch        | a <sub>g</sub>       | 598      | a <sub>g</sub>       | 461      |
|                                        | Asymmetric stretch     | e <sub>g</sub>       | 662      | e <sub>g</sub>       | 522      |
|                                        | Symmetric Deformation  | a <sub>g</sub>       | 289      | a <sub>g</sub>       | 289      |
|                                        | Out of plane           | e <sub>g</sub>       | 244      | e <sub>g</sub>       | 244      |
|                                        | Asymmetric Deformation | e <sub>g</sub>       | 244      | e <sub>g</sub>       | 244      |
| Table 8: Straight Cyclic $S_5$         |                        |                      |          |                      |          |
| Mode                                   | Description            | Symmetry             |          | Position             |          |
|                                        |                        | Symmetry             | Position | Symmetry             | Position |
| v                                      | Symmetric stretch      | a <sub>g</sub>       | 608      | a <sub>g</sub>       | 522      |
|                                        | Central stretch        | a <sub>g</sub>       | 598      | a <sub>g</sub>       | 461      |
|                                        | Asymmetric stretch     | e <sub>g</sub>       | 662      | e <sub>g</sub>       | 522      |
|                                        | Symmetric Deformation  | a <sub>g</sub>       | 289      | a <sub>g</sub>       | 289      |
|                                        | Out of plane           | e <sub>g</sub>       | 244      | e <sub>g</sub>       | 244      |
|                                        | Asymmetric Deformation | e <sub>g</sub>       | 244      | e <sub>g</sub>       | 244      |

| Table 9: Single Layer Symmetric S-CI |                                   |                |          |
|--------------------------------------|-----------------------------------|----------------|----------|
| Mode                                 | Description                       | Symmetry       | Position |
| v <sub>1</sub>                       | Stretch                           | a              | 196      |
| v <sub>2</sub>                       | Antisymmetric Bend                | a              | 196      |
| v <sub>3</sub>                       | Antisymmetric Bend                | a              | 257      |
| v <sub>4</sub>                       | Compress Stretch                  | b <sub>1</sub> | 519      |
| v <sub>5</sub>                       | S-S and S-C Symmetric Stretch     | a              | 549      |
| v <sub>6</sub>                       | S-S and S-C Antisymmetric Stretch | a              | 558      |

| Table 10: Branched S-CI |                           |          |           |
|-------------------------|---------------------------|----------|-----------|
| Mode                    | Description               | Symmetry | S.C.I.    |
| v <sub>1</sub>          | S-C-O Bend                | a'       | 238 / 237 |
| v <sub>2</sub>          | S-C-O Bending             | a''      | 250 / 250 |
| v <sub>3</sub>          | Dynamical Deformation     | a'       | 409       |
| v <sub>4</sub>          | Antisymmetric Deformation | a''      | 409       |
| v <sub>5</sub>          | S-C-O Symmetric Stretch   | a'       | 479       |
| v <sub>6</sub>          | S-C-O Stretch             | a'       | 552 / 556 |

| Table 11: C-I  |             |          |          |
|----------------|-------------|----------|----------|
| Mode           | Description | Symmetry | Position |
| v <sub>1</sub> | Bending     | a'       | 241      |
| v <sub>2</sub> | C-I stretch | a'       | 530      |
| v <sub>3</sub> | S-C stretch | a'       | 530      |

| Table 12: Singlet (Triplet) Open S- |                       |                |           |
|-------------------------------------|-----------------------|----------------|-----------|
| Mode                                | Description           | Symmetry       | Position  |
| v <sub>1</sub>                      | Symmetric stretch     | a <sub>g</sub> | 519 / 523 |
| v <sub>2</sub>                      | Antisymmetric stretch | b <sub>u</sub> | 550 / 553 |

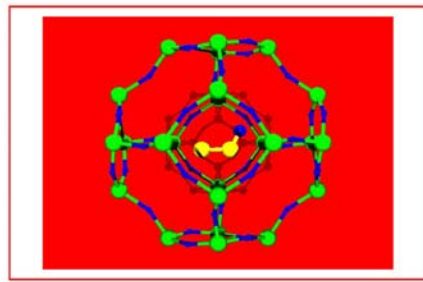
| Table 13: Singlet Closed S- |                       |                |          |
|-----------------------------|-----------------------|----------------|----------|
| Mode                        | Description           | Symmetry       | Position |
| v <sub>1</sub>              | Stretch               | a <sub>g</sub> | 455      |
| v <sub>2</sub>              | Dynamical Deformation | a <sub>g</sub> | 613      |

| Table 14: Singlet GDS |                    |                |          |
|-----------------------|--------------------|----------------|----------|
| Mode                  | Description        | Symmetry       | Position |
| v <sub>1</sub>        | Bending            | a <sub>g</sub> | 592      |
| v <sub>2</sub>        | Asymmetric stretch | a <sub>g</sub> | 592      |
| v <sub>3</sub>        | Dynamical stretch  | a <sub>g</sub> | 667      |

| Table 15: Singlet GDS |             |                |        |
|-----------------------|-------------|----------------|--------|
| Mode                  | Description | Symmetry       | S.C.I. |
| v <sub>1</sub>        | Bending     | a <sub>g</sub> | 594    |
| v <sub>2</sub>        | C-I stretch | a <sub>g</sub> | 594    |
| v <sub>3</sub>        | S-C stretch | a <sub>g</sub> | 594    |



Landman AA, De Waal D, *Vanadium in the Mullite Structure*, SACI Inorganic '03, Roode Vallei Country Lodge, Pretoria, 2003.



## What is Fly Ash?

Fly ash is obtained by separating the solids from the flue gases of furnaces fired with pulverised coal and is the predominantly inorganic residue of the minerals entrained in the coal.

Sphere-Fill (Pty) Ltd size-classifies the fly ash that it obtains from the Lethabo (a Tswana word, which means "good living" or "happiness" [1]) Power Station in the Northern Free State. The different size fractions are obtained by pneumatic control within cyclones at the power plant, a process described as air 'classification'. [2] The class F fly ash particles were of similar size: in the range of 1  $\mu\text{m}$  to 12  $\mu\text{m}$ , with an average diameter of less than 5  $\mu\text{m}$ .

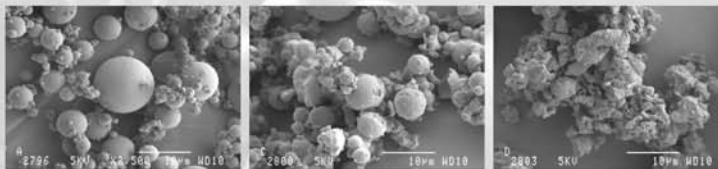


Figure 1: Scanning electron micrographs of fly ash, fly ash treated at 1000 °C, and fly ash reacted with ammonium metavanadate at 1000 °C

## Synthesis Procedures

Fly ash was heated to 1000 °C in an alumina crucible for 24 hours to establish the effect of heating on the microscopic and sub-microscopic structure of fly ash.

Fly ash has a grey colour. After the heat treatment fly ash had a cream colour.

Ammonium metavanadate AR (Associated Chemical Enterprises cc) is sparingly soluble in water and was dissolved in a 5 % nitric acid CP (Chemical Suppliers (Pty) Ltd) solution. The vanadium species were forced to precipitate by evaporation onto the insoluble fly ash. The obtained powder was milled and heated at 1000 °C in an alumina crucible for 24 hours. Samples were annealed after a first round of analyses at 600 °C for 24 hours, to obtain better Raman spectra.

The resulting products had, at some concentrations of vanadia (5, 7, 10 %), a yellow colour. This result was unexpected since the decomposition product of ammonium metavanadate is vanadium pentoxide, an orange-brown chemical species. The orange-brown colour was obtained at high concentrations of vanadia (25 %). In vanadium pentoxide the vanadium atom is found in a distorted octahedron (Tittle structure).

Ammonium metavanadate AR was placed in a porcelain dish with aluminium nitrate CP (uniLab, SAARCHM (Pty) Ltd) and silicic acid (precipitated extra pure light, Merck). The mixture was heated at approximately 140 °C in the presence of the water of hydration. At this stage the nitrate started to decompose. The dry fine solid was ground in a mortar and pestle and calcined in an alumina crucible at 600 °C in a muffle furnace for 1 hour, to remove the remaining waters of hydration. After grinding the mixture again, the mixture was placed in the furnace and calcined at 1000 °C for 24 hours.

The silicate-alumina-vanadia mixtures had a yellow colour, surpassing the yellow colour of fly ash reacted with ammonium metavanadate.

## Scanning Electron Microscopy

Fly ash has a predominantly spherical microscopic structure (Fig 1). Upon heating fly ash, the scanning electron microscopy micrographs changed only slightly.

Scanning Electron Micrographs showed that there was *more than just a difference between the fly ash and the fly ash treated at 1000 °C*. The spherical shape of fly ash was destroyed during the reaction of fly ash with ammonium metavanadate. This reflected the fluxing nature of the vanadia species. The skeleton-like structures observed in the scanning electron microscopy micrographs were similar to the micrographs of HF etched fly ash particles [3].

## X-Ray Diffraction

In the current X-ray diffraction patterns only mullite and quartz could be identified (Fig 2). [4,5] The quartz peak is not clearly visible in the presented pattern.

Neither the heat treatment nor reaction with ammonium metavanadate caused significant changes in the X-ray diffraction patterns of fly ash. **This might indicate that the vanadium atom replaced either a silicon or an aluminium atom in the aluminosilicate structure, or that the vanadia species was not detectable.**

Some synthesised aluminosilicates, of which only the synthesis of mullite is presented in this poster, gave a yellow colour. X-ray diffraction powder analyses identified the successful **aluminosilicate species as mullite** (Fig 2).

## Mullite Structure and Vanadium

Several types of interaction between the aluminosilicate and vanadia could be possible: adsorption of the formed vanadium pentoxide on the surface of the fly ash; inclusion of vanadia in an aluminosilicate structure in either an interstitial, silicon or aluminium site.

Vanadium in Zirconia ( $\text{ZrSiO}_4$ ) is believed to occupy tetrahedral  $\text{Si}^{4+}$  sites in the zirconia lattice [6].

In the crystal structure of mullite [7] (Fig 4) the **aluminium atoms occupy octahedral sites and the silicon atoms tetrahedral sites**. The (010) and (001) planes indicate that interstitial positions are available for the vanadium atom.

## References

1. Eskom - Lethabo Visitor Centre, Eskom, [http://www.eskom.co.za/education/visit/lethabo/lethabo\\_body.htm](http://www.eskom.co.za/education/visit/lethabo/lethabo_body.htm), 2002, downloaded 17 December 2002 - 15:30.
2. B.E. Scheetz, R. Earle, *Current Opinion in Solid State & Material Science*, 1998, 3, 510-520.
3. L.D. Hulett, A.J. Weinberger, *Environmental Science and Technology*, 1980, 14(8), 965-970.
4. R. Helmut, *Fly Ash in Cement and Concrete*, Portland Cement Association, Skokie, 1987, pp. 36-61.
5. J.L. Alonso, K. Wesche, *Characterization of Fly Ash*, in: K. Wesche (Ed), *Fly Ash in Concrete - Properties and Performance*, First edition, E & FN SPON, London, 1991, p. 8.
6. D. De Waal, A.M. Heyns, and others, *J. Raman Spectrosc.*, 1999, 27, 657-662.
7. R. Sadanga, M. Tokonami, Y. Takeuchi, *Acta Cryst.*, 1982, 15, 65-66.

## Acknowledgements

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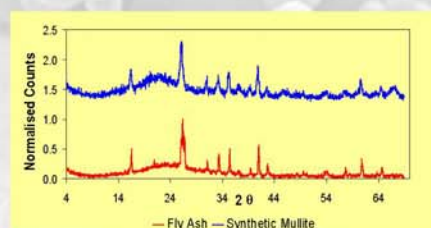


Figure 2: X-ray diffraction patterns

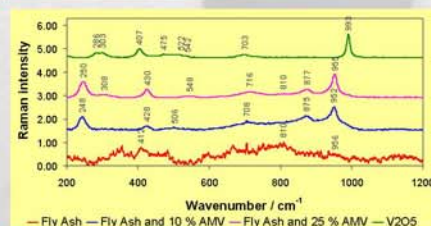


Figure 3: Raman spectra

## Raman Spectroscopy

Due to the combination of the small size and spherical microscopic structure of fly ash, no sensible Raman spectrum could be obtained for fly ash. The observed bands for fly ash treated with 10 % (a yellow product) and 25 % (a brown product) ammonium metavanadate (AMV) are similar to the bands for vanadium pentoxide (Fig 3). **This indicated that the vanadium could be in a distorted octahedral environment, as in vanadium pentoxide.**

## Conclusion

The yellow colour resulting after fly ash reacted with ammonium metavanadate was believed to be the result of vanadium in the mullite structure itself, or the amorphous precursor of mullite.

Due to the similarity of the Raman spectrum of the yellow product and the Raman spectrum of vanadium pentoxide, it can be concluded that **the vanadium atoms possibly replaced some of the aluminium atoms in the mullite structure.**

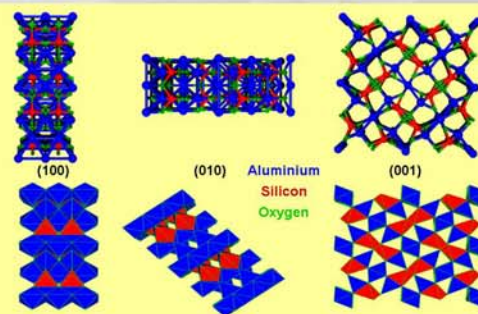


Figure 4: Crystal representations of Mullite

Landman AA, De Waal D, *Symmetry in Pigmentary Chromophores*, proc INDABA III, p , 8 August 2000.



# Orbital symmetry in pigmentary chromophores

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### Introduction

There is a growing interest in the study of the electronic structure of fly ash pigments. The fly ash pigments are a class of materials that are formed during the combustion of coal. They are composed of a variety of inorganic compounds, including silicates, aluminates, and oxides. The fly ash pigments are known for their unique color and stability, and they are used in a variety of applications, including pigments, dyes, and coatings. The study of the electronic structure of fly ash pigments is important for understanding their properties and for developing new materials with improved performance.

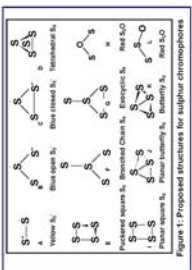
### Pictorial Molecular Orbital Theory

The pictorial molecular orbital theory (PMOT) is a method for determining the electronic structure of molecules. It is based on the principles of quantum mechanics and is used to calculate the energy levels and wavefunctions of molecules. The PMOT is a powerful tool for understanding the electronic structure of molecules and for predicting their properties. It is used in a variety of applications, including the study of pigments, dyes, and coatings.

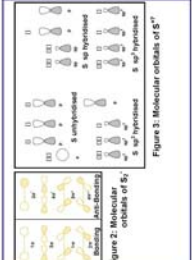
### The value of orbital symmetry

The value of orbital symmetry is a measure of the symmetry of the orbitals in a molecule. It is used to determine the electronic structure of molecules and to predict their properties. The value of orbital symmetry is a key factor in the study of pigments, dyes, and coatings, and it is used in a variety of applications, including the study of the electronic structure of molecules and the prediction of their properties.

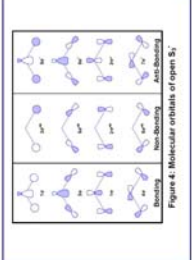
### Figure 1: Proposed structures for sulphur chromophores



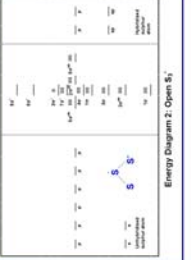
### Figure 2: Molecular orbitals of S<sub>2</sub>



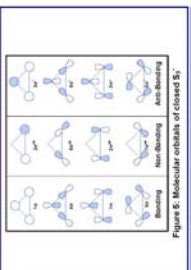
### Figure 3: Molecular orbitals of S<sub>4</sub>



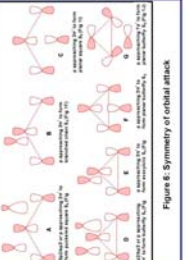
### Figure 4: Molecular orbitals of open S<sub>2</sub>



### Figure 5: Molecular orbitals of closed S<sub>2</sub>



### Figure 6: Symmetry of orbital attack



### Figure 7: Symmetry of orbital attack



### Theory applied

The theory applied in this study is the pictorial molecular orbital theory (PMOT). The PMOT is a method for determining the electronic structure of molecules. It is based on the principles of quantum mechanics and is used to calculate the energy levels and wavefunctions of molecules. The PMOT is a powerful tool for understanding the electronic structure of molecules and for predicting their properties. It is used in a variety of applications, including the study of pigments, dyes, and coatings.

### Yellow S<sub>2</sub> species

The yellow S<sub>2</sub> species is a class of materials that are formed during the combustion of coal. They are composed of a variety of inorganic compounds, including silicates, aluminates, and oxides. The yellow S<sub>2</sub> species are known for their unique color and stability, and they are used in a variety of applications, including pigments, dyes, and coatings. The study of the electronic structure of yellow S<sub>2</sub> species is important for understanding their properties and for developing new materials with improved performance.

### Blue open S<sub>2</sub> species

The blue open S<sub>2</sub> species is a class of materials that are formed during the combustion of coal. They are composed of a variety of inorganic compounds, including silicates, aluminates, and oxides. The blue open S<sub>2</sub> species are known for their unique color and stability, and they are used in a variety of applications, including pigments, dyes, and coatings. The study of the electronic structure of blue open S<sub>2</sub> species is important for understanding their properties and for developing new materials with improved performance.

### Blue closed S<sub>2</sub> species

The blue closed S<sub>2</sub> species is a class of materials that are formed during the combustion of coal. They are composed of a variety of inorganic compounds, including silicates, aluminates, and oxides. The blue closed S<sub>2</sub> species are known for their unique color and stability, and they are used in a variety of applications, including pigments, dyes, and coatings. The study of the electronic structure of blue closed S<sub>2</sub> species is important for understanding their properties and for developing new materials with improved performance.

### Conclusions

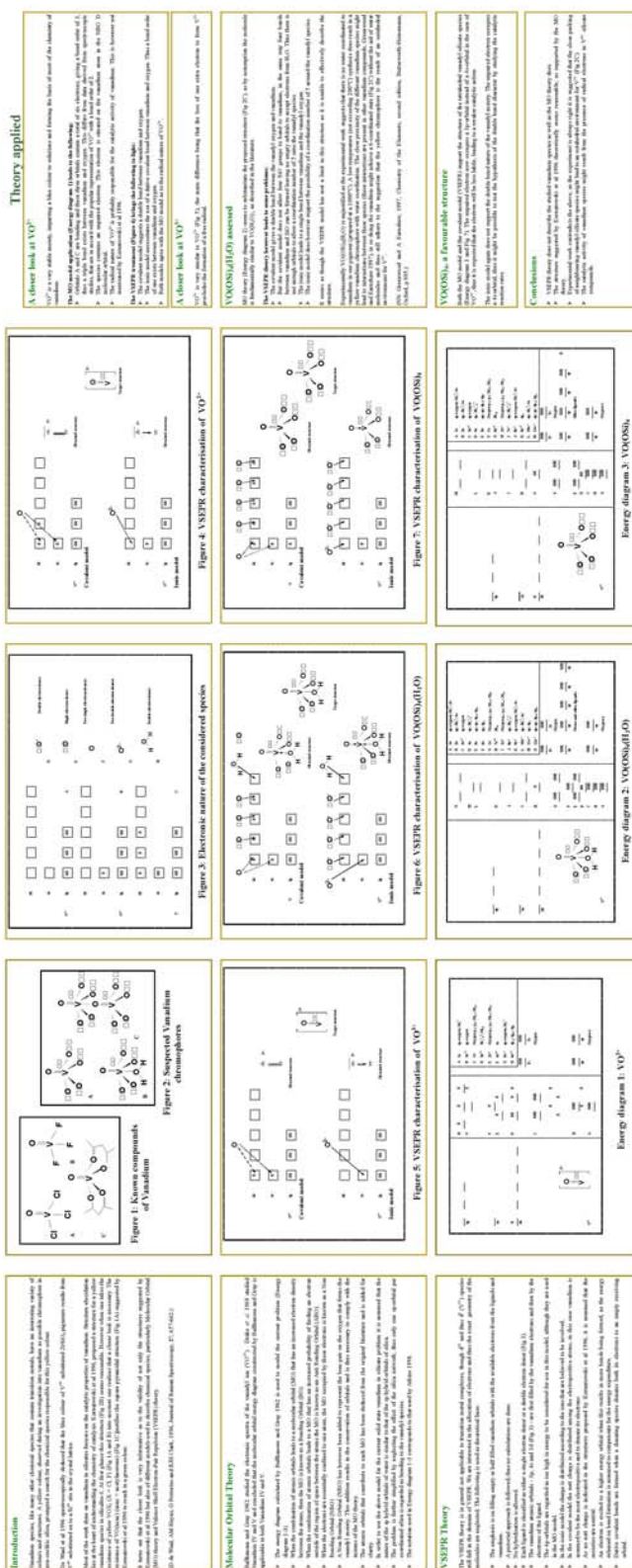
The study of the electronic structure of fly ash pigments is important for understanding their properties and for developing new materials with improved performance. The PMOT is a powerful tool for understanding the electronic structure of molecules and for predicting their properties. It is used in a variety of applications, including the study of pigments, dyes, and coatings.

Landman AA, De Waal D, *Vanadium electrons in Pigmentary Chromophores*, proc INDABA III, p, 9 August 2000.

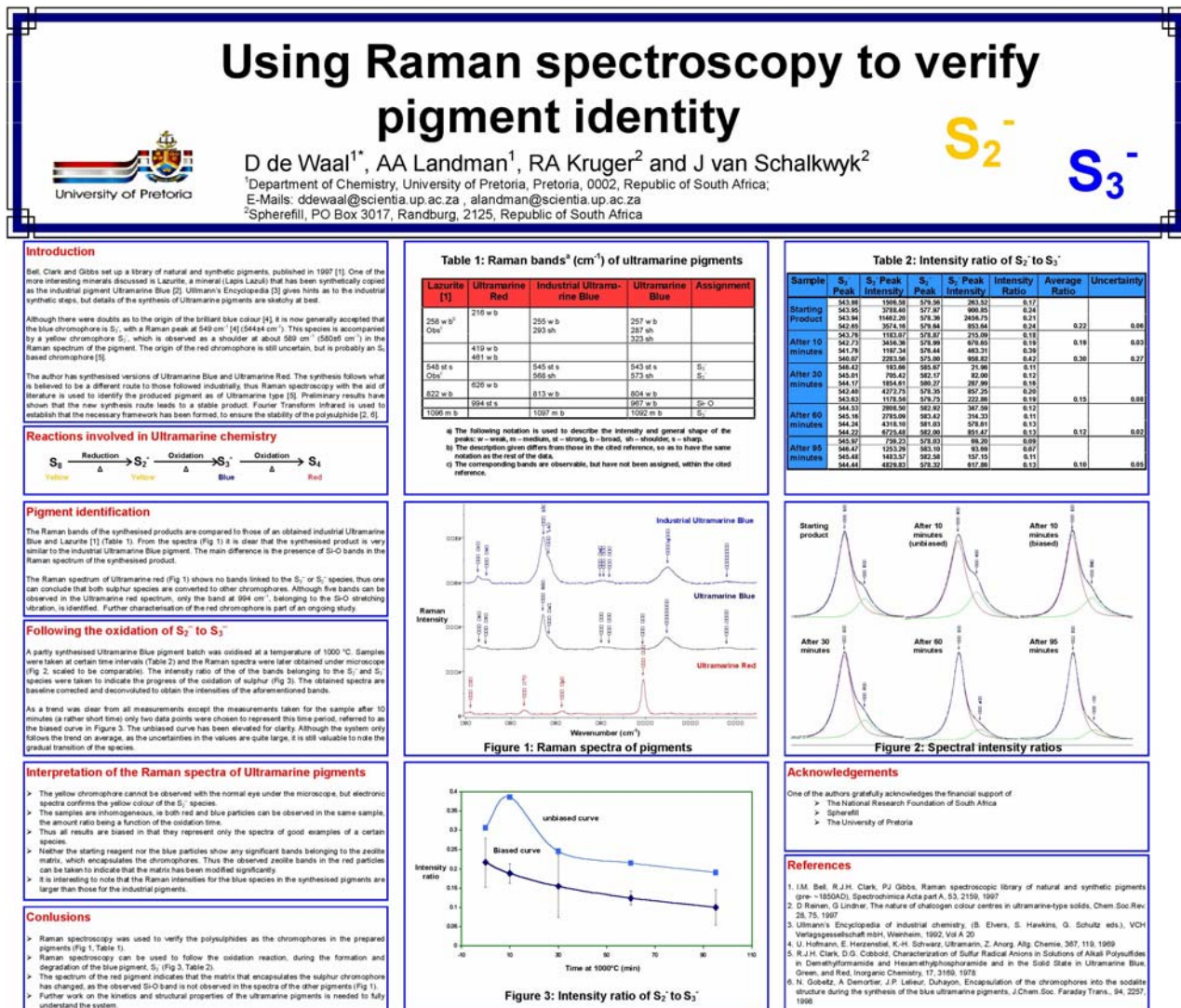
# Vanadium electrons in pigmentary chromophores



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De Waal D, Landman AA, Kruger RA, van Schalkwyk J, *Using Raman Spectroscopy to verify pigment identity*, proc Seventeenth International Conference on Raman Spectroscopy (ICORS 2000), Beijing, China, p , 20-24 August 2000.



# Vibrational Spectroscopy of Vanadia in Silicates

## What chemical species is responsible for the yellow colour?

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**The Journey** What I wanted to Say, but cannot

The journey of elucidating the structure of the chemical species responsible for the yellow colour of vanadia in Fe-ash, is like the blue space in the background. The spiral leads downwards, but is greatly distorted. This journey takes us to the depths of knowledge of the subject of silicates and should also, one day, lead to the depths of understanding of the chemical species responsible for the yellow colour.

Variable species, the many other chemical species that contain transition metals, have an interesting history of colour and structure in a yellow colour, observed during an investigation into vanadium, as well as the chemical species responsible for the yellow colour.

De Waal et al (1998) (1) spectroscopically deduced that the blue colour of V<sup>5+</sup>-substituted ZnO, originates from V<sup>5+</sup> substituted into a Zn<sup>2+</sup> site in the crystal lattice. Most of the data on vanadium in silicates focuses on the catalytic properties of vanadium (2). Little work has, however, been done on vanadium in silicates (3).

The amphibole species of the silicate starting reagent makes it difficult to identify new structural types independent decomposition of the spectra has, however, made it quite easy to strip where the band relating to V=O-V=O is located, band at 953 cm<sup>-1</sup> (Figure 16, spin content 0%). The band at 1030 cm<sup>-1</sup> (deformation band in the shoulder of Figure 16) for the amphibole species, obtained at 1000 °C, is used to identify the V=O-V=O band in Figure 16 in the vanadium-containing species.

In order to elucidate the structure of the chemical species responsible for the yellow colour various chemical, spectroscopic and structural studies were undertaken. The infrared (IR), Raman and X-ray diffraction (XRD) spectra were obtained and are discussed.

Unfortunately the IR spectra do not give any information as to the structure of the yellow vanadia species, not even for the work presented above. Back to square one.

**Wet lab work**

The samples were prepared from CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, MgO, and silicic acid by an extensive process involving crystallization of the salts into the silicate compound. The samples were compared with similar silicates in order to see, as the chemistry is deemed to be important, when incorporating silicate structures (3).

**Source Name** **Calculated theoretical spin content** **XRD Results**

| Source Name                                                     | Calculated theoretical spin content | XRD Results                                                     |
|-----------------------------------------------------------------|-------------------------------------|-----------------------------------------------------------------|
| CaO                                                             | 0.00                                | CaO                                                             |
| Al <sub>2</sub> O <sub>3</sub>                                  | 0.00                                | Al <sub>2</sub> O <sub>3</sub>                                  |
| Fe <sub>2</sub> O <sub>3</sub>                                  | 0.00                                | Fe <sub>2</sub> O <sub>3</sub>                                  |
| Na <sub>2</sub> CO <sub>3</sub>                                 | 0.00                                | Na <sub>2</sub> CO <sub>3</sub>                                 |
| MgO                                                             | 0.00                                | MgO                                                             |
| CaO-Al <sub>2</sub> O <sub>3</sub>                              | 0.00                                | CaO-Al <sub>2</sub> O <sub>3</sub>                              |
| Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub>  | 0.00                                | Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub>  |
| Fe <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> | 0.00                                | Fe <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> |
| Na <sub>2</sub> CO <sub>3</sub> -MgO                            | 0.00                                | Na <sub>2</sub> CO <sub>3</sub> -MgO                            |
| MgO-Al <sub>2</sub> O <sub>3</sub>                              | 0.00                                | MgO-Al <sub>2</sub> O <sub>3</sub>                              |
| CaO-MgO                                                         | 0.00                                | CaO-MgO                                                         |
| Al <sub>2</sub> O <sub>3</sub> -MgO                             | 0.00                                | Al <sub>2</sub> O <sub>3</sub> -MgO                             |
| Fe <sub>2</sub> O <sub>3</sub> -MgO                             | 0.00                                | Fe <sub>2</sub> O <sub>3</sub> -MgO                             |
| Na <sub>2</sub> CO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> | 0.00                                | Na <sub>2</sub> CO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> |
| Al <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> | 0.00                                | Al <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> |
| Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>  | 0.00                                | Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>  |
| Na <sub>2</sub> CO <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> | 0.00                                | Na <sub>2</sub> CO <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> |
| MgO-Fe <sub>2</sub> O <sub>3</sub>                              | 0.00                                | MgO-Fe <sub>2</sub> O <sub>3</sub>                              |
| CaO-Fe <sub>2</sub> O <sub>3</sub>                              | 0.00                                | CaO-Fe <sub>2</sub> O <sub>3</sub>                              |
| Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub>  | 0.00                                | Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub>  |
| Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>  | 0.00                                | Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>  |
| Na <sub>2</sub> CO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> | 0.00                                | Na <sub>2</sub> CO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> |
| Al <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> | 0.00                                | Al <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> |
| Fe <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> | 0.00                                | Fe <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> |
| Na <sub>2</sub> CO <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> | 0.00                                | Na <sub>2</sub> CO <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> |
| MgO-Fe <sub>2</sub> O <sub>3</sub>                              | 0.00                                | MgO-Fe <sub>2</sub> O <sub>3</sub>                              |
| CaO-Fe <sub>2</sub> O <sub>3</sub>                              | 0.00                                | CaO-Fe <sub>2</sub> O <sub>3</sub>                              |
| Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub>  | 0.00                                | Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub>  |
| Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>  | 0.00                                | Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>  |
| Na <sub>2</sub> CO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> | 0.00                                | Na <sub>2</sub> CO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> |
| Al <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> | 0.00                                | Al <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> |
| Fe <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> | 0.00                                | Fe <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> |
| Na <sub>2</sub> CO <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> | 0.00                                | Na <sub>2</sub> CO <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> |
| MgO-Fe <sub>2</sub> O <sub>3</sub>                              | 0.00                                | MgO-Fe <sub>2</sub> O <sub>3</sub>                              |
| CaO-Fe <sub>2</sub> O <sub>3</sub>                              | 0.00                                | CaO-Fe <sub>2</sub> O <sub>3</sub>                              |
| Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub>  | 0.00                                | Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub>  |
| Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>  | 0.00                                | Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>  |
| Na <sub>2</sub> CO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> | 0.00                                | Na <sub>2</sub> CO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> |
| Al <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> | 0.00                                | Al <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> |
| Fe <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> | 0.00                                | Fe <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> |
| Na <sub>2</sub> CO <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> | 0.00                                | Na <sub>2</sub> CO <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> |
| MgO-Fe <sub>2</sub> O <sub>3</sub>                              | 0.00                                | MgO-Fe <sub>2</sub> O <sub>3</sub>                              |
| CaO-Fe <sub>2</sub> O <sub>3</sub>                              | 0.00                                | CaO-Fe <sub>2</sub> O <sub>3</sub>                              |
| Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub>  |                                     |                                                                 |

 **The benefits of deconvoluting vibrational spectra of pigments based on aluminosilicates**

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Figure 7: Possible route to an easy deconvolution of complex spectra

## **E. BENEFICIARIES**

### **E1. SPHERE-FILL (PTY) LTD**

"Sphere-Fill (Pty) Limited is a wholly owned subsidiary of Ash Resources, South Africa. Ash Resources currently sells over 1,2 million tons/annum of the finest quality fly ash in Southern Africa and the Middle East." (Contact Details - Company profile, Sphere-Fill, <http://www.superpozz.com/contact1.html>, 2002, downloaded 10 September 2002 - 10h00.) The spherical form of fly ash makes it potentially functional in improving the workability of plastics. The current grey colour of fly ash is however a deterrent, since this colour hides the colour of added pigments and fly ash is not marketable in its grey state. Sphere-Fill (Pty) Ltd needed to know whether it is possible to colour fly ash. The new colours observed in fly ash will make fly ash more marketable, especially the heat treated fly ash. Any company utilising the proposed pigment syntheses will be expected to sign a contract with Sphere-Fill (Pty) Ltd as exclusive supplier of fly ash.

### **E2. ROLFES COLOUR PIGMENTS INTERNATIONAL**

Rolfes Colour Pigments International is interested in producing ultramarine blue locally. They can now consider using fly ash to produce the pigment.

### **E3. UNIVERSITY OF PRETORIA**

"The University of Pretoria's mission is to:

- be an internationally recognised academic institution which provides teaching, undertakes research and renders community service;
- fulfil the educational, cultural, social, economic and technological needs of the South African and Southern African communities; and
- be a member of the international scientific community." (University of Pretoria Mission statement, University of Pretoria, <http://www.up.ac.za/history/mission.html>, 05 May 2001, downloaded 5 May 2001 - 22:30.)

This project aids in achieving these goals by:

- Research that is relevant to local companies
- Research output, with international exposure, in the form of journal articles (1 published, 1 accepted, 2 submitted and 4 prepared), conference contributions in the form of posters (9) and lectures (4) and a thesis/dissertation.
- Research grants help in extending and improving the facilities at the University of Pretoria.

### **E4. SCIENCE**

Fly ash is a powerful starting reagent in the synthesis of ultramarine blue, and could possibly be used in other applications as well. Science gained from this research a methodology for studying the solid-state reactions of fly ash.

### **E5. ENVIRONMENT**

Man harnesses energy for beneficial purposes. Unfortunately this often has a price. In the Republic of South Africa the price of using low grade, abundantly available coal in generating electricity is mountains of fly ash. The aim of this project is to find other uses for fly ash and therefore reduce the problem of unused resources that pose environmental problems. Less fly ash in the environment will benefit not only the Republic of South Africa but also all countries that use coal-fired power plants.

## **F. PUBLISHED ARTICLE**