

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.¹ Pretorius² 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.

Harden³ 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 1945.⁴ 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.^{5,6} 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 briquettes⁴ and the use of milder oxidizing agents, like sulphur dioxide⁴ and water in air⁷ can be studied. Hydrothermal methods^{8,9} 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).

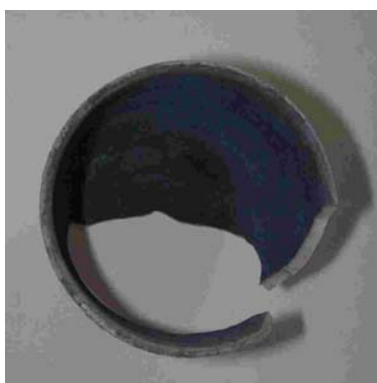


Figure 7-1: Broken alumina crucible used for the synthesis of ultramarine blue

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.¹⁰ 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

Jaeger¹¹ 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.¹¹ 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.¹¹ Jaeger¹¹ 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.¹²

Choosing not to assign specific positions for the sulphur atoms for the S_3^- group in ultramarine blue, Tarling and others¹³ 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.¹³ Furthermore, the sulphur - sulphur bond distances were in the order of 1 Å, a situation that was unacceptable to Gordillo and Herrero.¹⁴ This question could be studied by electron diffraction.

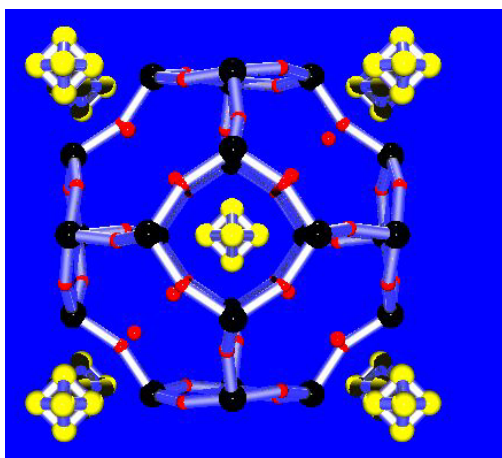


Figure 7-2: Ultramarine blue crystal structure suggested by Tarling and others¹³

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

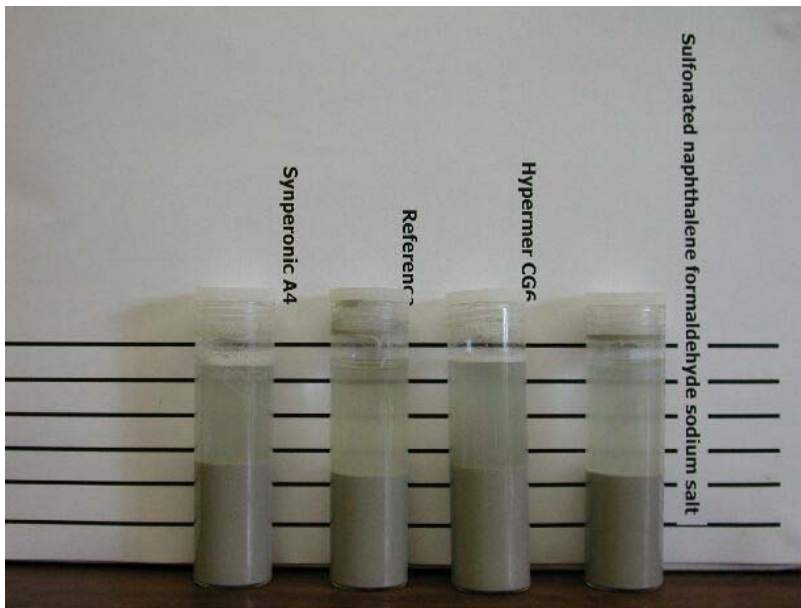


Figure 7-6: Synperonic A4 (successful), Hypermer CG6 (successful), and sulphonated naphthalene formaldehyde sodium salt used to suspend fly ash in water, after 5 minutes of settling time

7.4. Adding Colour to Fly Ash

The original aim was to change the colour of fly ash, so that fly ash would be more marketable (Chapter 0). To this end several different elements in the periodic table were tested to see whether any colour could be imparted to fly ash (Figure 7-7).

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
H																		He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuh		Uuo
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Figure 7-7: Periodic table of experiments and colours obtained. Grey indicates elements that were not tested, and the coloured cells indicate the colour obtained with the aid of the element

7.4.1. Alkali Metals

Sodium is regarded as something that did not work, because the white colour sodium imparts is not very strong and 30 % m/m sodium carbonate needs to be added to obtain this colour. At a 3:1 mass ratio of sodium carbonate to fly ash a green mineral-type colour is obtained. This hard green product of fly ash and sodium carbonate (BDH AnalR) is worth investigating, since the green colour is believed to result from reduced iron, which seems chemically improbable due to the oxidizing atmosphere in the muffle furnace.

7.4.2. Alkaline-earth Metals

Magnesium as magnesium sulphate anhydrous (BDH AnalR), barium as barium thiosulfate·H₂O (ICN Pharmaceuticals Inc) and calcium as calcium carbonate (Merck) were tested. Fly ash does not seem to react with the alkaline-earth metals. Higher temperatures, like in the clinkering of cement, might be needed.

7.4.3. Main Group Elements

Phosphorus (di-ammonium hydrogen phosphate - GR/ACS Merck; Iron(III)phosphate - Aldrich Chemical Company, Inc.), tin (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. NH_4VO_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 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 % NH_4VO_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.¹⁵ 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 PeakFit¹⁶ 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 ⁻¹)	Width (cm ⁻¹)	Fraction Gaussian
Decimal places Required		3	1	1	2
430	Min	0.047	416.1	9.2	0.00
	Max	0.524	444.0	87.2	1.00
472	Min	0.320	462.8	24.3	0.00
	Max	0.784	481.7	71.3	1.00
507	Min	0.089	498.2	19.7	0.13
	Max	0.507	517.8	50.2	1.00
566	Min	0.022	555.0	9.1	0.16
	Max	0.491	577.9	72.1	1.00
617	Min	0.008	611.6	14.7	0.00
	Max	0.264	623.4	39.8	1.00
685	Min	0.000	677.4	0.0	0.00
	Max	0.322	693.9	55.7	1.00
725	Min	0.085	708.7	24.7	0.21
	Max	0.355	742.0	73.7	1.00
831	Min	0.042	815.7	40.2	0.44
	Max	0.373	847.5	99.0	1.00
890	Min	0.128	872.4	62.6	0.20
	Max	0.611	907.5	126.9	1.00
981	Min	0.245	963.3	111.4	0.55
	Max	1.139	999.4	187.3	1.00
1092	Min	0.326	1076.5	79.7	0.00
	Max	0.966	1107.3	177.3	1.00
1164	Min	0.065	1142.5	48.1	0.00
	Max	0.548	1184.7	147.7	1.00
1438	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 MOME97¹⁷ or PEFF¹⁸ to develop a force field with parameters for vanadium. An example of such an endeavour is the work of JJP Stewart¹⁹ 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.²⁰

7.7. Density Functional Theory

The **Amsterdam Density Functional**^{21,22,23} program can be used to calculate geometries, energies, infrared spectra^{24,25} and Raman scattering.²⁶ The **Electron Paramagnetic Resonance (EPR)**^{27,28} and **Electron Spin Resonance (ESR)** spectra^{29,30} 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 (ZrSiO₄) and Zirconia (ZrO₂)*, 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.