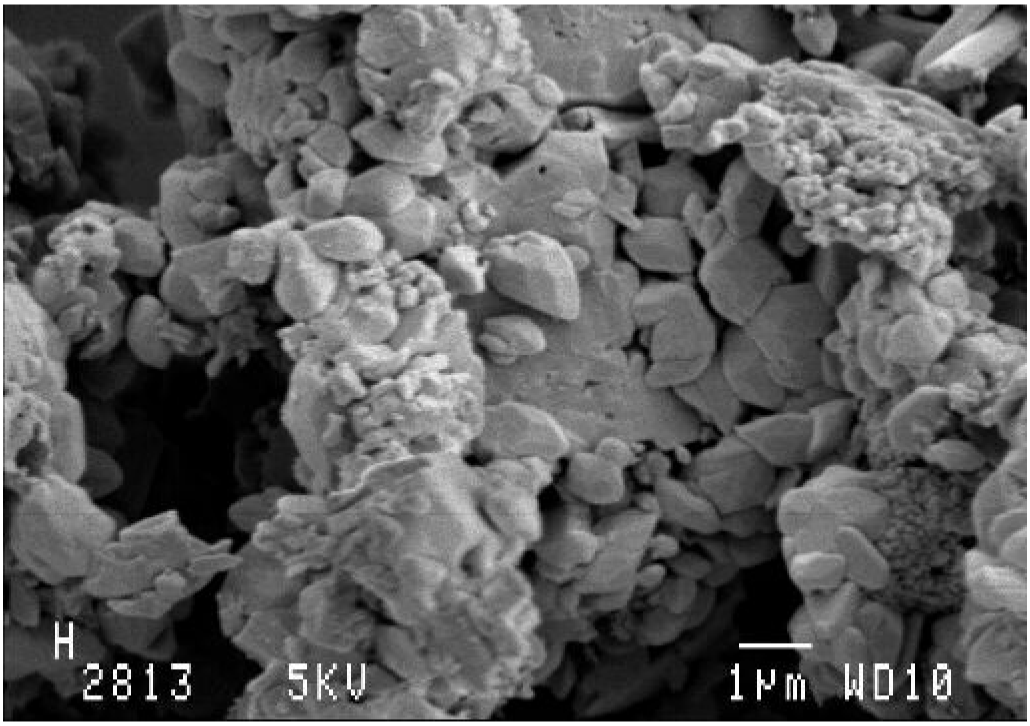
CHAPTER 4

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, $S_2^{-\bullet}$ and $S_3^{-\bullet}$, thereby stabilising the radical. The $S_3^{-\bullet}$ and $S_2^{-\bullet}$ were stable in the aluminosilicate framework,[1] and the quality of the synthesised pigment depended on the quality, that is defect-free, aluminosilicate framework.[2] The main building block of this aluminosilicate framework was the β-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[3] 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, $(Na,Ca)_{4\text{-}8}[Al_6Si_6O_{24}](SO_4,S)_{1\text{-}2}$. Based on powder X-ray diffraction results Jaeger[4] 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).[4] This fixed framework was cubic, and closer to nosean than to sodalite,[4] a notion supported by the work of Weller and others.[5]

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.[4] The selenium and tellurium ultramarine analogs were also known.[4,6-8]

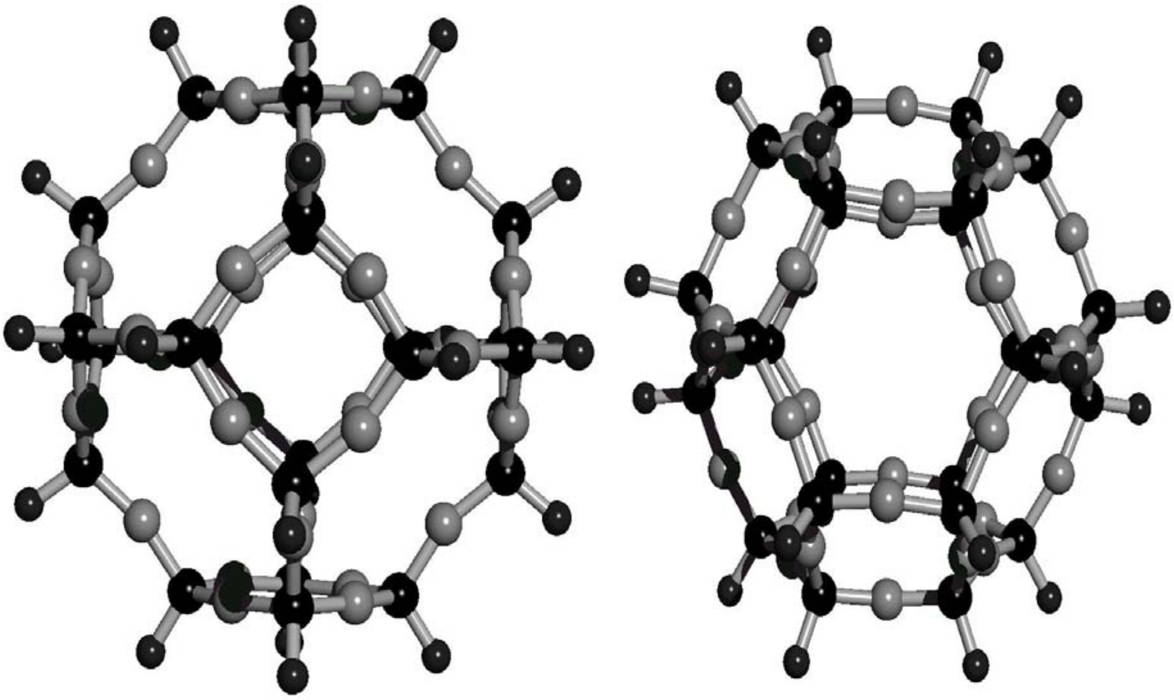


Figure 4-1: POV-Ray[9] images of AM1 force field[10]-generated β-cages

The industrial process for the manufacture of ultramarine blue[4,11-13] involved the activation of kaolinite, also known as Chinese clay, at approximately 700 ºC. 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 ºC 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 ºC. 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.[4,11-13]

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.[12] Gessler and Kumins[14] 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[14] 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_2S_3, Na_2S_4 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."[14] Gessler and Kumins[14] first synthesized the zeolite species by wet precipitation at 60 ºC, and then incorporated the sulphur species into the zeolite framework at high temperature, preferably between 750 ºC and 850 ºC, with the exclusion of air and preferably in the presence of hydrogen sulphide gas. They[14] 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.[14] Gobeltz-Hautecoeur and others[15] 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[16] reviewed the state of knowledge on ultramarine pigments. They[16] 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."[16] In my opinion, this statement was unjustified, and was researched in literature.

4.2. Synthesis

Fly ash was heated to 1 000 ºC (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 ºC, 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. [17,18-50] Quantitative work by energy dispersive X-ray analysis evidenced the heterogeneous nature of the fly ash particles[17,41-50] (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).[24] 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[a]

	Fa I	Fa[b] II	Fa1000 I	Fa1000 II	FaNa50 I	FaNa50 II	UMB I	UMB II	UMB III	UMB2 I	UMB2 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 ± 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[17,51] (Figure 4-2a). Some anorthite was also present.[52]

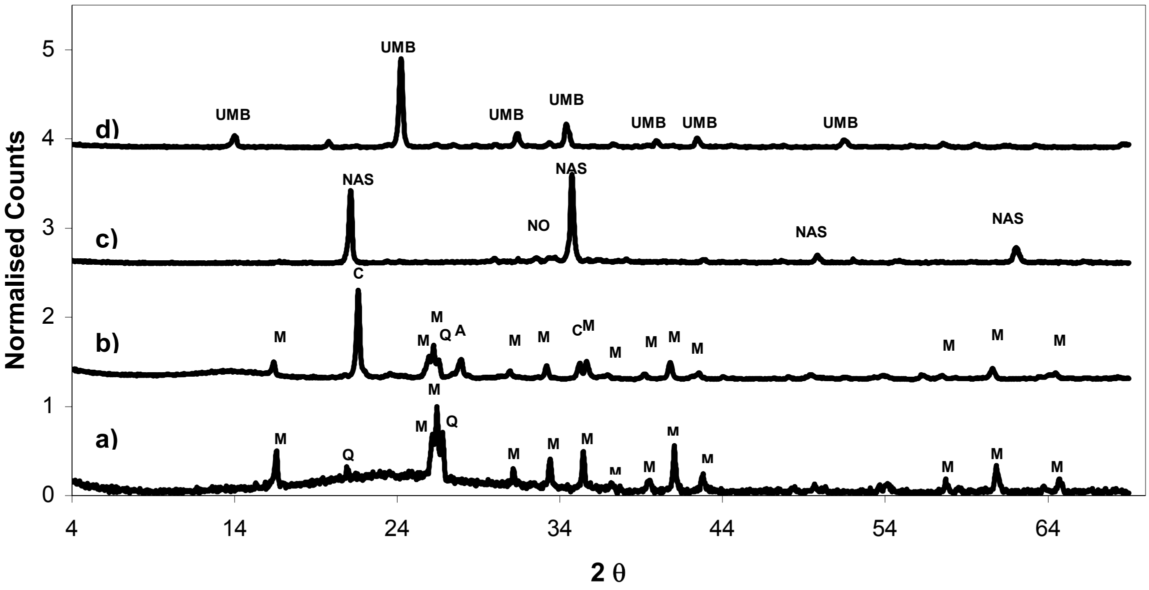


Figure 4-2: X-ray diffraction patterns of a) fly ash, b) fly ash treated at 1 000 °C, c) fly ash treated with sodium carbonate at 860 °C, d) ultramarine product; A: anorthite, C: cristobalite, M: mullite, Q: quartz, UMB: ultramarine product

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

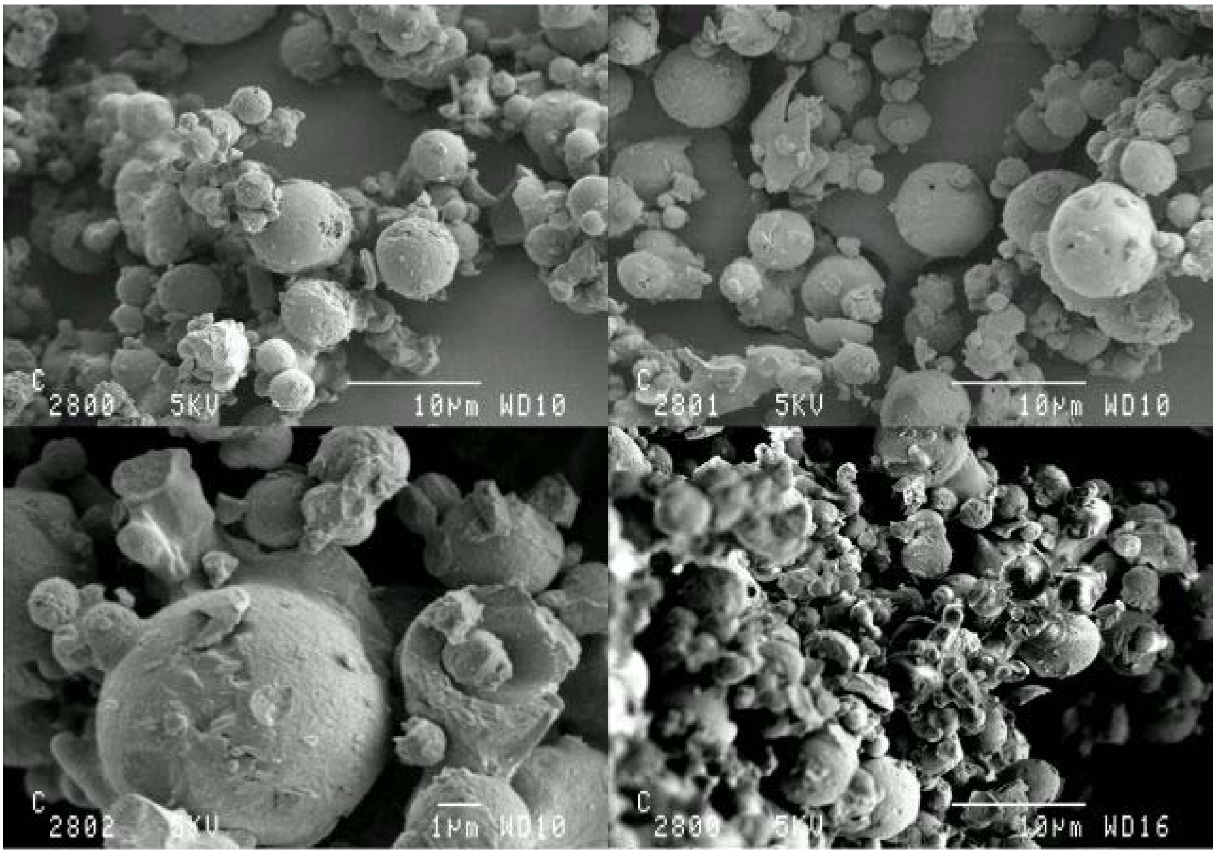


Figure 4-3: The predominantly spherical microscopic structure of fly ash was intact after treatment at 1 000 °C

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.[53] 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 $(Na_2O)_{0.33}NaAlSiO_4$ structure (Figure 4-2c).

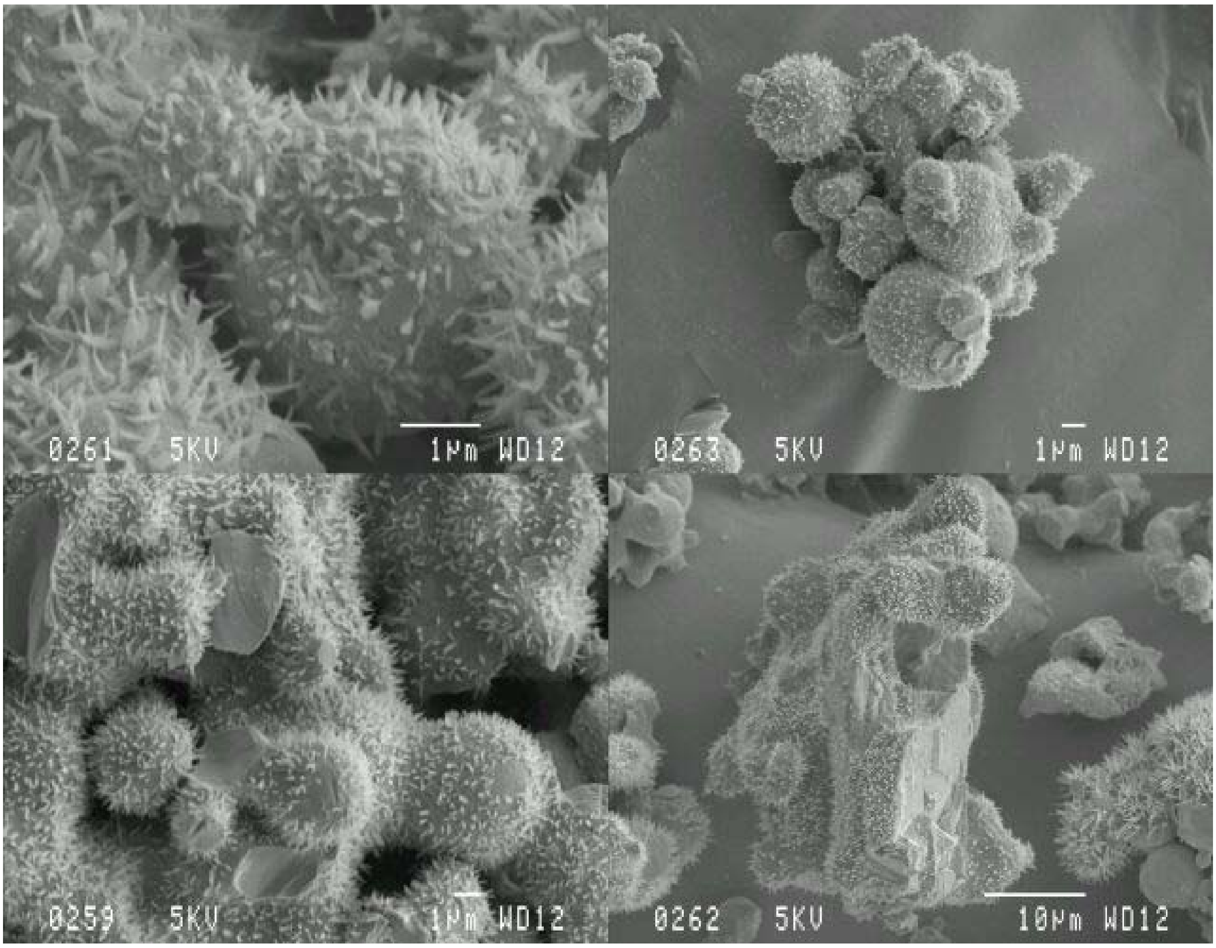


Figure 4-4: The microscopic structure of fly ash treated with sodium carbonate at 860 °C was characterised by needle shapes crystals growing from the spherically shaped particles

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

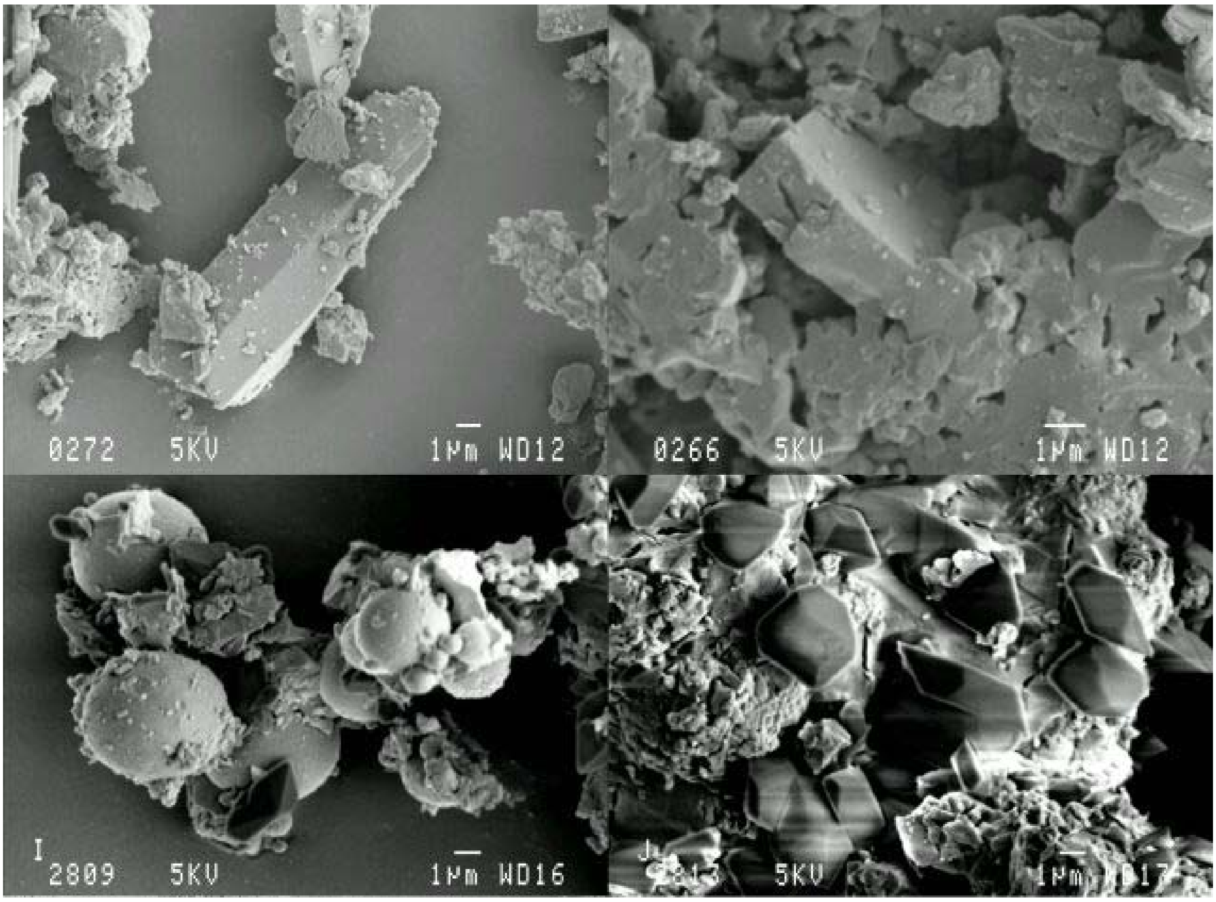


Figure 4-5: The microscopic structure of the ultramarine product showing that the spherical shape of the fly ash particles was lost and that the regular shape of zeolite-type material was formed

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 ºC.[54,55,56] Sulphur polymerised at approximately 159 ºC.[54-56] The boiling point was accepted to be 444.6 ºC.[54-56] 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.[57] 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.[31,53,58,59] 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, β-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[60] 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.[60] They[60] believed that the sulphur had a structure-directing effect.[60] Gorshtein[61] 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[62] hydrothermally synthesised sulphur-doped sodalite crystals, by adding the sulphur to the sodalite cage after the formation of the cage. They[62] claimed that $Na_2S•H_2O$ was less successful in imparting colour to the sodalite crystals. The addition of Na_2S_4 led to a blue product, when concentrated.[62] Prener and Ward[63] showed that the polysulphide could be added to the sodalite structure after the β-cages were formed.[63] Gobeltz and others,[1] and Jaeger[4] also observed this trend. Gobeltz and others[1] 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,[64] but also after the formation of the sodalite structure.[1] Treating hydroxysodalite with ammonium polysulphide, $(NH_4)_2S_6$ led to the formation of ultramarine blue type products.[64] 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.[60] 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.[14] 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.[65] The resulting aluminosilicate was washed free of excess hydroxides and was found to have ion exchange properties.[65] 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[60] 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

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1 N. Gobeltz, A. Demortier, J.P. Lilieur, 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 Persitence 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. Burragato, *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. Schrodt, *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.

60 S. Kowalak, M. Pawłowska, M. Miluśka, M. Stróżyk, J. Kania, W. Przystajko, *Colloids and Surfaces A: Physiochemical 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.