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.
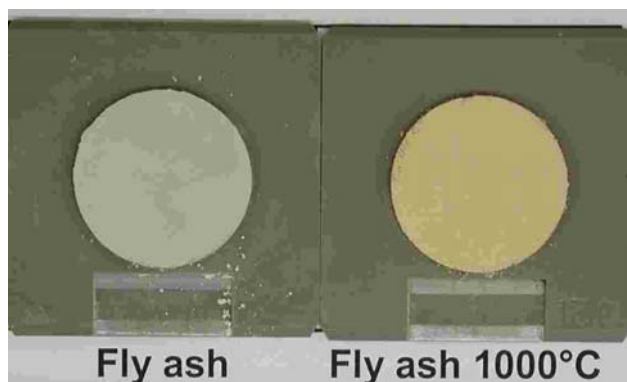

Figure 0-1: Samples of fly ash and fly ash treated at 1000 °C, indicating the colour of fly ash and heat treated fly ash
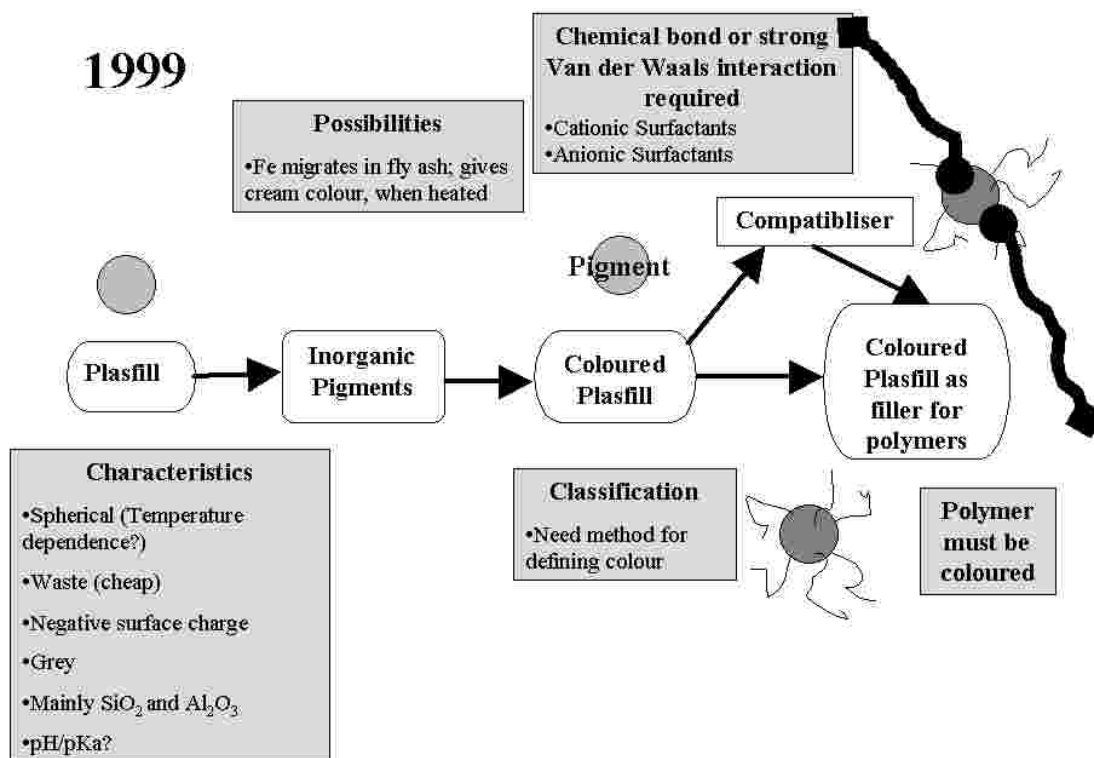
1999

Possibilities
•Fe migrates in fly ash; gives cream colour, when heated

Chemical bond or strong Van der Waals interaction required
•Cationic Surfactants
•Anionic Surfactants

Pigment

Compatibliser

Plasfill → Inorganic Pigments → Coloured Plasfill → Coloured Plasfill as filler for polymers

Characteristics
•Spherical (Temperature dependence?)
•Waste (cheap)
•Negative surface charge
•Grey
•Mainly SiO_2 and Al_2O_3
•pH/pKa?

Classification
•Need method for defining colour

Polymer must be coloured

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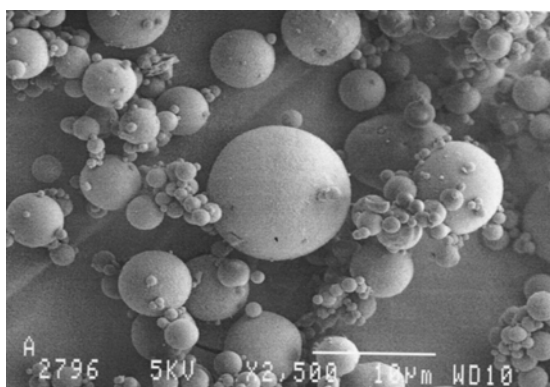

Figure 0-3: The spherical microscopic structure of fly ash as observed by scanning electron microscopy

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 ºC 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).
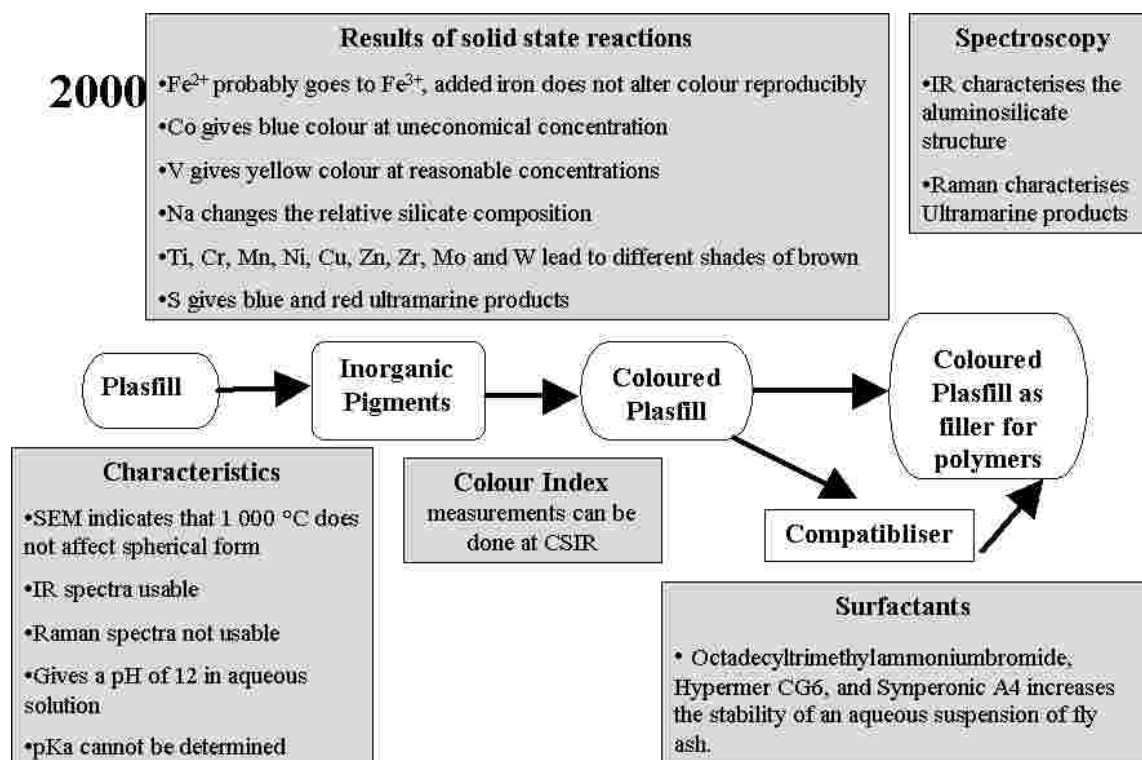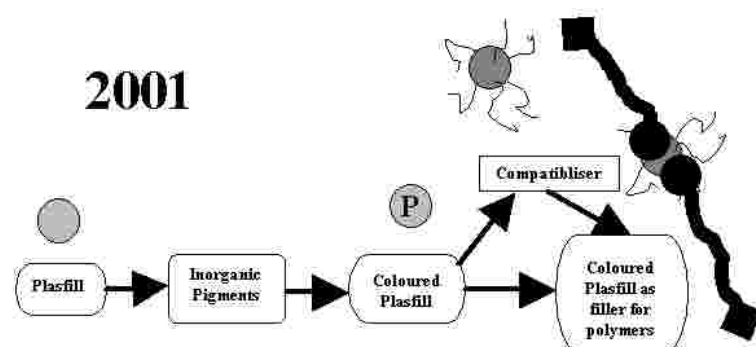

Figure 0-4: The results of the project as in 2000

| Ultramarine-Raman | •Kinetic study
•Structural elucidation |
| Vanadium-Raman/IR | •Chemical species responsible for the yellow colour
•Extent of vanadium content |
| Aluminosilicate IR | •Structural classification of aluminosilicates
•Elucidation of structural change
•Cement quality analysis |

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 ºC 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 Na_2CO_3 below 900 ºC in the crucible to act as a flux. The Na_2CO_3 is then reacted with concentrated HCl while boiling. Platinum crucibles have limited resistance to sodium carbonate at temperatures higher than 900 ºC 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 ZrO_2 undergoes a phase change at 950 °C, from a monoclinic to a tetragonal phase.[1] The phase transition of ZrO_2 is associated with a 3-5 % change in volume,[1] 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 ZrO_2 is possible,[1] 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.[2]

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)
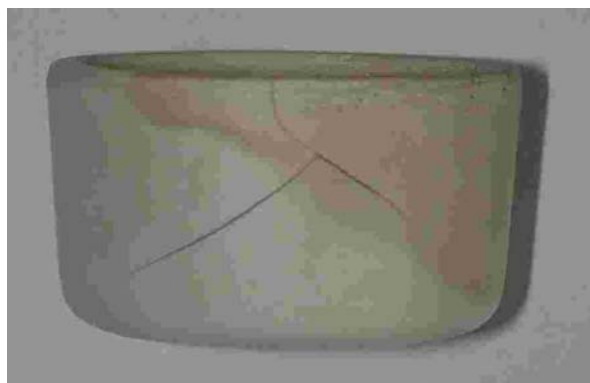

Figure 0-7: Damage to a zirconia crucible due to phase changes

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

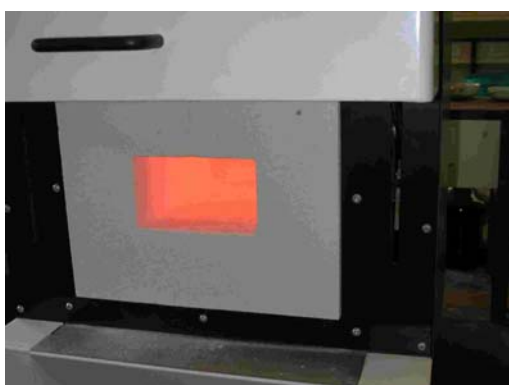Figure 0-9: Cracking of alumina crucibles due to acid washing

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[1] bubbled the SO_2 resulting from the thermal decomposition of $Zr(SO_4)_2$ through an ammonia solution forming $(NH_4)SO_3$, 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.[3-6] 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

1   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, 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.