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A thesis entitled

SLURRY ATOMISATION SYSTEM FOR PROCESS CONTROL

presented by

BENEDICT EVELYN FAIRMAN, B.Sc., G.R.S.C.

in part fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

of the

COUNCIL FOR NATIONAL ACADEMIC AWARDS

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Department of Environmental Sciences Polytechnic South West Drake Circus, Plymouth, U.K.

Collaborating establishment

E.C.C. International

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St. Austell, Cornwall, U.K.

March 1990



EXPERTO CREDITE

(Virgil)

SLURRY ATOMISATION SYSTEM

FOR PROCESS CONTROL

Benedict Evelyn FAIRMAN, B.Sc., G.R.S.C.

ABSTRACT

The mechanistic processes of slurry atomisation - Direct Current Plasma - Atomic Emission Spectroscopy (DCP-AES) were investigated using excitation temperature (Texc) measurements, simplex optimisation, particle transport experiments and computerised tomography. It was found that the observed analyte signal suppression for several analytes, which was linked to slurry concentration analytes, which was linked to slurry concentration (>10% m/m), was due to several factors. For kaolin slurries above 17% m/m, the amount of clay reaching the plasma was reduced due to viscosity effects at the nebuliser. It was shown that Texc decreased with increased slurry concentration, in the presence of 5 g dm⁻³ lithium. Using the simplex optimisation technique it was demonstrated that this decrease could be ameliorated by the addition of higher concentrations of Easily Ionisable Elements (EIE). It was suggested that when analysing high slurry concentration samples, in the presence of EIE, that ionic lines be used. Computerised tomography supplied spatial comformation for the Miller proposed mechanisms for argon emission in the DCP.

It has been shown that for kaolin analysis the slurry concentration and slurry atomisation effects in the DCP can be compensated for. This was achieved by using aluminium or silicon as intrinsic internal standards.

Slurry atomisation - DCP - AES was successfully applied to several china clay production processes. Using multiple regression analysis, the abrasiveness of clay samples, from a commercial froth flotation plant, were successfully predicted. With eight elemental and sample identification predictors, 98.3% of the variation in abrasion was predicted. It was also demonstrated that the slurry atomisation predictive technique had the capability for the on-line monitoring and control of the froth flotation process.

The slurry atomisation - DCP - AES system was also sucessfully applied to the prediction of the montmorillonite content and viscosity characteristics of china clay samples. The suitability of the system for assisting with the mining of china clay from poor quality stopes has been proven.

The monitoring of Dispex, and hence the conductivity, in 20-30% m/m Carbitol slurry samples has been accomplished. Boric acid was dissolved in the Dispex and successfully monitored in the Carbitol, providing a calibration for conductivity measurements.

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CHAPTER 1 INTRODUCTION

1.1 THE CHINA CLAY INDUSTRY

Ever since the composition of china porcelain (white kaolin and china stone) was finally characterised in the 18th Century, china clay or kaolin has been mined in Cornwall, especially around the St. Austell granite outcrop. Britain William Cookworthy (1705 - 80), a Plymouth apothecary, was the first to recognise the kaolin mineral deposits in Cornwall in 1746. He later took out a patent for the manufacture of porcelain from Cornish china clay and china stone in 1768 (1). From this period until the early 19th Century, Cornish china clay was almost exclusively sold to the Staffordshire potteries, although a small proportion was also used by the tin industry for refractory purposes. In the mid-19th Century, the development of china clay as a filler in the paper making industry dramatically increased demand for the mineral. Α further increase was initiated at the turn of the 20th Century when kaolin was first used as a paper coating material. At the present time approximately 80% of the 3 million tonnes extracted annually in the U.K. is used by the paper industry either as a paper filler material or a coating grade clay (1).

1.1.1 <u>Raolinisation of Cornish Granite</u>

Kaolinisation is one of only three main post-emplacement alterations which the parent granite rock can undergo. The other two being tourmalisation and greisemisation.

The primary factors governing these alteration processes include the chemical nature of the parent material, the physiochemical environment and the environment of deposition and diagenesis (2). Generally in the case of the primary kaolin deposits of Cornwall, the parent granite, or rather its alkali feldspar (principally sodic plagioclase) component, has been altered hydrothermally by hot gases and secondary weathering. Smectite (montmorillonite) is thought to be an important intermediate product, and kaolinite formation dependent on the destruction of secondary mica and smectite. Ouartz and tourmaline veins occur throughout the kaolin deposits. These are mainly unchanged by the kaolinisation process and provide a vein system with channelways through which the kaolinising fluids moved. Such veins also include other associated minerals such as anatase, rutile, mica and fluorspar (3). A kaolin content of 15 - 20% is typical of Cornish clay deposits, however, the final yield after extraction decreases to 10 - 15% for filler grade clay, and to around 10% for the finer coating grade clays.

The presence of associated minerals affects the commercial value of the product clay. The iron content significantly affects the natural and fired brightness of the clay. Smectite has a seriously detrimental effect on the rheological properties of kaolin which is important for coating clays. Tourmaline and other minerals with high Mhor (hardness) values, and with a particle size distribution overlapping that of the kaolinites, are found

to affect the abrasiveness of the clay and thus have important commercial implications for filler grade clays.

1.1.2 Mineralogy of Kaolinite

Kaolinite is a two layered silicate mineral (one having tetrahedral and one octahedral symmetry) and is part of the dioctahedral subgroup of the phyllosilicates (sheet silicates). From x-ray diffraction studies and numerous elemental analyses (3 - 5) the general mineral formula of kaolinite has been determined as $Al_2(Si_2O_5)(OH)_4$. However, this is very seldom, if ever, found in nature since samples nearly always contain mineral impurities or have undergone some form of cation substitution. Therefore most clay mineral chemical analyses always include Fe₂O₃, TiO₂, MgO, CuO, K₂O and Na₂O as well.

The structure (Figure 1.1) is composed of a single silica tetrahedral (SiO₄) sheet with 3 of the oxygens being shared between adjoining tetrahedra. All the tips of the silica tetrahedrons point in the same direction and towards the centre of the two layer unit. Because of the similarity in the size of the triangular face of the alumina octahedra units, it is possible for the composite octrahedral - tetrahedral layers to form. In the layer common to the octahedral and tetrahedral groups, twothirds of the atoms are shared by the silicon and aluminium and are found as 0 instead of OH.

The charges within the structural unit are balanced,

Figure 1.1 Structure of the Kaolinite dioctahedral layer. (From Grimm, R.E., "Clay Mineralogy", 2nd Ed., McGraw-Hill, New York, 1968, p.58).



although a negative edge charge is experienced. If the octahedral cation is divalent <u>e.g.</u> Mg^{2+} , each cation site is occupied and these phyllosilicates belong to the trioctahedral group. When the octahedral cations are trivalent, <u>e.g.</u> Al^{3+} (as in kaolinite), the charge balance is maintained when one out of every three cation sites is unoccupied <u>i.e.</u> when each 0 or OH group is surrounded by 2 cations. This describes the dioctahedral group. The octahedral-tetrahedral layers are bonded together by weak van der Waals forces.

Kaolinite exhibits a low cation exchange capacity typically in the range 3 - 15 meq/100g. In kaolinite hardly any substitution of cations occurs within the basic lattice structure and it is generally thought that cations are adsorbed to balance the unsatisfied edge-charges of broken silica-aluminium units (4).

1.1.3 The Paper Industry

Kaolin has a wide industrial base. Major users are the ceramics industry (15% of production) <u>e.g.</u> whiteware ceramics like sanitaryware, and the manufacture of rubber where it is used as a filler. It is also used in a variety of processes related to plastics, cement and agricultural chemicals, and by pharmaceutical companies, although strict regulations govern the quality of clay used for pharmaceutical applications. Even so 80% of the U.K. output is sold to the paper industry.
Kaolin is involved in two separate processes in paper making, filling and coating. Each process has its own quality specifications. There are three main white mineral fillers used at the present time, kaolin, calcium carbonate and talc, of which kaolin is the most important. The properties required by a good filler material are a fine, uniform particle size, low degree of abrasiveness, high brightness, chemical inertness and good attraction to the cellulose fibres. Most of these can be controlled by particle size. However, abrasion is not solely particle size dependent and is found to be a function of type, amount and particle size distribution of mineral impurities (6, 7). The incorporation of the filler kaolin between the cellulose fibres (approximately 5 - 15% m/m) produces a smoother paper with improved printing characteristics. Abrasion is important since the use of high abrasion filler clays drastically reduce the lifetime of the paper rolling machinery as well as the printing type.

Coating clays are applied to the surface of finished paper as a thin film of slurry/adhesive mixture. Machine made paper is produced with an uneven surface which is covered by the coating clay to produce a brighter, glossier surface for high quality printing. Coating grade clays are finer, and hence brighter, than filler clays. As they are applied to the surface of the paper at high speeds and in a high slurry concentration (approximately 70% m/m) the rheology of the clay is critical. The presence of

smectite (montmorillonite) clays, even in small quantities, has a seriously detrimental effect on the rheology properties of coating clays and hence the effectiveness of the coating process.

1.1.4 Froth Flotation and Abrasion

The kaolin is extracted from the china clay deposits by hydraulic mining. A schematic diagram of the whole production process is shown in Figure 1.2. Currently English China Clay International (ECCI) are the only china clay company to use froth flotation as one of their industrial processes. The purpose of the froth flotation plant is to remove the clay fraction containing the kaolinite from the mineral impurities that cause a degradation of the product clay's quality i.e. abrasiveness. The clay that passes through the flotation plant (the feed) has already passed through the primary and secondary kaolinite removal processes (Figure 1.2). Also under certain circumstances, the feed clay is supplemented with dam clay, (clay that has already been processed and discarded), to provide a feed of sufficient specific density for the plant to operate efficiently. Therefore it may contain a high proportion of abrasive mineral impurities.

The feed clay slurry is kept at a constant density (approximately 18% m/v slurry) by a water aduct system (Figure 1.3). The feed passes through a bank of three flotation cells where water and an appropriate dosage of ⁻ frothing agent are added. This renders the clay particles

Figure 1.2 The China Clay production process. (From Highley, D.E., "China Clay", H.M.S.O., London, 1984, p.17).



Figure 1.3 Schematic diagram of the Froth Flotation

process.



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RESIDUE

hydrophobic. Air is then blown through the tanks producing a froth to which the kaolinite particles preferentially attach themselves, because of their particle size, platelike shape and charge. The clay, carryed by the froth, bubbles over the sides of the tanks and is washed down to form the product clay. Sand grinders are then employed to breakdown the kaolin aggregates and to maximise the < 2 µm fraction. The underflow clay (residue) is removed from the last tank and is pumped to waste.

The amount of product clay that is recovered from the feed clay is dependent mainly upon froth reagent dose rate and quality of the feed clay, although the pH and temperature of the system also affects the efficiency of the flotation process. The percent recovery is calculated from the feed and residue clay densities. The abrasion of both the product and residue fractions rises with increased percent recovery. This is because as the recovery increases the product clay will consist of a higher fraction of mineral impurities and the residue clay a smaller proportion of the less abrasive kaolinite.

1.1.4.1 <u>Einlehner Abrasion Test</u>

This test has recently been developed for slurry samples to replace the Valley Abrasion Test and is now used as a standard test by ECCI and the paper industry for the characterisation of the abrasiveness of china clay.

The abrasion test rig is shown in Figure 1.4. A phosphor





bronze abrasion disc is washed in acetone, dried and weighed. The clay sample is prepared as a 10.0% m/v slurry and the pH is adjusted to be within the range 4.5 -A polyvinyl chloride (PVC) abrasion head is then 5.5. ground against the bronze disc, while immersed in the slurry, for 30 minutes. The disc is removed, washed, dried and weighed. The weight loss of the disc is then converted into Einlehner abrasion units.

At the present time it takes approximately 24 hours for a clay sample from the flotation plant to be tested for abrasion and for the running of the plant to be altered. As a result, the efficiency of the flotation plant has never been optimised <u>i.e.</u> running at the highest percent recovery possible while still producing product clay within the abrasive limits required. This is because an operational safety margin has to be used to allow for variations in the feed clay quality.

1.1.5 <u>Viscosity Concentration</u>

As described in Section 1.1.3, the rheology of the product clay is extremely important in application of clay as a paper coating material. The quality of clay used for coating purposes is specified by its viscosity concentration. The viscosity concentration is defined as the percentage by weight of a chemically deflocculated pigment, in an aqueous slurry, which has a viscosity of 5 poise at 22^oC when measured with a Brookfield RVF 100 Viscometer (Brookfield Engineering Laboratories Inc.,

Stoughton, Massachusetts, USA). ECCI and the paper industry use ECC Test Method P106 as the standard test method for viscosity concentration. This method has been highly characterised with a standard deviation of 0.3%.

Coating clays, to produce best quality paper finish, must have a viscosity concentration in the range 68 - 72%. If the viscosity concentration is lower than this the high quality gloss finish cannot be achieved. As mentioned above in Section 1.1.3 smectite or montmorillonite are the main mineral impurities that cause a degradation in the viscosity characteristics of the coating clay. This is due to the fact that most smectite clays (although not all) are "expanding lattice" minerals <u>i.e.</u> they can absorb water into their internal lattice structure thus "swelling" and therefore adversely affecting the rheological properties of a clay slurry.

1.1.5.1 <u>Montmorillonite</u>

As described above smectite and other expanding lattice minerals such as montmorillonite are the major cause for a degradation in the viscosity properties of commercial clay. Montmorillonite demonstrates this "swelling" characteristic due to its three-layer structure consisting of two silica tetrahedral sheets with a central alumina octahedral sheet. (Figure 1.5). All the tips of the tetrahedrons point in the same direction and toward the centre of the unit. The outstanding feature of this structure is that water and other polar molecules such as

Figure 1.5 Lattice structure of Montmorillonite. (From Grimm, R.E., "Clay Mineralogy", 2nd Ed., McGraW-Hill, New York, 1968, p.79).



organic molecules can enter between the unit layers causing the lattice to expand. Montmorillonite also exhibits a high cation exchange capacity (70 - 120 meg/100 g (3)) because of this inter-unit polar layer. The theoretical formula for montmorillonite is $Al(Si_2O_5)OH.nH_2O$ although this is never realised as the lattice is always unbalanced by cation substitutions. These are mainly Mg^{2+} for Al^{3+} in the octahedral layer, and a smaller amount of Al^{3+} for Si^{4+} in the tetrahedral Iron (both Fe^{3+} and Fe^{2+}) also substitute lavers. depending on availability. This net charge deficiency is balanced by exchangeable cations adsorbed between the unit layers (80%) and around their edges (20%). Sodium, calcium and magnesium are the most common interlayer cations found in nature.

1.1.5.2 Montmorillonite Measurement

There is no direct instrumental techniques for the identification and quantification of montmorillonite. An infra-red adsorption technique has been developed, but is only sensitive for "expanding" lattice clays. However, this technique is used by ECCI to give an indication of montmorillonite content (8). A complex is formed between 2,2'-dipyridyl and montmorillonite. The complex replaces water molecules in inter-sheet positions in the clay structure. The montmorillonite-2,2'-dipyridyl complex gives a 9 peak characteristic infra-red spectrum which is easily identifiable from other clay minerals such as kaolinite, chlorite and illite. Two peaks are

particularly strong and can be used for quantitative work with appropriate montmorillonite standards.

1.1.6 Carbitol

Carbitol is the name given to calcium carbonate when it is in slurry form with an added dispersant called Dispex (polyacrylic acid). Calcium carbonate has been used as a paper filler since the 1950s. It produces paper of greater strength and dimensional stability which is more durable than paper produced by conventional systems due to increased filler loadings of up to 30%. Since carbitol is also cheaper than kaolin, the demand for calcium carbonate fillers has increased over the last few years.

In paper coating there is a distinct disadvantage in using natural chalk whitings (calcium carbonate deposits) since the material is relatively coarse with a significant proportion having a particle size > 10 µm. However, this has been overcome recently by the use of high quality marble from Italy. Thus coupled with the low cost, high brightness and improved viscosity characteristics, calcium carbonates are today in increasing demand as a raw matrial for the paper industry.

1.2 DIRECT CURRENT PLASMA - ATOMIC EMISSION SPECTROMETRY Direct current plasma - atomic emission spectrometry (DCP-AES) has been used for elemental analysis since the late 1950s (9). The development of today's 3-electrode plasma (10) can be traced back to the 2-electrode flowing argon plasma arc of Valente and Schrenk (11). In this early design the anode and cathode were positioned at a 30° angle to each other. This was further refined by Elliot (12) who introduced the sample aerosol from below this inverted V configuration independently of the two electrodes providing an improved analytical zone.

The inverted Y, 3-electrode direct current plasma was developed in the mid 1970s commercially by Spectrametrics (Andover, Massachussetts). Adding an extra anode and positioning the cathode above the two anodes improved stability and reduced source drift.

In the configuration used today (Figure 1.6), the plasma jets have a total argon flow rate of approximately 8 dm³ min⁻¹ of which 4 dm³ min⁻¹ is used by the ceramic, crossflow, pneumatic nebuliser, 1 - 1.2 dm³ min⁻¹ for each of the graphite anodes and 1.5 - 2 dm³ min⁻¹ for the cathode sleeve gas.

Although temperatures in excess of 9000 K are generated in the current carrying plasma core, the temperature in the analytical zone is in the range 4000 - 6000 K (13, 14). This temperature is sufficient to produce 100% atomisation





efficiency for most elements. The versatility of the DCP with respect to sample introduction is well documented (9, 15-17). Slurry atomisation, hydride generation, laser ablation, direct insertion, electrothermal vaporisation, flow injection analysis and coupled chromatographic separation techniques have all been used with DCP-AES detection either for single or multielement analysis. The performance of the DCP has been compared to other emission techniques and, for many elements, can provide equal if not better analytical performance to that of the inductively coupled plasma (ICP) (18-20). This versatility of the DCP, plus its ability to tolerate high solids, organic solvents and slurry samples, has made it a popular emission source.

1.2.1 Excitation Mechanisms

The DCP inverted shaped plasma jet is a flowing, gasstabilised electrical discharge. Optimal plasma stability only occurs when the nebuliser and anode argon flows impose forced, convective conduction cooling on the current carrying argon core inducing the "thermal pinch" effect (21). This effect is characterised by elevated electron number density (n $_{\rm e}$) values in the high current zones and by steep radical n $_{\rm e}$ gradients (21-23).

Early excitation models for the DCP tended to assume that the plasma jet is in a state of vlocal thermal dynamic equalibria (LTE) (13, 24, 25), <u>i.e.</u> energy level densities could be calculated using the Saha-Boltzmann equation, and

that the excitation temperature (T_{exc}) equalled the electron temperature (26). However the assumption contradicts theorectical calculations (14, 25, 27) and reported observations (14, 23, 26-29). Electron densities are found to be 100-200 times lower than those expected from a system at LTE (30).

The mechanism proposed by Miller <u>et al</u>. (14, 31) has gained general acceptance and describes the DCP as a recombining plasma in a state of partial thermodynamic equilibrium (PTE). The two major excitation processes in the plasma have now been identified as:

- (i) radiative transfer of energy from the plasma continuum to the plasma margins via argon resonance lines.
- (ii) collisional redistribution of energy involving metastable argon species via primary ionisation of the analyte (22).

1.2.2 Enhancement Mechanisms

Analyte emission signal enhancement by easily ionisable elements (EIE) in the DCP is a well documented phenomenon (13,14,21,22,25,27-32,43). The signal enhancements, induced by EIE, follow a set pattern for all enhanced elements. At low concentrations of EIE there occurs substantial signal enhancement. The increase in signal enhancement decreases with higher EIE concentrations

(approxiamately 1 mol dm^{-3}) until a plateau region is reached. On further addition of EIE the magnitude of the enhancement begins to decrease. This is due to a slow quenching process which becomes dominant over the enhancement-inducing process at higher concentrations of EIE (14). If unbuffered (by saturation with other EIE) the enhancement is seen as a major interference because of its non-stoichiometric nature (14, 31, 32). Miller <u>et</u> <u>al</u>.(14, 27, 31) have also constructed a hypothesis as to the mechanisms of EIE enhancement of analyte emission signal. A synopsis of their theory is given below:

- (i) EIE provide additional channels for the radiative transfer of energy from the plasma core to the analytical zone via EIE resonance lines. This is inferred from the fact that although EIE do not enter the plasma core, a cooling of the core temperature occurs and a drop in n_e inside the continuum is observed (13, 27, 30).
- (ii) excited EIE have a large, total cross-section for resonance interaction with analytes.
- (iii) enhancement is increased because of the quenching of analytical background and argon molecular emissions caused by the accelerated cooling of the plasma upon the addition of EIE (13, 27).

Approximate models (31) have now been formulated for

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atomic and ionic resonance lines that can predict the enhancement of transition metal emissions caused by sodium (0.01 M) to ± 15 %.

1.2.3 <u>Slurry Atomisation</u>

The use of slurry samples for elemental analyses has only been developed for plasma spectroscopy over the last ten years. Other methods for introducing solid samples into the DCP, for example laser ablation (33), either require major modifications to the existing instrumentation or encounter calibration problems as a high degree of matrix matching is required. With slurry atomisation, aqueous suspensions of finely powdered material are calibrated directly with aqueous solutions, and minimal modification to the commercial DCP instrumentation is required (34-40).

However, one requirement that is stressed by all workers using slurry atomisation is that for the DCP the slurry material must have a fine particle size preferably < 15 μ m and with a sizeable fraction below 8 μ m. Saba <u>et al</u>. (37) using a filtration technique found that for metallic iron particles, the DCP ceramic nebuliser plus a cylindrical spray chamber quantitatively transported < 7 μ m particles and 62% of the 7 - 14 μ m particles.

One of the most important advantages of slurry atomisation is the reduced sample preparation time. For some sample types <u>e.g.</u> food stuffs such as mechanically separated turkey (39), particle size reduction is achieved by

homogenisation in under 3 minutes and coal has been reduced to < 5.7 µm in ten minutes by a micronising mill (40). An inexpensive and versatile method of particle size reduction has been developed in these laboratories (34,41,42) using 3 mm zirconium oxide beads as the grinding medium. This method has successfully been used on soil, grass, coal and various minerals. Dried milk powder has also been successfully analysed directly.

Slurry atomisation is particularly suited to the analysis of clay minerals such as kaolinite. Firstly kaolin samples, especially after refining, have a particle size range of < 20 μ m with a majority of particles < 2 μ m (the kaolinite fraction). For coating clays 80% of the particles should be < 2µm and for filler grade clays about Thus for many kaolin samples no particle 70-75%. reduction is needed and Ebdon et al. have successfully analysed kaolin samples by both DCP and ICP (43,44). Apart from the increased speed of analyses achieved by direct aspiration of the sample, slurry atomisation also avoids the tedious and time consuming dissolution of geochemical samples. This is a well known disadvantage for geochemists wanting to use emission detection techniques (45). In addition slurry atomisation avoids the use of hazardous chemicals such as HF and reduces the possibility of errors due to contamination or incomplete dissolution often encountered with fusion methods.

1.3 CHEMOMETRICS

Ever since 1972 when Wold coined the term chemometrics (derived from the word biometrics used by biology statisticians), and the development of the modern microcomputer, the use of statistical methods for data collection, interpretation and manipulation by the chemistry community has increased dramatically.

Chemometrics has developed along two broad fronts: firstly, in the integration of laboratory instrumentation and the processes involved in analytical analyses including sampling strategies, optimisation techniques, signal identification and interpretation, calibration and the detection of analytical bias; secondly, since modern instrumentation has the ability to rapidly acquire large amounts of data, techniques for the interpretation of large multivariate data-bases have been developed. The literature abounds with examples of pattern recognition techniques such as factor analysis, fuzzy sets, principal component analysis (PCA), cluster analysis and the evolution of several commercial packages (46-48). These have been applied to the identification, from chemical composition data, chromatographs etc, of numerous samples e.q. olive oils, petroleum, peat and tea samples.

Still the most popular method is that of multiple regression analysis (MR) (49, 50). In chemistry the partial least-squares (PLS) regression method (50) which is claimed to be more robust than the classical MR

algorithms, is increasing in popularity.

1.4 <u>TOMOGRAPHY</u>

A tomogram may be defined as a picture, or display, of a plane section of an object body at a given orientation. Computerised tomography (CT) or computer assisted tomography (CAT) are reconstruction tomographical methods. These have found a wide range of applications in science, although mainly in medical radiology (51).

Unlike other methods for gaining spatial information about emission sources, e.q Abel transformations, computerised tomography requires no spatial symmetry and is more tolerent to noise; important factors when applied to the DCP emission source. So far there has been no application of tomography to plasma sources, although Hill and Ebdon (52) have demonstrated the power of the technique for emission sources. They were able to show the internal structure of a 7 jet laminar flow flame from the individual jets at the base of the flame, to the laminar flow characteristics at the top. The potential of this technique as a diagnostic tool for plasma spectrometry has been discussed (52). The application of tomography to plasma sources would clearly bring new insight into the internal characteristics of the plasma gas under various operating conditions. The technique would also provide, in the case of the DCP, as to the interaction of EIE and slurry samples with the excitation mechanisms of the plasma.

1.5 <u>AIMS</u>

The principal aim of this project was to study the application of slurry atomisation - direct current plasma - atomic emission spectrometry for the control of china clay refining and quality assurance processes. Previous work (44, 53) had established that it is possible to perform elemental analysis of china clay by ICP-AES and DCP-AES without prior sample dissolution. This has important implications in the design of on-line process control systems. In addition, it was shown (53) that certain properties of china clay e.q. abrasion appear to be related to the presence of indicator elements. Such elements are associated with certain mineral impurities in the kaolin which greatly contribute to the commercially important properties of china clay (abrasion and viscosity concentration). Chemometric methods such as MLR can be used for the development of predictive models for these physical properties as well as for the control of industrial plant. Also studies into performance of the DCP sample introduction system when dealing with the nonideal slurry samples encountered in the production processes is necessary. Sample introduction anomalies have to be identified and compensated for if on-line monitoring of slurry streams is to become a reality. To aid these studies theoretical investigations will be used e.g. temperature and tomographical measurements to elucidate slurry atomisation excitation and enhancement mechanisms in the DCP.

CHAPTER 2 SAMPLE INTRODUCTION STUDIES

2.1 INTRODUCTION

When using conventional slurry analysis the sample is usually pre-ground (via various methods some of which have been outlined in Chapter 1, Section 1.2.3) until the particle size of the material has been reduced to below 8 However, for the application of slurry atomisation um. DCP - AES for on-line analysis of kaolin samples, minimal sample preparation is desired. In the case of the froth flotation process (Chapter 1, Section 1.1.4), three types of clay samples are encountered: the feed, product and residue. The particle size distributions of a typical product clay and that of a residue clay are shown in Figure 2.1 and Figure 2.2 respectively. This data was provided by ECC Central Laboratories (St. Austell, Cornwall) using industry standard particle size techniques. The differences in the particle size characteristics between the product and residual clay are clearly seen. The product clay has a mass distribution mean diameter of 6.28 microns with 75% m/m of its particles below 8 µm, whereas the residue clay has a mass distribution mean of 9.81 µm and 46% m/m below 8 µm. This, plus the fact that samples from the flotation plant can have slurry concentrations from 4 - 20% m/v, indicate that different samples will have varying transport, nebulisation and atomisation characteristics. This has already been investigated for the analysis of kaolin by ICP (44), showing that where for slurry concentrations of



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china clay above 10 - 12% m/v, analyte signal suppression occurs. Since this ICP data was obtained using a 'SPS' grade clay (ECCI classification) <u>i.e.</u> a clay with at least 80% of the particles below 2 µm and all below 5 µm, the suppression effect on the analyte signal was attributed to viscosity effects at the nebuliser, rather than to transport or atomisation effects. However these conclusions were based on the ICP sample introduction system, <u>i.e.</u> a high solids nebuliser and a double-pass spray chamber. Therefore an investigation was undertaken into how the DCP sample introduction system, (ceramic crossflow nebuliser with diamond-shaped cone spray chamber) performed with clay samples obtained from the froth flotation plant, described above.

2.2 VARIATION OF ANALYTE EMISSION SIGNAL WITH SLURRY CONCENTRATION

2.2.1 Experimental

A series of clay slurries were prepared containing 0, 5, 7, 10, 13, 17 and 20% m/v solids. The clay used was a froth flotation product clay with the particle size characteristics shown in Figure 2.1. The slurries were analysed using a Spectrospan IIIA DCP instrument (Applied Research Laboratories, Crawley, Sussex, UK). Operating conditions were those obtained by simplex optimisation as described by Ebdon <u>et al.</u> (43,54), and shown in Table 2.1. Each slurry contained ammonia solution (AnalaR Grade, BDH Chemicals, Poole, Dorset, UK), in the ratio of 1 ml of ammonia to 100 ml of sample, as a dispersant. Also each

Table 2.1

Direct Current Plasma Operating Conditions

Argo	on Supp	1 y		Commercia	1 g	rade	(99.5%	pure)
Flo	w rate			8 dm ³ min	-1			
Neb	uliser	pressure		24 psi				
Slee	eve pre	ssure		50 psi				
Powe	er supp	ly		7 A (d.c.)			
Samj	ple upt	ake		1.6 cm ³ m	in ⁻	1		
. Enti	rance s	lit widt	hs	Vertical Horizonta	= 1 =	300 50	មក មក	
Exi	t slit	widths		Vertical Horizonta	= 1 =	300 100	um um	

sample had 5 g dm⁻³ lithium solution (lithium nitrate, AnalaR Grade, BDH Chemicals, Poole, Dorset, UK) added as an EIE buffer. To avoid any errors being introduced from the water content of the china clay, all the clay samples were dried in an oven at 105°C for 24 hours, and kept in a dessicator until use. Each slurry was analysed for six elements which are shown in Table 2.2 together with the spectral lines used for this work. Calibration was achieved using aqueous standards.

2.2.2 Results and Discussion

The variations in elemental concentration of the product clay with slurry concentration are shown in Figures 2.3 -2.8.

Apart from boron (Figure 2.3) all the elements show a reduction in recovery with increasing slurry concentration. There does seem to be some correlation between the fall in recovery between 5% m/v and 20% m.v slurries and the spectral wavelength used (Table 2.2), <u>i.e.</u> the deviation from the expected signal increases along with the wavelengths. However, this is not supported by the excitation potentials for each line, or whether the lines used were either atomic or ionic resonance lines. For all the elements studied the aqueous calibration standards were linear up to the concentrations analysed and were within the linear working range for each line (55).

Table 2.2

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Elements and spectral lines used for the investigation of the effect of slurry loading on Analyte Signal

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Element	Wavelength/nm	Order
В	249.773 I	90
Ti	323.456 II	70
Sr	407.771 II	50
Ba	455.403 II	49
V	309.311 II	73
Ca	445.474 I	50





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This indicates that the loss of signal with increasing slurry concentration is not a simple excitation phenomena but either a sample introduction or slurry atomisation or nebulisation effect.

2.3 TRANSPORT EFFECTS

As stated above the decrease in analyte emission signal with increasing kaolin slurry concentration for the ICP was attributed to viscosity effects at the nebuliser and transport effects of spray chamber (44,53). To investigate this for the standard DCP sample introduction system an experiment was designed to measure the homogeneity of the sampling of the slurry from the sample container, viscosity effects on the sample uptake rate, and the transport efficiency of clay particles reaching the plasma plus their particle size distribution. A postnebuliser particle trap was designed and is shown in Figure 2.9. The clay which would have reached the plasma was collected by this system of 2 U-tubes in series containing silica gel to act as the particle traps.

2.3.1 Experimental

All the results for this experiment were determined gravimetrically. A series of clay slurries were prepared containing 5, 7, 10, 13, 17 and 20% m/m product clay. Sodium pyrophosphate 1% m/m (AnalaR, BDH Chemicals, Poole, Dorset, UK) was added as a dispersant. This was instead of the ammonia used previously since it not only performed as well for clay materials as ammonia (53,56) but also

Figure 2.9 Schematic representation of the postnebulision particle trap system.



DCP SAMPLE INTRODUCTION SYSTEM

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avoided weight loss problems due to the high volatility of ammonia. No lithium buffer was added to the samples, and each sample was nebulised for a period of 10 minutes using standard gas settings as described in Section 2.1.

The mass of clay for all experiments was only recorded after being dried at 105⁰C to constant weight. The experiment was repeated 3 times.

2.3.2 <u>Results and Discussion</u>

The slurry concentration of the samples, both before and after sampling are plotted in Figure 2.10. From Figure 2.10 it can be seen that the agitation of the slurries during sampling appears to have been sufficient to prevent any sedimentation of the clay particles, and that a homogeneous sample of slurry was introduced to the nebuliser for all slurry concentrations. This is confirmed by a study of the rates of sample uptake shown in Figure 2.11. From Figures 2.10 and 2.11 it can be concluded that increasing the slurry concentration of samples has no effect on the mass transfer of sample to the nebuliser.

However, from the data on the amount of clay collected that would have reached the plasma (Figure 2.12), a clear deviation from the expected amount of clay for 20% m/m slurries is shown. The amount of clay collected increased linearly up to 17% m/m (linear correlation coefficient (r) = 0.9988), but the amount of clay collected by the






Slurry Concentration **%** m/m 1

silica gel traps for the 20% m/m of slurry sample was only 73% of the expected mass.

This change in transport behaviour may be explained by the changes in the viscosity characteristics of slurry samples with increasing slurry concentration. From the Nukiyama and Tanasawa equation (57) (Equation 2.1), the mean diameter of aerosol droplets produced by the nebuliser can be predicted. This equation can only give an indication of droplet size as it was developed for jet injection nebulisers with different geometries and scale differences than those of modern analytical nebulisers (58).

$$d_{o} = \frac{585}{v} \left[\frac{\sigma}{p} \right]^{0.5} + 597 \left[\frac{n}{(o \ p)^{0.5}} \right]^{0.45} \left[10^{3} \frac{Q_{liq}}{Q_{gas}} \right]^{1.5}$$

Equation 2.1

do = droplet diameter / um
V = velocity of the gas / ms⁻¹
O = surface tension / dyne cm⁻¹
p = density of the liquid / g cm⁻¹
n = viscosity / poises
Q_{liq} = volume flow of the liquid
Q_{gas} = volume flow of the gas

What this equation does demonstrate is that the viscosity of the fluid is an important nebuliser parameter. The reduction in the amount of 20% m/m slurry clay reaching the plasma can be explained by the change in the viscosity

behaviour of the slurry. Ebdon <u>et al</u>. (44) have shown that viscosity does increase with increasing slurry concentration. Clay slurries of concentrations up to 15% m/v, display "Newtonian" behaviour <u>i.e.</u> the viscosity is independent of rate of shear (the speed at which the intermediate layers of the fluid move with respect to each other). This is typical of the behaviour of water and certain oils. However, 20% m/v slurries exhibited "non-Newtonian" behaviour <u>i.e.</u> there is an increase in viscosity with a decrease in shear rate. This change in viscosity behaviour coincides with the fall in the mass of clay reaching the plasma and could be the cause of the shortfall in clay transport to the plasma.

The average transport efficiency for clay particles in samples up to 17% m/m slurry concentration was 2.5% m/m. For the 20% m/m slurry samples this fell to 1.6% m/m, whereas the transport efficiency for water, calculated from rate of sample uptake and rate of drainage from the spray chamber, was 11% m/m. This low transport efficiency for the slurries can be explained by particle size data. Figure 2.1 shows the particle size distribution of the product clay used in these experiments. The clay has not been pre-ground and therefore has a high percentage of particles over 5 µm. Particle size measurements were obtained for pre- and post-nebulised samples of clay by Coulter Counter model TA II (Coulter Electronics Ltd., Luton, Beds, UK) and are shown in Figure 2.13. The use of a Coulter Counter was not ideal since it is principly



Figure 2.13 Effect of nebulisation on the particle size distribution of slurry samples.

based on the change in conductivity in an electrolyte solution. This change occurs when a particle passes through a small aperture between two electrodes. This causes a positive bias in particle size measurements for kaolin of between 2 - 4 times since it assumes that each particle is a sphere whereas kaolin, and most clay mineral particles, are plate like. This can be seen when comparing Figure 2.1 and 2.13. This apart, it can be seen that there was a major shift in the particle size distribution of the clay after nebulisation and that (taking the bias into account) few particles of over 6 µm reached the plasma. However from Figure 2.1 50% by mass of the particles of the product clay can be seen to be over 5.5 µm. This probably explains why the clay particle transport efficiency was approximately 70% lower than that for water.

2.4 CONCLUSIONS

Analyte signal suppression linked to increasing slurry concentration was observed for a range of elements. It was shown that this suppression was not of a simple nature. It has been demonstrated that the non-Newtonian behaviour of slurries (above 17% m/m) is the probable cause for the decrease in the expected slurry signal for several elements for 20% m/m slurries due to a reduction in the amount of sample reaching the plasma. Also, due to the particle size distribution of the samples from the flotation plant, the transport efficiency for clay particles was approximately 70% of that of water.

Different clays with different particle size distributions may exhibit varying degrees of transport efficiency. Therefore some kind of internal standardisation is necessary if these particle size and viscosity effects are to be corrected for an on-line analytical situation.

However the viscosity effects discussed above do not explain the signal suppression seen in Figures 2.3 - 2.8 for slurry concentration above 10% m/m. This does not appear to be a transport, viscosity or particle size problem and it may be either a slurry induced atomisation or excitation interference, and this is discussed further in Chapter 3.

CHAPTER 3 Mechanistic Studies

3.1 SLURRY ATOMISATION AND THE DIRECT CURRENT PLASMA

During the last decade, there have been numerous papers published concerning both the excitation and EIE enhancement mechanisms in the DCP. The generally accepted model, proposed by Miller et <u>al.</u> (14,21,27,30,31), for both the excitation and EIE enhancement mechanisms has already been discussed in Chapter 1, Section 1.2. However, the majority of these investigations concern solution analysis, whilst most workers using slurry atomisation for the DCP have limited themselves to sample preparation and introduction (34, 38-40).

This imbalance has recently been redressed by Sparkes and Ebdon (43). In their work they concentrated on the mechanistic aspects of slurry atomisation using electron density (n_e) , and excitation (T_{exc}) and ionisation (T_{ion}) temperatures as diagnostic tools for kaolin analysis. In addition they also touched upon the effect of EIE on these diagnostic parameters. They found that the Tion of the plasma remained constant with increasing slurry concentration, both with and without the addition of 5 g dm⁻³ lithium. This result has also been observed by Eastwood et al. (27) for aqueous solution samples spiked with EIE. From these observations it might be assumed that the introduction of particulates to the DCP does not alter the ionisation-recombination equlibrium that exists

between ionic states in the plasma. However, Sparkes and Ebdon (43) did observe a decrease of both T_{exc} and n_e values, with increasing slurry concentration in the presence of 5 g dm⁻³ lithium. Both these trends occur at similar slurry concentrations, namely >10% m/v, and coincide with the decrease experienced in analyte emission intensities described in Chapter 2. From this work the authors put forward the hypothesis that the results indicated that a "cooling" of the plasma had occured, caused by high concentrations of slurries in the presence of lithium. It is known that although EIE and samples are excluded from the plasma core, the core temperature and no do fall with the addition of EIE (13,14,60). This is shown by argon resonance line intensity and line halfwidths decreasing upon the addition of EIE.

In the present study these initial observations and experiments are extended. Principally T_{exc} measurements have been used but with significant contributions from signal-to-background ratio (SBR) data, simplex optimisation and computerised tomography.

3.2 EXCITATION TEMPERATURE MEASUREMENTS

3.2.1 Theory

The T_{exc} of argon plasma emission sources has been used as a diagnostic parameter, especially for the inductively coupled plasma (ICP), for many years. T_{exc} is said to characterise the populations of atomic energy levels. There are several methods for the measurement of T_{exc} and

a synopsis of these has been presented by Mermet (61). The method used in this investigation was the line pair intensity ratio method. This method, as well as the Boltzmann plot method, uses relative line intensities. This has a number of practical advantages over other methods since it is not necessary to measure absolute line intensities or to know the concentration of the radiating species.

The derivation of the practical formula used, shown in Equation 3.1, is described by Boumans (62) and concisely by Mermet (61).

$$T_{exc} = \frac{0.625 \ (E_1 - E_2)}{\log \frac{g_1 A_1 \lambda_2}{g_2 A_2 \lambda_1} - \log \frac{I_1}{I_2}}$$
 Equation 3.1

Here, I_1 and I_2 represent the two line intensities of an element in the same ionisation state; E_1 and E_2 are the energies in cm⁻¹ of the two states; g_1 and g_2 are the statistical weights of the two levels; A_1 and A_2 are the transition probability (s⁻¹) for spontaneous emission, and λ_1 and λ_2 are the wavelengths of the two lines.

The line pair method is less accurate than the Boltzmann plot method. The main source of error is introduced by the transition probabilities, and Mermet (61) claims that an uncertainty of at least 20% must be allowed for. Also it has been shown that there is no unique excitation temperature of a plasma using this method, as the T_{exc} is dependent on the energy levels of the line pairs and

emitting species selected when the plasma is not in Local Thermal Equlibrium (LTE) (63). However, this method has acceptable precision if the two lines have a large enough energy difference. Additionally, this is the most practical method for measuring T_{exc} . This is an important point since the relative variation of T_{exc} can be followed when one or more of the parameters are modified. This is borne out by the simplex experiments descirbed below in Section 3.2.3.

3.2.2 <u>Variation of Excitation Temperature with Slurry</u> <u>Concentration and Vertical Viewing Position</u>

Earlier studies (43) have been largely concerned with the differences in T_{exc} caused by slurry concentration in the presence of 5 g dm⁻³ lithium. These experiments centered upon the physical effect of the slurry particles on the plasma rather than the interaction between slurry samples, vertical viewing position and EIE.

3.2.2.1 <u>Experimental</u>

A series of kaolin slurries were prepared at 0, 1, 5, 10, 15 and 20% m/v solids concentrations. The 0% sample contained aqueous solution of an iron with the concentration of 350 μ g g⁻¹. The kaolin used was an SPS grade clay (ECCI, St.Austell, Cornwall, UK) with а particle size distribution of 80% below 2 μm (diameter), and with all particles below 5 µm. A11 the samples contained 5 g dm^{-3} lithium solution and the slurry samples had ammonia added (Analar grade,

s.g.0.880, BDH, Poole, Dorset, UK) to the ratio of 1 ml of ammonia to 100ml of total sample, to act as a dispersant.

The excitation temperatures were determined using relative line intensities on the DCP under normal operating conditions outlined in Chapter 2. The T_{exc} was obtained for each sample at 5 different viewing heights in the plasma, starting at -1.4 mm (away from the plasma continuum), -0.7 mm, 0 mm, +0.7 mm and +1.4 mm. The zero position in this case was taken as the apex of the angle between the two plasma "legs" and the continuum. The atom line pair used for the temperature measurements was the Fe I 371.993 nm / Fe I 372.762 nm pair. These were used as the statistical weights and transition probability data are well known (63,64). Also this was the pair used by Sparkes and Ebdon (43) in their initial study.

3.2.2.2 <u>Results and Discussion</u>

The results for this series of T_{exc} measurements are shown in Table 3.1 and graphically in Figure 3.1.

From Figure 3.1 it can be seen that for all slurry concentrations the steep temperature gradient, characteristic of the DCP analytical zone, is visible. Also, after the start of the continuum (position 0), a plateau region for T_{exc} is reached. The T_{exc} values for 0%, 1% and 5% m/v slurry samples of between 6000-7000 K in this region generally agree with other published values; Decker (13) 6000-6500 K, Miller et al. (14) 6000-8000 Κ,

<u>Table 3.1</u>

Variation of T_{exc} with slurry concentration and vertical viewing position.

Plasma viewing position / mm	Excitation temperature values / K							
	Fe solution 350 µg g ⁻¹	Slu 1	rry conc 5	entratio 10	n / % n/ 15	v 20		
-1.4	1600	1100	<u>1</u> 200	1300	1250	2000		
-0.7	2600	1825	3275	3000	1650	1200		
0.0	5850	4250	5100	4200	3600	2250		
+0.7	5550	5350	4750	4350	4125	3775		
+1.4	6200	6900	6000	4625	3600	4400		



VERTICAL VIEWING POSITION mm

Eastwood <u>et al.</u> (27) 6000-7000 K and Sparkes and Ebdon (43) 5500-6000 K.

What does seem to be the case is that although the values, and trends, for the 0, 1 and 5% m/v slurry samples are very similar, a fall in the continuum Texc is experienced for slurries >10% m/v. These results confirm those of Sparkes and Ebdon (43) as discussed above. From this, one can assume that above 10% m/v slurry concentration, the extent of the inversion of excited state populations caused by EIE addition is altered. This inversion, caused by EIE, enhances the relative intensities of those atomic lines which have the higher excitation potentials (14). This is why apparent T_{exc}, deduced from atomic spectra, rise sharply upon EIE addition (27,29). Therefore for higher slurry concentrations, for a refractory material like kaolin, an increase in EIE concentration or alteration of plasma characteristics is needed to achieve maximum T_{exc} values.

3.2.3 Simplex Optimisation

After considering the results of the T_{exc} measurements it was decided to optimise T_{exc} for a range of slurry concentrations. The optimisation procedure chosen was simplex optimisation. This procedure was first used for plasmas by Ebdon <u>et al.</u> (65). Since then it has been widely used in emission spectroscopy as a simultaneous, multi-parameter optimisation technique. One of the advantages of simplex optimisation is that it allows an

appraisal of a problem via the study of univariate searches, based around the optimised conditions. As an optimisation technique no prior decisions are needed to be taken as to the location of the optimum region. Simplex optimisation has previously been applied to the DCP for solution analysis (54,66). From these studies the important instrumental parameters were identified. These were the vertical viewing position, nebuliser gas flow and horizontal viewing position. Obviously the first two of these parameters are inter-linked, as the optimum viewing position is dependent on the nebuliser gas flow. The last parameter, horizontal viewing position, has а sharp optimum, but since this is always in the center, or apex, of the analytical zone, it can be discounted as a critical operating parameter if left in this position.

Simplex optimisation has been used for kaolin slurry analysis by Sparkes and Ebdon (43). For that study six parameters were optimised; horizontal viewing position, sleeve argon flow-rate, nebuliser argon flow-rate, aqueous ammonia concentration, lithium concentration and slurry concentration with SBR as the criterion of merit. It was found that an 8.1% m/v slurry with 4.35 g dm⁻³ lithium addition gave the best SBR for the magnesium II 279.079 nm line with the vertical viewing position and nebuliser argon flow-rate being the critical parameters. These results, especially for slurry concentration and lithium addition, certainly agree with the observation that with a low concentration <u>ca.</u> 0.6 M of EIE, the optimum slurry

concentrations to use for analysis are below 10% m/v.

3.2.3.1 Experimental

The maximum T_{exc} using each of the five kaolin slurry concentrations (1, 5, 10, 15 and 20% m/v) were optimised using the simplex optimisation procedure outlined by Ebdon et al. (54). In this case T_{exc} was used as the criterion Four operating and of merit. sample preparation parameters were optimised. These were the lithium concentration, vertical viewing position, nebuliser gas pressure and aqueous ammonia concentration. The horizontal viewing position (zero) and sleeve argon gas pressure (50 psi) were kept constant throughout.

As in earlier studies an SPS grade clay was used to prepare the kaolin slurries. The simplex procedure was considered complete when there was no significant increase in T_{exc} with successive vertices to a precision of 1.5%. The optimised parameter values were investigated further using univariate searches.

Some difficulty was experienced in calibrating the vertical viewing position of the DCP. This was finally achieved by aspirating a 10 μ g g⁻¹ solution of iron before each simplex and by obtaining the same emission intensity at position zero each time.

The boundary ranges selected for the optimisation for each of the four parameters were: 0.1-3.5 M lithium solution,

1-10% v/v of ammonia solution (s.g.0.880, 35%), -1.5 mm -+1.5 mm vertical viewing position, and 18-30 psi nebuliser gas pressure. The T_{exc} for each of the vertices were obtained as in Section 3.2.2 using the iron atomic line pair Fe I 371.993 nm / Fe I 372.762 nm.

3.2.3.2 <u>Results and Discussion</u>

The optimised parameter values for the five simplexes are displayed in Table 3.2. As described in Section 3.2.3.1, univariate searches were performed on all four parameters for each simplex. For the five slurry concentrations the univariate searches were essentially the same, and so for conciseness only the four univariate searches for 1% m/v slurry concentration are included here. These are shown in Figures 3.2-3.5. These graphs not only include the centroids of the simplex optimisation, as listed in Table 3.2, but also the ranges of the parameters present in the final vertices.

From Figures 3.2 and 3.3 it can be seen that both the nebulisation gas prassure, and amount of ammonia added, have little if any effect on the apparent Texc. This was found for all the slurry concentrations, and suggests that even for high slurry concentrations only a small amount of dispersant is required. The optimum values shown for these parameters in Table 3.2 are quite varied, but this is a feature of the simplex procedure, *i.e.* if there is no sharp optimum then the optimisation wanders back and forth along the parameter range. In the case of the nebuliser

Table 3.2

Optimum conditions for T_{exc} for various kaolin slurry concentrations.

Optimum parameter values

Slurry conc. / % m/v	Lithium concentration / M	Ammonina ^a addition / % v/v	Vertical height / mm	Nebuliser gas pressure / psi	^T exc / K
1	0.96	6.2	+0.31	24	4750
5	1.73	6.5	+0.23	23	4485
10	2.08	3.5	-0.30	22	4458
15	2.44	5.7	-0.10	23	4551
20	3.02	8.3	-0.41	27	4553

(a) from a stock solution of s.g. 0.880 35% concentrated ammonia

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gas pressure it was surprising that no recognisable optimum could be seen for any of the slurry concentrations. For other workers (43,66) the optimum for this parameter found to be very weak, and so with the inherent error of the T_{exc} calculations, any optimum present in this study may not be readily noticeable.

The univariate search for the vertical viewing position is shown in Figure 3.4. Here there is a maximum which the simplex has correctly identified. However, the decrease in T_{exc} at viewing heights closer to the plasma continuum is not so marked as seen in the other univariate searches with the higher slurry concentrations. In these a plateau region is reached with only a slight decrease in T_{exc}. This is consistent with the Texe data shown in Figure 3.1. In cases such as this the simplex procedure usually identifies the edge of the plateau region as the optimum position. This occurred with other slurry concentrations. The optimal vertical viewing positions also show a marked trend with slurry concentration. This is shown in Figure 3.6 with a linear correlation coefficient (r) of -0.8804 between vertical position and slurry concentration. Unexpectedly, the trend is for the optimal viewing zone to move away from the continuum with increasing slurry concentration.

The final parameter, lithium concentration, exhibited the sharpest optimum for all the slurries. The 1% m/v slurry concentration univariate search gives a typical sharpe



optimum peak. As with the vertical viewing position, the optimal lithium concentration shows a strong correlation (r=0.9832) with slurry concentration, as seen in Figure This trend is significant for several reasons. 3.7. The increase in the lithium concentration optima can be used to explain why the vertical viewing position optima move away from the plasma continuum. This is because as the lithium accelerates the radiative diffusion of energy away from the plasma core, the plateau region of Texc, shown in Figures 3.1 and 3.4, migrates away from the core, which in turn becomes progressively cooler. This process has also been described as the plasma core becoming more indistinct and with the plasma migrating upward towards the cathode (14).

It has already been described that on EIE addition apparent temperatures, as measured from atomic or neutral spectra relative line intensities, rise sharply. However at higher EIE concentrations a slow quenching process becomes dominant. This cycle is shown in Figure 3.5. Α sharp rise in T_{exc} was observed with an equally sharp fall after the optimum EIE concentration had been exceeded. However, if the slurry concentration is increased, the T_{exc} optimum is shifted towards higher EIE concentrations. This inter-relationship could exist for several reasons. Firstly there could be a direct relationship between analyte concentration and lithium concentration. This is improbable since there is no decrease in the apparent Texc for solutions, with the equivalent analyte concentrations,



in the presence of 5 g dm⁻³ lithium. More plausible the extra energy requirement needed is that to dissociate the slurry particles causes the apparent decline in Texc. The addition of higher concentrations of lithium could ameliorate this in several ways. The most obvious is the acceleration of the radiative diffusion of energy away from the plasma continuum to the plasma margins. This causes what some observers call а "swelling" of the plasma (14,21,23,30). The plasma swells because some of the current from the EIE cooled continuum is shunted to the plasma margins whose electron densities have been raised by the EIE addition. Therefore the plasma appears to swell as the EIE emit visible resonance lines in the plasma margins (21). One consequence of this "swelling" effect would be that the stagnent zone, directly underneath the plasma, would increase in volume. This would allow for the accommodation of a higher density of slurry particles, as well as increasing the residence time of the sample in the analytical zone. This would be achieved while maintaining the level of energy available to the sample throughout the increased volume of the analytical zone.

3.3 SIGNAL-BACKGROUND RATIO ENHANCEMENT

In order to verify the simplex optimisation results, a series of enhancement studies were undertaken using the signal-to-background ratio (SBR) as the measured parameter. This change from T_{exc} as the criterion of merit was undertaken to produce a measure that was

related to the enhancement of the signal for each line but independent of other lines.

3.3.1 Experimental

Three series of slurries were prepared consisting of 0, 1, 5, 10, 15, 20% m/v slurry concentrations using an SPS grade kaolin. The 0% m/v samples contained 40 μ g g⁻¹ iron solution. The three series contained no lithium, 5 g dm⁻³ lithium, and the simplex optimised lithium concentrations respectively. The SBR for three analyte lines were determined for all three series on the DCP under normal operating conditions. The analyte lines used were the Fe I 371.993 nm, Fe I 372.762 nm and the Fe II 259.940 nm lines. The slurry samples also contained aqueous ammonia solution (s.g.0.880, 35%) as a dispersant in the ratio of 1ml of ammonia to 100ml of sample.

3.3.2 Results and Discussion

The SBR results are shown in Figures 3.8-3.10. The SBR were calculated using Equation 3.2.

Figures 3.8-3.10 show the changes in the relative SBR of each line, as calculated by Equation 3.3, caused by the two types of lithium addition.

SBR enhancement= SBR with lithium Equation 3.3 SBR without lithium



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The two graphs for the two atomic lines (Figures 3.8 and 3.9) used for the T_{exc} measurements are very similar. It is clear that for the atomic lines, the best SBR for >5% m/v kaolin slurries are achieved with considerably more concentrated lithium additions as dictated by the simplex results. However, regarding the ionic line SBR (Figure 3.10), increasing enhancements the lithium concentration along with slurry concentration does not bring any improvement in SBR over the enhancement caused by 5 g dm⁻³ lithium. This conforms to the premise that the excitation of atomic and ionic analyte lines involve different sets of resonant collisions (14,32). Also that a refractory substance such as kaolin, for higher concentrations of EIE can overcome the effect that concentrated slurries have upon these redistribution processes.

3.4 COMPUTERISED TOMOGRAPHY

The equations governing image reconstruction (tomography) were first solved by Radon in 1917. The initial formula allowed an estimation of the spatial characteristics of a target object to be calculated. This was only possible the projection angles of the emitted when all or transmitted rays, from or through the object, were known. is extremely difficult in practice and so various This algorithms (known as Radon Transformations) have been developed based on line-integral formulae. These allow for an estimation of the object under investigation from a discrete number of angular projections.

Reconstruction tomography differs from conventional tomography, in that in conventional tomography the emitted or transmitted rays pass through all the object planes before reaching the detector. Unwanted planes are blurred while the desired plane is kept in focus. In reconstructive tomography the unwanted sections are completely excluded and mathematical procedures are used to reconstruct the required plane section.

There are several reconstructive techniques which have mainly been used in radiology. These have been extensively reviewed by Brooks and Di Chiro (51). The system used in this work is based on an analytical method (as compared to an iterative method) called filtered backprojection.

3.4.1 Filtered Back-Projection

In filtered back-projection, projected profiles are collected at a number of projection angles (or sets of ray sums) around the source. These profiles are modified or filtered (by either a fourier or convolution integral method) before being back-projected. The back-projection process is shown in Figure 3.11. Here the signal intensity, corresponding to a given ray sum, is applied to all points that make up that ray. Therefore for a given image point, the reconstructed density is the sum of all the ray-projections that pass through it (51). The purpose of the filtering of the profiles is that although conventional back-projection eliminates unwanted planes,

Figure 3.11 Back-projection profiles of a rectangular object. (a) back-projected across the plane (b) superimposed to form an approximation of the object.

(from Brooks and Di Chiro, Radiology, 1975, 117, 561)





it is at the expense of blurring the desired plane. Ideally the reconstruction is exact, with the filtering process counter-acting the blurring artifact of the backprojection process. Also the more projections used, the better the reconstruction.

3.4.2 Instrumentation and Experimental

The instrumentation used for the tomography work is shown in Figure 3.12. The DCP was mounted on a turntable, rotated by a stepper motor. The height of the DCP could also be altered on the turntable. The image was focussed onto a Czerny-Turner monochromator with a photodiode array detector mounted at the exit slit. The data aquisition and source rotation was computer controlled. The complete system and software package has been previously described by Hill and Ebdon (52).

A similar procedure was used for all the tomograms obtained. The monochromator was set to the argon I 415.82 nm emission line. For each tomogram 60 projection profiles were obtained. Once the image had been reconstructed it was visually enhanced by using a colour table to assign a "false" colour to each intensity band of the tomogram. For reference purposes the order of colours with regard to argon emission intensity is given in Table 3.3.

Figure 3.12 Schematic diagram of the tomographical system.


Table 3.3

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Colour assignment for the intensity bands of the tomographical data.

Band	Colour	Argon emission intensity
1	Blue	Low Intensity
2	Light blue	
3	Green	
4	Light green	
5	Cyan	
6	Light cyan	
7	Yellow	
8	Brown	
9	Light Red	
10 .	Red	
11	Light gr e y	
12	Black	High Intensity

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3.4.3 <u>Results and Discussion</u>

3.4.3.1 Effect of Slurry Samples on Argon Emission Intensity

For this study three sets of tomograms were obtained from the DCP. Each set consists of five tomograms, collected at a range of viewing heights comparable with the heights used for the T_{exc} measurements in Section 3.2 <u>i.e.</u> approximately 1 mm apart. The three sets differed only in the type of sample being aspirated. In one, no sample was aspirated with just the dry nebuliser gas reaching the plasma. The second set was obtained when introducing distilled water and the third set with a 10% m/v kaolin slurry sample being nebulised. The slurry sample contained 1% m/v sodium pyrophosphate to act as а dispersant. The operating conditions of the DCP were maintained as described in Chapter 2.

The tomograms are displayed in Plates 3.1-3.15. The tomograms are shown not by series, but by sampling height, so that a comparison can be made between the three different samples at the same observation height.

From this series of tomograms the changes in the argon emission intensity as the viewing height is moved up the plasma, <u>i.e.</u> towards the cathode, is readily noticeable. All three sets follow the same pattern. Plates 3.1-3.3 show the cross-section through the plasma approximately 2mm below the apex of the join between the two plasma "legs". Plates 3.4-3.6 were taken approximately.1 mm



<u>Plate 3.1</u> Tomogram of Argon emission at the -2.0 mm vertical viewing height. Dry nebuliser gas only.



vertical viewing height. Distilled water sample.



<u>Plate 3.3</u> Tomogram of Argon emission at the -2.0 mm vertical viewing height. 10% m/v slurry sample.



vertical viewing height. Dry nebuliser gas only.





<u>Plate 3.6</u> Tomogram of Argon emission at the -1.0 mm vertical viewing height. 10% m/v slurry sample.

higher and can be described as being on the bottom edge of the analytical zone. The next set (Plates 3.7-3.9) are of the apex of the inverted Y. For all three aspirated media the same trend is observed in that ... the argon emission intensity of the plasma decreases slightly the further the observation is away from the anodes. Of more importantance is that there is no appreciable difference between the tomograms for argon, distilled water or 10% m/v kaolin slurry. This absence of change in the argon core emission is continued through the plasma continuum as shown by Plates 3.10-3.12 and even closer to the cathode by Plates 3.13-3.15.

These observations supplement those from the Texc There, no change in apparent T_{exc} measurements. was observed with increasing slurry concentration, in the (43). Therefore it seems that absence of EIE slurry do not seem to affect either the particles argon excitation mechanisms or the "Thermal pinch" effect in the DCP.

The internal structure of the DCP is clearly illustrated by these tomograms. The "cooler" plasma margins and analytical zone with less argon emission together with the "hotter" plasma core, identified by a continuum of strongly emitting argon plasma, can clearly be observed. Another aspect characteristic of the DCP is that of the two plasma "legs". From the tomograms it is clear that one has a noticeably larger cross-section and displays



<u>Plate 3.7</u> Tomogram of Argon emission at the 0.0 mm vertical viewing height. Dry nebuliser gas only.



vertical viewing height. Distilled water sample.



<u>Plate 3.9</u> Tomogram of Argon emission at the 0.0 mm vertical viewing height. 10% m/v slurry sample.



vertical viewing height. Dry nebuliser gas only.





<u>Plate 3.12</u> Tomogram of Argon emission at the +1.0 mm vertical viewing height. 10% m/v slurry sample.



<u>Plate 3.13</u> Tomogram of Argon emission at the +2.0 mm vertical viewing height. Dry nebuliser gas only.





Plate 3.15 Tomogram of Argon emission at the +2.0 mm vertical viewing height. 10% m/v slurry sample.

more intense emission than the other one. This nonsymmetrical behaviour can be minimised by adjusting the angle between the two anodes and by adjusting the sleeve argon gas flow, but it can not be eliminated completely.

3.4.3.2 Effect of Lithium on Argon Emission Intensity

To show the effect of EIE upon the plasma argon emission two further series of tomograms were obtained from the DCP. Both sets contained five tomograms, one from each of the viewing heights described in Section 3.4.3.1. One set had ordinary distilled water aspirated throughout and the other a 5 g dm⁻³ lithium solution. The tomographical series are shown, in height pairs, in Plates 3.16-3.25.

Again, for both series, the non-symmetry of the plasma "legs" is quite noticeable. Also, the internal argon intensity distribution is seen in the progression from the anodes, through the analytical zone, towards the cathode. is most marked is the large decrease in the argon What emission in the presence of 5 g dm^{-3} lithium. This is not so marked between Plates 3.16 and 3.17 since this is too far away from the plasma core, and lithium contact with it, for any effect to be observed. However the tomogramsfrom the bottom edge of the analytical zone, Plates 3.18 and 3.19, show a marked effect caused by the lithium. The two legs are much less intense in the presence of lithium This is highlighted even more by Plates than without. 3.20 and 3.21. These were taken at the apex of the analytical zone as shown by Plate 3.20. Again there has



<u>Plate 3.16</u> Tomogram of Argon emission at the -2.0 mm vertical viewing height. Distilled water sample.



<u>Plate 3.17</u> Tomogram of Argon emission at the -2.0 mm vertical viewing height. 5 g dm⁻³ lithium solution.



<u>Plate 3.18</u> Tomogram of Argon emission at the -1.0 mm vertical viewing height. Distilled water sample.



solution.



<u>Plate 3.20</u> Tomogram of Argon emission at the 0.0 mm vertical viewing height. Distilled water sample.



vertical viewing height. 5 g dm⁻³ lithium solution.

been a slight decline in intensity from the earlier "distilled water" tomograms (Plates 3.16 and 3.18) taken closer to the two anodes. However compared to the tomogram obtained using lithium solutions at this height, a change has occurred to the plasma structure. The area of argon emission has contracted. Other observers have described this process by saying that the plasma becomes optically thin and moves towards the cathode upon EIE addition (14,27). Although the argon emission is much reduced the plasma body or "Thermal pinch" is still present providing an impenetrable plasma core. The decrease in argon emission intensity and plasma area is due to the lithium "cooling" the plasma by radiative redistribution of energy, as described in Sections 3.2 and 3.3. Because of this, the core argon can not carry the entire current loading, and therefore some of the current is carried by argon in the plasma margins or the lithium itself.

The series continues with Plates 3.22 and 3.23. These are of the continuum above the analytical zone, and again the reduction in argon intensity and plasma area on lithiun addition is clearly seen. In addition the core emission is becoming more intense <u>i.e.</u> "hotter" (Plate 3.22) as the cathode is approached. This is confirmed by Plates 3.24 and 3.25 although the tomogram produced using the lithium solution is still much less intense than the distilled water tomogram.



<u>Plate 3.22</u> Tomogram of Argon emission at the +1.0 mm vertical viewing height. Distilled water sample.



<u>Plate 3.23</u> Tomogram of Argon emission at the +1.0 mm vertical viewing height. 5 g dm⁻³ lithium solution.



Plate 3.24 Tomogram of Argon emission at the +2.0 mm vertical viewing height. Distilled water sample.



<u>Plate 3.25</u> Tomogram of Argon emission at the +2.0 mm vertical viewing height. 5 g dm⁻³ lithium solution.

3.5 CONCLUSIONS

It has been shown that when using the atomic relative line ratio method the T_{exc} decreases for slurry concentrations > 10% m/v in the presence of 5 g dm⁻³ lithium. Using the simplex optimisation procedure this decrease in Texc for high concentration slurries, can be somewhat negated by the use of higher concentrations of EIE addition. It was shown that in accordance with the Miller model (14) atomic line excitation involves additional steps which are more prone to EIE induced changes in the plasma. It is suggested that these atomic excitation steps can be disrupted by high slurry concentrations in the presence of This can be compensated for by a linear increase EIE. in with slurry concentrations above 10% m/v. EIE In practical terms this suggests the use of ionic lines when high concentration slurry samples are to be analysed in the presence of EIE.

Initial spatial studies using computerised tomography has spatially confirmed many of the proposed mechanisms about argon emission in the DCP. The technique was used with both slurry and EIE samples and the results indicated that tomography could become a powerful diagnostic tool for plasma sources.

CHAPTER 4 ABRASION IN CHINA CLAY

4.1 IDENTIFICATION OF ELEMENTAL MARKERS FOR ABRASION

As discussed in Chapter 1, the abrasive properties of china clay are caused by mineral impurities that are inherently harder than kaolinite, although they may not necessarily exist as larger particles. The impurities are the remains from residual, or primary, kaolinisation of granite deposits induced by volcanic, hydrothermal or weathering processes. The kaolinite-rich product produced by the froth flotation process (outlined in Chapter 1, Section 1.1.4) contains between 5-15% mineral impurities depending on the operating parameters fo the plant. The important minerals remaining after, or produced by, the kaolinisation process are shown in Table 4.1 together with their Mohr (hardness) values. Also listed are those elements that are particularly associated with these minerals (3-5,68,69).

Gray (53) has already established strong links between boron, barium, vanadium and abrasion using slurry atomisation - ICP-AES. Lithium, rubidium and cesium were also identified as elemental markers but due to instrumental restrictions were not quantitatively These initial studies have been extended determined. further by performing a comprehensive elemental scan of the periodic table by DCP-AES. Two 10% m/v samples from the flotation plant were analysed. The first of these was a product clay (Einlehner abrasion value 78) and the

Table 4.1

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Minerals produced by the Kaolinisation of granite with associated elements.

Mineral	Mohr Value	Associated Trace and Minor Elements
Kaolin	2.0 - 2.5	Mg, Ca, Fe, Li
Muscovite	2.5 - 3.0	V, Rb, Cs, Li, K, Na, Mn, Ti, Cr, Mg
Anatase	5.5 - 6.0	Ti
Potassium Feldspar	6.0 - 6.5	Ba
Rutile	6.0 - 6.5	Fe, Nb
Tourmaline	7.5	B (major), Mn, Li, Na, Ca, Mg
Quartz	7.0 - 7.5	-

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second a residue clay (Einlehner abrasion value 328). From this elemental scan several other elements were identified as showing a significant difference in concentration between the two samples. Six (lanthanium, neodymium, praseodymium, rhodium, yttrium and ytterbium) were all identified, but at concentrations very near or on the detection limits for DCP-AES. These elements were therefore not deemed suitable for further investigation. Rubidium, at 421.556 nm, also looked very promising at first, but spectral overlap from strontium (421.552 nm) and spectral interference from calcium (422.673 nm) rendered it unsuitable. Therefore six elements: barium, boron, calcium, strontium, titanium and vanadium, were identified as exhibiting promising correlations with abrasion.

4.2 INTERNAL STANDARDS

Due to the varying properties (slurry concentration, particle size and viscosity) of slurry samples obtained from the flotation plant, some form of internal correction procedure was required. This procedure had to compensate for transport or atomisation effects (described in Chapters 2 and 3) as well as the prediction of slurry concentration.

For the initial abrasion study, thirty-six samples were collected from the Goverseth froth flotation plant (ECC Internation, St. Austell) over a period of four days. On each day three sets of slurry samples at different set

recoveries were collected. Each set consisted of a feed, product and residue sample taken at plant recoveries of 35%, 55% and 75%.

4.2.1 Aluminium and Silicon

Kaolin provides two intrinsic internal standards, aluminium and silicon. Their relative concentrations do vary within the different clay types obtained from the flotation plant, but only to the degree of 2 3%. Earlier work, by Gray (56), has shown a good correlation (r = 0.82) between the measured silicon content, by slurry atomisation ICP-AES, and percentage slurry m/v, (determined gravimetrically). The thirty-six samples described above were analysed for aluminium and silicon using the aluminium I 396.150 nm and silicon I 288.158 nm lines. Standard DCP instrumental conditions as described above (Chapter 2, Section 2.2) were used. Samples were prepared by the addition of 0.5% v/v ammonia solution (AnalaR, s.g. 0.880, 35%, BDH, Poole, Dorset, UK) as a dispersent, and contained 5 g dm^{-3} lithium solution (lithium carbonate, AnalaR, BDH, Poole, Dorset, UK) as a spectroscopic buffer. For the silicon analysis the original slurry samples were diluted by a factor of 100 before the ammonia and lithium were added. This was because the silicon oxide content of clay is in the range 45 - 50% m/m, so that an 18% m/m slurry sample would of have a silicon concentration far above the linear working of DCP-AES for the silicon line used. range The correlation between these two elements and slurry

concentration were similar, r = 0.955, as shown in Figures 4.1 and 4.2. This improvement over the earlier value of r= 0.82 is probably due to the fact that the feed clay density was regulated in later work, before passing through the flotation plant. This is the cause of the tight cluster of feed data points in both Figures 4.1 and 4.2, and hence the reason for the improvement in the correlation coefficients.

4.2.2 Ratio Procedure

To predict the abrasiveness of the three types of samples from the flotation plant a ratio procedure was employed. This was used to compensate for slurry concentration, viscosity and temperature effects. As discussed in Section 4.2.1, aluminium and silicon can be used to correct for varying slurry concentration. Since the aluminium and silicon signals from the samples originate from the clay particles, these two elements can be used to correct, to some extent, for any differences encountered emission signal between samples, caused by in the temperature and transportation effects of varying slurry samples.

For the ratio procedure each sample was analysed for the six elements identified in Section 4.1. The analyte signals were then divided by the silicon or aluminium signals. Thus, assuming that for the same slurry concentration the aluminium and silicon contents for the three types of samples are the same, there would be





correction for slurry concentration plus any effects due to changes in slurry concentration as discussed above.

This approach has been used successfully by Mackey and Murphy for the slurry analysis of zeolites by ICP-AES (70). These workers were able to determine the sodium : aluminium and potassium : aluminium ratios of zeolite reference materials by direct slurry atomisation without any calibration procedure.

4.3 INITIAL ELEMENTAL ANALYSIS

A series of samples were prepared as in Section 4.2.1 and analysed by DCP-AES. The elements determined, together with the wavelengths used, are shown in Table 4.2. Nobackground correction procedure was used and calibration was achieved by using aqueous standards. For these first set of analyses aluminium was not determined.

4.3.1 <u>Correlation between Individual Elements and</u> <u>Abrasion</u>

Of the thirty-six samples in the sample set only thirtythree were analysed in this study. This was because three of the Einlehner abrasion values (supplied by ECCI) were deemed invalid for various reasons. The determined elmental concentrations for the six elements were ratioed to their determined silicon concentrations as described in Section 4.2.3, and also with slurry concentration data. Linear correlation coefficients for the ratioed data for individual elements with abrasion are shown in Table 4.3

Table 4.2

Elements and wavelengths used for initial Abrasion study.

Element	Wavelength/nm	Order
В	249.773 I	90
Ti	323.456 II	. 70
Sr	407.771 II	55
Ba	455.403 II	49
v	309.311 II	73
Ca	445.475 I	50
Si	212.415 I	106
Al	396.152 I	57

Table 4.3

Linear correlation coefficients of the relationships between Einlehner abrasion values and elemental Data. The elemental data being ratioed to silicon as well as slurry concentration.

Element	Correlation Coefficient (r)		
	Slurry Concentration ratioed data	Silicon ratioed data	
Ca	-0.351	0.545	
Sr	0.322	0.374	
Ва	0.399	0.340	
В	0.362	0.371	
A	-0.578	0.233	
	0.442	0.706	

Figure 4.3 Relationship between boron and Einlehner abrasion values. A) silicon ratioed data and





Figure 4.4 Relationship between strontium and Einlehner abrasion values. A) silicon ratioed data and B) slurry concentration ratioed data.



Figure 4.5 Relationship between barium and Einlehner abrasion values. A) silicon ratioed data and B) slurry concentration ratioed data.



Figure 4.6 Relationship between titanium and Einlehner abrasion values. A) silicon ratioed data and B) slurry concentration ratioed data.



Figure 4.7 Relationship between calcium and Einlehner abrasion values. A) silicon ratioed data and B) slurry concentration ratioed data.





VANADIUM/SLURRY CONCENTRATION RATIO
and diagrammatically in Figures 4.3 - 4.8.

A comparison of the two sets of correlation coefficients (Table 4.3), shows that for three elements B, Ba and Sr there is little difference between slurry and silicon ratioed data. Although titanium shows a improved correlation with internal standard ratioed data, the calcium and vanadium correlations decrease significantly. This, plus a study of Figures 4.3 - 4.8, indicates that each element may not have a linear relationship with abrasion. Certainly calcium, vanadium and titanium in the product clays (Einlehner values 30 - 110), seem to exhibit a different relationship than that of the feed (Einlehner abrasion values 140 - 220) and residue clays (Einlehner abrasion values 150 - 350).

4.3.2 Preliminary Multiple Regression Analysis

A predictor model for abrasion was obtained using multiple regression analysis. The Minitab statistical package (Version 5.1.3, V.S. Federal Government Users, U.S.A., 1985) was used on a Prime 950 mainframe computer. The predictors used were the six elements determined above, with all data being either ratioed to silicon, aluminium or slurry concentration. The regression analysis procedure was performed with all the predictors (ratioed data) included in the database. Statistical telemental values were obtained and the predictor with the lowest tvalue was discarded. The t-values are an indication of an individual predictors significance to the regression

after taking model. This is into account the contributions of the other predictors. The regression analysis was performed again with the modified database and new t-values obtained. This procedure was repeated until all the remaining predictor t-values were significant at the 5% level. When this occurred the regression analysis was considered complete. The computer package provides a regression model as in equation 4.1 and regression coefficient R-squared, in percent. The a regression coefficient is a measure of how much of the variation in the dependant data (in this case abrasion) may be explained by the regression model.

Dependent = $B_0 + B_1x_1 + B_2x_2 \dots B_mx_m + e$ Equation 4.1 variable

 B_0 = Constant (intercept) B_1-B_m = Constants (slope or sensitivity) x_1-x_m = Predictors m = Number of predictors e = error

4.3.2.1 <u>Results and Discussion</u>

The regression procedure above was implemented on the elemental data obtained in Section 4.3. The elemental data for each sample was ratioed to its silicon signal. The final regression model had a R-squared value of 85.7% and is shown in equation 4.2.

Abr = 39.4 - 14031 Ca + 801566 Sr + 98006 Ba

Equation 4.2

In this case Abr is the Einlehner abrasion units. Ca, Sr and Ba are the calcium, strontium and barium elemental predictors.

study of the individual elemental relationships From а with abrasion it may seem surprising that boron is not included in the regression model. With multiple regression it is not always the case that the best (or one of the best) individual predictor is included in the final model. This is because if boron depicts the same, or even less, variation in abrasion than say strontium and barium together, then, although a good individual predictor, the boron contribution is not deemed significant. That is to say the model gives boron a low t-value and this would be eliminated under the procedure outlined in Section 4.3.2.

The R-squared value of 85.7% was seen as very encouraging, although a study of the residuals from the model, shown in Figure 4.9, caused some concern. The residual plot exhibits a trend indicating that the model overpredicts for low abrasion samples (products) and under-predicts for high abrasion samples (including residues). This means that the regression model either lacks sufficient, or the correct, information. If the model was satisfactory, then the residual plot would exhibit random scatter above and below zero. Alternatively other contributing factors may be present and one possibility could be the complex relationship exhibited by several elements with abrasion as shown in Figures 4.3 - 4.8.



Figure 4.9 Plot of the residuals from the first silicon

4.4 SECOND ELEMENTAL ANALYSIS

During the analysis of the samples described in Section 4.3 several analytical problems were encountered. The first was that the vanadium results were rather higher than expected. It was realised that the aluminium Ι 309.271 nm line strongly affected the vanadium II 309.311 nm line. This was due to the high aluminium concentration present in the kaolin. Therefore, for subsequent analysis the vanadium II 292.403 nm line was used. It was also noticed that for several elements the clay samples exhibited an elevated background signal compared to that the aqueous standards. A background of correction procedure was therefore employed where the background for each sample was obtained by scanning of signal the emission peak and subtracting this signal from the peak The samples were prepared and analysed by DCP-AES signal. described in Section 4.3 using as the background correction procedure explained above.

For this and later work the DCP's data acquisition computer was bypassed and the detector linked to a BBC B+ microcomputer (Acorn Ltd., Cambridge, U.K.). This allowed the background correction procedure, and all instrumental data collection and manipulation, to be implemented online by computer.

4.4.1 <u>Correlation between Individual Elements and</u> <u>Abrasion</u>

The elemental data obtained from the second analysis of the flotation samples were ratioed to their aluminium, silicon and slurry concentration data. Individual elemental linear correlations with abrasion for all three data sets were obtained. These are presented in Table 4.4 and shown graphically in Figures 4.10 - 4.27.

From an appraisal of the correlation coefficients and graphs for all three types of ratioed data several conclusions can be deduced. Comparing the aluminium and silicon ratioed data with that obtained by ratioing with slurry concentration demonstrates that the first two are the preferred methods with respect to r-values and the scatter of the data. There seens little to differentiate between the aluminium and silicon ratioed data except in the case of titanium. Here the data shows a more linear relationship with abrasion when ratioed to aluminium than with silica. The use of background correction for the second analyses did not produce any significant effect on the correlations of boron, calcium, titanium, strontium. Vanadium showed a marked improvement although this may be due to the changing of the wavelength rather than the background correction procedure. The relationship for barium changed from being similar to boron and strontium to mirroring that of calcium.

Table 4.4

Linear correlation coefficients of the relationship between Einlehner abrasion values and elemental data. The elemental data being ratioed to measured aluminium, silicon and slurry concentrations.

Element	Correlation Coefficient (r)		
	Aluminium ratioed data	Silicon ratioed data	Slurry Concentration. ratioed data
Ca	0.628	0.605	0.310
В	0.916	0.919	0.905
Ba	0.586	0.562	0.233
Sr	0.899	0.562	0.847
v	0.650	0.577	-0.319
Ti	0.802	0.614	0.445









STRONTILS/ALLMINILS RATIO





TITANIUM/ALLMINIUM RATIO

Figure 4.14

Relationship

between the calcium:aluminium



CALCIUM/ALLMINIUM RATIO



ratio data and Einlehner abrasion values.



Figure 4.16 Relationship between the boron:silicon ratio data and Einlehner abrasion values.









STRONTILM/SILICON RATIO



Figure 4.18 Relationship between the barium:silicon ratio









ratio data and Einlehner abrasion values.











4.4.2 <u>Multiple Regression Analysis</u>

For a slurry atomisation DCP-AES system to be used for online analysis of china clay, minimal sample preparation is Using this criteria, and the results shown prefered. above, it was decided to use only aluminium ratioed data for the development of any predictive model. Although aluminium and silicon performed equally well as а compensator for slurry concentration and other analytical characteristics, for the silicon analysis the samples have to be subsampled and diluted. Thus for an on-line situation aluminium has this advantage. Therefore subsequent regression models used aluminium ratioed data as the predictors.

Using the background corrected aluminium ratioed data, and the regression technique described in Section 4.3.2, a regression model with an R-squared value of 96.5% was obtained (Equation 4.3),

Abr = 9.9 + 2093 Ca + 708 B - 2260 Ba + 15029 Sr + 12742 V Equation 4.3

where Abr, Ca, Sr and Ba are as before. V and B represent the vanadium and boron elemental predictors.

This model was a vast improvement on the earlier model using non-background corrected data, but again a study of the residuals, shown in Figure 4.28, revealed certain undesirable trends. Firstly, the feed samples seemed to be overpredicted for low abrasion feeds and underpredicted



for the higher abrasion feed samples. This was mirrored by the residue samples which were overpredicted at the highest abrasion samples and under predicted at the lower residue abrasion samples.

From these observations it was clear that another component needed to be included into the data-base to overcome these differentials between the three types of samples. Initially it was thought that because of the seemingly non-linear nature of some of the individual elemental relationships with abrasion, taking logarithms of the data would help overcome the problem. However this procedure did not offer any advantage over the existing model, either in predicting ability or in the integrity of the model.

A closer study of the best individual elemental predictor suggested that each type of sample did have a linear relationship with abrasion, but with different characteristics i.e. intercepts. Also some kind of structuring between each sample type would have to be used since the regression analysis assumed that all the samples had the same relationship towards abrasion. This may be shown to be incorrect since the three samples, product feed and residue, have varying abrasion ranges (30 - 110, 140 - 220 and 180 - 750 respectively) and cannot be treated identically within the regression model.

4.4.2.1 Product and Residue Identifiers

To compensate for the anomalies described above, two extra predictor columns were incorporated into the data-base. These extra predictors were for the identification of product and residue samples. With two of the three sample types recognised it is not necessary for a feed identification column. These columns consist of a series of 1's and 0's. For the Product identification column, if the sample was a feed or residue then the row would contain a 0, and for a product sample contain a 1. The residue column was constructed in the same manner but with the residue rows containing 1's and the feed and product rows containing 0's.

To demonstrate how these new predictors would affect the regression analysis, an example using two sets of samples, feeds and products, and one elemental predictor <u>e.g.</u> boron is described. If the boron concentration, in the feed and product samples, behaves the same towards abrasion, then the regression equation (Equation 4.1) would be as Equation 4.4. This equation can also be shown graphically as in Figure 4.29.

$$ABR = B_0 + B_1$$
 (boron) Equation 4.4

Where ABR = abrasion, $B_{\chi} = constants$, (boron) = boron concentration predictor.

However, if as discussed above, the feed and product boron concentrations possess different relationships towards







abrasion, and a product identifier predictor can be added to the data-base, Equation 4.4 becomes Equation 4.5. This new equation can also be shown graphically as in Figure 4.30.

$$ABR = B_0 + B_1$$
 (boron) + B_2 (product) Equation 4.5

A further model was formulated as before using these two extra predictors in the data-base. An R-squared value of 98.3% was obtained and the model is shown in Equation 4.6

Abr = 118 + 1927 Ca - 1438 Ba + 13171 Sr + 115958 V - 21279 Ti - 71.6 P

Equation 4.6

In this case the P is the symbol for the product identification predictor. The residue predictor was eliminated because the analysis could not discern any statistically significant difference in the intercepts between the feed and residue samples, and therefore no correction was required. A plot of the residues from this shown in Figure 4.31. These residues model is do look less structured than those shown in Figure 4.28. It seems that the inclusion of the two identifier columns has improved the predictive ability and removed some of the bias that was present in earlier models.



4.4.2.2 <u>Calibration of Final Regression Model</u>

To ascertain whether the model was performing adequately the data-base was re-calibrated. This consisted of removing a fraction of the data-base, and the remainder being regressed in the usual way. The removed data is then applied to the regression equation and the predicted abrasion values compared to the actual Einlehner abrasion values.

With only thirty three samples in the data-base to start with, the number of calibrant samples was critical. Six samples were chosen at ramdom. This number was chosen as it still left 82% of the original data-base and would provide enough information to indicate whether the models were performing correctly.

The regression analysis for the reduced data-base gave an R-squared value of 98.0% and the model shown in Equation 4.7.

```
Abr = 47.9 + 2157 Ca - 1704 Ba + 12926 Sr + 133013 V
- 57.1 P
```

Equation 4.7

The six calibration samples, (three products, two feeds and one residue), were applied to Equation 4.7 and the results shown in Figure 4.32. The predicted abrasion values give a linear correlation coefficient (r) of 0.9766 against the observed values, with an intercept of -3.6 and more importantly, a slope of 1.0034. These results are

1.37



OBSERVED ABRASION VALUES

extremely encouraging since the data indicates that the model was performing adequately. One of the criticisms of multiple regression analysis techniques is that the model may not be very robust <u>i.e.</u> may change dramatically when calibration samples are removed as above. This has not happened in this case, although titanium was removed by the regression analysis where as before it was included.

4.5 CONCLUSIONS

It has been shown that the abrasiveness of the three types of samples obtained from the froth flotation plant can be predicted. Also slurry concentration and slurry atomisation effects in the DCP can be compensated for, using aluminium or silicon as intrinsic internal standards. Background correction is necessary for the slurry analysis of kaolins as shown by the vast improvement in the regression models when background correction was employed. Inspite of the non-linear behaviour of individual elemental predictors towards abrasion, the multiple regression approach performed exceptionally well. However it was only after identification columns were included into the data-base in the model between sample that bias types was Further development of the model, plus eliminated. more rigorous statistical analysis are hampered at this stage . by the size and shape of the data-base. Since the product and residue samples were sampled at the same time as the feed, they do not bear a direct relation to the feed clay the half-life of clay in the flotation plant as is

approximately one and a half hours. In addition, the data-base is rather small although the calibration procedure described in Section 4.4.2.2 was successful. Therefore the next stage of development was to consider a new data-base, unconstrained by the problems discussed above.

CHAPTER 5 CONTROL OF THE FROTH FLOTATION PROCESS

5.1 **INTRODUCTION**

As discussed in Chapter 4, the use of using a slurry atomisation based-multiple regression system, successfully allows the abrasiveness of china clay samples to be predicted. However, as outlined in Section 4.5, several additional factors have to be taken into consideration when applying this method to the control of the froth flotation process. For this purpose the control system would have to predict the abrasiveness of the product clay from the analytical data of the feed clay and the plant operating conditions (percent recovery). Using such a model the percent recovery of the plant could be adjusted to produce a product clay within-the desired abrasion specification.

5.2 <u>REVISED SAMPLING PROCEDURE</u>

To improve the relationship between the product (and residue) samples, and the feed samples from the flotation plant, the product (and residue) samples were collected one and a half hours after the feed samples. During this time the percent recovery of the plant was kept constant. This meant that any changes in the feed clay quality (abrasiveness) would be apparent in the quality of the product clay. Three sets of feed, product and residue samples, in duplicate, were taken at 35, 45, 55, 65 and 75% recoveries. Thus, over a period of five days, 90 samples were obtained. All the samples were tested for

abrasion using the Einlehner abrasion test. Subsequently however, the results obtained at 35% recovery were discarded from the sample set since it was found that the flotation plant did not operate consistently at this recovery level. This was due to the poor reproducibility of the frothing process compared to that of higher operating recoveries, a fact highlighted by the abrasion results which yielded unacceptable variation in the duplicate sample values. Therefore the new sample base consisted of 72 samples containing 24 feed and product linked pairs.

5.3 ELEMENTAL ANALYSIS

The samples were prepared as in Chapter 4, Section 4.2.1, except that they were dispersed with sodium pyrophosphate in the ratio of 1 g of sodium pyrophospate to 100 ml of sample, giving a 1% m/v concentration of dispersent. This is an acceptable substitute for ammonia in the dispersion of kaolin (56), and would be easier to handle in an online situation. The slurry analysis was performed as before (Chapter 4, Section 4.4), and calibration was achieved using aqueous standards. The DCP unit was now interfaced to a PC compatable micro-computer (Amstrad PC 1512, Brentwood, Essex, UK). This was to facilitate any necessary interfacing with the flotation plant controllers, as well as to provide the capacity for the regression analysis needed for the development of the predictive models.

5.3.1 Duplicate Samples

As mentioned in Section 5.1, all the samples were taken in duplicate. This was to provide a check on the Einlehner abrasion test, and to compare the precision between this test and the slurry atomisation-aluminium ratio method of analysis that had been developed in Chapter 4. Correlation coefficients for the duplicate subsets (A and B) for individual elements ratioed to aluminium, Einlehner abrasion values and aluminium levels are shown in Table 5.1 and graphically in Figures 5.1-5.8. As can be seen the scatter (possibly with the exception of the vanadium ratioed data) between the Einlehner values and the slurry atomisation data is very similar. This indicates that both methods have similar precision which is desirable for any on-line system.

5.4 DEVELOPMENT OF CONTROL MODEL

5.4.1 Einlehner Model

Although the Einlehner abrasion test cannot operate as an on-line process at the present time, it would be instructional to test the proposed model (Section 5.1) with real abrasion values, rather than slurry atomisation obtained data. Initially this was to see whether the proposed method would function correctly, as well as providing a yardstick for any subsequent models.

Present in the data-base there were 24 pairs of feed and product samples. Using the feed abrasion values, and the percent recovery at which each pair of samples were

<u>Table 5.1</u>

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Linear correlation coefficients between duplicate samples with predictor elements ratioed to aluminium data, Einlehner abrasion values and aluminium concentration.

Element	Correlation Coefficient (r)
B/Al	0.979
Sr/Al	0.954
Ba/Al	0.975
V/Al	0.862
Ti/Al	0.949
Ca/Al	0.982
Al	0.988
Einlehner Abrasion Values	0.971



SUBSET A EINLEHNER VALUES












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collected, as the two predictors, a regression model for product abrasion was obtained. This model had an Rsquared value of 58.5% and is shown in Equation 5.1.

$$P = 20.4 + 1.29 R - 0.214 F$$
 Equation 5.1

Where P is the product Einlehner value, R is the percentage recovery of the flotation plant, and F the feed Einlehner abrasion value.

The reason for the poor R-squared value is revealed by a study of the residual plot from the model shown in Figure 5.9. Whereas most of the residuals are within ± 12 abrasion units, one sample had a residual of 42 units. This sample had a abrasion value of 96 units whereas its duplicate had a value of 53 units. From the percent recovery of the plant at the time these samples were collected, and from data obtained from other samples taken at this time, the 96 unit value is clearly elevated. This variation in the Einlehner abrasion values is more of a problem at the low end of the abrasion scale. Therefore for the remaining sections of this chapter, several models are presented and analysed with a number of samples which have erroneous abrasion values removed. As well as the poor R-squared value, this initial model also indicated that the feed abrasion predictor was not significant *i.e.* it lay outside the 5% significance limit explained in Chapter 4.



The sample with the 96 abrasion value was removed from the data-base and the regression procedure run again. This produced the model shown in Equation 5.2 with a R-squared value of 81.9%.

P = 18 + 1.36R - 0.235F Equation 5.2

This is a dramatic improvement in the predictive power of the model with the removal of a single sample, and highlights one of the problems encountered in this study, <u>i.e.</u> the identification of "false" data. This is especially important in this case, since using such a small data-base each sample is a significant percentage of the whole. In this type of situation, the inclusion of such a sample, as described above, would severly affect the regression analysis.

From the model shown in Equation 5.2 three more samples were found to have abnormally "elevated" abrasion values. These three samples, like the sample described above, had large variations in their duplicate Einlehner abrasion values, and were therefore removed from the database. A third model was obtained from the remaining 20 samples. This is shown in Equation 5.3 with a R-squared value of 94.3%.

P = 1.7 + 1.48R - 0.167F Equation 5.3

This was highly encouraging and a study of the residual plot (Figure 5.10) shows an even distribution of the residuals above and below the zero line.



5.4.1.1 <u>Conclusion</u>

From these results it is clearly possible to predict the abrasion of a product sample using the feed abrasion values, and the operating parameters of the flotation plant. However, the quality of the data-base has to be monitored. The problems encountered above are exaggerated because of the relatively small data-base.

5.4.2 <u>Slurry Atomisation Model</u>

For the on-line control of the flotation plant the feed abrasion predictor needs to be replaced by the feed elemental data. Concerning the regression models described below there are two major points to consider. Firstly, that calcium has been discarded as a predictor This was not because it demonstrated little element. significance during the modelling process, but for operational considerations. ECC International uses vast volumes of water in its mining and extraction processes. and the majority of this water is re-cycled. So although calcium had been included in several models, it was feared that the calcium level in the water supply could change dramatically, and invalidate the predictions from any model useing calcium data. Therefore the remaining five elemental predictors were used, plus two predictors for the percent recovery. This was the second major It was noticed that the response between development. product abrasion and percent recovery was possibly of a non-linear nature at the extremes of the plant operating capabilities. Therefore as well as a normal percent

recovery predictor, another predictor was introduced, consisting of squared percent recovery data. It was expected that the regression procedure would identify which predictor was most related to the operating characteristics of the plant.

5.4.2.1 <u>Multiple_Regression Analysis</u>

As in Section 5.4.1, initially all 24 samples were included in the data-base for the first regression model. This model is shown in Equation 5.4 and had an R-squared value of 66.7%.

P = -10.5 + 94214 V + 0.00959 RSQ Equation 5.4

Where P is the product abrasion value, V the vanadium/aluminium ratioed data and RSQ is the squared percent recovery data.

The same procedure was followed as in Section 5.4.1 with the removal of the most erroneous data point, and the data regressed again. This new model gave an R-squared value of 82.1% and is shown in Equation 5.5.

P = -1.69 + 60732 V + 0.0103 RSQ Equation 5.5

Again, the last three flawed samples were removed from the data-base and the regression procedure applied to the reduced data-base. This final model produced Equation 5.6 with an R-squared value of 96.7%.

P = 111 - 4.3R +10109 Sr + 41053 V + 0.0478 RSQ Equation 5.6

Where R, V and RSQ are as before and Sr is the strontium/aluminium ratioed data.

A study of the residuals from this final model (Figure 5.11) reveals a ramdom scatter around the zero line, indicative of a healthy model.

These three models show directly comparible predictive ability with those outlined in Section 5.4.1. Indeed these latest three models show improvements over those in Section 5.4.1. One interesting feature of the final model is that both percent recovery predictors were deemed significant. Infact, the squared percent recovery data was included in all the later models described in Section 5.5. It is probable that the retention of both at the present time is a reflection of the small data-base used.

5.4.2.2 <u>Conclusion</u>

It has been demonstrated that using feed analysis data, plus the percent recovery data from the flotation plant, the abrasiveness of the product clay can be predicted. The models using slurry atomisation data performed better than those containing feed Einlehner abrasion values. Thus, for an on-line control or monitoring situation the slurry atomisation-DCP-AES method is clearly a viable proposition.



5.5 ON-SITE TRIAL

With the success of the slurry atomisation models, described in Section 5.4.2, an on-site trial for the DCP system was performed. The DCP instrument was installed in the Goverseth flotation plant complex (St.Austell, Cornwall), and all analyses were performed on-site.

5.5.1 <u>Sampling Procedure</u>

Initially a six week sampling strategy was planned, each week containing six sampling days. On each day the percent recovery of the plant was changed to a predetermined level and two samples taken of the feed clay, and then 1.5 hours later two taken of the product clay. The percent recovery of each sampling day was chosen at ramdom from the set 50, 55, 60, 65, 70, 75%. Each week would therefore provide twelve new feed samples, two from each of the above recoveries, plus their corresponding product samples for calibration purposes.

The feed samples were analysyed on-site by slurry atomisation -DCP-AES, with the product clay undergoing the Einlehner abrasion test, so that the validity of the models could be determined. It had been hoped that for the first three weeks of the trial the new samples would be added to the data-base week-by-week. In this way the first weeks samples would be applied to the initial model, outlined in Section 5.4.2, and the predicted product abrasion values compared to the actual Einlehner values determined from the product clay samples. Then these 12

samples would be added to the initial data-base and a new regression model obtained. All this constitutes what is later refered to as one trial Cycle. The feed sample data from the second week would then be applied to this new model, predicted and observed abrasion values compared, and the data-base enlarged again with these new samples and a new regression model obtained, thus completing a second cycle. This process was to continue for three weeks to ascertain whether the model was predicting the product clay quality accurately. If this was so then on the addition of the 12 samples from week 4 to the database, the 12 oldest samples (from the initial 24) would be This would have limited the data-base to 60 discarded. The intention was to test whether the model samples. could be up-dated in this way, as well as ensuring that the data-base would reflect any changes in the chemical composition of the china clay passing through the plant.

In reality only the samples for three cycles, or weeks, were collected over a seven week period. This was due to the operational requirements of ECC Interanational, plus an unfortunate series of malfunctions of the flotation plant. Because of this, the on-site trial could only be of a monitoring nature.

5.5.2 Experimental

The slurry samples were prepared as in Section 5.4 and aqueous standards were used for calibration. Five elemental predictors, boron, strontium, barium, titanium

and vanadium, plus aluminium, were determined using the wavelenths and methology descirbed in Chapter 4. All data manipulation was performed on the Amstrad PC 1512 microcomputer except for the regression analysis which was performed on a Prime mainframe computer.

5.5.3 <u>Results</u>

For the purposes of comparison three models were run simultaneously. The initial models are those described in Section 5.4.2 and listed in Equations 5.4-5.6. This was done to determine whether any significant changes occurred with the removal of several data points and to see what influence the initial R-squared value had on the predicting ability of the models. The three models have been called Model 1, Model 2 and Model 3. The difference between the models lies in the number of samples in the initial data-base. Model 1 contained all 24 original samples, Model 2 had one data point removed and Model 3 had five datapoints removed. Each model underwent three sampling cycles as described in Section 5.5.1.

The results for Model 1 are shown in Table 5.2 and Figures 5.12-14, for Model 2 in Table 5.3 and Figures 5.15-17, and finally the results for Model 3 are shown in Table 5.4 and Figures 5.18-20.

It should be noted that in Cycles 1 and 2, twelve samples were applied to the regression equations and subsequently added to the data-base, whereas Cycle 3 only contained

<u>Table 5.2</u>

Evolution of the first product abrasion model. All 24 initial samples included in the data base.

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	Size of data base	Regression model for product abrasion	R~squared value / %	Correlation between predicted and actual product values (r) ^a
Cycle 1	24	-10.5 + 94214 V	66.7	0.897
		+ 0.00959 RSQ		
Cycle 2	36	5.4 -5136Ba +99777V	71.8	0.920
		+ 0.00975 RSQ		
Cylce 3	48	5.71 -4393Ba +90763V	76.0	0.977
		+0.00993 RSO		

Where	V	=	vanadium/alumin	nium,
	Ba	=	barium/aluminiu	שנ
	RSQ	=	squared percent	recovery

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(a) These correlations are depicted graphically in Figures 5.12-5.14.







<u>Table 5.3</u>

Evolution of the second product abrasion model. One sample removed from the initial data base.

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	Size of data base	Regression model for product abrasion	R-squared value / %	Correlation between predicted and actual product values (r) ^a
Cycle 1	23	-1.69 + 60732 V	66.7	0.897
		+ 0.0103 RSQ		
Cycle 2	35	2.26 +16740Sr +54724V	71.8	0.920
		-5029Ti + 0.00975 RSQ		
Cylce 3	47	1.6 +11137Sr +73273V	76.0	0.977
		-4596Ti +0.00932 RSQ		
•				

Where	V	=	vanadium/aluminium		
	Sr	=	strontium/aluminium		
	Ti	=	titanium/aluminium		
	RSQ	=	squared percent recovery		

(a) These correlations are depicted graphically in Figures 5.15-5.17.







<u>Table 5.4</u>

Evolution of the third product abrasion model. Five samples removed from the initial data base.

	Size of data base	Regression model for product abrasion	R-squared value / %	Correlation between predicted and actual product values (r) ^a
Cycle 1	19	111 -4.3R 10109Sr	66.7	0.897
		+41053V +0.0478 RSQ		
Cycle 2	31	3.21+18828Sr -4304Ti	71.8	0.920
		+26072V +0.0105 RSQ		
Cylce 3	43	1.85 -3822Ti +55517V	76.0	0.977
		11097Sr +0.0105 RSQ		

Where	V	=	vanadium/aluminium
	Sr	=	strontium/aluminium
	Ti	=	titanium/aluminium
	R	=	percent recovery
	RSQ	=	squared percent recovery

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(a) These correlations are depicted graphically in Figures 5.18-5.20.

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eleven samples. This was because, as described above, one sample in Cycle 3 was provided with an erroneous abrasion value and therefore could not be used for correlation purposes.

5.5.4 Discussion

5.5.4.1 <u>R-Squared Values</u>

From Tables 5.2-5.4 it can be seen that the R-squared values increase for the initial regression equations in order of Model 1 - Model 2 - Model the 3. This is expected since the most wayward sample points have been progressively removed (Section 5.4). One interesting observation is that although the R-squared values increase in Models 1 and 2 with the enlargement of the data-base, the R-squared values for Model 3 actually decrease slightly. This is probably due to the fact that as Models 1 and 2 contain some dubious data-points, the increase in the size of the data-base increases the predictive ability of the models. In the case of Model 3 the initial Rsquared value is probably the best that can be achieved practically. Thus, the slight fall in the R-squared value could be due to the difference between the initial samples and the on-site trial samples. Variations in the elemental composition must exsist between the two groups since they were collected over a year apart. Inspite of this, it can be assumed that the inherent predictive ability of this method is in the 90%-95% R-squared region. Also that the size of the data-base needs to be around 50 data points.

5.5.4.2 Model Composition

In all the three models used, the squared percent recovery predictor was included in the final equation rather than the simple percent recovery predictor. This comfirms some of the observations about the linearity of the flotation process discussed in Section 5.4.2.

The major difference in model composition occurs between Model 1, and Models 2 and 3. After Cycles 2 and 3, Models 2 and 3 both contain the same four predictors, vanadium, strontium, titanium and squared percent recovery. Model 1 has the substitution of the barium predictor for the titanium and strontium predictors of Models 2 and 3. This demonstrates the power that a single data-point can have on the regression analysis. The extra samples removed between Models 2 and 3 do not have the same effect on the final regression equation. Therefore some ambiguity exsists as to whether they should have been removed in the first place.

5.5.4.3 Accuracy of Predictions

For the purpose of this study accuracy was expressed by the linear correlation coefficients shown in Tables 5.2-5.4. This is a rather limited method, therefore a study of the correlation plots and the slopes of the regression lines (Figures 5.12-20) is nescessary. All three models exhibited the same overall trend. As the data-base is supplemented with new samples the linear correlation coefficients increase, with all the models achieving

similar values regardless of the R-squared values. However a study of the correlation plots revealed that although the linear correlations between the predicted and actual abrasion values were increasing, the slopes of the correlation plots were decreasing. It is difficult to speculate about this trend. Since samples were collected on only three cycles, it is not clear whether this is a general trend, a random variation, or whether additional cycles would reverse this trend. Some of this distorsion could be due to the fact that the old, initial data is still present in the data-base of the models. As mentioned in Section 5.5.1, it had been hoped to replace the oldest data after the data-base had reached 50-60 samples in size. It was not possible to collect sufficient samples for this process, so in this respect the on-site trial was incomplete.

5.6 CONCLUSIONS

It has been shown that the slurry atomisation, ratio procedure has the same precision as the Einlehner abrasion test. Also, that the product abrasion can be predicted, by a regression model consisting of feed clay analytical data, plus the percent recovery of the flotation plant. This type of model was shown to be better than the corresponding Einlehner test models.

A successful on-site trial was performed, showing that both the DCP instrumentation and regression analysis can work in an industrial environment. The on-site trial was

not as rigorous as intended due to a lack of samples. However it has been shown that a regression model for product abrasion can be obtained, and updated, with acceptable accuracy. Some problems were encountered with the quality of the data-base. Further development of this slurry atomisation system, plus some possible solutions to the problems outlined above, are discussed in Chapter 8.

CHAPTER 6 VISCOSITY CONCENTRATION

6.1 Introcduction

As discussed in Chapter 1, Section 1.1.5 viscosity concentration is of vital importance to the quality of coating clays for the paper industry and also to a lesser in the transportation of bulk extent china clay. Impurities such as montmorillonites ("expanding lattice" minerals) are the major or "swelling" causes of unfavourable viscosity characteristics in china clay. Therefore a study was initially performed on the prediction of the montmorillonite content of china clays being extended to include general viscosity before properties.

6.2 MONTMORILLONITE STUDY

Initially three sets of samples, varying in type and content of montmorillonite, were prepared by ECCI Central Laboratories (St. Austell, Cornwall). Pure montmorillonite was extracted from source clays and a SPS high quality coating clay was used for the bulking clay. The sample sets were as follows.

- Set A Consisted of six samples with increasing montmorillonite content (0.25, 0.5, 1.0, 2.0, 5.0 and 10% m/m).
- Set B Consisted of three samples containing montmorillonite from a drilling operation near

Bugle, Cornwall. These were labelled HM1, HM2 and HM3.

Set C - Consisted of three samples, spiked with montmorillonite from Littlejohns Pit, St. Austell, Cornwall. These were labelled L1, L2 and L3.

Slurry samples were prepared in the range 1% - 4% m/v containing aqueous ammonia (AnalaR grade, BDH Chemicals, Poole, Dorset, UK), as a dispersing agent in the ratio of 1 ml of ammonia to 100 ml of sample. The slurries were made up in a 5 g dm⁻³ lithium buffer solution, (hydrous lithium nitrate, AnalaR grade, BDH Chemicals, Poole, Dorset, UK). The prepared slurries were each sonicated for 2 minutes to aid the dispersion of any clay aggregates.

Each of the slurries were analysed by DCP-AES using the standard conditions listed in Chapter 2. Calibration was achieved using aqueous standards (Chapter 1, Section 1.2.4). Recovery was assumed to be 100% because, as discussed in Chapter 3, all these samples particles were below 5 µm in size. For the purpose of providing a 'blind trial' the montmorillonite content of the samples in Sets B and C were not provided until the analyses and predictive models were completed.

6.2.1 Identification of Predictor Elements

In order to identify which of the elements present could be used as possible predictor elements two approaches were A survey of the literature and consultations adopted. with ECCI suggested that magnesium, calcium, iron, sodium and manganese should be studied because of their known association with montmorillonite minerals. In addition, these elements are also known to be exchanged into the layered lattice of these 'swelling' minerals (5,71). То confirm the relationship with montmorillonite content, a series of photographs were taken of the spectrum produced by the excitation of a montmorillonite sample. This was achieved by utilising the DCP photographic attachment, which enables a polaroid picture to be taken of the entire spectrum produced by the echelle grating. This provides a rapid qualitative analysis method. Elemental identification was achieved by a series of transparent overlays indicating the positions of the major spectral lines of each element. Accurate identification of spectral lines was possible as each sample was spiked with a solution of mercury and the transparencies positioned correctly with respect to four mercury lines which are easily identifiable (55). This technique clearly confirmed the presence of the above elements, together with strontum, zinc and lead as possible predictor elements.

Other elements such as chromium, gallium and lithium were also identified but not investigated further in this study

since they were found at concentrations near the detection limits of the DCP (55). The seven elements determined, together with the spectral lines used, are shown in Table 6.1.

6.2.2 <u>Results and Discussion</u>

A11 the elemental concentrations obtained are given in Table 6.2. The elemental data was plotted against montmorillonite content for each element and the correlation coefficents obtained. Only magnesium and calcium showed significant relationships with montmorillonite content and with sufficient slope to be useful in any predictive model, as shown in Figure 6.1. The correlation coefficients for magnesium and calcium with montmorillonite content were r = 0.9988 and r 0.9994 respectively. The other elements, iron, sodium, zinc, manganese and strontium exhibited various degrees of correlation for sample Set A, but the values lay in differing concentration ranges compared to the other two sample sets, and therefore had limited value as predictors in a general model. Therefore further prediction work concentrated upon magnesium and calcium.

6.2.2.1 Identification of Sample Source

The relationship between magnesium and calcium for all three sample sets is shown in Figure 6.2. It is well documented (3) that for all types of montmorillonite mineral the magnesium, calcium, sodium and lithium content is enhanced above usual kaolinite levels, although to what

Table 6.1

Elements and wavelengths used in the montmorillonite study.

Element	Wavelength/nm	Order
Mg	259.533 II	87
Ca	317.933 II	71
Mn	257.610 II	87
Na	589.592 I	38
Sr	407.771 II	55
Zn	202.548 II	. 111
Fe	259.940 II	37

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Table 6.2

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Elemental concentrations for all montmorillonite samples.

Sample		Element	tal Con	centrat:	ion (µg	g ⁻¹)	
	Mg	Ca	Mn	Na	Sr	Zn	Fe
Set A							
0.25%	681	315	19.0	136	31.2	22.5	2359
0.5%	711	333	19.3	149	36.1	23.0	2346
1.0%	802	380	19.7	133	26.9	23.6	2321
2.0%	929	479	20.8	129	33.4	23.5	2444
5.0%	1351	778	24.3	124	27.5	24.6	2460
10.0%	1935	1343	31.3	132	33.3	26.8	2604
Set B							
HM1	993	462	29.5	268	27.9	23.7	5429
HM2	834	364	11.8	153	44.2	22.1	5240
нмз	1493	945	35.9	693	23.9	37.8	6200
Set C							
L1	1201	121	11.3	1040	15.4	12.6	2957
L2	810	198	8.8	349	32.7	17.0	1842
L3	940	178	10.1	759	27.4	15.7	2101


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extent will depend on the source and montmorillonite type. Taking this into consideration for Sets A and B, both magnesium and calcium content increased with montmorillonite content (Figure 6.1). The samples from Set C (Littlejohns), however, show that with increasing magnesium content (and hence montmorillonite content) there is a decrease in the calcium levels indicating a different mineralogy.

To distinguish Set A samples from Set B samples, the magnesium : calcium ratio was plotted against total iron content (Figure 6.3). As Figure 6.3 shows, three quite distinct linear groupings occur enabling simple pattern recognition of the sample source.

6.2.2.2 <u>Prediction of Montmorillonite Content for Set B</u> (HM) Samples

It can be seen from Figure 6.2 that Sets A and B were similar in their magnesium and calcium contents. Using the data from Set A a regression model for predicting montmorillonite, using magnesium and calcium as the two predictors, was obtained via the Minitab ^(TM) program and methology described in Chapters 4 and 5. An R-squared value of 100.0% and equation 6.1 were obtained.

M = 3.69 + 0.00329 Mg + 0.00545 Ca Equation 6.1

Where M is the montmorillonite content (% m/m), Mg is the magnesium concentration and Ca is the calcium



concentration. The R-squred value of 100.0% may seen surprising, but it can be explained by the small size of the data-base. Using two predictors which are highly correlated with each other, and with only 5 data points, it is possible to produce R-squared values of this nature. Using equation 6.1, predicted values for Set B samples were calculated and are shown in Table 6.3, together with the values provided by the ECCI infra-red technique described in Chapter 1, Section 1.1.5.2. Although not identical, the predictive values are in the same range as the ECCI values. These results were also confirmed by the the other elements in both sample order of sets. Manganese, sodium, zinc and iron all follow the HM3 > HM1 > HM2 pattern where as strontium was inversely correlated HM2 > HM1 > HM3. This suggests that stronium is more associated with the kaolinite bulking clay which is borne out by the results observed in Chapter 4. These showed that strontium had a high, positive, individual correlation with abrasion and was obviously associated with the physically harder type of mineral impurity found in the china clay product.

6.2.2.3 <u>Prediction of Montmorillonite Content for Set C</u> (Littlejohn) Samples

The Set C samples could not be applied to equation 6.1 because of the inverse relationship shown between magnesium and calcium in these samples and Set A samples. By only using magnesium values from Set A, however, a linear regression equation (Equation 6.2) was obtained

having a correlation coefficient (r) of 0.9988. Predictor values for Set C samples using equation 6.2 are shown in Table 6.3.

$$M = -5.13 + 0.00772 Mg$$
 Equation 6.2

As with the results for Set B, the predictor values show slight variation but the model has successfully identified the order of the samples in terms of increasing montmorillonite content <u>i.e.</u> L1 > L3 > L2. This sample also differed from the other two in that it set had an inverse trend for zinc versus montmorillonite content which highlighted the different nature and location of the samples.

6.2.3 <u>Conclusions</u>

With laboratory prepared samples, spiked with montmorillonite from various sources, the elemental prediction technique using the minor elements magnesium, calcium and iron was very successful in predicting both the location and montmorillonite content for a range of samples. Α blind trial for the prediction of montmorillonite content was successfully conducted although this highlighted the need for information or data about a sample's origin to be included in any predictive models. This variation in sample origin explains why the predictor elements varied between sample sets both in terms of concentration and type of relationship. A multielement model should be flexible enough to overcome this

Table 6.3

Predicted Montmorillonite Content for Set B (HM) and Set C (Littlejohns) samples.

Sample	Hontmorillonite/% m/m		
	ECCI	Predicted	
Set B			
HM1 ·	3.3	2.1	
HM2	1.5	1.0	
НМЗ	9.5	6.4	
Set C			
L1	3.3	4.1	
L2	1.0	1.3	
L3	1.5	2.2	

problem if sample source or elemental relationships relating to sample origin is taken into consideration.

6.3 DEVELOPMENT OF VISCOSITY PROJECT

The montmorillonite study discussed in Section 6.2 was taken a stage further by ECCI. The work described in this section was undertaken by Dr. G. Glegg for ECCI. ECCI has kindly given permission for these results to be included and discussed here, in order to provide continuity between this projects montmorillonite and viscosity concentration work. Glegg moved from analysing laboratory synthetic samples in the first instance, to real samples collected from various pits in the St. Austell area. The was moved to viscosity concentration emphasis from montmorillonite content. This was because as far as production control is concerned, the viscositv concentration is a measure of the rheological properties a clay, whereas montmorillonite content can only give of indication an to a clay's potential viscosity concentration. Also the standard test procedure for viscosity concentration (described in Chapter 1, Section 1.1.5) has a s.t.d. of 0.3% which is far superior to the infra-red technique for the analysis of montmorillonite.

Clay samples, from a variety of pit sources, were bleached, pugged, made up to 5% m/m slurries with 5 g dm⁻³ lithium solution (Analar grade, Hydrated Lithium Nitrate, BDH Chemicals, Poole, Dorset, UK) as an ionic buffer, and 0.02% m/m Dispex (TM) (sodium polyacrylic acid) as a

dispersant (Dispex is the standard dispersant used by ECCI). Each sample was then analysed by slurry atomisation DCP-AES for a range of elements. The elements determined were aluminium, magnesium, barium, strontium, chromium, lithium and potassium.

Using slurry atomisation - DCP - AES and the multiple regression procedure described in Chapters 4 and 5, the viscosity concentrations for these samples were predicted.

From the multiple regression analysis, models for viscosity concentration with R-squared values between 65.0-96.0%, were obtaied from single pit data. A combined data-base was formulated containing data from the five sources involved, plus source identification predictors. These pit identification predictors were in the same form the sample identification predictors, developed as in Chapter 4, for the abrasion regression analysis. With this extented data-base, a regression model, with an Rsquared value of 78.0%, was obtained. Although this was encouraging, the residuals from this model did exhibit some organised structure, indicating that there was some bias present in the model (72,73).

In parallel with these multi-element experiments, a study was conducted into the correlation between the ability of sample clays to absorb chelated nickel and copper organic species, plus inorganic copper, with viscosity concentration. This approach was adopted to try and

utilise the high cation exchange capacity of montmorillonite type minerals, and to correlate this to viscosity concentration. The idea is very similar in concept to that used to determine the montmorillonite content by infar-red analysis described in Chapter 1. Section 1.1.5.2. Experiments with the chelated organic material provided little encouragement but those with the inorganic copper showed some success. Samples were prepared as described in Section 6.4.1. The absorbed copper concentration was determined by slurry atomisation - DCP - AES and the results regressed against viscosity concentration. The regression model had an R-squred value of 98.0% (73).

6.4 FURTHER INVESTIGATIONS

Continuing the work undertaken by Glegg and ECCI (outlined above) a further series of samples were prepared. These differed from previous samples since they came from а single pit (Littlejohns, St. Austell) although they included samples from five different stopes (pit faces). These samples were prepared directly from pit washings. The object was to develop a quick, reliable analytical method to indicate the quality of each stope to aid pit management, thereby allowing an optimisation of the mining Thirty one samples were provided together with process. their solid contents and viscosity concentration. For twenty four samples, the copper absorption investigation was continued and again the solids content and viscosity concentration values were provided by ECCI.

6.4.1 <u>Copper Absorption</u>

The copper doping procedure was developed by ECCI, Central Laboratories. The clay samples were passed through a 300 mesh screen (providing particles of < 5.3 µm), made up to а 10% m/m slurry in a 0.5 M copper nitrate solution (AnalaR grade, BDH Chemicals, Poole, Dorset), and left for hour. The samples were then centrifuged, the one supernatant removed, and the clay washed four times with distilled water. This was to remove any unabsorped copper from the clay particles. After dispersion with Dispex (0.02% m/m), slurries in the range 3 - 10% m/v were prepared for analysis by slurry atomisation - DCP - AES in a 5 g dm⁻³ lithium solution. The Cu I 224.7 nm line was used for the analysis. Aqueous standards were used for calibration.

6.4.1.1 <u>Results and Discussion</u>

A plot of the copper concentrations in the clay samples $(\mu g g^{-1})$ versus viscosity concentration (%) plus the origin (stope) of the sample is shown in Figure 6.4. A regression model for viscosity concentration for this data, shown by Equation 6.3 yields a R-squared value of 62.9%.

Where V% is the viscosity concentration and Cu the determined copper concentration.





However a plot of the residuals from this regression (Figure 6.5) shows undesirable structuring to be present. Α close study of Figure 6.4 provides a possible explanation for this. Firstly for stopes 3 and 4 there was very little change in either the copper concentration or in viscosity concentration. For stope 6 samples, variation in copper concentration does not appear to produce any marked effect on the viscosity concentration. Finally, for stope 20 samples, there appeared to be in the viscosity concentration values differences for samples providing the similar copper concentrations.

When dummy variables were introduced into the data-base as an indication of stope source, as in Chapter 4 for sample identification, the correlation coefficient (R-squared) rose to 83.6%. However a plot of the residuals (Figure 6.6) still shows some structure as before. From this evidence it is obvious that the mineralogy of each stope distinctly different, especially in the case of is stope 6. It is known that, although 80% of the cation exchange capacity of 'swelling' clays occur via substitution of the interstitial water molecules within the lattice structure, 20% is due to the charges on the edge of the tetrahedral sheets. Thus it is possible that the copper attracting mineral in stope 6 is not of the absorptive montmorillonite (smectite) classification but of another adsorption 'non-swelling' type with highly charged lattice layers (3).



6.4.2 <u>Multi-Element Approach</u>

From earlier research (72,73) six elements have been identified which demonstrate a relationship with viscosity concentration. These elements, magnesium, potassium, chromium, titanium, barium and strontium, together with aluminium, were determined in a series of samples from Littlejohns Pit, St. Austell by slurry atomisation - DCP -AES. The thirty one samples were from the same five stopes as in Section 6.4.1 and distributed as shown in Table 6.4.

6.4.2.1 <u>Experimental</u>

The samples were passed through a 300 mesh screen as in previous studies and dispersed with 0.02% m/m Dispex. The slurries were prepared in the range 3.9 - 10% m/v, in a 5 g dm⁻³ lithium solution, and analysed for the elements mentioned above using the spectral lines listed in Table 6.5. Standard DCP - AES conditions were used as described in Chapter 2, and aqueous standards were used for calibration. For each sample the solids content (% m/m) and their viscosity concentration were provided by ECCI, Central laboratories.

6.4.2.2 <u>Results and Discussion</u>

In these determinations, and for the subsequent multielement regression analysis, aluminium was used as an intrinsic internal standard as discussed in Chapters 4 and 5. Thus, the elemental concentration of each sample was ratioed to its aluminium content as determined by slurry

<u>Table 6.4</u>

Distribution of multi-element samples with respect to stope origin.

Stope	Number of Samples
3	6
4	5
6	10
20	9
8	1

Table 6.5

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Elements and spectral lines used in the multi-element analysis.

Element	Spectral Line /nm	Order
Al	308.215	73
líg	280.270	08
к	404.414	56
Sr	407.771	55
Ba	614.172	37
Cr	425.455	53
Ti	323.452	69

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atomisation - DCP - AES.

6.4.2.2.1 <u>Single Element Correlations</u>

Individual element : aluminium ratios correlated with viscosity concentration (%), including stope identification, are shown in Figures 6.7 - 6.12. These element correlations proved to single be quite disappointing although the shape of some of the graphs were similar to earlier work on the Littlejohn Pit bv Glegg (73). From these plots it is clear that the single sample from Stope 8, has a large influence on any apparent relationship between the elements and viscosity concentration. Firstly, it has the lowest viscosity concentration value, and thus becomes very important in any regression correlation. Secondly, from all six plots, it clearly has a different mineralogy and hence chemical composition. This was also borne out by the sample's dirty brown appearance as compared to the relative whiteness of the other samples.

6.4.2.2.2 Multi-Element Regression Analysis

An initial multi-element analysis using the Minitab package and the six elemental predictors was performed. As before predictors that lay outside 95% confidence limits were removed from the model. The regression model produced had a correlation coefficient (R-squared) of 71.1% and is shown in equation 6.4.

V% = 78 - 343 Mg - 8097 Sr + 42603 Cr Equation 6.4













Where V% is the viscosity concentration and Mg,Sr and Cr are the aluminium ratioed, elemental predictors.

A plot of the residuals (Figure 6.13) obtained from this model shows, as in the copper model, some bias <u>i.e.</u> over prediction at low viscosity concentration and under prediction at high viscosity concentration. As with the work of Glegg and the copper absorption study, some type of stope identification is needed for an adequate multielement model to be developed. This was further investigated by the regression analysis of each individual This was only possible for stopes 6 and 20, since stope. the other stopes did not have a large enough data-base for regression analyses to be performed with six predictors. From the regression analyses of stopes 6 and 20, Equations 6.5 (R-squared = 80.2%) and 6.6 (R-squared = 99.4%) were obtained respectively.

V% = 71.8 + 3.2 K - 3290 Ba + 2257 Ti Equation 6.5

V% = 82.5 - 542 Mg - 304 K - 47781 Cr + 2257 Ti Equation 6.6

A close appraisal of the two models shown in Equations 6.5 and 6.6, points to several reasons why bias exists in the overall models developed without any indication of stope source. Three points support this premise:

(i) The intercept constants are markedly different.



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- (ii) The models contain different elemental predictors.
- (iii) Although the potassium predictor is included in both models the sign is different in each equation.

6.4.2.2.3 <u>Multi-Element Regression Analysis with Stope</u> <u>Identifiers</u>

The simplest method of including stope source in the data base would be to include extra predictors, one for each stope present in the data base. These columns contain a series of 1's and 0's as shown in Chapter 4 for the product and residual flotation samples.

The problem with this approach is that it assumes that within each stope, the relationship between all the elemental predictors and viscosity concentration are the same <u>i.e.</u> possess the same slope (Chapter 4, Figure 4.30). From Figures 6.7 and 6.12 it can clearly be seen that even for the same stope <u>e.g.</u> stope 20 samples, the relationship between the magnesium : aluminium and titanium : aluminium predictors and viscosity concentration do not possess the same intercept or slope.

To overcome this, each elemental predictor was multiplied by each stope identifier predictor, thereby creating for each elemental predictor, as many new predictors as there are stopes in the data-base. This was performed for stopes 3, 4, 6 and 20 creating a database of twenty four

predictor columns. The data for stope 8, containing only data from a single sample was removed from the database since data manipulation of this sort would isolate this data set from the main regression model and provide a perfect fit for this one sample. Using the identification predictors in this way, and for two stopes (1 and 2) and one element (boron), the regression equation shown in Equation 4.5 would have the format shown in Equation 6.7. This equation is shown graphically in Figure 6.14.

 $ABR = B_0 + B_1(boron) + B_2(Stope 2) + B_3(boron * Stope 2)$ Equation 6.7

A regression model was obtained as before with a correlation coefficient (R-squared) of 99.2%. Because of the size of the equation it is shown in tabular form in Table 6.6.

A plot of the residuals, shown in Figure 6.15 shows that the bias present in the earlier models, and for the copper absorption work, has been eliminated.

6.5 CONCLUSIONS

For laboratory prepared montmorillonite samples, both the montmorillonite content and sample origin were elucidated using minor element concentrations and simple statistical techniques. The slurry atomisation - DCP - AES technique compares quite favourably with ECCI's infra-red method for the determination of montmorillonite content. Although the predicted values for montmorillonite were not totally





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<u>Table 6.6</u>

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Regression model for multi-element data plus stope identification.

Coefficient	Element /Aluminium	Stope
81.4		
-480	Mg	3
20214	Sr	Ē
-11548	Ва	3
-6.43	к	4
-9430	Sr	4
174	Mg	6
-6177	Ba	6
-75914	Cr	6
4646	Ti	6
-531	Mg	20
-291	К	20
-4453	Cr	20
8569	Ti	20

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satisfactory (Table 6.3), the discrepancy can be attributed to the small number, and size, of samples multi-element technique holds analysed. The some avantages over the infra-red method in that with a greater data-base a more accurate prediction of montmorillonite content of clays would be possible. In addition, not only can the montmorillonite content be predicted, but the source and even type of montmorillonite present is revealed by the slurry technique; information which the infra-red method cannot provide. For 'real' samples from the pit wash and from different stopes, a more complicated but flexible model had to be developed. The absorption, and from the subsequent analyses, probably adsorption, of inorganic copper proved to be inadequate in overcoming different up-take processes and stope individuality. Also the preparation of the copper samples does not lend itself towards an on-line monitoring system.

It was only when the scope of the differences between the mineralogy were recognised that stopes а multiple model, with adequate unbiased regression prediction ability, could be developed. It is shown that the size of the data-base is critical for correct modelling. As а technique to maximise pit operation by the on-line blending of washes from each stope to produce a marketable clay within the viscosity concentration specification, the slurry atomisation - multiple regression procedure seems to meet most of the necessary criteria.

CHAPTER 7 CARBITOL

7.1 INTRODUCTION

As described in Chapter 1, Section 1.1.6, Carbitol is the name for the commercial product consisting of calcium carbonate and the dispersent Dispex (TM) (polyacrylic It is only relatively recently that carbitol has acid). been used as a paper coating material. Carbitol is marketed in various grades, each grade corresponding to the percentage of particles below 2 µm. As with kaolinite, the brightness characteristics of the carbitol, and hence the quality of the finished paper, is related to the proportion of particles below 2 µm in size. The larger the sub-2 µm fraction the better the coating properties of the material. One of the advantages of carbitol is that the strength of the paper, which is somewhat dependent on the particle size distribution of the coating material, is not affected as much as paper manufactured with kaolinite.

Carbitol is produced when calcium carbonate (marble), water and the dispersent (Dispex) are mixed and ground together to produce a slurry with the required particle size range. The amount of Dispex in the Carbitol is usually in the range 0.4-1% m/m. However a problem arises with the control of the Dispex addition. This is because the mass flow controllers used for the addition cannot accurately measure the Dispex owing to its high viscosity. ECCI employ a conductivity test method for Dispex

addition, but this method, at the present time, has not been accurately calibrated. Thus there is a requirement for a method to be developed for the measurement of Dispex in the carbitol product, against which the ECCI conductivity test could be calibrated. A once only calibration was required so as to minimise any interference with the carbitol production plant. Since the conductivity test is an on-line procedure, once calibrated, it could be left for long periods of time.

7.2 INFRA-RED_INVESTIGATIONS

Initially it was thought that infra-red techniques such as those described in Chapter 1, Section 1.1.5.2, for montmorillonite identification, could be used to monitor the amount of Dispex (polyacrylic acid) in the Carbitol. The structure of polyacrylic acid is shown in Figure 7.1. Infra-red scans were obtained from three samples supplied by ECC Calcium Carbonate Ltd. The samples used consisted of a pure sample of Dispex, a Carbitol 90 sample (90% of the particles <2 μ m, and approximately 65% m/m solids) containing 0.7% m/m Dispex, and a Carbitol 90 sample containing approxiamtely 2.0% m/m Dispex. The scans were recorded on an infra-red spectrometer (Model 298, Perkin Elmer, Beaconfield, Bucks., U.K.) using sodium chloride windows, 0.5 scale expansion, and 4 minute scan time with a narrow slit program. The scans are shown in Figures 7.2-7.4.

Figure 7.1 Molecular structure of Dispex (polyacrylic acid).

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$$-C - CH - CH_{2} - C - CH_{2} - C - CH_{2} - C$$

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The two peaks at 1640-1660 and 1400-1440 cm^{-1} from the two Carbitol 90 scans (Figures 7.2 and 7.3) are due to the ionised CO₂ stretching from the calcium carbonate (74). These peaks also occur in the pure Dispex spectrum shown in Figure 7.4. The main peak of interest occurs between these two peaks at 1550-1570 cm^{-1} , and can be seen in Figures 7.3 and 7.4. This peak is markedly stronger in the pure Dispex scan than in the Carbitol, 2.0% m/m Dispex scan, and is not present in the Carbitol, 0.7% m/m Dispex, scan at all. The peak, plus the two weak peaks at 1450 and 1330 cm^{-1} (Figures 7.3 and 7.4), are indicative of the ammonium (NH₄) salts of carboxylic acids. This seemed to be comfirmed by a comparison with a standard spectrum of polyacrylic acid (ammonium salt) (75). The standard scan for the ammonium salt also shows the extra peak at 1550-1570 cm^{-1} whereas the standard scan for polyacrylic acid powder (76) does not. Further conformation of the presence of the ammonium salt was obtained by a series of positive test-tube identification tests for ammonia in the Dispex sample (77). However, ECC Calcium Carbonate claimed that the polyacrylic acid they now used was of the sodium salt, although they had used the ammonium salt in the past. With obvious contradiction in experimental and supplied data there was a reluctance to use the peak at 1550-1570 cm^{-1} as a calibration method for the conductivity procedure.



7.3 INTRINSIC ELEMENTAL MARKER

Following the infra-red investigation it was decided to use slurry atomisation-DCP-AES as a method for determining the amount of Dispex in the Carbitol product. To facilitate this, photographs of the spectra of a Carbitol 90, 0.7% m/m Dispex sample, and a pure Dispex sample were obtained. This was achieved using the DCP photographic unit and the methology outlined in Chapter 6, Section 6.2. As the Carbitol 90 sample was approximately 60% m/m solids and the Dispex sample extremely viscous, each was diluted to a third of their original concentrations, so that they would not block the sample introduction system of the DCP.

From the photographs no elements were identified in the pure Dispex sample that could be used as a intrinsic internal marker. However, there was an absence of the higher transition metals in both samples <u>e.g.</u> manganese and chromium, as well as boron.

7.4 BORIC ACID

As described above, Dispex contained no obvious intrinsic internal marker, although certain elements were apparently absent in both pure Dispex and Carbitol samples. As the calibration of the conductivity measurements would be on a plant scale <u>i.e.</u> approximately a tonne of Dispex produced at a time, the cost of any elemental marker had to be considered. Boron is easily determined by DCP-AES, and if added as boric acid (H_3BO_3) , it is relatively cheap, easily available in bulk quantities and absent from the

spectra obtained. Two samples, one of Carbitol 90, 0.7% m/m Dispex, and one of pure Dispex were analysed for boron by DCP-AES using the boron I 249.977 nm line and the standard plasma condition described in Chapter 2. The samples were diluted by a factor of three and were prepared with a concentration of 10 g dm⁻³ lithium solution. No boron was found to be present in either sample, although the Carbitol 90 sample exhibited an elevated background, probably due to the high concentration of calcium, and so background correction was used on subsequent analyses.

7.4.1 Boric Acid Concentration

Several factors had to be considered when calculating the concentration of boron to be added to the Dispex. It was decided that a concentration of 5 μ g g⁻¹ of boron, in a Carbitol product containing 0.4% m/m Dispex, would be sufficient to obtain adequate accuracy and precision. However, before analysis by DCP-AES, the Carbitol sample would have to be diluted by a factor of three, as described above, to produce a sample of aprroximately 20% m/m solids concentration. The final concentration of boron required in the Dispex was 3750 μ g g⁻¹. This meant that for a plant trial 21.453 kg of boric acid would have to be dissolved in a tonne of Dispex. There was some concern about the ability of the dispex to dissolve the boric acid in this quanity. Scaled down laboratory trials established that with rigorous stirring, the desired concentration of boric acid was soluble in Dispex.

A laboratory trial was performed on the recovery of boron from a sample of Carbitol 90 spiked with 1.6% m/m Dispex. The Dispex contained the appropiate concentration of boric The Carbitol sample was diluted with a lithium acid. solution giving a lithium concentration of 10 g dm⁻³. An internal standard of lanthanum was also incorporated to monitor the recovery of the boron. The lanthanum was determined using the La I 394.910 nm line and the boron with the B I 249.977 nm line. Standard plasma conditions outlined in Chapter 2 were used and calibration was achieved using aqueous standards. As can be seen from the results shown in Table 7.1, the recovery of boron and lanthanum from the samples were approximately the same. Therefore the lanthanum was able to adequately correct for the low boron recovery value. That the recovery for both elements is low is probably due to the viscosity effects encountered with high slurry concentration samples discussed in Chapter 2.

7.4.2 Laboratory Trial

Following the success of the analysis of Carbitol containing boron spiked Dispex, a laboratory trial was undertaken. Thirty samples of Carbitol 90, with increasing amounts of boron spiked Dispex (0.01%-1.0% m/m), were prepared by ECCI Research Laboratories. Each sample contained 10 g dm⁻³ lithium buffer and 10 ug g⁻¹ lanthanum as an internal standard, the solids content of the samples being approximately 25% m/m. The boron content of the samples was determined as described in

<u>Table 7.1</u>

Laboratory trial for the recovery of boron from Carbitol 90.

Element	Calculated concentration yg g ⁻¹	Determined concentration µg g ⁻¹	Recovery %	Corrected concentration µg g ⁻¹
В	23.6	17.9	75.8	24.3
La	94.1	68.5	72.8	

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Section 7.4.1. A plot of the boron concentration verses spiked Dispex content is shown in Figure 7.5. A linear correlation coefficient (r) of 0.9888 was obtained from this data. However, the recoveries for boron were found to be between 100-150 % higher than what was expected. This was without any correction for expected low recoveries of boron using the lanthanum internal standard. The lanthanum content of the samples was not determined, mainly because of concern over the integrity of the samples with the recovery of two to three times the expected amount of boron. Dispite this, the experiment did prove that the addition of various concentrations of Dispex to Carbitol samples could be monitored by this method.

7.4.3 Plant Trial

Following the laboratory trial described in Section 7.4.2, a limited plant trial was performed. A one tonne sample of boron spiked Dispex was prepared by ECC Calcium Carbonate at their Salisbury carbitol plant. Various samples of Carbitol 75 i.e. 75% of the particles were <2 µm, containing various amounts of the boron Dispex, were produced and their conductivity recorded. The samples were then prepared and analysed for boron as before. The plot of the boron concentration (as determined by DCP-AES) versus the conductivity measurement values is shown in Figure 7.6. As seen from Figure 7.6 the relationship between the determined boron concentration and the conductivity measurements is not a linear one. This



comfirms the suspicions of ECC Calcium Carbonate that their mass flow meters do not accurately measure the flow of Dispex through the carbitol plant. Owing to production pressures, the lanthanum content was again not determined. This was not a serious loss since the main purpose of this preliminary plant trial was to demonstrate that the boron spiked Dispex could be monitored through the plant, and that a calibration procedure for the conductivity measurement was possible. The project has now been handed over to, and concluded by, ECCI Research Laboratories.

7.5 CONCLUSIONS

ECC Calcium Carbonate required a calibration technique for a conductivity test that measured the amount of Dispex (polyacrylic acid) being added to crushed marble to produce Carbitol, a commercial paper filler and coating material.

Initially infra-red studies proved promising, but qualitative infra-red data was at variance with the sponsors knowledge of the type of Dispex salt used.

Slurry atomisation-DCP-AES proved to be a far more successful approach. Boron was added to the Dispex as boric acid and was successfully recovered from Carbitol samples using lanthanum as an internal standard. Minimal sample preparation was required. Inaccuracies in the mass flow measurements used for the addition of Dispex to the calcium carbonate were highlighted by a non-linear

relationship between recovered boron and conductivity measurements. Thus is seems that slurry atomisation-DCP-AES is a viable technique for the calibration of conductivity measurements for the determination of the Dispex content of Carbitol.

CHAPTER 8 CONCLUSIONS AND FURTHER WORK

8.1 CONCLUSIONS

Analyte signal supression, linked to increasing slurry concentration, has been observed for a range of analytes. It has been demonstrated that the non-Newtonian behaviour kaolin slurries (above 17% m/m) is probably the cause of of a decrease in the expected signal for slurry samples for certain elements. Different clays, with varying particle size distributions, may exhibit different transport efficiences. Therefore some type of internal standardisation is required to compensate for particle size and viscosity effects, when such samples are analysed together. However, it was shown that the analyte signal suppression was not of a simple nature. The viscosity effects do not explain the signal suppression experienced between 10% and 17% m/m slurry concentration. It was shown that using the atomic pair, relative line intensity ratio method of measurement, the T_{exc} decreased for slurry concentrations >10% m/m, in the presence of 5 g dm⁻³ lithium. Using the simplex optimisation procedure, it was shown that this decrease in T_{exc} can be somewhat negated increase of EIE addition with slurry by a linear In practical terms, it is suggested that concentration. ionic lines be used for high slurry concentration samples, when in the presence of EIE.

Initial studies using computerised tomography has supplied spatial information which supports the proposed mechanisms

for argon emmision in the DCP suggested by Miller.

It has been shown that kaolin slurry concentration and slurry atomisation analytical effects in the DCP, such as viscosity effects and temperature effects, can be compensated for by using aluminium or silicon as intrinsic internal standards.

Inspite of the non-linear behaviour of individual elemental predictors towards abrasion, the abrasiveness of feed, product and residue clay samples from a froth flotation plant were successfully predicted. This was achieved using a multi-variate, linear regression technique with slurry atomisation elemental data ratioed to aluminium as the predictors.

The slurry atomisation ratio procedure has been shown to have the same precision as the Einlehner abrasion test. In addition, the product clay abrasion can be predicted, using a regression model consisting of feed analytical data, plus the percent recovery of the flotation plant.

A successful on-site trial was performed, showing that both the DCP instrumentation, and regression analysis functioned well in an industrial environment. The on-site trial showed that it would be possible to control, and optimise the froth flotation process via the slurry atomisation method.

The slurry atomisation predictive technique has also been successfully applied to the prediction of both the montmorillonite content and the viscosity concentration of china clays. However, it was only when the differences between the mineralogy of the pit stopes was recognised chemically, that a multi-element, linear regression model, with adequate flexibility, could be developed for the prediction of viscosity concentration.

The absorption of inorganic copper by 'swelling' minerals, proved to be inadequate in overcoming different up-take processes and stope individuality.

Slurry atomisation - DCP - AES was also shown to be an effective technique for the analysis of high (>20% m/m) solids samples of Carbitol. It was demonstrated that the amount of the dispersent 'Dispex' added to the Carbitol, could be monitored by determining boron. The boron was to the Dispex in the form of boric acid. added This was shown to be a viable method for the calibration of а conductivity test, which is used to monitor the amount of Dispex in Carbitol.

8.2 FUTHER_WORK

Several approaches could be taken in further developing the work on the mechanisms of slurry atomisation - DCP -AES. As regards the sample introduction studies, the use of a cascade impactor and standard particle size samples, would help in the design of more 'particle friendly'

introduction systems. With respect to the sample and simplex optimisation temperature measurement investigations, the use of either Boltzmann plot, or ionic-atomic relative line intensity methods, for the measurement of T_{exc}, should be used. This would eliminate any EIE effect on the T_{exc} measurements as discussed in Chapter 3. This should isolate, and highlight, any slurry concentration effects on the physical characteristics of the plasma.

The use of computerised tomography on an analytical plasma source opens up an entirely new area of research. The initial studies performed in this work could be extended in many directions. Firstly, instead of the argon line, tomograms could be obtained when monitoring the appropiate EIE resonance line. This would show how EIE interact with the argon plasma core. Secondly, analyte resonance lines, both atomic and ionic, could be monitored. The resulting tomograms would provide invaluable information for the development of different plasma configurations, sample introduction systems and slurry atomisation effects. The ultimate development of this tomographical work would be the production of 3-dimensional representations of the whole plasma. Obvously, the tomographical system can be modified to accommodate other plasma sources such as the inductively coupled plasma (ICP), in which there is probably a greater research interest at the present time.

Several matters have to be addressed before a complete, automatic system for the control of the froth flotation process can be produced. Firstly the use of aqueous standards must be replaced with a quick, reproducible, multi-element calibration technique. This could be using standard clay samples. achieved One possible procedure would involve the analysis of a standard clay sample for all the predictor elements plus aluminium prior to every abrasion sample. A multi-element instrument would record the signals form all the elements from both samples. The signals from the abrasion sample could then be ratioed with the signals from the standard clay sample. This would provide a quick calibration method for the multi-element analysis, plus enabling compensation for changes in the instrumentation e.g. monochromator drift.

A method for evolving the predictive model has already been discussed in Chapter 5. Extra security could be incorporated into the process to eliminate the possiblity of faulty data entering the data-base or affecting the accuracy of the predictions. This could be achieved using statistical techniques such as Cu-Sum, and would work by checking whether each element signal falls into the expected range. If too great a deviation occured, then either the sample could be discarded completly, or a new regression analysis performed for that sample excluding data for that element from the data-base.

As discussed in Chapter 5, the data-base would have to be constantly updated to account for changes in the feed

clay. Since it takes approximatly two hours for the flotation plant to stablise after a change in operating conditions, it would be expected that samples would be taken three to four times during a eight hour shift. On a data-base of about sixty samples, this should provide ample circulation of data. When each new sample was added to the data-base, the oldest data would be removed simultaneously.

The flotation plant is now under computer control. All the points mentioned above, plus the regression analysis, could be performed on a micro-computer linked to the DCP. This in turn could be interfaced with the flotation control computer, producing an entirely computer controlled system.

The only area that has not recieved any attention from this study is that of the automatic sampling of slurry streams. At the present time there are few sampling systems for high flow, high soild, liquid streams (56). This would have to be addressed if a fully automatic control system was to be developed.

Development of the viscosity project would be more complex than the abrasion work. The remarks about standard clay samples, and statistical monitoring of the regression process made above, could also be applied to the viscosity work. The slurry atomisation system could be used as an on-site monitor of pit wash. This would provide

information about the clay quality, which the pit managers could use to maximise the efficiency of the mining process.

Other applications for this slurry atomisation, regression technique exsist within the china clay industry. The most obvious one of these is that of brightness. Brightness is a vital, commercial, physical property of coating clays. The brightness, or reflectance, of clay is adversly affected by high concentrations of iron in the clay. Thus by monitoring for iron and elements associated with iron substitution in the clay lattice, the brightness chracteristics of clay samples could be predicted. Again this technology could be implemented on-line in the production process.

The greatest strengths of the slurry atomisation - DCP -AES systems decribed above, are flexibility and speed. Even when using a calibration clay sample, it is possible for all the analytical and predictive work to be completed within a ten minute period. Using a fully computerised, muti-element instrument, all the physical properties described in this work; abrasion, viscosity concentration, montmorillonite content, brightness and others, could be predicted and controlled. This multiplex system is not constrained to production matters, but could be easily used by managers to ensure efficient transportation, recycling of waste and effective management generally of the clay industry.

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LECTURES AND ASSOCIATED STUDIES

- RSC Lecture, 30/10/1986, Plymouth Polytechnic,
 Dr. J.D.R. Thomas, 'Liquid and Enzyme Membrane
 Electrodes'.
- (ii) RSC Lecture, 23/1/1987, Exeter University, Professor J. Miller, 'Illumination in Analytical Chemistry'.
- (iii) RSC Lecture, 20/2/1987, Plymouth Polytechnic,Dr. A. Ure, 'Atomic and Ion Spectra'.
- (iv) SERC Vacation School, 13-18/9/1987, UMIST, 'Instrumentation and Analytical Science'.
- (v) RSC Lecture, 13/11/1987, Plymouth Polytechnic,Dr. A. Howard, 'Speciation'.
- (vi) RSC Lecture, 29/1/1988, Plymouth Polytechnic, Professor A. Townsend, 'Flow Injection Analysis -The First Decade'.
- (vii) SERC Vacation School, 1-8/7/1988, University of Sheffield, 'Trends in I.T.'
- (viii) Research Visit, 18/10/1988, ICI Brixham.
- (ix) RSC Lecture, 20/1/1989, Plymouth Polytechnic, Dr. P. J. Worsfold, 'Flow Injection: Hands-off Analysis'.
- (x) RSC Lecture, 17/2/1989, Plymouth Polytechnic,Professor M. Barber, 'Modern Mass Spectrometry'.
- (xi) Departmental Research Colloquia, weekly meetings, 10/1986-9/1989.

MEETINGS OF THE ROYAL SOCIETY OF CHEMISTRY

- Atomic Spectroscopy Group AGM, 16/12/1986,
 'Combination Techinques in Analytical Atomic Spectroscopy', Imperial College, London.
- (ii) Analytical Division meeting, 8-9/7/1987, 'Research and Development Topics in Analytical Chemistry', University of Strathclyde.
- (iii) Joint Analytical Division and Western Region
 meeting, 3-4/9/1987, 'New Perspectives in Atomic
 Spectroscopy', Plymouth Polytechnic.
- (iv) Joint Analytical Division, Western Region and Chemometrics Group meeting, 29/10/1987, 'What can Chemometrics do for you', University of Bristol.
- Joint Analytical Division and Atomic Spectroscopy
 Group/Molecular Spectroscopy Group meeting,
 29/3/1988, 'Recent Advances in Atomic and Molecular
 Spectroscopy, University of Hull.
- (vi) Analytical Division joint meeting with the Spectroscopy Group of the Institute of Physics, 29/6-1/7/1988 the Fourth Biennial National Atomic Spectroscopy Symposium, University of York.

- DC Plasma User Group Meeting, 17/6/1988, PlymouthPolytechnic.
- (ii) Austrian Society for Microchemistry and Analytical Chemistry jointly with the German Working Group for Applied Spectroscopy, 8-14/1/1989, European Winter Plasma Conference, Reutte, Austria.

Publications and Presentations

- A) <u>Publications</u>
- (i) 'A Selected Review and Bibliography of Direct Current Plasma - Atomic Emission Spectrometry for 1984-1988' Les Ebdon, Janet A. Armstrong and Ben Fairman.
 ICP Information Newsletter, 1989, <u>14</u>, 459.
- (ii) 'Chemical Generation of Silicon Tetrafluoride With Direct Current Plasma-Atomic Emission Spectrometry for the Determination of Fluorine'. Neil Barnett, Hugh Beere, Les Ebdon and Ben Fairman. J. Anal. At. Spectrom., 1989, <u>4</u>, 805.
- B) <u>Presentations</u>
- (i) 'Slurry Atomisation DCP AES for On-line Process
 Control'. Presented at 'New Perspectives in Atomic
 Spectroscopy', 3-4/9/1987, Plymouth Polytechnic.
- (ii) 'Slurry Atomisation for Process Control', DC PlasmaUser Group Meeting, 17/6/1988, Plymouth Polytechnic.
- (iii) 'Mechanistic Aspects of Slurry Atomisation-Direct Current Plasma-Atomic Emission Spectrometry', Forth Biennial National Atomic Spectroscopy Synposium, 29/6-1/7/1988, University of York.
- (iv) 'Process Control by Slurry Atomisation', Research and Development Topics in Analytical Chemistry, 18-19/7/1988, Plymouth Polytechnic.
- (v) 'Further Insight into Slurry Atomisation Direct
 Current Plasma-Atomic Emission Spectroscopy',
 European Winter Plasma Conference, 8-14/1/1989,
 Reutte, Austria.

(vi) 'Computer Controlled Slurry Atomisation System For Process Control', Research and Development Topics in Analytical Chemistry, 21-22/3/1989, NIHE, Dublin, Eire.