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THE
MAGNETIC TREATMENT OF FLUIDS

EFFECTS OF APPLIED FIELDS ON CHARGED SPECIES IN SOLUTION

A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

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FOR DAD AND GRANDAD

CONTENTS

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DECLARATION

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Mark Gray.

ABSTRACT

The results of a number of investigations on the general phenomenon of the magnetic treatment of fluids are presented. The effects of applied magnetic fields on charged species in aqueous solution are considered in light of these results and the work of other authors. It is proposed that the magnetic treatment effects are due to a direct magnetic field/charge interaction, which causes changes in the nature and degree of interionic associations within the treated solutions. This would influence the stability and number of pre-nucleation ionic clusters and increase the mobility of the ions and, hence, the activity of the solution.

A number of precipitation and scaling processes are shown to be influenced by magnetic treatment. This is characterized by changes in the rate of precipitation, the particle size, the degree of aggregation, the suspension settling rate and the morphology of the crystals and their propensity to form scale. These changes are shown to be consistent with the proposed theory.

Magnetic treatment is shown to increase the proportions of both calcium and magnesium ions precipitated from an equimolar solution of the two ions, by the addition of a phosphate solution. The magnitude and duration of the effect are determined under different conditions and evidence in support of the suggested mechanism is obtained.

The magnetic treatment of sodium chloride and acid solutions is shown to alter the corrosion rate of steel and the composition of the corrosion products. The observed changes are explained by effects on the charge transport near to the metal/solution interface. The magnitude and endurance of the effect are investigated under a variety of conditions

The kinetics of the reaction

$$2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$$

(the Harcourt-Esson Reaction) are shown to be influenced by magnetic treatment. A study is made of the effects of varying the reaction parameters on the degree of the change in the reaction rate. The results of the investigation are shown to be consistent with the proposed theory and allow additional comments to be made about the mechanism.

CHAPTER 1

INTRODUCTION

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1.1. Introduction and Historical Background

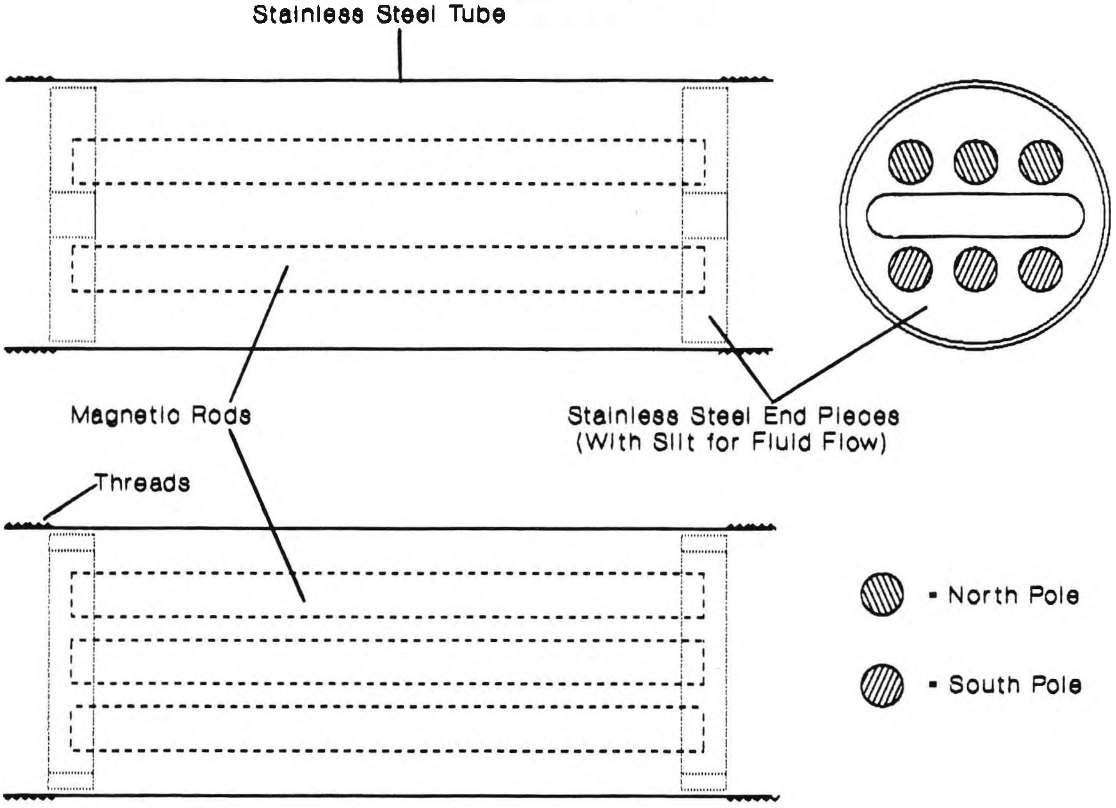
The magnetic treatment of fluids is a topic which is concerned with the interaction of magnetic fields on charged species in solution or suspension in fluids. For many years reports have appeared in the literature suggesting that passing a solution through a relatively weak magnetic field (e.g. 2500 gauss for 1" magnetic units produced by HDL Fluid Dynamics Ltd.) can alter the reactions of the species in the fluid after it has left the field.

The main use to which the treatment has been put is for scale prevention in a wide range of applications, most commonly for boilers and heat exchangers. The first record of this form of scale prevention dates from 1865 (Parry, G.T. "Improvement in Preventing Incrustation of Steam Boilers." U.S. Patent No. 50.773). Since 1865 a huge industry has developed around the effect. Chowdhury and Tanzosh (1984) state that almost 200 U.S. Patents were issued on 'Magnetic Water Treatment' between 1954 and 1984 and, as early as 1958, one manufacturer had sold several hundred thousand units (Eliassen et al, 1958).

The hundreds of different types of magnetic scale prevention devices which have been manufactured can be classified into a number of different categories. Donaldson and Grimes (1991a) discuss the types of magnetic unit available under four headings; (i) flow-through units with permanent magnets, (ii) clamp-on units with permanent magnets, (iii) units with electromagnets, and (iv) electronic devices generating an electromagnetic field. The most successful unit in the U.K., in industrial situations, is the HDL

Fluid Dynamics design which is a flow-through type unit, consisting of an array of magnetized PTFE-coated magnetic bars in a stainless steel tube. These units deserve particular mention, since they were used in much of the work presented in this thesis. The units come in a range of sizes and generally have a field of 2500 gauss. Figure 1.1 shows the geometry of the HDL 1" unit.

Figure 1.1



HDL 1" Magnetic Unit.

The reason for the massive market for a cheap method of scale prevention is readily appreciated when the enormous world-wide costs due to scaling problems are considered. Scaling occurs in hard water areas where solids are deposited from a supersaturated solution onto a surface. It has been termed as 'one of the curses of industry' (Feather, 1990). The deposited material can narrow pipes, block jets and severely reduce the efficiency of heat transfer processes.

Grutsch and McClintock (1984) comment on the fact that a 0.61mm coating of calcium sulphate scale on boiler tubes leads to a 183°C temperature drop across the scale. This not only contributes to energy inefficiency, but also, due to the higher tube skin temperatures, causes serious metallurgical problems with the tubes. Feather (1990) presents a conservative estimate for the cost of scaling due to hard water in the U.K. for 1989 - £830 million. This estimate does not include the increased costs due to the additional energy required for pumping water through clogged pipework and heating scale-encrusted boilers.

Many techniques are available to industry to prevent and remove scale, as follows:

(a) <u>The ion exchange process.</u>

In this method, the water is passed over NaCl so that the calcium and magnesium ions are exchanged with the sodium ions. Corrosion can, however become a primary problem with this type of treatment.

(b) <u>Prevention of suspended solids entering the system.</u>

This can be achieved by the filtration of the incoming water or by the removal of colloid suspensions by chemical additions.

(c) <u>Prevention of the formation of scale.</u>

Scale can be prevented by chemical addition of hardness stabilizers such as polyphosphates or dispersants to prevent the agglomeration of particles.

(d) <u>Removal of existing scale.</u>

Scale can be removed by chemical treatment and/or mechanical removal.

All of the processes described above are expensive to operate and those involving the use of chemical treatment also have waste disposal problems. The magnetic treatment of fluids for scale prevention has been promoted as a solution to this 'curse of industry'. It has been found to have an effect on the precipitation and/or propensity to scale for many crystal systems, including zinc phosphate, calcium carbonate, calcium sulphate, barium sulphate, aluminium hydroxide and basic tin sulphate (Grimes, 1987). The units are inexpensive to run, easy to install, environmentally friendly and require little or no maintenance. The savings reported for industrial applications are startling. HDL units have been installed at over 500 sites around the country with a great deal of success. This is discussed in section 1.3.i.

Magnetic units, in addition to being promoted as scale prevention devices, have been credited with possessing other beneficial properties:

(1) Reduction of algae, bacteria and fungi growing in water (Adverts for 'ALGARID' manufactured by MMR Ltd., Middlesex and 'TURBOMAG' which is sold by Australia PTY Ltd., Australia and New Zealand).

(2) Corrosion protection ('HYDROPATH' manufactured by HPL Ltd., Nottingham and 'Superior Water Conditioners' which are made by Kemtune, inc., Fort Wayne, U.S.A.).

(3) Increased fuel efficiency ('MAGNETIZER' produced by Magnetize Group, inc., California, U.S.A. and 'MAGNA-BURN' which is distributed by International Imperial Trading Co. Ltd., U.S.A.).

(4) Accelerated curing of concrete ('TURBOMAG' made by Australia PTY Ltd., Australia and New Zealand).

(5) Improved quality of metal pretreatment phosphate coatings (HDL units).

Magnetic fields have also been reported to influence a diverse range of chemical and biological systems and phenomena. Peev et al (1987) reported changes in the composition of corrosion products on steel plates in the presence of an external magnetic field. In Chinese medicine, drinking tea from a pot containing a magnet is believed to remove gallstones (Yue et al, 1983). Donaldson (1985) reports that barley yields were increased by 10% when their water supply was passed through a magnetic field. Klassen et al (1968) believed that magnetic fields could influence the structure of water and other authors (Piccardi, 1959; Delhez, 1961; Duffy, 1977) have reported changes in the surface tension, viscosity and pH of water. Domka (1979) used magnetic fields to produce finely divided calcium carbonate. Kestelman et al (1988) found that the use of a magnetic field can increase adhesive bond strengths. The effects of magnetic fields are not limited to inorganic aqueous systems. Evans (1985) found that the crystallization pattern of 4-n-octylbiphenyl grown from a saturated solution in benzene was profoundly effected by magnetic fields. A large number of authors (e.g. Werner et al., 1978; Turro and Weed, 1983; Scaiano and Lougnot, 1984) have reported magnetic field effects on the behaviour of radical ion pairs.

Perhaps surprisingly, in view of the reported success of the method in combatting scale problems in industrial installations and the number of other beneficial claims made, the effect has always been, and still is surrounded by a great deal of controversy. Hundreds of papers have been published concerning the phenomenon and many unjustified and contradictory claims have been made. Söhnel and Mullin (1988) comment on this fact in light of the claims made for the effects of magnetic treatment on nucleation. They state*:

> "Quantitative experimental data published on the influence of a magnetic field on crystallization have, so far, been sparse and often conflicting. For example, nucleation has been reported as being promoted ($MgSO_4$ [Nývlt and Krickova, 1976], $CaCO_3$ [Torbjoern and Kristiansen, 1979; Rubezhanskii et al., 1981], $CaSO_4$ [Rubezhanskii et al., 1979]), suppressed ($CaCO_3$ [Dotts, 1977]) and uninfluenced ($CaSO_4$ [Konak, 1974])."

The range of opinions concerning the effect are clearly demonstrated in the following literature review.

[Note : * = References added.]

1.2. Literature Review

1.2.i. Literature Sources.

The reports made in the literature on the magnetic treatment of fluids are very confusing due to the number of contradictory claims which have been made for the phenomenon. It seems that for every author who presents details of an effect, there is another whose results totally refute those findings. This fact is often used by the sceptics to disprove the existence of an effect of magnetic fields on fluids. These discrepancies can be more easily understood if the range of sources for the publications is considered.

By far the smallest number of publications on the magnetic treatment of fluids are reports of carefully controlled laboratory-based experimental work (though this situation is being improved as the results of the work carried out by the research groups at City and Brunel Universities are published). The bulk of the literature is concerned with industrial case studies of magnetic units. These papers are usually non-scientific and the testing procedures reported are often very inadequate. In many instances they were written by people involved with a particular unit manufacturer and, in some cases, it seems possible that the reports may have been exaggerated. A large proportion of the papers are simply reviews of the literature on the subject while others consider theoretical explanations for the reported effects.

The literature presented in this review has been divided into three groups. The first of these deals with reports of successful applications of magnetic units (Note: the results of trials with HDL units are presented in section 1.3). The second section considers the negative results and criticisms of the phenomenon, while the third contains details of some of the mechanisms and theories which have been advanced to explain the observations.

1.2.ii. Successful Applications.

The claims made by Vermeiren (1958) are typical of the reported beneficial properties of magnetic treatment. He states that treating hard water solutions with a magnetic antiscale device would a) reduce the amount of calcium carbonate scale formed; b) cause any scale which was produced to be soft and easier to remove; c) alter the morphology and size of the crystals formed; d) reduce corrosion; e) reduce the growth of algae; f) increase the pH of acidic solutions; g) transform rust to powdery black magnetite; and h) remove any existing scale in the system.

Reports of startling results of the use of magnetic treatment for a number of different applications have been published in journals from all around the world. Russian journals are a particularly rich source of references. It is plain from the tenor of these papers that magnetic treatment has been widely used in the Soviet Union as a scale prevention method for several decades. Indeed, several seminars and conferences have been held which were totally devoted to the magnetic treatment of fluids (e.g. Moscow, 1966; Novosibirsk, 1968; Tbilisi, 1969). Mibbeu (1973) reviews the Russian literature. He states that magnetic units were widely used in industry with great economic benefits and that no one questioned the fact that they retarded scale formation, only the mechanism of the effect was in doubt.

Tel'nov et al. (1973) were particularly interested with the problem of scaling in engines.

> "The problems of preventing scale in the cooling systems of automotive and tractor engines has long interested operators and scientists. For a fixed thermal engineering unit, there are a number of methods, chiefly reagent methods. However, the use of many of them requires the construction of costly devices and teams of specialists, and turns out to be unprofitable. Non-reagent methods (magnetic, ultrasonic), of which the method of water treatment using a magnetic field, is the most economical, therefore, have found application in recent years."

Kozlov (1971) reported on the widespread applications of magnetic treatment units on ships. He reports on the use of the treatment for the feed water of ships' boilers:

> "In our opinion, reagent-less (magnetic) treatment of water can guarantee, under conditions of the boilers being fed with 70-90 per cent condensate and 10-30 percent coastal (fresh) water, a scaleless regime for any modern designs of ship steam boilers."

Kozlov also describes several case histories, including details of the equipment, performance and water properties. He makes many recommendations for the successful application of the technique. An additional benefit of the technique reported is the dispersal of oil in the boiler feed waters:

> "Magnetic treatment with observance of the rules of technical operation of boilers prevents greasing of the heating surfaces. With prolonged proper operation of the magnetic device and the boiler, oil zones almost completely disappear, as verified by the quite complete elimination of oil from the water. Observations of the piston mechanisms established that gland packings and cylindro-piston groups of engines operate better and with less wear under conditions of the magnetic treatment of water."

The Norwegian government has funded a number of research projects on the magnetic treatment of fluids. Ellingsen and Kristiansen (1979) carried out an investigation into the precipitation rate of calcium carbonate from supersaturated solutions after passing through a number of magnetic units. They found that the effect increased the rate of precipitation, though they did note that some of the tested units did not function as claimed.

Hoff (1973) reports on serious scaling problems in a lime transporting pipeline at the Baerum Waterworks, Baerum, Norway. Every week or 10 days the pipeline was becoming clogged with sludge and hard scale. A magnetic unit was installed in the pipeline and the scaling stopped. Hoff comments:

> "The lime transporting pipeline was now cleaned and put back into service. After another three months' period with the same lime dosage as before, the dosage was stopped.... Now there was hardly any scale in the pipeline and mixing chamber.... Thus, it is possible to avoid all problems with lime in the pipeline.
>
> From certain quarters, it has been stated that magnetical treatment of water is sheer nonsense. It is pointed out that there is no theory which can explain what is said to happen, for instance, in ships' boilers. Regardless of theoretical background, the permanent-magnetic unit has abolished a laborious practical problem for us."

Guo and Chen (1987), working at the South China Institute of Technology, examined the use of magnetic treatment in the sugar refining industry. They conclude:

> "The characteristics of scale can be changed by magnetic treatment in such a way that the overall heat transfer coefficient of process vessels can be maintained. The results of magnetic treatment vary depending on the composition of the sugar solution and stability of operation under the same magnetizing conditions.
>
> Even though the mechanism of magnetic treatment is not clear and it remains necessary to find a quick method for determining the magnetizing effect, magnetic treatment can be regarded as one way of saving the consumption of steam.
>
> With further investigation, more advantages should be gained from magnetic treatment."

Laureys and Pourbaix (1957) investigated the effects of magnetic antiscale devices on water distillation. During thirty 48-hour trials they found that in 28 cases the magnetic treatment reduced the scale by an average of 55%. Davies (1983) considered the use of magnetic treatment in gold extraction processes in South Africa and concluded that, "...there are numerous advantages to descaling and scale prevention..." by the technique. Similarly, Raisen (1984) concluded from the results of a number of trials of magnetic units in diverse industrial situations that, "...the magnetic water treatment is an excellent way to control scale and corrosion in water systems."

Thomas' (1992) thesis contains details of a number of carefully controlled laboratory investigations into the interaction of charged species in fluids with applied magnetic fields. He concludes;

> "The work in this thesis has shown unequivocally that the magnetic treatment of fluids...,is a general phenomenon.... The results confirm that applied fields can alter the properties of simple systems..."

The cited literature is intended to demonstrate the wide range of applications of magnetic treatment for which beneficial observations have been reported. In addition to the references quoted, the successful use of the technique has been reported by many other authors (e.g. Rybak, 1961; Kuna, 1964; Skorobogatov, 1970; Shakhov and Dushkin, 1971; Lapotyshkina et. al., 1972). Additional information can be found in the literature reviews produced by Mibbeu (1973), Duffy (1977), O'Brien (1979), Grutsch and M^{c}Clintock (1984), Thomas (1992) and Stimpson (1993).

1.2.iii. Negative Results and Criticisms.

A common feature of negative reports is the scathing and sceptical tenor in which they are written. This is perhaps understandable when some of the outlandish claims that have been made in the media concerning non-chemical methods of scale prevention are considered. Davies (1983) reviews some of these:

> "...our patented magnetic power unit creates a force field which Scientists call a diamagnetic phenomenon."

> "...descales constantly! This is accomplished through a patented process which utilizes the principle of electrostatic deionization."

> "The units are sealed and the magnets being permanent will

> not diminish in intensity, consequently the units continue to be fully effective indefinitely."
>
> "The neutralizer is a self-energizing cell or electric couple composed of dissimilar metals which will create a definite rateable voltage potential when immersed in an electrolyte."
>
> "The...physical properties control process unit consists of a cylindrical metal casing that contains a coaxial element made of a special alloy."
>
> "...is a device built and successfully used using the so called catalytic property of surface tension."

Though comments of this type have been made to promote the non-chemical treatment of fluids for scale prevention, it was decided to include them in this section, since they have fuelled many of the arguments against the effect. This is probably the main reason for the large number of 'gadget bashing' papers which have been published. A good example of this type of approach is found in a paper published by two professors at the Massachusetts Institute of Technology. Eliassen and Uhlig (1952) made a study of the advertising literature for some of the commercially available devices. The paper constitutes a devastating indictment of the type of pseudoscientific terminology and wild claims highlighted above. The authors conclude that, "Many frauds are being perpetrated on an unknown and gullible public" and they relegate these "...fraudulent devices and processes..." to a position of suspicion.

The sceptics' attack on the phenomenon was taken up by Wilkes and Baum (1979) who updated the literature on these 'gadgets'. They reported no positive results with electrostatic and magnetic units. However, Grutsch and M^{c}Clintock (1984) comment on their conclusions;

> "In one case where 70 cycles of concentration were achieved in a cooling tower with no recurrence of a historic condenser heat exchanger deposit problem, the reason for success was argued to be low load operation and magnesium precipitation of silica."

The scathing attacks which some authors make on their devices, are not the only problems facing manufacturers of magnetic treatment devices. Chowdhury and Tanzosh (1984) comment:

> "Hydromag Ltd. (Pella, Iowa), for instance, has been sued by its home state on behalf of over a dozen presumably unhappy customers. It was their written complaints, says Jim Peters, assistant attorney general for consumer protection (Des Moines), that prompted Iowa to file in civil court. The users complain that the Hydromag units, which, according to Hydromag..., reduce chemical use by 50% and replace water-softening units entirely, have failed to meet these claims."

In addition to authors of non-technical literature who dispute the existence of the effect, many have reported negative results for apparently carefully controlled scientific tests of various units. Alleman (1985) produced an impressive research report, 151 pages long, on tests with six commercially available permanent magnetic devices. He concluded;

> "Simply stated, none of the six (6) permanent magnetic water conditioners tested during this study appeared capable of 'conditioning' the employed ground water in a fashion which would uniformly yield beneficial changes in its chemical, physical, and scaling characteristics."

Limpert and Raber (1985) conducted a number of experiments on heat exchangers to evaluate ten non-chemical scale and corrosion control devices. They conclude;

> "None of the magnetic devices, whether permanent magnet type or electromagnetic type which were tested, significantly reduced the amount of calcium carbonate scale formed under the test conditions."

The Israeli national water supply authority, 'Mekorot', sponsored tests of a magnetic device under well-controlled laboratory conditions. Hasson and Bramson (1985) report the results of these tests, and conclude;

> "It does not seem plausible to expect magnetic treatment to exert a meaningful scale suppression effect at sufficiently high supersaturation conditions. This has been demonstrated in the present study.... Thus, magnetic treatment, despite its long existence, remains in the status of a technology unbacked by adequate development requirements and unsupported by essential characterizing data."

It must be noted, however, that the tenor of this paper suggests that the authors may have held certain preconceptions concerning the outcome of the tests.

Chowdhury and Tanzosh (1984) discuss a detailed evaluation of magnetic treatment units which was carried out by the U.S. Army Corps of Engineers. They state that the final report concluded;

> "...the MWT* devices don't work - i.e., they did not reduce or prevent pipe scaling in lab and field tests. In fact,..., corrosion increased and there was a greater need for fungicides when the units were used."
>
> [Note * : MWT = Magnetic Water Treatment.]

The report that magnetic treatment increased corrosion is one which has caused a great deal of interest amongst many researchers. Indeed, it has been suggested that any scale-preventing properties of magnetic units are due solely to increases in the concentration of iron in the water, due to an increased rate of corrosion (Duffy, 1977; Busch et al., 1986; Lindegaard-Anderson, 1987; Herzog et al., 1989). Busch et al. (1986) conclude:

> "These results suggest that MTD* operation may simply accelerate an already spontaneous process that, in essence, is no more than the corrosion of iron."
>
> [Note * : MTD = Magnetic Treatment Device.]

More will be said on the effects of the magnetic treatment of fluids on corrosion processes in Chapter 4.

It was stated in the previous section that some of the literature supporting the reported effects of magnetic treatment was almost certainly biased. This is also the case for some of the critical papers (see quote from Hasson and Bramson (1985) above) and is commented on by Grutsch and M^{c}Clintock (1984), who question the influence of bias on the design of the performed experiments and the interpretation of results. For example, Eliassen et al. (1958) published their evaluation of the performance of three 'gadgets' on scale formation, scale dissolution and corrosion. All of the reported results were entirely negative. However, the earlier paper by Eliassen and Uhlig (1952), which has already been mentioned, shows the authors extreme scepticism concerning the effect, before the reported trials were carried out.

Another group of authors, who express doubt concerning the claims made for the treatment, also concede the paucity of controlled test results and comment on the need for 'hard facts' on the phenomenon. Dromgoole and Forbes (1979) and Söhnel and Mullin (1988) are good examples of this type of attitude. The latter conclude;

> "Surely, the time has come to establish unambiguously, whether magnetic pretreatment of aqueous feedstocks does or does not affect scaling. More reliable and reproducible experimental data are urgently needed. A definite answer to the problem, however, can only be provided by long term statistically designed industrial experiments..."

It is hoped that the results presented in this thesis will satisfy the authors' request.

1.2.iv. Theories and Mechanisms.

Many authors have proposed mechanisms and theories to account for the magnetic field effects. In common with every aspect of the literature on the phenomenon there is little agreement in this area. The mechanisms which have been advanced fall into three categories. The first of these suggests that the magnetic field has no direct effect on scaling, but rather, influences some other system, which, in turn, affects scale deposition. The second assumes that the field alters the properties or structure of water itself and the third that the effect is on the nature of suspensions or ions in solution.

Proponents of the first category include Kristiansen (1974), who states;

> "Examination of scale deposits from magnetically treated and untreated water indicate that the effect is due to carbon dioxide being more readily released from magnetically treated water. The conditions for the formation of carbonate are thus reduced, the pH value of the water increased and the calcium carbonate becomes more soluble."

Delhez (1961), has advanced a similar theory. He has postulated that the primary effect of magnetic treatment is to increase the pH of acid solutions. He believes that the magnetic field causes localized pressure variations in the solution, which, in turn, causes a decrease in the solubility of CO_2. He has suggested that this would bring about a shift in the equilibrium between calcium bicarbonate and calcium carbonate, causing local areas of high $CaCO_3$ concentration and consequent growth of crystal nuclei.

Many authors have considered the effect of increased corrosion on the deposition of calcium carbonate scale to be the major process involved in the magnetic treatment phenomena, e.g. Pourbaix, 1953; Duffy, 1977; Busch et al., 1986; Lindegaard-Anderson, 1987; Herzog et al., 1989). The latter authors suggest that;

> "A plausible mechanism explaining magnetic water treatment is the introduction of ferric hydroxide seed crystals into the water, thus providing sites for heterogeneous nucleation of $CaCO_3$ - sites that compete with equipment walls."

The second theory, that the properties or structure of the water itself are affected, has been exhaustively examined. Klassen et al. (1968, 1970, 1971a & 1971b) reported that changes in the infrared spectrum of magnetically treated water indicated a change in the structure of the water. These findings were supported by Ivanova and Makhnev (1970 and 1971) and Burns et al. (1966) who obtained similar results with ultraviolet, visible and infrared spectroscopy. All of these authors postulate a disaggregation of the water molecules to account for the observed changes. This idea was tested by Klassen and Zinovev (1967), who determined the aggregation rates of kaolin particles both in water exposed to a magnetic field and in unexposed water. They found that the magnetic treatment increased the rate by 16%. The authors concluded from this that the magnetic field caused a breakup of associated water molecules.

Yarolavskii and Dolglnosdov (1971), Vilimek (1969) and Kirgintsev (1971) proposed that the disaggregation of the water molecules due to the magnetic treatment was caused by an increase in the oxygen-hydrogen bond strength, thus decreasing the ability of the water molecules to form intermolecular bonds. Kirgintsev also proposed that this effect would increase the number of high energy boundary areas between aggregates and that $CaCO_3$ would preferentially nucleate and grow in these areas rather than forming scale on pipe walls.

Since the early nineteen-seventies, a large number of authors have commented on the findings presented above. Baranov et al. (1970), Mirumyants et al. (1972), Duffy (1977) and Gonet (1985) all found no differences in the optical transmission spectra of magnetically treated water, while the results presented by Ksenofontov et al. (1976) were in good agreement with those previously reported by Klassen et al. (1968, 1970, 1971a & 1971b).

Joshi and Kamat (1966) reported changes in the pH, surface tension and dielectric constant of magnetically treated water. They claimed that both pH (initially near 7) and surface tension increased with increasing field strength between 1.9 and 5.7 kgauss. Other investigators (e.g. Piccardi, 1959; Klassen, 1966; Klassen et al., 1965, 1970 and 1971c) have shown similar physicochemical changes for magnetically treated water, including effects on surface tension and the heat of hydration. However, for each of the claimed effects at least one contradictory paper has been published stating exactly the opposite, e.g. Kirgintsev et al., 1968; Evdokimov and Zubarev, 1969; Mueller et al., 1970; Ushakov and Sherbakov, 1970.

Before considering the mechanisms suggested in the third category of theories, i.e. those concerned with field effects on particles in solution, there are a number of papers which link this and the previous group of theories. Drost-Hansen (1971, 1972 and 1978), Kvajic and Drost-Hansen (1978), Cini et al. (1969) and Wiggins (1975) discuss the anomalous properties of 'vicinal water', i.e. the water adjacent to suspended material. They consider the unusual magnetic and ion selective properties of 'vicinal water' and its rejection of "water structure-making" ions over "structure-breaking" ions . It is proposed that the magnetic field may change the nature or extent of this 'vicinal water'. This theory, though suggesting a structural modification to the water, requires the presence of suspended particles in the bulk of the water.

The greatest number of the mechanisms which have been advanced to account for the reported changes in scale deposition following magnetic treatment belong to the final category. The authors of these papers suggest that the magnetic field influences very small particles (e.g. colloids or crystal nuclei) in suspension or ions in solution. This influence is often explained in terms of the force, F, on a charged particle moving through a magnetic field which is given by;

$$F = B.q.v,$$

where B is the magnetic field strength, q is the charge on the particles and v is their velocity through the field. The force is a maximum when the field is perpendicular to the direction of movement of the charged particles and it displaces positive and negative ions in opposite directions, which, according to Belova (1972), should;

> "...reduce the freedom of movement of the charged particles!... The limitations of the motion of the particles in the field leads to an increase in the number of collisions and the formation of centres of crystallization."

Umanskii (1966) and Tebenikhin and Gusev (1968) have suggested that increases in the number of crystallization centres would promote precipitation in the bulk of the solution, rather than on the walls of the vessel. Narasiah (1970) also supported this mechanism, but he suggested that the effect only operated when the solution was nearly saturated with calcium bicarbonate. This is an area of controversy between the supporters of the mechanism. Half of the papers published, e.g. Martynova et al., 1969; Skorobogatov, 1969; Zaslavskii and Dobrzhanskii, 1973, suggest that the solution must be saturated or nearly so for the effect to operate, while the rest reported that magnetic treatment accelerated crystallization when unsaturated solutions were passed through the field, e.g. Koubikova, 1969; Iovchev, 1966; Golubtsov et al., 1971). It has, however, been pointed out by Donaldson and Grimes (1991a) and Söhnel and Mullin (1988) that the size of the force on the charged particles is very small under the usual operating conditions of magnetic units (i.e. flow rate and field strength) and, therefore, these authors question its influence.

One of the major aims of the research group at City and Brunel Universities has been to develop a theory which accounts for the observed effects.

1.3. Research Projects at City University

1.3.i. Monitored Industrial Case Studies

For the last decade the research group under Professor Donaldson, initially at City University and now at Brunel University, has been investigating the general phenomenon of the magnetic treatment of fluids. Part of this work has involved the monitoring of industrial trials of HDL units, which have been installed at over 500 sites in Britain. For these trials, the units were installed by technical staff and every care was taken to ensure that the tests were carried out under rigorously controlled conditions. This section contains details of the scientific results and the economic and industrial benefits which have been found for the treatment.

In many cases the monitoring of industrial trials of units was accompanied by laboratory-based studies on particular systems. An example of this is presented in Chapter 3, on the reaction of a solution containing calcium and magnesium ions with a phosphate solution. The investigation was originally prompted by the findings of tests with a unit at a sewage treatment plant. Another example is the work on barium sulphate (see Chapter 2), which was particularly designed as a precursor to tests with units in offshore oil production processes. The following examples show the range of applications found for the units, and also give an indication of the monitoring techniques which were used.

The results of the monitored industrial trials of HDL units are often startling. Holloway (1990) describes the response of one of his colleagues when the heating bundle of a calorifier was examined three months after a magnetic unit was installed: "I don't believe it. It's magic!". The unit was at Goodmans Fields, the London data centre of Nat West Bank. The centre uses 80,000m^3 of water a year, which was conditioned by water softeners requiring 250 tonnes of salt per annum. Despite this the domestic hot water calorifiers at the site still experienced a scaling problem which necessitated regular chemical treatment at a cost of £12,000 a year plus two man days labour. After the magnetic unit was installed the scaling of the calorifiers ceased totally. Since then several more units have been installed and in the first five years of their operation no further work or costs were incurred. The estimated annual savings in this case were over £22,000.

The independent Hertford brewers, M^{c}Mullens and Sons, also found a magnetic unit to have great economic benefit. They suffered from extensive scaling in a 28,800 gallon tank, which was used to store hot water for the brewery, and in two heat exchangers. The problem became so acute that, despite regular acid descaling of the tank, eventually a team of brewery operators, using scaffolding, had to chisel away the thick coating of hard scale from the inside of the tank. After the installation of an HDL unit the scaling was reduced to a thin soft layer which was easily removed by power washing and one man using a wooden scraper. As a result the amount of acid used annually for descaling was reduced from 2,400 to 800 litres and the labour time was cut down by two-thirds. Similar beneficial results have been found with units at other breweries.

The British Airports Authority installed an HDL unit at Gatwick Airport. The air conditioning system at the airport's multi-storey office complex was suffering from acute scaling. The buildup of the scale in cooling towers and water chillers was greatly reducing their efficiency. Chemical dosing of the system was found to be ineffective, so a trial was arranged with an HDL unit. Due to the difficulty of regularly examining the cooling towers and water chillers, the effects of the treatment were inferred from the electricity consumption of the two pumps which circulated the water in the system. On the system's Number 1 pump consumption per phase fell from 15.75 to 15.5 amps in the first month. Four weeks later consumption had been reduced still further to 15.0 amps per phase. The savings on the No.2 pump were even more significant. Consumption per phase fell from 17.5 to 16.5 amps in the first month, then to 16.0 amps after eight weeks. At the end of the monitoring period (six months) the figure was down to 15.25 amps - a reduction of almost 13%.

The results of these industrial trials are representative of the type of beneficial effects that the magnetic treatment has been found to have at many of the 500 sites where units have been installed.

1.3.ii. Laboratory Investigations.

A large number of laboratory-based investigations have been carried out on the interactions of magnetic fields and a diverse range of systems. Some studies have been aimed at specific uses of magnetic units, for example, the work with domestic expansion boilers, presented in Chapter 2. Menzies (1989) considered applications for the manufacture of chocolate and Bell (1990) investigated magnetic treatment scale prevention for coffee percolators and reverse osmosis water purification. The precipitation of many crystal systems have been considered (e.g. $CaCO_3$, $CaSO_4$, $BaSO_4$, $Zn_3(PO_4)_2$). Changes in these systems have been characterized by a variety of techniques (see section 1.4).

Thomas (1992) and Stimpson (1993) have studied the rate of scaling of a number of crystal systems (e.g. $BaSO_4$, $CaCO_3$) using back pressure measurements with narrow bore tubes under a wide range of conditions. Thomas has also carried out work with polymerization reactions, optical absorption of dye solutions and crystal growth in static situations (i.e. where the solutions were not circulated through a field, but were crystallized within a magnetic field). Prosser (1989) carried out similar studies under static conditions and also made measurements of electrolytic conductivity.

In addition to the investigations described above, tests have also been carried out on pH, double layers on oxides, the settling rate of clays, the growth of pea and bean plants and the take-up of cloth dyes. From the results of the scaling, precipitation and crystallization studies Donaldson (1988a) has identified a number of common effects due to the magnetic treatment. These are changes in;

1) Particle size,
2) Crystallinity,
3) Crystal morphology,
4) Crystal phase,
5) Solubility, and,
6) Rate of precipitation.

Examples of all of these changes will be presented in subsequent chapters.

1.3.iii. Theories and Mechanisms.

The results of the various investigations discussed in the previous section have suggested several possible explanations for the magnetic treatment effects. Some of these are discussed here.

One of the first mechanisms to be proposed to account for the observed effects of magnetic treatment was that of 'Crystal Nucleation Modification' (Donaldson, 1988a). The nuclei on which crystals start growing and the growing crystallites themselves are very small. These charged particles would be subjected to a force as they pass through the magnetic field. This would act on the surface charges on the particles and modify their nature and, as a consequence, modify the growth of the crystals both in general and on specific planes.

The six effects of magnetic treatment presented in the previous section can be explained by such a modification of the nucleation process. Changes in crystal size would result from the alteration to the general growth pattern and changes in crystallinity and morphology would be due to differences between the relative growth rates of specific planes. Changes in the crystal phase would result from changes in the energy available to the growing crystals, with and without magnetic treatment. Changes in the solubility of the precipitates in fluids, including the dissolution of existing scale, would arise from changes in the fluid-precipitate equilibrium as a direct consequence of changes in crystal growth in the system. Changes in the rate of precipitation would also be a consequence of changes in the rate of growth of the crystals.

There are, however, certain problems with this theoretical mechanism. Thomas (1992) comments on one of these:

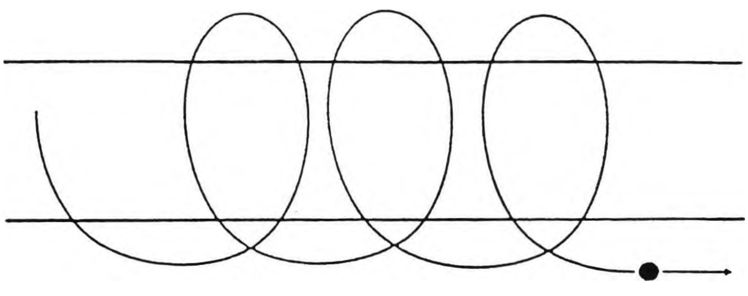
> "This theory provides a satisfactory explanation of the effects of magnetic fields on crystallization, <u>when the applied field acts at the point of crystallization</u>, but it cannot account for the downstream phenomena observed in this work, principally because it is very unlikely that the undersaturated aqueous solutions of calcium ions that were magnetically treated in this work contained any stable nuclei."

Thomas ascribes an alternative explanation to the magnetic phenomena which he observed. This concerns effects, similar to those suggested for crystal nuclei, on clusters of ions forming prior to the development of nuclei. The evidence for the existence of these clusters is given in Neilson and Enderby (1983). These clusters would essentially consist of hydrated ions in close proximity to each other. Thomas suggests that such species would have a high surface charge and be stable enough to have a finite lifetime in the fluid.

Recently, two theories have been used to explain the observed effects. The first of these is that of Magnetokinetic Energy Level Modification (Steiner and Ulrich, 1989). In this the observed effects arise because of interactions between the magnetic field and specific energy levels and results in Zeeman splitting of radical pairs. This type of effect is known to influence radical ion pair reactions, micellar reactions, emulsion polymerization reactions and biological systems.

The second theory suggests that the observed changes are due to direct magnetic field-charge interactions (Donaldson and Grimes, 1991a), which result from the mutual interaction between the magnetic field and the charged species as they move through the field. The physical basis of these interactions involves alterations in the random course of charged particles while leaving neutral particles unaffected. A charged particle moving in a plane perpendicular to the magnetic field executes a circular motion (Furuse, 1970; Akcasu and Hammouda, 1985), with the direction of the motion being opposite for positive and negative particles. If a particle has a velocity component parallel to the field then it produces a helical motion instead of a circle (Belova, 1972) - see Figure 1.2.

Figure 1.2



Helical Motion of a Charged Particle in a Uniform Magnetic Field.

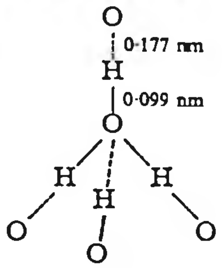
Several authors (e.g. Söhnel and Mullin, 1988) have attempted to show that magnetic treatment would not influence the behaviour of a solution, by calculating the energy supplied to the system by the magnetic field. The authors show that this energy would be insufficient to break any of the bonds between the various species in solution. Belova (1972) advances two main objections to this type of argument:

Firstly, it is well known that, in a large number of situations, very great effects can be caused by a small initial force (e.g. pushing a small pebble down a slope can cause an avalanche). Vonsovsky (1966) describes the exploitation of weak forces (in particular those caused by magnetic fields) as controlling factors in science and engineering. Secondly, since the microscopic structure of water and solutions is not yet understood, the microscopic effects of magnetic fields can only be inferred from experimental data. The calculations mentioned above usually assume that hydrogen bonds would need to be ruptured for any effects to be seen. However, there is evidence that this is not necessarily the case. Belova discusses the two modifications of water which can be distinguished by the arrangement of the nuclear spins of the hydrogen atoms in the water molecules. In ice all of the molecules show the paramodification, in which the spins are in opposite directions. At higher temperatures orthomodification, where both spins are in the same direction, predominates. The transition from the para- to the ortho-modifications requires only 150 J/mole (Note: the strength of hydrogen bonds in water are between 20 and 35 kJ/mole).

To appreciate the consequences of the possible effects of magnetic treatment described above, it is important to have an understanding of the theories concerning the physical nature of liquid water and the environment of ions in aqueous solutions. The following is a brief, simplistic description of the 'structure' of liquid water and its interactions with ions, and it is not intended to be a comprehensive account of the interactions occurring in such situations. These are considered in much greater detail in the six volumes of 'Water - a comprehensive treatise' (1971 to 1979) edited by Franks and also in Neilson and Enderby (1983). In both of these references it is stressed that there are many aspects of the microscopic behaviour of water and aqueous solutions which are still not explained or fully understood. This fact should be kept in mind when aspects of the magnetic treatment of fluids are discussed.

Water and aqueous solutions exhibit a number of unusual properties due to the dipolar nature of the water molecule. This causes the formation of relatively strong intermolecular hydrogen bonds in liquid water and also explains why it is such an excellent solvent for electrolytes. One of the consequences of this is that some of the tetrahedral distribution of the water molecules, present in ice (see Figure 1.3), persist in the liquid phase. This has been shown by the production of X-ray and neutron scattering intensity patterns, which indicated the existence of a 'structure' within the liquid (Franks, 1983). Supporting evidence for this is the very small latent heat of fusion for ice. This association of water molecules in the liquid phase leads to the formation of polymeric molecules of formula $(H_2O)_n$, where n varies from about eight at 0°C to near unity at the boiling point.

Figure 1.3



Tetragonal Structure of Water Molecules in Ice.

The microscopic structure of water has not yet been fully described, but, it is widely accepted that its nature depends greatly on temperature and pressure, and also on the nature and concentration of any solute dissolved in it. For example, shifts in the infrared absorption spectrum for water have been found with solute concentrations as low as 0.001%.

When an ionic substance is dissolved in water the ions become dissociated from each other and hydrated. These 'hydration spheres' separate and insulate the ions from each other. Such solutions are called electrolytic due to their ability to conduct electricity. The conductivity (the reciprocal of the resistance) of such a solution depends on two factors: the concentration of the ions present (i.e. the total charge) and, the speed with which the ions move towards the electrodes. The second of these depends, for a particular ion and solvent, on the temperature of the solution and the potential gradient applied. Therefore, the molar conductance, which is the conductance of one mole of an electrolyte enclosed between two electrodes spaced one centimetre apart, at a particular temperature would be expected to be independent of the concentration (since the measurement is always made with one mole of ions). However, in practice this is not the case. Table 1.1 shows the molar conductance values for sodium chloride solutions at various concentrations.

Table 1.1

Concentration (mol dm^{-3})	Dilution, V_m (cm^3 mol^{-1})	Conductivity (Ω^{-1} mol^{-1})	Conductance, Λ_v (Ω^{1-} cm^2 mol^{-1})	$\alpha = \Lambda_v/\Lambda_\infty$
1.0	1,000	0.0936	93.6	0.74
0.1	10,000	0.01067	106.7	0.85
0.02	50,000	0.00232	116.0	0.92
0.01	100,000	0.00118	118.0	0.94
0.001	1,000,000	0.000124	124.0	0.98
	∞		126.4	(1.00)

Apparent Degree of Dissociation, α, for $NaCl_{(aq)}$.

It can be seen that the values rise as the solution is diluted. The 'molar conductance at infinite dilution', Λ_∞, for the electrolyte is obtained by repeatedly diluting a solution until no further change in its molar conductance is found. It was discoveries of this type that led Arrhenius to propose the theory of electrolytic dissociation. He suggested that the anomalous behaviour of electrolytic solutions occurred because not all of the ions in a solution become dissociated, unless the solution is sufficiently dilute. i.e. the differences between the predicted and measured values are due to changes in the concentration of the charge carriers. Arrehnius proposed that the degree of dissociation of the ions for a particular solution, α, is the ratio of the molar conductance, Λ_v, of the solution and the molar conductance at infinite dilution for the electrolyte. These values are given in the last column of Table 1.1.

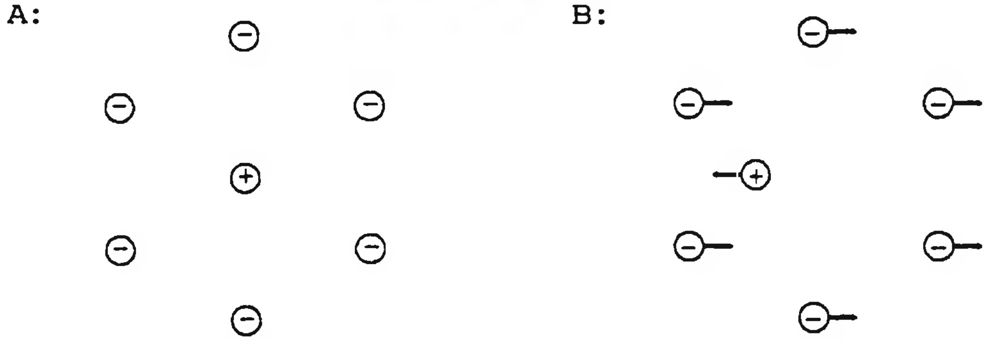
It is now known that, for strong electrolytes, the ions dissociate totally at all concentrations in solution. The anomalous behaviour of such solutions is now thought to be due to changes in the velocity of the charged particles. The ionic mobility of an ion in a solvent is the velocity of that ion in a potential gradient of one volt per centimetre at a particular temperature. For most ions in aqueous solution at room temperature its value lies between 3 x 10^{-6} and 8 x 10^{-6} m/s (about 2cm/hour), but H^+ and OH^- ions move considerably faster. The main retarding force which limits the movement of ions in an electric field is the frictional drag experienced by the ion and its attendant solvent molecules owing to the viscosity of the solvent. It has been suggested that the higher ionic mobilities for H^+ and OH^- are due, in part, to the fact that they are not hydrated.

It is believed that, in a concentrated solution of a strong electrolyte, each ion, in addition to its hydration sphere, is surrounded by a cloud or atmosphere of ions which are mostly of the opposite charge. It is obvious that the extent of such an ionic cloud would depend on the concentration of the solution. In the absence of a potential gradient this arrangement would be symmetrical (see Figure 1.4A), but, under the action of an electric (or magnetic) field, asymmetry arises, as in Figure 1.4B, because the positive and negative ions are attracted in opposite directions. Thus, as each ion moves through the solution its ionic atmosphere exerts a drag on it, owing to the excess of oppositely charged ions in its wake. The effect of this is to slow down the movement of the ion considerably.

This effect is greater with more concentrated solutions and is described graphically by Hicks (1977):

> "The situation is rather like a man trying to force his way through a dense crowd, many members of which are moving in the opposite direction. The analogy is all the more realistic if we imagine each person in the crowd to be carrying a couple of large cases (adhering molecules of solvent) which continually get caught in those of other people. Just as the denser the crowd the more the man's progress is impeded, so the more concentrated the solution the greater is the retarding effect of interionic attraction."

Figure 1.4



A: Ion/Ionic 'Atmosphere' System Without an External Field.
B: Ion/Ionic 'Atmosphere' System Within an External Field.

The situation described above is a precursor to the ionic clusters present in solutions prior to the formation of crystal nuclei. The degree of the effect is quantified in the same way as the degree of dissociation proposed by Arrhenius. The value obtained is termed the 'apparent degree of dissociation' or conductance ratio.

Many phenomena depend on both the ionic concentration and also on the extent to which the ions have become free from interionic action (i.e. their mobility). This, in fact, encompasses most areas of ionic chemistry since most ionic reactions in solution are diffusion controlled and, therefore, the mobility of the ions will influence the kinetics and equilibria of reactions involving ionic solutions. The two quantities are therefore often combined into a single quantity, activity, which can be considered as the 'effective concentration' of the solution. The relationship between the activity, a, and concentration, c, of the ions in a solution is given by;

$$a = f.c,$$

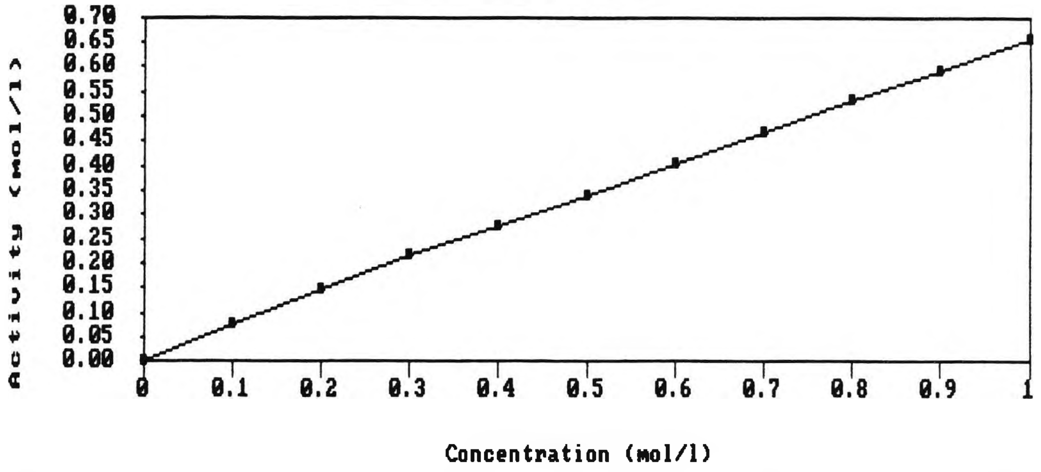
where f is known as the activity coefficient and is related to the degree of interionic association. The value of f can be determined from molar conductance, freezing-point, boiling-point or osmotic pressure data. Table 1.2 shows values of f and a for sodium chloride solutions at 25°C and Figure 1.5 is a graph of a against c.

Table 1.2

c (mol/l)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
f	0.778	0.735	0.710	0.693	0.681	0.673	0.667	0.662	0.659	0.657
a = f.c (mol/l)	0.078	0.147	0.213	0.277	0.341	0.404	0.467	0.530	0.593	0.657

Activity Coefficients, f, and Activities, a, for $NaCl_{(aq)}$ at 25°C.

Figure 1.5



Graph of Activity against Concentration for NaCl Solutions at 25°C.

The value of f, at a particular concentration, depends on the temperature and pressure and is also influenced by the presence of other species in the solution. Hence, activities are usually not known and concentrations are used instead. Graphs of rate against concentration, for a particular reaction, would be very similar to those plotted against activity (see Figure 1.5), but the gradients, and hence the rate constants would be lower. This can be demonstrated by considering the rate of a reaction, which is first order with respect to one of the reactants, X, given by;

$$-d[X]/dt = k.f.[X],$$

where k is the velocity constant and f is the activity coefficient. It can be seen that a graph of -d[X]/dt against f.[X], the activity of X in the solution, would give a straight line with gradient k. If, however, the graph is plotted against [X], a good straight line would be produced, with gradient k', where k' = k.f. Either method is equally acceptable, since the value of k is linked to the number of collisions between the reactants and, hence, for ionic reactions, to the activity of the ions in solution.

According to Arrhenius' theory, the rate constant, k, for a reaction is given by;

$$k = A.e^{-(E/RT)},$$

where E is the activation energy, R is the gas constant, T is the absolute temperature and A, the frequency factor, depends on the number of collisions between the reactants per unit time. If the value of k is determined using the activities of the reactants, then the frequency factor, A, is a constant representing the collision frequency at unit activity. If, however, k is calculated from the concentrations, then the value of A represents the actual number of collisions. For this work the second method was usually used.

1.4. Analytical Techniques and Test Apparatus

1.4.i. Analytical Techniques.

The analytical methods described here are those which were most commonly used for the work. The theory and operation of the techniques are briefly reviewed with their application to the study of the magnetic treatment of fluids.

Particle Size Analysis.

Many of the solid precipitate samples which were produced showed differences in their particle sizes. The determinations of the particle size distributions were made using 'Malvern' analyzers and computer software. These use laser scattering measurements to determine the percentage of the total amount of solids in different size bands. The software and computer system control all of the processes and carry out the calculations. The results are printed out as a table of percentage weight in band and cumulative weight below for each of the size bands, as shown in Table 1.3.

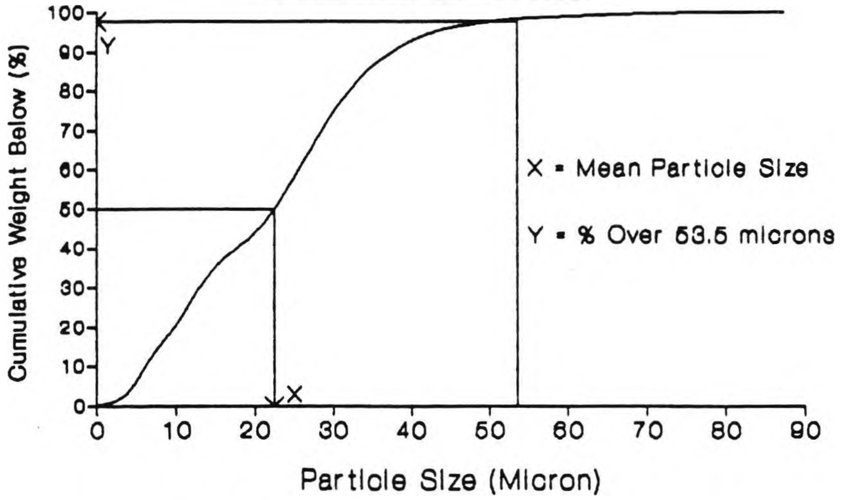
The results of the particle size analyses are presented graphically in two formats, which allow different information to be obtained concerning the size distribution of the particles. Figure 1.6 shows a set of data presented as cumulative weight below against particle size (i.e. the percentage of the total weight of the precipitate below a particular size). This format allows the mean particle size to be determined directly from the graph by finding the size corresponding to a cumulative weight below of 50% (X in Figure 1.6). It is also possible to determine a numerical indication of the level of aggregation of the particles (Y in the figure). This is

Table 1.3

Size Band		Weight in Band (%)	Cumulative Wt Below (%)
Upper	Lower		
188.0	87.2	0.0	100.0
87.2	53.5	0.1	99.9
53.5	37.6	3.4	96.4
37.6	28.1	26.4	70.0
28.1	21.5	25.2	44.8
21.5	16.7	5.4	39.4
16.7	13.0	8.7	30.8
13.0	10.1	10.7	20.1
10.1	7.9	4.8	15.3
7.9	6.2	4.9	10.4
6.2	4.8	5.0	5.3
4.8	3.8	2.3	3.0
3.8	3.0	1.1	2.0
3.0	2.4	0.6	1.4
2.4	1.9	0.5	0.9

Example of Output from Malvern Particle Size Analyzer.

Figure 1.6

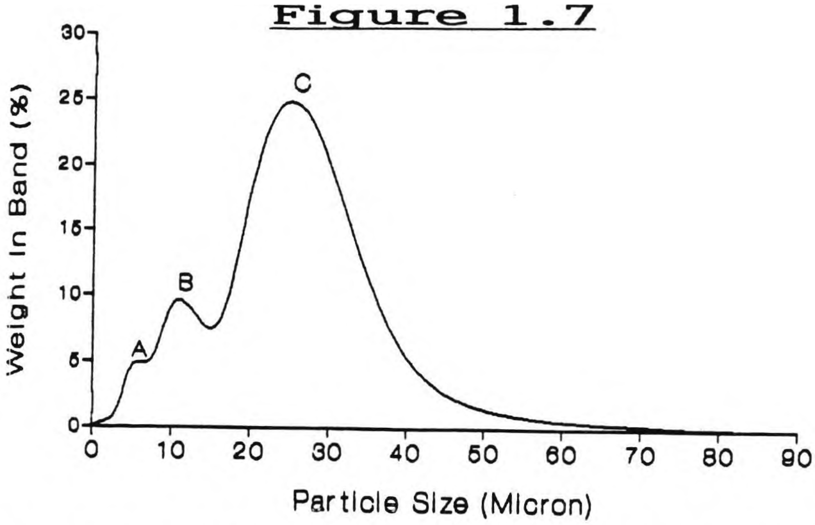


Particle Size Analysis as Cumulative Weight Below vs. Particle Size.

achieved by finding the percentage of the particles which are above a certain particle size. In the example shown, 53.5 microns was chosen as the 'critical' value, since the electron microscopy study had shown that all of the individual crystals were below this size.

Figure 1.7 is a graph of the results of an analysis plotted as weight in band vs. particle size (i.e. the percentage weight at each particle size). A graph of this type allows any preferential growth sizes for the crystals to be identified. Three distinct maxima can be seen in the distribution curve, indicating three separate preferential crystal sizes. These could not be identified with the previous presentation format. (N.B. The second method of presentation is, in effect, the differential of the first.)

Figure 1.7

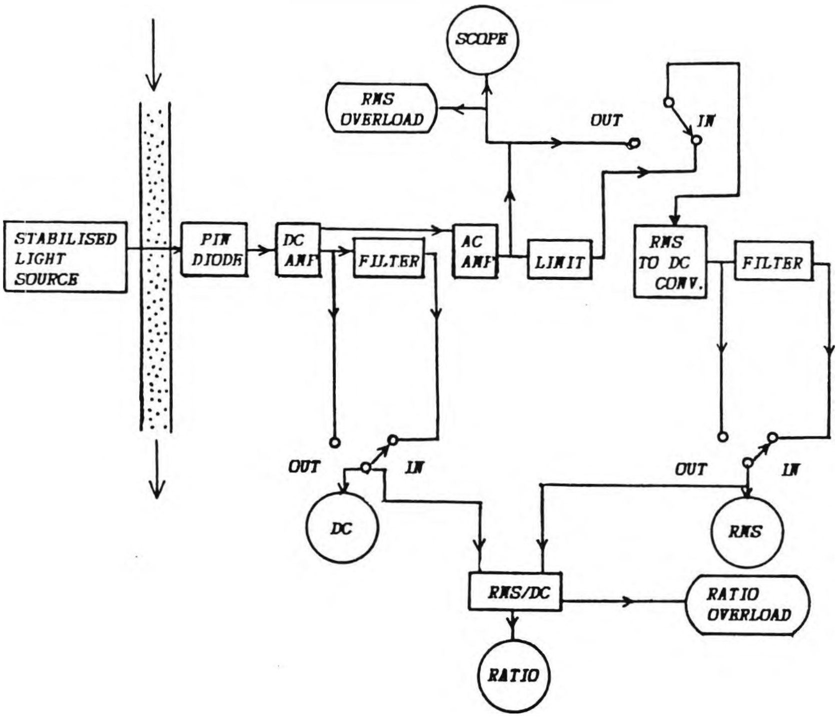


Particle Size Analysis as Weight in Band vs. Particle Size.

Photometric Dispersion Analysis.

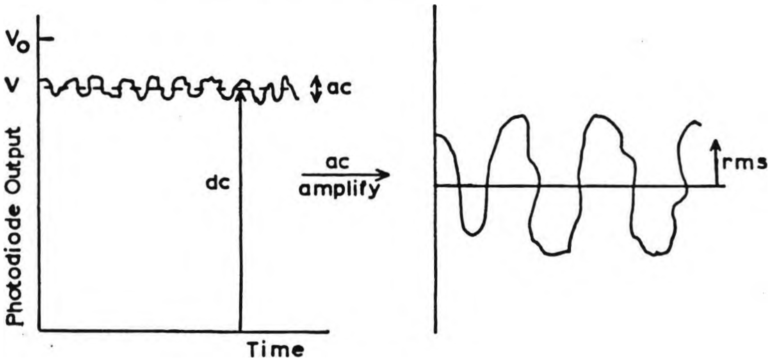
The photometric dispersion analyses were carried out using a PDA2000 dispersion analyzer (see Figure 1.8), which is particularly well suited to the study of the effects of magnetic treatment on precipitation processes, since it provides a continuous qualitative measurement of the total solids and particle size of a flowing suspension. The technique is based on the continuous measurement of fluctuations in the intensity of a transmitted light beam through a flowing suspension. The suspension is passed through a narrow transparent flexible tube which fits into a perspex block housing two precisely aligned fibre optics. The transmitted light intensity is

Figure 1.8



Schematic Diagram of PDA2000 Photometric Dispersion Analyzer.

Figure 1.9



a.c. and d.c. Components of Photodiode Output.

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monitored by a sensitive photodiode detector. The electrical output from this consists of a large d.c. component and a small fluctuating a.c. component (see Figure 1.9). The variations are caused by the inevitable local fluctuations in the particle concentration and size, as the suspension passes through the light beam.

Gregory (1985) has shown that the d.c. component of the photodiode output is related to the total solids in the suspension, while the root mean squared (r.m.s.) value of the a.c. component is influenced by the average number concentration and size of the suspended particles. The PDA2000 instrument separates the two components and displayes voltages, which are proportional to their values, on a digital display and/or a chart recorder.

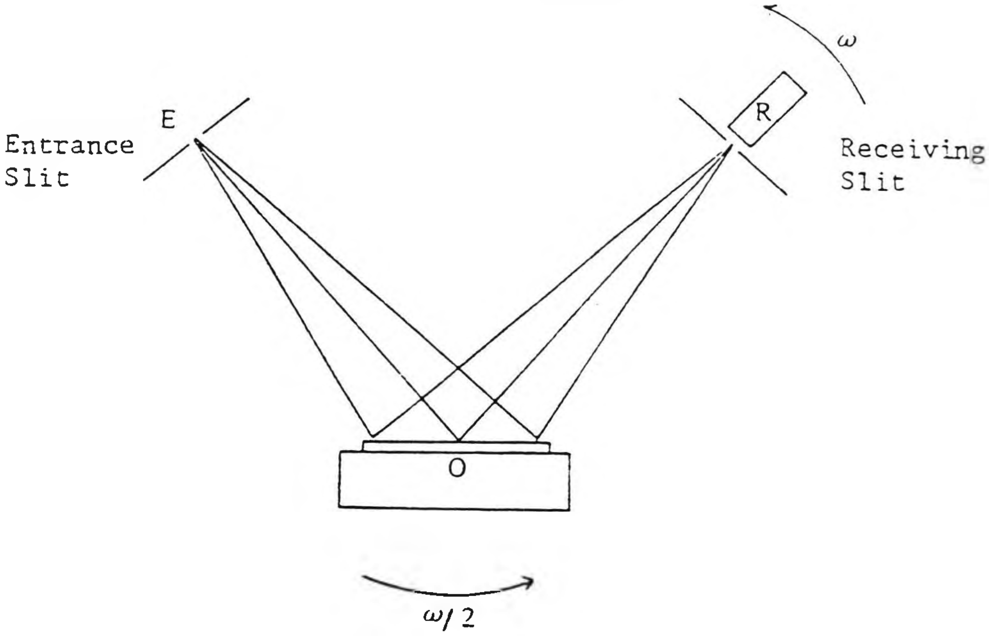
Electron Microscopy.

In an electron microscope a beam of electrons is reflected from the object being examined. The reflected intensities are detected and converted into an optical picture on a screen, which can then be photographed. Since the electron beams can have effective wavelengths of 0.4nm (of the order of 10^5 times shorter than visible light), detailed examination of very tiny objects is made possible. The electron micrographs presented in this work have magnifications of between 300 and 3000x, though greater resolution is possible using the technique.

Powder X-ray Diffraction.

For crystalline materials, the individual atoms exist in a symmetrical lattice which exhibits three-dimensional repeat symmetry. Such an arrangement can act as a diffraction grating. The lattice spacings in a crystal are such that X-rays, with wavelengths between 0.02 and 0.2nm, can be diffracted and this is the basis of the technique. The diffractograms are produced by rotating the powdered sample at a constant angular speed, while, at the same time, a detector is rotated around the sample, with twice the angular velocity. Figure 1.10 is a schematic diagram of the main components of such a diffractometer. In the way described, a diffraction pattern is built up of intensity of the reflected beam, which depends on the electron density within the lattice and, therefore, its size,

Figure 1.10



Schematic Diagram of a X-Ray Diffractometer.

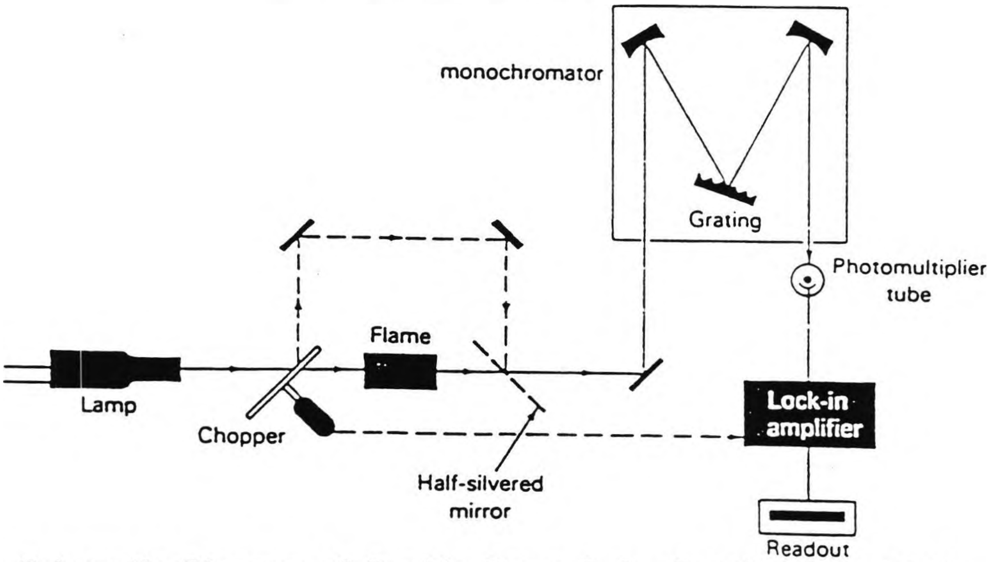
shape and symmetry, against angle of incidence. Since each crystalline material is unique in the arrangement of the atoms in its lattice, the technique gives a diffractogram which is characteristic (a 'finger print' for the crystal). The relative intensities of the diffracted X-rays depend on the electron densities within the lattice.

In some cases, during the course of the work, X-ray diffraction was used in a novel manner. The precipitated crystals from some of the experiments were not powdered prior to their X-ray analyses. The intensities of the lines in the diffraction pattern, in this instance, are not solely dependent on the electron cloud densities. The morphology (external shape) of the crystals may cause them to lie in a particular orientation. For example, needle-like crystals of aragonite (calcium carbonate) would be unlikely to stand on their 'points'! In this way, any changes to the external shape of the crystals, following magnetic treatment, could be identified by changes in the relative intensities of the lines in the diffraction pattern. The diffractograms presented in this work were produced using a Phillips PW1010 Diffractometer with copper K*α* radiation (wavelength = 1.54178nm).

Atomic Absorption (A.A.) Spectroscopy.

This technique involves the absorption of electromagnetic radiation in the visible and ultraviolet regions of the spectrum, resulting in changes in the electronic structure. Radiation characteristic to the particular element being determined is passed through an atomic vapour of the sample, which is produced by the aspiration of the test solution into a flame. The absorbed radiation excites electrons from the ground state to higher energy levels (excited states) and the degree of absorption is a quantitative measure of the concentration of ground state atoms in the vapour. If the absorption for a sample of known concentration is determined, then unknown concentrations can be calculated. This technique was used to determine the residual concentration after precipitation reactions. Figure 1.11 shows a typical A.A. spectrophotometer.

Figure 1.11

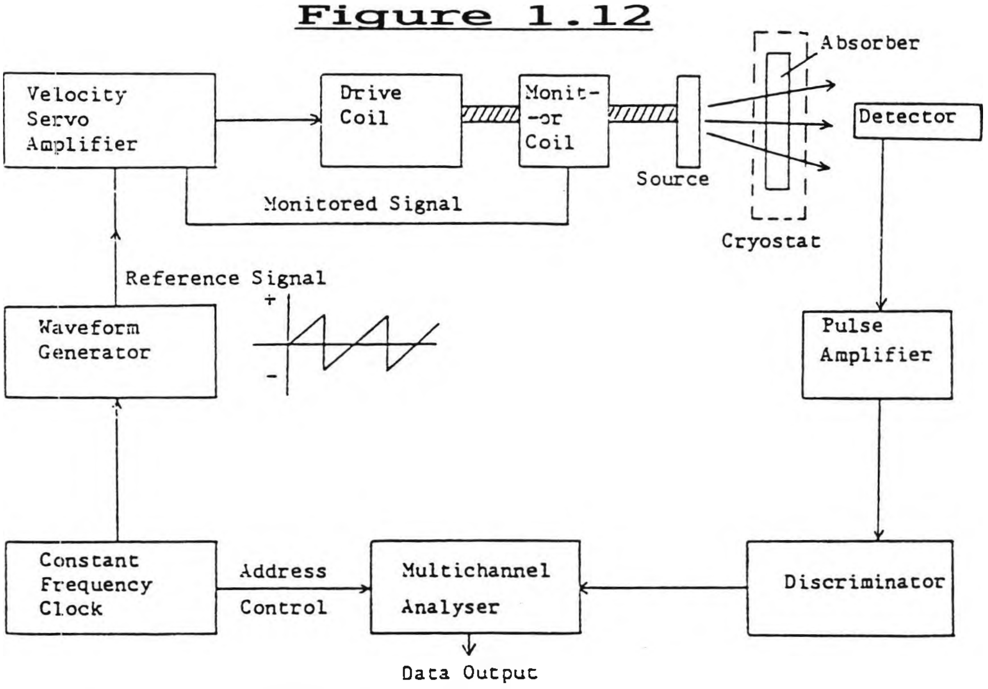


Schematic Diagram of Double Beam A.A. Spectrophotometer.

Mössbauer Spectroscopy.

The Mössbauer effect is defined as the emission or absorption of gamma rays by a nucleus, without loss of energy due to the recoil of the nucleus and without thermal broadening. It is not appropriate to consider the detailed working of a Mössbauer spectrometer here, but it is useful to understand the general processes which take place. Figure 1.12 shows the basic components of a typical spectrometer.

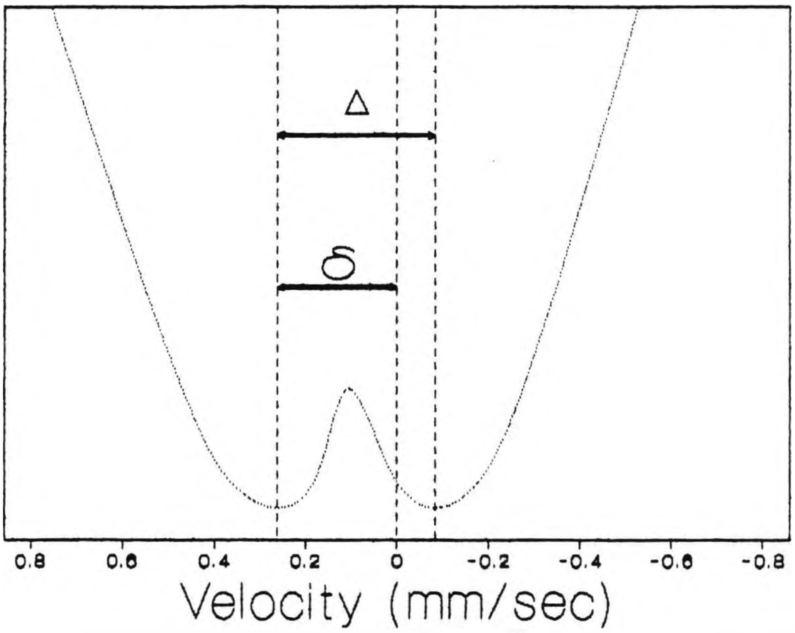
Figure 1.12



Schematic Diagram of a Mössbauer Spectrometer.

The source of gamma radiation consists of excited nuclei bound into the lattice of a solid, which allows recoiless emission of gamma rays as the nuclei relax to their ground state. If the ground state nuclei of a target were identical to those of the source (i.e. the same element in the same chemical environment), then the emitted gamma radiation would be absorbed. However, if the target nuclei were different from those in the source (due to differences in their electronic environment), the gamma rays would be transmitted and could, therefore, be detected. If a small relative motion is produced between the source and the target (the Doppler velocity), the frequency of the emitted radiation is modified. At a particular velocity the modified frequency of the gamma rays will be such that they will be absorbed and immediately re-emitted in all directions as resonance fluorescence. The Mössbauer spectrum is obtained by plotting the percentage transmission of the gamma rays through the sample against the Doppler velocity.

Figure 1.13



Measurement of δ and Δ for a Mössbauer Spectrum.

Three features of the target can be characterized using the technique. The chemical isomer shift (δ) is a measure of the s-electron density at the nucleus. Quadrupole splitting (Δ) is a measure of the asymmetry of the s-electron density at the nucleus. Figure 1.13 shows the measurement of δ and Δ on a typical spectrum. Magnetic hyperfine (Zeeman) splitting arises if there is a magnetic field at the nucleus. This splits the nuclear level of spin 'I' into (2I+1) equi-spaced states between which Mössbauer transitions can take place. These features can be detected in the Mössbauer spectra.

Hall Effect Gaussmeter.

In order to accurately determine the strength of the magnetic fields used for the work, an Omitec model 700 Hall effect gaussmeter was obtained. The instrument relies on the fact that when a current-carrying laminar conductor is inserted into a transverse magnetic field, the electrons are deflected in the direction given by Fleming's left hand rule. This gives rise to the 'Hall effect voltage' between the conductor edges. This voltage is proportional in magnitude to the magnetic field strength since the force on the free electrons is given by;

$$F = I.l.B,$$

where I is the current, l the length of the current carrying-conductor and B is the magnetic field strength. The instrument gives a digital readout of field strengths of up to 20 kgauss.

Microcomputer Applications.

During the course of the present work three programs for a BBC 'Master' microcomputer were written for particular applications:

'Ca-MgCAL'.

This program was written for the work on calcium/ magnesium phosphate (Chapter 3). It accepted the input of the data obtained for the samples using atomic absorption spectroscopy (see earlier), and provided the calculated concentrations of each ion in the solution in ppm. In addition, the program gave the number of moles and the percentage of the available amount of each ion reacted, and the molar ratio of calcium to magnesium in the precipitate. An example printout from the program is presented in Table 1.4.

'Corcalc'.

This program was written to carry out a number of calculations

Table 1.4

Run N°.	Ion	ppm in Solⁿ.	N° Moles in ppt ($x10^{-4}$)	% Used	Molar Ratio	$\frac{[Mg^{2+}]}{[Ca^{2+}]}$
1	Ca	961.5	1.0579	22.72	72.36	0.382
	Mg	736.4	0.4041	8.17	27.64	
2	Ca	549.8	2.5984	55.81	81.63	0.225
	Mg	707.1	0.5848	11.82	18.37	
3	Ca	228.4	3.8015	81.64	80.37	0.244
	Mg	651.4	0.9287	18.76	19.63	
4	Ca	94.5	4.3023	92.40	74.87	0.336
	Mg	567.9	1.4444	29.19	25.13	

Output of Calculated Values from 'Ca-MgCAL' Program.

Table 1.5

Time (Hours)	Weight (gms)	Wt.Loss (gms)	Wt.Loss/unit surface area ($x10^{-3}g/cm^2$)
0	145.8574	0.0	0.0
18	145.2386	0.6188	5.4417
42	144.4404	1.4170	12.5017
66	143.5970	2.2604	20.0184
90	142.7846	3.0728	27.3179
162	140.7822	5.0752	45.4179
330	135.7258	10.1316	92.2071

Output of Corrosion Rate Results from 'Corcalc' Program.

Table 1.6

Entry Number	x Values	y Values
1	0	0.0
2	17.0	4.2713
3	39.5	9.5028
4	72.0	15.7313
5	137.5	28.8826

Gradient = 2.075 (±0.073) x 10^{-1}.
y-intercept = 6.401 (±0.051) x 10^{-1}.
Coefficient of Determination = 99.809%.

Typical Output from the 'Curfit' Program.

for the corrosion rate determinations in the work presented in Chapter 4. In this work the weight of a number of corroding steel balls was measured at various time periods. The time and weight values obtained were entered into the computer. The program then calculated the weight loss and weight loss per unit surface area values for each of the entries. The surface area values were calculated as the averages between two successive readings, from the mass and density of the balls. The technique for this will be explained in the relevant section. A typical output of these values is given in Table 1.4. A further feature of the program was that it allowed the user to save the data onto a disc in such a format that it could be accessed by the '<u>Curfit</u>' program described below.

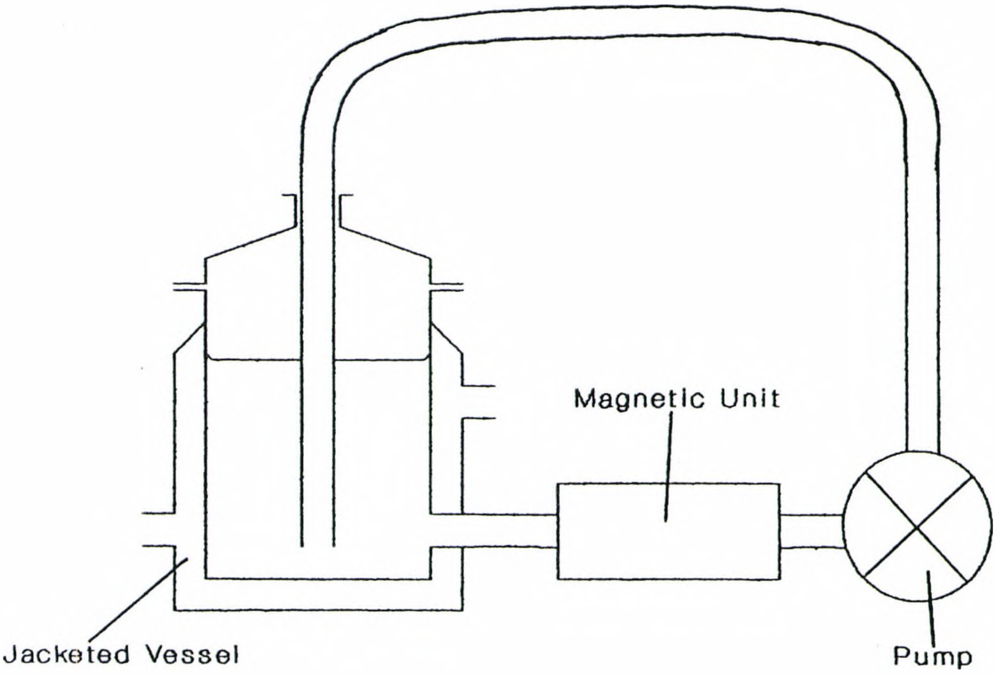
'<u>Curfit</u>'.

This program carries out a linear regression analysis on a set of data entered into it. The gradient and y-intercept of the 'best fit' line are calculated with a coefficient of determination and a standard deviation or range. These give an indication of how good the fit is between the entered values and the calculated straight line. The closer the coefficient of determination is to 100%, the better the fit, and lower values for the range, in relation to the size of the gradient, also indicate a better match. The program was particularly useful for the calculation of reaction rates with the work on corrosion (Chapter 4) and the Harcourt-Esson reaction (Chapter 5). A typical printout from the program is given in Table 1.5 and full listings of all three of the programs described can be found in Appendix A.

1.4.ii. <u>Test Apparatus.</u>

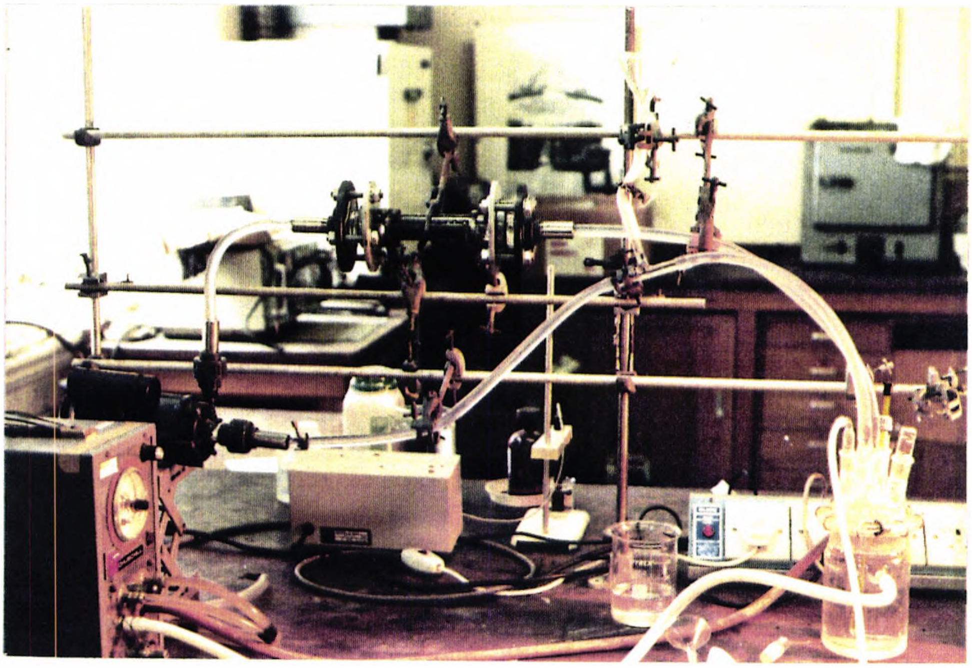
One particular type of test rig was used for the majority of the

Figure 1.14



Schematic Diagram of Jacketed Vessel Test Rig.

Figure 1.15



Photograph of Jacketed Vessel Test Rig.

present work. It consisted of a jacketed glass vessel (which was produced in a range of sizes) with a 'quick-fit' flanged top, which allowed the vessel to be sealed with a lid, so that inlet and outlet tubes and various probes (most commonly temperature probes) could be submerged in the solution in the vessel. The outer jacket of the vessel was connected to temperature-regulating devices so that the temperature of the test solution could be accurately maintained at a particular value.

The test solution in the vessel was circulated through transparent plastic tubing with a range of internal diameters (between 1 and 15mm) by either Totton EMP50 pumps or Watson Marlow Model 2011 peristaltic pumps. The pump heads and impellers for the Totton pumps were made from PTFE and, therefore, there was no contact between the solution and any metal (other than when HDL magnetic units were used).

The magnetic fields for the tests were produced in a number of different ways. The HDL 1" magnetic units have already been discussed in section 1.1 of this chapter. In addition to these units, a number of glass housed units of identical design were used for some of the tests (see Chapter 3). The majority of the present work was carried out using external magnetic fields. These were produced either by permanent magnets or electromagnets supported on either side of the circulation tubing.

Figure 1.14 is a schematic diagram of a jacketed vessel test rig and Figure 1.15 is a photograph of a typical test arrangement comprising a jacketed vessel, a Churchill temperature-regulating device, a Totton pump and a glass housed magnetic unit.

1.5. Objectives, Scope and Presentation

The major impetus behind this work was to improve the understanding of the phenomenon of the magnetic treatment of fluids. In order to achieve this, the aim of the experimental work was to carry out a wide range of carefully controlled and monitored laboratory investigations. These were designed in an attempt to prove that the magnetic treatment effect existed and to show that it is a general phenomenon influencing charged species in solution. It was also hoped that the results would enable a mechanism to be developed to account for the observed effects.

The work has been divided into chapters. Chapter 2 deals with three sets of experiments on precipitation and scaling reactions. The fourth piece of work, in Chapter 3, though dealing with a precipitation reaction, was not included in Chapter 2 since the aim of the work was to determine the effects of treatment on two 'competing' reactions (two cations reacting with a limited amount of a single anion). In the fourth chapter the effects of the treatment on corrosion processes are considered and in Chapter 5 the results of tests on a historical 'rate-determining' reaction are presented. In each chapter the theoretical implications of the findings are discussed and a theory to account for the observations is developed. Chapter 6 contains the final conclusions from the work. A substantial list of references and a bibliography are given in Chapter 7 and the experimental data for the tests are presented in Appendices B to E.

CHAPTER 2

THE EFFECTS OF APPLIED FIELDS ON PRECIPITATION, SCALING & CRYSTALLIZATION PROCESSES.

PAGE

2.1. Introduction

The work presented in this chapter describes experimental investigations of the effects of magnetic treatment on precipitation reactions. The research programme at City University has been largely based on this aspect of the magnetic treatment of fluids, much of the work being involved with the scale-preventing properties of the phenomenon.

Three pieces of work are described and they provide good examples of the analytical techniques used and the type of results obtained with different crystal systems. The first of these dealt with the precipitation and crystallization of calcium oxalate from aqueous solutions. The second was concerned with scale prevention in domestic water boilers, which is the main use of the commercially available magnetic units. The final area of work involved determining the effects of magnetic treatment on the precipitation of barium sulphate. This was carried out as part of a larger research project into the problems of scale in offshore oil production facilities.

Prior to presenting the results of the three investigations, it is useful to consider the theory and mechanism of precipitation processes, with particular reference to scaling. It must be emphasized that this discussion is a simplification of an exceedingly complex phenomenon, which is influenced by many factors, such as temperature and rate of temperature change, pressure, pH, agitation and dissolved impurities. All of these factors can affect the processes within the whole solution or in a very localized region of the bulk volume. The two main factors which influence all crystallization and precipitation reactions are (i) the solubility of the solid being deposited in the solvent in which it is dissolved, and (ii) the nucleation process which induces the precipitation and crystallization of the dissolved solute.

A precipitate will form from a solution only when the concentration of the dissolved salts is greater than an equilibrium value (saturation), i.e. when the solvent is supersaturated. Supersaturation can occur as a consequence of the much higher solubility of the exceedingly small crystal nuclei which form in the initial stages of precipitation. The solubility of a solute in a solvent is temperature dependent, as shown by the solubility curve in Figure 2.1.

It is believed that a definite relationship exists between solute concentration and the temperature at which crystals will spontaneously form from an initially unseeded (i.e. no nuclei present), supersaturated solution. The form of this relationship is a supersolubility curve roughly parallel to but above the normal solubility curve, as shown in Figure 2.1. In the region between the two curves (metastable zone) there will be no appreciable spontaneous nucleation, but in the labile region, above the supersaturation curve there will be copious spontaneous nucleation. Supersaturated solutions can arise in industrial processes for a number of reasons including mixing of incompatible streams, concentration of the solution (e.g. through evaporation), temperature changes, pressure changes and pH changes.

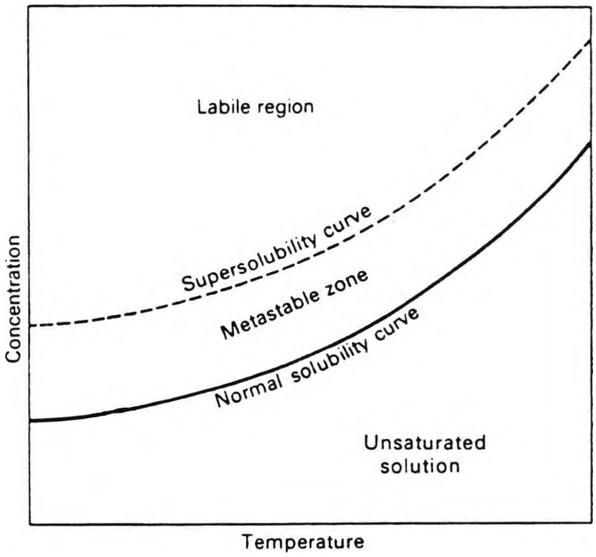
Nuclei for crystal growth can originate in two ways:

(a) Spontaneously due to changes in an unseeded solution (homogeneous nucleation).

(b) Seeds of minute crystals of another species (heterogeneous nucleation).

For the first of these, it is necessary that the solution be in the labile region. In the second situation, significant precipitation would occur, on the heterogeneous nuclei, if the concentration of the solution were in the metastable zone. In industrial processes heterogeneous nucleation is the most important.

Figure 2.1



Solubility Curves.

There is considerable evidence that stable clusters of ions form, prior to the formation of stable nuclei, even in unsaturated solutions (Neilson and Enderby, 1983). The gradual closer association of the ions in these clusters can be considered as a preliminary stage in the formation of homogeneous nuclei. The reason for this is that nuclei will appear where there is the greatest local concentration, i.e. where there are stable ionic clusters.

Once nuclei have formed in the solution (or have been added) the subsequent crystal growth proceeds by a number of steps, which occur simultaneously in the bulk of the supersaturated solution. The first of these processes is the diffusion of ions or molecules to the solution/crystal interface and their subsequent adsorption onto the crystal surface. The ions or molecules then move to energetically favourable positions on the crystal surface and are orientated to fit into the fixed lattice. The diffusion processes set up a diffusion layer close to the solution/crystal interface. This is shown in Figure 2.2, with the concentration gradient and convection current associated with it.

The stages described above for the precipitation of a solid from a solution can be considered as a 'chain reaction', the progression of which can be characterized by the degree of ionic association within the solvent (this is usually due to changes in the level of saturation of the solution). These processes are summarized in Table 2.1.

Scale deposition is an even more complex specific example of a crystallization process. All of the influences on precipitation and crystallization also affect scale deposition. However, in addition to these, there is also competition between the formation of crystals in the bulk solution and the formation of scale on the walls of the vessel. This is determined by a number of factors including the number of nuclei, the precipitation rate and the temperature and composition of the vessel walls.

The details of the investigations carried out on the effects of magnetic treatment on precipitation, crystallization and scaling are given in the relevant section and the experimental data for the experiments are given in Appendix B.

Figure 2.2

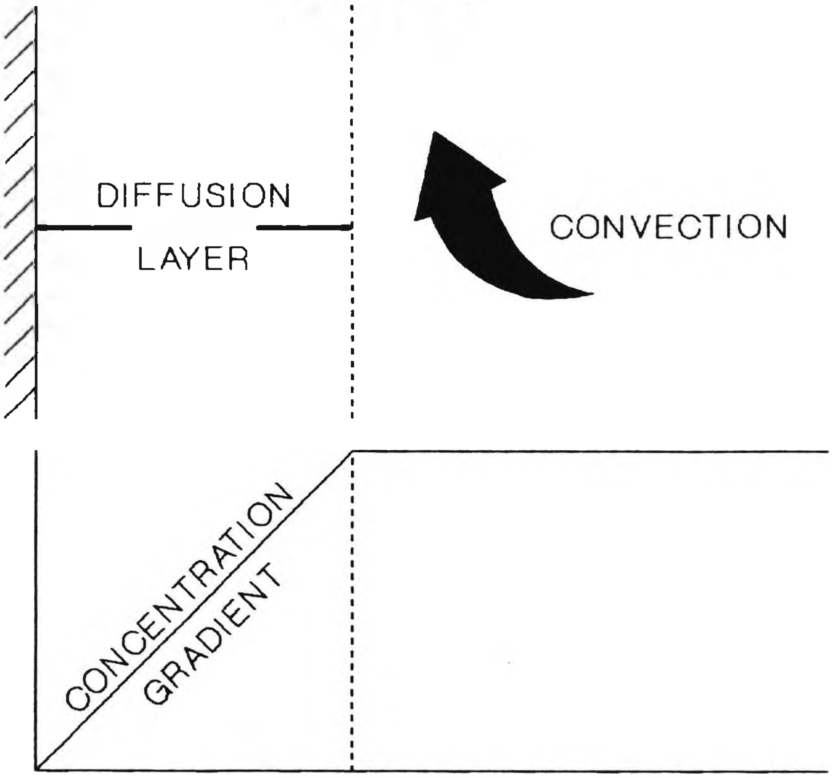


Diagram of Diffusion Layer Near to a Crystal/Solution Interface.

Table 2.1

INCREASING
DEGREE
OF IONIC
ASSOCIATION

Ions randomly distributed through the solution (totally dissociated).

Ions become associated with each other due to electrostatic attraction.

Stable clusters of ions form and become more extensive.

Localized areas of high concentration form as ionic clusters attract more ions and contract.

Stable crystal nuclei are formed from the clusters of ions.

Diffusion layer forms around nuclei. Ions diffuse to the surface of the nuclei and are incorporated into the crystal lattice.

Crystals form and continue to grow.

Small crystals aggregate to form larger particles.

V

Processes Involved in the Formation of Crystals.

2.2. The Precipitation of Calcium Oxalate

2.2.i. Introduction.

The experimental work on the precipitation of calcium oxalate was the first system which was studied as part of the work presented in this thesis. The reaction was originally chosen for investigation to provide experience of the various experimental and analytical techniques which are most commonly used to test the effects of the magnetic treatment of fluids on precipitation reactions. Calcium oxalate was picked as the subject for this investigation since no previous tests had been carried out with it and it is a 'well behaved' crystal system, having only one crystal form (tetragonal), unlike calcium carbonate which can exist in three different crystal forms. The oxalate is also less soluble than the carbonate (0.0067 g/l in cold water compared with 0.014 g/l for calcite).

The experimental test rigs used in the investigations were of the jacketed vessel type described in the previous chapter. A temperature-regulating device was used to maintain the solution temperatures at 25°C for all of the tests. The magnetic field was produced using 1" HDL units. For the control runs units of identical geometry containing non-magnetized rods were fitted. 0.01 molar calcium and oxalate stock solutions were made up for the experiments, using 1.47 g/l of $CaCl_2.2H_2O$ and 1.42 g/l of $(NH_4)_2C_2O_4.H_2O$. Different experimental procedures were used depending on the particular test which was being carried out. These procedures are described with the relevant results.

2.2.ii. Results.

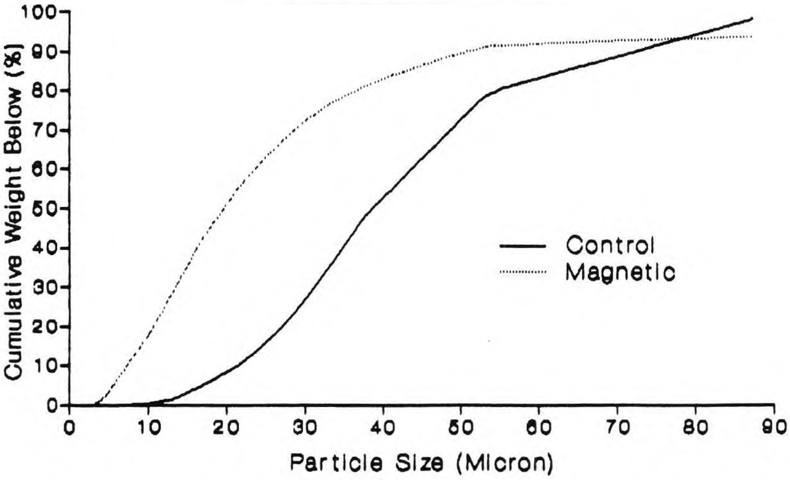
For the initial tests 500ml portions of the calcium chloride solution were circulated through magnetic and dummy units for several hours. After the circulation period, 500ml of the oxalate solution was added to the vessels and the mixtures were stirred for 20 minutes, after which samples of the oxalate suspension were removed. One of these was kept for particle size analysis. Another portion was filtered off on a sintered glass crucible with vacuum suction. The filtered solid was dried in an oven at 120°C for 24 hours and analysed by X-ray diffraction and electron microscopy. The filtrates were also kept for atomic absorption analysis. Many of the analyses which were carried out on the samples showed marked differences between the magnetic and control samples.

Particle Size Analysis Results.

The calcium oxalate suspensions obtained from the experiments were analysed using a Malvern Particle Size Analyzer. In every case the effect of the magnetic treatment was found to be a reduction in the particle size. There was also evidence for an increased degree of particle aggregation following treatment. Figures 2.3 and 2.4 are graphs of particle size distribution for typical control and magnetic runs. The results have been presented as both cumulative weight below vs. particle size and weight in band vs. particle size, since different information can be obtained on size distribution from the two presentation formats (see section 1.4.i).

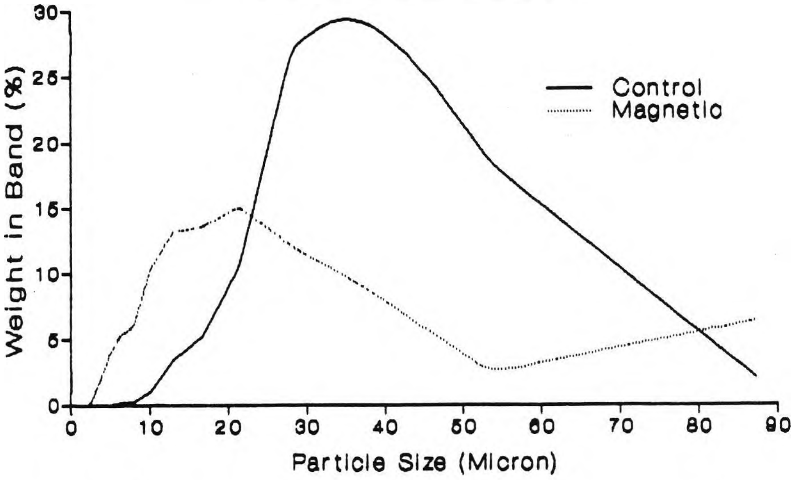
Figure 2.3 clearly shows the reduction in the particle size of the precipitate following the magnetic treatment. The mean particle sizes for the two samples, calculated from the graphs, were found to be 38.4 microns for the control run and 19.8 microns for the magnetic run, a reduction of 48%. The graphs also show that a greater number of large aggregated particles were produced, due to the magnetic treatment. This is demonstrated by the greater number of particles above the 90 micron range of the graph for the magnetic run.

Figure 2.3



Particle Size Distribution - Cumulative Weight Below.

Figure 2.4



Particle Size Distribution - Weight in Band.

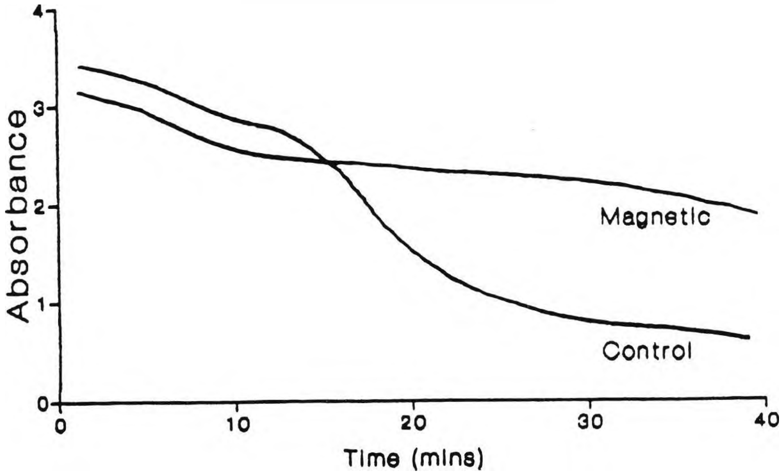
The second graph (Figure 2.4) allows more information to be gained on the distribution of the particle sizes. It can be seen that, for the control, the particles exist in a size band between 7 and 87 microns with a maximum at 35 microns. The plot also shows no appreciable aggregation of the crystals (98% of the particles being below 87 microns). For the magnetic run the particles were formed between 3 and 53 microns with a maximum at 21 microns. In this case there is clear evidence for aggregation giving particles above 53 microns. It is interesting to note that the plots both show similar changes of gradient between 0 and 20 microns, indicating the existence of 'preferential' growth sizes for the crystals.

Suspension Settling Rate Studies.

These tests were prompted by the findings of another member of the research group at City University. Demetriou (1988) had found that the settling rate of clay suspensions was affected by magnetic treatment. Experiments were set up to determine whether magnetic treatment would influence the rate at which calcium oxalate settled out of suspension. To achieve this a UV/visible spectrophotometer was used. Magnetic and control suspensions were placed into glass cells, shaken vigorously and positioned in the instrument. The spectrophotometer was set to measure the absorption of the sample at one particular wavelength, which gave a high absorption with calcium oxalate. Since it took some time to insert the test sample and start the machine, one minute was timed from when the shaking was stopped to when the analysis was started. As the suspended oxalate particles fell through the solution the absorption in the narrow light beam fell proportionately to the rate at which the suspension was settling. Figure 2.5 is a graph of absorbance against time for a typical run.

It can be seen that the particles in the control run settled at a much greater rate than those from the magnetic run. This is consistent with the differences found in the particle sizes, but the large difference between the rates suggests that an additional effect of the treatment is to cause the solids to remain in suspension for a longer time.

Figure 2.5



Graph of Absorbance vs. Time for Precipitate Settling Rate.

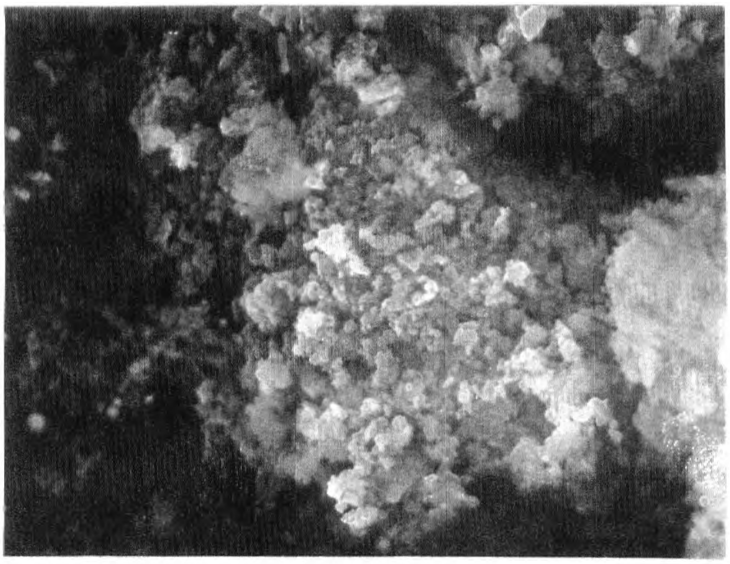
Electron Microscopy Studies.

The filtered, dried calcium oxalate samples were analyzed using electron microscopy. The resulting micrographs showed that the precipitated solid produced in the magnetic runs was less obviously crystalline than for the control experiments. The studies also showed a reduction in the particle size and an increased degree of particle aggregation following the treatment. Figure 2.6 is a typical electron micrograph of the precipitate formed during a control run and Figure 2.7 is representative of the micrographs obtained for the magnetic runs.

X-ray Diffraction Studies.

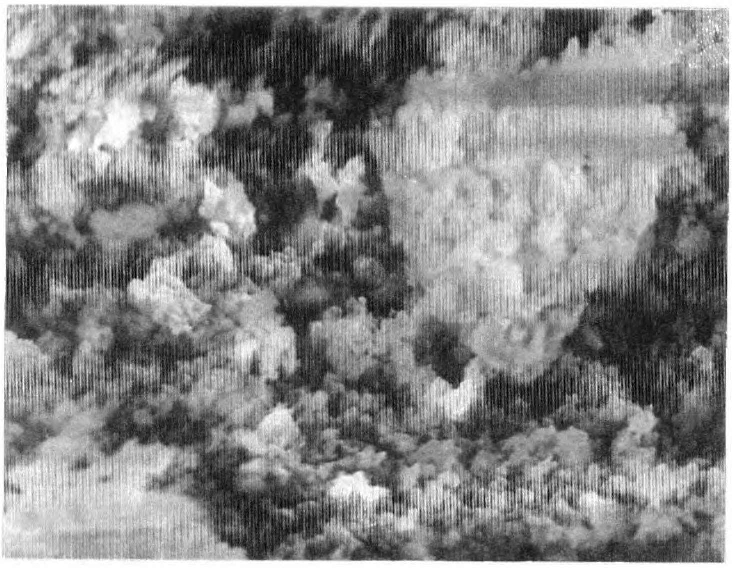
The solid samples obtained were characterized by X-ray diffraction, using a Philips PW1051 diffractometer with copper Kα radiation. Some indication of changes in the morphology of the precipitated calcium oxalate were detected by changes in the relative

Figure 2.6



Electron Micrograph (x3000) - Control Run Calcium Oxalate Sample.

Figure 2.7



Electron Micrograph (x3000) - Magnetic Run Calcium Oxalate Sample.

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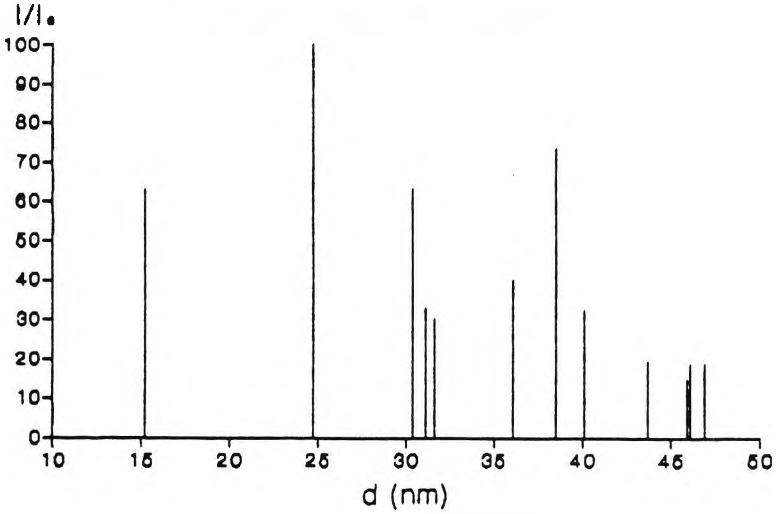
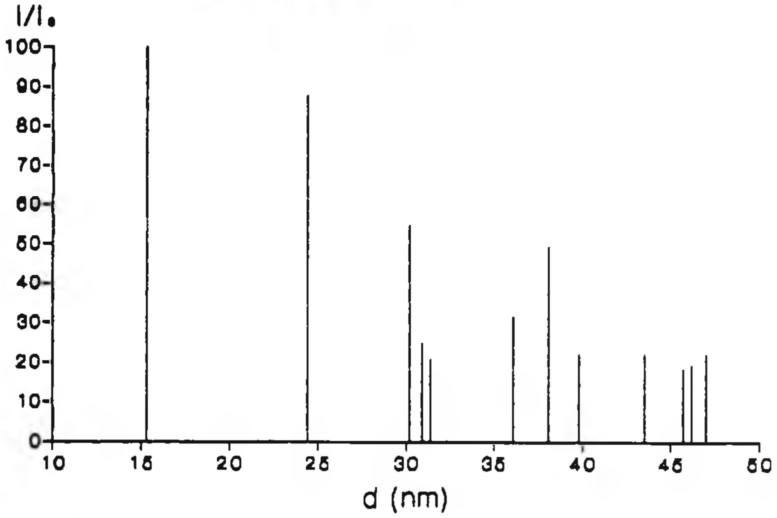
intensities of the reflections in the patterns. These changes in the intensities are due to differences in the external faces of the growing crystals giving different sample alignments. The external faces seen on a crystal are the slowest growing faces. Chemical addition can alter the relative growth rate of one set of crystal planes to another. One of the effects of magnetic treatment must, therefore, also be to alter the relative crystal plane growth rates.

Figure 2.8



X-ray Diffractogram - Control Run Sample.

Figure 2.9



X-ray Diffractogram - Magnetic Run Sample.

There is also evidence for a reduction in the unit cell dimensions for the magnetically treated samples (characterized by shifts to lower d-spacing values). Figures 2.8 and 2.9 show typical diffractograms for control and magnetic test runs. The changes in the relative intensities of some of the lines can clearly be seen (e.g. the lines at 15.2 and 24.5 nm). The unit cell dimensions for the crystals from the control run were calculated to be a_o = 121.6nm and c_o = 72.2nm. The corresponding values for the magnetic run were a_o = 120.8nm and c_o = 72.0nm.

Analysis of Residual Calcium.

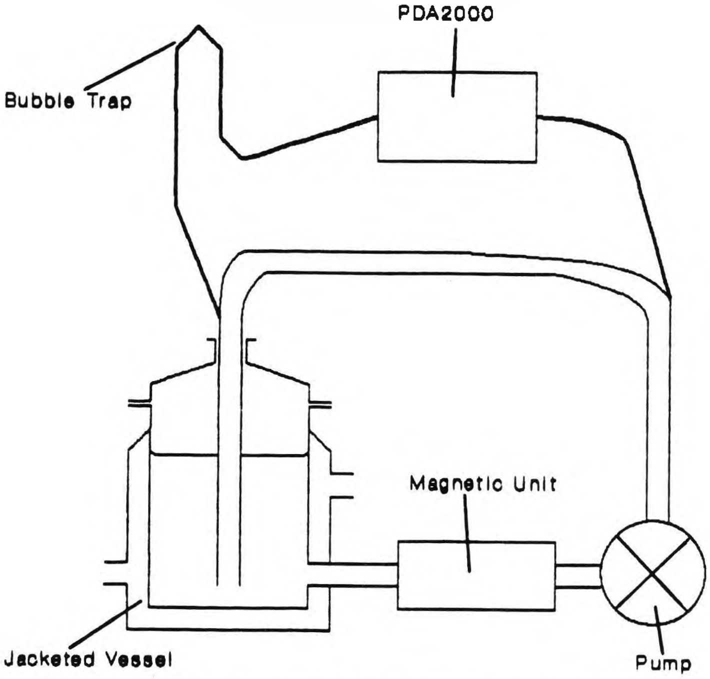
The residual calcium concentrations in the solutions, left after the oxalate suspensions had been filtered off, were determined by atomic absorption analysis. In every case the residual calcium concentration was found to be very low (between 2 and 4 ppm), which is consistent with the very low solubility of calcium oxalate in cold water. The treatment was found to have no significant or consistent effect on the residual calcium concentration, though this may have been due to the potentially high errors associated with such low values.

Photometric Dispersion Analysis.

These tests were carried out using a PDA2000 photometric dispersion analyzer. In order to use this instrument to monitor the effect of magnetic treatment on the precipitation of calcium oxalate, it was necessary to modify the test rig and experimental method.

The dispersion analyzer works by measuring changes in the intensity of a light beam passing through the circulating suspension. The Totton pumps, used to circulate the test solutions through the magnetic and control units, produced a great deal of turbulence and bubbles in the system. Clearly, any bubbles in the tubing would disrupt the output from the instrument and render any results obtained with it worthless. To overcome this problem a much smaller bore tube was attached to the main circulating tubing to divide the flow. A glass inverted U-tube was used as a bubble trap. The tubing was then passed through the flow cell block of the dispersion analyzer. This arrangement prevented bubbles from passing through the instrument and the flow rate through the light beam was reduced to within the operating range for the instrument. The test arrangement is shown in Figure 2.10.

Figure 2.10

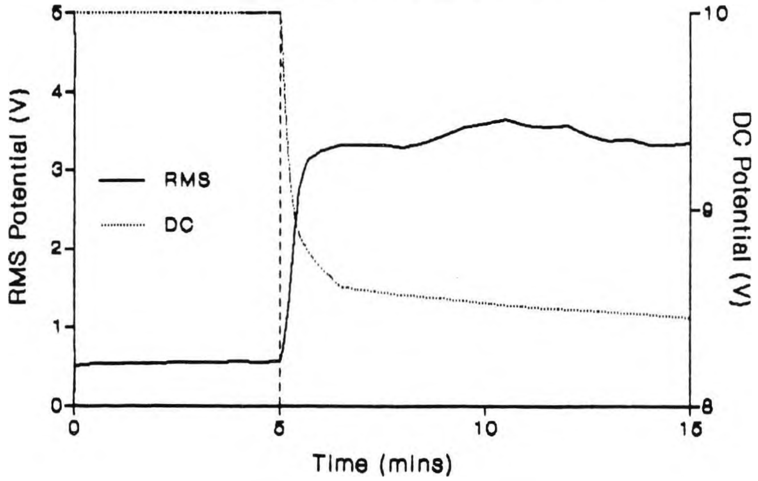


Modified Apparatus for Photometric Dispersion Analyses.

Many tests were carried out using this apparatus. For these experiments the oxalate solution was added to the vessel after five minutes and the circulation of the solution was continued. The results of these analyses were in very good agreement with the particle size results previously presented, i.e. the effect of the magnetic treatment was to give smaller particles. Figures 2.11 and 2.12 show typical results of control and magnetic test runs.

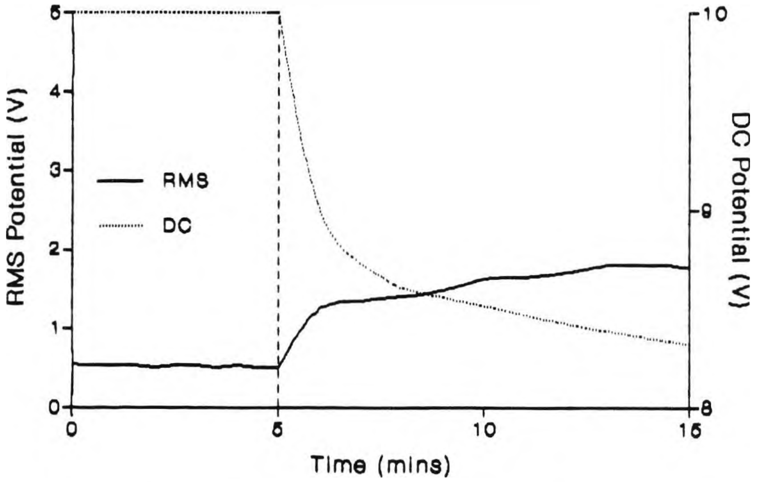
Several deductions, in addition to those on particle size, can be made from the graphs. For the control run the DC value fell very sharply immediately after the addition of the oxalate solution and continued to fall at a very slow rate for the remainder of the test. The RMS value, similarly, increased rapidly initially and then fluctuated slightly around a mean value after about two minutes. For the magnetic run the DC potential initially fell at a much slower rate than for the control, but then continued to decrease more slowly but faster than the corresponding rate for the control. This indicates that the precipitation rate was initially decreased after the magnetic treatment, but that the precipitation continued for

Figure 2.11



PDA2000 Graph - Control Run.

Figure 2.12



PDA2000 Graph - Magnetic Run.

a longer time. The RMS value for the magnetic run increased more slowly and to a lesser degree than for the control, but then continued to rise steadily for the remainder of the test. This is indicative of the smaller particle size and the increased degree of aggregation, caused by the magnetic treatment effect.

The rates of change for the DC values were calculated to give an indication of the magnitude of the effect. It was found that the initial rates of change were 0.95 V/min for the control run and 0.28 V/min for the magnetic run - a decrease of 71%. Comparing the final rates of change for the DC values (0.002 V/min for the control and 0.006 V/min for the test run) shows a three-fold increase following the magnetic treatment. There was also a 50% decrease in the maximum RMS value which is in excellent agreement with the particle size analysis results (i.e. the 48% reduction found for the mean particle size).

2.2.iii. Discussion.

The results of the analyses clearly show that magnetic treatment has a profound influence on the precipitation of calcium oxalate. This effect is characterized by changes in the rate of precipitation, the particle size, the degree of aggregation, the suspension settling rate and the morphology of the crystals.

The observed changes in the precipitate are consistent with a direct magnetic field-charge interaction of the type discussed in section 1.3.iii, i.e. one which influences the relative motion, and hence the association between the particles in solution. It is clear from the results that this influence is such that the processes involved in the subsequent nucleation and precipitation of the ions from the solution are disrupted. In order to explain these effects it is necessary to consider the distribution of ions and ionic clusters and their energies of association within the solution.

It is believed that clusters of ions form in a solution (see section 1.3.iii), giving areas of localized low and high concentration. These would exist in a range of sizes and stabilities. Some of the clusters would consist of a small number of ions, which may be associated with each other to a greater or lesser degree. Others would be much larger, with ions near to the centre of the cluster being more strongly associated with each other than those near to the periphery. The size, charge and concentration of the ions would, obviously, control the nature of these clusters within the solution. Therefore, the range of energies for these interionic interactions would be large and could be represented by a normal distribution curve.

If, as suggested, the magnetic field influences the motion of the ions, and hence their associations with each other, this would effect the particle distribution, described above, within the solution. Ions in the less stable clusters and those at the edges of larger clusters would become more dissociated, while the more stable clusters would either be largely unaffected, or could possibly be made more stable, due to the action of the magnetic field. The field may cause changes in the orientation and/or relative motion of ions in the more stable clusters, bringing about a greater degree of association between them. The overall effect of these phenomena would be to cause a decrease in the total number of clusters, an increase in the proportion of smaller (and possibly more stable) clusters, and an increase in the activity of the solution as a whole, due to the reduction in the degree of interionic association. This altered ionic distribution within the solution must be stable, since its effects are observed for a measurable period of time following the magnetic treatment.

In addition to the possibility of the magnetic field influencing the interionic associations, it is also possible that the nature or degree of the hydration sphere around the ions in solution could be affected. This idea is supported by the work of Dukhanin and Klyuchnikov (1973), who reported that the degree of hydration of Li^+, Mn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and $\underline{Ca^{2+}}$ was reduced by the application of a magnetic field with a magnetizing field strength of 1000 Oe. Effects of this type would also increase the activity of the ions in the solution.

Given the changes proposed above, it would be expected that the initial nucleation stage of the crystallization processes would be slowed down, due to the reduction in the number of clusters in the solution. However, once nucleation had finished, the rate of the subsequent incorporation of ions into the crystal lattice would be higher, since the rate of this process is diffusion controlled and the mobility of the ions would be increased as a consequence of their greater activity in the solution.

Both of the events described above were observed with the photometric dispersion analyses. The sharp initial fall in the DC values corresponds to the predominance of nucleation, due to the high level of supersaturation following the mixing of the two solutions. The slower rate of decrease characterizes the situation when spontaneous nucleation no longer occurs, due to the lower concentration, and the adsorption of ions onto the surface of the crystals is the predominant process. These events can be better understood by considering the first situation as occurring when the solution concentration is in the labile region and the second when it is in the metastable region of the solubility curves shown in Figure 2.1 on page 58.

The general increase in the proportion of smaller crystals would be due to both the larger proportion of smaller clusters and also the increased activity of the solution. The proposed alterations to the microscopic structure of the solution would also explain the observed changes in the morphology of the precipitated crystals. Any alteration to the stability, degree of association or orientation of the ions within the clusters would influence the subsequent nucleation and growth processes. It is well known that very small changes in a precipitating system can totally alter the morphology of the produced crystals (e.g. small additions of inhibitors can retard the growth along one particular set of planes). It would, therefore, be surprising if changes of the type suggested did not influence the morphology of the growing crystals.

Since the size and morphology of the precipitated particles were found to be altered by the magnetic treatment, it would be expected that the charge distribution on the surface of the crystals would also be changed. This would influence both the settling rate of the suspension and also the degree of aggregation of the crystals.

2.3. Scale Prevention and Removal in Domestic Expansion Boilers

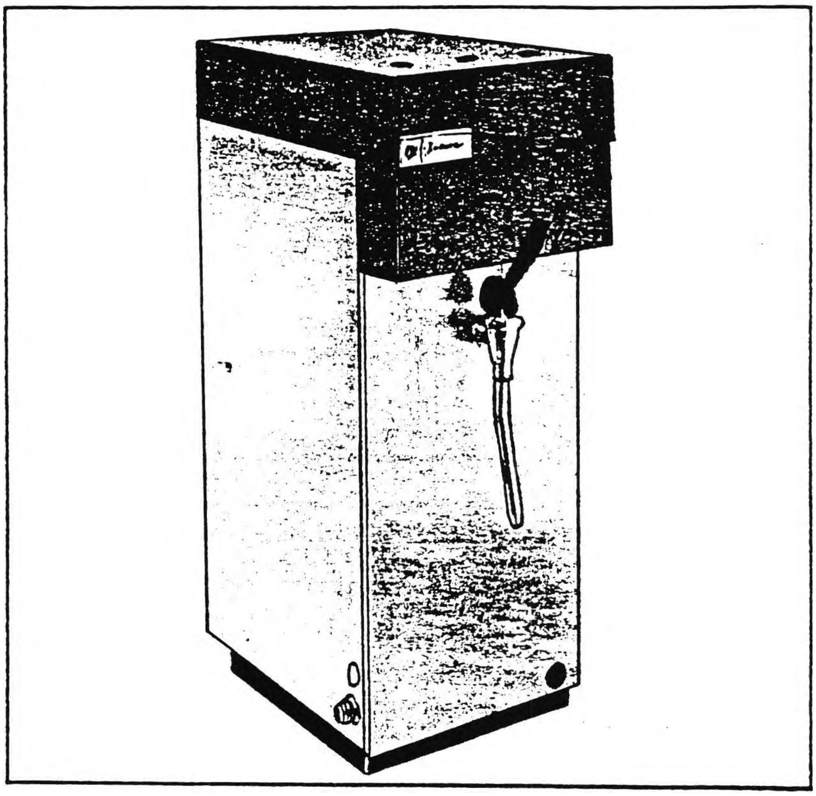
2.3.i. Introduction and Aims.

Investigations into the effects of magnetic fields on the scaling of boilers are very important to the work on magnetic treatment effect as a whole. Magnetic treatment devices were initially developed as boiler descalers (Parry, 1865) and by far the greatest number of them are still produced for this purpose (see Chapter 1). In this section the results of tests on scale prevention and removal in domestic water boilers by the magnetic treatment of fluids are presented. These investigations took place as part of an industrially sponsored trial of electrically heated expansion boilers. The boilers used in the study were of the JEM 20 type supplied by Jackson Catering Equipment Ltd. of Leeds. These, in common with all similar water heaters, suffer from scaling in hard water areas and the manufacturers recommend that complete descaling should take place every three months. This involves a complete strip down of the boilers and either mechanical or, in cases of extreme scaling, chemical and mechanical removal of the scale.

A JEM 20 boiler of the type used in the investigation is shown in Figure 2.13. The boiler consists of a tin-plate boiling chamber, an immersion tin-plated top plate, a rubber bonded stainless steel condenser, two immersion heaters totalling 3kW, and a solenoid water valve contained in a stainless steel outer casing.

The tests with the water heaters were carried out in two phases. The first of these was to determine whether a permanent magnetic field (produced by a HDL 1" magnetic unit) would inhibit or retard the formation of scale in an initially unscaled boiler. The second was to discover if the magnetic unit would perform as a scale removal device on an already scaled boiler.

Figure 2.13

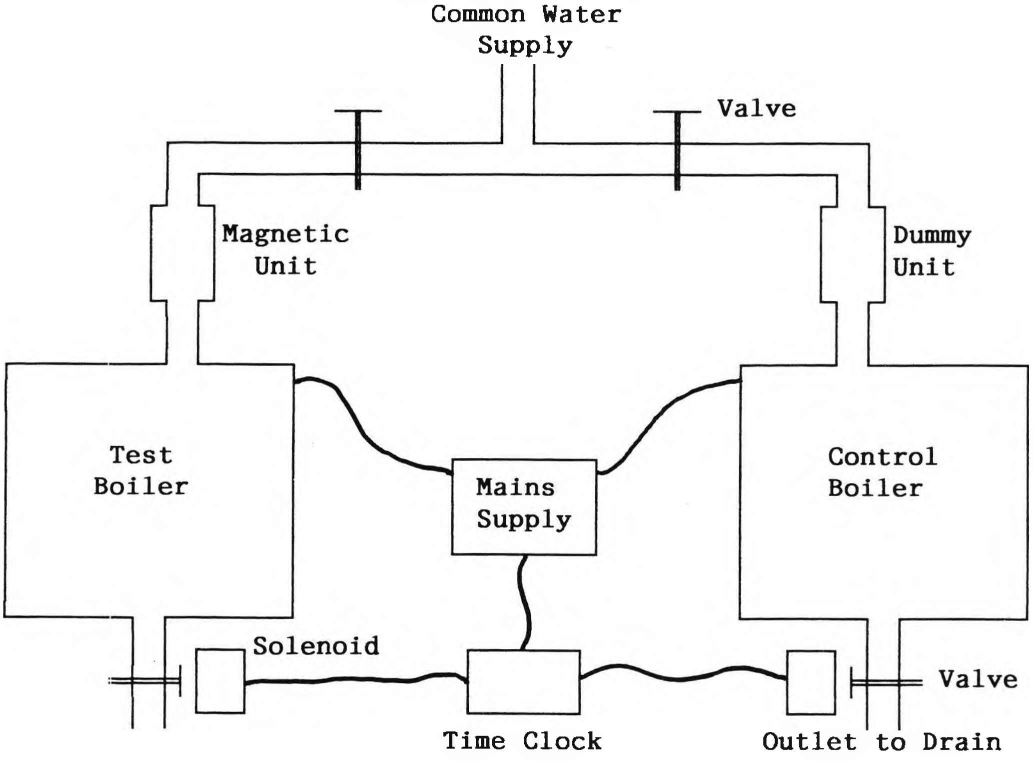


JEM 20 Expansion Boiler used for Scale Prevention Tests.

2.3.ii. Scale Prevention - Test Procedures and Results.

The two expansion boilers used in the tests were connected, following the manufacturer's instructions, to suitable common water and electricity supplies. The water inlets were fitted with valves so that the water pressures of the supplies to each of the boilers could be equalized. The boiler's outlets were fitted with solenoid water valves which were electrically connected, via a time switch, to the mains supply. The time switch was set so that, at certain time periods, the solenoid would open the valves and allow the hot water to be drawn off. In this way normal working conditions for the boilers were reproduced, while ensuring that both underwent exactly the same periods of heating and draw-off. One of the heaters (the test boiler) had an HDL copper housed 1" unit fitted in line with the inlet feed pipe. The control boiler had a dummy unit of identical geometry to the magnetic unit, but fitted with non-magnetized rods, connected in the same position and manner as the test unit. Figure 2.14 is a schematic diagram of the test arrangement.

Figure 2.14



Arrangement of Boilers for Scale Prevention Experiments.

The boilers were switched on and allowed to run under normal operating conditions for three weeks after which time they were dismantled and examined. The boiler containing the dummy unit had begun to scale up, while the test boiler showed no sign of any scaling. The boilers were reassembled and the test was continued for a further three weeks. The test was then stopped and the boilers were opened up again, inspected and photographed. Figures 2.15 and 2.16 show the collecting chambers of the control and test boilers and

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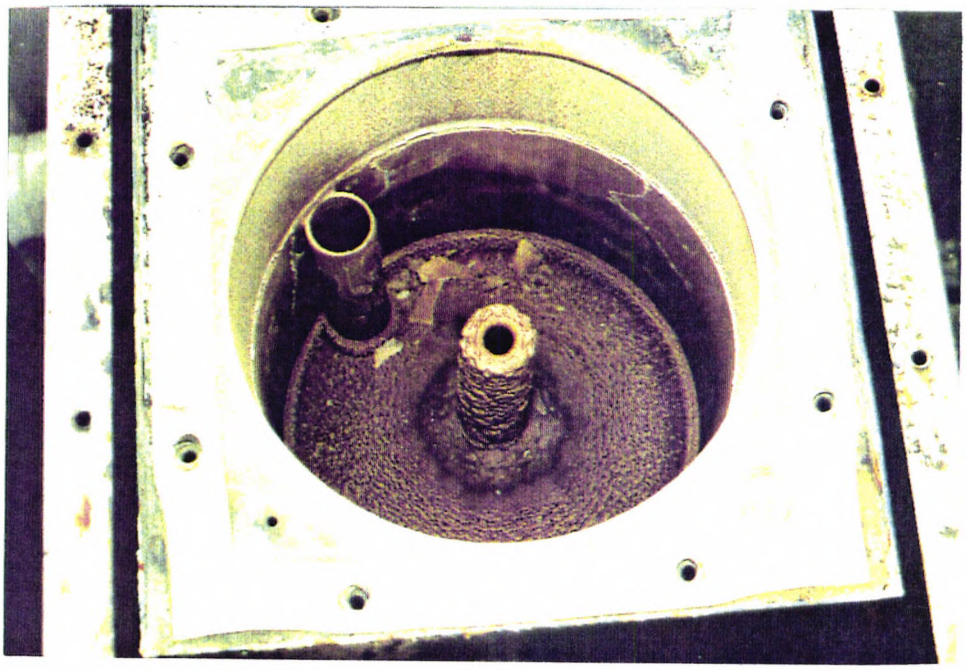
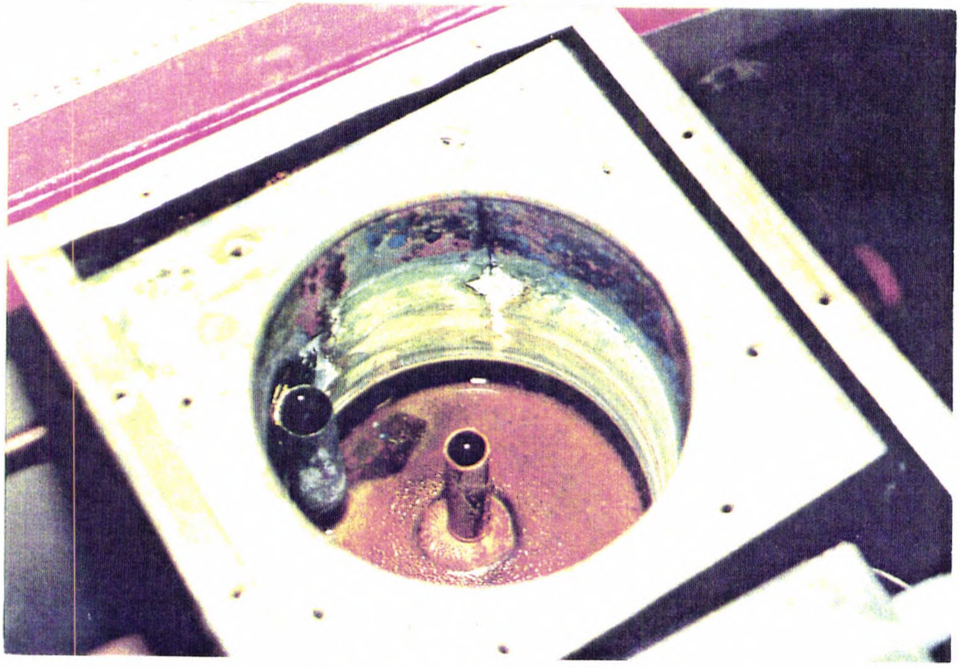
Figure 2.15



Control Boiler Collecting Chamber.

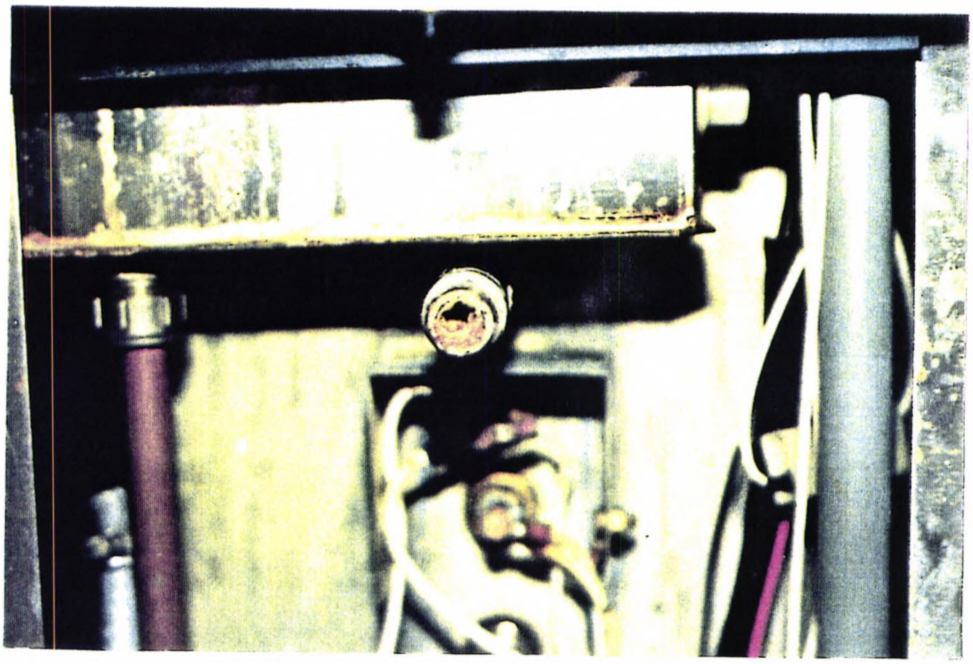
Figure 2.16



Test Boiler Collecting Chamber.

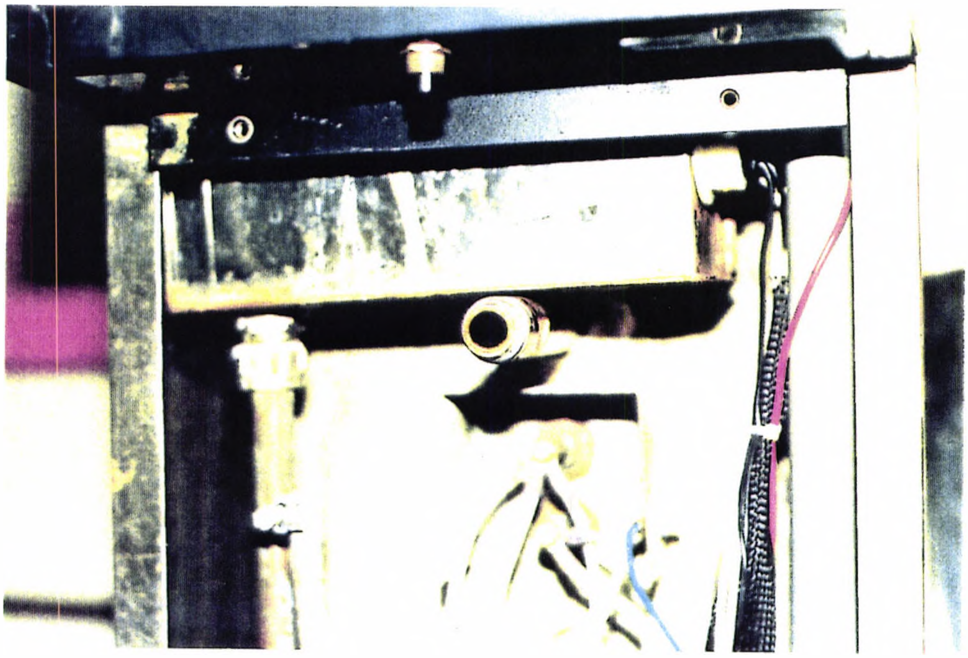
Figures 2.17 and 2.18 are of the draw-off pipes. It can be seen that the boiler fitted with the dummy unit had undergone a far greater degree of scaling than the one using magnetically treated water.

Figure 2.17



Control Boiler Draw-off Pipe.

Figure 2.18

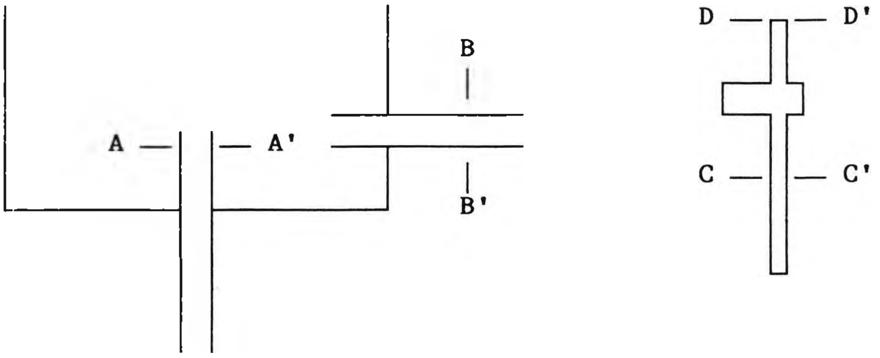


Test Boiler Draw-off Pipe.

The scale in the control was hard, compact and difficult to remove. That in the test boiler was soft, loose and was easily dislodged by hand.

In order to quantify the observations made concerning the scaling of the two boilers, the dimensions of various parts of each boiler and the total weights of scale deposited were determined. The measurements were taken for the positions shown in Figure 2.19 and are given in Table 2.2. The beneficial effect of the magnetic treatment can be easily seen from these results.

Figure 2.19



Collecting Box

Top Plate

Position of Measurements for Degree of Scaling Determination.

Table 2.2

Measured Dimension	Control Boiler	Test Boiler	Difference Between Control and Test
A-A'	26.50mm	20.00mm	6.50mm
B-B'	-	12.10mm	≈10.0 mm
C-C'	1.84mm	1.20mm	0.64mm
D-D'	1.30mm	1.20mm	0.10mm
Wt. of Scale	1038g	250g	788g

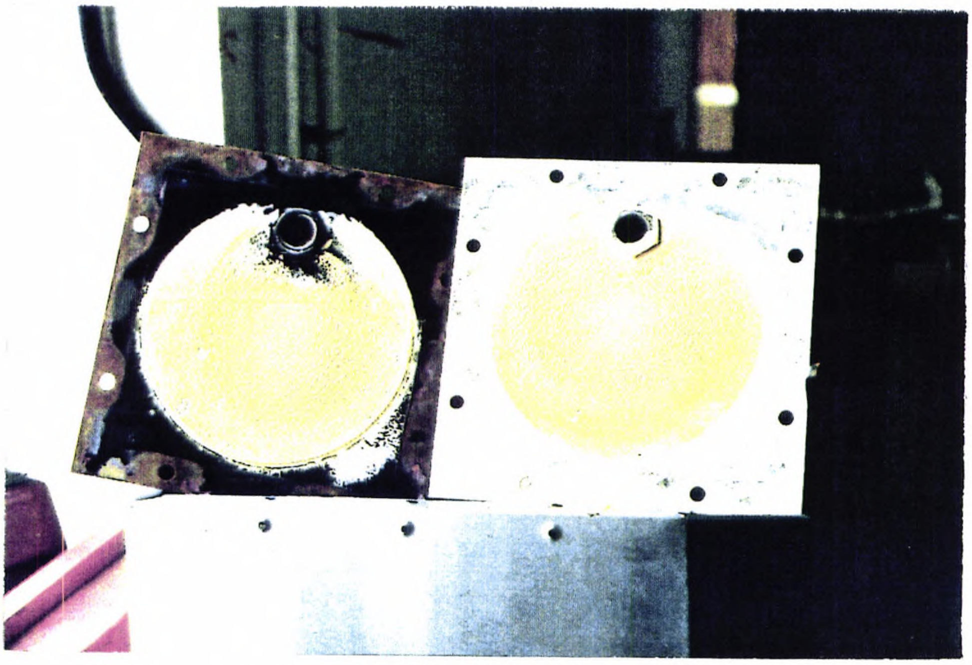
Dimensions Showing Degree of Boiler Scaling.

2.2.iii. Scale Removal - Test Procedures and Results.

The two boilers used for the previous investigation were completely dismantled and the parts thoroughly cleaned and descaled using dilute hydrochloric acid, distilled water and dilute sodium hydroxide. The boilers were then reassembled and set up as before, without the magnetic and control HDL units. After two weeks of continuous use the boilers were dismantled and inspected. Extensive scaling of the boiling chamber, collecting box, heating elements, circulating tube, draw off outlet and top plate was seen to have occurred. Due to their accessibility and particularly heavy scaling, the top plates were chosen as the test site for the investigation. The extensive scaling in this area of the boilers was due to the fact that the top plate came into contact with the hottest part of the system, the boiling chamber, and the coldest, the condenser. One of the boilers was chosen to be the test, and the other the control. The magnetic and control units were fitted in the cold water supply in the manner described previously. Figure 2.20 shows the scaled top plates of the boilers before reassembly (the control is on the left).

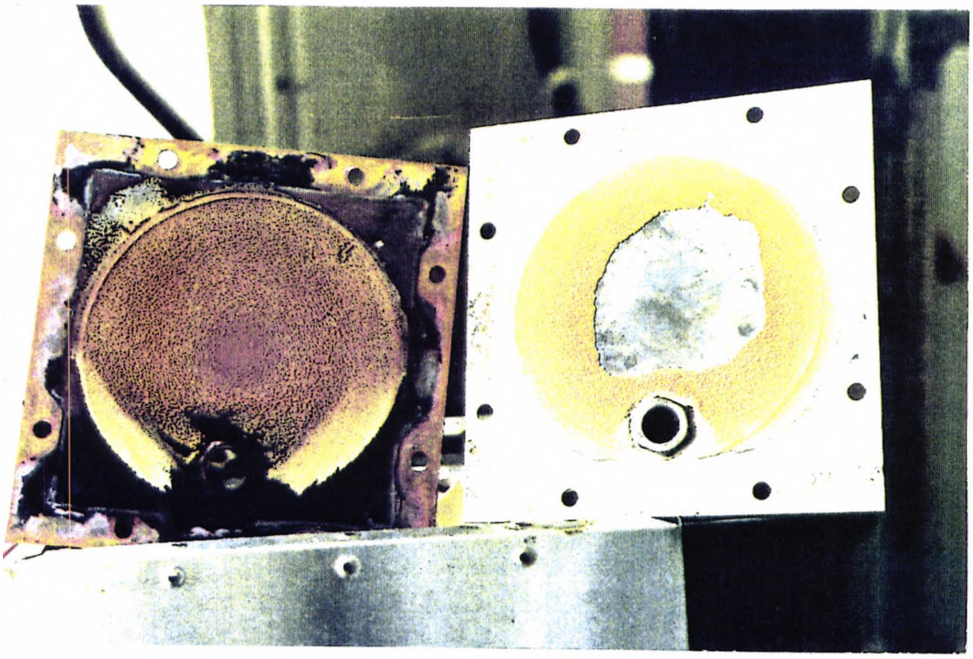
The boilers were operated, as before, for one month. After this time the boilers were again dismantled and examined for scaling. It was noticed immediately that the nature of the scale in the test boiler was different. The orientation of growth and the texture of the scale had changed. Also, it was seen that in places the scale had fallen off the metal surfaces and there was a pile of loose scale in the bottom of the boiling chamber and in the collecting box. The deposit in the control had, meanwhile, remained virtually unchanged. Figure 2.21 shows the top plates after one month. The effect of magnetic treatment can clearly be seen, with the top plate from the test boiler (right) showing flaking scale which had begun to fall off, while that from the control showed no marked change from when the test was started.

Figure 2.20



Boiler Top Plates Prior to Test.

Figure 2.21



Boiler Top Plates After One Month.

2.3.iv. Discussion.

The results of the two parts of the investigation have clearly shown that the magnetic units have a very beneficial effect on the scaling of the boilers. The magnetic treatment has been found to inhibit the deposition of scale and to bring about a degree of removal of existing scale. There is also evidence for a change in the nature of the deposits following magnetic treatment. No direct deductions can be made from the results concerning the mechanism by which the treatment influences the scaling of the heaters. However, the theory presented in the previous section can easily account for the observed effects, since changes in the ion/solution system of the type suggested, which have been shown to have a great effect on precipitation processes, would be expected to have a marked influence on the more complex phenomena associated with scale deposition.

2.4. The Precipitation of Barium Sulphate from Formation/Sea Water Mixtures

2.4.i. Introduction.

The experimental work on the precipitation of barium sulphate was carried out as part of a larger research project and was specifically designed to match the conditions likely to be encountered in off-shore oil rig situations. Prior to considering the research plan used in the work it is important to understand the specific scaling problems encountered in oil production facilities and the treatments which are currently being used to combat these problems.

One of the most serious scaling problems encountered in oil production facilities occurs when sea water, injected to maintain reservoir pressure, mixes with formation water in the oil-bearing rocks. This combination often results in the deposition of scale as the mixed fluids approach and enter the well-bore. The solid scales formed in off-shore production wells arise directly from the ions dissolved in the formation and sea waters and particularly from the levels of calcium, barium, strontium, sulphate and carbonate ions in solution. Some formation waters have a natural scaling potential but most of the problems arise when injected sea water breaks through to the producing wells. Mixing can also occur prior to the fluid entering the well-bore which can lead either to the entry of supersaturated barium or strontium sulphate or to the precipitation of these sulphates deeper in the formation rock structure.

A formation water will have a natural tendency to scale formation if it contains concentrations of all of the component ions of the scale in excess of the solubility of the scale material, i.e. when the product of the concentrations of the component ions exceeds the solubility product for the solid in the solvent. For example, the reported composition of the formation water at the Murchison oil field, in Table 2.3, shows levels of calcium and bicarbonate ions high enough to give calcium carbonate scaling in the well as the pressure reduces from the reservoir. However, it contains only low levels of sulphate ions and, because of this, does not have a natural tendency to form barium or strontium sulphate scale. The levels of Ba and Sr ions in this formation water would, however, lead to the precipitation of their sulphates if sea water break-through occurs. This is because sea water contains about 2,800 mg/l of sulphate ions. Under these circumstances the tendency to form sulphate scale will depend upon both the formation water composition and the degree of the sea water break-through.

Table 2.3

Ion	Ca^{2+}	Ba^{2+}	Sr^{2+}	HCO_3^-	SO_4^{2-}
Concentration (mg/l)	212	42	42	960	<5

Composition of Murchison Field Formation Water.

The scale build-up in the well-bore requires some form of treatment for maintenance purposes. The looser, more friable scales, including calcium carbonate, may be treated with wireline intervention, which mechanically breaks the scale off the host metal. The treatment is, however, expensive and does not provide a complete answer. By far the most common offshore scale problem results from barium sulphate. This is deposited as a very cohesive material and, consequently, resists removal by mechanical methods.

Even where mechanical removal is partially successful, the particles resulting from the break-up of the barium sulphate pose further problems. During the early processing and separation of the product train the barium sulphate has to be removed from the product and disposed of at an additional cost. This problem is increased further since many of the barium sulphate scales are radioactive due to radium leached from the formation rocks. Because of this there are only limited and costly disposal opportunities available to the operator. The material cannot be simply dumped either at sea or on-shore but must be disposed of by licensed disposal companies. In some cases reperforation of the well has been used in an attempt to bypass these problems.

Chemical methods of scale prevention are used in a number of different oil production operations. These methods fall into two main classes: (a) those designed to prevent scale formation through the injection of inhibitors by squeeze treatments or continuous injection, and (b) those designed to remove sulphate ions from the sea water used in the oil production processes. Details of these treatments can be found in the "Offshore Europe" conference papers published by the Society of Petroleum Engineers (see references).

Where neither mechanical scale removal nor efficient chemical treatment can be achieved, the operator would normally be required to carry out a full work-over of the well-bore. This is not an attractive proposition for the following reasons:

(1) It is very expensive, as it requires either the dismantling of the complete production string and subsequent mechanical removal of the scale from the components, or their replacement.

(2) It interferes with production, as it requires a total

well shut-down.

(3) It increases the risk of an accident because of the increased human involvement in the production processes.

It was because of the problems described above that the project to investigate the effect of magnetic treatment on the precipitation and propensity to scaling of barium sulphate was instigated.

2.4.ii. Aims and Experimental Methods.

The research described in this section was designed to determine whether barium sulphate precipitation (and hence scale formation) was affected by magnetic treatment. The research was specifically designed to match the conditions likely to be encountered when formation water meets sea water in off-shore oil rig situations. The present work was the preliminary part of the larger research programme mentioned earlier. The aim was to examine the effects of the magnetic treatment on barium sulphate precipitation from a number of different solution combinations, as follows:

(1) Both barium and sulphate in aqueous solutions.

(2) Both barium and sulphate in 2.9% NaCl solutions.

(3) Barium in aqueous solution and sulphate in a 2.9% NaCl solution.

(4) Barium in a saturated barium sulphate solution and sulphate in a 2.9% NaCl solution.

(5) Barium in aqueous solution and sulphate in a 2.9% NaCl solution containing calcium, strontium and bicarbonate ions.

For each of these solution combinations a series of six different experiments were performed. These are shown in Table 2.4, in which ——— M ———> and ——— O ———> represent a magnetically treated fluid and a non- magnetically treated fluid, respectively. In order to make the presentation of the experimental work results easier to follow, codes were assigned to each of the experiments.

Table 2.4

Experiment Number	Symbol used in Research Proposal		Code used for Samples
	Formation Water	Sea Water	
(i)	—— O ——>	<—— O ——	O-O
(ii)	—— M ——>	<—— O ——	M-O
(iii)	—— O ——>	<—— M ——	O-M
(iv)	—— M ——>	<—— M ——	M-M
(v)	O ↓		O
(vi)	M ↓		M

Codes used for Experiments on Barium Sulphate Precipitation.

The formation water test solutions used in the experiments were made up using 0.89g/l $BaCl_2.2H_20$, giving solutions containing 500ppm of Ba^{2+} ions. The sea water solutions contained 500 ppm of SO_4^{2-} ions, which were made up using 0.68 g/l of Na_2SO_4. The solutions containing calcium, strontium and bicarbonate ions were made up with the following concentrations, which were chosen to simulate typical sea water conditions:

320ppm Ca^{2+} (1.18g/l of $CaCl_2.2H_2O$),

33ppm Sr^{2+} (0.10g/l of $SrCl_2.6H_2O$), and,

2920ppm HCO_3^- (3.88g/l of $NaHCO_3$).

In order to distinguish between the different solution combinations tested, the following codes were used in addition to those given in Table 2.4:

Solutions in water - Code as given in table.

Solutions in 2.9% $NaCl_{(aq)}$ - '*' on solution code.

Solutions in saturated $BaSO_{4(aq)}$ - 's' on solution code.

Solutions containing other ions - '#' on solution code.

So, for example, if an experiment was carried out in which a formation water solution (containing barium), in distilled water, was circulated through a dummy unit and then mixed with a sulphate solution, in $NaCl_{(aq)}$, which had been magnetically treated, the code for the experiment would be O-M*. If an experiment was carried out in which a barium solution with sodium chloride was mixed with a sulphate solution in the presence of calcium, strontium and bicarbonate ions and then circulated through a dummy unit, the code would be *#O.

The test rigs used for the experiments were of the jacketed vessel type described in the introductory chapter. The temperature for all of the tests was maintained at 30°C. The magnetically treated solutions were circulated through HDL 1" magnetic units and the control solutions were passed through dummy units of identical geometry with non-magnetized bars.

The O-O, O-M, M-O and M-M tests were carried out using the following technique. The formation and sea water solutions were both circulated through the relevant units for one hour after which the pumps were switched off. 50ml portions of the two solutions were removed. The two solutions were then poured into a vessel together, with stirring. The stirring was continued for five minutes after which the barium sulphate suspension was divided into two portions which were prepared for various analyses.

The O and M tests were carried out in a very similar manner as that described above, with the same operations being carried out in the reverse order. 200ml portions of the two test solutions were stirred together in a vessel for five minutes. The resulting suspension was then transferred to the jacketed vessel of one of the test rigs and was circulated through the control or magnetic unit for one hour. The pump was then switched off and 100ml of the barium sulphate suspension was removed and divided into two portions which were prepared for the analyses.

One of the suspensions obtained from each run was used for particle size analysis. The other portion was filtered through a number 4 sintered glass filtering crucible using vacuum suction. The filtered barium sulphate was dried at 120°C for 48 hours and was then characterized by X-ray diffraction and electron microscopy. The solutions left after the filtration were analysed by atomic absorption spectroscopy (A.A.) to determine the residual barium content.

All of the experiments were replicated to ensure that any changes were not due to random variations between the tests. The results presented are, where applicable, the averages for several experiments. Where this was not possible (for example in the case of electron microscopy) representative results are given.

2.4.iii. Results.

Particle Size Analyses.

Since the six tests for each solution combination comprise two different experiments, the particle size results are presented as two separate graphs, the first for the O-O, O-M, M-O and M-M cases and the second for the O and M runs. The graphs of the particle size distributions are given in the two different formats discussed in section 1.4.i. Therefore, four particle size distribution (P.S.D) graphs for each solution combination are presented. For each figure these are numbered 1 to 4 as follows:

(1) P.S.D. graph for O-O, O-M, M-O and M-M runs as cumulative weight below vs. particle size.

(2) P.S.D. graph for O-O, O-M, M-O and M-M runs as weight in band vs. particle size.

(3) P.S.D. graph for O and M runs as cumulative weight below vs. particle size.

(4) P.S.D. graph for O and M runs as weight in band vs. particle size.

It was found that, for many of the weight in band vs. particle size graphs, there were three distinct peaks in the distribution curves (see section 1.4.i.). The positions and heights of these peaks were found to be influenced by both the different solution combinations used and also by the magnetic treatment. Any changes in the particle size could, therefore, be due to either changes to the sizes of these 'favourable' crystals or changes in their relative abundances. For example, a decrease in the mean particle size could be caused by a shift to the left of one of the peaks (i.e. a reduction in the preferential growth size) or an increase in the relative height of the smaller particle size peaks (i.e. an increase in the abundance of particles with that preferential size). In many cases both of these changes were seen to occur.

In order to quantify the particle size data for each set of experiments tables are presented giving the mean particle size, the percentage above 50 micron and the particle size and percentage weight at that size for the characteristic peak particle sizes described above. The values for the three peaks are labelled A, B and C in order of increasing particle size. A 'X' in any of these columns indicates that there was no peak at that size but that there was a change of gradient and a '-' indicates that there was not even a change of gradient in the graph at the expected point.

The results of the first set of experiments, with both the barium and sulphate in aqueous solution, are presented in Table 2.5 and Figure 2.22. It can be seen that, in every case, the effect of the magnetic treatment was to reduce the mean particle size of the barium sulphate crystals. The greatest change occurred when only the sulphate stream was treated (O-M case). The graphs of weight in band vs. particle size show that the particles were produced with two distinct preferential sizes. For the M-O and M-M runs the effect of the treatment was to decrease the preferential growth sizes and, to a lesser degree, reduce the abundances of particles with those sizes. For the M-M run the number of particles at the lower size was much increased, while very few were of the larger size. In addition to this there is evidence for a much increased level of aggregation in this case. Similar differences can be seen for the O and M runs. For the control there is also evidence of a third preferential growth size for the precipitate, of about 21 microns.

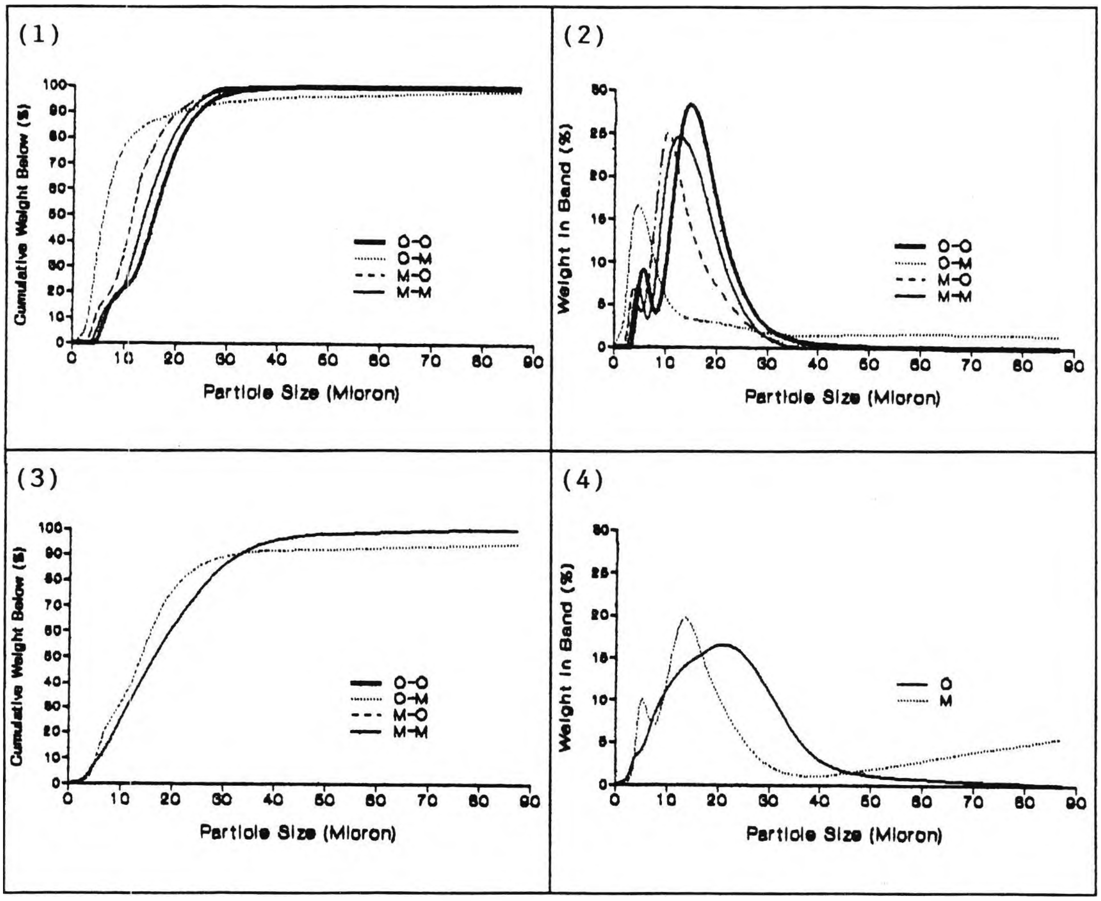
The results of the particle size determinations for the second set of experiments (those with both the barium and sulphate solutions in 2.9% NaCl) are presented in Figure 2.23 and Table 2.6. For the **O and **M runs the ranges of particle sizes were determined up to 260 microns, since for the magnetic run there was evidence of a great deal of aggregation giving particles much larger than 50 microns. It appears, from the graph of cumulative weight below vs. particle size, that for these runs the magnetic treatment actually brought about an increase in the particle size. The second representation of the results, however, shows that this was, in fact, due to the much increased degree of aggregation in this case. The graphs show that

Table 2.5

Run	Size (Abundance) for Peak: [µm (%)]			Mean Particle Size (µm)	Weight Over 50 µm (%)
	A	B	C		
O-O	5.8 (9.1)	14.7 (28.2)	-	15.8	0.0
O-M	4.8 (16.5)	X	-	6.2	3.9
M-O	4.1 (6.8)	10.6 (25.2)	-	11.6	0.0
M-M	4.8 (7.0)	12.3 (24.6)	-	14.0	0.0
O	X	X	21.2 (16.5)	16.6	0.5
M	5.5 (10.1)	13.2 (19.7)	-	14.0	7.9

Characteristic Particle Size Data - Both Barium and Sulphate in Aqueous Solution (X-Y).

Figure 2.22



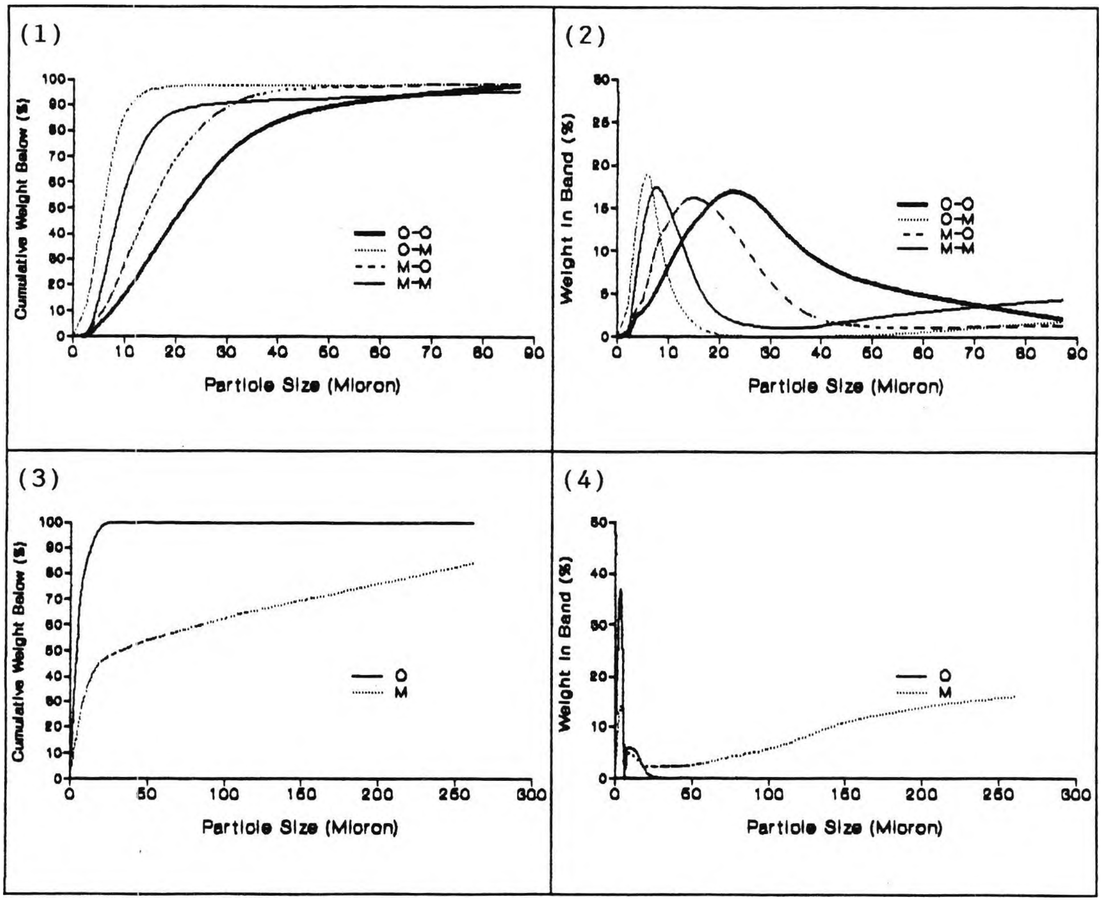
Particle Size Distribution Graphs - Both Barium and Sulphate in Aqueous Solution (X-Y).

Table 2.6

Run	Size (Abundance) for Peak: [µm (%)]			Mean Particle Size (µm)	Weight Over 50 µm (%)
	A	B	C		
O-O	X	-	22.9 (16.9)	21.2	10.6
O-M	6.2 (18.9)	-	-	5.8	0.5
M-O	X	15.1 (16.1)	-	14.4	1.6
M-M	7.5 (17.3)	-	-	8.9	7.3
O	4.6 (36.9)	9.1 (6.0)	-	4.8	0.0
M	4.6 (14.1)	8.0 (4.7)	-	32.1	46.2

Characteristic Particle Size Data - Both Barium and Sulphate in 2.9% NaCl$_{(aq)}$ (X*-Y*).

Figure 2.23



Particle Size Distribution Graphs - Both Barium and Sulphate in 2.9% NaCl$_{(aq)}$ (X*-Y*).

the barium sulphate crystals were produced in three distinct size bands. As was the case with the previous experiments, the effect of the magnetic treatment was found to be a decrease in the particle size, which was greatest when the sulphate stream alone was treated $(O^{*}-M^{*})$. There was also evidence for an increased degree of aggregation of the crystals.

The third set of experiments was carried out with the barium in aqueous solution and the sulphate in a 2.9% sodium chloride solution. Similar observations were made concerning the particle sizes of the precipitated barium sulphate produced following treatment, i.e. the crystals were smaller and were preferentially produced in the lower size bands (maxima). The results of the analyses are presented as graphs in Figure 2.24 and the characteristics of the graphs are given in Table 2.7.

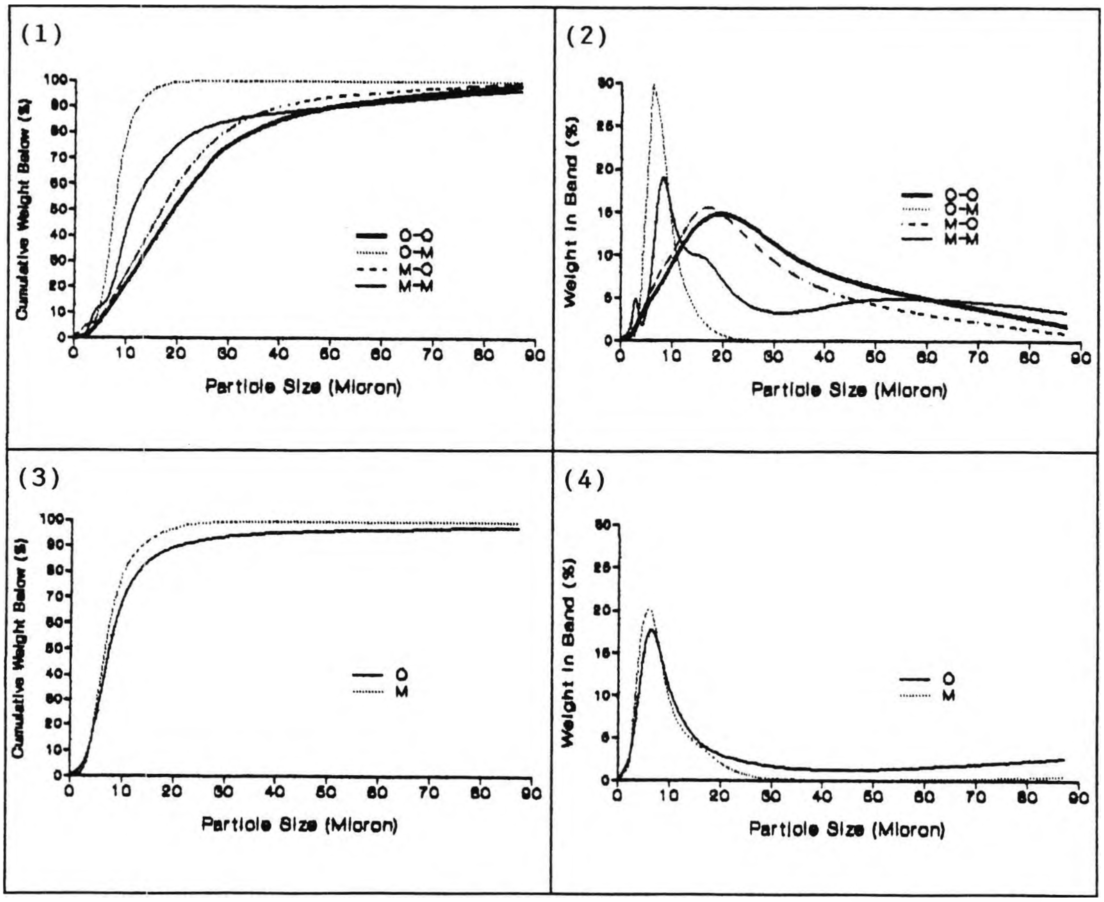
Slightly different results from those obtained previously were found for the fourth set of tests, in which the barium was in a saturated barium sulphate solution and the sulphate was in a 2.9% NaCl solution. The results of the analyses are given in Table 2.8 and Figure 2.25. The effect of magnetic treatment on the sulphate solution alone $(O^{s}-M^{*})$ was a marked decrease in the particle size, as was found in the previous cases, but the treatment of the barium solution $(M^{s}-O^{*})$ and both solutions $(M^{s}-M^{*})$ had a much reduced effect. The control run for these tests $(O^{s}-O^{*})$ showed a much greater propensity to particle aggregation than had previously been observed and the magnetic runs showed a lower degree of aggregation. The tests in which the solutions were mixed prior to treatment $({}^{s*}O$ and ${}^{s*}M)$ gave the same effects as had been seen with the earlier experiments, i.e. a small reduction in particle size and an increased degree of aggregation.

Table 2.7

Run	Size (Abundance) for Peak: [µm (%)]			Mean Particle Size (µm)	Weight Over 50 µm (%)
	A	B	C		
O-O	-	-	19.9 (14.9)	19.2	10.2
O-M	2.4 (0.8)	6.3 (29.8)	-	7.5	0.0
M-O	-	-	17.1 (15.7)	17.1	6.3
M-M	3.1 (4.8)	8.2 (19.1)	X	11.2	10.3
O	-	6.5 (17.7)	-	7.5	3.9
M	-	6.2 (20.1)	X	6.5	0.0

Characteristic Particle Size Data - Barium in Aqueous Sol^n and Sulphate in 2.9% NaCl$_{(aq)}$ (X-Y*).

Figure 2.24



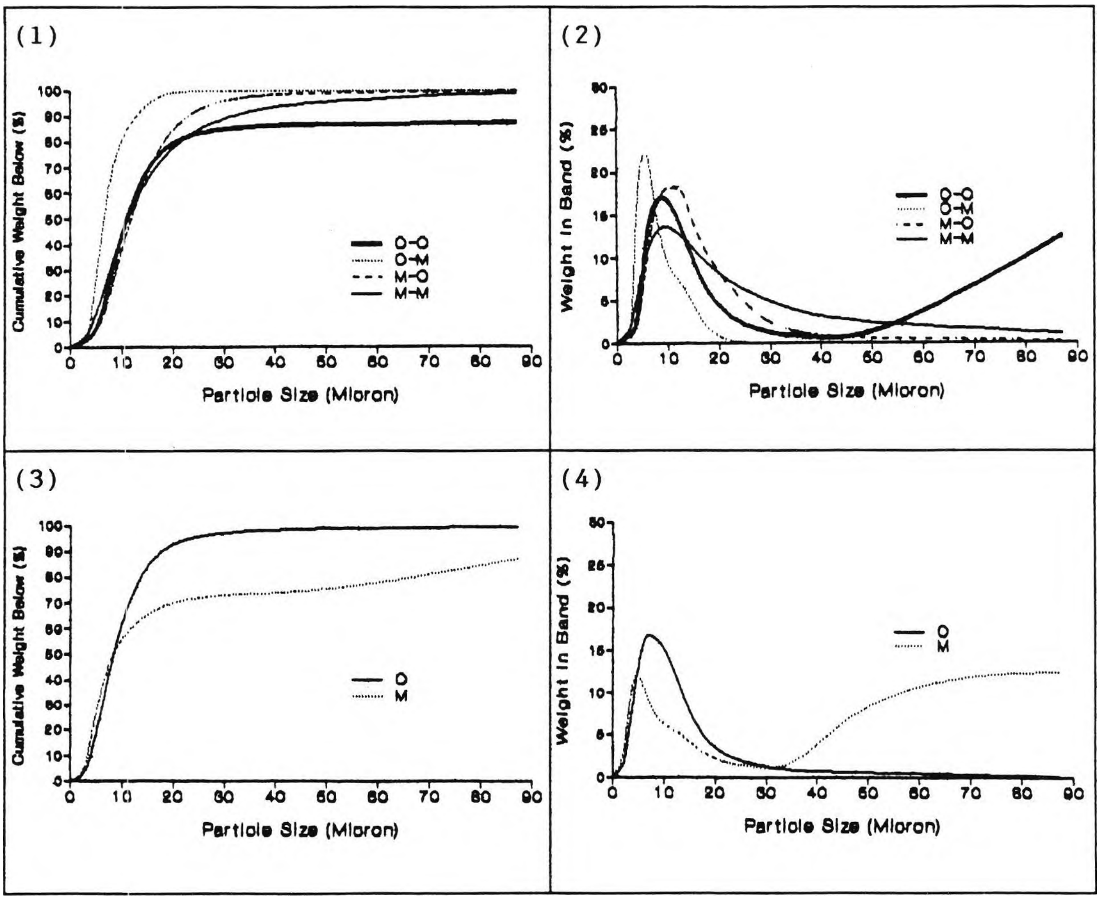
Particle Size Distribution Graphs - Barium in Aqueous Sol^n and Sulphate in 2.9% NaCl$_{(aq)}$ (X-Y*).

Table 2.8

Run	Size (Abundance) for Peak: [μm (%)]			Mean Particle Size (μm)	Weight Over 50 μm (%)
	A	B	C		
O-O	X	8.9 (16.9)	-	9.6	13.4
O-M	5.5 (22.1)	X	-	6.7	0.0
M-O	X	10.9 (18.5)	-	11.6	0.8
M-M	X	9.9 (13.7)	-	9.6	4.4
O	-	7.5 (16.9)	-	8.6	0.8
M	4.8 (12.0)	X	-	8.6	24.6

Characteristic Particle Size Data - Barium in Saturated $BaSO_{4(aq)}$ and Sulphate in 2.9% $NaCl_{(aq)}$ (X^s-Y^*).

Figure 2.25



Particle Size Distribution Graphs - Barium in Saturated $BaSO_{4(aq)}$ and Sulphate in 2.9% $NaCl_{(aq)}$ (X^s-Y^*).

The particle size distribution graphs and characteristic data for the final solution combination tested (barium in aqueous solution and sulphate in 2.9% $NaCl_{(aq)}$ with calcium, strontium and bicarbonate ions) are given in Table 2.9 and Figure 2.26. Many of the features observed with the previous runs can be seen and, as before, the effect of the treatment was a reduction in the particle size. The greatest effect was again seen with the O-M$^{\#}$ case.

Electron Microscopy Studies.

The filtered and dried barium sulphate samples obtained from the tests were analysed using electron microscopy. The resulting micrographs showed crystal size distributions which were in excellent agreement with the results of the particle size analyses, i.e. a reduction in particle size following magnetic treatment. The analyses showed that the solution combination used for the test, in addition to the magnetic treatment, had a marked effect on the size (and in some cases crystallinity and morphology) of the crystals. The preferential growth sizes for the crystals, which were characterized by the peaks in the particle size distribution curves, were also clearly seen in the micrographs.

The micrographs presented are representative of the analyses which were carried out. Figure 2.27 was taken at a magnification of 300x for the **M run [see Table 2.6 and Figure 2.23 (3) and (4)]. It shows one of the aggregated masses which were identified by their particle size analyses.

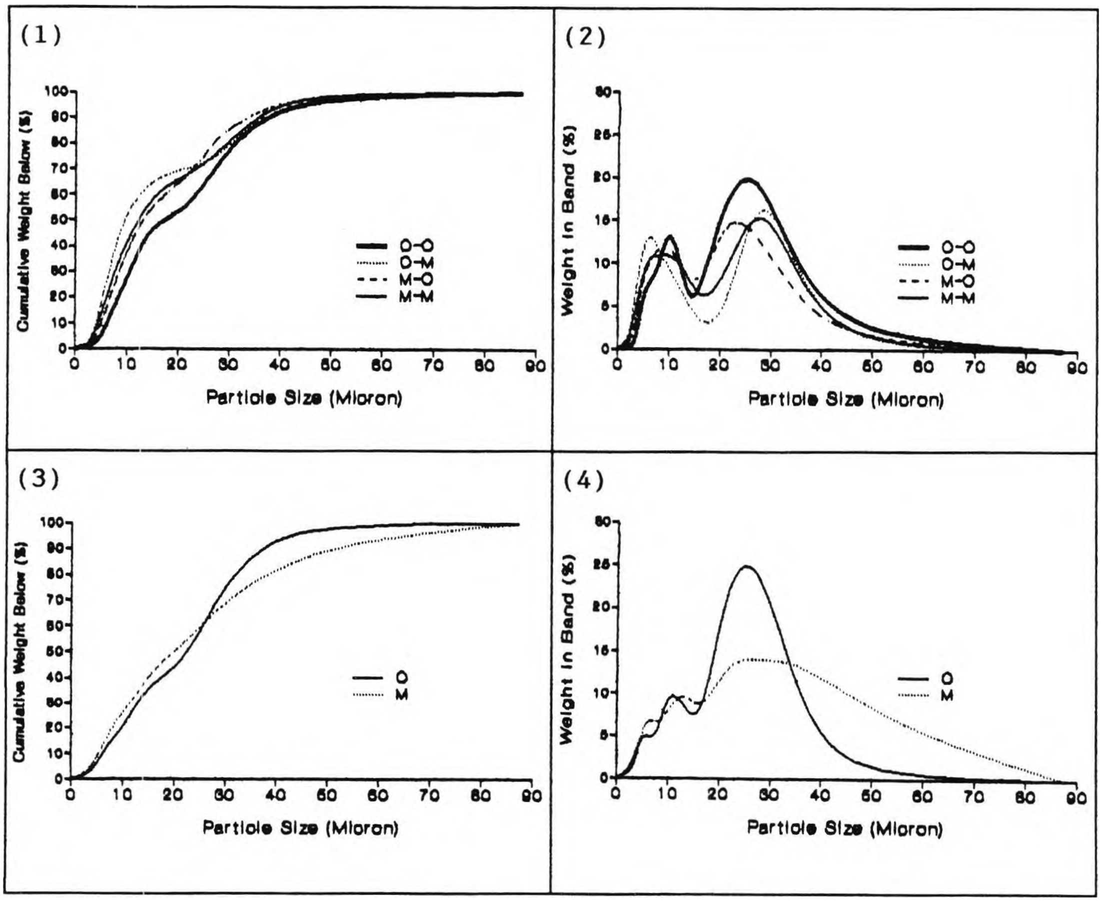
All of the remaining micrographs were taken with a magnification of 1000x. Figures 2.28 to 2.30 are micrographs of O-O, O^{s}-O* and O-O$^{\#}$ runs; these show the effect of different solution combinations on the morphology of the crystals. Figure 2.31 shows the crystals

Table 2.9

Run	Size (Abundance) for Peak: [μm (%)]			Mean Particle Size (μm)	Weight Over 50 μm (%)
	A	B	C		
O-O	X	10.1 (12.9)	25.4 (20.0)	17.2	3.2
O-M	6.2 (12.9)	-	28.5 (16.1)	9.6	1.2
M-O	X	9.6 (11.9)	23.4 (14.7)	13.1	1.6
M-M	6.9 (10.9)	9.6 (11.0)	27.8 (15.3)	12.0	1.2
O	4.8 (4.8)	9.6 (9.7)	25.1 (25.0)	22.7	1.9
M	6.2 (6.7)	12.7 (9.7)	24.0 (14.1)	19.9	10.6

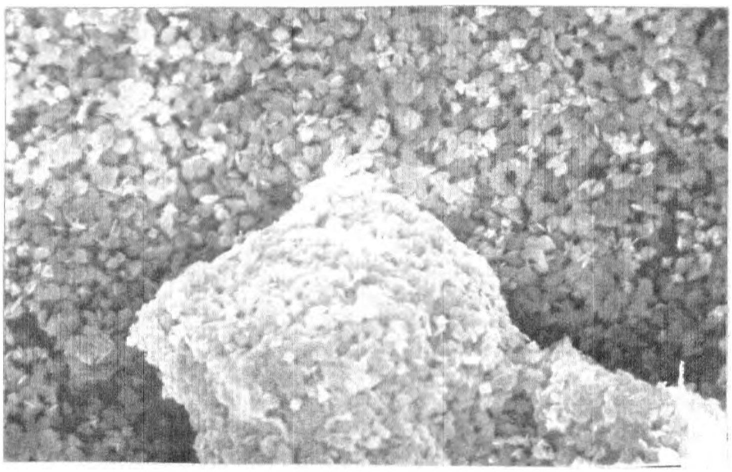
Characteristic Particle Size Data - Barium in Aqueous Sol^{n} & Sulphate in 2.9% NaCl$_{(aq)}$ with Ca^{2+}, Sr^{2+}, HCO_3^- (X-Y#).

Figure 2.26



Particle Size Distribution Graphs - Barium in Aqueous Sol^{n} & Sulphate in 2.9% NaCl$_{(aq)}$ with Ca^{2+}, Sr^{2+}, HCO_3^- (X-Y#).

Figure 2.27

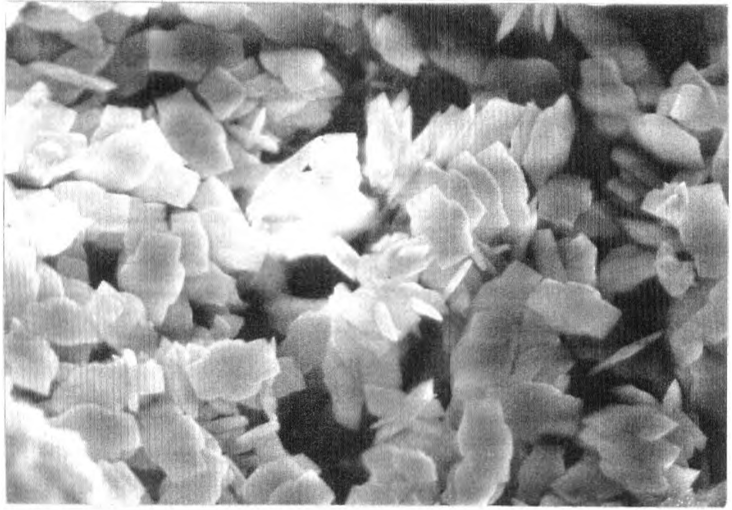


Electron Micrograph (x300) of **M Run Sample.

Figure 2.28

Electron Micrograph (x1000) of O-O Run Sample.

Figure 2.29



Electron Micrograph (x1000) of O^s-O* Run Sample.

Figure 2.30

Electron Micrograph (x1000) of O-O# Run Sample.

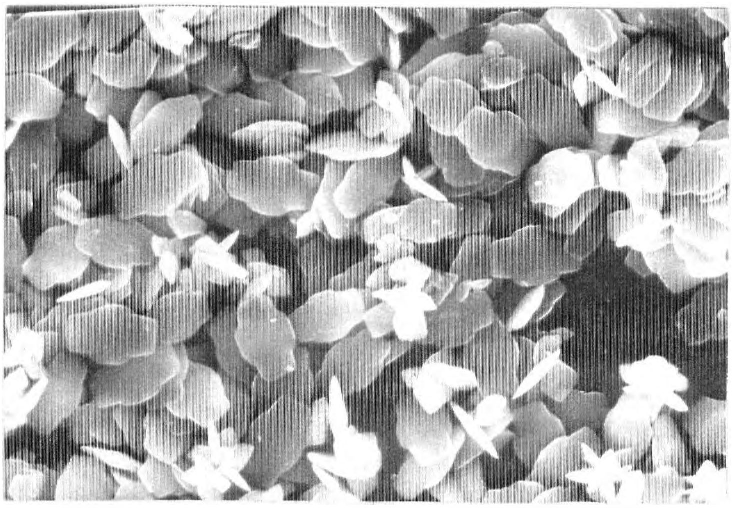
Figure 2.31

Electron Micrograph (x1000) of M-M# Run Sample.

for the M-M# case (compare with Figure 2.30). It can be seen that, in this case, the effect of magnetic treatment was to both reduce the particle size and alter the morphology of the particles.

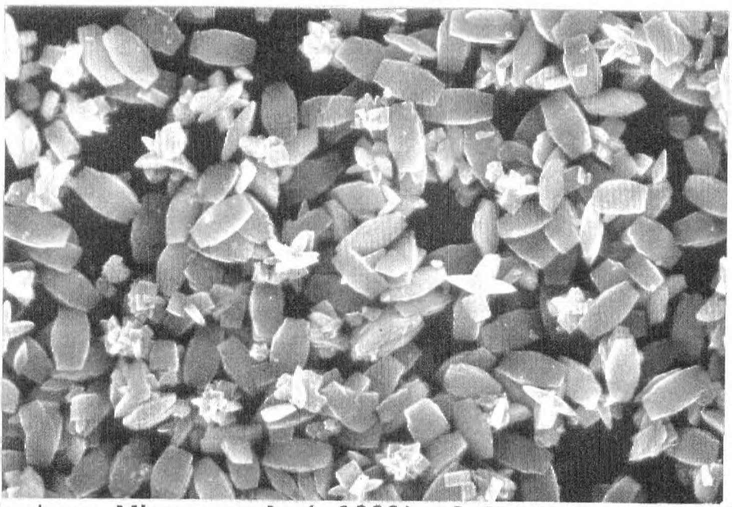
Figures 2.32 to 2.35 are for the O-O*, O-M*, M-O* and M-M* runs. The differences between the particle sizes which can be identified in the micrographs are in very good agreement with the particle size data given in Table 2.7 and Figure 2.24. In addition there is also evidence for changes in the relative dimensions of the crystals, which is shown by a reduction in the relative length of the longest axis of the crystals. This can be seen to be particularly pronounced for the O-M* run. Figure 2.36 shows the crystal growth habit of a barium sulphate crystal. The ratios of the a and b axes were determined for five crystals chosen at random from each of the four

Figure 2.32



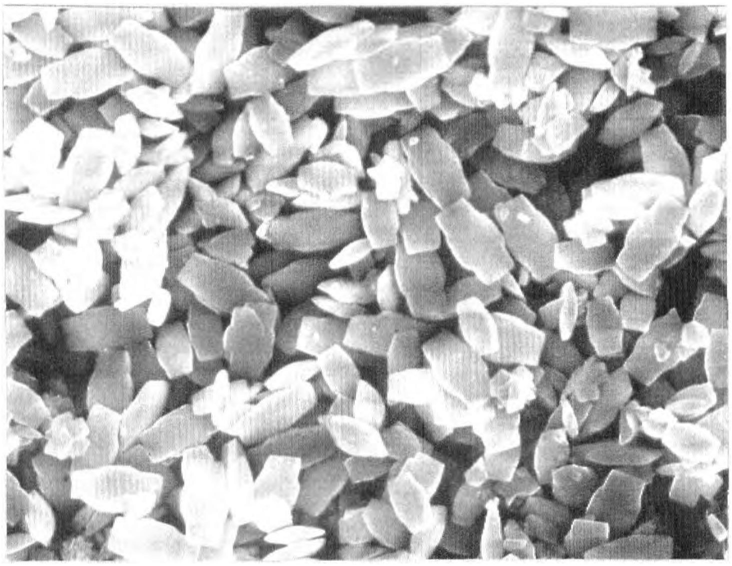
Electron Micrograph (x1000) of O-O* Run Sample.

Figure 2.33



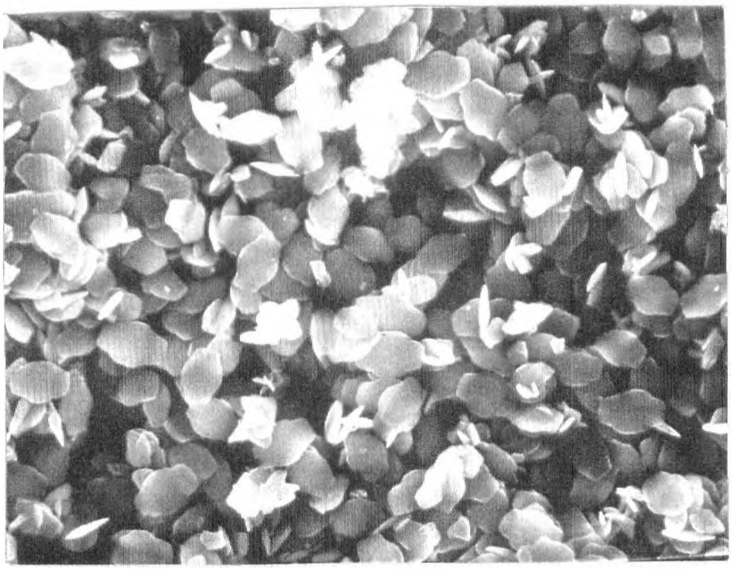
Electron Micrograph (x1000) of O-M* Run Sample.

Figure 2.34



Electron Micrograph (x1000) of M-O* Run Sample.

Figure 2.35



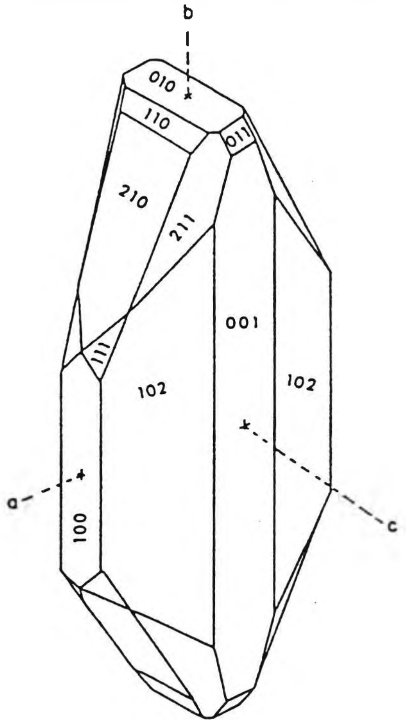
Electron Micrograph (x1000) of M-M* Run Sample.

micrographs. The average b/a ratios were calculated to be:

O-O* = 1.497; O-M* = 1.896; M-O* = 1.798; M-M* = 1.471

So the magnetic treatment appears (for the O-M* and M-O*) to either inhibit growth along the a axis or promote preferential growth along the b axis. It is interesting to note, in light of these findings, that the function of organophosphorus inhibitors is to decrease the preferential growth along (010), i.e. the b axis.

Figure 2.36

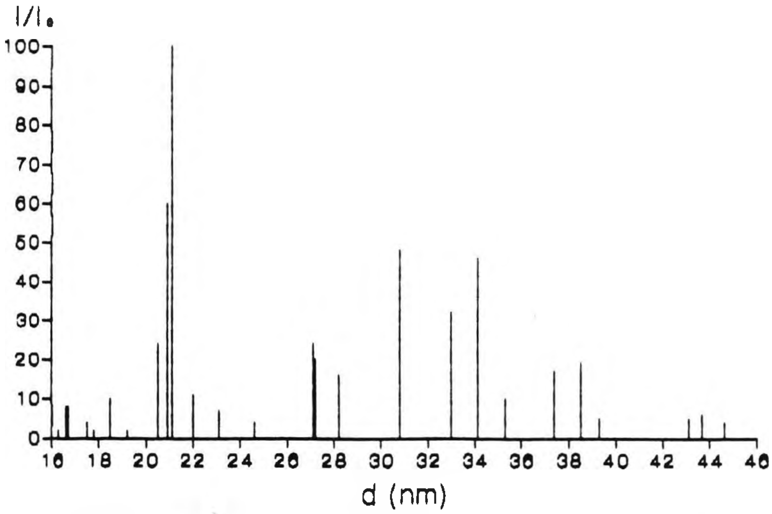


Crystal Growth Habit of Barium Sulphate.

X-ray Diffraction Studies.

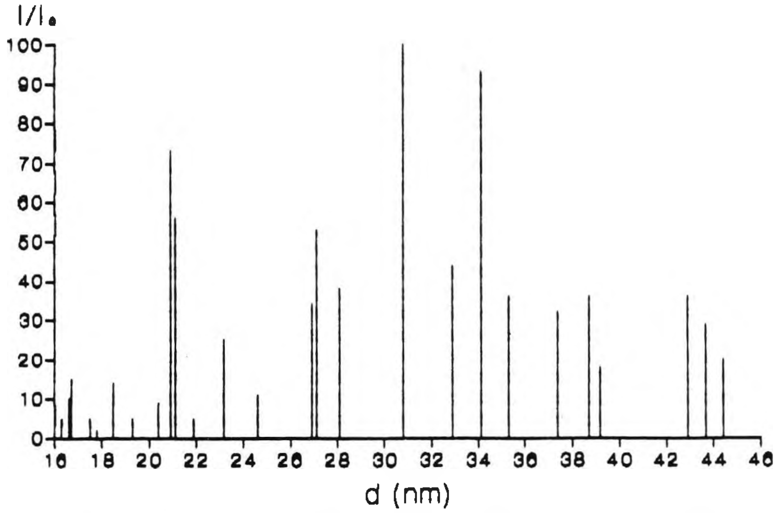
The changes in the morphology of the precipitated barium sulphate which were seen in the electron micrographs, were also detected by changes in the relative intensities of the reflections in the X-ray patterns. The differences between the intensities for the control and test samples are due to different sample alignments, caused by differences in the external faces of the growing crystals. So, one of the effects of magnetic treatment must be to alter the relative crystal plane growth rates. These effects can be seen in Figures 2.37 to 2.40 which are the diffractograms for the O-O, M-M, O-O# and M-M# runs, respectively. Figure 2.41 is the diffractogram for X-ray grade $BaSO_4$ for comparison.

Figure 2.37



X-ray Diffractogram for O-O Run Sample.

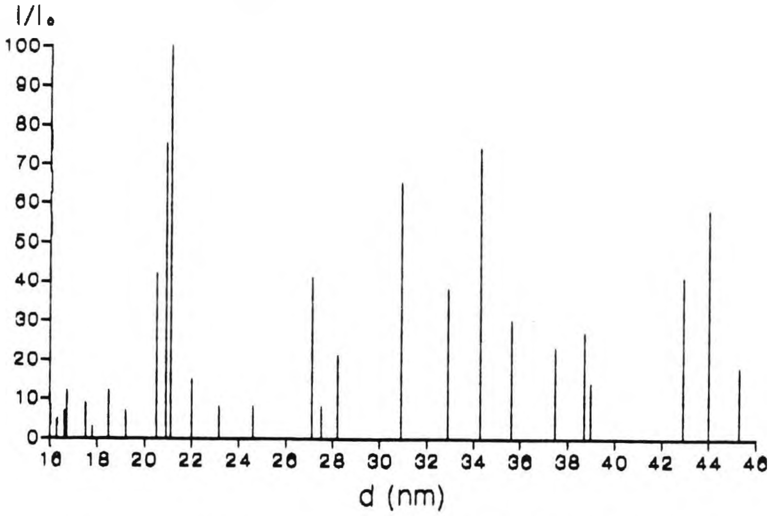
Figure 2.38



X-ray Diffractogram for M-M Run Sample.

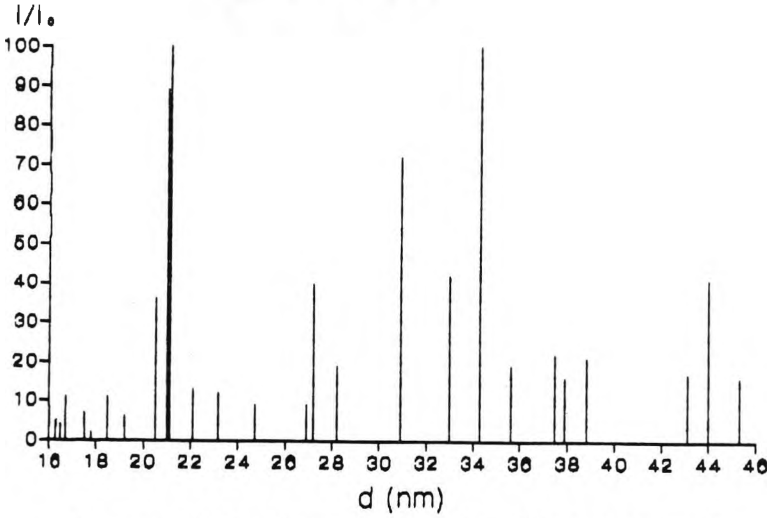
Another effect of the magnetic treatment was a reduction in the unit cell dimensions (characterized by shifts to lower d-spacing values). The unit cell dimensions were calculated for the crystals and are presented in Table 2.10. It can be seen that the solution combination used influenced the results and that the magnetic treatment only affected the a_o and b_o dimensions.

Figure 2.39



X-ray Diffractogram for O-O# Run Sample.

Figure 2.40



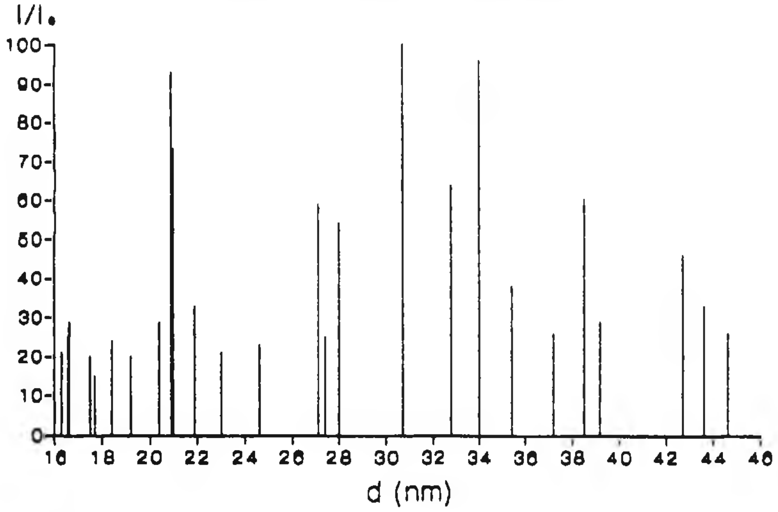
X-ray Diffractogram for M-M# Run Sample.

Table 2.10

Test Sample	Unit Cell Dimensions (nm)		
	a_o	b_o	c_o
X-ray Grade	89.2	54.8	70.8
O-O*	89.2	54.3	70.6
M-M*	88.8	54.0	70.6
O-O#	90.6	54.6	71.2
M-M#	89.2	54.1	71.2

Calculated Unit Cell Dimensions.

Figure 2.41



X-ray Diffractogram for X-ray Grade Barium Sulphate.

Analysis of Residual Barium.

The concentration of the residual barium left in solution after the precipitated barium sulphate had been filtered off was determined by atomic absorption analysis. A KCl ionization buffer was added to each of the samples. Due to the very small solubility of barium sulphate in cold water, the measured concentrations were very low. As was found for the calcium oxalate analyses, this means that any small errors in the measurements would have a greater effect. Consequently the standard deviations for the average values are quite high. The average residual barium concentrations for each of the solution combinations are presented in Table 2.11.

The results of the analyses show that the solution combination used had a marked effect on the residual barium content. This observation can be easily explained when the effect of sodium chloride concentration on barium sulphate solubility is considered. Thomas (1992) states that the solubility of $BaSO_4$ was thirteen times greater in a 3.0% NaCl solution than in distilled water. The results show that for the O-M, M-O and M-M runs there was a decrease in the amount of barium left in solution, i.e. a greater proportion of the barium had reacted.

Table 2.11

Run Type	Residual Barium Concentration (ppm)				
	X-Y	X^*-Y^*	$X-Y^*$	X^s-Y^*	$X-Y''$
O-O	0.42	2.43	2.25	2.09	3.19
O-M	0.33	1.48	0.87	1.80	1.33
M-O	0.39	1.46	0.99	1.46	2.25
M-M	0.35	2.30	0.55	1.37	2.30
O	0.64	0.59	1.00	0.59	1.89
M	0.53	0.89	1.10	0.94	1.56

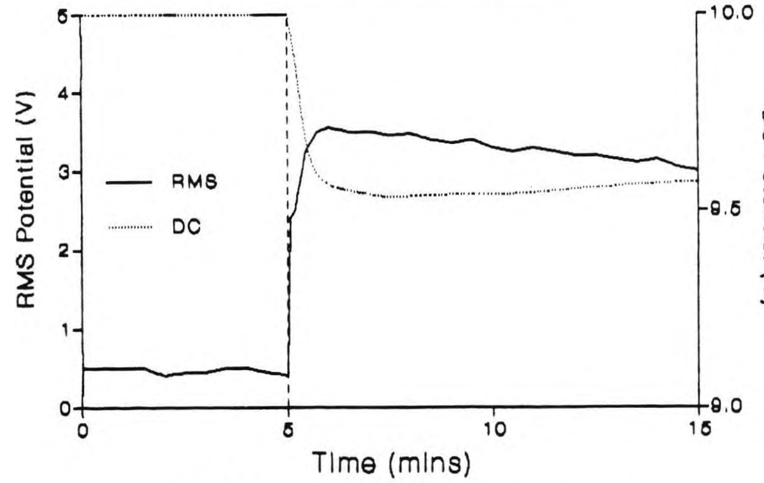
Analysis of Residual Barium Results.

Photometric Dispersion Analyses.

In addition to the analyses described above, a number of 'one-off' dispersion analyses using the PDA2000 analyzer were carried out. For these the same solution concentrations were used, with both the barium and sulphate in aqueous solution. 50ml portions of the barium solution were circulated through an electromagnetic field of strength 2500 gauss, by peristaltic pumping. Part of the circulatory tubing was passed through the flow cell of the instrument. After five minutes, 5ml of the sulphate solution was added to the vessel. Figures 2.42 and 2.43 are typical traces from a control and magnetic run, respectively.

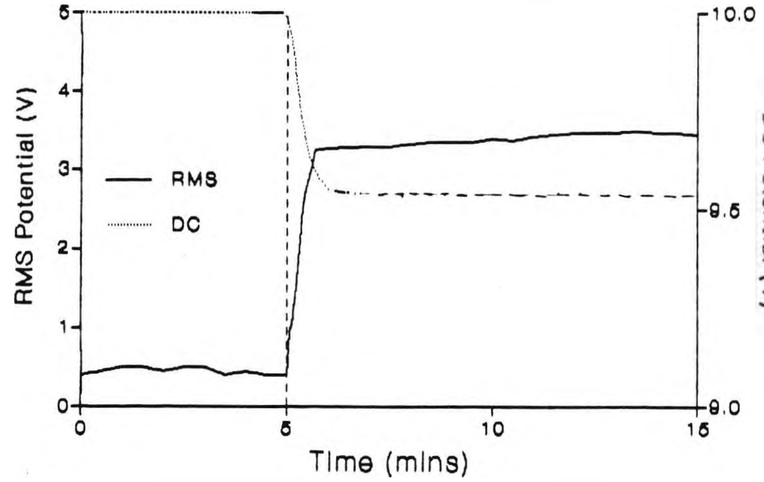
The initial rate of fall of the DC value is the same for both runs (0.93 V/min), but, the final rates of change are different. For the control, the DC value rises slightly in the second stage of the precipitation, while the value for the magnetic run continues to fall. The rate of increase for the control run was 0.04 V/min and the rate of fall for the magnetic run was 0.01 V/min.

Figure 2.42



PDA2000 Graph - Control Run.

Figure 2.43



PDA2000 Graph - Magnetic Run.

The events described above can be explained when the RMS values are considered. The initial rate of change in the RMS value is slower for the test sample than for the control (46.7 V/min compared with 66.7 V/min) which indicates a reduction in the nucleation rate. In the latter stages the RMS value falls, at a rate of 0.06 V/min, for the control, and rises at a rate of 0.02 V/min for the magnetic run. This indicates that, in the second stage of the precipitation, a degree of re-dissolution was occurring in the control, while precipitation was continuing in the treated solution.

2.4.iv. Discussion.

The results of the analyses on barium sulphate, precipitated from different solution combinations, show that magnetic treatment has a profound effect on the precipitation reaction. The treatment was found to cause decreases in the particle size, increases in the degree of aggregation, and changes in morphology and the amount of barium precipitated. The rates of the precipitation processes involved in the reaction were also influenced. These changes are very similar to those observed with the precipitation of calcium oxalate. It is, therefore, justifiable to assume that the same mechanism caused the changes in both cases, i.e. a direct magnetic field/charge interaction, which disrupts the interionic associations, and, therefore the clusters, within the treated solution. The reduction in the residual barium concentrations is consistent with this mechanism, since an increase in the activity of the ions in the solution would shift the equilibrium between the reactants and products causing more of the barium sulphate to be precipitated.

The results for barium sulphate also show additional factors which influence the effect. The most interesting of these concerns the four different test combinations, O-O, O-M, M-O and M-M. It was found that the treatment of the sulphate solution alone (O-M cases) produced the greatest change in the particle size in every case tested. This means, in terms of the proposed theory, that the magnetic field must have a greater influence on the sulphate ions and sulphate-containing clusters than on the barium ions in the formation solutions. A possible interpretation of this can be advanced if the size and charge distribution of the ions in question are considered.

The barium ion contains a single nucleus and can be considered as a sphere with its charge evenly distributed. The sulphate ion, however, consists of a tetrahedral distribution of oxygen nuclei around a sulphur atom. The ion is therefore larger than the barium ion (with approximately twice the radius) and also has a more complicated charge and mass distribution. Hence, the interionic associations and hydration spheres for the two ions will be different. This is supported by the values of the apparent degrees of dissociation for barium chloride and sodium sulphate (0.75 and 0.69 respectively for 100ppm solutions at 25°C). These values suggest that there is a greater degree of association within the sea water solutions, and therefore a larger number and size of clusters, than for the barium solutions. Therefore, there is a greater potential for disruption of sulphate-containing clusters, than for barium clusters, and hence the magnetic treatment would be expected to influence the two solutions to different degrees.

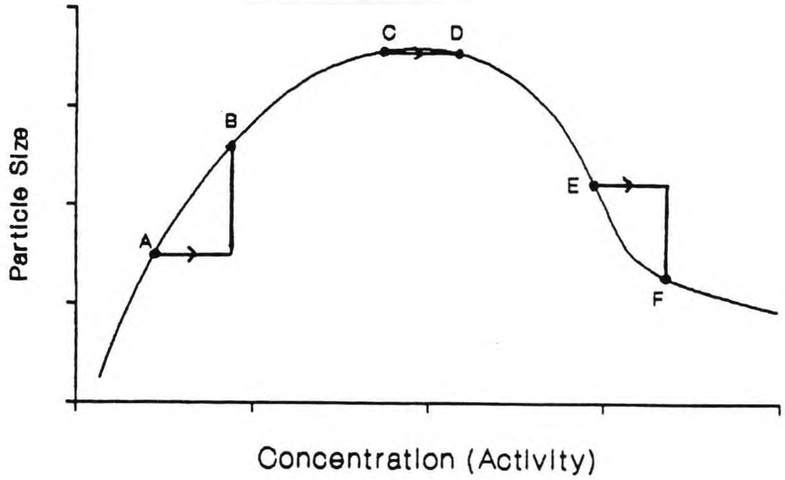
A second observation can be made concerning the O-O, O-M, M-O and M-M tests. It was found that the magnitude of the effect when both solutions were treated (M-M runs) was not greater than when the two solutions were treated separately (O-M and M-O runs). Instead the degree of the effect for the M-M runs appears to be between that for the O-M and M-O tests (i.e. the effect is 'averaged' rather than 'summed'). No obvious conclusions concerning the microscopic effects of the treatment can be drawn from this observation.

2.5. Conclusions

The results of the three pieces of work presented in this chapter have clearly demonstrated the profound effect that the magnetic treatment of fluids has on precipitation, crystallization and scaling processes. The effect has been shown to influence the rate of nucleation and subsequent crystal growth and, consequently, the amount of solids precipitated, and the particle size, degree of aggregation, crystallinity, and morphology of the crystals produced. It has been shown that effects of this type are consistent with changes in the ionic atmosphere and/or hydration sphere around the ions in solution, leading to alterations in the nature, size, stability and distribution of the ionic clusters and an increase in the overall activity of the solution.

It is interesting to consider the results presented by other authors in the light of the proposed theory. The literature review in section 1.2 demonstrated the controversy surrounding the claimed effects of the magnetic treatment of fluids. The main reason for this was shown to be the number of seemingly contradictory results which have been reported. The comments of Söhnel and Mullin (1988), that various authors have reported the crystal size of various precipitates to be increased, decreased or unchanged following magnetic treatment, have already been used to demonstrate this fact (see section 1.1). These seemingly conflicting claims can be accounted for if the effect of original solution concentrations on the subsequent precipitation is considered. It is well known that one of the major influences on the particle size of a precipitate is the level of supersaturation. In cases where two solutions are mixed together to cause precipitation, this is determined by the initial concentrations, or more accurately the activities, of the solutions. For more dilute solutions, increases in the concentration cause increases in the particle size. For more concentrated solutions, the effect is reversed. This is shown in Figure 2.44.

Figure 2.44



Effect of Initial Solution Concentrations on Particle Size.

If one of the effects of the magnetic treatment is to increase the activity of the solutions, it can be seen that this could cause an increase (A-B), a decrease (C-D) or no change (E-F) in the particle size of the produced crystals, depending on the initial concentrations of the treated solutions. This goes some way to explaining the different results given in the literature, which at first sight appear to be mutually contradictory.

CHAPTER 3

THE EFFECTS OF APPLIED FIELDS ON THE PRECIPITATION RATIO OF CALCIUM/MAGNESIUM PHOSPHATE

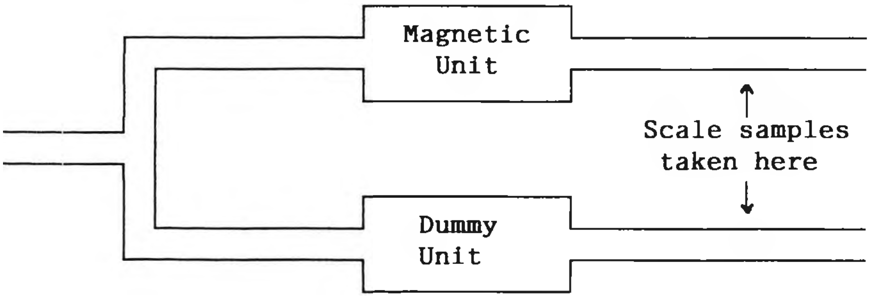
3.1. Introduction and Industrial Test Results

In common with much of the laboratory-based work on the magnetic treatment of fluids, the experimental work on the calcium/magnesium phosphate system was initially prompted by the findings of an industrial trial of a magnetic treatment device. In this case the trial took place at Crossness Sewage Treatment Plant near Dartford, Kent. Certain areas of the treatment process were affected by a serious scaling problem. Samples of the scale were collected from the site and analysed to determine their composition. The scale was found to have a complicated composition, with calcium phosphate being the major constituent.

Two identical, parallel lines of the sewage treatment process, with a common inlet, were chosen for the tests. One of these had a 2" HDL magnetic unit fitted in line, while, for the other a dummy (non-magnetized) unit of the same geometry was connected in the same manner and corresponding position. Figure 3.1 shows the test arrangements at the treatment plant. Scale samples were collected from the positions shown in the figure prior to the start of the tests. After six weeks of continuous, normal use further samples were collected from the same positions. The composition of all four scale samples were determined. The results of the analyses of the initial and final scale samples are presented in Table 3.1.

It can clearly be seen that the magnetic treatment had a very pronounced effect on the composition of the deposited scale. There are no significant or consistent differences between the initial and final control and the initial test sample, but the scale collected from the magnetically treated line, after the six weeks of the trial, was found to have a significantly different composition. The proportions of magnesium and phosphate in the scale had increased (by almost 20 times for magnesium and by 96% for the phosphate), while the concentrations of calcium and carbonate had fallen (by 94% and 100%).

Figure 3.1



Schematic Diagram of Industrial Test Site.

Table 3.1

Scale Component	Initial Control(%)	Initial Magnetic(%)	Final Control(%)	Final Magnetic(%)
Calcium	26.80	26.70	26.90	1.60
Phosphate	22.90	22.60	25.10	44.30
Carbonate	8.80	6.69	8.20	0.00
Carbon	8.31	1.20	6.25	1.20
Hydrogen	1.84	3.14	1.77	3.14
Nitrogen	1.15	2.23	0.91	2.23
Magnesium	0.78	0.75	1.20	14.85
Iron	0.12	0.37	0.61	0.10
Sodium	0.11	0.13	0.20	0.02
Zinc	0.05	1.03	0.20	0.02

Industrial Trial Results.

This type of change in the scale composition warranted further investigation in the laboratory. The analyses of the industrial trial samples had shown a change in the ratios of the constituents of the scale and the work described in this section concentrates on this aspect of the treatment effect. The composition of the deposited scale at the sewage treatment plant was very complex and contained too many components for a laboratory-based investigation, since the combined effects of the treatment on all of them would make the interpretation of the results more difficult. Therefore, it was decided to determine the effects of magnetic treatment on a much simpler system, viz. calcium/magnesium hydrogenphosphate.

Both calcium and magnesium phosphates are fairly insoluble in water (0.0316g/100ml for $CaHPO_4.2H_2O$ and 0.3g/100ml for $MgHPO_4.7H_2O$), and hence the addition of phosphate ions to a calcium/magnesium solution should cause the precipitation of a mixed phosphate. It was hoped that, since the calcium and magnesium ions in solution would be 'competing' for the available phosphate, any relative change between the rates of precipitation of the two ions could be detected by changes in the amount of each precipitated. The two competing reactions are:

$$Ca^{2+}{}_{(aq)} + HPO_4{}^{2-}{}_{(aq)} \rightleftharpoons CaHPO_{4(s)}$$

$$Mg^{2+}{}_{(aq)} + HPO_4{}^{2-}{}_{(aq)} \rightleftharpoons MgHPO_{4(s)}$$

The amounts of calcium and magnesium precipitated were determined by analyzing their concentrations in the residual solution after the precipitated solids had been filtered off. Consequently, the only analysis which was carried out on the samples was flame atomic absorption spectroscopy. The experimental data for all of the tests are presented in Appendix C.

3.2. Results

3.2.i. Equipment Design and Testing Procedures.

The laboratory-based experimental work on the calcium/magnesium phosphate system was carried out using two different types of test rig. The first of these used jacketed (i.e. temperature regulated) vessels and the test solutions were circulated, via Totton EMP50 pumps, through glass housed magnetic and dummy units, with the same internal geometry as the HDL 1" magnetic units. This type of test arrangement has been described in detail in Chapter 1 (Figure 1.15 is a photograph of one of the test rigs used in this investigation showing one of the glass housed magnetic units - see page 52).

With the second test arrangement the solutions were circulated through an electromagnetic field (with a simple geometry) using Watson-Marlow peristaltic pumps. The magnetic field was produced by a pair of coils with soft iron cores mounted on either side of the circulatory tubing, giving a field which was at 90° to the direction of flow. The coils were connected in series to a variable power supply, which gave potentials of 0 to 20V and field strengths of up to 5000 gauss (Note: For the highest field strengths, the coils required a cooling water supply to dissipate heat generated by the electric current). The vessels used were 250ml beakers which were supported in a temperature-regulated water bath. The temperature for all of the experiments, using either of the test rigs, was maintained at 20 (±0.5)°C, unless otherwise stated.

All of the tests were carried out using the same basic technique. A solution containing equimolar concentrations of calcium and magnesium ions was circulated through a magnetic field for a period of time. After this, portions were either removed from the vessel and mixed with phosphate solutions of various concentrations, or, a phosphate solution was added to the vessel and the circulation was continued (either with the magnetic field on or off). The two solutions were mixed for 20 minutes and then the resulting suspension was filtered through a number four sintered glass filtering crucible using vacuum suction. The residual solution was then analyzed for calcium and magnesium.

The quantitative analyses of the solutions were carried out using atomic absorption spectroscopy (A.A.). To prepare the solutions for this, they were divided into two portions and diluted with distilled water. The degree of dilution required depended on the initial solution concentrations and the linear range of the instrument for determining Ca^{2+} (0-7ppm) and Mg^{2+} (0-0.5ppm). For example, in order to analyze the residual solutions for Experiment 1, one portion was diluted by a factor of 500 times for the calcium determination and the other was diluted 2500 times for the measurement of the magnesium concentration. It was also necessary to add lanthanum chloride to the samples for the calcium analyses, since the determination of calcium is sensitive to the presence of phosphate ions. A computer program was written for a BBC microcomputer to carry out a number of calculations on the results of the analyses. The program output gave the concentration of each ion in the solution in ppm, the number of moles reacted (i.e. in the precipitate), the percentage of the initial number of ions reacted and the molar ratio of magnesium to calcium in the precipitate. A description of the program, which was called 'Ca-MgCAL', is given in Chapter 1 and it is listed in Appendix A (page 274).

3.2.ii. Initial Laboratory Experiments.

The initial experiments with the calcium/magnesium phosphate system were carried out by circulating portions of solutions containing calcium and magnesium ions through glass housed magnetic and dummy units and then precipitating the ions with a phosphate solution. The experiments used the first type of test rig, described earlier. The test solutions were made up as follows:

Calcium/magnesium solutions:

> 73.51g $CaCl_2.2H_2O$ and 65.63g $MgCl_2.2H_2O$ in 500ml of distilled H_2O. This gave an equimolar solution concentration of 1M Ca^{2+} ions and 1M Mg^{2+} ions.

Phosphate solutions:

> Saturated disodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$) solutions were used (approx. 1.0M).

500ml portions of the calcium/magnesium solution were circulated through the magnetic and dummy units for between thirty seconds and twenty four hours, after which 250ml samples were removed and transferred to other vessels. 250ml portions of the phosphate solution were then added with stirring. The stirring was continued for twenty minutes, after which the suspensions were filtered off and the residual solutions were diluted and analysed.

The A.A. analyses showed that, in every case, the concentrations of calcium and magnesium ions in the residual solutions were lower for the test samples than for the controls, i.e. a greater proportion of the available ions had reacted with the phosphate. Table 3.2 gives the results of the seven runs which were carried out for Experiment 1, after different periods of circulation through the magnetic unit and the control. Figures 3.2 and 3.3 are graphs of percentage calcium and magnesium reacted against time, respectively.

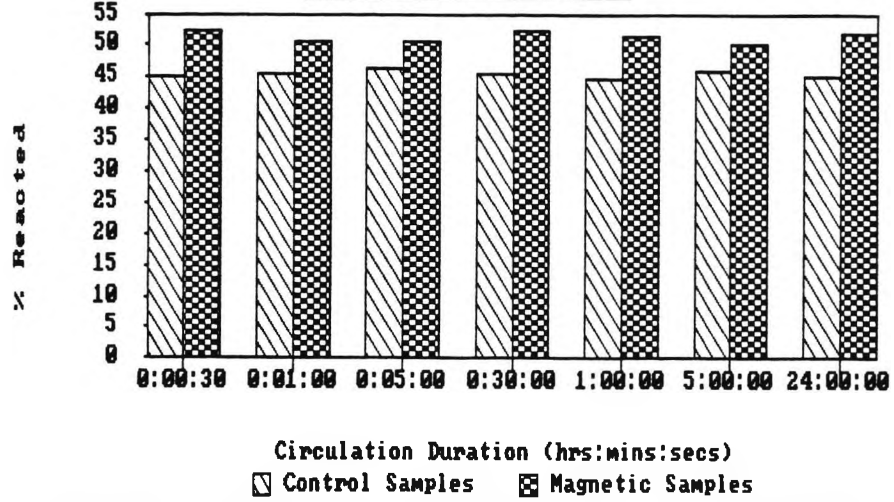
It can be seen from the table and graphs, that the results

Table 3.2

Time (hrs:min:s)	% Calcium Reacted		% Magnesium Reacted	
	Control	Magnetic	Control	Magnetic
0:00:30	45.1	52.1	40.8	44.1
0:01:00	45.6	50.6	40.8	43.6
0:05:00	46.6	50.8	39.1	44.9
0:30:00	45.4	52.1	40.4	43.6
1:00:00	44.9	51.6	39.1	43.2
5:00:00	46.1	50.3	39.5	44.9
24:00:00	45.1	51.8	39.1	44.9
AVERAGE (σ)	45.5 (0.6)	51.3 (0.7)	39.8 (0.7)	44.2 (0.7)

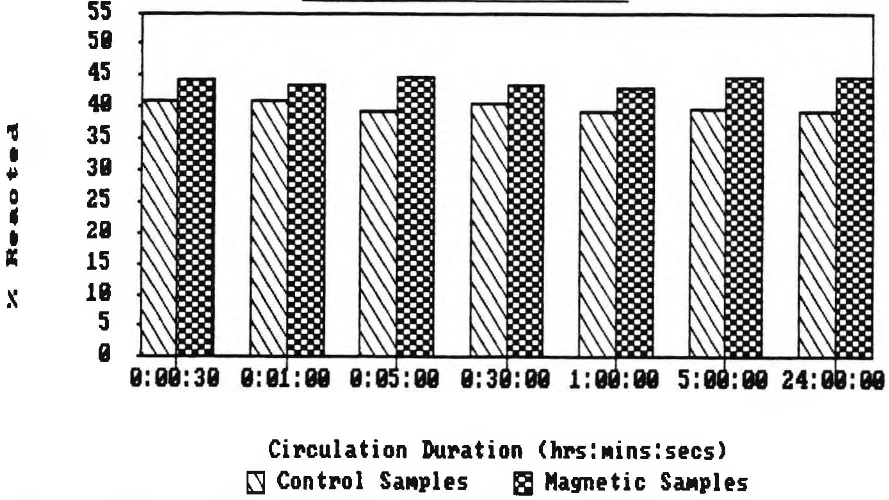
Results of Experiment 1.

Figure 3.2



Percentage Calcium Reacted Results for Experiment 1.

Figure 3.3



Percentage Magnesium Reacted Results for Experiment 1.

obtained for the experiments were very consistent, the standard deviations being less than 2% of the averages. This means that the length of time that the test solutions were circulated did not influence the magnitude of the effect to any significant degree. The magnetic treatment effect was found to cause increases in the amounts of calcium (12.7%) and magnesium (11.1%) precipitated by the phosphate. In view of the very low standard deviations for the results, it can be seen that these changes are significant. The results also indicate that the degree of the magnetic treatment effect was approximately the same for both the calcium and the magnesium.

3.2.iii. Influence of Continuing Treatment.

Following the interesting results obtained in the initial experiments, it was decided to determine whether continuing magnetic treatment after the phosphate had been added would have any further effect on the amount of calcium and magnesium in the residual solutions. To achieve this Experiment 2 was set up, in which control and magnetic test rigs were used and 500ml portions of the calcium/magnesium solution were circulated for 30 minutes. 500ml portions of the phosphate solution were then added to each vessel and the circulation was continued. At various time periods 50ml samples were removed from the vessels and filtered. The filtrates were analysed and the results processed as before. Table 3.3 gives the results of the analyses and the times at which the samples were removed and Figures 3.4 and 3.5 are the graphs of the proportions of calcium and magnesium reacted against the duration of circulation.

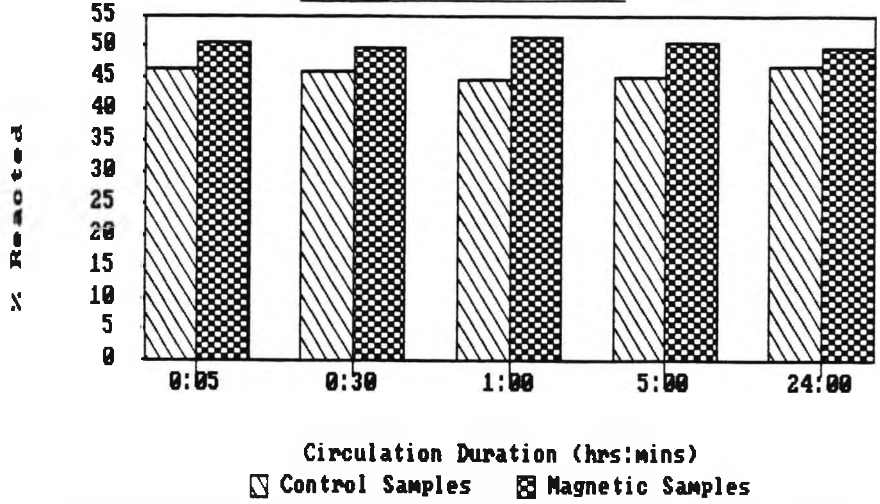
It can be seen that the continued circulation of the suspensions had no obvious additional effect on the proportions of the cations

Table 3.3

Duration of Circulation (hrs:min)	% Calcium Reacted		% Magnesium Reacted	
	Control	Magnetic	Control	Magnetic
0:05	46.6	50.6	41.2	44.1
0:30	45.9	49.9	39.5	45.7
1:00	44.9	51.3	40.4	44.1
5:00	45.1	50.6	39.1	45.7
24:00	46.9	49.9	39.1	45.3
AVERAGE (σ)	45.9 (0.8)	50.5 (0.5)	39.9 (0.8)	45.0 (0.7)

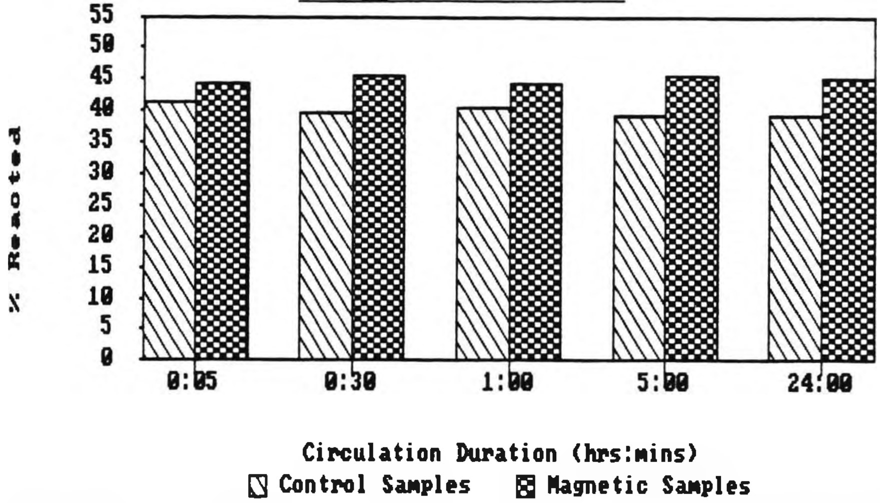
Results of Experiment 2.

Figure 3.4



Percentage Calcium Reacted Results for Experiment 2.

Figure 3.5



Percentage Magnesium Reacted Results for Experiment 2.

precipitated. This tends to indicate that the magnetic treatment affected the reaction in solution but had either no, or a much reduced, influence on the suspended precipitate once formed. Once again the results were very consistent, the standard deviations being less than 2% of the average values. The average percentage increases between the control and magnetic samples were 10.0% for calcium and 12.8% for magnesium.

3.2.iv. Influence of Phosphate Concentration.

For this experiment (No.3), the concentrations of the reactants were reduced, so that the dilution factors required for the atomic absorption analyses were lower. The new calcium/magnesium solution contained 0.1M Ca^{2+} (21.91g/l $CaCl_2.6H_2O$) and 0.1M Mg^{2+} (20.33g/l $MgCl_2.6H_2O$). A new phosphate solution was also made up with a concentration of 0.2M (71.6g/l of $Na_2HPO_4.12H_2O$). 500ml portions of the calcium/magnesium solution were circulated through magnet and dummy units, using the first type of test rig described in section 3.2.i., for 20 hours. Three 100ml portions were then removed from each vessel. For both the magnetic and control samples, one portion was mixed with 100ml of the phosphate solution, one with 50ml and the third with 25ml. In each case the solutions were stirred for ten minutes after the addition of the phosphate.

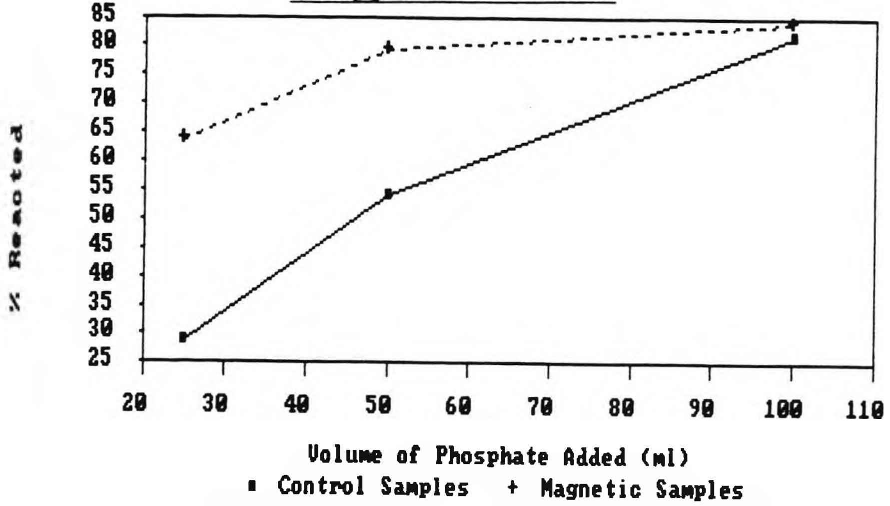
The resulting suspensions were then filtered off and the filtrates were diluted and analysed. The analyses of the calcium and magnesium concentrations were 'corrected' for volume. This was necessary, since the three residual solution samples were diluted by different factors due to the addition of different volumes of the phosphate solution (i.e. the samples had volumes of 200, 150 and 125ml following the additions of the phosphate solution). Table 3.4

Table 3.4

Volume of Phosphate Added /ml	% Calcium Reacted			% Magnesium Reacted		
	Con^{t}	Mag^{n}	% Change	Con^{t}	Mag^{n}	% Change
100	81.8	83.9	+2.6%	60.1	65.4	+8.8%
50	54.0	79.2	+46.7%	38.7	61.3	+58.4%
25	29.0	63.5	+119.0%	27.2	34.4	+26.1%

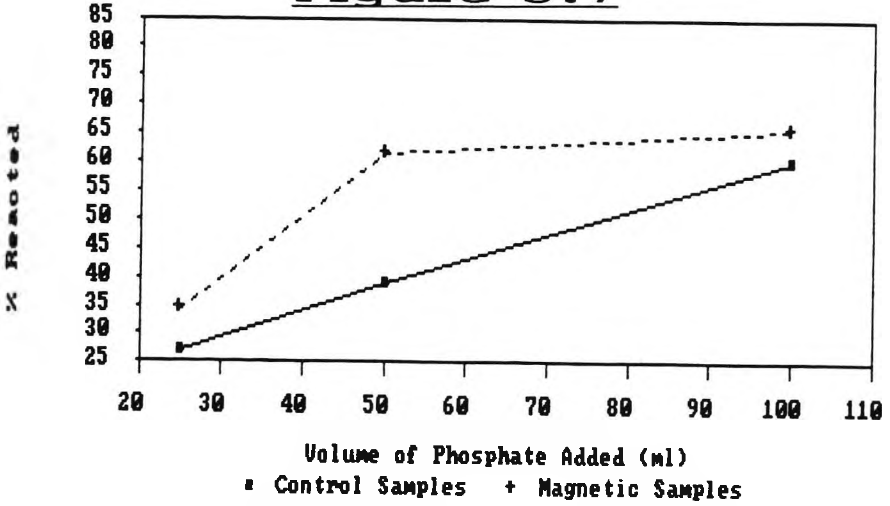
Results of Experiment 3.

Figure 3.6



Percentage Calcium Reacted Results for Experiment 3.

Figure 3.7



Percentage Magnesium Reacted Results for Experiment 3.

shows the 'corrected' results of the analyses, and graphs of percentage calcium and magnesium reacted against volume of phosphate solution added are presented in Figures 3.6 and 3.7.

It can be seen, from the table and graphs, that the effect of the magnetic treatment was again an increase in the proportion of both calcium and magnesium precipitated. It also appears that the effect was greatest when the lower volumes of phosphate were added. This is easily understandable for the calcium results, since the amount of calcium not reacted would be almost at the maximum solubility concentration for calcium phosphate, below which no more would precipitate out of the solution. The same argument may be applicable to the results for magnesium. The maximum percentage reacted figure would be expected to be lower than that for calcium, since the solubility of magnesium phosphate is about ten times greater than that of calcium phosphate. However, the observed effects may also have been influenced by the large volume of phosphate added, which may have 'diluted' the effect. Therefore, it was decided that for the remainder of the tests, the same volume of phosphate solution would be added and the concentration of the solution would be varied. It was also decided to add only a small volume, to minimize any 'dilution' of the magnetic treatment effect.

3.2.v. Initial Tests With New Procedures.

For the rest of the experimental work on the calcium/magnesium phosphate system, new testing procedures were used. The new test rigs have been described in section 3.2.i. The magnetic field was produced using electromagnets which were not in direct contact with the solution. The solutions were circulated using peristaltic pumps, which gave much lower flow rates than those used in the previous work. The solution concentrations and volumes were also reduced.

New stock solutions were made up with different concentrations. It was decided, in view of the results of the previous experiments, to precipitate each test solution with four different phosphate solution concentrations. The stock solutions were made up as follows:

Calcium/magnesium solutions:

11.81g/l $Ca(NO_3)_2.4H_2O$ and 12.82g/l $Mg(NO_3)_2.6H_2O$ in distilled water. This gave a solution containing 0.05M Ca^{2+} ions and 0.05M Mg^{2+} ions.

Phosphate solutions:

Disodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$) solutions were used. These were made up in four concentrations:

0.20M (71.63g/l) = 100% solution.
0.15M (53.72g/l) = 75% solution.
0.10M (35.81g/l) = 50% solution.
0.05M (17.91g/l) = 25% solution.

The percentage figures given correspond to the molar ratio of phosphate ions to calcium and magnesium ions in the solution, if 5ml of each of the phosphate solutions was added to 10ml of the calcium/magnesium solution.

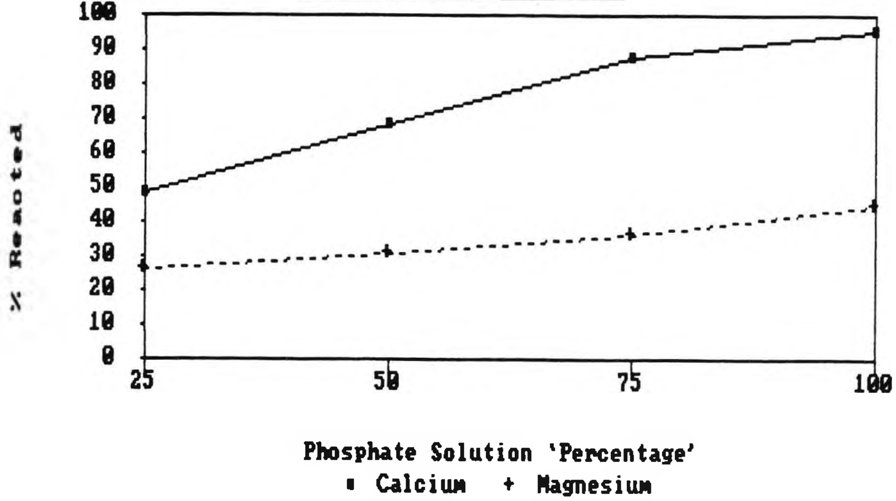
Experiment 4 was a series of replicate control runs to determine the reproducibility of the tests using the new techniques. Portions of the calcium/magnesium solution were circulated through the rigs for 1 hour with the electromagnets in place, but switched off. The peristaltic pumps were set to give a solution flow rate of 1.5l/hour. 10ml samples were then removed and mixed with 5ml portions of each of the phosphate solutions, with stirring. After 10 minutes the resulting suspensions were treated and analysed in the same manner as for the previous experiments. The results of four replicate control experiments are given in Table 3.5 and the average results are shown as a graph against phosphate solution 'percentage' in Figure 3.8.

Table 3.5

Replicate Run Nº	% Ca Used with % PO_4 Sol^{ns}				% Mg Used with % PO_4 Sol^{ns}			
	100%	75%	50%	25%	100%	75%	50%	25%
1	94.4	86.9	68.5	48.5	44.4	36.0	30.9	26.6
2	95.3	87.7	68.7	48.5	45.4	36.1	30.5	26.2
3	95.0	86.8	68.1	48.3	44.5	36.7	30.5	26.8
4	94.6	87.3	68.1	47.9	45.1	36.2	30.2	26.2
AVERAGE	94.8	87.2	68.4	48.3	44.6	36.4	30.5	26.5

Results of Experiment 4 - Replicate Control Runs.

Figure 3.8



Graphs of Average Replicate Control Runs for Experiment 4.

It can be seen that the new techniques and solutions gave very reproducible results. The analyses showed that, in every case, more of the calcium in the solution reacted with the phosphate than magnesium (approximately twice as much). This indicates that the reaction rate for the production of calcium phosphate is roughly twice that of the corresponding reaction with magnesium. The results also show that, for the 25%, 50% and 75% phosphate solutions, the percentage reacted for both calcium and magnesium was proportional to the concentration of the phosphate solution added. For the 100%

solution addition it can be seen that the graph for the calcium was beginning to level out as the maximum solubility concentration of calcium phosphate was approached. This was accompanied by a corresponding increase in the relative amount of magnesium reacted.

3.2.vi. Influence of Flow Rates and Duration of Effect.

Having demonstrated the reliability of the experimental methods, it was decided to determine the effect of magnetic treatment on the test solution at the reduced flow rate, and to investigate how long the effect persisted following treatment (the 'memory effect'). An experiment (number 5) was set up in which 200ml of the calcium/ magnesium solution was circulated through a field of 485 gauss. The flow rate was set at 1.5 l/min. After 30 seconds the pump was stopped and the electromagnets were removed. 10ml portions of the solution were removed at various time periods, mixed with 5ml of the phosphate solution for five minutes, filtered and analysed. The results of the analyses are presented in Table 3.6 and are shown as graphs of percentage reacted against time, after treatment for calcium and magnesium, in Figures 3.9 and 3.10 respectively. Both graphs have been plotted to the same scale for comparison. The horizontal lines shown on the graphs correspond to the control values determined for each phosphate solution.

The results show that the magnetic treatment effect, under the new conditions, again caused an increase in the proportions of both calcium and magnesium reacted with the phosphate solutions. It can be seen that the magnitude of the effect appeared to increase for a short time following the treatment, and then 'decayed' back to the control value over a period of several hours. The graphs indicate that the 'memory effect' has a duration of between five and eight hours under the given conditions. It is not possible to be any more specific than this due to the small random variations between the four sets of data. The results also show that the magnitude of the effect is approximately equal for both the calcium and the magnesium ions in the solutions, as was found in the previous tests. So the magnetic treatment influences both of the electrolytes to the same degree.

Table 3.6

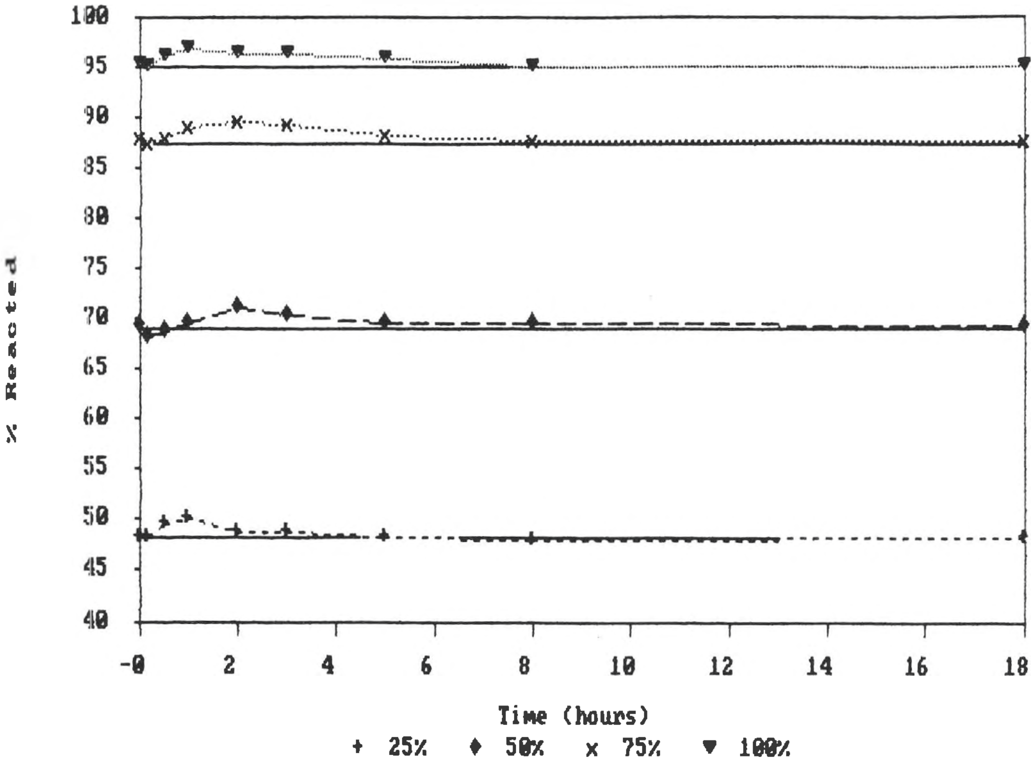
Time After Treatment (hrs:mins)	% Ca Used with % PO_4 Sol^{ns}				% Mg Used with % PO_4 Sol^{ns}			
	100%	75%	50%	25%	100%	75%	50%	25%
CONTROL	94.8	87.2	68.9	48.3	44.6	36.4	30.5	26.5
0:01	95.1	87.7	69.3	48.2	45.5	38.0	31.8	27.0
0:10	94.9	87.4	68.2	48.2	46.6	40.1	31.1	28.1
0:32	95.9	87.9	68.6	49.7	47.7	38.8	33.6	28.4
1:00	96.8	88.8	69.5	50.2	47.5	38.2	33.6	28.0
2:00	96.3	89.3	71.1	48.9	45.9	36.9	33.0	27.7
3:00	96.2	89.2	70.2	48.7	46.2	37.1	32.4	28.2
5:00	95.6	88.1	69.5	48.2	44.8	36.6	30.9	27.1
8:00	95.0	87.6	69.5	48.0	44.4	36.2	30.0	26.8
18:00	94.9	87.6	69.2	48.3	44.9	36.1	30.1	26.7

Results of Experiment 5.

3.2.vii. Influence of Flow Parameters.

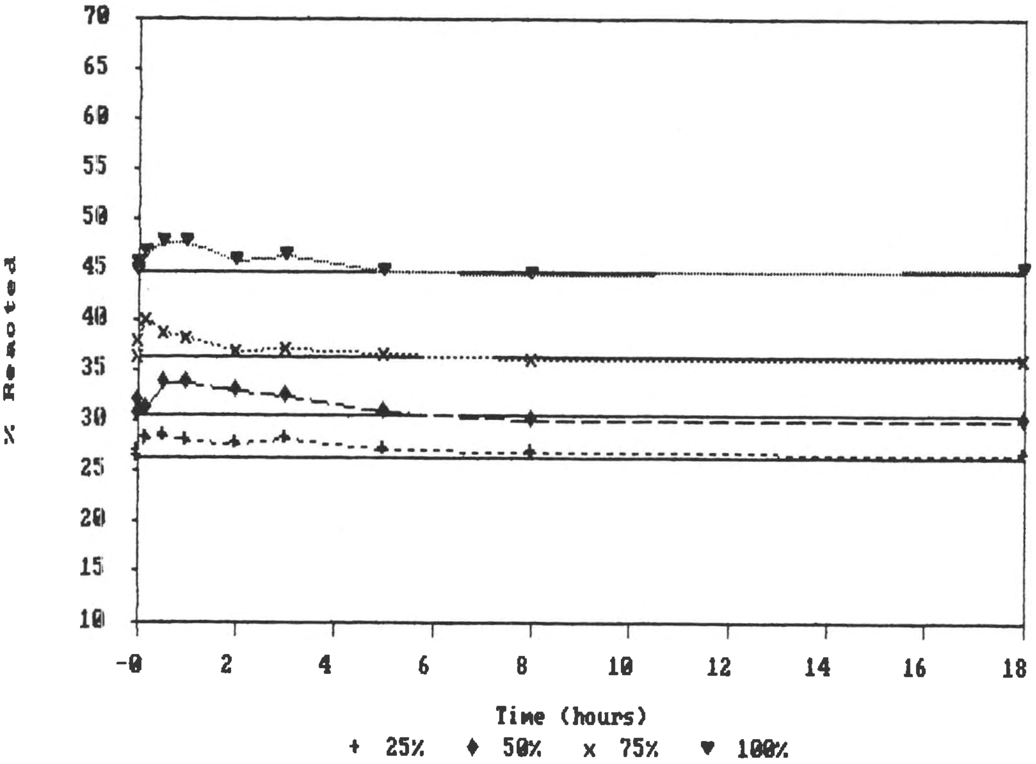
A number of experiments were set up to test the influence of different types of flow (i.e. circulating or single pass) and different flow rates on the magnetic treatment effect. These were all set up in the same manner as described earlier, with a field strength of 485 gauss. New stock solutions were made up with the same concentrations as those used in the previous experiment. The temperature for all of the tests was maintained at 22°C.

Figure 3.9



Percentage Calcium Reacted Results for Experiment 5.

Figure 3.10



Percentage Magnesium Reacted Results for Experiment 5.

For the recirculating experiments the calcium/ magnesium solutions were circulated through the apparatus for 10 minutes. The solutions were then allowed to stand for 5 minutes before the phosphate was added. The suspensions were then stirred for a further 5 minutes prior to being filtered. The standing and stirring periods for the single pass experiments were the same as those described above, but the solutions were only passed through the field once.

A further degree of variation in the flow parameters was achieved by using two different diameter tubes (with internal diameters of 3.0 and 4.5mm) for the peristaltic pump. The results of the recirculating tests with the small and large diameter tubes (Experiments 6 and 7) are presented in Tables 3.7 and 3.8 and those for the single pass runs (Experiments 8 and 9) are given in Tables 3.9 and 3.10. The graphs of percentage reacted against flow rate for calcium and magnesium, for all four experiments, are presented in Figures 3.11 to 3.18.

The results of Experiments 6 to 9 show that the effects of the magnetic treatment are the same, irrespective of whether the solution is only passed through the field once or recirculated through it many times. The magnitude of the effect can be seen to increase up to a maximum with increasing flow rates through the field. Above a certain flow rate there is no significant subsequent increase in the magnitude of the effect, i.e. there was a minimum flow rate required to achieve the maximum effect. With the narrow tubing this minimum flow rate was found to be between 0.3 and 0.5 l/hour, while with the wider tube it was between 0.5 and 1.0 l/hour. This indicates that velocity, rather than flow rate is the controlling factor.

Table 3.7

Flow Rate (1/hour)	% Ca Used with % PO_4 Sol^{ns}				% Mg Used with % PO_4 Sol^{ns}			
	100%	75%	50%	25%	100%	75%	50%	25%
Control	93.1	87.1	70.1	51.4	53.3	47.2	40.7	35.0
0.1	93.2	87.3	71.0	51.4	53.7	47.6	41.1	35.4
0.2	93.1	87.4	70.5	52.1	53.6	47.9	43.1	35.5
0.3	95.4	87.9	70.6	52.7	55.2	48.8	42.7	36.3
0.5	95.0	88.0	71.8	52.8	55.8	48.6	44.3	36.8
1.0	95.0	88.0	72.0	53.3	56.3	49.2	43.8	36.5
1.5	95.7	89.2	72.5	53.0	55.4	49.2	44.2	37.0
2.0	95.0	88.9	72.2	52.9	55.9	48.8	44.5	36.6
2.5	95.5	89.0	72.4	53.2	55.7	48.5	44.0	37.3
3.0	94.9	89.0	71.9	53.3	56.1	49.1	43.9	36.5

Results of Experiment 6 - Flow Rate Tests.
(Recirculating - Narrow Tube)

Table 3.8

Flow Rate (1/hour)	% Ca Used with % PO_4 Sol^{ns}				% Mg Used with % PO_4 Sol^{ns}			
	100%	75%	50%	25%	100%	75%	50%	25%
Control	93.4	86.8	70.1	51.8	53.5	47.0	40.9	34.8
0.1	93.3	87.1	70.0	51.6	53.5	47.5	41.0	34.4
0.2	93.5	86.9	69.7	51.8	53.8	47.2	41.2	34.5
0.3	93.2	87.4	70.6	51.9	53.2	47.6	40.9	35.3
0.5	94.0	87.4	70.3	52.8	54.1	48.1	42.0	34.8
1.0	94.9	88.1	72.2	52.3	54.4	48.6	41.9	35.5
1.5	95.5	89.1	71.9	53.0	55.0	48.6	42.2	36.0
2.0	95.2	88.6	72.1	53.1	54.9	48.6	42.3	36.6
2.5	94.9	88.9	72.6	53.2	55.2	48.8	42.0	36.3
3.0	95.0	89.2	72.3	53.0	55.2	48.5	42.5	35.9

Results of Experiment 7 - Flow Rate Tests.
(Recirculating - Wide Tube)

Table 3.9

Flow Rate (l/hour)	% Ca Used with % PO_4 Sol^{ns}				% Mg Used with % PO_4 Sol^{ns}			
	100%	75%	50%	25%	100%	75%	50%	25%
Control	92.8	87.0	69.9	51.7	53.3	47.0	40.5	34.9
0.1	93.0	87.1	70.0	51.5	53.5	47.2	40.8	35.4
0.2	92.9	87.3	70.2	51.8	53.9	47.2	40.6	35.5
0.3	95.6	88.3	71.6	52.8	56.5	48.9	41.0	37.3
0.5	95.8	89.2	72.1	53.2	56.2	49.2	42.0	36.8
1.0	95.5	89.1	72.4	53.2	56.8	48.9	42.6	36.6
1.5	95.7	89.4	72.0	53.4	56.7	48.9	42.5	37.1
2.0	95.5	89.7	72.3	53.6	57.0	49.1	42.2	36.9
2.5	95.5	89.3	72.4	53.3	56.9	48.9	42.8	36.8
3.0	95.8	89.3	72.4	53.5	57.1	49.2	42.6	36.9

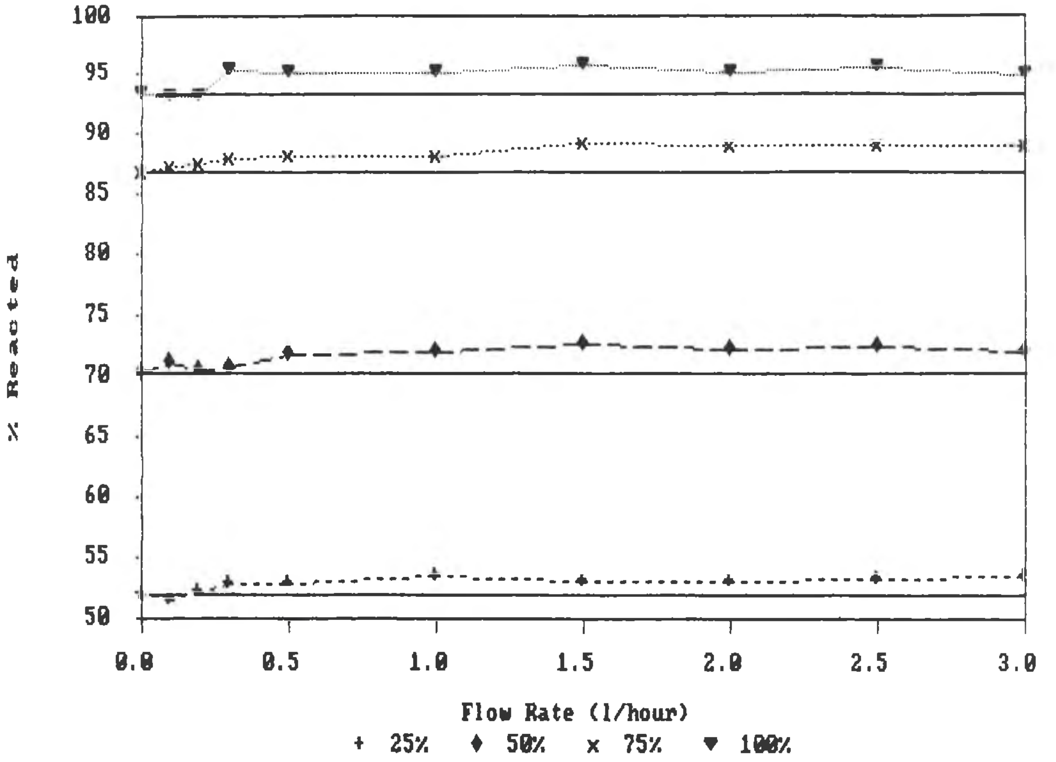
Results of Experiment 8 - Flow Rate Tests.
(Single Pass - Narrow Tube)

Table 3.10

Flow Rate (l/hour)	% Ca Used with % PO_4 Sol^{ns}				% Mg Used with % PO_4 Sol^{ns}			
	100%	75%	50%	25%	100%	75%	50%	25%
Control	93.3	86.6	69.7	52.2	53.0	47.5	41.1	34.6
0.1	93.0	86.4	70.1	51.9	52.9	47.6	40.9	34.4
0.2	93.4	86.7	69.8	52.2	53.4	47.4	41.3	34.5
0.3	93.3	86.9	69.7	52.2	53.2	47.7	40.9	34.8
0.5	93.8	87.5	70.2	53.8	55.1	48.7	42.4	37.2
1.0	95.6	88.5	71.9	53.6	55.3	48.6	42.7	36.5
1.5	95.9	89.1	72.4	53.6	55.5	48.9	42.4	37.0
2.0	95.9	89.3	72.6	53.9	55.2	49.0	42.9	36.6
2.5	95.7	89.0	72.7	54.0	55.5	48.8	42.6	36.3
3.0	95.8	89.3	72.7	53.8	55.3	48.7	42.5	36.5

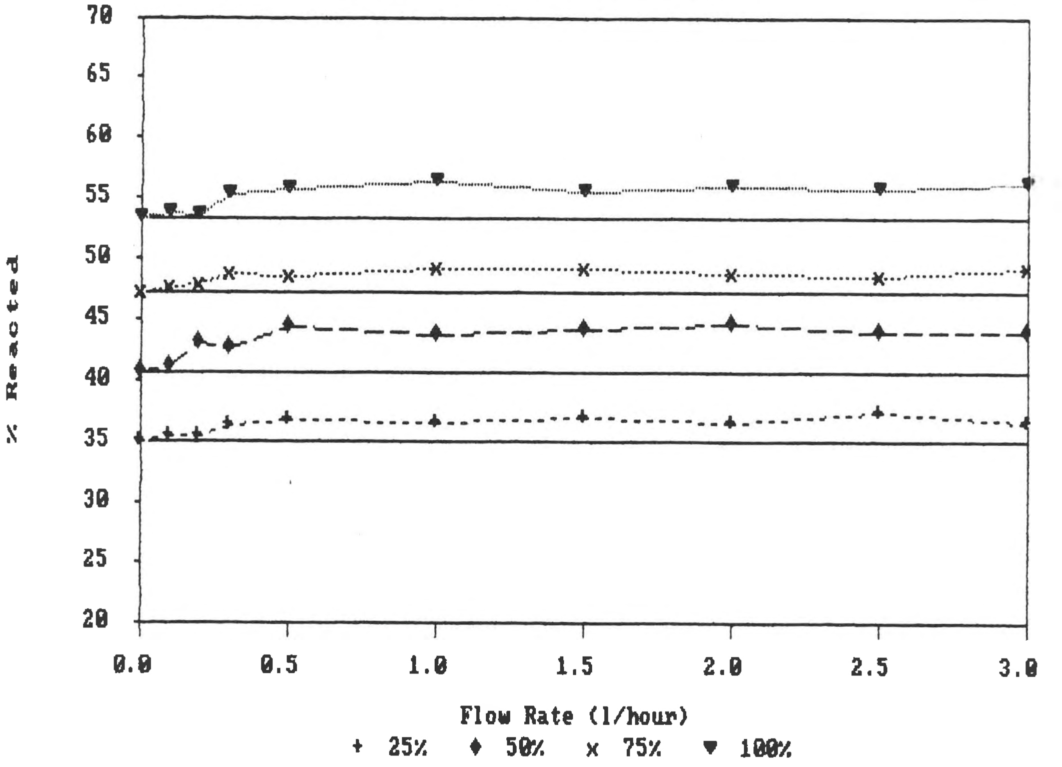
Results of Experiment 9 - Flow Rate Tests.
(Single Pass - Wide Tube)

Figure 3.11



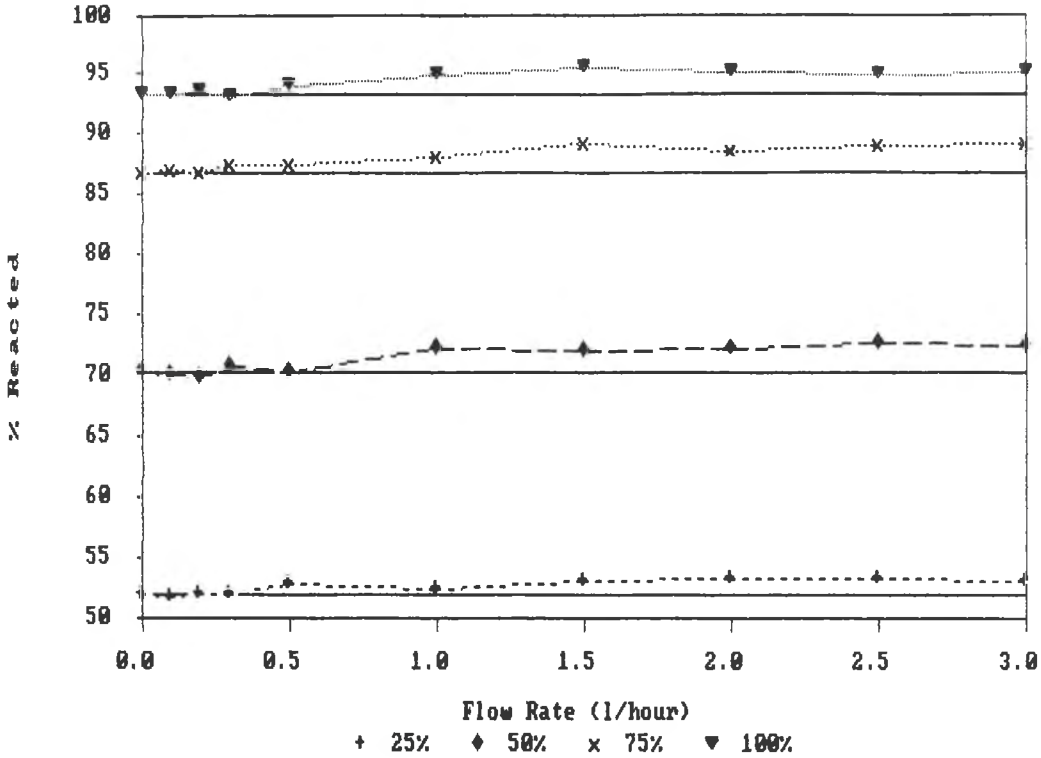
Percentage Calcium Reacted Results for Experiment 6.
(Recirculating - Narrow Tube)

Figure 3.12



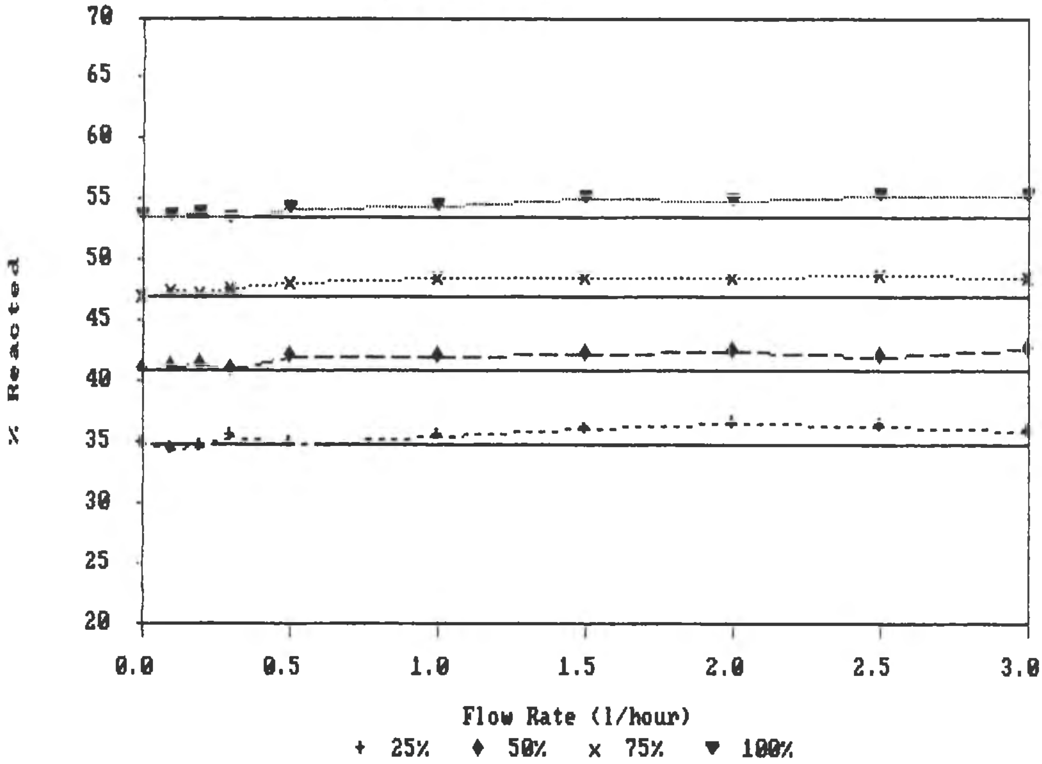
Percentage Magnesium Reacted Results for Experiment 6.
(Recirculating - Narrow Tube)

Figure 3.13



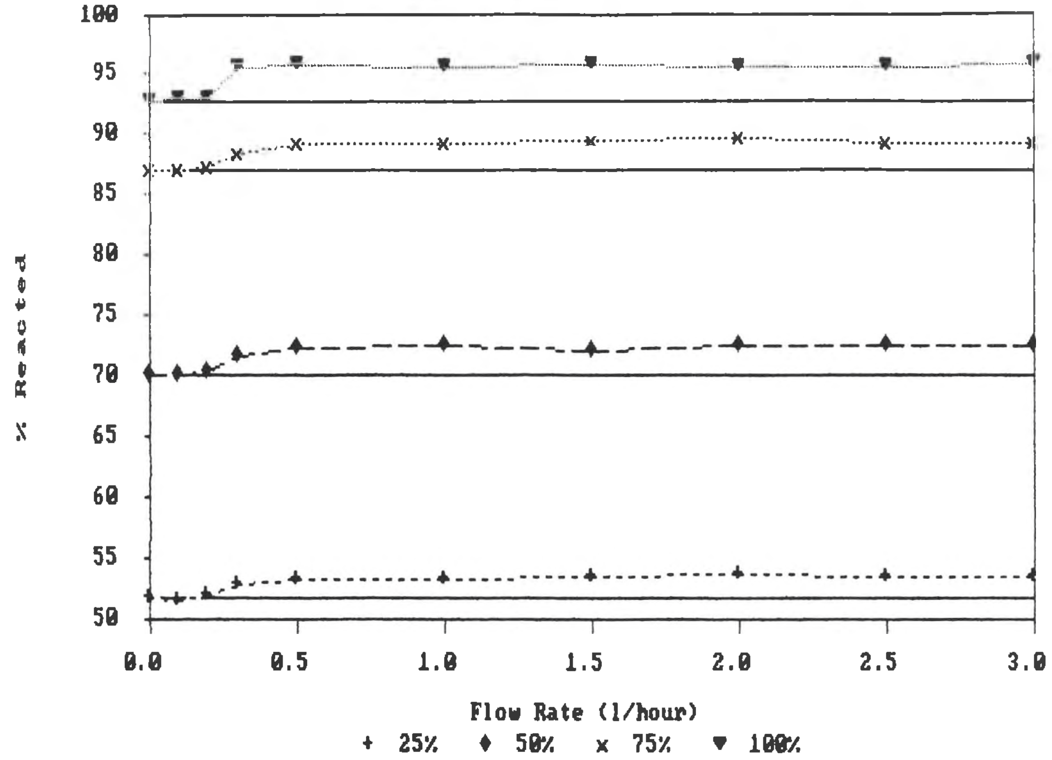
Percentage Calcium Reacted Results for Experiment 7.
(Recirculating - Wide Tube)

Figure 3.14



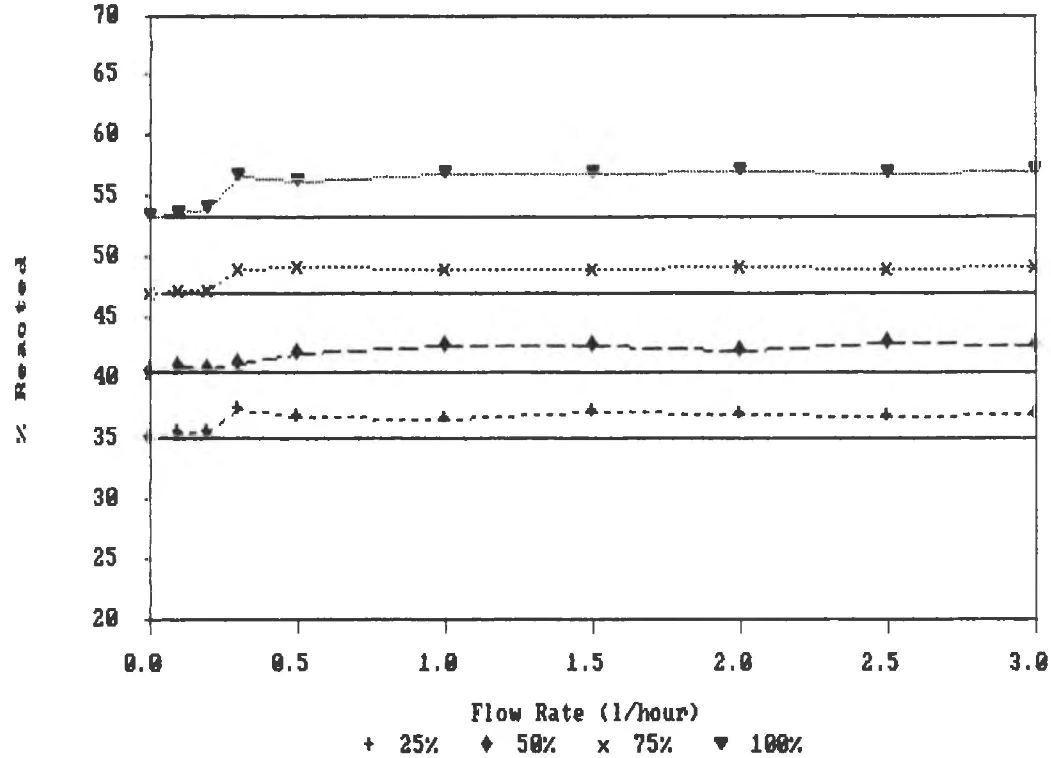
Percentage Magnesium Reacted Results for Experiment 7.
(Recirculating - Wide Tube)

Figure 3.15



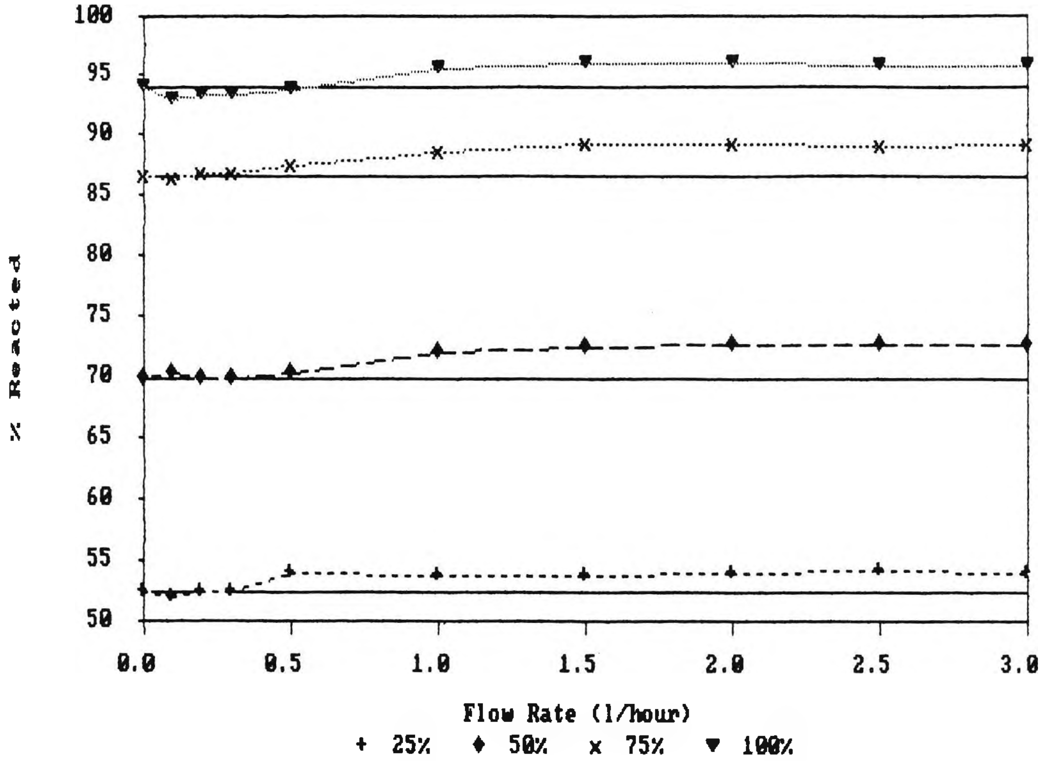
Percentage Calcium Reacted Results for Experiment 8.
(Single Pass - Narrow Tube)

Figure 3.16



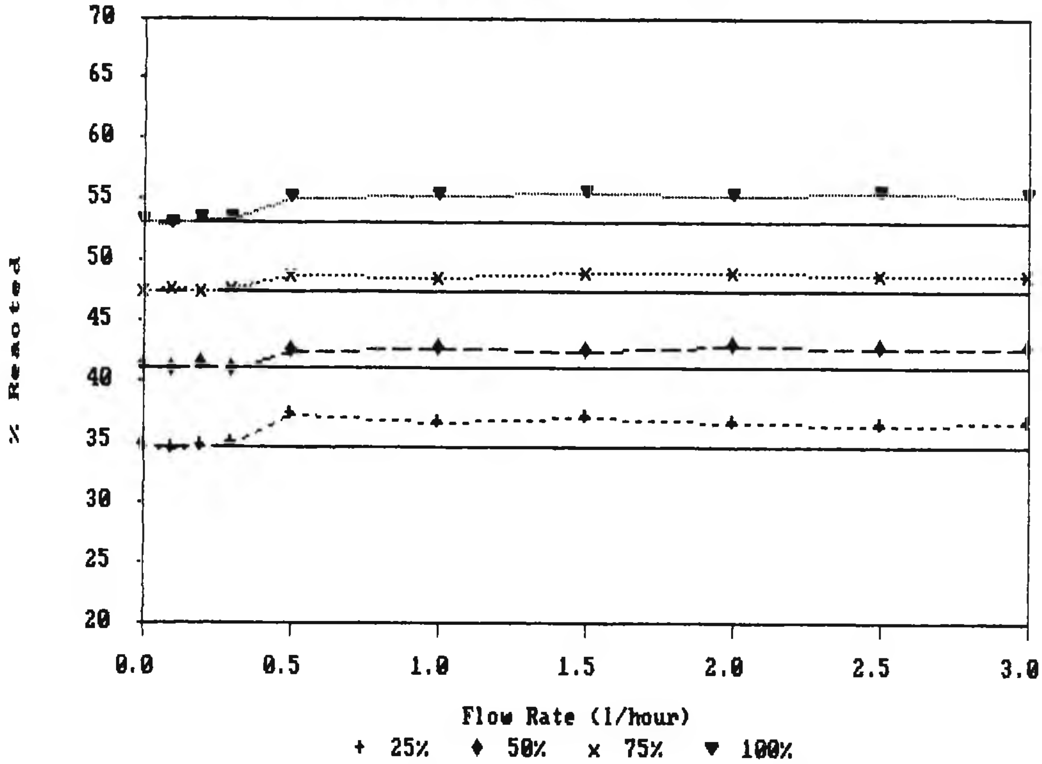
Percentage Magnesium Reacted Results for Experiment 8.
(Single Pass - Narrow Tube)

Figure 3.17



Percentage Calcium Reacted Results for Experiment 9.
(Single Pass - Wide Tube)

Figure 3.18



Percentage Magnesium Reacted Results for Experiment 9.
(Single Pass - Wide Tube)

3.2.viii. Influence of Magnetic Field Strength.

Given the results of the previous experiments, a number of tests were carried out with different field strengths at one flow rate (1.5 l/hour) and using only the narrow tubing. These tests (Experiment 10) and the residual solution analyses were carried out in the same manner as for Experiments 6 to 9, with temperatures of 20 (±0.5)°C. Table 3.11 gives the field strengths used and percentage reacted results for calcium and magnesium and Figures 3.19 and 3.20 are graphical representations of the results.

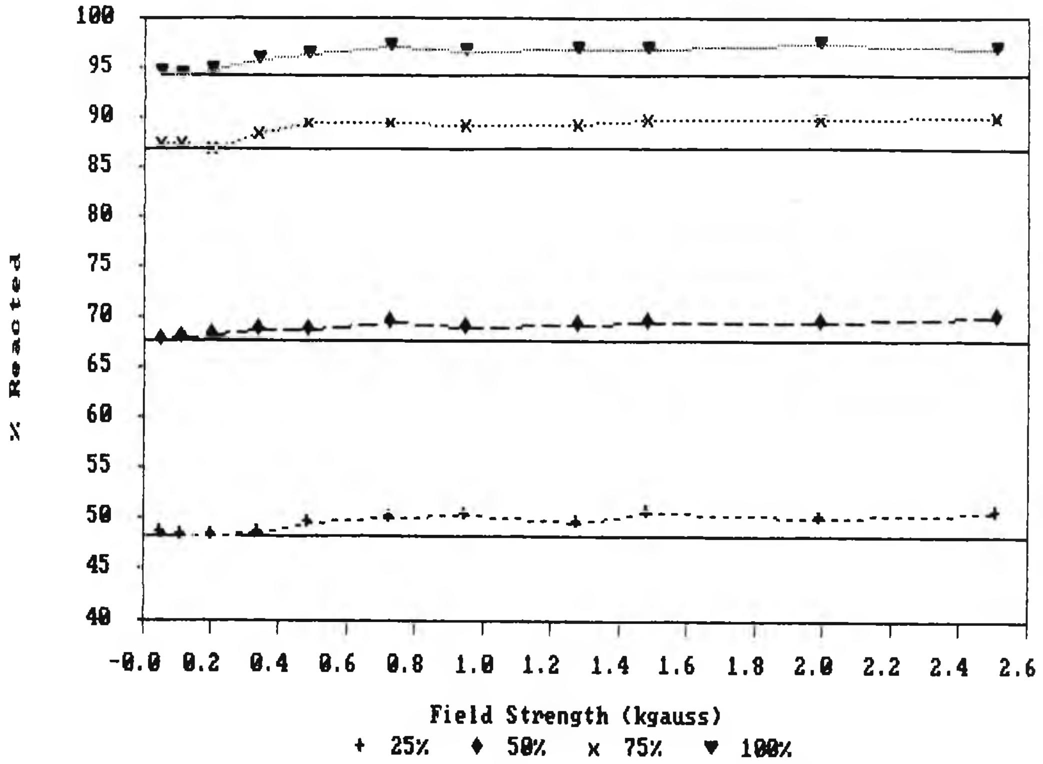
The graphs are very similar to those obtained at different flow rates (Experiments 6 to 9). At very low field strengths the magnetic treatment can be seen to have had little or no effect on the amount of calcium or magnesium reacted. Between about 200 and 500 gauss the degree of the treatment effect increased quite rapidly. Above 500 gauss increases in the field strength had only a very small influence on the magnitude of the changes.

Table 3.11

Field Strength (gauss)	% Ca Used with % PO_4 Sol^{ns}				% Mg Used with % PO_4 Sol^{ns}			
	100%	75%	50%	25%	100%	75%	50%	25%
CONTROL	94.2	86.8	67.7	48.2	45.3	37.0	31.4	26.9
52	94.3	87.2	67.7	48.4	45.1	36.6	31.4	27.1
114	94.0	87.2	67.9	48.3	45.9	36.7	31.1	27.5
207	94.7	86.7	68.1	48.3	45.8	37.9	31.7	27.9
340	95.7	88.4	68.6	48.5	46.7	39.2	32.6	28.9
485	96.2	89.3	68.6	49.7	47.4	38.9	33.4	28.5
727	97.1	89.4	69.4	50.2	47.7	38.6	33.6	28.9
951	96.6	89.1	68.9	50.4	47.4	38.6	33.2	28.6
1278	96.8	89.1	69.2	49.7	47.6	39.1	33.5	28.5
1484	96.8	89.6	69.6	50.5	47.8	39.0	33.5	29.0
1993	97.2	89.6	69.5	50.2	47.3	38.6	33.8	28.8
2515	96.7	89.8	69.9	50.5	47.7	38.8	33.4	28.5

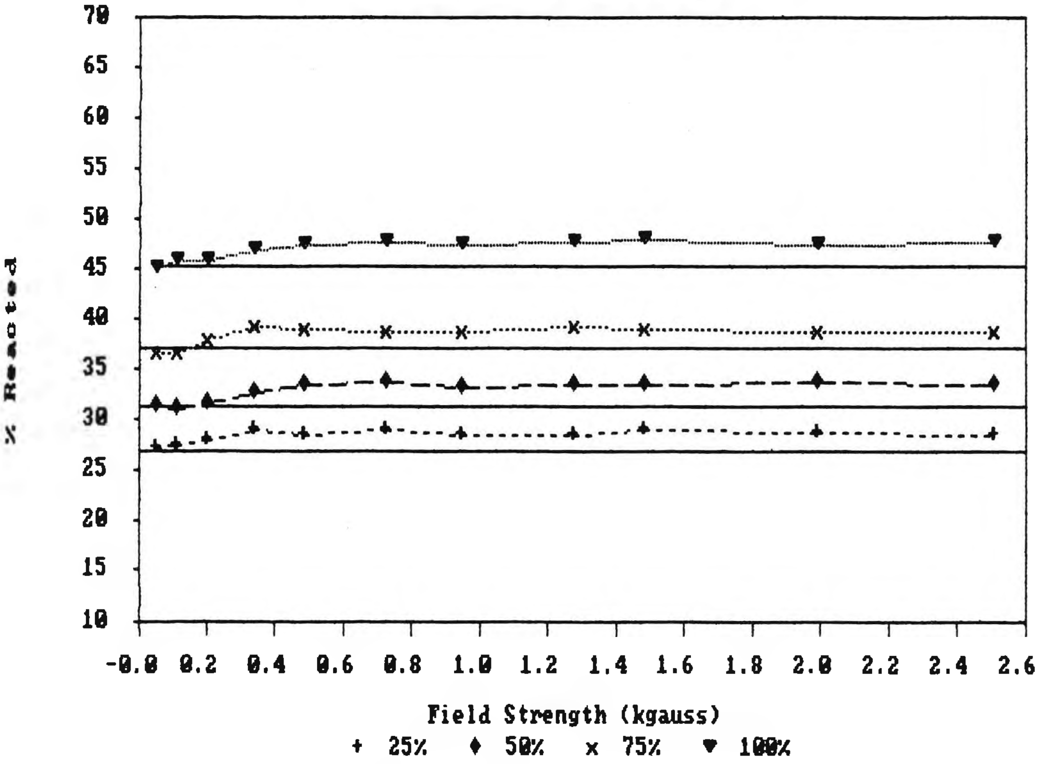
Results of Experiment 10 at Different Field Strengths.

Figure 3.19



Percentage Calcium Reacted Results for Experiment 10.
(Field Strength Tests)

Figure 3.20



Percentage Magnesium Reacted Results for Experiment 10.
(Field Strength Tests)

3.3. Discussion

3.3.i. General Comments.

All of the experiments with the calcium/magnesium phosphate system showed that the magnetic treatment of the calcium/magnesium solutions caused an increase in the proportion of both cations subsequently precipitated. This effect is consistent with the theory suggested in the last chapter. For this theory it was proposed that the magnetic field influenced the associations between ions in solution. The consequences of this would be to change the size, nature and distribution of stable clusters and to cause an increase in the activities of the charged species in the solution. For this work, only the proportions of the cations precipitated were determined, and therefore it is changes in the solution activity which are of particular interest. To understand the effects of such changes on the reactions, their kinetics and equilibria must be considered (see section 1.3.iii).

It is known that the equilibrium between the forward and backward reactions of a generalized reaction of the form;

$$aA + bB + cC + \ldots \rightleftharpoons xX + yY + zZ + \ldots$$

is expressed by the thermodynamic equilibrium constant, K_e, which is defined by;

$$K_e = \frac{[X]^x[Y]^y[Z]^z\ldots}{[A]^a[B]^b[C]^c\ldots}$$

The square brackets are usually taken to represent the concentrations of the products and reactants. However, the activities rather than the concentrations should be used.

The kinetics of the forward and back reactions are related to the value of K_e. If k_1 and k_2 are the two rate constants, then the rates of the forward and back reactions, r_1 and r_2, are;

$$r_1 = k_1[A]^a[B]^b[C]^c\ldots,\text{ and,}$$

$$r_2 = k_2[X]^x[Y]^y[Z]^z\ldots$$

At equilibrium, $r_1 = r_2$, so;

$$k_1[A]^a[B]^b[C]^c\ldots = k_2[X]^x[Y]^y[Z]^z\ldots$$

Therefore;

$$\frac{k_1}{k_2} = \frac{[X]^x[Y]^y[Z]^z\ldots}{[A]^a[B]^b[C]^c\ldots} = K_e$$

So, the equilibrium constant is the ratio of the two velocity constants for the forward and backward reactions. Since velocity constants usually alter to different degrees when the temperature is varied, it follows that the value of the equilibrium constant varies with temperature.

Another important consideration is LeChatelier's principle, which can be stated as:

> "If a system is in equilibrium and one of the factors pressure, temperature, or the concentration of a component , is altered, then the system responds in such a way as to oppose, or tend to oppose, the change that has been made."

In the introduction to this chapter the equations for the two competing reactions were presented. For these the equilibrium constants, K_{e1} and K_{e2}, are given by;

$$K_{e1} = \frac{[CaHPO_4]}{[Ca^{2+}][HPO_4^{2-}]}$$

and,

$$K_{e2} = \frac{[MgHPO_4]}{[Mg^{2+}][HPO_4^{2-}]}$$

It can be seen that, if the magnetic treatment of the calcium/magnesium solution caused an increase in the activities of the Ca^{2+} and Mg^{2+} ions (i.e. the values of $[Ca^{2+}]$ and $[Mg^{2+}]$), this would tend to reduce the values of K_{e1} and K_{e2}. However, by

LeChatelier's principle, the equilibrium would shift to oppose this change. In consequence the forward reaction (i.e. that leading to the production of the precipitate) would be promoted. The increase in the amount of calcium and magnesium reacted can therefore be explained.

If the above theory is accepted then the increases in the percentage reacted values can be attributed to changes in the activity of the solutions. There is, however, an obvious limit to the magnitude of this effect - the concentration of the solution! So, however much the magnetic treatment influences the association between ions in solution, its activity can never exceed its concentration. For more dilute solutions, the activity coefficient is lower, and hence the values of the activity and concentration are closer. Therefore, it would be expected that the maximum degree of any change caused by the magnetic treatment would be determined by the concentration of the solution and that the magnitude of the effect on the activity of the solution would be smaller for more dilute solutions.

Evidence in support of these ideas can be obtained by comparing the maximum magnitude of the magnetic treatment effect at the different concentrations used. For experiments 1 and 2 the calcium/magnesium solution contained one mole/l of each cation. The minimum increase in the percentage reacted values, as a result of the magnetic treatment, was 10.0%. For experiments 5 to 10 the solution concentration was reduced to 0.05M for both cations. For these experiments the increases in the percentages of calcium and magnesium reacted were found to be much lower (between 1.6% and 3.8%).

During the course of the tests no significant differences were found between the magnitude of the effect on the two cations. For the proposed theory to be consistent with this observation, the activity coefficients for equimolar concentrations of calcium and magnesium chloride would have to be very similar. Activity coefficients are determined from the apparent degrees of dissociation of a solution, which in turn can be found from the molar conductance values. The CRC Handbook of Chemistry and Physics gives values for the molar conductance of calcium and magnesium chloride solutions at 25°C, which are presented in Table 3.12.

Table 3.12

Concentration (mol/dm^3)	Calcium Chloride		Magnesium Chloride	
	Conductance, Λ_v (Ω^{-1} cm^2 mol^{-1})	$\alpha = \Lambda_v/\Lambda_\infty$	Conductance, Λ_v (Ω^{-1} cm^2 mol^{-1})	$\alpha = \Lambda_v/\Lambda_\infty$
0.1	102.40	0.754	97.10	0.750
0.05	108.47	0.799	103.08	0.797
0.02	115.65	0.851	110.04	0.850
0.01	120.36	0.886	114.55	0.885
0.005	124.25	0.915	118.31	0.914
0.001	130.36	0.960	124.11	0.959
0.0005	131.93	0.971	125.61	0.971
'Infinite Dilution'	134.84	(1.000)	129.40	(1.000)

Molar Conductance Values for Calcium and Magnesium Chloride.

The values for the apparent degree of dissociation, α, show that the degree of interionic activity for calcium chloride and magnesium chloride solutions are very similar. Hence, no significant difference between the magnitude of the effect on the two cations would be expected.

The ionic mobilities of calcium and magnesium were calculated from their conductance at 'infinite dilution' values and found to be 6.23×10^{-4} cm/second for calcium and 5.59×10^{-4} cm/second for magnesium. It is interesting to note that the calcium ions move faster than the magnesium ions even though they are larger (the ionic radius for calcium is 0.099nm, while that for magnesium is 0.066nm). This is a consequence of the fact that small ions tend to have a greater degree of hydration than larger ions. This is also consistent with the fact that the rate of formation of calcium phosphate was found to be greater than that for magnesium phosphate.

3.3.ii. Initial Experiments.

The initial experiments, which used the glass housed HDL design magnetic units, produced some useful and interesting results. The first tests showed that the duration of circulation of the calcium/ magnesium solution was not an important factor in determining the magnitude of the magnetic treatment effect. More will be said concerning this when the influence of different flow parameters is considered.

Experiment 2 was concerned with the effects of continuing the circulation through the control and magnetic units after the addition of the phosphate. Similar results were obtained as for Experiment 1, suggesting that the continued treatment had little significant additional influence. This indicates that the effect is much more pronounced on species in solution than on already precipitated solids. This observation will be considered further when the 'memory effect' is discussed.

The final experiment for which the glass housed units were used was an attempt to determine the level of the effect when different volumes of the phosphate solution were added. The results showed that the addition of a large volume of the phosphate solution

(100ml), relative to the volume of the cation solution, caused a much smaller change in the percentage reacted figures than were achieved with the smaller volumes. There are two possible explanations for this. The first is that the percentage of each ion precipitated was close to the maximum amount which could be precipitated (i.e. the percentage not reacted was equivalent to the maximum solubility concentration for calcium and magnesium phosphates). The second possible explanation is that the large volume added 'diluted' the treated solution, and hence reduced the effects of the magnetic treatment.

3.3.iii. The 'Memory Effect'.

The results of Experiment 5 showed that the effect of the magnetic treatment persisted for several hours after the magnetic field was removed. The degree of the effect was found to fall, approximately linearly, to the control value over a period of between five and eight hours. This effect has long been one of the 'stumbling blocks' to developing an accepted mechanism to describe the observed changes. The relaxation time of any change in the energy of ions in a solution caused by a magnetic field has been calculated by many authors (e.g. Söhnel and Mullin, 1988), and found to be of the order of nano- or even pico-seconds. However the validity of performing this type of calculation on a system which shows many anomalies and is not yet fully understood on a microscopic scale, can be questioned. This is clearly demonstrated by Franks (1983), who carried out a number of calculations on relaxation times of changes in water caused by electric fields. The values obtained were discussed in relation to the viscosity and self-transport properties of water molecules and to the results of NMR and dielectric analyses. He comments:

> "At first sight such self-consistency and agreement between results obtained from different techniques may seem gratifying, but the actual results raise questions as to the mechanism of molecular transport in water. Thus, the theory of dielectric relaxation and rotational diffusion takes as its starting point the diffusion of an isotropic sphere in a viscous continuum. The theory therefore does not apply to liquids the molecules of which are associated by hydrogen bonds. Indeed, the results from dielectric measurements on alcohols or amines do not fit [the] equation..., because such liquids are believed to contain linear branched chain and/or cyclic aggregates. It is surprising, therefore, that water which is probably the most associated liquid, obeys this simple relationship which is based on a molecular model that can hardly represent the state of affairs in liquid water."

Franks goes on to discuss several other unexplained anomalies of the transport and other properties of water and concludes;

> "...no model has yet been devised that can account for all the physical properties of water."

In view of these comments, the results of investigations such as those presented in this thesis have to be taken on their own merit, rather than with preconceived opinions, since these can only be based on a background which is itself in doubt. Indeed, it is possible that the results of experiments on the influence of applied magnetic fields on species in aqueous solution may eventually help in the development of a microscopic description of water. It seems possible that the explanation for the 'memory effect' may be connected with the microscopic structure of solutions. However, no further comments can be made concerning the effect until fundamental studies have been carried out and/or an accurate microscopic description of water is developed.

A second important observation was made concerning changes in the magnitude of the effect after the magnetic field was removed. The results show that the degree of the effect increased for several minutes, or even tens of minutes after the treatment had finished.

This is thought to be a new discovery, since no mention of changes of this type has been found in the literature. Again little can be said concerning the microscopic changes which must be taking place in the solution. However, this discovery suggests that the changes in the interionic associations, proposed to account for the observed effects, may be a consequence of a 'chain' of microscopic events which were initiated by the passage of the solution through the magnetic field (an 'avalanche' effect). This argument also explains why continuing the circulation through the magnetic field after the addition of the phosphate had no additional influence on the magnitude of the effect.

3.3.iv. Flow Parameters and Magnetic Field Strength.

The results of Experiments 6 to 9, with different flow conditions, demonstrated several interesting aspects of the magnetic treatment phenomenon. The first conclusion which can be drawn from the results is that the magnitude of the effect is not significantly influenced by the number of times that the solution is passed through the magnetic field. This is demonstrated by the similarity between the results obtained for the recirculating and the single pass experiments. This supports the findings of many of the industrial trials of magnetic units, for which similar changes have been found in situations where feed water to the process area is recirculated and where it is constantly renewed.

The experiments prove conclusively that the velocity of the ions through the magnetic field is a very important factor in determining the degree of the effect. The tests showed that below a certain flow rate the magnetic treatment had no measurable effect on the percentages of the cations precipitated. This minimum flow rate was found to be greater when the wide diameter tubing was used than for the narrow tubing. For the narrow (3.0mm i.d.) tubing the minimum flow rate was found to be between 0.3 and 0.5 l/hour, which corresponds to a velocity between 2.9 and 4.9 x 10^{-3} m/s. For the larger (4.5mm i.d.) tubing the minimum flow rate was between 0.5 and 1.0 l/hour, giving a velocity between 2.2. and 4.4 x 10^{-3} m/s. These values suggest that the minimum flow rate required must be of the order of 3.5 x 10^{-3} m/s.

As the velocity of the solution increased above the minimum value determined above, the degree of the effect increased very rapidly to a maximum. At higher velocities little or no further increase in the magnitude of the effect was observed.

The results of the tests at different field strengths are remarkably similar to those obtained for the flow rate experiments. Indeed, the graphs for the two sets of tests are easily confused. The results showed that there was a minimum field strength, below which the magnetic treatment had no significant effect on the percentages of the cations which were precipitated. As the field strength was increased above this minimum, the degree of the effect increased to a maximum value, above which there was little subsequent change. The minimum magnetic field strength was found to be approximately 200 gauss, and the maximum effect was achieved with a field of about 500 gauss.

The changes determined between control and magnetically treated electrolyte solutions have been shown to be consistent with changes in the degree of interatomic association within the solutions. It is suggested that these changes are brought about by a direct interaction between the magnetic field and the hydrated ions. When a solution is passed through a magnetic field, any charged particles in it would experience a number of forces, including that due directly to the interaction of the charges on the particles and the magnetic field, F, which was discussed in section 1.2.iv and is given by;

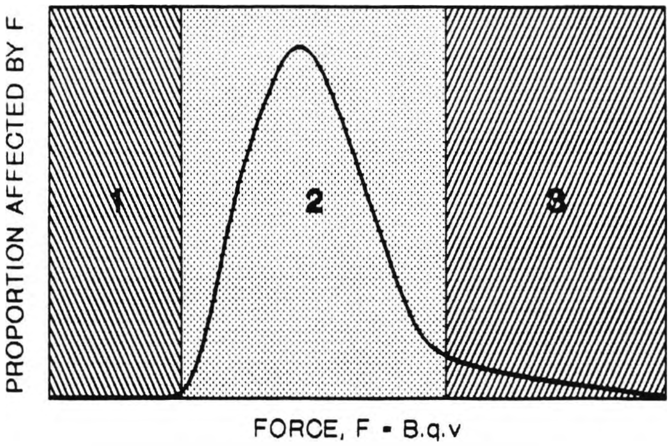
$$F = B.q.v,$$

where B is the magnetic field strength, q is the charge on the ions and v is their velocity through the field. It can be seen that the magnitude of this force increases with both increasing velocity and field strength. In view of the experimental results, it is justifiable to assume that this force contributes to the subsequent changes determined for the magnetically treated solutions.

In the light of the results of the present work, it is proposed that the force on the charged species in the treated solution, due to their interaction with the magnetic field, disrupts an energetically stable microscopic association between them. This, through a 'chain reaction', causes the macroscopic changes which were determined during the course of the present work. The influences of solution velocity and field strength on the effect can, therefore, be explained in terms of the range of energies associated with the degree of association of the species in the solution and, consequently, the minimum force required to disrupt these associations. A common feature of such energetic systems is that their range of energies conforms to a normal distribution (e.g. the kinetic energy of ions in a solution). Figure 3.21 shows the theoretical energy distribution for the degree of interionic association, suggested above.

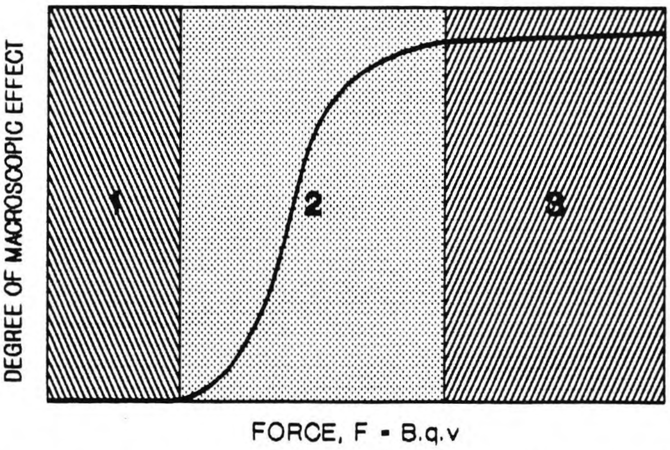
It can be seen that if the force, F, is below a certain value, no effect on the charged species would be expected (area 1 on the distribution graph) and, on a macroscopic level the magnetic

Figure 3.21



Theoretical Distribution of Energy of Interionic Associations.

Figure 3.22



Proposed Degree of Macroscopic Effect for Different Values of F.

treatment would have no effect. As F is increased by increases in the field strength and/or flow rate, some of the less strongly associated particles would be affected, and a macroscopic effect would be detected. Further increases in F would have a much reduced additional influence, as the majority of the associations between the species, which could be influenced, would already have been affected (area 3). Figure 3.22 shows the size of the macroscopic effects which would be observed as a result of these events.

3.4. Conclusions

The present results have shown conclusively that the magnetic treatment of fluids can influence the proportions of calcium and magnesium ions precipitated from an equimolar solution of the two ions by the addition of a phosphate solution. The results are consistent with changes in the degree of interionic association within the treated solution, and it is suggested that the effect of the magnetic field is to disrupt some aspect of its microscopic structure. This would promote a 'chain reaction' of events, affecting the microscopic structure of the solution. The eventual outcome of this would be increases in the mobility of the ions, which accounts for the macroscopic effects determined during the course of the experimental work. The details of the microscopic changes which may occur cannot be predicted, since the structure of water and aqueous solutions have yet to be adequately described.

The results of the investigation have also suggested that the initial effect may be 'fuelled' by the force on the ions due to their interaction with the applied magnetic field. The degree of the effect under different flow conditions and with different field strengths has been found to be consistent with the proposed mechanism.

CHAPTER 4

THE EFFECTS OF APPLIED FIELDS ON CORROSION PROCESSES

4.1. Introduction and Literature Review

In this chapter the results of a number of investigations into the effects of the magnetic treatment of aqueous solutions on the corrosion of steel are presented. Many manufacturers of magnetic water treatment devices, in addition to claiming the scale-preventing properties of their products, also promote then as corrosion inhibitors (see section 1.2). In the introductory chapter, the potential savings to worldwide industry of a cheap method of scale prevention were demonstrated, by an examination of the massive cost of scaling to various industries around the world. When the costs due to corrosion are considered in the same way, it is not surprising to find that the claims for the corrosion-inhibiting properties of magnetic treatment have caused a great deal of interest, in both the scientific and industrial communities.

Before considering the cost of corrosion and the claimed benefits of the hydrodynamic treatment of fluids in inhibiting it, it is useful to try to define the term itself and to briefly consider some of the factors which are known to affect it.

Friend (1935) describes the rusting of iron and steel:

> "Probably the commonest form of corrosion is the destruction of ferrous metals through oxidation; the hydrated oxide produced, being known as rust. This is a porous, friable material of composition represented approximately by the chemical formula, Fe_2O_3Aq, where Aq represents a fluctuating amount of more or less combined water."

Watts (1938) aptly and succinctly defines the same processes from an industrialist's point of view as;

> "a major industry in reverse - all loss, with never a profit."

It is very difficult to estimate accurately the worldwide cost of corrosion. One need only consider the huge amount of steel which is in use around the world to understand the reason for this. Speller (1935) estimated that there were about 1,200 million tons of steel in use in the world at that time, of which 75% required some form of protection before being put into use. It is obvious that in the 58 years since this estimation, the figure given would need to be increased several-fold. This is demonstrated in Table 4.1, which shows the progression in estimations of the cost of corrosion. It can be seen from the table that the estimated cost for the U.K., tripled from £200 million to £600 million in just nine years, and that by 1986 it had reached £1365 million.

Table 4.1

No.	Author	Cost of Corrosion	Country	Year
1	Hadfield	£ 600 million	World	1922
2	Hudson	£ 200 million	U.K.	1940
3	Uhlig	$ 6000 million	U.S.A.	1949
4	Vernon	£ 600 million	U.K.	1949
5	Linderborg	$ 47-62 million	Finland	1960-1
6	Linderborg	$ 39 million	Sweden	1960-1
7	Behrens	$ 6000 million	F.R.G.	1968-9
8	Kolotyrkin	$ 6900 million	U.S.S.R.	1969
9	Boshoku Gijutes	$ 9200 million	Japan	1976-7
10	Rajagopalan	£ 1365 million	U.K.	1986

Progress in the Estimation of the Cost of Corrosion.

Tretheway and Chamberlain (1988) graphically demonstrate the consequences of corrosion and the huge costs which it incurs:

> "It has been calculated that in the UK, 1 tonne of steel is converted completely to rust every 90 seconds. Apart from the waste of metal, the energy required to produce a tonne of steel from iron ore is sufficient to provide an average family home with energy for three months."

All of this information serves to highlight the worldwide cost of corrosion, and hence the potential importance of corrosion inhibition by the magnetic treatment of fluids.

Many authors (e.g. Kozlov, 1971; Mibbeu, 1973; Grutsch and M^cClintock, 1984) have reported that magnetic treatment reduces both scale and corrosion. Raisen (1984) presents positive descaling and corrosion-inhibiting results of industrial tests with a magnetic treatment device. He reports a reduction in corrosion in cooling towers, from 0.437 mm/Year to 0.206 mm/Year following the treatment, and states:

> "The reduction in corrosion was also evident by the colour of the scale, which changed from rust colour to white due to reduction in formation of iron oxide."

A colour change due to magnetic treatment is also reported by Vermeiren (1958). He reports on tests with lake water in Scandinavia and Canada:

> "This water attacks steel and forms ferric blisters which finally may block the pipes entirely or may perforate them. As magnetic treatment stops the corrosive action and transforms iron oxide to powdery black magnetite, these deposits disappear little by little; the piping is finally completely free and shows a smooth surface; corrosion does not continue."

Ar (1972) carried out a number of laboratory tests with magnetic treatment devices and, as with Raisen's industrial trials, found a beneficial effect for both scaling and corrosion. He reports on corrosion tests on aluminium foils:

> "There was a distinct qualitative difference in the appearance of the aluminium foils in the two tanks. The foils on the treated side were slightly dull in appearance and showed no brittleness. The foils on the untreated side were extremely brittle and immediately crumbled when touched."

It has also been reported (Vermerien, 1958; Joshi and Kamat, 1966; Duffy, 1977) that the pH of certain solutions is increased by magnetic treatment. Clearly, if true, this would reduce the acid corrosive properties of the affected solutions.

Other investigators have found that magnetic treatment only influences scale deposition, and has no effect on corrosion. Koubikova (1969) advanced the following conclusions of an investigation at the Prague Institute of Hydraulic Research:

> "a) The corrosive properties of water are not reduced by magnetic treatment.
>
> b) In the case of waters which have a tendency to form scale..., it is possible...to change the nature of scaling as well as to destroy old and tough scaling."

Those authors who repudiate the effect usually report their findings in a very scathing manner. Eliassen et al. (1958), evaluated the performance of three "gadgets" and found them to be ineffective for scale formation, scale dissolution and corrosion prevention. Chowdhury and Tanzosh (1984) take the sceptics attack one stage further:

> "The final report concludes that the MWT devices don't work...In fact...corrosion increased* and there was a greater need for fungicides when the units were used."

The idea that magnetic treatment increases corrosion, though only mentioned in passing by Chowdhury and Tanzosh, is one which has been advanced at length by many authors, e.g. Duffy, 1977; Busch et al., 1986; Herzog et al.,1989. Indeed, these authors have suggested that any changes in scale deposition, due to the treatment, are a consequence of increases in the iron concentration due to the increased rate of corrosion. Duffy's comments are typical:

> "These results suggest a mechanism by which commercial magnetic antiscale devices could indirectly retard $CaCO_3$ scale formation. According to this mechanism iron ions retard the growth of $CaCO_3$...and the function of the magnetic device is to increase the concentration of iron in solution by increasing the rate of corrosion of the attached pipe by either magnetic and/or galvanic effects."

[Note : * = Emphasis added.]

In conclusion Duffy states:

> "Due to the adverse effect of the magnetic devices on the corrosion rate of the iron pipe and the limited conditions under which the mechanism functions, it is not here recommended that these devices be used for scale control in commercial heat exchangers and boilers."

Grutsch and M^c^Clintock (1984), however, questioned the validity of Duffy's findings and made the following comments concerning the experimental techniques and testing methods which he had employed:

> "Our review of Duffy's thesis reveals his experimental protocol to measure such an effect was unequivocally inadequate."

There are a huge number of references on topics which support one or another of the arguments given above. However, in most cases these documents are as contradictory in their content as those which they are supporting. For example, it has been reported (Golubtsov et al, 1971; Martynova and Gusev, 1972; Kvajic and Drost-Hansen, 1978) that the presence of iron in treated water increases the descaling effect of magnetic treatment. However, this claim is refuted by the findings of Mibbeu (1973):

> "In addition, tests made to see how effective the magnetic method is for the treatment of the artesian well water used in some power stations indicate that the best results can be obtained by a combination of magnetic treatment and <u>removal of the iron content</u>*."

It is not surprising, given the number of contradictory claims and scathing attacks made in the literature, that there is so much confusion and disagreement about the possible effect of magnetic water treatment on corrosion. It was, therefore, the aim of the present work to conclusively validate, or otherwise, the claimed effects and, if proven, to investigate their properties.

[Note : * = Emphasis added.]

4.2. Results

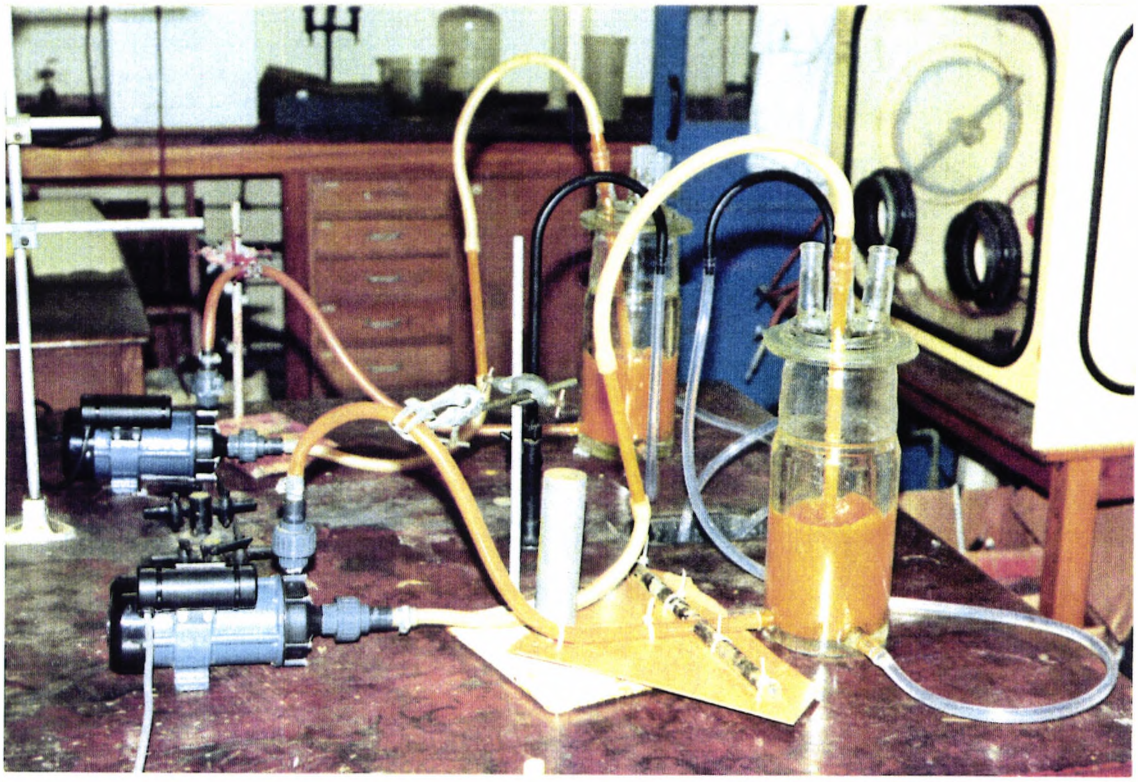
4.2.i. Aims, Equipment Design and Data Handling.

In view of the controversy surrounding a possible effect of magnetic treatment on corrosion, as shown in the previous section, it was decided that the initial work on this topic should have two goals. The first aim was to develop an experimental technique and test rig, which would allow reproducible corrosion rate experiments to be carried out. [Note : The development of the testing procedures continued thoughout the whole of the experimental work. Consequently, details of any minor changes to the test rig, and the reasons for these modifications are presented with the relevant results.]

The second goal of the work was to use this test arrangement to provide irrefutable evidence of the existence, or otherwise, of an effect on corrosion by magnetic treatment. If these investigations showed that there was indeed an effect, then the scope of the experiments would be extended to determine how various parameters, such as flow rate, magnetic field strength and ionic concentration, influenced the phenomenon.

During the course of the experimental work two main apparatus designs were used. The first of these was based on the jacketed vessel test rig, which was used for much of the work presented in this thesis and has been described in section 1.4.ii. The magnetic field was produced by two AlNiCo permanent magnetic rods, which were positioned on either side of the tubing, giving fields with simple geometries, perpendicular to the direction of the solution flow. Figure 4.1 is a photograph of two of the test rigs used.

Figure 4.1

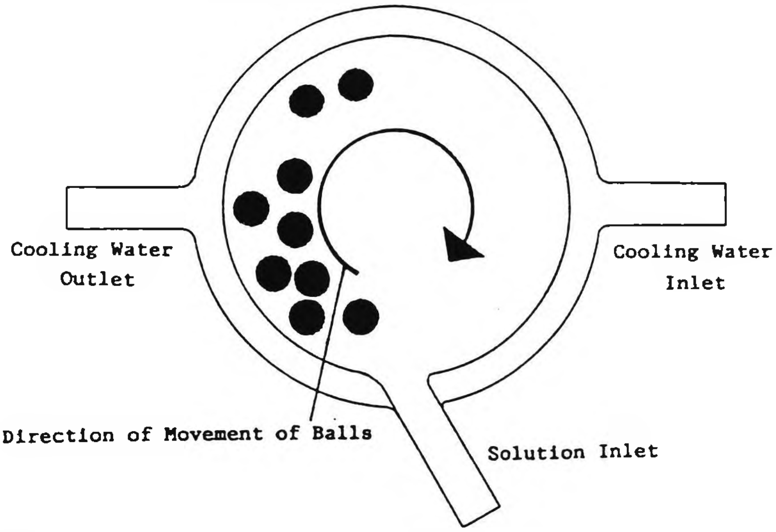


Corrosion Testing Apparatus (Single Test Rigs).

The test rigs were slightly modified for use with the work on corrosion. The pump was reversed, so that the inlet to the vessel was at the bottom. The inlet was also angled to the plane of the vessel, as shown in Figure 4.2. These two alterations were made so that the steel balls used in the experiments, would be moved around the vessel. This ensured even corrosion, since the whole of the surface of the balls was in contact with the solution, and prevented corrosion products adhering to the metal surface.

The second experimental design, which was used in much of the later work, was a multiple test rig. This was developed so that several experiments could be carried out, under the same conditions, concurrently, and so that the influence of reduced flow rates and interrupted flow on the magnetic treatment effect on corrosion, could be investigated. The apparatus allowed up to nine experiments to be

Figure 4.2



Modified Jacketed Vessel used in Corrosion Experiments.

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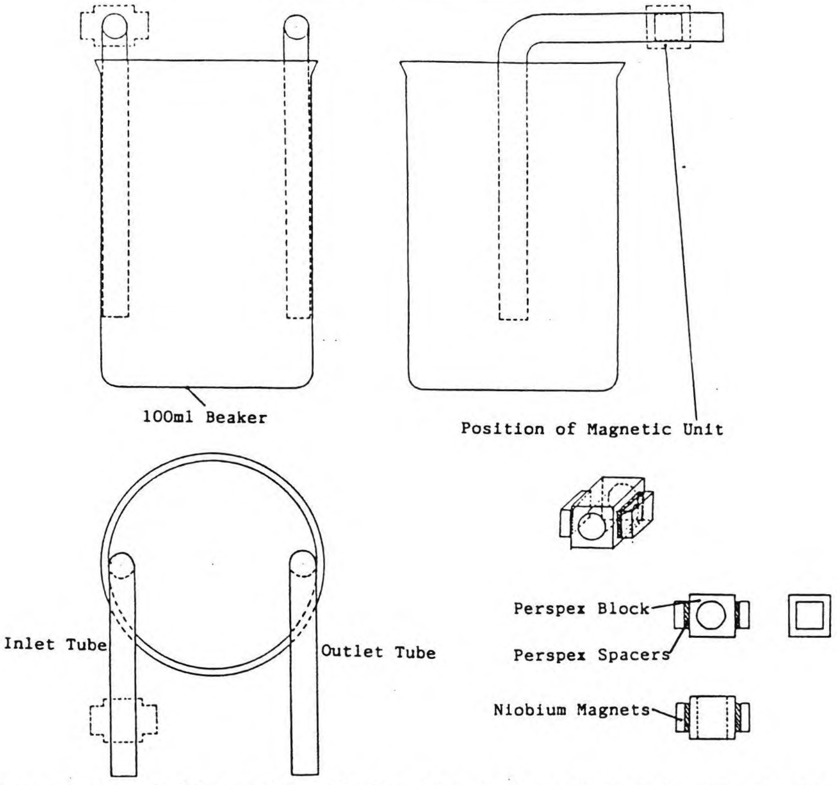
carried out at any one time. The vessels were 100 ml beakers with L-shaped inlet and outlet tubes. The magnetic fields were produced using two small Niobium permanent magnets supported on a perspex block which fitted around the inlets to the vessels. Different magnetic field strengths were obtained by altering the separation between the magnets using perspex spacers. Figure 4.3 shows the design of the vessels and the magnetic units.

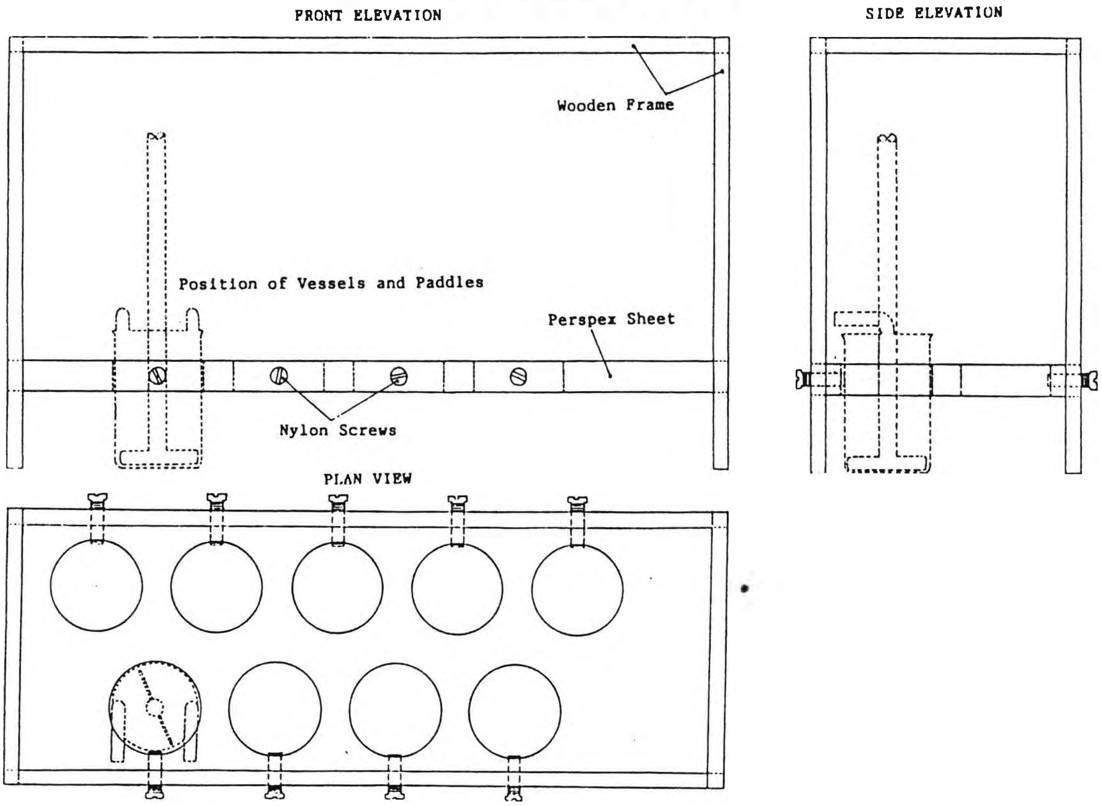
The nine vessels were held in holes in a perspex base by nylon screws. The base could be supported in a water bath to ensure that the temperature of the test solutions was kept constant. Figure 4.4 shows the design of the test rig base. A set of chain driven paddles was supported above the base, to move the balls around the vessel and ensure even corrosion over the whole of their surface. The paddle gears were held between two perspex sheets and the paddle rods themselves fitted into polypropene bushes. Figure 4.5 is a diagram of the paddle system, which was driven by a Citenco F.H.P. stirrer motor.

Figure 4.3



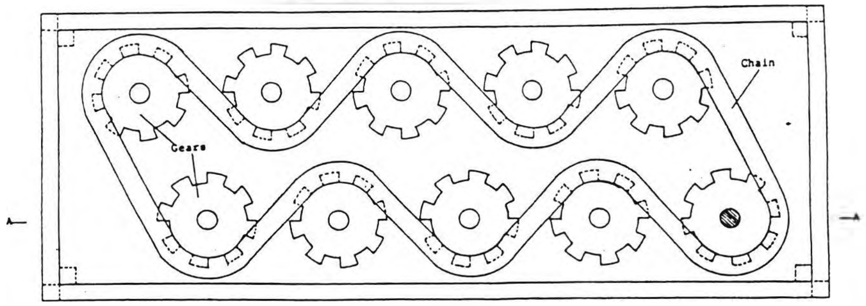
Vessels and Magnetic Units Used for Multiple Test Rig.

Figure 4.4

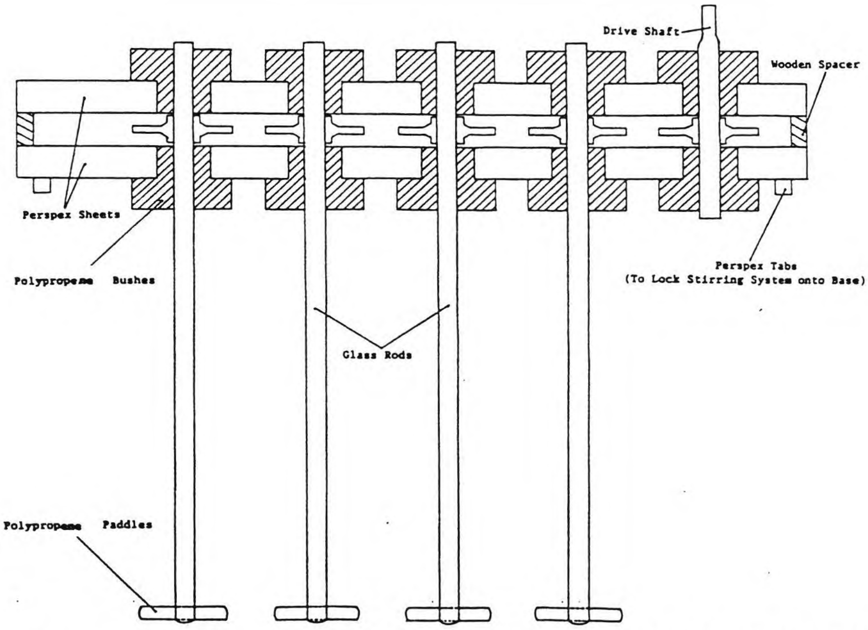


Multiple Test Rig Base and Vessel Holder.

Figure 4.5



Plan View of the Stirring System Used with the Multiple Test Rig. (N.B. Lid Removed).



Section A - A of Stirring System Used with Multiple Test Rig.

Having obtained the weight loss results from the experiments, by removing and weighing the test samples at various time periods, it was necessary to convert the results into standard units, so that they could be usefully compared with each other. One of the standard forms for expressing the corrosion rate of metals is as weight change per unit surface area per unit time, common units being $g/cm^2/hour$ and $g/m^2/day$. The weight change can be expressed as either weight loss, if the weight of uncorroded metal is considered, or weight gain if the total weight of uncorroded material and corrosion products is determined. For the present work, it was most convenient to measure the weight of uncorroded metal, and so the corrosion rates were calculated as weight loss per unit surface area per unit time.

For most of the work carried out on corrosion, steel balls, of the type used in ball bearings, were used as the test samples. In order to express the corrosion of these balls in standard units, as discussed above, it was necessary to determine their surface area. Initially this was achieved by measuring the diameter of the balls, using Vernier calipers, and applying the equation for the surface area of a sphere, $A = 4\pi r^2$, where A is the surface area and r is the radius. However, it was found that balls which had the same measured diameter and, therefore, the same calculated surface area, had different masses. In addition, since this method involved measuring the diameter of every ball used, and then calculating and summing the individual surface areas, it was also very time consuming. Therefore, it was decided to calculate the surface area of the balls from their masses. The method used to achieve this was developed in the following way:

If d is the density of the steel used in the balls, and the mass of n balls is measured to be M, then the total volume of the balls, V_n, can be found by;

$$V_n = M/d.$$

So, the average volume of one ball, v, is;

$$v = M/nd.$$

But, for a sphere, $v = 4\pi r^3/3$, so;

$$v = M/nd = 4\pi r^3/3.$$

Rearranging this gives;

(1) $$r = \sqrt[3]{(3M/4\pi nd)}.$$

The surface area of a sphere, S, with radius r, is;

(2) $$S = 4\pi r^2.$$

Substituting equation 1 into equation 2 gives;

$$S = 4\pi(3M/4\pi nd)^{2/3}.$$

So, the total surface area of n balls, S_n is given by;

$$S_n = \{6\surd(n\pi).M/d\}^{2/3}.$$

This method of determining the surface area also had the benefit that, as the balls corroded, their areas could be calculated at each mass determination. This is important, since while corroding, the active area of the balls decreased.

The steel balls used as the corrosion test samples were obtained in a range of sizes (3.2mm to 20.0mm), and were all of the same composition. They had been manufactured for use in automobile bearings, from a through-hardened, low-alloy, 1% carbon-chromium steel (EN31). The density of the steel was 7.6588 g/cm^3 and it contained the following alloying materials:

C = 0.90 - 1.20%
Mn = 0.30 - 0.75%
Cr = 1.00 - 1.60%
Ni = 0.05 - 0.08%

In order to make the determination of the corrosion rate for each experiment as accurate as possible, several mass readings were taken at different time periods. The surface area used for each determination was taken to be the average value calculated for two successive mass measurements. To simplify the calculations involved, two computer programs for a BBC microcomputer were used (see section 1.4.i and Appendix A). The first of these, called 'Corcalc', determined the results as weight loss per unit surface area and the second, called 'Curfit', was used to calculate the corrosion rates. The data for the programs are given in Appendix D.

The first use that was made of these programs was to validate the assumptions made about the surface area calculations. It was found that, when the results were treated in the way described and analyzed using the regression analysis program, a much better correlation was obtained for the corrosion rate determinations.

4.2.ii. Preliminary Results.

Even before the actual investigation into the influence of magnetic treatment on corrosion had begun, several observations had been made which indicated the existence of some form of effect. In the work on calcium oxalate precipitation (see section 2.2), it was noted that the magnetic units which were initially used for the tests (HDL 1" Units), corroded in the 0.1M calcium chloride solutions. On several occasions the corrosion was so severe that the solutions became coloured with dissolved cobalt corrosion products. Table 4.2 shows the results of an analysis of one such solution. (Note : The results presented in Chapter 2 were obtained with new units in which the metal surfaces and magnetic rods were PTFE-coated.)

Table 4.2

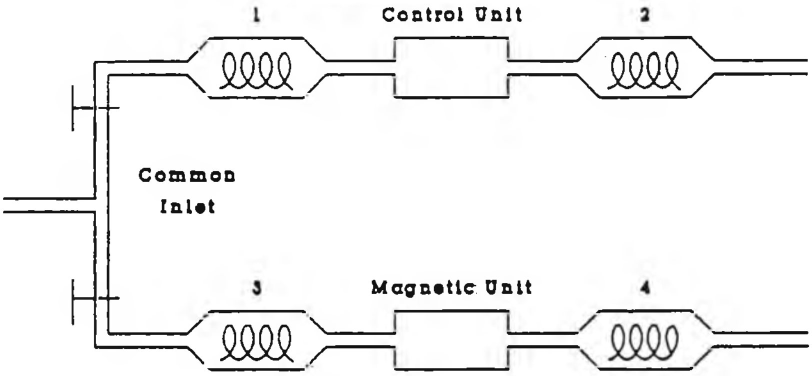
	Concentration of Ions in Solution (ppm)	
Run Type	Iron	Cobalt
Control	82	54
Magnetic	130	79

Concentrations of Fe and Co in 0.1M Calcium Chloride Solutions.

These results indicate that the magnetic treatment was affecting corrosion and that this influence caused an increase in the corrosion rate.

The initial testing apparatus used to obtain corrosion rate measurements is shown schematically in Figure 4.6. It consisted of two HDL units (one being an unmagnetised control) connected to a suitable common tap water supply. The inlet water to each side of the apparatus flowed around a weighed coil of 0.2 mm diameter iron wire, through the unit and then past a second coil of wire. The apparatus was fitted with valves and the flow rate through each unit was equalized to 120 l/hour.

Figure 4.6



Initial Corrosion Testing Apparatus.

The test was continued for two weeks, after which the apparatus was dismantled and the wire was removed and examined. It was seen that extensive corrosion had occurred. Indeed in places the wire had completely disappeared. However, when the samples were removed from the tubes they were found to contain a large quantity of powdery corrosion products and scale. Therefore, it was difficult to separate out the uncorroded metal. There was also a concern that some of the wire may have been washed out of the system. Table 4.3 shows the results of the investigation (Experiment 1). It can be seen that there is a large variation between the results, and though the sample after the magnetic treatment had the lowest weight loss, this was not considered to be conclusive proof of a magnetic treatment effect on corrosion.

Table 4.3

Test Position	Initial Weight/g	Final Weight/g	Weight Loss/g	Weight Loss/%
Pre-control	4.7768	3.8290	0.9478	19.8
Post-control	4.7782	3.9137	1.0567	22.1
Pre-magnet	4.7748	3.7181	0.8465	17.7
Post-magnet	4.7767	3.9546	0.8221	17.2

Results of Experiment 1.

Following the observations made for the first experiment, it was decided to replace the wire coils with 1/4" diameter steel balls. It was hoped that this would make it easier to accurately determine the mass of uncorroded metal left at the end of the experiments and that there would be no chance of uncorroded material being washed out of the system. It was also possible to calculate the surface area of the balls so that the corrosion rate could be expressed in standard units (see previous section). A series of four repeat tests (Experiments 2 to 5) were carried out to allow the reproducibility of the corrosion rate determinations to be ascertained.

The flow rate through each side of the apparatus was 120 l/hour and each experiment was allowed to continue for about one week. Before weighing the balls were cleaned in acetic acid, to remove any corrosion products on their surfaces, rinsed with distilled water and dried. Table 4.4 shows the results of the four experiments.

It can be seen from the tables that, for each experiment, there was a significant increase in the corrosion rate of the balls after magnetic treatment, when compared with both the control and the balls positioned before the magnetic unit. Table 4.5 show the average corrosion rates and standard deviations which were calculated for the results of the four experiments.

Table 4.4

Experiment 2 (Time = 188.25 hours.)

Test Position	Initial Weight(g)	Final Weight(g)	Wt. Loss ($\times10^{-3}$g)	Wt.Loss/S.A./Time ($\times10^{-7}$g/cm^2/h)
Pre-control	40.6508	40.6464	4.4	7.68
Post-control	40.6043	40.5992	5.1	8.91
Pre-magnet	40.6476	40.6422	5.4	9.42
Post-magnet	40.6627	40.6527	10.0	17.45

Experiment 3 (Time = 184.00 hours.)

Test Position	Initial Weight(g)	Final Weight(g)	Wt. Loss ($\times10^{-3}$g)	Wt.Loss/S.A./Time ($\times10^{-7}$g/cm^2/h)
Pre-control	40.6481	40.6449	3.2	5.71
Post-control	40.5977	40.5950	2.7	4.82
Pre-magnet	40.6047	40.5967	8.0	14.29
Post-magnet	40.6785	40.6653	13.2	23.55

Experiment 4 (Time = 191.25 hours.)

Test Position	Initial Weight(g)	Final Weight(g)	Wt. Loss ($\times10^{-3}$g)	Wt.Loss/S.A./Time ($\times10^{-7}$g/cm^2/h)
Pre-control	40.6667	40.6622	4.5	7.73
Post-control	40.6552	40.6503	4.9	8.42
Pre-magnet	40.5341	40.5279	6.2	10.67
Post-magnet	40.4922	40.4836	8.6	14.81

Experiment 5 (Time = 194.50 hours.)

Test Position	Initial Weight(g)	Final Weight(g)	Wt. Loss ($\times10^{-3}$g)	Wt.Loss/S.A./Time ($\times10^{-7}$g/cm^2/h)
Pre-control	40.5010	40.4938	7.2	12.19
Post-control	40.6520	40.6451	6.9	11.65
Pre-magnet	40.7047	40.6990	5.7	9.62
Post-magnet	40.6869	40.6744	12.5	21.10

Results of Experiments 2 to 5.

Table 4.5

Test Position	Average Corrosion Rate ($\times 10^{-7}$g/cm^2/h)	Standard Deviation (σ)
Pre-control	8.32	2.37
Post-control	8.45	2.43
Pre-magnet	11.00	1.96
Post-magnet	19.23	3.35

Statistical Comparison of Experiments 2 to 5.

Several observations can be made concerning the experimental technique:

1) The balls did not corrode evenly. The points at which they were in contact with each other, and with the walls of the tube could be seen to have corroded to a much lesser degree than those parts which were in clear contact with the liquid.

2) The results were obtained from only two weight measurements, due to the impracticability of repeatedly dismantling the apparatus. It was decided that it would be better to devise an experiment in which the balls could be easily removed and weighed. In this way it was hoped that several measurements could be taken for each run to improve the reliability of the results.

3) It was thought that the variation in the corrosion rates obtained for the four experiments could be explained in terms of changes in the tap water supply. When the supply was monitored for a week, it was found that there was a large variation in its pressure and temperature, both of which would have a marked influence on the corrosion rate.

4) The corrosion rate in London tap water was very slow. The weight loss of the balls was less than 0.02% of their original weight in one week. This meant that any errors in the weight measurement would have a large relative effect on the rate determination.

5) The surface of the balls soon became coated with a layer of scale and corrosion products, which would tend to protect the surface of the balls from further corrosion (stifling). It was also felt that if the magnetic treatment was acting as a scale inhibitor, this could account for the increase in the corrosion rate, as there would be less of this protective coating.

It was decided, in light the comments made above, that it was necessary to develop a new test rig and use new techniques to improve the reliability of the experiments. Figure 4.2 (see page 160) is a photograph of two of the new test rigs set up side by side. This arrangement had several advantages over the earlier testing procedures:

1) Scaling effects could be eliminated by using other corrosive solutions (e.g. $NaCl_{(aq)}$) instead of London tap water.

2) The balls used in the experiments could be removed and weighed several times during the course of each run.

3) The experiments could be carried out under closed and temperature-controlled conditions.

4) The design of the vessels was such that the balls could be kept in constant motion, ensuring even corrosion over the whole of their surfaces.

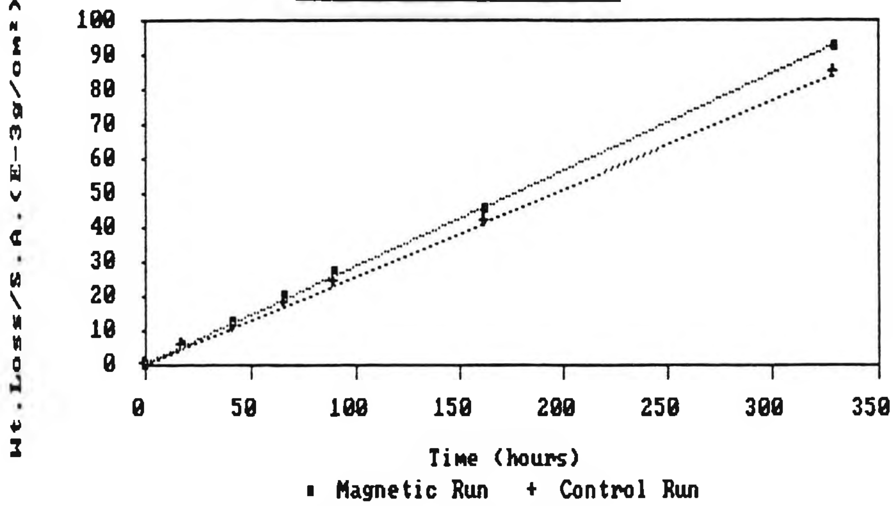
5) The magnetic runs of the experiments were set up with magnetic rods positioned around the circulating tubing, so that the only metal in contact with the solution was the balls themselves.

4.2.iii. Proof of an Effect.

The first set of experiments (Numbers 6 to 9), which were carried out with the recirculating test rigs, were set up to test how reproducible the results would be. For each experiment, 1.5 litres of 2.9% $NaCl_{(aq)}$ solution was circulated through a field of 1100 gauss for the magnetic run and 0 gauss for the control run. The temperature of the solutions was maintained at 18.0(±0.5)°C and the flow rates were measured to be 27 l/min. At various time periods, the flow was stopped and the balls were removed, cleaned and weighed. The corrosion rates were determined using the two computer programs.

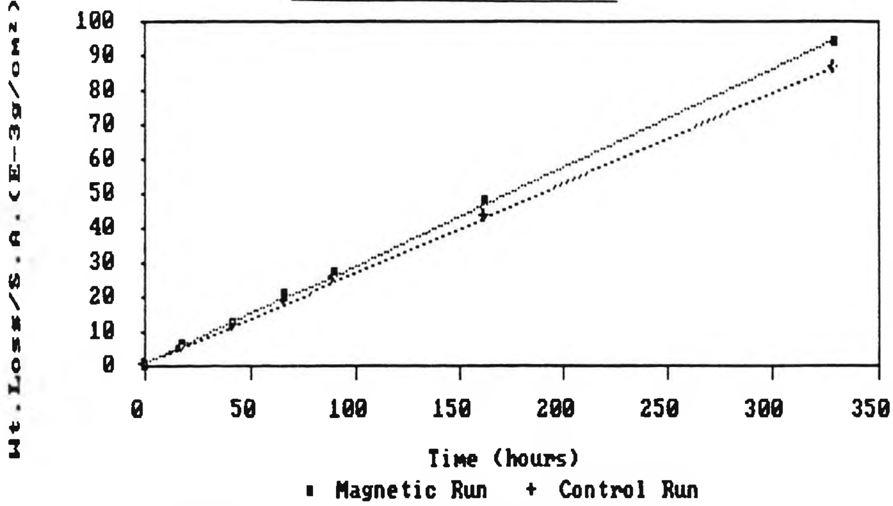
To ensure that any changes which were found were not due to differences between the two test rigs (A and B), the magnetic rods were swapped from one set of apparatus to the other for each test (i.e. for Experiments 6 and 8 test rig A was the control and test rig B was used for the magnetic run. For Experiments 7 and 9 this was reversed). Experiments 6 and 7 were carried out using thirty-six, 5.0mm diameter balls and Experiments 8 and 9 used six, 6.0mm diameter balls. This was to allow the assumptions concerning the surface area of the test samples to be checked. Figures 4.7 to 4.10 are graphs of weight loss per unit surface area against time for the magnetic and control runs of each experiment. The corrosion rates for the four experiments, calculated using the regression analysis program, are presented in Table 4.6 and Figure 4.11 is a graphical comparison of these results.

Figure 4.7



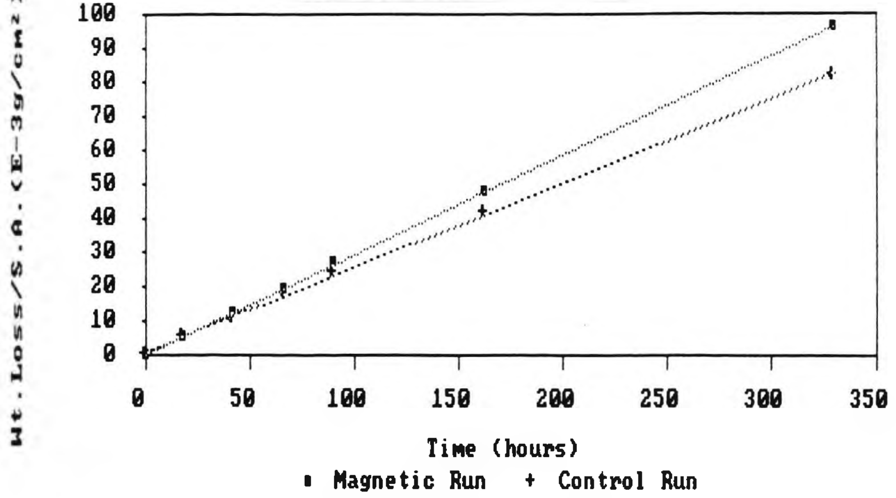
Graph of Results for Experiment 6.

Figure 4.8



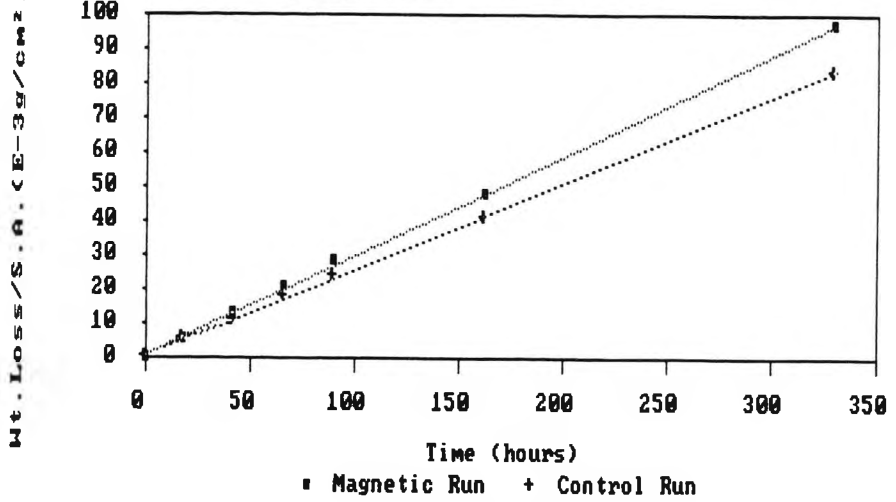
Graph of Results for Experiment 7.

Figure 4.9



Graph of Results for Experiment 8.

Figure 4.10



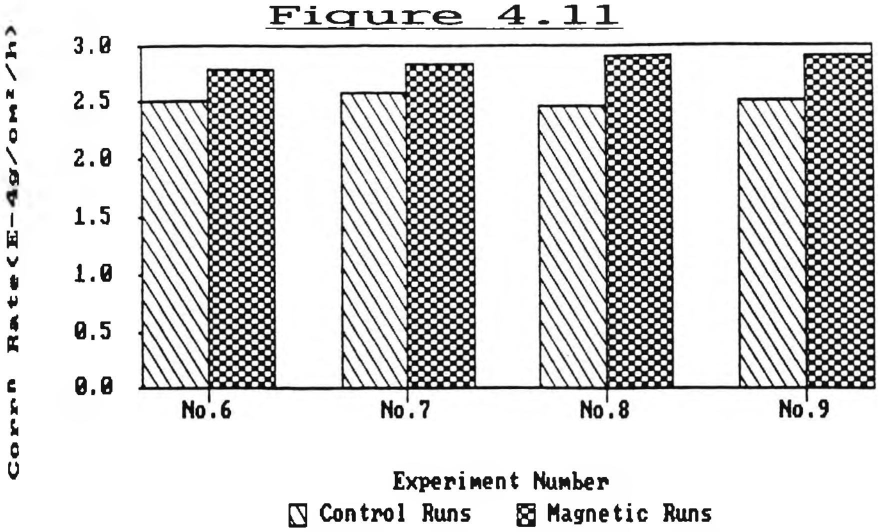
Graph of Results for Experiment 9.

Table 4.6

Exp^t Nº	Test Rigs	Nº/size of Balls (mm)	Corrosion Rate ($x10^{-4}g/cm^2/h$) Control Runs	Magnetic Runs	Percent Change
6	A/B	36 / 5.0	2.541 ± 0.016	2.775 ± 0.033	+9.2%
7	B/A	36 / 5.0	2.583 ± 0.029	2.828 ± 0.030	+9.5%
8	A/B	6 / 6.0	2.459 ± 0.027	2.900 ± 0.009	+17.9%
9	B/A	6 / 6.0	2.500 ± 0.020	2.899 ± 0.031	+16.0%
AVERAGE :			2.521(σ=0.062)	2.851(σ=0.076)	+13.1%

Comparison of Corrosion Rates for Experiments 6 to 9.

Figure 4.11



Comparison of Corrosion Rates Determined for Experiments 6 to 9.

The very low relative values for the ranges for the individual control results and the standard deviation (σ) for the average, indicate that the assumptions made concerning the surface area determination were sound and that the experimental design and testing procedures were good. The experiments carried out with the new test rig provide conclusive evidence of a magnetic treatment effect on the rate of corrosion of steel in a sodium chloride solution. The effect of the treatment was found to be an increase in the corrosion rate, by an average of 13.1%. Given the confidence in the experimental technique, it was decided to test how various parameters influenced the effect.

4.2.iv. Influence of Solution Concentration.

A number of experiments were set up using different sodium chloride concentrations, to determine how this influenced the magnetic treatment effect. It was decided to compare the rates calculated for Experiments 6 and 8 (using 5.0mm and 6.0mm diameter balls respectively), with a sodium chloride concentration of 2.9%, with those obtained using concentrations of 2.0% (Experiments 10 and

11) and 1.0% (Experiments 12 and 13). For one of the two experiments carried out at each concentration, thirty-six 5.0mm diameter balls were used (Experiments 10 and 12) and for the other, six 6.0mm balls were corroded (Experiments 11 and 13). Apart from the NaCl concentrations all the other parameters were the same as those described for the Experiments 6 and 8.

Table 4.7 shows a comparison of the corrosion rates for Experiments 6, 8, 10, 11, 12 and 13, and Figures 4.12 and 4.13 are graphs of corrosion rate against sodium chloride concentration for the two different ball sizes.

Several interesting observations can be made concerning the results of the investigation:

1) The very low ranges for the corrosion rate determinations again show the reliability and reproducibility of the testing procedures.

2) In every case the effect of magnetic treatment was to increase the corrosion rate.

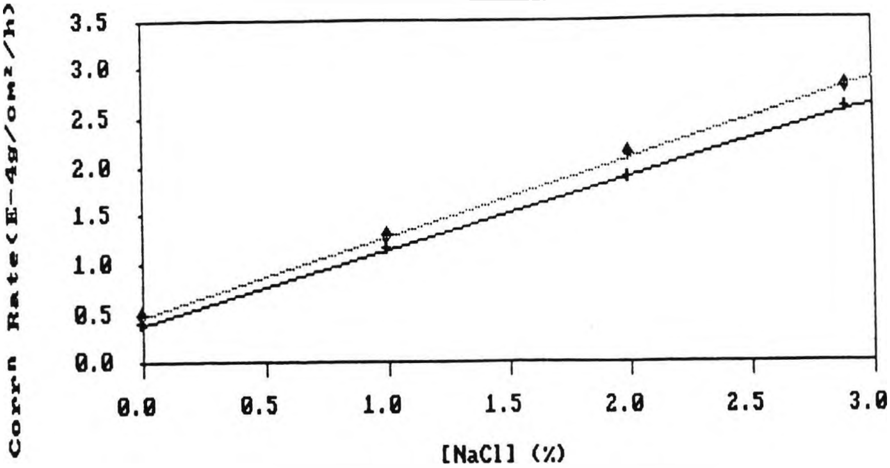
3) The determined corrosion rates were proportional to the sodium chloride concentration, for all four sets of data. This suggests that the corrosion reaction is first order with respect to sodium chloride.

Table 4.7

Exp^{t} Nº	[NaCl] (%)	Ball Radius(mm)	Control/ Magnet(c/m)	Corrosion Rate (x10^{-4}g/cm^{2}/h)	Percent Change
6	2.9	5.0	C	2.541 ± 0.016	
			M	2.775 ± 0.033	+9.2%
8		6.0	C	2.459 ± 0.027	
			M	2.900 ± 0.009	+17.9%
10	2.0	5.0	C	1.867 ± 0.003	
			M	2.086 ± 0.004	+11.7%
11		6.0	C	1.874 ± 0.017	
			M	2.211 ± 0.011	+18.0%
12	1.0	5.0	C	1.132 ± 0.003	
			M	1.262 ± 0.003	+11.5%
13		6.0	C	1.119 ± 0.011	
			M	1.304 ± 0.017	+16.5%

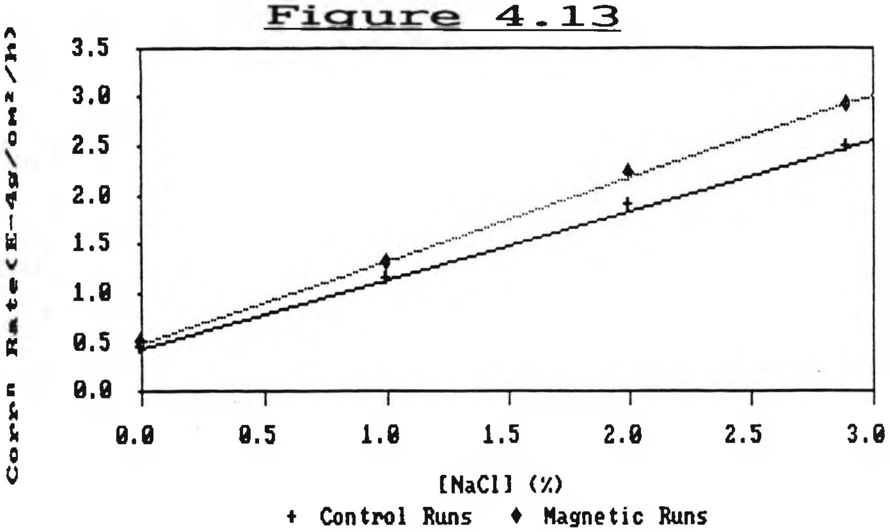
Comparison of Corrosion Rates at Different NaCl$_{(aq)}$ Concentrations.

Figure 4.12



Corrosion Rates at Different [NaCl] Concentrations (5.0mm Diameter Balls).

Figure 4.13



Corrosion Rates at Different [NaCl] Concentrations (6.0mm Diameter Balls).

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4) The experiments showed that the percentage increase in the rate was significantly higher, in each case, when the six larger balls were used (17.9%, 18.0% and 16.5% compared with 9.2%, 11.7% and 11.5% for the smaller balls). This observation warranted further investigation, the details of which are dealt with in the next section.

5) The increase in the corrosion rate, given the same ball size (see 4 above), was greater with the more concentrated solutions, i.e. the magnitude of the effect was found to be proportional to the concentration of the sodium chloride solution, with the greatest effect being achieved when the 2.9% solution was magnetically treated.

4.2.v. Influence of Size of Test Samples.

It has been shown that the corrosion rates obtained with different numbers, sizes and masses of balls under the same conditions, in the absence of a magnetic field, could be compared when divided by the surface area of the balls. The previous experiments had indicated, however, that the degree of the effect of the magnetic treatment was influenced by the nature (size) of the balls themselves. In order to check and further investigate this observation, Experiments 14 and 15 were set up. Both experiments were carried out in the same way as the earlier investigations with a sodium chloride concentration of 2.0%. For Experiment 14 five 10.0mm radius balls were used as the test sample, and for Experiment 15 ten 4.8mm radius balls were used.

Table 4.8 shows a comparison of the corrosion rate measurements for Experiments 10, 11, 14 and 15. The results are presented with details of the radius, number, total and individual masses, and total and individual surface areas for the different ball sizes used. It can be seen that there is no linear relationship between the degree of the magnetic treatment effect and the number, or the total mass or the total surface area of the balls. However, a relationship is apparent between the size of the effect and the radius of the balls.

The discovery of a relationship between the magnitude of the effect and the size of the balls used as the test samples required further investigation. Therefore, Experiment 16 was set up in which three different sized balls were corroded together in one litre of 2.9% $NaCl_{(aq)}$. This was done to ensure that all of the balls underwent exactly the same conditions. The three different sizes and numbers of balls chosen are shown in Table 4.9, along with their

Table 4.8

Exp^t No.	Radius (mm)	No. of Balls	Mass (g)		Surf.Area (cm^2)		Mag/ Con^t	Corrosion Rate (x10^{-4}g/cm^2/h)
			Total	Single	Total	Single		
15	4.8	10	35.2	3.5	28.8	2.9	C	1.865 ± 0.041
							M	2.075 ± 0.055
10	5.0	36	145.8	4.1	113.8	3.2	C	1.867 ± 0.003
							M	2.086 ± 0.004
11	6.0	6	41.0	6.8	26.9	4.5	C	1.874 ± 0.017
							M	2.211 ± 0.011
14	10.0	5	161.9	32.4	63.2	12.6	C	1.854 ± 0.022
							M	2.258 ± 0.053

Corrosion Rate Results and Physical Dimensions of the Balls Used.

Table 4.9

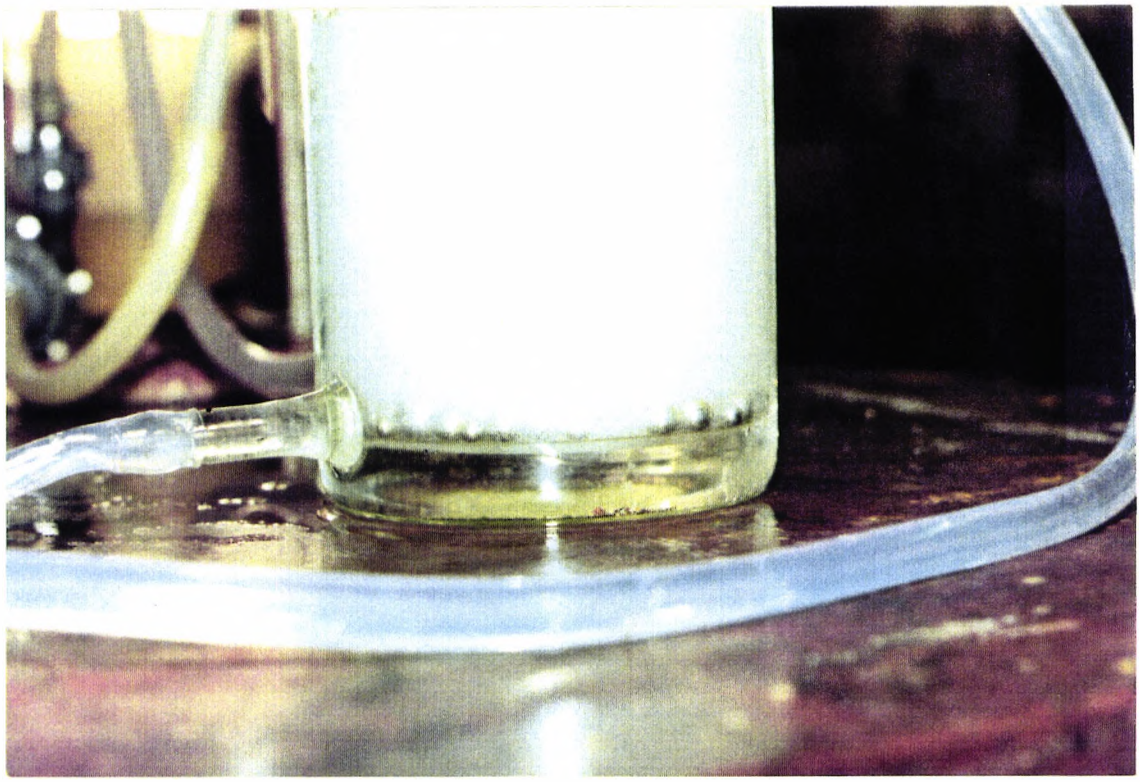
Radius (mm)	No. of Balls	Mass (g)		Surf.Area (cm^2)		C/M	Corrosion Rate (x10^{-4}g/cm^2/h)
		Total	Single	Total	Single		
3.2	15	15.6	1.04	19.2	1.3	C	2.353 ± 0.018
						M	2.812 ± 0.019
4.8	20	70.4	3.52	57.6	2.9	C	2.301 ± 0.026
						M	3.023 ± 0.045
6.4	10	83.1	8.31	51.0	5.1	C	2.332 ± 0.031
						M	3.241 ± 0.050

Physical Dimensions and Corrosion Rates for the Balls Used in Experiment 16.

respective corrosion rates. Figures 4.14 to 4.17 are photographs of the control and magnetic test rigs after 45 minutes and after four days. It can be seen that, after 45 minutes, the balls in the magnetic test rig were obviously corroding, unlike those in the control.

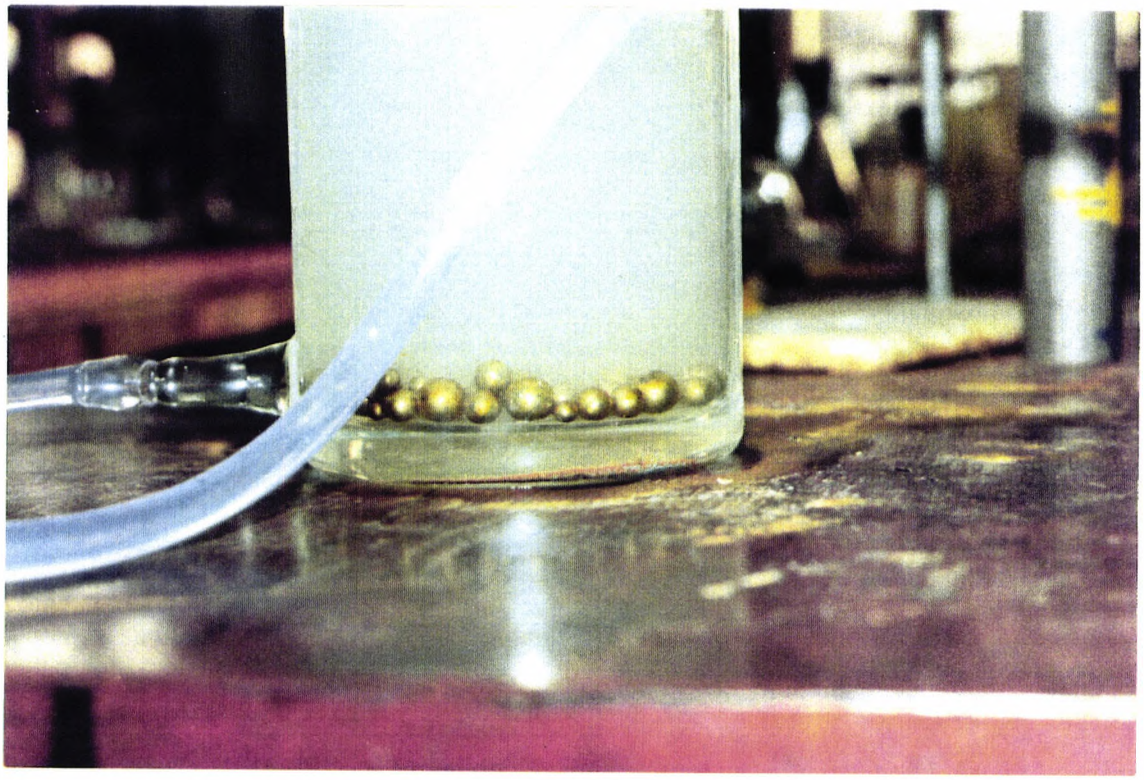
Figure 4.18 shows the control run results for the three sets of balls, as graphs of weight loss per unit surface area against time. It can be seen that all three of the lines are very nearly concurrent, their gradients differing by only 2%. This demonstrates the accuracy of the surface area determinations. Figure 4.19 shows

Figure 4.14



Control Run of Experiment 16 after 45 Minutes.

Figure 4.15

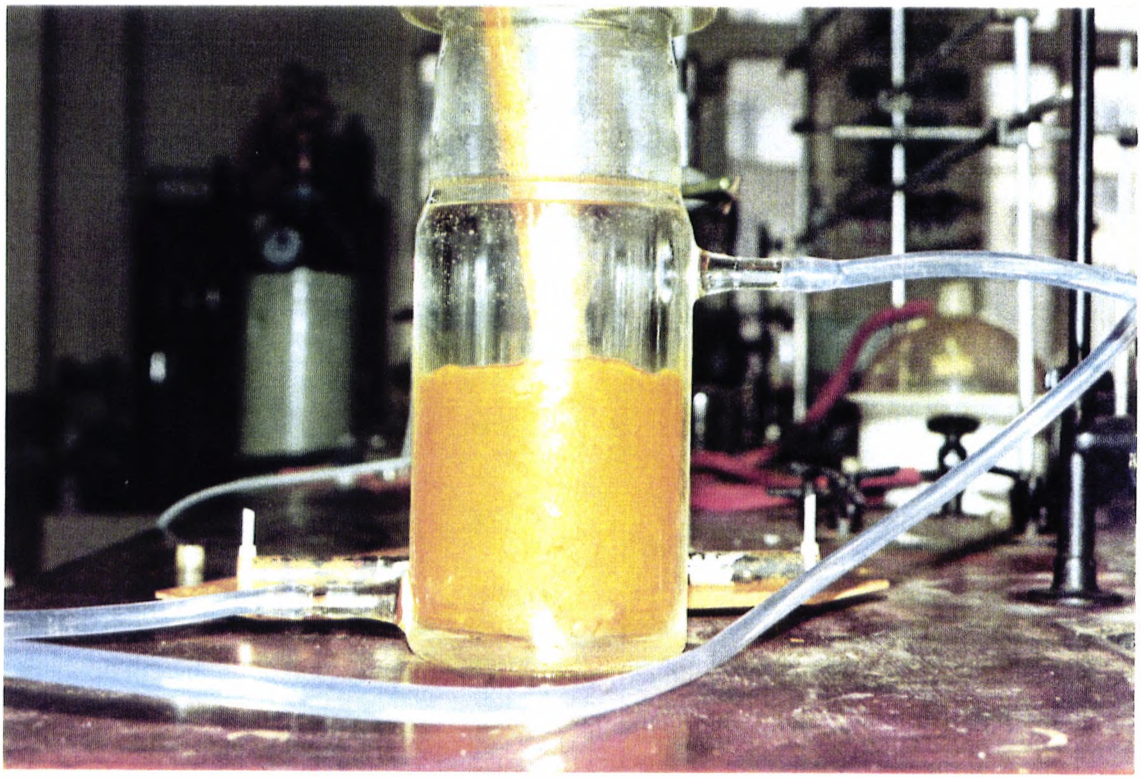


Magnetic Run of Experiment 16 after 45 Minutes.

Figure 4.16

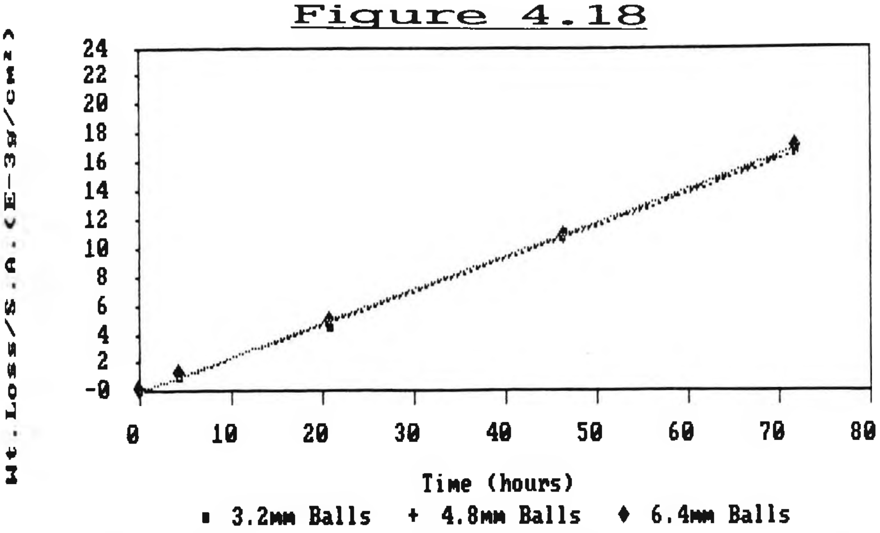
Control Run of Experiment 16 after Four Days.

Figure 4.17



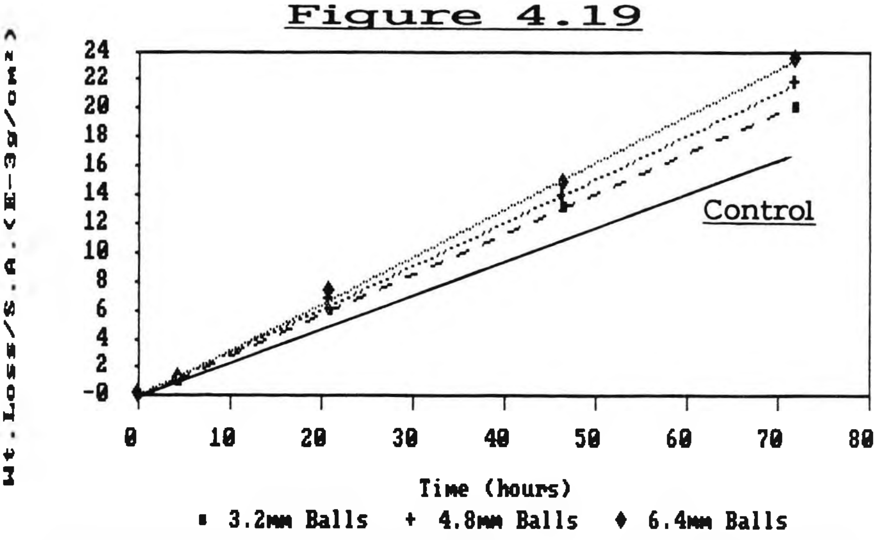
Magnetic Run of Experiment 16 after Four Days.

Figure 4.18



Control Corrosion Rate Results for Experiment 16.

Figure 4.19



Magnetic Corrosion Rate Results for Experiment 16.

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the corresponding graphs for the magnetic runs. In this case there is an obvious difference between the gradients of the three graphs, which differ by 13%. The control shown on this graph is the average.

Regression analyses were carried out on the corrosion rates for the three ball sizes as functions of their dimensions. Table 4.10 shows the coefficients of determination calculated for the relationships. These show conclusively that there is a relationship between the degree of the magnetic treatment effect and the size of the test samples. The best correlation, with a coefficient of determination of 99.991%, suggests that the magnitude of the effect is proportional to the radius of the balls.

Table 4.10

Corrosion Rate as a Function of :	Coefficient of Determination
Number of Balls	25.820%
Total Surface Area	59.045%
Total Mass	87.914%
Individual Mass	97.070%
Individual Surface Area	99.337%
Ball Radius	99.991%

Comparison of Corrosion Rates with the Dimensions of the Balls Used.

4.2.vi. Influence of Magnetic Field Strength.

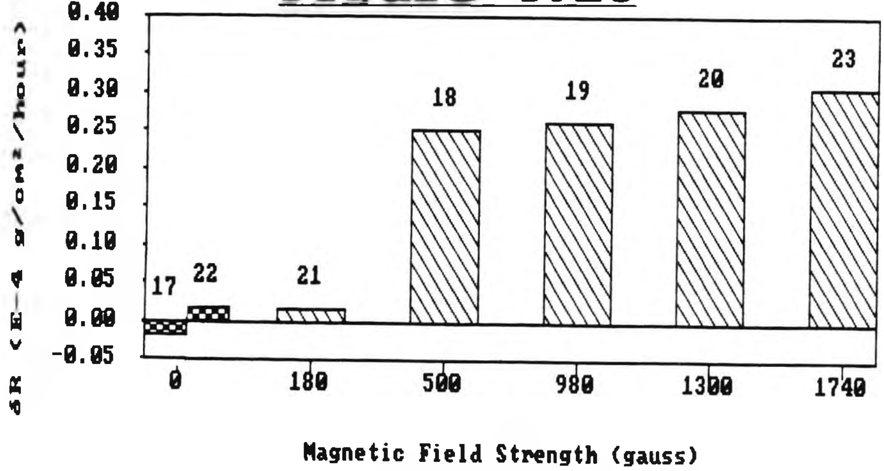
The most obvious factor to be tested in any investigation of magnetic treatment, is the influence of the magnetic field strength. All of the previous experiments had been carried out with a field strength of 1100 gauss. A series of experiments (Nos. 17 to 23) were set up in which all of the parameters were the same as for the earlier tests, with the exception of the field strength. In each case ten 6.0mm radius balls and a 2.9% sodium chloride solution were used. The temperature was maintained at 17.5(±0.5)°C. The field strength was varied by increasing or decreasing the gap between the two poles of the magnets. The calculated corrosion rates for the experiments are presented in Table 4.11 with the field strength used for each experiment and Figure 4.22 is a graph of δR, the difference between the calculated corrosion rates and the average control corrosion rate, against magnetic field strength.

Table 4.11

Exp^t No.	Magnetic Field Strength (gauss)	Corrosion Rate ($x10^{-4}$g/cm^2/h)	% Change in Rate w.r.t. Exp^t 17
17	0 (control)	2.504 ± 0.007	0.0%
18	500	2.770 ± 0.003	+10.6%
19	980	2.780 ± 0.006	+11.0%
20	1300	2.798 ± 0.004	+11.7%
21	180	2.537 ± 0.008	+1.3%
22	0 (control)	2.537 ± 0.004	+1.3%
23	1740	2.827 ± 0.007	+12.9%

Corrosion Rate Results at Different Field Strengths.

Figure 4.20



Results of Experiments 17 to 23 Against Field Strength.

Three observations can be made concerning the magnetic treatment effect from these results:

1) The effect of the magnetic treatment is to increase the corrosion rate at all of the field strengths tested, above a certain value (see 2. below).

2) There is a minimum field strength, between 180 and 500 gauss, below which the magnetic field has no significant effect on the corrosion rate.

3) Above this minimum value the effect is only slightly influenced by increasing the field strength (particularly when considered in light of the sensitivity of the effect to ionic concentration or the size of the test samples).

4.2.vii. Influence of Flow Parameters.

A series of experiments was carried out to determine the influence of altering both the field strength and the flow rate on the magnitude of the magnetic treatment effect. In order to carry out these investigations, and to allow more corrosion rate experiments to be carried out at one time, a new, multiple test rig was designed and built. This rig has already been described in Section 4.2.i.

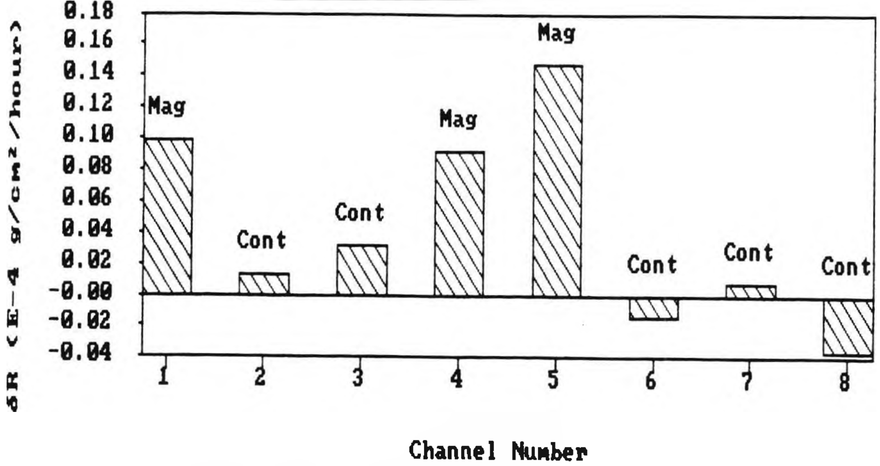
Experiment 24 was set up to test the new apparatus and to determine the magnetic treatment effect under the changed conditions. Five of the test rig channels were used for control runs and three for magnetic runs, each with a field strength of 1190 gauss. The particular channels chosen for each were picked at random. 75ml of a 2.9% $NaCl_{(aq)}$ solution was used as the corrosive medium and ten 3.2mm diameter balls were used for the test samples. The pump was set at 99%, giving a flow rate of 3.0 l/hour for each channel. The results of the experiment are presented in Table 4.12 and Figure 4.21.

Table 4.12

Control/ Magnetic	Channel Number	Corrosion Rate ($x10^{-4}g/cm^2/h$)	% Change in Rate w.r.t. Ave.Cont.
Control:	2	1.062 ± 0.039	+1.1%
	3	1.081 ± 0.023	+2.9%
	6	1.035 ± 0.027	-1.4%
	7	1.058 ± 0.019	+0.8%
	8	1.014 ± 0.013	-3.4%
	AVERAGE	1.050(σ=0.023)	-
Magnetic:	1	1.149 ± 0.056	+9.4%
	4	1.142 ± 0.030	+8.8%
	5	1.198 ± 0.028	+14.1%
	AVERAGE	1.163(σ=0.025)	+10.8%

Results of Experiment 24 using Multiple Test Rig.

Figure 4.21



Graph of Corrosion Rate Results for Experiment 24.

It can be seen that the results are very consistent. The average corrosion rate for the control channels is 1.050 x 10^{-4} g/cm^2/hour, with a standard deviation of 0.023 x 10^{-4}. For the magnetic channels the average is 1.163 x 10^{-4} g/cm^2/hour, with a standard deviation of 0.025 x 10^{-4}. There is an obvious difference between the control and magnetic run corrosion rates. Comparing the average rates in the two cases gives an increase of 10.8 % due to the magnetic treatment. This shows that the magnetic effect operates at a much lower flow rate than had previously been used. It was calculated that, with the Totton pumps, all of the test solution would pass through the field, on average, every 3.3 seconds. With the new test arrangement this was increased to once every 90 seconds.

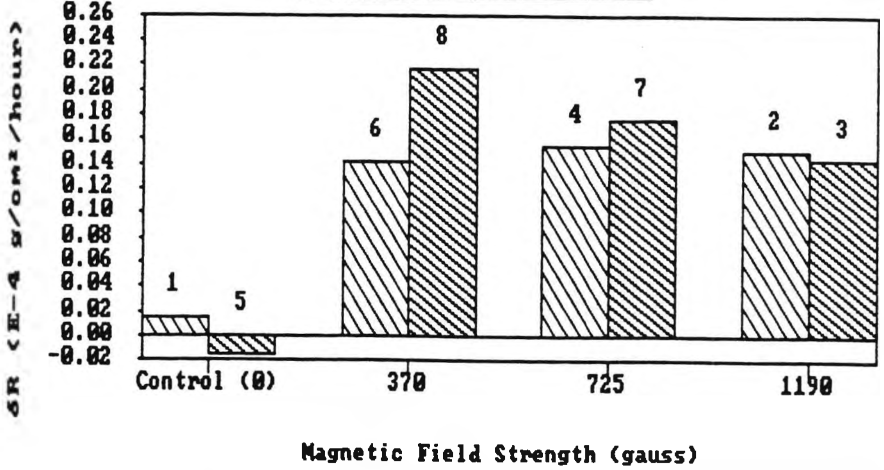
Having shown that the results obtained using the new test rig were very reproducible and that the effect operated under the changed conditions, it was decided to determine how different field strengths would affect the corrosion rate under different flow conditions. Experiment 25 was set up in the same way as the previous experiment, with three different field strengths used on different channels. The peristaltic pump was set at 50% giving an average pass rate through the magnetic field of once every 3 minutes. Table 4.13 shows the field strengths and corrosion rates for the experiment and Figure 4.22 is a graph of δR against field strength.

Table 4.13

Field Strength (gauss)	Channel Number	Corrosion Rate ($x10^{-4}g/cm^2/h$)	% Change in Rate w.r.t. Ave.Cont.
0	1	1.182 ± 0.053	+1.2%
	5	1.154 ± 0.014	-1.2%
	AVERAGE	1.168(σ=0.014)	-
370	6	1.309 ± 0.027	+12.1%
	8	1.385 ± 0.024	+18.6%
	AVERAGE	1.347(σ=0.038)	+15.3%
725	4	1.322 ± 0.023	+13.2%
	7	1.343 ± 0.041	+15.0%
	AVERAGE	1.333(σ=0.011)	+14.1%
1190	2	1.317 ± 0.046	+12.8%
	3	1.311 ± 0.035	+12.2%
	AVERAGE	1.314(σ=0.003)	+12.5%
ALL RESULTS:	AVERAGE	1.331(σ=0.027)	+14.0%

Results of Experiment 25 using Multiple Test Rig.

Figure 4.22



Graph of Corrosion Rate Results for Experiment 25.

As was the case with the higher flow rate experiments (Nos. 17-23), the magnitude of the change in the corrosion rate was not significantly influenced by changes in the field strength at the lower flow rate. In every case, the magnetic treatment was found to cause an increase in the corrosion rate.

For the next experiment (No.26) a time clock was used to interrupt the flow of the corrosive solution and to give periods of circulation and non-circulation. The experiment was set up in the same manner as before, with the clock set so that the pump would only circulate the solution for five minutes every hour. The field strengths and corrosion rates for each channel are presented in Table 4.14 and Figure 4.23 is a graph of δR against field strength.

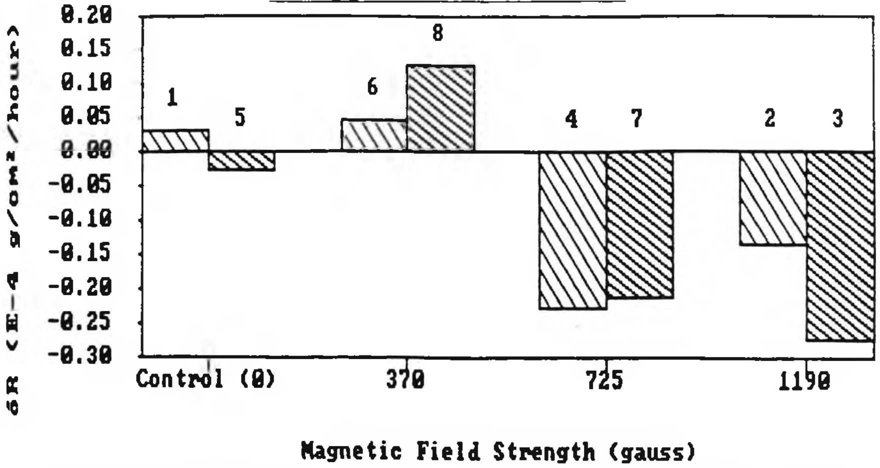
Table 4.14

Field Strength (gauss)	Channel Number	Corrosion Rate ($x10^{-4}g/cm^2/h$)	% Change in Rate w.r.t. Ave.Cont.
0	1	1.263 ± 0.034	+2.4%
	5	1.204 ± 0.024	-2.4%
	AVERAGE	1.234(σ=0.030)	-
370	6	1.279 ± 0.040	+3.6%
	8	1.359 ± 0.035	+10.1%
	AVERAGE	1.319(σ=0.040)	+6.9%
725	4	1.006 ± 0.036	-18.5%
	7	1.023 ± 0.017	-17.1%
	AVERAGE	1.015(σ=0.009)	-17.7%
1190	2	1.101 ± 0.048	-10.8%
	3	0.963 ± 0.038	-22.0%
	AVERAGE	1.032(σ=0.069)	-16.4%

Results of Experiment 26 using Multiple Test Rig.

With interrupted flow, the magnetic treatment on the corrosion rate was different to that previously observed. The rate was found to be increased at certain field strengths and decreased at others. With field strengths of 725 and 1190 gauss, the rates were 17.7% and 16.4% lower than the control value. However, the average corrosion rate with a field strength of 370 gauss was increased by 6.9%.

Figure 4.23



Graph of Corrosion Rate Results for Experiment 26.

The results of Experiments 17 to 25 show that, above a certain flow rate and field strength, the effect of the treatment is to increase the corrosion rate. Below this minimum flow rate, lower field strengths were found to cause an increase in the corrosion rate, while higher field strengths caused a reduction.

4.2.viii. Tests with Acid Corrosion.

The previous experiments had shown that, given the right conditions, the magnetic treatment of a sodium chloride solution could cause a reduction in the corrosion rate of steel submerged in it. It was decided to determine whether this would also be the case for corrosion in other solutions. Experiment 27 was set up, in the same manner as before, using dilute (0.2M) hydrochloric acid as the corrosive solution. Three of the channels were chosen as controls and five for the magnetic runs, using three different field strengths. The results of the investigation are presented in Table 4.15 and Figure 4.24.

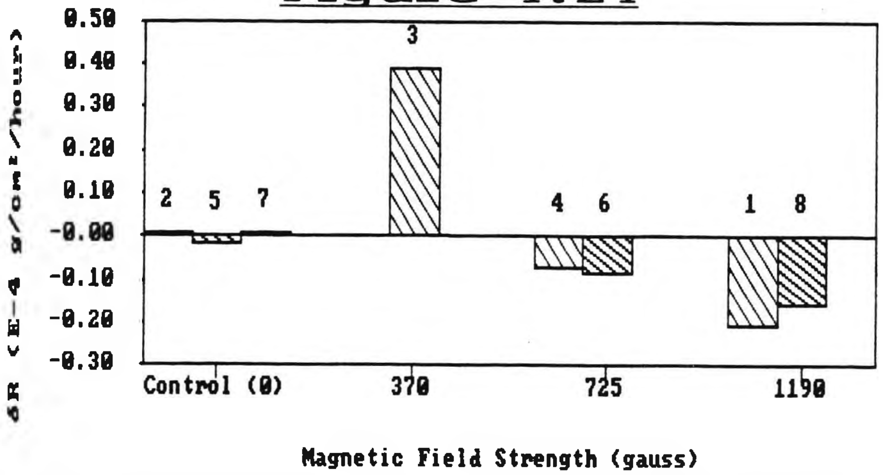
The results show that the effect observed in the earlier experiments with sodium chloride solutions operated in a similar way with $HCl_{(aq)}$. As was found for Experiment 26, the two higher field strengths (725 and 1190 gauss) caused decreases in the corrosion rate of 5.1% and 12.5%, while the lower field strength (370 gauss) caused an increase of 25.9%.

Table 4.15

Field Strength (gauss)	Channel Number	Corrosion Rate ($x10^{-4}g/cm^2/h$)	% Change in Rate w.r.t. Ave.Cont.
0	2	1.485 ± 0.020	+0.3%
	5	1.467 ± 0.020	-0.9%
	7	1.490 ± 0.017	+0.6%
			-
	AVERAGE	1.481(σ=0.010)	-
			-
370	3	1.864 ± 0.013	+25.9%
			-
725	4	1.409 ± 0.026	-4.8%
	6	1.398 ± 0.028	-5.5%
			-
	AVERAGE	1.404(σ=0.006)	-5.1%
			-
1190	1	1.276 ± 0.025	-13.8%
	8	1.323 ± 0.020	-10.6%
			-
	AVERAGE	1.300(σ=0.028)	-12.5%

Results of Experiment 27 using Multiple Test Rig.

Figure 4.24



Graph of Corrosion Rate Results for Experiment 27.

4.2.ix. Mössbauer Analysis of Corrosion Products.

Samples of the corrosion products were collected for many of the experiments and in some cases colour differences were noted between the control and magnetic run samples. Two sets of samples were collected, the bulk samples were the loose particles in suspension in the test solutions and the surface samples were taken from the surface of the balls. These were separated by ultrasonic treatment and filtration and dried under vacuum at 25°C for 48 hours.

The corrosion product samples were analyzed using Mössbauer spectroscopy. The spectra were produced at room temperature and the results obtained for four of the corrosion product samples are presented in Table 4.16. It can be seen that all of the control samples show no trace of any magnetic structure, while the magnetic run bulk samples all exhibit a trace, and the surface sample shows a definite (ca. 6%), magnetic structure, due to Zeeman splitting of some of the Fe nuclei. Figure 4.25 shows the spectra for the control and magnetic, bulk and surface samples from Experiment 16.

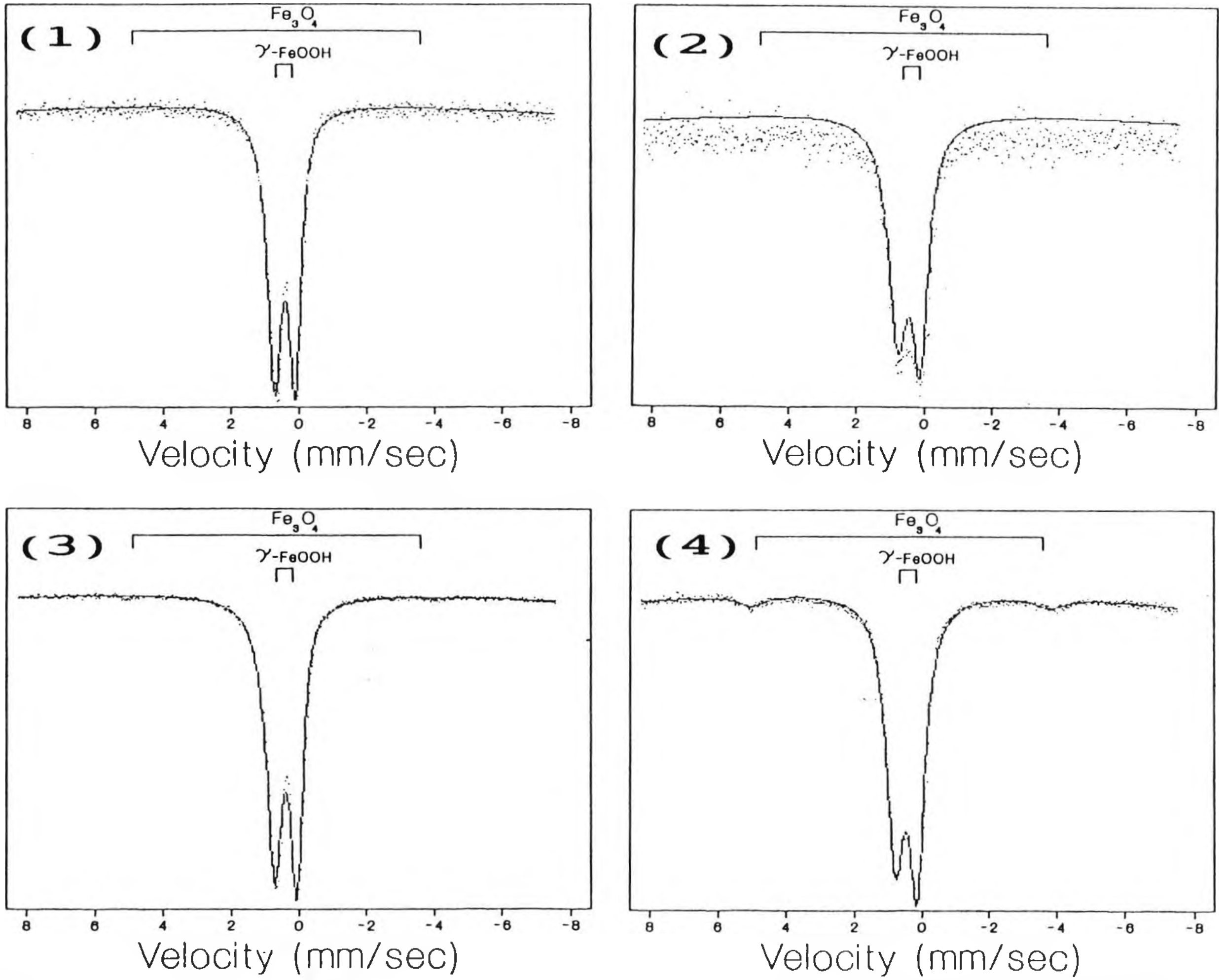
Table 4.16

Exp^{t} Nº	Sample Type	Isomer Shift (δ, ±0.02 mm/sec)	Q.M.S.F. (Δ, ±0.04 mm/sec)	Magnetic Structure
6	Con^{t}/Bulk	0.38	0.64	-
	Mag^{n}/Bulk	0.38	0.65	Trace
7	Con^{t}/Bulk	0.37	0.53	-
	Mag^{n}/Bulk	0.32	0.65	Trace
16	Con^{t}/Bulk	0.29	0.57	-
	Mag^{n}/Bulk	0.26	0.64	Trace
16	Con^{t}/Sur^{f}	0.36	0.64	-
	Mag^{n}/Sur^{f}	0.29	0.64	ca.6%

Q.M.S.F. = Quadrupole Magnetic Splitting Field.

Mössbauer Parameters of Corrosion Product Samples.

Figure 4.25



Room Temperature Mössbauer Spectra of Corrosion Products from Experiment 16
(1)Bulk Control (2)Bulk Magnetic (3)Surface Control (4)Surface Magnetic.

4.3. Discussion

4.3.i. Choice and Suitability of the Testing Procedures.

The results of the experiments have shown that the magnetic treatment of fluids has a very marked effect on corrosion processes. This is characterized by an increase in the corrosion rate under most of the conditions investigated. The effect is influenced by a number of factors, including field strength, flow conditions, size of test samples and concentration. Before discussing the implications of these influences, it is worth while considering the testing procedures used for the investigation.

Much has been written about the conditions and methods for testing corrosion. Evans (1948) devotes a whole chapter to this topic, in which he discusses some of the common problems encountered. In particular he considers the importance of the choice of the test samples. He states:

> "One difficulty keeps recurring in scientific testing - the disturbance due to points, angles and edges on specimens."

Evans suggests that to reduce the complications due to sharp edges, the test specimen may be a wire coiled into a helix or a cylinder. However, when this technique was used for the preliminary work, reproducibility could not be achieved. Much accurate work has been carried out using plates and rods or bars, but problems have been found with uneven corrosion due to special phenomena at edges, and disturbances due to the flow of corrosion products 'down hill' when the plates or rods were inclined at an angle.

Authors who have investigated the effects of magnetic treatment on corrosion have used a variety of techniques. Duffy (1977) carried out a series of experiments using vertically mounted rods, Ar (1972) considered the corrosion of aluminium foils, and Peev et al (1987) used low carbon steel coupons (50 x 50 x 1 mm). Other authors (e.g. Vermeiren, 1958; Mibbeu, 1973; Raisen, 1984) conducted their tests on industrial equipment such as boilers and cooling towers.

In this work steel balls were chosen as the test samples. Though no mention of this method of testing was found in the consulted literature, it was chosen since edge effects would be eliminated and even corrosion could be ensured, by keeping the balls in constant motion, so that there would be no cranny areas between the metal surface and the vessel. The movement of the balls would tend to dislodge corrosion products from their surface and would also give no constant 'down hill' direction for the flow of adhering rust particles. The particular balls chosen for the tests were manufactured for use in automobile bearings and hence had very uniform surface characteristics.

The experiments were all carried out under temperature-controlled conditions. Though the temperature coefficients for corrosion processes are relatively low, it was felt that any temperature differences between different parts of the test rig could set up convection currents, which would affect the accuracy of the results, particularly at the lower flow rates.

Another factor which can influence corrosion is the treatment of the test samples prior to the experiments. Because of this all of the balls were prepared in the same manner. Before the start of a test, the samples were cleaned in an ultrasonic bath, first in acetone, to remove any oil or grease, then in acetic acid, and finally in distilled water. During and after these processes, the balls were handled using polypropene tweezers to prevent any subsequent surface contamination. The methods used to prepare the test samples for weighing were also standardized (following the recommendations of Evans). The balls were removed from the vessel using tweezers and placed in a beaker containing 10% acetic acid. The beaker was put into an ultrasonic bath for five minutes, after which the acid was replaced and the process was repeated. Finally, the balls were rinsed in acetone and dried in a warm air stream. The length of time that the balls were out of the solution and the time that the circulation was interrupted were standardized.

The single test rigs for the initial experimental work produced a great deal of turbulence in the solutions. This can clearly be seen in Figures 4.14 to 4.17 on pages 179 to 181. This turbulence would have two effects: the solutions would be saturated with oxygen, and corrosion products would tend to be dislodged from the metal surface, preventing stifling of the reaction. Both of these effects would maximize and standardize the corrosion of the balls. Using the multiple test produced different conditions: the degree of oxygenation would be lower and the propensity to stifling would be increased. This is demonstrated by the lower corrosion rates achieved with the second test rig ($1.035 - 1.263 \times 10^{-4}$ g/cm^2/h compared with $2.459 - 2.583 \times 10^{-4}$ g/cm^2/h with the single test rigs for control runs using 2.9% sodium chloride). These observations will be considered in greater detail in section 4.3.ii.

It can be seen that every effort was made to ensure that, for each experiment, the conditions for the control and magnetic runs were the same and constant throughout the test. The success of these steps is demonstrated by the very reproducible results which were obtained using both of the testing procedures.

4.3.ii. General Comments.

It was stated in the introduction that the major aim of this work was to prove conclusively (or disprove) that the magnetic treatment of fluids influenced corrosion processes. The results have clearly achieved this goal and allow a number of conclusions to be made about the nature and possible mechanism of the effect.

The experiments show that, under most of the conditions tested, one of the effects of the treatment is to cause a significant increase in corrosion rates. This is consistent with the theory developed in the previous chapters, describing the disruption of interionic associations within a solution following its exposure to a magnetic field. However, it was found that, under certain conditions, the corrosion rate could be reduced by the magnetic treatment. At first sight this appears to inconsistent with an increase in the mobility of the charged species due to the magnetic treatment. In order to explain this observation, it is necessary to consider the events which take place during corrosion and particularly those which occur at the metal/solution interface.

It has already been stated that the processes involved during corrosion are very complicated. Much has been written on the subject and many reaction schemes have been advanced to describe these events. Corrosion is an electrochemical reaction and it proceeds by a series of consecutive steps. Fontana and Greene (1967) suggest that the corrosion of iron in an acid medium occurs in the following stages:

1. Diffusion of H^+ to the reaction site.

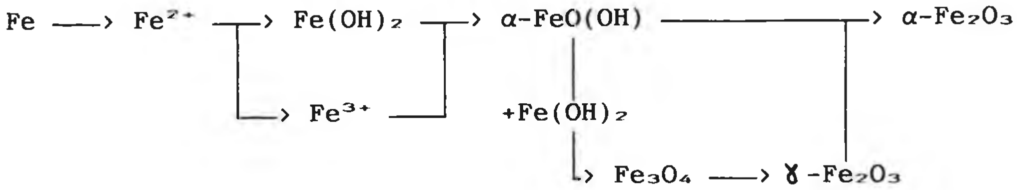
2. Absorption of $2H^+$ in solution onto the metal surface.
3. $2H^+$ combines with $2e^-$ giving $2H^o$.
4. $2H^o$ on the metal surface combine to give H_2.
5. nH_2 on the metal surface combine to give a bubble.
6. Movement of H_2 bubble away from the reaction site.

The rate of the overall reaction is controlled by the rate of the slowest step (the rate-determining step). If this controlling step is one which occurs at the reaction site (i.e. the metal/ solution interface), then the reaction is said to be activation polarized. If, however, the rate is determined by the diffusion of the reactants to the reaction site, then it is concentration polarized. Fontana and Greene found that the corrosion of iron in a sodium chloride solution was concentration polarized.

Hiller (1966) developed a scheme describing the mechanism of the corrosion process (Figure 4.26). The first product, $Fe(OH)_2$, is formed at the metal/solution interface, passes into the solution and diffuses away from the reaction site. At a certain distance from the metal, where more oxygen is available, the iron (II) hydroxide is oxidized to iron (III) oxide $\{Fe_2O_3.H_2O$ or $FeO(OH)\}$, which can then undergo further reactions to produce a number of corrosion products. These are less soluble than the iron (II) hydroxide and are precipitated as brown rust. This reduces the concentration of the hydroxide at the point of precipitation, and therefore sets up a concentration gradient, causing more of the $Fe(OH)_2$ to diffuse away from the metal.

The nature of the diffusion layer near to the metal/solution interface depends on a number of factors. Increasing the supply of oxygen would reduce the width of the diffusion layer due to the increased $[O_2]$ near to the reaction site and increase the

Figure 4.26



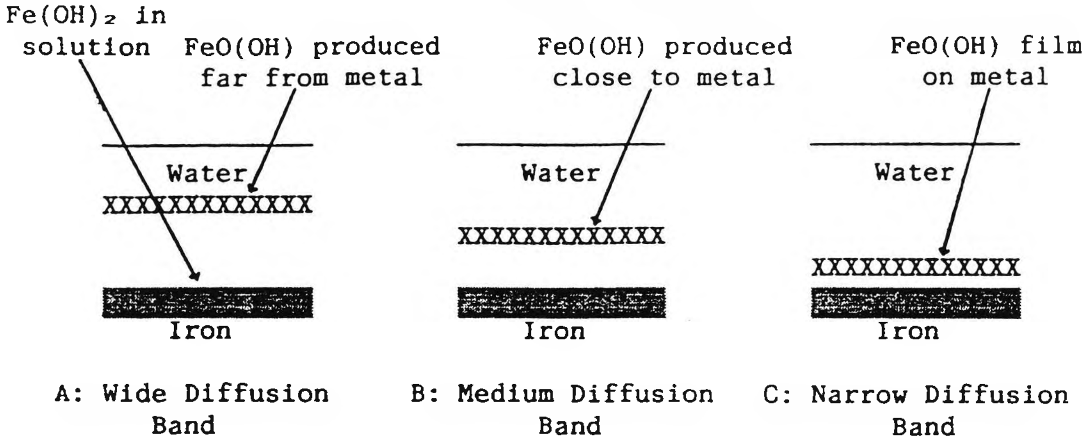
Hiller's Scheme for the Mechanism of Corrosion.

concentration gradient because of the increased rate of oxidation of the iron (II) hydroxide. The supply of oxygen depends on both the dissolved oxygen concentration and on the movement of the solution close to the metal surface (which is determined by the flow rate and turbulence of the solution and on the relative motion of the balls). Another factor which will alter the nature of the diffusion layer is the rate of production of iron (II) hydroxide at the reaction site. If the rate increases, the concentration of $Fe(OH)_2$ near to the metal/solution interface will be greater and this will increase the concentration gradient.

A second factor, stifling, also affects the rate at which a metal will corrode. This occurs when a protective film of corrosion products builds up on the metal surface and depends on where the oxidation of the $Fe(OH)_2$ occurs. If the diffusion layer at the metal/solution interface is sufficiently narrow and the concentration gradient is sufficiently high, then the insoluble corrosion products will be precipitated very close to the reaction site, protecting it from further attack. This is shown in Figure 4.27, in which the effects of changes in the diffusion layer on the precipitation of FeO(OH) are considered.

Forrest et al (1930, 1931a,b,c,d) conducted an exhaustive series of investigations into the effects of the flow rate of a solution

Figure 4.27



Influence of Width of Diffusion Layer on Precipitation of FeO(OH).

over a metal surface on the corrosion of the metal. They found that at low velocities, where the rate of replenishment of oxygen was small, and hence the diffusion layer was relatively wide, the corrosion proceeded quite slowly and there was no stifling of the metal surface. Increasing the velocity was found to increase the corrosion rate, due to the reduction in the thickness of the diffusion layer, caused by the enhanced supply of oxygen. At higher flow rates the corrosion rate was found to diminish, because of a significant degree of stifling, which increased with increasing oxygen supply. At the highest velocities the rate once again increased, owing to the mechanical removal of the protective layer. These events are summarized in Figure 4.28 (see page 201).

If, as suggested, the primary effect of the magnetic treatment is to influence the mobility of the ions in solution, this would influence all of the phenomena occurring at the metal/solution interface. The concentration gradient would be increased and the width of the diffusion layer decreased, due to the increased rate of production of iron (II) hydroxide at the reaction site. The corrosion rate and propensity to stifling would therefore be influenced, and the distribution and transport of charge across the metal surface and within the bulk of the metal would be altered. These changes account for all of the observed magnetic treatment effects found during the present work.

The mechanism proposed to account for the observed effects is supported by the findings of Duffy (1977), who reported that the corrosion rate of steel rods in 3.0% NaCl solutions was increased by 5.1 to 18.6% following magnetic treatment. These results are quantitatively in very good agreement with those found for the present work, using a sodium chloride concentration of 2.9% (corrosion inreased by 9.2 to 17.9%). Duffy suggests that the effect of the magnetic treatment may be to influence the diffusion of H^+ or OH^- ions or O_2 molecules to or from the reaction site.

4.3.iii. Influence of Field Strength and Flow Conditions.

The results of Experiments 17 to 23, at different field strengths, show that the magnitude of the magnetic treatment effect increases rapidly between 180 and 500 gauss, above which little additional change is observed. Very similar findings have been reported by Forestier (1930), Sborgi (1931) and Verizhskaya and Klyochnikov (1969). These observations are entirely consistent with those for the calcium/magnesium phosphate system and, therefore, the same explanation, concerning the range of energies of the species in the solution, is proposed (see section 3.3.iv.).

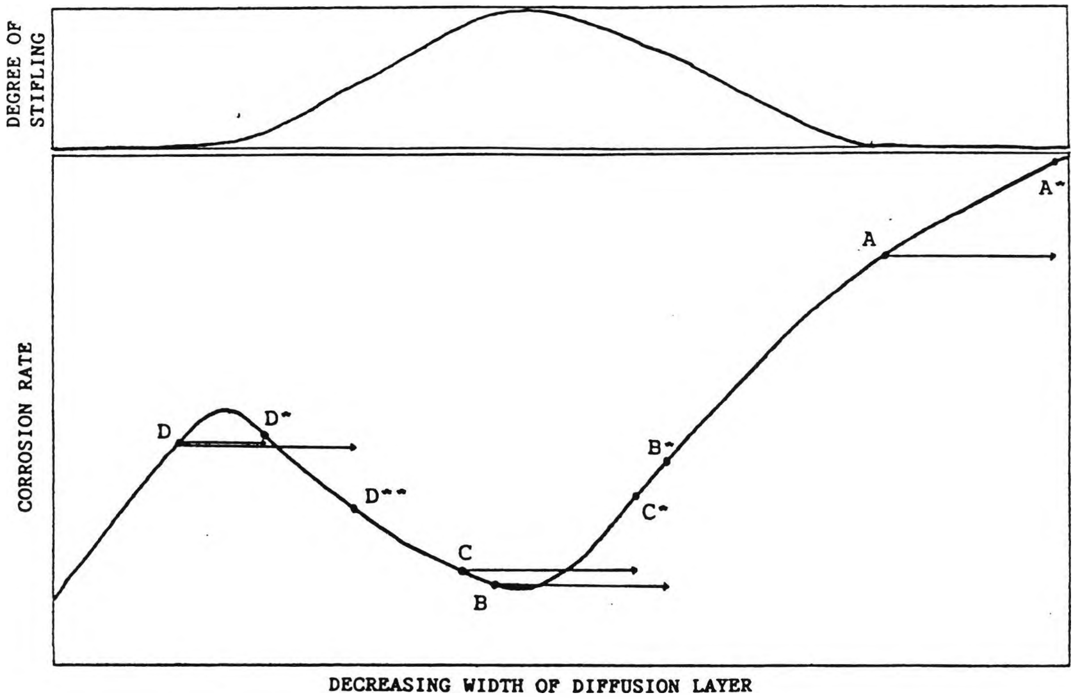
It has been shown that the corrosion rate is very sensitive to the flow conditions. This has been explained in terms of changes in the amount of dissolved oxygen, the rate of oxygen supply to the reaction site and the degree of mechanical removal of corrosion products from the surface of the balls. These changes would influence the diffusion layer near to the metal/solution interface. If the proposed effects of the magnetic treatment are considered in the light of this and the findings of Forrest et al, concerning the effects of changes in the width of the diffusion layer (see section 4.3.ii), the observed phenomena can be explained as follows. [Note: The positions A to D and A* to D** refer to Figure 4.28.]

With the single test rigs, the corrosion rate was increased by the magnetic treatment, under all of the conditions used. For these tests, the flow rate was very high and therefore the diffusion layer would be very narrow. Hence, it is suggested that the situation for the control runs correspond to position 'A' on the graph, while 'A*' shows the proposed effect of the magnetic treatment on the diffusion layer width, giving an increased corrosion rate.

When the multiple test rig was used for Experiments 25 and 26, the control corrosion rates were lower than those obtained with the single test rigs, due to the increased width of the diffusion layer, reduced degree of mechanical removal of stifling materials, and hence increased stifling. Therefore, positions 'B' and 'C' correspond to the control runs of Experiments 25 and 26 respectively. The reduced degree of stifling explains the higher control corrosion rate for Experiment 26, when the flow rate was lower, than that for Experiment 25 (1.168×10^{-4} g/cm^2/h compared with 1.050×10^{-4} g/cm^2/h). The proposed effects of the magnetic treatment would cause shifts to 'B*' for Experiment 25 and 'C*' for Experiment 26, giving increases in the corrosion rate in both cases.

When interrupted flow conditions were used, the control corrosion rate was higher than the rates for Experiments 25 and 26

Figure 4.28



Effect of Decreasing Diffusion Layer Width on Stifling and Corrosion.

(1.234×10^{-4} g/cm^2/h compared with 1.168×10^{-4} g/cm^2/h and 1.050×10^{-4} g/cm^2/h). This is a consequence of the increased width of the diffusion layer and reduced degree of stifling (position 'D'). Given the comments made concerning the field strength tests, the degree of the magnetic treatment effect on corrosion would be less with a field strength of 370 gauss than with field strengths of 725 or 1190 gauss. Therefore, it is proposed that 'D*' represents the situation with the lower field strength (giving a small increase in the corrosion rate) and 'D**' corresponds to the effect with the higher field strengths (i.e. a large decrease in the corrosion rate).

The discovery that magnetic treatment, under different conditions, can reduce or increase corrosion rates, goes a long way to explaining the controversy which has surrounded the effect for so long. If the interpretation of the results of this work are correct, then it is possible to reconcile the work of authors who have, under carefully controlled conditions, found that corrosion rates were reduced by magnetic treatment (e.g. Bhatnagar et al., 1929; Grigorev et al., 1971) with that of researchers who found the opposite (e.g. Forestier, 1930; Duffy, 1977).

4.3.iv. Influence of Solution Concentration.

The control tests with different sodium chloride concentrations show that the corrosion rate of the steel balls was proportional to the solution concentration (or activity), over the range tested. This suggests that the corrosion reaction is first order with respect to sodium chloride, and its rate, expressed as weight loss per unit surface area per unit time, $-d([Fe]/S)/dt$, would be represented by;

(3) $$-d([Fe]/S)/dt = k.\{f.[NaCl] + C\},$$

where k is the velocity constant, f is the activity coefficient and C is a constant, which is included in the equation to represent the corrosion rate in oxygenated distilled water (i.e. when $[NaCl] = 0$). Therefore, a graph of corrosion rate against activity would give a straight line, with gradient k and y-intercept k.C. Since the activities are not known, the corrosion rates for Experiments 6, 8, 10, 11, 12 and 13 (Figures 4.12 and 4.13 on page 176) are plotted against concentration. This still gives straight lines since, over the range tested, the concentration is approximately proportional to the activity of the solutions (see Figure 1.5 on page 38).

Given the relationship shown by Equation (3), the gradient of the control graphs in Figures 4.12 and 4.13 is k' and the y-intercept is k'.C, where k' = k.f (see section 1.3.iii). These values were calculated using regression analysis;

$$\text{Gradient} = k.f = 4.23 \times 10^{-4} \text{ g/cm}^2\text{/h/mole.}$$

$$\text{y-Intercept} = k.C = 0.41 \times 10^{-4} \text{ g/cm}^2\text{/h.}$$

The results of the magnetic runs are consistent with a relationship of the form;

$$-d([Fe]/S)/dt = k.\{(f^{*} + r.g^{*}).[NaCl] + C^{*}\},$$

where f^{*} is the altered activity coefficient for the sodium chloride solutions, $r.g^{*}$ is a factor representing the change in the rate due to the different ball sizes used (r is the radius of the balls - see sections 4.2.v. and 4.3.v.) and C^{*} is due to the change in the width of the diffusion layer and consequent change in the transport of reactants and products to and from the reaction site. The gradients and y-intercepts for the two magnetic run graphs are;

For 5.0mm balls:

$$\text{Gradient} = k.(f^{*} + r.g^{*}) = 4.66 \times 10^{-4}\ g/cm^{2}/h/mole.$$

$$\text{y-Intercept} = k.C^{*} = 0.47 \times 10^{-4}\ g/cm^{2}/h.$$

For 6.0mm balls:

$$\text{Gradient} = k.(f^{*} + r.g^{*}) = 4.92 \times 10^{-4}\ g/cm^{2}/h/mole.$$

$$\text{y-Intercept} = k.C^{*} = 0.48 \times 10^{-4}\ g/cm^{2}/h.$$

These values show that the magnetic treatment influences three aspects of the corrosion reaction:

(1) The degree of interionic association within the sodium chloride solution. This is characterized by the change in the activity coefficient (f to f^{*}).

(2) The 'effective concentration' of the metal in the reaction. This is demonstrated by the inclusion of the $r.g^{*}$ term in the relationship.

(3) The transport processes near to the reaction site. This is due to the changes in the diffusion layer and is characterized by the change in the value of C to C^{*}.

4.3.v. Influence of the Size of Test Samples.

The present work has shown that the degree of the magnetic treatment effect is influenced by the size of the balls used as the test samples. There is very strong evidence for the existence of a relationship between the radius of the individual balls used (irrespective of the number present) and the degree of the change in the corrosion rate following magnetic treatment. So, for example, the treatment would have a greater effect in an experiment using a small number of large balls than it would if a large number of small balls, with the same total surface area, was used. The control runs of the same experiment would have the same corrosion rates, since the rate, in these cases, has been shown to be proportional to the total surface area.

A relationship between individual ball radius and the magnitude of the magnetic treatment effect is not easy to explain as it stands. However, it is possible to achieve a more easily acceptable interpretation of the results.

Corrosion reactions occur at the metal/solution interface and are electrochemical in nature. It has been shown that changes in the associations between ions in solution, due to the magnetic treatment, would influence many aspects of the corrosion processes occurring at and near to the reaction site. This would affect the distribution and transport of charge across the metal surface and within the metal itself. Clearly, the nature and magnitude of these influences would depend on both the surface area and on the volume of the test sample. In view of these two factors, it is proposed that the observed differences between the magnetic treatment effect on different sized test samples, rather than being due to the radius of the individual balls, is due to the ratio of the total volume to the total surface area of all of the balls, as shown below:

If n balls of radius r are used in a corrosion experiment, the total volume of the balls, V, is given by;

$$V = n.(4/3)\pi r^3$$

The total surface area, A, of the balls is given by;

$$A = n.4\pi r^2$$

Therefore, the ratio of the total volume to the total surface area for the balls is;

$$V/A = r/3$$

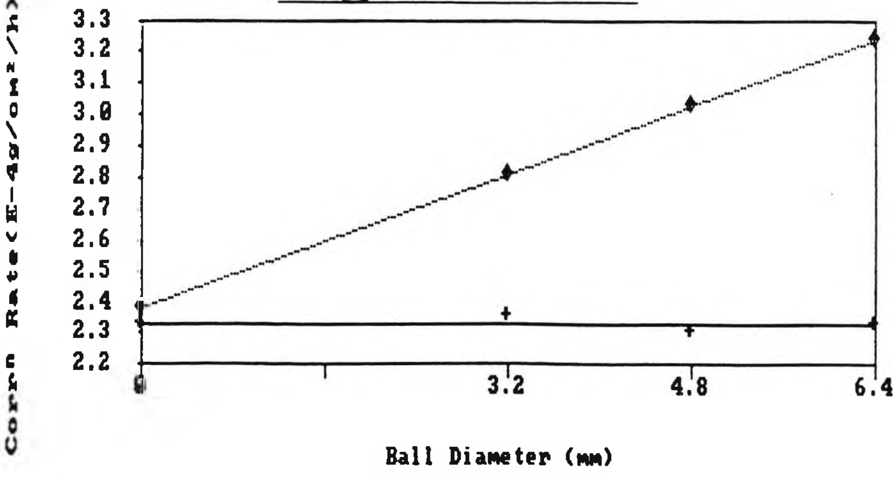
This is consistent with the fact that the degree of the magnetic treatment effect was found to be proportional to the radius of the individual balls used.

The control corrosion rates have been shown to be proportional to the total surface area of the test samples, i.e.;

$$-d([Fe]/S)/dt = k.b,$$

where $-d([Fe]/S)/dt$ is the corrosion rate expressed as weight loss per unit surface area per unit time, k is the velocity constant for the reaction and b is a constant, the value of which will depend on the events taking place at and near to the metal/solution interface. Therefore, a graph of $-d([Fe]/S)/dt$ against the radius of the balls used would have zero gradient and y-intercept, k.b. The control graph shown in Figure 4.29, for the results of Experiment 16, shows that this is the case.

Figure 4.29



Graph of Corrosion Rate vs. Ball Size for Experiment 16.

For the magnetic runs, the corrosion rate has been shown to be proportional to the ratio of the total volume to the total surface area of the balls. This has been explained in terms of the charge transport and distribution within the metal, due to changes in the nature of the diffusion layer. The magnetic run graph in Figure 4.29, is consistent with the relationship;

$$-d([Fe]/S)/dt = k.(b^* + r.g^*/3),$$

where the increased value of b, b^*, is due to the changes in the activity of the sodium chloride solution and the improved transport of oxygen and $r.g^*$ represents the change in the 'activity' of the metal. It can be seen that this corresponds exactly to the relationship suggested in section 4.3.iv, concerning the tests with different sodium chloride concentrations. In fact the two equations both represent the changes in the nature of the diffusion layer caused by the magnetic treatment of the NaCl solutions.

4.3.vi. Acid Corrosion Tests.

The results of the experiments with acid corrosion are consistent with the mechanism proposed to account for the magnetic treatment effects. The corrosion rate of the steel balls in 0.2M HCl was increased with an applied field strength of 370 gauss and was decreased with field strengths of 725 and 1190 gauss, as was found for the tests with sodium chloride solutions. However, the degree of the increase at the lower field strength was greater with the acid corrosion than had previously been measured (25.9% compared with a maximum of 18.6% with the sodium chloride solutions). Also the reduction in the corrosion rate at the higher field strengths was lower than with $NaCl_{(aq)}$ as the corrosive medium (5.1% and 12.5% compared with 17.7% and 16.4%).

The differences between the magnetic treatment effects using the two solutions are easily explained when the increased solubility of corrosion products in the acid is considered. For the acid corrosion tests, the propensity of the corrosion products to stifle the reaction site would be lower. Hence, the degree of increase in the corrosion rate with the lower field strength would be expected to be greater, and the degree of decrease with the higher field strengths, lower, with the acid solution than with $NaCl_{(aq)}$.

4.3.vii. Analysis of Corrosion Products.

The analyses of the corrosion products show that the changes in the corrosion processes influence the products of the reaction. The Mössbauer analyses of the samples show that, for the magnetic runs, Fe_3O_4 was present (particularly for the surface samples). In none of the corresponding control samples was there any evidence for the production of magnetite. These changes in composition must be due to the changes in the events taking place at the reaction site, which would make some reaction routes more energetically favourable than others. This idea is supported by Peev et al (1987), who carried out Mössbauer analyses on bulk and surface corrosion products from magnetic treatment corrosion tests. The authors found that the magnetic field promotes the reaction:

$$2FeO(OH) + Fe(OH)_2 \longrightarrow Fe_3O_4 + 2H_2O.$$

Many other authors have reported similar changes in reaction paths. Kohout (1962), Matejka (1966) and Zubarev (1971) found independently that the dehydration of $Fe(OH)_3$ was accelerated and Iovchev (1966) reported that the rate of the reaction;

$$6\text{-}\alpha Fe_2O_3 \longrightarrow 4Fe_3O_4 + O_2.$$

was markedly increased following magnetic treatment.

4.4. Conclusions

The following conclusions can be drawn about the effects of the magnetic treatment of fluids on corrosion processes.

1. The magnetic treatment of fluids has conclusively been shown to influence corrosion reactions.

2. The determined changes are consistent with the theory developed in earlier chapters, i.e. that the magnetic field causes a disruption of interionic associations within the treated solution.

3. The magnitude of the effect is proportional to the concentration of the corrosive solution (over the range investigated), i.e. there is a relatively greater change at the higher concentrations than with lower concentrations.

4. The degree of the effect is also proportional to the radius of the individual steel balls used as the test material. This observation can be explained if the ratio of the volume to the total surface area of all the balls used is considered.

5. The size of the effect depends on the field strength used. Below 180 gauss there is no measurable change in the corrosion rate. Between 180 and 500 gauss the corrosion rate increases rapidly. Above 500 gauss the rate continues to increase, but much more slowly than was seen with the lower field strengths.

6. The magnetic treatment effect operates over a wide range of solution flow rates, i.e. no minimum flow rate was determined.

7. The influence of stifling of the metal surface is very important in determining the overall effect of magnetic treatment on corrosion

rates. If the flow is sufficiently slow, so that the propensity to stifling is high, the magnetic treatment can cause an increase in the surface stifling and, consequently, a decrease in the overall corrosion rate.

8. The mechanism governing the effect is similar for acid corrosion, but the changed solubility of the corrosion products alters the degree of the observed corrosion rate changes, due to the reduced influence of stifling.

9. The corrosion products obtained following magnetic treatment are quantitatively different from control samples, containing a greater proportion of Fe_3O_4. These observations can be explained by changes in favourable reaction routes due to the altered diffusion layer width.

10. The results of this work and the associated theory can be used to explain the disagreements and controversy which have always surrounded the effect.

CHAPTER 5

THE EFFECTS OF APPLIED FIELDS ON THE KINETICS OF THE HARCOURT-ESSON REACTION

5.1. Introduction and Historical Background

The work presented in this thesis has shown that a common effect of the magnetic treatment of fluids is to change the rates of various processes. For example, the rates of precipitation of calcium oxalate and barium sulphate (Chapter 2), which were determined using the PDA2000 photometric dispersion analyzer, and the corrosion rate of steel in sodium chloride and acid solutions (Chapter 4). The mechanism which has been advanced to account for these and other observed effects of the magnetic treatment of fluids, concerns a direct magnetic field/charge interaction, which causes a disruption of interionic associations within the treated solutions. It has been shown that effects of this type would alter the kinetics of many chemical processes. Therefore, it was decided to investigate the effects of magnetic treatment on a reaction, the kinetics of which could be more directly determined. Three criteria were used in choosing such a reaction for the tests:

(1) It should proceed at a slow enough rate that its kinetics could be determined directly without requiring any specialist monitoring equipment.

(2) It should be one which has been extensively studied and its kinetics well documented, to reduce to a minimum the amount of preliminary work required.

(3) It should have been studied over a long period of time and been shown to be predictable and 'well behaved'. It was felt that, for such a reaction, any observed changes in its rate, caused by the magnetic treatment of the reactants, would be less open to criticism.

The reaction which was chosen for the investigation was that of iodide and peroxide in acid conditions (the Harcourt-Esson reaction);

$$2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O,$$

which satisfies the three criteria suggested above: The rate constants for the reaction are relatively low and, hence, its rate can be easily determined. Its kinetics have been extensively studied for over a century and a quarter; indeed, it was the first reaction to have its rate quantitatively determined. Because of the predictability of its behaviour and the ease with which its rate can be determined, it has been widely used in schools and colleges as a standard practical experiment to demonstrate chemical kinetic measurements and calculations involving the Arrhenius equation.

Prior to considering the testing procedures and the results of the investigation, it is useful to discuss the historical background to the experimental work with the reaction.

Harcourt (1867) and Harcourt and Esson (1867) reported on the first successful quantitative investigation of the kinetics of a reaction. The authors found that the rate of the iodide/peroxide reaction was proportional to the amounts of iodide and peroxide present and that it was 'accelerated' by the addition of an acid. Magnanini (1891) demonstrated how the rate of the reaction was related to the amount of acid used. Noyes (1895 and 1896), whose chief interest was in the classification of the concept of the order of a chemical reaction, was the first author to combine this information, and show that the rate of the reaction was consistent with a differential equation of the form;

$$d[I_2]/dt = k_1[H_2O_2][I^-] + k_2[H_2O_2][I^-][H^+],$$

where k_1 and k_2 are rate constants. He also advanced the idea that the role of the acid in the reaction was catalytic, even though it was consumed. In 1906, Bray proposed a new interpretation of Noyes' rate equation, which he suggested represented two independent rate-determining steps for the reaction:

$$H_2O_2 + I^- \longrightarrow H_2O + IO^-, \text{ and,}$$

$$H_2O_2 + I^- + H^+ \longrightarrow H_2O + HIO.$$

The two constants, k_1 and k_2, in Noyes' rate equation are the rate constants for these two reactions, the first of which is a compensating reaction in the catalytic decomposition of hydrogen peroxide by the iodine-iodide couple, which was extensively studied by Abel (1920 and 1928). The second reaction was investigated by Bray and Livingston (1928) as a means of quantitatively determining hydrogen peroxide.

During the nineteen-thirties many aspects of and influences on the kinetics of the reaction were studied at the University of California (Bray and Liebhafsky, 1931; Bray and Caulkins, 1931; Liebhafsky 1931a,b & c and 1932a & b; Bray, 1932; Liebhafsky and Mohammad, 1933) as part of a larger research project on the interaction of hydrogen peroxide with iodine compounds of all valencies.

A literature search for the reaction yielded only one reference since 1950. Bell et al (1951) investigated the influence of salt effects on the reaction, to determine whether these were consistent with Bronsted's theory of salt effects. The paucity of more recent papers can be attributed to the predictability of the behaviour of the reaction, i.e. it was believed that its kinetics had been fully described and that no additional information could be gained by further studies.

5.2. Results

5.2.i. Experimental Methods and Data Handling.

For the calculation of the rate of the Harcourt-Esson reaction, it is necessary to determine the concentration of hydrogen peroxide at various time periods during the course of the reaction. Different authors have used slightly different techniques to achieve this but, for all of these, the peroxide concentration is inferred from the iodine concentration, which is found by titration with a thiosulphate solution. The experimental protocol of Liebhafsky and Mohammad (1933) is typical:

> "In such experiments all the reaction mixture...except the peroxide, contained in a glass stoppered flask, was placed in a thermostat at the desired temperature and shielded from direct light. After temperature equilibrium had been reached, a measured volume of hydrogen peroxide solution from a reservoir in the bath was added to start the reaction, zero time being taken when the addition was half complete. From time to time 25cc samples were withdrawn with a pipet and permitted to flow into 125cc of water at 0°C, in order to retard the reaction by cooling and dilution. The time of sampling was recorded when the pipet was half emptied. So soon as was convenient, these samples were titrated with a 0.004N thiosulphate solution. The increase in the thiosulphate titre of the samples served to measure the rate of the reaction."

For the work presented in this chapter, a slightly modified technique was used, for which the titration with the thiosulphate solution was carried out within the reaction vessel. Stock solutions of the reactants were made up, using deionized water with the following concentrations:

HCl - 0.625M,

KI - 0.1M,

$Na_2S_2O_3$ - 1.0M, and,

H_2O_2 - 10volume.

These values were chosen after a series of preliminary experiments was carried out to find the concentrations required to give an easily measurable rate (neither too fast nor too slow) for the reaction. Once made up, the solutions were kept in cool dark conditions, since the peroxide and, to a lesser degree, the iodide and thiosulphate solutions all had a tendency to decompose after a period of time. In order to minimize the effects of this, new stock solutions were made daily and the circulation of the solutions and the reactions themselves were carried out under a nitrogen atmosphere.

The first step of the experimental technique was to determine the amount of iodine which was liberated from a known volume of the iodide solution, by a measured volume of the peroxide solution. This was achieved by mixing a volume of the iodide solution with a large excess of the acid (to ensure that the reaction had reached completion before the titration was carried out, by increasing its rate) and then adding a known volume of the peroxide solution. The volumes of the iodide and the peroxide solutions used for the titration were the same as were used for the rate determination tests themselves. The liberated iodine was then titrated with the stock thiosulphate solution, using a few drops of starch solution as an indicator. The titration was repeated several times, at the beginning and end of each day's work, to ensure that none of the solutions had decomposed, and hence distorted the results.

For the rate-determining tests, one or more of the solutions were circulated through a magnetic field for a period of time. Volumes of the iodide and acid solutions were then transferred into a temperature controlled vessel with a small, measured volume of the thiosulphate solution and a few drops of the starch solution. The volume of thiosulphate used was much lower than the titration value determined earlier (commonly about 1/20th of it). The reactants were stirred together for a few minutes until temperature equilibrium was achieved. The same volume of the peroxide solution as had been used for the titration was then measured into the vessel and a stop-watch was started. The control runs were carried out using a similar technique, but the test solution was not passed through the magnetic field.

The vessel was positioned so that there was a clear view through it and any solution colour change could be seen (A white board was placed behind the vessel to make this easier). Initially, the liberated iodine reacted with the thiosulphate, so no colour change was seen. However, once the reaction had reached a certain point, and all of the thiosulphate had been reacted, the continued production of iodine caused the solution to change from colourless to blue (due to the presence of the starch). When this was seen, the stop-watch was paused and another volume of the thiosulphate solution was added to the vessel. This process was repeated several times to give a table of volume of thiosulphate against time. The volume of thiosulphate added at each colour change, was many times lower than the total volume of the reactants (about 1/400th), and therefore dilution effects due to its addition were negligible and were ignored.

The rate constants for the experiments were calculated from the times between the thiosulphate additions. The concentrations of acid and iodide in the reaction mixture were in great excess over the hydrogen peroxide concentration. Therefore, they can be considered as being virtually unchanged during the course of the reaction, which is first order with respect to the peroxide (Harcourt and Esson, 1867). The reaction as a whole can be considered as first order and the overall reaction rate constant, k_o, can be found as follows:

> Let a represent the initial concentration of hydrogen peroxide in the reaction mixture and (a-x) the concentration remaining at time t. Then, since the reaction is first order, the rate of the reaction, dx/dt, will be proportional to the concentration of peroxide at time t, i.e. (a-x). So;
>
> $$dx/dt = k_o.(a-x).$$
>
> Thus,
>
> $$dx/(a-x) = k_o.dt.$$
>
> On integration this gives;
>
> $$-\log_e (a-x) = k_o.t + C.$$
>
> where C is the integration constant. When t = 0, x = 0, substituting these values in the equation gives;
>
> $$C = -\log_e a.$$
>
> So;
>
> $$\log_e a - \log_e (a-x) = k_o.t.$$
>
> Which on rearrangement gives Equation (1);
>
> $$k_o.t = \log_e a/(a-x).$$

Therefore, it is necessary to calculate the hydrogen peroxide concentration at each of the noted times, and then to calculate a/(a-x) for each measurement, as follows:

> If the total volume of the KI, HCl and H_2O_2 solutions used for the reaction, and hence for the titration, was y ml and the 1M thiosulphate solution titration value was z ml, then the initial H_2O_2 concentration, a, is given by;
>
> $$a = z/y,$$
>
> since one mole of iodine is liberated by the reaction of one mole of hydrogen peroxide. The fall in the peroxide concentration, x, after n additions of v ml of the thiosulphate solution, is, therefore, equivalent to the increase in the iodine concentration, and is given by;
>
> $$x = nv/y$$
>
> Substituting these values for a and x into (1) gives;
>
> $$k_o.t = \log_e [(z/y) / \{(z/y) - (nv/y)\}],$$

i.e.;

$$k_o.t = \log_e [z / (z - nv)]$$

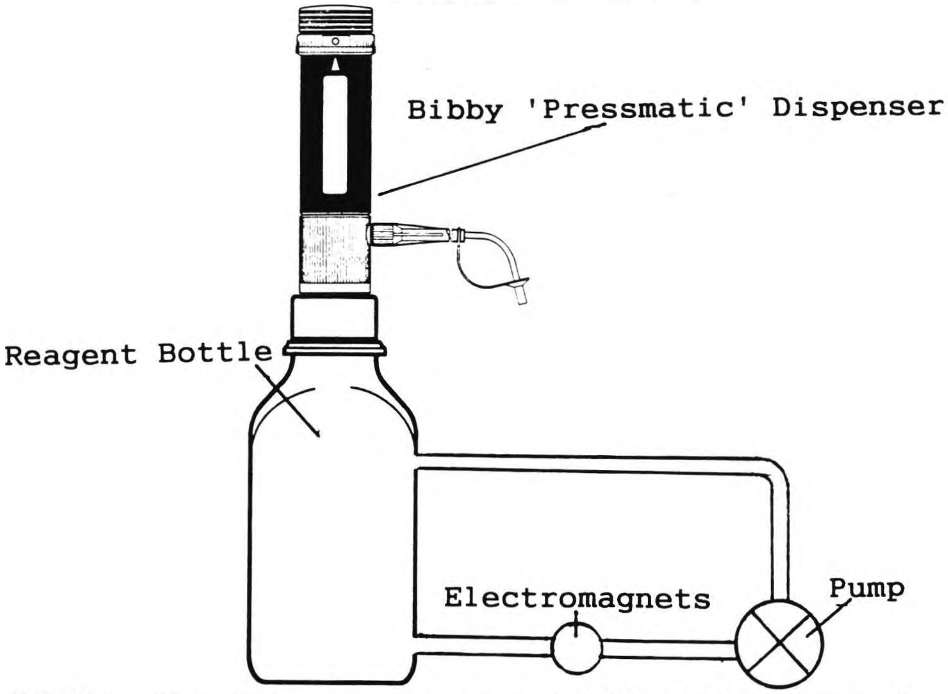
So, if values of $\log_e [z/(z-nv)]$ are plotted against time, a straight line graph through the origin is obtained, the gradient of which is k_o, the rate constant (N.B. the calculated value for k_o is the combination of the two rate constants, k_1 and k_2, in Noyes' equation - see section 5.1).

In practice, rather than plotting the graphs and then finding their gradients, the regression analysis computer program ('Curfit'), which is described in section 1.4.i, was used to calculate the rate constants.

Several different experimental methods were used for the work with the Harcourt-Esson reaction. For the initial experiments the test apparatus was of the jacketed vessel type, described in section 1.4.ii. Totton pumps were used to circulate the solutions, and the magnetic fields were produced using a pair of electromagnets mounted on either side of the tubing. The iodide and acid solutions were mixed in the vessel and circulated through the magnetic field for a period of time, after which the starch and thiosulphate solutions were added. The hydrogen peroxide was then pipetted into the vessel and the rate of liberation of iodine was monitored. The reaction mixture was circulated through the apparatus for the whole of the test.

For the second test procedure, standard reagent bottles were modified with inlets and outlets, which allowed the solutions to be circulated through magnetic fields using peristaltic pumping. Bibby 'Pressmatic 2000' dispensers were fitted to the bottles, so that the solutions could be quickly and accurately measured into the reaction vessel. This test arrangement is shown in Figure 5.1.

Figure 5.1



Solution Circulating Apparatus and Bibby 'Pressmatic' Dispenser.

A number of specially designed, small glass jacketed vessels (with capacities of 50ml) and stirring paddles to fit in them, were made. The dispensers were used to transfer 30.0ml of the acid solution and 10.0ml of the iodide solution into the new vessel. The stirring paddle was then inserted and connected to a stirrer motor. When temperature equilibrium was reached, micro-pipettes were used to dispense between 50 to 200µl of the thiosulphate solution and 1000µl of the peroxide solution into the reaction mixture.

The experimental data for all of the tests are presented in Appendix E.

5.2.ii. Preliminary Results.

The first experiment (No.1) was set up to determine the reproducibility of the reaction rate measurements and also to find whether the magnetic treatment would, in fact, influence the kinetics of the reaction. The tests were carried out using the first of the experimental procedures described in section 5.2.i., so that the reaction mixture was circulated through the apparatus for the whole of the run. Twenty runs were carried out, ten as controls, in the absence of a magnetic field, and ten using an electromagnetic field of 1400 gauss. The order in which the control and magnetic runs were carried out was chosen at random, and the temperature for all of the tests was maintained at 16.5 (±0.1)°C.

The values of the rate constant, k_o, calculated from the results of the control and magnetic runs are presented in Tables 5.1 and 5.2, with their associated coefficients of determination, calculated for the regression analyses.

The very high values for the coefficients of determination and low ranges for the results show that the experimental technique was very good. The very small standard deviations for the averages of

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Table 5.1

Run Number	Rate Constant, k_o ($\times10^{-3}$ $l^2mol^{-2}s^{-1}$)	Coefficient of Determination (%)
1	1.1819 ± 0.0032	99.992
3	1.1885 ± 0.0033	99.991
5	1.1799 ± 0.0041	99.987
6	1.1862 ± 0.0038	99.989
7	1.1896 ± 0.0033	99.992
8	1.1832 ± 0.0042	99.986
10	1.1842 ± 0.0039	99.988
11	1.1856 ± 0.0040	99.988
13	1.1896 ± 0.0058	99.974
16	1.1826 ± 0.0054	99.977
AVERAGE	1.1851(σ=0.0052)	_

Reaction Rate Constants for the Control Runs of Experiment 1.

Table 5.2

Run Number	Rate Constant, k_o ($\times 10^{-3}$ $l^2 mol^{-2} s^{-1}$)	Coefficient of Determination (%)
2	1.2157 ± 0.0046	99.984
4	1.2062 ± 0.0023	99.996
9	1.2121 ± 0.0035	99.991
12	1.2156 ± 0.0044	99.986
13	1.2091 ± 0.0038	99.989
15	1.2208 ± 0.0034	99.991
16	1.2175 ± 0.0045	99.985
18	1.2170 ± 0.0039	99.989
19	1.2161 ± 0.0034	99.992
20	1.2159 ± 0.0033	99.992
AVERAGE	1.2146(σ=0.0084)	_

Reaction Rate Constants for the Magnetic Runs of Experiment 1.

the two sets of results (0.0052 x 10^{-5} and 0.0084 x 10^{-5}) demonstrate the great reliability and reproducibility of the reaction for calculating rate constants, and the suitability of the experimental procedure.

It can be seen that the magnetic treatment has a marked effect on the kinetics of the reaction. There is an obvious and significant increase in the calculated values for the rate constant, and hence in the reaction rate, due to the magnetic treatment.

5.2.iii. Influence of Temperature.

Having demonstrated that the rate of the reaction could be accurately determined using the experimental method described for Experiment 1, and that the magnetic treatment significantly influenced its rate, it was decided to investigate how various parameters influenced the effect. The first of these was temperature, since, by determining the magnitude of the effect at different temperatures, it is possible to gain more information about which aspects of the reaction are affected by the magnetic treatment.

The Arrhenius equation gives the relationship between the rate constant for a reaction, at different temperatures, and the activation energy for the reaction. The equation is;

$$k = A.e^{-(E/RT)}$$

where E is the activation energy, R is the molar gas constant (= 8.314 J K^{-1} mol^{-1}), T is the absolute temperature and A is the frequency (or collision) factor. The value of A is determined by the collision frequency of the reacting ions. Taking natural logs of both sides of the equation gives;

$$\log_e(k) = \log_e(A) - (E/RT)$$

So, if values for the rate constant are obtained at different temperatures and their natural logs are plotted against 1/T, a straight line graph would be obtained. The gradient of this line would be -(E/R) and the y-intercept would be $\log_e$ (A). However, the value of the frequency factor, A, for a bimolecular reaction, is given by;

(1) $$A = 10^{-3}.N_A.\pi.(r_a + r_b)^2.v,$$

where N_A is the Avagadro number, r_a and r_b are the collision radii and v is the average speed of the molecules or ions, given by;

$$v = \surd(8.R.T/\pi.\mu),$$

where R is the molar gas constant, T is the absolute temperature and μ is the reduced mass which is given by;

$$\mu = m_a.m_b/(m_a + m_b),$$

where m_a and m_b are the molecular masses of the reactants. [N.B. this definition of A encompasses the activities of the reactants since the effects of their mobilities (i.e. v) are included within the equation - see section 1.3.] So, A is proportional to $\surd T$, and the Arrhenius equation can be re-written as;

$$k = \surd T.A'.e^{-(E/RT)},$$

where $A' = A/\surd T$. Taking natural logs of both sides now gives;

$$\log_e(k) - \log_e(T)/2 = \log_e(A') - (E/RT).$$

Hence, to nullify the effect of temperature on A, the graph should be plotted as $\log_e(k) - \log_e(T)/2$ against $1/T$. This graph would have gradient $-(E/R)$ and the y-intercept would be $\log_e(A')$.

For Experiment 2 a number of control and magnetic runs (field strength = 1400 gauss) were carried out at different temperatures, between about 10 and 20°C. The relatively low temperatures were used since the hydrogen peroxide decomposes quickly at higher temperatures. The experimental procedures used for the tests were the same as those described previously for Experiment 1.

The temperatures at which the tests were carried out and the values of the rate constant, k_o, calculated using regression analysis, from the results of the tests, are presented in Table 5.3. Figure 5.2 shows the graphs of $\log_e(k) - \log_e(T)/2$ against $1/T$ for the control and magnetic runs. It can be seen that the graphs for the two sets of runs are parallel to one another, with the line for the magnetic tests above that for the controls. This indicates that the magnetic treatment effect does not influence the activation energy for the reaction, but alters the pre-exponential collision frequency factor, A'.

Table 5.3

Run Number	Con^t/ Mag^n	Temp (°C)	Rate Constant, k_o ($\times10^{-3}$ $l^2mol^{-2}s^{-1}$)	Coefficient of Determination (%)
1	C	9.9	0.6413 ± 0.0028	99.982
2	M	10.2	0.6792 ± 0.0023	99.993
3	C	10.9	0.6937 ± 0.0014	99.990
4	M	11.0	0.7225 ± 0.0023	99.994
5	M	14.9	0.9496 ± 0.0018	99.991
6	C	15.0	0.9239 ± 0.0019	99.998
7	M	19.4	1.2973 ± 0.0029	99.995
8	C	19.7	1.2776 ± 0.0029	99.997

Reaction Rate Constants for Experiment 2.

The values for the activation energy and the frequency factor were calculated using the regression analysis program, and found to be:

Control Runs:

Activation Energy, E = 47.02 kJ/mol.

Frequency Factor, A' = 1.84×10^4 $l^2mol^{-2}s^{-1}$.

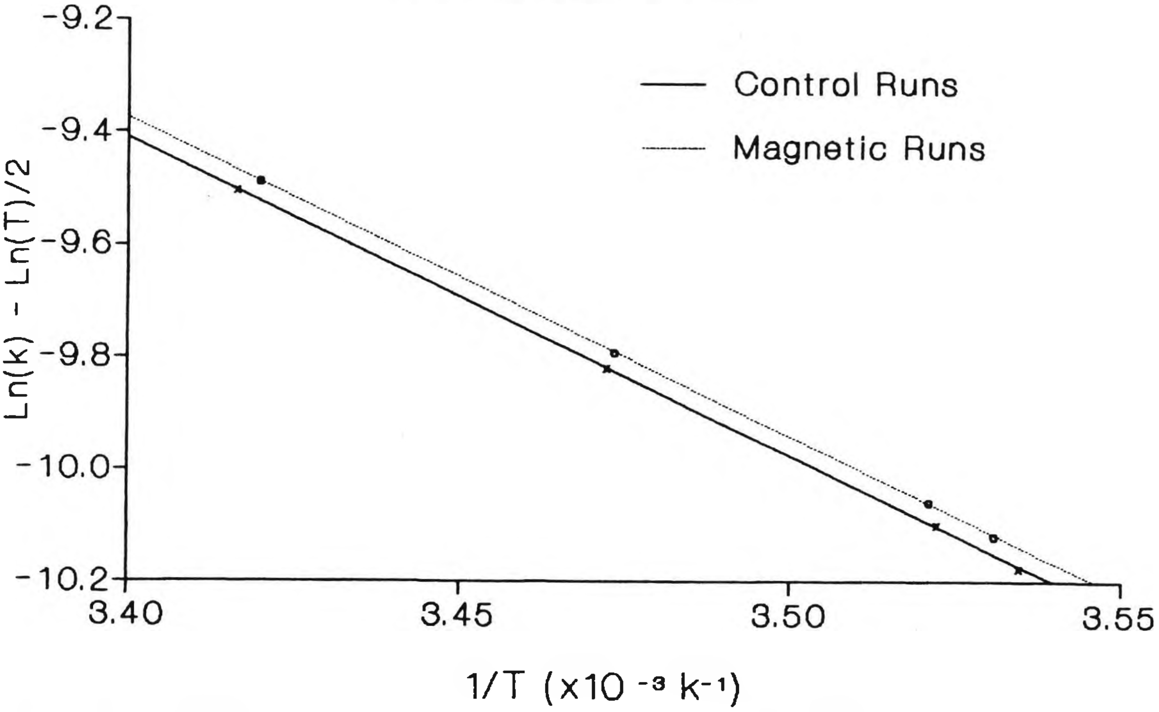
Magnetic Runs:

Activation Energy, E = 47.08 kJ/mol.

Frequency Factor, A' = 1.95×10^4 $l^2mol^{-2}s^{-1}$.

The coefficients of determination for the regression analyses were 99.993% and 99.996%, which demonstrate the very high levels of accuracy which can be achieved for the determination of the kinetics of the reaction. It can be seen that the two values for the activation energy are, within the experimental bounds, the same (differing by only 0.1%), while the value for A' is significantly changed, by 6.2%, following the magnetic treatment.

Figure 5.2



Graph of Results of Experiment 2 for the Determination of E and A'.

5.2.iv. Treatment of Individual Species.

For the remainder of the present work, the second experimental procedure and test apparatus were used (see section 5.1). Some initial experimental work was carried out to test the reproducibility of the results obtained with the new techniques. It was found that very good results could be obtained, and the reaction rate determinations were as accurate as those achieved using the previous method.

With the new techniques it was possible to determine the effect of the treatment on the individual species involved in the reaction (i.e. I^-, H_2O_2 and H^+). For each of these tests one of the solutions was initially circulated through the apparatus without the electromagnets in place. At various time periods volumes of the solution were dispensed into the reaction vessel, with the other reactants, and the rate was determined in the same manner as for the previous tests. After several of these control runs the circulating tubing was positioned between the poles of the electromagnet, which was set to give a field strength of 1400 gauss, and further rate determinations were carried out. In every case, the reaction was started, by the addition of the peroxide, one minute after the treated solution was dispensed into the reaction vessel. The temperature for all of the tests was maintained at 16.8 (±0.1)°C.

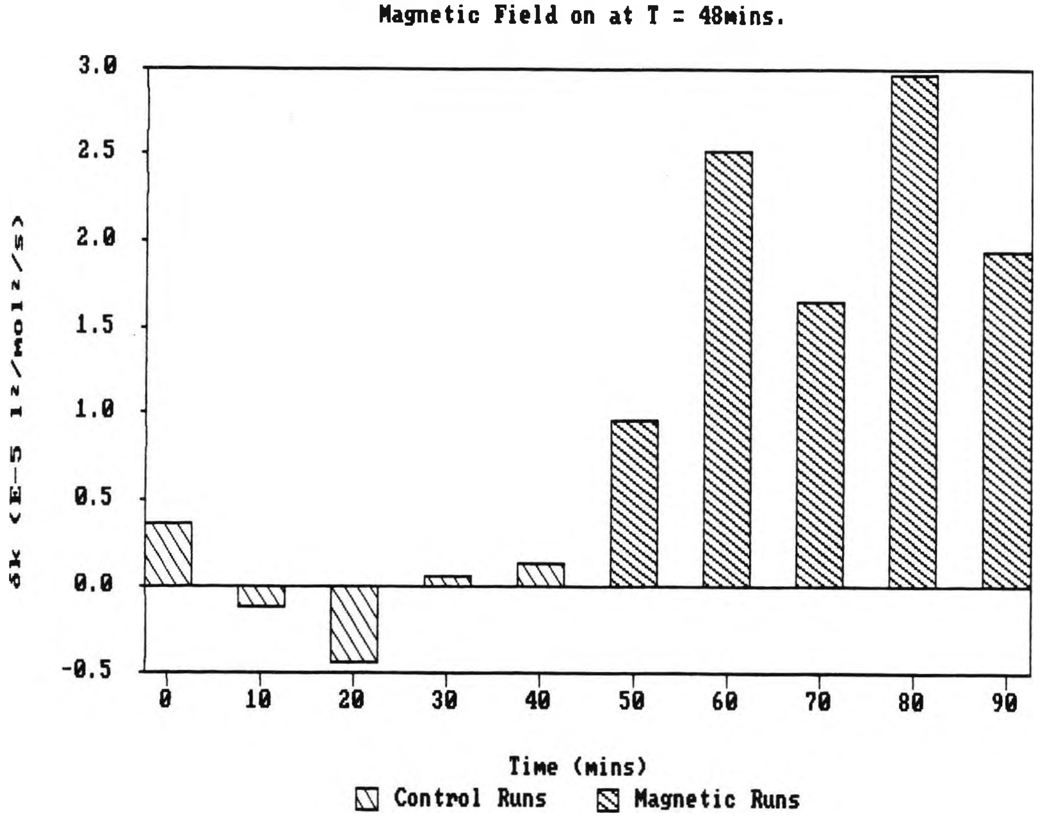
The calculated values for the rate constant for the treatment of the iodide solution (Experiment 3), the hydrogen peroxide solution (Experiment 4) and the acid (Experiment 5) are presented in Tables 5.4, 5.5 and 5.6, respectively. Figures 5.3, 5.4 and 5.5 are graphs of δk, the difference between the determined rate constant and the average control rate constant, against time of circulation.

Table 5.4

Run Number	Time (mins)	Rate Constant, k_o ($\times10^{-3}$ $l^2mol^{-2}s^{-1}$)	Coefficient of Determination (%)
1	0	1.1857 ± 0.0007	100.000
2	10	1.1807 ± 0.0014	100.000
3	20	1.1776 ± 0.0020	99.999
4	30	1.1826 ± 0.0013	100.000
5	40	1.1834 ± 0.0017	99.999
AVERAGE	-	1.1820(σ=0.0027)	-
MAGNETIC FIELD ON AT T = 48 MINS.			
6	50	1.1916 ± 0.0011	100.000
7	60	1.2072 ± 0.0011	100.000
8	70	1.1985 ± 0.0011	100.000
9	80	1.2116 ± 0.0060	99.990
10	90	1.2014 ± 0.0021	99.999
AVERAGE	-	1.2021(σ=0.0069)	-

Reaction Rate Constants for Experiment 3 (Iodide Treated).

Figure 5.3



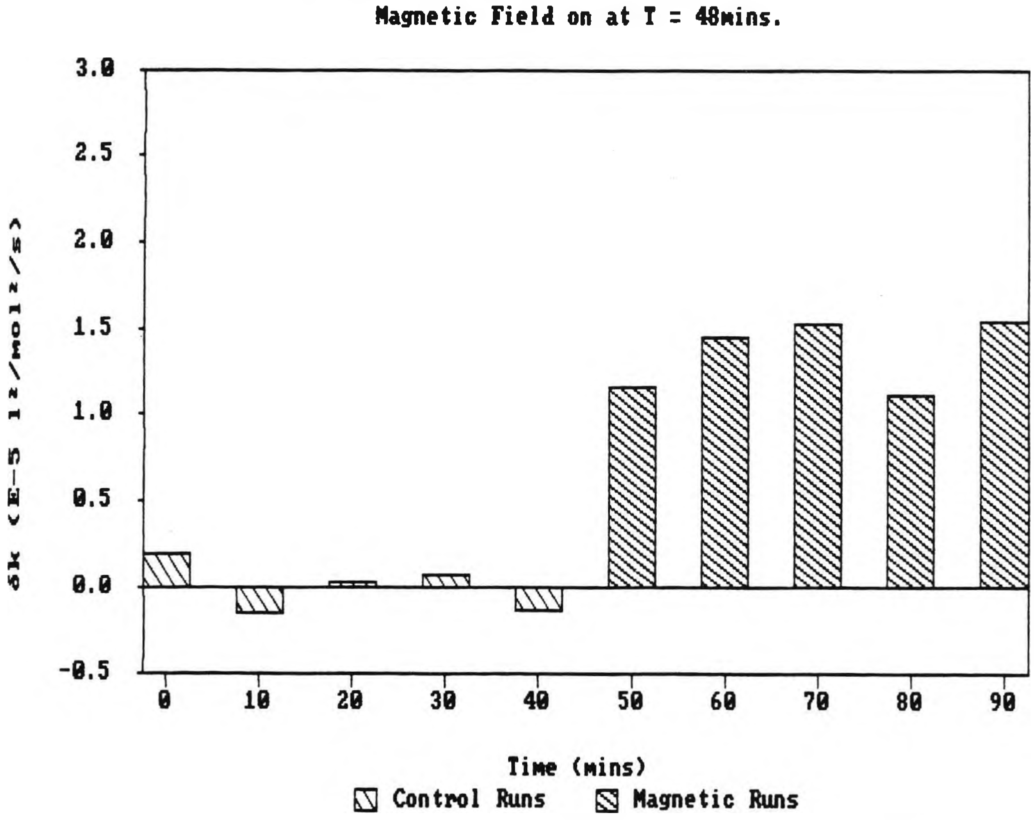
Graph of Change in k with Respect to Average Control, δk, vs. Time.

Table 5.5

Run Number	Time (mins)	Rate Constant, k_o $(x10^{-3}\ l^2mol^{-2}s^{-1})$	Coefficient of Determination (%)
1	0	1.1859 ± 0.0028	99.998
2	10	1.1824 ± 0.0017	99.999
3	20	1.1843 ± 0.0011	100.000
4	30	1.1848 ± 0.0021	99.999
5	40	1.1826 ± 0.0014	99.999
AVERAGE	-	1.1840(σ=0.0013)	-
MAGNETIC FIELD ON AT T = 48 MINS.			
6	50	1.1956 ± 0.0016	99.999
7	60	1.1985 ± 0.0030	99.997
8	70	1.1992 ± 0.0012	100.000
9	80	1.1952 ± 0.0016	99.999
10	90	1.1994 ± 0.0006	100.000
AVERAGE	-	1.1976(σ=0.0018)	-

Reaction Rate Constants for Experiment 4 (Peroxide Treated).

Figure 5.4



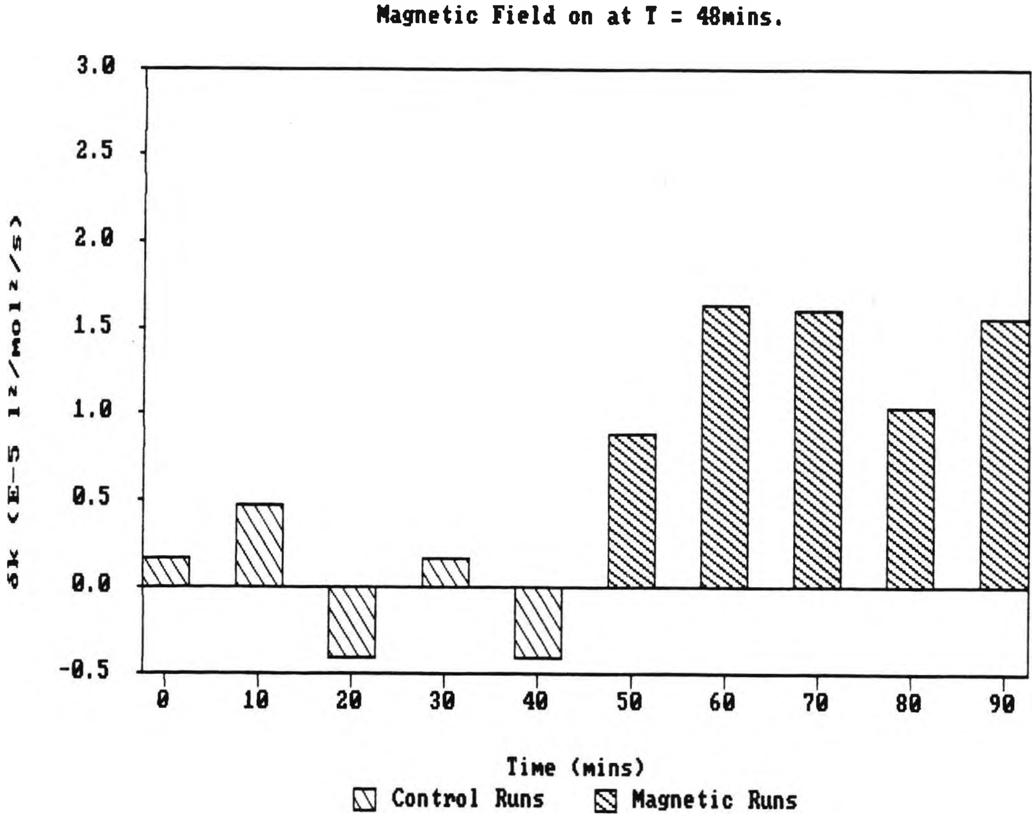
Graph of Change in k with Respect to Average Control, δk, vs. Time.

Table 5.6

Run Number	Time (mins)	Rate Constant, k_o ($\times10^{-3}$ $l^2mol^{-2}s^{-1}$)	Coefficient of Determination (%)
1	0	1.1855 ± 0.0026	99.998
2	10	1.1884 ± 0.0025	99.998
3	20	1.1796 ± 0.0020	99.999
4	30	1.1854 ± 0.0027	99.998
5	40	1.1797 ± 0.0021	99.999
AVERAGE	-	1.1837(σ=0.0035)	-
MAGNETIC FIELD ON AT T = 48 MINS.			
6	50	1.1926 ± 0.0028	99.998
7	60	1.2000 ± 0.0011	100.000
8	70	1.1998 ± 0.0006	100.000
9	80	1.1941 ± 0.0030	99.997
10	90	1.1992 ± 0.0018	99.999
AVERAGE	-	1.1971(σ=0.0031)	-

Reaction Rate Constants for Experiment 5 (Acid Treated).

Figure 5.5



Graph of Change in k with Respect to Average Control, δk, vs. Time.

It can be seen that, in every case, the effect of the magnetic treatment was to increase the rate of the reaction. The duration of the treatment was found to have no significant additional influence on the magnitude of this change, which was greatest when the iodide solution alone was treated. Consequently, all the remaining experiments with the reaction were carried out by treating the iodide solution only.

5.2.v. Determination of the 'Memory Effect'.

For the first of these tests (Experiment 6), the iodide solution was initially circulated through the apparatus without the magnets in place. After a number of rate determinations, the tubing was positioned between the poles of the magnets (field strength = 1400 gauss) for four minutes. The magnets were then removed and the rate of the reaction was determined every few minutes, until it had returned to its control value. The second set of tests (Experiment 7) was carried out using a very similar technique, but the iodide solution was only passed through the magnetic field once. The temperature for all of the tests was 16.7 (±0.1)°C and the peristaltic pumps were set to give a flow rate of 3.0 l/hour. The results of the two experiments are presented in Tables 5.7 and 5.8 and Figures 5.6 and 5.7. are graphs of δk, the difference between the determined rate constant and the average control value, against time.

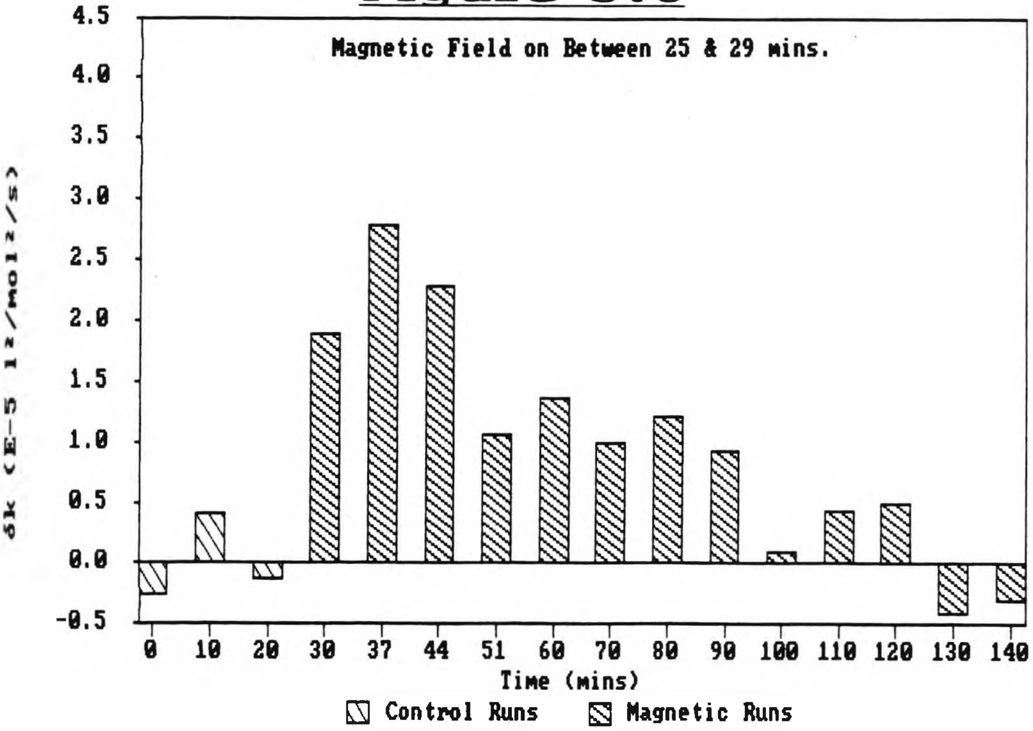
For both experiments, there is evidence that the degree of the treatment effect continues to increase for a period of time after the magnetic field has been removed. This is in good agreement with the observations made for the work on calcium/magnesium phosphate (see section 3.2.vi). The subsequent 'decay' of the increase in the reaction rate back to the control value is also very similar to that

Table 5.7

Run Number	Time (mins)	Rate Constant, k_o ($\times 10^{-3}$ $l^2 mol^{-2} s^{-1}$)	Coefficient of Determination (%)
1	0	1.1766 ± 0.0041	99.995
2	10	1.1832 ± 0.0036	99.996
3	20	1.1777 ± 0.0041	99.995
AVERAGE	-	1.1792(σ=0.0029)	-
MAGNETIC FIELD ON BETWEEN 25 and 29 MINS.			
4	30	1.1982 ± 0.0049	99.993
5	37	1.2071 ± 0.0020	99.999
6	44	1.2020 ± 0.0043	99.995
7	51	1.1899 ± 0.0043	99.995
8	60	1.1928 ± 0.0048	99.994
9	70	1.1891 ± 0.0049	99.993
10	80	1.1914 ± 0.0036	99.996
11	90	1.1885 ± 0.0045	99.994
12	100	1.1800 ± 0.0039	99.996
13	110	1.1835 ± 0.0025	99.998
14	120	1.1842 ± 0.0024	99.998
15	130	1.1750 ± 0.0047	99.994
16	140	1.1760 ± 0.0032	99.997

Reaction Rate Constants for Experiment 6 (Recirculating).

Figure 5.6



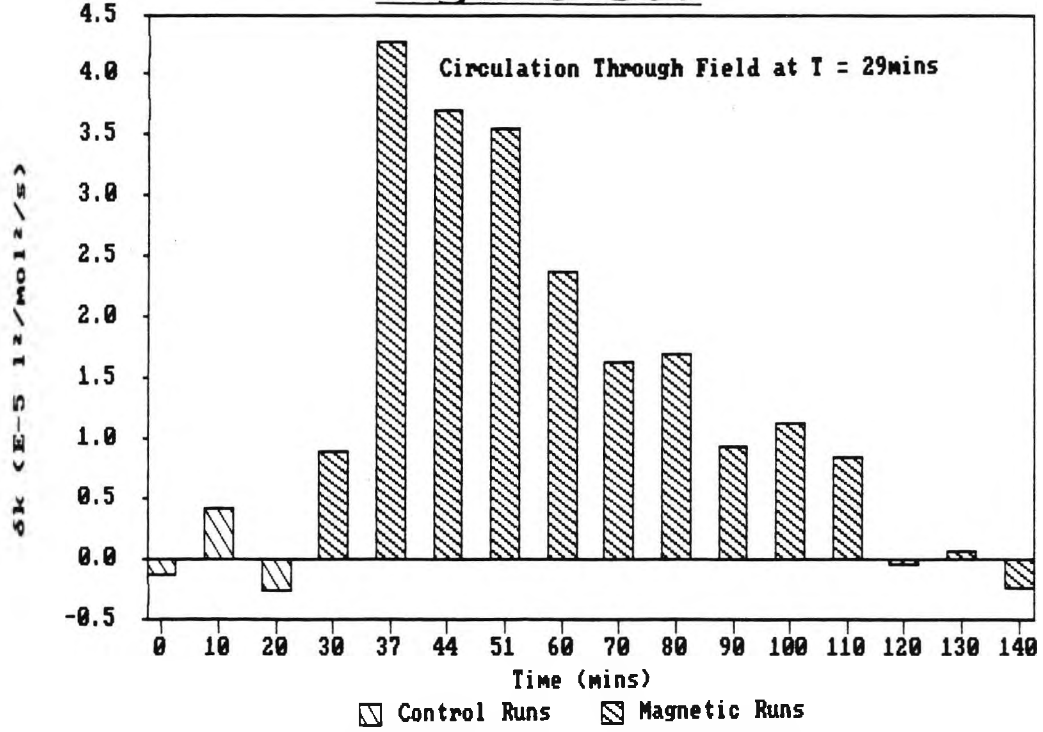
Graph of Change in k with Respect to Average Control, δk, vs. Time.

Table 5.8

Run Number	Time (mins)	Rate Constant, k_o ($x10^{-3}$ $l^2mol^{-2}s^{-1}$)	Coefficient of Determination (%)
1	0	1.1739 ± 0.0031	99.997
2	10	1.1793 ± 0.0022	99.999
3	20	1.1725 ± 0.0029	99.998
AVERAGE	-	1.1752(σ=0.0029)	-
SOLUTION PASSED THROUGH MAGNETIC FIELD AT T = 29 MINS			
4	30	1.1841 ± 0.0035	99.997
5	37	1.2180 ± 0.0024	99.998
6	44	1.2123 ± 0.0040	99.996
7	51	1.2109 ± 0.0029	99.998
8	60	1.1990 ± 0.0024	99.998
9	70	1.1916 ± 0.0029	99.998
10	80	1.1921 ± 0.0025	99.998
11	90	1.1845 ± 0.0012	100.000
12	100	1.1864 ± 0.0030	99.998
13	110	1.1836 ± 0.0033	99.997
14	120	1.1747 ± 0.0019	99.999
15	130	1.1758 ± 0.0028	99.998
16	140	1.1727 ± 0.0031	99.997

Reaction Rate Constants for Experiment 7 (Single Pass).

Figure 5.7



Graph of Change in k with Respect to Average Control, δk, vs. Time.

found for the calcium/magnesium phosphate system. The effect can be seen to last for approximately 1.5 hours after the magnets were removed.

5.2.v. Influence of Flow Conditions and Field Strength.

The results of Experiments 6 and 7 had shown that the magnetic treatment had a greater effect on the kinetics of the reaction when the iodide solution was passed through the field once only. It was decided to investigate this observation further, using different field strengths. In the light of the rate at which the effect had been found to decay, the experimental technique was very slightly modified. For the earlier experiments, from five to twelve time measurements and additions of the thiosulphate solution were made for the rate determination, which took up to seven minutes. For the remainder of the present work, the number of thiosulphate additions was reduced to three, so that the rate determination took only two or three minutes.

In order to ensure that the determination of the velocity constant, using only three points for the regression analysis, would be accurate, the constants for some of the earlier experiments were re-calculated using only the first three time measurements. It was found that the values of k_o were very close to those calculated using all of the data. The ranges and coefficients of determination for the regression analyses were, however, meaningless, since useful values can only be obtained with a larger data set. To compensate for this and to check the accuracy of the rate determinations, two or three repeat runs were carried out at each field strength and the average values and standard deviations (σ) were calculated.

The previous experiments had indicated that the magnitude of the effect continued to increase for a period of time after the magnetic field was removed. Consequently, the reactions were started, by the addition of the peroxide solution, exactly five minutes after the iodide solution was passed through the magnetic field. The experimental procedures used for the tests were the same as those used for Experiments 6 and 7.

For the first experiment (No.8), which was carried out to determine the influence of field strength on the magnetic treatment effect, the iodide solutions were continuously circulated through the magnetic fields for five minutes. A measured portion of each solution was then transferred to the reaction vessel and, after five minutes, the reaction was started and its rate constant was determined in the manner described previously. The temperature was maintained at 16.5 (±0.1)°C and the flow rate was 3.0 l/hour. Table 5.9 shows the calculated values for k_o at the given field strengths and Figure 5.8 is a graph of the results.

It can be seen that the magnetic treatment influenced the rate of the reaction at the lowest field strength investigated (495gauss). The value of δk with this field is about $1 \times 10^{-5}\ l^2mol^{-2}s^{-1}$. As the field strength was increased the value of δk also tended to increase, but to a much lesser degree than with the lower field strength. So, by about 3000gauss (which gave the greatest change) the value of δk had only increased by a further $0.7 \times 10^{-5}\ l^2mol^{-2}s^{-1}$.

Experiment 9 was carried out using the same technique and conditions as for Experiment 8, but the solution was passed through the field once only. The values of k_o, and the field strengths, are given in Table 5.10 and Figure 5.9 is a graph of the results.

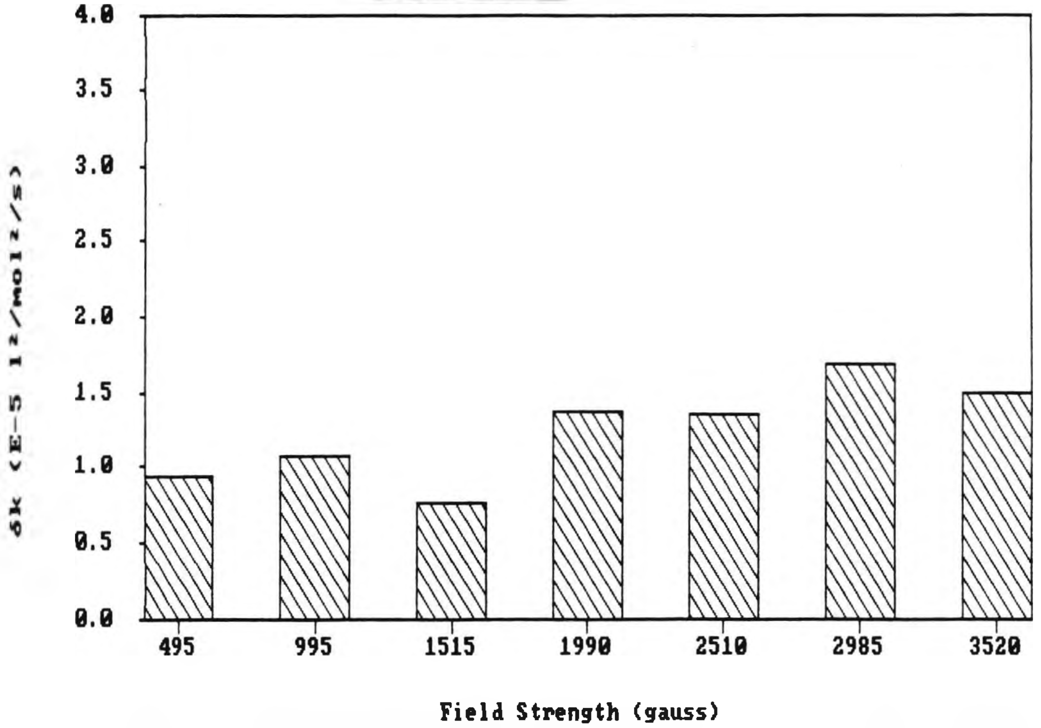
Table 5.9

Run Nº	Field (gauss)	Rate Constant, k_o $(x10^{-3}l^{2}mol^{-2}s^{-1})$
1	0	1.1851
2		1.1826
9		1.1831
16		1.1867
21		1.1824
27		1.1866
AVE		1.1850 (σ=0.0018)
6	495	1.1938
13		1.1928
20		1.1966
AVE		1.1944 (σ=0.0016)
3	995	1.1909
17		1.2009
23		1.1956
AVE		1.1958 (σ=0.0040)
7	1515	1.1958
10		1.1919
22		1.1910
AVE		1.1929 (σ=0.0021)

Run Nº	Field (gauss)	Rate Constant, k_o $(x10^{-3}l^{2}mol^{-2}s^{-1})$
8	1990	1.1927
18		1.2012
26		1.2021
AVE		1.1987 (σ=0.0042)
4	2510	1.1975
15		1.2007
25		1.1972
AVE		1. 985 (σ=0.0016)
5	2985	1.2112
11		1.1945
19		1.2001
AVE		1.2019 (σ=0.0069)
12	3520	1.1967
14		1.2021
24		1.2008
AVE		1.1998 (σ=0.0023)

Reaction Rate Constants for Experiment 8 (Recirculating).

Figure 5.8



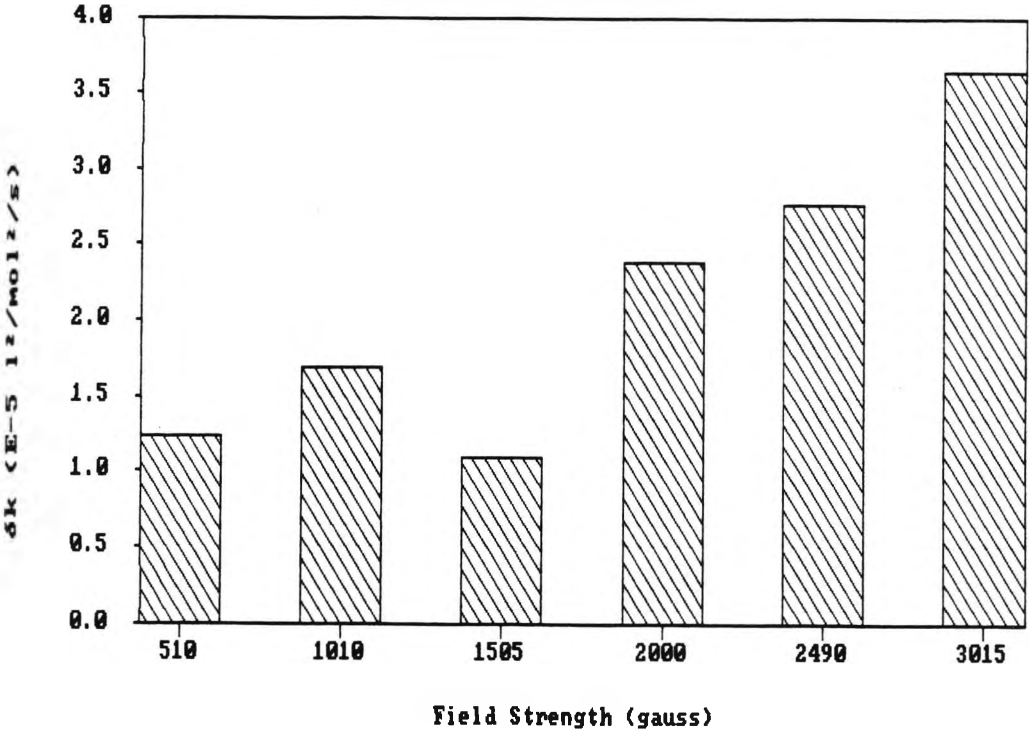
Graph of δk against Magnetic Field Strength - Recirculating Tests.

Table 5.10

Run Nº	Field (gauss)	Rate Constant, k_o $(\times 10^{-3} l^2 mol^{-2} s^{-1})$
1	0	1.1841
5		1.1871
11		1.1858
16		1.1821
AVE		1.1848 (σ=0.0019)
4	510	1.1956
14		1.1986
AVE		1.1971 (σ=0.0015)
7	1010	1.1996
15		1.2036
AVE		1.2016 (σ=0.0020)
2	1505	1.1953
10		1.1962
AVE		1.1958 (σ=0.0005)
6	2000	1.2211
13		1.1962
AVE		1.2087 (σ=0.0120)
8	2490	1.2097
12		1.2153
AVE		1.2125 (σ=0.0028)
3	3015	1.2270
9		1.2153
AVE		1.2212 (σ=0.0059)

Reaction Rate Constants for Experiment 9 (Single Pass).

Figure 5.9



Graph of δk against Magnetic Field Strength - Single Pass Tests.

The results of this experiment are very similar to those obtained for Experiment 8, but the magnitude of the effect was greater with the single pass tests. Figures 5.8 and 5.9 have been plotted to the same scale and it can be seen that the values of δk increase more rapidly, and the maximum change is approximately twice as great, than when the test solution was circulated through the magnetic field.

The results of Experiments 8 and 9 show that the magnetic treatment effect influenced the kinetics of the reaction with field strengths as low as 500gauss. It was decided to investigate the influence of weaker fields, below 500gauss, on the rate of the reaction. Therefore, Experiment 10 was set up using the same techniques and procedures as were used for Experiment 9 (i.e. single pass tests). The field strength was varied, by varying the supply to the electromagnets, between 0 and 500gauss. The pump was set to give a flow rate of 3.0 l/hour and the temperature was maintained at 16.3 (±0.1)°C throughout all of the tests. The calculated values for the rate constant are presented in Table 5.11 and Figure 5.10 is a graph of δk against field strength.

The results of this investigation were particularly interesting; it was found that the rate of the reaction was increased at certain field strengths and decreased at others. At the lowest field strengths (up to about 100gauss), the rate can be seen to be slightly increased. With fields between 100 and 250gauss the rate was significantly reduced. Above 250 gauss the rate increased, initially very sharply, and then (above about 450gauss) more slowly. This indicates that the magnetic treatment has a different effect on the species in the solution at the lower field strengths than with higher ones. There is evidence that this may have occurred for the calcium/magnesium phosphate system (Chapter 3), but as fewer field strengths were tested, it is not possible to be categorical about this.

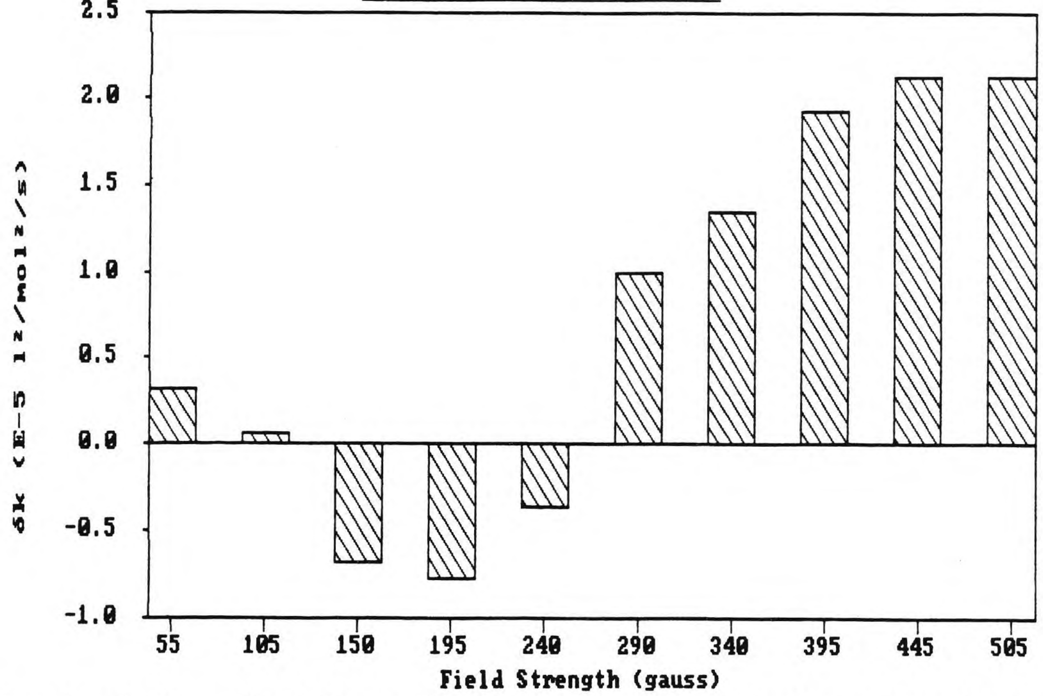
Table 5.11

Run Nº	Field (gauss)	Rate Constant, k_o ($x10^{-3}l^2mol^{-2}s^{-1}$)
1		1.1748
7		1.1818
16	0	1.1816
24		1.1751
AVE		1.1783 (σ=0.0034)
11		1.1883
19	55	1.1748
AVE		1.1816 (σ=0.0068)
4		1.1753
14	105	1.1827
AVE		1.1790 (σ=0.0037)
3		1.1711
22	150	1.1716
AVE		1.1714 (σ=0.0003)
9		1.1713
15	195	1.1696
AVE		1.1705 (σ=0.0009)

Run Nº	Field (gauss)	Rate Constant, k_o ($x10^{-3}l^2mol^{-2}s^{-1}$)
10		1.1701
18	240	1.1792
AVE		1.1747 (σ=0.0046)
2		1.1900
17	290	1.1866
AVE		1.1883 (σ=0.0017)
5		1.1916
8	340	1.1917
AVE		1.1917 (σ=0.0001)
12		1.1990
23	395	1.1962
AVE		1.1976 (σ=0.0014)
6		1.1935
20	445	1.2056
AVE		1.1996 (σ=0.0061)
13		1.1966
21	505	1.2023
AVE		1.1995 (σ=0.0029)

Reaction Rate Constants for Experiment 10 (Single Pass).

Figure 5.10



Graph of δk against Magnetic Field Strength - Recirculating Tests.

5.3. Discussion

5.3.i. Experimental Methods and Testing Procedures.

The extremely good and reproducible rate determinations which were made during the course of the work reflect both the suitability of the reaction for this type of investigation, and the care which was taken in the development and use of the testing procedures. In particular the results have shown that the decision to 'incorporate' the thiosulphate titration into the reaction was sound.

In addition to the method which was used to monitor the progression of the reaction for the presented work, (see section 5.1), the possible use of two other techniques was also investigated. For the first of these a colorimeter and chart recorder were used. The colorimeter was calibrated using a number of iodine solutions of known concentration. The iodide, thiosulphate and acid solutions were then dispensed into a cell which was positioned in the light beam of the instrument. The output from the colorimeter was connected to a chart recorder, which was switched on when the peroxide solution was added. There were, however, a number of drawbacks to using this technique:

1) The reaction mixture could not be stirred adequately, since the movement of the stirring paddle blades was found to affect the output. Because of this the reaction did not proceed evenly throughout the solution, and reproducibility could not be achieved.

2) It was not possible to accurately control and measure the temperature of the solution, because of the design of the cells which had to be used with the instrument.

3) The absorbance of the light beam passing through the sample was not as accurate a measure of the changing hydrogen peroxide concentration as the techniques used for the present work.

The second technique which was investigated as a method of following the progression of the reaction, involved monitoring the iodide concentration using an ion-selective electrode. The electrode and a single-junction reference electrode were connected to an amplifier, the output from which was fed into the A-D converter port of a BBC microcomputer. It was hoped that it would be possible to program the computer to directly calculate the reaction rate constant when the electrodes were submerged in the reaction mixture. Though some very promising results were obtained initially using this technique, in the end it was abandoned since the development of the hardware and software required was taking too much time.

5.3.ii. General Comments.

The results of the experiments with the Harcourt-Esson reaction have shown that the effect of the magnetic treatment, with fields over 250gauss (see section 5.3.vii), was to increase the rate of the reaction. This is entirely consistent with the theory which has been proposed and developed to account for the observed effects on other systems, presented in Chapters 2, 3 and 4. The effects of the proposed changes in the degree of interionic association, due to the magnetic treatment, on the kinetics of chemical processes have been discussed in terms of collision kinetic theory and the Arrhenius equation. However, the effects are also consistent with transition state theory, which is concerned with the equilibrium between the reactants and an activated complex which is formed as a transition state in the reaction. For a general bimolecular reaction this can be represented by;

$$A + B \rightleftharpoons AB* \longrightarrow \text{products.}$$

AB*, the activated complex, can be considered as a normal molecule, except that one of its vibrations is equivalent to a translational degree of freedom along the direction leading to the formation of the products. The frequency of this vibration, v, is the frequency at which AB* reacts to form products and is given by;

$$v = KT/h,$$

where K is Boltzmann's constant, h is Planck's constant and T is the absolute temperature. Therefore, the rate of the reaction is;

$$-d[A]/dt = v.[AB*]$$

In order to explain the observed changes in the rate of the reaction due to the magnetic treatment it is necessary to consider the equilibrium constant, K*, for the equilibrium between the reactants and the activated complex:

$$K* = [AB*]/[A].[B].$$

It has been shown (see section 3.3.i) that, as a consequence of LeChatelier's principle, the proposed changes in the activities of the reactants, A and B, would cause a shift in the equilibrium and, consequently, an increase in the concentration of AB*. In terms of transition state theory, this increase explains the observed changes in the kinetics of the studied processes. The theory proposed to account for the observed magnetic treatment effect has, therefore, been shown to be consistent with both the collision and transition state kinetic theories.

5.3.iii. Determination of Activation Energy.

The reaction rate constant, calculated at various temperatures, was used in conjunction with the Arrhenius equation to calculate the activation energy, E, and the pre-exponential collision frequency factor, A'. It was found that the magnetic treatment had no significant effect on the value of the activation energy for the reaction, which was calculated to be about 47kJ/mol. The literature values, given in the US National Bureau of Standards, Tables of Chemical Kinetics, for the two rate-determining steps of the reaction;

(1) $H_2O_2 + I^- \longrightarrow H_2O + IO^-$, and,

(2) $H_2O_2 + I^- + H^+ \longrightarrow H_2O + HIO$.

are (1) 56kJ/mol and (2) 43kJ/mol, which are consistent with the determined value for the overall reaction.

The magnetic treatment effect was found to influence the collision frequency factor, A', the value of which is determined, as its name suggests, by the number of collisions between the reactant species per unit time. This provides very strong evidence in support of the theory which has been proposed to account for the observed effects.

5.3.iv. Treatment of Individual Species.

The results of experiments 3, 4 and 5, for which only one of the reactant solutions was exposed to the magnetic field, show that the degree of the magnetic treatment effect depends on the species treated. This observation has also been made for the treatment of the barium and sulphate solutions used with the work on the precipitation of barium sulphate (see Chapter 2). In both cases, it is justifiable to assume that the different magnitudes of the observed changes are due to differences between the extent and nature of the interionic associations within the treated solutions. This is determined by the concentration of the species in the solution, the concentration and nature of other species present, and the size and charge distribution of the ion under consideration.

It would be expected, if the suggested magnetic treatment effect mechanism is accepted, that the species which has the greatest degree of interionic association, would exhibit the greatest magnetic treatment effect. Hydrogen peroxide is a polar molecule and, due to the relatively small charges associated with its polarity, it would be expected to have a smaller degree of association with other species, than would be the case for an ionic electrolyte. Activity coefficients have been shown to be determined by the extent of the ionic atmosphere and hydration sphere around an ion. The CRC Handbook of Chemistry and Physics gives values for the activity coefficients for potassium iodide and hydrochloric acid solutions of various concentrations at 25°C. These are shown in Tables 5.12 and 5.13, with the associated values of activity, and Figure 5.11 shows the graphs of activity against concentration for potassium iodide and hydrochloric acid solutions.

It can be seen that the values of the activity coefficients for the acid are much higher than those for the iodide. This suggests that there is a much greater degree of interionic association within

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Table 5.12

c (mol/l)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
f	0.778	0.733	0.707	0.689	0.670	0.661	0.654	0.650	0.646	0.645
a = f.c (mol/l)	0.078	0.147	0.212	0.276	0.335	0.397	0.458	0.520	0.581	0.645

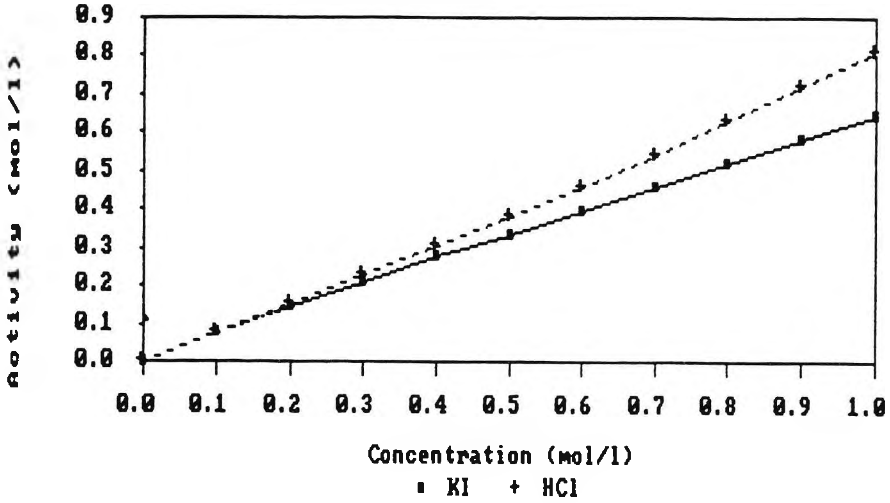
Activity Coefficients, f, and Activities, a, for $KI_{(aq)}$ at 25°C.

Table 5.13

c (mol/l)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
f	0.796	0.767	0.756	0.755	0.757	0.763	0.772	0.783	0.795	0.809
a = f.c (mol/l)	0.080	0.153	0.227	0.302	0.379	0.458	0.540	0.626	0.716	0.809

Activity Coefficients, f, and Activities, a, for $HCl_{(aq)}$ at 25°C.

Figure 5.11



Graphs of Activity Against Concentration for $KI_{(aq)}$ and $HCl_{(aq)}$.

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the iodide solutions and, as a consequence of this, the magnetic treatment of the iodide solution would be expected to give a greater effect than the treatment of the hydrogen peroxide or acid solutions.

5.3.v. The 'Memory Effect'.

The successive determinations of the rate of the reaction, carried out for Experiments 6 and 7, is an extremely good method for determining the duration of the magnetic treatment effect. The results of the investigation show that the magnitude of the effect increases for several minutes after the magnetic field is removed.

Once the maximum degree of the effect has been reached, it 'decays' back to the situation which existed in the untreated solution over a period of between 1 and 1.5 hours. Very similar observations were also made for the work with calcium/magnesium phosphate (see Chapter 3), except that the duration of the effect was longer (5 to 8 hours). No obvious conclusions concerning the mechanism of the effect can be draw from this observation.

In terms of the suggested theory, the decay of the magnetic treatment effect must be due to the reformation of the disrupted ionic associations and ionic clusters within the solution. The consequences of this and the objections to it made by several authors have already been discussed in section 3.3.iii, and the same arguments can be used for the work with the Harcourt-Esson reaction.

5.3.vi. Influence of Flow Conditions.

The results of Experiments 6 to 10, with recirculating and single pass flow conditions for the magnetic treatment, have shown that the magnitude of the effect is greatest when the test solution is passed through the field once only. This suggests that the magnetic field has two opposing effects on the charged species in the treated solution. This can be explained if the range of the degree of association between the charged particles in the solution is considered.

It has been proposed (in section 3.3.iv.) that the individual ions in a solution are associated with other charged particles to a greater or lesser degree. The range of this degree of interionic association would be represented by a normal distribution (see Figure 3.21 on page 151), with some ions almost totally 'dissociated', while others would have a very high level of association (e.g. those near to the centre of ionic clusters). The magnitude of the magnetic treatment effect, using different flow rates and field strengths, has been explained in terms of this distribution and the force on the charged species exerted by the magnetic field/charge interaction. The proposed effect of this interaction is a decrease in the overall degree of association of the species within the solution, giving an increased solution activity.

The observed differences between the magnitude of the magnetic treatment effect under different flow conditions can be shown to be consistent with the mechanism proposed above, if the immediate and wider environments around ions with different degrees of association are considered and the magnetic treatment is assumed to cause a physical movement of the charged particles. In Chapters 1 and 2 the areas of localized high concentration (clusters) which are believed to exist in ionic solutions, were discussed. The area between these clusters would have a comparatively low concentration. Given this, it is obvious that those ions at the centre of large ionic clusters would have a very high level of interionic association with other charged particles, while those in areas of low concentration would have the lowest level of interaction with other ions. Due to the normal distribution for the degree of association, relatively few ions would exist in either of these extreme situations. The majority would have a degree of association between these two values, existing either in smaller clusters or near to the periphery of larger ones.

For the most strongly associated ions, their mobility, under the influence of the external field, would be low, and hence they would only be moved by a relatively short distance. Since these ions exist at the centre of a large area of high concentration, the vast majority would be held in the ionic cluster and their degree of association would be virtually unchanged by the magnetic treatment.

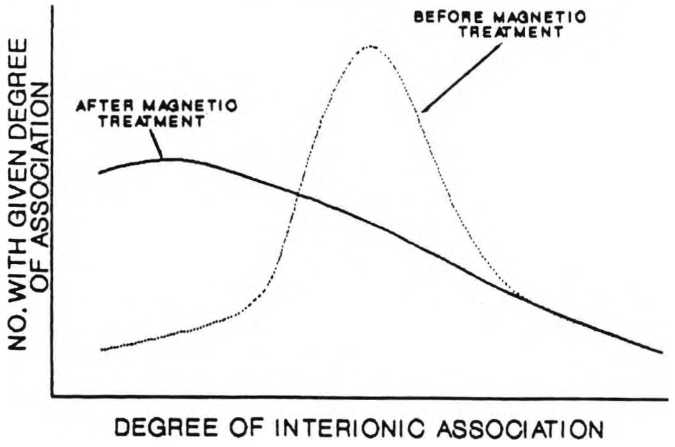
The less strongly associated ions would move a greater distance under the action of the magnetic field and the majority of these, which exist in small clusters, would be moved into the areas of low concentration. This would disrupt the clusters, increase the interionic separation, and hence decrease the degree of association.

The force due to the magnetic field/charge interaction on the least strongly associated ions would cause them to move a relatively long distance, and since they exist in areas of low concentration, this would tend to bring them into closer proximity with other ions and clusters causing an increase in their interaction with other species in the solution, i.e. the degree of association would increase.

In summary, the effects of passing an ionic solution through a magnetic field would leave the most strongly associated ions unaffected, increase the degree of association of the least strongly associated ions and decrease the degree of association for ions between these two extremes. The last of these processes would predominate overall, due to the larger number of ions in that area of the distribution of interionic association, so the overall effect would be a reduction in the total degree of interionic association within the solution. These events are shown diagrammatically in Figure 5.12.

It can be seen that the events described above would tend to shift the distribution of the degree of association for the charged particles in the solution to the left (see Figure 5.12), giving a higher proportion of more weakly associated ions and a lower

Figure 5.12



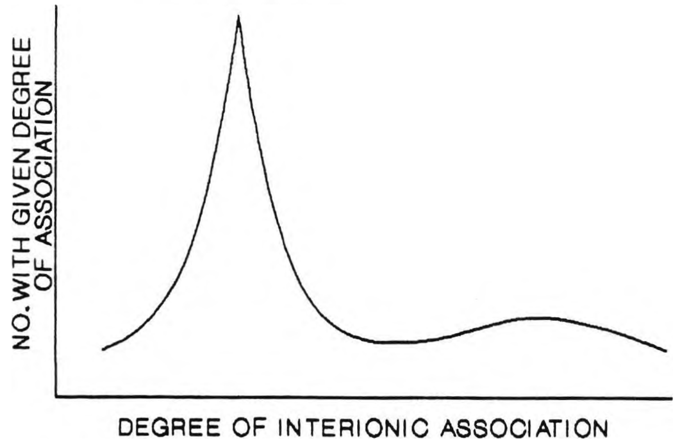
Magnetic Field Effects on the Degree of Interionic Association.

proportion in the centre of the distribution. If this is assumed to be the situation after the solution has passed through the field once, the effects of continued circulation can be predicted.

When a circulating solution passes through the field for the second time, the altered distribution of the degrees of association of the ions would give a predominant increase in the overall degree of interionic association within the solution. Subsequent passes through the field would cause the distribution to shift from side to side until an equilibrium is achieved. This would occur when the degree of association for the affected ions existed in a very small range, for which the reduction in the association of ions in the centre of the distribution is balanced by the increase for the ions to the left of the distribution. A hypothetical distribution of this type is shown in Figure 5.13.

The mechanism suggested above accounts for the greater magnitude of the magnetic treatment effect for the single pass tests. The situation shown in Figure 5.13 must be created after a relatively small number of passes through the field, since the results of

Figure 5.13



Distribution of Degree of Association After Recirculating Tests.

Experiments 3, 4 and 5 show that the magnitude of the effect does not change significantly with continued circulation, after the treatment had been continued for two minutes.

The proposed mechanism is also consistent with the results of the precipitation rate determinations for calcium oxalate and barium sulphate (see Chapter 2). To account for the observed magnetic treatment effects on these systems, it was suggested that the effect of the magnetic treatment was to reduce the number of ionic clusters, increase the stability of certain clusters and increase the activity of the solution as a whole. It can be seen that the events proposed above would have precisely these effects on the charged species in the solution.

5.3.vii. Influence of Field Strength.

The results of Experiments 8 and 9, for which field strengths of between 500 and 3500gauss were used, are entirely consistent with those obtained for the calcium/magnesium phosphate system and the work on corrosion (see sections 3.3.iv. and 4.3.iii.). The same mechanism is, therefore, proposed to account for the observed changes in the kinetics of the Harcourt-Esson reaction (see above). However, the results of Experiment 10, using fields of 50 to 500gauss, show that weaker fields can cause increases or decreases in the rate of the reaction. For extremely weak fields (50 to 100gauss) the magnetic treatment caused a slight increase in the rate. With field strengths between 100 and 250gauss the reaction rate was reduced. Above this value the magnitude of the effect increased in the manner described earlier. These observations can be interpreted in the light of the mechanism proposed in the previous section (5.3.vi.).

The weakest field strengths investigated would only have a very small effect on the least associated ions in the solution. This would give an extremely small increase in the rate of the reaction due to the slight increase in the kinetic energy of some of these ions. Slightly stronger fields would still only be expected to influence those ions with the smallest degree of association, but to a greater degree. Since the predominant effect of the magnetic treatment on such species has been proposed to be an increase in their degree of association, a decrease in the reaction rate would be predicted. The magnitude of this effect would increase with increasing field strength up to a point where the more associated ions begin to be influenced and their degree of association is reduced. When this occurs, the reaction rate would begin to increase. At a certain field strength, the fall in the degree of association of the more associated ions would exactly balance the rise for the less associated particles and the reaction would proceed at the same rate as for the control runs. Increasing the field strength above this value would cause a net reduction in the overall degree of association and the reaction rate would be progressively increased by increases in the field strength.

The results presented by McLauchlan (1989) are in excellent agreement with the proposed effects of weak magnetic fields on the degree of association of charged species in solution. McLauchlan investigated the effects of magnetic fields on the extent of mixing of singlet (S) and triplet (T) state radical pairs. He found that the application of very weak fields (about 100gauss) caused the extent of the T-S mixing to increase. As the field strength was increased (between about 200 and 400gauss) the degree of mixing decreased to below the control value. With higher field strengths a plateau was reached, above which subsequent increases in the field strength had little additional effect on the extent of the mixing. If these events are related to the proposed changes in the degree of association following the magnetic treatment, it can be seen that they correspond almost exactly.

One final interesting comment can be made concerning the proposed effect of weak fields at low flow rates on the degree of interionic association. For the work on corrosion, the observed reduction in the corrosion rate under these conditions was interpreted as representing an increase in the degree of stifling. The results of the investigations presented in this chapter, however, suggest that an increase in the overall degree of association of the ions in the sodium chloride and acid solutions used for the tests may also have had a significant effect on the corrosion rate.

5.4. Conclusions

The magnetic treatment of fluids has conclusively been shown to influence the kinetics of the Harcourt-Esson reaction. With field strengths over 250gauss, this effect caused an increase in the rate of the reaction. However, very weak fields were found to reduce the reaction rate. The magnitude of effect has been shown to be influenced by a number of factors:

1. The species which is treated.
2. The time lapsed since the solution was passed through the magnetic field
3. The flow conditions (i.e. circulating and single pass tests).
4. The field strength.

All of these observations and influences are consistent with the proposed theory, that the major effect of the magnetic treatment of fluids is to alter the degree of interionic association within the treated solution.

The changes in the value of the reaction rate constant, k_o, are due to changes in the pre-exponential collision frequency factor, A'. This shows that the number of collisions occurring between the reactants per unit time, was increased as a consequence of the magnetic treatment. The most justifiable interpretation of this is that the mobility, and hence the activity of the ions in the treated solution was influenced. This would be caused by a change in the degree of the interionic association within the solution, as is suggested by the proposed theory, and hence lends it excellent support.

CHAPTER 6

CONCLUSIONS

The magnetic treatment of fluids has been shown to be a general phenomenon, which influences charged species in solution or suspension in such a way that their subsequent behaviour, in a wide range of chemical processes, is altered.

The treatment has been shown to have a profound effect on precipitation, crystallization and scaling processes (for calcium oxalate, barium sulphate and scale deposition in domestic expansion boilers - see Chapter 2). This effect is characterized by changes in the particle size, the degree of aggregation, the crystallinity and the morphology of the precipitated crystals. The effect also influences the total amount of solids precipitated and the amount of scale deposited. These effects are consistent with changes in the rates of nucleation and the subsequent crystal growth, both of which are shown, by photometric dispersion analyses, to be influenced by the treatment.

The precipitation ratio of calcium and magnesium phosphates from an equimolar solution of calcium and magnesium ions (i.e. the ratio of calcium to magnesium in the precipitate - see Chapter 3) was found to be only slightly influenced by the treatment. However, the total amount of both of the cations precipitated from the solution by the addition of a phosphate was significantly increased, to approximately the same degree in each case (hence only the very small change in the precipitation ratio). These effects have been shown to be consistent with a shift in the equilibrium between the forward and back reactions, leading to increased yields of both phosphates. The magnitude of the effect continues to increase for a period of time after the magnetic field is removed and it then 'decays' back to the control situation over a period of several hours. The degree of the changes caused by the effect depends on a number of factors, including the concentration of the treated solution, the velocity of the solution through the field and the magnetic field strength.

The magnetic treatment effect has been found to have a marked influence on corrosion processes. This influence is characterized by changes in the corrosion rate and the composition of the corrosion products. The magnitude of the observed effects depends on the 'concentration' of the reactants (i.e. the concentration of the corrosive solution and the size of the steel balls used), the solution used, the flow conditions and the magnetic field strength.

The kinetics of the reaction between an iodide and hydrogen peroxide in acid conditions (the Harcourt-Esson reaction) have been shown to be affected by magnetic treatment. This influence causes a change in the rate of the reaction, which is due to changes in the collision frequency of the species in the treated solution. The magnitude of the magnetic treatment effect depends on the solution treated and the length of time after it was treated, the flow conditions and the magnetic field strength.

A theory is proposed which can be used to explain all of the observed effects of the magnetic treatment of fluids, and the influence of various parameters (e.g. flow conditions), which have been found to affect the magnitude of these effects. This theory is based on the suggestion that the interaction between the charged species and the magnetic field causes changes in the interionic association within the treated solution. By considering the range of these degrees of association for individual particles (i.e. their immediate and wider environments) and the magnitude of the force due to the magnetic field/charge interaction the observed phenomena can be interpreted.

If the results of the present work, and the associated theory which has been proposed to account for them, are considered, much of the confusion and apparent contradictions, which have always been associated with the phenomenon, can be explained.

Though much more work is required before the complete mechanism to describe the effects of applied fields on charged species in solution is developed, it is hoped that the work presented in this thesis has gone some way towards the development of such a description.

CHAPTER 7

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APPENDICES

APPENDIX A

COMPUTER PROGRAM LISTINGS

'Ca-MgCAL'

```
1000MODE7
1010@%=FNdp(0)
1020PROCgetinfo
1030CLS
1040PROCcalcs
1050DIMCa(N%),Mg(N%)
1060CLS
1070PROCgetresults
1080MODE3
1090VDU2
1100PROCoutput
1110VDU3
1120PRINT:PRINT:REPEAT:INPUT"DO YOU WANT TO RERUN THE PROGRAM (Y/N) :"N$:UNTILN
$="Y"ORN$="N"
1130IFN$="Y"GOTO1000
1140END
1150:
1160DEFFNdp(W%)=&20009+256*W%
1170:
1180DEFPROCgetinfo
1190INPUT"Enter Initial Run No. :"A%
1200INPUT"Enter  Final  Run No. :"Z%
1210PRINT
1220INPUT"Enter Ca/Mg Solution Vol :"CMVol
1230INPUT"Enter  PO4  Solution Vol :"POVol
1240TotVol=CMVol+POVol
1250PRINT
1260PRINT"For Calcium :"
1270PRINT
1280INPUT"Enter Standard Conc.     :"CaConc
1290INPUT"Enter Standard Reading   :"CaRdg
1300INPUT"Enter Stock Sol Reading  :"CaStk
1310INPUT"Enter Dilution Factor    :"CaDil
1320PRINT
1330PRINT"For Magnesium :"
1340PRINT
1350INPUT"Enter Standard Conc.     :"MgConc
1360INPUT"Enter Standard Reading   :"MgRdg
1370INPUT"Enter Stock Sol Reading  :"MgStk
1380INPUT"Enter Dilution Factor    :"MgDil
1390ENDPROC
1400:
1410DEFPROCcalcs
1420CaFM=40.08
1430MgFM=24.305
1440N%=Z%-A%
1450CaFactor=(CaConc/CaRdg)*CaDil
1460MgFactor=(MgConc/MgRdg)*MgDil
1470CaStkMol=(CaStk*CaFactor*CMVol)/(CaFM*100)
1480MgStkMol=(MgStk*MgFactor*CMVol)/(MgFM*100)
1490ENDPROC
1500:
1510DEFPROCtop
1520CLS
1530PRINT"Run No.        Ca Rdg.        Mg Rdg."
1540PRINT;STRING$(35,"-")
1550ENDPROC
1560:
1570DEFPROCgetresults
1580PROCtop
1590FORI%=0TON%
1600PRINTTAB(2,(I%MOD21)+3);I%+A%;:INPUTTAB(13)Ca(I%)TAB(29,(I%MOD21)+3)Mg(I%)
1610IF(I%+1)MOD21=0THENPROCtop
1620Ca(I%)=Ca(I%)*CaFactor
1630Mg(I%)=Mg(I%)*MgFactor
1640NEXT
1650ENDPROC
1660:
1670DEFPROCoutput
1680PRINTTAB(31)"Run Nos ";A%;" to ";Z%
1690PRINT:PRINT" Calcium :"
1700@%=FNdp(2):PRINT:PRINT"Stock Sol. Conc. (ppm) : ";CaStk*CaFactor
1710@%=FNdp(4):PRINT:PRINT"Moles in 10ml Samples : ";CaStkMol;"x10^-4 Moles"
1720PRINT:PRINT:PRINT" Magnesium :"
1730@%=FNdp(2):PRINT:PRINT"Stock Sol. Conc. (ppm) : ";MgStk*MgFactor
1740@%=FNdp(4):PRINT:PRINT"Moles in 10ml Samples : ";MgStkMol;"x10^-4 Moles"
1750PRINT:PRINT;STRING$(68,"-")
```

```
 1760PRINT"Run     Ion     ppm in      Moles in       % Used      Molar       Ratio Mg"
 1770PRINT"No.              Sol.       ppt(E-4)                   Ratio        to Ca"
 1780PRINT;STRINGS(68,"-")
 1790FORI%=0TON%
 1800C=CaStkMol-(Ca(I%)*TotVol)/(100*CaFM)
 1810M=MgStkMol-(Mg(I%)*TotVol)/(100*MgFM)
 1820D=(100*C)/CaStkMol
 1830N=(100*M)/MgStkMol
 1840E=(C*100)/(C+M)
 1850F=M/C
 1860@%=FNdp(0):PRINT:PRINTTAB(0);I%+A%;TAB(7);"Ca";:@%=FNdp(1):PRINTTAB(14);Ca(
I%);:@%=FNdp(4):PRINTTAB(26);C;:@%=FNdp(2):PRINTTAB(39);D;TAB(50);E;:@%=FNdp(3):
PRINTTAB(61);F
 1870@%=FNdp(0):PRINTTAB(7);"Mg";:@%=FNdp(1):PRINTTAB(14);Mg(I%);:@%=FNdp(4):PRI
NTTAB(26);M;:@%=FNdp(2):PRINTTAB(39);N;TAB(50);100-E
 1880NEXT
 1890ENDPROC
```

'Corcalc'

```
100REM" RUST 20/11/89
110:
120CLOSE#0
130DIMTM(N%),WT(N%),SA(N%),RES(N%),TEMP(N%)
140MODE7
150PROCinfo
160PROCfac
170PROCgetdata
180PROCresult
190REPEAT:PRINT"DO YOU WANT A PRINT OUT (Y/N) ":Y$=GET$:UNTILFNok
200IF Y$="Y" VDU2
210MODE3
220PROCprint_out
230MODE7
240REPEAT:PRINT"DO YOU WANT TO SAVE THE DATA (Y/N) ":Y$=GET$:UNTILFNok
250IFY$="Y" PROCsave
260REPEAT:INPUT"DO YOU WANT TO RERUN THE PROGRAM (Y/N) "Y$:UNTILFNok
270IFY$="Y"RUN
280END
290:
300REM" CHECKS Y/N INPUT
310:
320DEF FNok
330=INSTR("YN",Y$)
340:
350REM" GETS INFORMATION ABOUT THE RUN
360:
370DEF PROCinfo
380INPUT"ENTER RUN NO. : "RN%
390INPUT"MAGNETIC/CONTROL RUN (M/C) : "M$
400INPUT"ENTER NO. OF READINGS : "N%
410INPUT"ENTER DENSITY : "DEN
420INPUT"ENTER NO. OF BALLS : "KL%
430ENDPROC
440:
450REM" ALLOWS INPUT OF RESULTS
460:
470DEF PROCgetdata
480CLS
490PRINT"ENTER READINGS : "
500PRINTTAB(5,2)"NO.";TAB(12,2)"TIME/HOURS";TAB(25,2)"WEIGHT/GRAMS"
510FORI%=1TON%
520PRINTTAB(5,I%*2+2);I%
530INPUTTAB(15,I%*2+2)TM(I%):INPUTTAB(27,I%*2+2)WT(I%)
540SA(I%)=(WT(I%)*FACTOR)^(2/3)
550NEXT
560ENDPROC
570:
580REM" PERFORMS CALCULATIONS ON RESULTS
590:
600DEF PROCresult
610RES(1)=0
620FORI%=2TON%
630RES(I%)=FNcalc(WT(1),WT(I%),SA(1),SA(I%))
640NEXT
650:
660REM" CALCULATES WT.LOSS/SURFACE AREA
670:
680DEF PROCfac
690FACTOR=6*SQR(KL%*PI)/DEN
700ENDPROC
710:
720REM" CALCULATES SURFACE AREA FACTOR
```

```
 730:
 740DEF FNcalc(a,b,c,d)=(a-b)/FNave(c,d)
 760REM" CALCULATES AVERAGE SURFACE AREA
 770:
 780DEF FNave(a,b)=((a+b)/2)
 790:
 800REM" DECIMAL PLACE CALCULATION
 810:
 820DEF FNdp(a)=(INT(a*10000+.5))/10000
 830:
 840REM" PRODUCES PRINT OUT OF RESULTS
 850:
 860DEF PROCprint_out
 870 IF M$="M" THEN N$="MAGNETIC RUN" ELSE N$="CONTROL RUN"
 880PRINTTAB(16);"RUN NUMBER ";RN%;" : "N$'
 890PRINTTAB(1)"TIME"TAB(9)"WEIGHT"TAB(20)"WT.LOSS"TAB(30)"WT.LOSS/SA"
 900VDU11:PRINTTAB(44)"WT.LOSS/SA/TIME"
 910PRINTTAB(0)"(hours)"TAB(9)"(grams)"TAB(20)"(grams)"
 920VDU11:PRINTTAB(29)"(E-3 g/sq.cm)"TAB(43)"(E-4 g/sq.cm/hour)"
 930FORI%=0TO60:PRINTTAB(I%)"_";:NEXT:PRINT
 940PRINT;TM(1)TAB(9);WT(1)
 950FORI%=2TON%
 960PRINT;TM(I%)TAB(9);WT(I%)TAB(20);FNdp(WT(1)-WT(I%))
 970VDU11:PRINTTAB(32);FNdp(RES(I%)*1000)TAB(48);FNdp(RES(I%)*10000/TM(I%))
 980NEXT
 990VDU3
1000PRINTTAB(30,22)"PRESS ANY KEY TO GO ON"
1010REPEAT UNTIL GET
1020ENDPROC
1030:
1040REM" SAVES DATA ONTO DISC
1050DEF PROCsave
1060CLS
1070PRINT"ENTER YOUR CHOICE :"'
1080PRINT"1 : SAVE RAW DATA"'
1090PRINT"2 : SAVE WT.LOSS DATA"'
1100PRINT"3 : SAVE WT.LOSS/SA DATA (AS E-3 g/sq.cm)"
1110PRINT"4 : SAVE WT.LOSS/SA/TIME DATA (AS E-4 g/sq.cm/h)"
1120INPUTC%
1130IFC%=1 F$="RD"+STR$(RN%)+M$:FORI%=1TON%:TEMP(I%)=WT(I%):NEXT
1140IFC%=2 F$="WL"+STR$(RN%)+M$:FORI%=1TON%:TEMP(I%)=WT(1)-WT(I%):NEXT
1150IFC%=3 F$="WS"+STR$(RN%)+M$:FORI%=1TON%:TEMP(I%)=RES(I%)*1000:NEXT
1160IFC%=4 F$="WT"+STR$(RN%)+M$:FORI%=2TON%:TEMP(I%)=RES(I%)*10000/TM(I%):NEXT
1170IFC%=4 TEMP(1)=0
1180X%=OPENOUT(F$)
1190PRINT#X%,N%:FORI%=1TON%
1200PRINT#X%,TM(I%),TEMP(I%)
1210NEXT:CLOSE#X%
1220REPEAT:INPUT"DO YOU WANT TO SAVE MORE DATA (Y/N) "Y$
1230IFY$="Y" PROCsave
1240ENDPROC
```

'Curfit'

```
1000REM" CURVE FIT ANALYSIS
1010REM" 16-6-89
1020:
1030DIM O% 8,C% 8:zro=1E-9:log=FALSE
1040H$="POINT     X VALUE    Y VALUE"+CHR$13+CHR$10+STRING$(40,"_")
1050@%=10:MODE7:VDU15:R%=-1:PROCindata
1060ON ERROR GOTO1070
1070PROCsums(N%):F%=&20409:REPEAT
1080@%=&A:MODE7:A$=FNopt:CLS
1090IF A$="L" PROClist(FNprint)
1100IF A$="E" PROCedit:PROCsums(N%)
1110IF A$="S" R%=NOT R%:PROCsums(N%)
1120IF INSTR("XY",A$) PROCresa
1130IF A$="F" F%=FNform
1140IF A$="P" MODE4:PROCplot
1150IF A$="R" RUN
1160IF A$="T" PROClog:PROCsums(N%)
1170IF A$="C" PROCcurve
1180IF A$="Q" PRINT''"üIf you need to reenter the program type GOTO50":END
1190UNTIL FALSE
1200
1210DEF FNopt
1220VDU3:PRINT'"āOPTIONS"SPC20"PRESS KEY"
1230PRINT'" LIST DATA"TAB(30)" L"
1240PRINT'" EDIT X & Y VALUES"TAB(30)"ėE"
1250PRINT'" CHANGE FORMATING"TAB(30)" F"
1260PRINT'" CALCULATE m, c FOR y=m*x+c"TAB(30)" Y"
1270PRINT'" CALCULATE m, c FOR x=m*y+c"TAB(30)" X"
1280PRINT'" LEAST SQUARES/REGRESSION FIT"TAB(30)" S"
```

```
 1290PRINT'" POLYNOMIAL CURVE FIT"TAB(30)" C"
 1300PRINT'" PLOT POINTS & FITTED LINE"TAB(30)" P"
 1310PRINT'" TAKE LOGS OF DATA POINTS"TAB(30)" T"
 1320PRINT'" RERUN PROGRAM"TAB(30)" R"
 1330PRINT'" QUIT PROGRAM"TAB(30)" Q"
 1340=FNuc
 1350
 1360DEF PROCedit
 1370LOCALa$:@%=F%:L%=0
 1380PRINT''"The points will be listed one at a time.If you wish to change them
type both thenew X and Y values (or expressions).  Tostop editing, presséS.ç If
you do not   wish a point to be included in the"
 1390PRINT"analysis set X= @çfor that point.  Press @çto restore the point."'
 1400PRINTH$:REPEAT L%=L%+1
 1410IF pt%?L% V$="  " ELSE V$="  "
 1420PRINTV$STR$L%;TAB(10);X(L%);TAB(23);Y(L%)
 1430INPUT"X= ",a$
 1440IF a$="S" L%=N%:GOTO1500
 1450IF a$="@" pt%?L%=NOT pt%?L%:GOTO1500
 1460IF a$<>"" X(L%)=EVALa$
 1470INPUT"Y= ",a$
 1480IF a$="S" L%=N%:GOTO1500
 1490IF a$<>"" Y(L%)=EVALa$
 1500UNTIL L%=N%:ENDPROC
 1510
 1520DEF PROCindata
 1530REPEAT INPUT''" NUMBER OF POINTS (0 TO LOAD DATA) :ç"N%
 1540UNTIL N%>=0:CLS:LOCALa$
 1550IF N%=0 PROColddata:ENDPROC
 1560DIM X(N%),Y(N%),pt% N%
 1570PRINTH$:FOR L%=1TO N%:pt%?L%=0
 1580V%=VPOS:IF V%=24 V%=23
 1590PRINTTAB(2);L%;:INPUTTAB(12)a$
 1600X(L%)=EVALa$:INPUTTAB(26,V%)a$
 1610Y(L%)=EVALa$:NEXT
 1620ENDPROC
 1630
 1640DEF PROCsums(N%)
 1650sx=zro:sy=zro:sx2=zro:sy2=zro:sxy=zro:xmin=X(N%):ymin=Y(N%)
 1660I%=1:REPEAT I%=I%+1:UNTIL pt%?I%=0
 1670xmax=X(I%):ymax=Y(I%):B%=0
 1680FOR L%=1TO N%
 1690IF pt%?L% B%=B%+1:GOTO1780
 1700IF xmin>X(L%) xmin=X(L%)
 1710IF xmax<X(L%) xmax=X(L%)
 1720IF ymin>Y(L%) ymin=Y(L%)
 1730IF ymax<Y(L%) ymax=Y(L%)
 1740sx=sx+X(L%):sy=sy+Y(L%)
 1750sx2=sx2+X(L%)*X(L%)
 1760sy2=sy2+Y(L%)*Y(L%)
 1770sxy=sxy+X(L%)*Y(L%)
 1780NEXT:n%=N%-B%
 1790xbar=sx/n%:ybar=sy/n%
 1800PROCscale(xmax-xmin,xmin)
 1810xmax=hi:xmin=lo:PROCscale(ymax-ymin,ymin):ymax=hi:ymin=lo
 1820IF R% PROCrfit ELSE PROClsqfit
 1830ENDPROC
 1840
 1850DEF PROCrfit
 1860dx=FNsd(sx,sx2):dy=FNsd(sy,sy2)
 1870r=FNcc(0,n%):r2=r*r
 1880LOCALa:a=sxy-n%*xbar*ybar
 1890my=FNgrad(sx2,xbar)
 1900mx=FNgrad(sy2,ybar)
 1910dmy=FNdm(sy,sx):dmx=FNdm(sx,sy)
 1920cy=FNint(ybar,my,xbar)
 1930cx=FNint(xbar,mx,ybar)
 1940dcy=FNsdi(dmy,sy2)
 1950dcx=FNsdi(dmx,sx2)
 1960errX=FNerr(dx):errY=FNerr(dy)
 1970ENDPROC
 1980:
 1990DEF FNsd(sum,sum2):LOCALa
 2000a=sum/n%:a=sum2/n%-a*a
 2010=SQR(n%/(n%-1)*a)
 2020
 2030DEF FNgrad(sq,bar)=a/(sq-n%*bar*bar)
 2040DEF FNdm(s1,s2)=SQR(s1*s1/s2/s2*(1-r2)/(n%-2))
 2050DEF FNint(bar,m,bar2)=bar-m*bar2
 2060DEF FNsdi(m,sq)=m*SQR(sq/n%)
 2070DEF FNerr(sd)=sd*SQR(1-r2)
 2080
 2090DEF PROCres(M,dM,C,dC,err)
 2100@%=F%:PRINT'"GRADIENT = ";M;
 2110PRINTTAB(20)"+/- ";dM'
```

```
 2120PRINT"INTERCEPT= ";C;
 2130PRINTTAB(20)"+/- ";dC'':@%=&2030A
 2140IF R%=0 ENDPROC
 2150PRINT'"Correlation Coefficient       =ā";r
 2160PRINT"Coefficient of Determination =ā";100*r2"ç%"
 2170PRINT"Standard Deviation in "A$"       = ";err
 2180ENDPROC
 2190
 2200DEF PROClist(p%)
 2210@%=F%:IF p% VDU2:PRINT''' ELSE CLS:VDU14
 2220IF R% PRINT'"Correlation Coefficient =ā";r
 2230PRINT'TAB(4)"X-value"TAB(13)"Y-value"TAB(23)"Stat."TAB(30)"Inf. Fun."'STRIN
G$(39,"_")
 2240FOR L%=1TO N%:@%=2:PRINTL%TAB(3);:@%=F%
 2250IF X(L%)<0 PRINT;X(L%); ELSE PRINT" ";X(L%);
 2260IF Y(L%)<0 PRINTTAB(12);Y(L%) ELSE PRINTTAB(12)" ";Y(L%);
 2270IF pt%?L% PRINTTAB(30)"éignored" ELSE PROCinf(L%)
 2280NEXT
 2290IF p% VDU12,3 ELSE VDU15:A$=GET$
 2300ENDPROC
 2310:
 2320DEF FNprint
 2330VDU3:PRINTTAB(0,22);:=FNyn("the printer on")
 2340:
 2350DEF PROCresa
 2360IF R% a$=" Linear regression analysis" ELSE a$=" Least-squares fit"
 2370PRINT''a$'" of the ";
 2380IF (A$="X" AND R%) PRINT"X-values (x=m*y+c) gives :":PROCres(mx,dmx,cx,dcx,
errX) ELSE PRINT"Y-values (y=m*x+c) gives :":PROCres(my,dmy,cy,dcy,errY)
 2390IF FNprint VDU12,2:PROCresa
 2400ENDPROC
 2410
 2420DEF PROCplot
 2430LOCALnos,bar:VDU19,0,4;0;
 2440xscale=1000/(xmax-xmin)
 2450yscale=800/(ymax-ymin)
 2460xs=xscale*xmin:ys=ymin*yscale
 2470VDU28,0,0,39,0,24,0;0;1279;980;29,220-xs;136-ys;
 2480PROCaxes:PROCpldat
 2490VDU24,0;0;1000;800;
 2500IF FNyn("the Y-fit line plotted") GCOL4,1:MOVExs,(my*xmin+cy)*yscale:DRAWxm
ax*xscale,(my*xmax+cy)*yscale
 2510IF R% IF FNyn("the X-fit line plotted") GCOL4,1:MOVE(mx*ymin+cx)*xscale,ys:
DRAW(mx*ymax+cx)*xscale,ymax*yscale
 2520GCOL0,1
 2530nos=FNyn("the points numbered"):IF nos PROCpldat
 2540bar=FNyn("error bars"):IF bar PROCpldat
 2550IF FNyn("a printing of the above") PROClabel:PROCdump
 2560ENDPROC
 2570
 2580DEF PROCpldat:LOCALd
 2590VDU5:d=errY*yscale:FOR I%=1TO N%
 2600IF pt%?I% GOTO2630
 2610IF nos MOVE X(I%)*xscale+12,Y(I%)*yscale-12:PRINTSTR$I% ELSE PROCpt(X(I%)*x
scale,Y(I%)*yscale)
 2620IF bar PROCbar(X(I%)*xscale,Y(I%)*yscale,d)
 2630NEXT:VDU4:ENDPROC
 2640
 2650DEF PROCbar(x,y,d)
 2660MOVEx,y+d:PLOT0,-8,0:PLOT1,16,0
 2670MOVEx,y+d:DRAWx,y-d
 2680PLOT0,-8,0:PLOT1,16,0
 2690ENDPROC
 2700
 2710DEF PROCscale(range,min)
 2720E%=1
 2730IF range<1 E%=10^(-INTLOG(range))
 2740range=range*E%:min=min*E%
 2750IF min<1 AND min>0 range=range+min
 2760P%=10^INTLOGrange
 2770hi=(((range+min MODP%)DIV P%)*P%+P%)/E%
 2780lo=(min DIVP%)*P%/E%:hi=hi+lo
 2790lo=lo-lo
 2800ENDPROC
 2810
 2820DEF PROCaxes
 2830MOVExs,ys:PLOT1,0,ymax*yscale-ys:MOVExs,ys:PLOT1,xmax*xscale-xs,0
 2840VDU5:step=(xmax-xmin)/5:V=xmin
 2850FOR x=0TO1000STEP50
 2860MOVExs+x,ys:IF x MOD200=0 tick=16 ELSE tick=8
 2870PLOT1,0,-tick
 2880IF x MOD200=0 V$=LEFT$(STR$V,3):PLOT0,-16*LEN(V$),-16:PRINTV$:V=V+step
 2890NEXT:V=ymin:step=(ymax-ymin)/4
 2900FOR y=0TO800STEP40
```

```
2910MOVExs,ys+y:IF y MOD200=0 tick=16 ELSE tick=8
2920PLOT1,-tick,0
2930IF y MOD200=0 V$=STR$V:PLOT0,-32*LEN(V$)-12,-8:PRINTV$:V=V+step
2940NEXT:VDU4
2950ENDPROC
2960
2970DEF PROCpt(x,y)
2980MOVEx-8,y+8:PLOT1,16,-16:PLOT0,0,16:PLOT1,-16,-16
2990ENDPROC
3000
3010DEF PROClabel
3020LOCALT$:VDU29,0;0;24,0;0;1279;980;
3030REPEAT INPUT'"X-axis label ",T$:UNTIL LENT$<20
3040VDU5:MOVE1200-(LENT$*32),52
3050PRINTT$:VDU4:REPEAT
3060INPUT'"Y-axis label ",T$:UNTIL LENT$<20
3070X%=O% MOD256:Y%=O% DIV256:A%=10
3080FOR M%=1TO LENT$
3090?O%=ASCMID$(T$,M%,1):CALL&FFF1
3100FOR I%=1TO8:C%?I%=0:NEXT
3110FOR J%=1TO7:L%=2^(8-J%)
3120FOR I%=8TO2STEP-1:S%=2^(I%-1)
3130IF O%?J%>=S% C%?I%=C%?I%+L%:O%?J%=O%?J%-S%
3140NEXT:NEXT
3150VDU23,(239+M%),C%?1,C%?2,C%?3,C%?4,C%?5,C%?6,C%?7,C%?8,5
3160NEXT:X%=16:Y%=940-LENT$*32
3170FOR M%=1TO LENT$:MOVE X%,Y%
3180VDU(M%+239):Y%=Y%+32:NEXT
3190VDU4:INPUT'"Title ",T$
3200PRINT'TAB(19-LENT$/2)T$;
3210ENDPROC
3220
3230DEF PROClog
3240IF log PROCalog:ENDPROC
3250FOR I%=1TON%
3260IF X(I%)=0 OR Y(I%)=0 pt%?I%=-1:GOTO3280
3270X(I%)=LOGX(I%):Y(I%)=LOGY(I%)
3280NEXT:log=TRUE
3290ENDPROC
3300
3310DEF PROCalog
3320FOR I%=1TON%
3330IF (X(I%)=0 OR Y(I%)=0)AND pt%?I% pt%?I%=0:GOTO3350
3340X(I%)=10^X(I%):Y(I%)=10^Y(I%)
3350NEXT:log=FALSE
3360ENDPROC
3370
3380DEF FNform
3390REPEAT INPUT"No. of Decimal Places ",I%
3400UNTIL I%>-1 AND I%<9
3410=&20009+256*I%
3420
3430DEF FNuc=CHR$(GET AND&5F)
3440:
3450DEF PROColddata
3460REPEAT CLS:*.
3470INPUT''"åFILENAME ",F$:UNTIL LENF$>0 AND LENF$<8
3480X%=OPENUP(F$):INPUT#X%,N%
3490DIM X(N%),Y(N%),pt% N%
3500FOR I%=1TO N%:INPUT#X%,X(I%),Y(I%)
3510pt%?I%=0:NEXT:CLOSE#X%
3520ENDPROC
3530
3540DEF FNyn(a$)
3550LOCALb$:REPEAT PRINT'"Do you want "a$" ?";
3560b$=FNuc:UNTIL INSTR("YN",b$)
3570=(b$="Y")
3580
3590DEF FNcc(a%,n)
3600LOCALsx,xx,sy,yy,xy,sq
3610FOR I%=1TO N%:IF I%=a% OR pt%?I% GOTO3650
3620sx=sx+X(I%):xx=xx+X(I%)*X(I%)
3630sy=sy+Y(I%):yy=yy+Y(I%)*Y(I%)
3640xy=xy+X(I%)*Y(I%)
3650NEXT
3660sq=(xx-sx*sx/n)*(yy-sy*sy/n)
3670=(xy-sx*sy/n)/SQRsq
3680
3690DEF PROCinf(J%)
3700IF R%=0 PRINT:ENDPROC
3710LOCALstat,func:@%=&20306
3720REM" influence functions
3730stat=FNcc(J%,n%-1)
3740func=(n%-1)*(r-stat)
3750PRINTTAB(22)stat,func:@%=F%
3760ENDPROC
```

```
3770:
3780DEF PROClsqfit
3790LOCALd,SD:dmy=0:dcy=0:errY=0
3800IF n%=2 my=(ymax-ymin/(xmax-xmin):cy=xmin-my*xmin:ENDPROC
3810d=n%*sx2-sx*sx
3820IF d=0 my=1E37:cy=1E37:ENDPROC
3830my=(n%*sxy-sx*sy)/d
3840cy=(sx2*sy-sx*sxy)/d
3850SD=SQR(ABS((sy2+my*my*sx2+n%*cy*cy+2*(-my*sxy-cy*sy+my*cy*sx))/(n%-2)))
3860dmy=SD*SQR(n%/d):dcy=SD*SQR(sx2/d)
3870errY=dcy
3880ENDPROC
3890:
3900DEF PROCdump
3910VDU26,2,1,10,1,10,1,10
3920*$.dump
3930VDU1,12,3
3940ENDPROC
3950:
3960DEF PROCcurve
3970CLS:DIM A(6),P(6,6,6),Pi(6,6)
3980PRINTTAB(5)'"Order of Polynomial (0-5)";:REPEAT INPUTnt%:UNTIL nt%>0 AND nt
%<6
3990nt%=nt%+1:PROCpoly
4000PROCcurdat:PROCdhold
4010ENDPROC
4020:
4030DEF PROCpoly
4040LOCALsm,k%,I,J,K
4050FOR I=1TO nt%
4060FOR J=1TO nt%:Pi(I,J)=0
4070FOR K=1TO nt%:P(I,J,K)=0:NEXT
4080NEXT:NEXT
4090FOR I=1TO nt%:FOR J=1TO nt%
4100FOR M=1TO N%
4110P(I,J,1)=P(I,J,1)+X(M)^(I+J-2)
4120NEXT:NEXT:NEXT
4130FOR I=1TO nt%:FOR M=1TO N%
4140Pi(I,1)=Pi(I,1)+(Y(M)*(X(M)^(I-1)))
4150NEXT:NEXT
4160FOR K=2 TO nt%
4170FOR I=K TO nt%:k%=K-1
4180Pi(I,K)=((Pi(I,k%)*P(k%,k%,k%))/P(I,k%,k%))-Pi(k%,k%)
4190FOR J=k%TO nt%
4200P(I,J,K)=((P(I,J,k%)*P(k%,k%,k%))/P(I,k%,k%))-P(k%,J,k%)
4210NEXT:NEXT:NEXT
4220A(nt%)=Pi(nt%,nt%)/P(nt%,nt%,nt%)
4230FOR K%= nt%-1 TO1STEP-1
4240sm=0:FOR J=K%+1 TO nt%
4250sm=sm+(A(J)*P(K%,J,K%)):NEXT
4260A(K%)=(Pi(K%,K%)-sm)/P(K%,K%,K%)
4270NEXT
4280ENDPROC
4290:
4300DEF PROCcurdat
4310CLS:LOCALfit
4320PRINT'" Polynomial Coefficients"'
4330@%=&20809:FOR I%=1TO nt%
4340PRINTTAB(10)"a(X^";STR$(I%-1)") = ";A(I%)
4350NEXT
4360PRINT'" ","       X","       Y","   Y(CALC)"
4370@%=F%:FOR I%=1TO N%
4380PRINTSTR$I%,X(I%),Y(I%),FNy(X(I%))
4390NEXT
4400IF FNprint VDU12,2:PROCcurdat
4410ENDPROC
4420:
4430DEF FNy(x)
4440LOCALfit:FOR J%=1TO nt%
4450fit=fit+A(J%)*(x^(J%-1))
4460NEXT:=fit
4470:
4480DEF PROCdhold
4490LOCALx,inc,no%:no%=30
4500inc=(X(N%)-X(1))/no%
4510X%=OPENOUTLEFT$("fit"+F$,7)
4520PRINT#X%,no%+2
4530FOR x=X(1)-inc TO X(N%)+inc STEPinc
4540PRINT#X%,x,FNy(x)
4550NEXT:CLOSE#X%
4560ENDPROC
```

APPENDIX B

EXPERIMENTAL DATA
FOR CHAPTER 2

Data for Calcium Oxalate.

Particle Size Data.

		Control Run:		Magnetic Run:	
Size Band		Weight in Band (%)	Cumulative Wt Below (%)	Weight in Band (%)	Cumulative Wt Below (%)
Upper	Lower				
188.0	87.2	2.1	97.9	6.4	93.6
87.2	53.5	18.4	79.5	2.4	91.3
53.5	37.6	31.8	47.8	8.9	82.3
37.6	28.1	27.1	20.6	12.1	70.2
28.1	21.5	10.7	10.0	15.1	55.1
21.5	16.7	5.2	4.7	13.6	41.5
16.7	13.0	3.4	1.3	13.2	28.3
13.0	10.1	1.0	0.3	10.4	17.8
10.1	7.9	0.2	0.1	6.0	11.8
7.9	6.2	0.1	0.0	5.2	6.6
6.2	4.8	0.0	0.0	3.7	2.8
4.8	3.8	0.0	0.0	1.9	0.9
3.8	3.0	0.0	0.0	0.8	0.1
3.0	2.4	0.0	0.0	0.1	0.0
2.4	1.9	0.0	0.0	0.0	0.0

X-Ray Diffraction Data.

Control Run:

d Spacing (nm)	I/I_o (%)
15.2	63.0
24.7	100.0
30.4	63.0
31.1	32.9
31.6	30.1
36.1	36.9
38.5	67.6
40.1	29.9
43.7	17.7
45.9	13.7
46.1	17.2
46.9	17.2

Magnetic Run:

d Spacing (nm)	I/I_o (%)
15.3	100.0
24.4	81.0
30.2	50.6
30.9	22.8
31.4	19.0
36.0	29.1
38.1	45.6
39.8	20.2
43.5	20.2
45.7	17.0
46.2	17.7
47.0	20.2

Data for Barium Sulphate.

Particle Size Data (X-Y).

Size Band		Weight in Band (%)					
Upper	Lower	0-0	0-M	M-0	M-M	0	M
188.0	87.2	0.0	1.5	0.0	0.0	0.1	5.5
87.2	53.5	0.1	1.8	0.0	0.0	0.7	2.4
53.5	37.6	0.3	1.2	0.1	0.0	1.7	0.4
37.6	28.1	2.0	1.8	1.0	0.6	13.8	2.3
28.1	21.5	11.5	2.9	5.8	8.5	17.6	8.1
21.5	16.7	28.6	3.1	10.1	20.9	15.3	15.0
16.7	13.0	29.7	3.5	18.1	25.7	14.1	22.7
13.0	10.1	7.1	5.4	29.5	23.5	11.5	12.4
10.1	7.9	1.9	9.8	14.3	4.7	9.0	5.9
7.9	6.2	10.0	14.9	4.3	2.0	5.6	7.8
6.2	4.8	8.7	16.8	3.5	8.7	3.6	11.9
4.8	3.8	0.1	16.5	8.6	5.1	3.6	3.3
3.8	3.0	0.0	11.4	4.2	0.1	1.9	0.6
3.0	2.4	0.0	5.2	0.4	0.0	0.6	0.4
2.4	1.9	0.0	2.1	0.0	0.0	0.4	0.5

Particle Size Data (X*-Y*).

Size Band		Weight in Band (%)			
Upper	Lower	0-0	0-M	M-0	M-M
188.0	87.2	2.2	1.9	1.4	4.4
87.2	53.5	5.2	0.2	1.0	2.9
53.5	37.6	8.1	0.0	1.4	0.8
37.6	28.1	16.2	0.0	7.5	1.1
28.1	21.5	17.7	0.1	13.7	1.8
21.5	16.7	14.4	0.6	16.3	4.2
16.7	13.0	11.8	2.6	16.3	10.5
13.0	10.1	8.2	5.9	13.3	15.2
10.1	7.9	5.6	13.3	11.4	18.1
7.9	6.2	3.8	20.3	6.9	16.6
6.2	4.8	2.7	17.7	3.7	11.7
4.8	3.8	2.5	13.7	3.4	7.7
3.8	3.0	1.2	8.9	2.0	3.4
3.0	2.4	0.3	4.5	0.7	1.0
2.4	1.9	0.1	2.8	0.4	0.3

Size Band		Wt in Band/%	
Upper	Lower	0	M
564.0	261.6	0.0	16.0
261.6	160.4	0.0	13.1
160.4	112.8	0.0	6.2
112.8	84.3	0.0	4.8
84.3	64.6	0.0	3.5
64.6	50.2	0.0	2.4
50.2	39.0	0.0	2.4
39.0	30.3	0.0	2.3
30.3	23.7	0.2	1.8
23.7	18.5	1.6	2.6
18.5	14.5	5.2	3.8
14.5	11.4	5.8	4.5
11.4	9.1	6.0	5.1
9.1	7.2	6.1	4.8
7.2	5.8	9.4	4.5

Particle Size Data (X-Y^*).

Size Band		Weight in Band (%)					
Upper	Lower	O-O	O-M	M-O	M-M	O	M
188.0	87.2	1.9	0.0	0.9	3.4	2.6	0.5
87.2	53.5	5.5	0.0	3.4	6.1	1.2	0.0
53.5	37.6	7.9	0.0	5.9	3.3	1.1	0.0
37.6	28.1	12.3	0.0	10.1	3.1	1.8	0.2
28.1	21.5	15.2	0.1	14.0	5.2	2.6	1.1
21.5	16.7	14.7	1.5	16.5	10.5	3.7	3.8
16.7	13.0	12.2	5.0	13.7	9.6	6.4	5.2
13.0	10.1	9.0	11.1	10.1	13.5	10.0	8.4
10.1	7.9	6.6	26.1	8.4	22.7	15.7	15.7
7.9	6.2	5.1	32.0	6.2	9.2	18.9	21.3
6.2	4.8	3.7	15.5	4.1	1.6	15.1	19.1
4.8	3.8	2.6	3.2	3.0	1.6	9.1	14.3
3.8	3.0	1.6	0.4	1.8	6.0	5.0	6.6
3.0	2.4	0.8	0.3	0.9	3.4	2.8	2.2
2.4	1.9	0.4	1.1	0.5	0.4	1.7	0.9

Particle Size Data (X^s-Y^*).

Size Band		Weight in Band (%)					
Upper	Lower	O-O	O-M	M-O	M-M	O	M
188.0	87.2	12.6	0.0	0.2	1.1	0.1	12.5
87.2	53.5	0.5	0.0	0.5	2.1	0.6	12.6
53.5	37.6	0.5	0.0	0.7	3.2	0.6	0.8
37.6	28.1	1.4	0.0	2.6	5.2	1.4	1.2
28.1	21.5	3.1	0.1	6.9	7.4	2.6	1.7
21.5	16.7	6.7	2.0	12.7	9.9	5.1	3.2
16.7	13.0	13.0	7.1	18.7	12.4	10.9	5.2
13.0	10.1	17.3	8.4	18.6	13.9	15.5	6.1
10.1	7.9	17.1	13.7	17.0	13.4	16.7	7.3
7.9	6.2	14.9	23.0	11.8	11.4	17.2	11.5
6.2	4.8	7.0	22.2	4.5	8.2	12.7	13.0
4.8	3.8	2.1	16.2	1.6	5.1	8.1	11.1
3.8	3.0	1.0	3.3	1.4	2.8	4.4	7.3
3.0	2.4	0.9	0.8	1.2	1.5	2.0	3.5
2.4	1.9	0.7	1.2	0.7	1.0	1.0	1.5

Particle Size Data (X-Y#).

Size Band		Weight in Band (%)					
Upper	Lower	O-O	O-M	M-O	M-M	O	M
188.0	87.2	0.0	0.0	0.0	0.0	0.0	0.0
87.2	53.5	0.9	0.0	0.5	0.0	0.1	5.9
53.5	37.6	4.3	3.5	3.5	3.9	3.4	13.6
37.6	28.1	21.3	22.5	12.9	19.5	26.4	14.2
28.1	21.5	19.7	4.1	16.7	9.3	25.2	14.2
21.5	16.7	3.8	2.3	7.3	4.7	5.4	7.2
16.7	13.0	7.8	6.1	8.5	9.4	8.7	10.6
13.0	10.1	15.3	9.3	12.5	11.2	10.7	8.0
10.1	7.9	9.0	11.6	11.5	10.7	4.8	6.1
7.9	6.2	8.0	13.8	10.5	11.0	4.9	7.2
6.2	4.8	6.0	11.4	7.9	8.5	5.0	5.2
4.8	3.8	1.8	7.8	4.0	5.5	2.3	3.1
3.8	3.0	0.4	4.6	1.9	3.4	1.1	2.0
3.0	2.4	0.2	1.9	0.9	1.6	0.6	1.1
2.4	1.9	0.4	0.7	0.5	0.6	0.5	0.7

X-Ray Diffraction Data.

	Literature Values		X-ray Grade		O-O*	
hkl	d (nm)	I/I_o (%)	d (nm)	I/I_o (%)	d (nm)	I/I_o (%)
200	44.4	17	44.6	26	44.6	4
011	43.4	36	43.6	33	43.7	6
			42.7	46	43.1	5
111	39.0	57	39.2	29	39.3	5
			38.5	60	38.5	19
002	35.8	31	35.4	38	35.3	10
210	34.4	100	34.0	96	34.1	46
102	33.2	67	32.8	64	33.0	32
211	31.0	97	30.7	100	30.8	48
112	28.3	53	28.0	54	28.2	16
020	27.3	47	27.4	25	27.2	20
					27.1	24
220	23.2	15	23.0	21	23.1	7
113	21.2	80	21.0	73	21.1	100
312	21.0	76	20.9	93	20.9	60

	M-M*		O-O″		M-M″	
hkl	d (nm)	I/I$_o$ (%)	d (nm)	I/I$_o$ (%)	d (nm)	I/I$_o$ (%)
200	44.4	20	45.3	18	44.8	16
011	43.7	29	44.0	58	44.0	41
	42.9	36	42.9	30	43.1	17
111	39.2	18	39.0	14	38.8	21
	38.7	36	38.7	27	37.9	16
002	35.3	36	35.6	30	35.6	19
210	34.1	93	34.3	74	34.3	100
102	32.9	44	32.9	38	33.0	42
211	30.8	100	30.9	65	30.9	72
112	28.1	38	28.2	21	28.2	19
020	27.1	53	27.5	8	27.2	40
	26.9	34	27.1	41	26.9	9
220	23.2	25	23.2	8	23.2	12
113	21.1	56	21.1	100	21.1	100
312	20.9	73	20.9	75	21.0	89

APPENDIX C

EXPERIMENTAL DATA
FOR CHAPTER 3

Data for Experiment 1.

Time (hrs:min:s)	Residual $[Ca^{2+}]$ (ppm)		Residual $[Ma^{2+}]$ (ppm)	
	Control	Magnetic	Control	Magnetic
0:00:30	22,000	19,200	14,400	13,600
0:01:00	21,800	19,800	14,400	13,700
0:05:00	21,400	19,700	14,800	13,400
0:30:00	21,900	19,200	14,500	13,700
1:00:00	22,100	19,400	14,800	13,800
5:00:00	21,600	19,900	14,700	13,400
24:00:00	22,000	19,300	14,800	13,400

Data for Experiment 2.

Time (hrs:min)	Residual $[Ca^{2+}]$ (ppm)		Residual $[Ma^{2+}]$ (ppm)	
	Control	Magnetic	Control	Magnetic
0:05	21,400	19,800	14,300	13,600
0:30	21,700	20,100	14,700	13,200
1:00	22,100	19,500	14,500	13,600
5:00	22,000	19,800	14,800	13,200
24:00	21,300	20,100	14,800	13,300

Data for Experiment 3.

Vol. of PO_4 Added /ml	Residual $[Ca^{2+}]$ (ppm)		Residual $[Ma^{2+}]$ (ppm)	
	Control	Magnetic	Control	Magnetic
100	728	644	970	840
50	1839	832	1490	940
25	2840	2456	1770	1595

Data for Experiment 4.

Replicate Run Nº	Residual $[Ca^{2+}]$ (ppm)				Residual $[Ma^{2+}]$ (ppm)			
	100%	75%	50%	25%	100%	75%	50%	25%
1	70	163	392	641	446	513	554	589
2	59	153	389	641	438	512	557	592
3	62	164	397	643	445	508	557	587
4	67	158	397	648	440	512	560	592

Data for Experiment 5.

Time (hrs:mins)	Residual $[Ca^{2+}]$ (ppm)				Residual $[Ma^{2+}]$ (ppm)			
	100%	75%	50%	25%	100%	75%	50%	25%
Control	65	159	387	643	444	510	557	589
0:01	61	153	382	645	437	497	547	585
0:10	64	157	396	645	428	480	553	577
0:32	51	151	391	626	419	491	533	574
1:00	40	139	380	620	421	496	533	577
2:00	46	133	360	636	434	506	537	580
3:00	47	134	371	638	431	504	542	576
5:00	55	148	380	645	443	508	554	585
8:00	62	154	380	647	446	512	561	587
18:00	64	154	383	643	442	512	561	588

Data for Experiment 6.

Flow Rate (l/hour)	Residual $[Ca^{2+}]$ (ppm)				Residual $[Ma^{2+}]$ (ppm)			
	100%	75%	50%	25%	100%	75%	50%	25%
Control	86	161	372	605	375	423	476	521
0.1	85	158	361	605	371	420	472	518
0.2	86	157	367	596	372	418	456	517
0.3	57	151	366	589	359	411	460	511
0.5	62	149	351	587	354	412	447	507
1.0	62	149	348	581	350	407	451	509
1.5	54	134	342	585	358	407	448	505
2.0	62	138	346	586	354	411	445	508
2.5	56	137	343	582	355	413	449	503
3.0	64	137	350	581	352	408	450	509

Data for Experiment 7.

Flow Rate (1/hour)	Residual $[Ca^{2+}]$ (ppm)				Residual $[Ma^{2+}]$ (ppm)			
	100%	75%	50%	25%	100%	75%	50%	25%
Control	82	166	372	600	373	425	474	523
0.1	83	161	373	602	373	421	473	526
0.2	81	163	377	600	371	423	472	525
0.3	85	157	366	598	375	420	474	519
0.5	75	157	370	587	368	416	465	523
1.0	64	148	346	593	366	412	466	517
1.5	56	136	350	585	361	412	464	513
2.0	60	142	347	584	362	412	462	508
2.5	64	138	341	582	359	411	465	511
3.0	62	134	345	585	359	413	461	514

Data for Experiment 8.

Flow Rate (1/hour)	Residual $[Ca^{2+}]$ (ppm)				Residual $[Ma^{2+}]$ (ppm)			
	100%	75%	50%	25%	100%	75%	50%	25%
Control	90	162	375	601	375	425	477	522
0.1	87	161	373	603	373	423	475	518
0.2	88	158	371	600	370	423	476	517
0.3	55	146	353	587	349	410	473	503
0.5	52	134	347	582	351	407	465	507
1.0	56	136	343	582	346	410	460	508
1.5	54	132	348	580	347	410	461	504
2.0	56	129	345	577	345	408	464	506
2.5	56	133	343	581	346	410	459	507
3.0	52	133	343	579	344	407	460	506

Data for Experiment 9.

Flow Rate (1/hour)	Residual $[Ca^{2+}]$ (ppm)				Residual $[Ma^{2+}]$ (ppm)			
	100%	75%	50%	25%	100%	75%	50%	25%
Control	83	167	377	595	377	421	472	524
0.1	87	169	372	598	378	420	474	526
0.2	82	166	376	595	374	422	471	525
0.3	83	163	377	595	375	419	474	523
0.5	77	156	371	575	360	411	462	504
1.0	55	143	350	577	359	412	460	509
1.5	51	136	343	577	357	410	462	505
2.0	51	133	341	574	359	409	458	508
2.5	54	137	340	572	357	411	460	511
3.0	52	133	340	575	359	411	461	509

Data for Experiment 10.

Field (gauss)	Residual [Ca^{2+}] (ppm)				Residual [Ma^{2+}] (ppm)			
	100%	75%	50%	25%	100%	75%	50%	25%
Control	72	164	402	645	439	505	550	586
52	71	159	402	642	440	508	550	585
114	75	159	399	643	434	508	553	581
207	66	166	397	643	435	498	548	578
340	54	144	391	641	427	488	541	570
485	47	133	391	626	422	490	534	573
727	36	132	381	620	419	492	533	570
951	42	136	387	617	419	492	536	573
1278	40	136	383	626	420	488	533	573
1484	40	129	378	616	419	489	533	569
1993	35	129	380	620	423	492	531	571
2515	41	127	375	616	419	491	534	573

APPENDIX D

EXPERIMENTAL DATA
FOR CHAPTER 4

Data for Experiments 6 and 7.

Time (Hours)	Experiment 6 - Weight (g)		Experiment 7 - Weight (g)	
	Control Run	Magnetic Run	Control Run	Magnetic Run
0	146.0126	145.8574	145.9826	145.9903
18	145.4174	145.2386	145.3456	145.2956
42	144.7687	144.4404	144.6569	144.5595
66	143.9870	143.5970	143.8363	143.6528
90	143.3254	142.7846	143.1416	142.8950
162	141.3696	140.7822	141.0893	140.6538
330	136.7128	135.7258	136.4295	135.5549

Data for Experiments 8 and 9.

Time (Hours)	Experiment 8 - Weight (g)		Experiment 9 - Weight (g)	
	Control Run	Magnetic Run	Control Run	Magnetic Run
0	40.9655	41.0506	41.0297	41.0441
18	40.8234	40.9041	40.8849	40.8889
42	40.6691	40.7093	40.7328	40.6937
66	40.4860	40.5234	40.5455	40.4804
90	40.3300	40.3402	40.3590	40.2894
162	39.8712	39.7951	39.9336	39.7720
330	38.8304	38.5484	38.8953	38.4197

Data for Experiments 10 and 11.

Time (Hours)	Experiment 10 - Weight (g)		Experiment 11 - Weight (g)	
	Control Run	Magnetic Run	Control Run	Magnetic Run
0	145.9502	145.5799	41.0154	40.9742
18	145.5450	145.1516	40.9151	40.8645
42	145.0320	144.5936	40.8045	40.7176
66	144.5247	144.0284	40.6747	40.5784
90	144.0217	143.4577	40.5576	40.4356
138	143.0065	142.3294	40.3220	40.1591

Data for Experiments 12 and 13.

Time (Hours)	Experiment 12 - Weight (g)		Experiment 13 - Weight (g)	
	Control Run	Magnetic Run	Control Run	Magnetic Run
0	138.8304	138.8582	39.1306	39.1444
18	138.6154	138.6065	39.0581	39.0829
42	138.3081	138.2696	38.9817	38.9926
66	138.0115	137.9364	38.9174	38.9106
90	137.7127	137.6056	38.8443	38.8345
138	137.1196	136.9481	38.7048	38.6774

Data for Experiments 14 and 15.

Time (Hours)	Experiment 14 - Weight (g)		Experiment 15 - Weight (g)	
	Control Run	Magnetic Run	Control Run	Magnetic Run
0	161.7396	161.8922	35.1735	35.1686
17	161.5510	161.7046	35.0716	35.0458
39.5	161.2760	161.4004	34.9344	34.8961
72	160.9266	160.9424	34.7732	34.7189
137.5	160.1348	159.9592	34.4378	34.3473

Data for Experiment 16.

Time (Hrs)	3.2mm - Weight (g)		4.8mm - Weight (g)		6.4mm - Weight (g)	
	Control	Magnetic	Control	Magnetic	Control	Magnetic
0	15.6155	15.6170	70.4526	70.4442	82.9822	83.1304
4.5	15.5942	15.5970	70.3907	70.3825	82.9298	83.0722
21	15.5218	15.5032	70.1918	70.0631	82.7531	82.7664
46.5	15.4100	15.3692	69.8424	69.6552	82.4326	82.3718
72	15.2926	15.2358	69.5050	69.2018	82.1340	81.9482

Data for Experiments 17-23.

Time /hrs	Weight (grams) for Experiment No.						
	17	18	19	20	21	22	23
0	68.3284	68.3897	68.3432	68.3539	68.4246	68.3539	68.4032
24	68.0668	68.0896	68.0436	68.0561	68.1550	68.0561	68.1405
48	67.7969	67.7953	67.7468	67.7554	67.8876	67.7554	67.7997
72	67.5261	67.5018	67.4515	67.4569	67.6194	67.4569	67.5011
96	67.2660	67.2025	67.1488	67.1626	67.3427	67.1626	67.2015
168	66.4620	66.3233	66.2567	66.2683	66.5314	66.2683	66.2951

Data for Experiment 24.

T	Weight (grams) for Channel No.							
hrs	1	2	3	4	5	6	7	8
0	10.4554	10.4494	10.4450	10.4431	10.4734	10.4654	10.4457	10.4474
22	10.4229	10.4284	10.4182	10.4115	10.4346	10.4405	10.4156	10.4165
32	10.3986	10.4061	10.4015	10.4010	10.4200	10.4269	10.4046	10.4064
44	10.3816	10.3945	10.3816	10.3770	10.4008	10.4134	10.3874	10.3890
70	10.3485	10.3547	10.3494	10.3387	10.3659	10.3730	10.3542	10.3550
94	10.3174	10.3256	10.3166	10.3087	10.3266	10.3436	10.3176	10.3257

Data for Experiment 25.

T	Weight (grams) for Channel No.							
hrs	1	2	3	4	5	6	7	8
0	10.4384	10.4765	10.4437	10.4595	10.4777	10.4590	10.4382	10.4473
16	10.4147	10.4501	10.4175	10.4325	10.4560	10.4314	10.4145	10.4193
40	10.3833	10.4134	10.3784	10.3895	10.4176	10.3893	10.3754	10.3804
64	10.3494	10.3635	10.3321	10.3484	10.3838	10.3481	10.3394	10.3330
88	10.3026	10.3314	10.2992	10.3124	10.3486	10.3133	10.2867	10.2927

Data for Experiment 26.

T	Weight (grams) for Channel No.							
hrs	1	2	3	4	5	6	7	8
0	10.4546	10.4465	10.4375	10.4345	10.4471	10.4669	10.4408	10.4533
16	10.4357	10.4216	10.4196	10.4147	10.4245	10.4350	10.4208	10.4334
40	10.3904	10.3935	10.3856	10.3896	10.3901	10.4040	10.3882	10.3860
64	10.3540	10.3619	10.3638	10.3516	10.3485	10.3599	10.3551	10.3451
88	10.3153	10.3191	10.3278	10.3224	10.3133	10.3213	10.3274	10.3037

Data for Experiment 27.

T	Weight (grams) for Channel No.							
hrs	1	2	3	4	5	6	7	8
0	10.4784	10.5108	10.4624	10.4071	10.4375	10.3973	10.4497	10.3934
18	10.4451	10.4825	10.4172	10.3831	10.4052	10.3627	10.4161	10.3570
42	10.4075	10.4320	10.3647	10.3338	10.3568	10.3157	10.3678	10.3187
66	10.3763	10.3914	10.3055	10.2882	10.3167	10.2830	10.3276	10.2839
90	10.3328	10.3457	10.2464	10.2446	10.2646	10.2401	10.2825	10.2399
152	10.2283	10.2240	10.1034	10.1405	10.1562	10.1246	10.1606	10.1356

APPENDIX E

EXPERIMENTAL DATA FOR CHAPTER 5

Data for Experiment 1.

$z = 17.1$ ml, $v = 0.5$ ml.

$\ln \frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:									
	1	2	3	4	5	6	7	8	9	10
0.0	0	0	0	0	0	0	0	0	0	0
0.02968	25	27	27	27	27	28	27	27	27	27
0.06026	50	52	53	52	52	52	52	51	51	52
0.09181	76	77	79	77	78	78	78	78	77	78
0.12438	104	102	106	104	105	105	105	104	103	105
0.15806	131	130	133	132	134	133	133	133	130	133
0.19290	161	158	162	161	162	162	162	161	159	162
0.22901	191	188	192	190	193	192	192	192	188	193
0.26647	223	219	224	221	225	224	223	224	219	224
0.30538	257	250	257	254	257	257	256	257	252	256
0.34587	291	285	292	288	292	292	291	292	286	292
0.38807	328	320	328	323	330	328	327	328	321	328
0.43213	366	359	366	360	369	367	363	368	359	368
Con/Mag	C	M	C	M	C	C	C	C	M	C

$\ln \frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:									
	11	12	13	14	15	16	17	18	19	20
0.0	0	0	0	0	0	0	0	0	0	0
0.02968	25	27	27	27	27	28	27	27	28	27
0.06026	53	51	51	51	51	53	51	52	52	51
0.09181	78	77	77	77	77	78	77	77	77	77
0.12438	105	102	103	102	104	104	102	102	104	103
0.15806	133	129	130	130	129	132	130	130	134	131
0.19290	162	159	159	158	158	160	158	158	162	159
0.22901	193	187	188	188	187	190	187	188	192	188
0.26647	224	220	220	218	218	223	219	220	223	220
0.30538	257	250	252	250	250	256	251	252	257	251
0.34587	292	284	286	284	284	292	285	286	291	284
0.38807	327	321	322	319	320	326	319	320	329	321
0.43213	368	358	360	357	358	367	358	359	369	358
Con/Mag	C	M	M	M	M	C	M	M	C	M

Data for Experiment 2.

z = 21.7 ml, v = 0.5 ml.

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:							
	1	2	3	4	5	6	7	8
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.02331	36.69	36.72	35.52	34.52	27.72	24.97	17.99	18.28
0.04718	74.24	69.88	68.84	66.80	51.49	50.37	36.42	36.98
0.07163	110.19	105.19	103.01	99.71	76.79	76.57	56.77	57.31
0.09669	151.05	141.82	138.37	133.54	103.74	104.51	74.64	75.80
0.12240	191.15	180.00	175.16	169.10	129.59	132.34	94.49	95.96
0.14879	228.31	218.02	213.91	205.38	157.74	160.46	115.29	116.83
0.17589	274.76	258.19	251.52	243.71	186.20	189.72	135.79	137.90
0.20375	318.96	300.20	293.71	282.36	215.50	220.72	157.29	159.74
0.23240	359.24	342.77	336.42	322.39	246.12	250.60	179.22	181.83
0.26190	410.54	387.26	378.76	364.44	277.98	283.49	202.19	205.33
Temp/°C	9.9	10.2	10.9	11.0	14.9	15.0	19.4	19.7
Con/Mag	C	M	C	M	M	C	M	C

Data for Experiment 3.

z = 1.625 ml, v = 100 µl.

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:									
	1	2	3	4	5	6	7	8	9	10
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.06351	53.2	54.2	54.3	53.9	54.3	53.4	52.7	52.8	54.0	53.9
0.13134	110.5	111.1	111.1	110.7	111.8	110.4	108.6	109.7	109.8	109.4
0.20410	172.1	173.3	172.9	172.2	172.5	171.5	168.6	170.5	170.5	169.9
0.28257	238.1	239.7	239.6	138.8	139.3	136.8	234.1	236.0	235.6	235.4
0.36773	310.0	311.4	312.7	311.1	311.2	308.8	304.7	306.6	303.0	306.6
T(mins)	0	10	20	30	40	50	60	70	80	90

Magnetic Field on at T = 48 mins.

Data for Experiment 4.

z = 1.625 ml, v = 100 µl.

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:									
	1	2	3	4	5	6	7	8	9	10
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.06351	54.3	54.4	53.4	54.8	53.9	53.4	52.7	52.9	53.0	53.0
0.13134	110.9	111.0	111.1	111.3	110.9	110.1	109.2	109.0	109.2	109.3
0.20410	172.4	172.3	171.9	172.6	172.1	170.8	169.8	169.8	170.2	170.3
0.28257	237.6	239.3	238.4	138.9	139.1	135.9	235.4	235.4	236.4	235.5
0.36773	310.9	311.3	310.6	310.9	311.0	308.0	306.9	306.7	307.5	306.6
T(mins)	0	10	20	30	40	50	60	70	80	90

Magnetic Field on at T = 48 mins.

Data for Experiment 5.

z = 1.690 ml, v = 100 μl.

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:									
	1	2	3	4	5	6	7	8	9	10
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.06100	52.8	51.3	50.9	51.0	52.4	52.2	51.3	51.1	51.3	50.2
0.12595	107.1	105.0	106.1	105.3	107.7	105.8	105.0	105.0	104.6	104.3
0.19543	165.6	163.5	165.2	163.7	166.0	163.5	162.9	162.8	162.7	162.2
0.27009	228.0	227.0	228.1	127.1	128.9	126.5	225.4	225.3	225.8	224.9
0.35078	296.7	295.2	297.3	296.0	297.9	294.8	292.4	292.4	294.1	292.3
T(mins)	0	10	20	30	40	50	60	70	80	90

Magnetic Field on at T = 48 mins.

Data for Experiment 6.

z = 1.750 ml, v = 100 μl.

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:							
	1	2	3	4	5	6	7	8
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.05884	49.34	49.30	49.82	48.21	48.27	48.56	48.77	48.68
0.12136	101.80	101.29	102.17	99.28	99.76	99.79	100.02	100.21
0.18805	158.14	157.64	158.24	155.00	155.05	154.97	156.07	155.53
0.25951	219.50	218.37	219.28	215.58	214.38	214.77	216.29	216.88
0.33647	286.12	284.58	286.22	280.69	278.75	280.29	282.91	282.07
T(mins)	0	10	20	30	37	44	51	60

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:							
	9	10	11	12	13	14	15	16
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.05884	48.53	48.77	49.54	49.90	49.60	49.71	49.54	49.76
0.12136	100.22	100.15	102.19	102.91	102.05	102.53	102.11	102.96
0.18805	156.40	156.78	156.35	157.73	158.00	157.82	157.93	158.43
0.25951	216.79	217.01	218.51	220.07	218.64	219.24	220.00	220.53
0.33647	283.06	282.29	283.31	285.33	284.63	284.26	286.58	286.21
T(mins)	70	80	90	100	110	120	130	140

Magnetic Field on at T = 25mins and off at T = 29mins.

Data for Experiment 7.

z = 1.725 ml, v = 100 µl.

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:							
	1	2	3	4	5	6	7	8
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.05972	50.58	50.69	49.39	48.57	48.11	47.70	48.22	49.10
0.12323	104.71	103.92	103.90	103.07	100.27	100.57	100.94	101.79
0.19106	161.28	161.30	162.10	160.09	155.90	156.25	156.66	158.33
0.26382	223.43	223.18	224.22	221.80	215.88	216.13	216.88	219.38
0.34229	291.39	290.53	291.34	288.52	280.82	282.23	282.58	285.37
T(mins)	0	10	20	30	37	44	51	60

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:							
	9	10	11	12	13	14	15	16
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.05972	49.69	49.44	50.15	49.55	49.23	50.79	50.13	50.22
0.12323	102.45	102.39	103.46	102.89	102.90	104.53	103.82	104.59
0.19106	159.18	159.19	161.10	159.72	159.82	161.90	161.13	161.59
0.26382	220.62	220.62	222.37	221.53	222.13	224.18	224.18	224.06
0.34229	287.40	287.07	288.93	288.49	288.86	291.61	290.83	292.06
T(mins)	70	80	90	100	110	120	130	140

Solution Passed Through Magnetic Field at T = 29mins.

Data for Experiment 8.

z = 1.700 ml, v = 150 µl.

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:								
	1	2	3	4	5	6	7	8	9
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.09237	75.6	75.2	75.3	75.1	75.0	75.6	74.2	75.5	75.6
0.19416	160.0	159.8	159.6	158.7	158.5	159.3	158.1	159.6	160.2
0.30748	256.5	257.0	255.8	254.7	252.5	255.8	254.1	255.8	257.3
Field (gauss)	0	0	995	2510	2985	495	1515	1990	0

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:								
	10	11	12	13	14	15	16	17	18
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.09237	75.8	75.5	75.5	75.0	74.5	75.2	75.8	74.8	75.2
0.19416	160.4	159.7	159.8	158.9	158.1	158.8	160.5	158.4	159.8
0.30748	256.3	255.6	255.2	255.2	253.4	254.3	257.0	253.8	254.3
Field (gauss)	1515	2985	3520	495	3520	2510	0	995	1990

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:								
	19	20	21	22	23	24	25	26	27
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.09237	75.3	75.8	75.0	76.3	74.3	75.6	75.4	75.4	74.8
0.19416	158.3	160.3	159.5	160.4	158.3	159.2	159.4	158.8	159.3
0.30748	254.5	255.5	256.9	256.8	254.2	254.7	255.0	254.3	256.0
Field (gauss)	2985	495	0	1515	995	3520	2510	1990	0

Data for Experiment 9.

$z = 1.600$ ml, $v = 100$ µl.

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:							
	1	2	3	4	5	6	7	8
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.06454	54.70	54.52	51.99	54.14	54.21	53.35	54.66	54.06
0.13353	113.29	112.04	109.10	112.07	112.09	109.56	111.96	110.50
0.20764	175.26	173.79	170.69	173.63	174.97	170.15	173.19	171.86
Field (gauss)	0	1505	3015	510	0	2000	1010	2490

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:							
	9	10	11	12	13	14	15	16
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.06454	51.62	53.59	54.82	52.34	54.45	53.45	53.93	55.13
0.13353	108.26	110.38	113.08	108.99	111.60	111.31	111.05	113.20
0.20764	169.05	171.91	175.10	169.34	173.76	173.12	172.59	175.77
Field (gauss)	3015	1505	0	2490	2000	510	1010	0

Data for Experiment 10.

$z = 1.650$ ml, $v = 100$ µl.

ln $\frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:							
	1	2	3	4	5	6	7	8
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.06252	52.95	52.23	53.37	52.89	52.44	52.42	52.64	52.11
0.12921	109.79	108.53	110.08	109.27	108.45	108.08	109.03	108.01
0.20067	170.78	169.07	171.43	170.83	168.39	168.21	169.80	168.36
Field (gauss)	0	290	150	105	340	445	0	340

$\ln \frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:							
	9	10	11	12	13	14	15	16
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.06252	53.45	53.83	52.50	51.48	51.59	52.57	52.93	52.61
0.12921	110.16	110.78	107.96	107.00	107.68	108.98	109.94	108.75
0.20067	171.40	171.53	169.07	167.31	167.56	169.66	171.55	169.91
Field (gauss)	195	240	55	395	505	105	195	0

$\ln \frac{z}{z-nv}$	Time of Colour Change (seconds) for Run Number:							
	17	18	19	20	21	22	23	24
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.06252	52.00	53.40	53.04	51.55	51.37	53.00	52.03	53.33
0.12921	107.91	109.55	110.26	106.66	107.03	110.21	107.62	109.96
0.20067	168.65	170.31	171.08	166.49	167.00	171.22	167.80	170.81
Field (gauss)	290	240	55	505	495	150	395	0