The nature of precipitated gypsum in a soil irrigated with gypsiferous water

by

Lindi Grobler

Dissertation presented in partial fulfilment
of the requirements for the degree of
MASTER OF SCIENCE
(Soil Science)

in the

Department of Plant Production and Soil Science
Faculty of Natural and Agricultural Sciences of the
University of Pretoria

January 2002

Supervisor: Prof A.S Claassens
Co-supervisor: Prof J.G. Annandale

ACKNOWLEDGEMENTS

The author would like to thank the following people for their contribution and assistance with this study:

My study leaders, Prof. Claassens and Prof. Annandale, for their advice, guidance and great patience,

The project sponsors: COM, DTI, UP, WRC, FRD, Amcoal and Kleinkopjé Colliery for making it possible to carry out this study,

Mias Pretorius for his help and patience in installing the glasshouse evaporation system under very unpleasant temperatures,

Dr. Christel Bühmann, from the Institute for Soil, Climate and Water, for her expert advice,

Mr. Chris van der Merwe, Andrè Botha and Allan Hall from the Department of Electron Microscopy at the University of Pretoria for their help in the sample preparations and interpretation of results,

My father, mother and brother for their continuos support and prayer,

My best friend and husband, Samuel Jacobs, for his encouragement, perspective and motivation and last but not least,

My Lord and Saviour for giving me the ability of mind and strength of character to persevere in the face of adversity.

SUMMARY

The Kleinkopjė Opencast coal mine near Witbank, in the Mpumalanga province has large volumes of gypsiferous water stored in the Jacuzzi and Tweefontein Pans. Utilising this mine water for irrigation may be a cost-effective way of solving several environmental problems, while at the same time increasing food production and generating revenue for the users and mines. The long and short term implications of using this mine water for irrigation needed to be researched to ensure the sustainable use of the soil.

This study had several purposes.

1. Developing a method of accelerating gypsum precipitation under controlled conditions.
2. Analysing the amount of precipitated gypsum in the soil.
3. Studying the nature of gypsum, once precipitated in the soil.
4. Assessing what effect such precipitation will have on the soil over a period of time.

A method by which the process of precipitation is accelerated, would allow researchers to study and analyse the changes and nature of certain physical soil properties caused by the precipitation of any compound over a period of time.

Soil columns were constructed by using PVC pipes that were filled with soil. These columns were watered and air flow was used to increase the drying rate of the soil after watering. This system with watering and drying cycles, optimised water evaporation from the soil to maximise gypsum precipitation. The in situ precipitation of gypsum took place much faster than would be expected under field conditions and this research, therefore, provided a method for successful precipitation of any compound in a soil at an accelerated rate compared to natural systems.

After several levels of precipitation were reached, the columns were cut into sections to assess the distribution and amount of precipitated gypsum in the soil. The gypsum content was analysed by treatment with a Na-and Cl-resin method. This method entailed suspending the soil sample, resin and water together whereafter the electrical conductivity of the filtrate was measured. The relation between electrical conductivity of the filtrate (after the adsorption of Ca and SO_4 by the resin had taken place) and applied gypsum levels were used to obtain a regression curve for the specific soil used in this project. The data showed that the centre of the column contained more precipitated gypsum than the top and bottom sections. Although this was the case, the gypsum distribution confirmed the expectations that the vacuum pump had, in fact, ensured that gypsum had precipitated throughout the column.

Examining the nature of the precipitated gypsum in the soil was an important aspect of this study and several techniques were used to study gypsum's nature after precipitation.

1. The Scanning Electron Microscope was used to observe the form in which gypsum precipitated.
2. An Energy Dispersive X-ray analysis was used to confirm the elemental composition of the elongated, prismatic crystals as being gypsum.
3. Epoxy impregnated samples were prepared and viewed under a light microscope with a light diffractor system to establish where gypsum precipitation took place. Examining the position of precipitation by using a light microscope, was not successful because of the diffractive light breaking index of gypsum and the soil being very similar.
4. A Mercury Porosimeter was used to study the changes in the pore size distribution in the soil caused by gypsum precipitation. The data from this study was inconclusive due to the fact that the levels of precipitated gypsum, that were analysed, were insufficient to change or clog soil pores or change pore size distribution.

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CHAPTER 1

INTRODUCTION

1.1. Background

The Highveld region in the Mpumalanga province of South Africa is known for its high potential agricultural soil. Unfortunately most of these soils are highly leached, acidic and continue to acidify as a result of cropping practises, fertilisation and acid rain. These conditions, coupled with low and unreliable rainfall conditions (66% of South Africa is classified as semi-arid to arid), often result in crop failure (Annandale, Jovanovic, Benadė & Tanner, 1999).

The mining industry is one of the country's most important contributors to national product and is widely scattered over a large portion of high potential arable land. The mines have one problem in common. There are huge volumes of contaminated water that are threatening the capacity of holding dams and are costing large sums of money in management and treatment.

South African coal formations always contain some pyrite that constitute a source of acidity. During the coal mining process these pyrite containing formations are exposed to oxygen, water and *Thiobacillus ferroxidans* bacteria that oxidise iron pyrite to sulphuric acid and iron sulphate (Van der Merwe, 1996; Annandale *et al*, 1999; Thompson, 1980). This leads to the production of acidic water (referred to as acid mine water). Simple discharging of this water into river systems is prohibited because of the resulting hazardous environmental impact.

There are several options available to the mines in regard to the usage, purification and dispensing of the water, but they are unfortunately very costly to implement. Utilising mine water for irrigation may be a cost-effective practise for solving several problems. Succeeding in using acid mine water for irrigation, will provide much needed water to the arid Mpumalanga province. This practise will increase food and animal feed production whilst also generating revenue for the users and mines.

It is, however, imperative that the long and short term implications of using this mine water for irrigation be considered. Research into this practice is therefore important, before full implementation of a program by which mine water is used to irrigate crops, on all mines with comparative problems. Careful research will also ensure the sustainable use of the soil for continuous crop production for future generations (Annandale *et al*, 1999).

1.2. Problem statement

The Kleinkopjé Opencast coal mine near Witbank, in the Mpumalanga province is a mine where large volumes of gypsiferous water are being stored in two pans known as Jacuzzi and Tweefontein. Research into the sustainable use of this gypsiferous mine water for irrigation, is presently underway at the Kleinkopjé mine.

Several important questions, related to the effect that large amounts of gypsum precipitation might have on the soil, need to be addressed:

i. What will happen to the soil after 30 years of prolonged irrigation with gypsiferous water? According to Annandale, Jovanovic, Benadè & Tanner (1999), an estimated 404 ton ha^{-1} gypsum will precipitate in the soil over this period.

ii. How will this affect the physical and chemical properties of the soil, in the short and long term? What form will the precipitation of gypsum take on, in the soil? This precipitation can be one or a combination of the following possibilities.
    - Gypsum will precipitate within pore spaces and subsequently clog these pore spaces.
    - Gypsum will precipitate around soil aggregates and thus coat the soil aggregates.
    - Gypsum will precipitate as crystals without interference with adjacent soil particles.

iii. How will this gypsum change the soil structure? Is it possible that the soil structure might actually improve or will there be degradation?

iv. How will this affect the hydraulic properties of the soil? Might the precipitate improve the flow of water, constrict it, or will there be no impact on the flow and distribution of water throughout the soil profile?

v. What other secondary effects can be expected to occur over such a long period of time? What effects can this precipitate have on plant development and physiology, fertilisation of crops, the sorption of plant and soil nutrients and gross harvest?

Any possible degradation of the soil has to be minimised to ensure sustainable use of the soil for optimum crop production. Answers had to be found for these questions, enabling the gypsiferous mine water irrigation plan to be implemented at other mines and sites.

It was, therefore, necessary to simulate the precipitation process under controlled conditions. This would provide the means for studying the physical and chemical property changes in the soil. A method to enhance and accelerate the process of precipitation in a glasshouse trial, had to be found and the form of precipitate had to be investigated.

1.3. Objectives of the research

The objectives of this study were fourfold.

1. Developing a method of accelerating gypsum precipitation, under controlled conditions in a glasshouse.
2. Analysing the amount of precipitated gypsum in the soil.
3. Studying the nature of gypsum, once precipitated in the soil.
4. Assessing what effect such precipitation will have on the soil over a period of time.

CHAPTER 2

LITERATURE REVIEW

2.1. The nature of gypsum in soils

Gypsum is a relatively common mineral found in agricultural soils. Gypsum ($CaSO_4{\cdot}2H_2O$) and its dehydrated products hemi-hydrate ("Plaster of Paris", $CaSO_4{\cdot}\frac{1}{2}H_2O$) and anhydrite ($CaSO_4$) are widely distributed minerals in sedimentary and interstratified deposits such as limestone and slate. In evaporation brines, gypsum is the first mineral to precipitate when water evaporates and it is usually found beneath rock salt deposits (Hurlbut, 1971; Shainberg, Sumner, Miller, Farina, Pavan & Fey, 1989).

Both gypsum and its dehydration products are slightly soluble salts in aqueous solution, dissolving to an extent of approximately 2.5 g ℓ^{-1}. Other common Ca salts are either much less soluble ($CaCO_3$) or much more soluble {$CaCl_2$, $Ca(NO_3)_2$}.

Anhydrite ($CaSO_4$) may precipitate before gypsum at high temperatures (> 50°C). The hydrated gypsum mineral is however much more commonly found because anhydrite instantly rehydrates to gypsum when exposed to water at a lower temperature.

Hemi-hydrate ($CaSO_4{\cdot}\frac{1}{2}H_2O$) is sometimes found in gypsiferous surface soil horizons at elevated temperatures, but this is geologically very rare. In the production process of "Plaster of Paris", gypsum is ground and heated to between 190°C and 200°C to ensure the removal of approximately 75% of the crystal water (Hurlbut, 1971; Shainberg *et al*, 1989). This hemi-hydrate when mixed with water, will harden due to the formation of $CaSO_4{\cdot}2H_2O$ and can then be used for many purposes such as making casts for interior decorations and broken bones (Hurlbut, 1971).

2.2. The influence of sulphates on pH

The continuous and prolonged irrigation of agricultural crops, with gypsiferous water will cause the precipitation of gypsum ($CaSO_4{\cdot}2H_2O$), due to the high concentration of calcium and sulphate ions. The question arises as to how this continuous irrigation with gypsiferous water will influence the soil reaction. This is important, since it have an effect on sulphate absorbtion and gypsum precipitation.

Results from a wide range of trials done in the United Kingdom (Curtin & Syers, 1990) and other continents, on soils with pH (H_2O) levels (between 6 and 7) show no capacity to adsorb sulphate (Alcordo & Rechcigl, 1993). The reason for this being that as the soil pH increases, the

CEC of the soil increases and less positive charges on the solid fraction are available to adsorb sulphates. At a neutral pH, most of the SO_4^{2-} in the soil will either precipitate in the soil as gypsum or be susceptible to leaching (Curtin & Syers, 1990; Adams & Rawajfih, 1977).

Farina and Channon (1988) state that precipitated gypsum has little or no effect on pH. Inspite of the large amounts of SO_4^{2-} being adsorbed from a saturated gypsum solution, the pH of the soil solution is not affected. Alva, Sumner and Miller (1990) proposed the following explanation for this process. When gypsum is added to the soil, the pH is the net effect of the balance between the release of protons (H^+) (due to the specific adsorption of Ca^{2+}) and the release of the OH^- (due to ligand exchange of SO_4^{2+} with OH^- ions). The OH^- released (as a result of a ligand exchange reaction) is counteracted by the release of H^+ resulting from the Ca^{2+} adsorption. This may be one of the reasons why the increase in pH with SO_4^{2-} adsorption is insignificant.

Some other researchers suggested that the simultaneous adsorption of an anion and a cation by soils, result in the neutralisation of the H^+ and OH^- ions which are released during the adsorption. This process was termed apparent salt adsorption (Farina and Channon 1988; Bolan, Syers & Sumner, 1993) and this is another reason why there is no change in pH.

Consequently, pH can therefore not be used as an indication of the amount of sulphates that may have precipitated in a soil.

2.3. Gypsum and soil mineralogy

Depending on the amount of gypsum added to the soil, the chemical conditions within the soil and the elements present in the soil solution, the mineralogy of the soil might change. This could influence the stability of the mineral being formed.

The adsorption of anions in a clay system is influenced by the broken bonds on the clay mineral edges, where $Al(OH)H_2O^{2+}$ is found. The 1:1 clay mineral is able to adsorb any oxy-anions on to the positively charged sites. It seems that the dominant factor during sulphate adsorption, is pH associated with the amphotheric characteristics of clay minerals. Therefore sulphate adsorption increases as the clay system acidifies. Kamprath, Nelson & Fitts (1956) and Harward & Reisenauer (1966) found that more sulphate is adsorbed by 1:1 clay minerals than 2:1 clay minerals. This is attributed to the greater amount of anion exchange sites in the 1:1 clay minerals and the higher negative charge associated with anion repulsion of 2:1 clay minerals (Alcordo & Rechcigl, 1993; Van der Merwe, 1996).

This effect of clay mineralogy on sulphate adsorption depends on the acid saturation of the clay mineral. A hydrogen saturated clay, for instance kaolinite, is able to adsorb more sulphate than acid saturated illite and bentonite. If the same clay becomes even more acid, more sulphate adsorption can occur due to the pH dependant charge of the clay. This sulphate adsorption takes place through the process of ligand exchange on the edges of the 1:1 clay minerals (Van der Merwe, 1996).

Gypsum does not have a unique mineralogy, but literature suggests definite associations with palygorskite. Precipitated gypsum is often found in a soil as individual crystals, widely scattered among soil particles (Eswaran & Zi-Tong, 1991).

A number of sulphate minerals may occur in association with gypsum precipitation. All of these are more soluble than gypsum and consequently reflect a specific environmental condition if they are present in the soil. These more soluble minerals frequently occur as efflorescence and their stability is a function of temperature (Eswaran & Zi-Tong, 1991).

An application of gypsum to soil may result in the precipitation of either an Alunite mineral $\{KAl_3(SO_4)_2(OH)_6\}$, a Jurbanite mineral $\{Al(SO_4)(OH)_{10}\cdot 5H_2O\}$, or a Jerosite mineral $\{KFe_3(SO_4)_2(OH)_6\}$, provided there is enough Al and Fe present in the soil (Shamshudin & Ismail, 1995).

Due to the fact that gypsum does not have a unique mineralogy and that the new minerals which might form are a function of changing environmental conditions, the possibility of mineralogical changes in the soil, are unlikely.

2.4. The influence of gypsum on soil physical properties

Field experiments done by Sharma (1971) showed several changes in soil physical characteristics due to increased gypsum content.

- There was increased volumetric water content in a soil profile 15 – 30 cm, due to increased unsaturated water flow, greater root ramification, greater hydraulic gradients and availability of larger pore spaces to fill up.
- Very little breakdown in the structure of soil occurred with gypsum added, although an increased hydraulic conductivity 30 cm and deeper in the soil profile was observed. This seemed to have been caused by the fact that the surface layer was coarser in texture, had lower exchangeable Na^+ and was richer in organic material. All of these factors favoured better structure and higher flow rates.
- A definite elevation of microbial activity as well as the carbon dioxide (CO_2) flux due to improved aeration.

Large quantities of gypsum induce some soil effects such as:

- the dissolution of precipitated Al and Fe on the surfaces of the silicate clays, which are known to reduce cation exchange capacity (CEC) (Alcordo & Rechcigl, 1993) and

- leaves the soil prone to erosion and soil loss (Eswaran & Zi-Tong, 1991).

2.5. Plant responses to gypsum

Several experimental results show that gypsum has a beneficial effect on root density (Farina & Channon, 1988; Shainberg *et al*, 1989). Gypsum treatments resulted in substantial deeper penetration of roots whereas in the control plots with no gypsum, few roots penetrated beyond 0.6 m. On both a mass and length basis the quantity of the roots in the subsoil of the gypsum treatments exceeded the control (Shainberg *et al*, 1989).

Studies done by both Farina & Channon (1988) and Shainberg *et al* (1989) proved that gypsum treatments increased the Ca level in the subsoil, decreased the Al levels, promoted root density and the overall growth and yield of the plants.

Initially, the best response to gypsum applications was during the dry seasons (indicated by low yields on plots not receiving gypsum) but it was later found that the same response was also found in good rainy seasons. There is therefore a possibility that the precipitation of gypsum might improve soil structure, which may lead to the improvement of root development and nutritional uptake.

CHAPTER 3

MATERIALS AND METHODS

At the present rate of irrigation it is predicted that between 340 – 404 tons ha^{-1} calcium sulphate ($CaSO_4$) will precipitate in the soil at the Kleinkopjé mine over a period of 30 years of irrigation with gypsiferous water. Apart from calcium, there are also especially large quantities of magnesium sulphate ($MgSO_4$) present in the irrigation water (Table 1). Due to $MgSO_4$ having a higher solubility than $CaSO_4$, it is predicted by the "Soil Water Balance" model (SWB-model), that the $MgSO_4$ will not precipitate but leach out of the soil profile and only $CaSO_4{\cdot}2H_2O$ will precipitated (Annandale *et al*, 1999; Annandale, Benadè, Van der Westhuizen & Campbell, 1996). In this study, only water saturated with gypsum was used to emulate the precipitation of gypsum in soil.

Table 1: Typical Kleinkopjé colliery irrigation water analysis from two different water sources.

Sources	**pH**	**EC ($mS\ m^{-1}$)**	**Ca^{2+} ($mg\ \ell^{-1}$)**	**Mg^{2+} ($mg\ \ell^{-1}$)**	**Na^+ ($mg\ \ell^{-1}$)**	**K^+ ($mg\ \ell^{-1}$)**	**SO_4^{2-} ($mg\ \ell^{-1}$)**
Jacuzzi Site	7.28	352	196	257	46.7	13.5	1929
Tweefontein Pan	7.20	273	405.4	195.6	46.8	19	1523.7

3.1. Enhancing gypsum precipitation in soil

3.1.1. Enhancing the precipitation process

Studying the influence of precipitated gypsum in a soil under normal field irrigation would take decades. It was therefore necessary to expedite the precipitation process, to be able to study it's effect on the soil. This precipitation process was accelerated by using soil columns.

Columns were constructed from 300 mm lengths of 110 mm diameter PVC pipes. Each pipe section was fitted to a steel base with an outlet hole. The outlet was covered with shade cloth to prevent soil from falling through (Figure 1). Each column was then filled with 3 kg of soil from the irrigation site Pivot Major at the Kleinkopjé mine. The soil from this site was chosen due to the ease of accessibility and sandy texture (Table 11 in the Addendum).

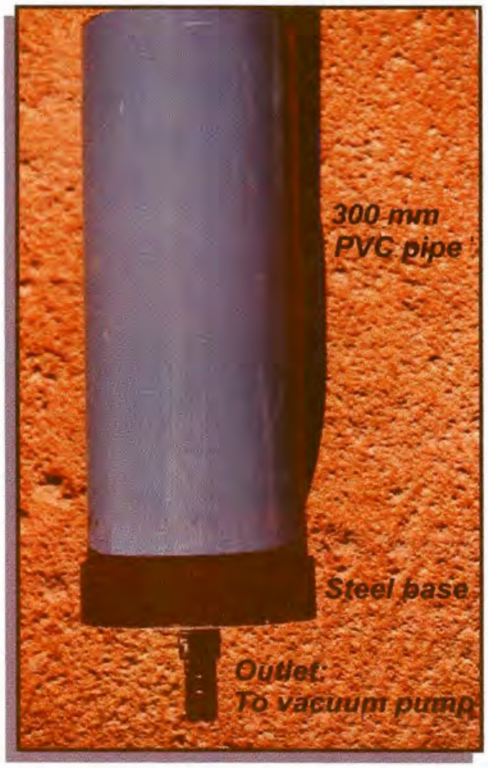

Figure 1: A soil column.

The outlet at the bottom of the columns were connected to an Ambassador vacuum pump which operated at its maximum capacity of -60 kPa. In order to prevent the pump from overheating (overheating occurs when exhaust temperature exceeds 85°C), it was connected to a timer which switched the pump on for two hours and off for one hour.

The reason for applying a vacuum was twofold.

- Firstly, it was assumed that the vacuum would enhance the evaporation rate of the gypsiferous water added to the columns, by drawing air through the column.
- Secondly, the assumption was that the vacuum would ensure that gypsum precipitated throughout the column. The reason for this being, that the air moving through the column of soil, would ensure the precipitation of the gypsum takes place in that spot where the water evaporated from.

The section of the glasshouse used for housing the columns was disconnected from the cooling system to obtain higher temperatures ensuring higher evaporation rates. Average summer temperatures varied between 38°C and 45°C during the day with night temperatures ranging from 27°C to 30°C. The winter day temperatures varied between 21°C and 29°C with night temperatures between 18°C and 20°C. The pump itself was installed in a cooled environment in an adjacent glasshouse since the surrounding temperature of the pump had to be kept below 30°C.

In order to ensure the maximum amount of gypsiferous water was added to the soil system in one day, an automated watering system was built that worked in conjunction with the timer system on the pump. The sequence worked as follows: the pump switched off for a one hour resting period. Fifteen minutes after the pump switching off, the watering system watered the columns, which took about 10 minutes. Thereafter, a 35 minute period lapsed so that an hour had passed without suction and then the pump switched on for the two hour air flow cycle. This sequence continued for 24 hours a day which meant that gypsiferous solution was added and evaporated from the soil column without supervision.

Table 2: A tabulated illustration of the vacuum pump cycles.

Time (minutes)	**Pump switch off**	**Start watering**	**End watering to allow water distribution in column**	**Pump working**
0.00	*			
0.15		*		
0.25			*	
1.00				*
1.15				*
1.25				*
1.45				*
2.00				*
2.15				*
2.25				*
2.45				*
3.00	*			
3.15		*		
3.25			*	
4.00				*
4.15				*
4.25				*
4.45				*
5.00				*
5.15				*
5.25				*
2.45				*
6.00	*			

The automated system consisted of a series of solenoid valves (Figure 2). A solenoid valve was fitted to each column to regulate the amount of water given every three hours. The amount of water applied to the soil was controlled by a Hunter irrigation computer and the gypsiferous water was supplied from a 100 ℓ reservoir containing a saturated gypsum solution (2.5 g ℓ^{-1} $CaSO_4 \cdot 2H_2O$).

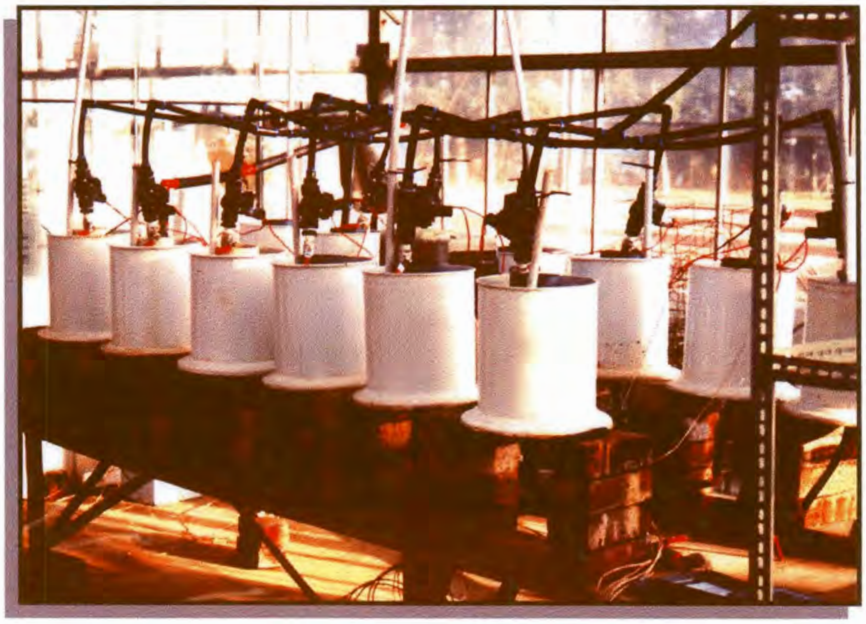

Figure 2: The automated watering system.

3.1.2. Treatments and sampling

The automated watering and evaporation system, accelerated and emulated the precipitation of gypsum that would have occurred after several years of irrigation with gypsiferous water under field conditions. Treatments consisted of five time scenarios, each of which was replicated three times (Table 3).

There would be a certain amount of precipitation per year under field conditions. It was simulated, by the SWB-model that there would be approximately 50 tons of gypsum precipitated in a 5 year period. This was used as the starting point from which the levels of precipitation were calculated.

Table 3: Time scenarios simulating field condition precipitation in the glasshouse.

Simulated time scenarios (years)	**$CaSO_4 \cdot 2H_2O$ to be precipitated (tons ha^{-1})**	**$CaSO_4 \cdot 2H_2O$ precipitated per column (kg column^{-1})**	**Gypsiferous water to be evaporated from each column (ℓ column^{-1} at 2.5 g ℓ^{-1})**
0	0	0	0
5	50	0.048	18
10	100	0.095	35
15	150	0.143	53
25	250	0.238	88

After the precipitation process for each time scenario (Table 3) was completed the columns were removed from the system. Before each section was cut, 30 to 40 mℓ of gypsiferous water was added to the soil column. This water ensured enough cohesion of the soil to prevent the loss of soil through the cutting of the sections. Each section was 40 mm in height (Figure 3) and cut by using a hack saw.

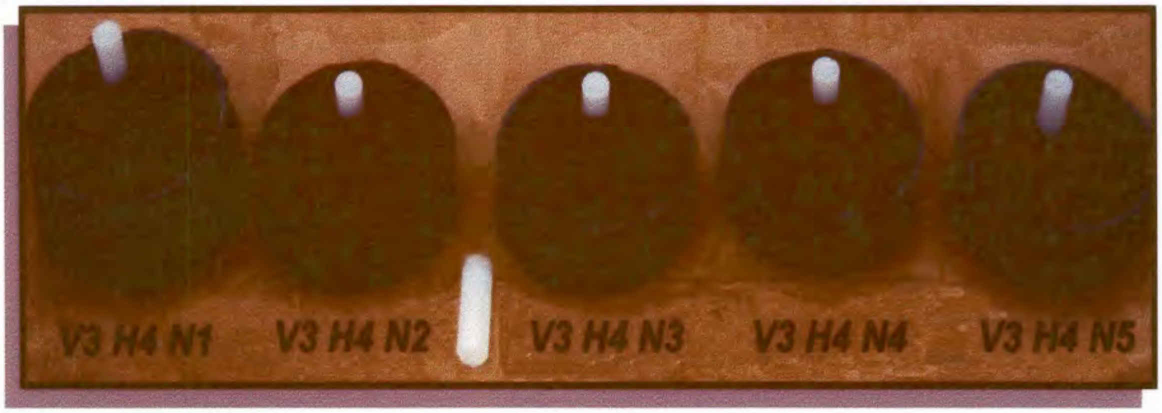

Figure 3: Soil column sections indicating sampling from each section.

The columns were numbered as follows (Figure 3):

- V, indicated the level at which gypsum was precipitated in the soil. The control was therefore V0 and the first level of 50 ton ha^{-1} precipitation was V1.
- Each level had replications indicated by H. There were between 2 and 5 replications for each level of precipitation written as H3 for replication 3.

- After the columns were sawn into sections, the section slices was numbered from N1 to N5. The sections were numbered from the bottom of the column. Thus, the steel base section was always numbered N1.

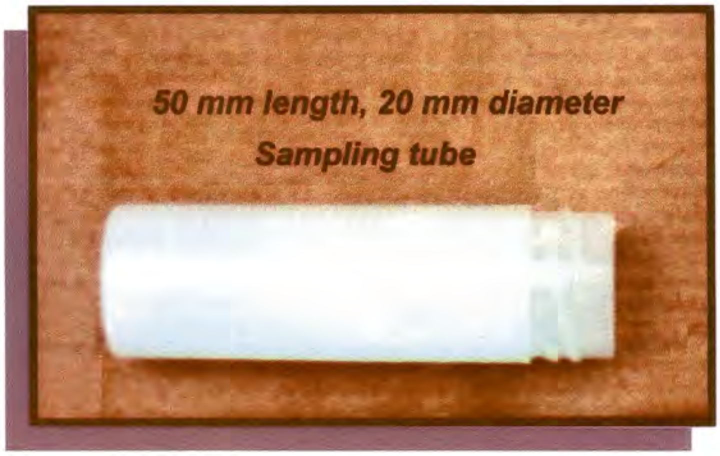

Figure 4: Polypropylene tube for sampling the soil.

Soil samples were taken from each section with a small polypropylene tube which was 50 mm in length and 20 mm in diameter (Figures 3 and 4). The columns were cut in this way to be able to assess whether the gypsum did in fact precipitate throughout the whole length of the column.

3.1.3. Vacuum pump efficiency and evaporation rate

Ensuring that the vacuum pump worked to optimise evaporation and maximise gypsum precipitation, the pump's efficiency had to be established.

To determine the optimum evaporation of water, two columns were saturated and left to drain freely for 24 hours. These two columns were weighed before the vacuum was applied and the water draining from the outlet hole was collected into an Erlenmeyer flask. In the first two hours the amount of water drained and the mass of the columns were measured every half an hour and as this water lessened, the columns were measured and weighed hourly. The resultant evaporation data (Table 4 & 5) are illustrated in Figure 6.

This data allowed the determination of the evaporation rate as well as the maximum amount of water that could to be added to each column over a certain time.

3.2. Analysing the amount of precipitated gypsum in soil

The extraction method of Frenkel, Gerstl & Van de Veen (1986) was used to determine the amount of gypsum precipitated in each column section. According to this method, Na-and Cl-resins are used to selectively adsorb calcium and sulphate precipitated as gypsum in soil.

$$Ca^{2+} + 2Na\ (resin) \rightarrow Ca\ (resin) + 2Na^{+}$$

$$SO_4^{2+} + 2Cl\ (resin) \rightarrow SO_4\ (resin) + 2Cl^{-}$$

Frenkel *et al* (1986) concluded from their findings that the amount of resin added to a certain amount of soil depends on an estimate of how much gypsum is suspected to be present in the soil. This optimal ratio in $mmol_c$ Na-resin to $mmol_c$ $CaSO_4$ is approximately 2. Sustaining this ratio ensures that no Ca will be present in the equilibrium solution.

A range of 1 g soil samples were prepared to which increasing amounts of gypsum were added (0.1 to 0.9 g $CaSO_4 \cdot 2H_2O$ per 1 g of soil). After applying the mixture of Na-and Cl-resins to the soil samples, 30 mℓ of water was added and shaken for two days to complete the exchange reactions. The samples were then centrifuged at 5000 rpm for 15 minutes, to separate the soil and resin from the suspension. The electrical conductivity of the solution was determined.

The EC of the solution increased depending on how much Na and Cl was released by the resin. This release of Na and Cl was due to the exchange with Ca and SO_4 precipitated at the beginning of the experiment.

The relation between electrical conductivity of the soution (Table 6) (after the resin adsorption of Ca and SO_4 has taken place) and gypsum levels created were used to obtain a regression curve (Figure 7) for the specific soil used in this project. The existing regression curve was derived for a specific soil used in the experiments of Frenkel *et al* (1986). Using the regression curve and the regression analysis determined for the soil from Pivot Major, the amount of precipitated gypsum in the soil samples was determined.

3.3. Examining the presence and nature of precipitated gypsum in soil

Examining the nature of the precipitated gypsum in the soil was the most important aspect of this study. This would include examining what the precipitated gypsum looked like, evaluating whether the precipitate was in fact gypsum, establishing where the majority of precipitation was and assessing whether the precipitated gypsum had any effect on the soil.

3.3.1. Scanning electron microscope (SEM) study

The Scanning Electron Microscope (SEM) is an electron optical instrument and as the name suggests, the SEM utilises a focused beam of high energy electrons that systematically scan across the surface of a specimen. This interaction of the beam with the specimen produces a large number of signals near the specimen surface. These interactions include lower energy electrons (secondary electrons) and the low energy of the secondary electrons, induces a signal that is convenient to collect for the SEM. The electron signal is eventually converted to an electronic signal which is portrayed on a television screen. (Chapman, 1986; Howard, Johnson & McMichael, 1980).

Work with the scanning electron microscope is generally regarded as the lower form of electron microscopy due to the fact that the SEM cannot quantify or chemically analyse constituents of any visual observation. The SEM can, therefore, only be used for surface observations, which means that this method cannot indicate whether there was clogging of pore spaces in a sample.

A small sample of air dried soil (all approximately the same size of about 0.5 mm by 0.5 mm) was mounted on an aluminium stub with glue. These samples were coated with five thin layers of gold (each layer being approximately 500 Armstrong (Å) (50 nm)) in a -60 kPa vacuum. An electron beam striking a specimen surface requires a conducting path in order to remove any electron charge that results. Conducting materials do not produce problems, but non conducting material need a conducting coating applied to the surface to enable viewing of the sample.

There are thus two reasons why a specimen needs to be coated prior to analysis. Firstly, because non conducting specimens build up a surface charge through which secondary electron information is unable to penetrate, therefore the image viewed may be distorted both in signal level and image form. Secondly, in order to provide a surface layer that produces a higher secondary electron yield than the specimen material (Chapman, 1986).

Subsequently, the JOEL 840 Scanning Electron Microscope (JOEL Ltd – Tokyo, Japan) was used for viewing the crystal precipitation in a sample.

3.3.2. Energy Dispersive X-ray analysis (EDX) study

X-ray analysis is widely referred to as a form of analytical electron microscopy (Postek, Howard, Johnson & McMichael, 1980). The LSM 5800 LV is one such instrument that does an Energy Dispersive analysis via X-ray's (EDX) (Voyger Version 2.0 Noran instruments – Madison, Wisconson). The analytical electron microscopy is accomplished by the coupling an x-ray analysis device with the SEM. Through the process of analysis the interaction of electron beams with a specimen in the SEM produces many signals, including x-rays. Some of the x-rays that are produced in this manner, have wavelengths and energies that are characteristic of elements in a specimen (Chapman, 1986). This results in samples being analysed for elemental composition in a certain area (Postek, Howard, Johnson & McMichael, 1980).

Where crystals were found in a sample, it was necessary to determine whether or not these crystals were in fact precipitated gypsum. Therefore the EDX was used for an elemental analysis.

To have an EDX analysis done, a sample approximately 0.5 mm by 0.5 mm was dried, mounted on an aluminium stub and coated eight to ten times with carbon (each layer being approximately 300 – 400 Å (30 – 40 nm)) at a vacuum of -60 kPa.

3.3.3. Light microscopy and light diffraction study

A light microscope with light diffractor system was subsequently used to establish where the gypsum precipitation took place. This would be important due to the fact that if the precipitation was on the outside of the soil particles, present not only as crystals, it would have the ability to clog the soil pores by coating the soil particles.

Dried soil, from the soil column sections was sampled in polypropylene tubes, 50 mm in length and 20 mm in diameter (Figure 4). Two tubes were were put into each of three 250 mℓ beakers and Embed-813, Embed-812, London-dry White epoxy's (Kushida, 1959; Van der Merwe & Coetzee, 1992) were prepared. The three epoxy's were poured into the three seperate beakers, with the samples, to allow the epoxy to infiltrate from the bottom to the top of the tube. A vacuum of -60 kPa was applied to enhance the infiltration of the epoxy. Allowing the infiltration of the epoxy from the bottom to the top prevents air bubbles from being trapped in the sample. The impregnated samples were placed in an oven at 60°C for 36 hours to complete the polymerisation process.

After the polymerisation process was completed the impregnated samples were removed from the tubes and cut up into 2 mm discs with a rotating blade. Sanding of the sample was done by hand, starting with a coarse paper (200 grit) and working through to a finer grain of 600 grit of approximately 10 - 12 µm thickness.

The thin sections were then viewed under the light microscope with a diffractor system. The light diffractor gave an image of colours (equivalent to the light breaking index of the sample composition) under the light microscope, by which it might be possible to distinguish between soil, epoxy and precipitated gypsum. It might then be possible to see whether the soil pores were blocked by the precipitated gypsum.

3.3.4. Mercury porosimetry

The Pascal 140 and 240 Mercury Porosimeter (Fisons instruments – Milan, Italy) is an instrument which is used to quantify the porous nature of solid material. The instrument provides information about the pore volume, pore size distribution and bulk density for most porous solids regardless of their nature and shape. The Pascal series mercury porosimeters consist of two interacting models (Figure 5).

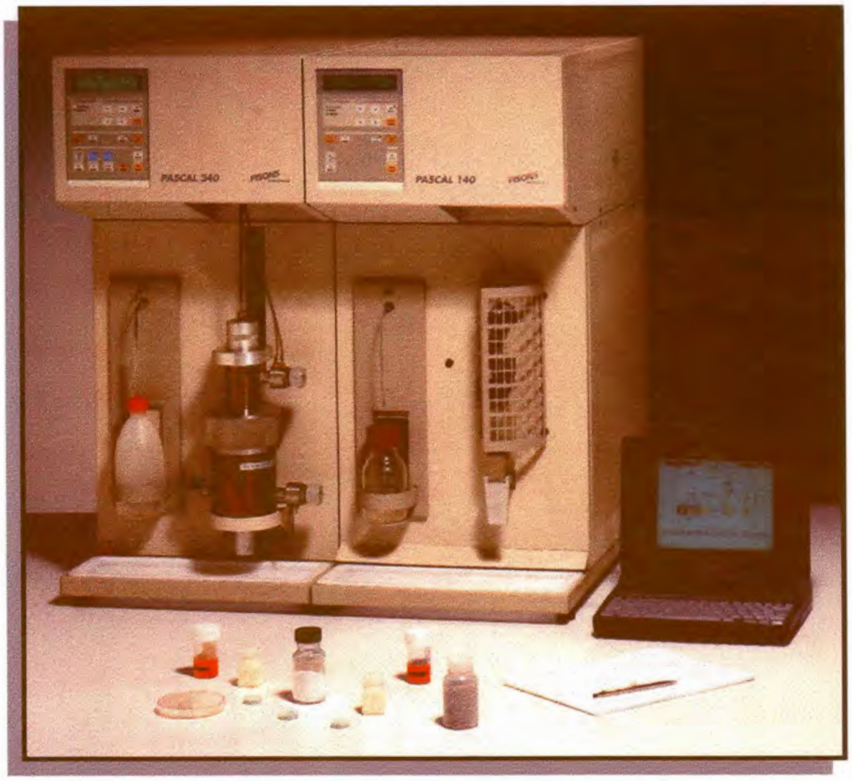

Figure 5: The mercury porosimeter.

Mercury porosimetry analysis is based on the measure of the intrusion of mercury into the pores of the sample at various pressures. The principle of this method is to evacuate an undisturbed sample and fill the pore spaces with either a liquid or powder mercury. The rate of mercury intrusion into the sample pores is then used to evaluate the pore size distribution.

The Pascal 140 is an automatic, low pressure, high resolution porosimeter operating from vacuum up to 400 kPa absolute pressure. Pascal 140 regulates sample preparation (which is the outgassing phase), dilatometer filling with fresh or powder mercury and carries out low pressure porosimetry measurements for macropore analysis.

The sample preparation process is started by outgassing the sample under vacuum. A special proportional valve starts the system and outgassing continues until the required degree of vacuum is attained. The pressure transducer for the analysis is automatically calibrated to zero and the system proceeds with the mercury filling operation. The dilatometer is automatically filled with mercury up to a preselected volume level. The quantity of mercury transferred is thus reproducible. The method used by the Pascal series, automatically determines the correct pressurisation speed according to the presence of pores and the actual mercury penetration rate into the sample.

Once the filling operation is completed, the analysis begins by reducing the vacuum at the rate determined by the Pascal system within the speed range selected by the operator. When reaching the minimum vacuum, the sample is depressurised at the rate determined by the Pascal system. The depressurisation speed range selected by the operator may differ from the pressurisation speed range. For powder samples, a second run must be made to ensure there is no aggregation thus permitting a correct particle size distribution.

The Pascal 240 (the second part of the system) takes over where the Pascal 140 leaves off to measure pores down to the micropore regions. This part of the porosimeter operates at maximum pressure of up to 200 MPa.

Samples from the control, first and second levels of precipitated gypsum were taken from column sections and replicated three times. These samples were sent to the "Instituto per la Genesi e l'Ecologia der Suolo" IGES – CNR, in Firenze, Italy, for analyses.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Gypsum precipitation study

4.1.1. Vacuum pump efficiency and evaporation rate

Saving time and hastening the evaporation rate of the water from the columns was imperative. Therefore, gypsiferous water had to be added to the columns in time intervals and these time intervals were important.

- The maximum amount of gypsiferous water had to be added to the columns and having an efficient watering and evaporating system would ensure effective and maximum evaporation and precipitation.
- The air flow through the column was much lower when the soil was at field capacity and then increased as the column dried. Therefore the time and sequence that allowed maximum evaporation had to be established.

As little water as possible was permitted to leach from the column, ensuring that no gypsum crystals were lost through leaching.

The experimental results determining the optimum rate of evaporation can be set out as follows (Tables 4 and 5).

Table 4: The mass loss (kg) of column 1 due to drainage (mℓ) and evaporation (mℓ) over an eight hour time period.

Column 1			
Time (hours)	**Mass of columns (kg)**	**Water drained (mℓ)**	**Water evaporated (mℓ)**
0.0	4.700	0	0
Pump switched on			
0.5	4.514	91	95
1.0	4.496	8	10
1.5	4.456	4	36
2.0	4.436	6	14
Pump switched off			
3.0	4.434	0	2
Pump switched on			
4.0	4.428	0	6
5.0	4.420	0	8
Pump switched off			
6.0	4.416	0	4
Pump switched on			
7.0	4.407	0	9
8.0	4.402	0	5

Table 5: The mass loss (kg) of column 2 due to drainage (mℓ) and evaporation (mℓ) over an eight hour time period.

Column 2			
Time (hours)	**Mass of columns (kg)**	**Water drained (mℓ)**	**Water evaporated (mℓ)**
0.0	4.554	0	0
Pump switched on			
0.5	4.356	78	120
1.0	4.342	12	2
1.5	4.330	5	7
2.0	4.314	2	14
Pump switched off			
3.0	4.308	0	6
Pump switched on			
4.0	4.292	3	13
5.0	4.283	0	9
Pump switched off			
6.0	4.281	0	2
Pump switched on			
7.0	4.278	0	3
8.0	4.274	0	4

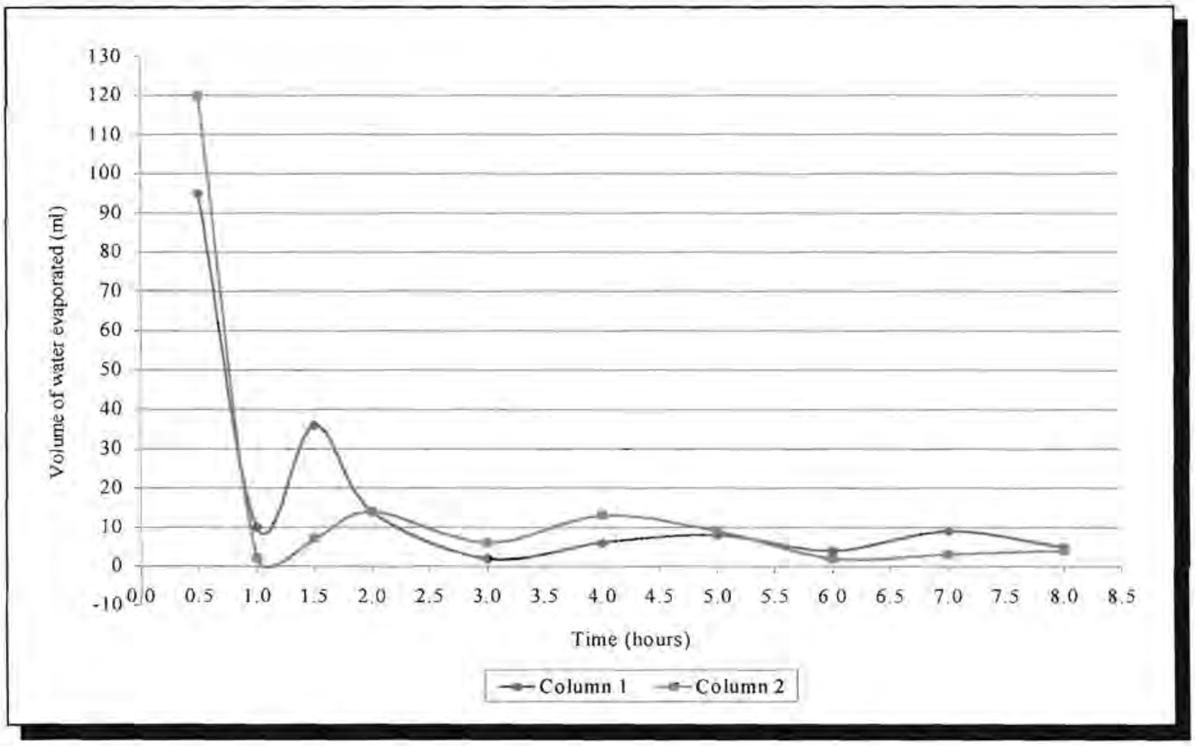

Figure 6: The rate of water evaporation (mℓ) due to the applied vacuum.

These results clearly show that the maximum evaporation rate was achieved within the first two hours of air flow. Thereafter evaporation diminished greatly for both columns with only another 34 mℓ for column 1 and 37 mℓ for column 2 evaporating in the following six hours.

Subsequently, it was decided to set the time intervals to a two hour vacuum and one hour rest cycle. The automated system watering 150 mℓ saturated gypsum water each time the vacuum ceased. By using 150 mℓ of saturated gypsiferous water the optimum amount of gypsum that had to be precipitated was easily reached. This operating system was implemented 24 hours a day resulting in the evaporation of 1200 mℓ water per day.

4.1.2. Gypsum precipitation rate in the soil columns

According to the volume of saturated gypsiferous water added to the soil in the columns every three hours the amount of gypsum precipitation can be calculated as follows:

The calculated surface area of the entire column, the 300 mm length, 110 mm diameter, was 0.009503 m^2 and within a column, 1 ton ha^{-1} $CaSO_4 \cdot 2H_2O$ equaled 0.9503 g $column^{-1}$ $CaSO_4 \cdot 2H_2O$. With the automated system giving 1200 mℓ saturated gypsum (2.5 g ℓ^{-1} $CaSO_4 \cdot 2H_2O$) a day, 4 g $column^{-1}$ day^{-1} $CaSO_4 \cdot 2H_2O$ was precipitated. This is equivalent to 3.1 ton ha^{-1} day^{-1} under field conditions.

According to the chosen time scenarios (Table 3) it would take approximately 16 days to reach the first level of precipitating 0.048 kg column^{-1} gypsum and 92 days to reach the 25 year level.

These levels of precipitation had to be evaluated and validated by analysing the precipitated gypsum, but more importantly, analysis must determine where the precipitation took place in the column.

4.2. Analysing the amount of precipitated gypsum

4.2.1. Determining a regression equation for the resin method

The electrical conductivity of the prepared soil samples with the increasing amounts of gypsum are given in Table 6. These EC values were used to determine a standard regression equation for the specific soil used in this trial and the determination of the precipitated gypsum in the soil column sections.

Table 6: Electrical conductivity (EC) (dS m^{-1}) of the prepared samples.

g Gypsum added to 1 g soil sample	Gypsum per gram of soil (g g^{-1})	Electrical conductivity (dS m^{-1})
Control	Control	0.22
0.1	0.091	4.20
0.2	0.167	6.71
0.3	0.231	10.04
0.4	0.286	12.14
0.5	0.333	15.10
0.6	0.357	16.90
0.7	0.412	17.40
0.8	0.444	20.30
0.9	0.473	22.00

The regression analysis obtained for the soil from Major pivot at Kleinkopjé colliery, which was used in the column study, differs markedly from that of Frenkel, Gerstl & Van de Veen (1986). This regression equation was confirmed by repeating the procedure and subsequently, it would be necessary to obtain an equation for each soil before this method can be used successfully. This standard regression equation (Figure 7) was used to determine the precipitated gypsum in the soil columns.

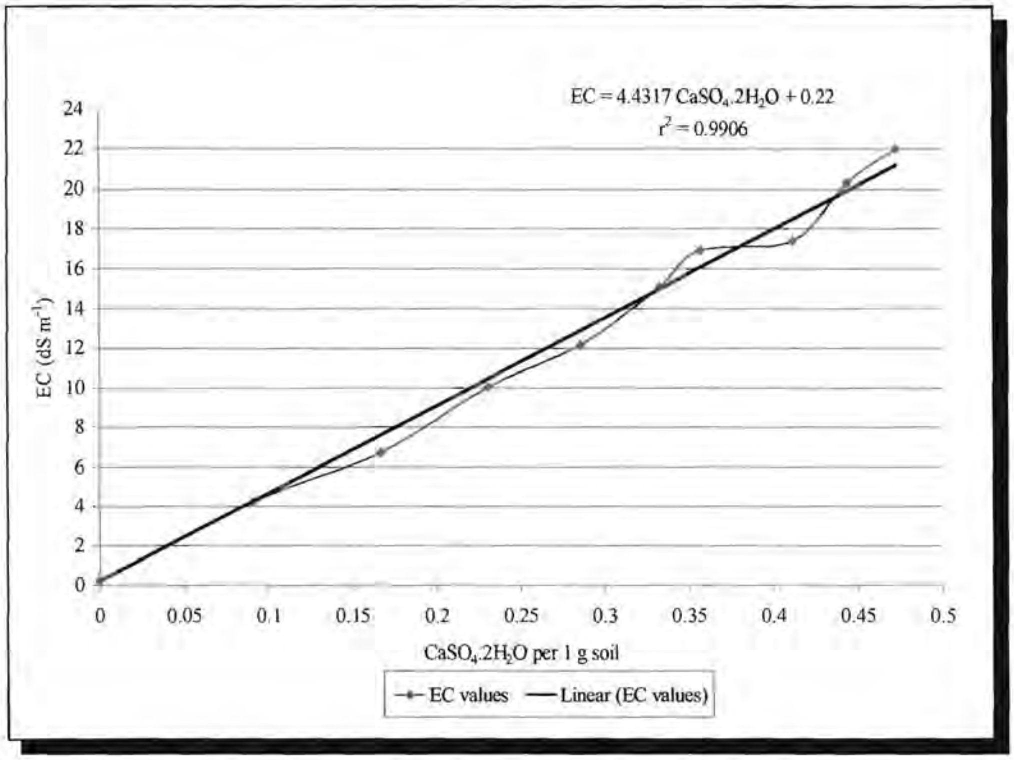

Figure 7: Regression equation for the resin method.

4.2.2. Determining the precipitated gypsum in each section of the columns

All the columns were sampled in each section (Figures 3 & 4). The EC (0.22 dS m^{-1}) of the control column was used in comparing the regression equation. This average electrical conductivity value and the average calculated amounts of gypsum precipitation are given in Table 7 (detailed values of EC and precipitation in Appendix (Tables 12 to 15)).

Table 7: Average EC and average amounts of precipitated gypsum in the soil column sections for all four precipitation levels.

Year time scenario (years)	Soil column and replication number *	Average EC (dS m^{-1})	Average amount of gypsum ($CaSO_4{\cdot}2H_2O$) precipitated		
			mg kg^{-1}	g $column^{-1}$	ton ha^{-1}
5	V1H1	94.79	1 835.24	5.51	8.08
5	V1H2	100.12	1 938.67	5.82	8.53
10	V2H1	337.23	6 539.83	19.62	28.78
10	V2H3	372.11	7 216.77	21.65	31.75
10	V2H4	388.96	7 543.75	22.63	33.19
15	V3H1	889.36	17 254.37	51.76	75.92
15	V3H2	899.07	17 442.84	52.33	76.75
15	V3H3	915.66	17 764.67	53.29	78.16
15	V3H4	833.08	16 162.19	48.49	71.11
25	V4H1	1 106.86	21 475.02	64.43	94.49
25	V4H2	1 089.97	21 147.30	63.44	93.05
25	V4H3	1 118.50	21 701.02	65.10	95.48
25	V4H4	1 060.57	20 576 70	61.73	90.54

* Level (V) and replications (H)

Table 6 shows the average EC and average amounts of gypsum precipitated on all four levels. Although the levels of precipitation are lower than the calculated reference levels, it none-the-less proves that this system can be used to speed up and emulate the process of gypsum precipitation. These lower levels can be attributed to several practical difficulties in refining the automated system used for the precipitation process. Due to automation breakdowns and subsequent manual management, the levels were thought to be higher at the time they were taken from the precipitation system for analysis.

It is, however, clear from the results of the resin analysis for precipitated gypsum, that the precipitation was distributed throughout the column since the largest amount of precipitation was evident in the middle section of the soil columns (Tables 12 to 15 in Addendum). Connecting the vacuum pump to the columns ensured that precipitation did not just take place on the surface soil. The original assumption that the vacuum pump would ensure the distribution of gypsum salts throughout the column, was verified.

4.3. The nature of precipitated gypsum in soil

4.3.1. Scanning electron microscope (SEM) study

The SEM proved useful in viewing gypsum crystal precipitation in a sample. All the section samples from the columns showed that gypsum crystalised as an elongated prismatic structure which can clearly be seen in between soil particles (Figures 8 & 9).

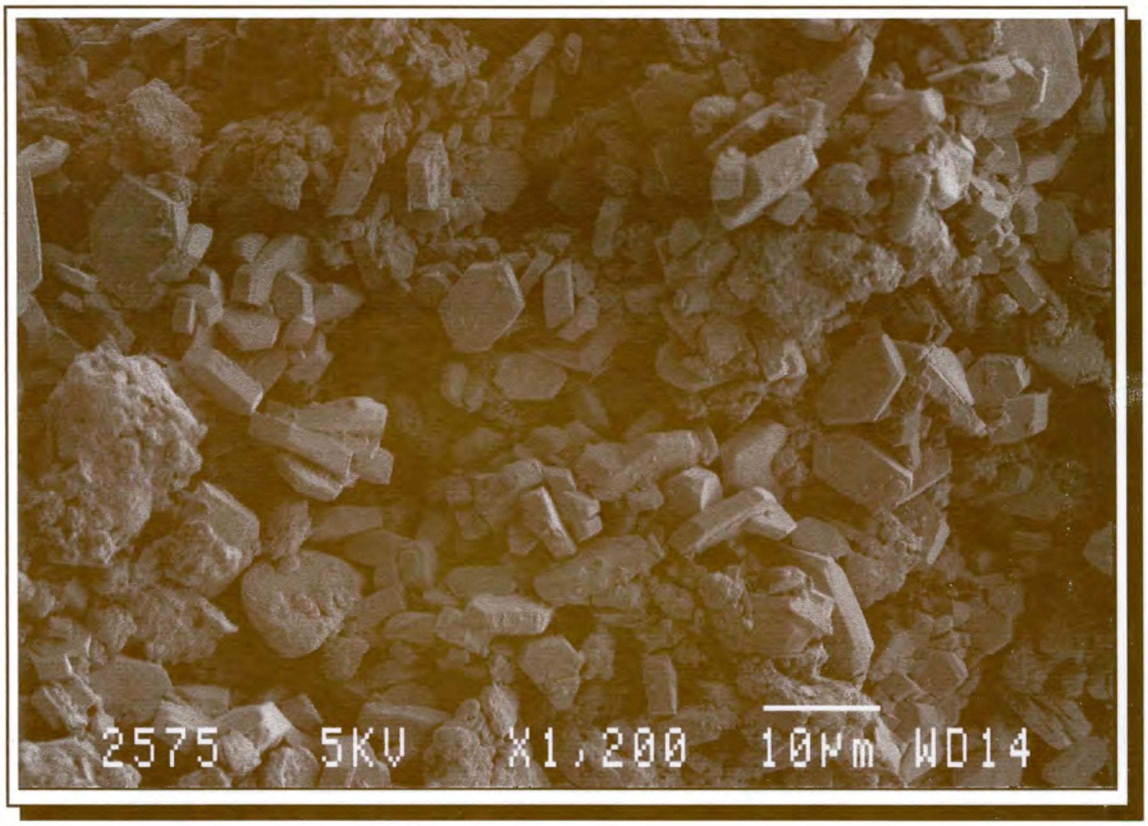

Figure 8: SEM image of crystals between soil particles.

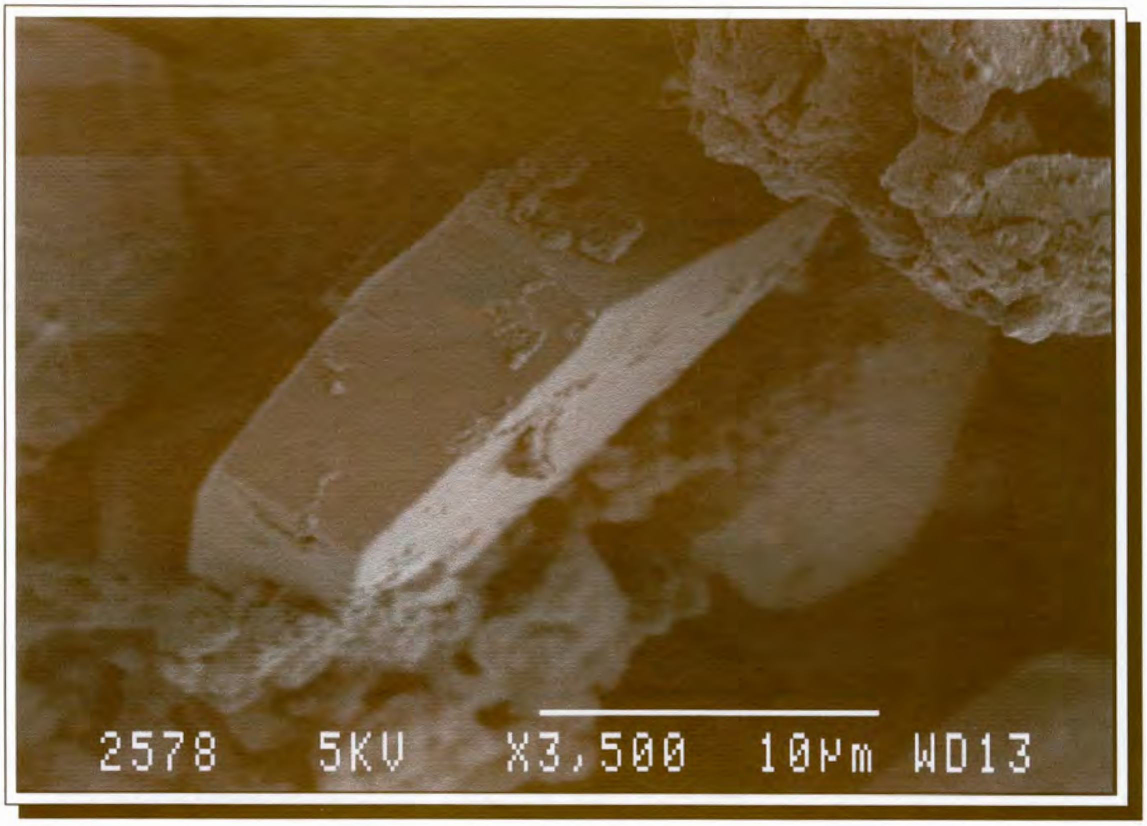

Figure 9: A second SEM image of crystal formation.

These photographs confirm the presence of gypsum in the soil as well as the fact that the gypsum will be precipitating as crystals. There were, however several disadvantages in using this method for analysis.

- During the gold coating of the sample, a relatively high vacuum is required even for the coating of a small soil sample. Most of the sample stayed intact, but often the applied vacuum and subsequent gold coating caused the sample to break into pieces. Great care had to be taken afterwards in handling the samples and mounting them in the SEM because they were very brittle.
- Due to the porous nature of the soil, it has to be coated a minimum of eight times with each coat of gold being approximately 500 Å thick. It leads to very small particles being completely covered with gold and subsequently the layer of gold is as thick or thicker than the soil particle. This particle can therefore not be observed or distinguished from other soil particles.
- If a sample, as in the case of soil, does not have a smooth uniform surface it is often found that the coating process is ineffective because there are particles laying under one another which are thus not coated. This affects the photography of the crystal in the sample. The soil particles which were not coated absorbed electrons instead of reflecting them to give a distorted image which was difficult to focus on and photograph.

Table 8: EDX analysis of the precipitated gypsum crystals.

Element	Element mass (%)
Mg	0.06
Al	6.07
K	0.24
S	32.05
Ca	38.61
Fe	6.82
P	0.35

Figure 11: Other crystals analysed by the EDX.

- To be able to have good resolution of the SEM photographs of crystal formation, it was necessary to coat the sample with gold which in turn prevents the user from doing an electron dispersive X-ray analysis. It is therefore unfortunate that the crystals can be viewed but there can be no elemental analysis of the sample composition.

4.3.2. Energy dispersive X-ray analysis (EDX) study

Neighbouring samples from those analysed by the SEM were coated with carbon for an EDX analysis. This elemental composition analysis proved not only the presence of gypsum in the soil but also that the crystals were in fact gypsum (Figures 10 & 11). These analyses of the crystals in the soil showed much higher Ca and S content than other samples where these crystals were not present (Table 8 & 9).

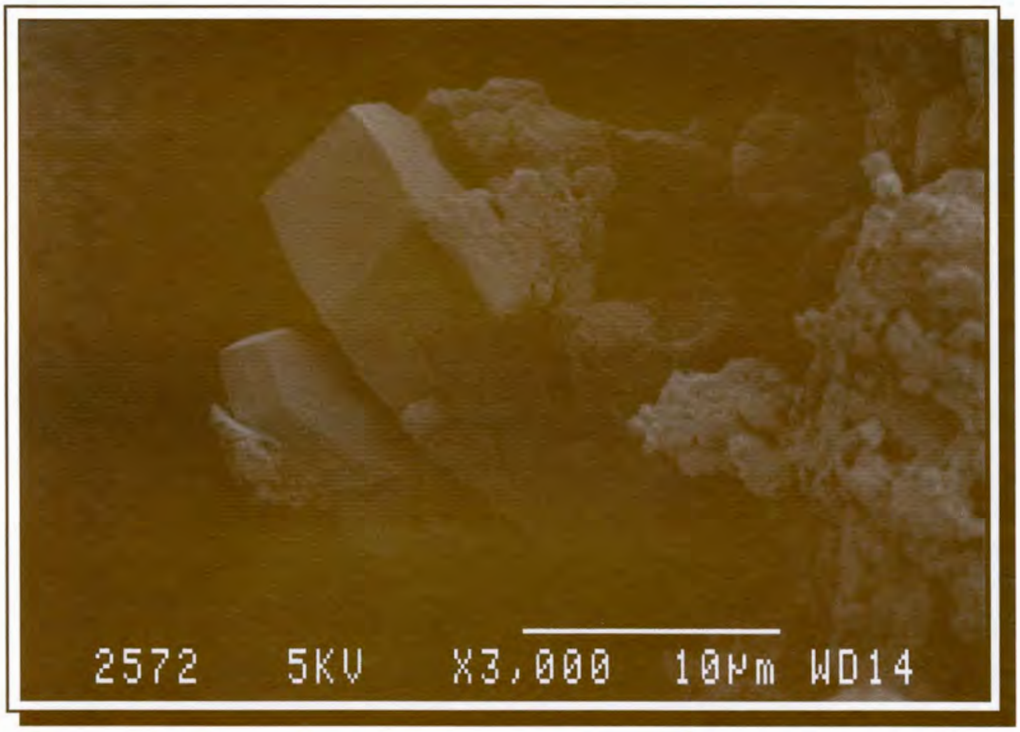

Figure 10: Crystals analysed by the EDX.

Table 9: A second EDX analysis of gypsum crystals.

Element	Element mass (%)
Mg	0.09
Al	7.24
K	0.34
S	27.24
Ca	33.81
Fe	11.40
P	0.19

Using the EDX for the elemental analysis of the crystals, it became clear that this method, also, had a few distinct disadvantages.

- Coating the samples for the EDX analysis, the vacuum required for coating, again, proved problematic since it broke the samples into pieces. The crystals were however very easy to find and to ensure that the elemental analysis of the crystals were that of gypsum, it was repeated several times. Each time the elemental analysis gave high levels of Ca and S.
- Due to the porous nature of the soil, the samples had to be coated ten times with each coat being approximately 500 Å thick. This did not interfere with the soil particles as much as with the SEM analysis since the EDX is not usually used to provide the operator with the best quality photographs, but it is used for elemental analysis. The process of vacuum and coating the samples, however, proved to be extremely time consuming.
- This instrument can not give an analysis of compounds such as SO_4^{2-}, but only of single elements such as S, Ca or Na etc. Thus, if a crystal is analysed, it is important to verify the crystal structure before assuming the nature of the given crystal.
- Furthermore there can not be an oxygen or carbon element analysis, because the sample is in an oxygen environment in the EDX instrument and the sample has to be coated with carbon for an EDX analysis to be done.

A soil mineralogist verified the elongated, prismatic structure of the crystals to be that of gypsum ($CaSO_4 \cdot 2H_2O$) (Bühmann, 1999).

In studying several samples with gypsum crystal formation, with the SEM and EDX, it proved clear that the gypsum crystals were scattered among the soil particles. This appearance of scattering confirmed the findings of Eswaran & Zi-Tong (1991). Although, not quantified and proved, it appeared that the precipitated gypsum were not coating the soil particles to reduce pores or block them. The SEM photographs (Figure 8) shows that the gypsum are separated from the soil and clustered together although connected to the some of the soil particles.

Basically two observations were apparent.

- Some of the viewed samples showed the crystals forming on top of and/or next to existing crystals which gave a stacked nature to the crystals. It stands to reason that the gypsum, (precipitating after initial precipitation had taken place) seemed to have grown onto existing gypsum. This could indicate that gypsum formation would take place onto gypsum crystals already present in the soil, rather than onto the soil.
- Other crystals were adjacent to the soil and seemed to be connected to the soil. These crystals were, however, formed as a gypsum crystals and were not distorted or misformed. The crystals had to have completed its formation cycle for them to be formed as elongated, prismatic structures as seen on the photographs (Figure 8). Although these crystals were connected to soil particles but they were still structurally distinguishable from the soil. These crystals were probably part of the initial precipitation where on the resulting gypsum then precipitated.

Both these methods (SEM and EDX) do prove helpful to substantiate, that the crystal in a soil sample is in fact gypsum. It does, however, not quantify the amount of gypsum or give an estimate of whether the precipitated gypsum will block soil pores.

4.3.3. Light microscopy

Only one of the prepared epoxy's proved to be suitable for impregnation of the soil samples. This was due to the polymerisation rates being different. The Embed-813 polymerisation rate was too fast and it produced a impregnated sample that was to hard to cut into pieces or sand down. The harder the impregnated sample the more difficult and time consuming it is to handle the sample.

On the other hand, the London-dry White polymerisation rate proved to be too slow and therefore there were areas in the sample that was not completely impregnated. The result was that when the samples were cut into pieces it broke and fragmented due to the sample still being very brittle.

Embed-812 was the most suitable epoxy for impregnation. After polymerisation the Embed-812 epoxy samples were easy to cut into pieces and the sanding process was much easier and less time consuming.

After the impregnation of the soil samples, the sanding down of the sample proved to be problematic. In the sanding of epoxy samples, water is usually used as a lubricant to wash the sample and ensure a smooth and even surface, even when a course sanding paper is used. Gypsum has a relatively high solubility and it was decided not to use water, but to dry sand the sample. This left a sample with an uneven surface (not visible with the naked eye) which is again difficult to coat with either gold or carbon for SEM or EDX analysis.

The EDX elemental analysis showed zirconium and titanium contamination. After analysing the sandpaper it became clear that the contamination originated from the colourants used on the sandpaper. Paraffin was used to sand down the sample which does not interfere with the precipitated gypsum. This ensures a relatively smooth surface which eliminates contamination to a great extent.

Viewing the impregnated sample under the light microscope with a diffracting light source, it was found that the light reflection index of gypsum and the epoxy was similar, to the extent that one could not distinguish between the two. Therefore, difference between the soil, precipitated gypsum and epoxy, was not prominent and it was impossible to see where the precipitation had taken place.

4.3.4. Mercury porosimetry

Samples from the control, first and second precipitation levels were analysed with the mercury porosimeter. The numerical data from the mercury porosimeter are given in Table 10.

Table 10: Numerical data of the mean total porosity and mean pore size of the samples from the control, first and second levels of precipitation.

Sample number	Total porosity ($mm^3 g^{-1}$)	Pore size distribution - r (μm)
V0H1N3	186	20
V0H1N4	181	20
V1H1N2	187	20
V1H1N3	218	20 –30
V2H2N3	209	30
V2H2N4	216	20
V2H3N2	200	30
V2H3N3	224	50

Using this method proved to be time consuming, costly and tedious. Since the porosimeter is usually used to analyse solid particles, the samples had to be dried before the analyses could take place. The soil is so brittle and unstable after drying that the standard method of using liquid mercury for intrusion, could not be used. Powder mercury replaced the liquid mercury and this not only increased the cost of analysis substantially but also prolonged the time of chamber evacuation and dilatometer filling with powder mercury.

The results for the porosimeter (Table 10), indicates that there were very little change in the pore size distribution of the samples, except that of the level V2H3N3. In general, on the basis of the results obtained, it is difficult to say if there were pores that, after gypsum precipitation, reduced in size by clogging. There could be two possible explanations for the inconclusive results.

- It was possible that for all the levels of precipitation, the amount of precipitated gypsum were not sufficient to clog or block a large enough number of pores. Should this be the case, changes would not have been detect with the mercury intrusion.
- It might be that precipitated gypsum, deposited on the walls of the soil pores in reducing such a small part of the pores that there was no marked reduction in pore size distribution.

On the other hand, level V2H3N3 show very different results from other samples. In fact, in these samples the porosity value of 224 mm^3 g^{-1} is higher in comparison to the values of the other samples. The most important result is that of the shifting in the radius of the samples, from 30 µm to 50 µm. This means that the presence of gypsum improved the porosity in this part of the column section. It would seem as if the level of precipitation improved the structure of the sample, and this would relate back to the findings of Sharma (1971) that there was very little breakdown in the structure of the soil with increased gypsum content in the soil.

It is however important to note that the section V2H3N3 of the column, showed a slightly higher level of gypsum precipitation (27.12 g column^{-1}) in comparison to section V2H3N2 with the level of 26.46 g column^{-1}. The same level of precipitation, on another replication (V2H2N3), however, shows a precipitation level of 27.56 g column^{-1} but the porosity has not changed from that of the first precipitation level V1H1N3 (Table 12 in Addendum).

Due to the fact that there was no conclusive data on the porosity and pore size distribution of the analysed samples, it would seem that the results of the porosimeter was inconclusive.

4.4. Estimated pore space occupation

Irrespective of the inconclusive nature of the Mercury porosimeter analyses, one can make a rough estimate, through calculation, as to the possible pore space clogging that might take place at a specific level of precipitation.

The equation used to determine the approximate volume of pores in a column is as follow:

$$\textit{Column pore volume} = \left[1 - \left(\frac{\textit{packed porosity} \times \textit{volume of column} - \left(\frac{\textit{mass of gypsum precipitated per column}}{\textit{density of gypsum crystal}}\right)}{\textit{packed porosity} \times \textit{volume of column}}\right)\right] \times 100$$

A 110 mm diameter column, 30 mm in length containing 3 kg of soil with an assumed density of 2.65 g cm^{-2}, has an approximate pore volume of 1718 cm^{-3} when loosely packed. This calculates to 573 mm^3 g^{-1} of soil (loosely packed).

Using the average amount of gypsum precipitated for the 25 year scenario (V4H1 = 46.43 g $column^{-1}$ (Table 7)) with gypsum's density at 2.314 g cm^{-3} (or 27.8 cm^3 $CaSO_4{\cdot}2H_2O$ $column^{-1}$), the gypsum occupies 1.62% (or 9.3 mm^3 g^{-1}) of the pore spaces, given that the bulk density of the soil stays unchanged. Assuming that the field bulk density of the soil is approximately 1.6 g cm^{-3}, the precipitated gypsum (for the 25 year time scenario) will occupy 2.5% of the total pore spaces.

This estimated calculation shows that if there is a precipitation level of 46.43 g $column^{-1}$, which equals 94.49 tons $CaSO_4{\cdot}2H_2O$ ha^{-1} under field conditions, the possible pore reduction in pore spaces will only amount to 2.5%. Clearly this amount of pore space occupation is negligible.

CHAPTER 5

CONCLUSIONS

The results of this study proved several original assumptions correct.

- It is possible to enhance the process of gypsum precipitation in a glasshouse. Coupling a vacuum pump and keeping the glasshouse temperatures relatively high, there is a rapid evaporation of water within the first two hours of water added. This ensures that more water can be added to the soil in a shorter period of time, which accelerates the precipitation process. Most importantly, it is not just gypsum that can be precipitated in this way. Any field condition salt precipitation can be emulated using this automated glasshouse system.
- Apart from the vacuum pump accelerating the precipitation of gypsum, it also ensured that the precipitation was distributed over the whole column. The simulation in the glasshouse gives a good idea of the precipitation distribution in a soil profile.
- Associated with this, the automated watering system ensured optimal watering of the soil coupled with the vacuum and high temperatures ensuring optimal evaporation.

The method of Frenkel, Gerstl & Van de Veen (1986) provided results as to the amount of gypsum precipitated in the columns. This method, however, requires an equation for each soil before this method can be used successfully and a separate regression equation had to be determined for the soil used in this study. Since the regression equation will differ from soil to soil, this method is not ideally suited for analyses of large quantities of samples originating from different soils and different sites.

The SEM and EDX, were two useful methods for viewing crystal formation between soil particles and confirmation of the chemical content of a specified crystal structure. However, these two methods do not quantify the amount or the placement of the precipitated gypsum in the soil.

Impregnating a soil sample with epoxy ensures a stable and reusable sample for several other analyses. Once the contamination from the sandpaper was eliminated and an even surface was produced, the sample could successfully used for light microscopy analysis. Unfortunately, the gypsum placement could not be viewed with the light microscope because of the diffractive light breaking index of gypsum and the soil being very similar.

This study concluded that the Embed-812 epoxy was in fact the best polymerisation agent. Several other epoxy combinations such as were tried like for instance the London-dry White. These epoxies were unsuitable for soil impregnation. Due to the polymerisation agents the polymerisation process were either too slow or too fast acting, which made the sample either too brittle or too hard to prepare for analyses.

The mercury porosimeter is the method with the most potential. The data received from the analysis were inconclusive which could be attributed to the levels of precipitated gypsum being insufficient to change, block or clog the soil pores. Thus no definite changes could be observed in the soil pore and there was no change in the pore size distribution.

Unfortunately this method is very costly, extremely time consuming and tedious. The reason for this being that the porosimeter is usually used to analyse solid particles. Due to soil's brittle and unstable nature when dry (since the sample has to be dry to be analysed) a deviation on the original method had to be found. Thus, powder mercury was use instead of the usual liquid mercury. This not only prolonged the process, but increased the cost of analyses substantially.

A rough calculation estimated that there will be a 2.5% reduction in pore spaces, at a precipitation level of 94.49 ton gypsum ha^{-1} under field conditions. This percentage of pore space occupation by gypsum, clearly proves to be negligible. Using this calculation substantiates the findings of the Mercury Porosimeter, that (even with a higher level of precipitate than analysed with the Mercury Porosimeter) there was, theoretically speaking, insufficient blocking or clogging of soil pores.

In light of the previous conclusions the following recommendations should be taken into account when further research is done:

- It would be most valuable if the other levels of precipitation were to be analysed via the mercury porosimeter. This method will give a very good idea of the change in aggregate pores, pore size distribution and will substantiate the calculated percentage of pore space occupation.
- A universal, easy to use, standard method should be found to analyse the amount of precipitated gypsum in soil.

CHAPTER 6

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CHAPTER 7

ADDENDUM

Table 11: Soil chemical analysis for three intensive monitoring sites at pivot Major (sugarbeans crop, end of 1997/98 summer season).

Strategy	Depth (cm)	pH (H_2O)	EC (mS m^{-1})	Bray I P (mg kg^{-1})	Soluble cations ($cmol_c$ kg^{-1})				Exchangeable cations ($cmol_c$ kg^{-1})				SO_4^{2-} ($cmol_c$ kg^{-1})
					Ca^{2+}	K^+	Mg^{2+}	Na^+	Ca^{2+}	K^+	Mg^{2+}	Na^+	
Leaching fraction	0-20	3.78	95.5	-	0.056	0.002	0.036	0.005	0.504	0.047	0.282	0	0.127
	20-40	4.38	0.9	-	0.078	0.005	0.065	0.164	0.522	0.047	0.147	0	0.193
	40-60	4.88	31.0	-	0.014	0.002	0.032	0.022	1.074	0.089	0.363	0.025	0.026
	60-80	4.38	6.0	5.90	0.002	0.001	0.003	0.008	0.194	0.053	0.295	0.015	0.002
	80-100	4.43	7.8	4.30	0.001	0.001	0.002	0.016	0.116	0.044	0.068	0.033	-
	100-120	6.64	8.3	5.95	0.010	0.001	0.005	0.005	0.230	0.067	0.486	0.056	0.002
Field capacity	0-20	3.96	82.0	-	0.098	0.010	0.114	0.013	0.553	0.110	0.487	0.001	0.273
	20-40	3.51	59.6	-	0.079	0.007	0.076	0.176	0.323	0.079	0.070	0.018	0.184
	40-60	3.79	37.8	-	0.029	0.006	0.036	0.016	0.428	0.027	0.196	0.007	0.101
	60-80	4.09	9.9	5.80	0.006	0.002	0.009	0.002	0.824	0.070	0.489	0	0.001
	80-100	4.21	15.8	6.70	0.011	0.002	0.013	0.003	0.417	0.042	0.197	0	0.001
	100-120	3.66	10.8	6.30	0.007	0.002	0.008	0.003	0.222	0.044	0.289	0	0.001
Deficit	0-20	4.96	134.0	-	0.129	0.009	0.263	0.210	3.296	0.109	1.489	0	0.495
	20-40	3.27	49.6	-	0.030	0.010	0.069	0.006	0.250	0.030	0.196	0	0.165
	40-60	4.64	20.7	-	0.015	0.002	0.016	0.003	0.495	0.054	0.409	0	0.020
	60-80	4.20	20.9	5.10	0.022	0.003	0.025	0.002	0.409	0.045	0.328	0	0.003
	80-100	4.01	20.2	-	0.020	0.003	0.024	0.003	0.119	0.029	0.209	0	0.027
	100-120	3.82	13.4	5.70	0.006	0.003	0.013	0.002	0.125	0.084	0.370	0	0.001

Table 12: Determination of the amount of precipitated gypsum in the soil column, level 1.

Soil section sample number *	EC (dS m^{-1})	$CaSO_4 \cdot 2H_2O$ precipitated		
		mg kg^{-1}	g $column^{-1}$	ton ha^{-1}
V1H1N1	98.00	1 722.83	5.17	7.58
V1H1N2	103.05	1 995.48	5.99	8.78
V1H1N3	100.60	1 947.94	5.94	8.57
V1H1N4	86.52	1 674.71	5.02	7.37
V1H2N1	92.05	1 782.02	5.35	7.84
V1H2N2	106.42	2 060.88	6.18	9.07
V1H2N3	101.95	1 974.14	5.92	8.69
V1H2N4	100.07	1 937.65	5.81	8.53

* Level 1 (V), replications 1 to 2 (H) and sections 1 to 4 (N)

Table 13: Determination of the amount of precipitated gypsum in the soil column, level 2.

Soil section sample number *	**EC (dS m^{-1})**	**$CaSO_4 \cdot 2H_2O$ precipitated**		
		mg kg^{-1}	**g column^{-1}**	**ton ha^{-1}**
V2H1N1	375.21	7 276.92	21.83	32.02
V2H1N2	356.94	6 922.38	20.77	30.46
V2H1N3	279.53	5 420.19	16.26	23.85
V2H2N1	300.24	5 822.08	17.47	25.62
V2H2N2	331.00	6 419.00	19.26	28.24
V2H2N3	468.56	9 088.44	27.56	39.99
V2H2N4	388.64	7 537.54	22.61	33.17
V2H3N1	312.92	6 068.15	18.20	26.70
V2H3N2	454.67	8 818.90	26.46	38.80
V2H3N3	466.00	9 038.76	27.12	39.77
V2H3N4	322.25	6 249.20	18.78	27.50

* Level 2 (V), replications 1 to 3 (H) and sections 1 to 4 (N)

Table 14: Determination of the amount of precipitated gypsum in the soil column, level 3.

Soil section sample number *	EC (dS m^{-1})	$CaSO_4 \cdot 2H_2O$ precipitated		
		mg kg^{-1}	g $column^{-1}$	ton ha^{-1}
V3H1N1	803.97	15 597.29	46.79	68.63
V3H1N2	806.98	15 655.70	46.97	68.89
V3H1N3	1 004.29	19 484.63	58.45	85.73
V3H1N4	930.24	18 047.64	54.14	79.41
V3H1N5	901.33	17 486.62	52.46	76.94
V3H2N1	897.26	17 407.64	52.22	76.59
V3H2N2	898.63	17 434.23	52.30	76.71
V3H2N3	929.81	18 039.29	54.12	79.37
V3H2N4	924.06	17 927.71	53.78	78.88
V3H2N5	845.61	16 405.34	49.22	72.18
V3H3N1	833.12	16 162.96	48.49	71.12
V3H3N2	898.39	17 429.57	52.29	76.69
V3H3N3	1 012.56	19 645.11	58.83	86.44
V3H3N4	923.91	17 924.80	53.77	78.87
V3H3N5	910.31	17 660.88	52.98	77.71
V3H4N1	766.53	14 870.74	44.61	65.43
V3H4N2	853.18	16 552.24	49.65	72.83
V3H4N3	877.94	17 032.72	51.10	74.94
V3H4N4	839.45	16 285.80	48.56	71.66
V3H4N5	828.30	16 069.43	48.21	70.71

* Level 3 (V), replications 1 to 4 (H) and sections 1 to 4 (N)

Table 15: Determination of the amount of precipitated gypsum in the soil column, level 4.

Soil section sample number *	**EC ($dS\ m^{-1}$)**	**$CaSO_4 \cdot 2H_2O$ precipitated**		
		mg kg^{-1}	**g $column^{-1}$**	**ton ha^{-1}**
V4H1N1	1 053.05	20 430.85	64.29	89.90
V4H1N2	1 083.83	21 028.15	63.08	92.52
V4H1N3	1 197.05	23 225.26	69.68	102.19
V4H1N4	1 148.56	22 284.28	66.85	98.05
V4H1N5	1 051.80	20 406.59	61.22	89.79
V4H2N1	1 088.57	21 120.13	63.36	92.93
V4H2N2	1 102.94	21 398.99	64.20	94.16
V4H2N3	1 135.61	22 032.91	66.10	96.95
V4H2N4	1 122.48	21 778.18	65.34	95.82
V4H2N5	1 000.25	19 406.23	58.22	85.39
V4H3N1	1 096.37	21 271.50	63.81	93.59
V4H3N2	1 128.27	21 890.54	65.67	96.32
V4H3N3	1 154.00	22 389.85	67.17	98.52
V4H3N4	1 132.21	21 967.00	65.90	96.65
V4H3N5	1 081.67	20 986.24	62.96	92.34
V4H4N1	1 026.22	19 910.19	59.73	87.60
V4H4N2	1 083.42	21 020.20	63.06	92.49
V4H4N3	1 105.64	21 451.39	64.35	94.39
V4H4N4	1 082.39	21 000.21	63.00	92.40
V4H4N5	1 005.16	19 501.51	58.51	85.81

* Level 4 (V), replications 1 to 4 (H) and sections 1 to 4 (N)