

**Study of Pollutant Spillage and
Electrokinetic Soil Remediation**

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The proposal for this work outlined a research programme separated in four parts as follows:

- (i) design and development of equipment and instrumentation,
- (ii) laboratory electrokinetic tests at 1 g for investigation of fundamental processes,
- (iii) 4 centrifuge tests on spillage of dense pollutant and analysis of results,
- (iv) 4 centrifuge tests on electrokinetic remediation and interpretation of data.

Part I was successfully undertaken and led to the design and manufacturing of a 1g electrokinetic cell and centrifuge test equipment and instrumentation for the two different sets of tests. All the centrifuge tests were undertaken on the CUED 10m arm centrifuge. The post-test investigations required an Atomic Absorption Spectrometer was necessary and this was the most substantial equipment purchase.

Part II. investigated both chemical and thermal effects on electrokinetic remediation. As the research progressed several interesting findings were encountered which led to a slight modification of the programme to enable detailed research and interpretation of those findings.

Part III accomplished 8 centrifuge tests on density driven flows in silty and sandy soils. The data were used to validate the computer code HST3D.

Part IV involved considerable development of equipment and instrumentation and comprised 5 centrifuge tests which led to a successful model configuration and meaningful data.

Over the course of the work it was found that it would be difficult to obtain a proven computer code for electrokinetic remediation. It was therefore decided that in addition to the proposed research a numerical code should be developed and used to provide predictions (Part V).

Despite various unforeseen circumstances during this work (i.e. three different Research Assistants and an one year sick leave for the principal investigator) the research was undertaken with success and led to many interesting findings, several research papers and two PhD dissertations.

This report summarises the findings of the work and is presented in four parts according to the proposed programme outlined above.

PART I

Several iterations of design and development produced the electrokinetic cell (Figs. 1-3) used in Part II of the research and the centrifuge equipment (Figs. 4-6) used in Part III and (Figs. 7- 11) used in Part IV.

PART II

Chemical tests

During electrokinetics electrolysis reactions occur around the wells producing alkaline conditions at the cathode and acidic conditions at the anode. These ions then migrate towards the oppositely charged electrode forming alkali and acid fronts. The migration of the acid is towards the cathode

remain adsorbed or form precipitates such as ferric hydroxide. When the two pH fronts meet at the pH jump, the impurities that are in solution and moving with the acid front, will form hydroxide or oxide precipitates. The high localised ion concentration produces a thin band of precipitates, which have a high resistance. A consequence of this may also be that the pore space is reduced locally resulting in an increase in local resistance. This causes a large localised voltage drop across the pH jump. The sodium concentration profile shows no effect of the pore fluid pH level (Fig. 15). Sodium hydroxide is soluble and conductive and will therefore migrate in both high and low pH environments. The profile shows that approximately 2/3 of the sample has been remediated.

This series of tests indicates the need to limit pH front development and migration during electrokinetics. Both fronts limit the process; the alkali front produces non-conductive precipitates, which stop the process, whilst the acid front causes impurities to be desorbed and moved through the system, causing a large percentage of the driving gradient to be used to move them rather than the main pollutant ions. This means that the percentage of the applied electrical power being used to remove the actual pollutant ions is reduced, hence influencing the efficiency of the remediation process. The formation of a highly resistive band also influences the remediation as it causes the voltage gradient, and hence the pollutant migration, to decrease across the majority of the soil.

Temperature tests

The samples were prepared as above. The tests were performed at a constant temperature - 25, 50 or 75°C (note that field scale studies have shown temperature increases of 40°C are possible after applying a current density of 4Amps/m² for four weeks) by placing the electrokinetic cell in a water bath 48 hours prior to testing. This allowed the clay samples to reach equilibrium.

A volume measuring device was connected to the cathode reservoir to monitor the electroosmotic flow rate, whilst the anode reservoir was flushed with deionised water. Constant head devices connected to both reservoirs prevented the development of hydraulic gradient across the sample. Table 3 describes the experiments undertaken; more detail can be found in Penn and Sawidou (1997). In the first two tests the supply voltage was monitored and adjusted manually to provide a constant voltage gradient across the soil until a constant electroosmotic flow rate was established. In the other tests the supply voltage across the whole system was constant resulting in varying voltage across the soil until the process was stopped due to the pH fronts meeting. The current was measured by the arrangement shown in Fig. 3.

Post test investigations involved sampling and measuring the pH, moisture content, sodium and sulphate concentrations in the pore fluid of each sample. Tests T1 and T2 showed an increase in electroosmotic permeability with increasing temperature (fig. 16). For the calculation of the electroosmotic permeability, values for dielectric constant and viscosity were obtained from Physical and Chemical constants references, but zeta-potential must be obtained experimentally. Since zeta-potential measuring equipment was not available at CUED the experimental electroosmotic permeability at 25°C was used to calculate a value for zeta-potential which was then used to calculate theoretical values for electroosmotic permeability at other temperatures. Three calculations were performed, with electroosmotic permeability assumed to be only dependent on either (i) viscosity, (ii) dielectric constant and viscosity, or (iii) dielectric constant, viscosity and zeta-potential. The theoretical values compare well with experimental values for both deionised water and sodium sulphate solution samples (Figs. 17 and 18).

Tests T7 - T9 investigated the effect of temperature on both electroosmosis and ionic migration. The tests were stopped after the formation of a blue line and corresponding fall in current described

processes. Further work would be necessary for evaluation of fingering and **circulation** mechanisms present in such experiments.

PART IV

Five electrokinetic centrifuge tests were performed in cylindrical models of E-grade kaolin clay mixed and saturated with copper sulphate solution. Figs. 7-10 show schematic diagrams of the equipment and Table 7 outlines the **different** tests. A constant direct current electrical potential was applied across the clay by inserting rectangular platinum electrodes. Contaminants that migrated to the electrodes during the processes were removed by flushing the wells with deionised water. The voltage field, temperature and pore water pressures within the model were measured by voltage pins, thermocouples and pore water pressure transducers. Voltage pins with a high resistance, potential divider circuit and isolation amplifiers were developed to monitor local voltages within a floating voltage field (Fig. 11). Each test duration comprised of a period of consolidation followed by remediation. Post test sampling and analysis were carried out to determine the **final** concentration of copper and sulphate ions in the pore fluid. The tests for copper used the atomic absorption spectrometer and for sulphate used the turbidity method with a spectrophotometer. Since this was the first time that anyone had attempted a study of electrokinetics in a centrifuge, tests 1 to 4 involved considerable development and improvement which then led to test 5 which provided the most reliable data (Penn & Savidou, 1996). The results **from** this test are described briefly below.

The initial and final voltage fields at a cross-section through the model, along the centreline of the electrodes are presented in Figs. 26 and 27, This shows the initially uniform voltage field becoming distorted and indicating a change in conductivity of the soil with time. The areas close to the electrodes (especially the cathode) become more resistive. The explanation for this can be given in terms of the resultant ions from the electrolysis reactions of the water in the wells migrating towards the oppositely charged electrode and forming acid and alkali fronts. The acid front migrates from the anode to the cathode whilst the **alkali** front does the opposite. The copper ions, which move towards the cathode, meet the hydroxide **front** close to the cathode and precipitate out of solution in the high **pH** environment forming copper hydroxide. This precipitate is not conductive and causes a high resistive band to build up close to the cathode. The wells are flushed with deionised water which is drawn into the soil around the anode due to electroosmosis. This high resistance **fluid** acts as a resistive band around the anode. The areas of high resistance develop within a relatively short time after applying the voltage and cause the current to reduce as a consequence (Fig. 28) and the heating effect also reduces (Fig. 29).

The **final** concentrations for a vertical cross-section through the model show some reduction in the concentration for both ions but mainly around the electrodes (Figs. 30 and 31). As expected, there is a greater reduction in copper ions at the anode as the positive copper ions migrate towards the cathode; the opposite occurs to the sulphate ions. The test highlights the fact that electrokinetic remediation is susceptible to small areas of high resistance between the electrodes which limit the process by reducing the driving gradient across the majority of the contaminated **soil**. The tests also showed that the migration of an alkali **front** through the soil causes areas of high resistance and is therefore detrimental to the remediation process. This is in line with the findings in Part **II**.

PART V

In addition to the research work outlined in the original proposal time was **invested** in **developing** computer codes that predict one dimensional electrokinetic **remediation**. This work was undertaken

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- Penn, M. and Sawidou, C. (1996). "Centrifuge **modelling** of the removal of heavy metal pollutants using electrokinetics", Second International Congress on Environmental Geotechnics, Osaka, Japan, November **5-8th**, (in press).
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- Penn, M., Neal, P., Lynch, R.J. and **Savvidou**, C. (1996). "Investigation of Electrokinetic Remediation in kaolinite clay using Inductively Coupled Plasma Atomic Emission Spectrometry", in preparation.

Test Y - Results of ICP-OES Analysis of Initial and pH Jump Samples.

ELEMENT	CONCENTRATION ($\mu\text{g/g}$ dry clay)	
	INITIAL	pH JUMP SAMPLE
Al	2224.5	6643.0
Ca	340.3	891.9
Cr	3.7	24.2
Co	0.0	2.5
Cu	19.2	52.4
Fe	2021.9	2858.1
K	755.9	719.2
Mg	112.8	1486.9
Mn	8.1	60.3
Na	4005.5	363.4
V	1.7	4.7
Zn	196.4	76.3
Zr	21.0	28.9

TABLE 2

Test	Description	Soil	AH plume /m	Contaminant and Conc. /M		Ratio R	R _{as}	i clean up		Total test time (hrs)
								Phase 1	Phase 2	
EEH2	A contaminant plume is created due to a hydraulic gradient between a leaking landfill and a base aquifer. Hydraulic clean up then conducted.	180 grade silt	0.16	NaCl	0.1	0.18	29.6	0.06	0.2	1.5 8
EEH3	Plume created by combined density driven flow and a small hydraulic gradient.	180 grade silt	0.02	NaCl	0.85	0.85	203.1	0.31	0.12	24
EEH4	Proof test of new air valves and package arrangement	sand	-	NaCl	1.0	-				2
EEH5	Plume created by density driven flow followed by hydraulic clean up.	180 grade silt	.	NaCl	0.667	>10	131.1	0.02	0.125	32
EEH6A	Plume created in sand by density driven flow at three different contaminant concentrations	100-170		NaCl	0.88	>10	106,780			6
EEH6B		sand	.	NaCl	0.48	>10	60,410	.	.	6
EEH6C				NaCl	2.10	>10	232,750			3
EEH7	Dense pollutant (copper sulphate) migrated into the soil due to density and hydraulic gradients.	180 grade silt	-	cusO4						

AH is the potential difference between the landfill and the base aquifer

TABLE 4 SUMMARY OF CENTRIFUGE TESTS (PART III)

Parameter Description	EEH6 A	EEH6 B	EEH6 C
Porous medium porosity		0.46	
Hydraulic conductivity /m/s		1.55x 10 ⁴	
Lonitudinal dispersivity /m		1.15x10 ⁴	
Transverse dispersivity /m		1.15x10 ⁻⁵	
β_w		0.7	
D_j m ² /s		1.38x10 ⁻⁹	
$\rho_{pore\ fluid}$ kg/m ³		998.62	
$\mu_{pore\ fluid}$ kg/m		0.001	
Temperature/deg C		15	
$C_{contaminant}$ Mols	0.867	0.480	2.01
$C_{contaminant}$ (mass fraction)	0.0482	0.0273	0.105
$\rho_{contaminant}$ kg/m ³	1034.0	1018.3	1076.3
$\mu_{contaminant}$ kg/m	1.034x10 ⁻³	1.0068x10 ⁻³	1.186x10 ⁻³

TABLE 6 HST3D INPUT PARAMETERS FOR EEH6A, B, and C

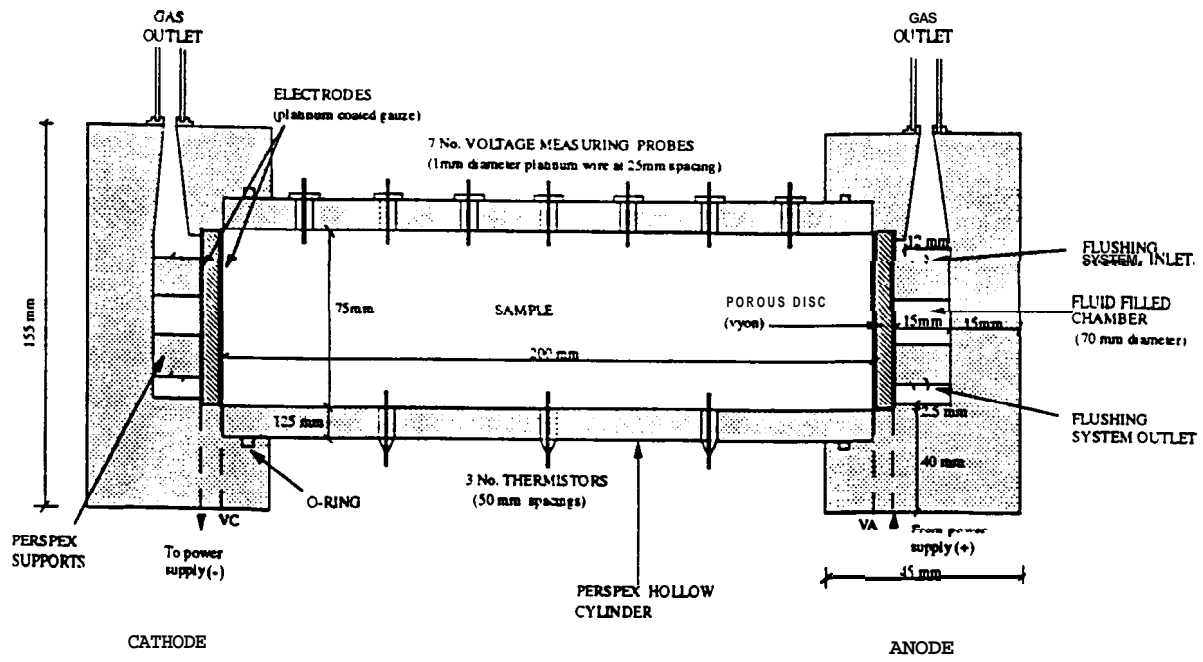


FIGURE 1 ELECTRO KINETIC CELL

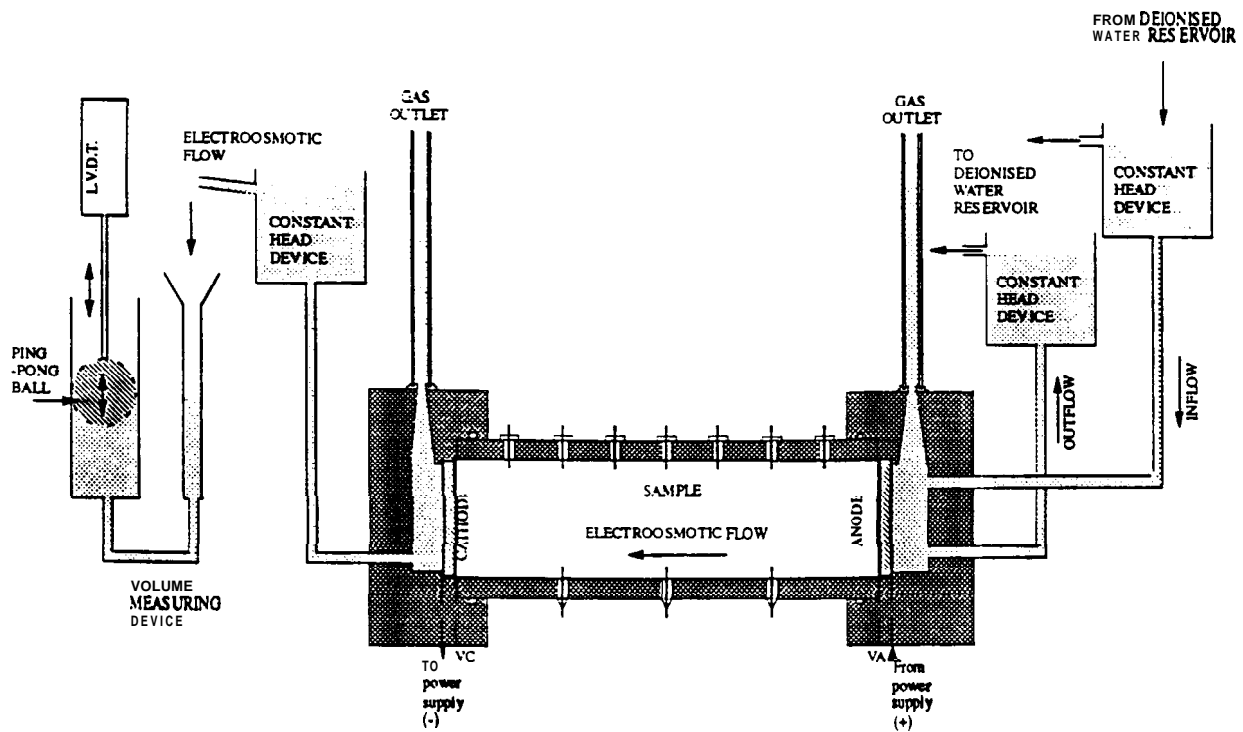
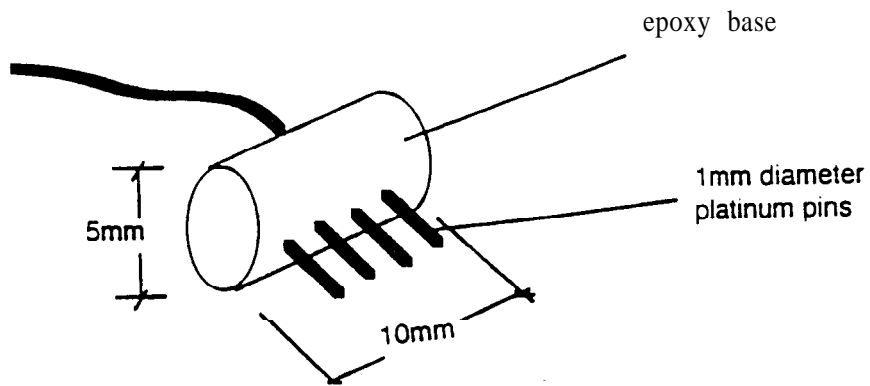
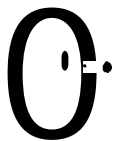
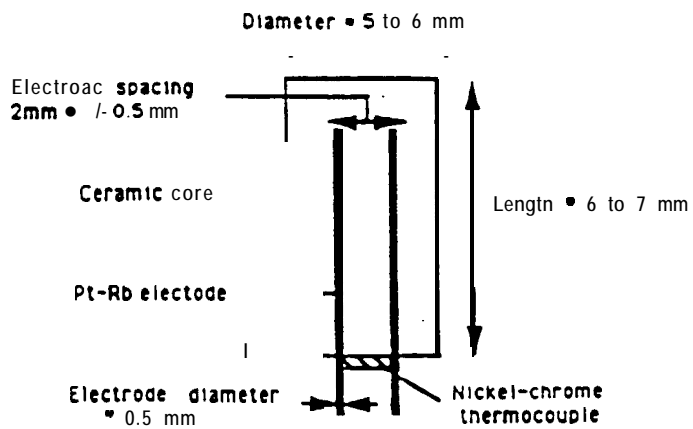


FIGURE 2 ELECTRO KINETIC CELL - PLUMBING



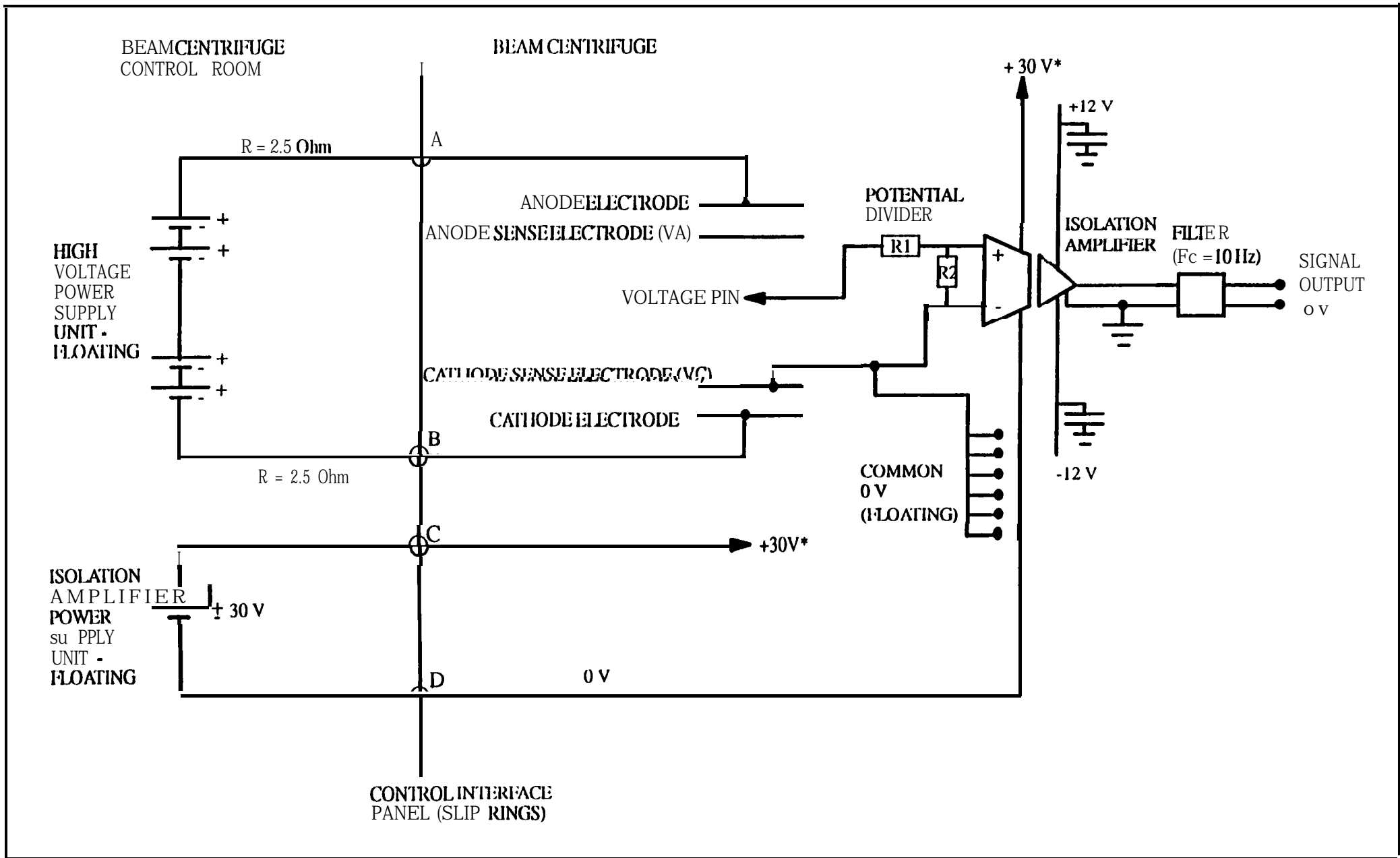
4 PIN CUED RESISTIVITY PROBE



Plan view of core showing position of electrodes

SECTION THROUGH UWA RESISTIVITY PROBE

FIGURE 4



MPEK5 - SCHEMATIC OF ELECTRICAL SET UP FOR VOLTAGE FIELD AND VOLTAGE PINS

FIGURE I I

Test Y - Aluminium Final Concentration Profile

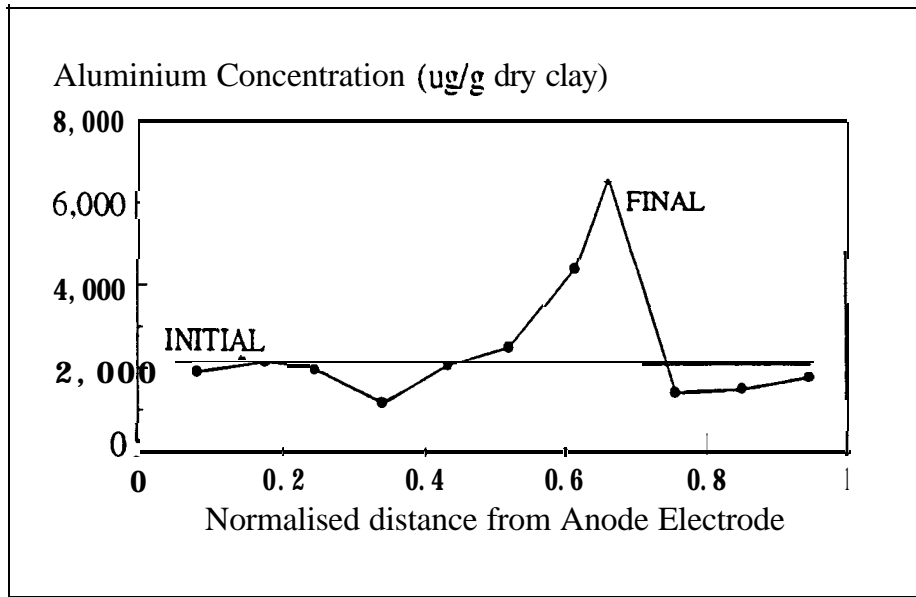


FIGURE 14

Test Y - Final Normalised Sodium Concentration Profile

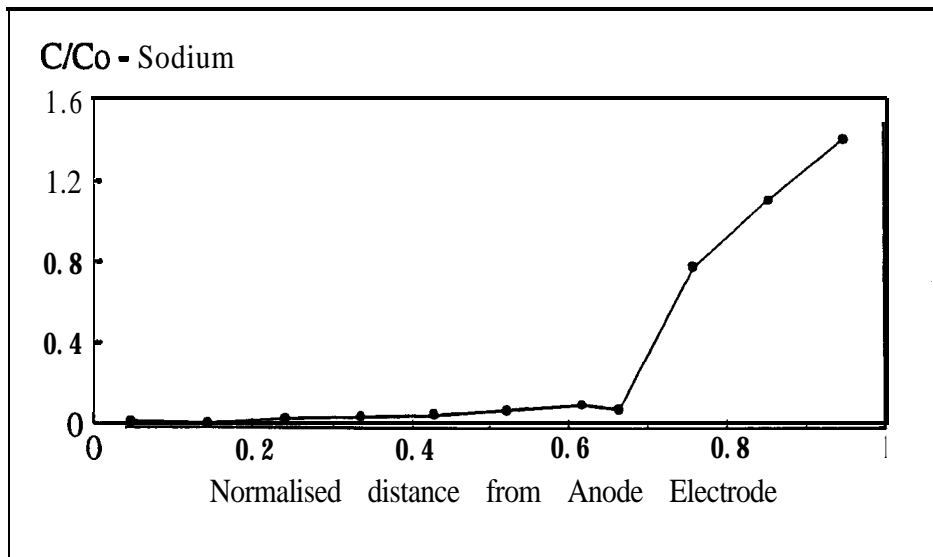


FIGURE 15

Kc • Electroosmotic Permeability (x 10⁻⁹ m²/Vs)

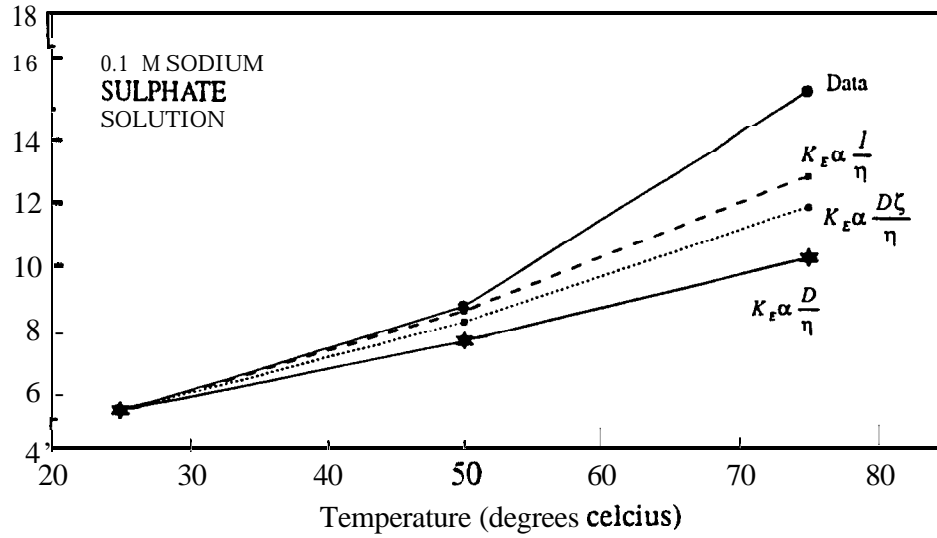


FIGURE 18 TEST SERIES T2: ELECTROOSMOTIC PERMEABILITY VERSUS TEMPERATURE - EXPERIMENTAL AND THEORETICAL VALUES

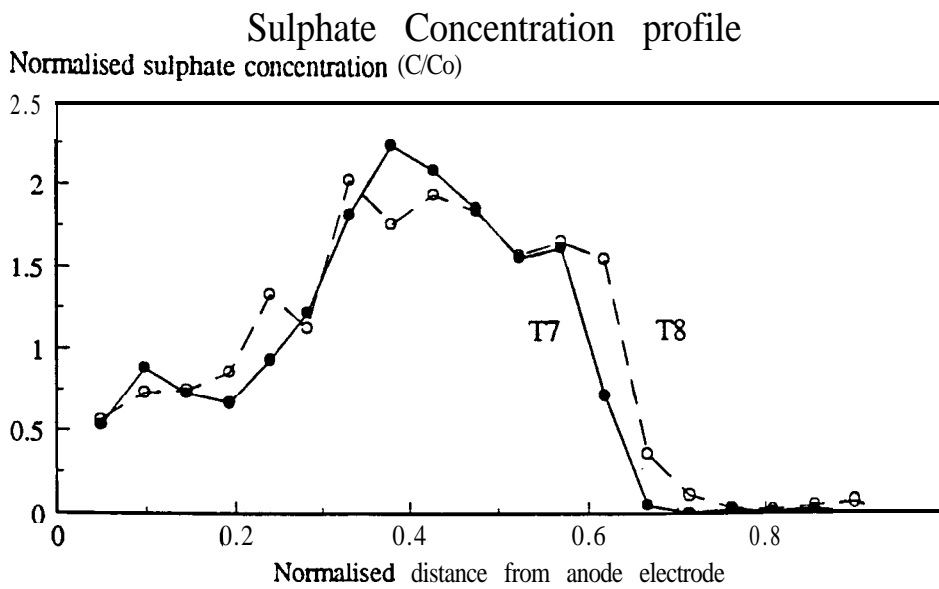


FIGURE 21 TEMPERATURE TESTS

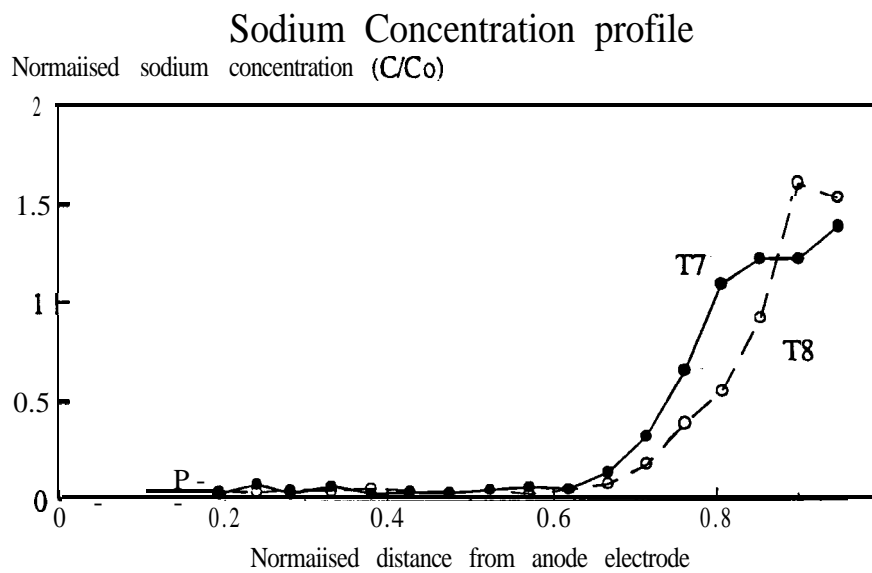


FIGURE 22 TEMPERATURE TESTS

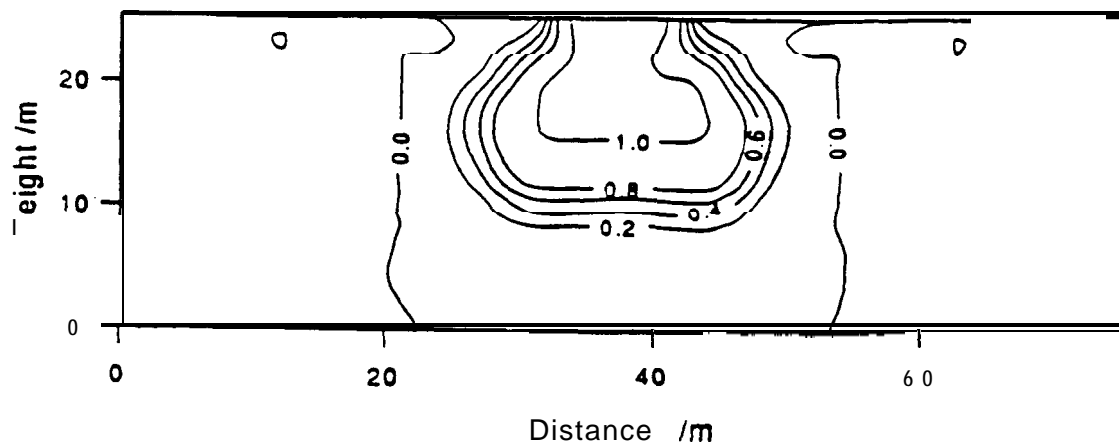


FIGURE 24 PREDICTED CONTOURS OF NORMALISED CONCENTRATION AFTER 16 YEARS

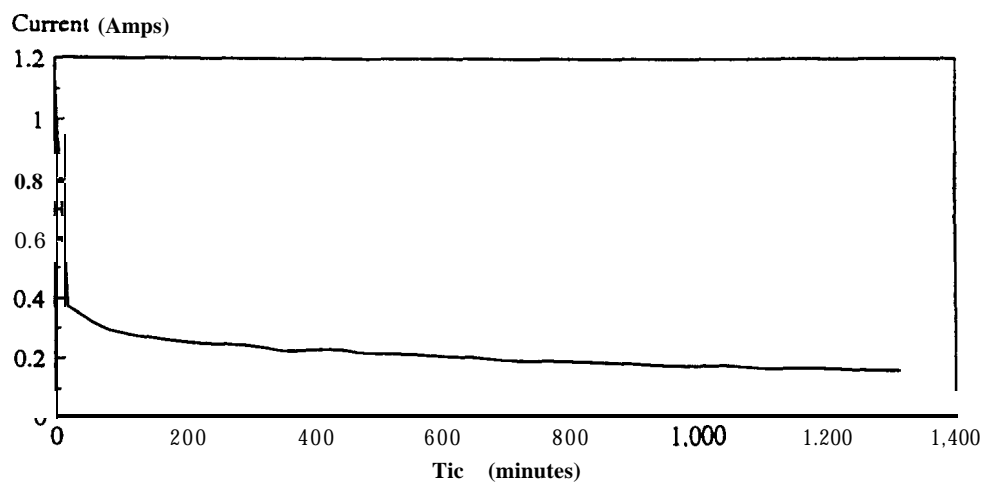


FIGURE 28 MPEKS - CURRENT PROFILE WITH TIME

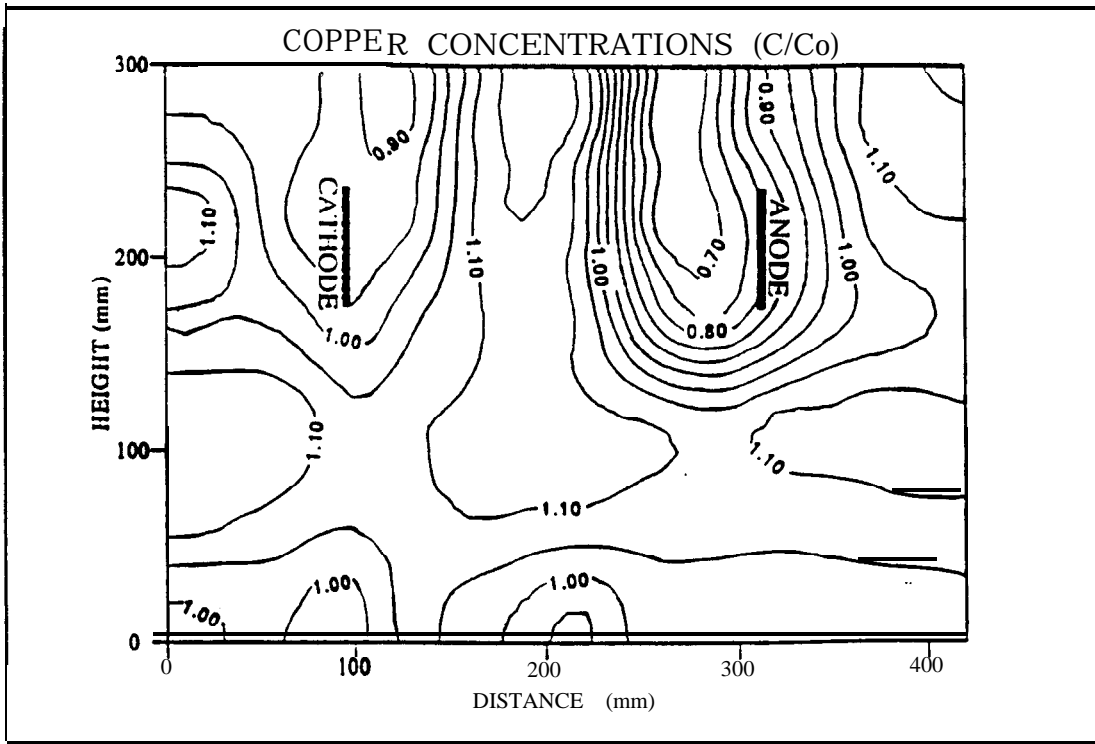


FIGURE 30 FINAL COPPER CONCENTRATIONS (CROSS-SECTION THROUGH THE MODEL, ALONG CENTRELINE OF ELECTRODES)

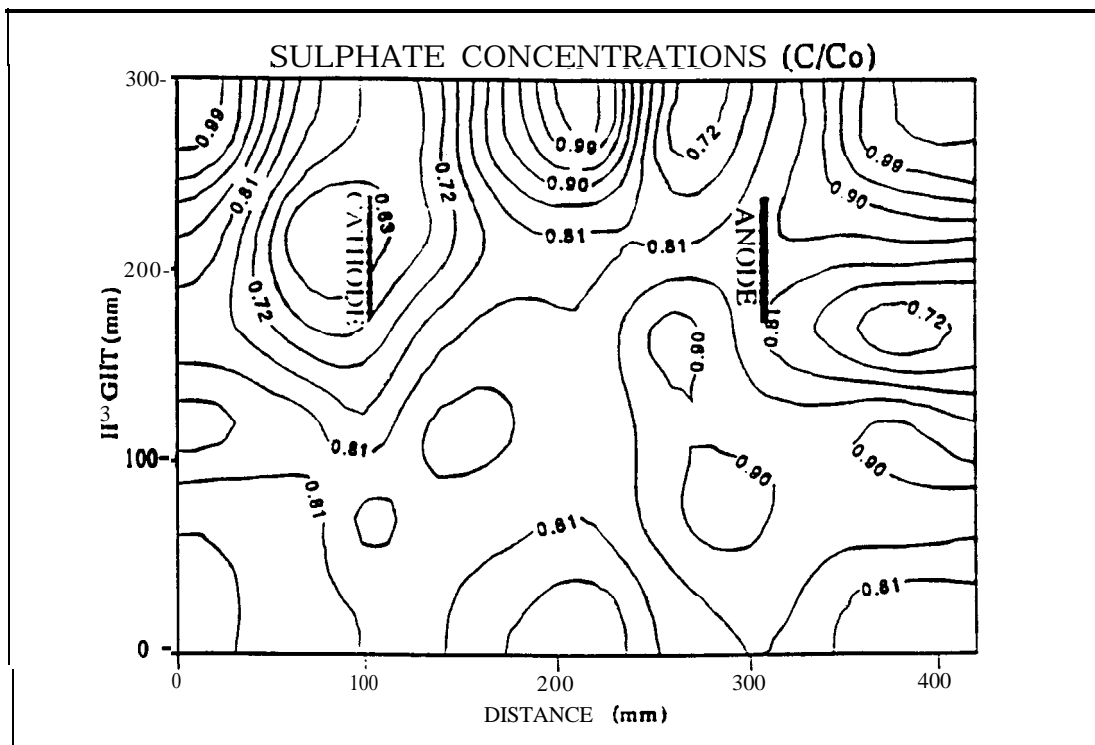
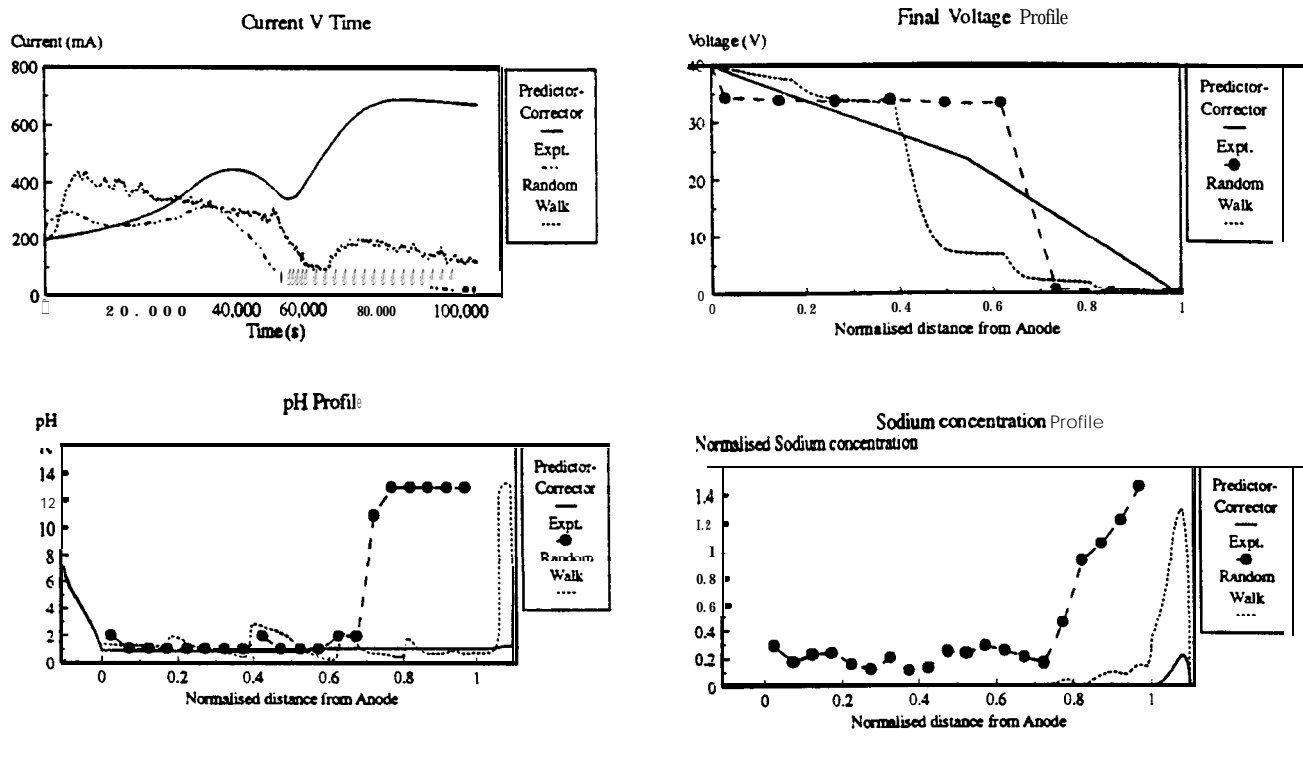


FIGURE 31 FINAL SULPHATE CONCENTRATIONS (CROSS-SECTION THROUGH THE MODEL, ALONG CENTRELINE OF ELECTRODES)

TEST Y • COMPARISON OF EXPERIMENTAL RESULTS, PREDICTOR CORRECTOR & RANDOM WALK EK MODELS
 Simulation of Sodium sulphate + E-grade in cell. 40V for 29 hrs. at 25 degrees



TEST Y • COMPARISON OF EXPERIMENTAL RESULTS, PREDICTOR CORRECTOR & RANDOM WALK EK MODELS
 Simulation of Sodium sulphate + E-grade in cell. 40V for 29 hrs. at 25 degrees

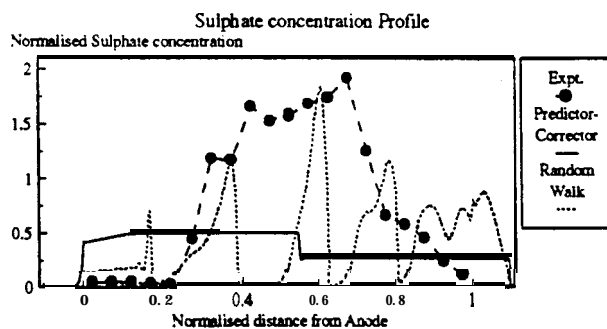


FIGURE 33