

## **Degradation of Piezoelectric Materials**

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**January 1999**

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### **Summary**

As part of the DTI programme on the development of test methods for characterisation of advanced materials, project CAM 7 *Electroactive materials properties under conditions of high stress or stress rate*, has the overall aim of defining and improving the measuring framework for electroactive materials which will enable them to be used with greater confidence by UK industry.

This report describes the results of experiments that have been developed to characterise piezoelectric ceramic materials at high electrical and mechanical stresses. The change in dielectric and piezoelectric properties with time at exposure to such stresses is reported in this document. Additionally, the experimental measurement methods - although described in a previous report (NPL Report CMMT (A) 116) - are re-visited and discussed in terms of the results which have been produced.

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**ISSN 1361-4061**

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## Executive Summary

Methods for controlled application of cyclic mechanical and electrical stressing and the subsequent piezoelectric characterisation have been investigated for a selection of hard and soft PZT materials.

The measurement of dielectric capacitance and loss is a convenient method of establishing degradation in these materials. The use of resonance analysis, especially coupling factor  $k_p$ , can also be used as sensitive indicators of degradation.

The soft materials are very sensitive to repeated mechanical loading with the softer composition PC 5H showing a greater rate of degradation with increasing stress than PZT 5A. Hard materials do not show degradation with repeated mechanical cycling, but are sensitive to extended periods under constant load.

A logarithmic law has been used to model the degradation behaviour under mechanical cycling in the soft materials, and a methodology for extracting the relevant coefficients has been devised. With this equation, given the material coefficients, it is possible to predict the degradation that will occur under a given stress and number of cycles.

The soft materials are generally more sensitive to the application of cyclic electrical stress than the hard materials and those which are placed under static mechanical constraint suffer even more rapid change in properties. The degradation caused under electrical stressing is minor when compared to that caused by even moderate mechanical cyclic loading.

# Mechanical Fatigue of Piezoelectric Ceramics

## *Introduction*

In previous reports<sup>1,2</sup> characterisation methods for piezoelectric materials has been developed, both under free and highly stressed conditions. The current work will extend these methods to examine the change of piezoelectric properties as the material undergoes an increasing number of stressing cycles. This process has been termed degradation rather than fatigue as it is intended to include both electrical and mechanical loss in performance, whereas the term fatigue is generally used to describe loss in mechanical performance prior to complete mechanical failure. The degradation process examined here is intended to cover the complete loss in piezoelectric activity due to mechanical cycling, which occurs at levels well before mechanical failure occurs.

The aim is to develop a measurement method which can be used to generate degradation data that can then be modelled in order to interpolate or extrapolate the information. This data will also be used in separate milestone within the CAM7 program which aims to use Finite Element Analysis to model real piezoelectric device behaviour.

The test methods discussed in the following section deal with simple uniaxial mechanical cycling of monolithic materials parallel to the polar direction under short circuit conditions. Real world applications rarely see such pure mechanical stressing except for some load sensing applications, however the electrical stressing of relatively simple devices such as bimorphs can lead to mechanical stresses that are difficult to introduce into monolithic samples by pure electrical stressing. How this mechanical degradation information will be incorporated into the modelling of mixed electrical and electrical stressing will not be considered here.

## *Measurement methods*

### Producing Degradation

Mechanical degradation was introduced into a variety of poled PZT ceramics, both hard and soft compositions by compressive mechanical cycling. The degradation was carried out on an Instron 8800 series Servo Hydraulic mechanical testing machine with a 25kN load cell. The frequency capability of the system is dependent on the tuning of the PID control for the machine, and the stroke that the hydraulic actuator needs to travel in order to achieve the required load i.e. the compliance of the sample and the holders. The system is designed mainly with long specimens (several cms) in mind, so achieving high speed load control for 1mm thick samples, with loads in the 0 - 5kN range was difficult. However it was possible to cycle at frequencies of up to 100Hz at loads up to 2kN. In the majority of cases there was little or no preload. For example when performing a 2kN loading cycle this meant cycling the load in a sine wave from 0 to 2kN compressive load. In practice there was usually a pre load of 0.05kN just so that the Instron crosshead would not come off the sample, and return to it with a jolt. Therefore the actual loading cycle was from 0.05kN to 2kN compressive. However to achieve some of the higher frequencies it was necessary to overcompensate the load amplitude demand to achieve required load amplitude, and effectively adding a pre-load. For example in

order to drive the system at 2kN p-p at 100Hz the programmed amplitude was 3kN p-p. Due to the inability of the control system to follow this, it meant that the actual amplitude was 2kN p-p, but around a mean of half 3kN (1.5kN), effectively a pre-load of 0.5kN. There was no evidence that this level of preload made any difference to the results, and that the important parameters in the degradation were the amplitude and number of cycles.

Two distinct shapes of samples were chosen for this work, flat disc shaped samples 10mm diameter, 1mm thick, and long cylinders 15mm long, 6.35mm diameter. For compressive loading it is generally recommended to use samples with a length to diameter ratio greater than 2 to 1 to reduce frictional end effects and maintain uniaxial loading. Berlincourt and Krueger found that problems from hydrostatic effects were negligible so long as the diameter was not greater than 3 times the thickness. More recently Audiger et al have achieved accurate results using the standard parts found in piezoelectric fire lighters, 15mm long, ¼" diameter. So although the cylinders fulfil the requirements for uniaxial loading, the flat discs do not. The reasons for using the discs are two fold, firstly there was a requirement to examine the effect of the degradation on parameters that are determined from disc shapes, such as  $d_{31}$ . Secondly most real world applications are based on thin disc shapes, simply because it is difficult to achieve sufficiently high voltages to drive thicker samples.

### *Sample holding and alignment*

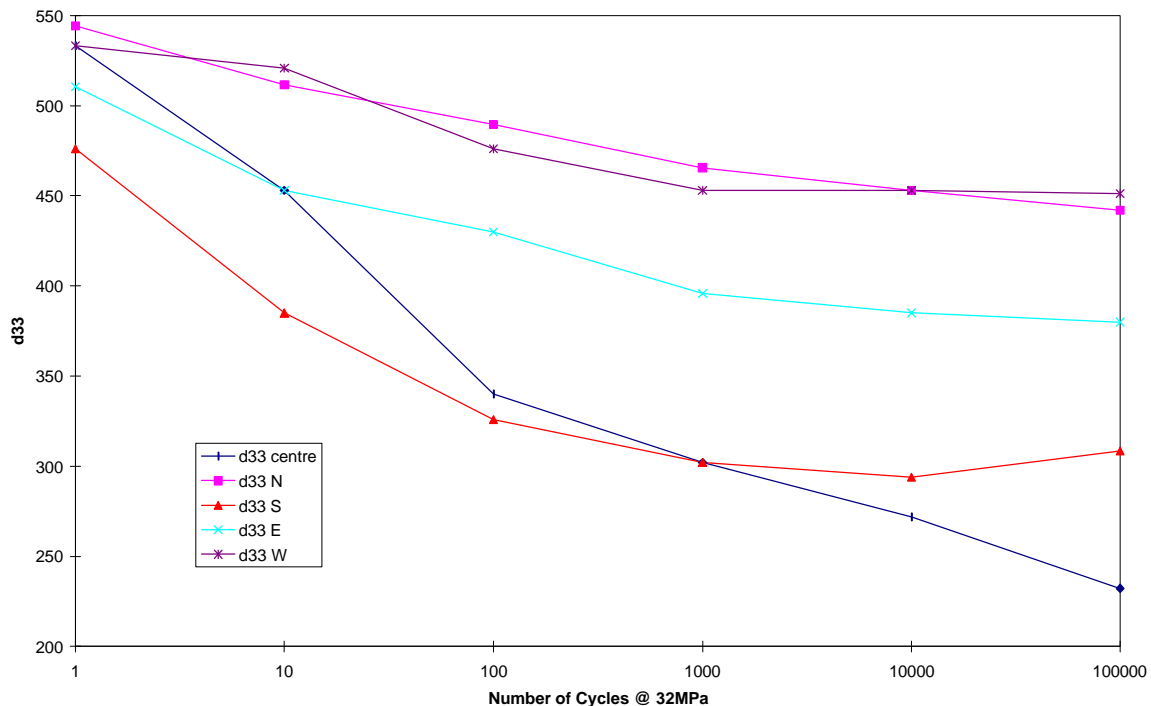
When carrying out compression tests a great deal of care is needed to make sure that the sample alignment is correct. Misalignment and non parallelism can cause bending in long samples, and hence tensile failures, or in shorter samples can lead to massively increased stresses as the load is carried by a small fraction of the area. In the early stages of this work two problems arose which were thought to be due to misalignment of samples. In a number of tests there was premature failure of the hard materials. In previous work<sup>3</sup> it was found that hard PZT compositions were mechanically stronger in biaxial flexure tests than the soft materials. However, in these tests the hard materials were failing mechanically under exactly the same conditions which only caused mild depoling in the soft materials. The failure occurred by brittle failure into a few small pieces, rather than by crushing into a powder, suggesting that tensile failure was being produced by bending. The profiles of the samples were investigated to see if the hard samples were somehow deformed, but profilometry showed no significant difference in the hard and soft sample dimensions, and the platens were also checked and found to be flat. At this point it was decided to concentrate on the soft materials and so the precise cause was not traced, however the possible causes might bear further investigation. It may be that the hard materials are more sensitive to loading rate, since the previous experiments<sup>3</sup> were carried out at fairly low loading rates. It has subsequently proven difficult to repeat these failures since the PID control of the hydraulic actuator has been improved, which points to the sensitivity of hard materials to high stress rates.

A second problem that occurred was the crushing of some of the disc shaped specimens on one side, indicating incorrect spreading of the applied load. The inclusion of various types of self aligning adjustments were investigated but proved unsuccessful at these frequencies and loads. The method which gave the best results was to use aluminium spacers 12mm diameter, and 10mm long between the sample and the loading platens. The disks have silver contact paste electrodes which, when fired, results in a silver loaded glassy type electrode for electrical

contact prior to poling and use. It is these electrodes which confer an additional degree of plastic deformation when the ceramic disk is uniaxially loaded. When combined with the aluminium spacers the overall sample/Instron misalignment can be compensated to some degree.

In order to investigate the effect of the uneven loading the piezoelectric activity of the sample was measured with a Berlincourt type  $d_{33}$  instrument before and after loading. The loading contact of the Berlincourt meter, and therefore the area measured, was sufficiently small such that different areas of a 10mm diameter, 1mm thick disc could be measured. The 10mm disk was divided into five regions, North, South, East, West and centre, and  $d_{33}$  measurements were made in these locations and the alignment in the Instron was suitably marked so that any problems with the holder could be detected. Figure 1 shows the difference in degradation of  $d_{33}$  for a sample as it undergoes extended mechanical cycling. This sample shows that although the  $d_{33}$  is decreasing in all regions, the worst affected area is south and centre. Obviously this indicates that the load has spread unevenly and therefore it is difficult to control the homogeneity of the stress levels throughout the sample.

Experimentation with the sample holding fixtures managed to remove this uneven loading, however in the flat discs it was always found that after cycling, the centre of the discs had a lower  $d_{33}$  than the surrounding areas. At first this was thought to be due to non planar samples or loading platens, however it is more likely that this is due to the non uniaxiality of the stress due to the unfavourable length to diameter ratio.



**Figure 1: Berlincourt measurements of  $d_{33}$  at various points on a 10mm diameter PZT-5A disc sample after mechanical cycling at 32MPa.**

All the experiments so far have been carried out under short circuit conditions, that is no electrical isolation between the ends, however it is a simple matter to add ceramic spacers to perform open circuit experiments.



## Assessing Degradation

It was difficult to monitor the degradation of the samples in situ, so the damage was assessed in several ways by removal of the samples from the Instron after a given number of cycles.

As discussed previously a Berlincourt  $d_{33}$  meter was used to measure  $d_{33}$  of the rod and disc samples. For the disc samples it was possible to measure the variation of  $d_{33}$  across the surface of the sample to detect any inhomogeneity. On some occasions it was difficult to measure  $d_{33}$  because of drift which at first was thought to be instrumental, but later found to be sample related. The Berlincourt measures the instantaneous charge developed in response to a small sinusoidal applied load, and any slow change in charge, perhaps caused thermally, can cause difficulties making the readings. It was found that some samples, particularly the long rods after encountering high mechanical loads, were still undergoing some kind of mechanical recovery tens of minutes after removal from the Instron. This was manifested in a slow drift in the charge signal in one sense, this was in contrast to thermal and electrical interference effects where the drift is much more variable.

In previous work <sup>2</sup> it was found that the change in resonance behaviour was one of the most sensitive methods of detecting changes in the sample. In this work the resonance spectra were analysed using PRAP piezoelectric resonance analysis program. This uses either the standard IEEE analysis<sup>4</sup> or an extended method based on Smits<sup>5</sup> work able to derive complex coefficients to get the relevant piezoelectric and elastic parameters from the particular resonance modes. For the disc samples the radial mode was used to get  $d_{31}$ , and for the rods the length extensional mode was used to determine  $d_{33}$  and other parameters.

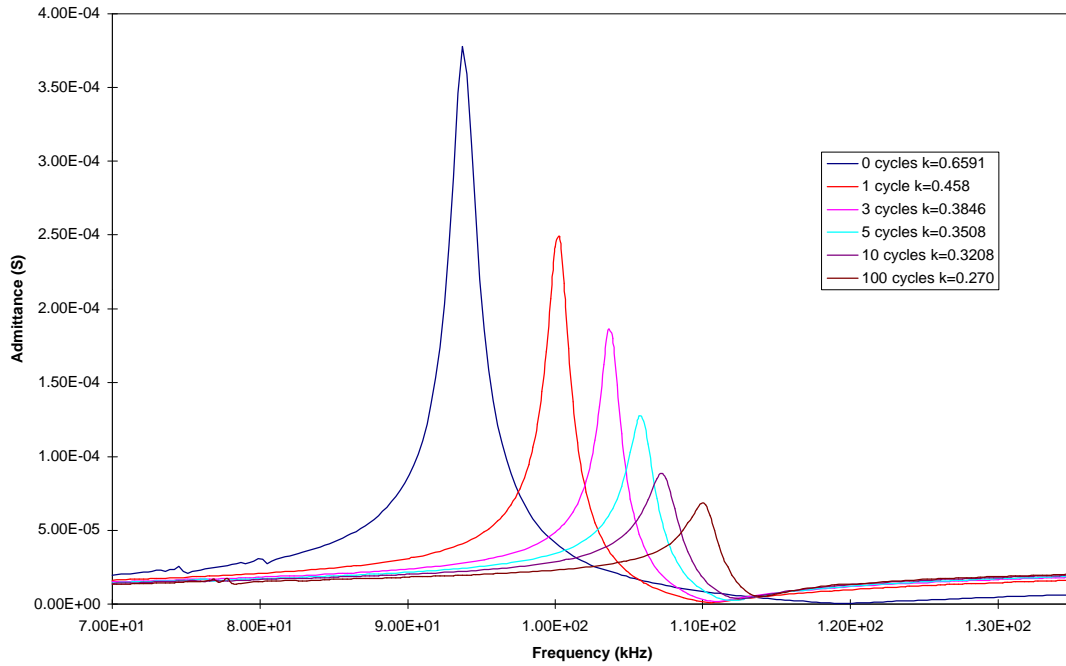
One problem with using resonance to assess degradation is that it is sometimes difficult to differentiate between degradation in the bulk material and gross mechanical defects such as cracks and loss of material. Often if a small part of material has broken off the sample during handling this can result in a large change in the apparent bulk material properties, however these kind of defects can usually be easily found.

The preceding two characterisation methods are low field, low stress measurements where the material is still behaving linearly. In order to examine the effects of the degradation in the high stress regime some high field measurements were carried out after the low field resonance measurements. For convenience, measurements of high field capacitance and loss measurements were made using the Solartron 1260 and 1296 as this could be carried out quickly and automatically, and any change in these would be likely reflected in high field piezoelectric displacement.

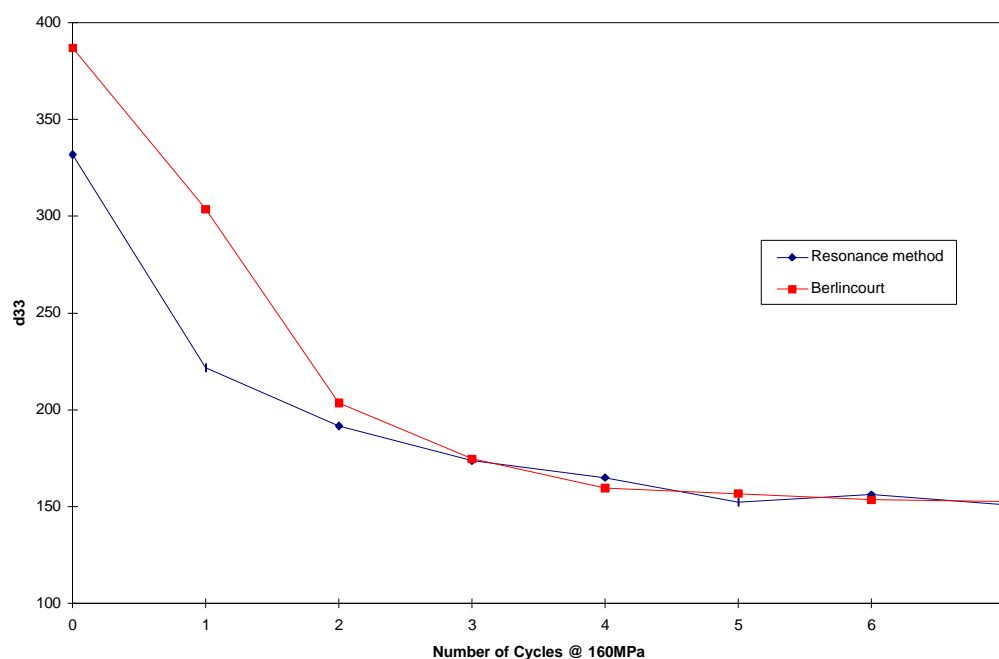
## Results

The degradation of piezoelectric properties with repeated exposure to mechanical cycling is evident in the change in the admittance spectra with the change in behaviour at resonance. Figure 2 shows the shift of the resonance peak of the length extensional mode of a soft PZT5A cylindrical sample with repeated exposure to a 160MPa stress, along with the calculated  $k_{33}$

values for each curve. The height of the peak also reduces with repeated cycling, and this is reflected in the general degradation of all the piezoelectric parameters. The  $d_{33}$  was also measured by the Berlincourt method and these values along with those calculated from the resonance spectra are plotted in Figure 3. There is reasonable agreement after a few cycles, however, there is some disagreement for early cycle data. This is probably because for these particular samples the maximum impedance at antiresonance is just above the maximum possible measurable with the HP 4192A ( $1.2\text{M}\Omega$ ), and as the material degrades the value of maximum impedance reduces giving improved results. Most of the other piezoelectric parameters are only minimally affected by this loss of accuracy at the antiresonance frequency, but since  $d_{33}$  is a combination of most of the others it is more easily affected.

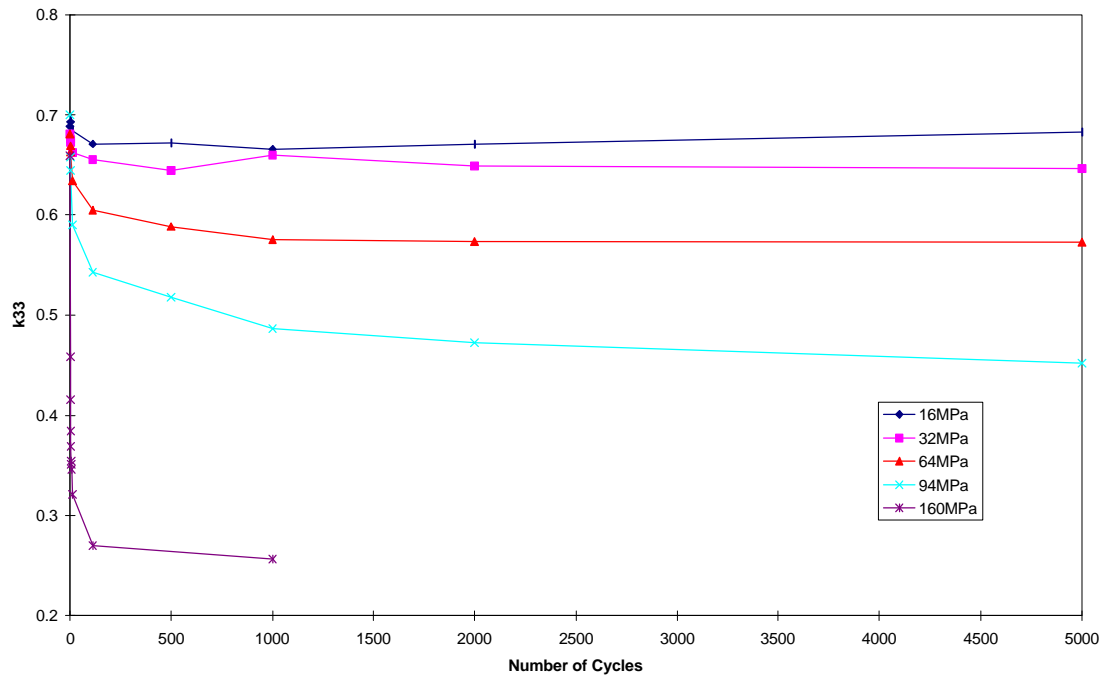


**Figure 2: Admittance spectra of 15mm long PZT-5A rod after mechanical cycling at 160MPa and the corresponding  $k_{33}$  values.**



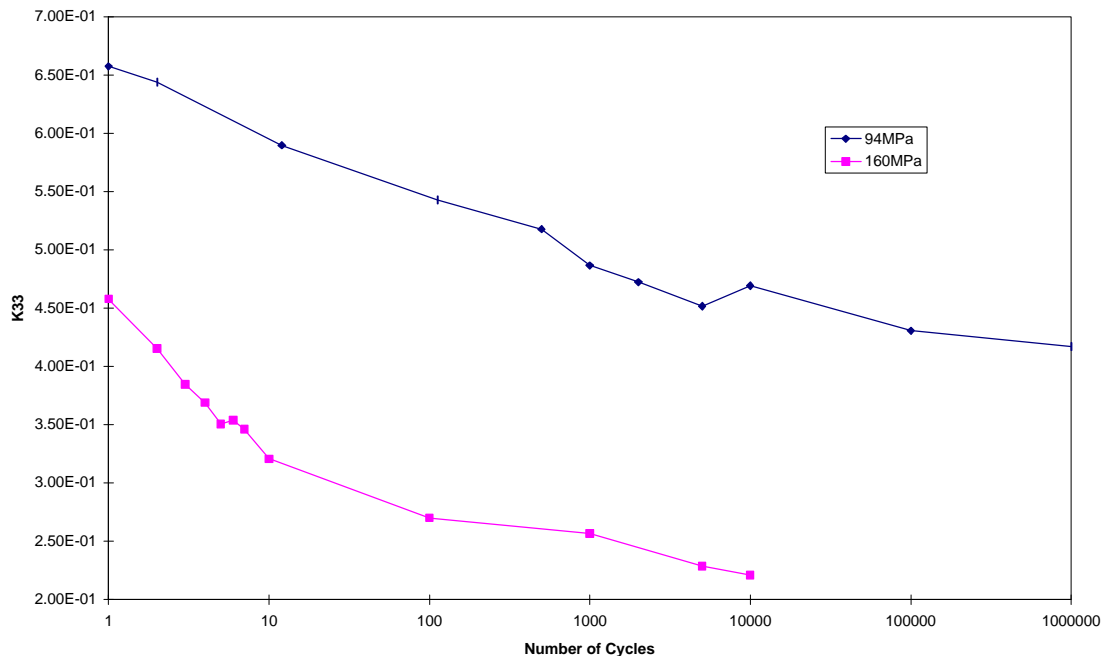
**Figure 3: Comparison of Berlincourt and PRAP  $d_{33}$  values for 15mm PZT-5A rod cycled at 160MPa.**

The effect of different stress levels on the cyclic degradation can be seen in Figure 4, with stresses ranging from 16 to 160MPa, up to 5000 cycles. Increasing the number of cycles decreases the piezoelectric performance, however the largest effect comes from increasing the stress level. If the curves are plotted against log of the number of cycles it appeared that there was a linear relationship, at least for the lower stress levels. Figure 5 shows such a plot where the number of cycles for the 95 and 160MPa has been increased from 5000 cycles to see if the linear relationship could be extended to predict behaviour at higher number of cycles. For example how many cycles would be needed at 95MPa to achieve the same degradation as using 160MPa for 1000 cycles? The experiment was stopped at  $10^6$  cycles as the then predicted number became  $10^8$  cycles as the 95MPa curve flattened out, and it was not possible to carry out the required cycles in a suitable time. It would appear that the logarithmic behaviour is not a satisfactory model at these stress levels.



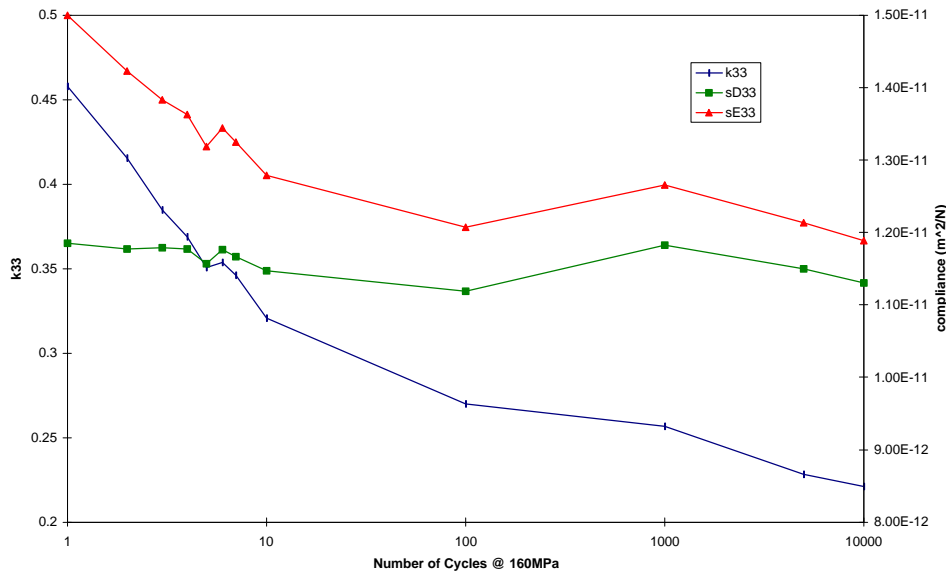
**Figure 4: Effect of different stress levels on mechanical cycling of PZT-5A rods.**

The frequency of the cycling during the course of selected experiments was changed according to the load applied and number of cycles needed. For the 1 to 10 cycle experiments the frequency was usually 0.1Hz in order to start and stop the test effectively. For the larger number of cycles frequencies up to 100Hz were used, however there was no evidence that changing frequency in this range had any effect other than changing the completion time of the experiment.



**Figure 5: Extended mechanical cycling of PZT-5A rods at stresses of 94MPa and 160MPa.**

The electromechanical coupling coefficient  $k$ , was found to be the most sensitive parameter to the effects of mechanical cycling, but there are other parameters that are calculated by the PRAP resonance analysis. Figure 6 shows the variation of the open and short circuit compliance coefficients with increasing cycles at 160MPa. As might be expected as the degradation progresses the two compliances converge, however this may be purely because of the dependency of the coefficients in the analysis. Clearly the short circuit compliance follows the coupling coefficient, but as the short circuit compliance is calculated using the coupling coefficient and the open circuit compliance (which is constant throughout), this is hardly surprising.



**Figure 6: Effect of mechanical cycling at 160MPa on compliance of PZT-5A rods.**

### *Modeling Degradation Behaviour*

The main aim of this work is to see if it is possible to develop some kind of predictive tools in order to estimate degradation behaviour. Although we have seen that at high load levels the logarithmic law was found to be unsatisfactory, however it was felt that at lower loads logarithmic behaviour might give a reasonable fit. In order to be able to plot the different samples on the same graph, values for  $k_{33}$  were normalised and plotted against log of the number of cycles. This gives the immediate problem of how to cope with the 0 cycle value, but since this is always 1 in the normalised state this can be ignored. The degradation curves then gave approximate straight lines which were a starting point for the empirical model. The fit to the equation should be able, given the stress cycle and the number of cycles, to predict the amount of degradation. A problem was found that for each stress level the intercept at 1 cycle was needed to be known, i.e. the equations took the form

$$k_{\# \text{ of cycles}} = f(\sigma) * \log(\text{number of cycles}) + k_{1\_cycle} \quad (1)$$

where  $k_{1\_cycle}$  is the  $k$  value after 1 cycle at a particular stress, and  $f(\sigma)$  is a function of the stress. This is unsatisfactory as it leads to another unknown, however if we plot the log of one minus the value of  $k_{1\_cycle}$  against the stress, we get a good straight line fit which gives  $k_{1\_cycle}$  as

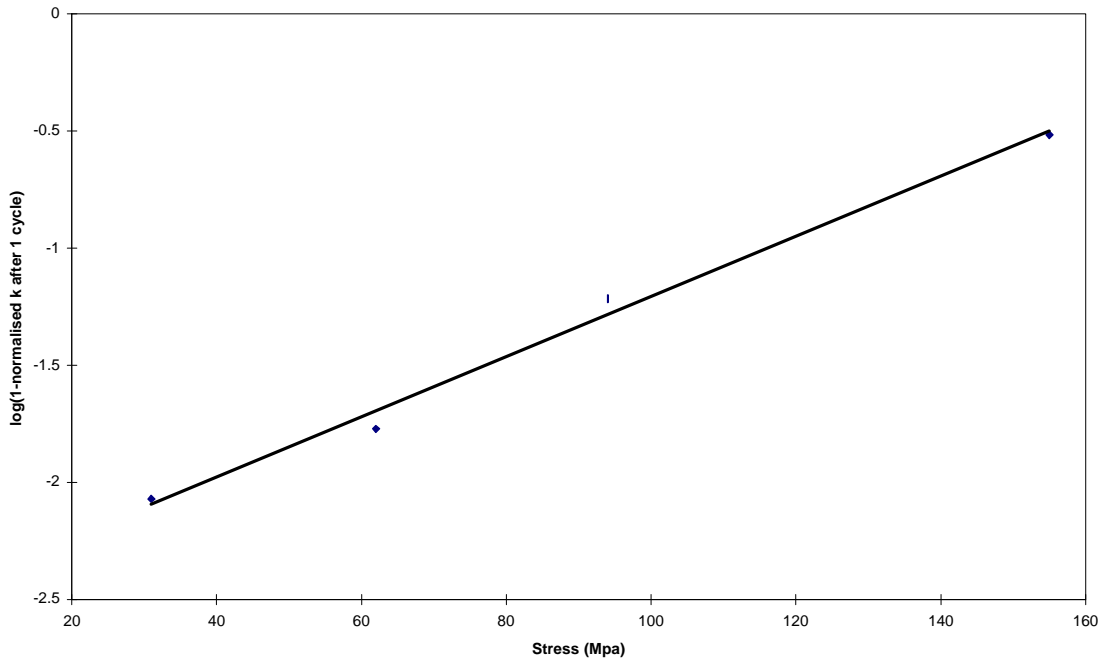
a function of stress. Figure 7 shows this plot for the degradation curves plotted in Figure 4, and this leads to an equation of the form

$$\log(1 - k_{1\_cycle}) = y_0 + \sigma/K_1 \quad (2)$$

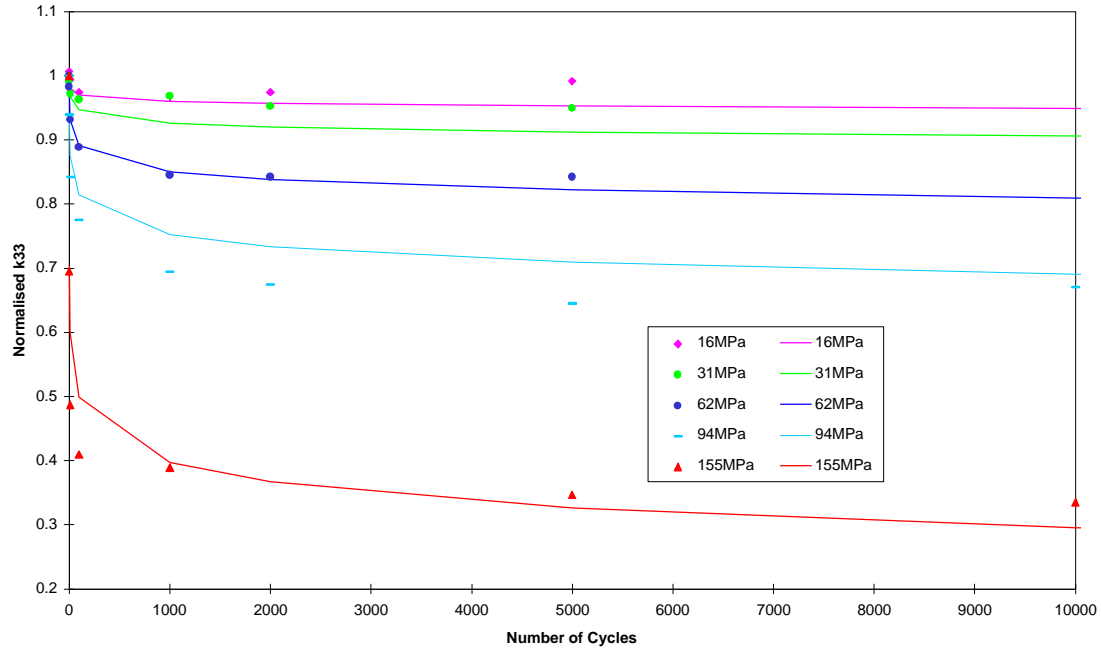
where  $y_0$  and  $K_1$  are the constants from the straight line fit to the data. If this equation for  $k_{1\_cycle}$  is substituted into equation (1) we get an equation of the form

$$k_{\# \text{ of cycles}} = 1 - 10^{(y_0 + \sigma/K_1) - \sigma/K_2 \cdot \log(\text{number of cycles})} \quad (3)$$

where there is now another material constant  $K_2$ , which can be determined from a plot of the slopes of the linear fits for each equation against the stress level. From the results plotted in Figure 4 the values for the constants were determined as  $K_1=90$ ,  $y_0=-2.25$ , and  $K_2=1520$ . The fits based on equation (3) using the constants previously determined are plotted in Figure 8 along with the experimental points. It can be seen that the fit is deficient in several areas, however this is because the equation is attempting to cover a wide range of stresses and cycles, and also there is an inherent material variability in the experimental curves. Obviously covering a narrower range of behaviour would enable better fits to the experimental points. For a design it is sufficient to know whether an intended stress regime will cause maybe greater than 10 percent degradation in properties. The preceding methodology should be able to provide some indication to cover most cases, where at present there is a lack of data.



**Figure 7: Determination of  $K_1$  coefficient by plot of (1- normalised k after 1 cycle) against stress level. Gradient of the straight line fit is  $1/K_1$ .**



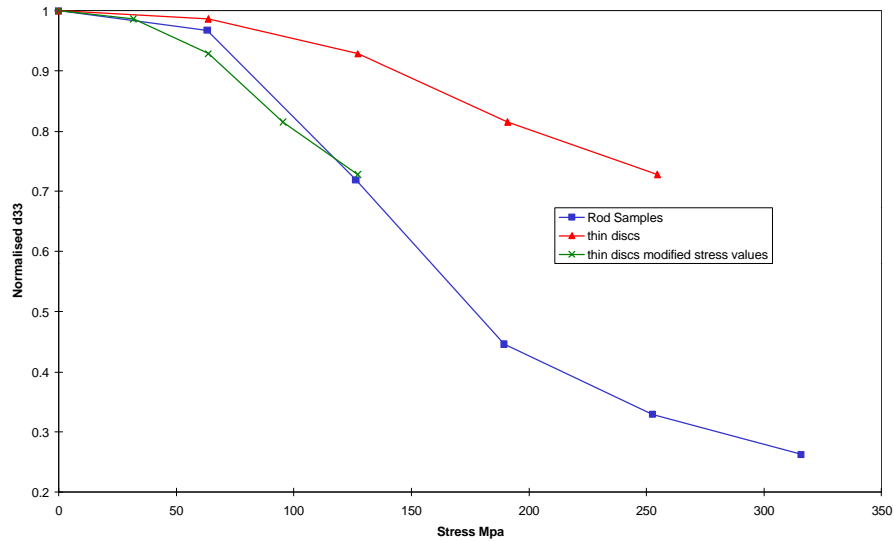
**Figure 8: Experimental points for PZT-5A rods at different stress levels and calculated curves based on equation (3) using the coefficients  $K_1=90$ ,  $y_0=-2.25$ , and  $K_2=1520$ .**

The procedure for determining the empirical fit for degradation has highlighted the importance of the stress level in determining the amount of degradation produced. The largest amount of degradation occurs in the first cycle, and the degradation in subsequent cycles will always decrease. This means that if no measurable degradation occurs in the first cycle at a given stress, it is unlikely that significant degradation will occur until at least  $10^9$  cycles have occurred. Conversely if there is considerable degradation after one cycle there is no need to perform extended tests, i.e. a single cycle test is a quick and simple indicator of degradation behaviour. The model developed so far only predicts behaviour for cycling at a constant stress level, and does not account for a situation where perhaps there are high stress cycles during manufacture or installation, yet a larger number of much lower stress cycles in actual operation. It may be that some form of iterative procedure based on the state before each cycle, and taking the stress level for each cycle into account would be more suitable.

### *Degradation of disc samples*

As previously discussed there was also a need to examine what happened when disc shaped samples were mechanically cycled. Again in order to examine the stress level at which degradation begins to occur, a one cycle experiment is quick and simple. Figure 9 shows what happened after one cycle for a PZT5A disc, along with the results for the rod shaped samples. It appears that much higher stresses are needed to produce degradation in the discs than in the rods. Of course the stress values are based on the applied loads and sample area, and not the actual stress state in the material. If we assume that the stress state in the long samples is uniaxial then it would appear that the applied stress in the flat discs is around half the calculated value. Figure 9 also shows an amended curve for the degradation in the disc where the effective stress has been halved, and it shows a much better agreement with the rod samples. This was also found when the number of cycles was increased, i.e. if the applied stress

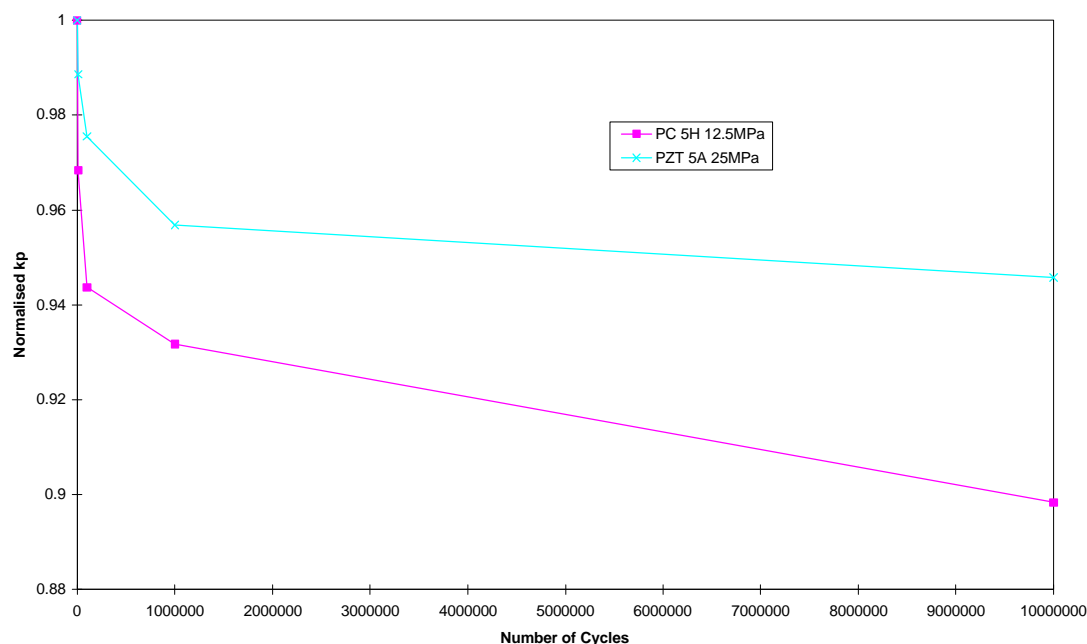
value was halved it gave better agreement with the rod results. This apparent reduction in degradation in disc shaped samples would appear to be beneficial for real world applications as it means the allowable stress range is increased two fold. Obviously the apparent uniaxial stress has been decreased, however the load must still be supported, so extra stresses must be introduced potentially causing degradation in other modes. With the disc samples the  $d_{31}$  can be determined from the radial resonance and this degraded at approximately the same rate as the coupling coefficient. It may simply be that in the flat discs the load is distributed more triaxially thus reducing the levels in any one axis, leading to reduced degradation.



**Figure 9: Effect of 1 cycle comparison of thin disc with rod samples**

A limited number of tests were carried out on PC5H material but only on disc samples. Figure 10 shows a comparison of PC5H against PZT 5A and even though the stress was only half that of the PZT 5A the degradation is much more rapid in PC5H. Using the methodology described previously equation (3) was fitted to the PC5H data and the constants obtained were  $K_1 = 30$ ,  $y_0 = -2.55$ , and  $K_2 = 800$ . Both  $K_1$  and  $K_2$ , which are the stress related coefficients, are much lower than the corresponding values for PZT 5A indicating a much more rapid degradation in PC5H with increasing stress.

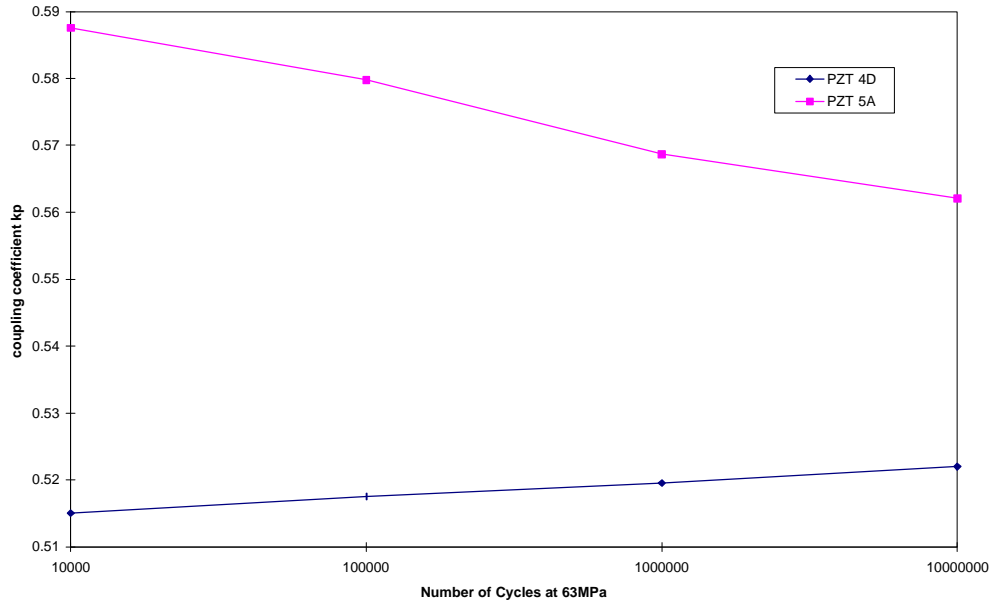




**Figure 10: Comparison mechanical cycling of 10mm diameter 1mm thick discs of PZT-5A at 25MPa and PC5H at 12.5MPa stress.**

### *Degradation in Hard Materials*

Up to now all the materials examined have been soft PZT. However, after the problem with premature failure of the hard materials was cured, some experiments on hard materials were carried out. Initially some cycling on disc shaped specimens were carried out under the same conditions that causes the onset of degradation in soft PC5H materials in order to compare behaviour. Figure 11 shows that there is no detectable degradation for the hard material, and indicates that they are generally more resilient to cyclic loading. In order to get some kind of estimate for the onset of degradation in PC4D materials a series of one cycle experiments were carried out. The outcome of this was that up to stresses of 63MPa no measurable degradation was introduced in 1 cycle, and at stresses of 315MPa there was actually a 10% increase in the  $d_{33}$ . This increase in  $d_{33}$  may have simply been some kind of deaging of aged samples. As Krueger<sup>7</sup> and Belincourt<sup>6</sup> noted, each exposure to stress, temperature or electrical fields begins a new aging cycle. They also noted that hard PZT materials were very sensitive to time under load, but less so to mechanical cycling. For instance maintaining a stress of 100MPa on a hard material for 100 minutes had a greater effect than mechanically cycling for 200 cycles, whereas for soft materials the opposite is true. That time applied rather than level of stress is more important in the hard materials is illustrated by the long recovery time for the DC drifting to settle in the Berlincourt meter after the samples had been exposed to high stress.

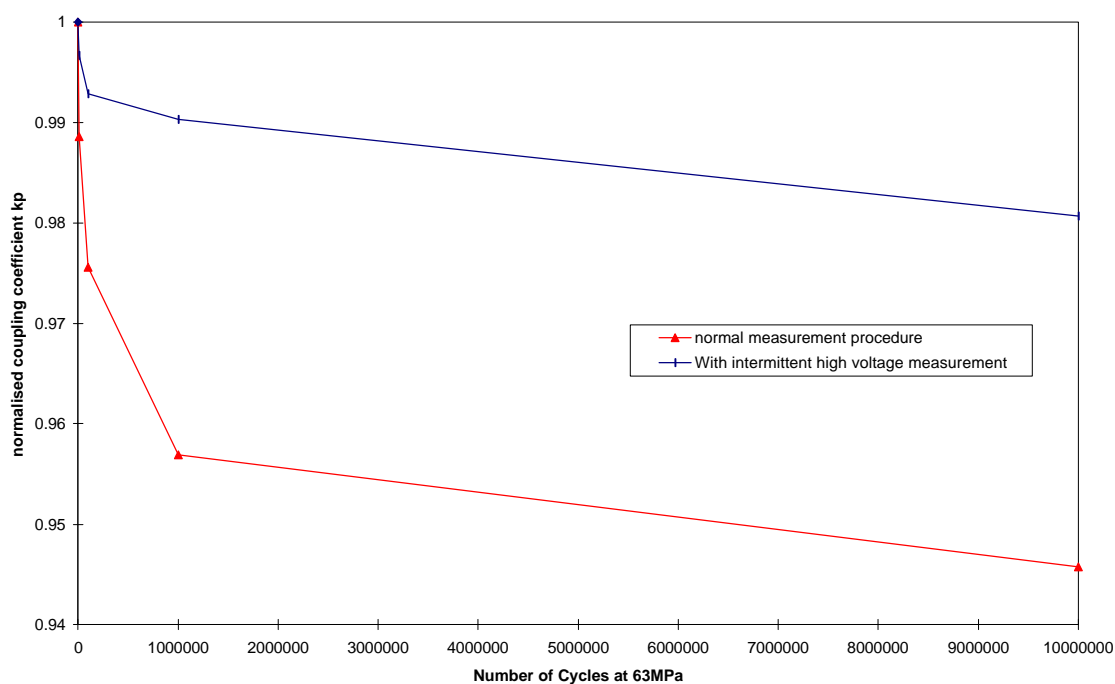


**Figure 11: Change in coupling coefficient  $k_p$  for a PZT 5A material compared with a PZT 4D material both at stress cycling of 63MPa.**

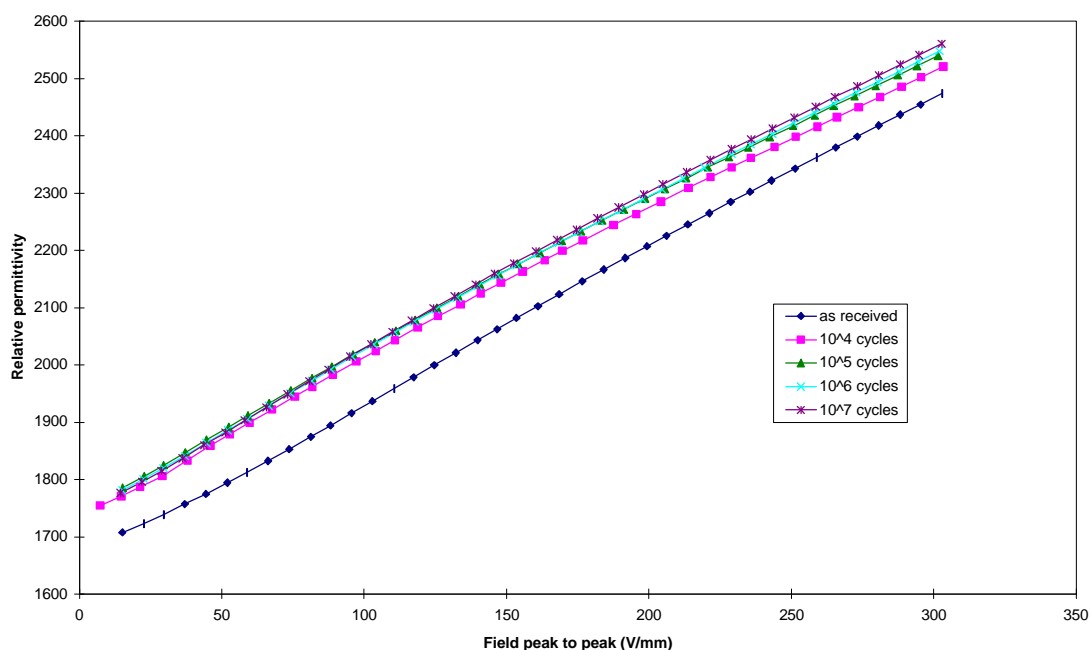
### *High field properties*

So far the assessment of degradation has been by measurement of the low field properties as these are a very sensitive yet relatively simple to measure. In many real applications the piezoelectric performance at high fields is the more important characteristic, so in some experiments the high field capacitance and loss were measured in addition to the resonance spectra. Figure 12 shows two degradation curves for disc samples seeing 25MPa stressing cycles, where for one of the samples the high field capacitance and loss measurements were made additionally.

There is some evidence that introducing this measurement which applies fields up to  $300V_{pp}/mm$  actually reduces the degradation, and the effect on the high field properties similarly is at the least harmless, if not beneficial. Figure 14 shows the high field properties, and it can be seen that the only effect is to make the low field permittivity increase, whilst the slope of the capacitance against loss curve remains unchanged. The samples used in the experiments had been aged for at least six months after poling, and it may be that this increase is just deaging by the application of mechanical and electrical stressing.



**Figure 12: Change in coupling coefficient  $k_p$  for a PZT 5A material, one sample using the normal measurement procedure, and one sample which has undergone high field measurements as well as low field measurements.**



**Figure 13: Changes in high field capacitance with mechanical cycling at 63MPa.**

## Conclusions

Methods for controlled application of cyclic mechanical stressing and the subsequent piezoelectric characterisation have been investigated for a selection of hard and soft PZT

materials. The soft materials are very sensitive to repeated mechanical loading with the softer composition PC 5H showing a greater rate of degradation with increasing stress than PZT 5A. Hard materials do not show degradation with repeated mechanical cycling, but are sensitive to extended periods under constant load.

A logarithmic law has been used to model the degradation behaviour in the soft materials and a methodology for extracting the relevant coefficients has been devised. With this equation, given the material coefficients, it is possible to predict the degradation that will occur under a given stress and number of cycles. A simple method to see the possible effect of mechanical cycling is to perform one cycle, and if measurable degradation occurs then obviously degradation will be a problem, but with two different stress levels an indication of the onset of fatigue at lower stresses can be derived.

## Electrical Fatigue of Piezoelectric Ceramics

### ***Introduction***

Measurement of the electrical properties of electroceramic materials using Impedance Spectroscopy and PE loop methods has been described in a previous report<sup>1</sup>. These methods were shown to provide reliable and robust data when measuring permittivity and dielectric loss as a function of frequency and electrical field for a range of piezoelectric ceramics 1. The aim of the work was to develop measurement good practice for the assessment of the electrical properties of piezoelectric ceramics when driven at high stresses and stress rates.

Permittivity and loss were used as a descriptor of the materials' degradation when measured as a function of elapsed time and electric field. These parameters were measured at the high driving field under which the samples were fatigued, but only for a short duration of time (up to  $10^4$  cycles). An increase in the samples' loss with time was recorded which has been observed by others (see references in Ref. 2).

The work described in this document attempts to guide the reader through the measurement methodology that can successfully be used to determine the degradation in piezoelectric material properties through electrical fatiguing. This report does not have the aim of providing tremendous amounts of fatigue data for a large variety of piezoelectric compositions. Rather, it is aimed at providing a set of robust, 'good practice' measurement guidelines in assessing the fatigue response of these materials.

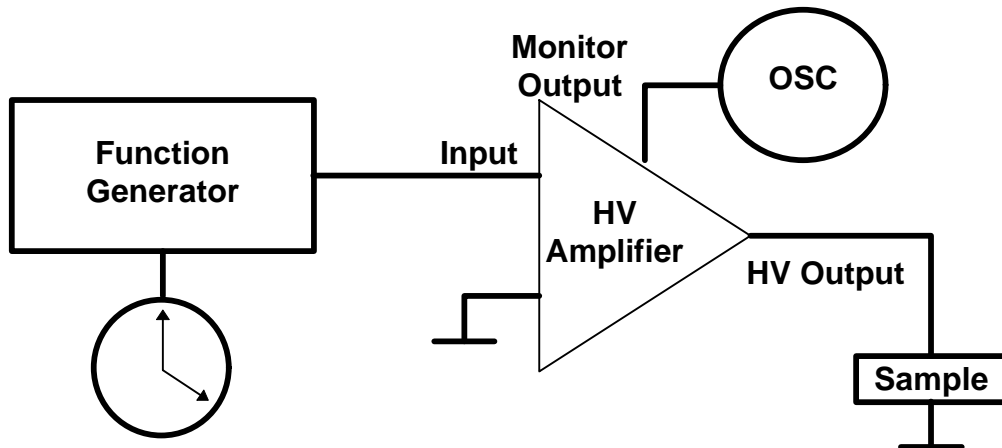
This section of the report is divided up into several parts which deal firstly with the measurement systems used, then describes the experimental checks and calibrations which may be carried out to add further confidence to the measured data and finally to describe the experiments, methodology and interpretation of data.

### ***Measurement Methods***

The measurement methods that will be described include those developed to actually produce the degradation through exposure to high electric field and those developed to actually measure certain dielectric and piezoelectric properties which may be used to assess degradation. Methods have been developed which are able to provide an assessment of fatigue using low field probes and an assessment of fatigue using high field probes. Finally, measurement methods based on Schering Bridge type systems used by our European project partner INSA, Lyon, France, are used to provide additional confidence in these techniques.

### ***Producing Degradation***

Electrical degradation has been introduced into a series of poled, hard and soft composition, PZT piezoelectric materials (PC4D and PC5H) using high voltage amplifiers and function generators<sup>1,2</sup>.

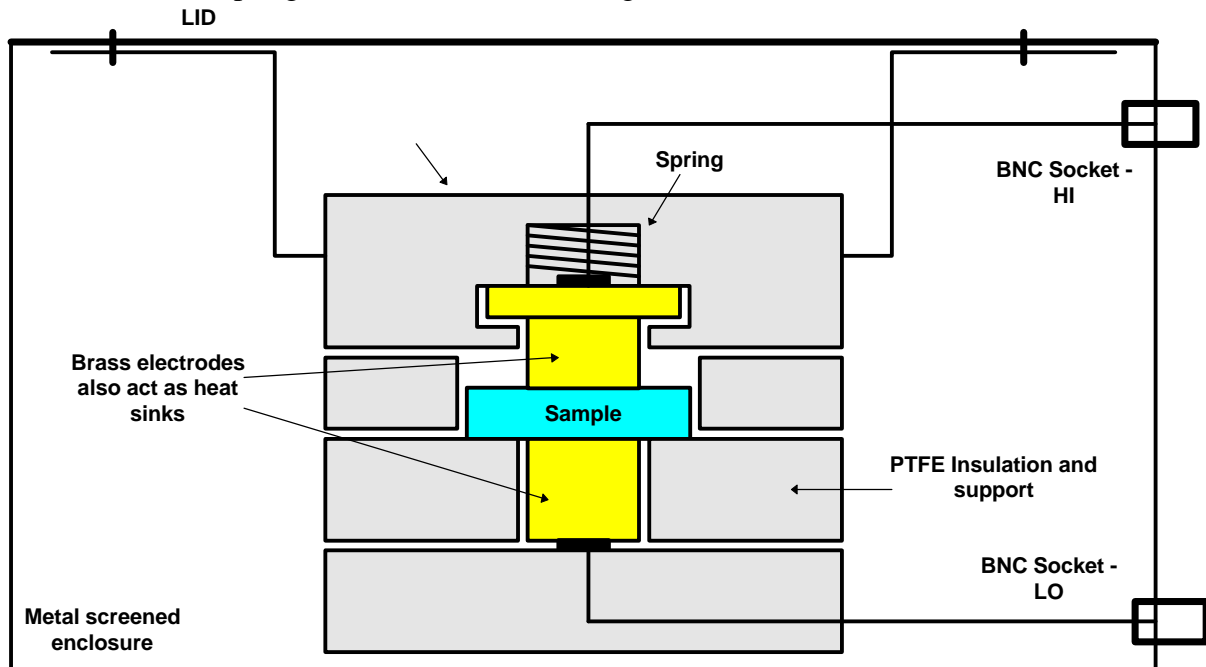


**Figure 14: Schematic showing method of electrically degrading the PZT samples.**

The schematic in Figure 14 represents one way in which to apply the high voltage to the sample. In the case of this work, the details of the generator and amplifier were:

- Function generator: Thurlby-Thandar TG1304 Programmable Function Generator.
- HV Amplifier: TREK 50/750 with  $\pm 750\text{V}$  plug inserted.

The sample is encased within a PTFE-lined closed-metal shell which has high voltage BNC connections and spring loaded brass contacts, Figure 15.



**Figure 15: Sample holder and metal screened enclosure for high voltage and low voltage dielectric testing of disc samples.**

The brass contacts provide adequate electrical conductivity to the silver electroded disks whilst maintaining a convenient heat sink to minimise thermal runaway during electrical stressing. The effect of driving frequency on thermal properties of piezoelectrics has been the subject of a recent piece of work undertaken for NPL, on the CAM7 project, entitled ‘Thermal modelling of ferroelectric ceramics under high electric stress : influence of thermal conditions and frequency on stress dependence’<sup>8</sup>. In this report, differences in dielectric loss and permittivity measured on similar samples but at different frequencies were linked to the changes in temperature experienced within the sample which was thought to be due to dielectric heating of the material. The heat generated is associated with the higher frequency of the applied electric stress and the difference in thermal conditions for the dissipation of heat between the two specimens. The study emphasised the need for precise definition of both the electrical and thermal conditions when making measurements of this kind. One particularly important conclusion is that for many instances of practical applied frequency and voltage a simple heat sink fabricated from thin slabs of brass is sufficient to prevent thermal runaway and to dissipate the heat generated so that loss and permittivity may be recorded at fairly constant temperature (Ref. 2, page 46).

Electrical stressing was accomplished using a sinusoidal signal of adjustable amplitude, measured as an rms value (for compatibility with the Impedance Analyser) and as a peak to peak voltage ( $V_{pp}=2\sqrt{2}V_{rms}$ ). The signal, generated using the Function generator, was applied to the input of the high voltage TREK amplifier and monitored using the TREK’s special Monitor output using an oscilloscope. The HV output signal was then applied to the disk shaped sample. In applying potentially several thousand volts peak to peak per mm to a ceramic disk sample the requirements of safety and electrical discharging or breakdown or even flash-over needs to be considered. The sample environment must be clean and grease free to avoid electrical discharge. The sample must also be cleaned and degreased and then never again handled by direct hand contact. Metal tweezers are useful to handle the sample for two reasons; 1. This avoids contamination by finger grease and moisture and 2. this effectively shorts the sample electrically which is the recommended methodology that should be adopted prior to any dielectric measurement taking place. Safety is always an issue when using high voltages. Suitable HV BNC connections and leads must be used and at the very least safety cages and warning notices must be used. At the frequencies that we have been using (up to 1kHz), it is less important to consider effects such as variable cable impedance and capacitance, which must be considered when working at frequencies of order MHz.

There are various methodologies which can be used when assessing degradation under electrical stressing. The low field dielectric properties may be measured *following* a period of electrical fatigue or high field dielectric properties may be measured *whilst* the material is being electrically fatigued. From work carried out in CAM7 project it is known that the low field and high field dielectric properties are not the same. In real applications, the material properties that will dictate the device’s performance are those associated with the high (driving) field values, clearly. Thus, there is an argument that fatigue measurements must be made at the higher voltages in which the materials will operate under. To meet this requirement we have developed measurement methods to be able to do this in addition to the low field measurements. Both types of measurement scenario will now be described.

### Measurement of low field properties to describe degradation

The material is fatigued in the manner described above and shown schematically in Figure 14. After a suitable time at stress the output from the function generator is disabled and the sample (contained within its enclosure) is taken out of the HV circuit. The sample is then electrically shorted to remove any charge build up (storage of charge arises from the materials capacitance) and placed within the Impedance Analyser circuit - described later. The low field dielectric properties are then measured. The sample and enclosure may then be placed back in the HV circuit and additional electrical stressing cycles applied. This procedure is repeated (with additional complexity described later) for the required number of cycles - in our case up to  $10^8$  cycles.

### Measurement of high field properties to describe degradation

The high field properties (that is the driving field) can also be used as an indication of degradation. In this measurement scenario the sample is contained within its enclosure and connected into a high-voltage-modified Impedance-Analyser circuit. Suitable software can control the timing of measurements and measure the capacitance and loss at the high voltage used to degrade the material. NPL used Solartron based equipment to do this. This equipment has an additional high sensitivity amplifier (called the 1296 dielectric interface) which may be used to measure the permittivity and loss to high levels of precision and through the use of a standard reference capacitor to high degrees of absolute accuracy. However, in these high-voltage experiments it is typically found that the currents flowing through the sample exceed the maximum permitted input current allowed by the interface unit. Thus, the Impedance Analyser *alone* can be used to drive the HV amplifier and to also monitor the capacitance and loss as a function of time. In this case, though, there is not the possibility of using a standard reference capacitor within the circuit and so absolute accuracy is lost. This type of circuit configuration has been described before<sup>1,2</sup> and will be expanded upon in the next sections.

### Degradation Parameters

The electrical driving characteristics applied to all the samples in this study are:

- Sinusoid, 50% duty cycle,  $\pm V_{pp}/2$
- Zero DC offset voltage
- Frequency of 1kHz (limited by the amplifiers output current)
- Amplitude: 200Vr.m.s. and 354Vr.m.s. (566Vpp and 1000Vpp)

The fatigue times were set at logarithmic decades as:

- Virgin, 0 cycles
- $10^4$  cycles
- $10^5$  cycles
- $10^6$  cycles
- $10^7$  cycles
- $10^8$  cycles (maximum time assessed owing to 1kHz drive resulting in approx. 1 full day fatiguing)

The samples were chosen to represent materials commonly used by industry:

- PC4D, hard PZT composition, 1mm thick, 10mm diameter disks, electroded and poled.
- PC5H, soft PZT composition, 1mm thick, 10mm diameter disks, electroded and poled.



### Quality of amplified signal

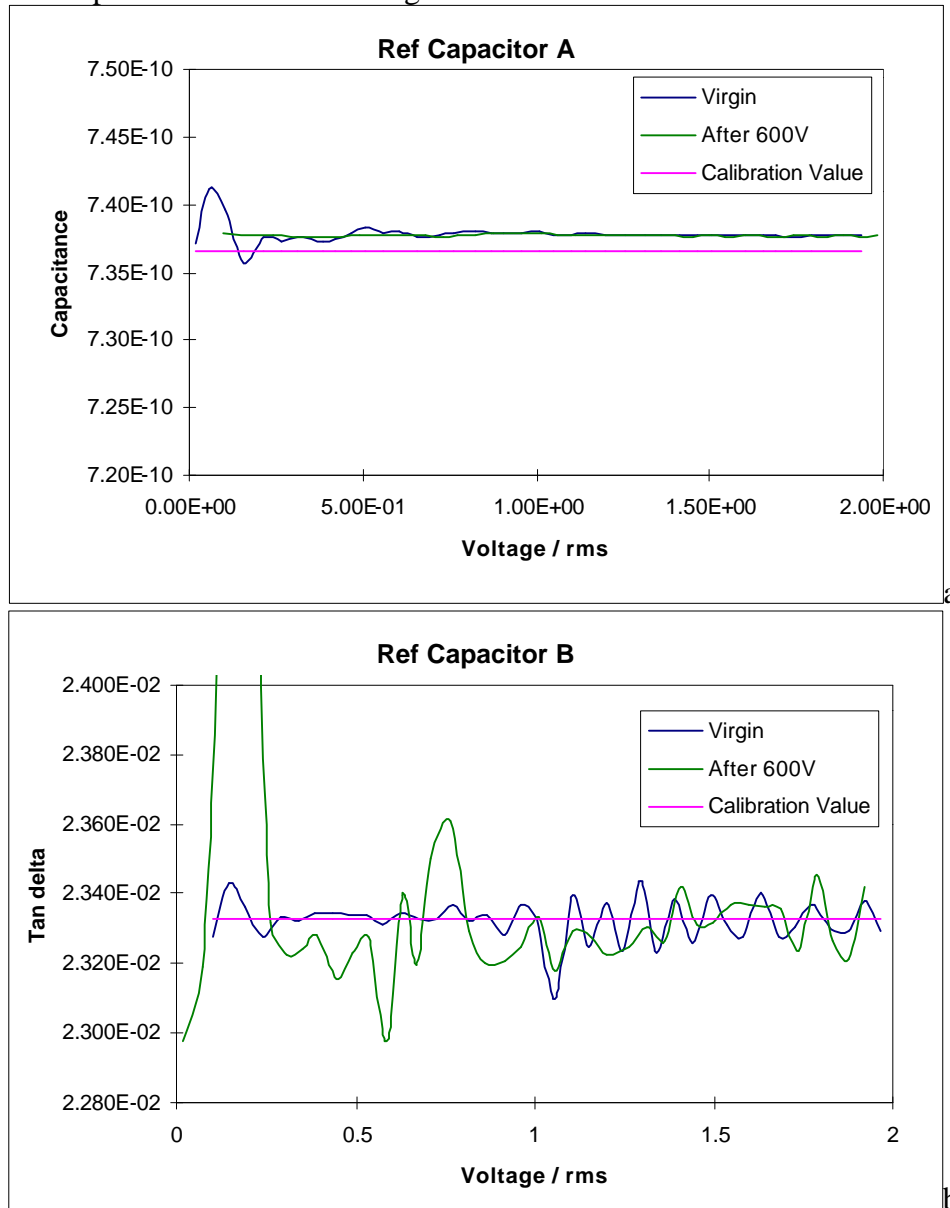
The output from the function generator or the Solartron Impedance Analyser is used as input for the high voltage amplifier. The distortion and linearity for the HV amplifiers are quoted within their own datasheets or manuals. One of the more important factors when assessing the experimental set-up is the quality of the HV signal that is actually applied to the sample. Most HV amplifiers have a 'Monitor' output which is simply an attenuated voltage taken off typically a linear resistor chain voltage divider from the HV amplifiers HV output. This signal may be viewed on an oscilloscope to provide a qualitative verification that the correct voltage and correct form of signal is applied to the sample. In many instances it will be found that, due to the excessive current requirements afforded by material impedance, frequency and voltage, the HV amplifiers maximum rated current is exceeded. In this instance, the voltage that appears on the HV output (and hence the Monitor output) is reduced. An additional complication arises due to the non-linear nature of piezoelectric materials. Since the piezo sample is now a part of the HV circuit, it is possible that its response may affect the amplifier characteristics. At the very least, the monitor output should be checked for voltage (taking into account the amplification - or attenuation - level stated by the amplifier manufacturer) and signal form.

### Calibration of Measurement Systems

Before any serious experiments are undertaken it is very important that the experimental set-up chosen to monitor degradation be carefully checked and if necessary calibrated. At NPL a standard reference capacitor artefact has been constructed to carry out this task. High field and low field measurements can be validated as well as any frequency dispersive relationships which may exist within the set-up. The standard reference capacitors are based on highly linear high-voltage polypropylene capacitors (available from RS Components) connected in series and parallel to afford the correct capacitance and voltage required. The soldered components may also incorporate fixed values of resistance in either parallel or series arrangement to be able to provide a standard with fixed and known capacitance and loss (RC circuit). The reference constructed at NPL contains one circuit of fixed capacitance (approximately equal in capacitance to the 1mm thick PZT samples) and one circuit of similar capacitance but with a parallel R element such that its loss at 1kHz is approximately equal to that of a 1mm thick soft composition PZT material. This equating of values is important for various reasons. Specifically related to the Solartron systems, equating a reference value to the samples value means that when the system measures both sample and reference no change in its internal sensing amplification occurs thus minimising errors associated with a change in the internal sensing amplifier characteristics.

The standard reference capacitor was calibrated using a HP4194A impedance analyser and Gen Rad transformer ratio arm bridge (calibrated traceably to national standards), at 1kHz and 10kHz and 100mV, 300mV and 1000mV r.m.s. applied field. The reference standard was left to equilibrate for 2 hours at room temperature before any measurements were made. Repeat measurements were taken over a period of two days using these two measurement methods. Regression analysis of 98% was calculated from the spread in results. The standard reference capacitor box was then checked for linearity at high electrical field, using the Solartron 1260 Impedance Analyser and the TREK high voltage 50/750 amplifier. The graphs in Figure 16 show that the capacitance and loss is unchanged after a field of 600Vpp at 1kHz is applied to the standards for a duration of 10 minutes. Additional tests ensure that the capacitance and loss do not change with driving field up to the maximum that will be used in the experiments. When

measurements are made on real piezo samples and then compared to this standard our level of confidence in the data is enhanced since any non-linearity in the sample data may be ascribed solely to the sample and not the measuring method.



**Figure 16: Standard reference capacitor a) Capacitor A showing capacitance vs low field drive and b) Capacitor B showing loss tangent vs low field drive.**

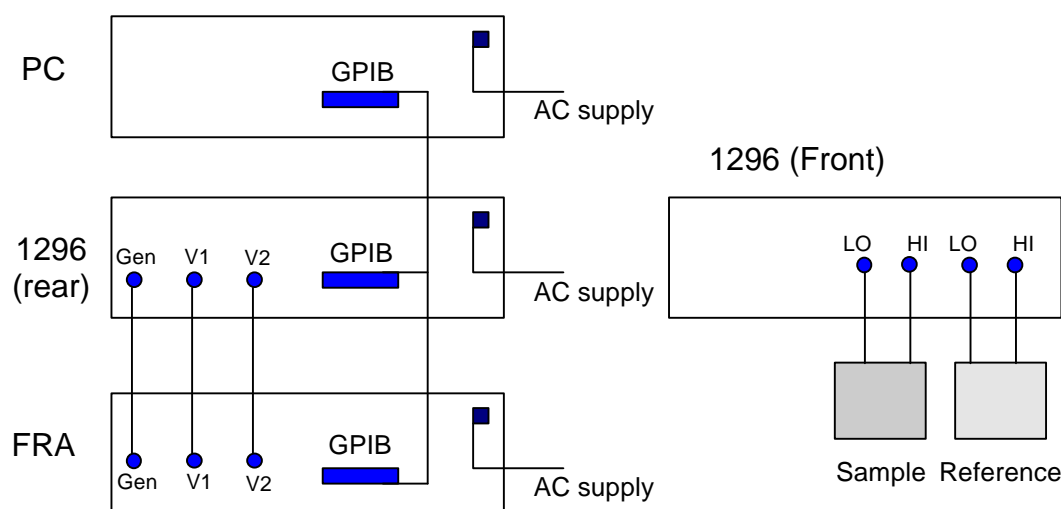
A similar standard reference capacitor was provided by Solartron with the 1296 dielectric interface unit. This has been calibrated by Solartron, but is only rated for use at low voltages. This reference was also used for many of the measurements.

### Impedance Spectroscopy - Monitoring of Degradation

As described in previous NPL reports (CMMT(A) 98 and 116), permittivity and loss may be measured at various frequencies and fields using an impedance analyser and associated high sensitivity dielectric interface unit. This system is able to automatically measure the dielectric

current, voltage and phase across the sample and compare this to the identical drive through either an internal or (in this case) an external standard reference capacitor, as described above. The reference measurement is used to eliminate the effects of extraneous capacitance and loss, since the absolute values of phase ( $\tan \delta$ ) which are measured will be affected by the connection cables and interfaces. Additionally, corrections for phase shifts introduced by the high voltage amplifier will need to be made for measurements made at high voltage. However, for measurements made at high voltage the maximum permitted input current of the 1296 is exceeded and so this unit can not be used. Operation of the 1260 alone precludes the use of a reference standard and so phase differences and cable impedance etc. is not eliminated in the dielectric measurements. This is a particular problem when measuring the loss from hard materials which possess losses of order  $<1\%$ .

The system that has been used to make the dielectric measurements at low signal voltage includes the 1260 Solartron Impedance Analyser and its 1296 Dielectric Interface Unit, Figure 17.



**Figure 17: Standard configuration (low voltage) dielectric interface measuring equipment for electrical fatigue measurements**

The system adopted to enable the application of high drive voltages, taken directly from the Solartron 1296 manual, shows how a reduced ‘monitor’ voltage may be taken from the main HV drive output of the amplifier, Figure 18. In most cases, HV amplifiers have this ‘Monitor’ signal available as a BNC output which can be used in this application circuit. Monitoring the attenuated output using a ‘scope is considered good practice especially when the system is being commissioned. The 1296 software enables various sweeps of frequency, time, temperature, AC and DC voltage to be applied to the sample (via the HV amplifier) whilst holding some parameters fixed. In these experiments where the degradation was measured using the 1296 option (low voltage measurement), the following procedure was used:

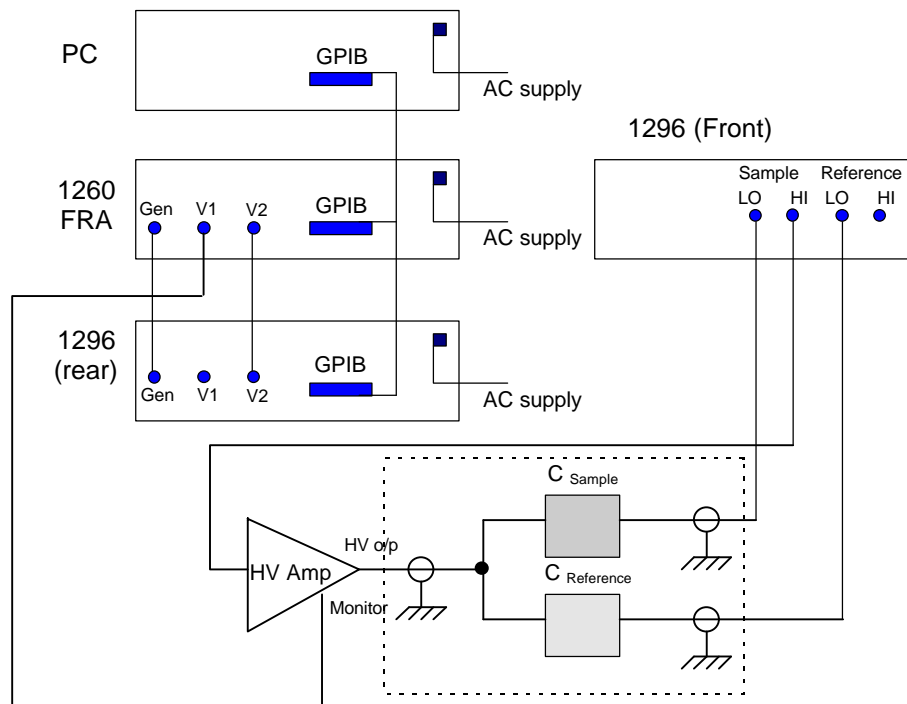
1. The sample was cleaned and its silvered electrodes shorted together.
2. Dielectric capacitance and loss were measured on virgin (but aged) samples using:
  - HP4192 LCR meter
  - Solartron 1260 + Solartron 1296 system set up as Figure 17.
  - The sample was then placed back in the HP4192 and a resonance scan was made from approx. 80kHz to 800kHz. This spectra was then analysed using the PRAP software (version 2.1) described in the Mechanical Fatigue section of this report. Parameters that can be used to monitor fatigue include resonant frequencies, loss,

- permittivity, coupling factors, piezoelectric coefficient  $d_{31}$  (radial mode analysis permits only  $d_{31}$  calculations), elastic strain tensor and many others.
3. The sample was then placed within its fatiguing enclosure. The HV BNC connections were made according to Figure 14, and the Function generator output enabled for a predetermined time - number of cycles = frequency (Hz) x time (s).
  4. The Function generator output was disabled, and the sample was taken out of the HV circuit but left in its enclosure. The BNC connections were then shorted together.
  5. The fatigued sample was measured using the 1260/1296 system. Capacitance and loss were measured at least twice, and their average values recorded.
  6. The sample was taken out of its enclosure and measured using PRAP on the HP4192.
  7. The sample was returned to its enclosure and reinserted into the HV fatiguing set-up ready for the next set of cycles.

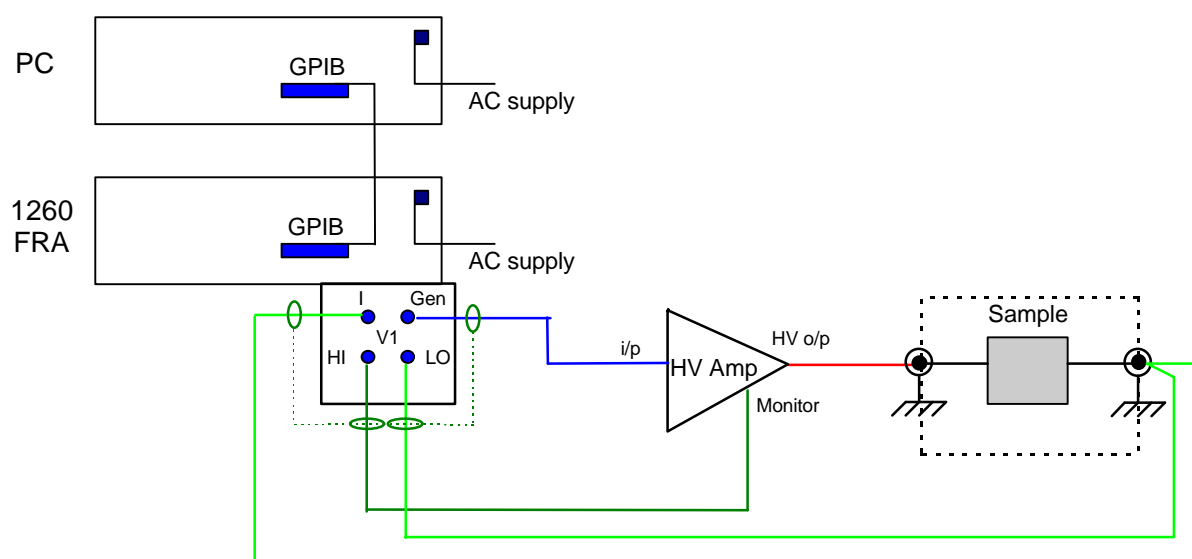
This procedure (3-7) was repeated as many times as necessary. The data was analysed and recorded graphically. The best indicators of degradation were determined from the large amount of information that the PRAP and dielectric measurements provide.

The second method of measuring degradation is based on the simultaneous electrical fatiguing and measurement of dielectric properties afforded through the use of the HV amplifier coupled into the Solartron 1260/1296 or Solartron 1260 stand-alone circuit configuration. The dielectric properties are then measured at high electrical stress. A disadvantage of this technique is that the sample is not removed from the fatiguing set-up to enable its resonance spectra to be made. However, the fact that the sample is never removed from its fatiguing stress is perhaps more representative of real-life applications.

The circuit used for these measurements is shown in Figure 18, for the combined 1260/1296 reference method and Figure 19 for the stand alone (non reference) 1260 method.



**Figure 18: High AC Voltage 1260/1296 configuration dielectric interface measuring equipment for electrical fatigue measurements**



**Figure 19: High AC Voltage 1260 configuration measuring equipment for electrical fatigue measurements**

The operation of the Solartron 1260 in stand alone mode, Figure 20, is in DC coupled, floating earth, differential input. This is why the BNC outer earth shells must be connected at one point - preferably on the sample enclosure, but also can be made on the 1260 front panel, as shown in the diagram.

There is some confusion in the literature concerning the terms fatigue and ageing. In this report we have used the term degradation to describe changes in properties brought about by an imposed mechanical or electrical stressing condition. The effects of ageing, or recovery through ageing has been observed in many instances as a reversion of degraded parameters back to values approaching the 'virgin' or 'before degradation' experiments. This has been observed during this programme of work and also in experiments conducted by our EC Actuate partners at INSA, Lyon, France. In the following sections the main experimental results will be summarised and compared to parallel experiments conducted at INSA. INSA also conducted fatiguing experiments under conditions of static applied mechanical stress. This more truly represents the conditions applicable to the real use of these materials.

### General Guidelines

There is some very important general guidance that should be considered when carrying out tests of this type. This is because of the inherent non-linear nature of ferroelectric and piezoelectric materials. It is often quite easy to accept data as valid materials property rather than an artefact of the experimental method or measurement set-up. Much time can be spent in endeavouring to piece together some reasoned explanation of how the data behaves based on piezoelectric theory where in essence the data has been distorted by the action of a complex experiment where parameters are not independent and due consideration has not been given to the interrelationships between them.

In fatigue type experiments it is vital to know;

- that the voltage and waveform that you think is being applied to the sample is actually present between its electrodes
- that the analyser is basing its calculations of permittivity and loss from its measurements of current, voltage and phase angle on robust principles and sound algorithms
- that the measurements are made at constant temperature and that temperature is controlled in some way to prevent thermal runaway
- that preload or static stresses are thoroughly assessed since the effect of preload on degradation is quite profound, as will be seen later
- that a well characterised calibrated capacitor is used within the experimental methodology to minimise uncertainties and that the experimental method adopted is precisely followed for each measurement.

### **Electrical Degradation Results**

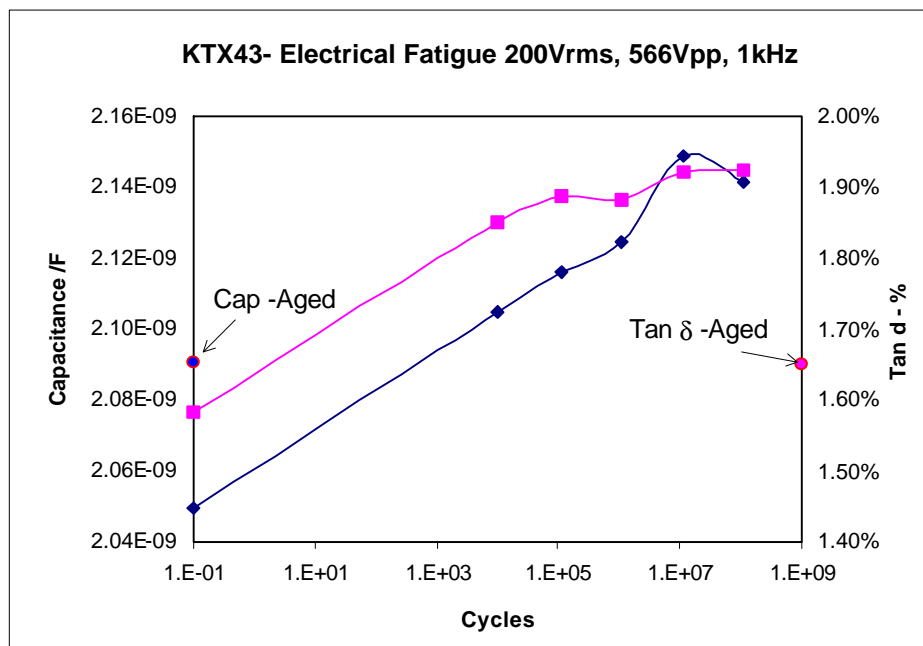
Piezoelectric disc samples have been subjected to various forms of electrical stressing. The monitoring of the change in properties has been carried out using Impedance Analysis and Resonance Analysis, described earlier. The table shows the material types and the electrical stressing that they have experienced. The results will follow this table and are split into materials types.

<b>Material Type</b>	<b>Max. Electrical Stress <math>V_{pp}</math></b>	<b>Max. number of cycles (at 1kHz)</b>	<b>Measured Parameters</b>	<b>Mechanical Stress</b>
PC5H 1mm thick x 10mm disc	566, 1000	$10^8$	C, $\tan\delta$ , $K_p$ , $f_s$ , $d_{31}$ ,	None
PC4D 1mm thick x 10mm disc	566	$10^8$	C, $\tan\delta$ , $K_p$ , $f_s$ , $d_{31}$ ,	None
PZT5A* 15mm thick x 6.25mm rods	566	$10^7$	C, $\tan\delta$ , $K_p$ , $f_s$ , $d_{31}$ ,	32MPa
PZT4D* 15mm thick x 6.25mm rods	566	$10^7$	C, $\tan\delta$ , $K_p$ , $f_s$ , $d_{31}$ ,	32MPa

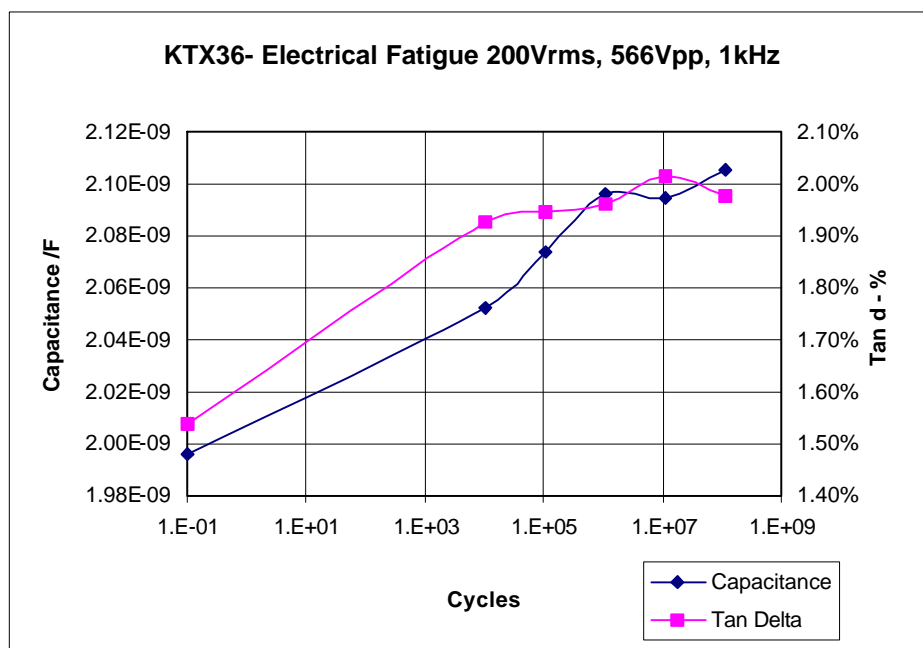
**Table 1: Experimental summary of electrical fatigue. \* denotes material tested solely at INSA, France.**

### **Electrical Fatigue of soft materials**

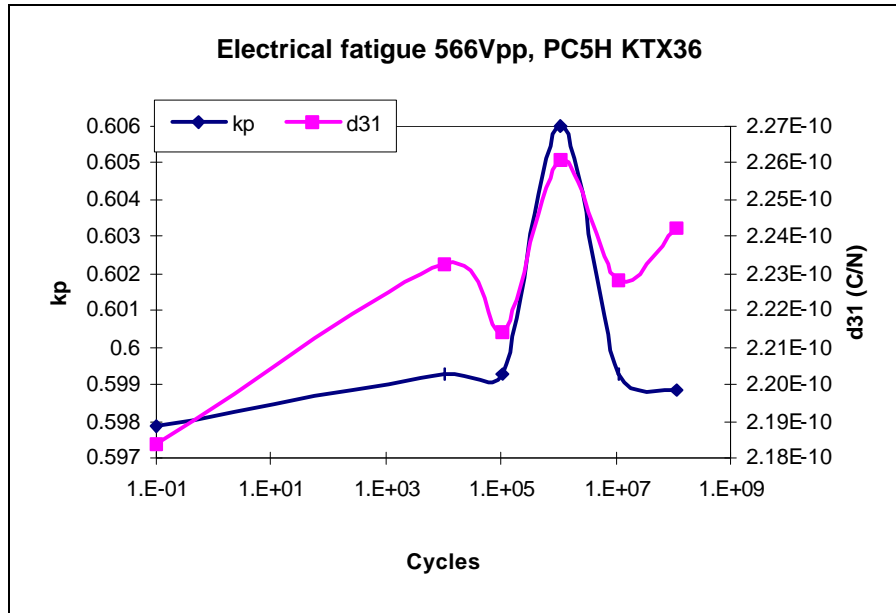
Application of an electric field of 200Vrms (566Vpp) across a 1mm thick PC5H sample over a period of many cycles causes the material to exhibit changes in capacitance and loss, Figure 20. As expected from the literature and parallel work in the EC-funded Actuate project, the capacitance rises with number of cycles as does its loss tangent. Unusual anomalies in the capacitance and loss between  $10^6$  -  $10^7$  cycles are evident. This has been observed before<sup>9</sup> and its origins are not well understood. Another sample of PC5H material exhibits a similar response, Figure 21 and Figure 22.



**Figure 20: Electrical fatigue of a PC5H material.**



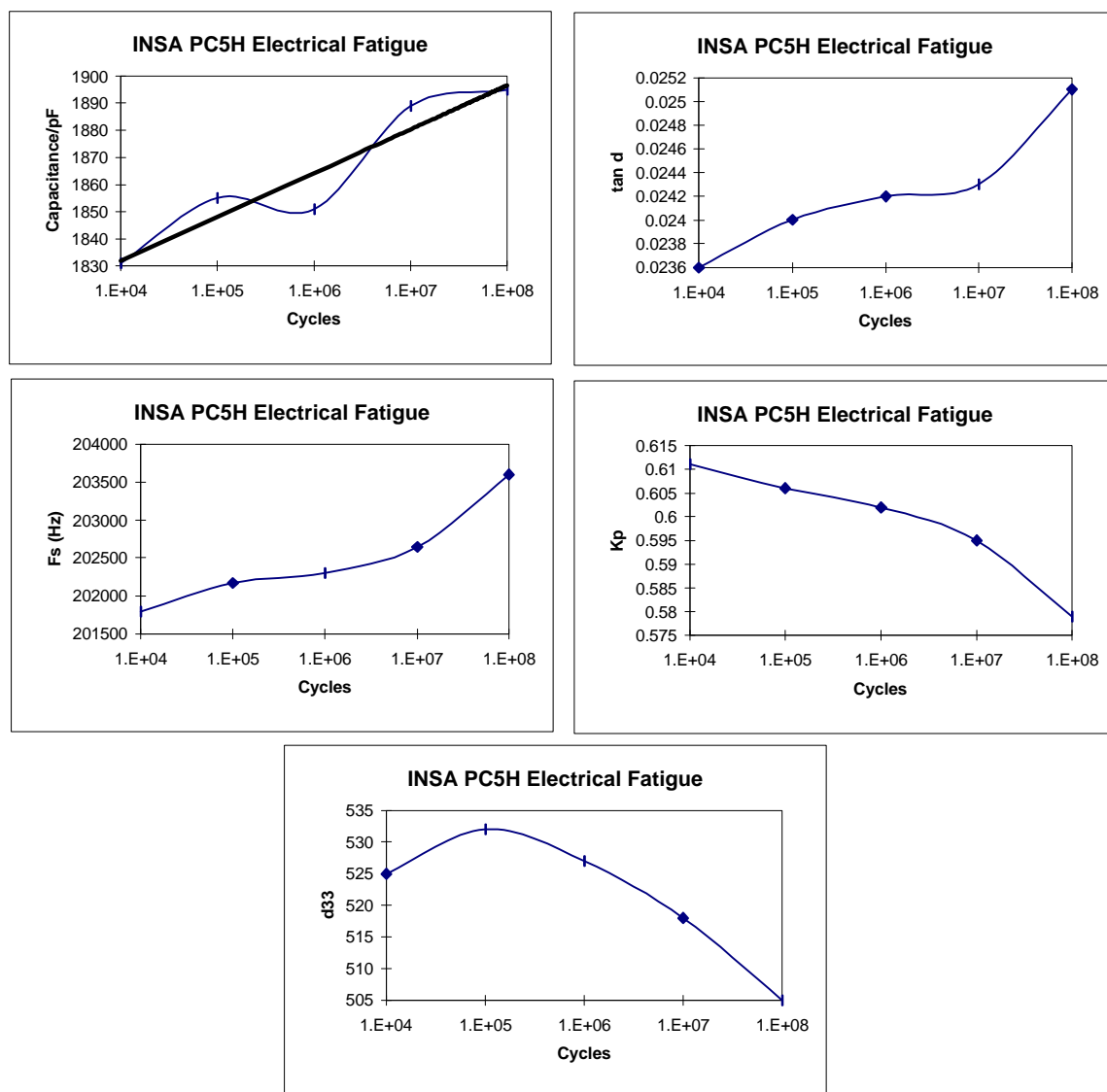
**Figure 21: Electrical fatigue of another PC5H material.**



**Figure 22: Electrical fatigue of PC5H at 566V<sub>pp</sub> drive. Resonance analysis calculates large increase at  $10^5$  cycles followed by drop in  $k_p$  and  $d_{31}$  after approx.  $10^6$  cycles.**

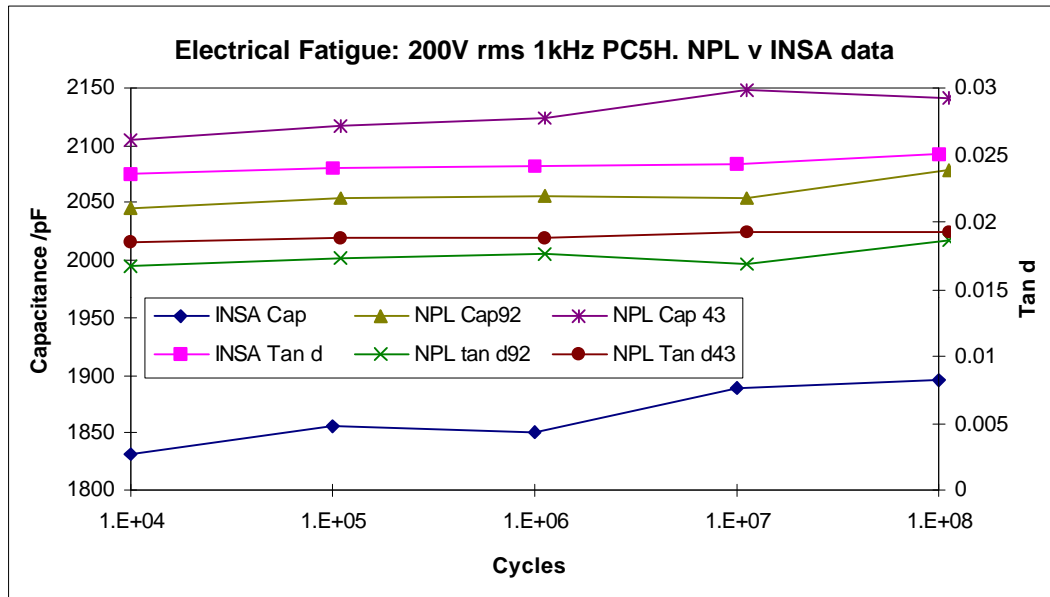
The data obtained by INSA shows very similar behaviour, Figure 23. In this series of graphs the resonance information is included with plots of  $k_p$ ,  $f_s$  and  $d_{33}$  vs cycles showing a variation expected from a reduced domain wall contribution to the materials activity, perhaps through increased domain pinning obstacles such as grain and domain boundaries. The INSA data show capacitance and loss both increasing with number of cycles, again as expected. Interestingly, measurements taken two days following the completion of their fatigue experiments, showed that for PC5H material the values of capacitance and loss did not fully 'recover' to their original values - as witnessed for other material types. This would seem to indicate that the PC5H material had exhibited some permanent depolarisation as a direct result of the electrical stressing.





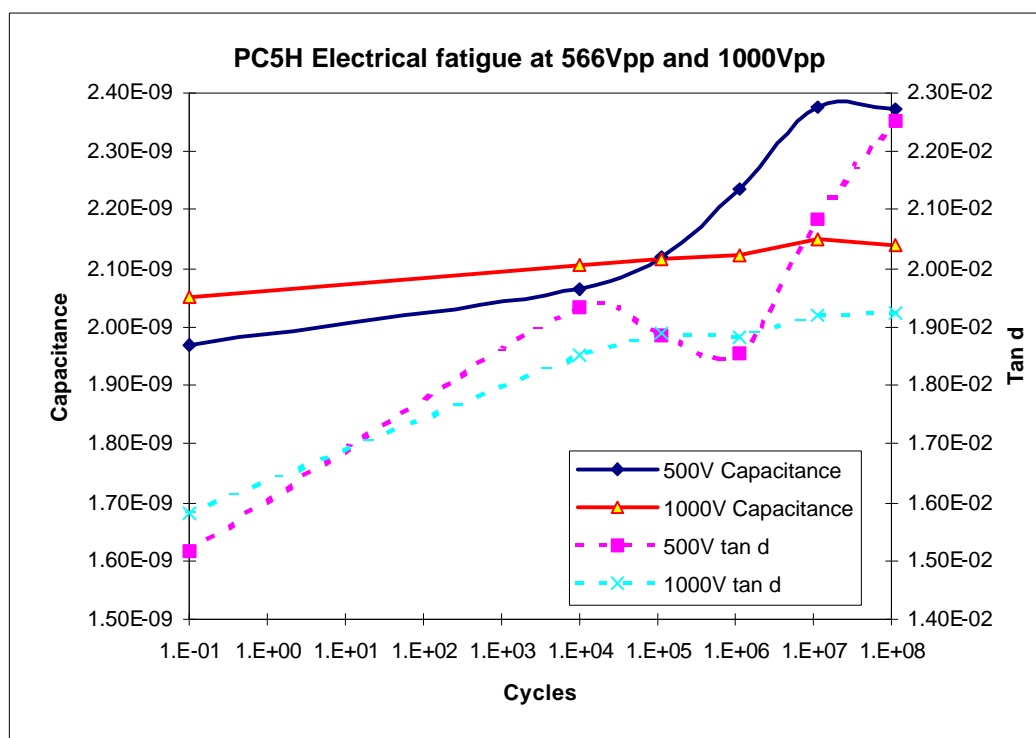
**Figure 23: INSA measured electrical fatigue on PC5H soft material at applied electric field of 200Vrms, at 1kHz.**

Comparisons between NPL and INSA data, Figure 24, shows that for a sample of 3 pieces (from the same batch of material) of PC5H, the variation and change in capacitance and loss tangent follows quite similar behaviour up to  $10^8$  cycles.

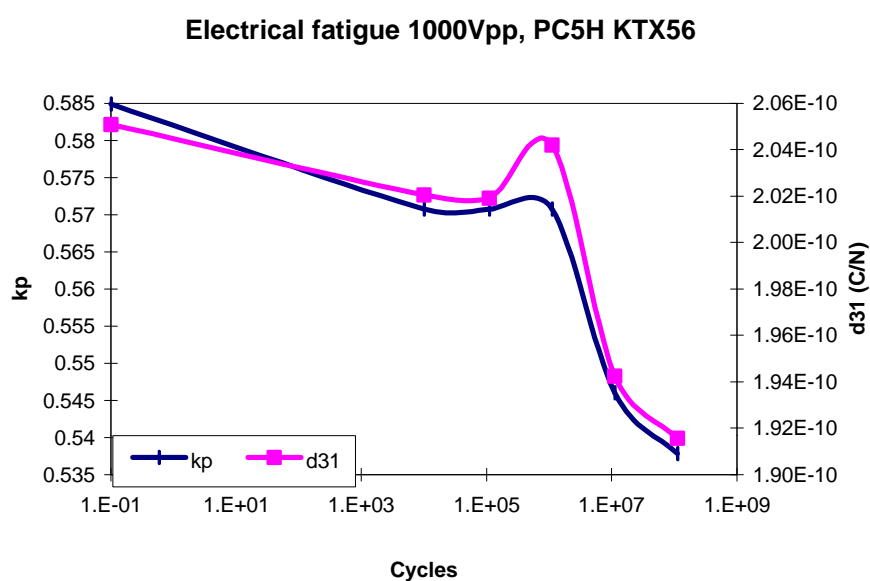


**Figure 24: NPL and INSA data for PC5H combined on one graph, shows that the behaviour is quite reproducible.**

Electrical fatigue at higher electric fields produces a similar but surprisingly less dramatic effect. Figure 25 superimposes data obtained at 566V<sub>pp</sub> (described above) with that obtained on a sample of the same batch fatigued at 1000V<sub>pp</sub>. It is clear that the same transitions in capacitance and loss occurs at approximately the same cycle times. A corresponding reduction in coupling coefficient and piezoelectric coefficient occurs around 10M cycles, with an apparent increase at around 1M cycles, Figure 26. This behaviour is not well understood but may arise from an initial increase in the materials polarisation as the alternating field preferentially aligns domains which would act to enhance piezoelectric activity. Once this has been optimised then domain wall motion may become hindered through a gradual build up in pinning sites such as domain boundaries and grain boundaries.



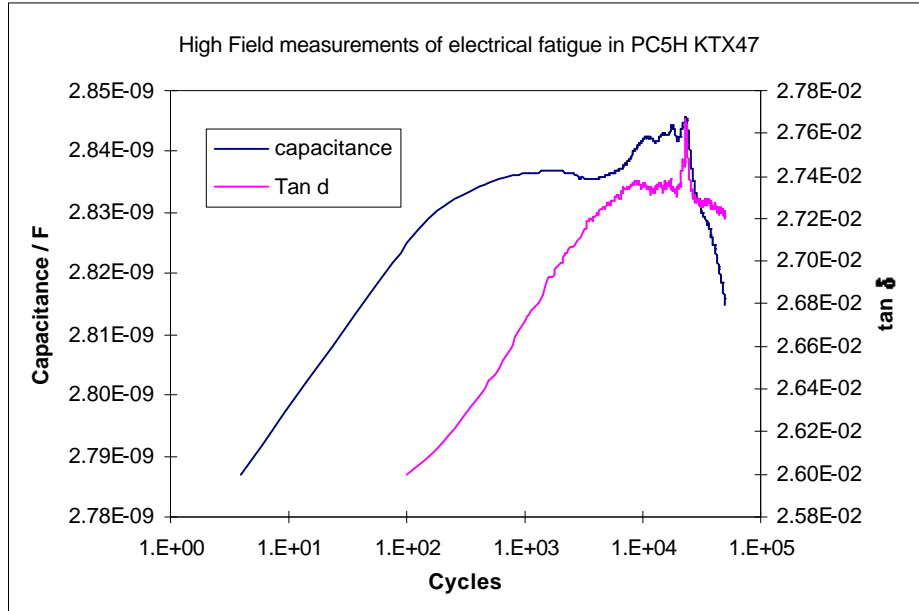
**Figure 25: Changing the electrical drive has some effect on the magnitude of degradation but overall the effects are comparable.**



**Figure 26: Electrical fatigue of PC5H at 1000Vpp drive. Resonance analysis calculates drop in  $k_p$  and  $d_{31}$  after approx.  $10^6$  cycles.**

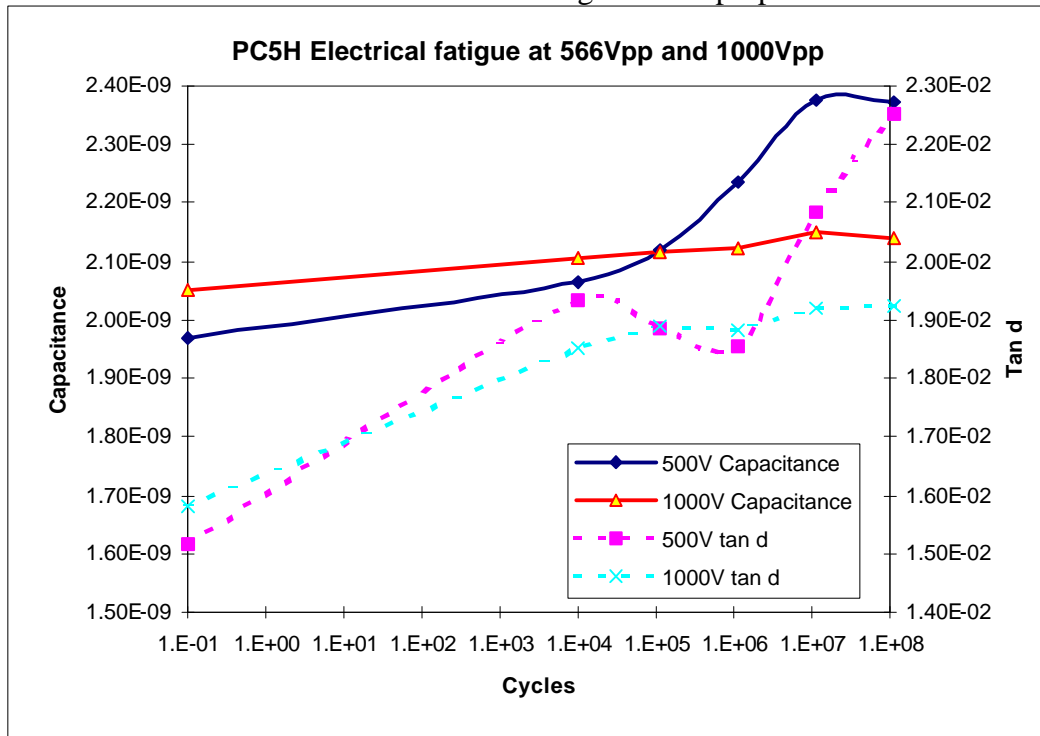
The second method of assessing degradation is to measure the dielectric properties at the electric stress used for the fatigue. This methodology has many benefits since the performance of actuators measured at high (operational) stress differs from that measured at low field - see

NPL report CMMT(A)98 and 116. Thus a soft PC5H material has been fatigued at 200Vrms (566V<sub>pp</sub>) at 1kHz using the Solartron 1260 set up described in Figure 19, whilst its dielectric properties, capacitance and loss tangent are simultaneously measured at 566V<sub>pp</sub>. Due to an instrumental issue data only up to 10<sup>5</sup> cycles were recorded, Figure 27.



**Figure 27: High field measurements of fatigue in a soft PC5H material.**

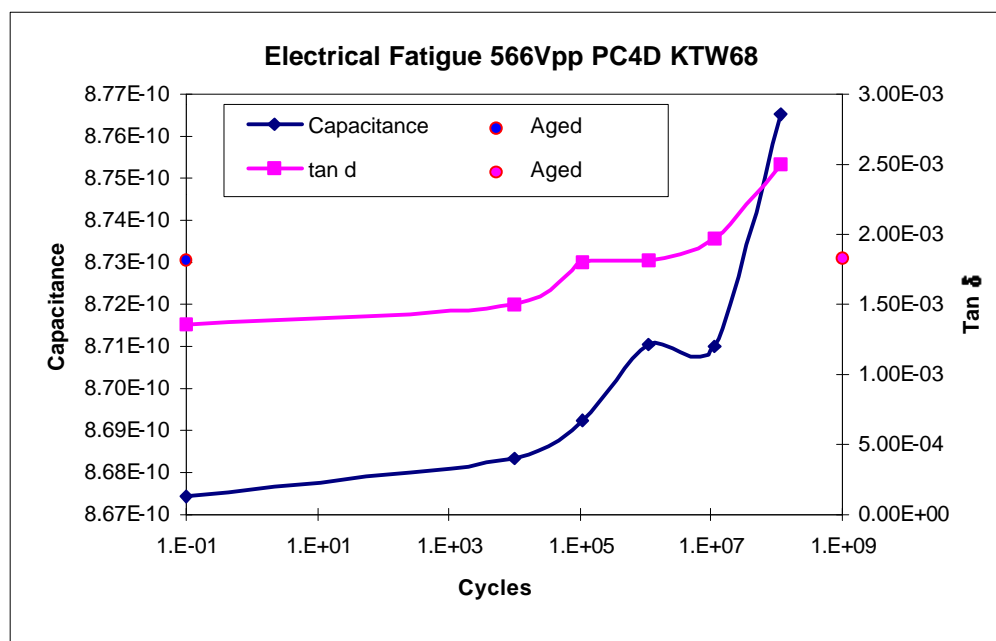
As expected the loss and capacitance increase as the material is fatigued. Various anomalies exist and the values of loss and capacitance start to decrease after approximately 5E4 cycles. This is also observed when measuring these properties at low stress, refer to



**Figure 25. Additional cycles are required to determine the degradation for long exposure times.**

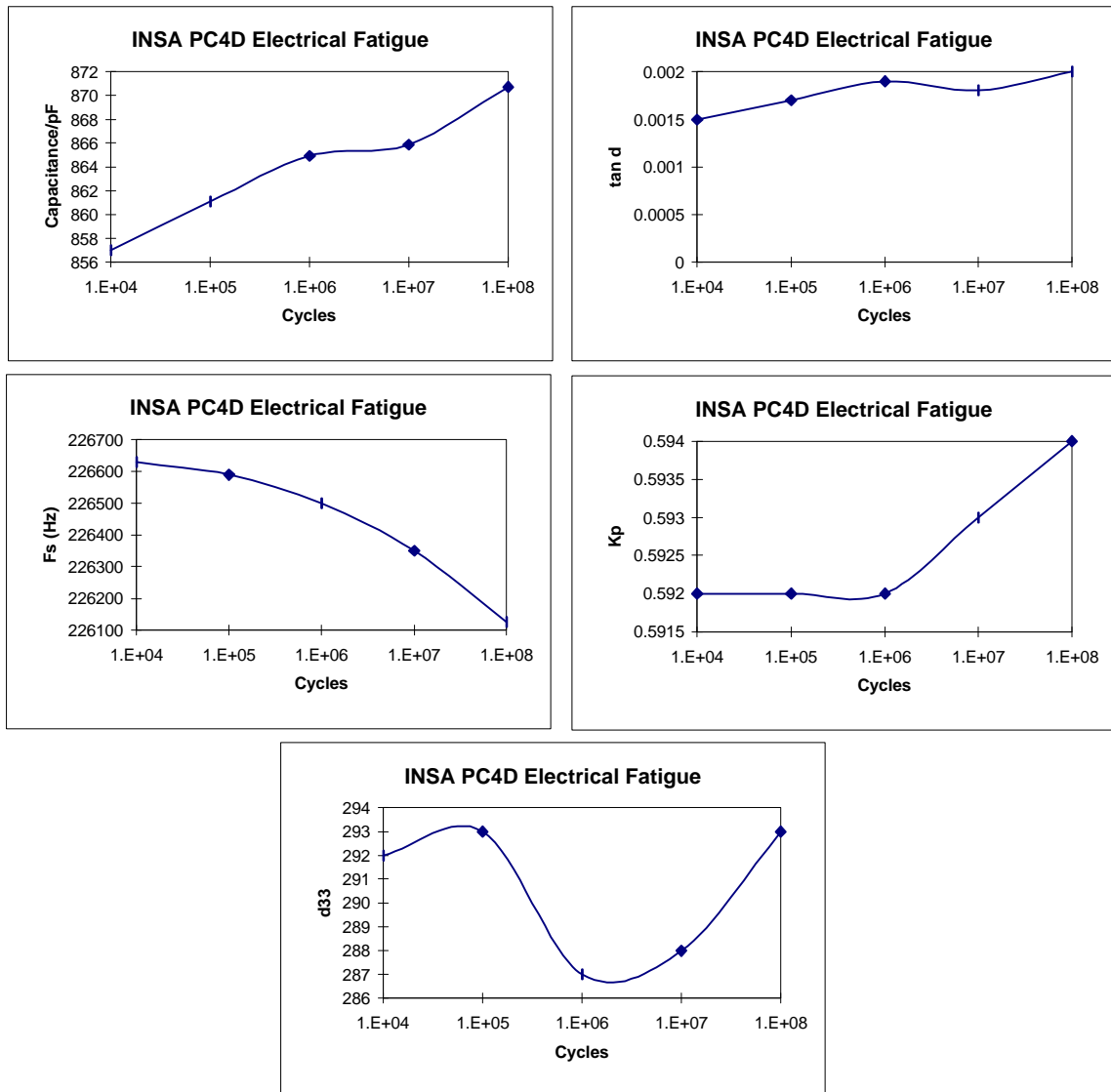
## Electrical Fatigue of hard materials

An identical series of experiments has revealed that the degradation exhibited by hard composition materials follows a similar pattern of behaviour, that is an increase in permittivity and loss and a corresponding decrease in coupling factor and piezoelectric coefficient. The absolute changes however are much reduced, although the measurement methods are sensitive enough for these differences to be determined. Figure 28 shows the change in  $C$  and  $\tan \delta$  with cycles for a PC4D composition cycled at 1kHz up to  $10^8$  cycles at 566V<sub>pp</sub> driving field. These measurements are all low field probes.



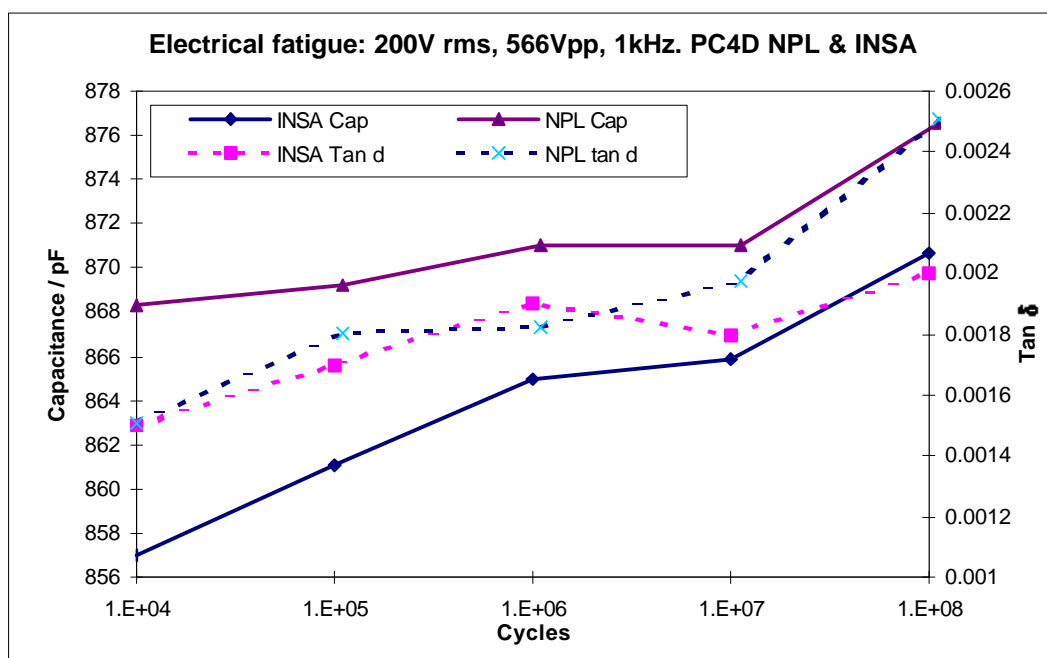
**Figure 28: Dielectric property changes with fatigue cycles for hard composition PC4D.**

Data obtained at INSA exhibited very similar trends with capacitance and loss increasing with the same inflexions in magnitude at around 1M cycles, Figure 29. The resonance data shows strikingly different behaviour to that observed for soft materials. Both  $k_p$  and  $d_{33}$  increase in value after a small drop to around 1M cycles. This was not observed in mechanical cycling measurements, reported earlier. This increase in piezoelectric activity may have origins in a development of an enhanced polarisation due to the effects of cyclically partially poling and depoling the material.



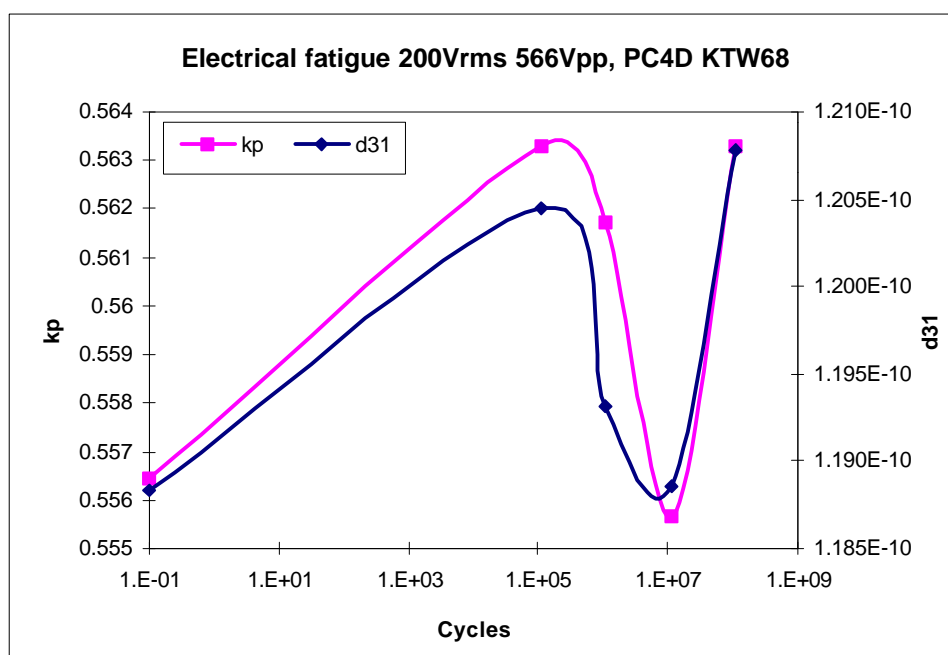
**Figure 29: INSA measured electrical fatigue on PC4D hard material at applied electric field of 200Vrms, at 1kHz.**

A comparison between data obtained at NPL and that obtained at INSA is shown in Figure 30. Similar, although not totally identical, trends in the variation of capacitance and loss with cycles are observed.



**Figure 30: NPL and INSA data for PC4D combined on one graph, shows that the behaviour is quite reproducible.**

Results from measurements of resonance spectra on the sample fatigued at NPL also exhibit increases in piezoelectric activity,  $k_p$  and  $d_{31}$  most notably, Figure 31.



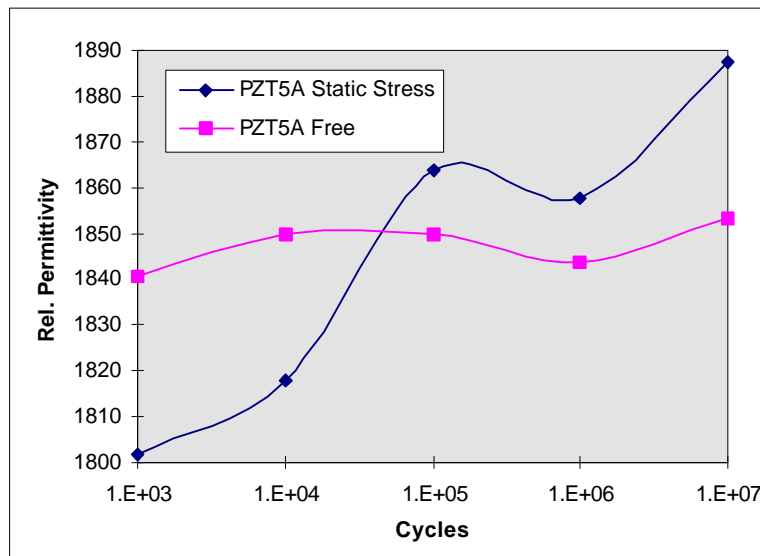
**Figure 31: Coupling coefficient and piezoelectric coefficient  $d_{31}$ , for PC4D from resonance measurements as a function of fatigue cycles.**

It should be noted that the absolute changes in actually very small and although error bars have not been included in these graphs the fact that INSA data matches qualitatively NPL data signifies that this is a real phenomena.

### Effect of static stress on degradation in PZT5A and PZT4D materials.

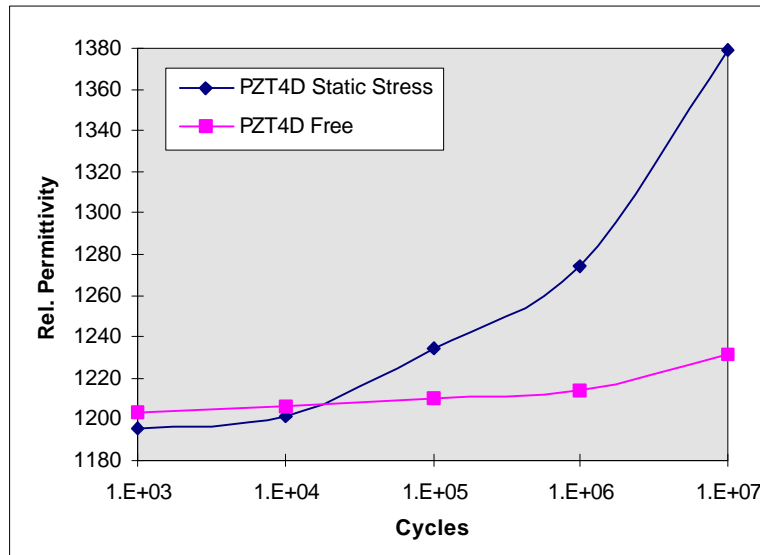
The effect of static stress on dielectric properties has been described in detail in previous reports<sup>1,2</sup>. Broadly, for soft materials the rate of change of capacitance with applied field decreases with increasing static stress and the absolute values of capacitance also decrease with increasing applied static stress. The same holds true for loss tangent. Hard materials (PZT4D) show quite the opposite behaviour, that is the rate of increase in capacitance and loss tangent increases with applied load and the absolute values also increase with applied load.

The degradation of piezoelectric materials is strongly dependent on applied mechanical stress, see earlier in this report. The application environment that many piezoelectric materials encounter is one of high electrical and mechanical stress. It is expedient then to measure the change in properties of the material with cycles whilst the material undergoes electrical fatiguing in a state of uniaxial static compression. INSA have performed these measurements and have shown that the rate at which the materials degrade is strongly influenced by the static mechanical stress, Figure 32 for soft PZT5A material and Figure 33 for hard PZT4D material. Two rod samples (approximate diameter 6.35mm and length 16mm) were connected head to foot in a test device allowing the application of a calibrated static mechanical stress. In order to avoid mechanical vibrations the electrical fatigue at  $8kV_{pp}$  ( $500V_{pp}/mm$ ) was limited to 100Hz up to  $10^7$  cycles. Similar experiments were conducted on samples under free conditions (zero applied mechanical stress). The rate of degradation was very small for the unclamped materials but were significantly higher under a static mechanical stress.



**Figure 32: Relative permittivity for soft PZT5A material under free conditions and static stress of ~32MPa.**





**Figure 33: Relative permittivity for hard PZT4D fatigue under free conditions and static stress of ~32MPa.**

### Conclusions

Methods for the controlled application of cyclic electrical stress and the subsequent piezoelectric and dielectric characterisation have been developed for a selection of hard and soft PZT materials. Comparison has been made with our EC Actuate project partner where cyclic degradation has been measured on similar materials using different techniques. Generally, there is reasonable agreement from both techniques.

The soft materials are generally more sensitive to the application of cyclic electrical stress than the hard materials and those which are placed under static mechanical constraint suffer even more rapid change in properties.

The measurement of dielectric capacitance and loss is a convenient method of establishing degradation in these materials. The use of resonance analysis, especially coupling factor  $k_p$ , can also be used as sensitive indicators of degradation.

Assessment of degradation using low field and high field probing techniques shows that, although the data obtained using both measurement methods differ quantitatively, the general trends in behaviour are similar.

To be able to define models describing degradation in PZT materials under cyclic electrical loading would require a more extensive series of experiments under different electrical loads to be performed. However, the degradation caused under electrical stressing is minor when compared to that caused by even moderate mechanical cyclic loading. This is why the effort in this programme of study has been placed on cyclic mechanical loading.

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## Acknowledgements

The static stress electrical fatigue data was supplied by LGEF, INSA, Lyon, France as part of the EC SMT funded project ACTUATE.