

REPORT

Accelerated Weathering of UPVC

A Turnbull, N Falla,
A Smith and D White

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A Turnbull*, N Falla†, A Smith† and D White*

* Division of Materials Metrology, National Physical Laboratory,
Teddington, Middlesex, TW11 0LW, UK

† Paint Research Association, 8 Waldegrave Road, Teddington,
Middlesex, TW11 8LD, UK

ABSTRACT

A detailed study has been conducted to assess the effect of various artificial weathering cycles on the degradation of three formulations of window-grade UPVC. The results were compared with samples which had been exposed outdoors in the north-east of England for periods of up to 16 years. Microhardness, loss of calcium carbonate filler, intensity of C-O stretching band, colour and gloss were used as measures of degradation.

The samples tested in the laboratory exhibited the characteristic surface degradation and partial recovery predicted for these materials. Cyclic variation of certain properties was exhibited for long laboratory exposures. In contrast, the naturally exposed material gave no definitive indication of a recovery process. The various measures of degradation employed gave reasonably consistent indications of degradation, particularly with regard to the onset of partial recovery.

The complexity of the degradation process for these materials inherently limits the establishment of quantitative rate equations to predict durability of naturally exposed materials. Nevertheless, four of the five exposure cycles gave consistent ranking of the different materials which compared well with the ranking deduced from natural exposure. An optimum artificial weathering cycle was derived.

It is recommended that laboratory tests should involve testing of a reference sample in parallel for the purposes of quality control, interlaboratory comparison. By choosing a material with established outdoor performance a basis for prediction of relative service life is also provided.

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National Physical Laboratory
Teddington, Middlesex, UK, TW11 0LW

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Director, Centre for Materials Measurement and Technology

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INTRODUCTION

Polymeric materials subjected to the atmospheric exposure effects of UV, temperature, wetting and drying cycles, and pollutants will degrade with exposure time resulting in loss of gloss, colour, and mechanical properties. In addition, the formation of a degraded surface layer creates difficulties in effective recycling of exposed material.

The very extensive research on weathering of polymers generally¹⁻³ and PVC in particular⁴⁻⁸, has led to significantly improved formulations, but there remains considerable debate concerning the efficacy of accelerated exposure tests in simulating natural exposure conditions^{2,9-11}. The inherent difficulties are the range of environmental factors and their complex time and spatial variation, coupled with the need to accelerate testing in a meaningful way. Advanced weathering machines with appropriate filtering can generate a reasonable simulation of the solar spectrum, with the acceleration factor being the intensity of the source and the time of exposure, coupled with elevated temperature, humidity and water spraying. Accelerated natural exposure is also used, in the context of using more severe environments compared to the intended application or using mirror reflection to intensify the irradiance.

The advantage of laboratory testing is control and convenience but the degree of success in relation to correlation with natural exposure has been very mixed and indeed it has been argued that there appears to be no correlation between natural and artificial weathering.^{1,9} However, the term correlation is often used without a clear definition. The principle requirements for a meaningful accelerated test are that ranking of materials should be successfully predicted and that a functional relationship should be established which enables long term prediction in service. In practice, a damage function which takes account of the range of weathering parameters and can be applied to a wide variety of locations and hence exposure conditions seems unrealistic. The more realistic goal would be to focus on predicting behaviour for a particular climatic condition.

The primary objective of this research was to evaluate the effect of artificial weathering parameters on chemical and mechanical properties of a commercial polymer and to assess the capability for correlation of the results with the effects of natural exposure. A parallel activity using plasma erosion as an ultrafast degradation process is described elsewhere¹². The main material for study was PVC-U window grade, the basis of choice being the availability of naturally weathered samples of known history and the provision of new extrusions of identical formulation. Material property variation was measured by FTIR, microindentation, colour and gloss measurement, and scanning electron microscopy. A range of techniques were used because of the broader interest in the correlation between different property measurements with exposure. Nanoindentation was also used in this study and the results are reported in detail in a separate publication¹³. Impact tests and tensile tests were not feasible because of the non-uniform geometry of the profiles.

EXPERIMENT METHOD

MATERIALS

Three formulations of PVC-U window profiles were used including Hostalit®Z (Hoechst AG) chlorinated polyethylene-modified window-sill section, denoted AHS8; acrylic modified "tropical" PVC window section denoted AHS7; RW00 acrylic modified window profile, denoted AHS2.

The composition of these materials is described in Appendix 1.

For the laboratory exposure tests newly extruded profiles of AHS8 and AHS7 with formulations identical to the naturally exposed material were utilised but equivalent material

could not be obtained for AHS2. Accordingly, sections of the original material not exposed to sunlight were used but the available material was limited and this is reflected in more limited laboratory exposure data.

EXPOSURE CONDITIONS

Artificial exposure

The samples were exposed in an Atlas weatherometer Model Ci 35A which utilises a xenon arc radiation source. For these tests the radiation was filtered using borosilicate glass to give a Miami "Average" 45 °S daylight spectrum in the range 300-800 nm. The radiant energy per unit area is measured only at 340 nm. The total radiant energy per unit area (irradiance) in the energy band 300-800 nm was estimated¹⁴ by multiplying the measured value at 340 nm by a factor of 1160.

The exposure conditions for this test programme are listed in Table 1 and involved five specific weathering cycles in which primarily the irradiance or temperature was modified. Cycle 1 is based on the draft CEN standard¹⁵. Cycle 4 is similar to Cycle 2 with the exception of an extended water spray period.

Natural exposure

The AHS8 and AHS7 were exposed with a south-facing aspect at Wilton, Cleveland, UK, (54 °N, 1 °W). The AHS8 was exposed for a total of 16 years between 10 December 1975 and 2 December 1991 and the AHS7 for about eight years between 20 August 1984 and 13 April 1992. The AHS2 was exposed at Newton Aycliffe, Co Durham, UK, (54 °N, 1 °W) over a nine year period between 18 April 1983 and 5 March 1992. The relevant climatological data for the locality are given in Table 2. All samples were exposed at an incline of 45°.

The solar spectrum extends from about 300 nm to 3000 nm. However, the spectrum of the artificial radiation source in this study extends from 300-800 nm. In calculating the solar radiant energy density in the range 300-800 nm it was assumed that this wavelength range represents about 55% of the total value, which is close to the value reported elsewhere¹⁶. For comparison with the artificial weathering the solar energy data have been scaled accordingly. A total radiant energy density of 10 GJ m⁻² calculated in this way would correspond approximately to 5.3 years of natural exposure at 54°N.

MEASUREMENT METHODS

Microindentation measurements were made using a Vickers microhardness tester with a 15s period at maximum load. The load applied was 0.29 N but the effect of varying this load on the hardness was evaluated in a few tests. Indents were made for any particular sample at ten different locations on the exposed surface. The repeatability of the mean value of the ten indents was within 10%. The choice of *ten* indents was based on repeated determination of hardness on a sample until the mean value of the hardness, as a function of the number of indents, converged.

Chemical composition was measured using FTIR (B10-Rad FTS-7) with photoacoustic cell attachment, and a scanning electron microscope with energy dispersive X-ray analysis. The SEM was used mainly in plan (ie from the top surface) but measurements were made also in profile after sectioning of the sample. In order to ensure reliable statistics at different depths in the latter case a rectangular section of height 6 µm and length about 20 µm was scanned and this was repeated at 10 to 12 different locations along a plane at the same distance from the top edge.

Colour measurements were recorded on a Pacific Scientific Spectrogard colour system and conformed to BS 3900 Pt D9. Gloss measurements were made generally using a Rhopoint

Labgloss instrument with a 60° head and a large port hole (about 420 mm²) in accordance with BS 3900 Pt D5. However, for assessment of the effect on gloss of ultrasonic cleaning of the samples a Rhopoint Novogloss Gloss Comparator with a port hole of about 75 mm² was used because of limitations in size of the particular samples evaluated.

Mechanical tests to fracture were not possible on the particular window profiles because of the distinctive non-uniform geometry of the extruded material and, in the case of naturally exposed samples, limited availability of material.

RESULTS

HARDNESS

The measured values of the microhardness of the artificially weathered AHS8 material are shown as a function of dose per unit area (for brevity this will be referred to simply as dose) and weathering cycle in Figure 1. The depth of indent for the 0.29 N load ranged from about 14 µm for the aged but unweathered material to 19 µm for Cycle 1 at a dose of 6.6 GJ m⁻². There is indication of the onset of recovery of properties, certainly in Cycles 1 and 2. These results would appear supportive of a loss of surface layer as reported elsewhere⁴ and indeed the surface is very powdery after this degree of exposure. Cycle 3, for which the temperature was elevated with respect to the other cycles, shows significant hardening. In practice, the surface was very powdery indeed at a dose of 4.0 GJ m⁻² and although tests at longer duration were conducted it was not possible to resolve optically the indents because of the degraded surface state.

The effect of varying the indenter load was evaluated for Cycle 1 (Figure 2). At a dose of 6.6 GJ m⁻² the nominal indent depths were 19 µm, 23 µm and 30 µm for the three loads applied. The details of the variation of hardness with dose changed slightly but the general trend was maintained. The lack of recovery in hardness at the lowest (standard) load is surprising in view of the evident recovery at the higher loads. For this pyramidal indenter, the layer constituting the first 10% of overall indent depth contributes 49% of the volume of the indent. A change in hardness of the very top surface could then have a significant effect on the hardness measurements. The lack of apparent recovery for the smallest load may reflect greater sensitivity to the very near surface conditions, and thus subsequent exposure damage to the newly exposed surface. Alternatively, the sustainment of softening of the shallower indents may be due to the gradual loss of the thin hard outer crust (<150 nm) detected in nanoindentation measurements¹³.

Cyclical variation in hardness is observed more obviously for AHS7 (Figure 3). The distinctive features in contrast to AHS8 are the more rapid onset of surface loss, indicated by the minimum at smaller values of dose, and the more limited degree of recovery relative to the initial hardness value. Mid-thickness measurement of hardness confirmed that the hardness of the unexposed material represents the bulk material and not simply a surface hardened region which had subsequently been removed by weathering. The minimum in hardness for Cycles 1 and 2 occurs at fairly similar values of radiant exposure, paralleling the results for AHS8. Cycle 4 shows the lowest value of hardness, although the minimum occurs at the same radiant energy density as for Cycle 2. In contrast to AHS8, there is a clear decrease and partial recovery in hardness for Cycle 3.

The limited availability of AHS2 material necessitated exposure to Cycle 1 only (Figure 4). Nevertheless, the data show the same trend as for the other materials. The minimum in hardness occurs at a somewhat smaller value of dose relative to AHS7.

The results for the naturally weathered samples (Figure 5) suggest a minimum in hardness for the AHS2 material but there is no recovery distinguishable for the AHS8 or AHS7

material despite being subjected to doses. Interestingly, the minimum in the value of hardness for naturally weathered AHS2 is similar to that for Cycle 1.

CHEMICAL COMPOSITION

Measurement of chemical composition was made by the complementary use of both scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX) and FTIR with photoacoustic attachment.

SEM-EDX

The SEM-EDX was used to monitor the relative concentrations of calcium, titanium and chlorine as a function of exposure conditions in plan and to a limited extent in profile. Estimation of the depth of sampling for composite material analysed in plan by this method is very uncertain but would be about 7 μm . The SEM gives information only about relative concentrations (ie relative to the total counts) of detectable species and should only be considered a semi-quantitative technique.

The loss of the percentage calcium was significant and strongly affected by exposure conditions and time.

TiO_2 is very insoluble and will have little tendency to be lost. Indeed, loss of adjacent material may leave TiO_2 standing proud on the surface with a consequent loss of gloss. The limitation with the SEM technique in this context is the depth of sampling which may not allow the very near surface detail to be resolved. No loss of Ti was observed for the naturally weathered material or artificially weathered material. The SEM data appeared to show a slight increase of Ti but this was probably an artefact associated with the loss of Ca and the derivation of concentration as a percentage of the total count.

The loss of Ca from AHS7 and AHS8 investigated in plan are shown in Figures 6 and 7 for the artificially weathered samples and in Figure 8 for the naturally weathered materials. The %Ca is observed to decrease in all cases but the magnitude and rate of change are strongly affected by exposure conditions and material. The AHS8 shows a slightly greater loss rate (versus dose) than the AHS7 under natural weathering conditions while both show indications of cyclical variation of calcium concentration. Cycles 1 and 5 would appear to be the less severe in relation to the rate of loss of calcium with radiant energy density for AHS8, although Cycle 1 was aggressive for AHS7. For both materials, the high temperature cycle, Cycle 3, was aggressive in terms of loss of calcium.

In assessing these data it is important to recognise that, for the same dose, the exposure *time* will be different for different levels of irradiance. The loss of calcium carbonate will be a time dependent process and, for example, the time-based rate of loss of calcium for Cycle 2 relative to Cycle 1 is even faster than apparent from Figure 6.

The reproducibility of these measurements was tested for a range of exposure conditions by a different operator. The maximum difference in measured value was less than 25%. In addition, measurements were made at different positions along the sample to allow for any variability in sampling position. The variability was less than 10%. Thus, the detailed variations in the %Ca for AHS7, Cycle 1, for example, would be inferred to be real.

Depth profiling of % calcium is time consuming because of the requirement for good statistics, and the range of investigation was confined mainly to AHS8 and to Cycle 1 and naturally-exposed material only. Examples of the profile for these exposure conditions are given in Figures 9 and 10. In order to simplify comparison, the depth of depletion relative to the bulk value was evaluated and plotted against dose as shown in Figure 11 and 12. An evident peak in value occurs between 4.0 GJ m^{-2} and 5.0 GJ m^{-2} for the artificially weathered material and matches the minimum in hardness for Cycle 1 in Figure 1. The rate of change

of the depth of the depletion zone of calcium after the peak (Figure 11) would imply that the surface is eroding at a rate of about 88 μm per annum for these artificial weathering conditions. The variation of depth of depletion of calcium with exposure period for the naturally weathered sample has a very similar characteristic trend to the variation in hardness.

FTIR

The measurement of interest from the perspective of FTIR were stretching bands associated with CO_3 , CO and polyene. However, problems of water vapour and CO_2 contamination in this instrument interfered with measurements in the critical wavenumber range of interest, 1400-1800 cm^{-1} . Accordingly, characterisation of the variation of the polyene absorbance peak with weathering was not feasible. Fortunately, the CO_3 moiety exhibits a characteristic absorbance band at 875 cm^{-1} associated with the three C-O bonds bending towards each other. Absorbance bands corresponding to aliphatic C-O (C-O-C or C-O-H) stretching in the range 1050-1150 cm^{-1} should give a measure of the build up of oxidation products such as ethers, peroxides and/or hydroxyl groups. No attempt was made to specifically identify the various degradation species since this was not a critical requirement of the project objectives and has been discussed elsewhere⁶. In quantifying the variation in carbonate concentration with exposure period the ratio of the peak area, after subtracting of the background, to that for a C-H deformation (1329 cm^{-1}) was used on the basis that the latter would be unaffected by exposure and there would be a consistent reference. In determining the variation in C-O concentration the peak height at 1095 cm^{-1} was used in calculating the relevant ratio to the reference peak. Peak height rather than area was used in this case because of overlap of neighbouring peaks. Where absorbance bands overlap there will be uncertainty in reliable quantification, whether using peak area or peak height. Much will depend on the detailed shape of the spectral bands and extent of overlap. The peak height was considered more reliable for these data.

The variation with radiant energy density of the intensity of the absorbance band associated with CO_3 for the naturally weathered samples is shown in Figure 13 and for the artificially weathered samples in Figures 14-16. The loss of carbonate detected by FTIR compares reasonably well with the loss of calcium determined by SEM for the AHS8 material in terms of the dependence on dose and exposure cycle (Figs 14 and 6). The basic cyclic variation of the data with dose is matched also for the AHS7 material (Figures 15 and 7) but there are specific differences, eg for Cycle 1. Comparison of the FTIR and SEM results for the naturally exposed samples (Figures 13 and 8) indicates similarity for AHS8 but less accord for AHS7 in relation to the rate of loss of calcium carbonate. The depth of sampling of the material for the SEM and FTIR technique will be different and hence some variations in detail might be expected although uncertainty in measurement may also be a factor.

The change with artificial weathering of the intensity of the absorbance band associated with the C-O stretching mode is shown in Figures 17-19. The range of uncertainty indicated in these figures represents the variability of results obtained for the unweathered sample determined in a series of repeat tests. This is reflective of general measurement variability associated with the particular measurement process.

In view of the magnitude of the uncertainty associated with the results, emphasis on detailed variation would be inappropriate. Nevertheless, some broad trends can reasonably be identified. For example, a peak at 5.0 GJ m^{-2} for exposure of AHS8 to Cycle 2 can be discerned, while an initial decrease and subsequent increase to a plateau can be identified for Cycle 1. The AHS2 material exposed to Cycle 1 appears to show a peak although, again, uncertainty levels for these measurements are significant.

The variation of C-O with exposure period in the naturally weathered samples (Figure 20) is comparatively small but some indication of a build up in concentration with exposure for

AHS2 and AHS8 material is evident although the loss of C-O for AHS2 is not easy to rationalise.

COLOUR

Colour variations with exposure were evaluated in terms of da, db, dL and dE. The results for db and for dE are reproduced in Figures 21-24 and 25-28 respectively. The most significant change in colour for these materials is generally towards the yellow. In the case of AHS8 material, the artificial weathering in Cycles 1 and 2 results in an initial peak in db associated with yellowing of the material followed by a subsequent minimum. Cycle 3 gives rise to an almost continuous increase in yellowing but with a maximum occurring towards the end of the exposure period. The AHS7 shows an initial increase in yellowing for Cycle 1 with a subsequent peak and then a minimum, but for Cycles 2 and 3 an initial decrease in db is observed before some degree of partial recovery ensues. The AHS2 material exposed to Cycle 1 shows a generally similar response with exposure but with the peak and the minimum shifted, and with the extent of change being different also.

The behaviour of the naturally weathered material (Figure 21) is more complex. A concern with these latter measurements was the long duration after removal from exposure before measurements were made. In order to investigate the effect of ageing, artificially weathered samples were stored in the dark and removed for colour measurement at regular intervals. The results are shown in Figure 29 and indicate a marked ageing effect. In contrast, variation in CO₃, for example, with storage period was minor. The consequence is that the colour measurements of the naturally weathered samples do not provide a good reference framework for evaluation of the effects of artificial weathering.

Whilst the shift in db was the most significant feature for most exposure cycles, the AHS8 material experienced a very significant shift to red for the higher temperature Cycle 3 with a correspondingly visible "pinking" of the material. This pinking is most probably associated with the photoactivity level of TiO₂ in the AHS8 material which results in production of radicals and enhanced degradation¹⁷. The photocatalytic activity of TiO₂ tends to become more pronounced with increasing temperature¹⁸.

Ultrasonic cleaning of the naturally weathered samples was carried out to assess the impact of dirt accumulation on the surface of the window profiles. The cleaning had a marked effect on the whiteness of the samples and for each sample an increase in whiteness of the order of 2-4 L units was observed. No discernible variation in the other colour parameters was observed.

GLOSS

The results of gloss measurement of the artificially weathered samples (Figures 30-32) show a fairly consistent pattern. A steady decrease in gloss with exposure period occurs followed by a more rapid fall off, consistent with surface erosion, and then a levelling off at a very low value. The dose corresponding to the onset of the more rapid degradation was sensitive to material and exposure condition. There was indication of a slight partial recovery of gloss of AHS7 prior to the onset of erosion which may reflect loss of surface asperities. The uncertainty in the reported gloss measurements arises mainly from variations across the sample, the magnitude of which varies with exposure conditions. The error bars in Figures 30-32 reflect the maximum uncertainty in the data.

In view of the accumulation of dirt on the naturally exposed samples, measurements were made after ultrasonic cleaning in distilled water also. Differences were observed but since tests carried out on artificially weathered samples also showed a significant change this approach was abandoned.

The results for AHS7 showing a marked increase in gloss of the naturally exposed samples (Figure 33) are exceptional. Manhandling of the material was considered unlikely since this would show up under optical observation. The likely explanation is inconsistency in gloss of the original sample with respect to the control, aged, sample. The rate of loss of gloss for the naturally exposed AHS8 shows very different behaviour from that of the artificially exposed with no evidence of the marked increased in rate associated with erosion observed for the artificially exposed samples. Indeed, the rate of loss of gloss decreases at the longer exposures.

DISCUSSION

The objectives of accelerated testing are to provide satisfactory ranking of materials and a measure of the potential life of a product. In both cases it is important that the degradation of properties generated by the artificial weathering follows the same mechanism path. The prediction of long term performance in natural conditions depends on the ability to predict the *rate* of degradation in natural weathering. It is insufficient to demonstrate that 2 months in the weatherometer with a specified weathering cycle is equivalent to 2 years say in natural conditions, for which data may be known as a reference point, unless there is a framework for predicting the extent of degradation at 15 years for example. In any degradation process there will usually be a single point equivalence.

For ranking of materials the requirement is less stringent and it is necessary simply to demonstrate that the relative performance of the different materials in terms of the extent of degradation is consistent with that observed in natural conditions. Nevertheless, it is conceivable that problems could arise if the rate of degradation is not varying consistently for the different materials, so that a cross-over occurs.

In assessing which weathering cycle best simulates natural behaviour a minimum requirement is that it should adequately rank the materials. In the absence of specific rate equations for degradation this enables confidence that broad predictions can be made based on comparison with practical experience of the performance of materials already in service for an extensive period.

A range of property measurements were made in this study, some directly related to performance such as colour and gloss and others indirect such as hardness. Direct in this context represents practical measures of degradation such as loss of cosmetic appearance or mechanical integrity while indirect measures may be considered indices of change in properties related to those parameters. A first step in the evaluation is to establish the extent of consistency in the varied measures of degradation and to use the critical parameters as a basis for identifying the most effective weathering cycle capable of predicting temperate exposure while retaining the maximum degree of acceleration.

Thus, the three key issues to be resolved are:

the extent to which individual measurement methods give consistent indicators of degradation;
the effect of changing artificial weathering parameters on the material properties;
the extent to which artificial weathering correlates with natural weathering in terms of rate prediction and ranking.

CONSISTENCY OF MEASUREMENT PARAMETERS

The parameters measured in this study reflect mechanical, chemical and physical properties of the material. An explicit functional relationship between these would be surprising. Nevertheless, it might be expected that similar trends in behaviour would be observed since in different ways they will reflect degradation of the material. The most distinguishing feature of accelerated degradation of this UPVC material is the recovery of properties in a

number of cycles associated with erosion of the surface. The steps in degradation of UPVC have been summarised succinctly by Magnus⁴:

- Dehydrochlorination leads to the formation of conjugated double bonds. When the number exceeds eight the double bonds absorb visible light and yellowing results.
- Oxidation of the double bonds causes disruption of the polyene sequence leading to the reduction and possible disappearance of yellowing. Also, water-sensitive molecules are formed and are removed from the surface. The oxidation can also lead to chain scission.
- Disintegration of the surface can result from oxidation and crosslinking leading to high surface stresses and microcracking. The microcracks cause a diminution of mechanical properties and the loss of surface due to erosion is accompanied by a loss of gloss. A recovery of certain properties is obtained and the process repeats itself leading to a cyclical variation in properties with exposure time.

The relative effects of UV bond dissociation and oxidation processes will be a function of distance from the exposed surface and exposure conditions. Thus, a high UV irradiance might be expected to consume oxygen close to the surface. The presence of a dark period in natural exposure can allow ingress of oxygen to greater depths and influence the detailed reaction processes.

In temperate climates the cyclical nature of the degradation process is not commonly observed. Nevertheless, the AHS2 material examined in this study does show some indication of the commencement of recovery in relation to hardness, and to some extent in the blue-yellow colour index db.

The accelerated artificial weathering provides a more extensive framework for comparing different measures of material properties. In that context, there is a consistent pattern of degradation and recovery identifiable for the most extended exposure cycles, Cycles 1 and 2. For AHS8 exposed to Cycles 1 and 2 this appears as a recovery in hardness after initial softening (Figure 2), in calcium concentration (Figures 6 and 11), in the colour parameter db (Figure 21), in the C-O concentration to some extent (Figure 17, Cycle 2), and as a discrete acceleration in the rate of loss of gloss (Figure 30). For example, the minimum in hardness for Cycle 1 occurs at about 5.0 GJ m^{-2} and this is consistent with the minima and/or maxima in the other parameters. Hence, all of the parameters show a consistent and characteristic trend for these two cycles. This is illustrated in Figure 34 in which the various property measurements have been compared using simple scaling.

There are more detailed fluctuations in colour, with a peak followed by a minimum. This behaviour reflects most probably initial yellowing due to the formation of the polyene sequence, oxidation causing bleaching, and then surface removal.

The depth of depletion of calcium carbonate (Figure 11) is interesting. Loss of calcium carbonate in laboratory exposures is due to dissolution in the presence of water and HCl generated by dehydrochlorination. The depth of depletion, up to about $15 \mu\text{m}$, implies that there is a pathway for ingress of water, reaction with the carbonate and removal of product. The conceptual image is a network of cavities linked by small cracks carrying the water. Indeed, examination of the weathered surface with the scanning electron microscope indicates a very porous structure (Figures 35 and 36). The porous structure appears to develop most significantly for the naturally weathered material. The calcium carbonate particles or their remnant cavities may act as local stress/strain raisers amplifying the thermal stresses and strains inherent in the heating and spraying cycle and causing cracking between. Loss of calcium carbonate will also affect the hardness of the material. The reduction in hardness will reflect not only chain scission but also loss of filler.

For Cycle 3, in which the temperature was significantly elevated, the exposure conditions were so severe for the AHS8 material that cyclic behaviour was not observed for all parameters. The hardness and colour index db did not show simple behaviour, in the former case because of very marked disintegration of the surface.

The pattern of behaviour of the AHS7 material is broadly similar to AHS8 in showing a correlation between different parameters with respect to the onset of recovery.

It may be concluded that all of the parameters measured at different exposure periods for the different cycles give a reasonably consistent indication of the recovery of properties, with the exception of Cycle 3. However, it does not appear possible to *predict* the onset of surface loss and recovery in properties in relation to any critical change in measured parameter.

Perhaps the surprising feature overall is that the recovery is a gradual process in all cases even with respect to the calcium level (Figure 11). If extensive microcacking and porosity is developing on the surface it might have been anticipated that when a sufficient degree of deterioration of the surface was achieved some discontinuous loss of material may have occurred. In practice, this may happen but on a small scale and in the approximate 500 hour exposure interval it would not be apparent as a discontinuous process. The surface removal appears as a slow continuous erosion which at the same time is "competing" with the effect of radiation on the newly exposed surface. It would imply that the onset of erosion may not be at the minimum in hardness but occurs prior to that perhaps in a very near surface region. As discussed in a later section, the rate of change of hardness undergoes a minimum at doses less than that associated with the minimum in hardness.

The indications from the long exposures are that the rate of degradation and surface removal reach a dynamic balance once the initial surface of the material is degraded. This is most clearly apparent for AHS7 exposed to Cycle 2.

EFFECT OF WEATHERING PARAMETERS

Five weathering cycles were investigated in this study focusing on the effect of changing the level of irradiance, of temperature and of water spray cycle. Cycle 1 corresponds to the draft CEN standard on artificial weathering.

In comparing Cycles 1, 2 and 5 the white panel temperatures are approximately the same with only the irradiance changing. Nevertheless, the exposure time at a given level of radiation will increase with a decrease in irradiance. Cycles 2 and 4 differ in the water spray cycle only. The variation in white panel temperature for these two cycles was insignificant.

In some cases, the exposure period was limited so that full evidence of the cyclic characteristics of the degradation process did not appear. This is true in particular for Cycle 5. Also, it was not possible to obtain the full range of property measurement in every case.

The perception of the effect of different cycles depends to an extent on the particular material and property measurement. In comparing Cycles 1 and 2 for AHS8, the hardness diminishes most significantly for Cycle 1, perhaps due to reduced oxygen penetration as a consequence of the higher irradiance (and hence oxygen consumption) of Cycle 2. The onset of recovery in hardness appears at a slightly value of the dose. The latter trend is observed also with respect to the measurements of colour index db, but for Cycle 5 there is little variation of db with exposure period. The loss of calcium carbonate with radiant energy density is more rapid for Cycle 2. There is also little difference with respect to the loss of gloss for the different cycles.

The response of AHS7 to Cycles 1, 2 and 3 is broadly similar to that for AHS8 with respect to hardness. There is not much sensitivity of this material with respect to colour changes. The

increased rate of loss of calcium carbonate for Cycle 2 in relation to Cycle 1 is repeated for this material also. The loss of gloss is somewhat more rapid for Cycle 2 relative to Cycles 1 and 5.

On the whole, the differences between Cycles 1, 2 and 5 are not particularly distinct in character or in magnitude. However, the test time for Cycle 2 is inherently shorter for the same level of dose. On the basis of the artificial weathering alone, Cycle 2 would be the optimum choice. This cycle is reasonably similar to that suggested in the draft ISO standard (ISO/DIS2 4892-2).

Comparison of Cycles 2 and 4 should give an indication of the impact of water spraying period. Differences in hardness were apparent only for AHS7 for which the minimum in hardness was lower for the longer spray cycle. There was no distinction of the different cycles in terms of dE but there was a difference in detail with respect to dB although the distinction for both AHS8 and AHS7 rests largely on single data points. The rate of loss of carbonate for AHS8 and AHS7 would appear to be broadly similar, within the measurement uncertainty, for both cycles. There was no discernible difference in gloss for the different cycles. Thus, it may be inferred that an extended water spray has a distinguishable but only a small impact on the material properties relative to the conventional test. This conclusion is in agreement with the summary of Decker⁷ although it would not apply to outdoor weathering for which acid rain and pollutants would potentially have an effect.

In essence, the differences overall between Cycles 1, 2, 4 and 5 may be considered to be minor. However, Cycle 3, in which the white panel temperature was 55°C, showed very distinctive behaviour. The AHS8 material developed a very powdery surface after a short period making hardness evaluation difficult and the loss of hardness and the onset of recovery was more rapid for the AHS7 material. Similarly, the loss of calcium carbonate from the surface was more rapid than for Cycles 1 and 2. The colour of samples exposed to Cycle 3 showed very marked variation in all parameters with respect to the other cycles. The loss of gloss of both AHS7 and AHS8 was most rapid for Cycle 3.

It may be suggested that raising the temperature significantly as a method of accelerating weathering will introduce very marked changes compared to the effect of the variations in level of irradiance investigated in this study. The appropriateness or otherwise of this approach depends on comparison with natural weathering and that is discussed in the next section.

CORRELATION OF ARTIFICIAL WEATHERING WITH NATURAL WEATHERING

Predicting rates of degradation

The difficulty in quantitative prediction of natural weathering is illustrated by comparison of the hardness data for AHS8 exposed to Cycle 1 (Figure 1) with the data for natural weathering (Figure 5). This is set out more explicitly in Figure 37 in which the rate of change of hardness with dose is plotted as a function of dose. In the case of the artificially weathered sample, the rate of change of degradation with dose achieves its maximum value at 3.0 GJ m⁻² (an apparent minimum in Figure 37 only because of the negative sign representing loss of hardness) and then diminishes as the character of the surface changes. This may represent shielding of the underlying sub-structure as the degraded layer builds up or the onset of gradual erosion of the surface.

Although not apparent for AHS8, the continuing exposure of the samples leads to a *cyclic* process of surface damage and erosion. This process is observed most evidently for AHS7 exposed to Cycle 2 (Figure 3). After the initial hard surface layer is removed the amplitude of the cyclic change diminishes and the hardness then depends dynamically on the competitive processes of damage and recovery. Dampening of the cyclic change with exposure period occurs until the cyclic change is small.

Resistance to colour change is probably the most important performance parameter for the application of these materials. Unfortunately, the dependence of colour on the time of removal from exposure, demonstrated in Figure 29, means that there is no reference basis in the naturally exposed samples with which to make comparison, since the samples were stored for years prior to measurement. The correlation in behaviour between colour and hardness described earlier suggests that predicting the rate of change of the colour parameters quantitatively will also be difficult.

The degradation of gloss is simpler in character with three stages apparent: initial decay; loss of surface and more rapid degradation; levelling off at a low level of gloss. Consideration of Figure 33 (eg AHS8 gloss data) suggests that the behaviour of the naturally weathered samples is not simple, with an initial high rate of degradation followed by a slower rate. It is inconceivable that fitting of equations to the gloss data of the artificially exposed samples (prior to surface erosion) can predict this behaviour even with scaling of the data. A problem here may be contamination of the naturally exposed samples with other material of one form or other, and the uncertain effect of pollutants on degradation. Unfortunately, the destructive effect of cleaning means that it is not possible to isolate the "intrinsic" gloss. The accumulation of dirt on the surface may be a factor also in the extent of absorption of UV.

In conclusion, the intrinsic dependence of the development of the degraded layer on exposure conditions and, for these materials, the subsequent erosion means that it can be inherently difficult to establish rate equations which can be transferred meaningfully from artificial weathering to natural exposure. Prediction of life then depends greatly on relative ranking based on known performance of specific materials.

Ranking of materials

For ranking of materials, it is necessary simply to demonstrate that the relative performance of the different materials, in terms of the extent of degradation, is consistent with that observed in natural conditions. Implicit in this evaluation is an assessment of the relevance of the weathering cycle since the relative performance of the material could change according to the artificial exposure conditions. The important performance criterion is resistance to change of the key parameters. The three materials will be compared with respect to a range of performance parameters.

In relation to colour change, for which satisfactory reference data for natural exposure are not available, the basis for comparison is with respect to the laboratory exposures only. In that context, AHS2 would appear the least resistant material in so far as it shows the greatest change in db and dE when exposed to Cycle 1. The AHS7 is more resistant to yellowing than AHS8 and does not show the marked deterioration in colour observed for AHS8 in the elevated temperature cycle, Cycle 3. The TiO_2 concentration in the AHS7 is almost double that for AHS8 and this most probably accounts for its increased resistance to colour change.

The AHS7 can be compared with the other materials with respect to loss of gloss based only on artificial exposure because of the anomalous natural weathering data. In terms of the exposure period to attain the minimum in gloss the AHS8 performs better than AHS7 which performs better than the AHS2. It would appear also that the more rapid decrease in gloss associated with surface erosion occurs at shorter exposure periods for the AHS7 with respect to AHS8 although the differences for the higher temperature cycle, Cycle 3, are less obvious. Comparison of AHS8 and AHS2 with respect to loss of gloss of the naturally exposed samples indicates little difference. However, this may reflect simply the limited period of exposure.

Comparison of the resistance to change in hardness requires consideration of the initial value of the hardness which is similar for the AHS2 and AHS7 but much lower for the AHS8. This is associated with the use of chlorinated polyethylene impact modifier in the AHS8 material. The rate of loss of hardness of materials exposed naturally is greatest for the AHS2 material

with the AHS8 showing the most modest rate of change. AHS8 also shows the greatest resistance to change in hardness for all cycles except Cycle 3 for which very rapid erosion of the surface appeared to occur.

The artificial weathering results may be summarised as follows:

AHS2 exhibits the poorest performance in all tests;
 AHS7 shows best resistance to colour change;
 AHS8 shows the greater resistance to change in hardness and surface erosion with the exception of Cycle 3;
 AHS8 shows the slowest rate of loss of gloss.

The natural weathering results may be summarised:

AHS2 shows the poorest performance in all reliable tests;
 AHS8 shows the greatest resistance to change in hardness.

It is evident that the ranking of these materials is consistent for the natural and artificial weathering provided that the artificial weathering is not too extreme, eg Cycle 3 with regard to its effect on AHS8. All of the cycles would have been satisfactory for ranking of the materials but Cycle 2 would be the most cost effective. In deciding which material has the best resistance to weathering the key issue is the critical performance criterion. Clearly, AHS2 performs less well generally, although the lack of reliable colour data for the natural exposures limits definitive conclusion with respect to this parameter. AHS7 shows much less tendency to yellowing than AHS8 although the magnitude of the change in either is comparatively small with the exception of AHS8 exposed to Cycle 3. AHS7 exhibits a greater rate of deterioration in hardness (reflecting likely mechanical properties) and gloss and a more rapid onset of surface erosion.

The explanation for the performance of AHS7, good colour stability but greater ease of erosion, may be associated with the suggestion that particular mixes of anatase and free chalking rutile grades of TiO_2 giving faster bleaching may lead to more rapid erosion⁸.

It should be emphasised that the materials tested no longer represent current formulations. Hence, while useful for indicating the effectiveness of the artificial weathering cycles in predicting natural exposure the results do not reflect the properties of materials currently supplied by the different manufacturers.

In view of the conclusion in the previous section with respect to long term prediction outdoors and the need to depend more on ranking rather than quantitative prediction it is reassuring that consistent behaviour is predicted. In that context, it is important that a reference material, for classes of material, should be adopted for laboratory testing. This would provide a basis for quality control and for comparison of different weathering apparatus. More importantly, by utilising a material whose long term outdoor performance is reasonably established there is then the possibility of getting an assessment of relative life prediction.

CONCLUSIONS

Exposure of three different formulations of window-grade UPVC to artificial weathering results in a process of surface damage followed by partial recovery which becomes cyclic in nature at long exposures, as described previously by Magnus⁴.

The rate of degradation and surface removal by erosion achieves a competitive dynamic balance with the cyclic amplitude of the variation in properties gradually diminishing with exposure period.

Exposure of these materials outdoors in the temperate climate of the north east of England gave no indication of recovery for two of the materials despite exposure in one case for up to 16 years. One of the materials did exhibit a trend towards some recovery but the data were limited and firm conclusions could not be drawn.

The varied measures of degradation employed, viz microhardness, loss of calcium carbonate filler, colour and gloss, gave reasonably consistent indications of degradation, particularly with regard to the onset of partial recovery.

Varying the incident irradiance in the range 0.25-0.5 W m⁻² at approximately the same white panel temperature had an impact on the details of the variation of properties with dose but the general trends were not affected. Similarly, increasing the water spray period from 18 min/120 min to 30 min/120 min had only a small influence on behaviour. In contrast, increasing the white panel temperature to 54°C from 44°C at the same irradiance resulted in a dramatic deterioration in the performance of one of the materials.

Cycle 2, which utilises the higher irradiance, is considered the most efficient weathering cycle, of the cycles studied, for characterising the weathering resistance of these materials.

The intrinsic dependence of the development of the degraded layer on exposure conditions and, for these materials, the subsequent erosion means that it can be inherently difficult to establish rate equations which can be transferred meaningfully from artificial weathering to natural exposure. Quantitative prediction of service life, based on laboratory testing, is not feasible in an absolute sense.

The four weathering cycles at moderate temperatures (1, 2, 4, 5) all gave consistent ranking of the different materials and within the range of reliable data available gave ranking consistent with natural weathering.

Prediction of the relative resistance to natural weathering depends on the performance criteria used. One of the materials exhibited greater colour resistance but was more sensitive to surface erosion.

It is recommended that a reference material, of a specific material class, be established for testing in parallel with other materials being evaluated. This would enable quality control of testing, interlaboratory comparison and, by choosing a material with an established outdoor performance, a measure of potential service life.

ACKNOWLEDGEMENTS

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TABLE 1

ARTIFICIAL WEATHERING CYCLES: CONDITIONS USED

	1st Cycle	2nd Cycle	3rd Cycle	4th Cycle	5th Cycle
Black standard temp Black panel temp $\approx 58^{\circ}\text{C}$	65	65	72	65	58
White panel temp ($^{\circ}\text{C}$)	44	44	54	44	46
Air temp ($^{\circ}\text{C}$)	36	36	48	36	41
Wet bulb depression ($^{\circ}\text{C}$) Relative humidity 65%	6	6	7	6	6
Light/dark cycle	Continuous light				
Water spray cycle	102 min/18 min (light/light + water spray)			90 min/30 min light/light + water spray	102 min/ 18 min (light/ light + water spray)
Irradiance @ 340 nm (Wm^{-2})	0.35	0.5	0.35	0.5	0.25
Inner filter	Borosilicate				
Outer filter	Borosilicate				
Maximum radiant exposure (MJm^{-2})	AHS2: 5116 AHS7: 5846 AHS8: 6577	AHS7:) 8352 AHS8:) 8352	AHS7:) 5846 AHS8:) 5846	AHS7:) 4176 AHS8:) 4176	AHS7:3654 AHS8: 3654
Maximum duration (hr)	AHS2: 3500 AHS7: 4000 AHS8: 4500	AHS7:) 4000 AHS8:) 4000	AHS7:) 4000 AHS8:) 4000	AHS7:) 2000 AHS8:) 2000	AHS7: 3500 AHS8: 3500

TABLE 2

Climatological data for naturally exposed samples *

Year	Temperature °C			Relative Humidity %			Rain (mm)	Rain (hrs.)	Wet (hrs.)	Solar max. °C	Bright sun hrs.	Sun(1) L
	Max.	Min.	Mean	Max.	Min.	Mean						
1975	30	-4	8.9	95	60	78	431	420	1864	36.7	1376	93855
1976	30	-9	8.9	93	62	77	552	488	2174	35.7	1294	85677
1977	26	-11	8.4	94	67	80	522	540	2406	35.4	1179	85103
1978	26	-11	8.4	94	62	79	636	610	2381	35.1	1056	65759
1979	26	-15	7.9	92	64	78	708	628	2017	32.6	1209	81087
1980	27	-7	8.6	93	61	77	646	573	2271	32.9	1158	78596
1981	26	-17	8.4	92	61	77	591	488	2475	34.8	1273	84788
1982	27	-16	8.9	93	61	77	521	476	2099	34.2	1313	85879
1983	29	-8	9.0	93	64	78	569	533	1920	33.4	1244	81214
1984	27	-8	8.7	91	58	75	540	517	2229	34.9	1303	86282
1985	25	-10	8.1	93	61	77	564	572	1981	Δ	1152	76584
1986	27	-12	7.2	92	56	74	644	366	1082	38.2	Δ	54769
1987	26	-7	8.2	96	71	84	667	552	1961	Δ	1174	75086
1988	26	-10	9.0	93	66	80	557	557	1945	40.8	1464	81243
1989	30	-6	9.5	93	64	78	339	334	1611	41.3	1645	87271
1990	34	-6	9.8	Δ	Δ	Δ	536	Δ	1556	40.9	1491	81187

NOTES

1. Wetness (hrs) - total wetness due to rain and dew.
2. Bright sun hours - measured using a Campbell-Stokes sunshine recorder.
3. The Solar max temperature refers to a standard black bulb thermometer (made by Solar Max).
4. Solar radiation data applies to surfaces facing south 45°.
5. L (Langley) = $4.19 \times 10^{-4} \text{ Jm}^{-2}$.
6. Symbol Δ: Equipment failure

Data supplied by Tioxide UK Ltd. Technical Service Dept. Weathering Station, Cleveland, England

APPENDIX 1**MATERIALS****AHS2 SPECIFICATION:**

Various naturally weathered, acrylic modified, window and window sill profile extrusions; no control specimens available.

Supplied by Hydro Polymers, Newton Aycliffe, Co Durham.

COMPOSITION:

Suspension PVC (K value, 66-68)	100 (phr)
Acrylic impact modifier	10.0
Acrylic processing aid	1.5
Ba/Cd/Pb-Lubricant master batch (stabilisers are in the ratio 1:1:1 as salts, actual % metal, 25% Pb, 4.5% Cd and 2.5% Ba; lubricants usually comprise PE wax, paraffin wax and/or long chain fatty acids $\approx$ 2.5 phr)	4.5-5.0
TiO ₂	4.0-6.0
CaCO ₃	6.0

NATURAL EXPOSURE HISTORY:

Samples were exposed at Newton Aycliffe, Co Durham (54 °N 1 °W) over a nine year period between the 18/4/83 and the 5/3/92. Sampling periods were 3, 6, 7 and 9 years.

AHS7 SPECIFICATION:

"Tropical" PVC window section; small control specimen and various naturally weathered cuttings from the faces of Corvic® (PVC resin) based, acrylic modified, profile extrusion; also $\approx$ 5 m of newly extruded profile based on the same composition.

Supplied by EVC UK Ltd, Runcorn, Cheshire.

COMPOSITION:

Corvic 68/173 (SPVC resin)	100 (phr)
Paraloid KM323B (impact modifier)	8.7
Stabiliser/Lubricant masterbatch (Pb/Ba/Cd)	6.5
Omyalite (CaCO ₃ filler)	6.5
Tioxide RS3230 (TiO ₂)	7.6

NATURAL EXPOSURE HISTORY:

Samples were exposed at Wilton, Cleveland (54 °N, 1 °W) over an eight year period between the 20/8/84 and the 13/4/92. Sampling periods were 1, 3, 5 and 8 years.

AHS8 SPECIFICATION:

Hostalit®Z (Hoechst AG) CPE modified window sill section; small control specimen and various naturally weathered cuttings from the exposed surface; also 3 m of newly extruded profile based on original formulation, kindly prepared by parent company in Sendenhorst, Germany.

Supplied by EVC UK Ltd, Runcorn, Cheshire.

COMPOSITION:

SPVC/70	100 (phr)
CPE impact modifier	10.0
Ba/Cd stabiliser	2.0
Lubricants	1.7
CaCO ₃	6.0
TiO ₂	4.0

NATURAL EXPOSURE HISTORY:

Samples were exposed at Wilton, Cleveland 54 °N 1 °W) over a 16 year period between the 10/12/75 and 2/12/91. The aspect of exposure was 45 ° south facing; sampling periods were 1, 3, 5, 8, 15 and 16 years.

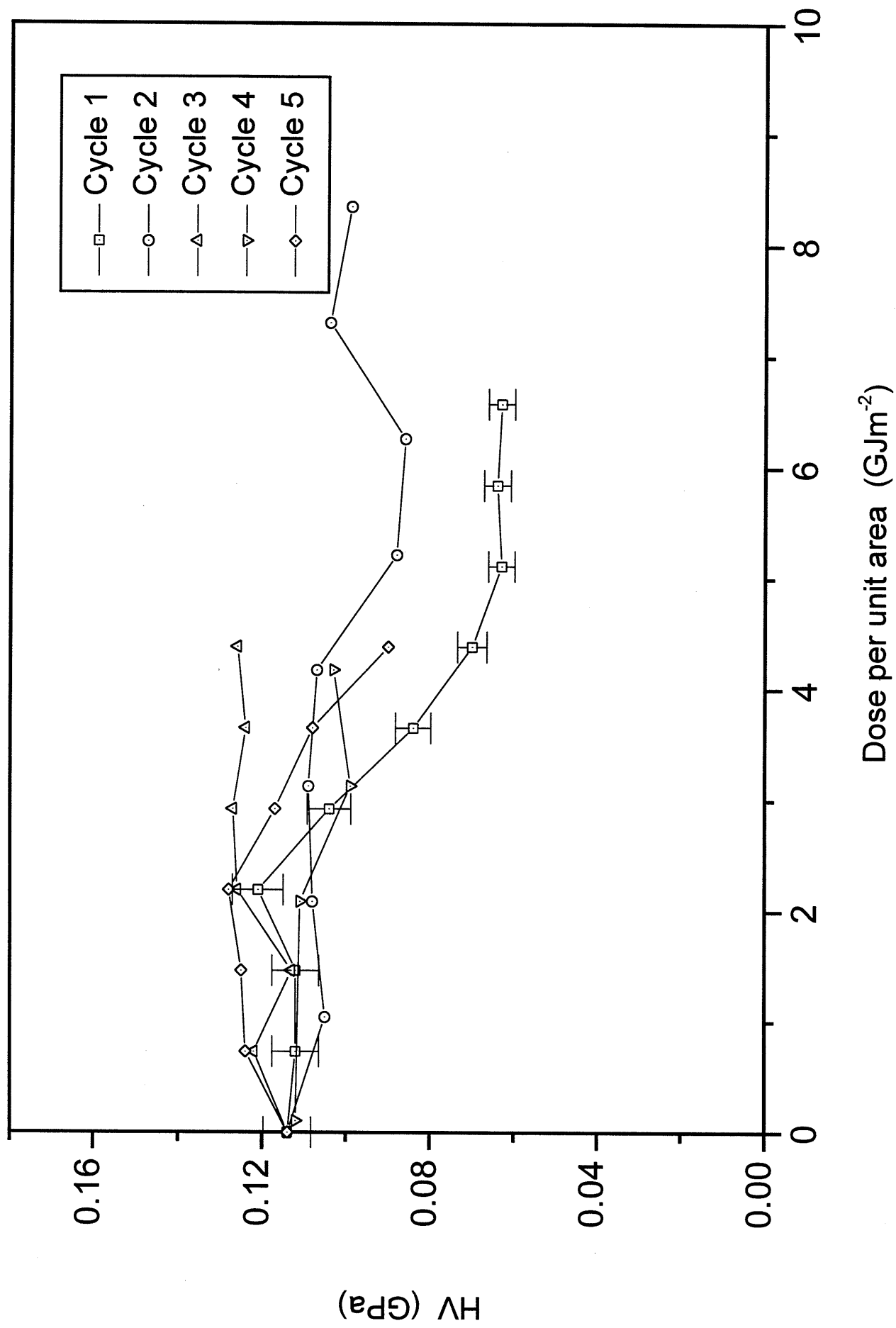


Fig.1 Variation of mean value of Vickers Hardness with exposure period for AHS8 material

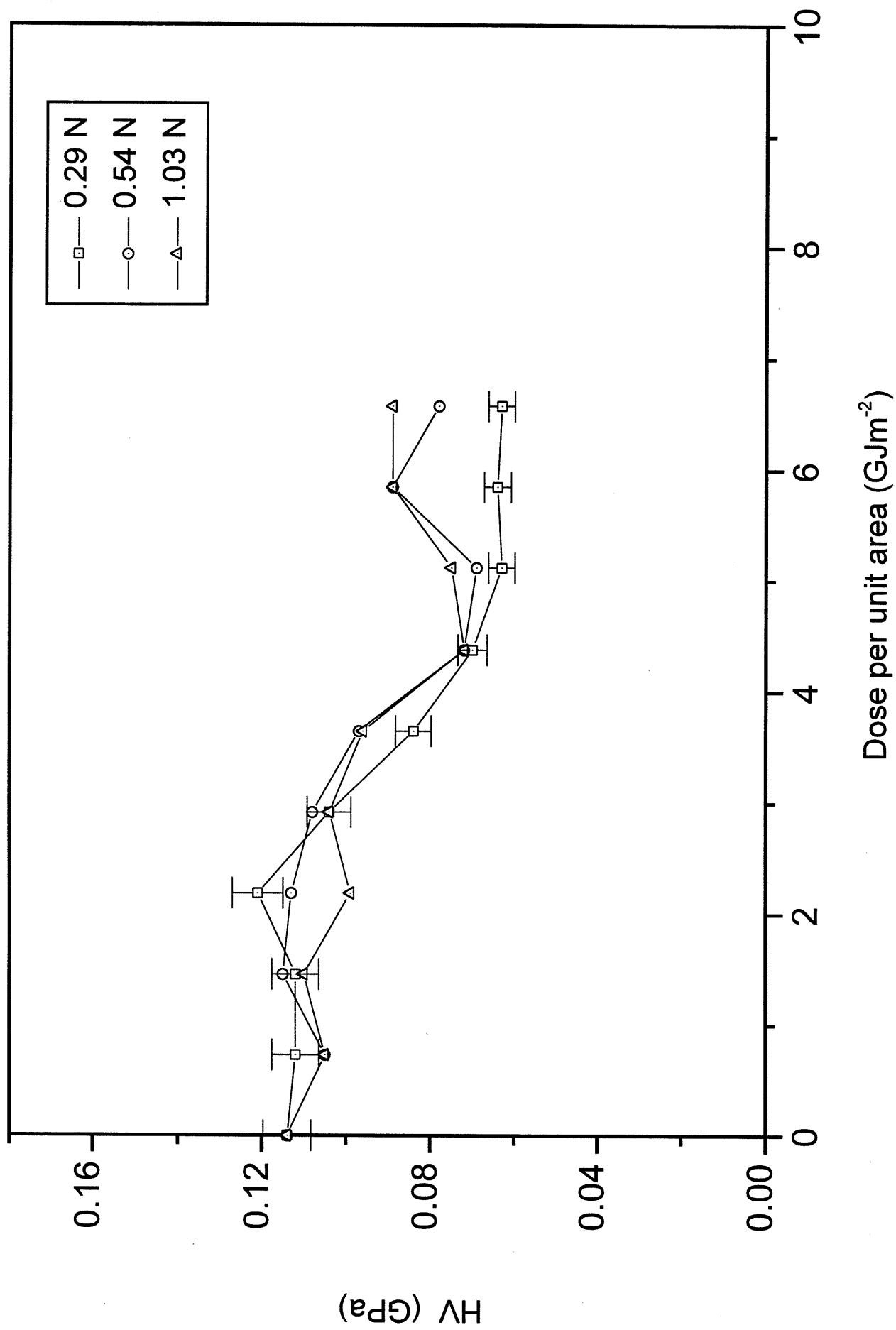


Fig.2 Effect of load on mean value of Vickers Hardness
with exposure period for AHS8 material (cycle 1)

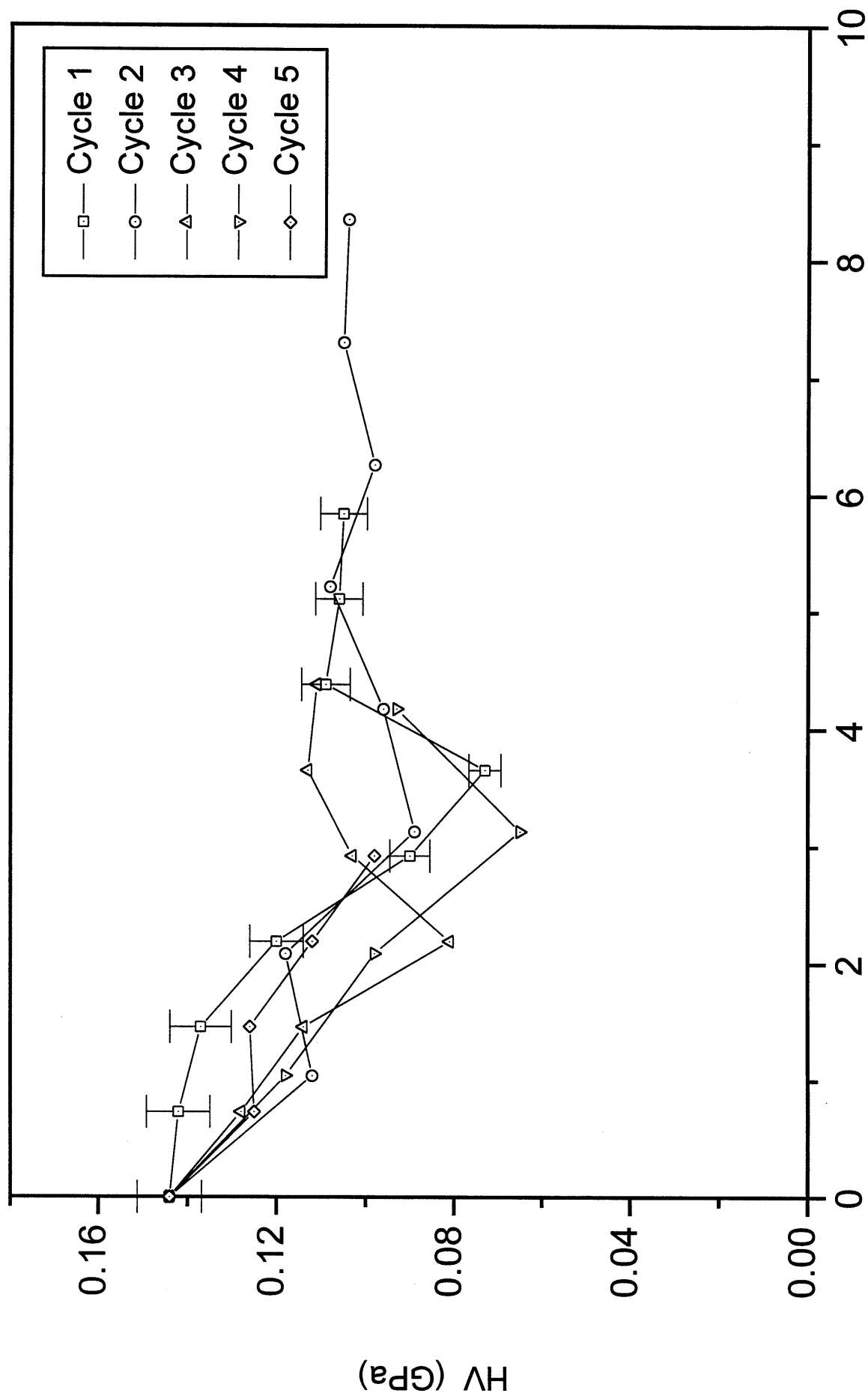
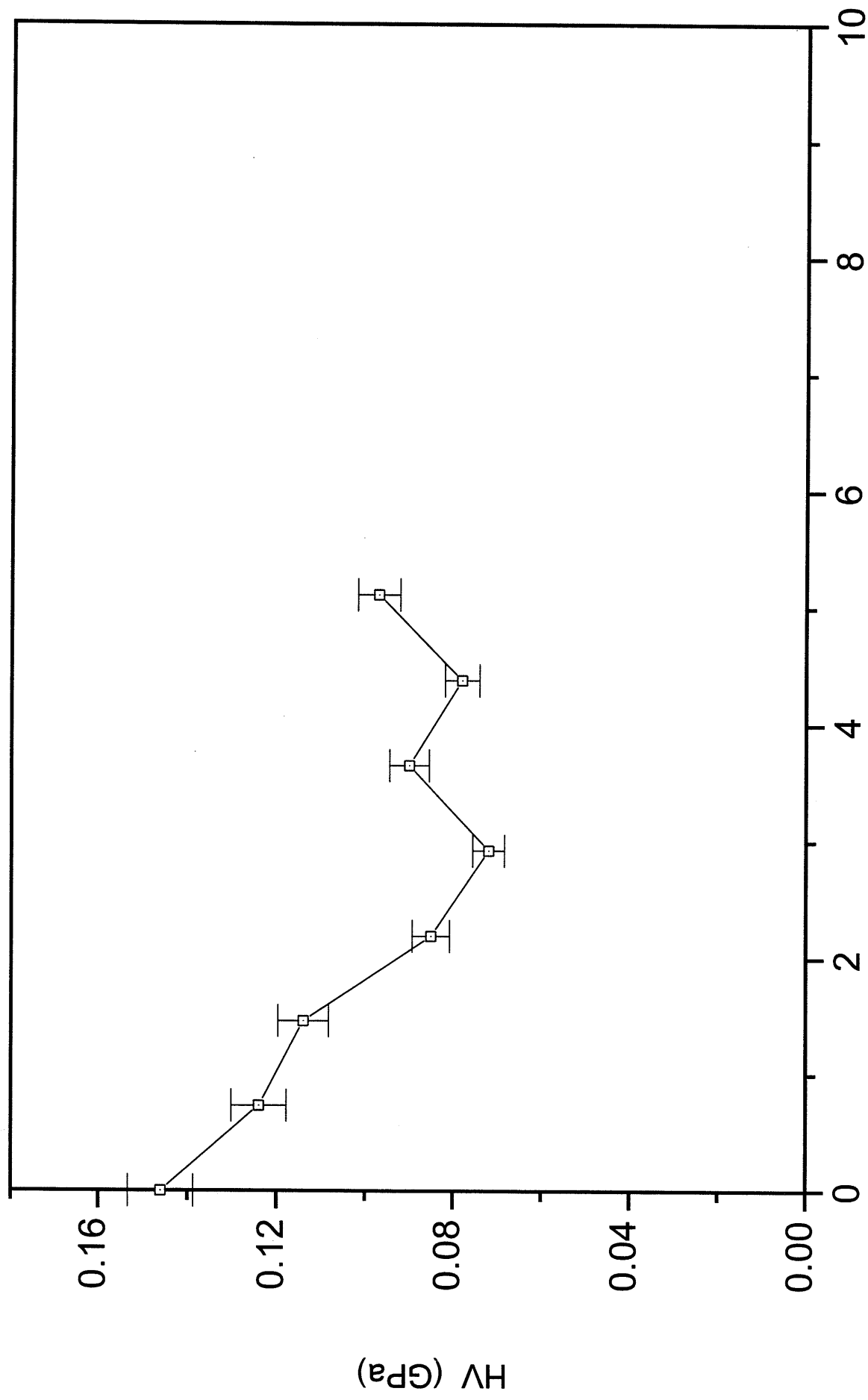


Fig.3 Variation of mean value of Vickers Hardness
with exposure period for AHS7 material



Dose per unit area (GJm⁻²)

Fig.4 Variation in mean value of Vickers Hardness with exposure period for AHS2 material (cycle 1)

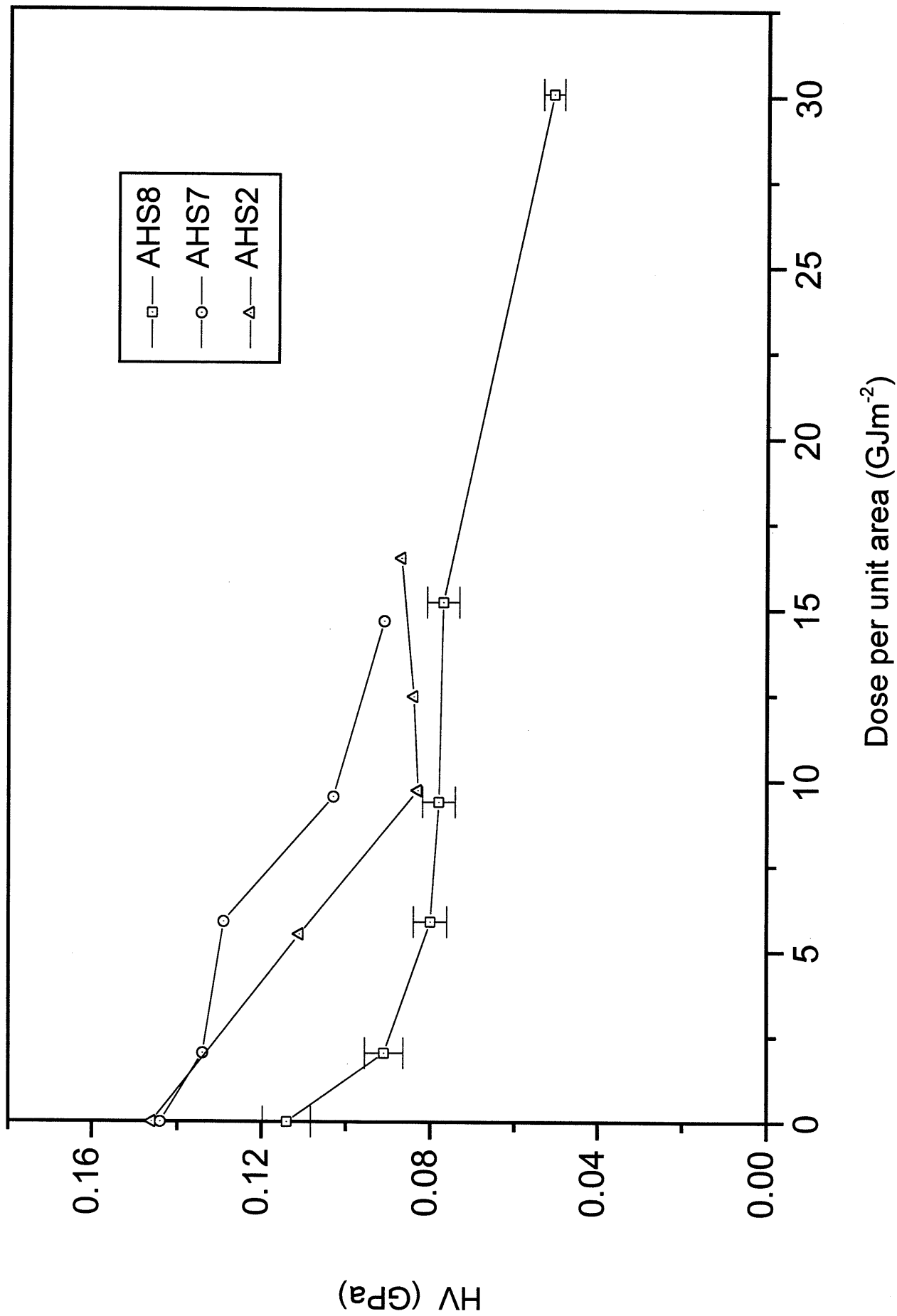


Fig.5 Variation of mean value of Vickers Hardness with exposure period for naturally weathered material

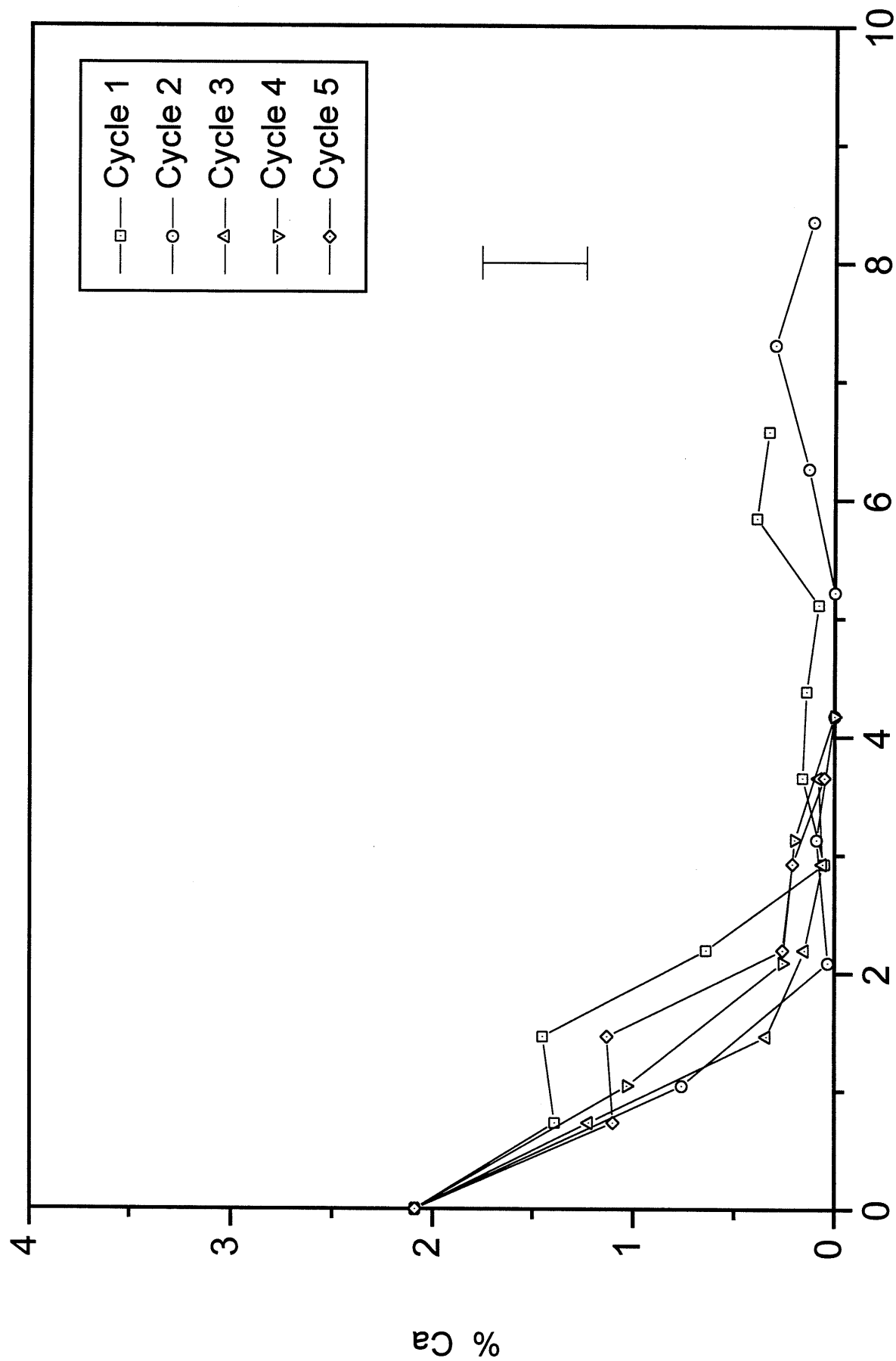


Fig.6 Variation of % Ca with exposure period for surface of AHS8 material

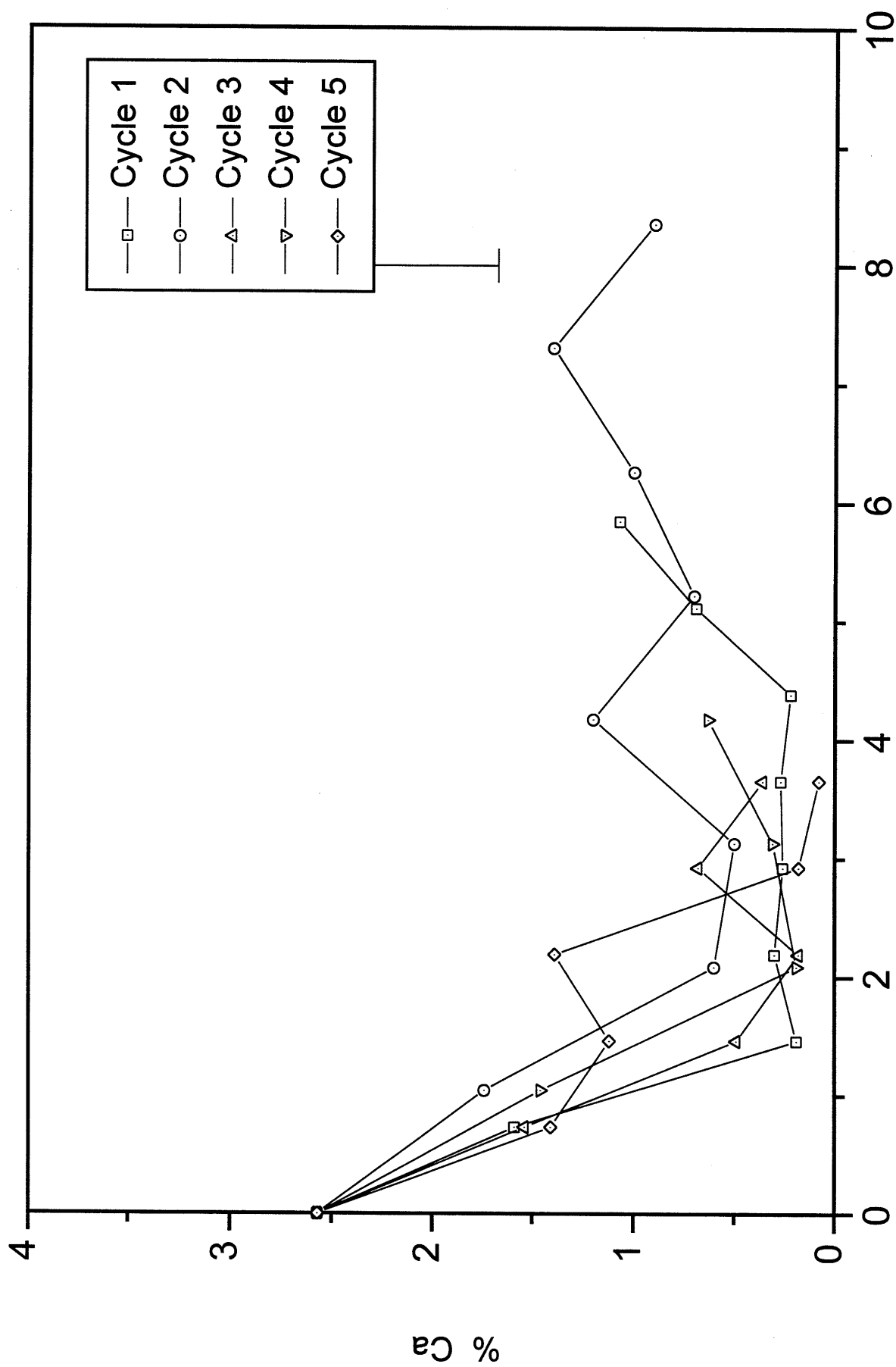


Fig.7 Variation of % Ca with exposure period for surface of AHS7 material

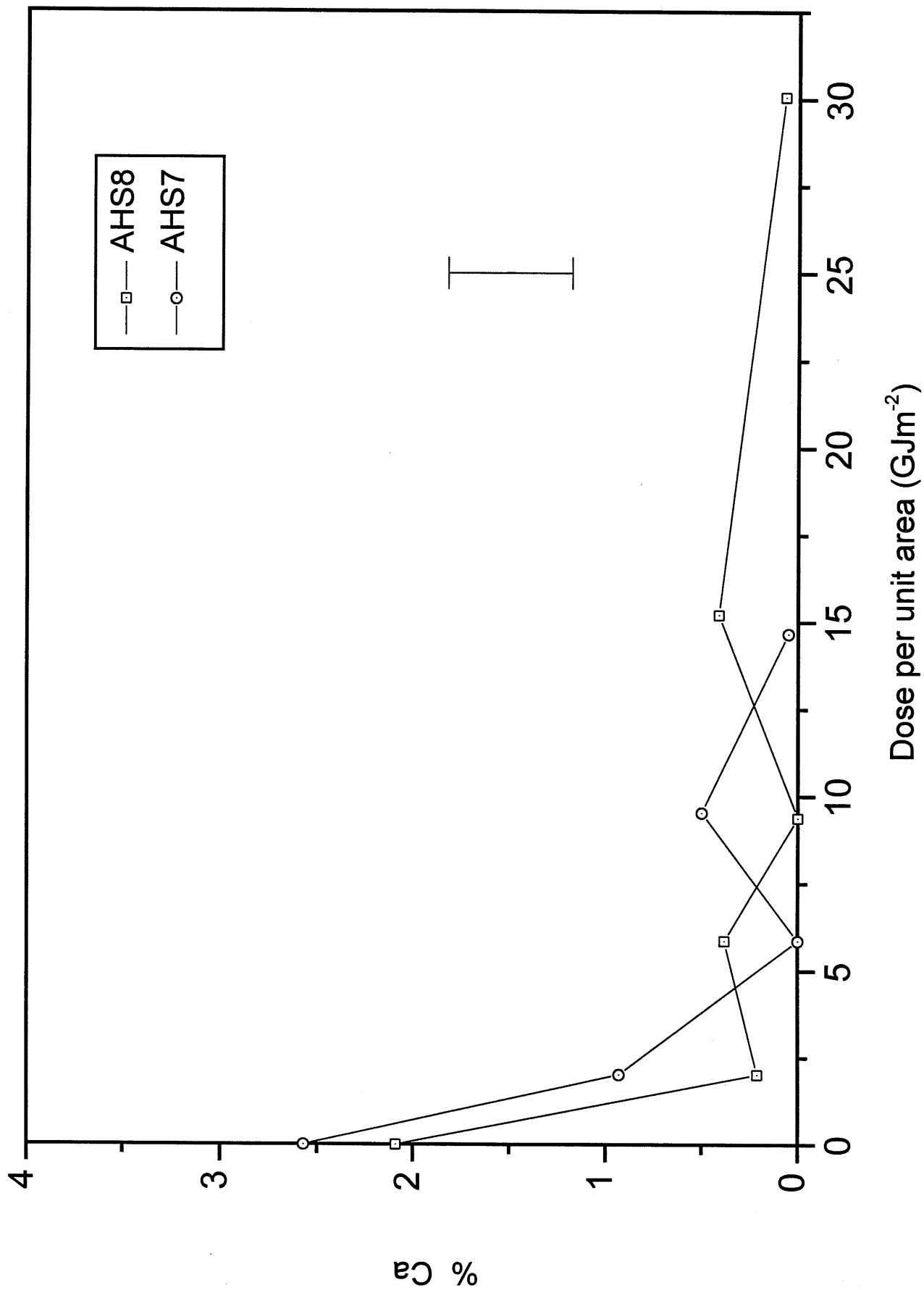


Fig.8 Variation of % Ca with exposure period for surface of naturally weathered material

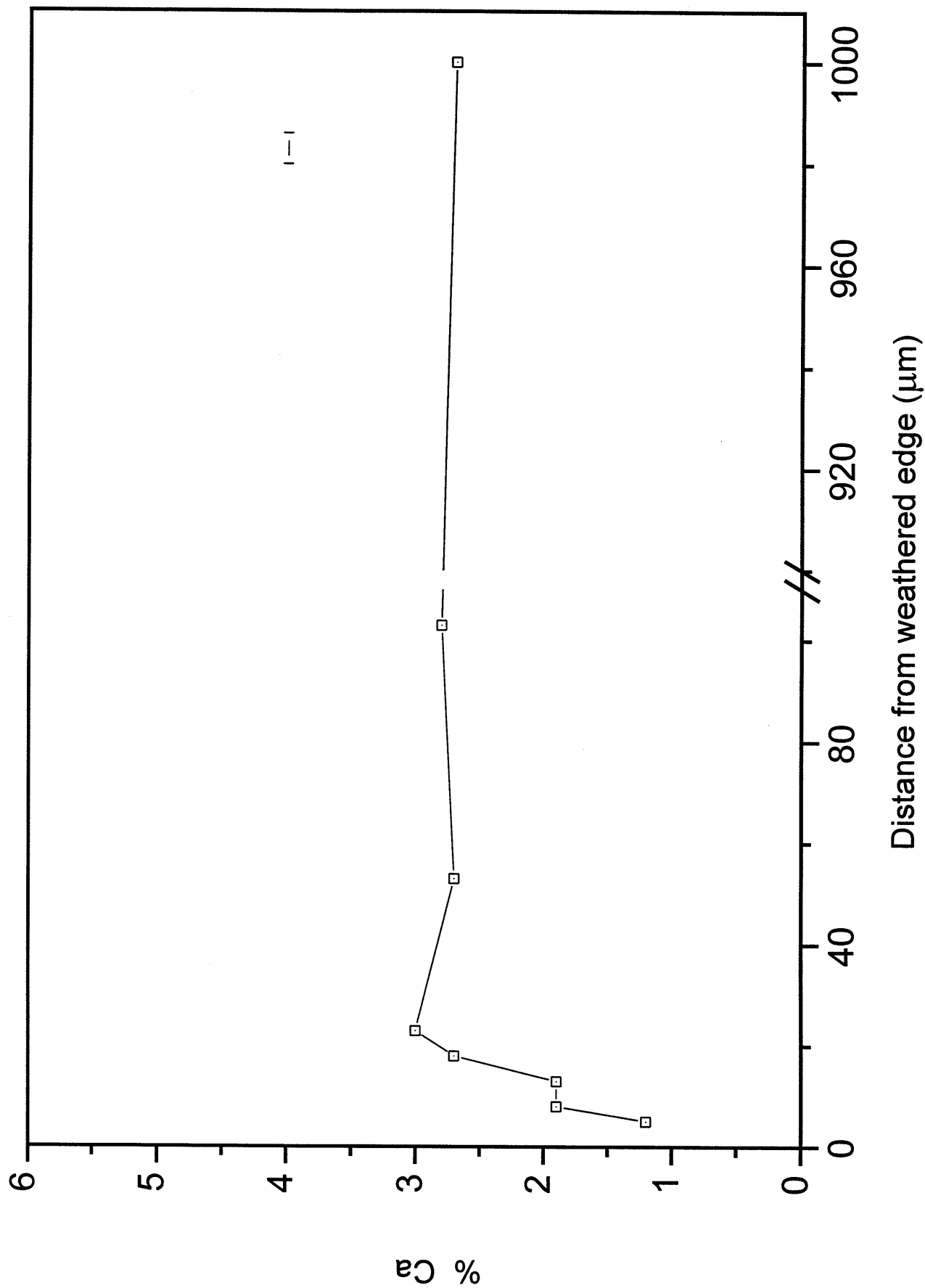


Fig.9 Variation of % Ca with cross-sectional depth for AHS8 material (cycle 1, 5.12 GJm^{-2})

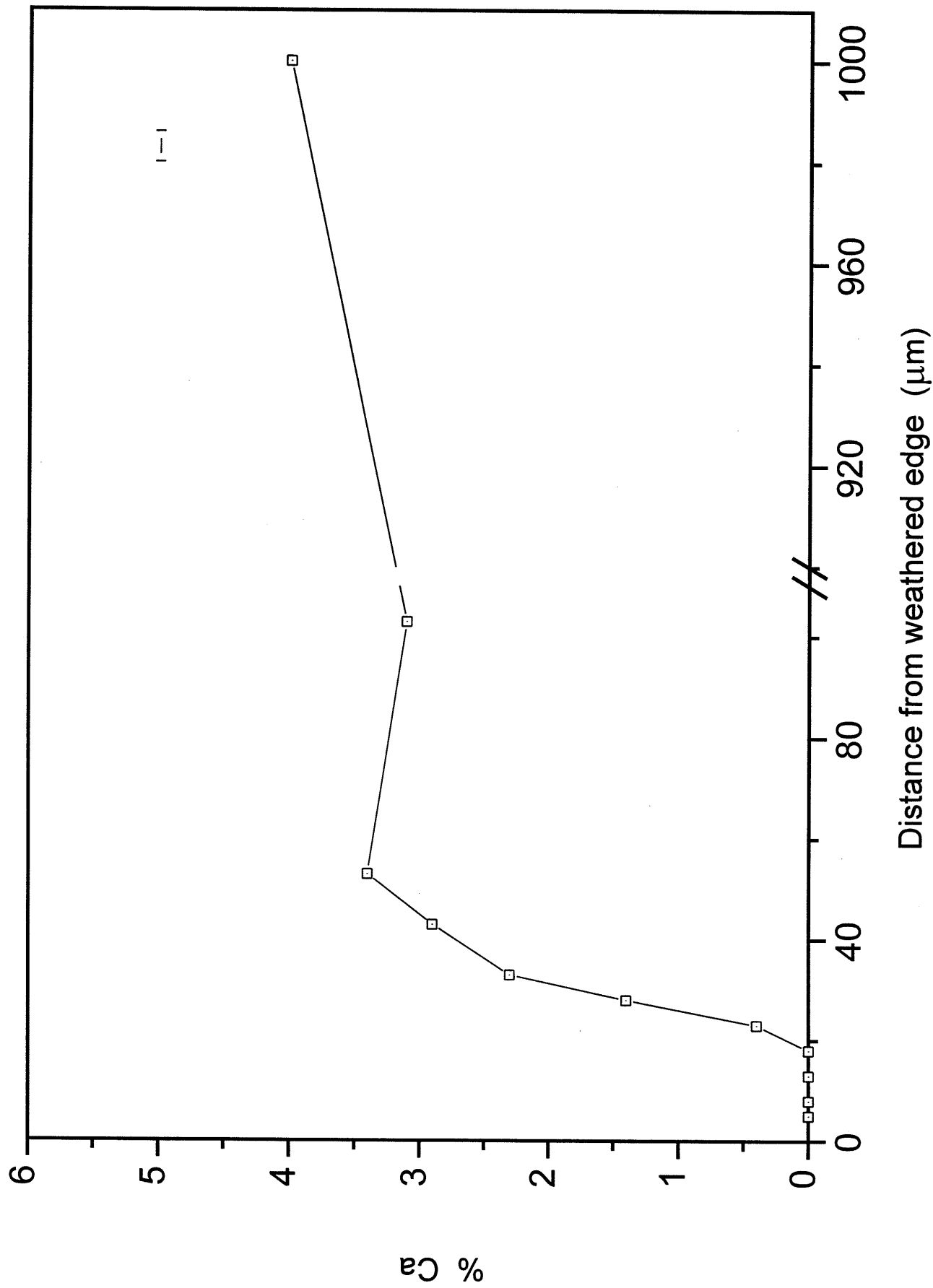
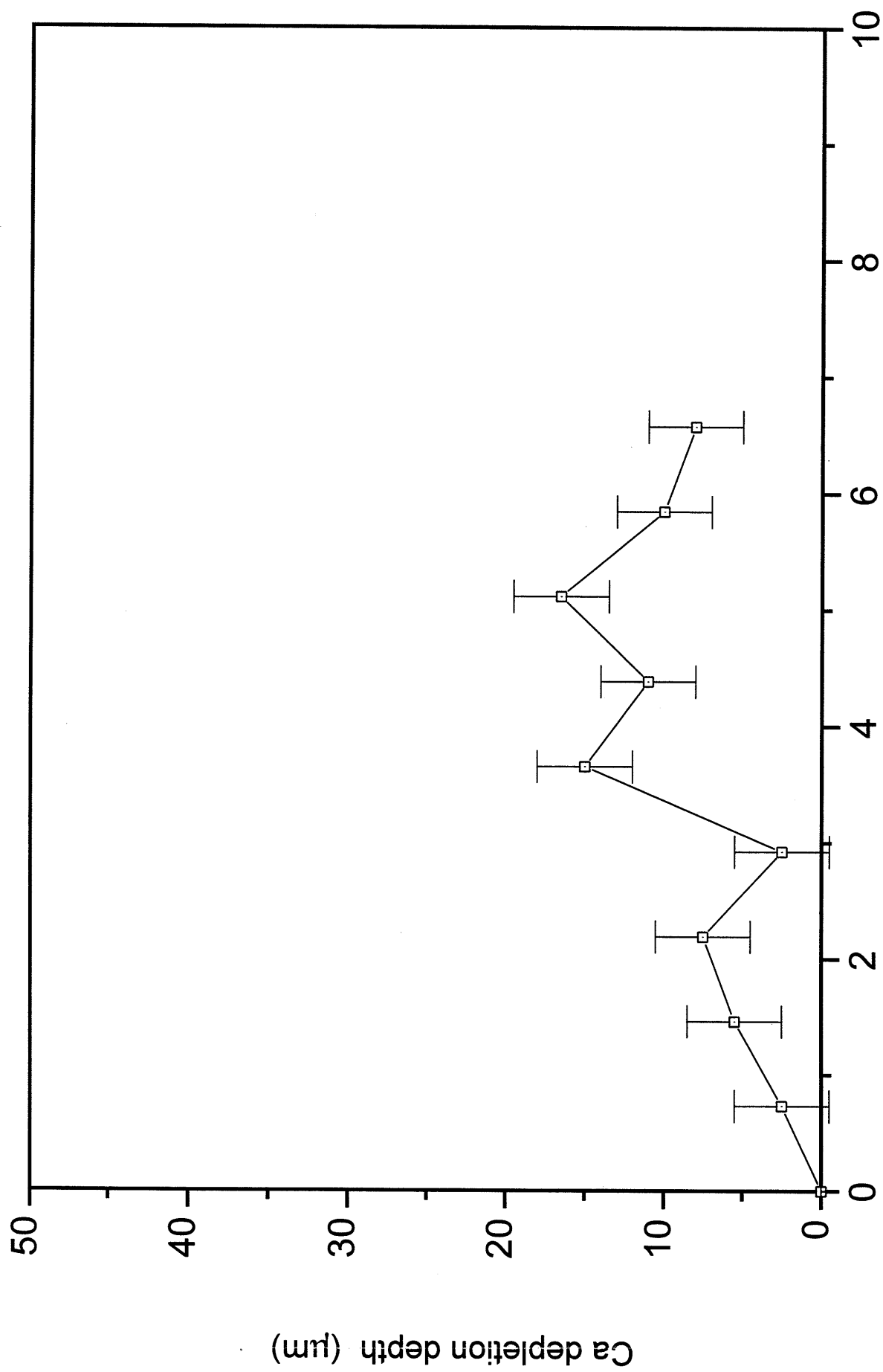


Fig.10 Variation of % Ca with cross-sectional depth
for naturally weathered AHS8 material (30.07 GJm^{-2})



Dose per unit area (GJm⁻²)

Fig.11 Variation of Ca depletion depth with exposure period for AHS8 material (cycle 1)

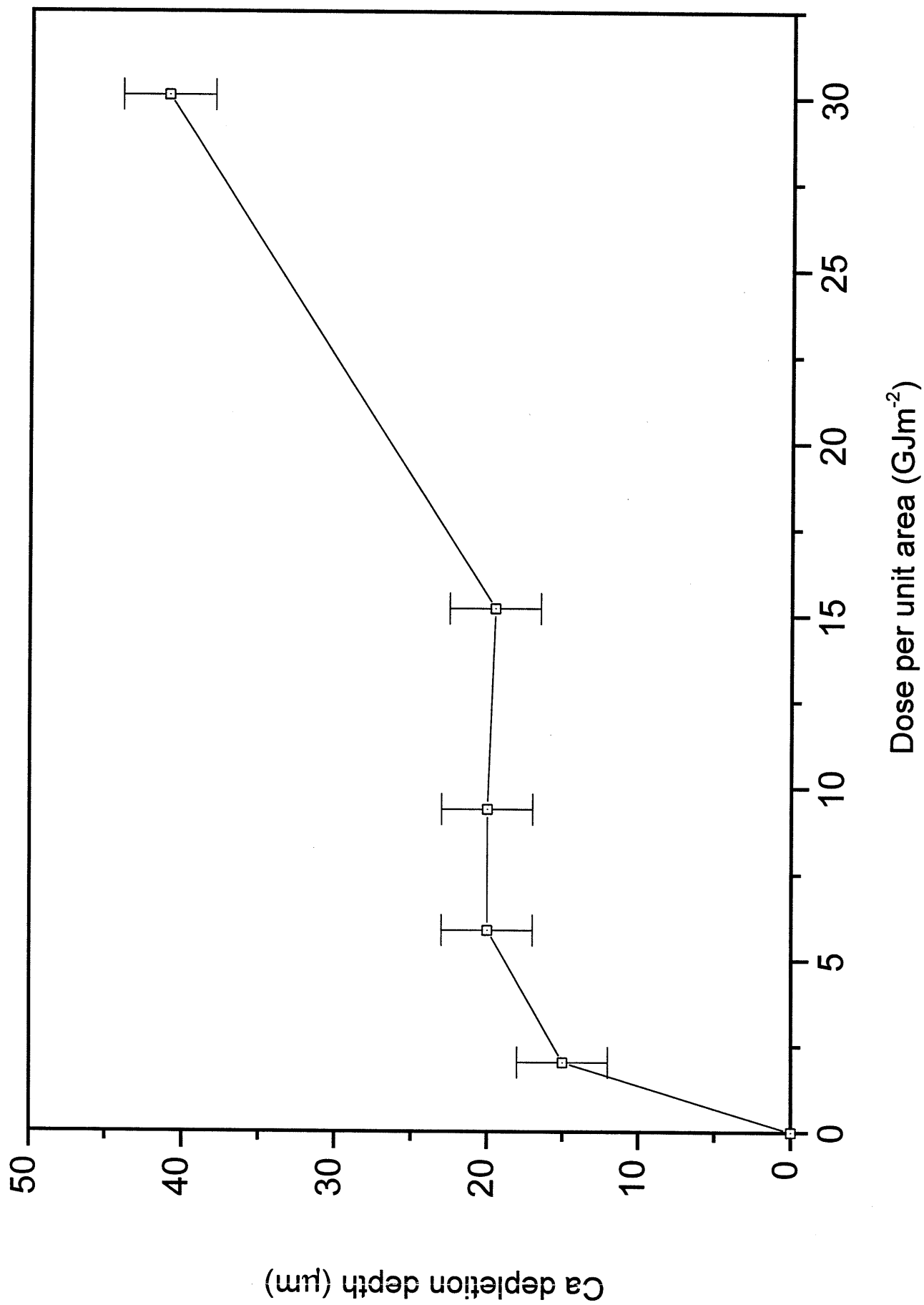


Fig.12 Variation of Ca depletion depth with exposure period
for naturally weathered AHS8 material

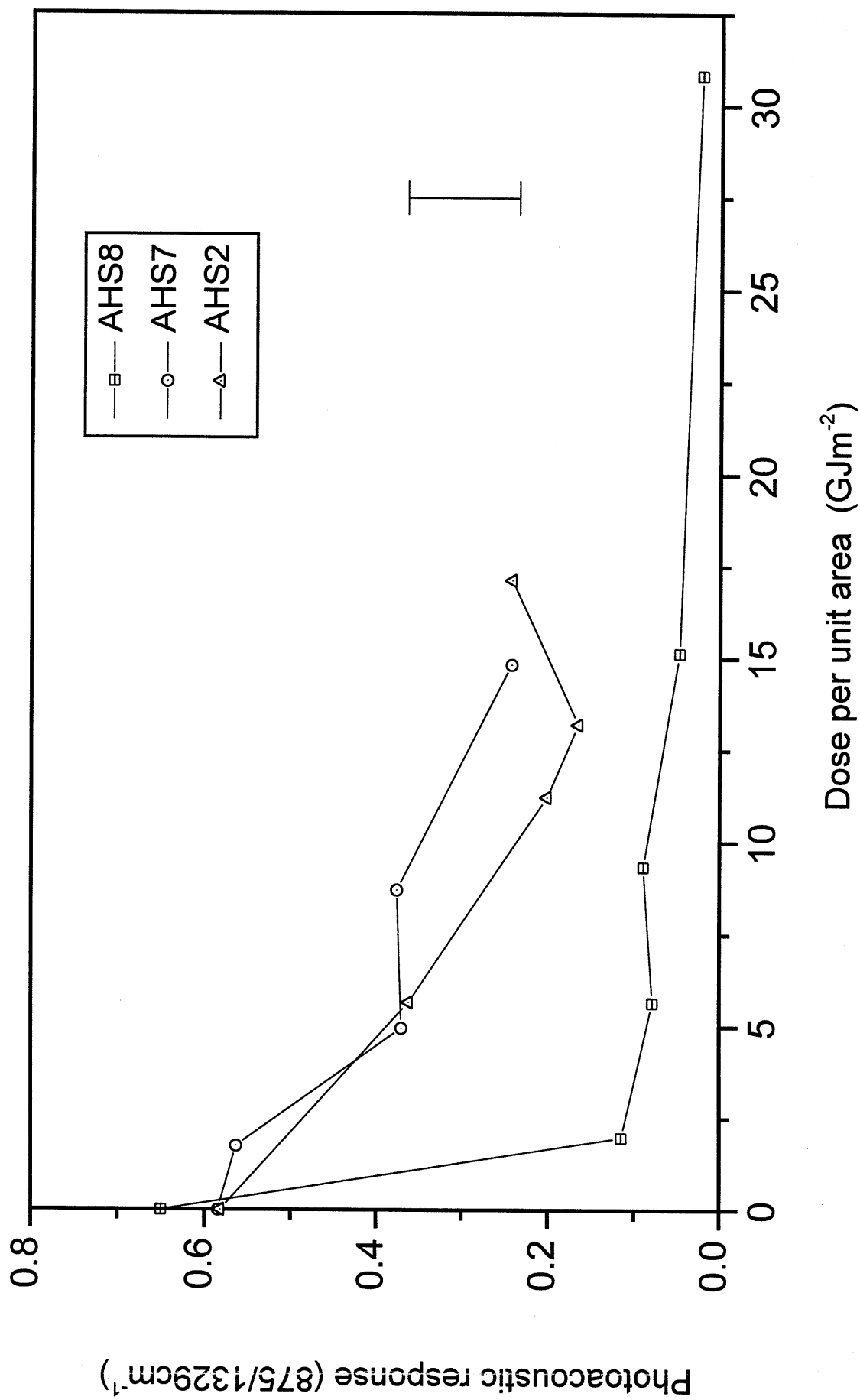


Fig.13 Variation of CO₃ with exposure period
for naturally weathered material

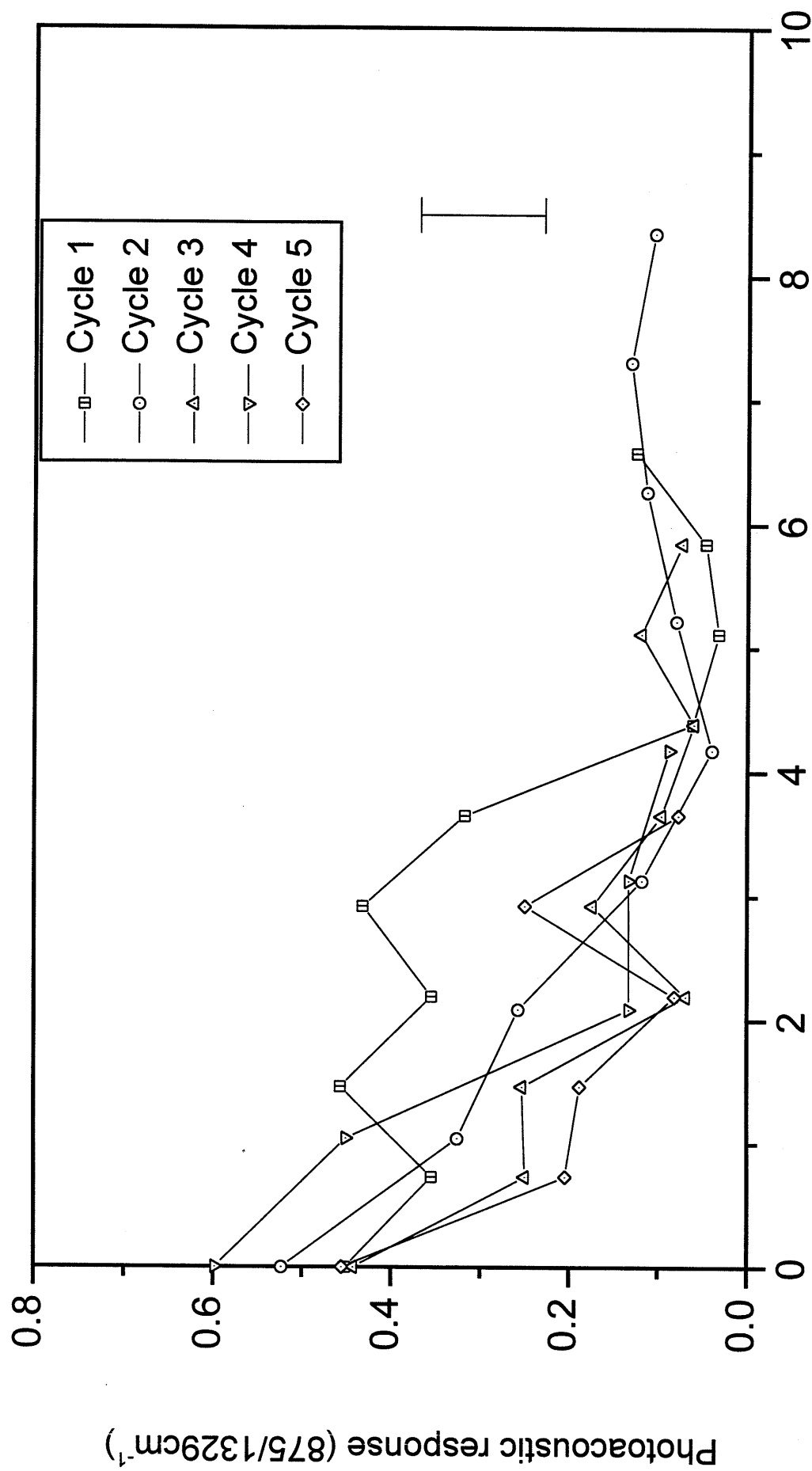


Fig.14 Variation of CO₃ with exposure period for AHS8 material

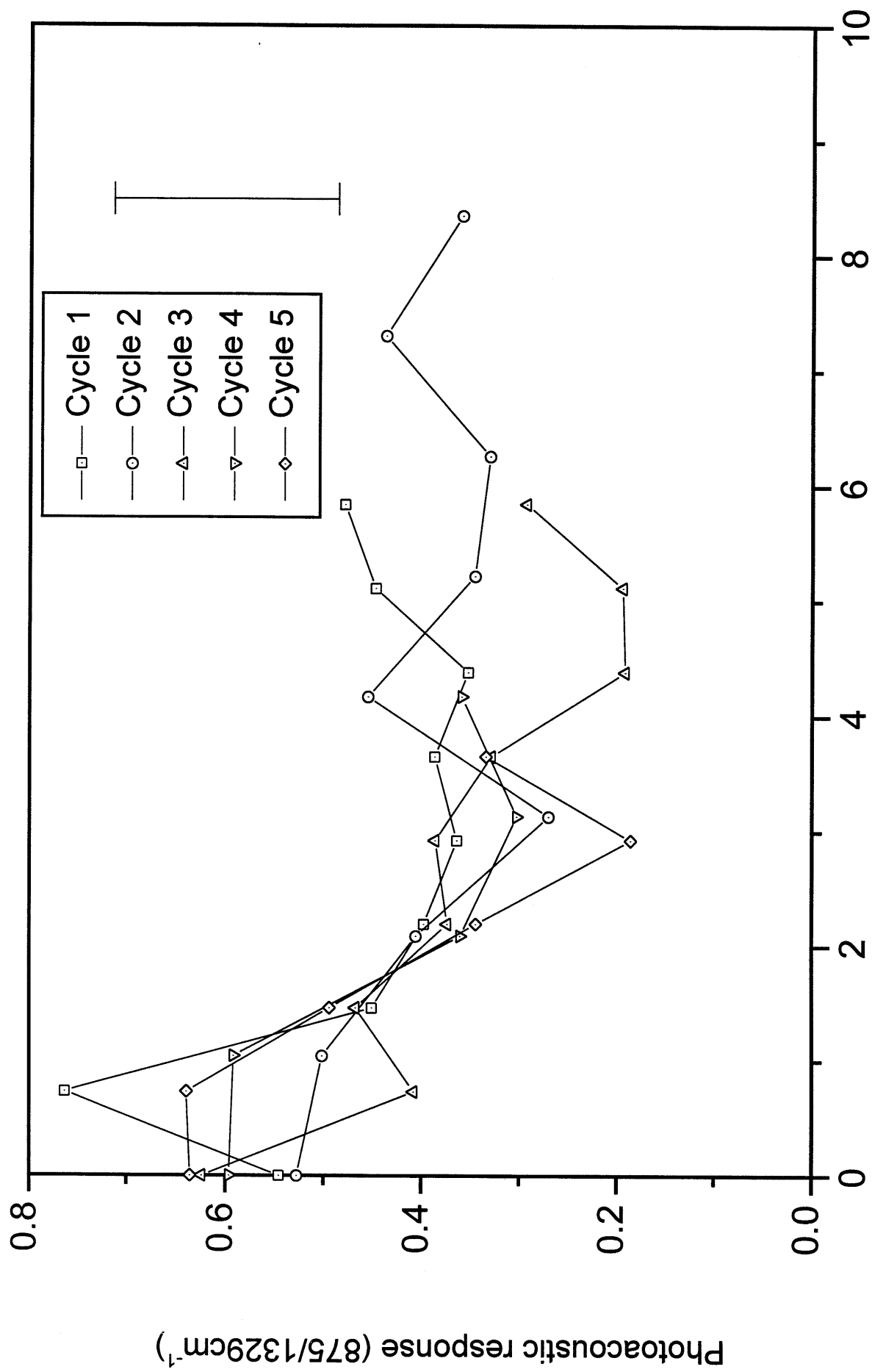


Fig.15 Variation of CO₃ with exposure period for AHS7 material

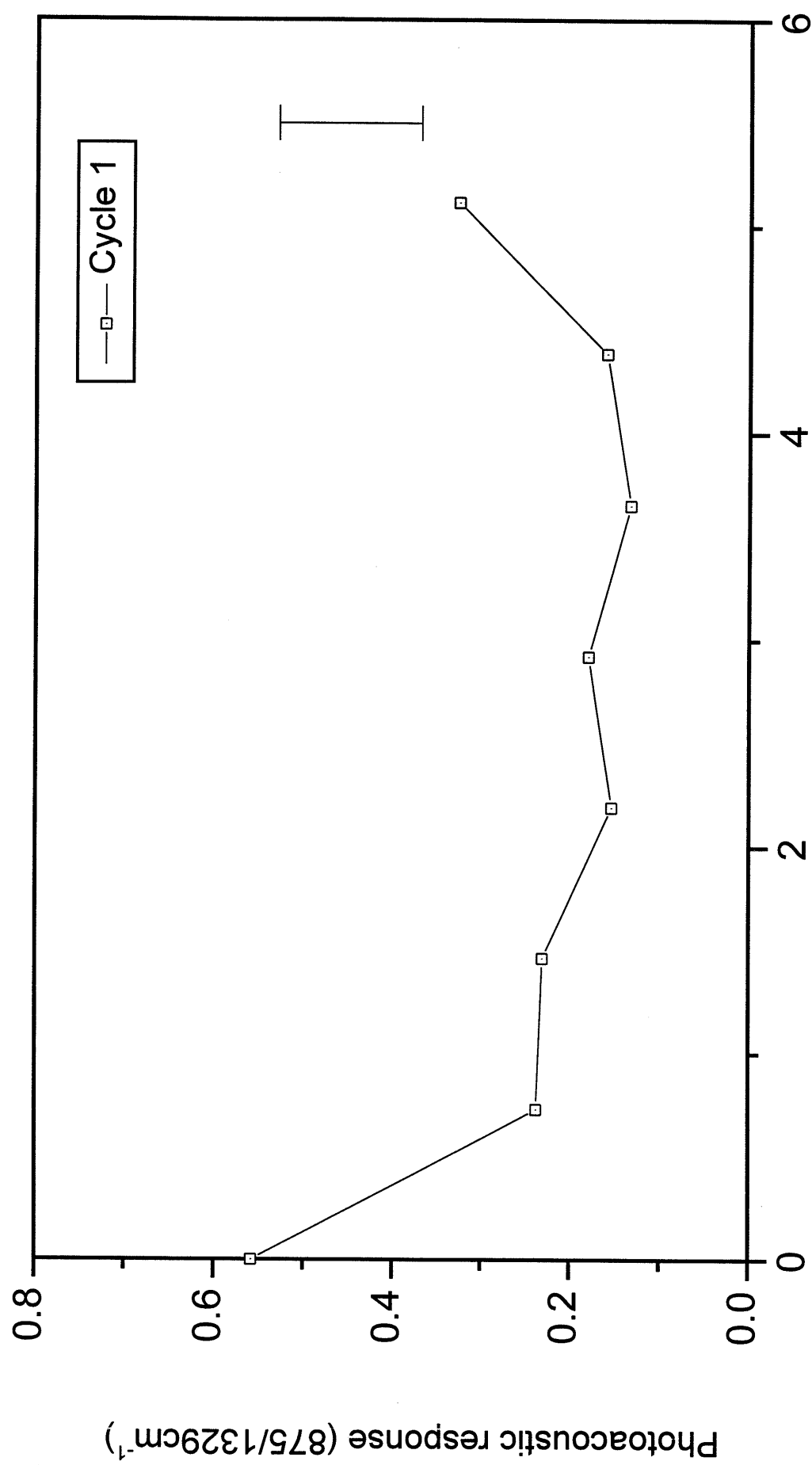


Fig.16 Variation of CO₃ with exposure period for AHS2 material

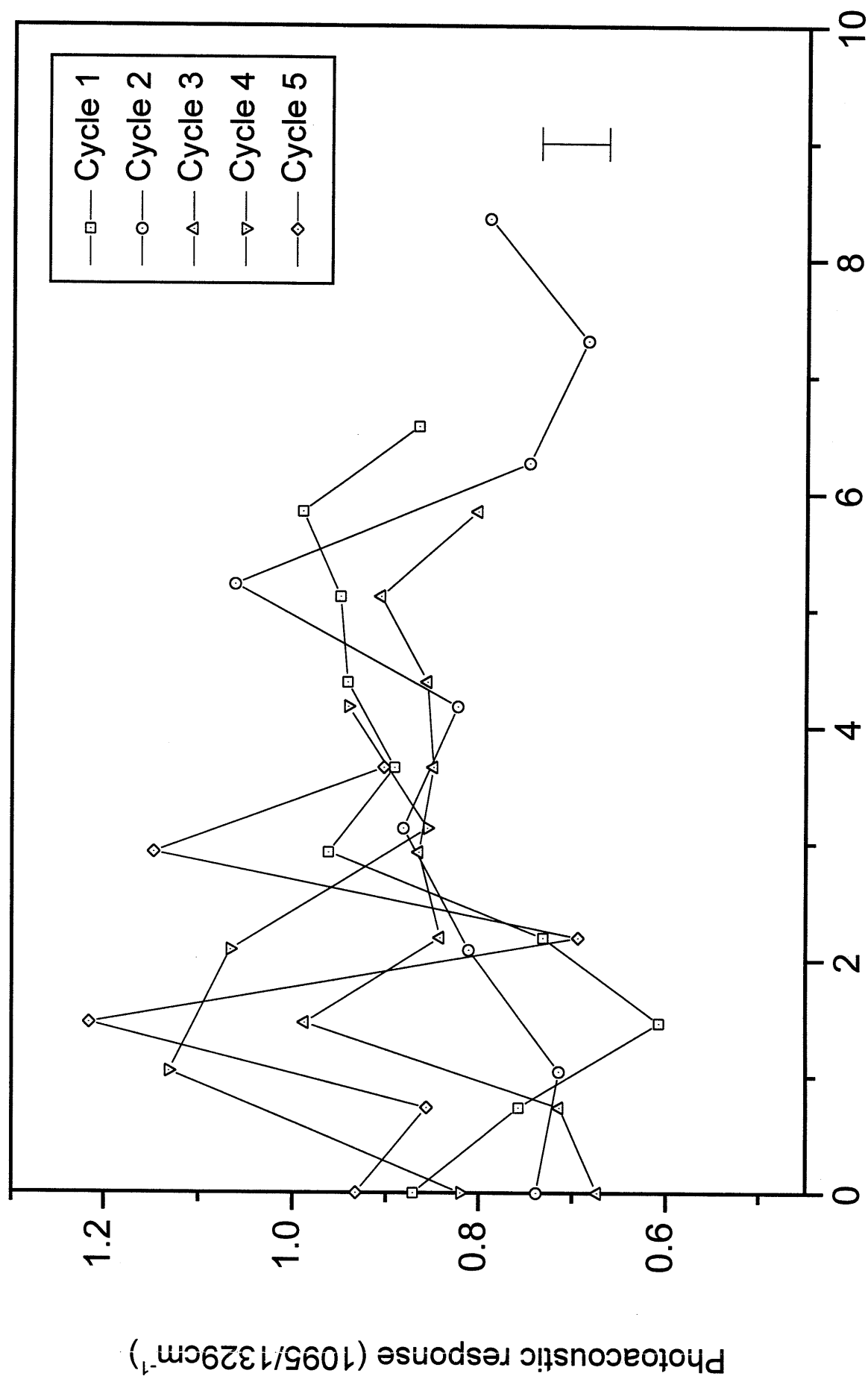


Fig.17 Variation of C-O abs. with exposure period for AHS8 material

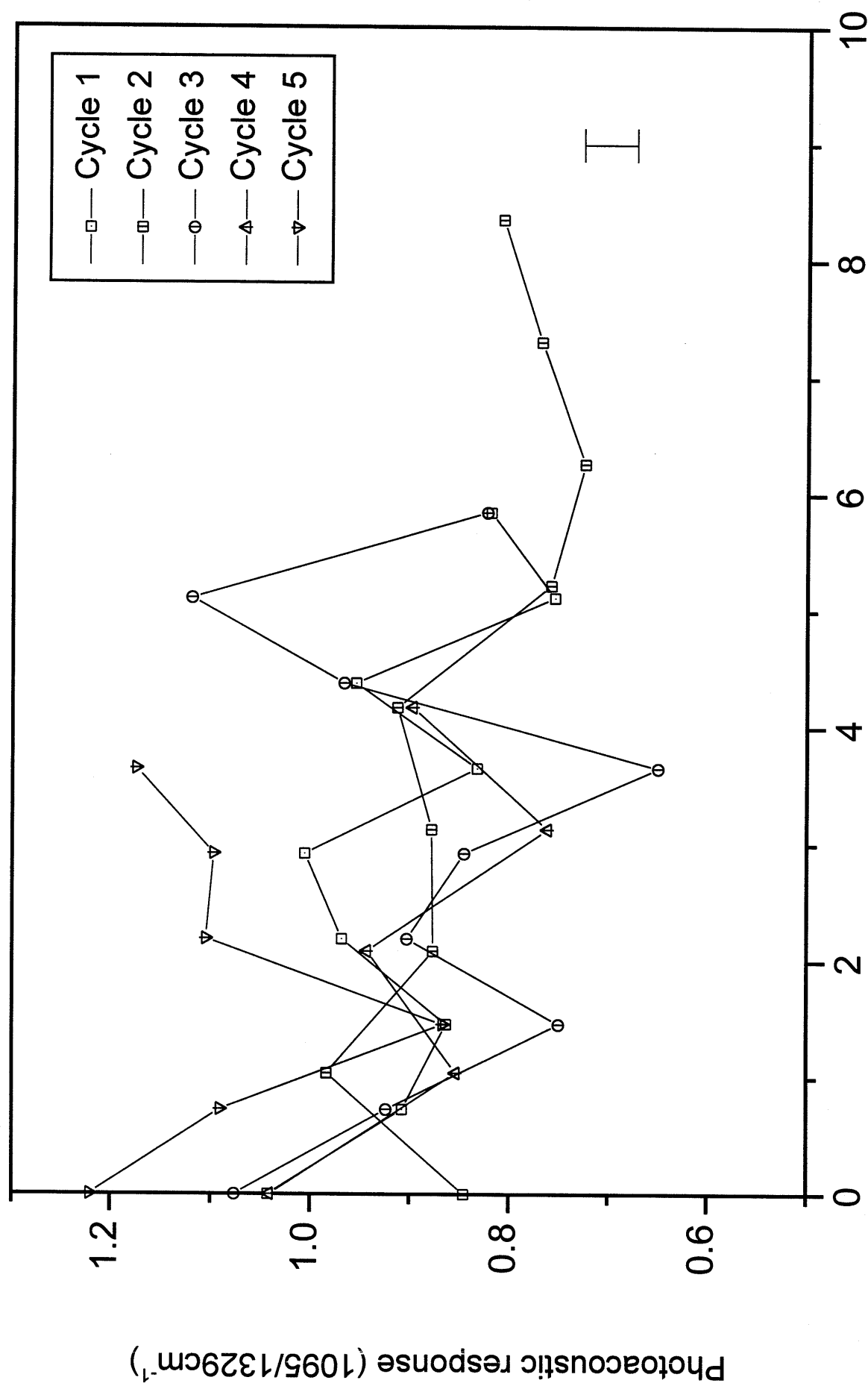
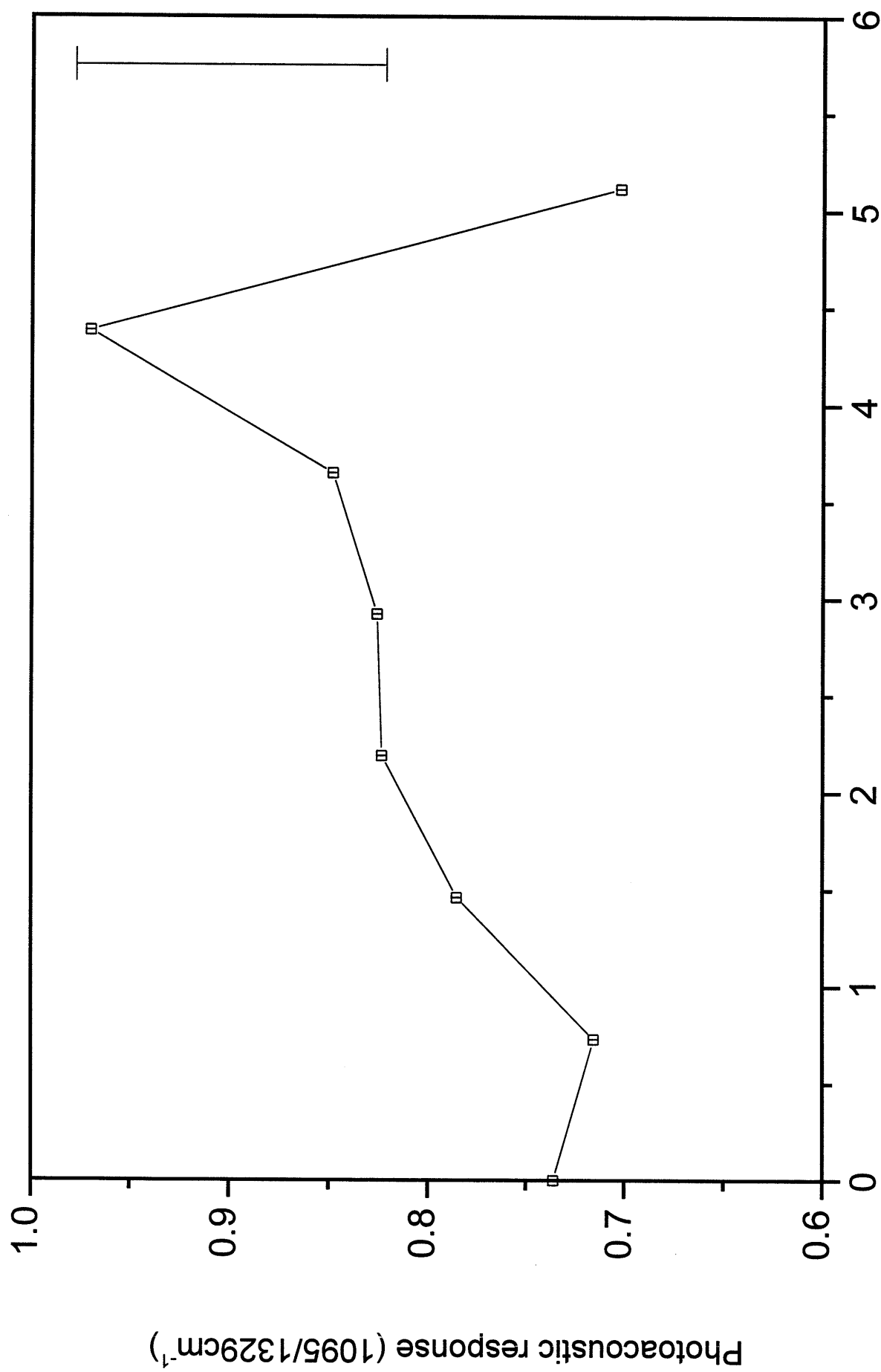


Fig.18 Variation of C-O abs. with exposure period for AHS7 material



Dose per unit area (GJm^{-2})

Fig.19 Variation of C-O abs. with exposure period
for AHS2 material

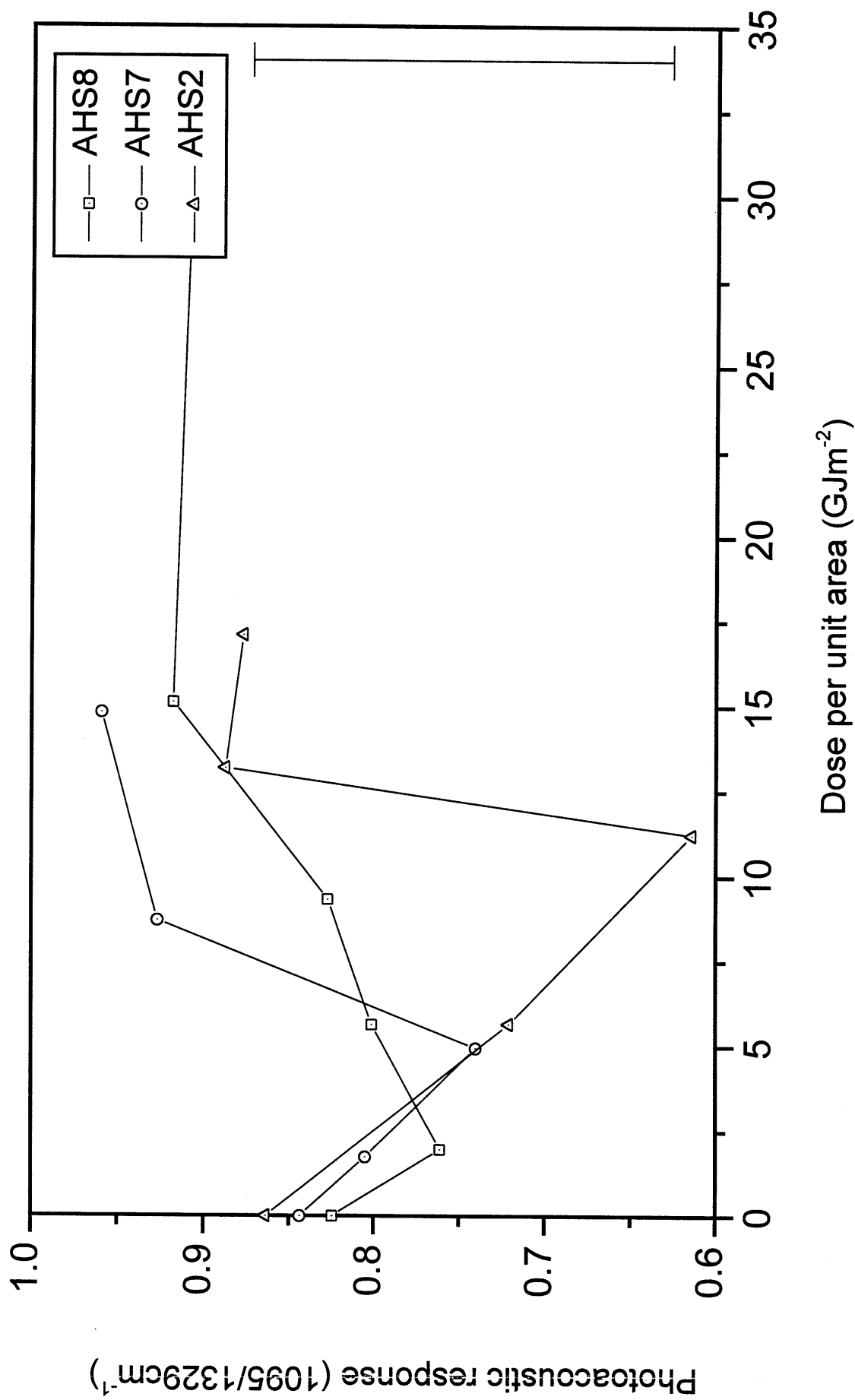
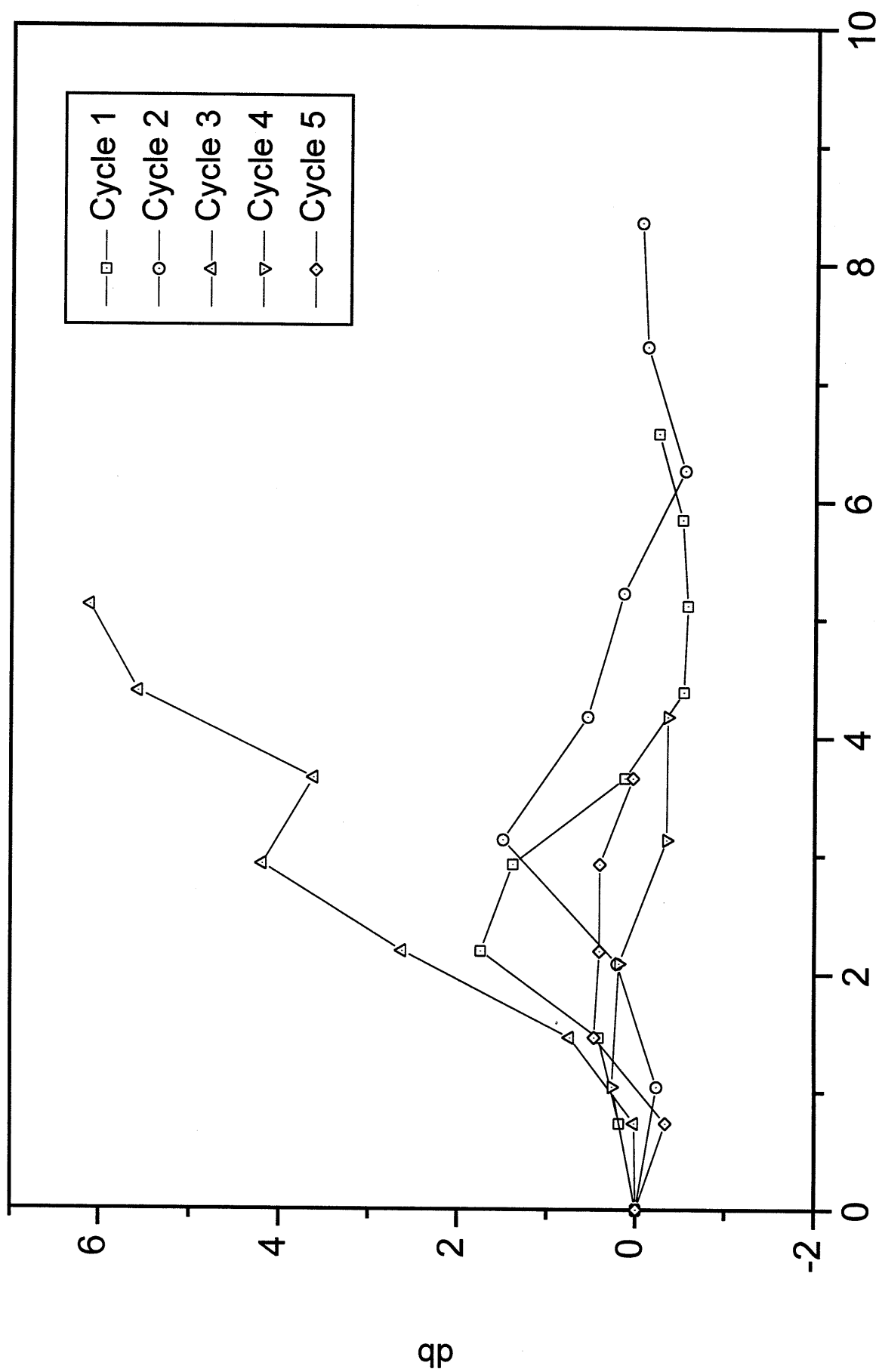


Fig.20 Variation of C-O abs. with exposure period for naturally weathered material



Dose per unit area (GJm⁻²)

Fig.21 Variation of colour (dp) with exposure
period for AHS8 material

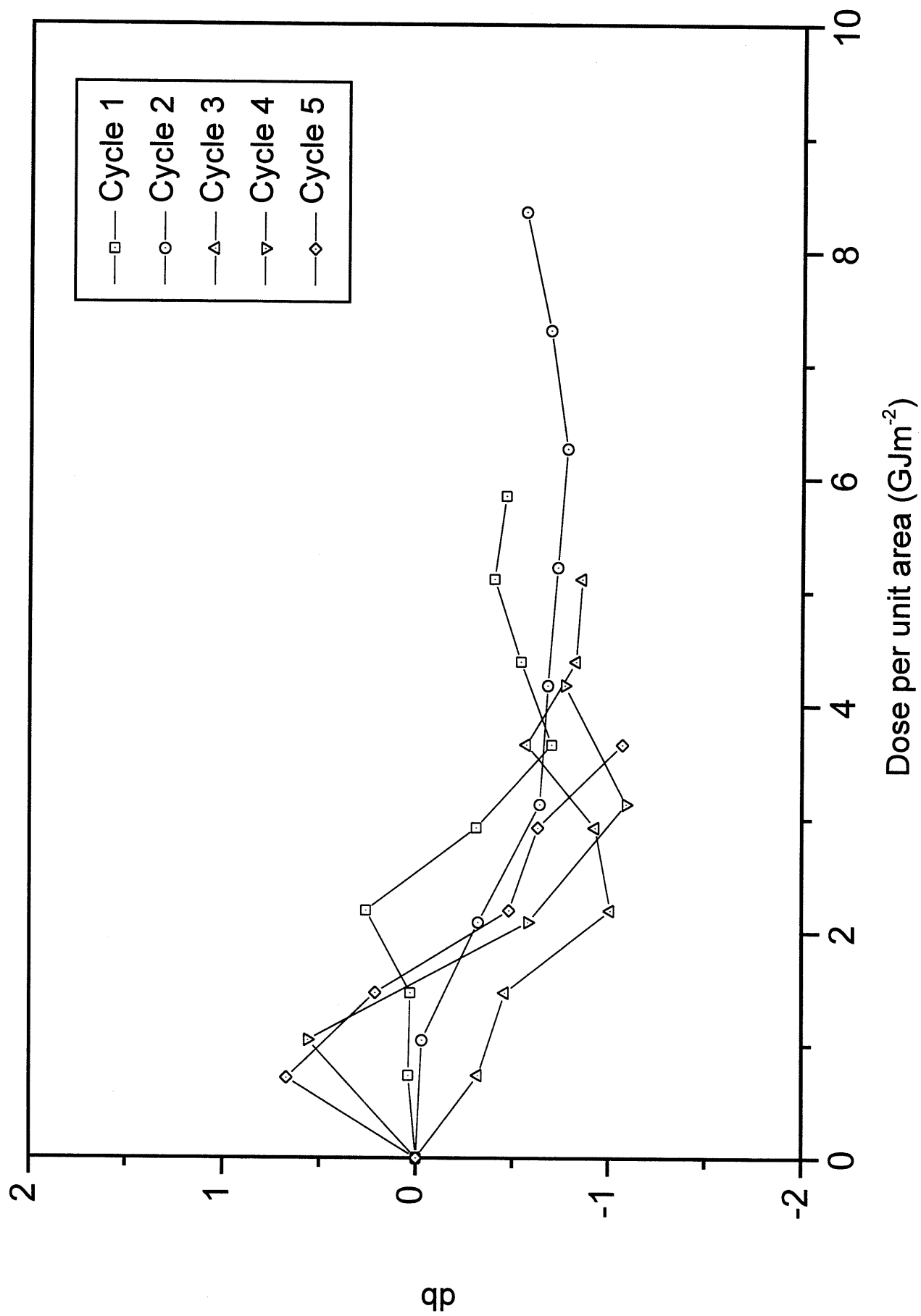


Fig.22 Variation of colour (db) for exposure period for AHS7 material

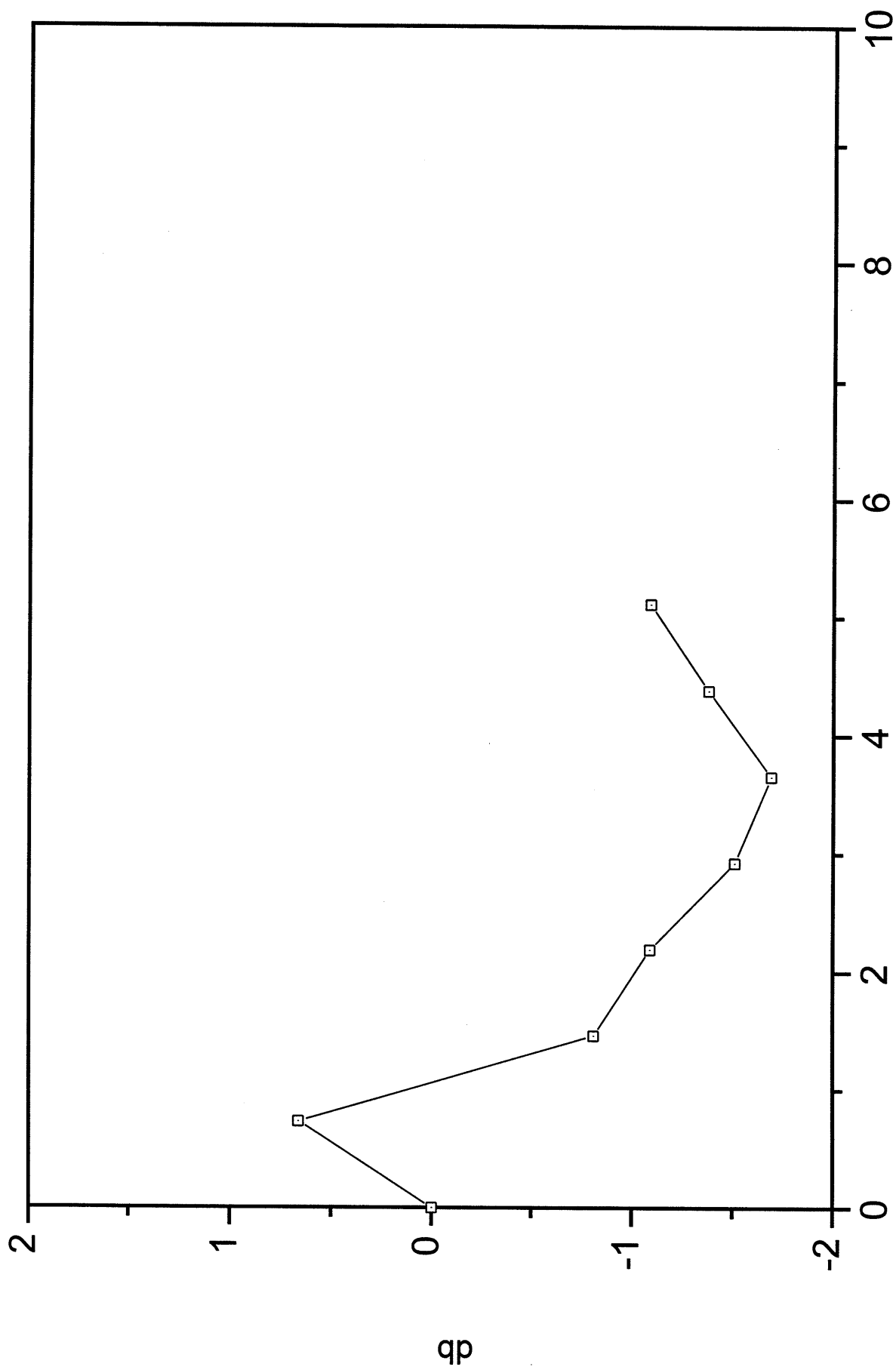


Fig.23 Variation of colour (db) with exposure period for AHS2 material (Cycle 1)

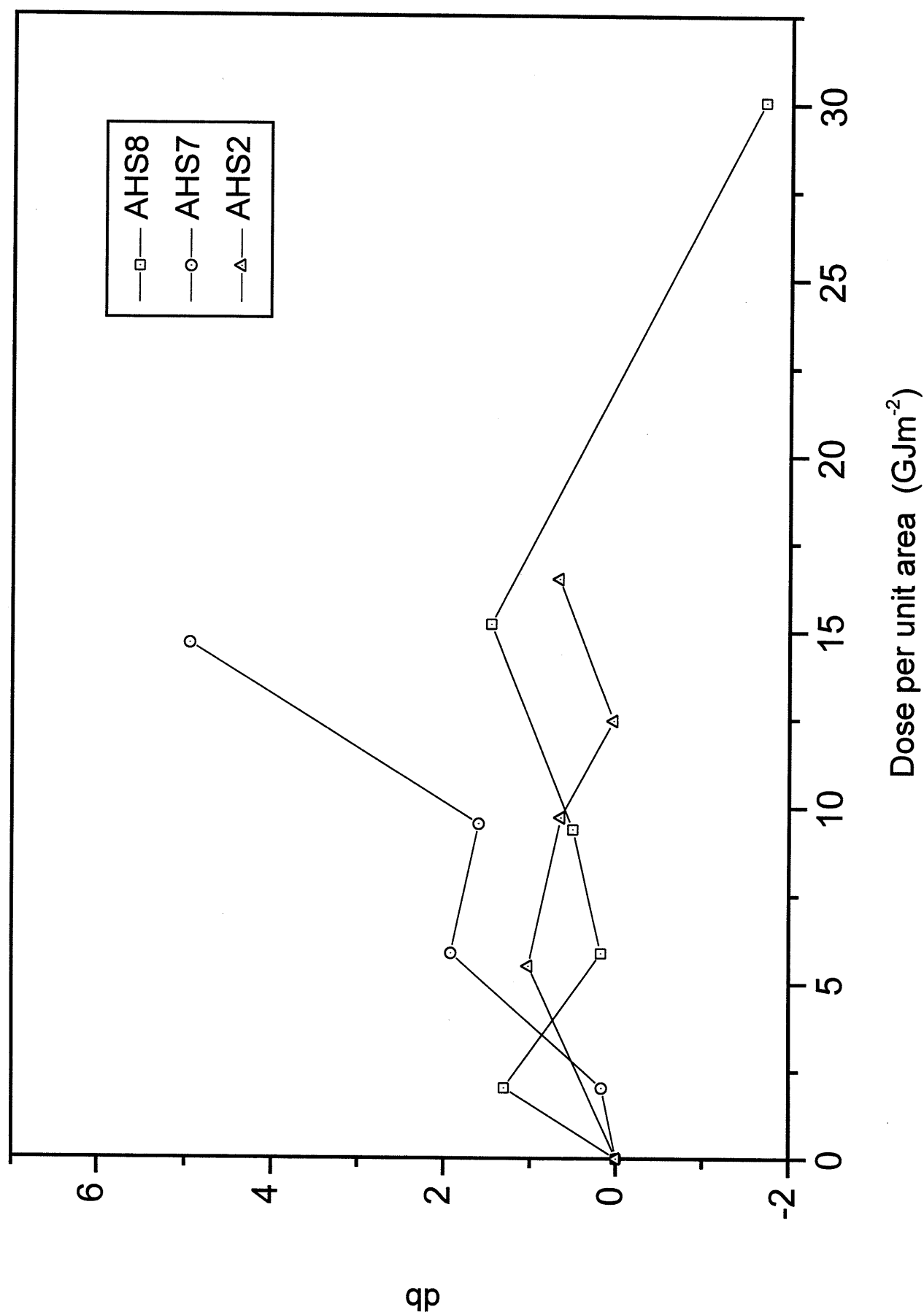


Fig.24 Variation of colour (dp) with exposure period for naturally weathered material

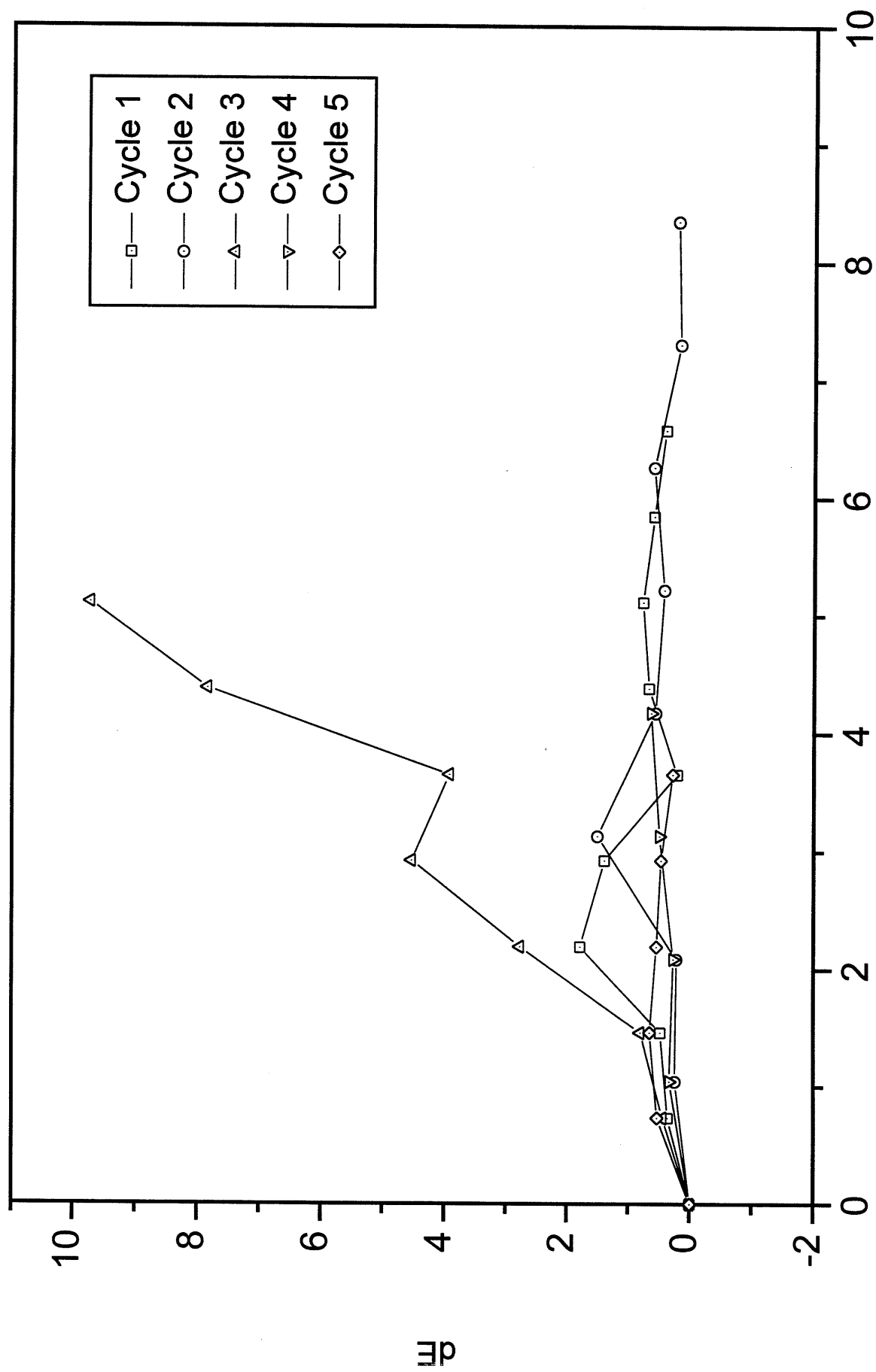
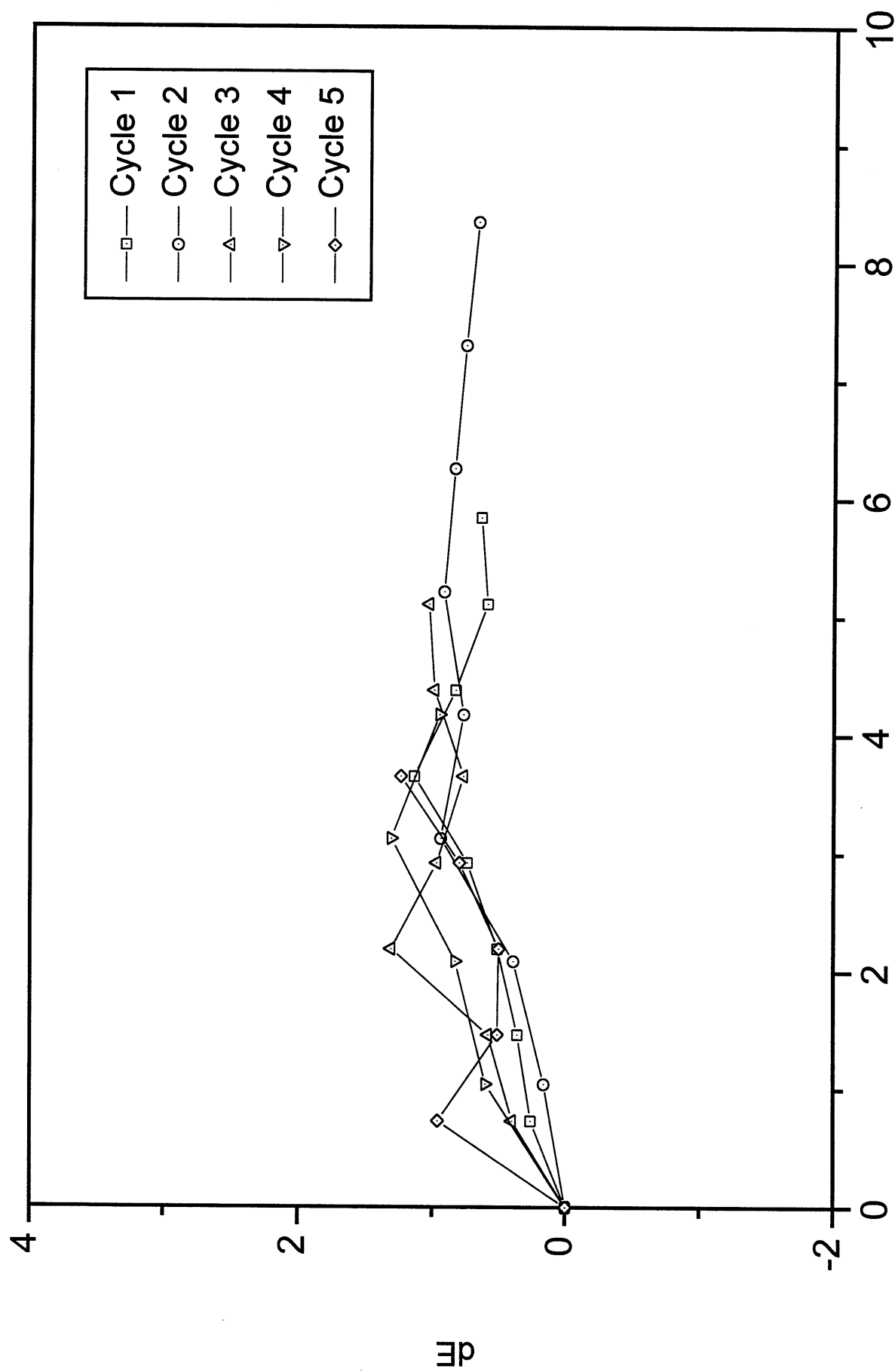
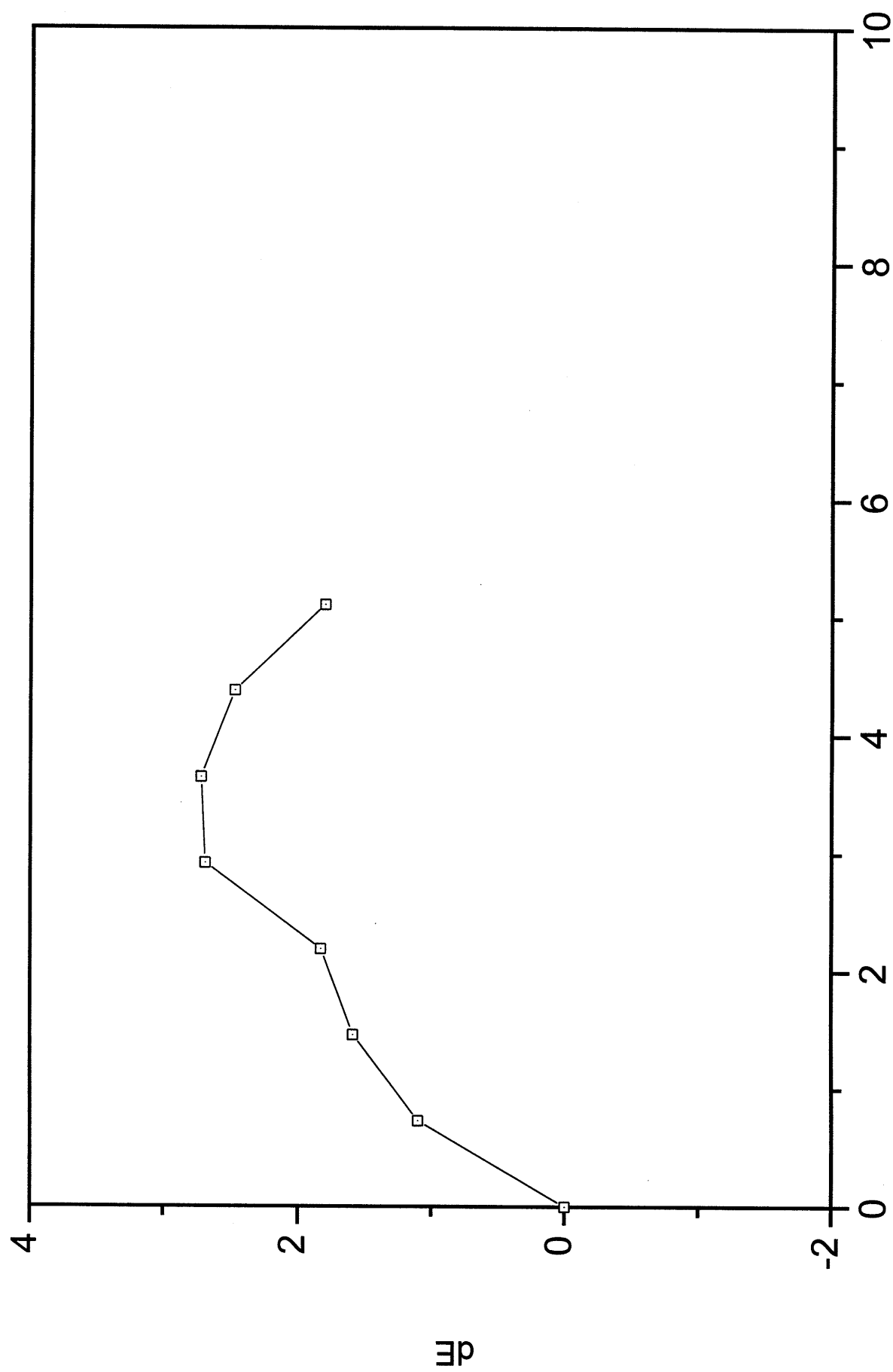


Fig.25 Variation of colour (dE) with exposure period for AHS8 material



Dose per unit area (GJm⁻²)

Fig.26 Variation of colour (dE) with exposure
period for AHS7 material



Dose per unit area (GJm⁻²)

Fig.27 Variation of colour (dE) with exposure
period for AHS2 material (cycle 1)

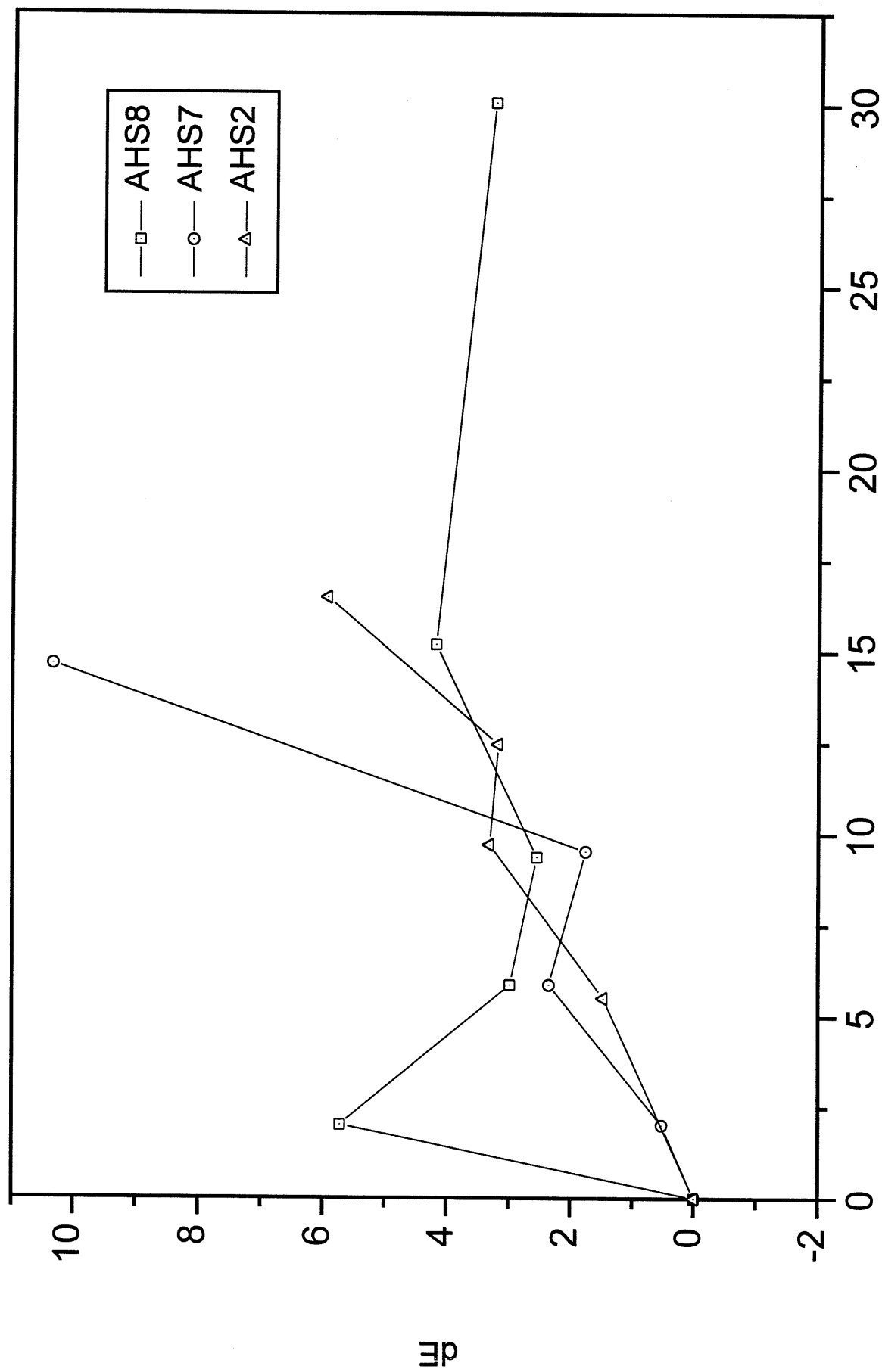


Fig.28 Variation of colour (dE) with exposure period for naturally weathered material

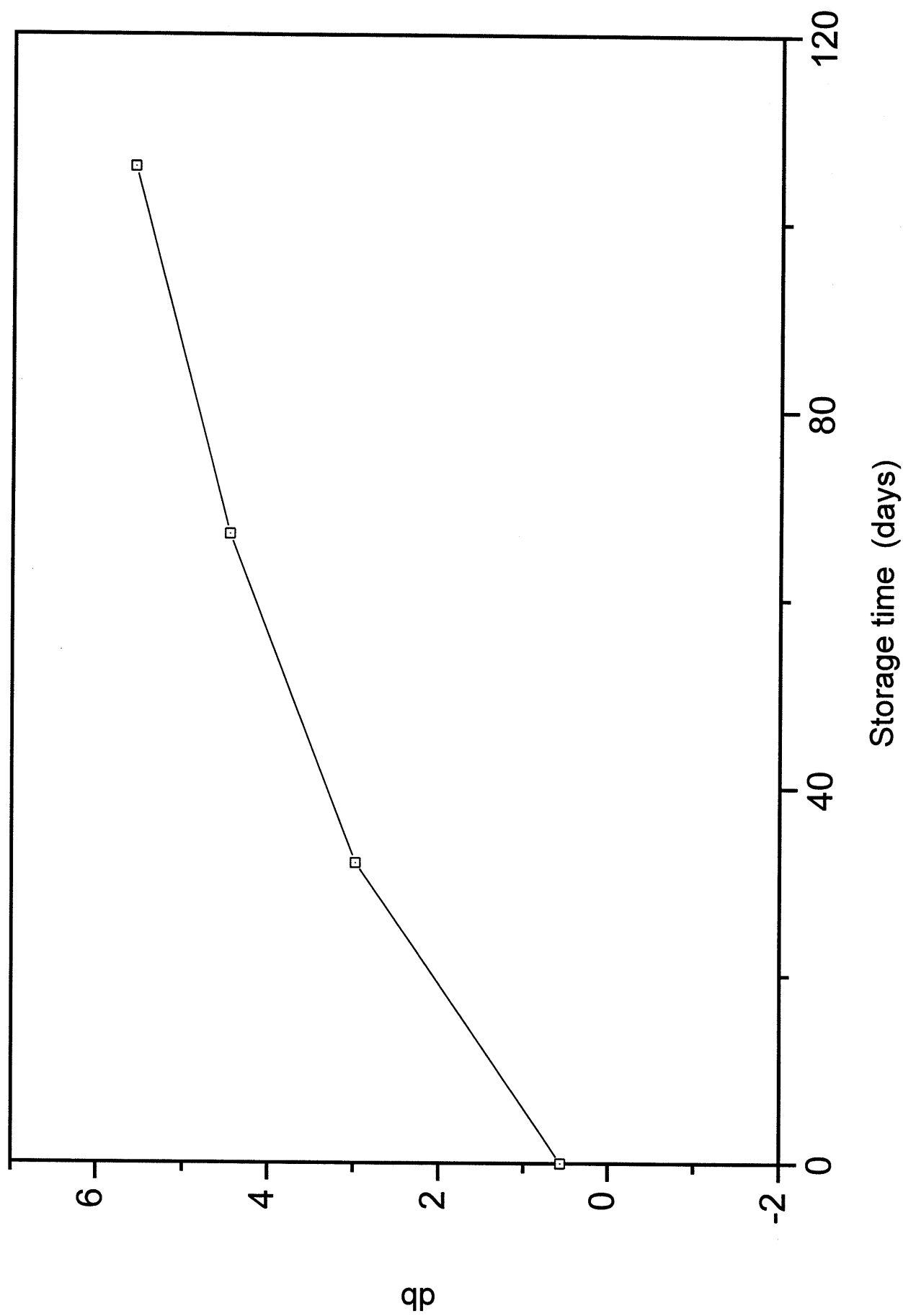


Fig.29 Colour (db) variation with storage period after 2000hrs. (2.92 GJm^{-2}) a/w of AHS8 material

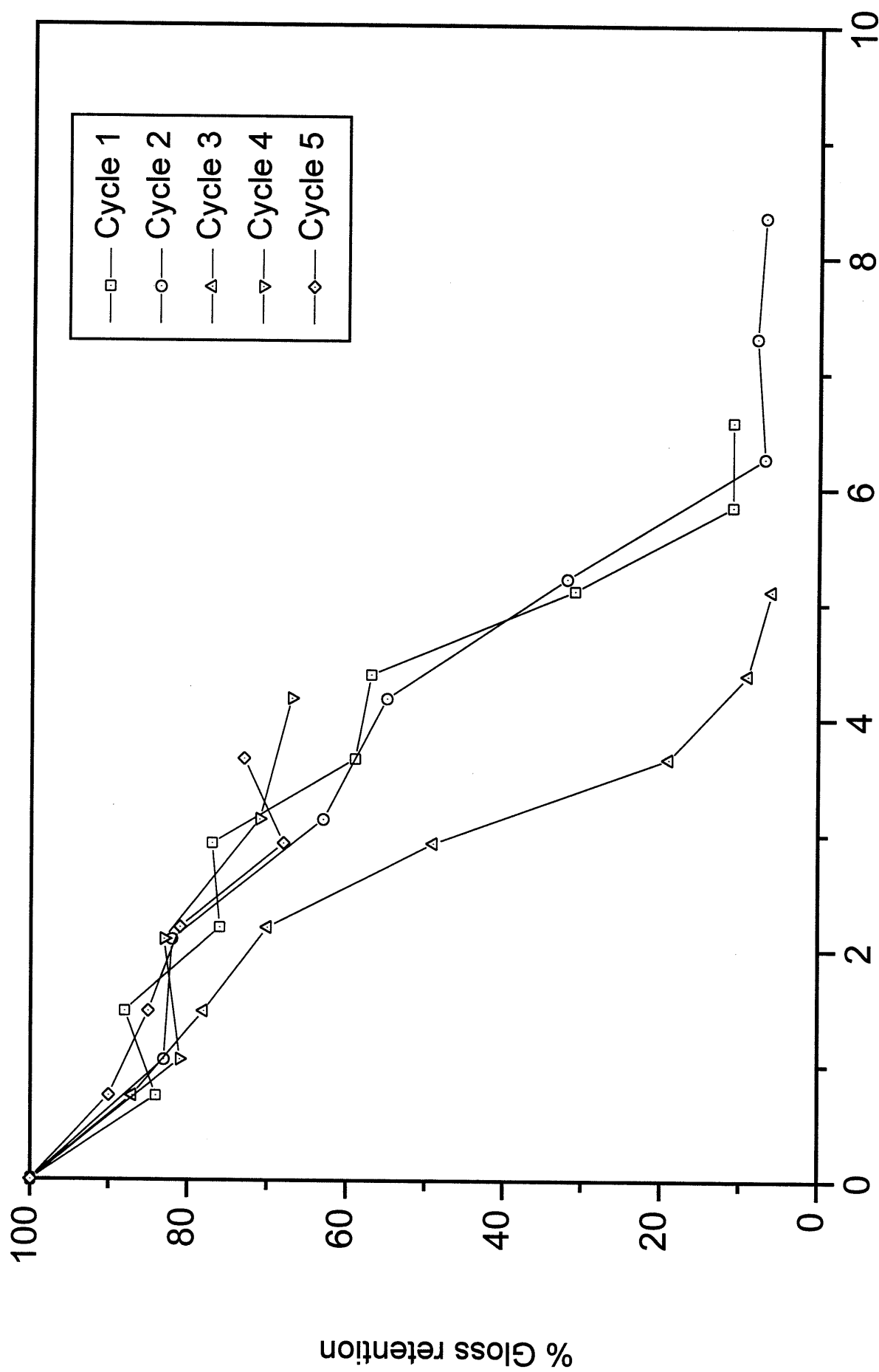


Fig.30 % Gloss retention with exposure period for AHS8 material

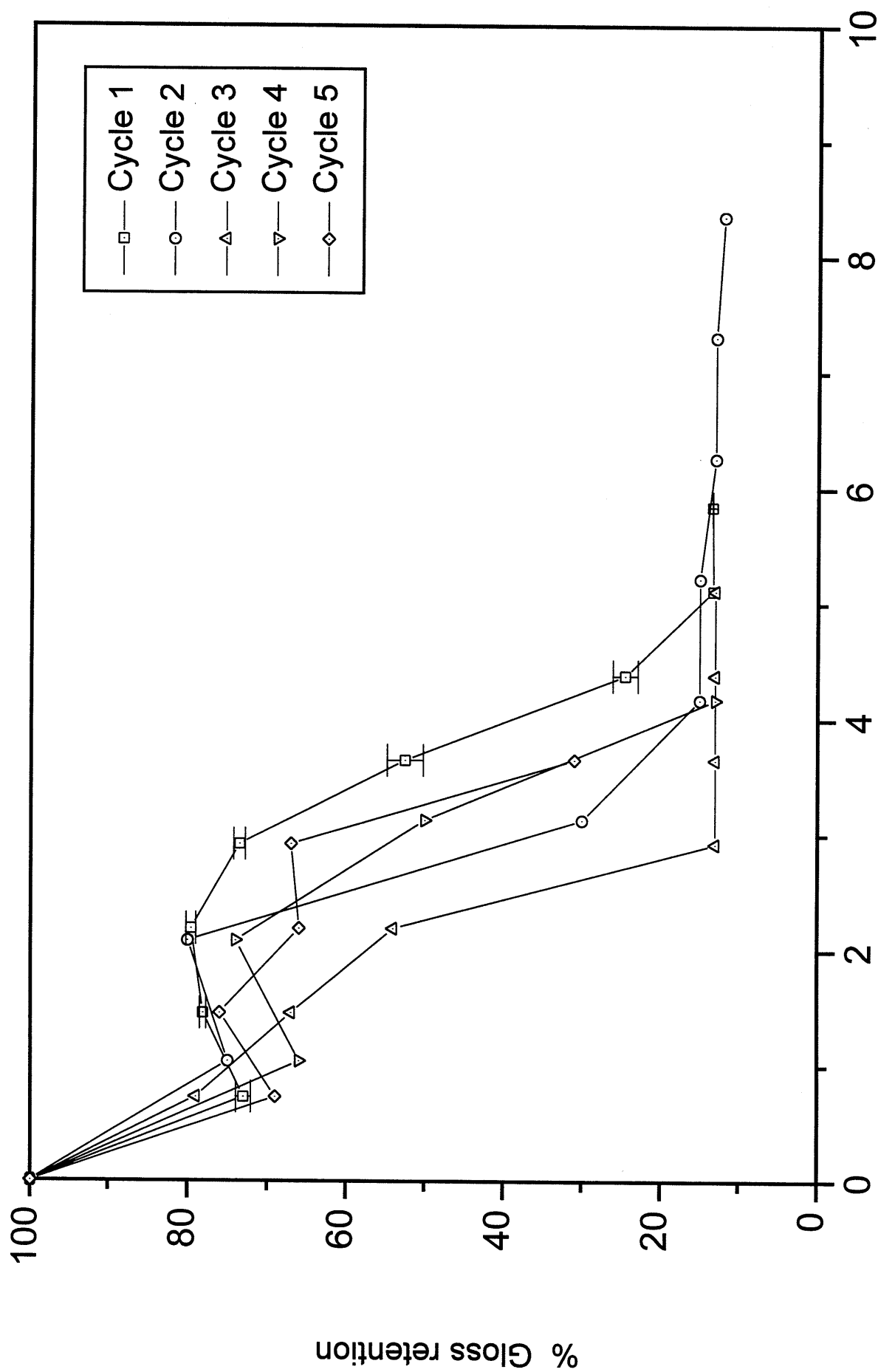


Fig.31 % Gloss retention with exposure period for AHS7 material

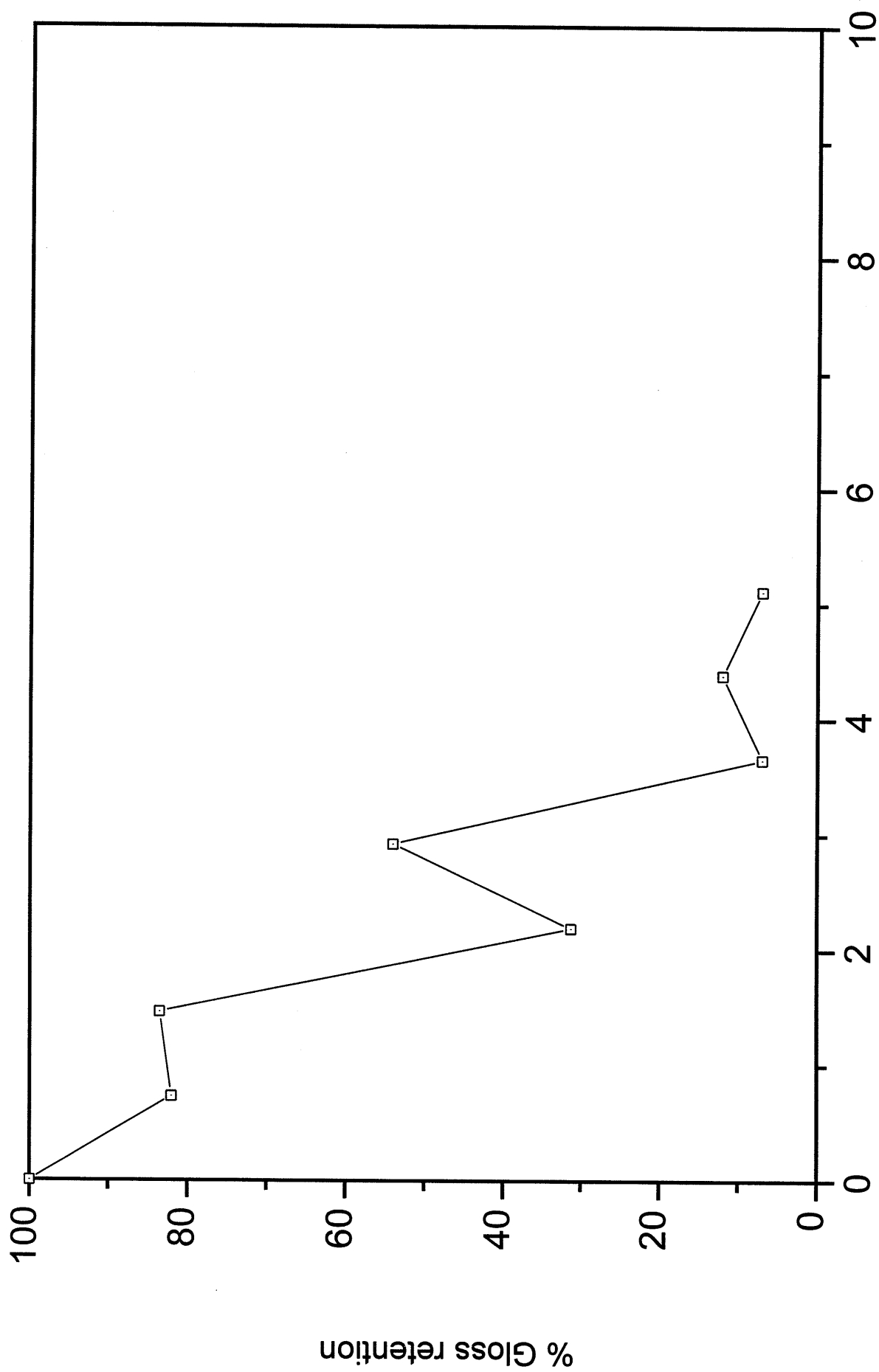


Fig.32 % Gloss retention with exposure
period for AHS2 material (cycle 1)

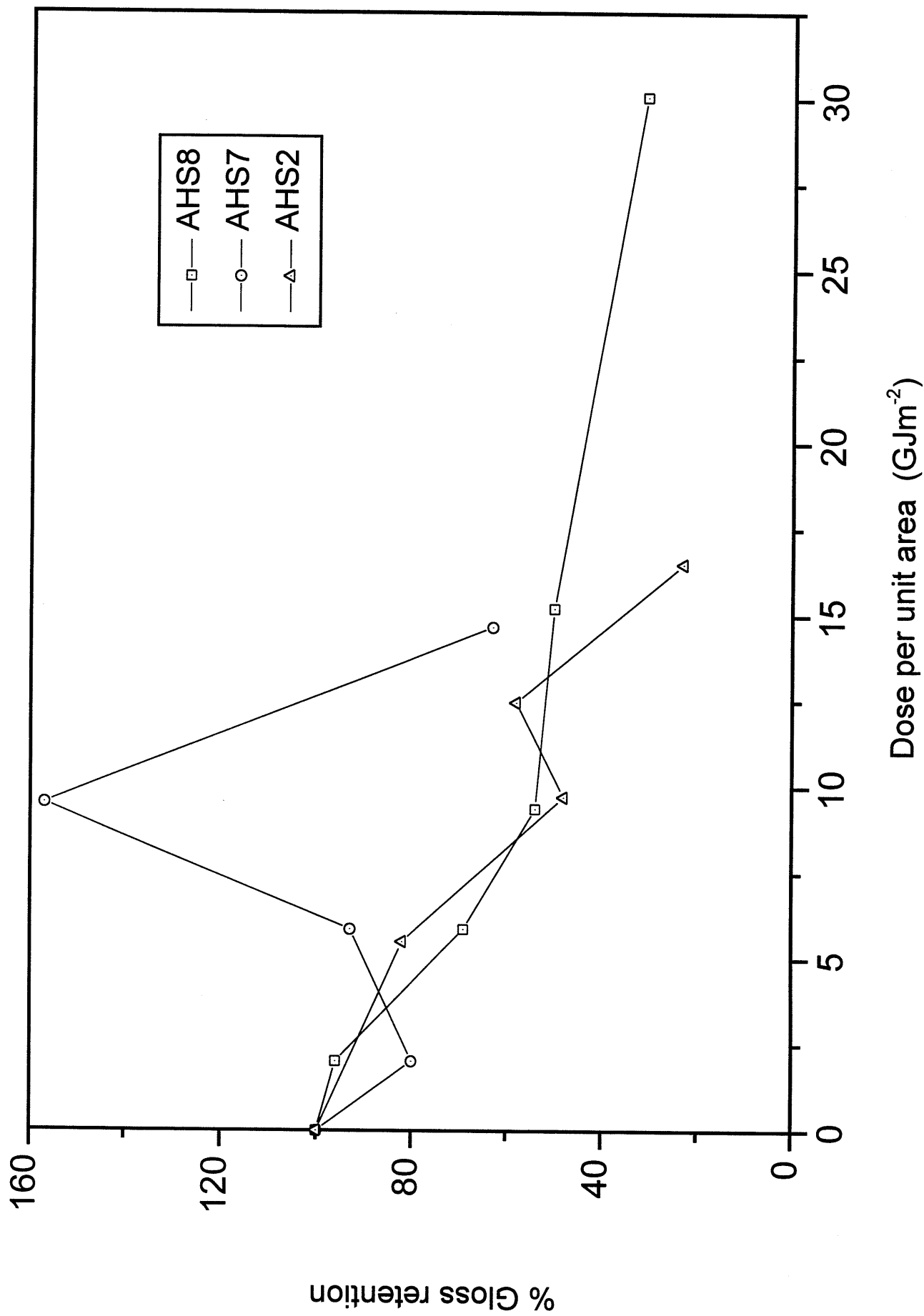


Fig.33 % Gloss retention with exposure period
for naturally weathered material

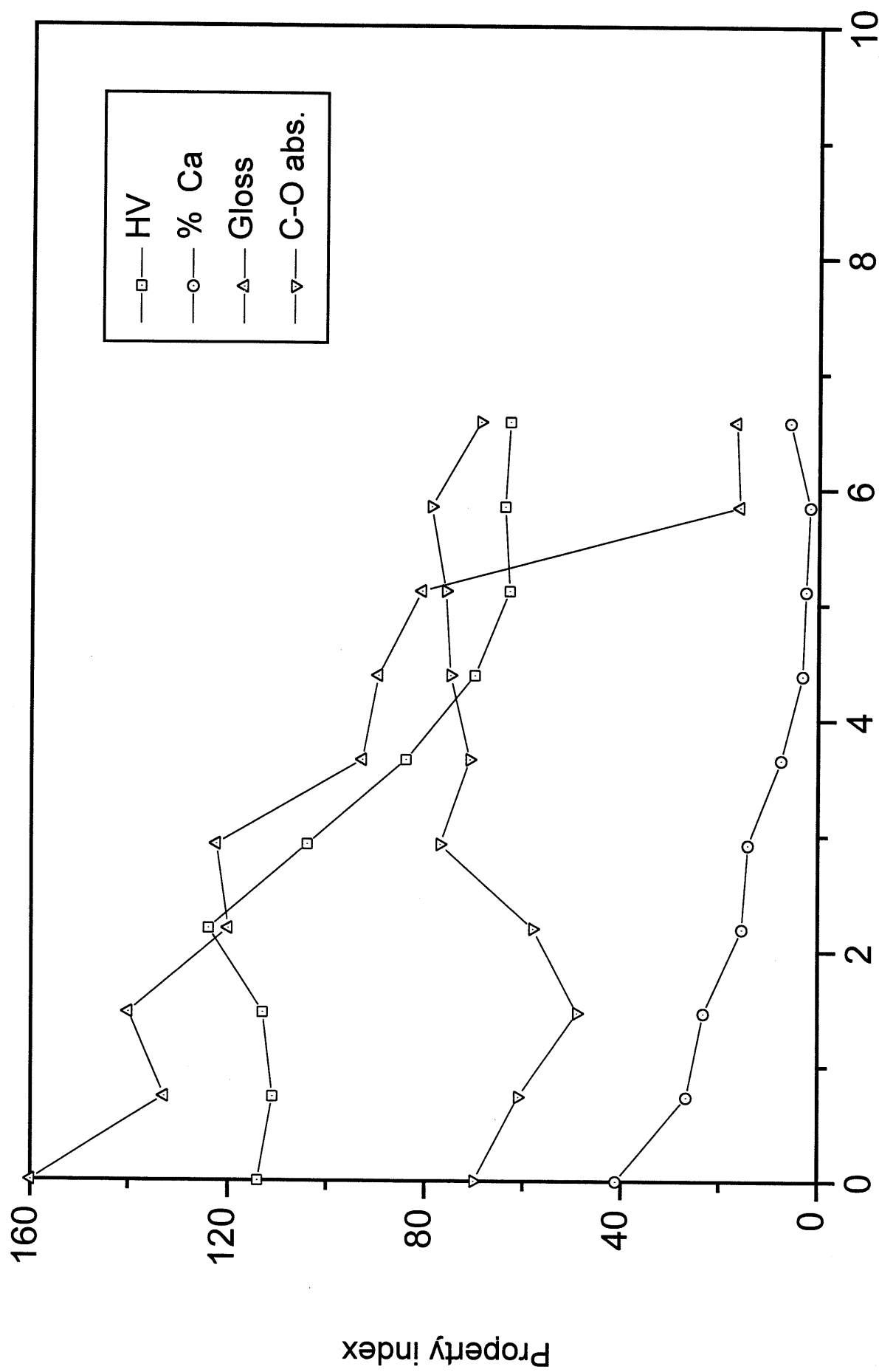
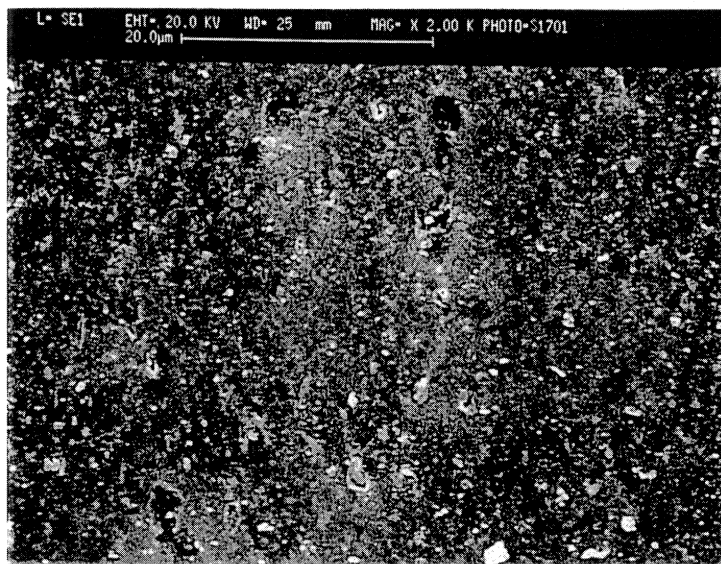


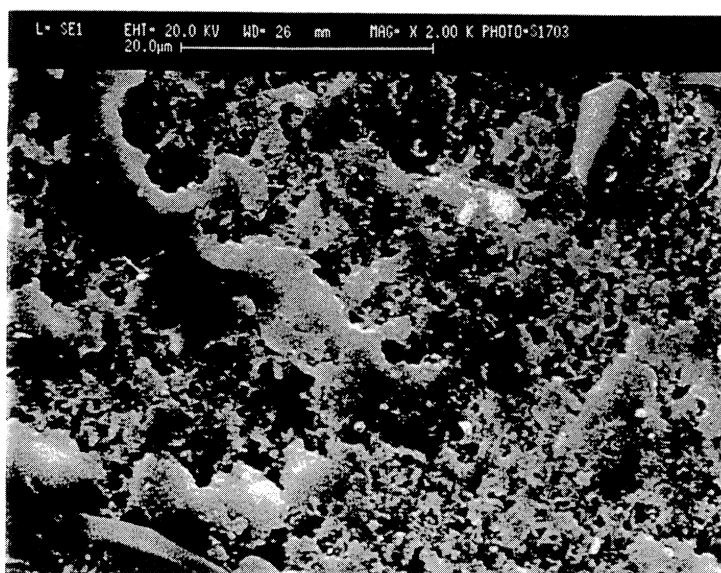
Fig.34 Variation of property measurements with exposure period for AHS8 material (Cycle 1)



a)



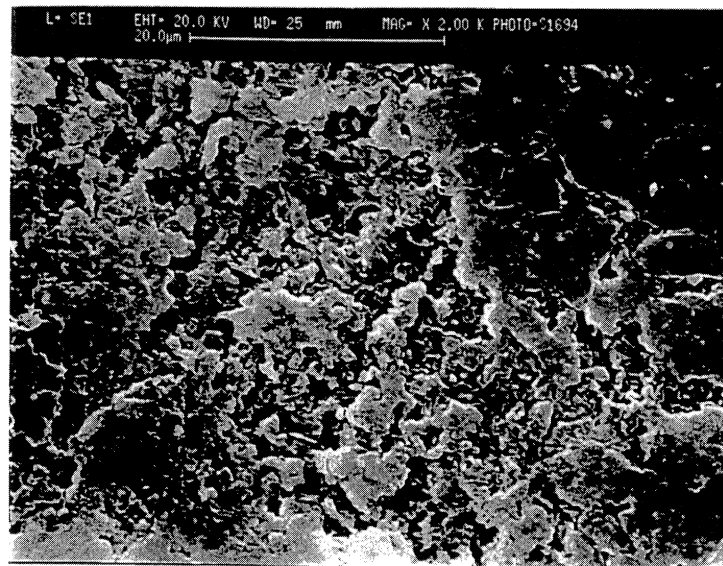
b)



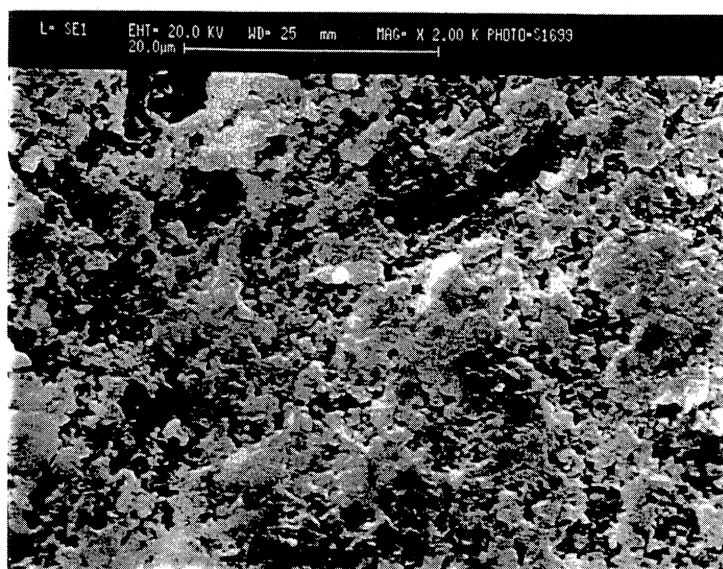
c)

Fig.35 SEM observations of artificially weathered samples of AHS8

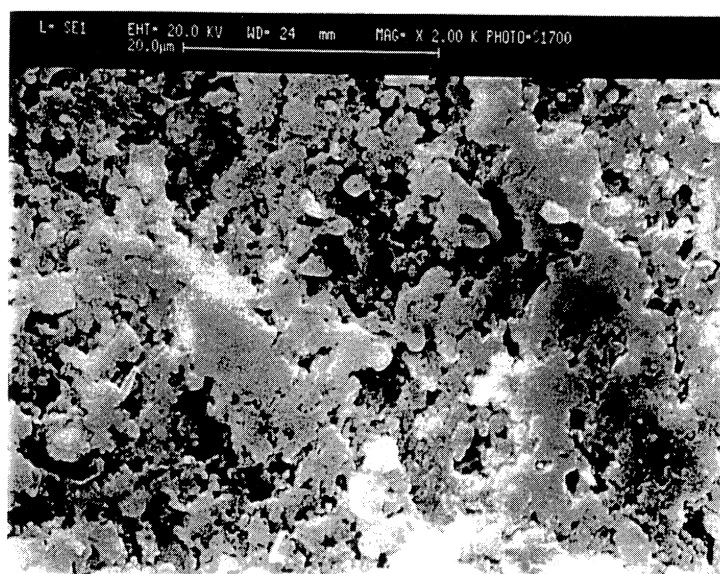
a) 2.02GJm^{-2} b) 15.22GJm^{-2} c) 30.07GJm^{-2}



a)



b)



c)

Fig.36 SEM observations of naturally weathered samples of AHS8

a) 2.09 GJm^{-2} b) 5.22 GJm^{-2} c) 7.31 GJm^{-2}

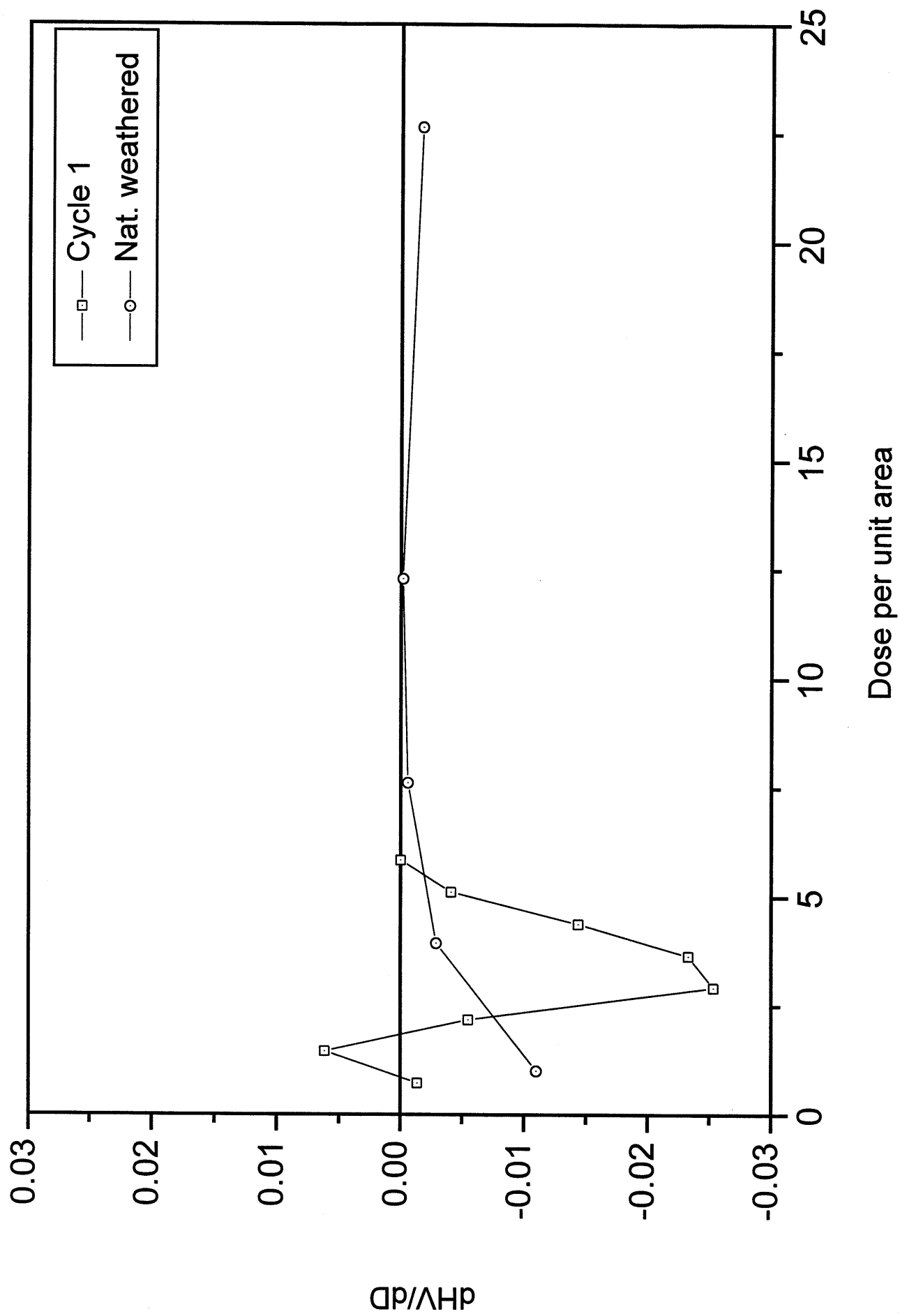


Fig.37 Rate of change of Vickers Hardness with dose for AHS8 material for a 0.29N load