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Corrosion of Dielectric Coated Aluminum in the Sudbury Neutrino Observatory

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Abstract

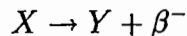
The Sudbury Neutrino Observatory has been designed to detect solar neutrinos by detecting Cerenkov radiation given off in the weak interaction between neutrinos and heavy water. To collect as much of this light as possible, light concentrators with mirrors composed of petals of dielectric coated aluminum are being used. They will be immersed in H₂O for the ten year life of the detector. They were tested in deionized water at temperatures greater than the SNO environment to accelerate aging. It was found that 24(3) percent of the petals would develop an interference pattern destroying their optical properties if exposed to non-degassed water for the ten year period. This destruction would begin 6.4(4) years into the detector lifetime. The decay occurred because of the reaction of the aluminum reflective layer with hydrogen ions in the test water. If the pH of the water is maintained at 7.00, the effect no longer occurs. The degradation in the mirrors could be avoided in the Sudbury Neutrino Observatory by covering the water surrounding the concentrators with a layer of CO₂ free air during filling and nitrogen during the run time.

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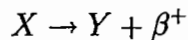
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1 Introduction

In the early part of this century, Wolfgang Pauli introduced a massless, chargeless particle to explain the apparent violation of conservation laws by the process of nuclear beta decay. According to the theory at the time, the two reactions of beta decay were:



[7]



[7]

The energy of the beta particle should have been equal to the energy equivalent to the mass lost in the reaction, but this was not observed. In time it was realized that spin and momentum also were not conserved. The addition of a third product to the reaction solved these problems, as the third particle could carry off the missing energy. Pauli's work was initially ignored, as the physicists of the time were more inclined to believe that energy was not conserved rather than introduce a new particle that was undetectable, but in 1933 Enrico Fermi published a brilliant mathematical solution to the decay showing that three particle decay accurately predicted the energies of the two detectable products. The new particle was named the neutrino, which in Fermi's native Italian means "Little Neutral One"

The neutrino remained a theoretical particle for many years despite many attempts to detect it. The neutrino was not detected until the advent of nuclear power created powerful neutrino sources. The detection at the Savanna river reactor by C. Cowen and F Reines involved a flux of 5×10^{13} neutrinos per second.[6] They watched for the interaction of neutrinos with the water in their detector. Even with this powerful source, they detected only two or three interactions per hour. [6]

It was realized that the neutrino, with its ability to pass through planets unaffected, was an excellent tool for studying the stellar interior. The nuclear reactions in the sun were known to create neutrinos along with photons. The photons, although easy to detect, carry no information about the solar interior as they undergo 100,000 year long random walk [9] from the sun's center to the solar surface. The neutrinos travel at the speed of light from the point of their creation to the Earth, and scientists realized their study could help to confirm some of the theories of solar power generation.

p-p chain	$p + p \rightarrow {}^2\text{H} + e^+ + \nu_e$
	$p + e^- + p \rightarrow {}^2\text{H} + \nu_e$
	${}^7\text{Be} + e^- \rightarrow {}^7\text{Li} + \nu_e$
	${}^8\text{B} \rightarrow {}^8\text{Be} + e^+ + \nu_e$
	${}^3\text{He} + p \rightarrow {}^4\text{He} + e^+ + \nu_e$
CNO Cycle	${}^{13}\text{N} \rightarrow {}^{13}\text{C} + \nu_e$
	${}^{15}\text{O} \rightarrow {}^{15}\text{N} + e^+ + \nu_e$
	${}^{17}\text{F} \rightarrow {}^{17}\text{F} + e^+ + \nu_e$

Fig 1: Solar Neutrino Producing Reactions

According to the standard solar model, eight neutrino producing reactions occur in the sun. These are shown as fig 1.

The p-p chain accounts for the greater part of the neutrino flux, with a maximum energy of 0.42 MeV per neutrino. The ${}^8\text{B}$ neutrinos have a maximum energy of 15 MeV and thus are much easier to detect.

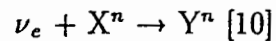
1.1 The Solar Neutrino Problem

Four solar neutrino detection experiments have returned substantial data at this time. All found that the flux of solar neutrinos from the sun was between one and two thirds of what was expected in theory. These experiments relied for the most part on the ${}^8\text{B}$ produced neutrinos. The entire emission curve was extrapolated from these neutrinos, as the theorists felt that they could accurately predict the ratio of these neutrinos to the low energy ones. As the results came in at such low values, it became apparent that more direct measurements of the neutrino flux was necessary. Detectors with lower background signals could possibly detect some of the lower energy neutrinos. More accurate data could help suggest the correct solution to the problem.

In the current standard model, neutrinos come in three flavours; electron, tau, and mu. The standard model allows only extremely limited conversion between the types in a vacuum. One solution to the solar neutrino problem is to allow neutrinos to switch flavours more readily. This is called neutrino oscillation. The neutrinos produced in the sun are electron neutrinos, and the detection reactions employed detect electron neutrinos. The missing neutrinos could be changing flavours on the way from the sun. To test this theory, a detector that detects all flavours of neutrinos is needed.

1.2 The Sudbury Neutrino Observatory

Two main types of neutrino detector have been employed so far in the detection of solar neutrinos. The first employs a large volume of one isotope of a certain atom, and then relies on the inverse beta decay reaction to convert atoms in the detector volume to atoms of the element with an atomic number one higher than the detector atom. The reaction involved is



The product atoms are separated out of the detector volume and counted to give a neutrino flux. This process has the drawback that no time or direction information is given, as it takes several months for a large enough number over product atoms to form to allow counting. To study neutrino events on an individual basis, scattering reactions are used. Neutrinos entering the detector give some of their momentum to electrons in the detector medium, accelerating them to speeds greater than that of light in the medium. The Cherenkov radiation given off can then be detected. By studying the pattern of PMT responses, an energy can be found for the neutrino. This makes these detectors ideal for determining the source of neutrinos. They require extremely low background radiation, as the Cherenkov radiation is extremely weak. The Sudbury Neutrino Observatory is such a detector. Fig 2 shows a diagram of the detector.

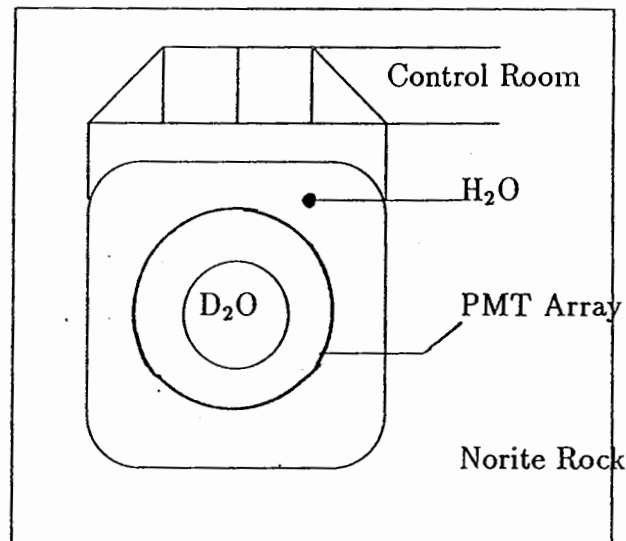


Fig 2: The SNO Detector

Medium	Reaction	Mechanism
D ₂ O	$\nu_e d \rightarrow p p e^-$	charged current
D ₂ O	$\bar{\nu} d \rightarrow n n e^+$	***
D ₂ O	$\nu_x d \rightarrow \nu_x p n$	***
D ₂ O	$\nu_x e \rightarrow \nu_x e$	scattering
H ₂ O	$\bar{\nu} p \rightarrow n e$	***
H ₂ O	$\nu_x e \rightarrow \nu_x e$	scattering

Fig 3: Reactions in SNO

1000 tons of heavy water will be contained in an acrylic vessel surrounded by 6000 tons of light water. Fig 3 outlines the reactions that will be studied in the various medium. To shield the detector from as much background radiation as possible, it will be located 2200 meters below the Earth's surface in the Inco nickel mine near Sudbury, Ontario. This excludes the majority of the cosmic rays and other surface radiation.

The components will give off very low quantities of background radiation. It will have a detection threshold of 5MeV, and thus provide the broadest measurement yet of the solar neutrino flux.

1.3 Light Concentrators

The Cherenkov radiation will be observed by 9000 photomultiplier tubes. This number does not cover the entire volume of the detector, and so concentrator mirrors will be used to increase the area covered. The concentrators will be composed of small "petals" of dielectric-coated aluminum or DCA. arranged in a sphere surrounding the inner acrylic vessel containing the heavy water. The PMT's are located in the region of light water, and will also detect the reactions taking place in the light water between them and the acrylic vessel.

As the concentrators will not be accessible during the working life of the detector, it is very important that they will last the full ten years of the proposed run time without their reflective abilities being degraded by the aqueous environment. Initial tests conducted by Dr. Chris Waltham at U.B.C. raised some doubts as to whether this goal was realistic. The dielectric coated aluminum has shown a peculiar aging pattern in which some of the petals develop a striped appearance accompanied by development of an interference pattern in the reflection curve. Throughout the document this shall be referred to as failure because the petals no longer do their job properly after this process occurs. The following pages will describe exhaustive tests on both

the properties of pure water and the petals themselves to achieve quantitative estimates of the lifetime of this component of the detector, as well as the reasons behind the problem, possible solutions will also be examined.

1.4 Aging of the Dielectric Coated Aluminum

The Sudbury Neutrino Observatory will basically be a closed system over its working lifetime. It is therefore very important that all of its components will last for the ten year run time without any serious breakdowns. It is my objective to determine whether the dielectric coated aluminum reflectors will function as planned, and to determine whether the failures of these petals observed in past tests are likely to occur in SNO. The SNO environment is one of ultra pure water at 8°, with slight current flow due to the circulation of the water. The net current flow in the concentrators will in all probability be very small.

There is not enough time to study these petals at SNO's temperature, so accelerated aging techniques will be used, and have been used on all previous runs. The chemical rule of thumb is that reaction rates roughly double for every 10°C. rise in temperature. I will attempt to verify that this is a valid assumption in this system by aging petals at several temperatures and then comparing the relative aging rates.

By varying the atmosphere over the samples, the effect of various cover gasses on the corrosion will be studied. SNO could employ a cover gas to prolong the detector lifetime by preventing the reaction that destroys the petals from taking place. I also hope to provide a quantitative estimate of how many of the reflectors will have failed after a set time, and explain the cause of the failing of the product in the deionized water.

2 Apparatus

The deionized water for these tests was produced with a Barnstead E-pure water system. The system took Vancouver tap water and removed all particulate matter, using a three stage charcoal filter. It also removed all of the charged ions in the water. This left only neutral gases behind. For some runs the water was degassed by evacuation in the vacuum oven.

A Corning Checkmate multimeter capable of measuring conductivity, pH, oxygen activity, and dissolved oxygen in mg/l was used throughout the experiments. Oxygen activity is a measure of the reactivity of oxygen in solution.

The petals were tested in uncut form when at all possible. They were stood

upright in the sample tubs in holders made of Lucite blocks with narrow cuts to support the petals. The Lucite blocks were well boiled in DI water before use to remove contamination. The effect of the lucite on the water quality was assumed to be low due to the small amount of lucite involved.

The tubs used for the bulk of the samples were made of Nalgene pp plastic. Both small bottles and larger tubs were used. The forty degree runs were performed in five gallon pp plastic buckets. Heat for these runs was provided with simple aquarium heaters with an accuracy of ± 5 degrees Celsius. The remaining tests were conducted in one of two ovens. The first of these allowed control within \pm two degrees Celsius under air, and the other was a vacuum oven, making partial degassing of the water possible, as well as allowing samples to be tested under various cover gasses. The vacuum oven was capable of reducing pressure to at least under 0.01 atmosphere, although the exact value has not yet been determined. A simple gas sparge was constructed from lucite to allow even bubbling of gas through the solutions. All of the gasses were purchased in bottled form. The gasses were bubbled in at the opposite end of the tubs from the samples to disturb the water as little as possible.

The vacuum oven had a nozzle for pumping out the air in the chamber. A small vacuum pump with an attached cold trap for removing water was used for creating the vacuum. Gas could then be let in to the oven through a different nozzle. Poly-flo tubing was used for bringing the gas from the tanks to the oven. After testing, the reflectance of the petals was tested on a Perkin Elmer spectrophotometer. This device used an integrating sphere to produce a measure of the petals reflectance. This device works by splitting a monochromatic light beam. Half of the beam is directed directly to the detector, and the other half enters the integrating sphere, a spherical cavity of highly reflective barium sulfate, and then to a detector. The sample is placed in a small window in the integrating sphere. Comparing the resulting signal to that received when a barium sulfate plate covers the sample window, the relative reflectance of the sample can be found. The range examined was 350 to 900 nm in 4nm increments. The data was then saved as ASCII files.

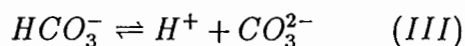
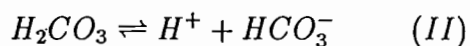
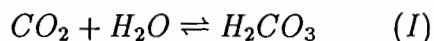
3 Theory

3.1 Chemistry of the Deionized water

The water in SNO will be 8° C, with most of the ions and gasses removed. In te lab, the water had a minimum contamination of 0.03mg/l During the filling, however, the SNO water may be exposed to the atmosphere above the

detector.

Exposure to lab air brings the water into contact with nitrogen, oxygen, carbon dioxide, and sulfur dioxide. The Barnstead filter is not designed to remove uncharged molecules. The oxygen content of the water will remain unchanged, as will the nitrogen content. Nitrogen is inert, and poses no threat to the aluminum. Oxygen is a potential oxidant, and will be studied. Oxygen can be removed from the water by processing in the vacuum oven. Sulfur dioxide is a small enough component of air to be ignored, and in any case can be lumped with the action of CO₂. The CO₂ in the air will lower the pH of the water. However CO₂ is removed along with the other elements of the carbonate chain.[4]



This equilibrium is dominated by the dissolved CO₂(g), but the cycling action of the filter combined with the fast (0.1 second) [4] return to equilibrium of this system removes all of the carbonates and the CO₂ present. The deionized water produced had a pH of 7.00(05), and a conductivity of 0.07(02) μS/cm. Conductivity is directly related to dissolved ion content, and is thus directly related to the amount of carbonate in the solution.

Once the water is exposed to air, it begins to return to equilibrium. If SNO does not have a cover gas, the same effect should occur in SNO.

3.2 Diffusion of CO₂ in 24° C DI water

Upon exposure to the atmosphere, CO₂ reenters the water according to Henry's law:

$$[CO_2] = K_H P_{CO_2} \quad (IV)[4]$$

K_H is Henry's constant, 10^{-1.5}M/atmosphere, at 25°C.; [CO₂] is in moles per litre(M) P_{CO_2} is the partial pressure of CO₂ in atmospheres, The hydrogen ion concentration in the water can be written in two forms:

$$[H^+] = K_{a1}[CO_2]/[HCO_3^-] \quad (V)$$

$$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (VI)$$

The last two terms of the above equation can be ignored as they are small. Making this approximation, and combining (VI) with (V),

$$[H^+]^2 \approx K_{a1}K_H P_{CO_2} \quad (VII)$$

[4]

By replacing the partial pressure with equation (I), we get the approximation

$$[H^+]^2 \approx K_{a1}[CO_2] \quad (VIIb)$$

where K_{a1} is the first ionization constant of the carbonate system. It has a value of 1.7×10^{-4} M. In terms of pH,

$$pH \approx pH_{\infty} - \frac{1}{2K_{a2}} \log[CO_2] \quad (VIII)$$

[4]

pH_{∞} is the pH under pure CO_2 . This can be determined experimentally. The concentration is directly related to conductivity. First it must be noted that pH and conductivity can be experimentally linked by

$$pH = Ae^{BS} + pH_{\infty} \quad (IX)$$

Where S is the conductivity and A, B are constants to be determined. The CO_2 moves downward through the water according to the equation of diffusion:

$$\frac{dn}{dt} = D \frac{d^2n}{dz^2} \quad (X)$$

[3]

Where n is the concentration in question. In this model z is the depth into the water, and if it is assumed that the gas is diffusing downward from a flat surface, the solution to the equation is [3]

$$[CO_2] = \frac{A}{\sqrt{t}} e^{-\frac{x^2}{4Dt}} \quad (XI)$$

From this material, the level at which the concentration of CO_2 is one half that of the surface value is:

$$x = \sqrt{2.77Dt} \quad (XII)$$

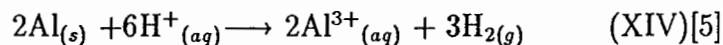
If the value for D is very small, the CO_2 will not penetrate downwards through the water fast enough to effect the samples over their run time.

3.3 Al reactions in Deionized Water

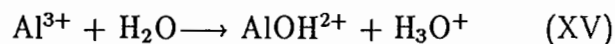
Aluminum is a highly reactive material that undergoes oxidation on exposure to water. The oxidation reaction involved is



The reaction requires that some oxygen be dissolved in the water. Additional chemistry must be considered to take into account the fact that the water becomes a weak solution of carbonic acid. When exposed to acid, aluminum undergoes the reaction:



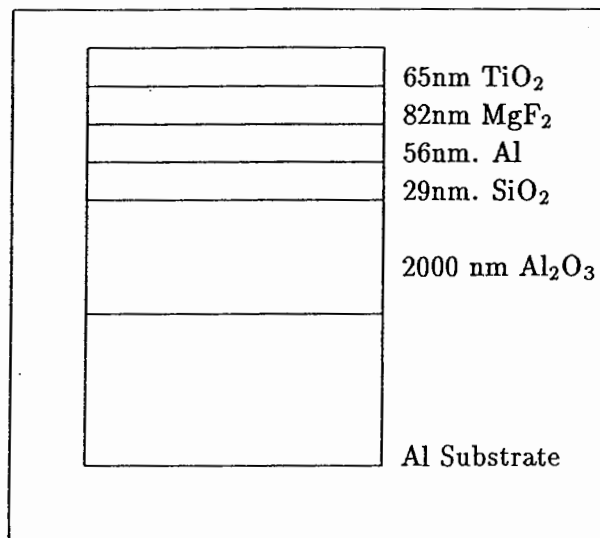
The aluminum ions then form aluminum hydroxide through the reaction



3.4 Dielectric Coated Aluminum

The petals were selected to be highly reflective over the wavelength range 280nm to 600nm. They have to physically survive the ten year run time in the water, as well as survive the filling period during which atmospheric contact is likely. They have to be low on nutrients for biological life, and low in radioactivity.

The choice of material was dielectric coated aluminum. Our design consists of an anodized aluminum base with a specular aluminum coating, further coated with several dielectric layers. The 0.3mm aluminum base is coated with 2000nm thick anodized Al_2O_3 . Next the 29nm of SiO_2 is added to prevent oxygen from leaching to the next layer, the 56nm. of aluminum. This is the reflecting surface. The next two layers act to increase reflection at the water/mirror barrier. They also seal the aluminum from the water. A diagram of the petals is shown as fig 4.



DCA PETALS

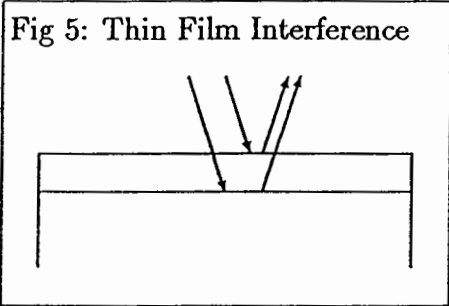
Fig 4: The Dielectric Coated Aluminum

Thin films create an interference pattern as reflection occurs as shown as fig 5. The interference creates minima and maxima that can be characterized in terms of film thickness, Incident light wavelength and index of refraction. The minima and maxima occur as

$$\lambda = \frac{2nd}{m + \frac{1}{2}} \quad (XVI) \quad (maxima)$$

$$\lambda = \frac{2nd}{m} \quad (XVII) \quad (minima)$$

Where m is an integer



A scan of the DCA used in the neutrino observatory is shown as fig 6. This plot of reflectance versus wavelength shows that the reflectance is very high in the range 330nm to 850nm. The interference minima is caused by interference in the outer coatings. The scan was performed on the Perkin Elmer Spectrophotometer, using a barium sulfate coated plate as a near one hundred percent reflecting reference surface.

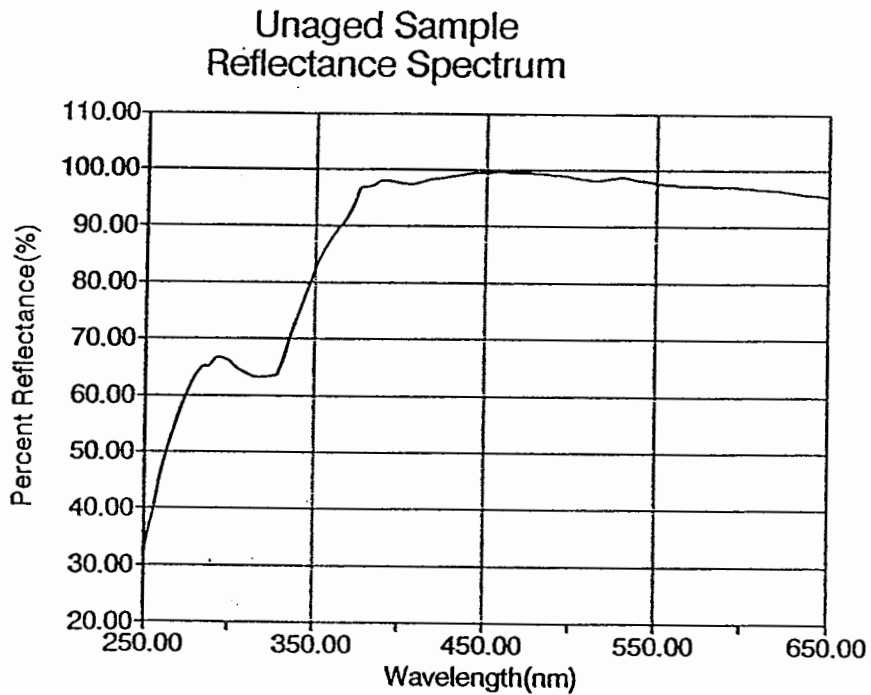


Fig 6: Reflectance of the Dielectric Coated Aluminum

The raw sheets of DCA are cut into 3cm by 9cm petals, and the edges sealed by TiO. A protective coating of plastic sheet is then stuck onto the optical surface with lines of non permanent adhesive.

4 Tests and Results

The tests undertaken began with qualitative studies of the deionized water and progressed over the year. The aging tests were started in September to allow time for the runs to be completed. Some runs had already been performed by Dr. Waltham. A few of these runs are discussed as they provided background material for this study.

4.1 Water Tests

Vancouver tap water was found to have a conductivity of 14.0(5) $\mu\text{S}/\text{cm}$. This was not clean enough for our purposes so the deionized water was used for all rinsing of the containers as well as the water for the runs. It was found that directly out of the purification system the water had a conductivity of $5.5(1) \times 10^{-8} \text{S}/\text{cm}$. which is a resistivity of 18.2 Mohms/cm.

Test One: Return to equilibrium of the Carbonate chain

In this first run 2 litres of deionized water was allowed to sit exposed to the air in the lab. A raised lucite roof was placed over the sample to prevent dust from settling in the water. The water temperature at the start of the run was 18°C and rose to 22°C at the end of the run. This can be ignored as the probe is self correcting with temperature on such a small range. The conductivity meter was placed in the water to study the return to equilibrium of the carbonate chain.

Test One (a) : Self correction of the multimeter for temperature.

In later tests it will be necessary to take the conductivity of the deionized water at many different temperatures. The multimeter is claimed to self adjust for temperature, giving a stable value between 0°C. and 100°C. I tested this by heating some deionized water at equilibrium with the air in the oven and testing at various temperatures. The data is plotted as fig 7. It shows that the conductivity remains fairly stable throughout the range. I noted that the conductivity falls at very high temperatures, but this can be explained by the fact that CO_2 is less soluble at 100°C than at 0°C.

Fig 7:
Stability of the Meter Response
Over a Temperature Range

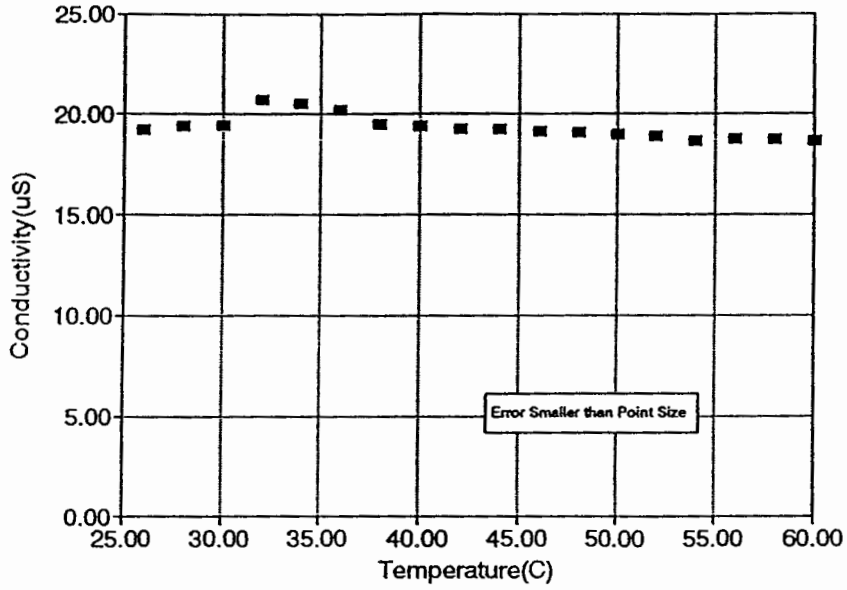
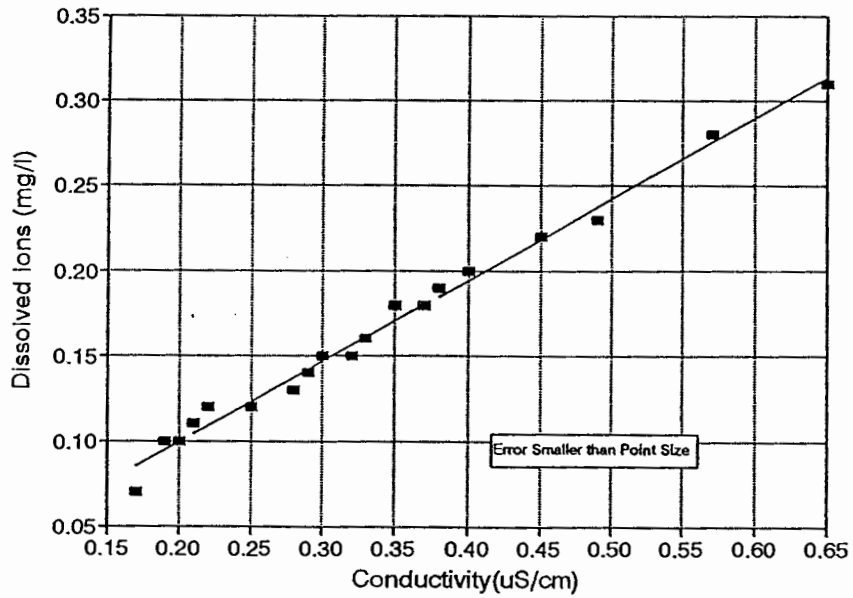


Fig 8:
Total Dissolved Ions
vs. Conductivity



Test One(b) Relating Conductivity to dissolved ions.

. The multimeter has a secondary mode that measures the total dissolved solids in mg/l.

This can be used to link conductivity to $[\text{CO}_2]$. All of the dissolved solids are dissociated ions from the carbonate chain. Half of these ions are hydrogen ions. I placed some deionized water in one of the two litre Nalgene tubs, and measured dissolved ions and conductivity as the water returned to equilibrium. I've plotted the results as fig 8. By taking a regression of this data in Quatro Pro, I found that

$$\text{TDI} = 0.476(1)\text{S} + 0.004(3) \text{ (XVIII)}$$

From this, and noting half of the dissolved ions are hydrogen, we can write

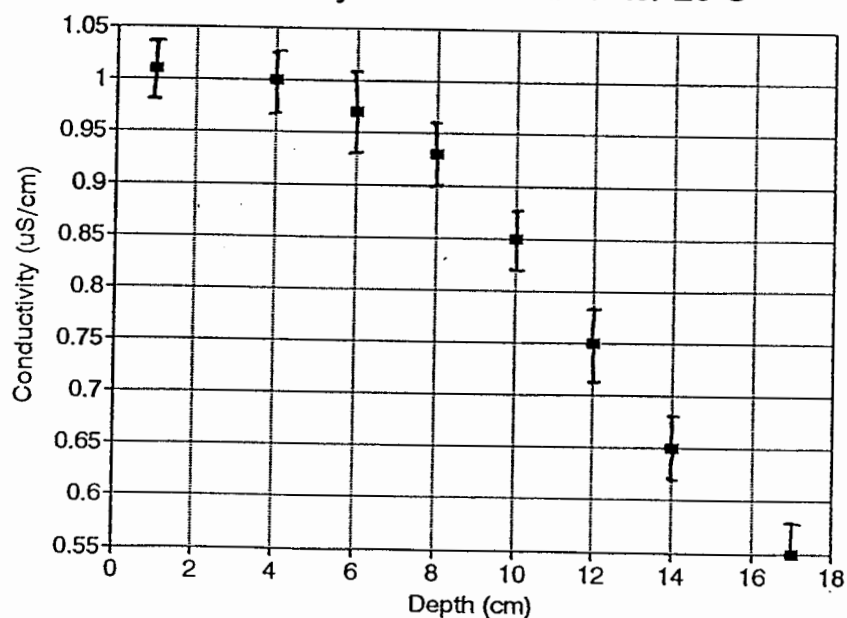
$$[\text{H}^+] = 0.5(0.476(1)\text{S} + 0.004(3)) \text{ (XIV)}$$

Test Two: Depth profile for the Deionized water

After run one was completed I removed the lucite lid and sampled the water at several depths in order to create a depth profile for the sample. The time was 70 minutes, and the water temperature was 23°C . I sampled from the top down, to avoid disturbing the underlying water. The data is given as fig 9.

Fig 9:

Depth profile after 70 Minutes
Conductivity in Deionized Water 23°C

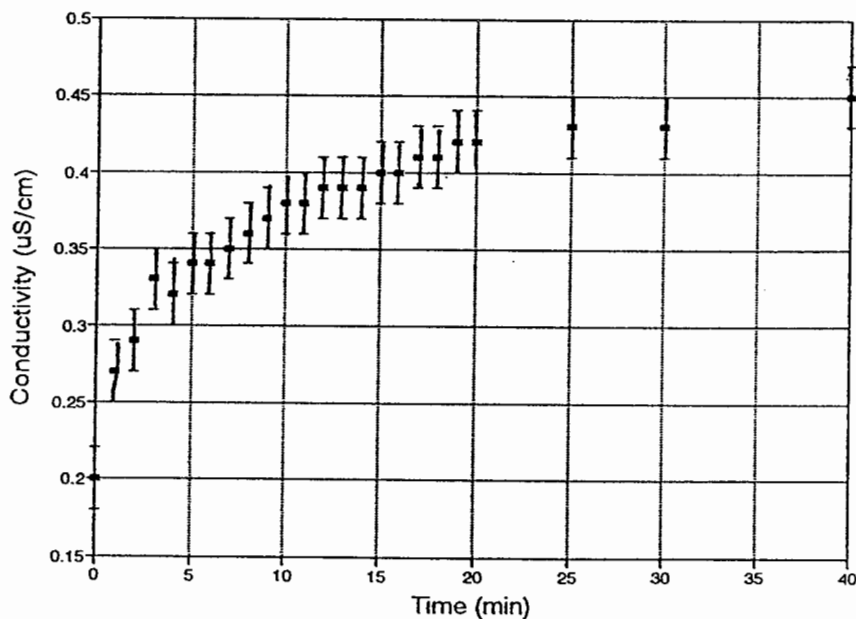


Test Three: deionized water under a cover of nitrogen

Under a nitrogen cover, the conductivity peaked at a value of $0.45(1)\mu\text{S}/\text{cm}$. This is shown in fig 10. The nitrogen cover was achieved by sparging nitrogen into the bottom of the container, and covering the top. A better method was then used. A sample of water was placed in the vacuum oven and the oven was pumped down and then filled with nitrogen. This was repeated a few times to ensure that no air remained. Measurements could not be taken every few minutes, but after an hour the conductivity had a value of $0.20(1)\mu\text{S}/\text{cm}$.

Fig 10:

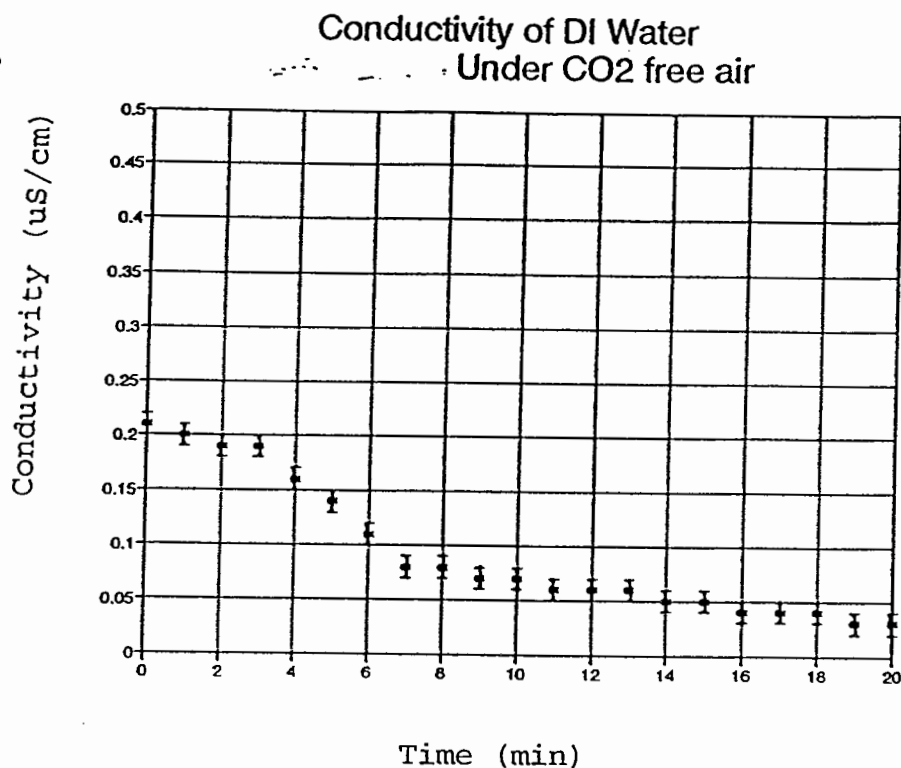
Conductivity of DI Water
Nitrogen Bubbled in



Test Four: Deionized water under CO₂ Free Air

CO₂ free air was sparged through a fresh sample of the deionized water. The result is plotted as fig 11. The results would suggest that almost all of the dissolved ions in the water comes from the carbonate chain. Thus minor components like the sulfate chain can be ignored

Fig 11:



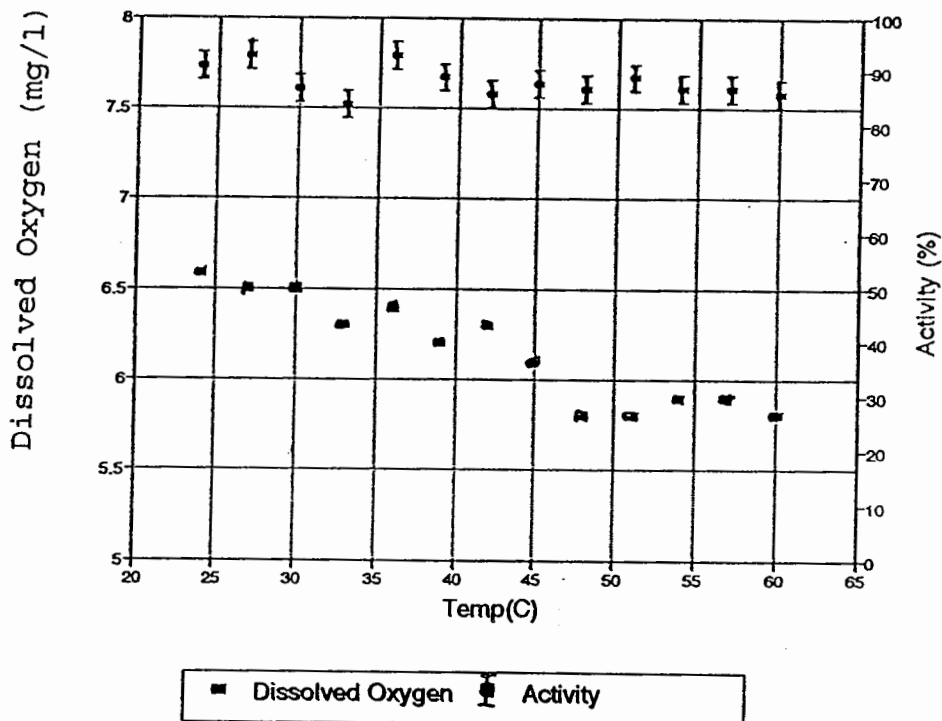
Test Five: Behaviour of the Dissolved Oxygen

The dissolved oxygen is not removed by the filter. The oxygen content was found to vary little in time, with a value of 7(1)mg/l. The examination of the behaviour of the dissolved oxygen showed that as temperature rises, concentration falls but the activity of the total oxygen remains about the same. The activity is proportional to the reaction rate of the oxygen, and is used because it is measurable by measuring the reaction rate of a catalyzed reaction in the meter tip. The activity is defined to be zero in a zero oxygen solution and 100 in cold water vapour over fresh running water.

Over time, the concentration and the activity of the water falls slightly as the water sits. This suggests that aging tests will not accurately predict the action of oxygen in SNO. Fig 12 shows both activity and content vs. temperature. It is clear that as the temperature rises the activity of the total oxygen remains the same as the concentration falls with higher temperature.

The reactions involving oxygen will occur at about the same rate over the temperature range 0°C to 90°C.

Fig 12:
Oxygen Content and Activity
In Deionized Water



Test five(a): Efficiency of Oxygen removal and return to equilibrium.

By pumping the vacuum oven down to below 0.01 atmospheres for one minute, about half of the oxygen in the DI water was removed. Further pumping for two minutes reduced the oxygen content to one tenth its initial value, and reduced the conductivity to 0.07(1) μ S, indicating the carbonates were almost totally removed. The degassed water was then exposed to the room air, and the oxygen content rose back to 8mg/l after twenty minutes.

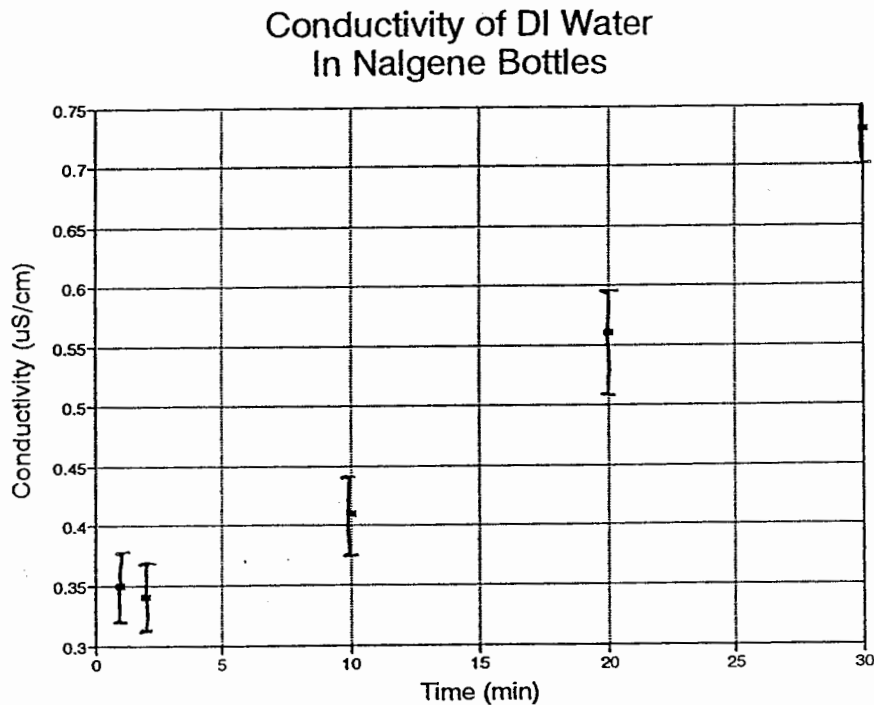
Test Six: CO₂ and pH_∞

From the theory section, pH_∞ was defined to be the pH of the deionized water under pure carbon dioxide. Carbon dioxide was sparged through a tub of deionized water for fifteen minutes. The measured pH was then 3.95(1). It was

found that when in equilibrium with the room air, the water had a conductivity of between 1.5 and 2.0. This varied from day to day. This corresponded to a pH of 5.5(5) at room temperature.

Test Seven: The effect of Nalgene plastic on the water To study the effect of the containers on the deionized water, several samples of the deionized water were placed in 500ml Nalgene bottles and sealed. They were filled to the top to prevent contact with air. Fig 13 shows the conductivity in the water over time. On very long runs in the small containers, this effect should be corrected for when measuring the conductivity to get the CO₂ content.

Fig 13:



4.2 Tests and Results on the Dielectric Coated Aluminum

Test One: Study of aged petals

I scanned many samples from a previous run that had been undertaken by Dr Waltham in 1994., in which sixty of the petals had been exposed to 90°C water overnight with CO₂ bubbled into it. Several things were noticed.

All samples showed no trace of the edge coating. The petals have the top layers applied to both surfaces and the edges to seal them from the water. The edge coating gives the edges a slight yellowy tinge. When the coating is gone the edges have the silver gray colour of oxidized aluminum.

The samples could be divided into two groups: Those with faint closely spaced, ragged grey lines running across them and those without. Small samples of each type were cut to size and examined using the spectrophotometer. Scanning the ones without revealed that the shape of the reflection curve was preserved, although reflection at all wavelengths had fallen by a few percent. Analysis of many samples showed this decay was always between one and four percent. This is shown in fig 14. Analysis of several of the "failed" petals revealed dramatic decreases in reflectivity, and the development of an interference pattern in the reflectance curve. Fig 15 shows a selection of these scans. The interference is more pronounced in some of the samples than in others. The maxima and minima occur at slightly different wavelengths, indicating differences in the dielectric coating thicknesses of approximately 10nm. or less.

Test Two: Placement of the discolouration

The horizontal stripes visible on the failed sample are very similar to the pattern of glue used to stick on the protective plastic sheet. A run was performed in which half of the sample's protective sheet was removed, and then the sample was placed in 90° water with CO₂ bubbling through it. When removed, it was observed that the failure occurred in between the lines of glue. This could be seen as the remaining glue lines under the plastic were aligned with the unchanged stripes of the exposed area. Thus the glue somehow prevents the water corrupting the surface layer. One possible solution is that the water penetrates micro cracks in the upper surface, and the glue seals these cracks. Also, if the hydrogen ion is responsible, it could possibly be penetrating through the layer as it is such a small ion.

Test Three: Test Under CO₂

Some of the degassed water was used in a run of 16 petals at 90°C. The

vacuum oven was then filled with CO₂. Only four of the petals failed, and none of the 16 samples showed sign of the minor 4 % loss of reflectivity.

Test Four: Test Under CO₂ free air

A run of samples was also undertaken under a cover of CO₂ free air. This run lasted for fourteen days at 90°C in order that it could be easily compared with test six. Of the nine samples tested there were no failures. Under the CO₂ free air the petals showed the 4 % drop in reflectivity seen in other runs. I continued the run and after four weeks in 90°C water no failures had occurred, an equivalent of roughly twenty years in SNO if the reaction rate doubles every 10°C

Test Five: Exposure to strong acid.

It seemed that the acidity in the water was causing the failure. A petal was exposed to a solution of hydrochloric acid. Acid with a pH of 1.0 was placed in a square Nalgene container. A petal was then placed face up in the solution. The petal was unaffected at first, but soon small bubbles began to appear in neat rows along the petals parallel to the short edge.

Fig 14:

Reflectivity Loss
After Four Days, 70C

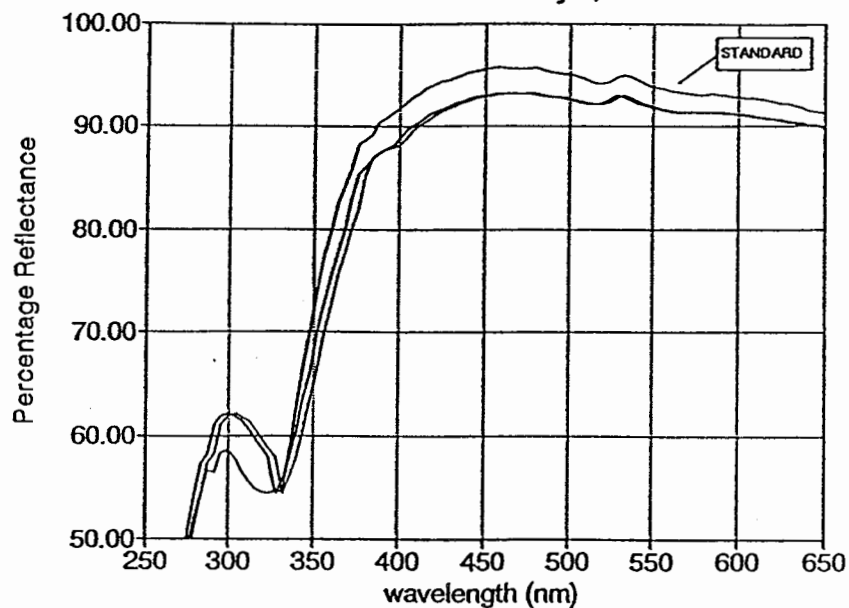
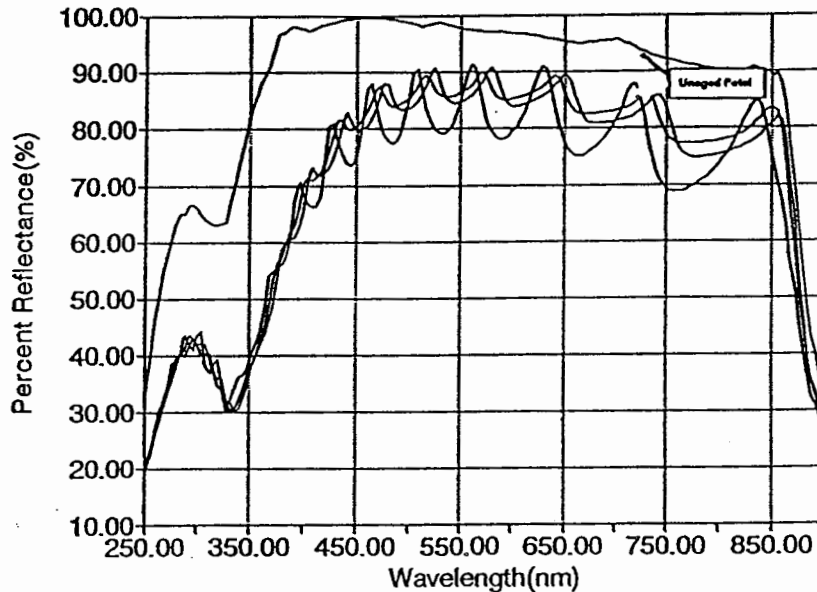


Fig 15:

Various Degrees of Petal Failures



Probing with a pin revealed that the small bubbles were forming under the outer dielectric layers. The edge coating quickly peeled off in strips, leaving the bare edges to bubble madly. I presume the gas was hydrogen, but I could not tell. The bubbles on the face grew larger and as they did formed on the surface, still in neat rows. The petal soon showed the usual failure pattern. After a few additional moments, the surface took on the dullness of corroded aluminum. A small quantity of white sludge could be seen in the container. The back face of the petal was also severely damaged. I repeated the test in a strong solution of NaOH, and the same pattern was observed.

Test Six: Nitrogen Test

The vacuum oven was used to degas the deionized water. The oxygen content was measured at 2.2 mg/l before degassing and fell to 0.4mg/l after five minutes at low pressure. I then tested ten petals at 90°C under a nitrogen atmosphere. Once again no failure was seen, and the scans showed that after

fourteen days the reflectivity had not decreased. Other tests run by doctor Waltham show some failure does occur under the nitrogen, but only after a run that is the equivalent of roughly forty years in the SNO environment.

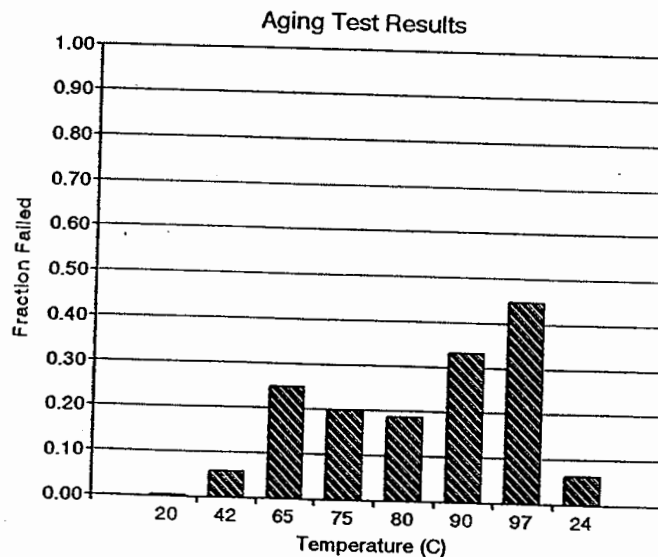
Test Seven: Aging Tests at many Temperatures

Several tests were run over the course of the year in an environment of normal air at various temperatures. The lowest temperature run was started by Dr. Waltham, and was in a large sealed container. Due to the sealing, the conductivity was only $1.2\mu\text{S}/\text{cm}$. The other samples were tested throughout their runs, and were found to have conductivities of $2.0(3)\mu\text{S}/\text{cm}$. The results are tabulated as figure 16, and in graphical form as fig 17

Test Number	Temperature(C)	Test Length(Days)	Failures	Total
i	20	365	0.05	20
ii	42	30	1	17
iii	65	70	2	8
iv	75	16	5	25
v	80	11	3	16
vi	90	14	3	9
vii	97	13	27	60
viii	24	100	1	16

Fig 16:

Fig 17:



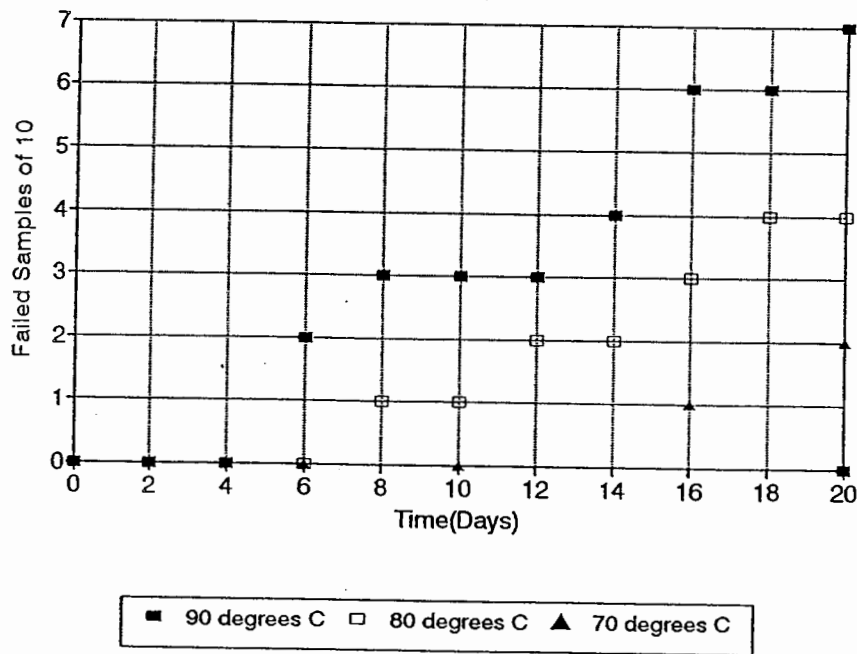
Test Eight: Effect of the Glue on the Petals The striped pattern on the failed petals closely resembles the pattern of the glue used to stick the protective plastic coating put on the petals for transport. To determine the effect of the glue, six petals were heated overnight at ninety degrees Celsius with CO₂ sparged through the deionized water. Half of the protective plastic was removed from each petal by making a cut in the plastic with an exacto knife parallel to the long edge of the petal. The next morning the petals had failed badly, and it was clear that the failed lines were in between the lines of glue used to stick down the covering. The process of gluing somehow protects the petals.

Test Nine: Response under air over time.

To compliment the various temperature test two runs were performed to see how the petals act over time at the same temperature. The two temperatures chosen were 80°C and 90°C. I cut petals into nine small pieces, and then put ten pieces per bottle in Nalgene bottles. A 70°C run was also performed, but for it whole petals were placed in a large tub and removed as necessary. Four petals were removed each time. The various results are shown as fig 18.

Fig 18:

**Aging over time
Constant Temperatures**



5 Analysis

The data from test one was fitted to an exponential model. It was found that at 22° the conductivity three cm. into the sample rose with time as:

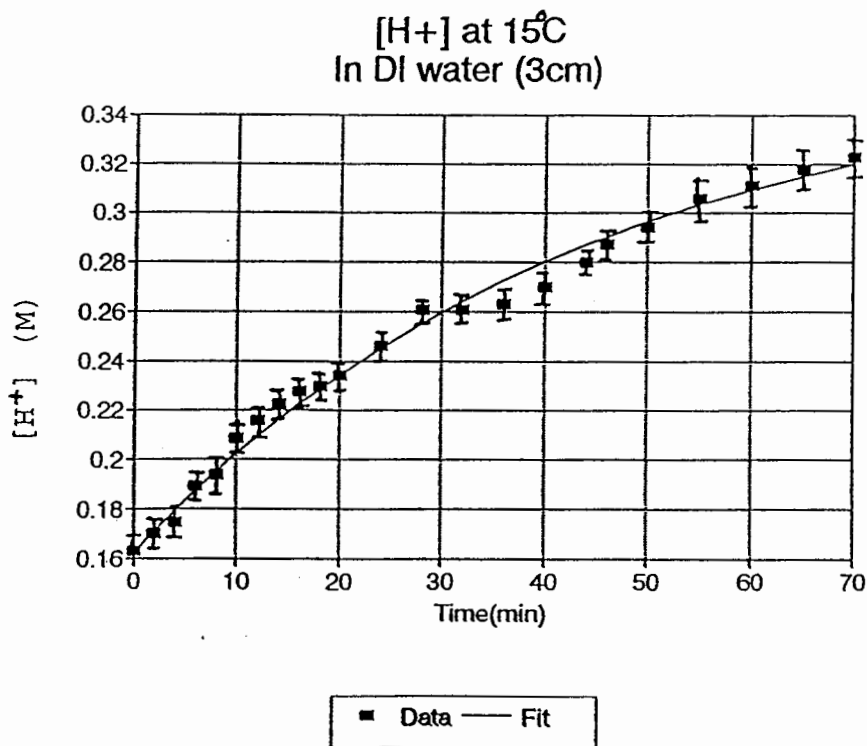
$$S = 1.50(05) - 0.90(05)e^{-0.024(03)t}$$

By using equation (I) to relate this to hydrogen ion content, it was found that

$$[H^+] = 0.24(1)S + 0.0003(5)$$

This is shown fitted to the data as fig 19. By letting S equal $0.75\mu\text{S}$ it can be seen that the concentration of $[H^+]$ rises to half of its equilibrium value in eight minutes.

Fig 19:

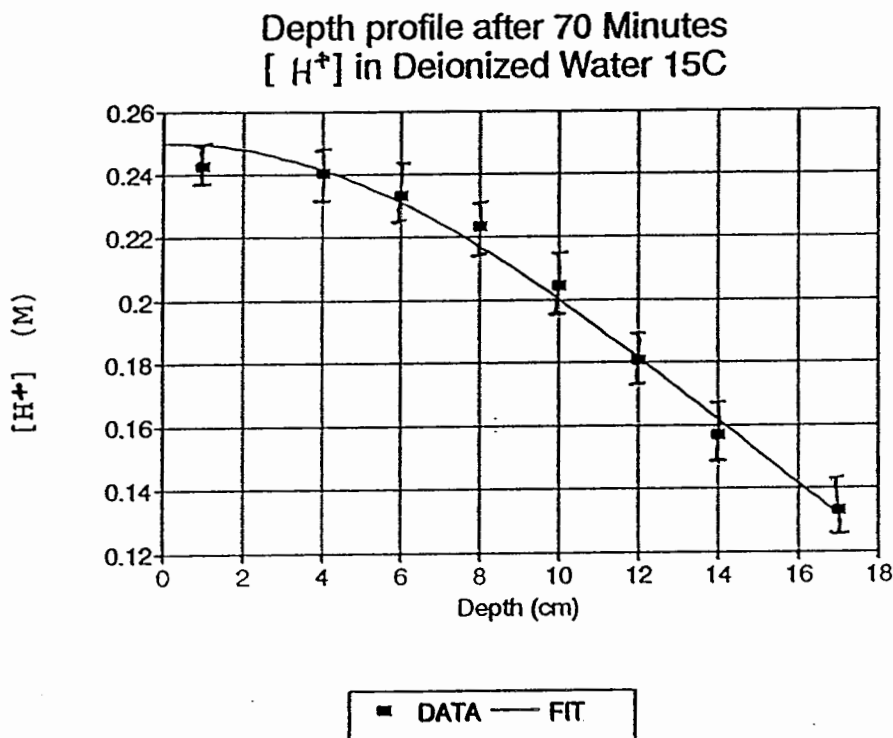


Analyzing the depth profile after 70 minutes, I fitted to Fick's equation to find

$$[H^+] = 0.25(3)e^{-0.0022(1)x^2}$$

This is plotted as fig 20.

Fig 20:



The diffusion constant was $0.27(1) \text{ cm}^2/\text{sec}$. With this value, the point in the water with a value of half of the surface value will travel downwards with a speed of $3 \times 10^{-4} \text{ m/s}$.

Under a cover of nitrogen, the conductivity rose to only about one third as high as it did under the atmosphere. The pH was thus about 6.5. The reaction rates should be slowed accordingly. Dr. Waltham's samples suggested that failure occurred only after aging equivalent to forty years in SNO.

The data from petal run number one was investigated. The scans showed varying degrees of interference, but the pattern was very similar for all three petals. I've tabulated a few of the minima for the three failure curves in fig 21. From the minima the thickness of the film can be calculated.

Knowing that for a thin film the minima can be found by

$$2nd = m\lambda \text{ where } m \text{ is an integer.}$$

The value of nd can be found to be 2479nm . The handbook of chemistry lists the index of refraction of aluminum as ranging from 1.2 to 1.6 for wavelength

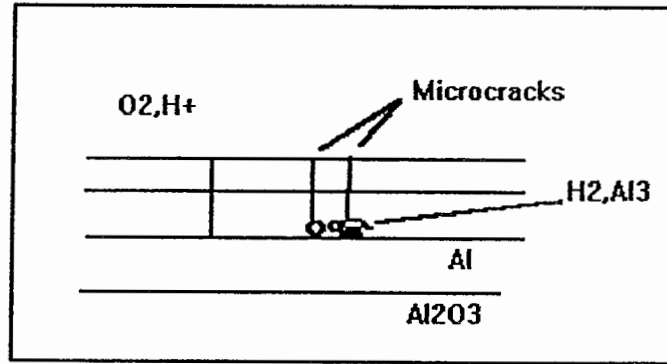
Fig 21: Failure Minima

A	B	C
772(2)	760(2)	780(2)
668	664	680
592	588	604

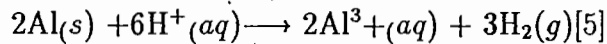
in the range important to SNO. The low end of this range gives $d = 2060$. The entire stack of films layered on the substrate is acting as a thin film. The Al layer goes from being reflective to translucent. The unfailed petals have one interference minima at 330nm. Thus $nd/m = 165\text{nm}$. If m is one and n is about 1.2, we find $d = 130\text{nm}$, the thickness of the two sealing layers. The aluminum is non spoiled and reflects the light that falls on it.

The various petals tests two through six indicate that two processes are occurring. One involves oxygen only, and one involves the action of acid on the aluminum. Fig 22 shows what is happening at various levels in the petal.

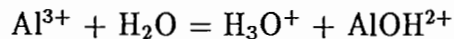
Fig 22: Corrosion of the DCA



The failure occurs as carbonic acid leaches through the protective surface to the bare aluminum, where it causes the reaction



The reaction below then takes place.



The various elevated temperature aging runs under air will be analyzed to provide a relation of reaction rate to temperature. This will allow the

extrapolation of a reaction rate in the SNO environment itself. Combined with the results of how the failures occur over time, these results will yield an idea of the fraction of petal failures in SNO. It was necessary to determine an estimate of the error on the values found in the various aluminum tests. The petals could be either failed or unfailed, and it is assumed that failure of one petal will not affect the remaining unfailed petals. The binomial distribution can then be applied to determine a value for the standard deviation for each run. It should depend on the number of samples in the run. Runs with more samples should be more accurate than those with less. For a binomial distribution,

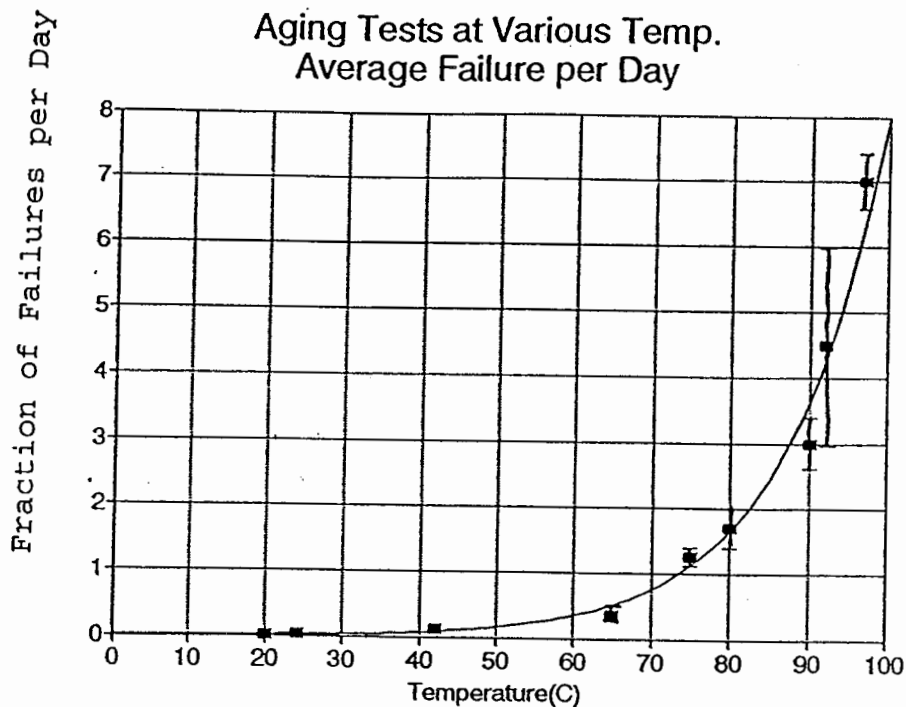
$$\sigma = \sqrt{np(1-p)}[11]$$

It has been fit to the model

$$\text{Fraction Failed per Day} = P_0 (a)^{T/10} \text{ with } T \text{ in degrees Celsius.}$$

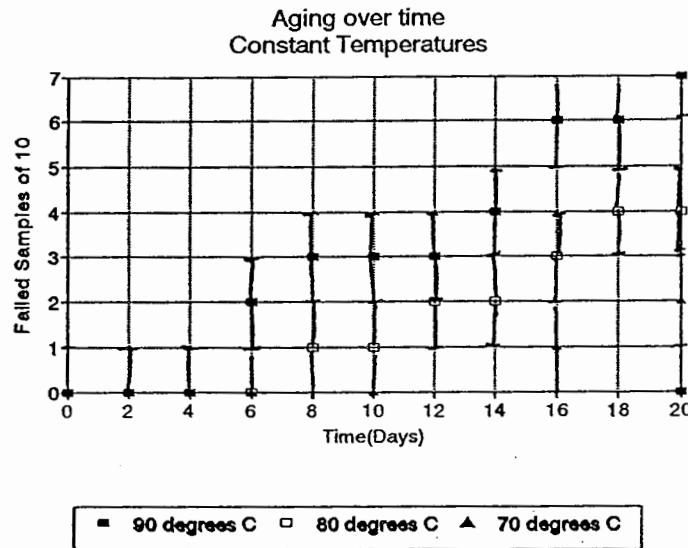
The data and a fit are shown as fig 23. The data fits the curve within error.

Fig 23:



Time Dependent Runs The time dependent runs are plotted as fig 24. The time t_b , explained below, is seen to become longer as the temperature increases.

Fig 24:



The time dependent runs reveal that the corrosion of the petals does not start right away, but takes a time t_b to begin. The number of petals corroded then increases until all of the samples are failed. The increase can be approximated by a linear increase. With a slope dependent on temperature. The starting time t_b should follow the same reaction rate rule as found in the temperature runs. With this model,

$$t_b = 4400(150) \times (2.2(1))^{-T/10}$$

If the SNO temperature is put into this relationship, the result is 6.4(6) years until the failures begin.

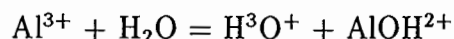
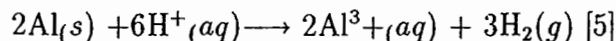
The data for the time dependent runs does not allow the precise fitting of a curve to the reaction process. The large statistical error leads to a large error in t_b and the shape of the curve. Sampling the pH in one of the final day bottles in the 90°C run, the pH was found to be 4.8(1). This is more acidic

than expected if the acid is produced from the carbonate cycle only. This could be explained by the acidic nature of the Al^{3+} ion. (See equation XV)

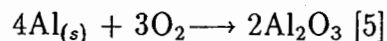
6 Conclusion

Water has often been described as a universal solvent. Part of its ability to attack metals such as aluminum comes from its quick absorption of carbon dioxide from the air. A solution of Carbonic acid soon forms, with a pH proportional to the partial pressure of the carbon dioxide in the atmosphere. It was found that pH_∞ was 3.86(02). P_{CO} in the lab was found to be 0.005(1) of an atmosphere causing the water to have a pH of 5.5(3) and a conductivity of $1.55\mu\text{S./cm}$. The point in the water column with a carbonate concentration half that of the equilibrium concentration moved downward at a rate of $3 \times 10^{-4}\text{m/s}$.

Exposure to the deionized water caused corrosion in the dielectrically coated aluminum. This effected the reflection curves in two separate ways. The curve was degraded by four percent, but maintained its shape, and some samples exhibited a sharp interference pattern. The development of this interference pattern was referred to as failure as it seriously damaged the optical properties of the petals. Analyzing the interference pattern with the laws of thin film interference, it was found that the pattern was that of one from a film of 2000nm thickness, implying that the aluminum layer had been rendered translucent. The reactions involved were:



The four percent degradation was most likely the result of oxygen causing the reaction



This effect took about two days to begin independent of temperature. One explanation is that penetration of the petals surface takes this amount of time. The layer of Oxide then protected the Al from further corrosion when acid was not present. The interference pattern did not develop. If acid is present the surface corrosion dissolves leaving the Aluminum exposed to further attack.

Under a cover of Nitrogen or CO_2 -free air, failure was seriously reduced or eliminated entirely. Under CO_2 -free air the failure is not seen, but the four

percent decrease in reflectivity does occur. Both are seriously discouraged under nitrogen. This agrees with the reactions above.

. Under a cover of CO₂ the decrease in reflectivity did not occur. Failures were seen, but slightly less than under regular air. Oxygen speeds the reaction by converting the aluminum to Al₂O₃ which is soluble in acid.

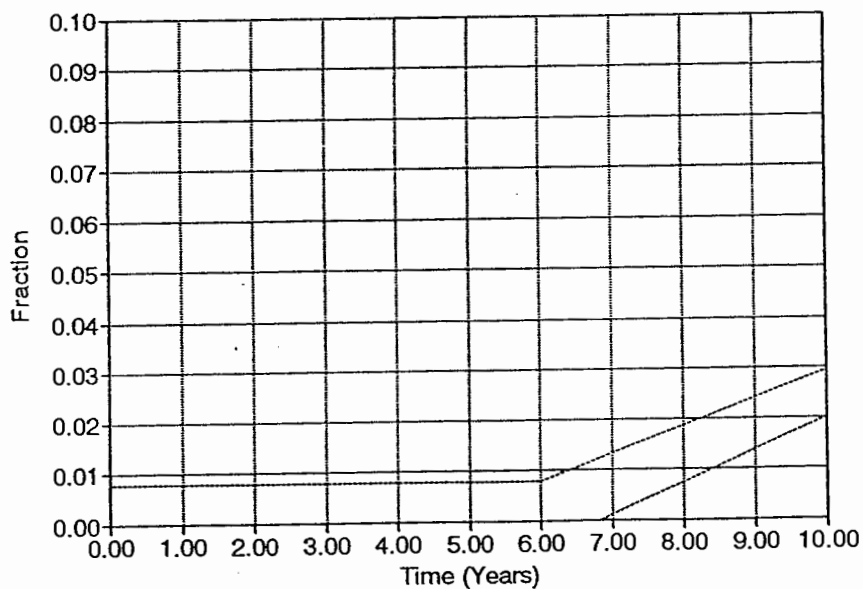
By aging samples at a variety of temperatures, it was found that the reaction rates increased by a factor of 2.2(1) every 10°C This supports the assumption used in early runs that the reaction rate doubled with every ten degree Celsius increase in temperature.

Over time, the failures began to occur after a time T_b and continued to completion at time T_c . They occurred in a roughly linear fashion. A slight increase in rate was observed at the ends of the runs due to lowering of the pH by the corrosion reaction. In a large container this is not observed.

At 8°C for ten years, 24(3) percent of the samples will have failed. The failures will begin 6.4(6) years into the detector lifetime. Figure 25 shows the probable failures in SNO over the ten years. The true failure curve will lie somewhere in the shaded area.

Fig 25

Fraction of Failed Reflectors In the sudbury Neutrino Observatory



The effects observed in these experiments could be decreased in the Sudbury Neutrino Observatory by keeping the water absolutely pure with no dissolved CO_2 or O_2 . This would be facilitated by a cover gas of nitrogen and a cover of CO_2 free air while filling. The first of these would seriously retard both forms of reflectivity degradation in the concentrators, and the second would prevent the more serious of the two problems. CO_2 free air does have the advantage that it could be produced in the mine with a cold trap and that it is breathable, allowing access to the upper surface of the detector.

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