

Moisture absorption and its effect on the electrical properties of high silica fabric

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Abstract. High silica fabric with a silica content $> 98\%$ can be prepared by removing the non-siliceous ions from the E-glass fabric using HCl as the leachant. The presence of Si-OH groups makes the material hydrophilic. The extent of moisture absorption depends on the extent of leaching. The moisture present in the leached fabric decreases the volume and surface resistivity values.

Keywords. Porosity; moisture absorption; diffusion; silanol groups; volume resistivity; surface resistivity.

1. Introduction

The absorption of water molecules to the glass surface or the absorption in the bulk material is of both practical importance and academic interest. When glass is used for vacuum envelopes and insulating the electrodes in vacuum devices, a knowledge of moisture absorption characteristics is important (Holland 1966). Alkali silicate glasses with alkali content greater than 20% have such poor resistance to water attack that they can be completely dissolved in water to form water glass. Various glass compositions show different types of hydration (Che-Kvang Wu 1980). The absorption of water vapour on glass surface is due partly to a firmly held (chemisorbed) monolayer which cannot be removed by pumping at room temperature and partly to a physically adsorbed film (Razouk and Salem 1948).

In the presence of atmospheric moisture the silica of the glass surface will rapidly be transformed into the hydroxylate state. The hydration process will not stop with the formation of silanol groups, since they can form hydrogen bond with water to multimolecular layer of adsorbate over the surface. Studies on E-glass showed the surface coverage of 1, 3, 5 monolayer of water at relative humidity 10, 50, 60 respectively (Broutman and Krock 1968; Gut Friend and Weber 1961). It was proved experimentally that water vapour absorption is

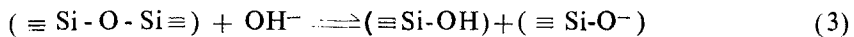
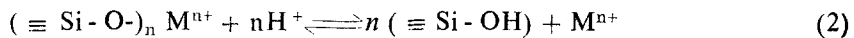
restricted to silanol sites on the glass surface even at high relative pressures (Young 1958). Various reviews are available on the interaction of water with glass (Scholze 1966; Moulson and Roberts 1961; Hvang 1971).

The moisture absorbed by the glass plays a vital role in effecting various of physical properties of the glass. Excellent reports are available on the effect of water on the properties of glass (Boulos and Kreidl 1972; Scholze 1966; Hetherington and Jack 1962).

It is generally agreed that water is mostly accommodated in the glass structure in the form of hydroxyl ions and a reaction of the type,



is generally postulated. Silanol group formation is also observed when the glass reacts with acids or alkalies



The silanol groups thus formed become the hydrophilic sites.

In the present work E-glass fabrics were leached in different normalities of HCl for a fixed time (4 hr), to remove the nonsiliceous ions and to create silanol groups. The moisture content and moisture absorption against time was studied. The effect of moisture on volume and surface resistivity was also studied. Protonic conduction was found to dominate in these high silica glass. Leaching studies on E-glass was carried out to prepare high silica glass (silica content > 98%). This material is used as a high temperature electrical and thermal insulator. It is used in rocket nozzles for ablative purposes and in furnaces for thermal insulation.

2. Experimental

E-glass fabric (Pilkington, UK composition) was employed in the present work. The composition ascertained by the chemical analysis was, SiO₂, 54.2; Al₂O₃, 14; CaO, 19.8; MgO, 2.2; B₂O₃, 8.2; Fe₂O₃, 0.3; Na₂O + K₂O, 0.56 (all wt%). The cut fabric pieces were leached in HCl solution for 4 hr. The normality of the solution was varied from 0.5 N to 4 N. The leached fabrics were heated to various temperatures (post-heat treatment 100-700°C) for 4 hr to remove the absorbed water in an oxidizing atmosphere. It was then cooled to room temperature in a desiccator and then weighed to find the weight loss. The same fabric was exposed to atmosphere of known humidity and the weight increase due to moisture absorption was also recorded.

In addition to moisture absorption experiments, leached and heat-treated fabrics were also used to measure volume and surface resistivity. Details of the equipment and procedure employed have been described earlier (Rama Chandran *et al* 1980).

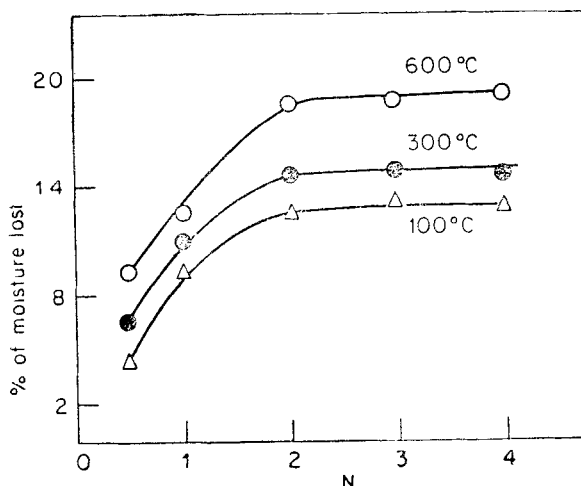


Figure 1. Percentage of moisture lost by the leached fabric (0.5-4 N) at various temperatures of heat treatment. Leaching time 4 hr.

3. Results and discussion

As indicated in equation (2), silanol groups can be formed by the removal of non-siliceous ions. These silanol groups become the potential sites for water absorption. The silanol group formed can be dehydrated by heating (equation 1.) Apart from the formation of silanol groups, due to the substitution of smaller H^+ ions in place of cations such as Ca^{2+} and Al^{3+} , the material becomes porous. The porous structure and silanol groups enable water absorption. During the post heat treatment, in addition to the water removal, the pore size distribution is also altered either by shrinkage and/or by the closure of the pores.

3.1 Moisture content

The moisture in the leached fabric depends on the number of silanol groups, which in turn depends on the number of cations removed. The ion removed depends on the concentration of the acid employed for the leaching treatment. Greater the concentration of the acid greater will be the moisture content as the leaching rate decreases. Figure 1 shows this effect at any fixed temperature for fabrics prepared by leaching in 4 N HCl for 4 hr. As the heat treatment temperature increases, the moisture lost at any fixed normality also increases.

3.2 Moisture regained

Figures 2 and 3 show the moisture reabsorption pattern for fabrics leached in 4N and 1N HCl for 4 hr and heat-treated to various temperatures for 4 hr. The heat-treated fabric can absorb moisture again when exposed to the atmosphere. The desorption-absorption process is reversible up to a heat-treatment temperature of

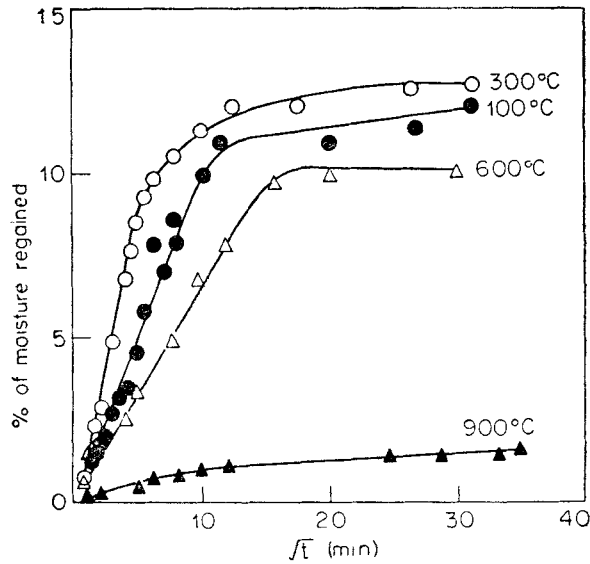


Figure 2. Percentage of moisture regained with time by fabrics leached in 4N HCl for 4 hr and heat-treated to various temperatures.

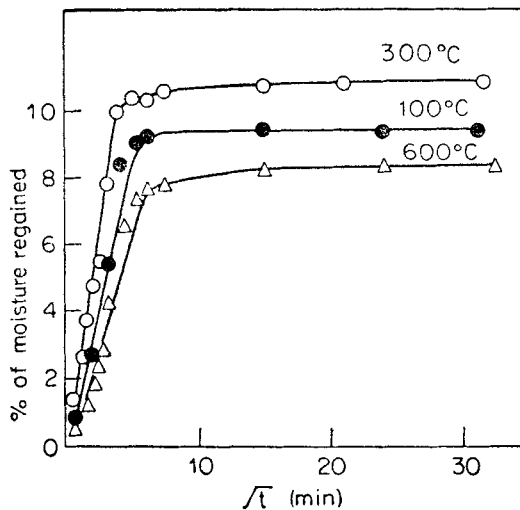


Figure 3. Percentage of moisture regained with time by fabrics leached in 1N HCl for 4 hr and heat-treated to various temperatures.

900°C. The reabsorption is a diffusion-controlled process (Hvang 1971). A heat-treatment of 100°C removes only physisorbed water, 300°C heat treatment removes completely absorbed water and a major portion of structural water by the interaction of -Si-OH groups. Heat treatment of 600°C leads to partial sintering as well. At 900°C the sintering process is completed and hydrophilicity of the material is minimized.

The fabric heat-treated to 100°C loses physically adsorbed water only while structural water (in the form of silanol group) remains in tact in the material. On exposure it recaptures only the free absorbed water. A 300°C heat-treated fabric loses all the adsorbed water and structural water and recaptures it again. Hence the moisture lost and regained will be higher compared to 100°C heat-treated fabric. Since sintering does not occur for heat treatment at $\leq 300^\circ\text{C}$ the reabsorption is not at all affected whereas in 600°C heat-treated fabric, sintering process affects the water reabsorption pattern (figures 2 and 3)

3.3 Effect of moisture absorption on volume resistivity

The moisture present in the fabric will decrease the volume resistivity (ρ_v) of the material. Any decrease in the moisture content will increase the resistivity (Rama Chandran *et al* 1979). It was pointed out earlier that as the post heat-treatment temperature increases the moisture content decreases resulting in a corresponding increase in volume resistivity. As can be seen from figure 4 the increase in ρ_v is linear with respect to the post heat-treatment temperature.

During the heat treatment apart from the dehydration of silanol groups, porosity is also reduced. Porosity of the fabric also determines the moisture absorbed. Fabrics prepared by leaching in 2N HCl for 3 hr were heat treated at 300, 600, 900°C and then exposed to the atmosphere. Fabrics heated to higher temperature absorb very little moisture and hence ρ_v decrease is also less. The decrease in porosity with post heat treatment also affects the mobility of water molecule into the material. Figure 5 shows the effect of post heat treatment temperature on moisture absorption of the E-glass fabric and its volume resistivity and as can be seen it shows the expected trend. The conducting species would be protons as was observed earlier (Tronovcova *et al* 1977). The diffusion of water in silica has been explained by lattice breaking model (Cockram *et al* 1969) and diffusion and reaction of molecular water model (Doremus 1969).

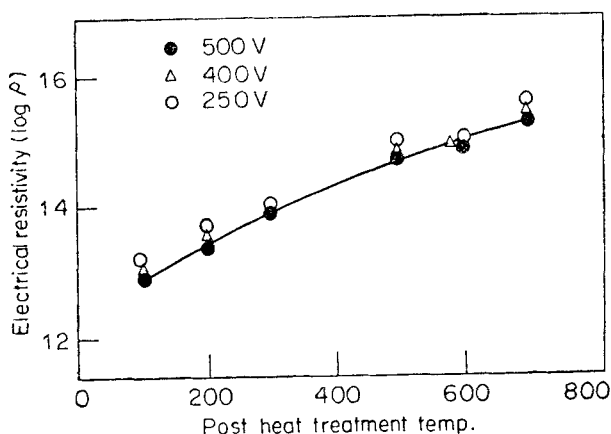


Figure 4. Variation of electrical resistivity with heat-treatment temperature. Fabric soaked in 2 N acid for 3 hr.

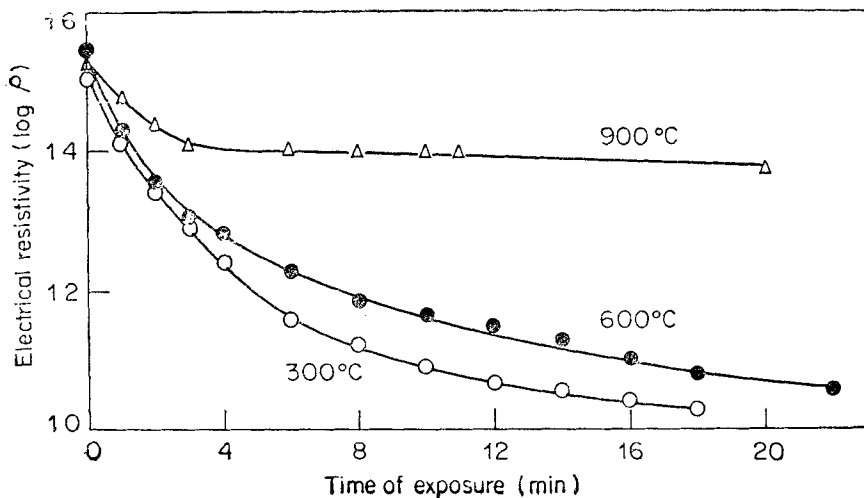


Figure 5. Effect of post heat-treatment on electrical resistivity of fabrics soaked for 3 hr in 2 N acid.

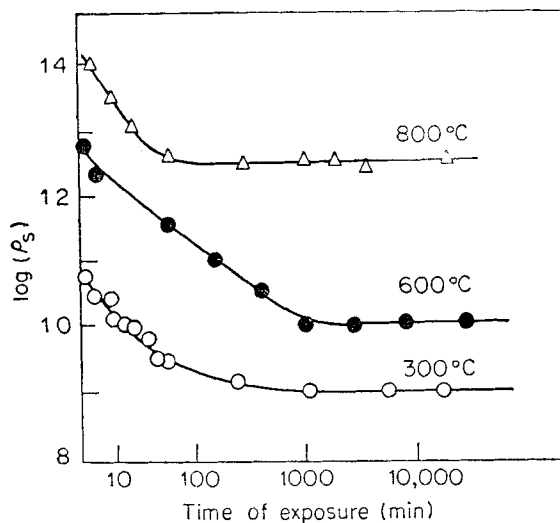


Figure 6. Change in surface resistivity with time exposure for heat treated fabrics.

3.4 Effect of moisture absorption on surface resistivity

Figure 6 shows the effect of moisture absorption on surface resistivity (ρ_s) for fabrics leached in 4N HCl for 6 hr and then heat treated at various temperatures. The change with time was recorded. The decrease is due to the moisture absorption. As the post heat-treatment temperature increases, the moisture absorption rate decreases and hence the decrease in ρ_s varies accordingly. As the moisture absorption increases with time, number of charge carriers also increases. The decrease in ρ_s may also be due to the enhanced and easy mobility of protons in the multimolecular layer of water formed over the silanol groups.

4. Conclusions

E-glass fabric on leaching with HCl gives rise to silanol groups which become the hydrophilic sites. The moisture absorption of the leached fabric depends on the extent of leaching. The moisture content increases as the concentration of the leachant increases. The reabsorption of moisture on completely leached and heat-treated samples leads to decrease in both volume and surface resistivities.

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