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Observation of chemical hydration in inorganic mineral fibres

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An experimental study has been carried out and it was observed that inorganic mineral fibres of the slag wool and rock wool types exhibit a physical disintegration and morphological modifications on the fibre surface when these fibrous products have been exposed to water vapour or immersed in a liquid water medium under heating at temperatures up to 100° C for a period of several months. The physical disintegration transformed the fine and thread-like fibres into small segments and granules. Scanning electron microscopic examinations showed that a rough and eroded fibre surface was formed for those fibres which have been immersed in water and heated at temperatures below 60° C for about 3 months and that a reticular network structure or "honeycomb morphology" was developed on the fibre surface for those fibres which have been immersed in water and heated at temperatures above 85° C and up to 100° C for about 4 weeks. Measurement of the pH value of the water solution and thermogravimetric analysis of the disintegrated fibres suggest that these modifications of the fibrous products are caused by two possible mechanisms: chemical leaching and chemical hydration. Thermal conductivity measurements showed that the disintegrated fibres have thermal insulating values about 15% lower than that of the normal and thread-like fibres.

1. Introduction

Studies of the durability of building materials and components due to environmental influences have been actively pursued in recent years and many interesting results have been reported in the literature [1–5]. However, studies of the durability of thermal insulating materials have not been revealed to the same extent, as very little information can be found in the literature. This is particularly so for the inorganic mineral fibres, such as glass fibres, slag wool and rock wool fibres, which are used extensively as thermal insulators in building envelopes to impede heat energy transfer so that energy conservation can be realized. These inorganic fibres are generally considered to be durable products for insulation applications because they are able to withstand high operating temperatures; they are chemically stable and they are also believed to be non-absorbent of water. However, there are several pieces of information in the literature indicating that the action of heat and water vapour could render detrimental effects to these inorganic mineral fibres. It has been reported that slag–rock wool fibres could become fragile and develop to the point of destruction of the fibre form by exposure of the fibres to heat and humidity [6]. Other studies have reported that the presence of a water vapour atmosphere could lower the surface tension of the fibrous soda–lime–silica glass products [7, 8].

Fibrous glass used as thermal insulators is generally made from the soda–lime–silica system with a silica content in excess of 55 wt %, lime in excess of 14 wt % and soda in excess of 10 wt % [9]. On the other hand, mineral fibres of the slag wool and rock wool types are fabricated primarily from mechanical mixtures of metallurgical slags and/or natural rocks which contain the main ingredients of silica (SiO_2), alumina (Al_2O_3), lime (CaO) and magnesia (MgO) with a small proportion of other oxides such as iron oxide (Fe_2O_3) and alkalies (Na_2O or K_2O). In order to control the melting temperature or the viscosity of the molten mixture, other oxide components are often added to the starting components. The common compositions of the slag–rock wool fibres contain silica in the range 35 to 45 wt %, lime in the range 20 to 40 wt %, alumina in the range 10 to 20 wt %, magnesia in the range 2 to 15 wt %, and soda in the range 0.5 to 2 wt % [10]. The chemical compositions among these inorganic fibres therefore differ quite significantly.

A laboratory study has been carried out and it was observed that heat and water not only caused the inorganic slag–rock fibres to become fragile but they also induced a physical disintegration and morphological change on the fibre surface. The disintegrated fibres also exhibited inferior thermal insulation properties. The purpose of this paper is to present some of the experimental results and discussions.

2. Experimental techniques

Three mineral fibre products of the slag–rock wool type were used for the study. These inorganic fibres were made primarily from the combinations of natural rocks and metallurgical slags by three different manufacturers. Fibres from source 1 were produced by Bishop Building Material Products Ltd, Toronto, Ontario. Fibres from source 2 were produced by Canadian Gypsum Co, Montreal, Québec. Fibres

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from source 3 were produced by Holmes Insulation Ltd, Sarnia, Ontario. They are commercially available in the form of loose pouring fibres for residential insulation applications. However, the chemical compositions of these slag–rock wool fibres obtained from the three sources are not readily identified by the manufacturers, nor were they experimentally determined for the study.

The study was divided into two groups of experiments. The first group of experiments was carried out by immersing ~30 g of the loose fibres in 500 ml distilled water in air-tight glass containers such that the fibres were constantly in contact with the liquid water. Each fibre sample was placed separately in an individual container. The second group of experiments was carried out with slightly modified procedures. About 50 ml distilled water was first placed in the bottom of the glass container and a layer of clean glass cullet, ~10 mm thick, was then placed in the water. About 30 g of the mineral fibres were then placed on top of the glass cullet such that the fibres were not in direct contact with the liquid water inside the container. Each fibre sample was also placed separately in the container. All glass containers were then closed with a forced lid to ensure that water evaporation from the container was minimized. These containers containing the mineral fibres were then placed in an electric furnace and heated at temperatures of 25, 45, 60, 85, 92 and 100° C, for a period varying from 2 weeks at 100° C to 8 months at 25° C, and other periods depending on the heating temperature. At the completion of the heat-water treatment, a small fibre mass was removed from the container and dried for inspection by scanning electron microscopy.

The chemical change in the distilled water before and after the fibre immersion process was analysed by measuring the pH of the water at ambient temperature with a custom built pH meter. The thermal behaviour of the normal slag–rock wool fibres and of the short fibres which were transformed by the degradation process was analysed, using thermogravimetric analysis (TGA), employing a DuPont 1090 differential thermal analyser (DuPont Inc, Wilmington, Delaware USA).

The thermal conductivity and the thermal resistance of the normal slag–rock wool fibres and of the disintegrated fibres were measured with a heatflow meter apparatus (the R-matic system, Dynatech R/D Co, Cambridge, Massachusetts, USA) according to an ASTM test method [11]. Test specimens of 25 mm thick and containing fibres of various pouring fibre density values were prepared for such measurements.

3. Results

Mineral fibres of the slag–rock wool type generally appear in the form of fine and thread-like filaments and the surface of the individual fibre is smooth and free from defects, as shown in Fig. 1. This fibrous form was observed to remain unchanged when the fibres were heated from ambient temperature up to 500° C for a period of 5 to 6 h and subsequently cooled back down to ambient temperature under a water-free environment. This dry heat treatment was observed to cause no physical modification on the fibres. However, when water, either in the form of vapour or in the form of liquid, was introduced to the fibres and the fibre–water system was then heated at the temperature levels selected for the present study, all three slag–rock fibres were observed to exhibit physical changes. The manner of this physical change in the fibres was observed to vary between those fibres immersed in the water and those exposed to the water vapour. These will be discussed separately in the following sections.

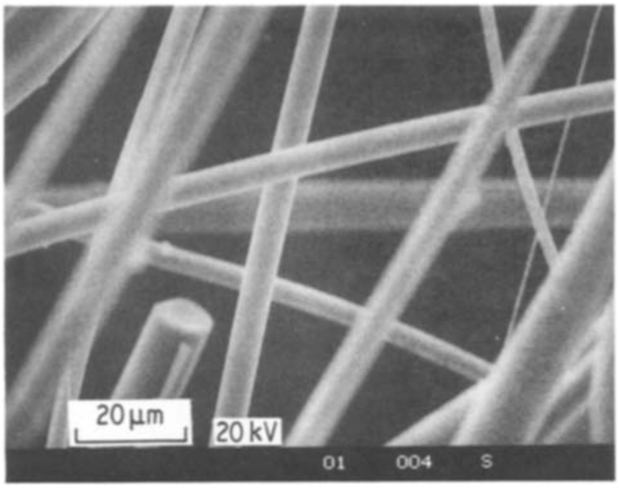

Figure 1 Scanning electron micrograph of normal mineral fibres.

Experiments of the first group, in which the mineral wool fibres were immersed in distilled water and heated at different temperatures, showed significant variations. After a continuous immersion in the distilled water at 25° C for 8 months, the fine and thread-like filaments of the test samples from sources 1 and 2 were found to break down into small segments very easily when the fibres and the water were mechanically agitated. However, the test fibre sample from source 3 was observed to remain essentially unchanged with similar mechanical agitation. When the water temperature was increased to 45° C for 4 months, fibres from sources 1 and 2 were again found to break down easily into small segments upon agitation. Upon close examination of the small segments of these transformed fibres with the scanning electron microscope, a rough and eroded surface

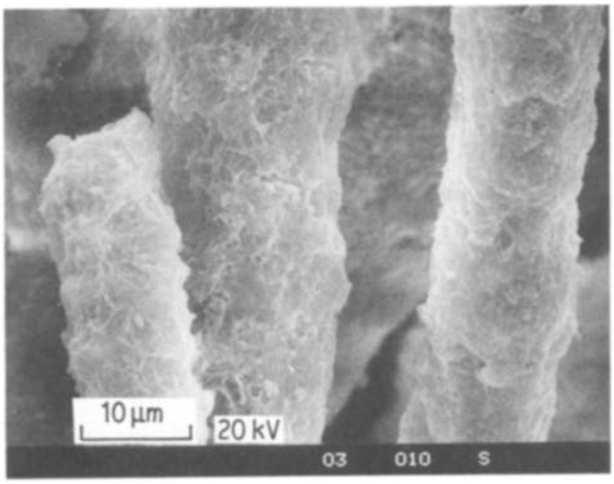

Figure 2 Scanning electron micrograph of slag–rock wool fibres after heating in liquid water at 45° C for 4 months.

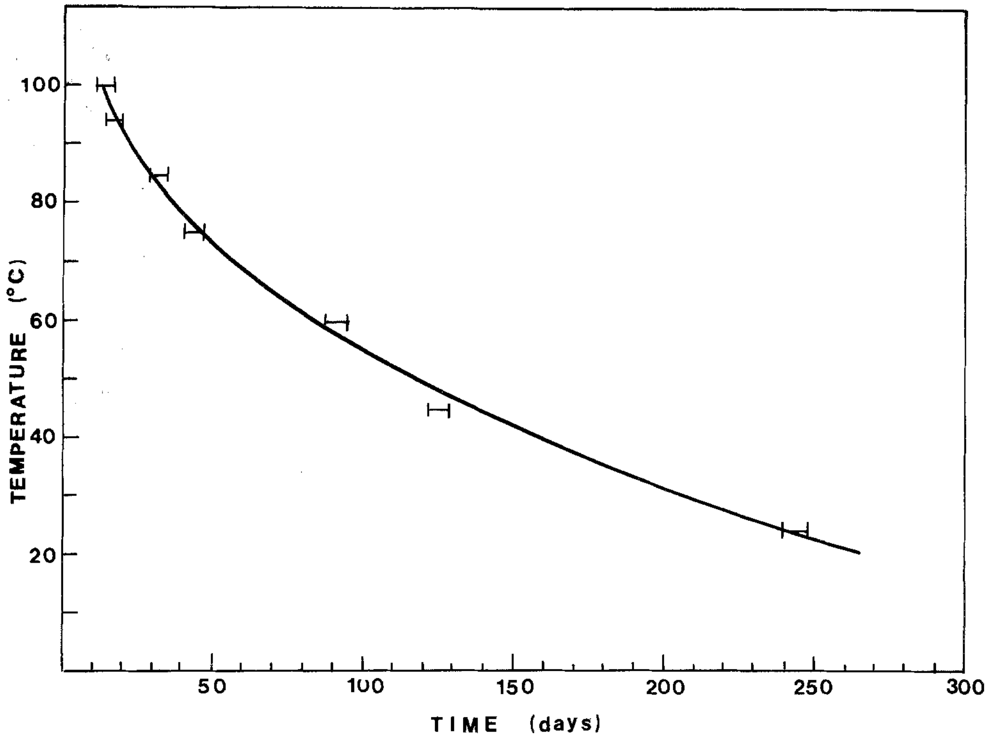

Figure 3 A simple correlation between heating temperature and the time for the material degradation of slag–rock wool fibres.

was observed as shown in Fig. 2. The nature of the physical change of the fibre surface suggests that it may have been caused by a chemical reaction process between the surface of the fibres and the water medium. When the heating temperature was further increased to 60° C, the fibre disintegration process was observed to be more acute. After only 3 months of heating, fibres from sources 1 and 2 were found to have transformed into a granular form upon only a slight agitation process in the containers. Upon heating at 85° C, similar results were observed after a time period of only 27 days. When the temperature of the water was increased to 92 to 100° C, the fibre samples from all three sources were observed to have partially transformed into the granular form after only 6 days of heating, and complete transformation was observed after 14 days. A simple trend between the heating temperatures and the time periods for the material disintegration process to materialize as observed in this group of experiments became evident as shown in Fig. 3. The error bars in the graph indicate the time period from the first sign of the physical change of the fibres to the final visualization of the disintegration process. Scanning electron microscopic examination of the disintegrated fibres which were produced by heating in water at 100° C for 14 days revealed a morphological change on the surface of the fibres. The fibres were observed to be surrounded by a "honeycomb morphology" or reticular network structure, as shown in Fig. 4.

Experiments of the second group in which the mineral fibres were exposed to water vapour and heated at the same temperature levels as those in the first group, also showed a fibre disintegration process but in a different manner. After 4 months of exposure to water vapour at 45° C, a spotty material growth or deposition was observed on the surface of the fibre stem for those slag–rock fibres obtained from sources

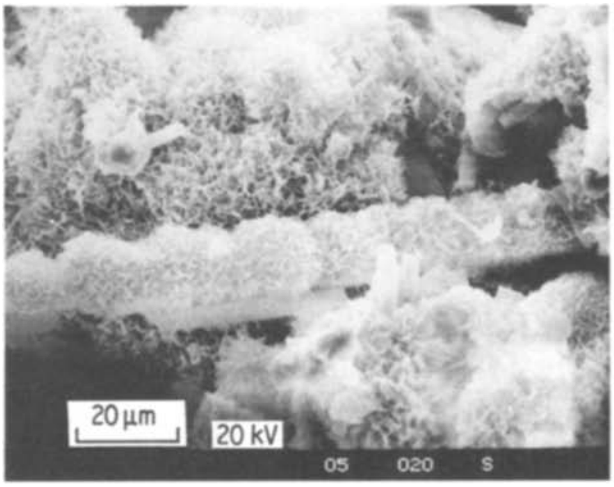

Figure 4 Scanning electron micrograph of slag–rock wool fibres after heating in liquid water at 100° C for 14 days.

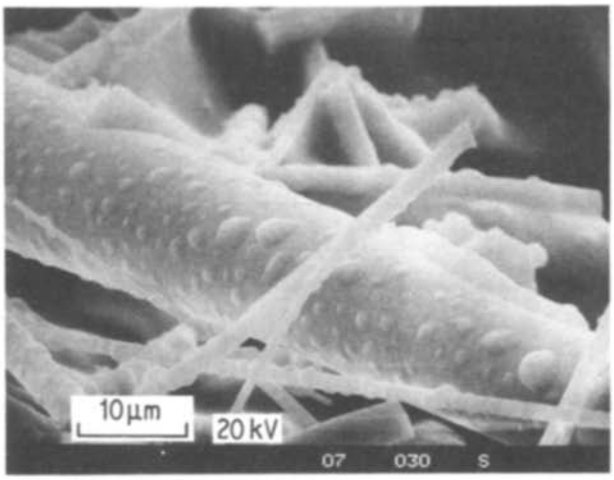

Figure 5 Scanning electron micrograph of slag–rock wool fibres after exposure to water vapour at 45° C for 4 months.

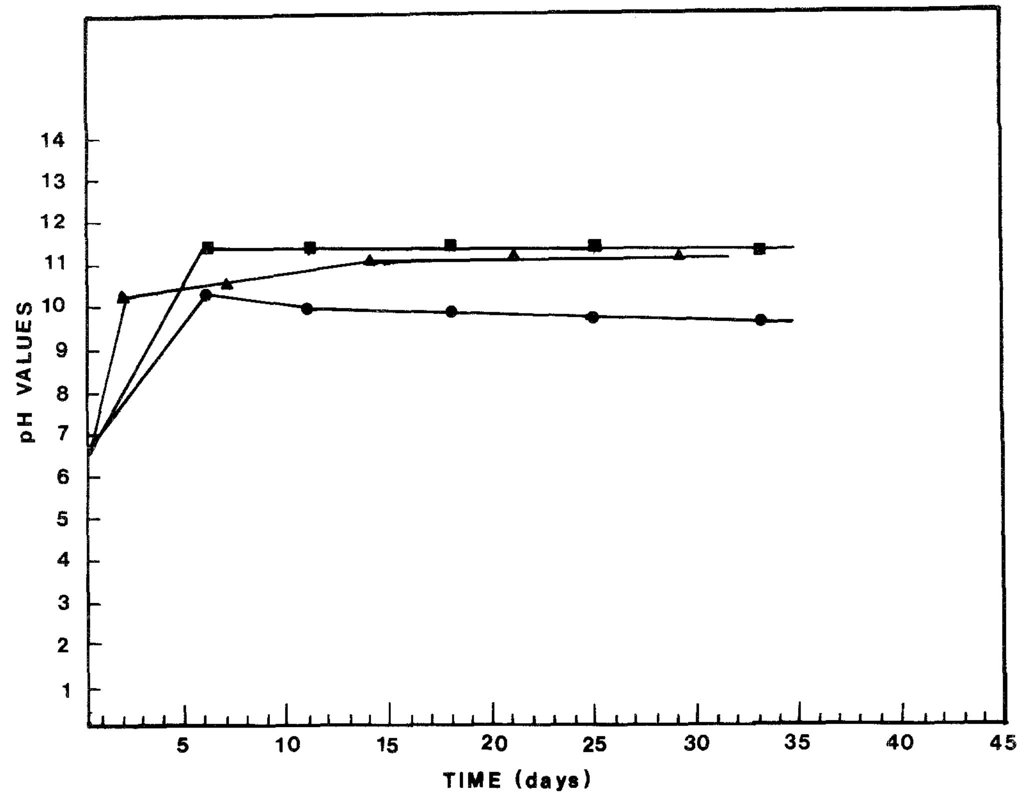

Figure 6 Modification of the pH values of distilled water by the immersion of slag–rock wool fibres: slag–rock wool fibres from ■, source 1; ▲, source 2; ●, source 3.

1 and 2, as shown in Fig. 5. However, under normal visual inspection, the larger fibre mass exposed to these conditions remained in the form of fine fibres and displayed no external breakage. After exposure to water vapour at 60° C for 3 months, fibres from sources 1 and 2 were found to break down easily into a granular form when the moist fibres were rubbed together gently with the fingers. Fibres from all three sources were found to break down easily into small segments and granules by this finger rubbing process after the fibres had been exposed to water vapour and heated at temperatures of 85 to 100° C for a period of about 40 to 50 days. It was noted that the slag–rock wool fibres exposed to the water vapour phase and heated at temperatures above 85° C also displayed a honeycomb morphology, similar to that observed in the fibres immersed in the distilled water and heated at the same temperatures, as shown in Fig. 4. The overall results of the second group of experiments indicate that the slag-rock wool fibres exposed to water vapour at the various temperatures encountered similar physical changes and material disintegration to those observed in the fibres immersed in the liquid water but in a less extensive manner. Table I gives a summary of the experimental results for the two groups of test samples as exposed to the water vapour phase and to the liquid water phase at the various heating temperatures.

Measurements showed that the pH of the distilled water prior to the immersion of the slag–rock wool fibres was near neutral (about 6.8) and increased to 10 to 12 after the mineral fibres were immersed in the water for a few days to a few weeks as shown in Fig. 6. This indicates that the distilled water had become an alkaline solution due to the fibre immersion process. It was observed that modification of the pH value of the distilled water occurred in the slag–rock wool fibres from all three sources. It was noted that the length of

TABLE I Observation of material change in mineral fibres after exposure to water treatments at various temperatures

Heating temperature (° C)	Exposure time (days)	Occurrence of material change	
		Vapour phase	Liquid water
25	240	No change	Fibres from sources 1 and 2 break down by shaking
45	120	Fibres from sources 1 and 2 surface change	Fibres from sources 1 and 2 break down by shaking
60	90	Fibres from sources 1, 2 and 3 break down by rubbing	Fibres from sources 1 and 2 break down by shaking
75	40	Fibres from sources 1, 2 and 3 break down by rubbing	Fibres from sources 1 and 2 break down by shaking
85	27	Fibres from sources 1, 2 and 3 break down by rubbing	Fibres from sources 1 and 2 break down no shaking
94	14	Fibres from sources 1, 2 and 3 break down by rubbing	Fibres from sources 1, 2, and 3 break down no shaking
100	14	Fibres from sources 1, 2 and 3 break down by rubbing	Fibres from sources 1, 2, and 3 break down no shaking

time for which the fibres were immersed in water and the temperatures to which the fibres were heated within the 25 to 100° C range have no influence on the modification of the pH value of the water solution. Modification of the pH of the water solution was also found to be unaffected by preheat-treatment of the mineral fibres up to 500° C for several hours, prior to immersion of the fibres in the distilled water. The preheat-treatment of the mineral fibres before immersion in the water was intended to remove any organic resin material which might have been sprayed on to the fibres as binding agent to hold the fibres together by the manufacturer during the fibre production stage. Removal of this organic matter did not appear to alter the pH value of the water solution, as the value remained in the 10 to 12 range. The pH of the water solution was also found to remain unchanged when the fibre–water system was frequently exchanged with fresh distilled water after each measurement. However, it was noted that mineral fibres immersed in distilled water with frequent water change also displayed easy breakage into small segments upon mechanical agitation, even without the heat-treatment process.

Thermogravimetric analysis (TGA) measurements showed that there is a distinctively different behaviour in the fibre mass between the normal long fibres and the disintegrated short fibres when they were subjected to heating at temperatures up to 1000° C. Fig. 7 shows the weight change as a function of the heating temperature for the normal slag–rock wool fibres (curve A) and for the disintegrated fibres (curve B). The disintegrated fibres used in this TGA measurement were small segments and granules which had been transformed from the normal fibres after heating in water at 85° C for 27 days. It is evident that the normal slag–rock wool fibres exhibited no weight change within the temperature range, while the disintegrated fibres showed a gradual weight loss as the heating temperature was steadily increased. An optimum weight loss of about 18% was observed at about 1000° C. When the derivative signal of the weight change as a function of temperature was plotted, a pronounced and abrupt weight change within the narrow temperature range 680 to 710° C became evident, as shown in Fig. 8. This indicates that within this narrow high-temperature range the disintegrated mineral fibres have experienced a sudden transition in the fibre mass.

Heat-flow measurements on loose pouring fibre mass showed that the thermal conductivity of the disintegrated fibres is considerably higher than that of the normal fibres. Fig. 9 shows the variation of the thermal resistance of a 25 mm thick test specimen as measured at the various pouring fibre density values. Curve A is the plot of R rendered by the normal, thread-like slag–rock wool fibres and curve B those by the small segments and granules of the disintegrated fibres. It is evident that the thermal barrier for the space filled with the disintegrated fibres is at least 15% lower than that of similar space filled with the normal, thread-like fibres in spite of the fact that the space is filled with fibres of similar fibre density. For test specimens containing fibres with very low fibre density values, the difference in thermal resistance rendered by the two forms of insulation materials between the normal and long fibres and the disintegrated and short fibres is even more pronounced. This is due to the fact that, at this low fibre density level, the small segments and granules of the disintegrated fibres became insufficient to occupy the entire container space thus creating a significant portion of the space unfilled with the insulating material.

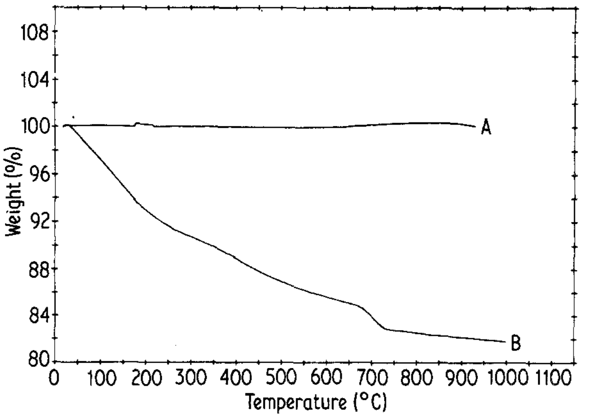

Figure 7 The weight change as a function of heating temperature between the normal slag–rock fibres and the disintegrated slag–rock wool fibres.

4. Discussion

The change in the pH of the water solution by the fibre immersion process and the physical disintegration of the slag–rock wool fibres as a result of immersion in the water solution, or of exposure to the water vapour in conjunction with heat-treatment at temperatures up to 100° C, are strong evidence that the changes are caused by some chemical reaction processes which are developed between the water medium and the surface of the mineral fibres. The observed experimental evidence suggests that there are two possible mechanisms which may be responsible for these material degradation processes. They can be interpreted by the following considerations.

The surface erosion on the fibre stem of those fibres which have been heated at temperatures up to 60° C is possibly a consequence of a chemical leaching process. When the water medium is in contact with the mineral

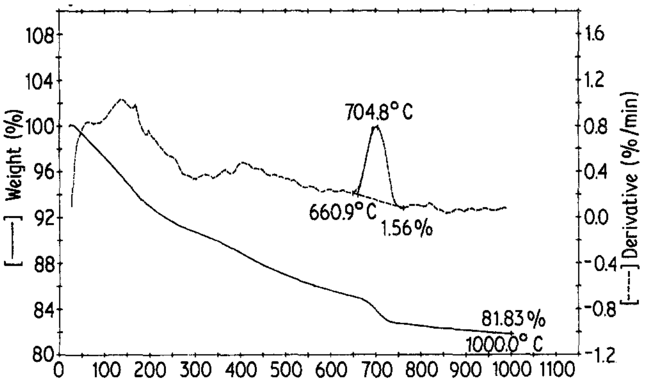

Figure 8 The derivative of the weight change of the disintegrated slag–rock fibres as observed in the thermogravimetric analysis measurement.

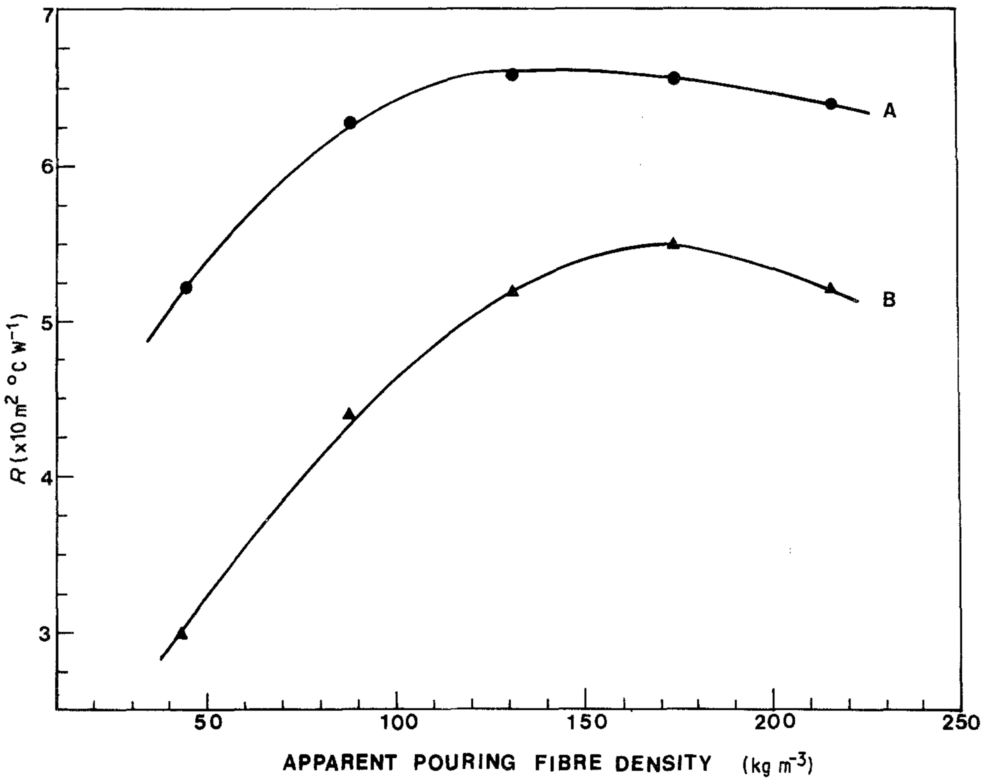

Figure 9 Variation of the thermal resistance of a 25 mm thick test specimen as measured at various pouring fibre density values.

fibre surface, certain chemical species are removed from the fibres and dissolved in the water solution thus changing the neutral water solution to an alkaline solution. Under continual removal and accumulation of these leached out components, some of the components begin to settle on some part of the fibres which are not affected by the water chemical reaction thus leading to the formation of the spotty growth on the fibres. On the other hand, the removal of chemical species from the fibres would result in the formation of weak spots or stress concentrators in the fibre stem. Movement of the fibres by external vibration, or by the hand shaking process would lead to fracture and subsequent disintegration of the fibrous form in the weakened spots, thus transforming the long and fine fibrous solids into small segments and granules.

The formation of the reticular network structure or honeycomb morphology on the surface of those fibres which have been immersed in water and heated at temperatures above 85° C is evidently developed from a different chemical process. It has been known that when Portland cement grains are in contact with the water medium, a hydration process is developed and the calcium silicate compounds in the cement become hydrated. This hydration often caused the formation of a reticular network structure on the surface of the calcium silicate hydrates [12]. A close comparison of the physical appearance of the reticular network structure between the slag–rock wool fibres and the calcium silicate hydrates in Portland cement is found to be very similar. Secondly, sources which contribute to the formation of such a honeycomb structure in these two types of materials is also very similar. Based on these similarities it seems not unreasonable to suggest that a chemical hydration process has also been developed on the slag–rock wool fibres when they are in contact with the water medium and activated by the heat-treatment at temperatures within the range 85 to 100° C.

The manifestation of this chemical hydration and chemical leaching processes between the inorganic slag–rock wool fibres and the water medium is not totally unrealistic in view of the chemical sources which are used to produce this type of inorganic fibrous product, as mentioned earlier. Apart from the complexity of the starting material components which are used for the production of these slag–rock wool fibres, there is the presence of other impurities in the mixtures. For example, sulphur is frequently present in the metallurgical slags and natural rocks and it is also invariably present in the coke which is the major fuel source in the mineral wool fibre production process employing the conventional cupola furnace technique. Intermixing all these chemical ingredients with homogeneity in the melting process and in the fibrization of the molten mass would become difficult. Many of the fibrous solids produced would contain various chemical contents with very little chemical homogeneity. It is quite possible that some silicate type and other related chemical compounds would have been formed during the high temperature melting and subsequent cooling processes. When these silicate and related compounds are in contact with the water medium and activated by the heating process, the initiation of the chemical leaching and chemical hydration processes is not impossible.

Apart from the evidence of microstructure modification, the postulation of the chemical hydration process in inorganic slack–rock wool fibres is also supported by the results of the thermal conductivity measurements and the thermogravimetric analysis. The thermal conductivity of the small segments and granules of the disintegrated fibres is found to be higher than that of the normal slag–rock wool fibres. If the disintegrated fibres have indeed become hydrated, the short fibres would contain a number of the hydrated water molecules in the fibre structure. This hydrated water will not be removed by a low-temperature heating process, such as oven drying. The presence of hydrated water in the fibre structure would therefore enhance the heat conduction mode through the fibre mass, thus contributing to a higher thermal conductivity of the small segments and granules of the disintegrated fibres. This increase in the thermal conductivity of the disintegrated fibres might have been accentuated by a secondary factor. This is the settlement of the short fibres in the container by the hand pouring process. A greater settlement of the short fibres would reduce the overall pore space in the fibre mass. It is generally known that decrease of porosity in a particulate medium in the presence of air would increase the thermal conductivity of the granulate material [13]. These two factors, the presence of the hydrated water molecules in the fibre structure and the reduction of porosity in the fibre mass, would contribute to a higher thermal conductivity value in the disintegrated fibres of the slag–rock wool fibres as compared to the normal thread-like fibres. The occurrence of the abrupt weight change and the large rate of weight loss in the small segments and granules of the disintegrated slag–rock fibres within the narrow temperature range 680 to 710° C in the thermogravimetric analysis measurement, is evidently related to a thermal dehydration process. There are a number of ceramic minerals which exhibit thermal dehydration around this temperature range [14].

5. Conclusion

Results of the present study have shown that the water medium, whether in the form of liquid or in the form of vapour, when in contact with the inorganic slag–rock wool fibres, initiates chemical processes. When the fibre–water system is heated to temperatures below 60° C, the chemical reaction in the form of a leaching process is developed, and this leaching action subsequently caused the fine and long thread-like fibres to break down into small segments and granules. On the other hand, when the heating process is elevated to temperatures above 85° C, the chemical reaction between the fibres and the water became a hydration process. The postulation of the development of the chemical hydration process is supported by the experimental evidence on the microstructure modifications of the disintegrated fibres which displayed the formation of a reticular network structure or honeycomb morphology on the fibre stem. The disintegrated fibres showed a higher thermal conductivity or lower thermal insulation value as compared to the normal fibres. The thermogravimetric analysis also showed that an abrupt and large weight loss occurred within the narrow temperature range 680 to 710° C, possibly due to a thermal dehydration process. Whether this material degradation process in the mineral fibres as observed in the laboratory study could occur in similar materials and products in the field, is uncertain. This is yet to be investigated.

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