

SURFACE MODIFICATIONS OF VOLCANIC GLASSES (PERLITES) BY WATER VAPOR

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Abstract— Hydrothermal treatments on expanded volcanic glasses (perlites) were studied. The main objective of this paper is to obtain an activated surface able to interact with specific chemical substances. The above mentioned treatment consists on exposing the glass surface to water vapor at temperatures over 250°C at the correspondent vapor pressure during different periods of time and for different size of particles. The glass surface modifications were studied by IR, DTA-TG and adsorption techniques. The grade of surface activation was tested by studying the chemical interaction with polysiloxane polymers.

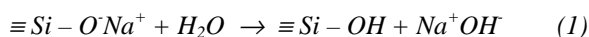
Keywords— glasses, surface modifications, perlite.

I. INTRODUCTION

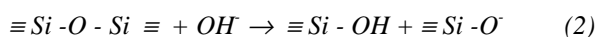
Amorphous materials, specially natural and synthetic glass have found a wide spectrum of practical applications as follows: polishing-free optical lenses, adsorbents, chemical species supports, like molecular sieves, ligand transport, biochemical, etc. (Moriya and Nogami, 1983).

The low superficial reactivity of this kind of materials is limited for its applications. However the superficial reactivity can be increased by different treatments. Hydrothermal treatments are adequate for expanded perlite. A hydrated glass with the characteristic of having OH groups on the surface is obtained by the exposure of expanded perlite to water vapor (Bathrolomew, 1980).

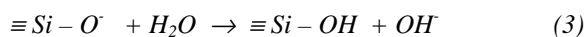
As reported in the literature (Goyal and Cutler, 1975; Abalos *et al.*, 1995), when the water vapor comes in contact with the soda-lime glass the following process takes place:



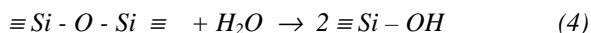
A free hydroxyl ion is formed in the hydrolysis reactions and a second important step in the glass corrosion takes place:



In reaction (2) the very strong bond (Si-O-Si) is broken and gives rise to another active group, which reacts with water as:



The overall reaction may be written as:



The OH groups on the surface can interact with special chemical groups, like organic polymers, in order to form materials useful in separation and adsorption technologies, for example. To make the above concept viable for an industrial process, the presence of hydroxyl groups in the glass surface as a function of vapor pressure and temperature must be investigated.

It is the aim of this work to present the results obtained from incorporating hydroxyl groups into a glass surface and the test of the materials obtained with polydimethylsiloxane.

II. EXPERIMENTAL

A. Material Description

Perlites are volcanic hydrated glasses, which are able to expand when exposed at high temperatures. Hydration water is eliminated during this expansion process. The obtained material is called “expanded perlite” with characteristics like low-chemical reactivity, porosity and mechanical resistance.

Chemically, perlites are glasses with a high silicon and alkali content (Destefanis *et al.*, 1987). The bulk chemical composition of the material is shown in Table 1:

TABLE 1. Expanded Perlite Chemical Composition (%mole)	
SiO ₂	75.36
TiO ₂	0.20
Al ₂ O ₃	13.85
Fe ₂ O ₃	0.67
FeO	0.00
MnO	0.08
MgO	0.29
CaO	1.07
Na ₂ O	3.58
K ₂ O	4.84
P ₂ O ₅	0.04
TOTAL	99.98

B. Materials Preparation

B1. Rehydroxilated perlite:

A fraction 14-18 US series (1.168-0.991mm) of green perlites was expanded at 1000°C during 5 minutes in an electric oven. The resultant material was separated in fractions of different size and these were rehydroxilated. The rehydroxilation process consists in exposing the solid to water vapor in a Parr High Pressure Reactor Model 4652. The experiences were carried out over a range of 250 to 320°C, 30 to 110 Kg/cm² of pressure, during different periods of time.

The material obtained was washed with distilled water, filtered and dried at 120°C.

B2. Impregnated rehydroxilated perlite:

The perlite rehydroxilated at 300°C was impregnated with polydimethylsiloxane. The polymer was synthesized using Braun et al. technique (1979) and the impregnation was carried out with solutions of the polymer in toluene at a 5% concentration. The impregnated materials were treated at 200°C to eliminate toluene during 2 hours.

C. Characterization

The materials were characterized using different techniques, such as:

C1. Granulometric Analysis: In order to obtain the size distribution due to the expansion process, a granulometric analysis was made on a perlite sample after expansion. The different fractions were rehydroxilated at 300°C during 20 hours in order to study the effect of the size of the particles on the rehydroxilation process.

C2. IR Techniques: The surface rehydroxilation and the interaction between the modified solid with the polysiloxanes were followed by Infrared Technique (IR). KBr pellets containing 3% and 90% in weight of sample compressed at 5 Tn/cm² were prepared and a Fourier IFS 88 Bruker Spectrophotometer was used. The spectra were recorded out over a range 4000 to 400 cm⁻¹.

C3. DTA-TG Techniques: A Rigaku ME 800 KP equipment was used to analyze the solid samples. The measurements were made from room temperature to 1000°C.

C4. Adsorption techniques: The rehydroxilated materials were characterized by adsorption methods with n-hexane using a Cahn RG Electrobalance

The material was pretreated at 180°C during 3 hrs. in vacuum to eliminate volatile impurities. The adsorption measurements were carried out at a pressure range of 10-120 mmHg and at a temperature of 45°C.

From the adsorption isotherms obtained it is possible to calculate the energy involved in the rehydroxilation process (Gregg, 1965) using the following equation:

$$\frac{P}{X(P_0 - P)} = \frac{1}{X_m C} + \frac{C-1}{X_m C} \frac{P}{P_0} \quad (5)$$

Where X_m is the adsorbed amount by the monolayer, X is the adsorbed amount, P is the equilibrium pressure of the adsorbate, P_0 is the partial pressure of the adsorbate at the experiment temperature, and C is a constant.

The adsorption enthalpy can be calculated as follows:

$$\Delta H = -RT \ln K, \quad (6)$$

$$\text{where } K = \frac{b}{a} + 1; \quad a = \frac{1}{X_m C} \quad \text{and} \quad B = \frac{C-1}{X_m C}$$

III. RESULTS AND DISCUSSION

The results obtained from different techniques used for the characterization of the materials subjected to hydrothermal treatment show that for the investigated conditions an important grade of rehydroxilation is obtained.

This observation is coherent with the high alkali content in the volcanic glass and the reaction conditions. These conditions assure the occurrence of the hydrolysis reaction (1) and generate hydroxyl ions in the interface water/glass. The reaction with water vapor proceeds with great speed due to a rapid increment in the pH at the interface water/glass.

Also, the Si-O-Si bond in the surface may be more reactive after the ionic exchange due to the biggest electronic attraction when the sodium ions are replaced by the hydrogen ions. The increase of load density favors the nucleophilic attack of the hydroxyl ions on the atom of silicon in the net, generating reactive new species (2).

In Fig.1 the IR spectra of expanded and rehydroxilated perlite is shown (Uchino *et al.*, 1991).

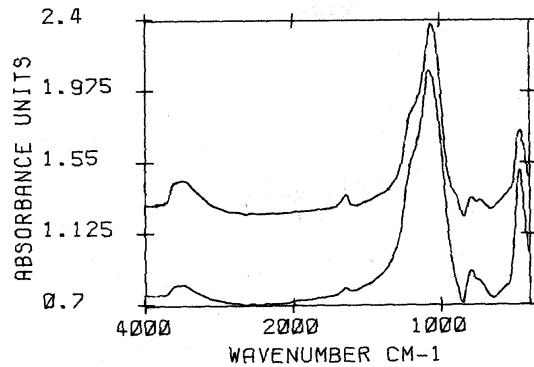


Figure 1. a) IR spectra of perlite with a rehydroxilation process of 300°C during 20 hours; b) expanded perlite.

According with Fig.1 (a) it is possible to assign the following bands to the rehydroxilated sample IR spectra:

- ✓ From 3750 to 3300 cm⁻¹ a broad band that includes the corresponding OH stretching in the SiOH group at 3600 cm⁻¹ and the corresponding OH stretching in the HOH group from 3500 to 3300 cm⁻¹ is presented
- ✓ H-O-H bending at 1637 cm⁻¹.
- ✓ From 1350 to 850 cm⁻¹ a broad band that includes the asymmetric stretching of SiOSi at 1050-1070 cm⁻¹, the stretching of Si-O in the SiO⁻Na⁺ at 960-

980 cm^{-1} and the bending of the OH bond and the SiO stretching in the SiOH group at 880 cm^{-1} appears.

- ✓ Symmetric stretching of the SiOSi group from 820 to 780 cm^{-1} .
- ✓ SiOSi and OSiO bending from 450-470 cm^{-1} .

The formation of the hydroxyl groups is proved by IR spectroscopy. In order to obtain a better definition of the silanol groups bands, the samples were treated in vacuum for 20 minutes at different temperatures. With this treatment it is possible to observe a better definition in the OH band (3700-3300 cm^{-1}).

In Fig. 1 we can also observe that the IR spectrum for the expanded perlite (without rehydroxilating) shows clearly the absence of the hydroxyl groups bonded to the silicon.

In Fig. 2, the IR spectrum corresponding to the rehydroxilated perlite impregnated with dimethylsiloxane is presented.

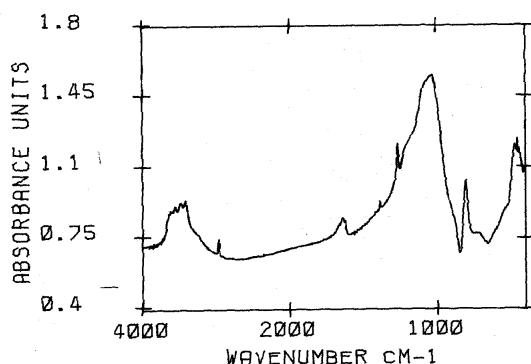


Figure 2. IR spectra of rehydroxilated perlite impregnated with dimethylsiloxane.

In this figure it is possible to observe not only the bands corresponding to the perlite but also the characteristic bands of the polymer, such as the 2964 cm^{-1} band corresponding to the vibration of the C-H bond in a CH_3 group, the 1261 cm^{-1} band corresponding to the swing of the CH_3 group and the 800 cm^{-1} band corresponding to the Si-C bond in the $\text{Si}(\text{CH}_3)_2$ group (Abalos *et al.*, 1995; Abalos and Destéfanis, 1995).

DTA spectra of expanded perlite, rehydroxilated perlite and polysiloxane impregnated perlite are shown in Fig.3.

In the DTA spectra of the rehydroxilated perlite it is clear that the endothermic changes at approximately 120°C-150°C correspond to weight losses due to the physisorption of OH groups onto the surface. The changes observed at 400°C correspond to losses of structural water incorporated during the rehydroxilation process of the material. All the above mentioned changes are not present in the DTA spectra of the polysiloxane impregnated perlite due to the interaction of the OH groups onto the surface with the corresponding polysiloxanes.

The absence of the same changes in the DTA spectra of the expanded perlite is due to the absence of the hydroxyl groups in the material.

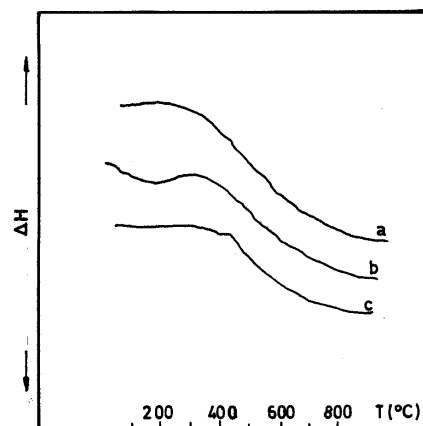


Figure 3: DTA spectra of expanded perlite (a), rehydroxilated perlite (b) and polysiloxane impregnated perlite (c).

From the results obtained by adsorption techniques it is possible to calculate the energy due to the adsorption phenomena between n-hexane and the rehydroxilated surface of the solid; considering the adsorption enthalpy (ΔH) as the latent heat of n-hexane vaporization (λ) plus the energy involved in the surface-gas interaction (E_I):

$$\Delta H = \lambda + E_I \quad (7)$$

Figure 4 shows the values of E_I vs. the rehydroxilation time and Fig 5 shows the values of E_I for rehydroxilated solids of different particle size, but at the same rehydroxilation conditions.

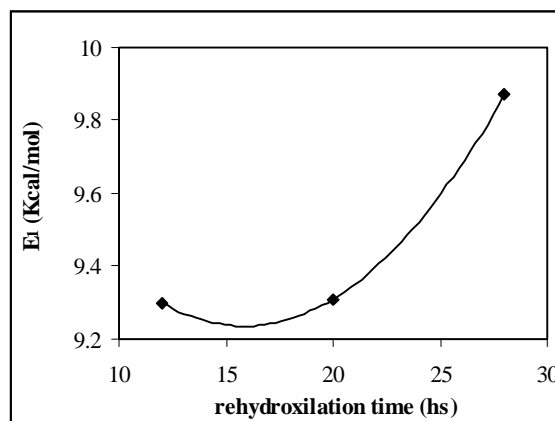


Figure 4. E_I vs. rehydroxilation time (hs.) for perlite rehydroxilated at 300°C.

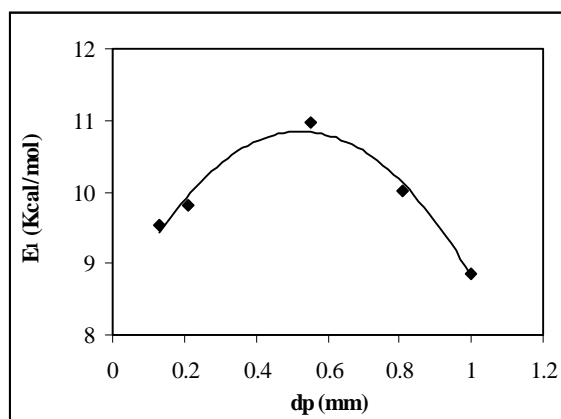


Figure 5. E_1 vs. dp (mm) for perlite rehydroxilated at 300°C during 30 hours.

The energy involved in the adsorption process (E_1) between the surface and the n-hexane vapor increases with the treatment time as shown in Fig.4, this result is coherent with the corrosion mechanism. This parameter is a measure of the rehydroxilation grade at a determined treatment time.

Finally in Fig.6 the specific surface (S_g) vs. the particle diameter (mm) for perlite rehydroxilated in identical conditions is shown.

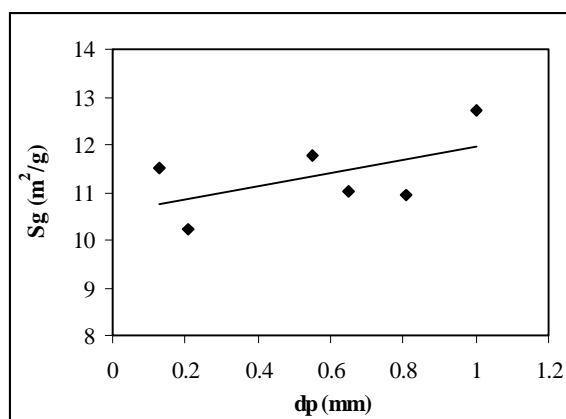


Figure 6. S_g (m²/g) vs. dp (mm) for perlite rehydroxilated at 300°C during 30 hours.

Figure 5 shows that the rehydroxilation process is better for solid size between 14-18 US series, but the specific surface of the materials is independent of the particle size (Fig.6).

IV. CONCLUSIONS

According with the results it is possible to conclude that volcanic glass is able to be transformed in reactive materials by hydrothermal treatments, like the rehydroxilation process.

The optimal conditions of rehydroxilation are temperatures over 280°C, during 30 hs. or more and with solids with particle size between 14-18 US series.

The techniques of characterization used are adequate to observe the surface changes of the solid and provide useful information to characterize the rehydroxilation phenomena.

Finally, the material obtained after the hydrothermal treatment is adequate to interact with polysiloxanes in the search for materials to be used in separation and adsorption technologies.

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