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A New Thermal Treatment Process of Low Value Volcanic Glass towards the Production of Expanded Material and its Use on CNTs' Synthesis as Substrate Material

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Abstract. Pitchstone is a naturally occurring volcanic glass that contains considerable amount of chemically bound water (> 6 % wt). Due to its high water content, its direct thermal processing in conventional expansion furnaces towards the production of lightweight material, similar to expanded perlite, is practically impossible. In the current research paper a sophisticated 2 stage process is presented that consists of a partial dehydration and an expansion stage towards the production of high quality expanded material. After proper treatment, low-value volcanic glass is transformed to frothy, lightweight material of closed external surface and apparent density of 52 $kg \cdot m^{-3}$ that can be used in various branches of the industry. The material produced is used as substrate for the development of multiwall CNTs through CVD method. Dense multiwall CNT clusters were identified on expanded pitchstone surface, thus rendering the material suitable for such application.

1. Introduction

Carbon nanotubes (CNTs) have attracted great research interest since they uniquely combine important properties, including chemical stability, high surface area and extraordinary mechanical strength and electric conductivity, as a result of their cylindrical nano-architecture. CNTs are currently used in a wide range of applications including electronic and optoelectronic devices, energy storage, high strength composites, sensors and catalysts [1].Chemical vapour deposition method (CVD) constitutes a widely applied technique for CNTs synthesis due to its low cost, low temperature and relative equipment simplicity, in comparison to other existing methods i.e. carbon-arc discharge and laser ablation of carbon. Hydrocarbon (carbon source), catalyst and catalyst support (growing media) constitute key materials that are involved in CNTs production through CVD method. Commonly used CNT precursors are purified carbon products, namely methane, benzene and acetylene, while concerning substrates graphite, quartz silicon, silicon carbide, silica, alumina, alumina-silicate have successfully being used. Fe, Co and Ni metals are used as catalysts since they provide with high solubility and diffusivity of carbon atoms at elevated temperatures [2]. An alternative natural CNTs' precursor, that successfully have been used for synthesis of single and multi-walled CNTs constitute camphor ($C_{10}H_{16}O$) that is obtained from cinnamomum camphora tree. Unlike petroleum by-products, camphor is eco-friendly and can be easily cultivated in as much quantity as required [3]. Recently, expanded perlite proved to be an effective substrate for multiwall CNT production with remarkable production yield [4]. Pitchstone is a naturally occurring volcanic glass, similar to perlite and obsidian. The major difference between these materials is their water content; obsidian, perlite and pitchstone water content range between 0-2, 2-5 and >6 wt. %, respectively. Due to the presence of chemically bound water, these materials expand when heated at a temperature that exceeds their softening point as contained water vaporizes and pushes its way out of the softened grains, resulting in the formation of granular, cellular material of significant low density. Since expansion phenomenon is affected by chemical composition, water content and also crystalline content of the glass, expansion potential is different for obsidian, perlite and pitchstone. Perlite constitutes best performance material, and after proper single step heating in expansion furnace at temperature above 800 ℃ attains loose bulk density (LBD) as low as 30-150 $kg \cdot m^{-3}$ [5]. In its expanded form, perlite become white, frothy and cellular, with a wide network of air bubbles in its structure. Expanded perlite is lightweight, inorganic, chemically inert, fire resistant, with superior thermal and sound insulating properties, while its properties are invariant in time, and is widely used in construction, horticulture, filtration and other applications.

High water content of pitchstone constitutes a barrier towards its transformation to lightweight material in traditional gas-fired expansion furnaces. As reported in a recently published work, in order to transform it to high-quality expanded material, sophisticated thermal treatment has to be implemented which combines partial dehydration in laboratory oven and expansion in vertical electric furnace [6]. One of the biggest pitchstone occurrence is located in north of Chillagoe, in north Queensland, Australia. The occurrence is owned by Perlco Pty Ltd and may contains 700 Mt resource [7]. 100 Mt of pitchstone exists, and on annual basis, 30% of pitchstone is crushed into fine stone-dust with particle size less than 500 μm [8]. As a consequence of its fineness and its relatively high water content, at present, this stone-dust is stockpiled since it has no economic value [9]. However, recent researches have proved the pozzolanic activity of pitchstone fines thus rendering suitable their use as cement replacement in concrete [9]-[11].

The objectives of the current research article are dual; (a) a processing method for transformation of low value fine pitchstone to high quality expanded material is presented through a two steps thermal treatment method for effective partial dehydration and expansion of pitchstone grains, and (b) the expanded material was used as substrate for the development of multiwall CNTs. Successful application of the new material will provide with a new application of low value volcanic glasses.

2. Materials and methods

2.1. Pitchstone characterization

The chemical analysis of raw pitchstone was performed using Energy Dispersive X-Ray Fluorescence instrument and the Al_2O_3 content was defined by flame Atomic Absorption Spectroscopy after dissolution in a $HF/HClO_4/HNO_3/HCl$ mixture. Pitchstone sample mainly consists of silicon and aluminum oxide (70.7 and 13.1 %, respectively), while its content in K_2O and Na_2O is 3.5 % wt. each. Minor contents in Fe_2O_3 and CaO were identified in amount 0.96 and 0.92 % wt, respectively. A commonly applied classification method of volcanic matter constitutes TAS classification. TAS classification can be used to assign names to many common types of volcanic rocks based upon the relationship between the combined alkali content and the silica content [12]. According to the chemical composition of the pitchstone sample, it is classified as rhyolite.

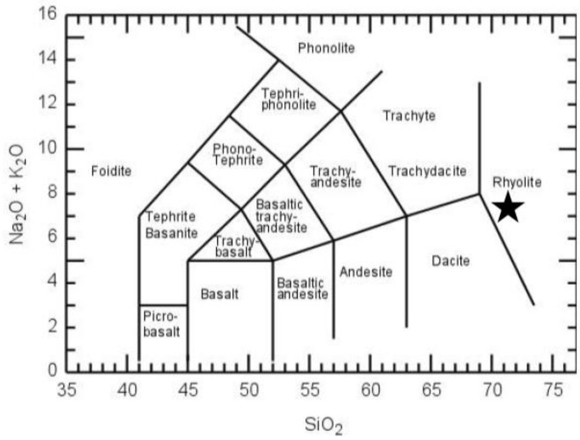


Figure 1 TAS diagram for the classification of volcanic matter. According alkalis and silica content of pitchstone sample it is classified as rhyolite (star sign)

Loss on Ignition (LOI) constitute weight loss after heating at 950 ℃ for 4 h as suggested by Perlite Institute, and is attributed to release of different forms of water. LOI of pitchstone sample was found to be 7.41 % wt. The mineralogical composition was examined on X-Ray diffraction device with Cu-Kα (Ni filtered) radiation (2 theta range from 5 to 75° and 0.02°·sec^{-1} step), and indicated the dominance of amorphous phase with minor quartz and feldspar content. The rough XRD pattern of pitchstone sample is characteristic for non-crystalline materials, while the hump between 15 and 30 2 theta (degree) is characteristic for volcanic glasses.

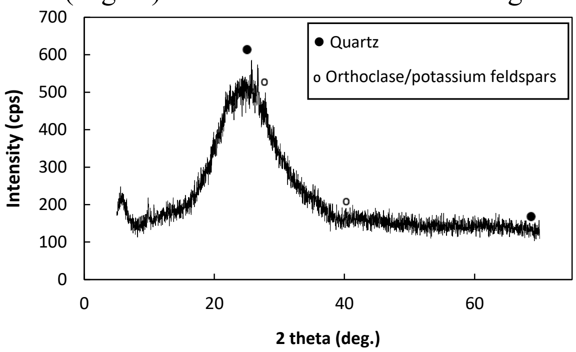


Figure 2 XRD pattern of pitchstone sample

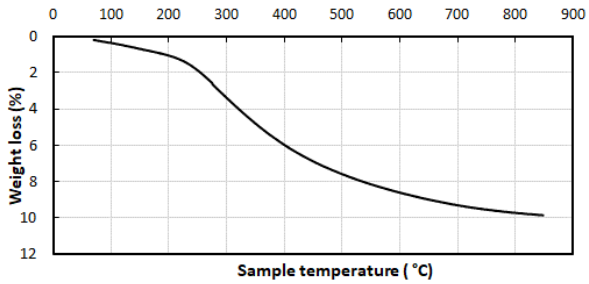


Figure 3 Weight loss of pitchstone in terms of heating temperature (thermogravimetry)

Thermogravimetric analysis was performed at a Labsys DTA/DSC Setaram device at sample heating rate 10 °C per min and under atmospheric conditions, and revealed two stages of weight loss, which are attributed to moisture and loosely held (up to 200 °C), and chemically bound water (over 200 °C) release.

2.2. Pitchstone processing towards production of expanded material

Raw pitchstone has been subjected to mechanical and thermal treatment towards the production of lightweight expanded material. Raw sample has been crushed, milled and sieved in order to produce a grade with particle size range between 100 and 300 μm. Equipment employed for this purpose consists of jaw crusher, rotor beater mill and continuous sieve device with aperture size of 100 and 300 μm. Then, sample heat treatment took place at 3 different units. First, moisture removal took place through sample heating at 105 °C overnight (16 h). Scoping the partial dehydration of the sample, pitchstone has been heated at 300 °C for 1 h. The LOI of partially dehydrated sample reached the desirable value of 3.92%. Finally, the partially dehydrated sample has been fed in the vertical electric furnace. The furnace was set to 1100 °C and the particle heating time did not exceed 4 s. It is noteworthy that the use of vertical electric furnace is inevitable since traditional gas fired furnaces are incapable to sufficiently treat such raw material due to its fineness [5].

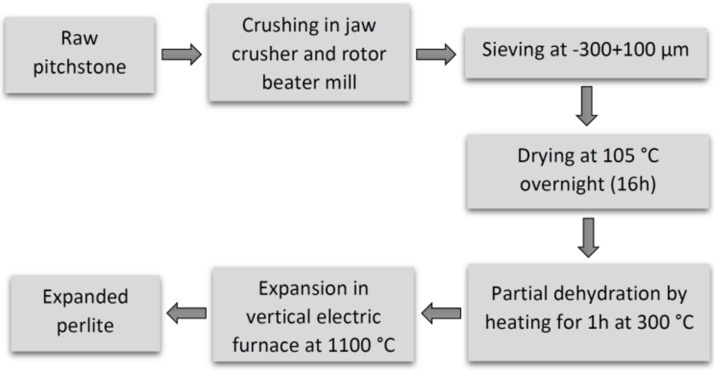


Figure 4 Mechanical and thermal treatment route of pitchstone towards the production of expanded material

2.3. CNTs' synthesis method

For multiwall CNTs' synthesis, a commonly applied synthesis process, namely, chemical vapour deposition (CVD) method has been applied. Camphor was used as carbon source, ferrocene as catalyst and expanded pitchstone as substrate. 100 gr of camphor and 5 gr of ferrocene were placed at the narrow part of quartz tube (diam=5 cm), which was heated at 200 °C. The vapors produced where drifted by mild nitrogen gas stream to the wide quartz tube (diam=10 cm) where expanded pitchstone (800 cm^3, 40 gr) was spread and heated peripherally at 800 °C by heating resistances. The synthesis duration was 30 minutes. After growth of CNTs on expanded pitchstone the product was diluted in 4N NaOH solution for 8 h, in order to dissolve the substrate and purify the CNTs.

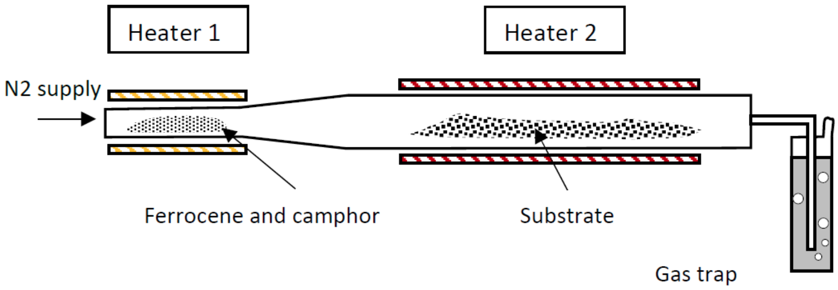


Figure 5 Experimental setup for CNTs' synthesis through CVD method

3. Results and discussion

3.1. Properties of expanded pitchstone

The sophisticated mechanical and thermal processing of low value pitchstone resulted in the production of high quality expanded material. The grains produced are cellular, white in colour and lightweight with LBD of 52 $kg \cdot m^{-3}$. The angular and non-symmetric raw pitchstone grains were transformed to expanded material of high sphericity, closed surface porosity and cellular structure, as shown in SEM images of Figure 6. Expanded material is characterised by high expansion ratio and low fragments content. It is worth noting that expansion experiments were also performed to non-dehydrated material, and the product obtained LBD value equal to 350 $kg \cdot m^{-3}$, thus rendering partial dehydration of pitchstone beneficial towards the production of high quality lightweight material.

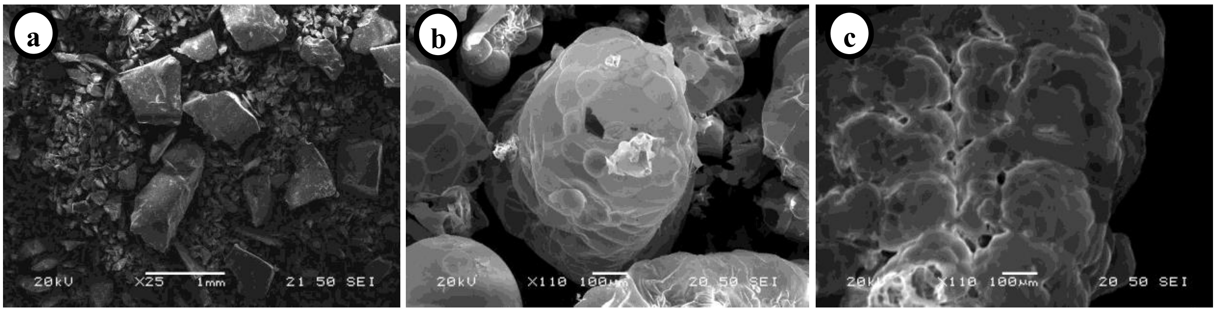
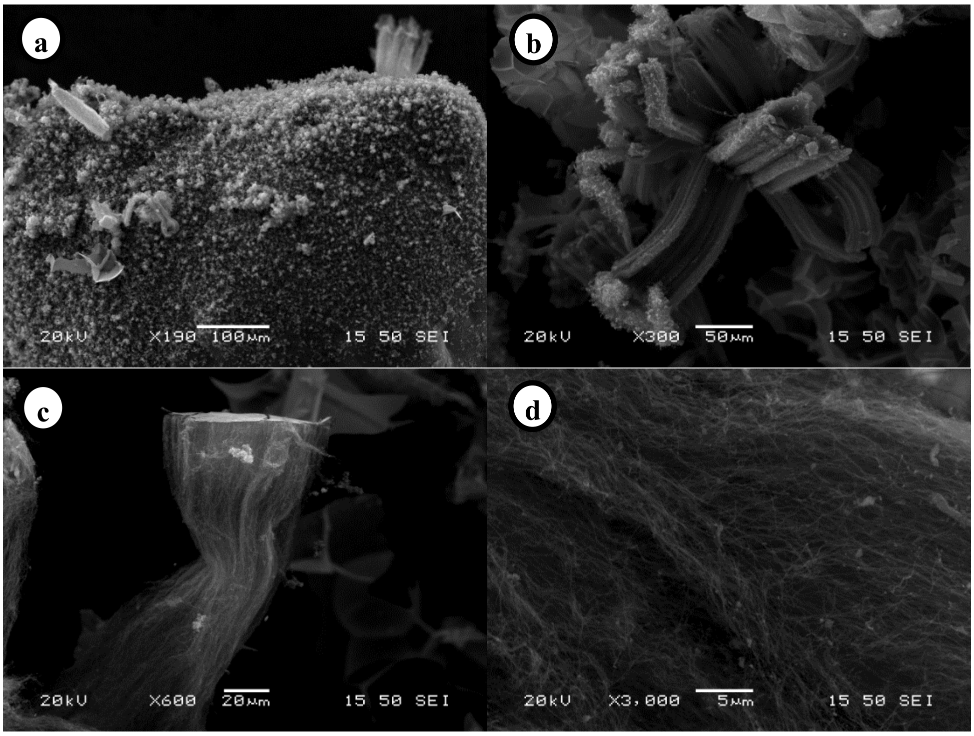


Figure 6. SEM micrograph of raw (a), and expanded pitchstone (b, c)

3.2. Properties of produced CNTs

The morphology of synthesized CNTs was investigated using scanning electron (SEM) and high resolution transmission electron microscopy (HR-TEM). As depicted in Figure 7a, a pitchstone grain has been covered by the synthesized CNTs. CNTs are well dispersed over the grain surface while in certain locations the growth is well-developed in the vertical direction. After CNTs purification through dilution in NaOH solution, the identified CNTs were found to be orthogonal and carpet type that macroscopically compose clusters and tangles (Figure 7b-d). As can be seen in Figures 7b and c, the dissolution of pitchstone matrix was not complete since pitchstone fragment are still present. It is thus proposed the increase of NaOH concentration and in parallel the solution heating for complete dissolution of pitchstone towards the production of pure CNTs. In Figure 7d, a CNTs' cluster is observed that encloses catalyst particles and tiny pitchstone fragments. In HR-TEM Figure 7e the characteristic multilayer morphology of multiwall CNTs is identified, while in Figure 7f a detailed view of CNTs produced is given, with the dark color denoting the catalyst particles



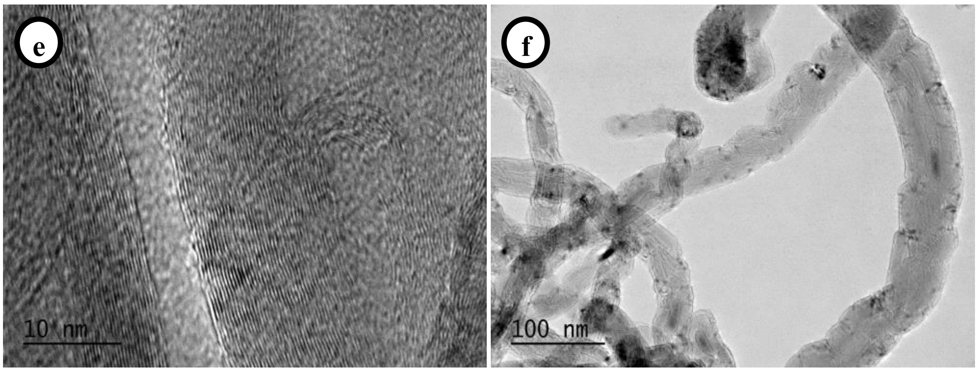


Figure 7 SEM micrographs of (a) CNTs on expanded pitchstone surface, (b) orthogonal growth CNTs, (c-d) CNTs clusters, and TEM micrographs of produced CNTs (e-f)

4. Conclusions

In the current research article a sophisticated thermal treatment method of low value volcanic glass towards their transformation to high quality expanded material is presented. The method incorporates primary sample heating at relative low temperature (300 °C) in order to reduce its water content below 4 wt. % , and subsequently expansion of the sample in a vertical electric furnace at 1100 °C. The material produced is frothy, granular with closed surface porosity and LBD value of 52 $kg \cdot m^{-3}$. Furthermore, expanded material produced was used as substrate for the development of multiwall CNTs through CVD method using camphor as precursor. CNTs were purified from substrate through dissolution of pitchstone by NaOH concentrate. It is shown that CNTs were developed at the majority of expanded pitchstone surface, while the CNTs structures vary due to surface inhomogeneity and thus catalyst polydispersity at substrate surface. It is thus shown here, that the expanded material produced though sophisticated treatment of low value volcanic glass can be used for high-end nanotechnology application such as substrate for CNTs synthesis.

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