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THERMAL BEHAVIOUR OF SILICA WASTE FROM A GEOTHERMAL POWER STATION AND DERIVED SILICA CERAMICS

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Abstract

The silica waste originating from a geothermal power plant in Mexico was investigated with the aim of finding its applicability as a raw secondary material for ceramics production. The thermal behaviour of the original silica waste (containing NaCl and KCl from marine brine) and of the purified silica was characterized by means of DTA/TG, emanation thermal analysis (ETA) and thermodilatometry (TD). The reactivity of the purified silica waste mixed with $CaCO_3$ (1.8 mass%) was characterized by means of ETA, DTA and TG. The microstructures and phase compositions of the final products prepared by heating in air were tested by means of X-ray diffraction and of scanning electron microscopy coupled with electron probe X-ray microanalysis. The thermal analysis methods allowed determination of the optimal conditions for thermal treatment of the silica waste in order to obtain partly sintered porous materials for use as refractory bricks.

Keywords: ceramics, emanation thermal analysis, geothermal waste, industrial waste, silica, thermal methods

Introduction

Geothermal energy power plants have been constructed as high-performance technology for electricity production in countries with capabilities for the transport of steam generated by thermal springs and/or 'fumaroles' located at a depth of 8–10 km. The decrease in steam temperature from approximately 573 to 373 K during its path towards the surface gives rise to the saturation of brine rich in silica and salts, resulting in their precipitation in the pipelines of the power plant. In the Cerro Prieto Geothermal Plant in Baja California, Mexico, the subsoil fluid is mainly composed of a silica brine with a high concentration of soluble salts. The hard crust deposited in the pipelines must be removed frequently, giving rise to an industrial waste rich in silica (98%), which is stored in landfields, with no applications so far [1]. This silica-rich residue and the product resulting from its purification were characterized in previous work [1, 2]. As demonstrated elsewhere, the purified silica

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waste can be used in the production of glasses [3], glass-ceramics [4], refractories [5] and ceramics [6]. For the development of ceramics by the recycling of silica geothermal wastes, the thermal characterization of impure silica geothermal waste (ISGW), purified silica geothermal waste (PSGW) and several ceramic products has been carried out [6]. Besides the more common thermal analysis methods such as DTA/TG and thermodilatometry (TD), emanation thermal analysis (ETA) has been used in this work. ETA is a less common method that furnishes information about the microstructures of powders and sintered materials under the *in situ* conditions of their heat treatment [7]. The microstructures and phase compositions of the final products heated in air to 1200 or 1500°C were characterized by means of hot stage microscopy (HSM), X-ray diffraction (XRD) and scanning electron microscopy coupled with electron probe X-ray microanalysis (SEM/EPXMA).

The aim of this paper is to use the results of ETA, TG, DTA, TD and other methods to characterize the thermal behaviour of both ISGW (containing salts from sea water) and PSGW, as well as mixtures with $CaCO_3$, to be used as feed mixtures for the production of partly sintered porous refractory bricks.

Experimental

Materials

Original ISGW, PSGW and a mixture of PSGW with CaO (1 mass%), but added as $CaCO_3$ (1.8 mass%) were investigated. The purification of ISGW was carried out by water washing under permanent stirring of a crushed powder (10 μm in particle size) at 80°C for 30 min [2]. The absence of chlorides from the PSGW was tested with a 0.1 N solution of $AgNO_3$. For sintering tests, cylindrical specimens measuring 15 mm ∅ 5 mm were prepared by axial pressing at 200 kg cm^{-2}. The particle size of the starting materials was lower than 60 μm. The sintered samples of PSGW and of PSGW+CaO were prepared by heating to 900, 1200 and 1500°C. The thermal treatment cycle was as follows: initial heating at a rate of 10°C min^{-1} to the respective temperature, followed by isothermal heating for 60 min and subsequent cooling at a rate of 10°C min^{-1}.

Methods

The following methods were used: DTA/TG (Mettler Apparatus, type TA2), TD (Adamel Lhomargy, type DI-24), HSM (type II A, produced by Leitz), XRD (Philips, Type 3710), and SEM/EPXMA (SEM: JEOL JSM 6300; EPXMA: KEVEX-8000 with Si(Li) detector and Be window). For SEM/EPXMA, carbon-coated specimens were prepared. For measurement of the apparent density of sintered samples, the mercury intrusion method was used.

The ETA equipment was constructed at NRI Řež, based on the Netzsch DTA 409 device. ETA consists in the measurement of an inert gas released from solids previously labelled with the inert gas or its parent radionuclide [7–9]. In ETA, the inert gas atoms are used as trace indicators of the solid state and its changes: the inert gas atoms do not react with the solid in which they are incorporated; the inert gas release is controlled by the diffusion in the solid, which is influenced by structural changes,

changes in morphology and porosity, interactions of the solid sample with the surrounding medium and/or chemical of reactions taking place in the solid and its surface. By means of ETA, processes taking place in solids and on their surfaces have been characterized even in cases where the processes were not accompanied by changes in mass or enthalpy [9]. Samples for the ETA measurements in this work were labelled by the adsorption of radioactive traces of ^{228}Th, serving as a quasi-permanent source of radon atoms ^{220}Rn. The atoms of ^{220}Rn formed by spontaneous alpha-decay were incorporated into a depth of at most 130 nm from the surface, due to the recoil energy (85 keV atom^{-1}) gained by every atom of radon during its formation by alpha-decay. A schematic drawing of the ETA apparatus is shown in Fig. 1.

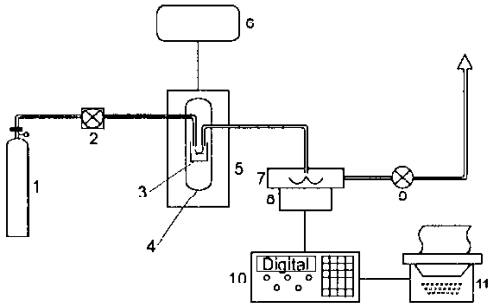

Fig. 1 Scheme of the ETA apparatus [9]: 1 – gas supply; 2 – gas flow stabilizer; 3 – labelled sample; 4 sample holder; 5 thermostat (furnace); 6 temperature controller; 7 – measuring chamber; 8 – radioactivity detector; 9 – flow ratemeter; 10 – count-meter; 11 – data processor and printer-plotter

The following experimental conditions were used for thermal analysis characterization of a sample of approximately 0.1 g. DTA/TG with heating in air in the temperature range 20 to 1500°C at a rate of 10 K min^{-1}; TD with heating in air in the temperature range 20 to 450°C at a heating rate of 10 K min^{-1} and subsequent cooling; and ETA with heating in an air flow (flow rate 50 ml min^{-1}) from 20 to 1450°C at a heating rate of 5 K min^{-1}, followed by cooling at a rate of 5 K min^{-1}.

Results and discussion

It follows from Table 1 that the apparent density values of the sintered products prepared by the heating of PSGW and the mixture of PSGW+1 mass% CaO are in the range 1.02–2.24 g cm^{-3}. It seems that the addition of CaO caused a decrease in the final density of the samples heated to 1200 and 1500°C. From the XRD patterns of PSGW, it has been observed [6] that at 900°C a disordered cristobalite is formed, which on heating to higher temperatures is converted to ordered cristobalite.

Figures 2a–c show ETA results as the temperature dependence of the radon release rate, with E (in relative units) obtained during the heating of ISGW, PSGW and the mixture of PSGW+1 mass% CaO, respectively.

Table 1 Densities of sintered products prepared from PSGW and PSGW+CaO

Sintering temperature/°C	Apparent density/g cm^{-3}	
	PSGW	PSGW + 1 mass% CaO
900	1.1234	1.3640
1200	2.1541	2.1045
1500	2.2136	2.0374

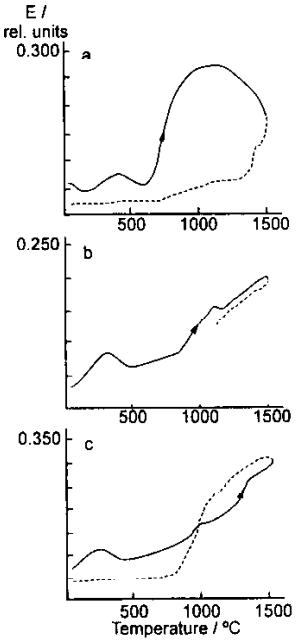

Fig. 2 ETA results on: a – original ISGW, b – PSGW and c– a mixture of PSGW + 1.8 mass% $CaCO_3$ [ETA curves measured during heating (full line) and cooling (dotted line)]. The cooling demonstrated in Fig. 2b was interrupted at 1100°C

Before describing the differences in thermal behaviour of the three samples, as reflected by the ETA curves, we shall point out the specific character of the information gained by means of ETA in this investigation. It follows from the theoretical background of ETA [7–9] that the rate of radon release from a single solid grain is related to the diffusion coefficient of radon in the solid (D), the density (δ) and the surface area (S) according to the simplified equation

$$E = \left[k_1 + k_2 \left(\frac{D}{\lambda} \right)^{1/2} \delta \right] S \tag{1}$$

where k_1 is a temperature-independent constant, proportional to the depth of penetration of recoiled radon atoms, k_2 is a constant characterizing the concentration of microstructure defects in the sample, D is the radon diffusion coefficient, λ is the radon decay constant, δ is the density, and S is the surface area of solid sample.

Consequently, an increase in the radon release rate E reflects the enhanced diffusivity of radon in a solid, and an increase in surface area and/or porosity, caused by the loosening of the structure and the formation of metastable phases in the reaction mixtures [7]. On the other hand, a decrease in E reflects a decrease in the surface area and/or porosity and the consolidation of the structure, due to sintering, phase transitions, etc.

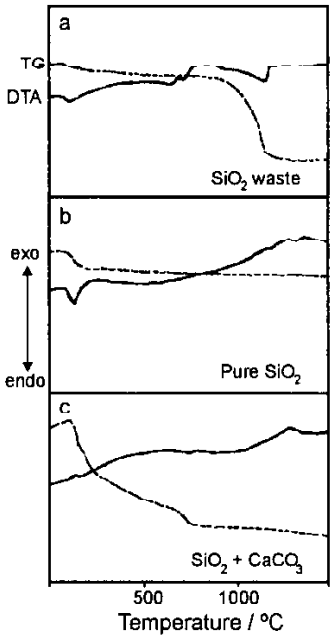

Fig. 3 DTA/TG results on: a – original ISGW; b – PSGW and c – PSGW with addition of CaO

Therefore, the effects observed in the temperature range 200–600°C in the ETA curves in Figs 2a–2c can be ascribed to changes in the surface area and microstructure of the samples, due to their dehydration. The increased radon release rate in Fig. 2a, observed on heating above 600°C, indicates loosening of the structure of the ISGW sample, presumably initiated by the ordering of initially highly disordered quartz, as indicated by the exothermal effect in the temperature range 600–700°C in the DTA curve (Fig. 3).

The presence of alkali metal halides in the ISGW probably facilitated the lattice loosening, as the ETA curves in Figs 2b and 2c, corresponding to PSWG and its mixture with CaO, revealed no similar increase in radon release rate, E.

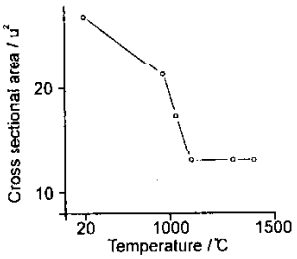

Fig. 4 Relative contraction observed at 1500°C by HSM for the pressed powder of the original IGSW sample

On further heating of the ISGW sample, the increasing trend of radon release slowed down in the temperature range 900–1000°C, indicating the annealing of the surface roughness and subsequent sintering of the sample. The changes observed in this temperature range in the ETA curve (Fig. 2a) correspond to the decrease in mass of the sample observed in the TG curve (Fig. 3) in the same temperature range, due to the volatilization of alkali metal halides from the ISGW sample. It should be mentioned that the DTA endothermal effect observed for the ISGW sample above

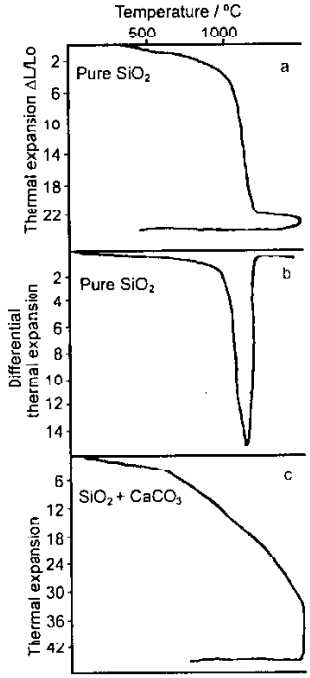

Fig. 5 TD results on a – PSGW silica sample; b – derivative curve of the same PSGW sample; c – the mixture of PSGW+1.8 mass% $CaCO_3$

1100°C (Fig. 3), corresponding to a phase transition in quartz, coincides well with the onset of the decreased in the radon release rate observed in Fig. 2a. Intense sintering of the ISGW sample was observed in this temperature range by means of HSM (Fig. 4). This confirms the characterization of the IPGW sample by the ETA results presented in Fig. 2a.

The ETA curve measured during cooling of the IPGW sample represents the temperature dependence of radon diffusion in the sample heated to 1450°C. From the comparison of the ETA heating and cooling curves it was obvious that heat treatment to 1450°C resulted in a highly compacted sample.

From Figs 2b and 2c, it follows that the thermal behaviour, of the PSGW sample and the mixture of PSGW+1 mass% CaO differs from that of IPGW, as reflected by the ETA results in Fig. 2a. The ETA curves in Figs 2b and 2c characterize the thermal behaviour of the respective samples in the temperature range 900–1100°C by a less intense increase in radon release rate than that observed in the ETA curve in Fig. 2a. The effect in the temperature range 1000–1100°C in the ETA curve of the PSGW sample (Fig. 2b) corresponded well to the sintering effect observed in the TD curve in Fig. 5.

The decreased radon release rate observed at temperatures above 1400°C in Fig. 2b indicated the next step of sintering indicated in Fig. 5 by TD. The ETA curve measured during sample cooling (interrupted at 1100°C) supported the above characterization of the thermal behaviour of the PSGW sample.

In the ETA curve in Fig. 2c, characterizing the thermal behaviour of the mixture PSGW+1 mass% CaO, two temperature ranges can be distinguished: 900–1200°C, where the initial solid-state reaction of PSGW silica with CaO takes place, and 1200–1450°C, where wollastonite crystals and other phases are formed, as detected by XRD and SEM/EPXMA in the sample heated to 1500°C (Fig. 6).

From the ETA curve measured during cooling of the sample heated to 1450°C (Fig. 2c), it follows that the product resulting after this thermal treatment is characterized by a higher radon diffusivity as compared to the sintered product prepared by heating of PSGW or even ISGW powders to the same temperature. The fact that the ETA cooling curve in Fig. 2 is situated in the temperature interval 950–1450°C, above the ETA heating curve, demonstrates the formation of disordered (microporous) ceramics after heat treatment of the mixture PSGW+1 mass% CaO to 1450°C.

The TG and DTA results (Fig. 3) characterizing the thermal behaviour of the three investigated samples are in agreement with the respective ETA curves (Figs 2a–2c) described above.

It should be pointed out that, due to the amorphous character of both the original ISGW and the PSGW [6], no effects corresponding to the α/β-transformation of quartz or silica phases were observed in the DTA curve (Fig. 3). The exothermal DTA effect detected during heating of the ISGW sample indicated progressive ordering of the silica structure on heating from 650°C. This effect was already correlated with the increase in radon release rate observed in the ETA curve in Fig. 2a.

The thermal behaviour of the samples characterized by the ETA curves was confirmed by the TD, SEM, XRD and density measurements. The sintering observed by TD and ETA for the PSGW sample in the temperature range 1000–1100°C corre-

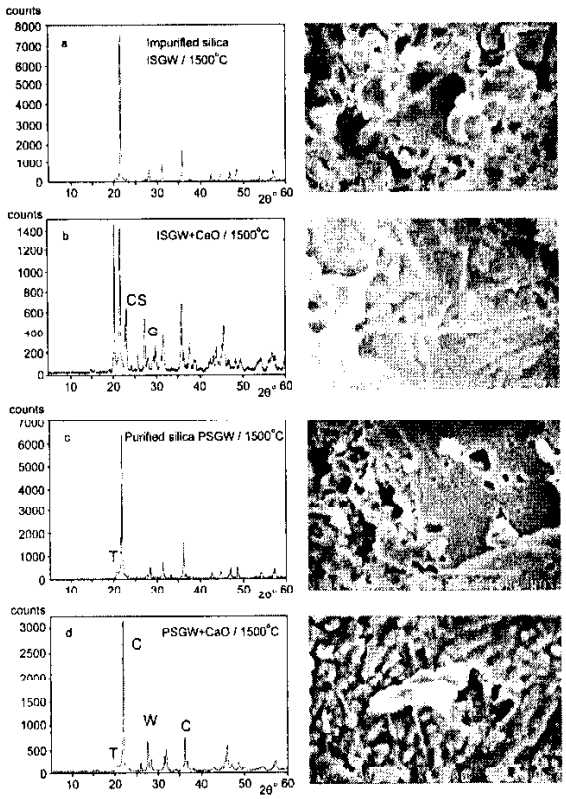

Fig. 6 XRD patterns and SEM micrographs of sintered products prepared by heating at 1500°C: a – ISGW; b – ISGW+CaO; c – PSGW and d – PSGW+CaO (C=cristobalite; T=tridymite; W=wollastonite; CS=calcium silicates; G=gehlenite)

lated well with the phase transformation of silica. From the results obtained via the various methods used, it follows that the addition of CaO did not accelerate the sintering of purified silica, supposing the formation of a wollastonite phase. The XRD patterns (Fig. 6) showed that in all cases α-cristobalite is the main crystalline phase present in the silica waste investigated, appearing at lower temperatures of thermal treatment [6]. The SEM micrographs of samples heated to 1500°C are presented together with the corresponding XRD patterns in Fig. 6.

It can be seen from the SEM results that, in the sample prepared by the heating of ISGW silica, well-distributed round cristobalite crystals (approx. 1 μm in size) were embedded in a glassy phase. From the XRD patterns and SEM micrographs of the ceramics prepared by the heating of mixtures of ISGW and PSGW silica with CaO, differences in microstructure were determined. In the ceramics prepared by

heating the mixture of ISGW+CaO, elongated crystals of wollastonite and other calcium silicates were embedded in the amorphous matrix. Very thin acicular crystals of wollastonite were clearly observed in the sample prepared by heating the mixture of PSGW+CaO. Large and smooth areas were observed in the micrographs of the material prepared from the PSGW silica. Cristobalite was readily identified, but tridymite was not easy to detect by SEM.

Conclusions

Several silica and wollastonite/cristobalite ceramics were prepared by sintering of a silica waste originating from a geothermal power plant by heat treatment of pressed mixtures of the original impure and purified silica waste at temperatures in the range 900–1500°C. DTA/TG, TD and ETA allowed characterization of the thermal behaviour of the feed materials. Moreover, the reactivity of the purified silica waste mixed with $CaCO_3$ (1.8 mass%) was characterized by means of ETA, DTA and TG. ETA furnished information on the microstructural changes in the feed materials obtained under *in situ* conditions of heat treatment A semiquantitative characterization of the compaction and microporosity formation in the samples treated to 1500°C, including partially porous wollastonite/cristobalite ceramics, was possible from the ETA results.

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