1. Introduction

Highly porous ceramics with interconnected cellular structures are used as media for storing liquid reactants in scrubber units. For example, aqueous solutions of urea absorbed in porous clay media are used in N$_2$O$_4$ scrubber units [1]. They are also used as catalyst-support and aquarium bio-filter media [2–5]. Cellular ceramic materials with spherical shapes (foam spheres) are highly desirable for the above applications, since a spherical shape provides high packing density, separation for reuse and diametrical compressive strengths in the ranges of 76.5 to 82.7 vol.%, 6.8 to 9.2 μm and 1.65 to 0.93 MPa, respectively, were produced from emulsions prepared from hydrogenated vegetable oil and aqueous clay slurries. The interconnected open cell structure and small cell size enabled fast absorption and 100% retention of urea solution for N$_2$O$_4$ scrubber application. The urea solution absorption capacity (71.5 to 80 vol.%) of the foam spheres was much higher than the capacity (45.6 vol.%) of the porous clay ceramic media currently used in N$_2$O$_4$ scrubbers.

2. Experimental

Kaolin clay [Al$_2$O$_3$(SiO$_2$)$_2$·2H$_2$O] with an average particle size of 0.27 μm and surface area of 6.2 m$^2$/g was used.
obtained from English Indian Clays Ltd., Thiruvananthapuram, India. Alumina powder (A165G) with an average particle size of 0.34 μm and surface area of 10.4 m²/g was procured from ACC Alcoa, Kolkata, India. A 40 wt% aqueous ammonium poly (acrylate) solution (Darvan 821 A) procured from Vanderbilt Company Inc., Norwalk, CT, USA, was used as the dispersant. Sodium dodecyl sulfate (SDS), urea and petroleum ether were procured from Merck India Ltd., Mumbai, India. A carrageenan gelling agent was procured from Aldrich Chemicals, USA. The hydrogenated vegetable oil (HVO) was procured from a local market. Distilled water was used for the preparation of powder suspensions.

20 vol.% aqueous suspensions were prepared by dispersing ceramic powders in distilled water using the ammonium poly (acrylate) dispersant followed by ball-milling in polyethylene bottles for 12 hours with zirconia balls measuring 10 mm in diameter. The concentration of ammonium poly (acrylate) was 1 wt% of the ceramic powder. The slurries were transferred to 1 liter round-bottomed flasks and the carrageenan gelling agent was added. The amount of carrageenan was 2 wt% of the water present in the slurry. The slurry was mechanically stirred using a Teflon paddle while keeping the round-bottomed flask in a water bath at 85°C for 30 minutes for dissolving the carrageenan. HVO was then added. The concentration of SDS was 0.6 wt % of the HVO. The molten HVO containing SDS was poured into the aqueous ceramic powder suspension at 85 °C, and mechanical stirring was continued for another 1 hour to form a stable emulsion. Emulsion taken into a 50 ml syringe was injected into the spherical cavities of a copper mold. The mold was then cooled using crushed ice to gel the injected emulsion. Gelled emulsion spheres were removed from the mold after 15 minutes, dried under ambient conditions and extracted with petroleum ether to remove the HVO. The spheres with HVO removed were sintered at 1500°C for 2 hours at a heating rate of 0.5°C/minute up to 600°C and 1°C/minute from 600 to 1500°C.

Viscosity measurements of the emulsions were carried out at 85°C using an RVT model Brookfield viscometer [Brookfield Engineering Inc., USA] with the help of a small sample adapter and cylindrical spindle. A thermo-cell accessory was used to maintain the emulsion temperature at 85°C during the viscosity measurements. XRD analysis was carried out using an X-ray diffraction analyzer [X’pert Pro, Philips, USA] by Cu Kα radiation. The microstructures of the foam spheres were observed on the fractured surfaces using a scanning electron microscope [SEM, Hitachi S-2400, Hitachi High Technologies Corporation, Japan]. The diametrical compressive strength of the foam spheres was measured using a Universal testing machine [Instron 5984, Instron USA]. The loading rate was 0.5 mm/minute.

The density of the foam spheres was calculated from their weight and dimensions. The open porosity of the foam spheres was estimated by the water absorption method as follows: the accurately weighed foam spheres were immersed in distilled water and heated for 2 hours in a boiling water bath. The foam spheres were removed from the water after cooling to room temperature, wiped with a wet linen cloth to remove the water from the surface and then weighed. The increase in weight of the foam spheres was the volume of absorbed water which was taken as the open porosity. The urea solution absorption capacity of the foam spheres was estimated using a 35 wt% aqueous urea solution. The increase in weight of the foams spheres after immersion in the urea solution for 12 hours was taken as the absorption capacity.

3. Results and discussion

Ammonium poly(acrylate) dispersant produces a well-dispersed suspension of clay in water. Molten HVO droplets were dispersed in 20 vol.% aqueous clay slurry (ACS) in the presence of SDS to form a stable HVO-in-ACS emulsion. The emulsion on cooling in an ice bath underwent gelation due to the physical cross-linking of the carrageenan as well as the freezing of HVO (freezing point 41°C) [40,41]. A photograph of the copper mold and a schematic of the injection molding set-up are shown in Figure 1(a,b), respectively. The emulsion injected into the spherical cavity of the copper mold solidified on cooling. Volume shrinkage during solidification resulted in cavity formation in the gelled emulsion spheres. In the foundry, formation of cavities by shrinkage during solidification of molten metal cast in a mold are generally avoided by using raisers which act as reservoirs for the liquid metal. In the present case, the syringe containing the emulsion was removed from the mouth of the mold cavity only after complete solidification of the injected emulsion. Here, the syringe containing the excess emulsion acted as a reservoir. That is, the emulsion present in the syringe was fed to the mold cavity as and when shrinkage occurred during solidification. A photograph showing a cavity formed in a gelled emulsion sphere when the syringe was removed immediately after injection and a perfect sphere formed when the syringe was removed after solidification are shown in Figure 1(c).

The setting time of the emulsion injected into the mold was estimated by measuring the temperature using a thermocouple and a digital thermometer. The temperature of the emulsion at the center of the spherical mold cavities was measured by properly inserting the thermocouple. A time-temperature graph of the injected emulsion is shown in Figure 1(c). The HVO-in-ACS emulsion formed a soft gel within
5 minutes of injection when the temperature fell below 40°C. The syringes containing the emulsion were removed from the mouths of the mold cavities at this stage. However, the gelled emulsion spheres did not have sufficient strength at this stage to be removed from the molds without deformation. On the other hand, the gelled emulsion spheres could be easily removed from the molds with no deformation after 15 minutes by which time the temperature of the gelled emulsion had decreased to 20°C. That is, with the current injection molding setup, gelled emulsion spheres can be produced at a rate of 4 sets/hour. However, a higher production rate could be achieved by adopting alternative faster cooling methods.

Ambient drying of gelled emulsion spheres prepared from HVO-in-ACS emulsion at an HVO-to-ACS volume ratio of 1.5 did not create any cracks, but instead produced uniform shrinkage. The diametrical shrinkage observed during drying was 8.6%. No shrinkage or deformation of the dried emulsion spheres was observed during the subsequent HVO removal by extraction with petroleum ether. However, sintering of the spheres at 1500°C after HVO removal resulted in clay foam spheres with hairline cracks as shown in Figure 3(a). It is well known that sintering of kaolin clay produces mullite and silica [42, 43]. XRD analysis of the clay foam spheres indicated that crystallization of mullite was initiated at 1200°C. The silica formed from kaolin existed in crystalline form up to 1400°C as evidenced by a peak at the 2θ value of 21.5° corresponding to the reflection from the (100) plane of quartz. The disappearance of the peak at 21.5° in the XRD spectra of foam spheres sintered at 1500°C indicates the transformation of crystalline silica to an amorphous state. XRD spectra of clay foam spheres sintered at various temperatures are shown in Figure 3(b). The diametrical sintering shrinkage observed is 27.7%. This corresponds to a volume shrinkage of 61.3%. The formation of cracks during sintering is due to the presence of a large amount of the glassy phase as well to significant shrinkage during sintering. Although hairline cracks were formed, the interconnected cellular foam structure was preserved as evidenced by the SEM microstructure shown in Figure 3(c). The average cell size observed in the SEM image is 10.12 μm. High-magnification image of the clay foam spheres show needle-shaped mullite crystals embedded in the glass phase. A high-magnification SEM image of a clay foam sphere is shown in Figure 3(d).

It is well known that the incorporation of alumina into kaolin produces secondary mullite growth during sintering which suppresses the amount of the glass phase [44, 45]. In addition, the formation of mullite results in volume expansion which reduces sintering shrinkage [46–48]. That is, the incorporation of alumina...
is expected to prevent the formation of cracks during sintering. Our trials with various mixtures of kaolin and alumina indicated that a minimum of 10 wt% alumina is required to prevent crack formation during sintering of clay foam spheres. Therefore, further studies on foam sphere preparation at various HVO-to-ACS volume ratios were carried out with a kaolin-alumina mixture containing 10 wt% of alumina. The kaolin-alumina suspension formed a stable emulsion up to an HVO-to-ACS volume ratio of 2.25. Further increases in the HVO-to-ACS volume ratio resulted in phase separation during cooling. Emulsions with HVO-to-ACS volume ratios in the range of 1.5 to 2.25 showed shear thinning flow behavior. Emulsions prepared from kaolin alone at an HVO-to-ACS volume ratio of 1.5 showed viscosities in the range of 2.5 to 0.39 Pa.s at shear rates in the range of 4.65 to 93 s$^{-1}$. Incorporation of alumina produced a slight decrease in viscosity, while emulsions with the same HVO-to-ACS volume ratio prepared from a kaolin-10 wt% alumina mixture exhibited lower viscosity (2.3 to 0.33 Pa.s at a shear rate in the range of 4.65 to 93 s$^{-1}$). This was attributed to modification of the particle size distribution upon the addition of alumina. At all the shear rates studied, the viscosity of the emulsions increased gradually when the HVO-to-ACS volume ratio was increased from 1.5 to 2.25. This increase in viscosity was due to increases in HVO droplet–HVO droplet and ceramic particle-HVO droplet interactions in the emulsion when the concentration of HVO was increased [40,41]. The viscosity observed at a shear rate of 4.65 s$^{-1}$ was in the range of 2.3 to 3.5 Pa.s for emulsions at HVO-to-ACS volume ratios in the range of 1.5 to 2.25. On the other hand, at a shear rate of 93 s$^{-1}$, the viscosities observed were in the range of 0.33 to 0.43 Pa.s. The viscosity of the emulsions was kept sufficiently low to enable easy suction into the syringe and easy injection into the mold cavities. A shear rate versus viscosity plot of HVO-in-ACS emulsions measured at 85°C is shown in Figure 4.

Gelled emulsion spheres produced at HVO-to-ACS volume ratios in the range of 1.5 to 2.25 took nearly 5 days to dry completely under ambient conditions (25°C). The diametrical drying shrinkage of the gelled emulsion spheres decreased from 11.8 to 8.7% when the HVO-to-ACS volume ratio was increased from 1.5 to 2.25. Gelled ACS in emulsion spheres underwent major shrinkage, whereas solidified HVO underwent only negligible shrinkage during drying. This explains why the diametrical drying shrinkage decreased with increases in HVO loading. Unlike foam spheres produced from kaolin, foam spheres produced from kaoline-10 wt% alumina mixture did not suffer any cracks during sintering. A photograph of foam spheres produced from kaoline-10 wt% alumina mixture is shown in Figure 5. These foam spheres have smooth surfaces. The diametrical sintering shrinkage observed increased from 24.8 to 28.9 when the HVO-to-ACS

Figure 3. (a) Optical image showing a crack formed during sintering of a clay foam sphere, (b) XRD spectra of clay foam spheres sintered at various temperatures, (c) SEM photomicrograph of the fractured surface of a clay ceramic foam sphere showing the cellular structure and (d) a high-magnification SEM image of a cell wall surface.
The volume ratio was increased from 1.5 to 2.25. The diametrical sintering shrinkage (24.8%) observed in foam spheres prepared from kaolin-10 wt% alumina mixture at an HVO-to-ACS volume ratio of 1.5 was considerably lower than that observed in foam spheres prepared from kaolin alone (27.7%). The lower sintering shrinkage observed in the foam spheres prepared from kaolin-10 wt% alumina was due to volume expansion during secondary mullite growth from the added alumina. The final diameters of the sintered foams spheres were in a close range of 2.2 to 2.35 cm.

SEM photomicrographs of as-formed and fractured surface of a sintered ceramic foam spheres (HVO-to-ACS volume ratio of 1.5) are shown in Figure 6(a,b), respectively. The fractured surface of a foam sphere exhibits an interconnected cellular structure with a near-spherical pore morphology. On the other hand, pores on an as-formed surface though well interconnected, deviate largely from a spherical morphology. Similar pore structures were observed in foam spheres prepared at higher HVO-to-ACS volume ratios. The cell size of the foam spheres increased, however with increases in the HVO-to-ACS volume ratio. The average cell size increased from 6.8 to 9.2 μm when the HVO-to-ACS volume ratio was increased from 1.5 to 2.25. SEM microstructures of fractured surfaces of foams spheres prepared at HVO-to-ACS volume ratios from 1.75 to 2.25 are presented in Figure 6(c–e). High-magnification SEM images of the cell walls show the presence of needle-type mullite grains. A remarkable decrease in the concentration of the glass phase and enhanced growth of mullite crystals is observed in foam spheres prepared from kaolin-10 wt% alumina mixture compared to those prepared from kaolin alone (Figure 3(d)). The high-magnification SEM microstructure of foam sphere prepared from kaolin-10 wt% alumina mixture is shown in Figure 6(f).

The bulk density of foam spheres decreased from 0.68 to 0.49 g/cm³ when the HVO-to-ACS volume ratio was increased from 1.5 to 2.25. The open porosity of foam spheres estimated by the water absorption method increased from 76.5 to 82.7 vol.% when the HVO-to-ACS volume ratio was increased from 1.5 to 2.25. It is worthy of note that the porous clay spheres currently used in N₂O₅ scrubbers have a much lower open porosity of 54.4 vol.%. The bulk density and open porosity of foam spheres prepared at various HVO-to-ACS volume ratios are given in Table 1. The foam spheres easily absorbed and retained the urea solution. The time required for the urea solution to saturate the foam spheres was ~10 minutes. On the other hand, the porous clay spheres currently used as N₂O₅ scrubbers achieve 95% saturation in 10 minutes. Further absorption of the urea solution was very slow taking ~12 hours to reach the complete saturation. The faster urea solution absorption by our foam spheres was due to the complete interconnectivity of the pores. The urea solution absorption capacity of the foam spheres is in the range of 71 to 80 vol.%. This is slightly lower than the open porosity (76.5 to 82.7 vol.%) estimated for the water absorption method. This indicates that a small fraction of pores that are accessible to water are inaccessible to urea solution due to the higher viscosity of the urea solution. In contrast, the porous clay spheres currently used in N₂O₅ scrubbers showed a urea solution absorption capacity of only 45.6 vol.%. Urea absorption capacities of the foam spheres prepared at various HVO-to-ACS volume ratio is presented in Table 1. Unlike the urea solutions absorbed by ceramic foams with large cell size, the urea solution absorbed into these foam spheres is retained without leakage.

Urea absorption capacities of the foam spheres prepared at various HVO-to-ACS volume ratio is presented in Table 1. Unlike the urea solutions absorbed by ceramic foams with large cell size, the urea solution absorbed into these foam spheres is retained without leakage.

Foam spheres for N₂O₅ scrubber application should have sufficient strength to resist breakage during urea absorption.
impregnation, charging and reactivation for a large number of times. The mechanical strength of foam spheres was measured by diametrical compression and the load-displacement graphs are shown in Figure 7. Foam spheres exhibit brittle fracture. Diametrical compressive strength, a measure of the tensile strength of the samples, was calculated by the following equation [49]:

$$\sigma_f = \frac{2.8P_f}{\pi D^2}$$

$\sigma_f$, $D$ and $P_f$ are the diametrical compressive strength, the diameter of the foam sphere and the load at fracture, respectively.

The diametrical compressive strengths of foam spheres prepared at various HVO-to-ACS volume ratios are given in Table 1. Diametrical compressive strength decreased from 1.65 to 0.93 MPa when the HVO-to-ACS volume ratio was increased from 1.5 to 2.25. The decrease in strength was due to an increase in the porosity of the foam spheres. Currently available porous clay spheres exhibited a lower diametrical compressive strength of 0.21 MPa in spite of their lower porosity. Foam spheres prepared by injection molding of HVO-in-ACS emulsion is far superior to those currently used in \(N_2O_4\) scrubbers (Fig S1) in terms of open porosity, pore interconnectivity, diametrical compressive strength, surface smoothness, closeness to

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**Table 1.** Characteristics of ceramic foam spheres prepared from kaolin-10 wt% alumina mixture at various HVO-to-ACS volume ratios.

| HVO-to-ACS ratio | Diametrical drying shrinkage of gelled emulsion spheres (%) | Diametrical sin-tering shrinkage (%) | Density of foam spheres (g/cm\(^3\)) | Open porosity (vol.%) | Cell size (\(\mu\)m) | Urea solution absorption (vol.%) | Diametrical compressive strength (MPa) |
|-----------------|---------------------------------------------------------------|-----------------------------------|-------------------------------------|----------------------|----------------|-------------------------------|--------------------------------------|
| 1.5             | 11.8                                                          | 24.8                              | 0.68                                | 76.5                 | 6.98 ± 1.16   | 71.55                         | 1.65                                 |
| 1.75            | 10.4                                                          | 25.16                             | 0.61                                | 78.5                 | 7.32 ± 1.35   | 75.16                         | 1.09                                 |
| 2.0             | 9.5                                                           | 26.01                             | 0.52                                | 80.8                 | 8.66 ± 1.6   | 78.30                         | 1.06                                 |
| 2.25            | 8.7                                                           | 28.9                              | 0.49                                | 82.7                 | 9.2 ± 1.85    | 80.00                         | 0.93                                 |
| Currently used porous clay spheres |                                                               |                                   | 1.059                               | 54.46                | 45.61         | 0.21                          |                                      |

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**Figure 6.** The SEM microstructure of (a) an as-formed surface at an HVO-to-ACS volume ratio of 1.5, fractured surfaces at HVO-to-ACS volume ratios of (b) 1.5, (c) 1.75, (d) 2, and (e) 2.25, and (f) high-magnification SEM micrograph of the cell wall surface of a ceramic foam sphere prepared from a kaolin-10 wt% alumina mixture.

**Figure 7.** Diametrical compressive load-displacement graph of ceramic foam spheres prepared at various HVO-to-ACS volume ratios from a kaolin-10 wt% alumina mixture. The photograph in the inset shows debris formed by the fracture of a foam sphere during the compression test.
a spherical shape, higher urea solution absorption capacity and faster absorption of urea solutions.

4. Conclusions

Injection molding of hydrogenated vegetable oil-in-aqueous clay slurry (HVO-in-ACS) emulsions has been studied for the preparation of clay ceramic foam spheres for use as media for storing urea solution in N₂O₅ scrubber. Foam spheres produced from kaolin tend to crack during sintering due to large-scale shrinkage and the presence of an excessive glass phase. Incorporation of a minimum of 10 wt% alumina prevents sintering cracks by promoting secondary Mullite growth that decreases both the shrinkage and the concentration of the glass phase. Foam spheres prepared at HVO-to-ACS volume ratios in the range of 1.5 to 2.25 exhibited well-interconnected pore structures with spherical cells in the interior and distorted cells on the as-formed surface. The open porosities, average cell sizes and diametrical compressive strengths of the foam spheres were in the ranges of 76.5 to 82.7 vol.%, 6.8 to 9.2 μm, and 1.65 to 0.93 MPa, respectively, at HVO-to-ACS volume ratios in the range of 1.5 to 2.25. The urea absorption capacity (71.5 to 80 vol.%) was slightly lower than that of open porosity as some of the finer pores that were accessible to water were inaccessible to urea solution due to its higher viscosity. The foam spheres produced are suitable for use as porous media in N₂O₅ scrubbers.

Acknowledgments

The authors wish to thank to Dr. V. K. Dadhwal, Director, IIST for his support and encouragement. The authors are also thankful to the ISRO Propulsion Complex, Mahendragiri for its financial support.

Disclosure statement

No potential conflict of interest was reported by the authors.

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