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# Cohesion Effects on Hydrogen Holdup in Granular Sediments with X-Ray Computed Tomography – 25354

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#### ABSTRACT

Nuclear energy production consumes a lot of water to protect against the release of radiation from nuclear waste. The effluent water must be treated to remove soluble radionuclides such as <sup>137</sup>Cs and <sup>90</sup>Sr. At the Sellafield Site (United Kingdom), it is treated at the Site Ion Exchange Effluent Plant (SIXEP) which has been in operation since 1985. The ion exchange material used in SIXEP is clinoptilolite, a naturally occurring aluminosilicate which has high selectivity for ions such as cesium. After 35 years in operation, SIXEP has reached the end of its lifecycle. In 2019, the plant was reported to be generating ion exchange material waste at a rate of 40 m<sup>3</sup>/yr with total stock at approximately 1335 m<sup>3</sup> which is projected to rise to 2975 m<sup>3</sup> by 2060. This waste is classified as intermediate level waste (ILW) with a composition of approximately 60 wt% clinoptilolite, 4 wt% sand and 36 wt% water. This consolidated ion exchange material is suspected to have trapped hydrogen from processes such as radiolysis in the presence of water. This needs to be incorporated into safety and cost evaluations of interim storage and long-term geological disposal facilities as well as engineering designs of storage containers and disposal environment selections. The volumes of hydrogen in the clinoptilolite and the extent to which the waste will expand are unknown. This work investigates hydrogen bubbles in granular sediments to better understand such systems simplified by using silica glass beads. Surface properties such as cohesion affect gas transport and the extent to which this impacts overall gas holdup is investigated by altering the silica glass bead surfaces through esterification. The impact of esterification with different alcohols was assessed using water droplet contact angle measurements. Hexanol was found to be the most efficient. Two size ranges (150–250 µm and 250– 425 µm diameter) of silica beads were esterified in hexanol. Hydrogen holdup and solid phase expansion in columns of 60 vol% esterified silica glass beads were measured in comparison to the non-esterified samples. The bubbles were imaged using x-ray computed tomography (XCT).

Studies of gas holdup in multiphase systems have shown that bubbles move through sediments via capillary invasion and sediment fracturing. Fracturing has not been identified in the silica bead columns. Granule size affects bubble invasion, pore sizes and the likelihood of slugging due to wall effects; invasion is inhibited with decreasing silica bead size. This trend is not changed with increased cohesion; however, the effect of esterification varies per size range. This was supported by shear yield stress measurements of the silica beads pre- and post-esterification. The volume of hydrogen holdup in the columns was lower for esterified versus non esterified samples of the 150–250  $\mu$ m size range whereas the opposite effect was observed for the 250–425  $\mu$ m range. XCT with a 203  $\mu$ m reconstruction pixel size was an effective method for single bubble imaging and no connected bubble networks were found. There was a difference in the distinct bubble sizes per particle size range. In summary, this work highlights the critical impact of granular particle size and degree of cohesion on total gas holdup and bubble size distributions. These findings will allow more accurate assessment of hydrogen holdup in clinoptilolite for Sellafield safety case assessments.

#### **INTRODUCTION**

Cohesive sediments such as the top 100 m of the seabed have bubbles produced by the presence of organic matter, and clay marine beds have a higher gas holdup than less cohesive sands [1][2]. Environmental studies of gaseous behavior of carbon dioxide and methane in cohesive muds have investigated release rate

dependence on factors such as nucleation sites, bubble size and sediment properties. In sludges, bubbles can be expected to start to rise once they have grown to a centimeter scale and not to keep increasing greatly in size due to limitations imposed by production rates and bubble populations [3]. Bubbles in aqueous sediments tend to be non-spherical with simulations in gelatin showing increased elongation with higher Young's modulus indicating sediment fracturing as the likely mechanism by which gas escapes [4].

In nuclear energy waste management, gas holdup in zeolite ion exchange materials, such as clinoptilolite, affect the storage capacity and increase hydrogen flammability risks. Granular clinoptilolite and sand waste from Sellafield Ltd's SIXEP is extrapolated to reach 2975 m<sup>3</sup> by 2060 [5]. This ion exchange material is stored in bulk storage tanks (BSTs) and the Medium Active Solid Waste Encapsulation Plant (MASWEP). Hydrogen gas holdup in these facilities is being researched to understand complications that may arise such as slugging effects from large horizontal bubbles leading to waste expansion. Such effects could have an impact on maintenance procedures such as purging of the tanks and planning of future storage facilities.

Thus, in the present study, the hydrogen gas holdup in silica glass beads has been investigated to correlate to the granular nature of the ion exchange material. While hydrogen in this waste form is most likely from radiolysis in the effluent water, hydrogen at the laboratory scale is being generated from corrosion of magnesium which achieves a random spread of nucleation sites. Cohesion is added via esterification of the glass beads; Ishikawa et al. [6] found decreased hydrophobicity in mesoporous silica crystals after reflux reactions with butanol and octanol, proving the reaction of the silanol groups with alcohols results in altered cohesion. Different alcohols were tested for efficiency of the esterification process with non-porous silica glass beads.

Measurements of hydrogen gas released from columns of silica glass beads, and the volumes of holdup are used to investigate the effects of cohesion on production rates and bed expansion. Holdup is calculated as the total volume of gas that is not released from the sediment that is trapped as a result of a combination of bubble invasion into the pores by displacement of water and movement of the solid particles by the bubble pressure. Differences in bed expansion and holdup in esterified and non-esterified samples can inform the correlation amongst particle size, cohesion, capillary entry pressures, bubble size populations, reaction rates and overall holdup over different time intervals. XCT has been used to visualize bubbles in silica glass beads and quantify the parameter measurements experimentally. This imaging technique allows for identification of bubble networks or established bubble transport networks. Post-processing volume estimations are based on a 203  $\mu$ m reconstruction pixel size may also be important in terms of overall holdup volumes.

# **MATERIALS AND METHODS**

# **Esterification and Characterization**

The process of altering surface properties of the glass beads was adapted from the esterification process used by Hunter, et al. [7]: batches of 250 g of silica glass beads were boiled in 650 g of hexanol as illustrated in Figure 1. Silanol groups react with alcohols as in Equation 1 which increases the hydrophobicity of the silica glass beads.

$$Si - OH + HO - R_x H_y \leftrightarrow Si - O - R_x H_y + H_2 O \qquad (Eq. 1)$$

Refluxing of silica glass beads in alcohol was performed over 7 hours with a calcium chloride drying tube to prevent hydration of the system. The esterified beads were washed in ethanol and acetone to remove alcohol residue then dried in an oven at 80 °C.



Figure1. Experimental set-up of esterification process.

Esterification with butanol, hexanol and octanol was trialed by esterifying glass slides and measuring water droplet contact angles using a tensiometer (Attension Theta Flex, Biolin Scientific, UK) as shown in Figure 2. The most efficient alcohol was taken to be that which resulted in the largest contact angles suggesting increased hydrophobicity.



Figure 2. Water droplets (left) and an example of contact angle measurements (right).

The surfaces of the glass beads were visually inspected using scanning electron microscopy (TM3030 Plus Tabletop Microscope, Hitachi, Ltd, UK). Changes in shear yield stress post-esterification were estimated from torque measurements using a viscometer (DV2TRV model, Brookfield AMETEK, USA) with cylindrical vanes.

# Gas Holdup

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Hydrogen holdup experiments in columns with mean bead sizes of diameter 203  $\mu$ m and 394  $\mu$ m were carried out using the method outlined in previous work Sibanda, et al. [8]. For this work 2 g of magnesium were added to a column with 450 g of esterified silica glass beads in a saline solution. Hydrogen generated was collected over 24 hours with the water displacement and solid bed expansion recorded by a camera. This was repeated with non-esterified silica glass beads.

## X-Ray Computed Tomography

Hydrogen bubbles were imaged using XCT (Brivo CT385 Series, GE Healthcare, UK) in aqueous samples with 450 g silica glass beads of 203 µm and 394 µm diameter, and 2 g magnesium with salinity of 113 ppt. The glass beads and liquid solution were separately degassed under vacuum prior to mixing then imaged over a 6-hour period. Post-processing was done using Dragonfly (Comet Technologies Canada Inc), ImageJ (National Institutes of Health, USA) and Avizo (Thermo Fisher Scientific, USA). This included using tools such as: thresholding to separate the different phases, connectivity to identify pore networks, separate objects tool for improved segmentation of individual bubbles and label analysis for measurements such as volume, area and sphericity. Volume clipping techniques were used to study the bubble size distributions at different depths and plane orientations. Three-dimensional volume rendering of initial and end sample scans can be used to measure bed expansion.

### **RESULTS AND DISCUSSION**

#### Characterization

Water contact angle measurements in Table 1 suggest that hexanol is the more efficient alcohol of the three alcohols tested. An increase in contact angle after esterifying the glass slides agrees with the expected increase in hydrophobicity which reduces the adhesion of water and the glass [9]. This effect was more pronounced when the esterification vessel was insulated to reduce heat loss and ensure boiling of the alcohol.

	e e
Alcohol	Average Contact Angle
Non-esterified	58.5
Butanol	61.1
Non-insulated hexanol	61.0
Insulated hexanol	70.2
Insulated octanol	60.4

Table 1. Water contact angles on glass slides.

Scanning electron microscopy (SEM) of the silica glass beads pre- and post-esterification indicate reduced fines as in Figure 3. A greater difference is noticeable with the 150 to 250  $\mu$ m sample where an increase in clustered beads is observed. There is no visually notable difference pre and post esterification from the SEM images. Both samples do not show formation of clumps of beads from the esterification, as found by Hunter et al. [7].



Figure 3. SEM images of (i) 150 - 250 μm non-esterified, (ii) 150 - 250 μm esterified, (iii) 250 - 425 μm non-esterified and (iv) 250 - 425 μm esterified silica glass beads.

Shear yield stress values of silica glass beads in water, Figure 4, show that larger particles have greater yield stress. The esterification process increases yield stress as the attractive bonds between the beads are strengthened and the liquid bridges. Studies have found greater hydrogen bonding at the surface-water interface of larger silica particles [10] suggesting correlation between capillary forces and particle diameter. These interactions are reduced during esterification as in Equation 1, increasing particle cohesion and consequently shear yield stress which lowers hold-up.



Figure 4. Shear yield stress measurements of non-esterified and esterified silica glass beads

#### **Gas Holdup**

As found in previous work in the literature [2][8], overall hydrogen production from corrosion is higher in smaller silica beads which have a more heterogenous distribution of magnesium powder. Figure 5 shows a reduction in yield with added cohesion which suggests reduced gas pore networks and access for the saline solution to corrosion sites. There are varying standard deviations of the total hydrogen generated for the different size ranges which may be due to different extents of esterification and changes in factors such as temperature when the experiments were run.



Figure 5. Hydrogen production in two esterified and non-esterified silica glass bead size ranges.

For non-esterified silica beads, overall gas holdup in all samples was initially higher than the bed expansion during the first 6 hours of corrosion as in Figure 6. After 6 hours the holdup and bed expansion level-off to the same percentages as their water displacement. The displacement of the solid bed contributes to all the

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holdup. Figure 6 (left) shows that for the smaller beads,  $150 - 250 \mu m$ , the bed expansion increases at approximately the same volumes as the water level above the bed while for the larger beads, Figure 6 (right), there can initially be greater water displacement which is then reabsorbed into the bed as the gas is released until the holdup is only from bed expansion. For esterified cases, hence more cohesive silica beads, the volume of hydrogen in the 150–205  $\mu m$  columns was reduced as the yield stress was now greater resulting in more temporary fracturing or distinct paths for gas escape. The esterified 250 - 425  $\mu m$  case had a higher holdup than the non-esterified columns as the sediment strength increased, but the hydrogen generation rate did not; an increase in fracture strength without an increase in diffusion would lead to more trapped bubbles as there is not enough bubble pressure for fracturing. The 250–425  $\mu m$  columns demonstrated reduced elasticity with increased cohesion as the trapped gas pores were not released, keeping the sediment fixed in its new structure and prohibiting water reabsorption, so while the bed expansion was lower with increased cohesion, overall holdup was increased. Boudreau [1] has observed this phenomenon in viscoelastic sediments where bubbles get trapped and expand in "low fracture-toughness zones" as "pseudo buoyancy" ceases to be relevant.



Figure 6. Bed expansion versus total gas holdup in 150-250  $\mu$ m and 250 – 425  $\mu$ m esterified and non-esterified glass bead columns.

#### X-Ray Computed Tomography

XCT of hydrogen bubbles in Figure 7 of the 150–250  $\mu$ m horizontal silica bed showed bed expansion after 6 hours. Avizo's label analysis tool was used for volume measurements of individual hydrogen bubbles which were found to be within the size range of 10<sup>-8</sup> to 6600 mm<sup>3</sup>. Over 50% of the bed expansion was from bubbles greater than 100 mm<sup>3</sup> and less than 25% from bubbles less than 20 mm<sup>3</sup>. There is a possibility of overestimation of the large bubbles from connections of neighboring bubbles during thresholding and underestimation of the microbubbles from XCT scanner resolution limits.



Figure 7. 3-D reconstruction of a silica glass bead sample (150 - 250  $\mu$ m) showing hydrogen gas pores at T=0 (left) and T= 6 hours (right).

The large contribution of the mesocale bubbles to the holdup supports the hypothised temporary fracturing and preferred transport paths. Some of these large pores are attributable to wall efffects mostly at the base of the scanning cell. Figure 8 shows these larger pores (greater than 100 mm<sup>3</sup>) preferentially at the base and the sides of the cell with the density of smaller bubbles increasing at the top of the cell. These bubbles are more similar to free bubbles at the top of marine sediments [1] and not representive of bubbles at lower depths under higher stresses. High bubble concentrations in the top layers promote a more steady seepage while bubbles at lower depths could cause more sudden outbursts [2].



Figure 8. 3-D XCT Images of hydrogen bubbles in a 150–250  $\mu$ m silica glass bead sample clipped in the XZ plane increasing in depth height from bottom to top (left to right). Plane points (x,y,z): (48,75,63), (48,65,63) and (48,0,63) mm respectively. Colors represent individual bubbles (color range limitations in the software resulted in color repetition which is not be interpreted as connectivity).

#### CONCLUSIONS

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The surface of silica glass beads can be manipulated by refluxing with alcohols like hexanol for an esterification reaction of the surface silanol groups which increases cohesion. The extent of esterification is dependent on the silica bead diameter which correlates to the arrangement of silanol groups and mixing capacity of the experimental set-up. Greater differences in hydrogen holdup may be observed if the silica beads are left to reflux for longer with stronger mixing of the alcohol and the beads for more surface exposure. For both the  $150-250 \mu m$  and  $250-425 \mu m$  size ranges, gas holdup in the non-esterified samples after 24 hours was from the bubbles expanding the bed. For samples with added cohesion, there is a difference between overall holdup and bed expansion meaning the holdup is a sum of the water displaced from the bed and expansion of the solid particles; this effect is more pronounced with larger silica beads suggesting a correlation between reaction rate and diffusion. Holdup increases in cohesive sediments as the sediment fracture strength increases without a greater increase in reaction rate.

XCT has identified micro- and meso-bubbles with resolution and threshold limits under and overestimating the contribution of each size scale to the holdup. At the scale used for this work, bubbles greater than 100 mm<sup>3</sup> contribute to most of the holdup but this could be reduced in wider sampling vessels. Future work will image bubbles in cohesive silica glass beads and study holdup in commercial clinoptilolite.

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