Nuclear Engineering and Design 270 (2014) 101–108

Contents lists available at ScienceDirect

Nuclear Engineering and Design

journal homepage: www.elsevier.com/locate/nucengdes

The start of ebullition in quiescent, yield-stress fluids

David J. Sherwood[a,*], A. Eduardo Sáez[b]

[a] URS Corporation, Hanford Tank Waste Treatment and Immobilization Plant Project, 2435 Stevens Center Place, Richland, WA 99354, United States
[b] Department of Chemical and Environmental Engineering, The University of Arizona, Tucson, AZ 85721, United States

HIGHLIGHTS

- Nuclear waste slurries evolve gases from radiochemical reactions.
- Evolved gases form bubbles that rise in the yield-stress slurry.
- Bubble buoyancy leads to expansion and ebullition, processes modeled here.

ARTICLE INFO

Article history:
Received 19 February 2013
Received in revised form
16 December 2013
Accepted 17 December 2013

ABSTRACT

Non-Newtonian rheology is typical for the high-level radioactive waste (HLW) slurries to be processed in the Hanford Tank Waste Treatment and Immobilization Plant (WTP). Hydrogen and other flammable gases are generated in the aqueous phase by radiolytic and chemical reactions. HLW slurries have a capacity for retaining gas characterized by the shear strength holding the bubbles still. The sizes and degassing characteristics of flammable gas bubbles in the HLW slurries, expected to be processed by the WTP are important considerations for designing equipment and operating procedures. Slurries become susceptible to degassing as the bubble concentration increases over a maximum value that depends on shear strength. This susceptibility and the process of ebullitive bubble enlargement are described here. When disturbed, the fluid undergoes localized flow around neighboring bubbles which are dragged together and coalesce, producing an enlarged bubble. For the conditions considered in this work, bubble size increase is enough to displace the weight required to overcome the fluid shear strength and yield the surroundings. The buoyant bubble ascends and accumulates others within a zone of influence, enlarging by a few orders of magnitude. This process describes how the first bubbles appear on the surface of a 7 Pa shear strength fluid a few seconds after being jarred.

1. Introduction

Radioactive waste slurries stored at the Hanford Site (Hanford, WA) form bubbles from radiochemical reactions after gases (*e.g.*, hydrogen, methane, and nitrous oxide; Delegard, 1980; Spinks and Woods, 1976) reach their low solubility limits (Hu et al., 2002). The radioactive waste generates gas at rates of about $\dot{G} \approx 1\ \text{mmol/m}^3$ day. By comparison, methane production from organic degradation reactions in marine sediment under harbors and lakes occurs in the range $\dot{G} \approx 1\ \mu\text{mol/m}^3$ day to $100\ \text{mmol/m}^3$ day (Winterwerp and van Kesteren, 2004). A sudden release of bubbles from the Hanford waste containing flammable gas to the airspace outside the system can be hazardous, mainly because of its flammability. In addition, transportation and storage of nuclear waste slurries for treatment and stabilization are subject to risks of overpressures from flammable gas evolution. Significant engineering efforts are expended to mitigate this type of risk at the Hanford Tank Farms and the Hanford Tank Waste Treatment and Immobilization Plant (WTP). There are similar concerns for humans living near coastal gas seeps of methane and hydrogen sulfide (Etiope et al., 2005).

In general, bubbles form in liquids from chemical reactions or by decreasing pressure or increasing temperature after becoming supersaturated with dissolved gas. This condensation method (Exerowa and Kruglyakov, 1998) for dispersing gas occurs whenever a liquid is boiled, when water vapor exsolves from magma during volcanic activity (Gaonach et al., 1996; Lovejoy et al., 2004), and in ocean sediments (Boudreau et al., 2001; Winterwerp and van Kesteren, 2004) and peatlands (Glaser et al., 2004) after organic decomposition reactions saturate the liquid phase with dissolved gases such as methane and carbon dioxide. Solid particles dispersed in the liquid interact to provide a cohesive matrix (Richefeu et al., 2006; Nowak et al., 2005) which traps the gas bubbles. Cohesion is reflected in the shear strength (or yield stress) of the fluid or granular material that surrounds the bubble (Winterwerp and van Kesteren, 2004).

* Corresponding author. Tel.: +1 509 205 8367; fax: +1 509 371 8987.
E-mail address: djsherwo@bechtel.com (D.J. Sherwood).

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http://dx.doi.org/10.1016/j.nucengdes.2013.12.050

Fig. 1. Appearance of a bubble on the surface of a bumped vessel. The still frame shows a bubble of about 6 cm in diameter emerging from a 0.49 m^3 vessel containing an aqueous slurry of kaolin and bentonite particles. Before the perturbation, the fluid was stationary and contained millions of oxygen bubbles generated by H_2O_2 decomposition of average diameter 0.3 cm. Bubble coalescence must have occurred to generate the observed bubble since the vessel depth (0.8 m) is too shallow for significant enlargement by decompression.

Unlike volcanic systems where the volatile species (mainly water and carbon dioxide) are fairly soluble, several weight percent being dissolved at typical characteristically high pressures (Moore et al., 1998), Hanford slurry gases are sparingly soluble, less than about 10^{-5} weight percent for the typically near-ambient storage conditions (Hu et al., 2002), and so exsolve into bubbles. A large number of bubbles are then dispersed into the fluid, reaching levels at which the fluid can be considered a gas–liquid emulsion. The bubbles are retained until liberated because there is evidently a limiting, critical volume fraction of gas for yield-stress fluids. The precise nature of the internal disturbances which might initiate gas release is not known but, presumably, relate to fluctuations in local properties, or to the bubble population over aging. Regarding the latter, after the nucleation and growth stage, the average bubble size increases as larger bubbles accumulate gas from the smaller bubbles in the late, aging stage of phase separation (Sagui et al., 1998). Brief mechanical loads (*i.e.*, a shock or jar) to the system's boundaries or intrusions into the system are examples of external disturbances. Stix (2007) notes that for volcanoes such triggers could be the rise of a larger gas bubble through a dispersion of smaller bubbles, or an earthquake.

The shear strength of suspensions and granular materials allows for trapping of bubbles of exsolved gas (Winterwerp and van Kesteren, 2004; Gauglitz et al., 1996; Dubash and Frigaard, 2004). Exsolution occurs by a first order phase transformation with the new gas phase separating from the liquid in stages: first by nucleation and growth, and second by aging (Boudreau et al., 2001). Growth of nuclei reduces the concentration of dissolved gas in the nonequilibrium, supersaturated liquid, moving the system toward equilibrium. But the bubbles have surface free energy and therefore the system will not be in equilibrium until the gas collects into a single location, separated from the saturated liquid with a flat interface. Unlike typically simple liquids where bubbles rise as they are nucleated, fluids with shear strength allow both the non-competitive and second stage competitive growth processes to occur *in situ*. Rather large amounts of gas, ~30 vol.% in some cases, are then able to be retained in bubbles with diameters as large as $D_b \sim 1$ cm (Gauglitz et al., 1996).

Bubbles in a suddenly fluidized gas–liquid emulsion rise in concert and rapidly degas the system in a bubble cascade gas release event (Gauglitz et al., 1996). One of these was captured on video and a still image is shown in Fig. 1. The fluid is an aqueous slurry of kaolin and bentonite clay particles simulating high-level radioactive waste with a yield stress of 7 Pa. The tank is a 0.49 m^3 vessel with 0.8 m depth provided with four pulse-jet mixers with tubes of 13.4 cm ID (see Meyer et al., 2005 and Russell et al., 2005, for more details on the apparatus). Oxygen from the decomposition of hydrogen peroxide in the aqueous phase was used to simulate the HLW slurry exsolved gases. All the gas exsolved from the liquid accumulated in many bubbles with average diameter of 0.3 cm. After the vessel was bumped, enlarged bubbles began emerging from the fluid. Fig. 1 shows one of such bubbles. This particular type of ebullitive release occurs in homogeneous, viscoplastic fluids with shear strengths typically between $\tau_y \approx 3$–70 Pa (Stewart et al., 2005); at the lower end of the range most bubbles are released and the system is effectively degassed. It is this lower range ($\tau_y \lesssim 30$ Pa) where HLW slurries will be processed in the WTP. Understanding the ramifications of sudden ebullitive releases is important for sizing vessel headspaces and ventilation systems and developing operating and safety procedures.

Somewhat similar ebullitions occur in natural systems, such as saturated sediment (Winterwerp and van Kesteren, 2004; Amos and Mayer, 2006), peatlands (Tokida et al., 2005; Kellner et al., 2006), and in gas-driven eruptions for some types of volcanic activity (Gaonach et al., 1996; Lovejoy et al., 2004; Stix, 2007), and lake and ocean activities (Zhang and Kling, 2006). Strack et al. (2005) described what could be essentially the same behavior as "potential episodic release of CH_4 *via* ebullition events." Some of these natural occurrences can, however, involve more complex processes than ebullition, and in the case of the eruptions, thrust the fluid