Chapter 32

Sonochemistry in Graphite Decontamination

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32.1 Decontamination Techniques for Graphite

Decontamination of materials refers to the process of cleaning of materials to remove radioactive contaminants from its surface completely or bring it down to an acceptable level to enable its reuse in the process. Graphite is one of the widely used structural materials in the nuclear industry. Therefore, decontamination of nuclear graphite is essential to reduce nuclear waste and facilitate its reuse in the nuclear facility.

The conventional methods of decontaminating graphite consists of: (a) disintegration of graphite to a suitable mesh size and leaching in acid and (b) graphite oxidation and (c) electrolytic graphite disintegration. But these methods of dissolution are destructive in nature and secondary wastes would require further processing before disposal. Moreover, the possibility of reuse of the structural element is less [285–291].

32.2 Challenges of Graphite Decontamination

The following are the challenges of decontaminating porous graphite substrates.

1. Recovery of deposits of radioactive materials from the pores of mesoporous substrates like graphite is a challenge. The problem is more severe in case of impingement of ions on graphite electrodes. Acid dissolution alone was ineffective in dislodging the entire contamination from the pores.
2. Grind-leaching technique, in which graphite will be crushed and the graphite powder of a suitable mesh size is leached in acid. But the possibility of reusing the graphite structural element is zero. Moreover, carbon residue is produced.
3. Preliminary studies show that the use of process intensification techniques like stirring may increase the external mass transfer in the macroscopic scale but the material from the microscopic pores cannot be recovered. Stirring does not influence the diffusion or recovery of materials from the pores. In case of use of aggressive catalyst, the graphite might get oxidized.

32.3 Mechanism of Sonochemical Decontamination

Use of cavitation, generated using ultrasound, as a process intensification technique is lucrative due to the mechanical effects of implosion of bubbles. Ultrasound propagates by phases of rarefaction and compression. In the rarefaction phase, the liquid pressure is low enough to generate bubbles, which grow in subsequent cycles and collapse in a later compression phase (Fig. 32.1). This phenomenon is known as cavitation. When a bubble implodes, areas of elevated temperatures (500–15000 K) and pressures (100–500 atm) are generated locally. Additionally, shock waves create microscopic turbulence in the boundary layers near solid particles, also referred to as micro streaming. When the bubble is imploding near a solid surface, micro-jets of solvent are formed, which impinge on the solid surface. These microscopic jets result in the removal of materials from the substrate. Turbulence increases mass and heat transfer across the film. This process intensification of the decontamination of nuclear structural materials will pave the path for economic recovery of the valuable nuclear materials and subsequent reuse of the structural element [285–287].

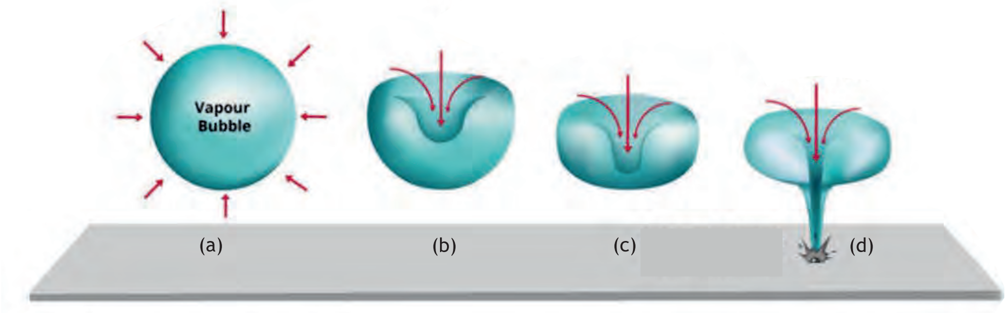

Figure 32.1: Schematic representation of the phases in acoustic cavitation indicating high pressure (red arrows): (a) vapour bubble, (b) vapour bubble collapse, (c) vapour bubble further collapse, and (d) microjet formation and surface erosion. [292]

32.4 The Transducers Generating Ultrasound

A transducer converts one form of energy into another. Acoustic transducers convert either electrical or mechanical energy into sound. Gas-driven, liquid-driven, and electro-mechanical types of transducers are generally available. The two main types of electro-mechanical transducers are based on either the piezo-electric or the magneto-strictive effect. The most commonly used are piezoelectric transducers, based on the piezo-electric effect:

a) When compressive stress is applied on a surface, charge generation takes place on each face equal in size but opposite in polarity. Reversal of polarities occurs if tension is applied on the surfaces.

b) When a charge is applied to one face of the piezoelectric crystal and an equal but opposite charge to the other face, the crystal will deform depending on the polarity of the charge applied on it.

On applying reversal of charges to a piezo-electric transducer, variations in dimensions will be seen [288]. This phenomenon can be utilized to generate the ultrasonic waves from the crystal section through the medium of propagation. The transducers may be mounted at the bottom of tanks or dipped in the reaction medium to generate ultrasonic waves depending on the application. Generally, the commonly used piezoelectric materials are barium titanate, lead salts (lead mataniobate, and lead zirconate titanate). Since single large crystal is difficult to fabricate, the materials are ground with binders and sintered under pressure to form a ceramic. The best performance of the transducer will depend on its natural resonance frequency and its dimensions [290]. Typical transducers are shown in Fig. 32.2.

32.5 Factors Affecting Cavitation

32.5.1 Frequency of ultrasound

The frequency of the irradiation governs the duration of rarefaction and compression phases. As the frequency of operation increases, higher input power is required to generate cavitation. This is because the molecules require finite time to be pulled apart to generate bubbles. At low frequencies, the acoustic cycles are sufficiently long to facilitate the quick generation of bubbles and their subsequent implosion. It is generally observed that the physical effects of the bubble implosion are more profound at lower frequencies.

Figure 32.2: Typical piezo-ceramic ultrasonic transducers.

Figure 32.3: Layout of the decontamination facility.

32.5.2 Intensity of ultrasound

A crucial factor affecting the effect of ultrasound is the intensity of ultrasound. The molecules will vibrate around their mean position in a sonication field. The sound pressure (P_a) will be adding on to the ambient pressure (in this case it is the hydrostatic pressure, P_h) present in the liquid. The total pressure (P) in the liquid at any time (t) is:

$$P = P_h + P_a = P_h + P_A sin(2\pi ft) \tag{32.1}$$

where P_A is the pressure amplitude, and f is the operating frequency. In case of acoustic wave, the wavelength (λ) is given by:

$$v_s = \lambda f \tag{32.2}$$

where v_s is the ultrasonic wave velocity and f is the operating frequency. Considering a film of the liquid of area (A) and thickness (dx) in a sonication field, the kinetic energy (KE) of the liquid film is shown as

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}(\rho A dx)v^2 \tag{32.3}$$

where m, v and ρ are the film mass, velocity, and density, respectively. The total energy of the ultrasound (E_t) is obtained by integrating Eq. (32.3) to give

$$E_t = \frac{1}{2}\rho A x v^2 \tag{32.4}$$

where ρ, A, x and v are the film density, area, thickness, and velocity, respectively. The energy density (E) of the wave is given by

$$E = \frac{1}{2}\rho v^2 \tag{32.5}$$

where ρ is the liquid film density of the film and v is its velocity. Sonic intensity (I) is the amount of sonic energy travelling per unit area per unit time.

$$I = E v_s \tag{32.6}$$

$$I = \frac{1}{2}\rho v p^2 v_s \tag{32.7}$$

At maximum velocity of the particle (v_{max}), the amplitude of the oscillating acoustic pressure (P_A) is given by

$$\frac{P_A}{v_{max}} = \rho v_s \tag{32.8}$$

Thus, the sonic intensity of the wave turns out to be

$$I = \frac{1}{2}\rho v_{max}^2 v_s = \frac{1}{2}\rho (P_A/\rho v_s)^2 v_s \tag{32.9}$$

Sonic intensity is directly proportional to the vibration amplitude of transducer [291]. However, indefinite increase in the input of ultrasonic energy input is not feasible for three reasons [290]:

1. Dimensional changes in the source of ultrasound will eventually fracture the material;
2. Higher vibration leads to decoupling as the source of ultrasound will find it difficult to maintain contact with the liquid throughout the complete cycle;
3. Larger power input will lead to larger bubble formation that will assist in dampening and cushioning the effects of ultrasound.

32.5.3 Solvent

Generation of cavitation is difficult in viscous liquids, where a large cohesive force has to be overcome to generate cavitation and to form microbubbles. Solvents with low surface tension generally offers lower cavitation threshold and facilitates bubble formation. A solvent having higher vapour pressure will facilitate easier bubble formation at low applied energy than a solvent with lower vapour pressure. However, the cavitational collapse of the vapour filled bubbles of solvent of higher vapour pressure is less violent than that of lower vapour pressure and hence optimum condition would exist similar to that discussed for effect of temperature.

32.5.4 Temperature

Temperature rise of the solvent increases the vapour pressure of the solvent while decreasing its viscosity and surface tension. This lowers the cavitation threshold. However, at temperature near the boiling point of the solvent, a host of bubbles filled with vapors are formed. They act as a barrier in sound transmission and leads to loss of energy and sonochemical effects. Also the collapse is less violent, again pointing to the existence of optimum temperature.

32.5.5 Dissolved gases and particles

It has been observed that the presence of impurities or dissolved gases help in the formation of cavities, thereby reducing the cavitation threshold. The gases act as nuclei for cavity formation. The higher the gas solubility, greater is the intensity of the bubble collapse. The intensity of bubble collapse may reduce if the gas is soluble as it will redissolve in the liquid during the compression phase of the acoustic cycle.

32.5.6 External pressure

Higher external pressure implies that higher rarefaction pressure will be required to initiate cavitation. Therefore, a higher acoustic intensity will be required to generate cavitation. Higher pressure will give rise to higher intensity of cavitational collapse and therefore, an enhanced sonochemical effect. Generally speaking, the sonochemical reactions are performed at ambient pressure conditions.

32.5.7 Attenuation of ultrasound

The propagation of ultrasound in a liquid medium is limited by the absorption or scattering of sound energy by the medium and its subsequent conversion into heat [290]. Depending on this acoustic impedance between the transducer and medium, there will be a rise in temperature the bulk medium during sonication [286]. The intensity of ultrasound I_d decreases exponentially from the starting value I_0 with distance d and depends on the absorption coefficient of the liquid medium.

$$I_d = I_0 \ exp(-2\alpha d) \tag{32.10}$$

The absorption coefficient α/f^2 (where f is the frequency of operation) is constant for most liquids.

32.6 Features of Power Ultrasound

A number of applications of sonication are found in the industries. These include non-destructive testing of materials and joints, intrusion detection, measurements of physical properties, medical applications and process control applications [293]. Effects of ultrasound can be briefly summarized by the following [293]:

1. **Temperature:** As sound propagates through a medium, the sound energy dissipated in the medium is in the form of heat. Loss of acoustic energy in the form of thermal energy vary depending on the properties of the medium of propagation. This leads to a rise in temperature of the medium.
2. **Stirring:** Agitation or turbulence is generated readily in a less viscous liquid medium and this leads to increased heat and mass transfer due to collapse of bubbles during sonication.

3. **Chemical effects:** Cavitation generated by ultrasound leads to effects that have been attributed to local high temperature zones in bubbles and also to radical generation. This hastens the reactions.
4. **Mechanical effects:** Stresses generated due to sonication can cause ruptures to occur in materials (especially biofilms and membranes). Stresses developed by the implosion of bubbles can cause severe pitting and erosion of surfaces.
5. **Diffusion:** Sonication enhances diffusion across cell walls, into gels, and across porous membranes.
6. **Cleaning:** The mechanical effects of bubble implosion leads to corroding of a protective layer from a substrate.

32.7 Advantages and Limitations of Sonochemistry

The benefits obtained by the use of cavitation-assisted dissolution include:

1. Higher rate of reaction due to efficient heat and mass transfer;
2. Decreased energy consumption for desired transformations compared to other intensification technologies;
3. Lower reaction temperature and pressure to achieve same conversion;
4. Reduction in the reaction time;
5. No sophisticated equipment or technology required;
6. Efficient utilization of the raw materials and the catalyst.

32.8 The Experimental Setup

Based on a few successful trials on a small scale, two ultrasonic baths were installed in Chemical Laboratory (Fig. 32.1). One is a vertical ultrasonic tank, which generally handling decontamination of metal wastes and other is a horizontal tank that is used for decontaminating graphite (Fig. 32.3). Both the tanks have blowers that carry out the NO_x gases generated during the dissolution of uranium in nitric acid. The PVC duct carries out the off-gases and discharges them at a level > 10 m from the ground level. Ultrasonic decontamination reduces the man-exposures as it is an unmanned process. The graphite plates were degassed [294] and used in material processing furnace. The contaminated plates are then submerged in the 10% acid bath for ultrasonic decontamination. The plates are taken out of the bath and the activity on the plates are checked with alpha-beta monitors after drying. The summary of the steps are given below.

1. Initial measurement of alpha counts on the extractor.
2. Initial measurement of gamma counts on the extractor.
3. Manual leaching with 30% (v/v) nitric acid of pre-decided sections of extractor plates.
4. Collection of samples for quality and quantity assessment.
5. Leaching of the plates in ultrasonic tanks
6. Draining and volume estimation of the leachant.
7. Drying and measurement of the alpha counts on the plate.
8. Collection of samples for quantity measurement.

The contamination on each plate is checked using alpha-beta contamination monitor before and after decontamination. The contamination is also sometimes cross checked using gamma-spectrometer before and after sonochemical cleaning.

Frequently Asked Questions

Q1. What is the main advantage sonochemical decontamination provides over the two widespread decontamination techniques used for nuclear graphite?

Q2. Why is stirring incapable of removing contaminants from pores?

Q3. How does piezoelectric transducer generate cavitation in a reaction medium?

Q4. Out of castrol and linseed oils, in which liquid, will sonication be more favourable and why?

Q5. Name of the effects produced by high power ultrasound.

Q6. Why can the ultrasonic intensity not be increased indefinitely?

Q7. Calculate the attenuation of sonic intensity I, when sound of 20 kHz frequency travels a distance of 1000 km in water having absorption coefficient $\alpha/f^2 = 21.5\text{x } 10^{-17}\ \text{m}^{-1}\text{s}^2$.