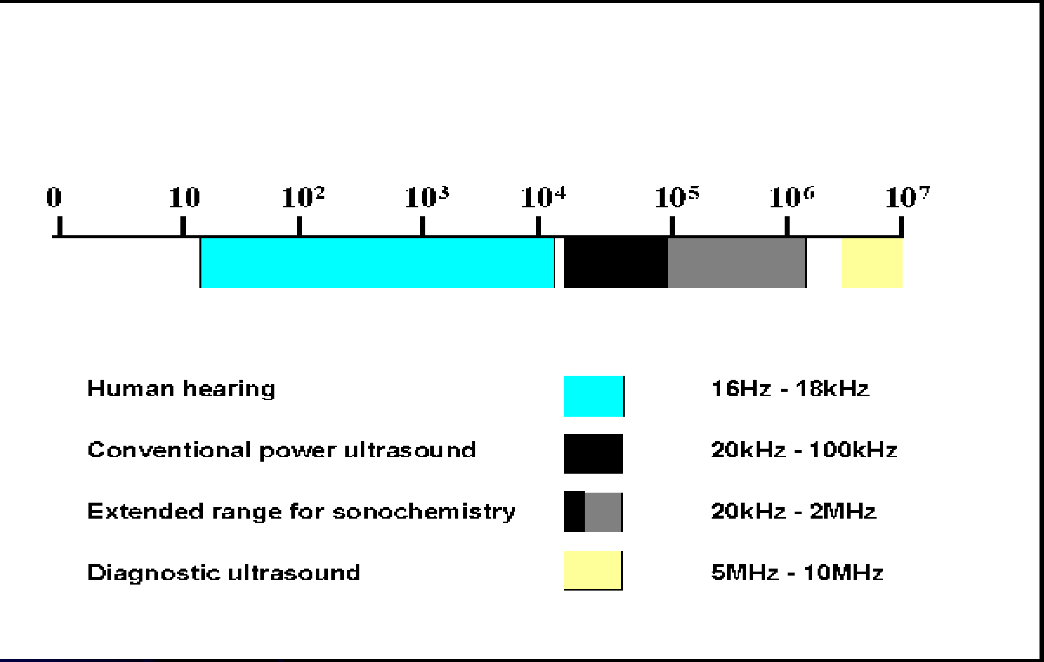
Ultrasound as an Advanced Oxidation Tool

Environmental Applications

Principles of Sonochemistry

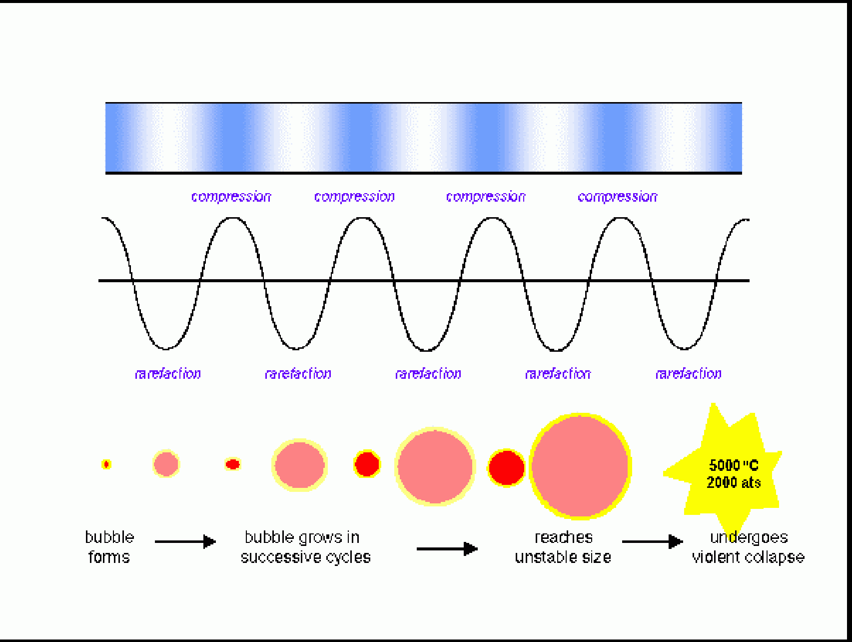
- Effects of US in water treatment are the result of ultrasonically induced acustic cavitation.
- Sound ranges applied must be those that generate cavitation.



- Large scale applications are in the low range.
- Extensive reserach on higher frequencies, but not the MHz range, where cavitation is difficult to achieve without very high powers.

Origin of Ultrasonic Effects

- Like all other sound waves, US is propogated via a series of compression and rarefaction waves induced in the molecules of the medium
- Cavitation bubbles form when the rarefaction cycle exceeds the attractive forces between molecules of the liquid (at sufficiently high power).
- Bubbles grow by “rectified diffusion” (entering of vapor during expansion phase, not fully expelled during compression)



The “Hot Spot” Theory

- Each cavitation bubble acts as a localized microreactor, which, in aqueous systems generates instanteneous temperatures of several thosand degrees and pressures in excess of 1000 atmospheres.
- Transient cavitations:exist for no more than a few acoustic cycles, during which they expand to at least double their initial radius before collapsing violently within a few microseconds. (F ≅ 300-1000 kHz; R ≅ 4-5 μm; bubble life ≅ 0.4 μs)
- Stable (inertial and non-inertial) cavitations:Collapse stage is delayed till after the elapse of a number of compression and rarefaction cycles, during which a large volume of dissolved gases flow into the gas phase.Occur at low frquency cavitation. Bubble life≅10 μs, R≅170 μm.

- Bubbles grow over a period of a few cycles to an equilibrium size related to the applied frequency.
- Bubbles collapase in succeeding compression cycles.
- Cavitation bubble collapse generates the energy for chemical and mechanical effects.

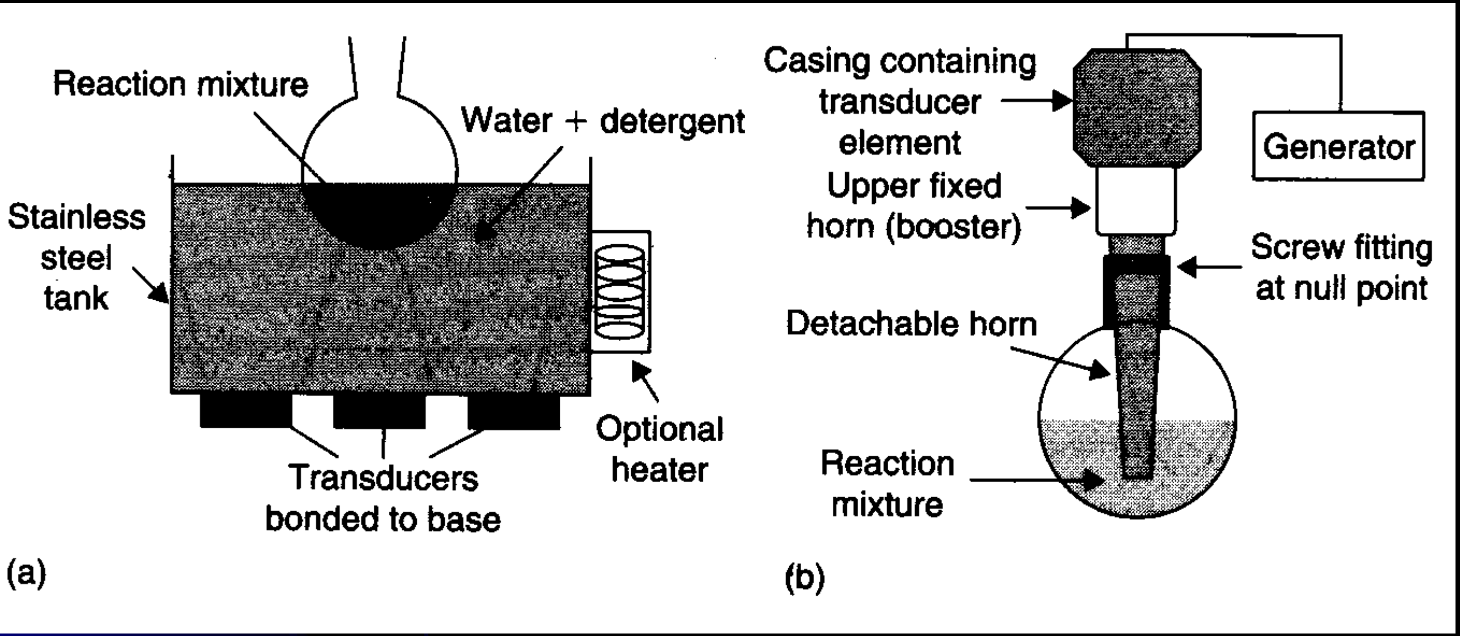
Uses of US in Environmental Protection

- Water decontamination
  - Biological: Direct mechanical action (cell rupture, break-up of bacterial clumps)
  - Chemical (direct oxidation)
- Efficient surface cleaning (decontamination of surfaces and biofilms)
- Control of air-borne contamination (agglomeration of smokes and aeresols)
- Sewage treatment (defoaming of liquids, stabilization and dewatering of sludge)

Lab-Scale Reactors

Two essential components

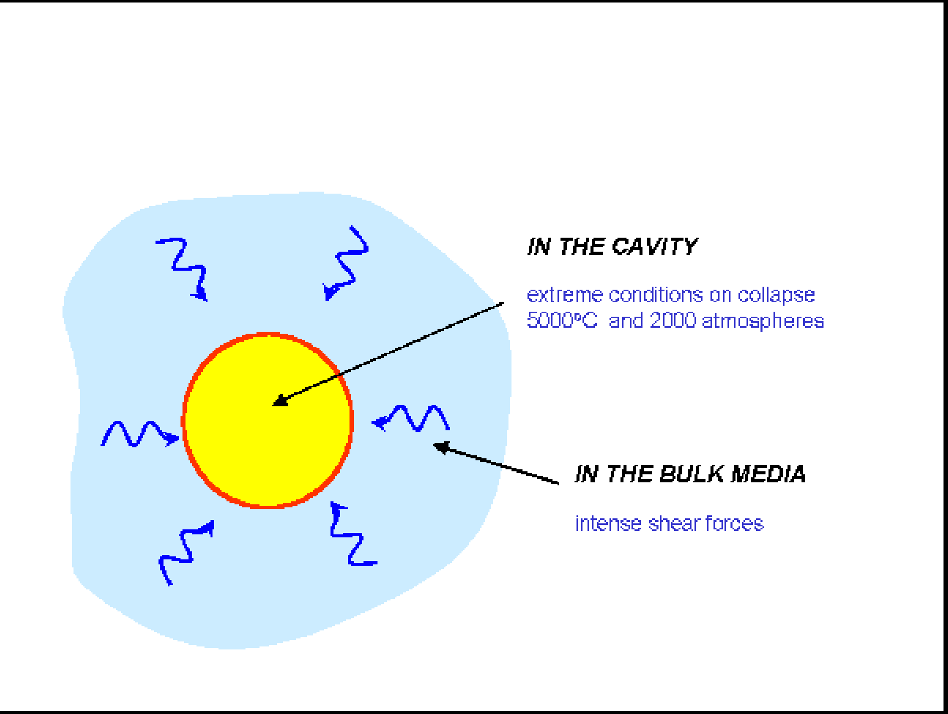
1. A liquid medium
2. A source of high energy vibration: transducer
    1. probe



Homogeneous liquid-phase reactions

Zones of Reaction

1. The bulk liquid, where bubble collapse generates shear forces that produce mechanical effects
2. Bubble itself, where species entrapped inside will be exposed to extreme conditons of T and P
3. The bubble-liquid interface, where semihydrophobic species accumulate and where radicals begin to react



Homogeneous reactions (cont'd)

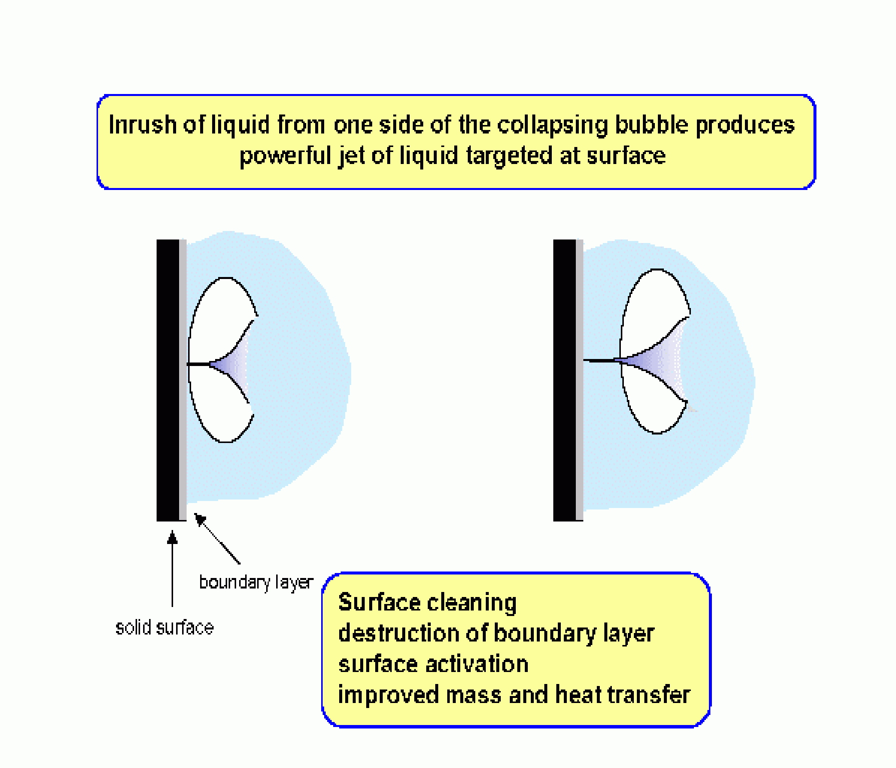
- Shear forces in the surrounding liquid are powerful enough to cause breaking of chemical bonds in compounds dissolved in the liquid.
- Disturbance by cavitation bubble oscilation and collapse also provides excellent mixing that results in rapid dissociation of chemicals and mixing of gases.
- If the liquid contains a dissolved gas, ultrasonic degasing occurs, because during rarefaction phase gases in the medium enter newly forming bubbles.

Degasing in homogeneous medium

- Such bubbles do not easily collapse in the comression cycle of the wave, because of their gas content and their contiual growth during rarefaction cycles (20,000-40,000 times per second by power US). As they fill with more gases they eventually float to the surface and degasing occurs instantaneously.
- Ultrasonic degasing is frequently used
  - to degas solvents for use in high performance liquid chromatography (HPLC)
  - to remove air from molten glass
  - to defob beer
  - to remove excess chlorine in disinfected water

Heterogeneous solid phase reactions

- Unlike cavitation bubble collapse in the bulk liquid, collapse on or near a surface is assymmetrical ➡ surface resistance to liquid flow from that side.
- Result is inrush of the liquid from the side of the bubble away from the surface, as a powerful liquid jet.
- The effect is equivalent to high pressure jetting ➡



•Cleaning
•Removal of biofilms
•Increase of mass and heat transfer to the surface by disruption of interfacial boundary layers

Radical Reactions in Homogeneous medium

$H_2O +))) \rightarrow \bullet OH + \bullet H$

$\bullet OH + \bullet OH \rightarrow H_2O_2$

$\bullet OH + \bullet OH \rightarrow H_2O + O$

$\bullet OH + \bullet OH \rightarrow H_2 + O_2$

$\bullet H + O_2 \rightarrow \bullet HO_2$

$\bullet HO_2 + \bullet H \rightarrow \bullet H_2O_2$

$\bullet HO_2 + \bullet HO_2 \rightarrow H_2O_2 + O_2$

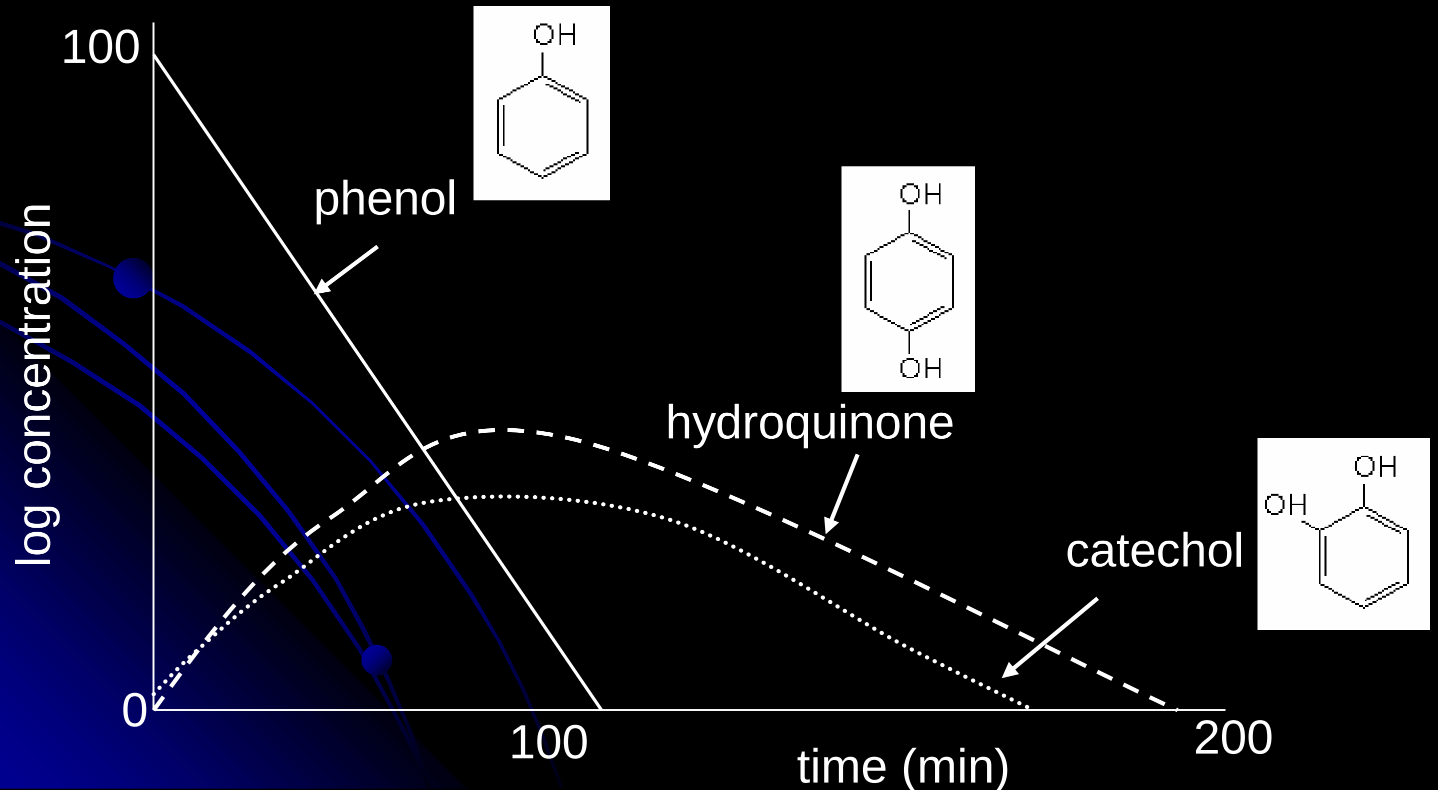
$\bullet OH + H_2O \rightarrow H_2O_2 + O$

$\bullet H + \bullet H \rightarrow H_2$

$\bullet H + \bullet OH \rightarrow H_2O$

Applications in Decontamination of polluted waters by ultrasound alone

- Phenols



2. Halogenated hydrocarbons

Initial concentration and chloride yield after 150 min sonication of chlorinated aromatics at 500 kHz

Chloroaromatic	Conc(mM)	Cl^- yield (%)
1,2-dichlorobenzene	0.4	90
1,3-dichlorobenzene	0.05	89
1,4-dichlorobenzene	0.2	95
1,3,5-trichlorobenzene	0.02	95
1-chloronaphthalene	0.04	98

- Destruction of chlorinated compounds and phenol take place at different sites and follows different pathways

H_2O_2 yields and rates of decomposition ($\mu Mmin^{-1}$) of chlorinated compounds and phenol

Frequency	20 kHz	200 kHz	500 kHz	800 kHz
H_2O_2 formation	0.7	5.0	2.1	1.4
Phenol degradation	0.5	4.0	1.9	1.0
CCl_4 degradation	19	33	37	50

- Chemical contaminants behave differently under ultrasonic irradiation
  - Phenol decomposes at the interface or the bulk liquid at an optimal frequency of 200 kHz

    ➡ two-step reaction pathway: i)radical production within the bubble; ii)migration of radicals to the interface or the bulk liquid to form peroxide or react with the target. As f increases, collapse occurs more rapidly and more radicals can escape from the bubble. But icreased f results in reduced cavitation intensity (violence) and reduced radical yields.
  - CCl_4 decomposes within the bubble and the rate increases with increasing frequency

Application of US with ozone

Provides 3 sources of •OH

1. From sonochemical decomposition of water
2. From chemical decomposition of ozone
3. From thermolytic decomposition of ozone inside the bubble as it collapses

Result is enhanced degradation of contaminants via:

1. Enhanced OH formation
2. Enhanced mass transfer of O_3 in solution

Assignment

- Combined Applications of US (e.g. with UV light, metal electrodes, O_3) for environmental remediation
- Applications of US for biological decontamination and sewage sludge treatment