Fundamentals and Applications of Micro/Nano Bubbles

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- Application of micro/nano bubble technology
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- Merit of using ozone bubbles
- Concluding remarks

Movies will be used for better understanding so far as they are available
Overview of Micro/Nano Bubble Technology
What micro/nano bubbles look like?

Microbubbles encountered in daily life
Dissolved air in hot water appear in tiny gas bubbles when it is mixed with cold tap water.

Artificially produced microbubbles
1,800L/min  (OHR Linemixer Ltd)

Microbubbles are visible!
Nano bubbles are too small to be detected with naked eye!!

Nano Bubble Generation (Direct method)
Nothing can be seen by eyes but can be seen by green laser light irradiation.

Nano Bubble Generation (Indirect method)
After microbubbles disappear, nano bubbles remain in water. Nano bubbles show Brownian motion.

Left: nano bubble water
Right: water without nano bubbles

(movie)

(movie)

(movie)
Size Range of Micro/Nano Bubbles

- **Clusters of Molecules**: Atoms, molecules of water are clustered.
  - **Atoms**:
    - Oxygen atom: 1.4 Å
    - Hydrogen atom: 1.2 Å
    - Molecular size of water: 0.3 nm
  - **Clusters of Molecules**:
    - A few 10 nm to a few 100 nm
    - Typical clustered molecule of water: \(H^+H_2O\) ... 5~10 nm

- **Bubbles**
  - Micro bubble: 1 μm
  - Nano bubble: A few 10 nm to a few 100 nm
  - Intermediate bubble: 100 μm
  - MM-order bubble

- **Picture of Nano Bubbles**
  - Taken by ultra-high voltage microscope.
  - Why not spherical?

- **Source**
  - Taken from NHK TV (science ZERO)

- **Diagram**: Bubble size range and molecular structure.
Recent Trends in Practical Application of Micro/Nano Bubble Technology

Microbubble Nanobubble

Medical Environment (Oxygen supply to activate microbe)

Agriculture Aquaculture (Oxygen-rich water supply to accelerate growth)

Industries

Wastewater Treatment Plants (removal of pollution by flotation, etc.)

Medical Treatment (to kill bacteria, virus)

To improve Fuel Consumption (fine bubbles improve fuel quality towards higher combustion efficiency)

Energy Saving (fine bubbles reduce flow resistance)

Closed Waters Purification

Sludge Purification

Aquaculture

Laundry Machine, Tableware (high performance cleaning effect by fine bubbles)

Bubble Bath (bubble-induced physiological functions)
Fundamentals of Micro/Nano Bubbles (Fine Bubbles)

- Characteristic features of micro/nano bubbles
- Short description of fine bubble generation
Why does Micro/Nano Bubble Technology Attract People’s Great Concerns?

Key: Excellent properties peculiar to fine bubbles (micro/nano bubbles) which are not encountered with normal-size bubbles

1) Extremely slow rise velocity: follows Stokes law
   \[ v = \frac{1}{18} \frac{\rho gd^2}{\mu} \]

   To assure long reaction time with uniform reaction field

How does bubble rise velocity differ for different bubble size?
2) Excellent Solubility:

- Large interfacial area concentration for constant gas volumetric ratio (void fraction)

\[ a_i = \frac{6\alpha}{d} \]

\[ a_i : \text{Interfacial area concentration (} m^3/m^2 \text{)} \]
\[ \alpha : \text{void fraction (-)} \]
\[ d : \text{bubble diameter (m)} \]

- Larger interfacial area for smaller bubble

- Bubble inside pressure higher than environment due to mechanical force balance to maintain stable curvature of a bubble

\[ \Delta P = \frac{4\sigma}{d} = \frac{2\sigma}{r} \]

(10μm: 0.3atm, 1μm: 3atm)

- Dissolution rate \( \propto (\text{driving force } (\Delta P)) \times (\text{interfacial area}) \)

Solubility follows Henry’s Law:

- Solubility is proportional to gas pressure

- Smaller bubbles is much easier to solve into water

Application
- chemical reaction
- purification of sludge, waste water etc.
- aquaculture, agriculture
  oxygen- rich water to enhance growth rate
Gas bubbles dissolve into water beyond equilibrium saturation concentration under forced circulation

Good reason for application to agriculture and aquaculture
3) **Fine bubbles (micro/nano bubbles) are electrostatically charged**

Zeta potential of fine bubbles ranges roughly from -10mV to -70mV under normal conditions, but it varies depending upon the value of pH of the liquid solution. In alkali liquid, fine bubbles show positive charge. It also depends upon how fine bubbles are generated.

Charged bubbles show either repulsion or attractive force like Coulomb's force when two bubbles or foreign particles approach to each other.

Charging mechanism has not been made clear yet.

**Application:** flotation
- physico-chemical absorption
- physiological function & effects
  - to enhance blood flow,
  - growth rate

**Zig-zag path of a microbubble motion according to the alternating electric field**
4) Surface adsorption

Organic substrate (surfactant) is adsorbed at the interface with hydrophobic group towards the gas side.

On still surface, organic substrate distributes uniformly over the surface at equilibrium condition. However, on moving surface, it distributes non-uniformly, which leads to non-uniform surface condition.

- Change of drag
- Partial break of mechanical equilibrium condition

A micro bubble breaks to form nano bubbles

[Diagram showing surface tension force and surfactant distribution]

Change of drag
Partial break of mechanical equilibrium condition

Drag coefficient

Taken after Takagi (2007)
**Oil separation by microbubble flotation in Oil-Water Emulsion**

An example showing adsorption/absorption of oil particles at microbubble surface
5) **Acoustic properties (Sono –chemistry)**

- Acoustic energy is significantly reflected at gas-liquid interface (for medical use)
- Applying external pressure fluctuation with resonant frequency causes high pressure and temperature fields inside the bubble up to the order of 100 MPa and 5,000K, leading sonoluminescence.
- Bubble collapse by external force induces shockwaves and radical formation.

![Acoustic reflection at interfaces](image1)

*Acoustic echo diagnosis*

![Generation of shockwaves by bubble collapse](image2)

*An example of sonoluminescence in wild life (pistol prawn)*

![Kidney stones smashed by acoustic shockwaves due to bubble collapse](image3)

*(movie)
6) Radical formation induced by bubble collapse:

Formation of free radicals has been experimentally confirmed when they crush. This phenomenon is often observed when the micro/nano bubbles are applied with ultrasonic waves to be collapsed, but popularly encountered with cavitation bubbles. It is however difficult to find evidence which shows free radical formation without any external forces acting on fine bubbles.

Hot-spot model to explain the mechanism

High temperature and pressure fields formed at bubble collapse induce decomposition of water molecules, and thus

\[
H_2O \rightarrow OH^- + H^+ 
\]

Most of free radicals thus generated tend to recombine

\[
+ H^+ \rightarrow H_2 \\
OH^- + OH^- \rightarrow H_2O_2
\]

\(OH^-\) radical has strong oxidization effect

\[\text{to decompose organic chemists sterilization}\]

Note: bubble collapse in course of time due to gas dissolution into water may not produce radicals.
7) Long life of nano bubbles

Nano bubbles can survive up to a few months. There are more than several models reported elsewhere to explain stabilization mechanism of nano bubbles, but none of them yet succeeded.

Possible application: aquaculture, agriculture, medicals,

(by courtesy of Kyowa Kisetsu Co. Ltd)
8) Physiological Effect

Micro/nano bubbles enhance
- blood flow
- growth rate of plants, fishes
- disinfectant

Enhanced blood flow in oyster (Ohnari, 2007)

Accelerated growth of eggplant

Enhanced growth of fish by NB

Microbubble bath

Blood flow

Enhanced blood flow in oyster (Ohnari, 2007)

Time trace of blood flow at wrist (Himuro, 2014)
9) Reduction of flow resistance (wall drag and skin drag)

Microbubble injection reduces skin friction

Applied to mercantile marine

Microbubble injection reduces wall drag in channel flow

Pseudo laminarization in wall drag

Energy saving
10) Change of physical properties of liquid caused by microbubble injection

After bubbling with microbubbles for a certain time, leave bubbly water for one day as it is. Then, physical properties of water were measured.

Change of network structure of water molecules caused by bubbling

cf: bubbling breaks hydrogen bond in water molecules

Tap water

cf: viscosity \( \propto \) molecular weight
break of hydrogen bond
smaller water clustering

ionization of chemicals in water caused by bubbling
**pH of water solution changes with different gas species by bubbling**

Air microbubble injection

In case of distilled water: pH decreases
In case of tap water: pH increase

cf. Air bubbling eliminates CO₂ and Cl₂ contained in tap water


(CO₂ + O₂) microbubble injection

Sea water 120 L
CO₂ : 1.4L/min, water 14L/min
O₂ : 0.2L/min, water 14L/min

Taken after AURA TEC report (2005)

In case of distilled water: pH decreases
In case of tap water: pH increase

Kaneko (2014)
How to Generate Micro/Nano Bubbles

There are various types of fine bubble generators commercially sold with different designs, but mechanisms used are however classified into shear flow, nucleation, cavitation and bubble break down by shockwave. Combination of these separate mechanisms is possible. A few examples are typically shown below.

**Depressurization type**

- The bubble generation mechanism is based on homogeneous/heterogeneous nucleation and cavitation through sudden depressurization of the system.
- High bubble number density is attained with use of a high pressure pump (Henry’s law).
  - Small scale device with a high pressure pump is appropriate for laboratory use.
  - Large scale device with a high pressure pump should be preferably avoided in view of cost performance unless otherwise necessary.

[Images and diagrams showing examples of bubble generation mechanisms]

- Use of a high pressure (~7atg) pump
  - Centrifugal pump
  - Use of a high pressure (~7atg) pump (Nikuni Co. Ltd.)

- Use of a low pressure (~3atg) pump
  - Use of a low pressure (~3atg) pump (Aura Tec Co. Ltd.)
Shear flow type

- Gas flow is broken down into fine bubbles by shear force.
- High pressure pump is difficult to use for ejection type generator because of air suction problem.

Ejection type

Gas flow is broken down into fine bubbles by shear force:

- Sophisticated honeycomb structure

(movie) (NHK TV Science Zero 2015.8.30)
**Swirl flow type (shear force)**

Water (or water-gas mixture) is running into the vessel in tangential direction to form swirl flow inside the vessel. This swirl flow induces negative pressure along the centerline of the vessel, which in turn sucks the air from the top of the vessel (left side picture). Air column is then torn off into fine bubbles by strong shear flows in the outside region of the vessel at the bottom or both ends (right picture).

- simple structure
- low cost
- fairy low bubble number density

**Single exit (Aura Tec)**

**Double exits (Yamaguchi Univ.)**
**Static line mixer**

A specially designed static structure with guide vanes and current cutters creates high speed swirl flow along the centerline of a cylinder. Strong shear fields are then formed locally by interactions between the swirl flow and current cutters. In addition, negative pressure regions appear both in the core region of the cylinder and in regions just behind the current cutters. Fine bubbles are generated by combination of nucleation, cavitation, shear force and by shockwaves. Usually a high pressure pump is used.

(OHR Laboratory Corporation)
Application of Micro/Nano Bubble Technology

Several typical examples of application of micro/nano bubble technology in specific fields such as
  • environments
  • agriculture
  • aquaculture
will be briefly mentioned.
Application in Environment Protection-I

Purification of water in closed water area (pond, lake and semi-enclosed sea)

**Use of micro bubble injection**

*before test*
Water clearness was only 20 cm

*one year after test*
After two months’ operation, the water was made so clear that all fishes in the pond (1300 m²) were visible.

**Purification mechanisms**

- floatation
- Sterilization
- Oxygen supply

(By courtesy of Aura Tec Co Ltd.)
Purification of sludge at sea bottom

Nano bubbles are easy to shrink when they are injected into nearly sea bottom because of increased ambient pressure. Thus, the air is successfully supplied to sludge in a form of nano bubbles. This phenomenon has been successfully applied to recover poor oxygen condition at the bottom through fresh air supply, and thus to activate marine life and to decompose organic substances as well. Purification of marine environment made fishes to live in again.

Copied from NHK World TV program (2014.3.3) Nanobubble technology
Purification of oil-contaminated soil by flotation

**Stage 1: to extract oil from contaminated soil**

- Sample emulsion
- Microbubble 10 µm
- Oil particle

**Stage 2: to separate oil from oil/water emulsion**

- Sample emulsion
- Extracted oil layer with α = 1.1%
- Extracted oil layer with α = 1.4%
- Extracted oil layer with α = 2.3%

70~80% oil was successfully extracted from oil-contaminated soil by flotation effect of microbubble.
Environment - IV

Nuclear decontamination of radioactive Cs from soil of rice fields in Fukushima by use of micro/nano bubbles

Radioactive Cs is chemically and electrostatically combined very firmly with extremely fine clay particles of the order of a few μm. These very fine clay particles with highly radioactively contaminated are extremely difficult to remove by conventional methods.

A mixture of micro and nano bubbles demonstrates a peculiar combined flotation effect on such small particles in terms of agglomeration (by nano bubbles) and convection (by microbubble flotation).

Classification of clay particles takes place effectively depending on particle size. Smaller clay particles with highly contaminated are going up by flotation.

More than 50% of radioactive Cs lies both in water and in the soil in the depth range 0~5cm below the surface.

What depth is the most seriously contaminated by Cs?

<table>
<thead>
<tr>
<th>ground depth</th>
<th>Surface below water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 cm</td>
<td>54.8 %</td>
</tr>
<tr>
<td>5 cm</td>
<td>34.0 %</td>
</tr>
<tr>
<td>10 cm</td>
<td>11.2 %</td>
</tr>
<tr>
<td>15 cm</td>
<td></td>
</tr>
</tbody>
</table>

How contaminated?

electrostatically combined very firmly with extremely fine clay particles of the order of a few μm.

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How remove Cs?

Smaller clay particles with highly contaminated are going up by flotation.

to be removed
Application of fine bubble technology in agriculture

Fine bubble technology is expected to be successfully applied in agriculture from the following view points.

1) To improve agricultural productivity by enhancing growth rate of vegetables,
2) To improve biological or physiological conditions for soil in production sites in terms of
   • suppression of a failure caused by continuous cropping
   • suppression of eutrophication in field soil caused by nitrogen chemicals
   • to increase a number of aerobic bacteria and microorganism
   • to encourage aerobic microorganism in decomposing organic matters
3) Agricultural water treatment by fine bubbles
   • oxygen dissolution with high efficiency
   • higher performance of water permeability through soil particles
4) Fine bubble water is a beneficial tool, as already used, for culture solution in hydroponics for the purpose of purification and sterilization (ozone bubbles)
Application in Agriculture – II

Air microbubble injection applied to rice field

Tamaki.M, Utilization of Micro/Nano bubbles in agriculture, paper presented at STAFF seminar (2009, 10.23)

- Air microbubbles enhanced the growth of rice plant
- An explosive increase in the number of triopsidae which prevents growth of weed in rice fields
- No Japanese barnyard millet grew

Good harvest without chemicals nor fertilizer

Original video copied from Interim Report Video (2006), Miyagi Women’s University, Institute of Living and Environmental Science
**Enhanced growth of vegetables by fine bubble-water splash**

Fine bubbles containing water is a good soil conditioner:
- excellent permeability to permeate into even stiff soil
- oxygen-rich water makes soil aerobic and water retaining

- decrease of ammonia production
- to help roots in expanding into the depth of the ground
- to enhance the growth of rootlets and hence ingestion of microelement of plant nutrient

**Application in Agriculture –Ⅲ**

Oxygen nano bubble-water adopted in hydroponics system in a vegetable factory:
- to enhance growth rate
- to eliminate bacteria

Oxygen nano bubble-water splash in ginger cultivation:
- significant growth of ginger roots

Air microbubble + water splash for potherb mustard:
- to enhance rooting

- MB+ water
- water only
Application of fine bubble technology in marine product industry and fishery

<table>
<thead>
<tr>
<th>objective</th>
<th>available system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shellfish culturing</td>
<td>oyster, scallop, pearl oyster, abalone</td>
</tr>
<tr>
<td>Fish culturing</td>
<td>red sea bream (red tai), prawn, shrimp</td>
</tr>
</tbody>
</table>
| Quality preservation/improvement for marine products | oyster: wash and clean after picking up  
Scallop: prevention of meat hardening  
Prawn/shrimp: removal of parasites  
Seaweed: quality preservation in drying process  
For all fishes:  
    improvement of fish transportation  
    improvement to keep freshness and taste  |
| others                                        | Improvement of oligoaerobic sea area for fishery  
Improvement of aeration effect in fish culture |

Fine bubble technology is expected to bring about prospective future possibility in sustainable marine product industry and fishery including all kinds of aquaculture.
**Disease control and enhancement of growth rate**

**Disease control**:  
Applicable to prawn or shrimp farming

**Enhancement of growth rate**  
Oxygen-rich sea water brought about by micro/nano bubble injection enhances blood flow and branchial respiration of fishes.

- Oxygen microbubbles brings about rapid growth of pearl oyster
- Scallop grows faster with air microbubble injection
- Oxygen nano bubble supply  
  upper: without oxygen NB  
  lower: with oxygen NB

Fishes grow faster and bigger.

Blood flow ratio between before and after microbubble injection

Time elapsed (min)

Blood flow ratio

(movie)
Aquaculture – Ⅲ

Freshness keeping technique for fishes using a slurry of (sea water ice) with ultra-low oxygen content

Requirements to keep fishes fresh are
- to prevent oxidization of oil and fat content
- to prevent activity and growth of aerobic bacteria

Solution
- to create extremely oxygen-deficient environment for fishes
  1) replace oxygen in water and ice with nitrogen by bubbling in a form of nano bubbles
  2) dissolved nitrogen can penetrate into fish meat through skin and visceral

Action
Use of a slurry consisting of sea water and ice with ultra-low oxygen content
Under such condition freshness is successfully kept at least 8 days with good taste

(movie)
Fishes treated with nitrogen nano bubble-sea water
(movie)
How to obtain sea water with low oxygen content
**Long distance transport of live fishes by letting them asleep**

Findings:
- In highly CO₂ gas dissolved sea water, fishes tend to sleep quickly.
- Once they are put back into normal sea water, they wake up soon.
- While they are sleeping, oxygen is supplied in a form of nano bubbles to maintain branchial respiration.
- After long distance transport, they are still fresh with beautiful taste.

Anesthetic effect of CO₂ dissolved sea water makes fishes asleep. To maintain branchial respiration, O₂ nano bubbles injected into sea water.

1,200Km, 17 hrs. drive to Tokyo

Fishes wake up in normal sea water

Even after a long journey, fresh taste is kept

Image of branchial respiration of fishes

Demonstration of fish sleeping and awaken
Wash and clean oyster meat in shell by microbubble cleaning

Application in Aquaculture – V

Oysters in carrying basket
Put them into sea water
Microbubble purging
Foam of foreign particles taken off from oysters
Enlarged picture

Oyster meat after cleaning
Right: washed by sea water
Left: washed by microbubbly water

Oyster meat (enlarged)
Upper: by sea water
Lower: by microbubbly water

Microbubble cleaning clearly removed the stains from oyster meat in shell.

Taken from You Tube: What are micro/nano bubbles? Surprising power of fine bubbles (2010/5/12)
Merit:
① to keep high dissolved oxygen to accelerate growth
② bactericidal effect of nano bubbles inhibits the growth of bacteria in rear water (safe method using sterilization sterilized equipment)
③ cleaning effect of nano bubbles make rear tanks, channels and pipings resistant to dirts no stress to fishes
④ bacteriostatic effect of nano bubbles prevents deterioration of water quality and bad odor

- High productivity and stable production
- Reducing costs significantly
- Expected to be applied to various fish species
Aquaculture – VII

A future prospect of shrimp farming using fine bubbles

Inshore fishery in Thailand (2010)

- Marine fish: 19,820t
- Mollusc: 328,250t
- Shrimp: 505,500t

Thailand: black tiger → vannamei
Japan: prawn (scampi, kuruma-ebi)
black tiger, vannamei shrimp

Key technology: water quality control
- Deterioration of water quality → lack of DO
- DO = 5~10mg/L (<3mg/L serious damage)
- pH = 8~8.5 (>9.5 serious damage)
- Anti viral infection, bacterial disease

Control of water quality
- Oxygen deficient water
- Suppression of disease

Causes of deteriorated water quality and poor bottom environment of breeding pond are:
- Over bait
- Corpse & exuvia
- Excreta

Inshore-based + land-based

- Shrimp pond design to collect biological waste
- Stirring paddle to increase DO
- Microbubble injection to improve water quality

Land-based
- Tillage of water bottom sediment

No results reported yet
**Merit of using ozone bubbles**

### Characteristic features of ozone are:

1. **Strong oxidation ability**
   
   Ozone (O₃) is chemically unstable and changes to stable oxygen O₂ by emitting oxygen atom as follow:
   
   \[ O_3 \rightarrow O_2 + (O) \]
   
   This emitted oxygen atom shows strong oxidization.

2. **Strong bactericidal effect**
   
   nearly 10 times stronger than chlorine-type sterilizing agents.

3. **High solubility in water**

4. **Easy ozone production by electromagnetic radiation** (i.e., corona discharge etc.)

5. **Ozone microbubble crushing yields complete decomposition of organic compounds.**

### Application of Ozone micro/nano bubble in agriculture and environmental protection area is promising:

- removal of agrochemical residues
- decomposition of organic substances
- waste water treatment
- etc.

### Table: Solubility of Ozone and Air in Water

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Ozone (mg/100g water)</th>
<th>Air (mg/100g water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>89.4</td>
<td>3.80</td>
</tr>
<tr>
<td>5</td>
<td>34.3</td>
<td>3.33</td>
</tr>
<tr>
<td>10</td>
<td>29.9</td>
<td>2.88</td>
</tr>
<tr>
<td>15</td>
<td>25.9</td>
<td>2.62</td>
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<td>20</td>
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<td>1.78</td>
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<tr>
<td>50</td>
<td>0.6</td>
<td>0.219</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Concluding remarks

Though fine bubble (micro/nano bubbles) is fairy a recent finding, its application has been drastically expanding in past ten years to a wider range of different fields, covering electronics, medical fields, environmental protection fields, industries, agriculture, aquaculture and etc. In fact, fine bubble technology application especially in both agriculture and aquaculture is very promising for future and should be expected to hold potentially a huge possibility.

However, it should be pointed out that our current knowledge of basic mechanisms associated with fine bubble phenomena are still quite limited with an exception of only a few made clear scientifically. Most of the successful applications of fine bubble technology are the results after thousands times trial and error, since operational performance of any type of fine bubble generators is quite sensitive to the conditions under which they operate.

In fact, we can now fabricate very easily ourselves a fine bubble generator at cheap price whatever bubble generation mechanism is, since key knowledge about efficient bubble generation methods is now almost open. However, operation is another issue and totally different from fabrication. We should chose correct type of bubble generator with sufficiently good specification which fits to the objectives.

When we try to use fine bubble technology, one of the most important things we should first consider about is to know what sort of properties of fine bubbles we really want to use among more than several. If we get a proper answer to this with confidence, then we can approach to our goal. Nevertheless, it is true that agriculture and aquaculture are good scope for future in practical application of micro/nano bubble technology.
Thank you for your kind attention