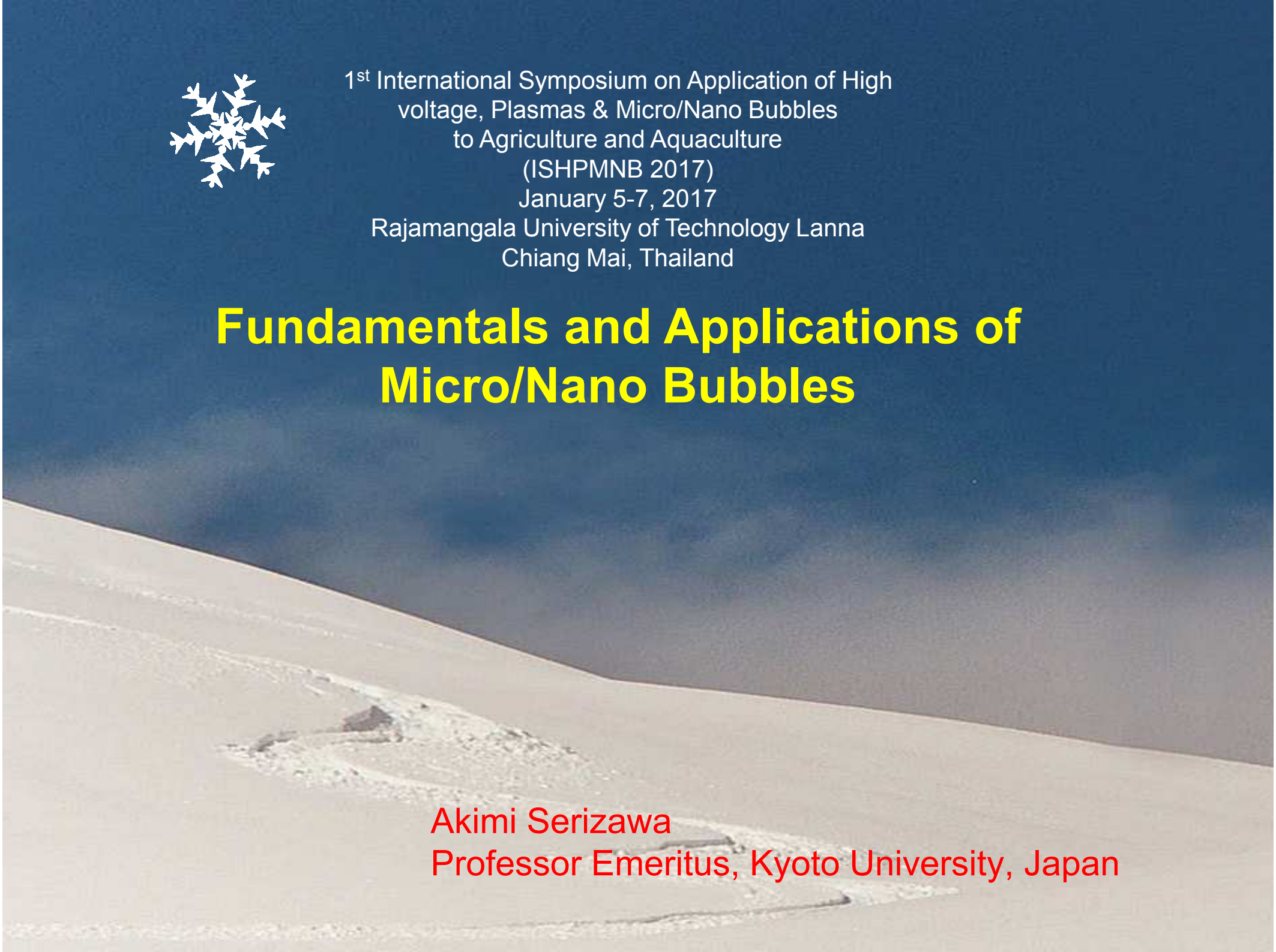

1st International Symposium on Application of High voltage, Plasmas & Micro/Nano Bubbles to Agriculture and Aquaculture
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Fundamentals and Applications of Micro/Nano Bubbles

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Professor Emeritus, Kyoto University, Japan

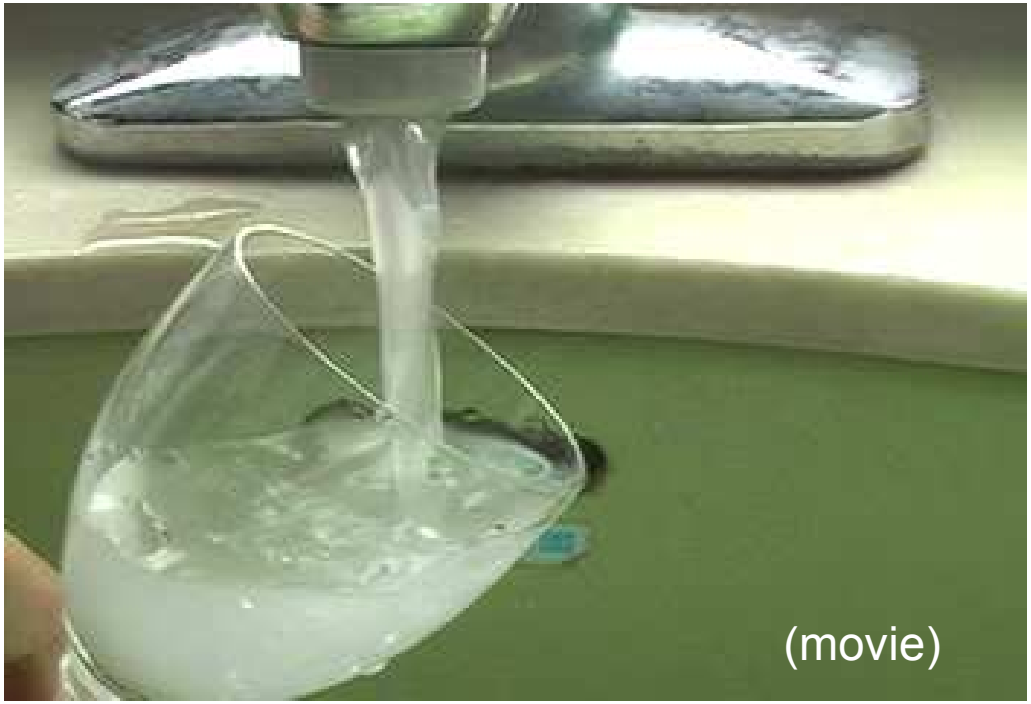
contents

- *Overview of micro/nano bubble technology*
- *Fundamentals of micro/nano bubbles (fine bubbles)*
- *Application of micro/nano bubble technology*
  - *application in environment protection*
  - *application in agriculture*
  - *application in aquaculture*
  - *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

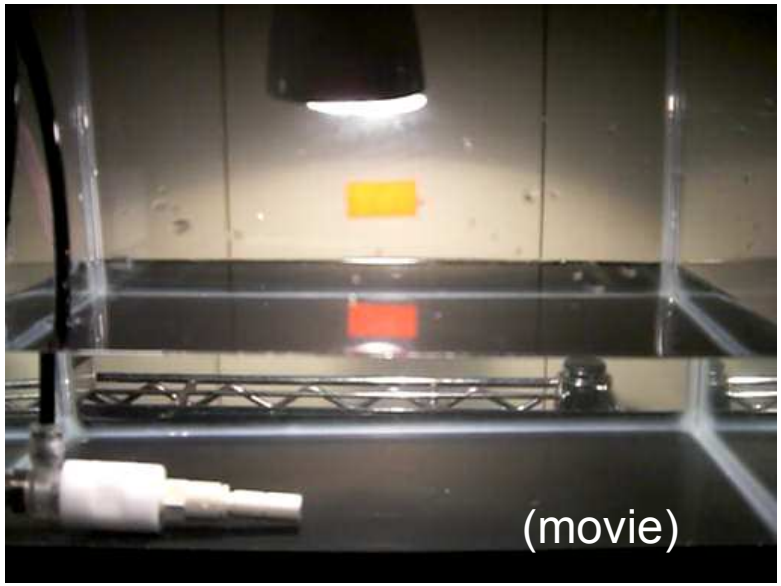
Dissolved air in hot water appear in tiny gas bubbles when it is mixed with cold tap water.

Microbubbles are visible !

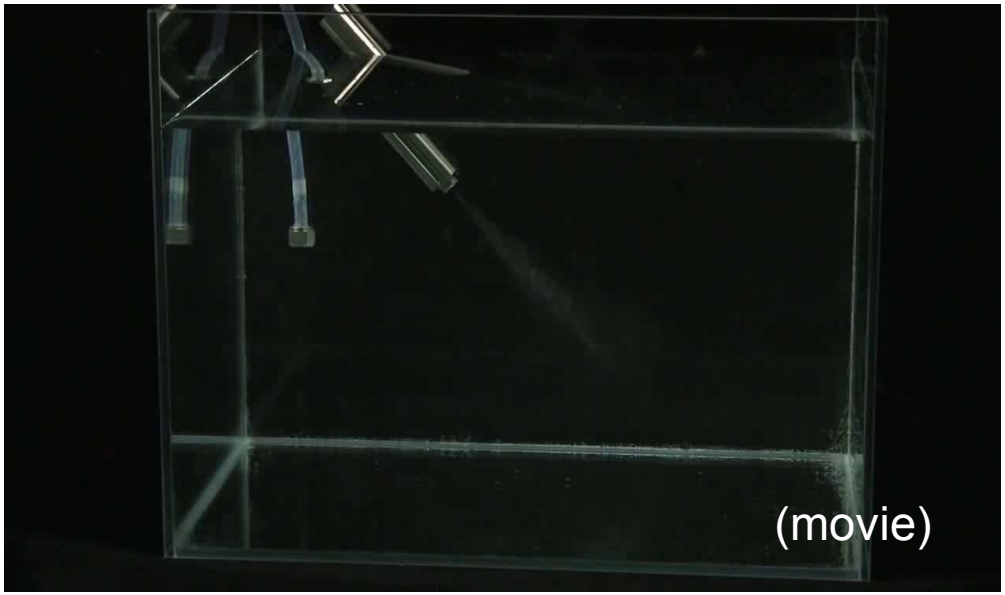
Artificially produced microbubbles

1,800L/min (OHR Linemixer Ltd)

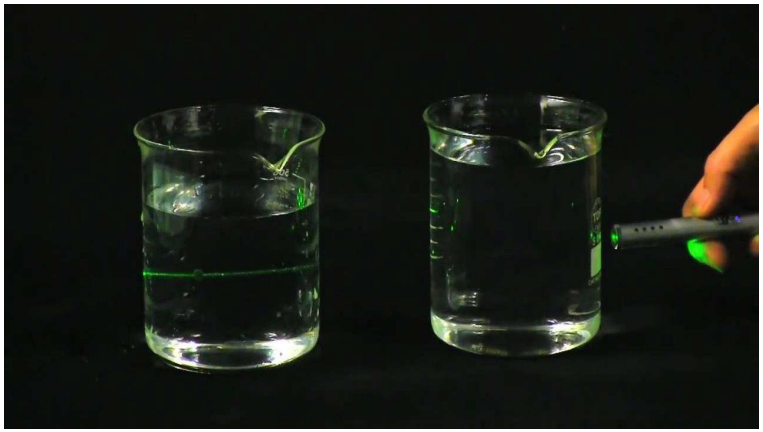
Nano bubbles are too small to be detected with naked eye !!



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



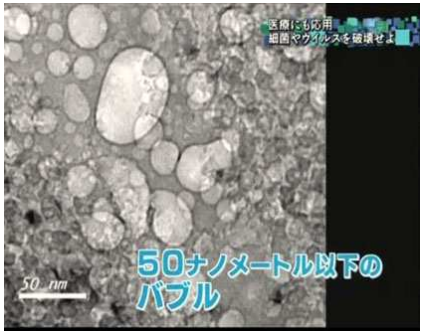
Nano Bubble Generation (Indirect method)
After microbubbles disappear, nano bubbles remain in water. Nano bubbles show Brownian motion.



Left: nano bubble water
Right: water without nano bubbles

Size Range of Micro/Nano Bubbles

taken from NHK TV
(science ZERO)



Picture of nano bubbles taken by ultra-high voltage microscope:
Why not spherical?

100μm

1μm

1nm

0.1nm

mm-order bubble

micro bubble

nano bubble
a few 10nm~ a few 100nm

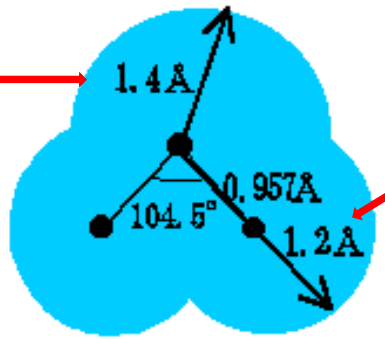
Intermediate bubble

micro/nano bubble

atoms, molecules

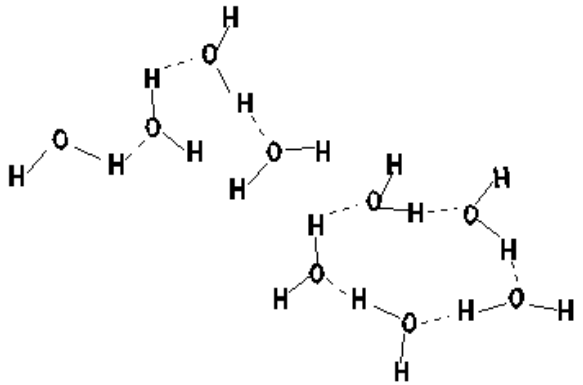
Clustered molecule of water

diam. of Oxygen atom



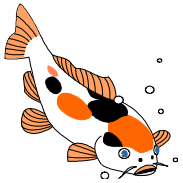
diam. of Hydrogen atom

molecular size of water（0.3nm)

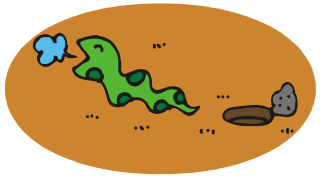


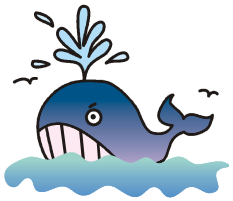
Typical clustered molecule of water（$H^+(H_2O)$ ….5~10nm）

Recent Trends in Practical Application of Micro/Nano Bubble Technology



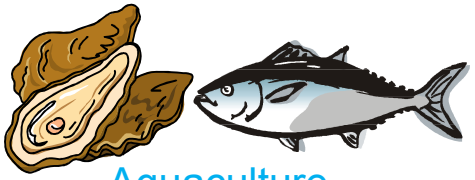
Closed Waters Purification





Sludge Purification

(Oxygen supply to activate microbe)



Aquaculture

Medical Treatment

(to kill bacteria, virus)

Medical Environment

Agriculture Aquaculture

Agriculture

(Oxygen-rich water supply to accelerate growth)

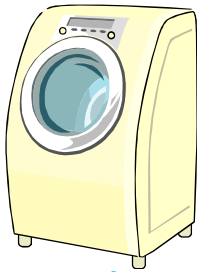
Microbubble Nanobubble

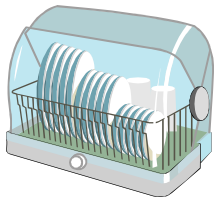
Wastewater Treatment Plants

(removal of pollution by flotation, etc.)

Industries

Electronic Household Appliances



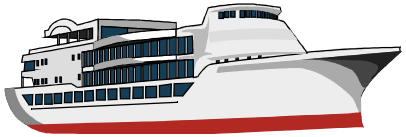


Laundry Machine, Tableware

(high performance cleaning effect by fine bubbles)

To improve Fuel Consumption

(fine bubbles improve fuel quality towards higher combustion efficiency)



Energy Saving

(fine bubbles reduce flow resistance)

Bubble Bath

(bubble-induced physiological functions)

Fundamentals of Micro/Nano Bubbles (Fine Bubbles)

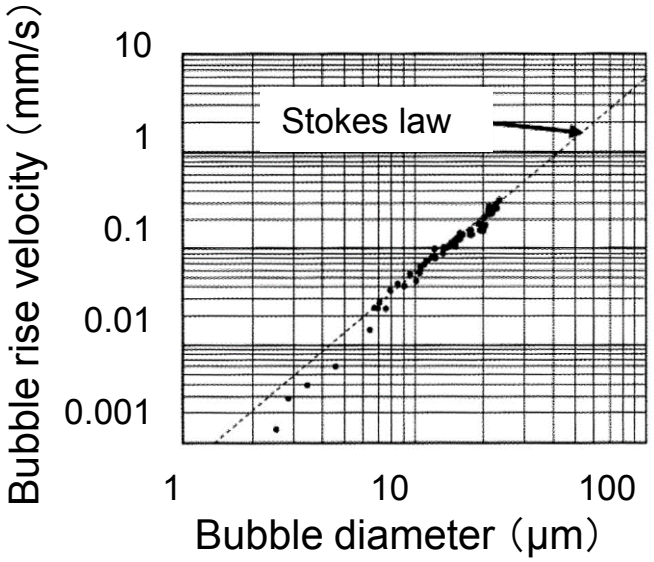
- *Characteristic features of micro/nano bubbles*
- *Short description of fine bubble generation*

Why does Micro/Nano Bubble Technology Attract People's Great Concerns?

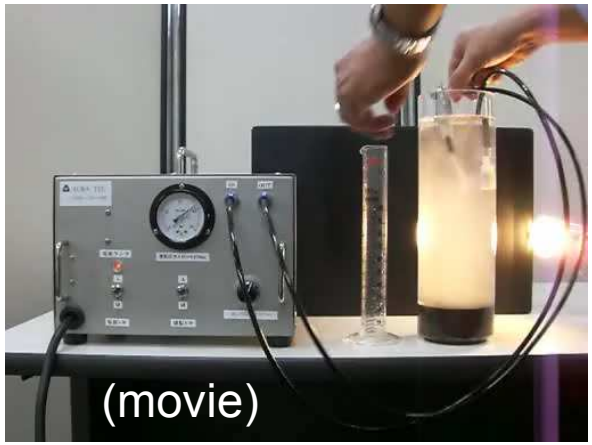
Key: Excellent properties peculiar to fine bubbles (micro/nano bubbles) which are not encountered with normal –size bubbles

1) Extremely slow rise velocity: follows Stokes law $V = \frac{1}{18}\frac{\rho g d^2}{\mu}$

➡ To assure long reaction time with uniform reaction field



How does bubble rise velocity differ for different bubble size ?



1μm

20μm

40μm

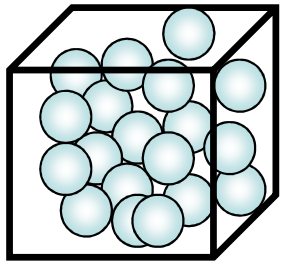
2) Excellent Solubility:

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

$$a_i = 6\alpha / d$$

a_i : Interfacial area concentration (m^3 / m^2)
α : void fraction (-)
d : bubble diameter (m)

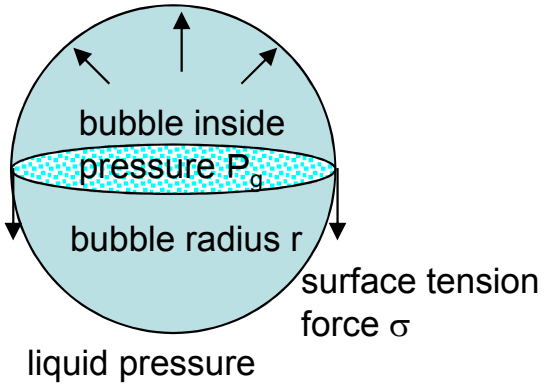
➡ Larger interfacial area for smaller bubble



N bubbles exist in unit volume

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

$$\Delta P = {}^{4\sigma}/_{d} = {}^{2\sigma}/_{r} \quad : \quad (10\mu m : 0.3atm,\ 1\mu m : 3atm)$$

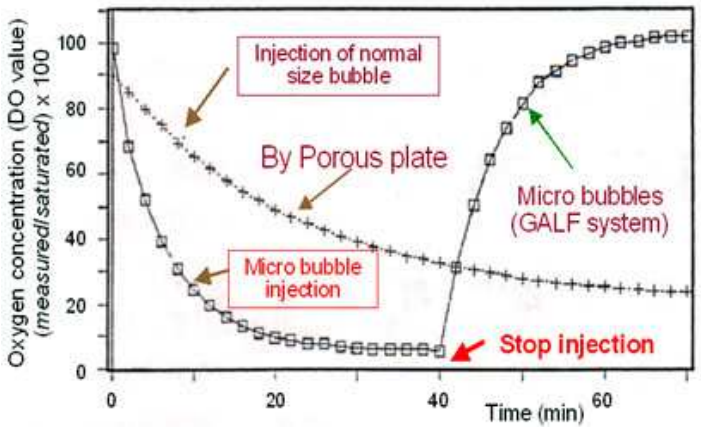


- Dissolution rate ∝ (driving force (ΔP)) x (interfacial area)

Solubility follows Henry's Law:

Solubility is proportional to gas pressure

➡ Smaller bubbles is much easier to solve into water

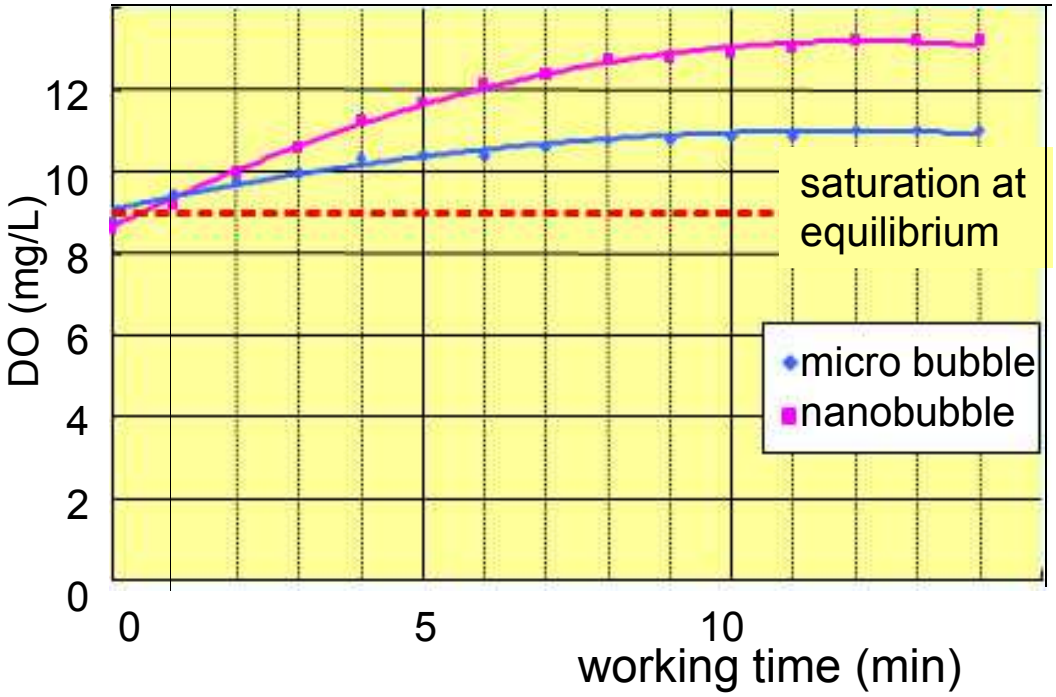


Application

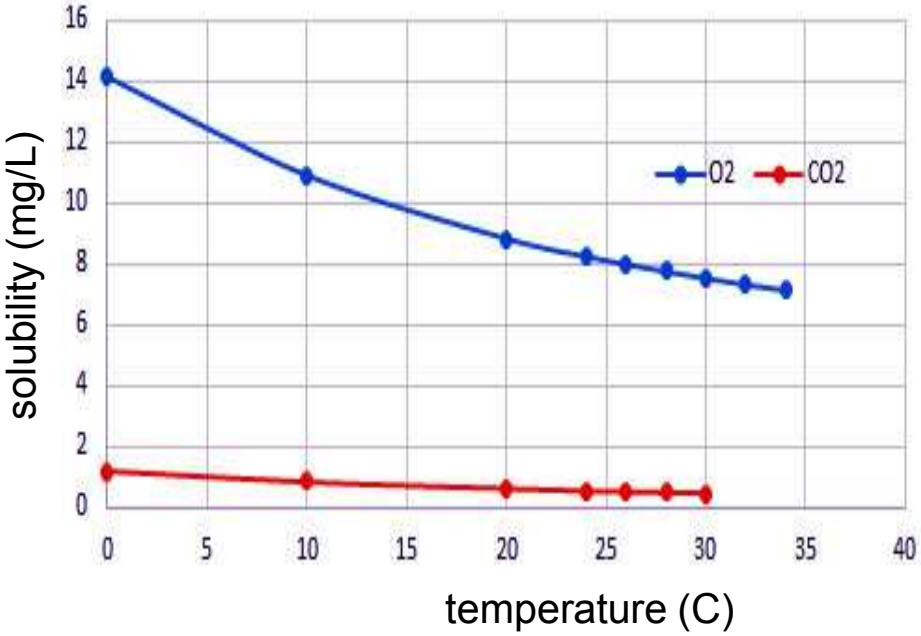
- chemical reaction
- purification of sludge, waste water etc.
- aquaculture, agriculture
  oxygen- rich water to enhance growth rate

Gas bubbles dissolve into water beyond equilibrium saturation concentration under forced circulation

Good reason for application to agriculture and aquaculture



saturation concentration at equilibrium for O_2 and CO_2

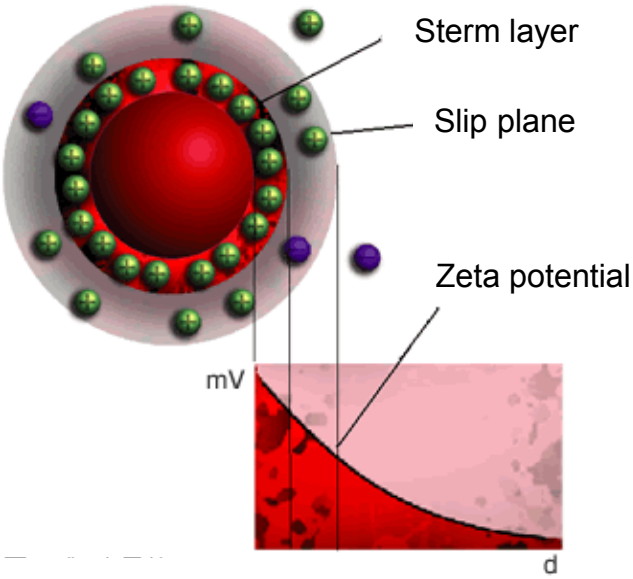


3) Fine bubbles (micro/nano bubbles) are electrostatically charged

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.

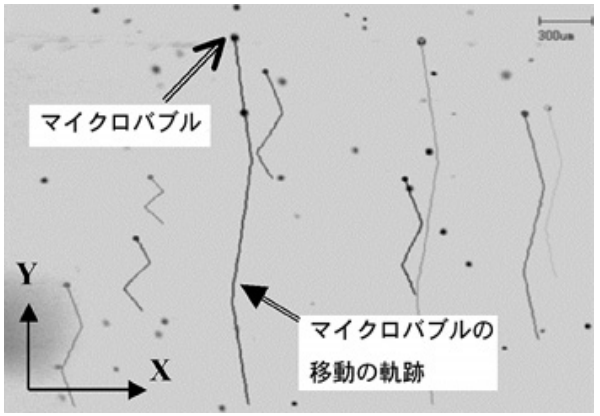
Charged bubbles show either repulsion or attractive force like Coulomb's force when two bubbles or foreign particles approach to each other.

Charging mechanism has not been made clear yet.



Definition of Zeta potential

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



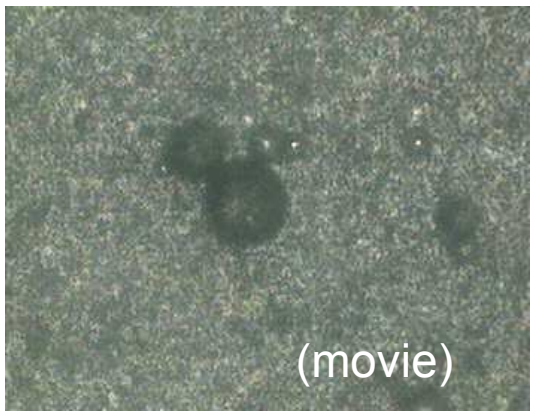
Zig-zag path of a microbubble motion according to the alternating electric field

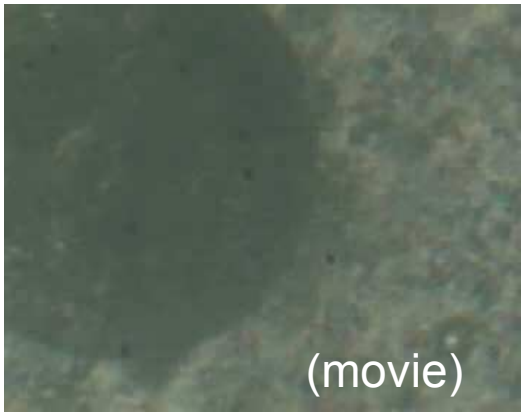
4) Surface adsorption

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

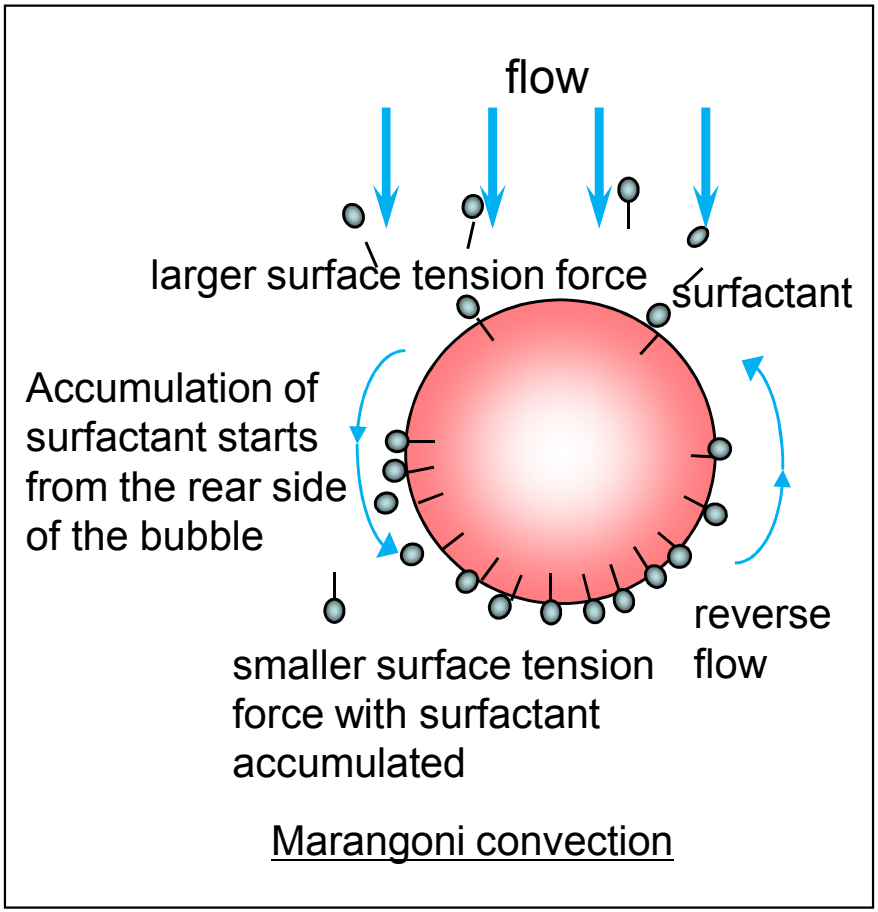
On still surface, organic substrate distributes uniformly over the surface at equilibrium condition. However, on moving surface, it distributes non-uniformly, which leads to non-uniform surface condition.

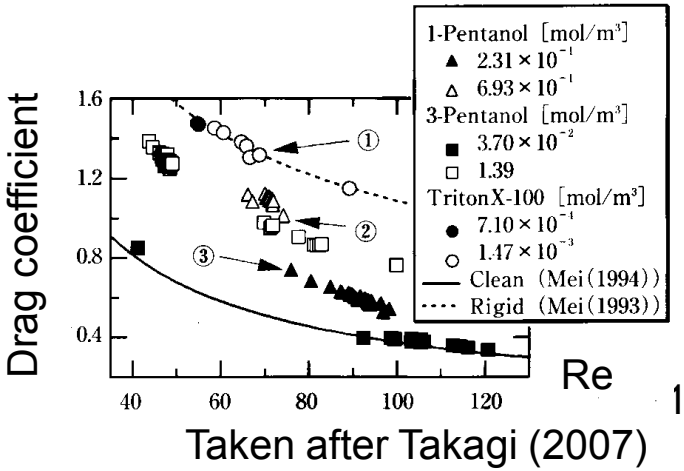
- Change of drag
- Partial break of mechanical equilibrium condition





A micro bubble breaks to form nano bubbles

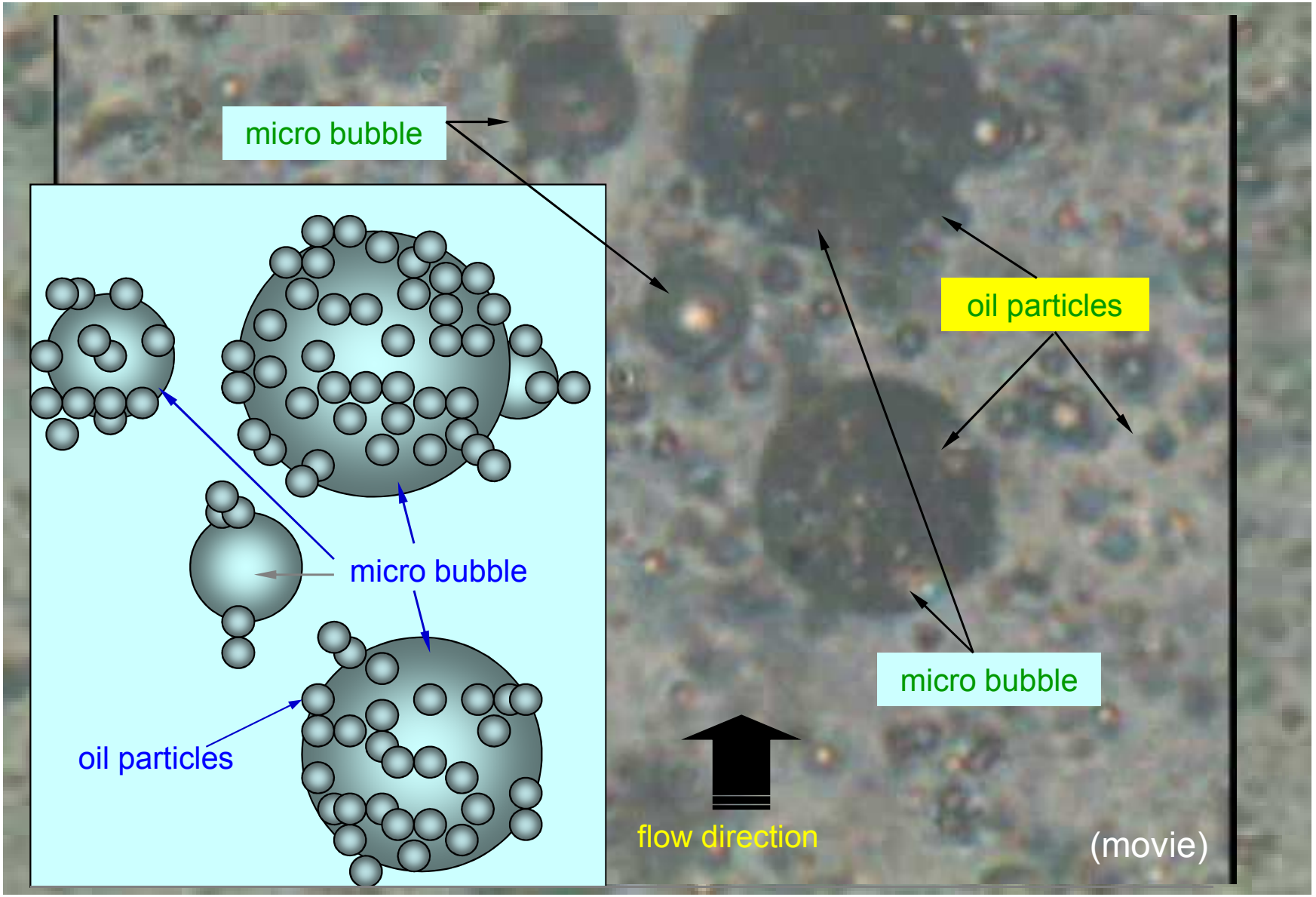




Taken after Takagi (2007)

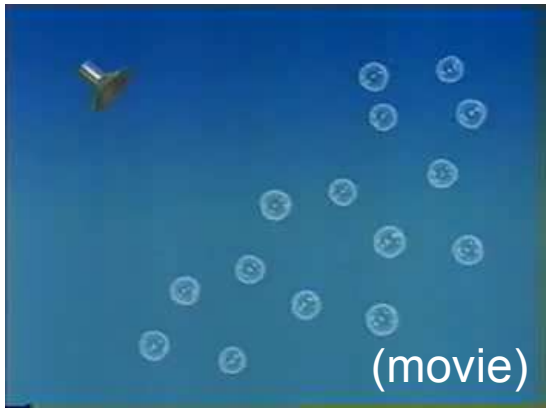
Oil separation by microbubble flotation in Oil-Water Emulsion

An example showing adsorption/absorption of oil particles at microbubble surface

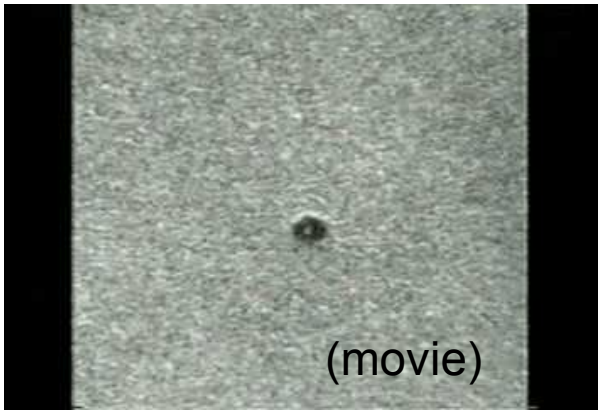


5) Acoustic properties (Sono –chemistry)

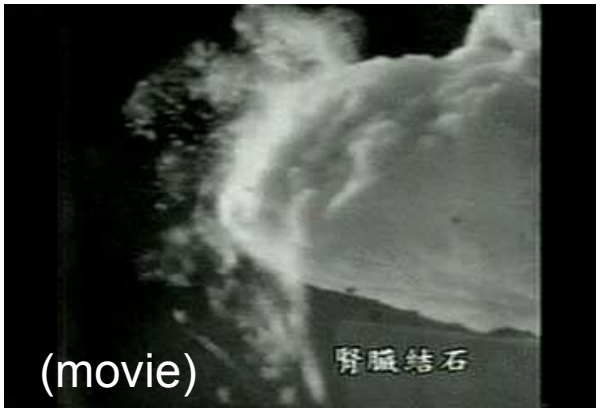
- Acoustic energy is significantly reflected at gas-liquid interface (for medical use)
- Applying external pressure fluctuation with resonant frequency causes high pressure and temperature fields inside the bubble up to the order of 100 MPa and 5,000K, leading sonoluminescence.
- Bubble collapse by external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



Acoustic reflection at interfaces
➡ Acoustic echo diagnosis



Generation of shockwaves by bubble collapse ➡



kidney stones smashed by acoustic shockwaves due to bubble collapse

An example of sonoluminescence in wild life (pistol prawn)

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

$$+ \quad H^+ \rightarrow H_2$$

$$OH^- + OH^- \rightarrow H_2O_2$$

OH^- radical has strong oxidization effect

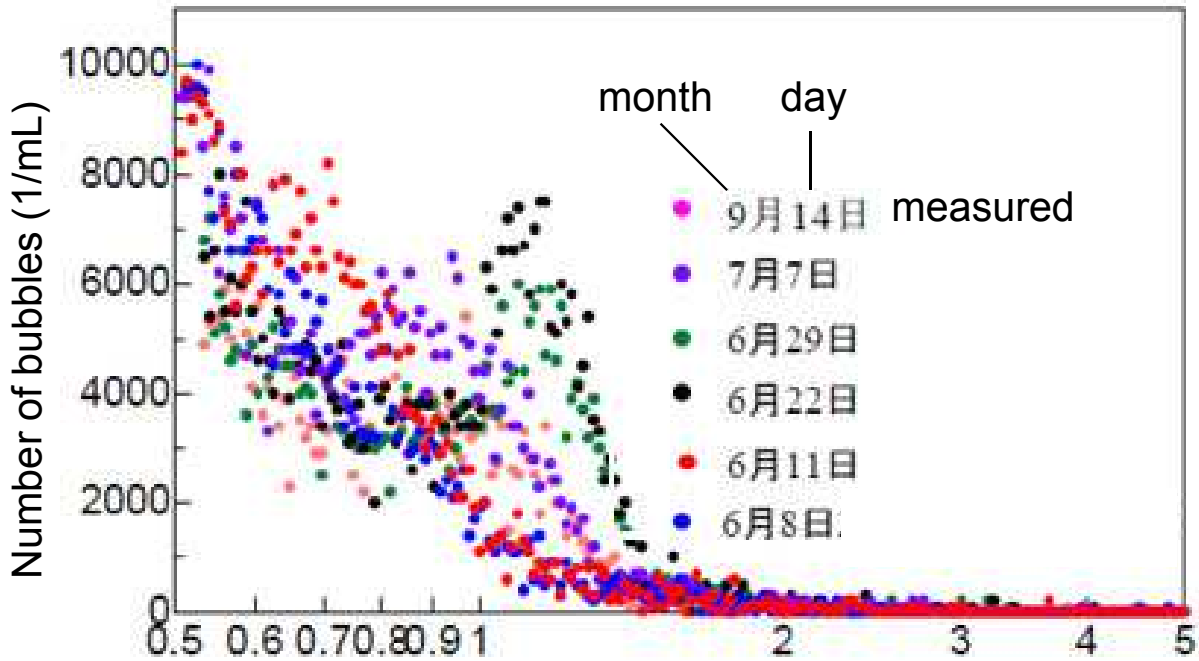
➡ to decompose organic chemists
sterilization

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,



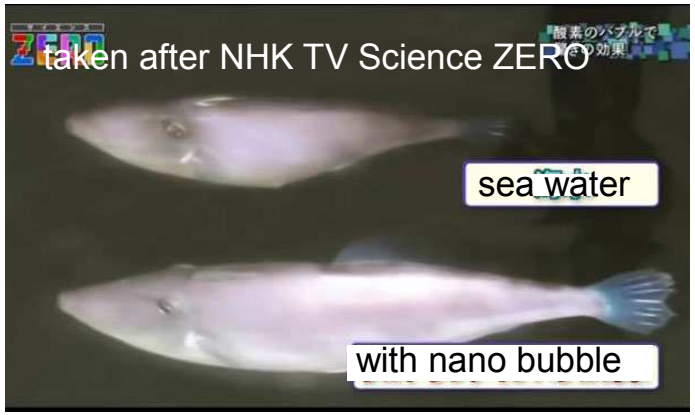
by courtesy of Kyowa Kisetsu Co. Ltd)

8) Physiological Effect

Micro/nano bubbles enhance

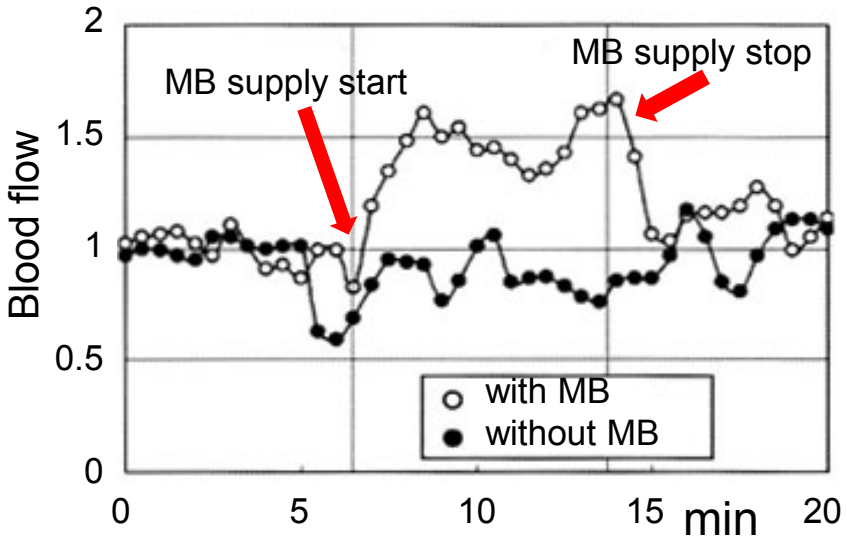
- blood flow
- growth rate of plants, fishes
- disinfectant

Accelerated growth of eggplant

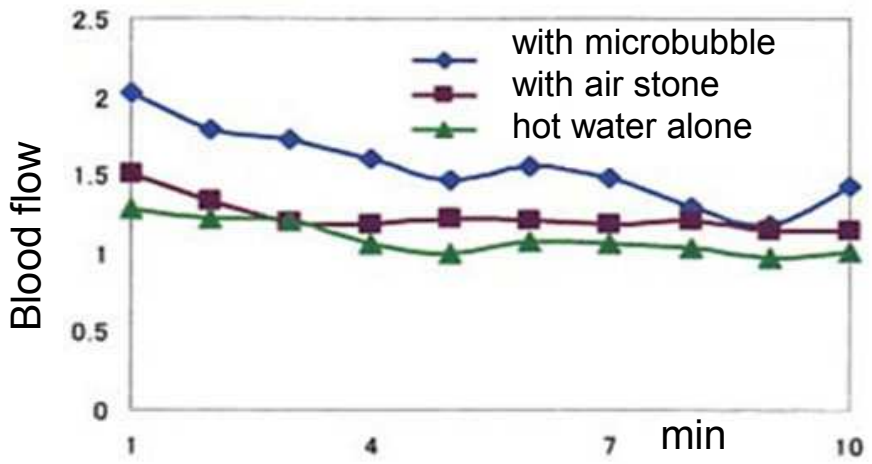


Enhanced growth of fish by NB

Microbubble bath



Enhanced blood flow in oyster
(Ohnari, 2007)



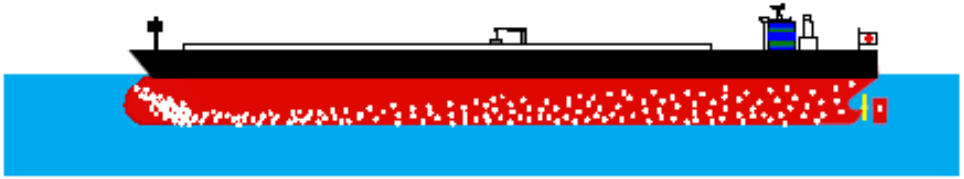
Time trace of blood flow at wrist
(Himuro, 2014)

9) Reduction of flow resistance (wall drag and skin drag)

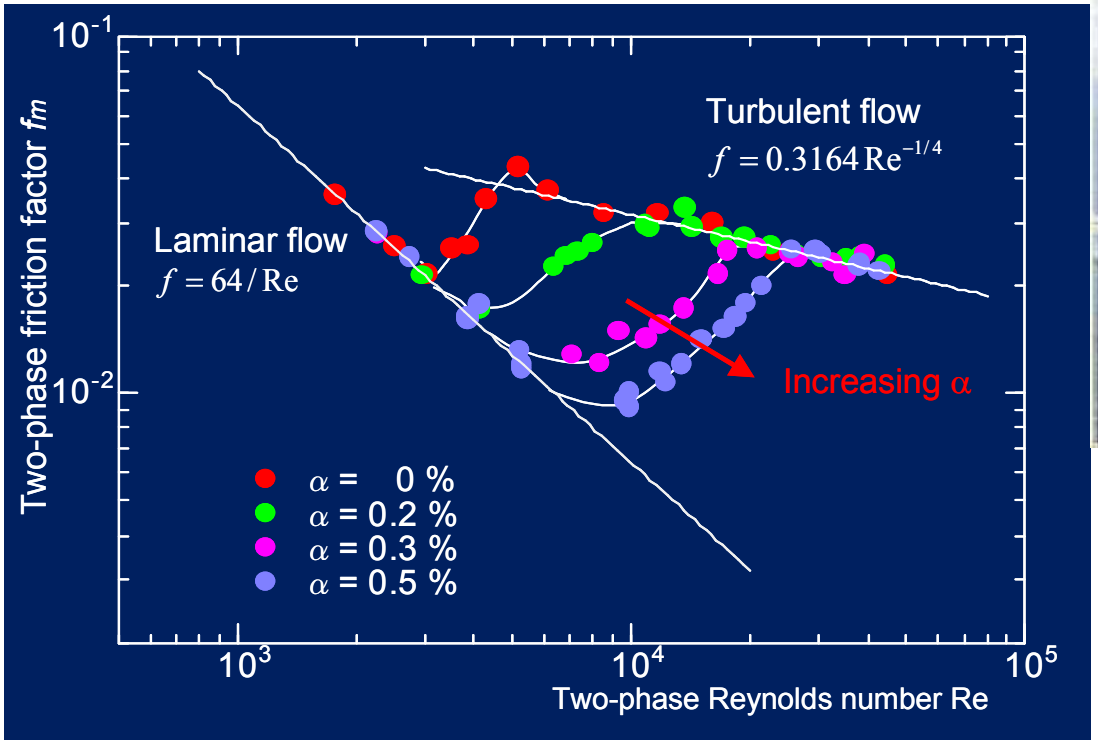
➡ Energy saving

Microbubble injection reduces skin friction

➡ Applied to mercantile marine



Microbubble injection reduces wall drag in channel flow



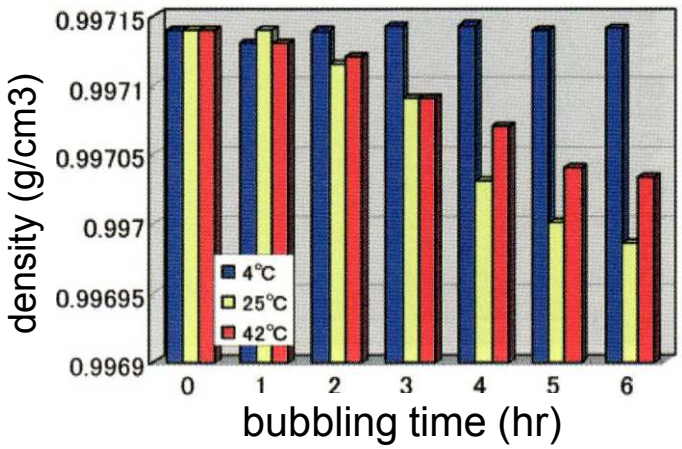
Pseudo laminarization in wall drag

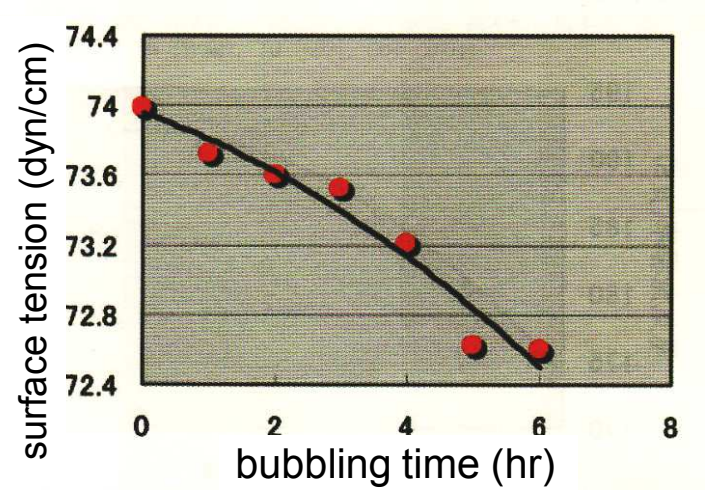
10) Change of physical properties of liquid caused by microbubble injection

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

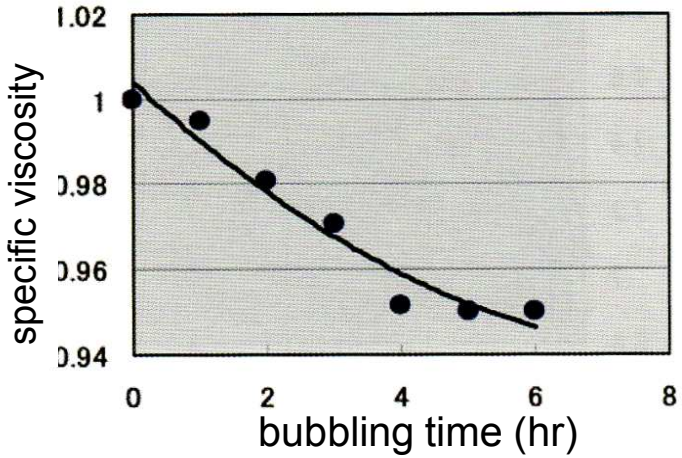
Change of network structure of water molecules caused by bubbling

Tap water

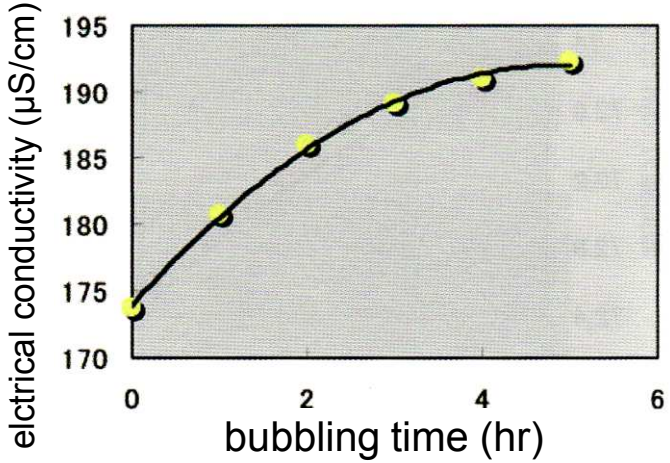




cf: bubbling breaks hydrogen bond in water molecules



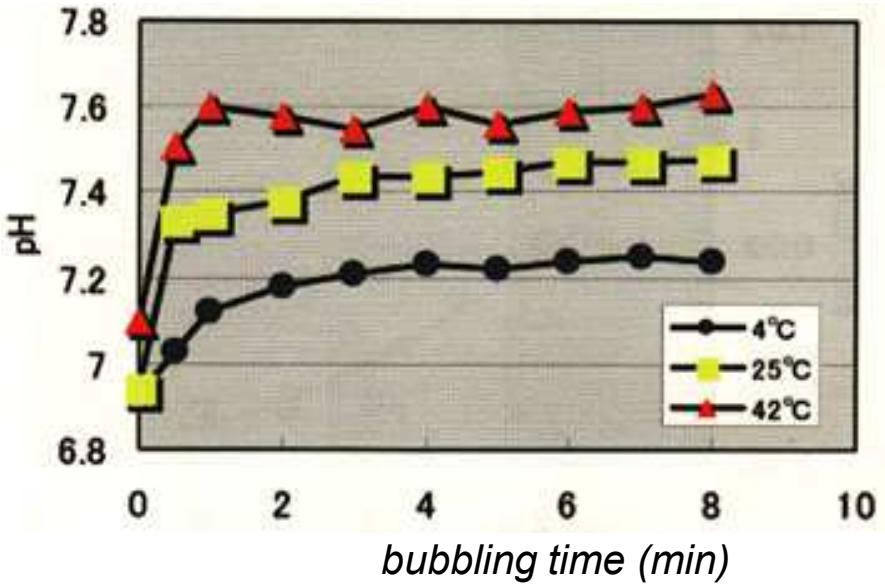
cf: viscosity ∝ molecular weight
break of hydrogen bond
→ smaller water clustering



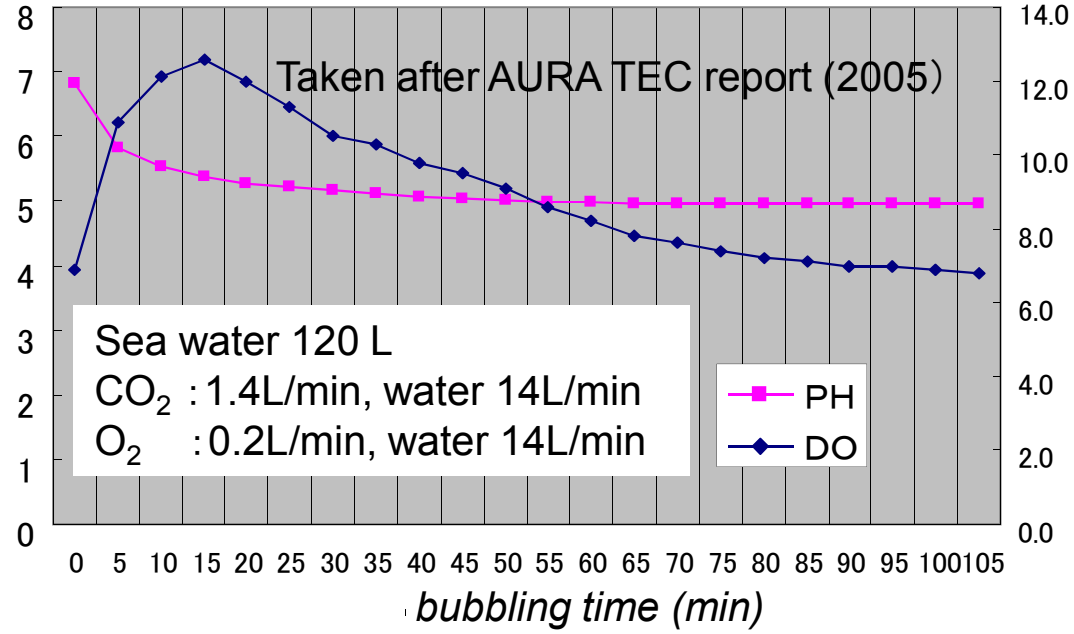
ionization of chemicals in water caused by bubbling

pH of water solution changes with different gas species by bubbling

air microbubble injection



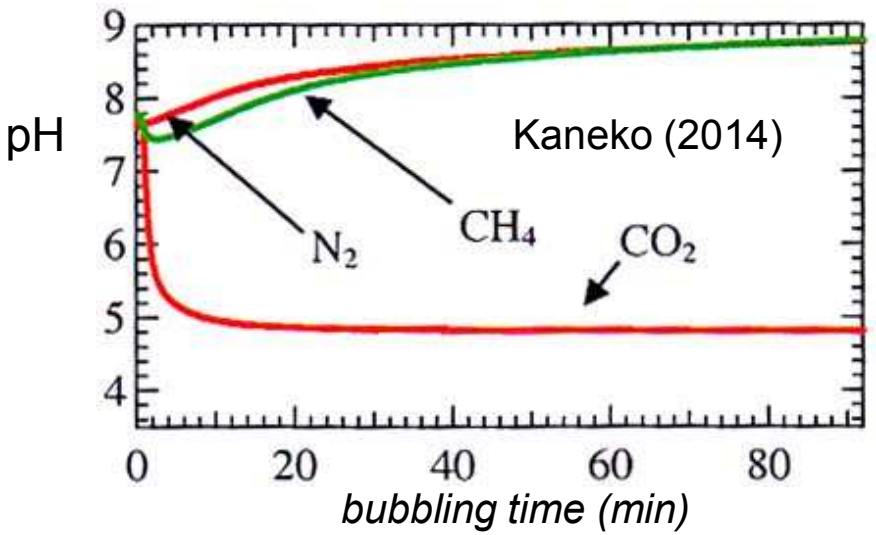
(CO_2+O_2) *microbubble injection*



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

cf. Air bubbling eliminates CO_2 and Cl_2 contained in tap water

(Himuro: J. Chem Eng.,Vol.71, No.3, 2007)

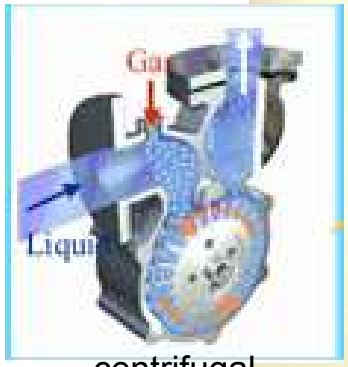


How to Generate Micro/Nano Bubbles

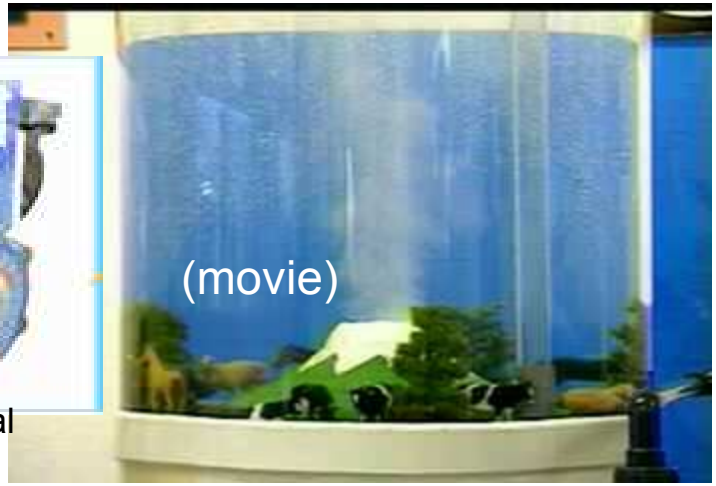
There are various types of fine bubble generators commercially sold with different designs, but mechanisms used are however classified into shear flow, nucleation, cavitation and bubble break down by shockwave. Combination of these separate mechanisms is possible. A few examples are typically shown below.

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.

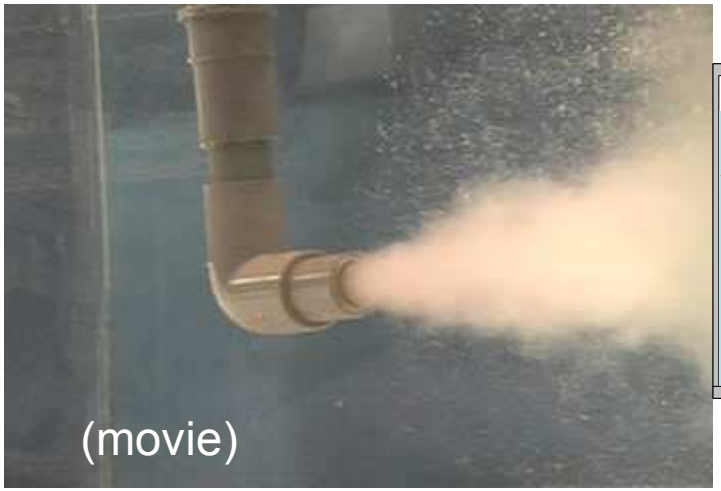


centrifugal pump



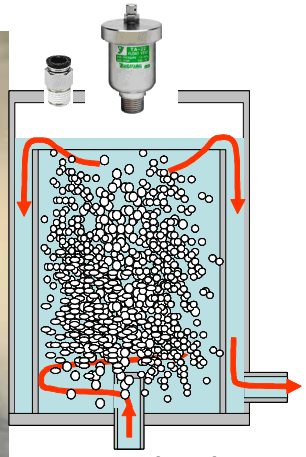
use of a high pressure (~7atg) pump

(Nikuni Co. Ltd.)



use of a low pressure (~3atg) pump

(Aura Tec Co. Ltd.)

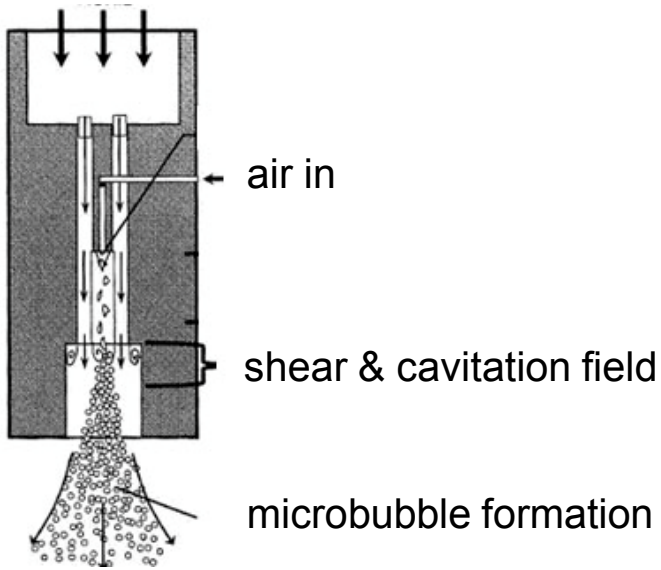


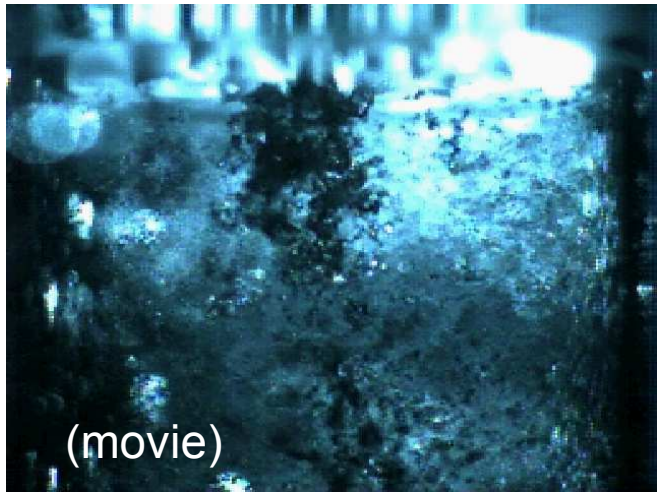
pressurized dissolver & accumulation tank

Shear flow type

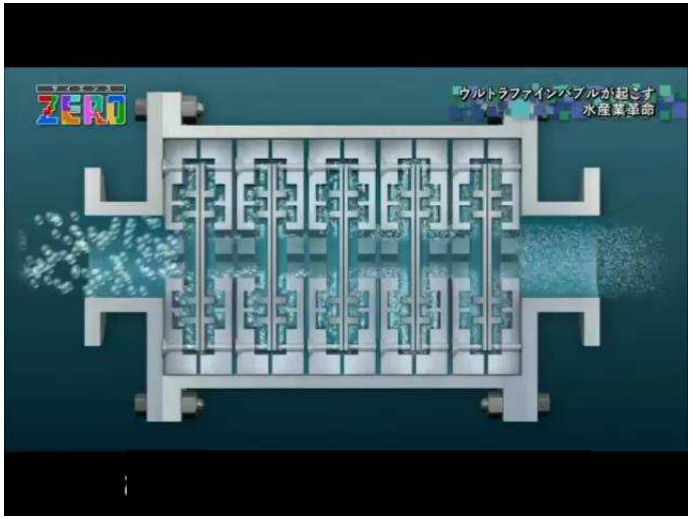
- Gas flow is broken down into fine bubbles by shear force.
- High pressure pump is difficult to use for ejection type generator because of air suction problem.

ejection type





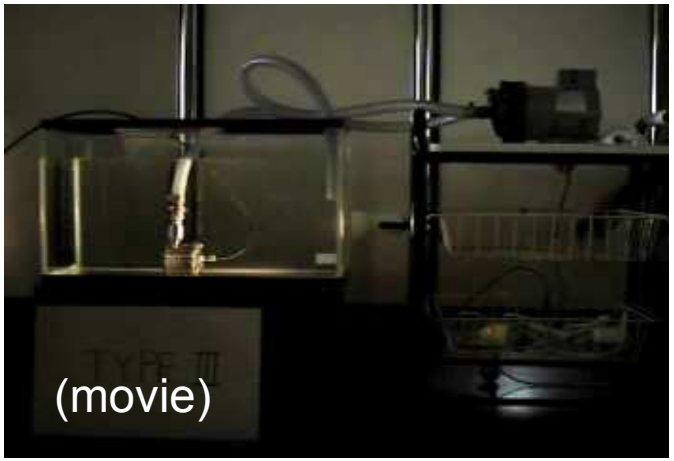
sophisticated honeycomb structure



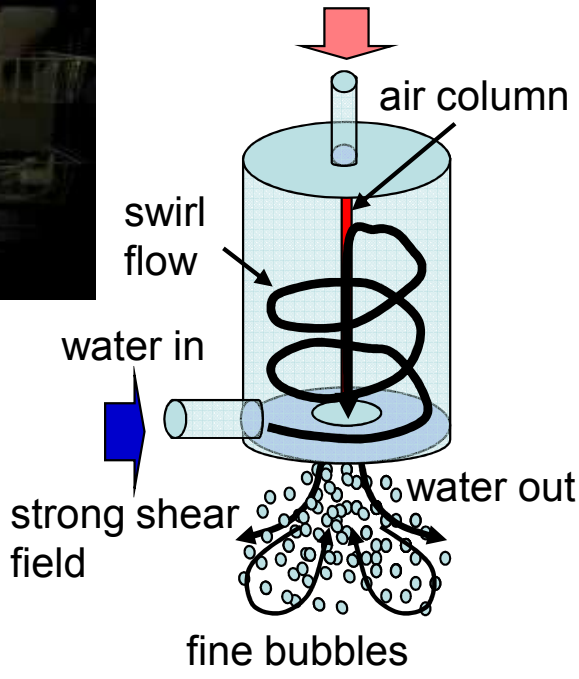
Swirl flow type (shear force)

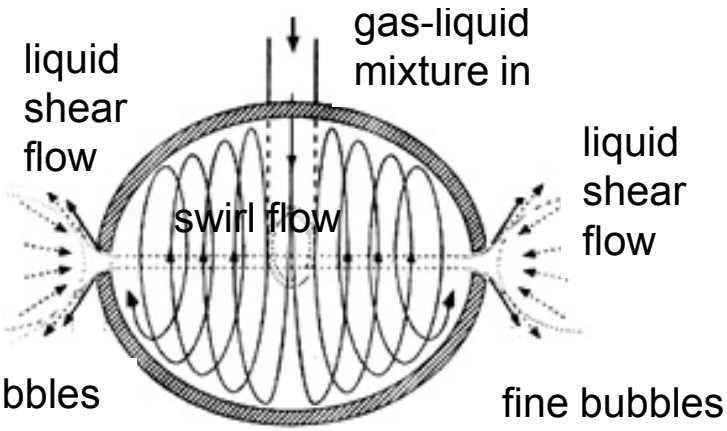
Water (or water-gas mixture) is running into the vessel in tangential direction to form swirl flow inside the vessel. This swirl flow induces negative pressure along the centerline of the vessel, which in turn sucks the air from the top of the vessel (left side picture). Air column is then torn off into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

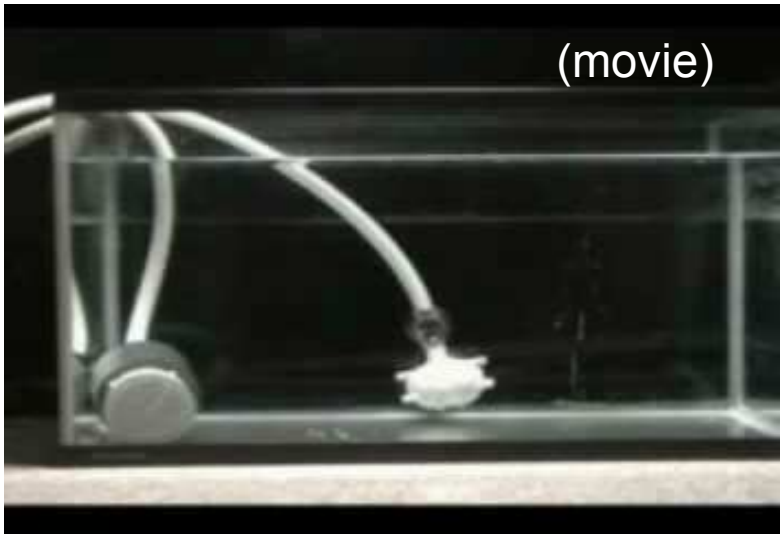
- simple structure
- low cost
- fairy low bubble number density



single exit (Aura Tec)



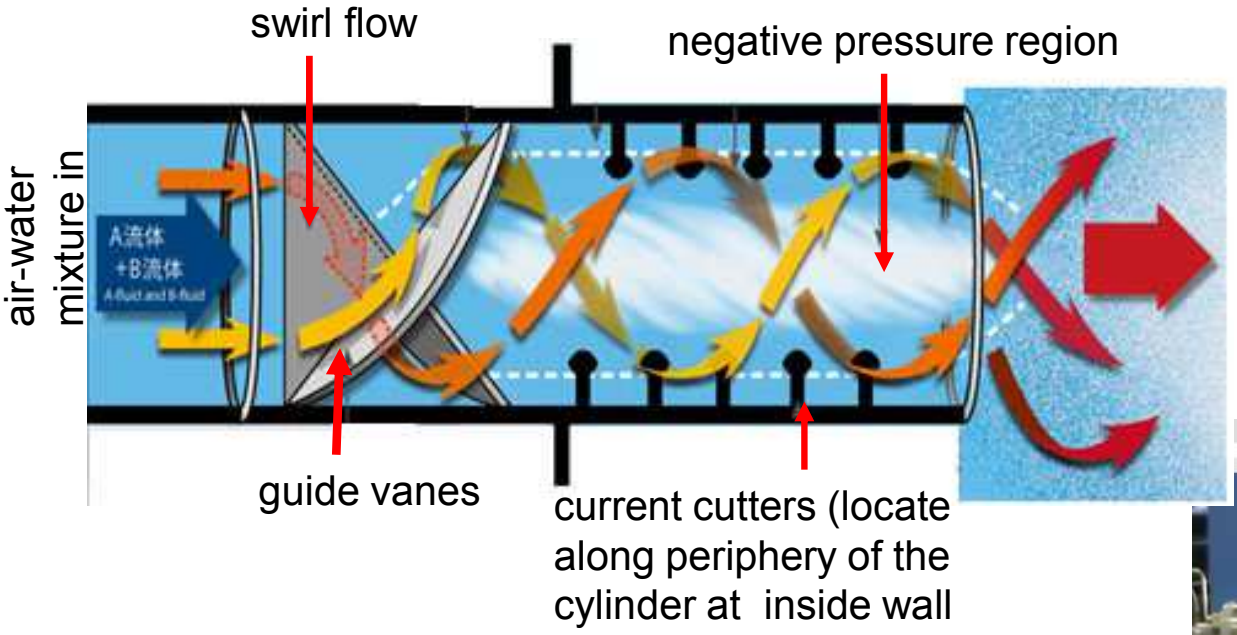




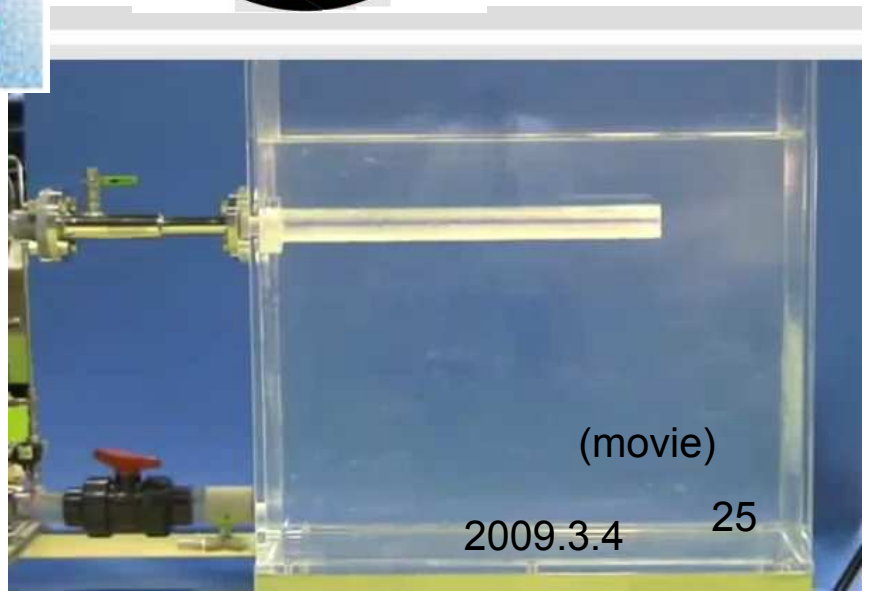
Double exits (Yamaguchi Univ.,)

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)



(movie)

Application of Micro/Nano Bubble Technology

Several typical examples of application of micro/nano bubble technology in specific fields such as

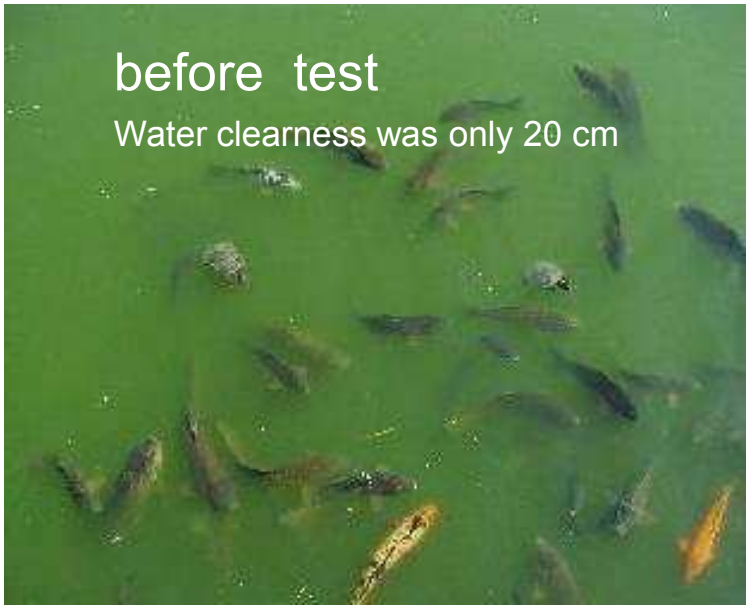
- *environments*
- *agriculture*
- *aquaculture*

will be briefly mentioned.

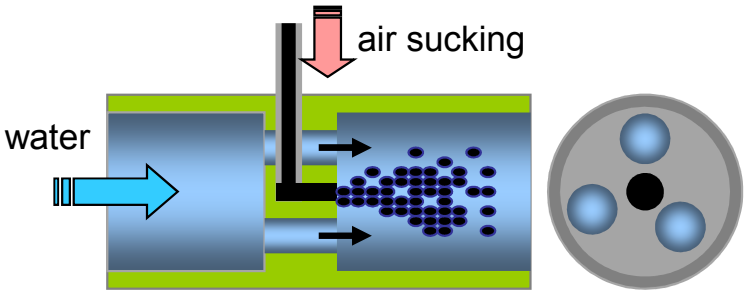
Application in Environment Protection-I

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

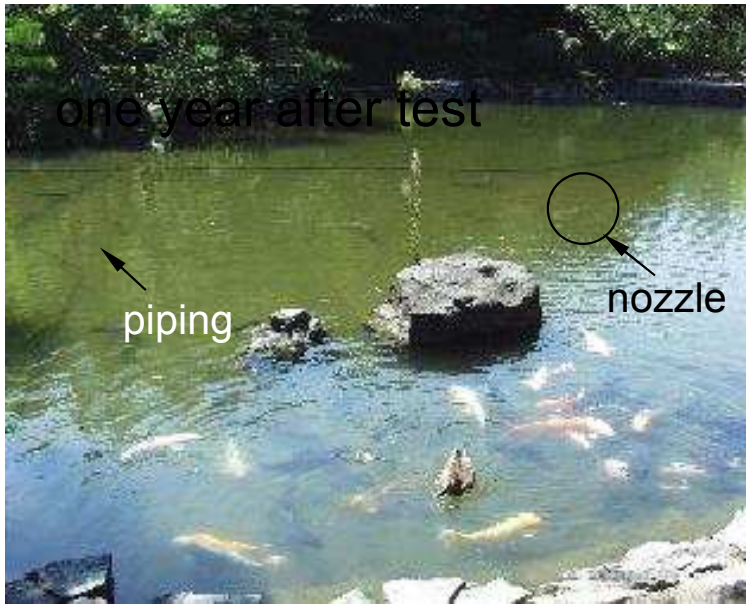
Use of micro bubble injection



After two months' operation, the water was made so clear that all fishes in the pond (1300 m^2) were visible.



Ejection type nozzle



Purification mechanisms

floatation

\+

Sterilization

\+

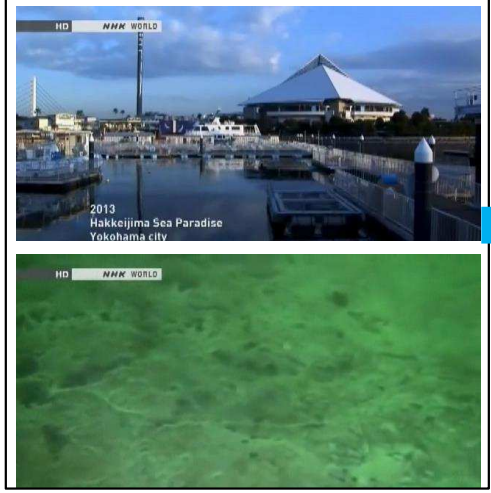
Oxygen supply

(By courtesy of Aura Tec Co Ltd.)

Purification of sludge at sea bottom

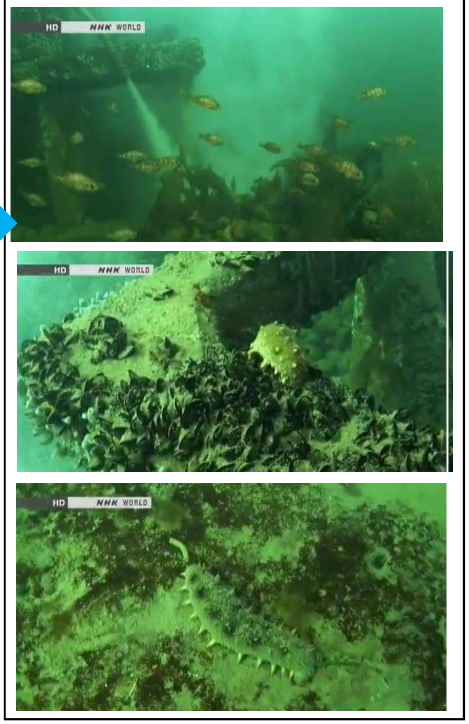
Nano bubbles are easy to shrink when they are injected into nearly sea bottom because of increased ambient pressure. Thus, the air is successfully supplied to sludge in a form of nano bubbles. This phenomenon has been successfully applied to recover poor oxygen condition at the bottom through fresh air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

Test place in Yokohama and view of sludge

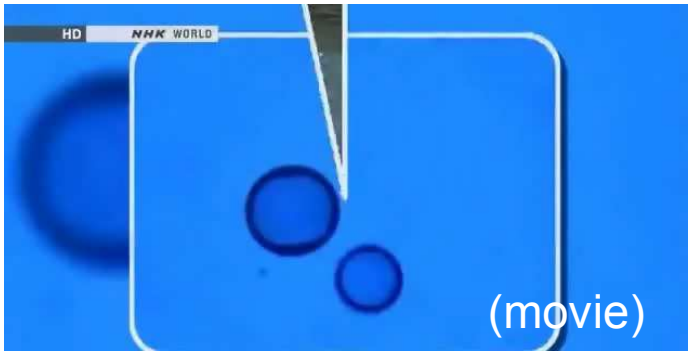


Ceramic nozzles & sea water before test

Revived sea water and fishes after test



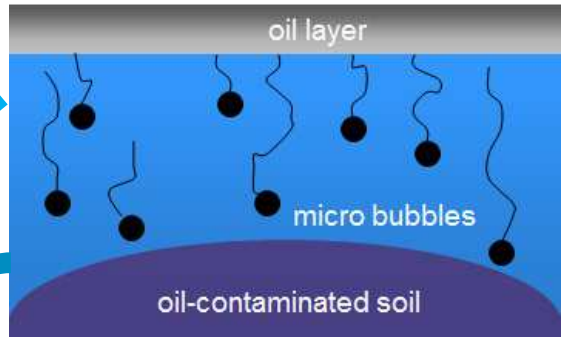
Shrink & vanishment of Oxygen nano bubbles



Copied from NHK World TV program (2014.3.3)

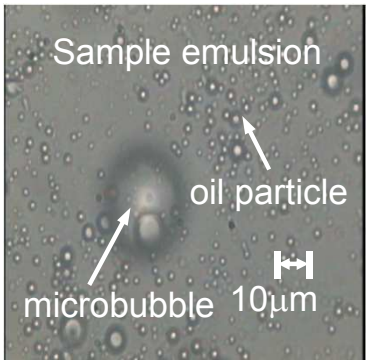
Purification of oil-contaminated soil by flotation

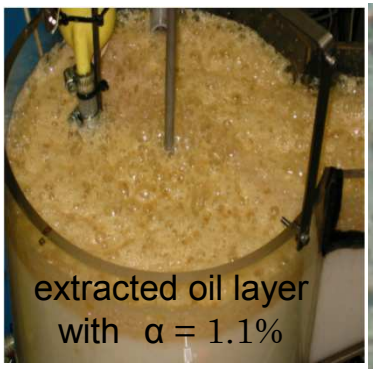
Stage 1: to extract oil from contaminated soil

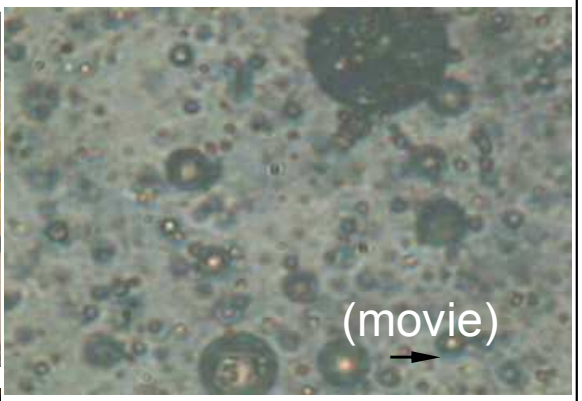


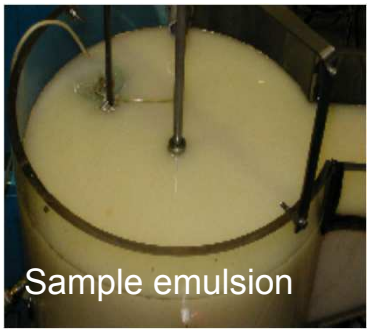
Condensed oil component after processed

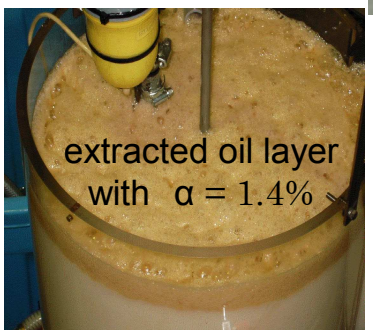
Stage 2: to separate oil from oil/water emulsion

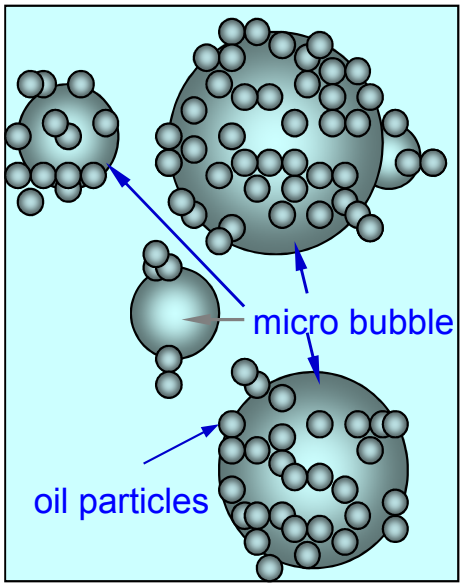


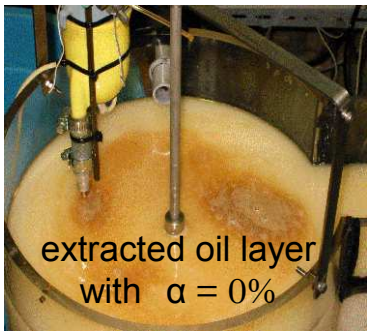


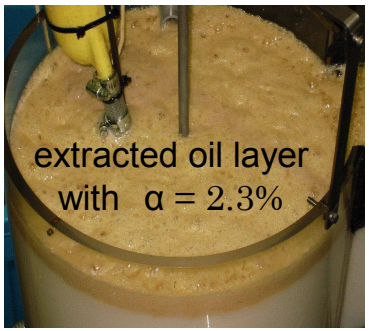










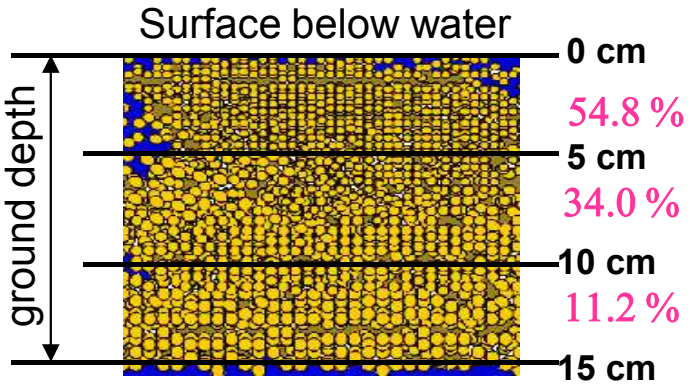


70~80% oil was successfully extracted from oil-contaminated soil by flotation effect of microbubble

Environment - Ⅳ

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

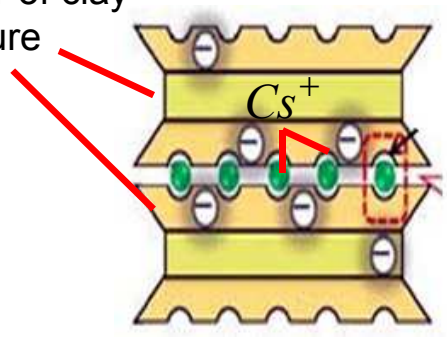
What depth is the most seriously contaminated by Cs?



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

How contaminated?

a layer of clay structure



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).

How remove Cs?

Classification of clay particles takes place effectively depending on particle size.

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)

Original video copied from Interim Report Video (2006), Miyagi Women's University, Institute of Living and Environmental Science

- 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

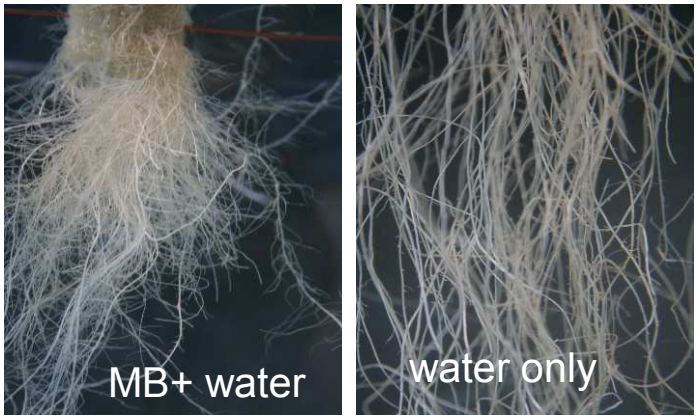
→ Good harvest without chemicals nor fertilizer

Application in Agriculture –Ⅲ

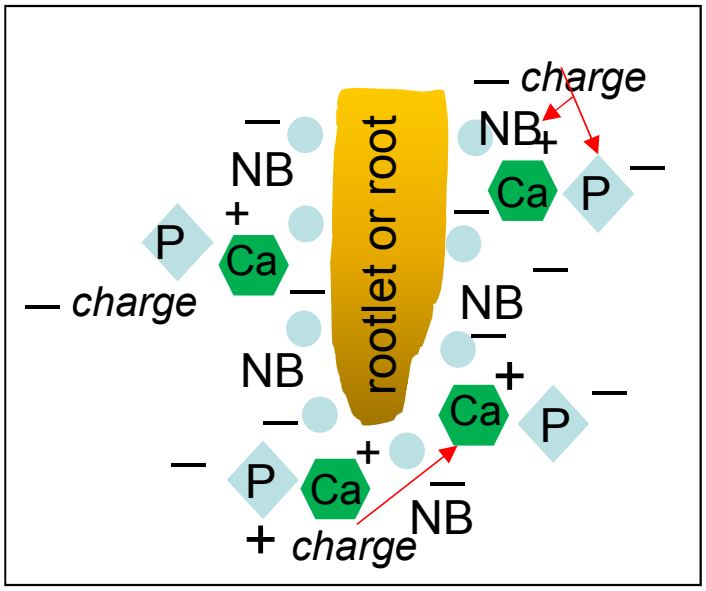
Enhanced growth of vegetables by fine bubble -water splash

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



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 of fine bubble technology in marine product industry and fishery

objective	*available system*
Shellfish culturing	*oyster, scallop, pearl oyster, abalone*
Fish culturing	*red sea bream (red tai), prawn, shrimp*
Quality preservation/ improvement for marine products	*oyster:* wash and clean after picking up *Scallop*: prevention of meat hardening *Prawn/shrim*p: 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

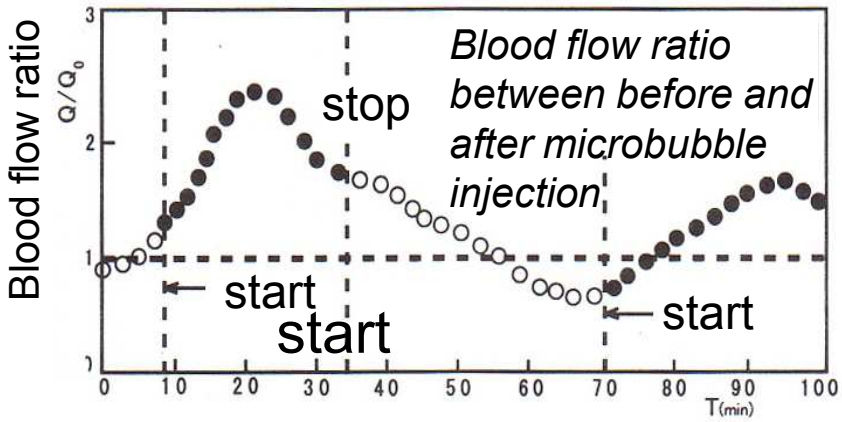
Fine bubble technology is expected to bring about prospective future possibility in sustainable marine product industry and fishery including all kinds of aquaculture.

Application in Aquaculture – Ⅱ

Disease control and enhancement of growth rate

Disease control :

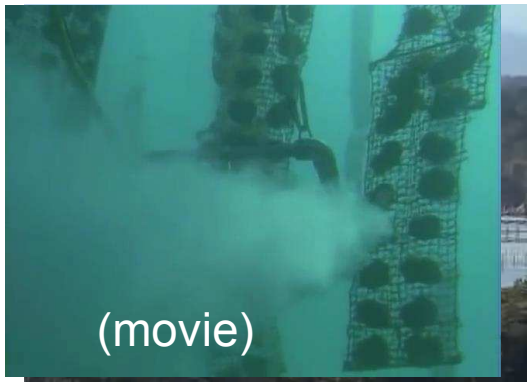
➡ Applicable to prawn or shrimp farming



Time elapsed (min)

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.

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

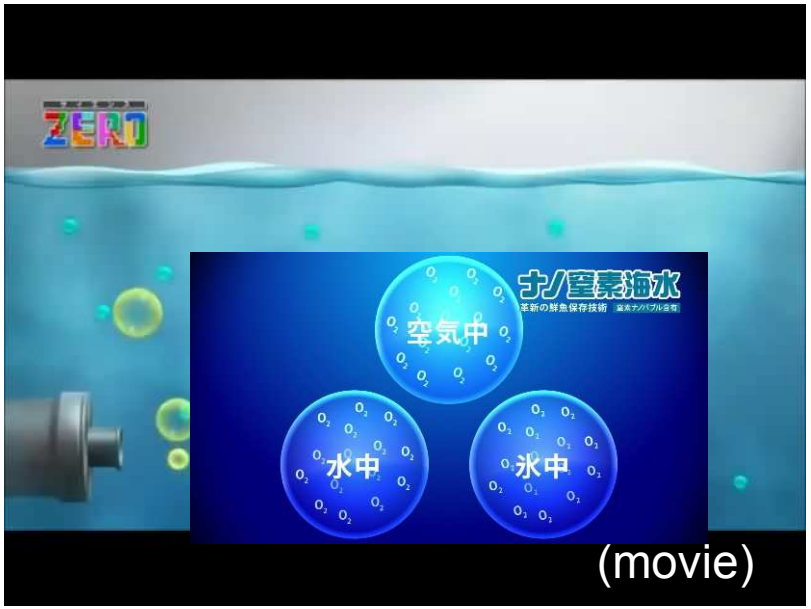
- to create extremely oxygen–deficient environment for fishes
  1) replace oxygen in water and ice with nitrogen by bubbling in a form of nano bubbles
  2) dissolved nitrogen can penetrate into fish meat through skin and visceral

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

Fishes treated with nitrogen nano bubble-sea water

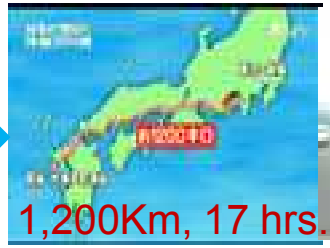


How to obtain sea water with low oxygen content

Application in Aquaculture – Ⅳ

Long distance transport of live fishes by letting them asleep

Findings:
- *In highly CO_2 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 CO_2 dissolved sea water makes fishes asleep. To maintain branchial respiration, O_2 nano bubbles injected into sea water

Fishes wake up in normal sea water

Even after a long journey, fresh taste is kept

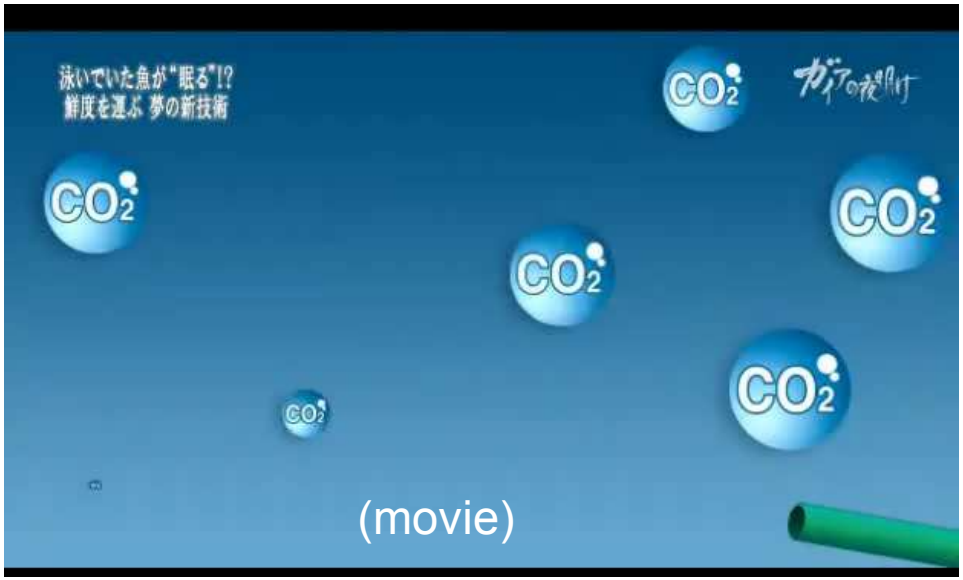


Image of branchial respiration of fishes

Demonstration of fish sleeping and awaken

Application in Aquaculture – V

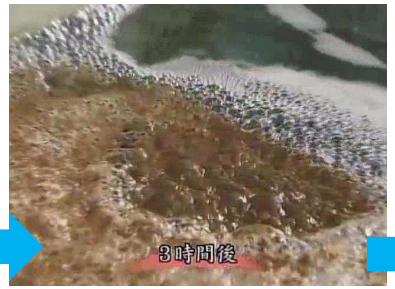
Wash and clean oyster meat in shell by microbubble cleaning

Oysters in carrying basket

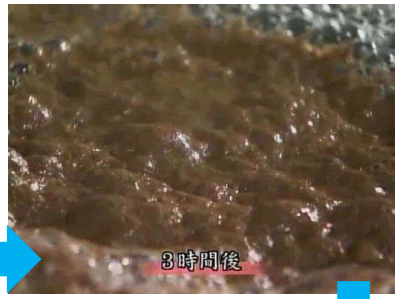
Put them into sea water

Microbubble purging

Foam of foreign particles taken off from oysters



Enlarged picture



Oyster meat after cleaning

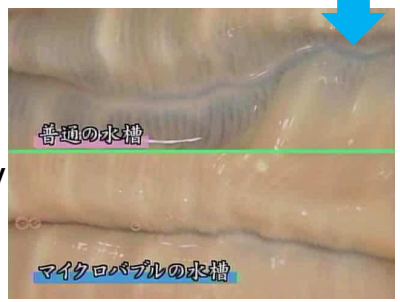
Right: washed by sea water

Left: washed by micro-bubbly water

Oyster meat (enlarged)

Upper: by sea water

lower: by micro- bubbly water



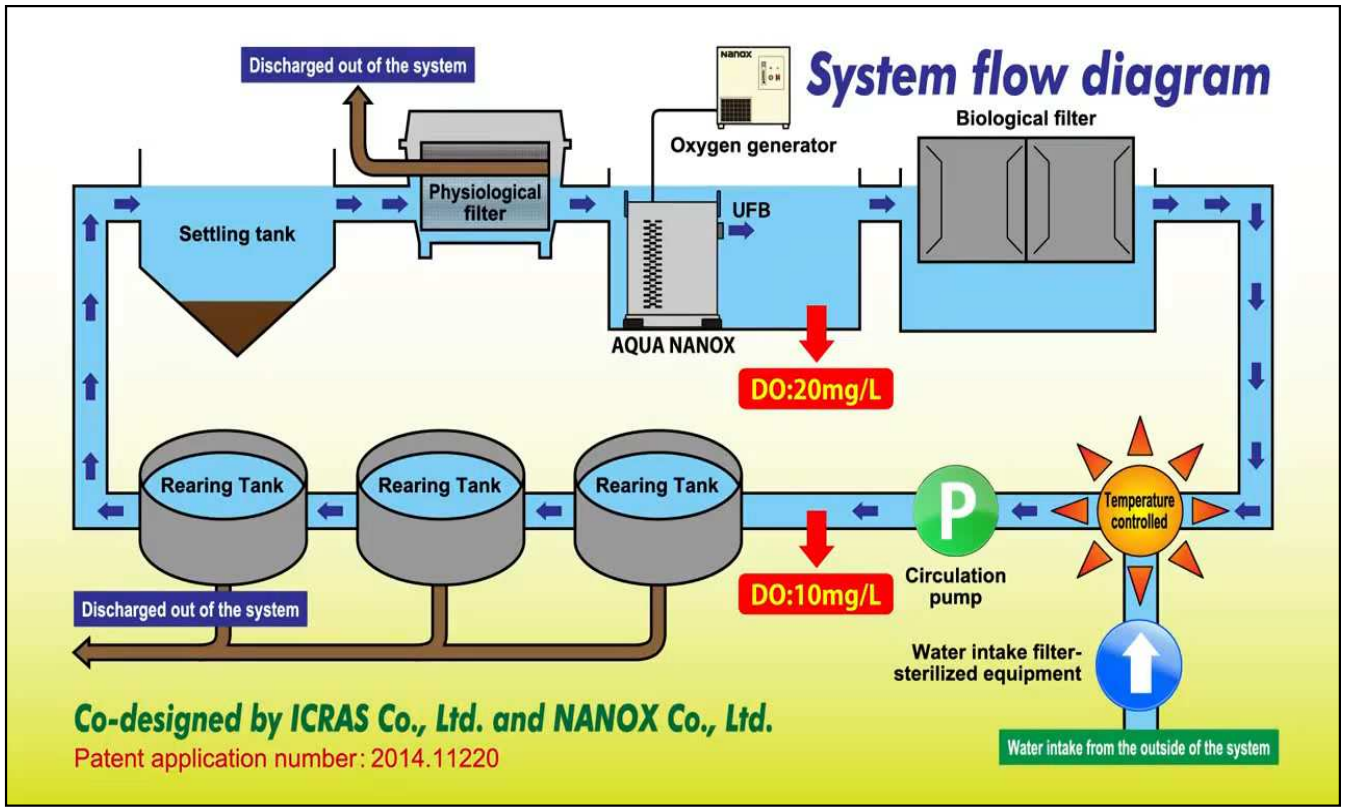
Microbubble cleaning clearly removed the stains from oyster meat in shell.

Taken from You Tube: What are micro/nano bubbles? Surprising power of fine bubbles (2010/5/12)

Aquaculture – Ⅵ

A closed recirculation aquaculture system using oxygenated nano bubbles

Edited from http://nano-x.co.jp (movie)



- High productivity and stable production
- Reducing costs significantly
- expected to be applied to various fish species

Merit:

① to keep high dissolved oxygen to accelerate growth

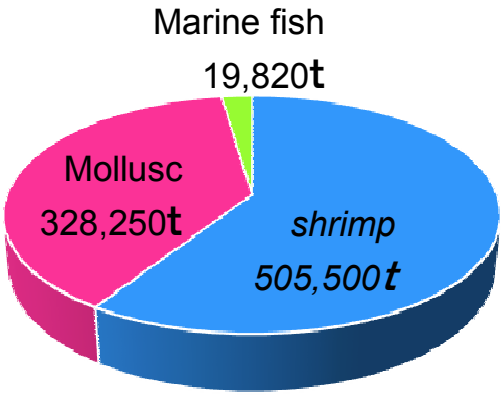
② bactericidal effect of nano bubbles inhibits the growth of bacteria in rear water ➡ safe method (sterilization using electrolyzed water or ozone involves residual chlorine and oxidant or oxidant).

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

A future prospect of shrimp farming using fine bubbles

Inshore fishery in Thailand (2010)



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

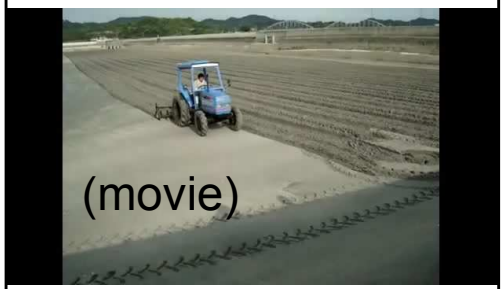
Causes of deteriorated water quality and poor bottom environment of breeding pond are:
over bait　corpse & exuvia　excreta

Inshore-based + land-based

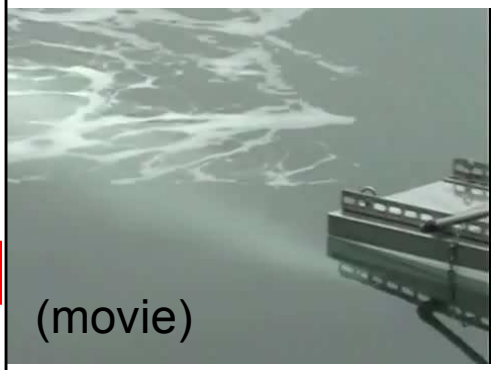
stirring paddle to increase DO

Land-based

shrimp pond design to collect biological waste



tillage of water bottom sediment



microbubble injection to improve water quality

No results reported yet

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

promising

kuruma-ebi

Merit of using ozone bubbles

Characteristic features of ozone are:

1) Strong oxidation ability
   Ozone (O_3) is chemically unstable and changes to stable oxygen O_2 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.

temp (C)	solubility in water (mg/ 100gwater)	
	ozone	air
0	89.4	3.80
5	34.3	3.33
10	29.9	2.88
15	25.9	2.62
20		2.32
25	18.9	2.14
30	7.7	1.98
35		1.89
40	4.2	1.78
50	0.6	
60		0.219

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

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

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