



«A new approach for the
removal of persistent
compounds from
wastewaters:
hydrodynamic cavitation»

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Information Engineering,
and of Economy (DIIE)

*Pilot technology for aerobic
Biodegradation of spent
TMAH Photoresist solution in
Semiconductor industries*

May 31th, 2017



Funded under the European Union's
Life Programme grant agreement
N. LIFE15 ENV/IT/000332
ENV/IT/000332



«A new approach for the removal of persistent compounds from wastewaters: hydrodynamic cavitation»

World water forum



The 8th World Water Forum will be held in Brazil, in the city of Brasília, March 18 to 23, 2018, and it will be the first time a World Water Forum is held in the Southern Hemisphere.

Growing populations have led to greater water needs and at the same time to pollution of natural water resources



Delhi
Photograph by Jonas Bendiksen,
National Geographic

An emerging environmental concern

RESEARCH ARTICLE

SUSTAINABILITY

Four billion people facing severe water scarcity

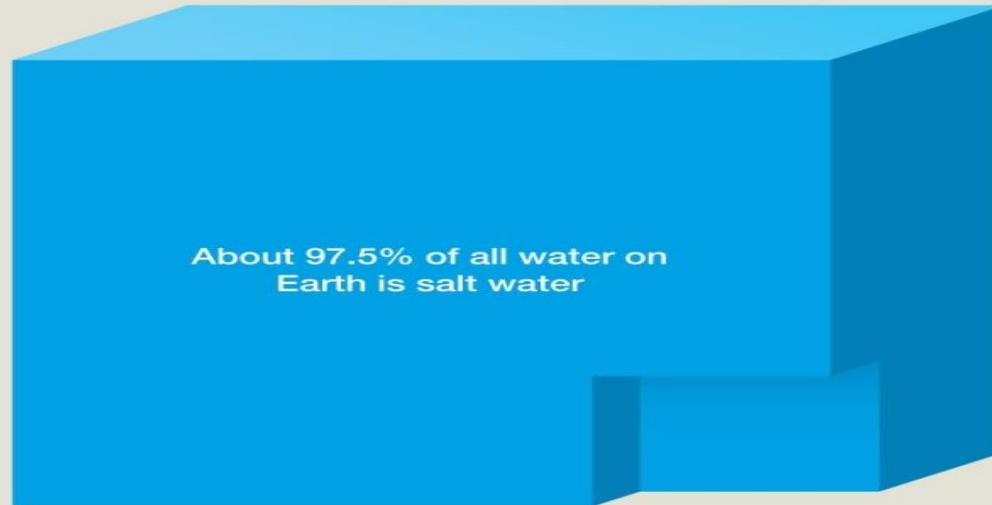
Mesfin M. Mekonnen* and Arjen Y. Hoekstra

Freshwater scarcity is increasingly perceived as a global systemic risk. Previous global water scarcity assessments, measuring water scarcity annually, have underestimated experienced water scarcity by failing to capture the seasonal fluctuations in water consumption and availability. We assess blue water scarcity globally at a high spatial resolution on a monthly basis. We find that two-thirds of the global population (4.0 billion people) live under conditions of severe water scarcity at least 1 month of the year. Nearly half of those people live in India and China. Half a billion people in the world face severe water scarcity all year round. Putting caps to water consumption by river basin, increasing water-use efficiencies, and better sharing of the limited freshwater resources will be key in reducing the threat posed by water scarcity on biodiversity and human welfare.

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World fresh water supply

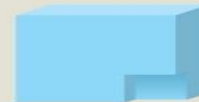


Only 2.5% of all the water on Earth is fresh water

Around 70% of fresh water is frozen in Antarctica and Greenland icecaps



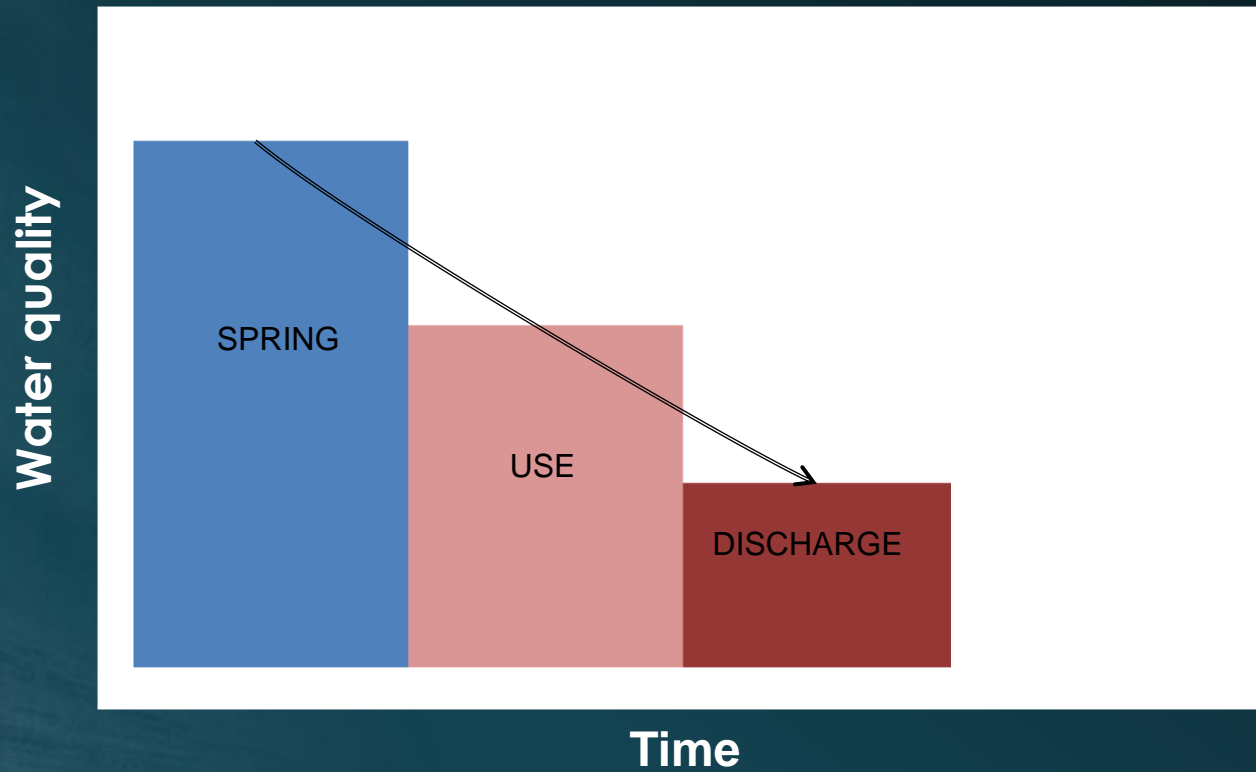
Most of the remaining freshwater lies too deep underground to be accessible or exists as soil moisture



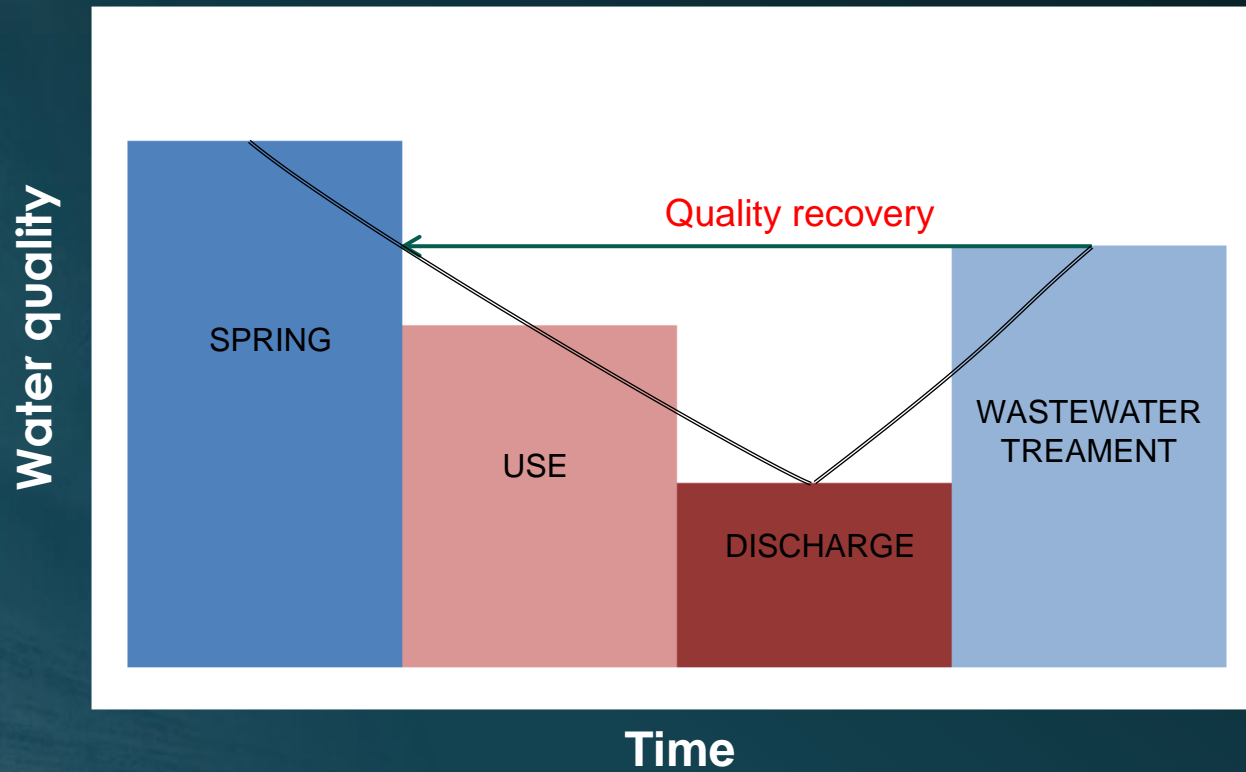
Only 1% of the earth's fresh water is available for withdrawal and human use



OPEN CYCLE → CLOSED CYCLE



OPEN CYCLE → CLOSED CYCLE



Industrial Reuse & Urban Uses

- **Industrial Recycling and Reuse**

- Cooling water
- Boiler feed
- Process water
- Heavy construction

- **Non-Potable Urban Uses**

- Fire protection
- Air conditioning
- Toilet flushing

- **Potable Reuse**

- Blending in water supply reservoirs
- Pipe-to-pipe water supply
- irrigation

- **Groundwater Replenishment**

- Groundwater recharge
- Saltwater intrusion control
- Subsidence control



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Chemical Engineering Journal

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

Process analysis applied to water reuse for a “closed water cycle” approach

Marina Prisciandaro^{a,*}, Mauro Capocelli^b, Vincenzo Piemonte^b, Diego Barba^b

^aDepartment of Industrial Engineering and Information and of Economy, University of L'Aquila, Viale Giovanni Gronchi 18, 67100 L'Aquila, Italy
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What is the key factor in water reclamation?

The removal of all
undesired and toxic
constituents must be
complete

REUSE + ENVIRONMENTAL
PROTECTION



ADVANCED TREATMENT

Constituents in Reclaimed Water

- **Conventional (mg/L)**

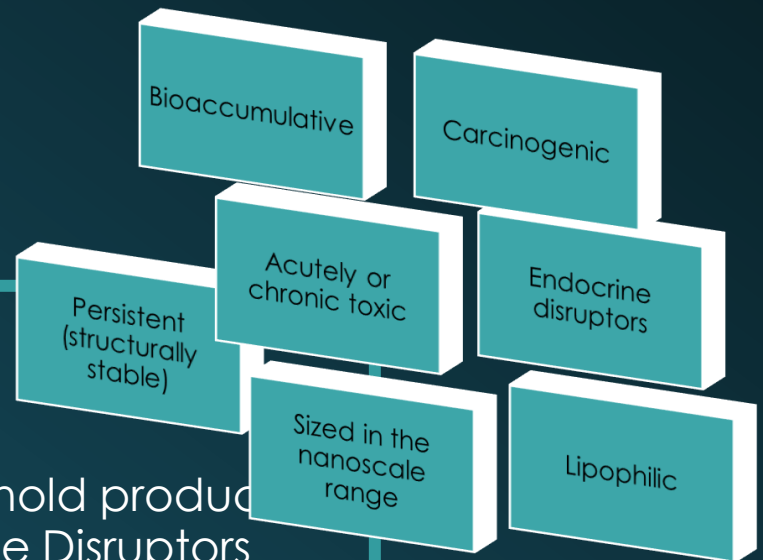
- TSS
- BOD; COD
- TOC
- Nitrogen (Ammonia; Nitrate; Nitrite)
- Phosphorus
- Microorganisms: Bacteria; Viruses ; Protozoan cysts & oocysts

- **Non-conventional**

- VOC
- Surfactants
- Metals
- TDS

- **Emerging ($\mu\text{g/L}$)**

- Refractory organics
- Antibiotics (veterinary & human)
- Home-care, industrial, and household products
- Hormones (steroids) and Endocrine Disruptors





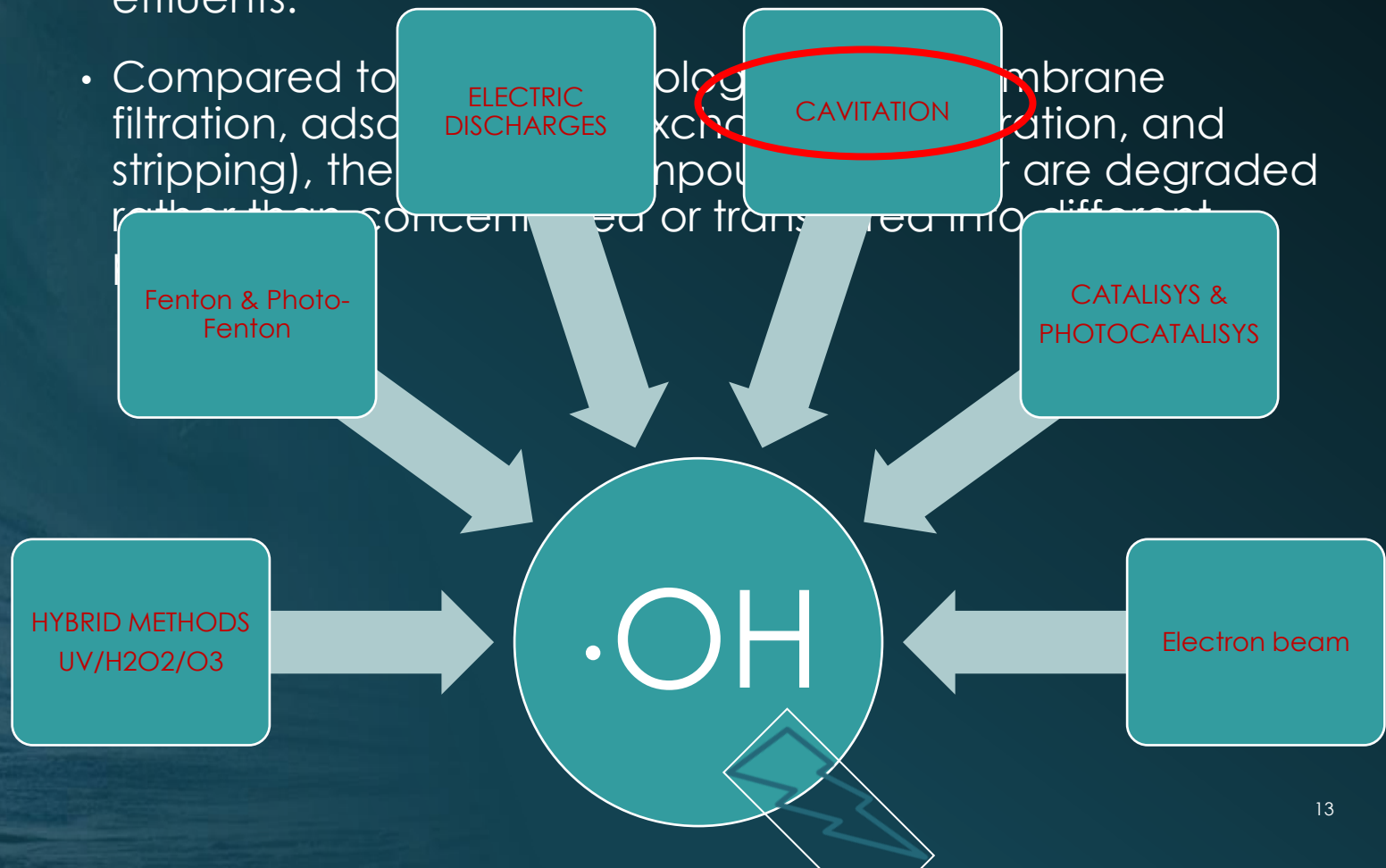
ADVANCED OXIDATION PROCESSES

*«A new approach for the removal of
persistent compounds from
wastewaters:
hydrodynamic cavitation»*

Advanced Oxidation Processes


- Advanced oxidation is used for various applications in wastewater treatment, water reclamation, indirect potable water reuse, drinking water production, and recently in micro-pollutant control of sewage treatment effluents.

- Compared to biological processes (e.g., membrane filtration, adsorption, ion exchange, and stripping), the pollutants (micro-pollutants) are degraded rather than concentrated or transferred into different



·OH radicals

- Advanced oxidation processes (AOPs) have the ability to generate elevated concentrations of hydroxyl radical ·OH, a strong oxidant capable of complete oxidation of most organic compounds into carbon dioxide, water, and mineral acids or salts.
- The advantage of AOPs is the relative high reaction power of hydroxyl radical.
 - As a result of the high reaction power, reactions with OH radicals are very fast, often close to diffusion-controlled rates, and nonselective
- Due to the high oxidative and nonselective character of hydroxyl radicals relative to other oxidants, AOPs enable the conversion of non-biodegradable into biodegradable compounds as well as the generation of undesirable by-products.
 - Therefore, AOPs often need careful control of oxidant dose and/or strategies to avoid or minimize by-product formation.
 - As a consequence, each application needs feasibility studies in laboratory and pilot scale before applying.

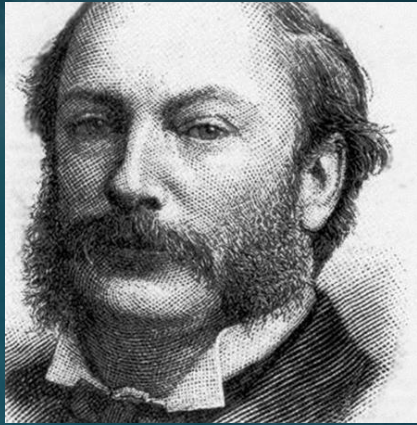


ULTRASONIC & HYDRODYNAMIC CAVITATION

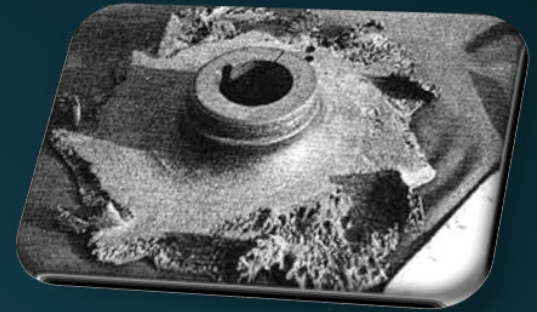
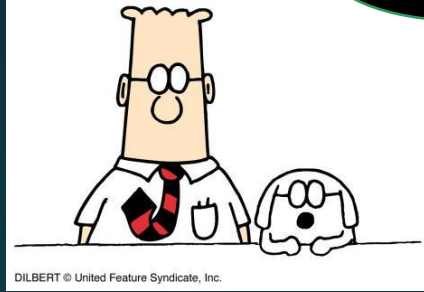
*«A new approach for the removal
of persistent compounds from
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hydrodynamic cavitation»*

Sonolysis_ the Sonoc...

PERFORMANCE REDUCTION
EROSION-DAMAGES



**John William Strutt, 3rd
Baron Rayleigh**
(1842 – 1919)



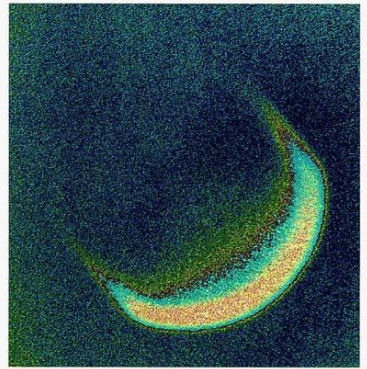
Earlier investigations dealing with hydrodynamic cavitation have been mainly directed towards avoiding it, e.g. cavitation erosion of propeller blades of ships



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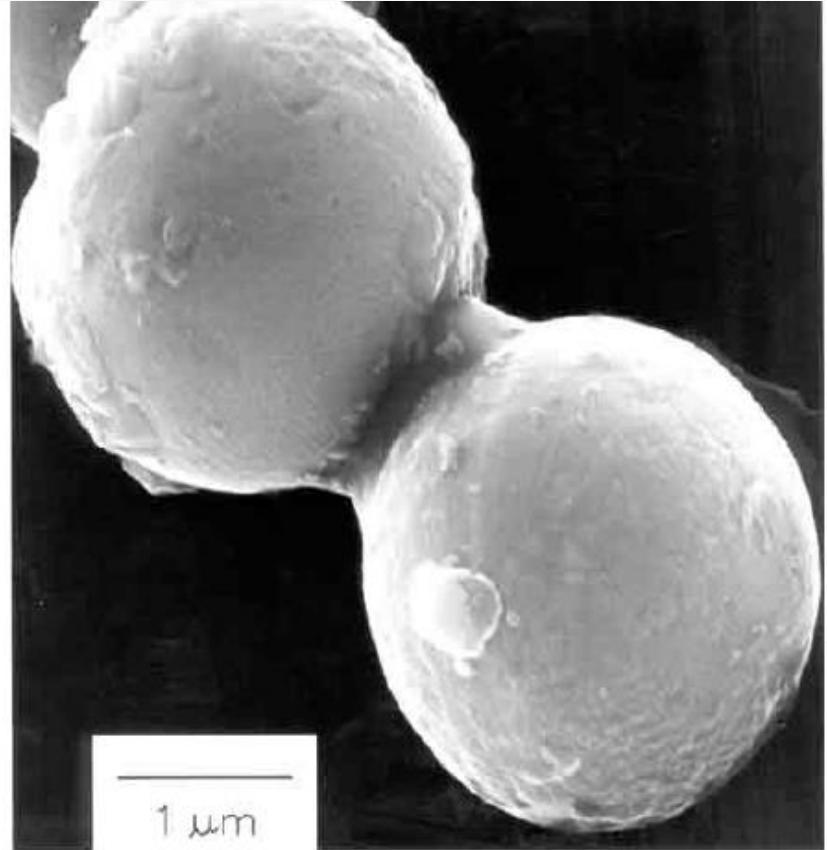
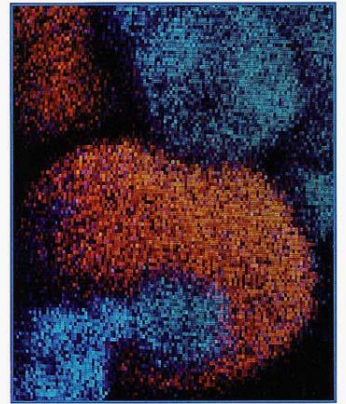
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VOL. 30 • PAGES 1325-1426



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23 MARCH 1990 \$3.50
VOL. 247 • PAGES 1275-1320
PART 1



25 July 2002

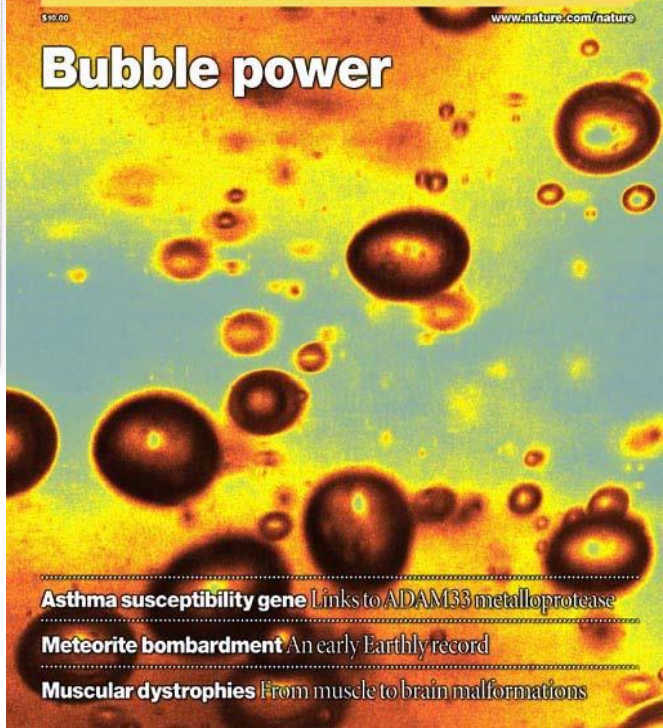
International weekly journal of science

nature

\$10.00

www.nature.com/nature

Bubble power



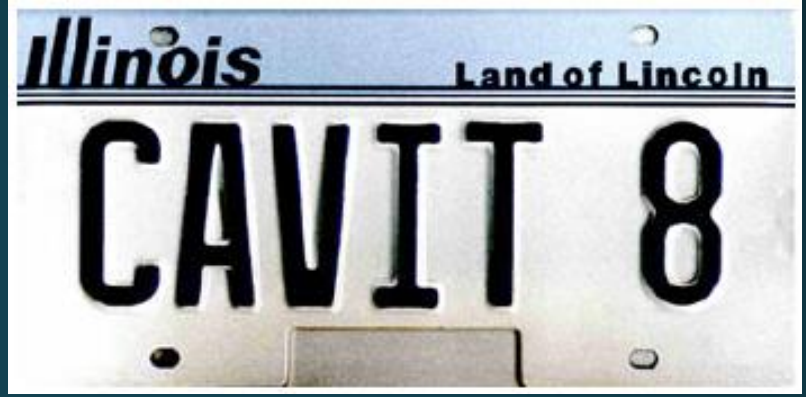
Asthma susceptibility gene Links to ADAM33 metalloprotease

Meteorite bombardment An early Earthly record

Muscular dystrophies From muscle to brain malformations

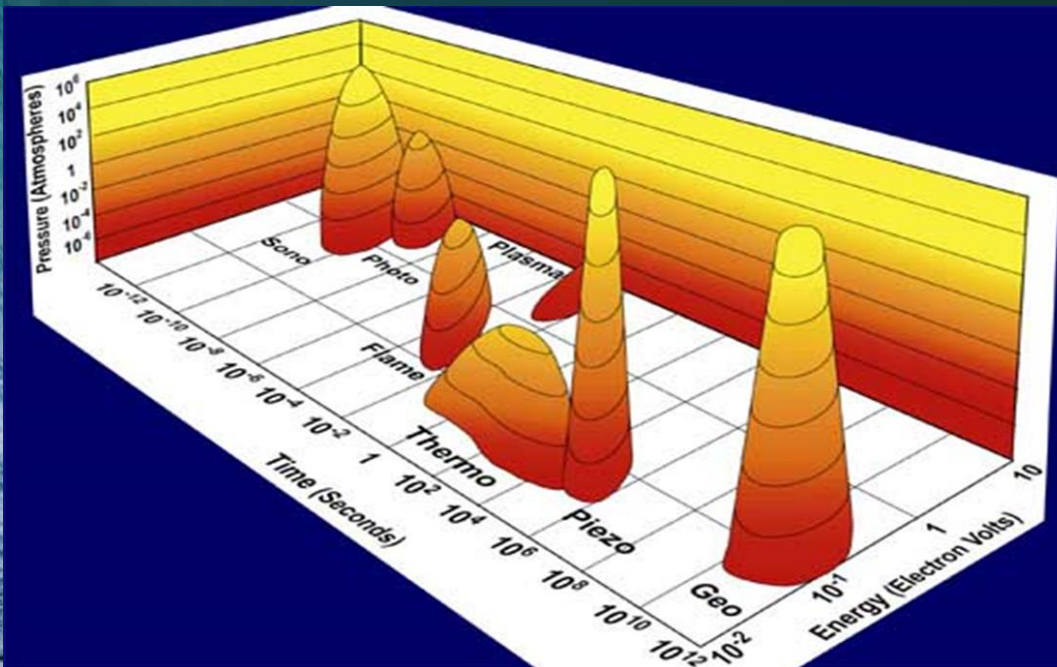


Kenneth S. Suslick
Dept. of Chemistry
University of Illinois



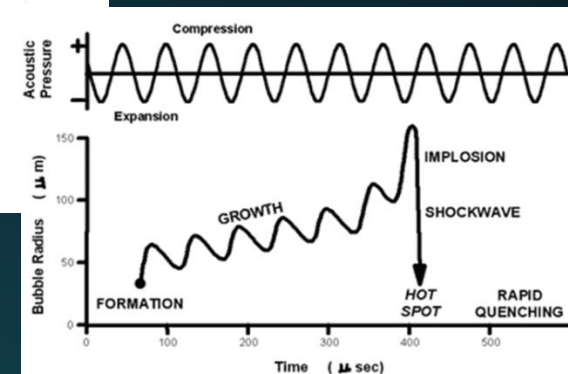
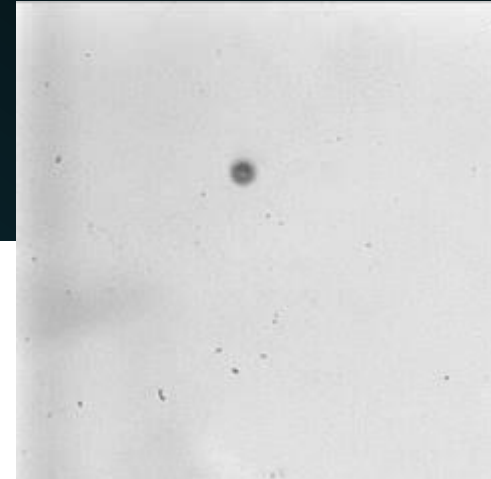
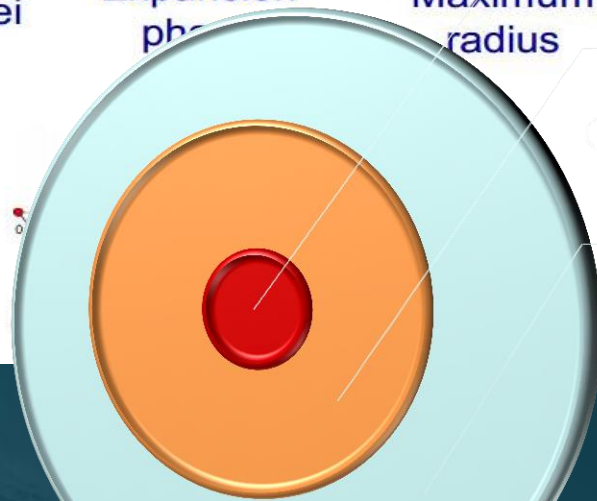
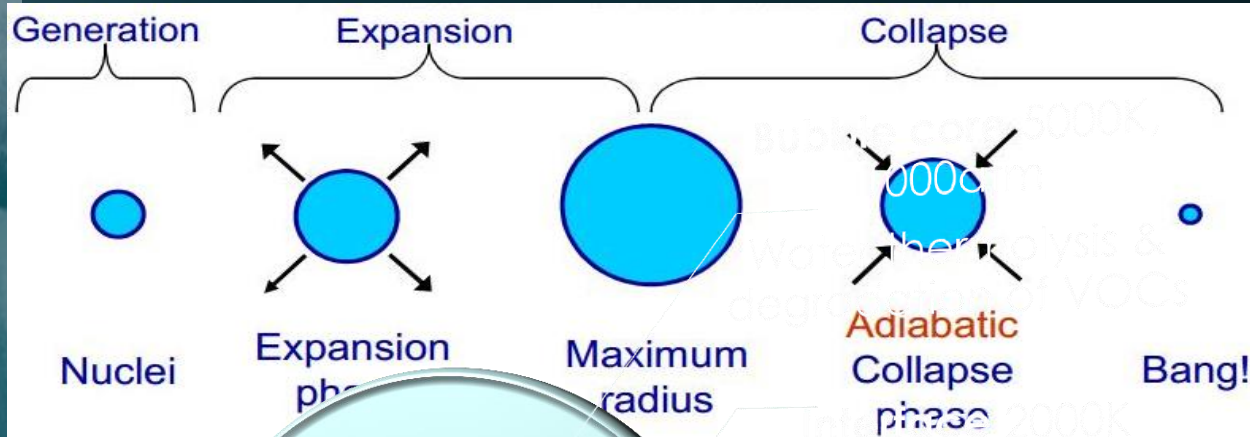
Cavitation

- Mechanism of Oxidation of pollutants
- Cavitation phenomenon includes vapor bubble formation and collapse in water.
- During bubble collapse, extreme local temperature and pressure conditions are reached and radical species, particularly $\cdot\text{OH}$ radicals, are released thanks to the dissociation of trapped water molecules



- ❑ High Magnitude Pressure Pulse, 100-5000 atm
- ❑ Extremely high Temperatures, 1000-15000 K
- ❑ Velocity in excess of 2-3 times that of sound in the case of compressibility media
- ❑ High energy densities 1-10x 10^{18} kW/m^3

What is cavitation?



- The generation of nuclei is a nucleation process, homogeneous or heterogeneous, that takes place when the pressure falls below the vapor tension at that temperature (saturation conditions)

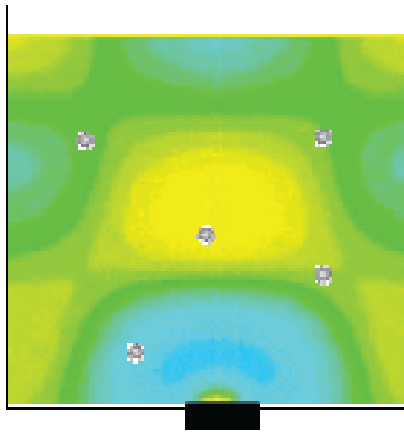


Nature also utilizes cavitation

- Use of Snapping Shrimp for actually visualizing hydrodynamic cavitation technique
- Study carried out at University of Twente, The Netherlands, indicated that the Snapping shrimp (*A. heterochaelis*) throws a cavity, which travels a certain distance and collapses.
- Aim of hydrodynamic cavitation reactors will be to replicate this natural phenomena but possibly at multiple locations simultaneously

Acoustic and Hydrodynamic Cavitation (HC)

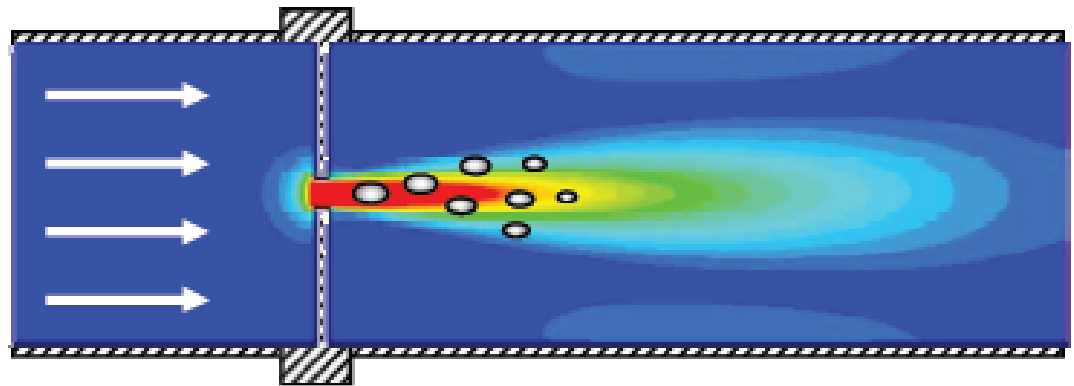
How is cavitation done?



Ultrasonic bath

Ultrasonic pressure field

Acoustic cavitation



Orifice plate

Turbulent fluctuating pressure field

Hydrodynamic cavitation



HYDRODYNAMIC CAVITATION

*«A new approach for the removal
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HC in WWT

In WWTP processes hydrodynamic cavitation (HC) conditions can be obtained by forcing water to pass through a constriction, such as an orifice or a convergent divergent nozzle.

Geometrical and operational parameters (flow conditions, device geometry, turbulence scale, rate of pressure recovery) directly influence bubble dynamics and chemical reactions in the various existent phases.

Because of the complexity of the system and the numerous interconnections between fluid dynamics, transport phenomena and chemistry, HC is still an open field of research

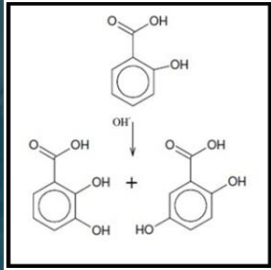


ADVANTAGES

- Energy efficiency
- Up-scalable
- Easy retrofit
- Low cost management
- Rugged and durable
- Suitable for hybrid methods
- Flexibility
- Huge theoretical background

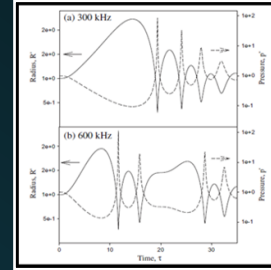


Investigation of HC



EXPERIMENTS

- Model compounds (dosimetry methods)
- New geometrical configurations
- Individuation of parameter effects



MODELING

- Kinetic modeling
- Single bubble dynamics
- Chemical reactions
- Nucleation
- Bubble population phenomena
- CFD computations

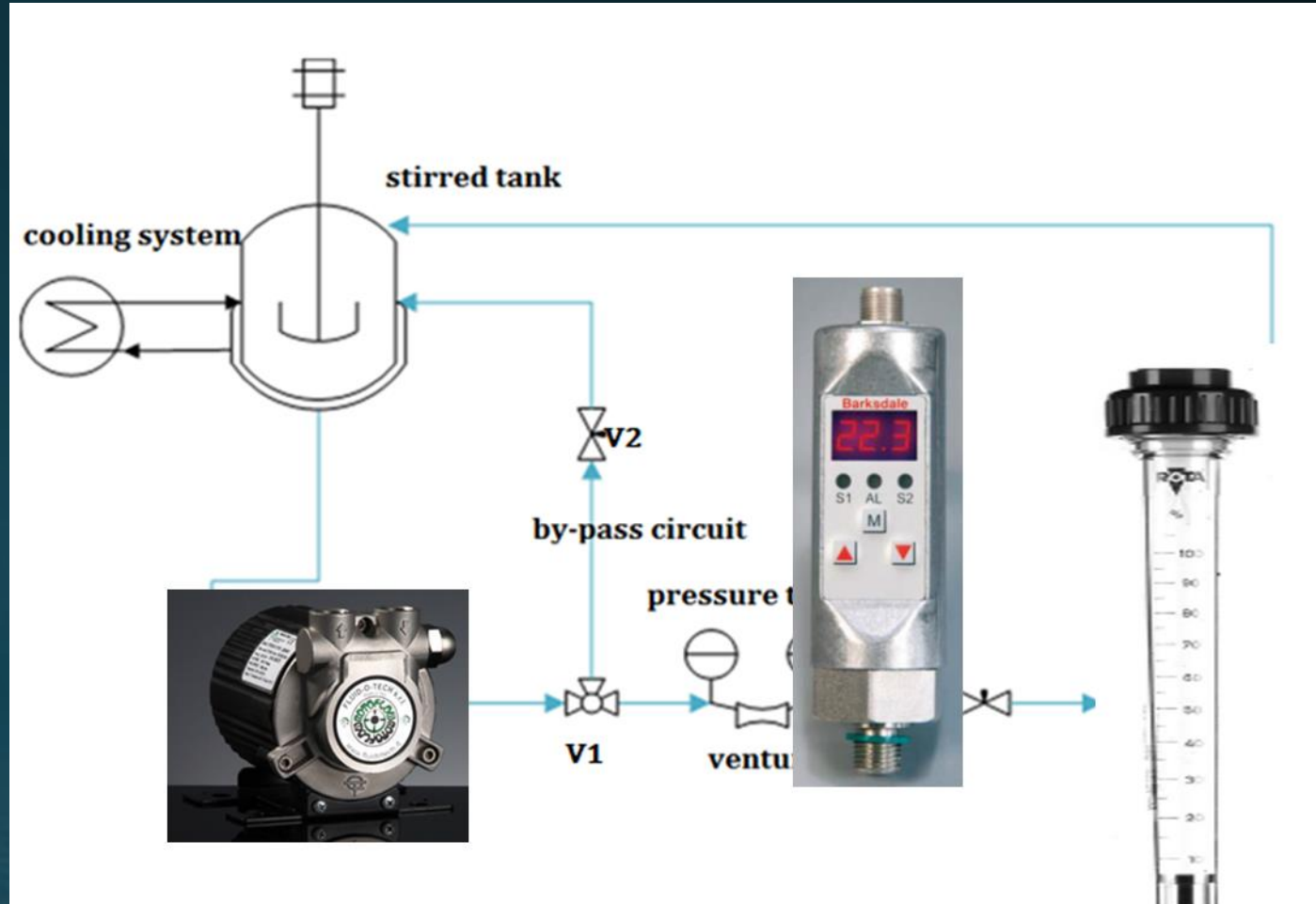
$$P_{collapse}, T_{collapse}, \cdot OH = C \left\{ R_0^\alpha \times P_{in}^\beta \times \left(\frac{d_o}{D} \right)^\gamma \right\}$$

**CORRELATIONS, EFFICIENCY
PREDICTION & DESIGN
PROCEDURES**

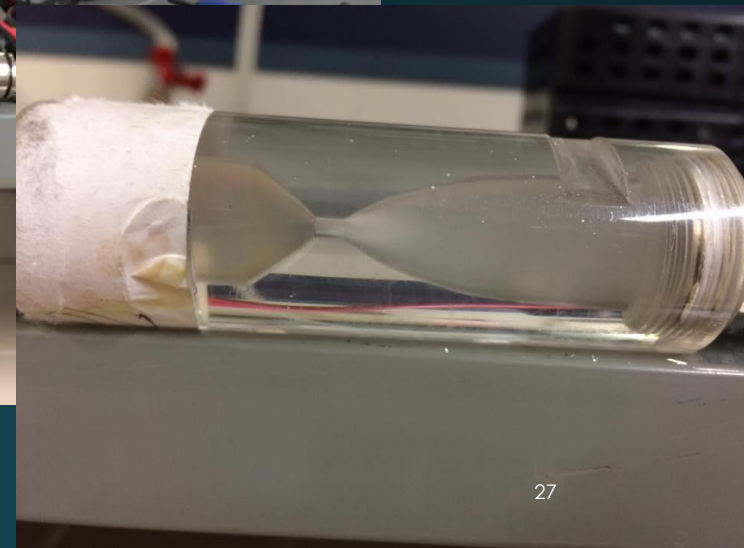
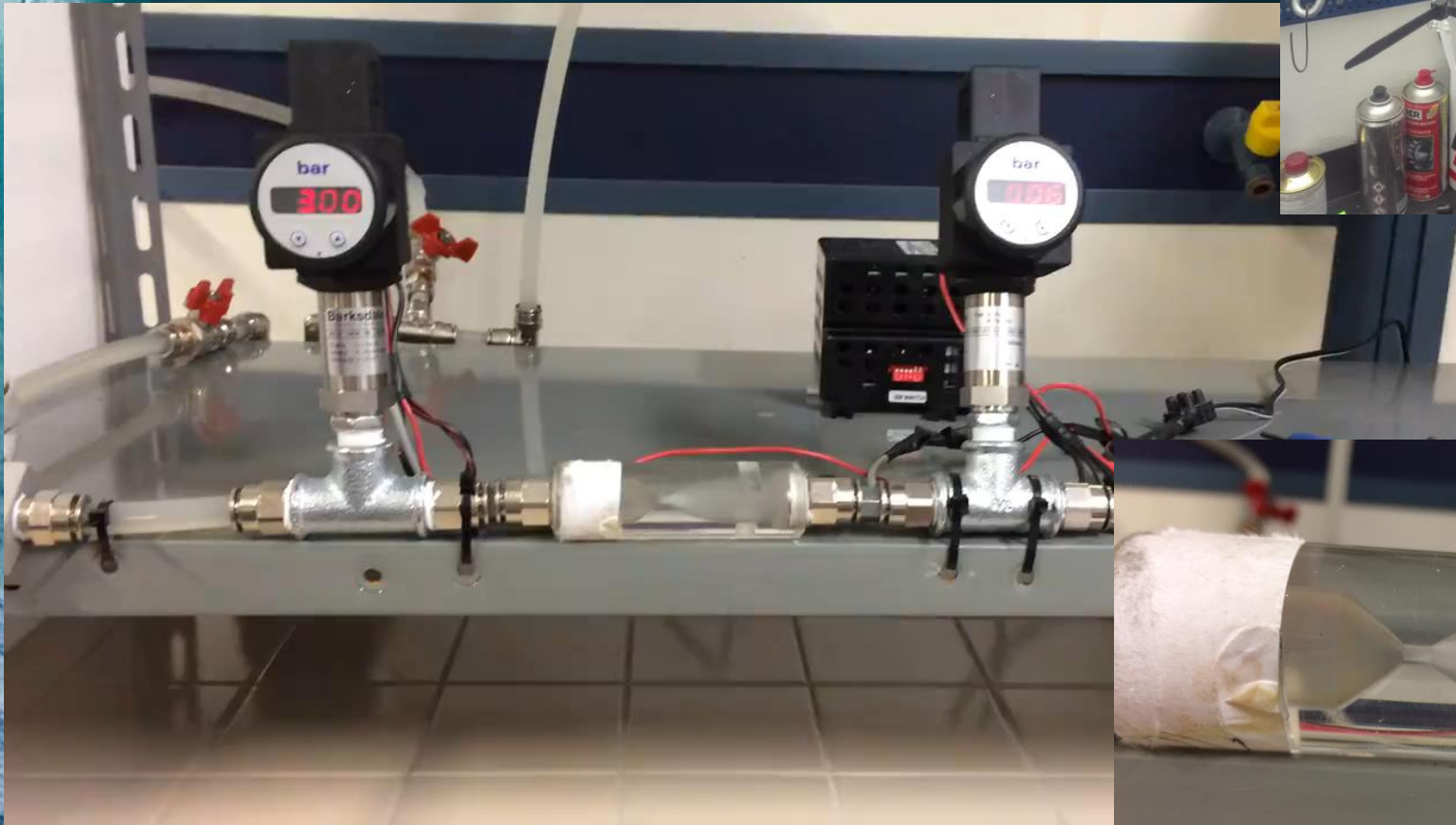
Experimental investigation



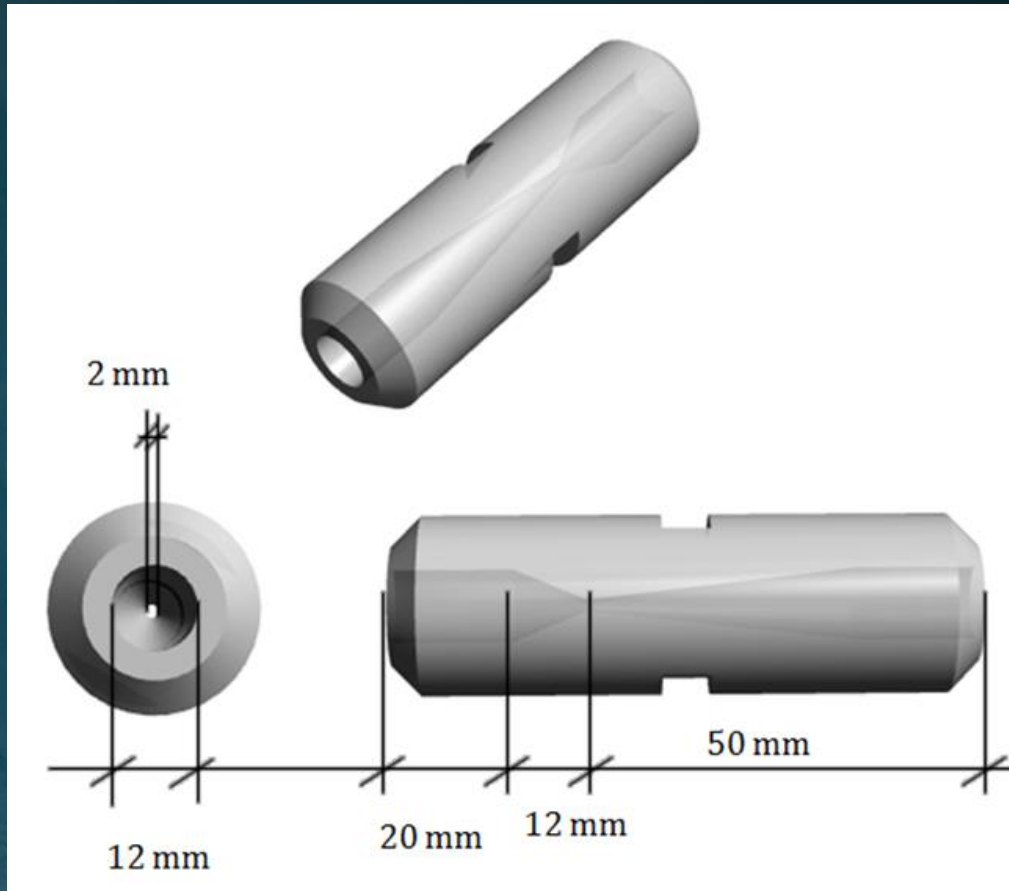
- Batch reactor with a recycling line
- Feed tank of 1.5 liter volume, a centrifugal pump and two control valves (V1-V2).
- $T=30^{\circ}\text{C}$.
- The main line passes through the Venturi, where cavitation occurs, and ends into the tank
- A bypass line with the regulating valve is provided in order to control the liquid flow in the main line.



EXPERIMENTAL LAB SCALE PLANT

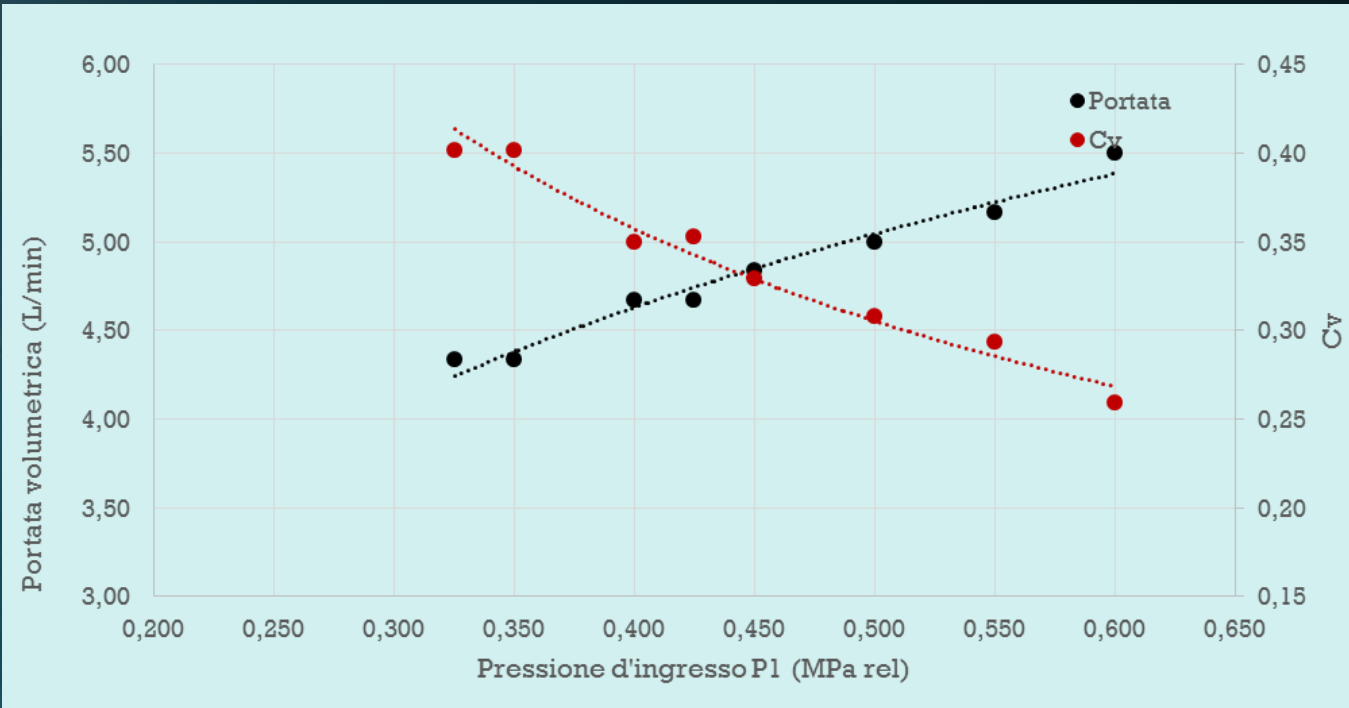


Venturi device



- Geometrical configuration of the convergent-divergent nozzle tested made in Plexiglass in order to make the cavitation regimes visible.
- The largest diameter corresponds to the pipe diameter $d_p=12$ mm, while the inner one is $d_o=2$ mm.

Experimental investigation



The characteristics of the hydraulic system were studied by measuring the main flow rate at different pump discharge pressures.

The Cavitation number C_v is a dimensionless parameter, extensively used to characterize this kind of devices

- p_2 is the fully recovered downstream pressure,
- p_v is the vapor pressure of the liquid,
- v_0 is the fluid velocity at the throat

$$C_v = \frac{p_2 - p_v}{1/2 \rho v_0^2}$$

**HYDRAULIC
CHARACTERISTICS**

Experimental studies

Degradation of ibuprofen by hydrodynamic cavitation: Reaction pathways and effect of operational parameters

Ultrasonics Sonochemistry 29 (2016) 76–83

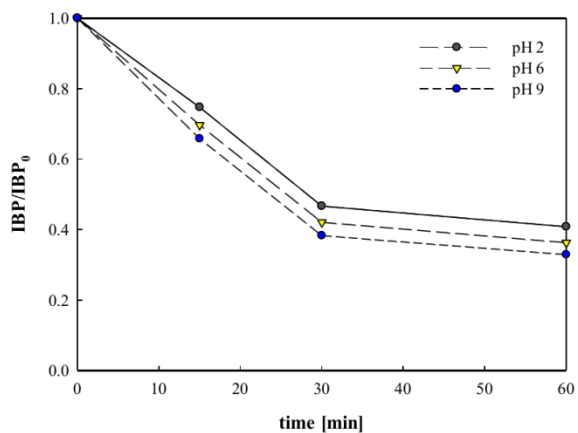


Fig. 8. Conversion of ibuprofen at different pH.

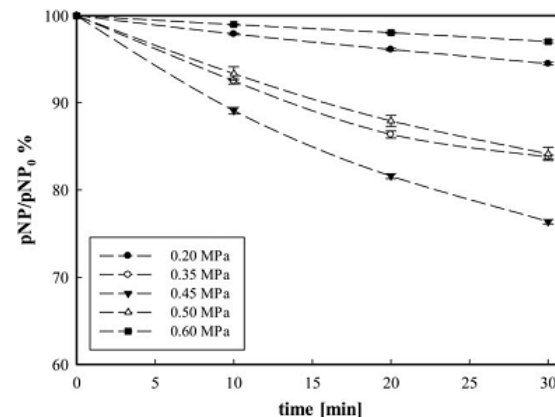
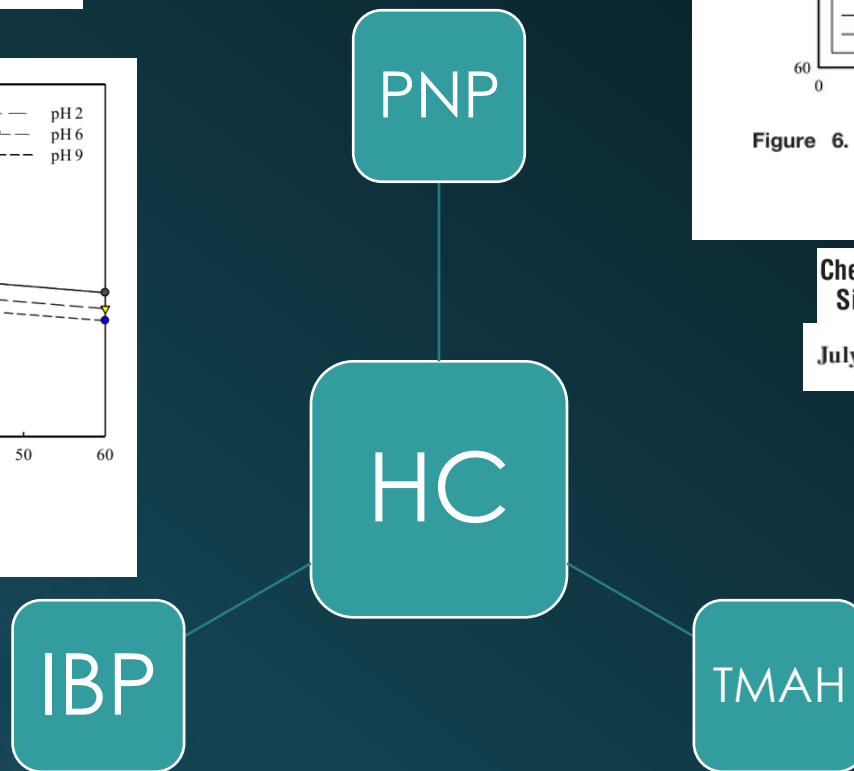


Figure 6. PNP degradation percentage versus time: inlet pressure: 0.6 MPa (■); 0.5 MPa (△); 0.45 MPa (▼); 0.35 MPa (○); 0.2 MPa (●).

Chemical Effect of Hydrodynamic Cavitation: Simulation and Experimental Comparison

July 2014 Vol. 60, No. 7

AIChE Journal

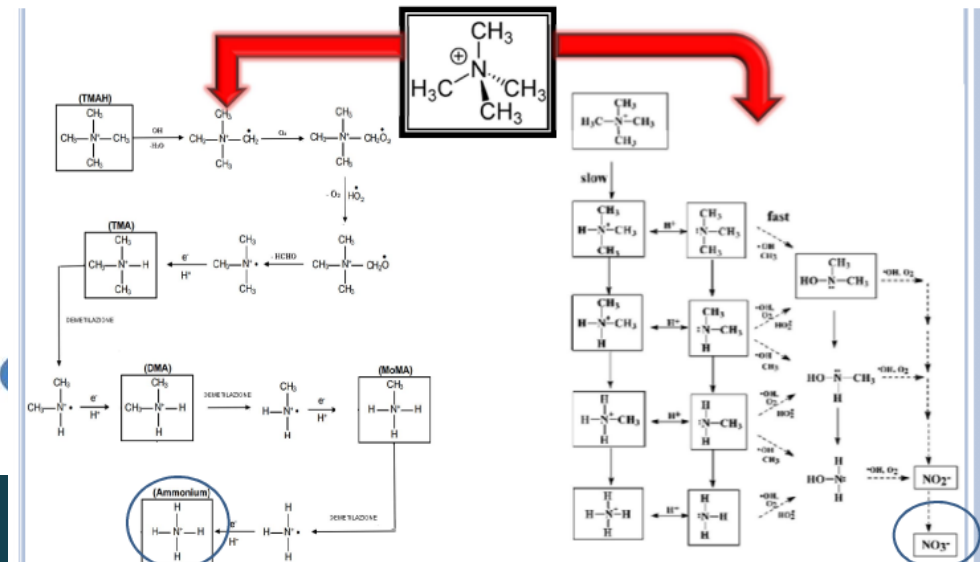
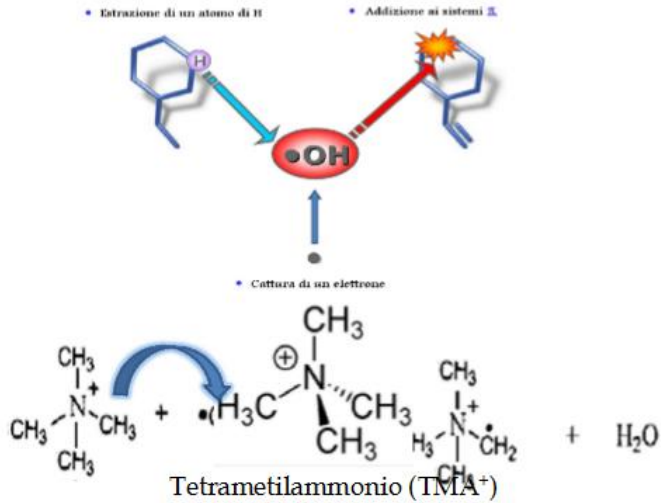


Work in progress



DEGRADAZIONE DEL TMAH

MECCANISMO DI ATTACCO DEL $\cdot\text{OH}$



Work in progress

DEGRADAZIONE DEL TMAH

PIANO SPERIMENTALE

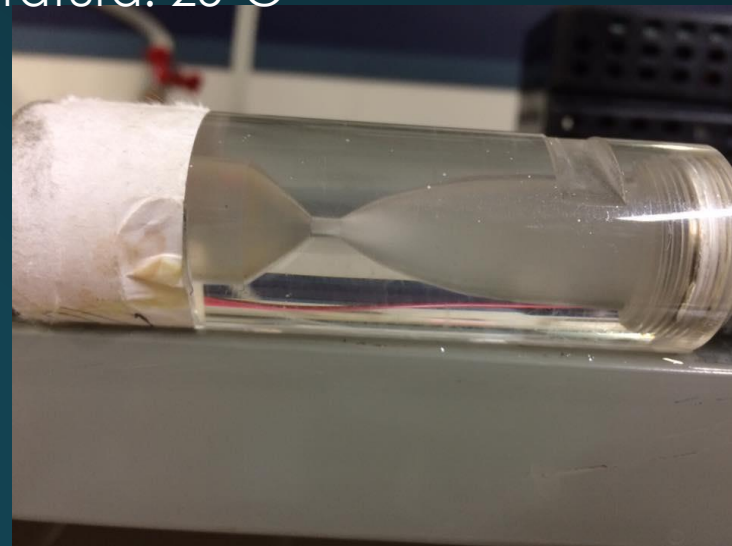
Studio dell'efficienza di degradazione del TMAH in funzione della concentrazione dell'inquinante e della pressione.

Range di concentrazione: 0.02 – 2 g/L

Range di pressione: 2-5 bar

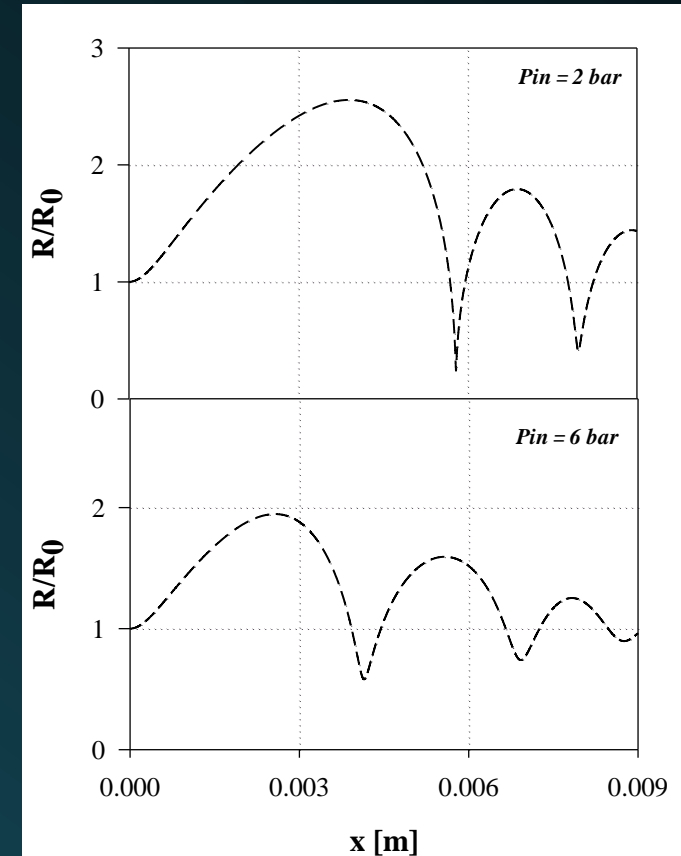
Range di tempo: 10 - 40 min

Temperatura: 25°C



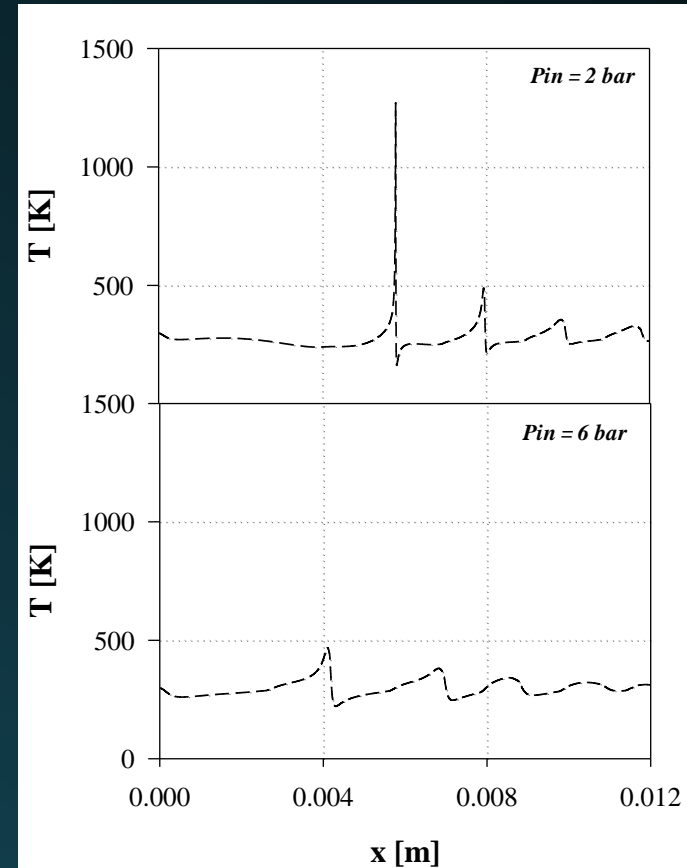
Modelling and Numerical Simulation

Description	Equations	Initial values
Rayleigh-Plesset Equation	$P_i = P_i - \frac{2\sigma}{R} - \frac{4\mu U}{R} \left(\frac{dR}{dx} \right) - \rho_L \left[R \left(U^2 \frac{d^2 R}{dx^2} + U \frac{dU}{dx} \frac{dR}{dx} \right) + \frac{3U^2}{2} \left(\frac{dR}{dx} \right)^2 \right]$ $P_i = \frac{N_{tot}(t) kT}{\left[\frac{4\pi}{3} (R^3(t) - h^3) \right]}$	$R(0) = R_0$ $R'(0) = 0$
Mass diffusion	$u \frac{dN_w}{dx} = 4\pi R^2 D_{ij} \frac{\partial C_w}{\partial r} \Big _{r=R} \approx 4\pi R^2 D_{ij} \left(\frac{C_{WR} - C_w}{l_{diff}} \right)$	$N_w(0) = 0$
Energy balance	$C_{v,mix} \frac{dT}{dx} = \frac{dQ}{dx} - P_i \frac{dV}{dx} + (h_w - U_w) \frac{dN_w}{dx}$ $u \frac{dQ}{dx} = 4\pi R^2 \lambda \frac{\partial T}{\partial r} \Big _{r=R} \approx 4\pi R^2 \lambda \left(\frac{T_o - T}{l_{th}} \right)$	$T(0) = T_w$
Continuity equation	$\left(u \frac{dA}{dx} + A \frac{du}{dx} \right) \left(1 - \frac{4\pi n R^3}{3} \right) = 4\pi n u A R^2 \frac{dR}{dx}$ $U(t) = u(t) + \bar{u}'(t) \sin(2\pi f t)$	$U(0) = U_0$
Momentum equation	$U \frac{dU}{dx} = - \frac{1}{\rho_L (1 - 4\pi n R^3 / 3)} \frac{dp}{dx}$	$p(0) = p_v$



Modelling and Numerical Simulation

Description	Equations	Initial values
Rayleigh-Plesset Equation	$P_i = P_i - \frac{2\sigma}{R} - \frac{4\mu U}{R} \left(\frac{dR}{dx} \right) - \rho_L \left[R \left(U^2 \frac{d^2 R}{dx^2} + U \frac{dU}{dx} \frac{dR}{dx} \right) + \frac{3U^2}{2} \left(\frac{dR}{dx} \right)^2 \right]$ $P_i = \frac{N_{tot}(t) kT}{\left[4\pi(R^3(t) - h^3)/3 \right]}$	$R(0) = R_0$ $R'(0) = 0$
Mass diffusion	$u \frac{dN_w}{dx} = 4\pi R^2 D_{ij} \frac{\partial C_w}{\partial r} \Big _{r=R} \approx 4\pi R^2 D_{ij} \left(\frac{C_{WR} - C_w}{l_{diff}} \right)$	$N_w(0) = 0$
Energy balance	$C_{v,mix} \frac{dT}{dx} = \frac{dQ}{dx} - P_i \frac{dV}{dx} + (h_w - U_w) \frac{dN_w}{dx}$ $u \frac{dQ}{dx} = 4\pi R^2 \lambda \frac{\partial T}{\partial r} \Big _{r=R} \approx 4\pi R^2 \lambda \left(\frac{T_o - T}{l_{th}} \right)$	$T(0) = T_w$
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Momentum equation	$U \frac{dU}{dx} = - \frac{1}{\rho_L (1 - 4\pi n R^3 / 3)} \frac{dp}{dx}$	$p(0) = p_v$



Conclusions

- Removal ECs is of fundamental importance for environmental protection and water reuse
- Cavitation techniques is an effective and low-cost advanced WWT
- Particularly if associated with a radical initiator it represents a promising solution for AOP up-scaling
- Research should be focused on addressing the parameter effect and developing design procedures and correlations
- It can be achieved by coupling experimental and numerical studies