The status and future of fine bubble technology in China

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Development of FB tech. in China
The present status in China
Looking forward
DEVELOPMENT IN CHINA

FB application

- Photosensitive materials (70s)
- Ultrasound contrast agent (80s)
- Flotation column (90s)
- FB generator (2000s)

From 2010

- Medical
- Flotation column
- Waste water treatment
- Oil extraction
- Chemical Indus.
- Cleaning
Photosensitive materials-70’

ISO/TC 42  ISO 18912-2002
Imaging materials - Processed vesicular photographic film - Specifications for stability
Ultrasonic contrast agent-80’ to now

- The FBs act as echo-enhancers by basically the same mechanism as that determining echo-scattering in all the other cases of diagnostic ultrasound, namely that the backscattering echo intensity is proportional to the change in acoustic impedance between the blood and the gas making the bubbles.

- The different acoustic impedance at this interface is very high and in fact all of the incident sound is reflected, even though not all of it will of course go back to the transducer. But the acoustic wave reflection, though nearly complete, would not be sufficient to determine a strong ultrasonic enhancement because the FBs are very small and are sparse in the circulation.

- Moreover, reflectivity is proportional to the fourth power of a particle diameter but also directly proportional to the concentration of the particles themselves.
Ultrasonic contrast agent-80’ to now

SECOND HARMONIC IMAGING:

- As we know, the FBs reached by an ultrasound signal resonate with a specific frequency depending on FB diameter.

- However, the main resonance frequency is not the only resonance frequency of the bubble itself, the second harmonic, is still strong enough to be used for diagnostic purposes.

- The theoretical advantage of the harmonic over the fundamental frequency is that only contrast agent FBs resonate with harmonic frequencies, while adjacent tissues do not resonate, or else their harmonic resonance is very little.
Fig. 1 The ablated lesion could be clearly defined under the mode of pulse inversion harmonic imaging after bolus injection of contrast agent.

Fig. 2 The necrotic lesion after local injection of absolute alcohol with coagulation necrosis circled by granulation tissue. There exists focal hemorrhage (noted by "*") with granulation tissue intrusion into the necrosis (noted by “↗”) (HE staining ×40).
DEVELOPMENT IN CHINA

Flotation column-90’
DEVELOPMENT IN CHINA

FB generator-2000’

Pressurization  Microporous Aeration  Electrolysis  Gyratory Shear
Medical Industry

- The FB contrast agents developed and introduced as safe and effective echo-enhancers in present-day clinical practice will open up new opportunities.

- With the developments and therapeutic applications of ultrasound techniques and advances in ultrasound contrast agents in recent years, the synergistic effects of ultrasonic cavitation and ultrasound contrast agents, as an efficient, safe, simple and targeted therapy with no pain, has shown great potential in biomedicine such as gene therapy, drug delivery, thrombus lysis and diagnosis and therapy for vascular diseases and tumors.

- Moreover, the application of the FBs create a new way in ultrasound medical examination without any damaging. It results the most progress on the techniques of preparation of FBs and introduces the microcapsule techniques.
THE PRESENT STATUS IN CHINA

Medical Industry

- The contents in FB: CO$_2$, O$_2$, Air, macromolecule inert gas, such as CF$_4$ or SF$_6$


- The way to produce FB: neutralizational process, adsorption, mechanical homogenization, acoustic cavitation, freeze-dry, and etc..
THE PRESENT STATUS IN CHINA

Medical Industry

4A  fine bubbles MB-NH$_2$ only

TEM micrograph of a freeze-dried fine bubble

4B  fine bubbles with PLGA nano

CLSM micrography of PLGA fine bubbles
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Flotation column

- Floated Product
- Feed
- Air Pressure
- Air
- Water Pressure
- Recycle
- Treated Effluent
- Microbubble Generator
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Flotation column

The basic principle of flotation column is the counter current flow of air bubbles and the interaction between particles and bubbles. The interaction includes:

1) Collision
2) Adherence
3) Fall off
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Flotation column

Bubble–particle collision and attachment interaction in flotation

\[ \theta_o : \text{Polar angle} \]
\[ \theta_{cr} : \text{Critical angle of attachment} \]
\[ \theta_c : \text{Collision angle} \]
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Flotation column

<table>
<thead>
<tr>
<th>time</th>
<th>Feed</th>
<th>Clean coal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dried Culm(t)</td>
<td>Ash(%)</td>
</tr>
<tr>
<td></td>
<td>Dried (t)</td>
<td>Ash(%)</td>
</tr>
<tr>
<td>1st month</td>
<td>1693</td>
<td>13.89</td>
</tr>
<tr>
<td>2nd month</td>
<td>1654</td>
<td>12.31</td>
</tr>
<tr>
<td>3rd month</td>
<td>2305</td>
<td>13.04</td>
</tr>
<tr>
<td>4th month</td>
<td>2222</td>
<td>14.52</td>
</tr>
<tr>
<td>Weighted mean</td>
<td>7897</td>
<td>13.49</td>
</tr>
</tbody>
</table>

An example of flotation column with Φ3000mm in a coal separating plant in 90’
## Flotation column

<table>
<thead>
<tr>
<th>Flotation type</th>
<th>Feed Cu</th>
<th>Feed Co</th>
<th>Cu concentrate Cu</th>
<th>Cu concentrate Co</th>
<th>Co concentrate Cu</th>
<th>Co concentrate Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flotation machine</td>
<td>14.44</td>
<td>0.374</td>
<td>20.83</td>
<td>0.377</td>
<td>0.743</td>
<td>0.358</td>
</tr>
<tr>
<td>Flotation column</td>
<td>14.44</td>
<td>0.374</td>
<td>21.10</td>
<td>0.287</td>
<td>0.235</td>
<td>0.550</td>
</tr>
</tbody>
</table>

An example of flotation column plant
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Waste water treatment
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Waste water treatment

- Much quicker and fewer floor space,
- The products contain a certain amount of oxygen, which is helpful to the following processing,
- Some aquatic organisms, such as cryptosporidium, can be well removed
- The amount of reagents used is much fewer.

An example of FB generator for waste water treatment
1 liquid inlet, 2 air inlet, 3 outlet
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Waste water treatment

Alga samples at different time

Effect of flotation time on the removal rate of alga
The present status in China

Oil extraction

Drilling fluid with FBs can be used:

- Reduce serious losses
- Cheaper
- Easy to handle
- Fewer complicated troubles
- Speed up the drilling footage
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**FB generator**

Jet type microbubble generator

Mixed-flow microbubble generator
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FB generator

The meshwork of generator is achieved by Gambit.
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FB generator

Static pressure curves in the central axis of generator
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FB generator

Turbulent kinetic curves of generator
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FB generator

Velocity magnitude curves in central axis of generator
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FB generator

Contours of Turbulent Kinetic Energy (k) (mixture) (m2/s2)

Formation of the turbulent kinetic energy peak
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FB generator

Distribution of diameter vs velocity
Chemical industries

- For ordinary bubbles (diameter > 0.1mm), $\Delta P \approx 0$;
- A FB would shrink gradually, resulting in dramatically increase of $\Delta P$ and the specific surface area;
- The gas in a FB would dissolve into the medium when it collapses, and the mass transfer efficiency would be enhanced.

**Self-pressurized Dissolution of a Fine Bubble**

\[ \Delta P = \frac{2\sigma}{r} \]
Lots of anions would gather at the FB-water interface;

With a FB shrinking, the interface charge would congest significantly;

A large zeta potential would be formed and lots of chemical energy would be released with the burst of a FB, resulting in the generation of reactive oxygen species (ROS) at the gas-water interface.
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Chemical industries

Microporous filter aerator
(size: 0.22μm, 30μm, 50μm, 80μm)

Experimental aeration

With the filter aerator with microporous, fine bubbles with diameter sizing from 0.22 to 100 μm would be generated by bubbling oxygen into the solution.
The optimum bubble size for ROS generation in KOH and NaOH solutions is 40μm.

The optimal alkali concentration for ROS generation in KOH solution is 5M.

The optimal temperature for ROS generation in KOH solution is 65 °C.
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Chemical industries

ROS Generation Comparison in NaOH and KOH Solutions

- KOH favors the generation of ROS in comparison with NaOH;
- Alkali concentration ↑, activity ↑, oxygen solubility ↓, diffusion coefficient ↓;
- Temperature ↑, activity ↑, oxygen solubility ↓, diffusion coefficient ↑.

The key for ROS generation is to increase the oxygen solubility and diffusibility in the medium.
Example I-Vanadium Leaching

- FB Generation: Microporous Aeration
- Operation Pressure: 1 atm
- Operation Temperature: 130 °C
- Medium: NaOH aqueous solutions
- Application: Institute of Process Engineering, CAS

Schematic diagram for vanadium slag treating

Comparison of the V Leaching Yield With and Without Microbubbles

<table>
<thead>
<tr>
<th>Method</th>
<th>Bubble Size</th>
<th>Temperature</th>
<th>Medium Conc.</th>
<th>V Yield</th>
<th>Cr Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aeration</td>
<td>50~100</td>
<td>130</td>
<td>60</td>
<td>97</td>
<td>~30</td>
</tr>
<tr>
<td>SMS(^1)</td>
<td>5000~10000</td>
<td>210</td>
<td>80</td>
<td>95</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Roasting</td>
<td>750~850</td>
<td></td>
<td>85</td>
<td></td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

1 Sub-molten salt method.

Longjie Liu et al., International Processing of Minerals, 2016 (Under Review)
THE PRESENT STATUS IN CHINA

Example II-Chromium Leaching

- FB Generation: Electrolysis.
- Operation Pressure: 1 atm;
- Operation Temperature: 150 °C
- Cell Voltage: 1.5~3.5 V.
- Medium: KOH aqueous solutions.
- Application: Institute of Process Engineering, CAS

Schematic diagram for chromite electrolysis

Comparison of the Cr Leaching Yield With and Without Microbubbles

<table>
<thead>
<tr>
<th>Method</th>
<th>Bubble Size</th>
<th>Temperature</th>
<th>Medium Conc.</th>
<th>Cr Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolysis</td>
<td>20~40 μm</td>
<td>150 °C</td>
<td>60 wt%</td>
<td>&gt;95</td>
</tr>
<tr>
<td>SMS²</td>
<td>5000~10000</td>
<td>300 °C</td>
<td>75 wt%</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Roasting</td>
<td>1200</td>
<td></td>
<td>75</td>
<td></td>
</tr>
</tbody>
</table>

1 Sub-molten salt method.

Zhonghang Wang et al., Minerals Engineering, 2014

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Example III-Gold Leaching

- FB Generation: pressure nozzle aeration.
- Aeration Amount: 0.62~5.0 m³/min
- Nozzle Numbers: 8, 6, 4
- Nozzle Diameter: 5 mm
- Application: BGRIMM,

Schematic diagram for cyanide gold leaching enhanced by microbubbles

Comparison of the Gold Leaching Yield With and Without Microbubble Aeration

<table>
<thead>
<tr>
<th>Cyanidation Apparatus</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas Amount, m³/min</td>
<td>Yield, %</td>
<td>Gas Amount, m³/min</td>
</tr>
<tr>
<td>Aeration Tank</td>
<td>5.00</td>
<td>89.65</td>
<td>3.75</td>
</tr>
<tr>
<td>Regular Tank</td>
<td>5.00</td>
<td>86.84</td>
<td>5.00</td>
</tr>
<tr>
<td>Difference</td>
<td>0</td>
<td>+2.81</td>
<td>-1.25</td>
</tr>
</tbody>
</table>
In alkaline solutions, the ROS generation would be significantly enhanced by FBs; FBs would greatly enhance the dissolved oxygen content and the oxygen diffusivity in the alkaline solutions; By using the FBs, Au, Cr and V could be effectively extracted from the minerals under much more moderate conditions.
LOOKING FOWARD

Published papers vs years
LOOKING FORWARD

Published papers vs years

![Bar chart showing the number of published papers from 2010 to 2016.](chart.png)
LOOKING FORWARD

Distribution of FB tech. in different industries

- Cleaning
- Chemical Indus.
- Waste water treatment
- Oil extraction
- Flotation column
- Medical

- Not necessary
- New tech.
- Not well-known
LOOKING FORWARD

What we should do?

- Well-organize-Chinese Society of Particuology
- Focus on the study of FB generators
- Make FB tech. more popular
- Good corporation with developed countries
LOOKING FORWARD

What we should do?

QUESTION:
FBs in hydraulic fluid or insulating oil are very harmful.

How to measure the contents of FBs, number of FBs and its distribution in these kind of oils? What is the ISO standard?
Acknowledgement

Prof. Z. Li from Kunming University of Science and Technology & Prof. H. Du from Institute of Process Engineering, CAS gave me lots of information about the FB technology. I would express my sincere thanks to them.
Thank you
For Your Attention