



## Water Towards Safety Sustainable Environment and Prosperity



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Application of Fluidized-Bed Homogeneous Crystallization Technology for Recovering Metal and Non-metal Resources from Wastewater

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## Content

- Principle of Homogeneous Crystallization Technology
- Technical Advantages
- Application
  - Metal and non-metal recovery
  - Carbon dioxide capture from flue gas
  - Resource recovery from brine
- Take-home messages

## Sludge after dewatering







Comparison of chemical precipitation and crystallization processes

4

**FBHC** 

### ■ Principle

Using a fluidized bed reactor to recover metal or non-metal ions in the form of homogeneous crystal granules as resources for reuse Unique in the world : The **homogeneous** crystallization technology

Comparison of chemical precipitation (CP), fluidized bed heterogeneous crystallization (FBC) and fluidized bed homogeneous crystallization crystallization (FBHC)

獨步全球的均質結晶技術 Seeded-Type 混凝 Fluidized-bed Heterogeneous Crystallization Crystallization FBC nucleation 膠凝 (FBC) 191 異質成核 異質結晶 Low Purity Coagulation **Our patents** Flocculatio 低純度 lomoaenou nucleation Fluidized-bed 均質成核 Homogeneous CP Granulation (FBHG) Coagulation Flocculation Crystallization **High Purity** 均質結晶 (Active growing site) 混凝 膠凝 高純度





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### COLLOIDAL STRUCTURE AND STABILITY



### Process of Agglomeration ✓ For agglomeration to occur, two particles have to collide and the attractive forces between the two particles have to exceed the force resulting from the inertia of the particles to disintegrate again. ✓ The particles hit, tumble and either disintegrate or agglomerate. This first binding has to be fast. Agglomeration



### ■ Application

□ Metal-Containing Wastewater Treatment and Resource Recovery

- ✓ calcium, magnesium, iron, aluminum, copper, nickel, zinc, lead, cobalt, strontium etc.
- Nonmetal-Containing Wastewater Treatment and Resource Recovery
  - ✓ phosphate, oxalate, sulfate, molybdate, tungstate, ammonium, sulfur etc.
- Carbon dioxide capture and resource recovery from flue gas









# **METAL REVOVERY**

碳酸鈣結晶粒

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# **NON-METAL REVOVERY**

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magnesium ammonium phosphate(MAP)

molar ratio. [pH 9.0; 300mg-

1 mm













Thi-Hanh Ha, Nicolaus N.N. Mahasti, Cai-Sheng Lin, Ming-Chun Lu\*, Yao-Hui Huang\*, 2023, Enhanced struvite (MgNH<sub>4</sub>PO<sub>4</sub>· $6H_2O$ ) granulation and separation from synthetic wastewater using fluidizedbed crystallization (FBC) technology, Journal of Water Process Engineering, 53, 103855.

# BOTH METAL AND NON-METAL REVOVERY





Lester Lee E. Bayon, Florencio C. Ballesteros Jr. Sergi Garcia-Segura, Ming-Chun Lu\*, 2019, Water reuse nexus with resource recovery: On the fluidized-bed homogeneous crystallization of copper and phosphate from semiconductor wastewater, Journal of Cleaner Production, 236, 117705.

### **Fluidized-bed reactor**





For 10 CMD

For 7000 CMD





### Technical advantages





- Less energy consumption due to operation at normal temperature and pressure
- **D** Removing both metal and non-metal salts in water.
- □ Saving at least 50% of the treatment cost because the moisture content of the crystals obtained is only 5%,
- High potential for subsequent resource recovery due to high purity of crystals obtained by homogeneous crystallization technology



□ High treatment efficiency and high operational flexibility



Integrating vertically the units in a single one to reduce land costs

#### **Comparison benchmark:**

Crystal grain moisture content 5% Dewatered sludge moisture content: 70 % Dewatered sludge moisture content reduced from 70% to 5% Reduce carbon emissions:

>234 kg CO<sub>2</sub>/ 1000 kg sludge

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# **CARBON DIOXIDE CAPTURE AND** CRYSTALLIZATION **FROM FLUE GAS**



### President Tsai Ing-wen presented the championship award

**gold medal** 2022 Taiwan Innovation Technology Expo Invention Competition



# **TTV News**

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搜尋





生成「碳酸鈣」可回收再利用減碳量驚人【發現科學】

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後 明 人	: 盧明俊					
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# The third one is under review

#### NaOH, KOH or other alkaline agents.....



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### □ According to the carbonate solubility curve pH 8-12 : HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> , pH > 12 : CO<sub>3</sub><sup>2-</sup> $CO_2 + H_2O \leftrightarrow H_2CO_3$ $H_2CO_3 \leftrightarrow HCO_3^- + H^+; K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3(aq)]} = 4.8 \times 10^{-11}$ $HCO_3^- \leftrightarrow CO_3^{2-} + H^+; K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.3 \times 10^{-7}$

• According to the calcium solubility curve

At pH>10.5, Ca(OH)<sub>2</sub> formed

Ca(OH)<sub>2(aq)</sub> ↔ Ca<sup>2+</sup> + 2OH<sup>-</sup>;  

$$K_{sp} = \frac{\gamma_{Ca^{2+}}[Ca^{2+}] \times \gamma_{OH-}[OH^{-}]^{2}}{[Ca(OH)_{2(aq)}]} = 7.9 \times 10^{-6}$$
  
☐ Operation range: pH 8.0-10.0



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## **Effect of pH**

#### **D** Removal efficiency

At pH 8, the removal and crystallization efficiencies were 96.9 and 93.7%, respectively, and those are 99.5% at pH 9, indicating that pH 9-10 was the optimum operating condition.

#### □ Size analysis

At a pH of 9, about 20% of the calcium carbonate particles were close to 1 mm in diameter. The granulation effect is significantly improved.





## **Effect of reactor type on granule size**

**One-stage reactor** •



Comparison of CaCO<sub>3</sub> size distribution at different concentration.  $([CO_3^{2-}]/[Ca^{2+}]=1, pH 9.0\pm0.3)$ 



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Comparison of CaCO<sub>3</sub> size distribution at different concentration.  $([CO_3^{2-}]/[Ca^{2+}]=1, pH 9.0\pm0.3)$
• One-stage reactor

Composed of relatively fine crystals and the density is approximately 2.06 g/cm<sup>3</sup>



one-stage

#### • Two-stage reactor

The center of the granule is composed of larger crystal particles, and the density is approximately 1.68 g/cm<sup>3</sup>

#### **Mechanism of granulation**



### **Mechanism of granulation**







#### Growth of calcium carbonate crystal grains

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#### **Effect of different chemicals on granulation**



Comparison of CaCO<sub>3</sub> size distribution at different different different ion sources.( $[CO_3^{2-}]=0.096 \text{ M}, [CO_3^{2-}]/[Ca^{2+}]=1, \text{pH } 9.0\pm0.3$ )

#### Cost evaluation of carbon dioxide capture and resource recovery from flue gas

	ltem	Cost (TWD/kg or TWD/Kwhr)	Consumption or Production (kg reactant or product/kg CO <sub>2</sub> )	CO₂removal c (TWD/ ∣	cost or benefit kg CO <sub>2</sub> )	Remark
Expense	Ca(OH) <sub>2</sub>	2.0-5.4	1.68	3.4-9.1	0	If recycled Ca is used, the cost is 0.
	Electricity	3.38		1.09-1.27	1.09-1.27	
	Capital			0.5-0.75	0.5-0.75	The amortization period is 10 years
Subtotal				4.99-11.12	1.59-2.02	
Income	CaCO <sub>3</sub>	1.7-4.9	2.27	3.9-11.1	3.9-11.1	
	Carbon fee	0.3-3.0		0.3-3	0.3-3	
Subtotal				4.2-14.1	4.2-14.1	
Total				-0.79 ~ +2.98	+2.61~+12.1	If recycled calcium is used, there is definitely profit.

# RESOURCE RECOVERY FROM BRINE

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#### TABLE 1 | Physicochemical composition of the desalination brine.

Desalination	Oman RO	Emirates RO	Qatar RO
Calcium (mg/L)	417 - 1020	220 -1 180	1350
Magnesium (mg/L)	260 - 1980	311 - 2660	7600
Sodium (mg/L)	1670 - 15,300	311 - 17,700	NR
Potassium (mg/L)	43.1 - 668	34.1 - 950	NR
Strontium (mg/L)	11.4 - 28.2	4.56 -21.10	NR
pH	3.07 -7.94	6.38 - 7.87	NR
Carbonate (mg/L)	NB	NR	NR
Bicarbonate (mg/L)	37 -859	100 - 656	3900
Chloride (mg/L)	1964 - 77,335	2,933 -34,839	29,000
Sulphate (mg/L)	1143 - 6139	756 -4602	3900
Nitrate as NO <sub>3</sub> (mg/L)	5.2-46.7	3 - 47.2	NR
Fluoride (mg/L)	-	<0.1 -2.3	NR
E.C (mS/cm)	9870 -	10,850 - 81,100	NR
S.A.R (me/L)	15.51 -64.65	6.8 - 67.25	NR
S.E.R (me/L)	61.77 -75.012	31.1 - 74.29	NR
Langelier Index (me/L)	-0.33 -	-0.28 - 1.2	NR
Ryzner Index (me/L)	4.38 - 9.27	4.47 - 7.69	NR
TDS (ma)	8,747 - 48,510	3700 - 61,587	NR
Total ions (mg/L)	8,765 - 48,618	33,765 - 61,645	NR
Total alkalinity (mg/L)	30 - 704	82 - 538	NR
Total hardness (mg/L),	2,211 - 9,951	1,730-12,872	NR
Iron (mg/L)	<0.05 -	<0.05 -0.33	NR
Manganese (mg/L)	<0.05 - 0.07	< 0.05 - 0.07	NR
Copper (mg/L)	<0.05	<0.05 - <0.5	NR
Zinc (mg/L)	<0.05	<0.05 - <0.5	NR
Chromium (ma)	<0.02	<0.05	NR
reference	(Ahmed et al., 2001)	(Ahmed et al., 2001)	(Bello et al.,

3

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44



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 $CO_3^{2-}$ ]=0.096M, pH=10.0±0.3, [Mg<sup>2+</sup>]/[CO<sub>3</sub><sup>2-</sup>]=1.0, [Mg<sup>2+</sup>]/[Ca<sup>2+</sup>]=10



# A POSSIBLE SOLUTION

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# Nanofiltration (NF) Mechanism

- NF is a pressure-driven separation process based on principles of size exclusion, charge, and polarity.
- This process selectively removes divalent ions, small organic molecules, and viruses from aqueous solutions.
- NF is promising for precision separation, with advantages like low energy use for ion and small molecule removal.

#### Nanofiltration membrane technology features and advantages

Membrane pore size	Driving force	Mechanism	Applications	Advantage
0.1–10 nm	Pressure difference (10–25 bar)	Solution diffusion	<ul> <li>Treatment of wastewater and brackish water desalination</li> <li>Chroma removal</li> </ul>	<ul> <li>Less energy for treatment</li> <li>Easy operation</li> <li>Better efficiency</li> <li>High water permeability</li> </ul>



# Take-home messages

- FBHC can recover both metal and non-metal resources from water at normal temperature and pressure
- FBHC is an technology with high treatment efficiency and flexibility
- **□** FBHC could be a carbon negative technology for CCUS
- Technology application must consider technological feasibility, economic feasibility, and carbon emission feasibility.
- FBHC has the potential to recover resources from brines but NaCl has to be removed first.

# Thank you very much for your kind attention







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# Sustainable high-performance energy free desalination

#### **Sheh-Yi Sheu**

Department of Life Sciences and Institute of Genome Sciences National Yang Ming Chiao Tung University, Taipei, Taiwan



https://www.aslo.org/what-is-aquatic-science/earths-water-resources/



#### Water Stress by Country - 2040



Extremely high (>80%) High (40-80%) Medium to high (20-39%) Low to medium (10-19%) Low (<10%)

Data source: World Resources Institute via The Economist Intelligence Unit



# **Desalination Methods**

- Reverse osmosis (RO)
- Thermal Distillation
  - Multi-stage flash distillation (MSF)
  - Multi-effect distillation (MED)
  - Vapor compression distillation (VC)
  - Solar-powered desalination
- Electrodialysis (ED)
- Nanofiltration (NF)
- Gas hydrate formation



### high pressure = energy

E Jones et al. Sci. Total Environ. 657, 1343 (2019)







# **Bioinspired** By **nature**

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#### **Unidirectional motion** $\rightarrow$ **Dissipationless**



YM Zheng et al. Nature 463, 640 (2010)





CC Liu et al. ACS Nano, 8, 1321 (2014)

AR Parker et al. Nature 414, 33 (2001)

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# **Unidirectional Liquid Flow**

Wettability and Liquid spread under nanoscale confinement are universal in biology — Asymmetric structures, Heterogeneity, and Surface roughness.

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## Amyloid Fibrils as Functional Materials



TP Knowles, et al. Adv. Mater. 28, 6546 (2016)

The physical nature of Amyloid Fibrils:

- Polyelectrolytes
- Hydrogen bonding network
- Chirality and polarity
- High Elastic moduli and Rigidity
  - (Compared to actin, tubulin, collagen, keratin, and silk)
- It is an Irreversible assembly process.





#### Water Pump – Fountain Effect



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### **Pressure-Driven Nanofiltration**



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#### **Desalination performance**

Туре	Materials**	Methods*	Water flux (L·cm <sup>-2</sup> ·day <sup>-1</sup> )	Salt Rejection	
Pressure-driven	PA	MD(RO)	0.3868 at 9.9 atm	100.0 % (NaCl)	
	CNT (6,6) CNT (7,7)	MD(RO)	0.27 (6,6) 0.42 (7,7) at 54.3 atm	100.0 % (6,6) (Na <sup>+</sup> ) 95.0 % (7,7) (Na <sup>+</sup> )	
	Mxene $(Ti_3C_2)$	MD(RO)	1.1532 per atm	> 99.0 % (NaCl, KCl)	
	ZFCNT	MD(RO)	0.1153 at 36.0 atm	98.6 % (NaCl)	
	GOQD	RO	0.090 at 15.8 atm	98.8 % (NaCl)	
	rGO/TiO <sub>2</sub>	NF-RO	0.1229 at 14.8 atm	99.5 % (NaCl)	
	AqpZ- DOPC/DOTAP biomimetic	NF-RO	0.053 at 4.0 atm	75.0 % (NaCl) 97.0 % (MgCl <sub>2</sub> )	
	Al membrane	DCMDL	0.0458	99.5 % (NaCl)	
Thermal-driven	Tubular ceramic	VMDL	0.0723	99.5 % (NaCl)	
Commercial		RO	0.0017 – 0.0054 per atm	> 99.6 – 99.9 % (NaCl)	
Our work	ABNT-DPPC	MD	24.68 at 0 atm 27.92 at 1 atm 30.49 at 3 atm 36 13 at 5 atm	100 % (NaCl)	



## Conclusions

- 1. Nano-dewetting facilitates the unidirectional motion of water molecules on the  $A\beta$  surfaces the ratchet structure and the broken detailed balance.
- 2. Water overflows from ABNT natural water pump.
- 3. The designed ABNT nanofilter shows 100% desalination efficiency with perfect NaCl rejection.
- 4. The production of ~ 2.5 tons (10 x 10 cm<sup>2</sup>) of pure water per day without any energy input.
- 5. Peptide-based nanotubes should be able to provide a more biocompatible environment for implant materials, while also providing flexibility, disposability and environmental **protection.**

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#### Dr. Yu-Cheng Liu

