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Phosphorous Recovery Technologies

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Outlines：

I. Struvite Recovery from Municipal Wastewater : Fluidized Bed Crystallization (FBC).

II.Phosphate Recovery from Industrial Wastewater : Selective Precipitation.

III.Other Technologies Applied for Sludge, Sludge Ash, etc.

I. Municipal Wastewater → **FBC** → Struvite（MAP）（$MgNH_4PO_4 \cdot 6H_2O$）

1.Conventional Biological Activated sludge Process to breakdown complex into NH_4^+,PO_4^{-3}, etc.

2.EBPR(enhanced biological phosphorus removal)and BNR (biological nutrient removal) processes make the〔PO_4^{-3}〕in the anaerobic liquor up to 100$^{mg}/_{\ell}$

1. High purity with low heavy metal contamination, low water content, and large size(3~5mm)crystals with hardness characterize a good slow-release fertilizer.

3.On-site anaerobic digestion is better than off-site hauling.

4.In conjunction with high 〔 PO_4^{-3} 〕, high level of 〔 NH_4^+ 〕 also characterize anaerobic digester liquors.

5.〔Mg^{+2}〕needs to be added and Mg : P ratio in turn controls the crystal size and hardness.

2.The small size(＜1mm) and brittleness of MAP have resulted in low market value. Sufficient hardness is necessary to meet the requirement of commercial fertilizer spreader.

3.Fertilizer recovered from sewage is forbidden in some local agencies.

4.The production cost is important in final product marketing.

I. Wastewater → Fluidized Bed Crystallization(FBC) → struvite

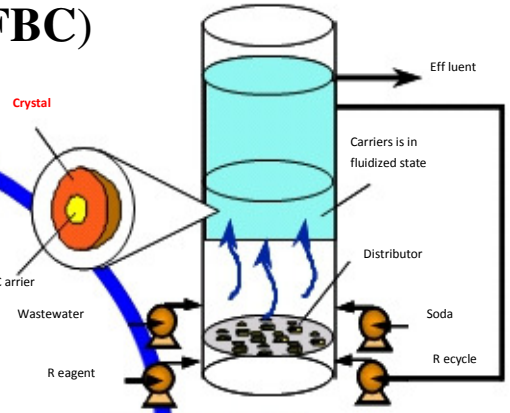
1.Feed : digester liquor, 〔$MgCl_2$〕dosing , 〔NaOH〕 dosing for pH control.

2.Control Variables : SSR（super-saturation ratio）, Mg : P ratio, and hydraulic shearing force controlled by liquid recycling rate.

Full-scale Applications of ITRI patented technologies

UASB/
Anaerobic MBR system

Fluidized Bed Crystallization
(FBC)



BioNET

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Fluidized-bed
Fenton Reactor
(FBR-Fenton)

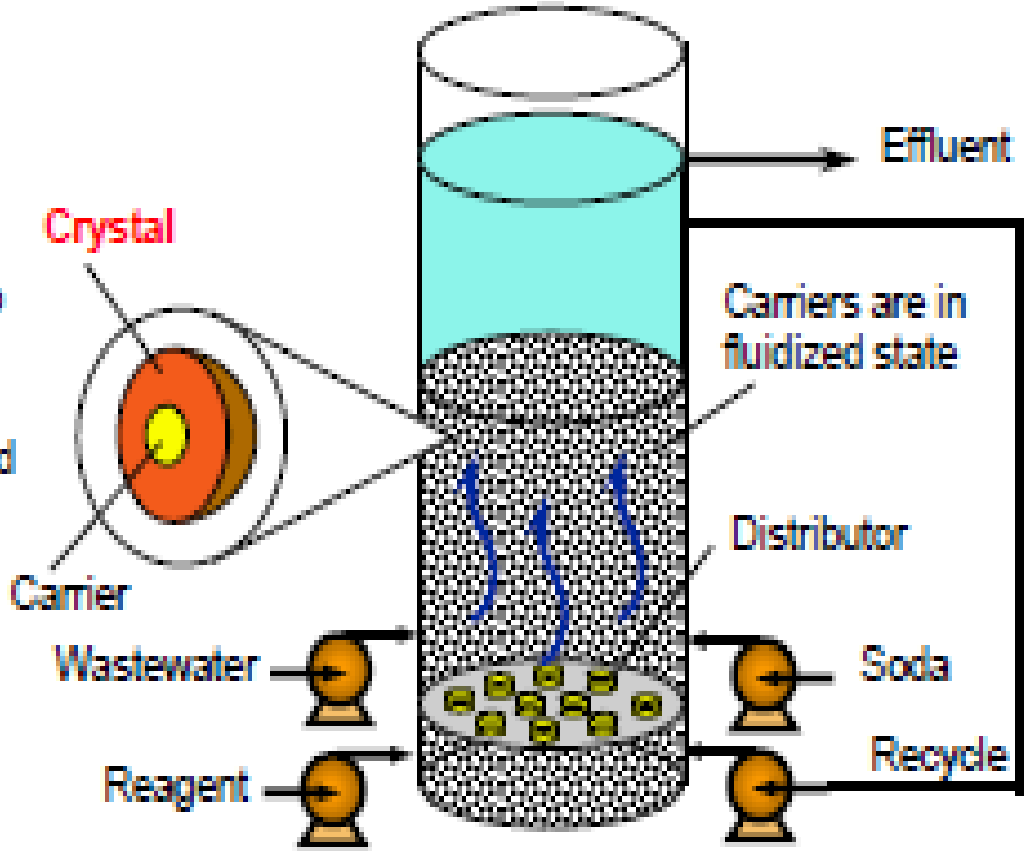
Web-MBR

Anaerobic Fluidized Bed
(AFB)

Fluidized Bed Crystallization Wastewater Treatment Technology

Introduction

Fluidized bed crystallization (FBC) uses silicate sands as carriers to recover metal salts or inorganic ions from wastewater in crystal forms. Properly controlled recycle flow provides mixing to maintain sand fluidization. Control of chemical reagent addition provides appropriate super-saturation to form crystals. Crystals are discharged when the size is grown to 1 to 2 mm in diameter.



Features

- Reactor and process control
- Influent flow distribution design
- Crystal growth control

Benefits

- Remove inorganic ions from wastewater
- Reduce sludge production by 75%
- Recover valuable resources in crystal form

Applications

- Fluoride-containing wastewater
- Arsenic-containing wastewater
- Water softening
- Phosphate / ammonia removal
- Heavy metal removal from wastewater

Case Examples

12 full-scale FBC plants have been constructed (capacity up to 24,000 m^3/d), of which seven are for fluoride removal (5 in semiconductor industry, 2 in TFT-LCD industry), two for ammonium removal (in TFT-LCD industry), two for calcium removal (drinking water softening and wastewater reuse), and one for heavy metal recovery (in PCB industry)..

8000 m³/d FBC water softening project for Taiwan Water Corporation

Colorful crystals discharged from FBC system for treating different wastewater

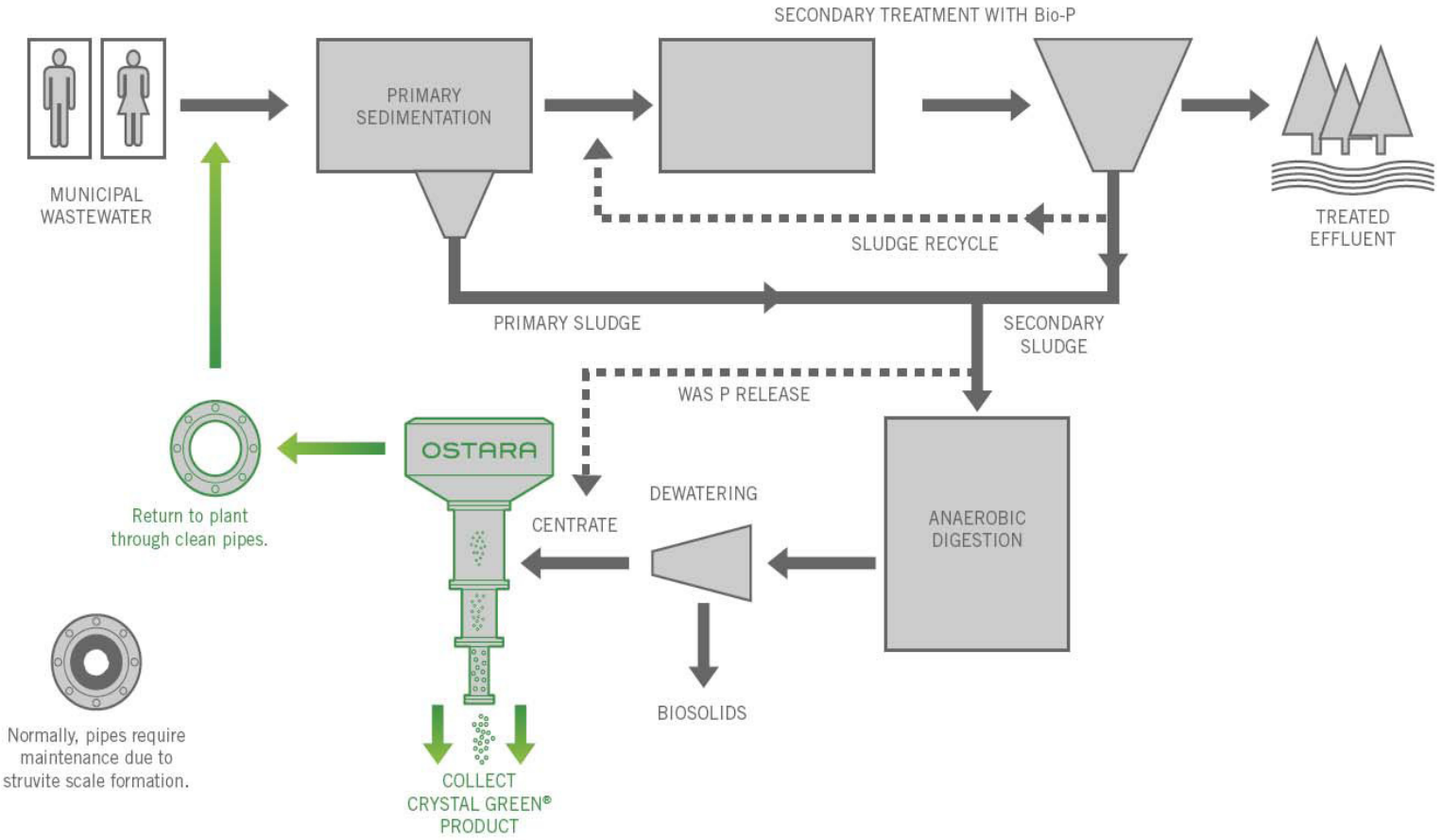
Patents

- US 6.235.203, 6.210.589
- NL 1004621, 1011698, 1014191,
- CN ZL96213888.6
- TW 088519, 122668, 143243, 161596, 189832

- **Fluidized Bed Crystallization Wastewater Treatment and Resource Recovery Technology by ITRI.**
- **7 FBC for Fluoride recovery（5 in semiconductor industry, 2 in TFT-LCD industry）2FBC for Ammonium removal（TFT-LCD）2FBC for calcium removal（1 in water softening and 1 in petrochemical wastewater reuse）**

1 FBC for Heavy metal removal（PCB industry）

- **Ostara Process**



Phosphorus recovery from Edmonton Goldban WWTP, Canada. 80% of phosphorus and 10-15% of the ammonia from a flow of 500 CMD can be recovered.

- **Combination of Phosphate and Ammonium Rich Streams for Struvite Recovery from Municipal Wastewater.**

- **Struvite($MgNH_4PO_4 \cdot 6H_2O$),a crystalline structure comprised of Mg^{+2},NH_4-N,PO_4-P, is commonly encountered in wastewater.**

- **The fluidized bed reactor can grow crystals to 5 mm in diameter with much greater crystal hardness and purity.**

II. Semiconductivity Indust. Wastewater —selective precipitation→ $Mg_3(PO_4)_2 \cdot 8H_2O$ or $Mg\ HPO_4 \cdot 3H_2O$

1.Wastewater contains high level of 〔F^-〕 and 〔SO_4^{-2}〕and 〔PO_4^{-3}〕and 〔NH_4^+〕 in wet etching unit.

1.Form three possible precipitates:

newberyite 〔$MgHPO_4 \cdot 3H_2O$〕

trimagnesium phosphate 〔$Mg_3(PO_4)2 \cdot 22H_2O$〕

bobierrite 〔$Mg_3(PO_4)2 \cdot 8H_2O$〕

2.Calcium reacts with both phosphate and fluoride, the calcium phosphate 〔$Ca_5(PO_4)_3OH$〕cannot be obtained in pure.

3.Magnesium salts($MgCl_2$) can be a good solution in recovering 〔PO_4^{-3}〕from Waste stream, Knowing that they have low reactivity with fluoride.

2.Further purification and processing depends on the final application.

II. Wastewater → Selective Precipitation (by Mg salts) → precipitates (further processing)

1.Pretreatment（pH＜3.0）

Selective Precipitation by $CaCl_2$to recovery $CaF_2$and remove metal ions.

2.Selective precipitation（pH at 3~10）

Selective precipitation by $MgCl_2$ to recovery phosphate :

Newberyite〔$MgHPO_4 \cdot 3H_2O$〕is predominant at pH＜6.0

Trimagnesium phosphate

〔$Mg_3(PO_4)_2 \cdot 22H_2O$〕 is favorably formed at pH＞9.0

Bobierrite 〔$Mg_3(PO_4)_2 \cdot 8H_2O$〕will form at pH＝8~10

3.Control Variables :

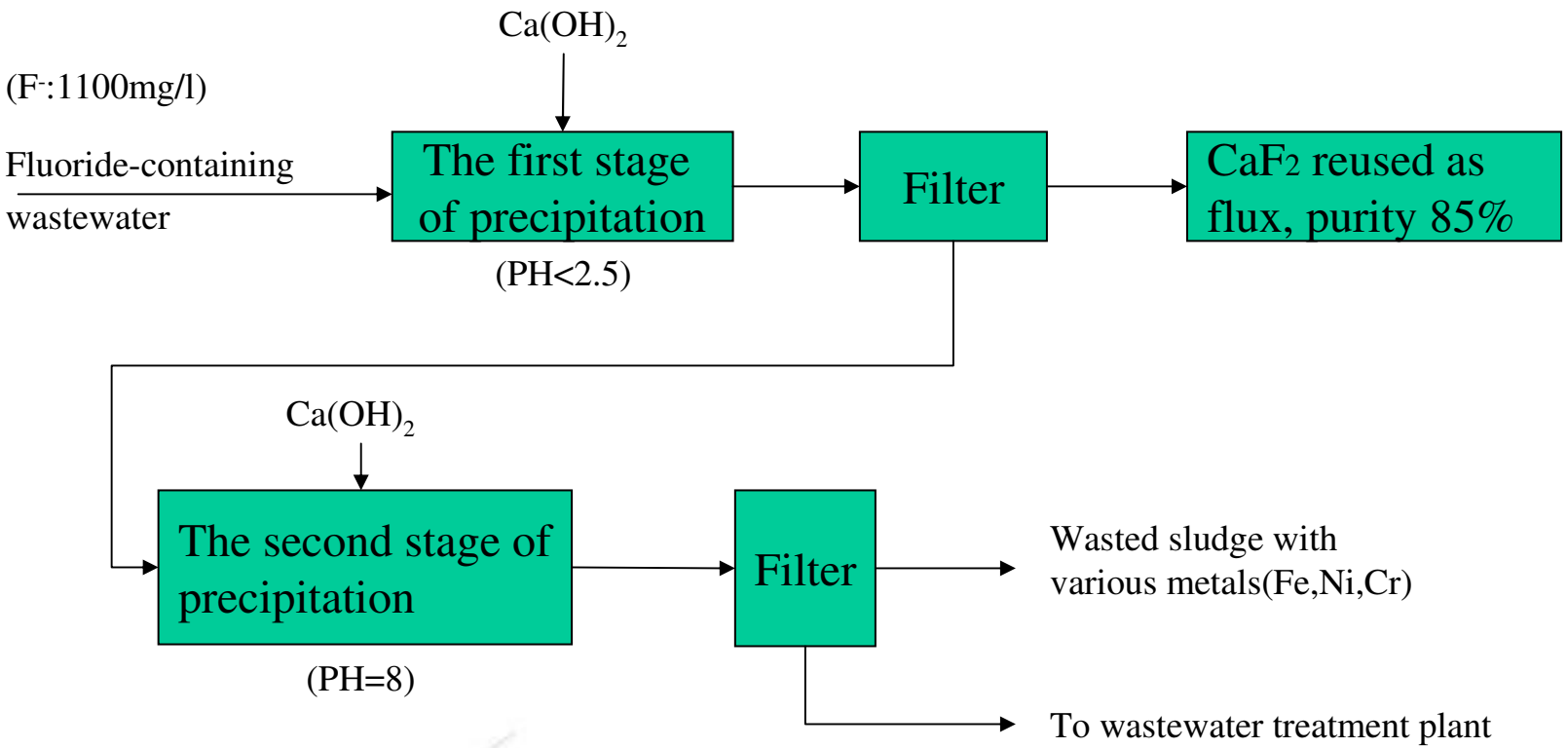
pH, molar ratio of 〔Mg^{+2}〕：〔PO_4^{-3}〕and other species competitivity and interferences.

Ⅱ. Selective Precipitation : Pretreatment

Selective Precipitation of Fluoride and Phosphate from High-tech Industries.

- **Armco Electrosteel Co.USA**

  Selective precipitation of Fluoride from Electrosteel waste stream by Two-Stage Lime Neutralization.



Selective precipitation to recovery CaF_2 in Armco ElectroSteel Co. USA

- **Basic Chemical Concept:**

  .The solution of CaF_2 at PH=2.0 is about 65 mg/l, therefore, around 95% of the influent of fluoride (F^-: 1100 mg/l) will be precipitated as CaF_2.

  .At PH < 3.0, reversely, the solubilities of $Fe(OH)_3$, $Ni(OH)_2$ and $Cr(OH)_3$ are all very high, and can be separated and get high quality of CaF_2.

  .Compare to the nature CaF_2 mineral, the product from selective precipitation process makes even higher purity (85%) than 77%-80% of nature one.

- **Selective Precipitation : Phosphate Recovery**

Selective Precipitation of Phosphate from Semiconductor Wastewater

Flow Characteristics:

Fluoride(F^-): 800-1000mg/l

Sulfate ($SO_4^{=}$): 500-650mg/l

Phosphate($PO_4^{\equiv}$): 100-120mg/l

Ammonium(NH_4^+): 20-30mg/l

- **Basic Concepts:**

  Magnesium salts have low reactivity with fluoride,therefore,can be a good separator for phosphorus from fluoride ions.

  Three possible magnesium phosphate precipitates,namely,$MgHPO_4 \cdot 3H_2O$,

  $Mg_3(PO_4)_2 \cdot 22H_2O$ and $Mg_3(PO_4)_2 \cdot 8H_2O$

  $MgCl_2$ is more effective than MgO.

- **Operation Conditions:**

  molar ratio of【Mg^{+2}】:【PO_4^{-3}】=3 to3:2

  pH=8-10

  phosphate recovery rate = 40-70%

  product $Mg_3(PO_4)2 \cdot 8H_2O$ is dominated when molar ratio is 3:1, pH=10 , and recovery rate is 70%.

Table C: Periodical system showing pellet reactor experience

1 H																	2 He
3 Li	4 Be					successfully recovered						5 B	6 CO3	7 NH4	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 PO4	16 SO4	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57/71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89/103 Ac-Lr	104 Rf-Ku	105 Ha-Ns	106 Unh	107 Uns	108 Uno	109 Une									

In some cases it has proved to be attractive to form metal phosphates. Anions are usually removed as calcium salts. Occasionally it is more desirable to form complex salts. For example, phosphate can be removed as NH_4MgPO_4 while simultaneously reducing the wastewater nitrogen content.

For industrial wastewater, magnesium salts have low reactivity with fluoride, therefore, can be a good separator for phosphorus from fluoride ions. Selective precipitation of phosphorus from semiconductor and TFT-LCD waste streams as the forms of magnesium phosphate precipitates seems a promising approach.

III.Other Technologies Applied for Sludge, Sludge Ash, etc.（www.phosphorous-recovery.tw）

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Thanks for your attention!