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Ministry of the Environment

Ravinteiden talteenoton yleiskatsaus

Ari Kangas
Ympäristöministeriö

Lieteresurssi tänään ja huomenna
Vesiyhdistys / Jätevesijaosto
28.11.2019

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Ravinteiden kierrätys

Mineraalifosforivarojen rajallinen riittävyys

- Arviot 60-130 vuotta

Fosforivarat keskittyneet harvojen valtioiden alueille

- Poliittisesti epävakaassa Marokossa jopa 70 %
- Seuraavaksi suurin varanto Kiinassa, joka käyttää fosforinsa itse
- Suomessa on Länsi-Euroopan ainoa fosfaattikaivos

Vuonna 2014 EU lisäsi fosfaatin kriittisiksi määrittelemiensä raaka-aineiden joukkoon

Typpilannoitteiden valmistus Haber-Bosch -menetelmällä

- Kuluttaa paljon energiaa, n. 10 kWh/kgN
- Perustuu yleensä fossiiliseen energiaan
- Noin 2 % maailman energiankulutuksesta käytetään tähän tarkoitukseen

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Ravinteiden kierrätys

Ravinteiden käytön tehokkuus on heikko

Käyttöön otetusta

- typestä noin 80 %
- fosforista 25-75 %

menetetään ravinnepäästöinä, hukkavirtoina tai energiankäyttönä.

Ravinnevuodot aiheuttavat ravinnepäästöjä vesistöihin

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Puhdistamoliete ja ravinteet

Suomessa vuosittain muodostuvat ravinteiden kierrätykseen soveltuvat biomassat [LUKE]

	Saatavilla oleva typpi [t/a]	[%]	[%] mineraali-lannoitteista	Saatavilla oleva fosfori [t/a]	[%]	[%] mineraali-lannoitteista
Kotieläinten lanta	74600	54,7	49,1	18500	58,9	168,2
Säilörehunurmi	26765	19,6	17,6	3032	9,7	27,6
LHP-peltojen ja suojavyöhykkeiden nurmi	6300	4,6	4,1	970	3,1	8,8
Olki	16000	11,7	10,5	3200	10,2	29,1
Yhdyskuntien jätevesiliete	8300	6,1	5,5	4540	14,5	41,3
Yhdyskuntien biojäte	2200	1,6	1,4	400	1,3	3,6
Teollisuuden biohajoavat lietteet	2240	1,6	1,5	770	2,5	7,0
Yhteensä	136405			31412		

Suomessa käytetään perinteisinä epäorgaanisina lannoitteina noin **152 000 t/a N** ja **11 000 t/a P**

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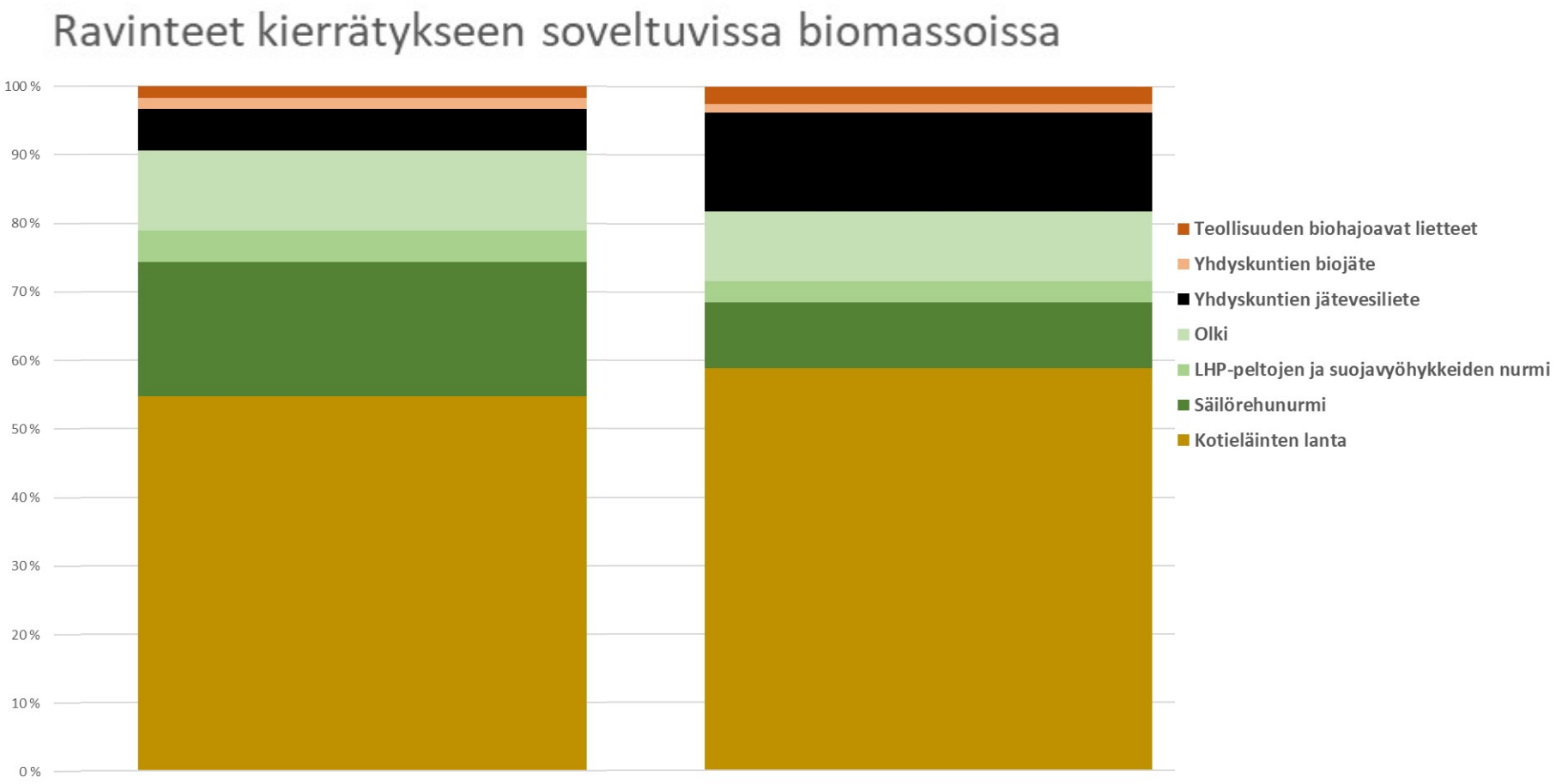
Puhdistamoliete ja ravinteet



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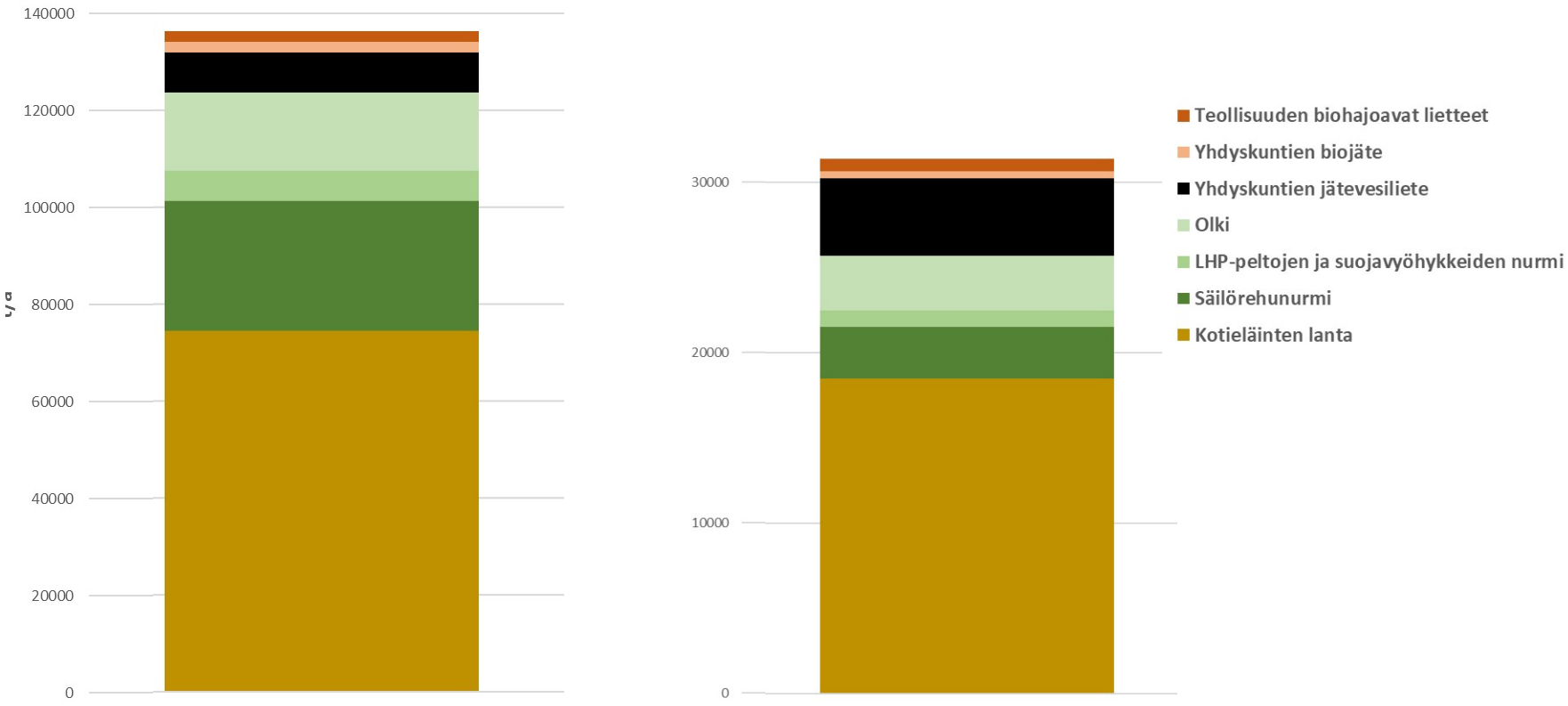
Puhdistamoliete ja ravinteet

Ravinteet kierrätykseen soveltuvissa biomassoissa



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Puhdistamoliete ja ravinteet

- Kierrätysravinteilla voidaan korvata perinteisiä lannoitteita
  - Lähes kaikki mineraalifosfori tulee EU:n ulkopuolelta
  - Saksa, Sveitsi, (Ruotsi?): lakisääteiset velvoitteet ottaa fosforia talteen
- Puhdistamolietteen fosforipitoisuus nelinkertainen muihin ravinnerikkaisiin biomassoihin verrattuna
- Lietefosfori 4 000 - 4 500 t/a
  - Kierrätettäväksi sopivan lietefosforin osuus kattaisi lähes 40 % koko Suomen vuosittaisen kasvintuotannon vaatimasta määrästä
  - Osankin kierrättäminen vakauttaisi markkinoita
- Lietetyppi 8 000 t/a (?)
  - Päästetään ilmaan tai vesiin

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Ravinteiden kierto jätevedestä

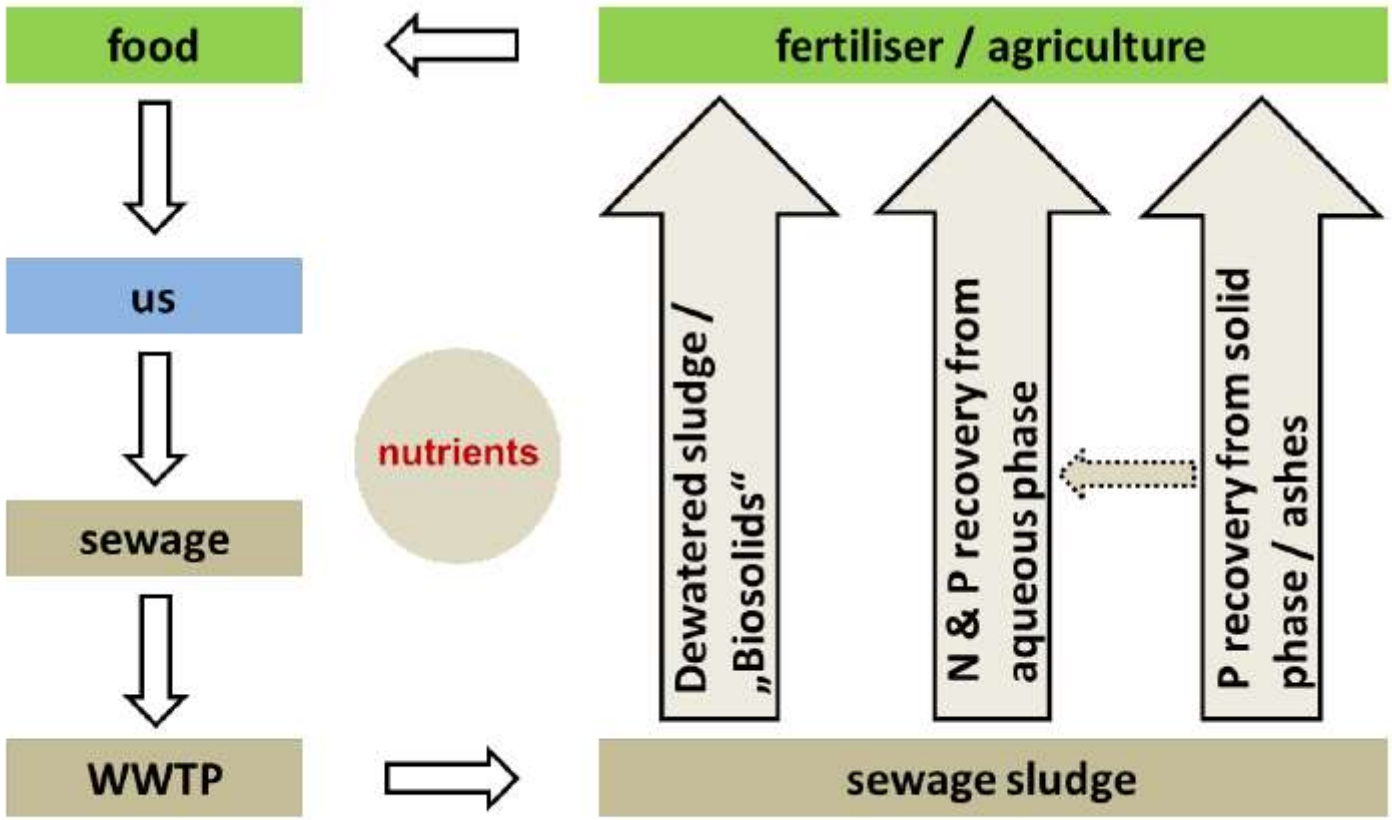

Figure 2: The three principal routes for P recovery and recycling from the wastewater stream as a nutrient (Kabbe,

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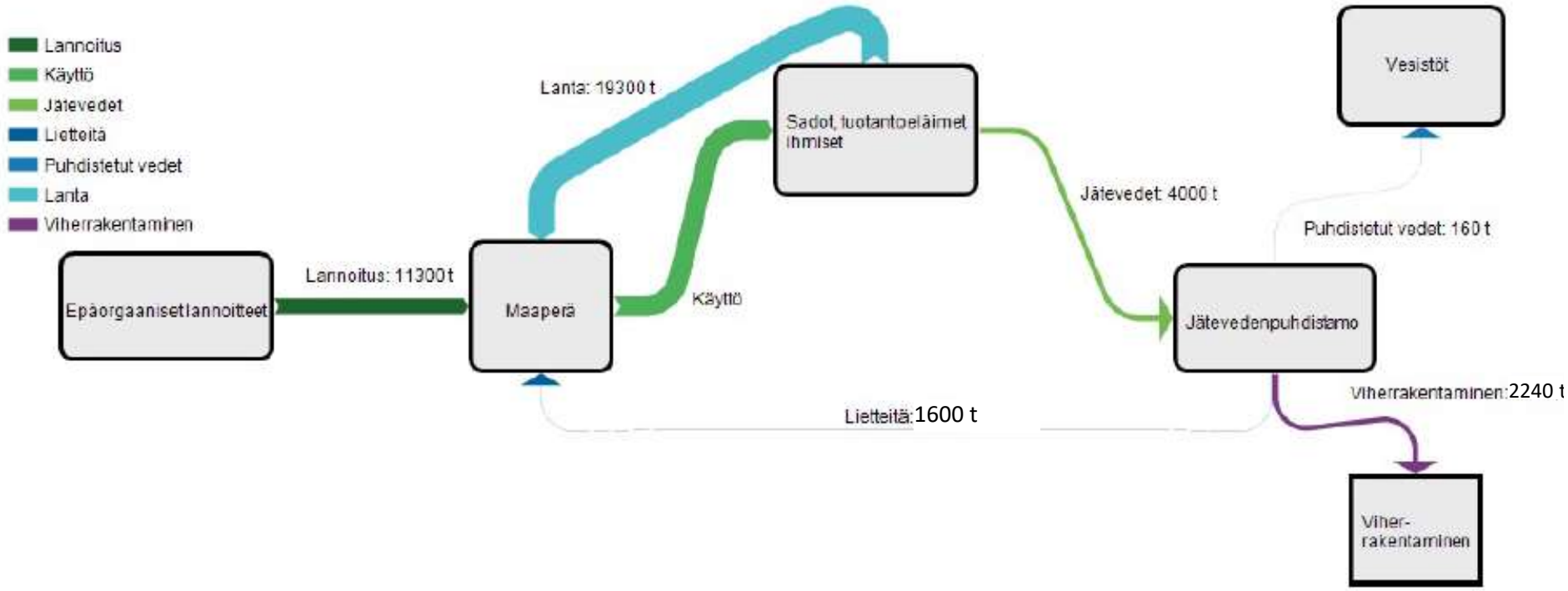
Fosforivirrat Suomessa



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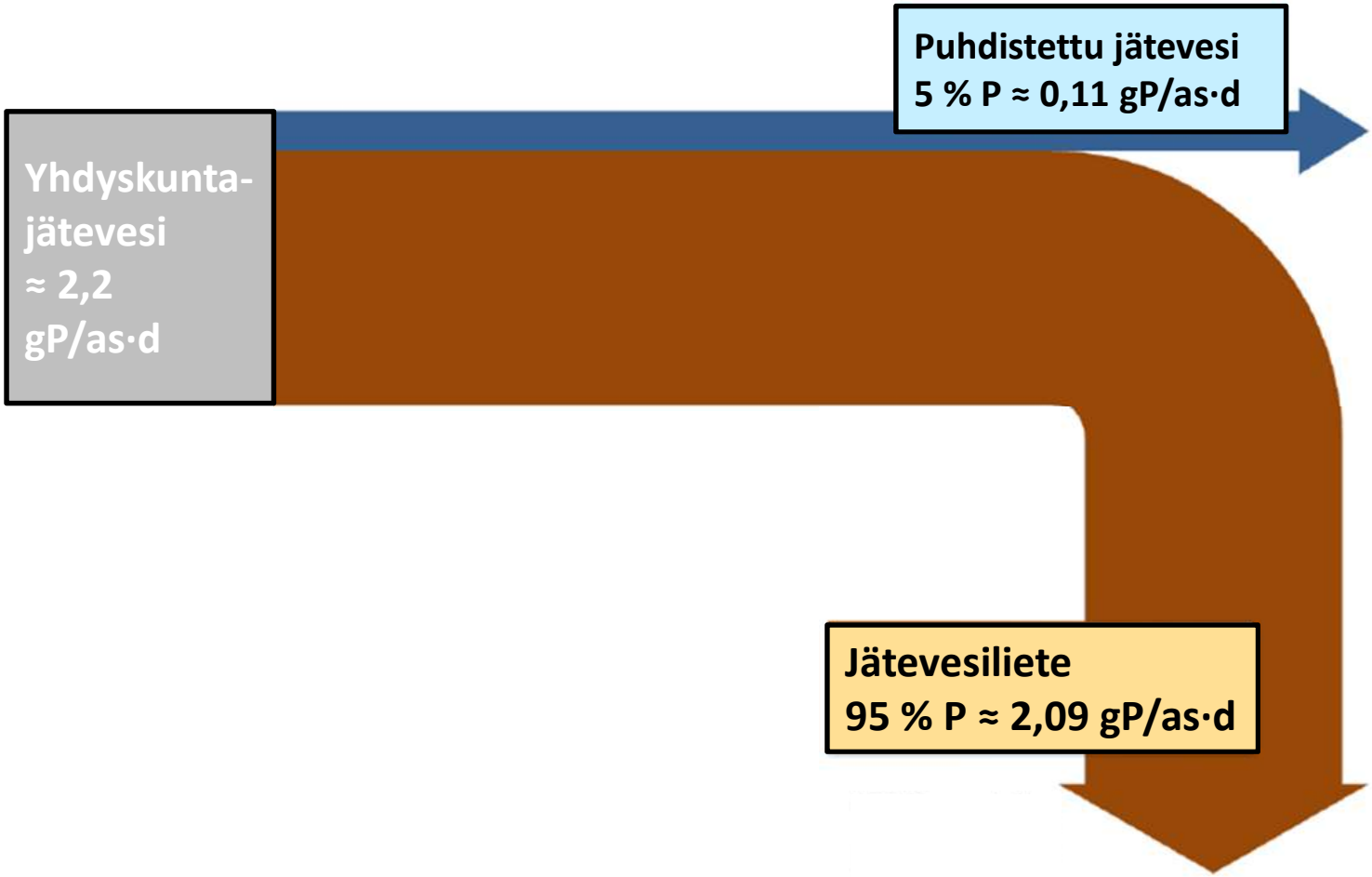
Fosforin talteenotto



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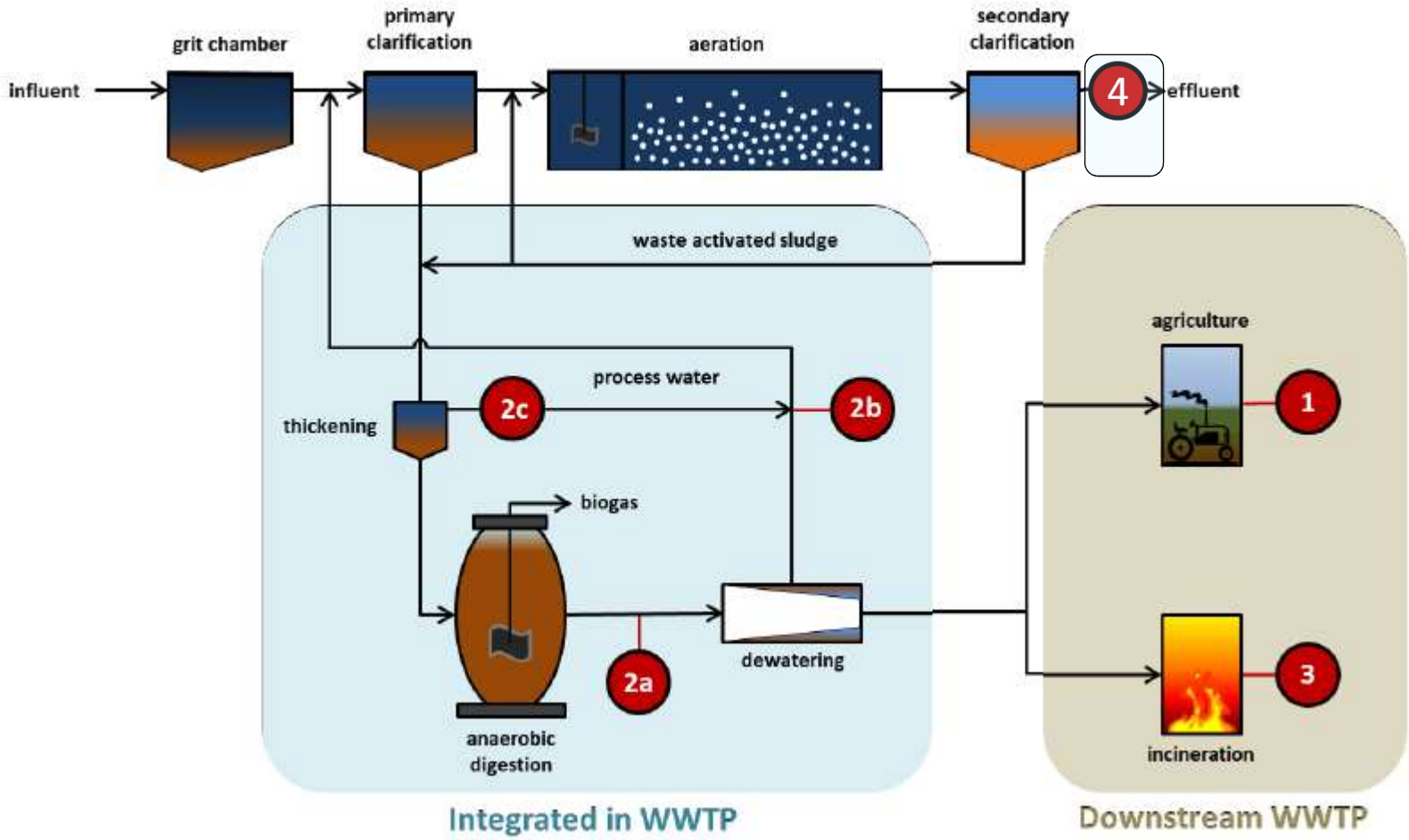
Fosforin talteenotto



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Fosforin talteenotto

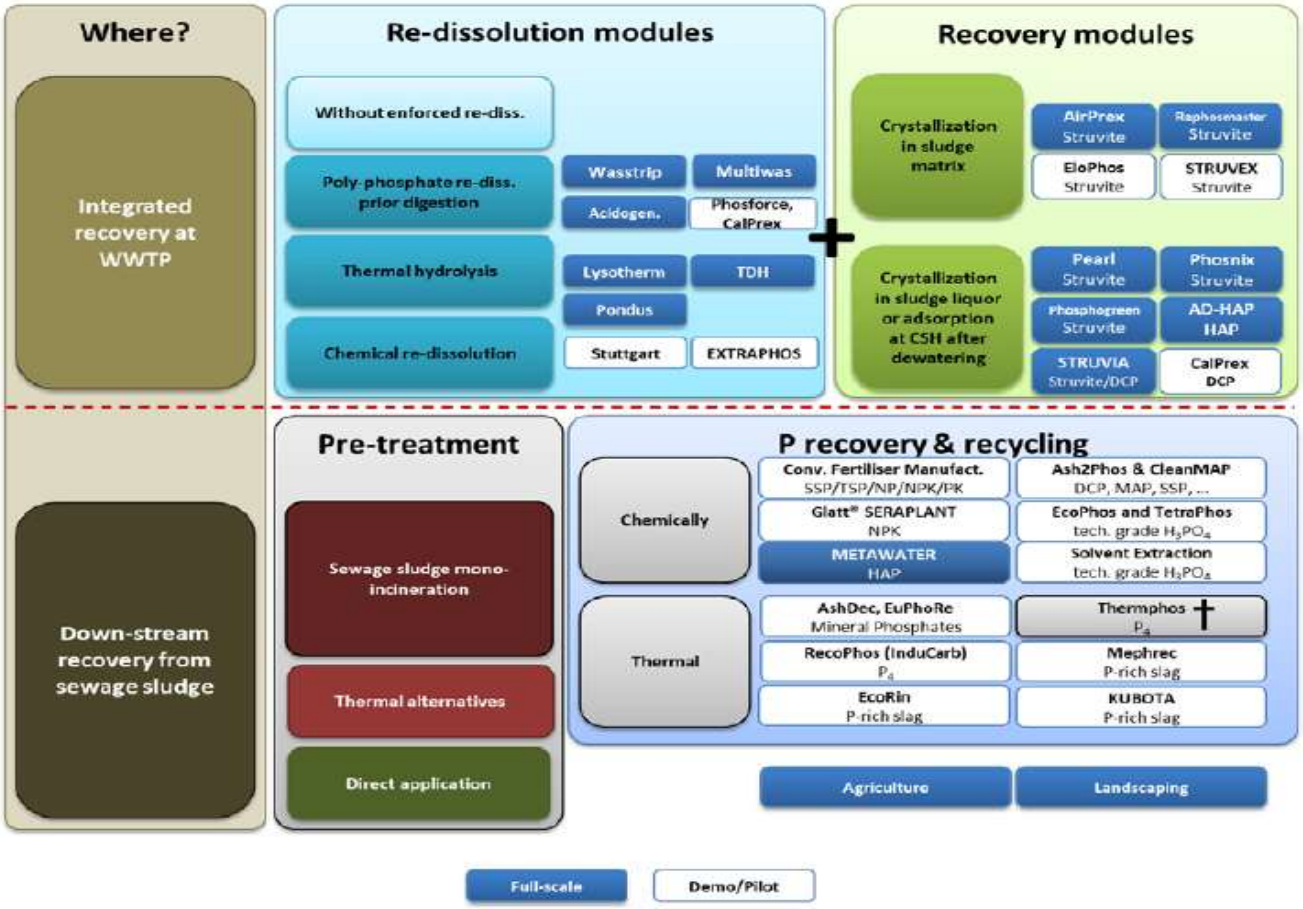

Figure 4: Prominent and already applied concepts for P recovery and recycling from sewage sludge.

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Fosforin talteenotto

Tuotettu fosfori

MAP, monoammoniumfosfaatti, ($NH_4H_2PO_4$)
DAP, diammoniumfosfaatti, ($(NH_4)_2HPO_4$)
MAP, magnesiumammoniumfosfaatti, ($NH_4MgPO_4 \cdot 6H_2O$) **struviitti**
HAP, kalsiumhydroksiapatiitti, ($Ca_{10}(PO_4)_6(OH)_2$)
DCP, dikalsiumfosfaatti (kalsiumvetyfosfaatti), ($CaHPO_4 \cdot 2H_2O$) brushiitti
P-CSH, fosfori absorboidaan struviittina kalsiumsilikaattihydraattiin

PA, phosphoric acid
MGP, Merchant Grade Phosphoric Acid, fosforihappo (H_3PO_4)

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Fosforin talteenotto

Technology	Location and operator	Operational since	Recovered material or product	Qty/a in tons
Onsite wastewater treatment plants				
AD-HAP (since 2014 by Hitachi Zosen)	Senboku Blackwater TP (JP), Senboku City	2007	HAP (from Night Soil)	15
	Totsugawa Village (JP)	2008		2
	Seihokugo Environment Improvement Assoc. (JP)	2009		40
	Kushimoto Town (JP)	2011		11
	Shimanto Town (JP)	2011		11
	Kofu Town (JP)	2015		4
AirPrex®	MG-Neuwerk (DE), Niersverband	2009	Struvite	100
	Wassmannsdorf (DE), Berliner Wasserbetriebe	2010		350
AirPrex®	Echten (NL), Drents Overijsselse Delta	2013	Struvite	n.i.
	Amsterdam-West (NL), Waternet	2014		500
	Salzgitter Nord (DE), ASG	2015		50
	Uelzen (DE), SE Uelzen	2017		n.i.
	Wolfsburg (DE), SE Wolfsburg	2017		50
	Tianjin (CN), Tianjin CEPG	2016		offline
	Liverpool, OH (USA), Medina County	2018		--
	Savage, MD (USA), Howard County	2018		--
	Denver, CO (USA), Denver Metro	2019		--
	Ft. Collins, CO (USA)	2019		--
	Göppingen (DE), SE Göppingen	2020		--

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Fosforin talteenotto

Technology	Location and operator	Operational since	Recovered material or product	Qty/a in tons
	Onsite wastewater treatment plants			
ANPHOS®	Well (NL), EcoFuels, (biomass digestion)	2005	Struvite	n.i.
	Odiliapeel (NL), Peka Kroef	2006		400
	Kruiningen (NL), Lamb Weston Meijer	2003		650
	Bergen op Zoom (NL), Lamb Weston Meijer	2007/16		290
	Budrio (IT), Pizzoli	2010		150
	Haps (NL), Waterschap Aa en Maas	2011		n.i.
	Oosterbierum (NL), Lamb Weston Meijer	2016		580
	Den Bosch (NL), Waterschap Aa en Maas	2018		n.i.
	Asturias (ES), Longas	2018		n.i.
	Tiel (NL), Waterschap Rivierenland	2019		n.i.
Crystalactor®	Nanjing (CN), Royal Haskoning DHV	2010	Struvite	n.i.
EloPhos®	Lingen (DE), SE Lingen	2016	Struvite	n.i.
EXTRAPHOS® (Budenheim)	Itzehoe (DE), Kommunalservice Itzehoe	2018 (demo)	DCP	n.i.
Gifhorn	Gifhorn (DE), ASG	2007	Struvite/CaP	70
J-Oil	Yokohama (JP), J-Oil Mills Co.		HAP	260
JSA	Kawasaki (JP), Japan Synthetic Alcohol Co.	1998	HAP	n.i.
KURITA	Fukuoka North, South and Wasui (JP), Fukuoka C.	1997	Struvite	120

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Fosforin talteenotto

Technology	Location and operator	Operational since	Recovered material or product	Qty/a in tons
Onsite wastewater treatment plants				
Kyowa Hakko	Hofu (JP), Kyowa Hakko Bio Corp.	2006	HAP	90
Multiform™	Yakima, WA (USA)	n.i.	Struvite	n.i.
	Boise, ID (USA)	n.i.		n.i.
	Massey, MD (USA), Jones Family Farms (dairy)	n.i.		n.i.
	Green Bay, WI (USA)	n.i.		n.i.
NASKEO	Castres (FR)	2015	Struvite	25
NuReSys®	Harelbeke (BE), Agristo	2008	Struvite	250
	2x Niewkuerke (BE), Clarebout Potatoes	2009/12		650
	Waasten (BE), Clarebout Potatoes	2012		n.i.
	Geel (BE), Genzyme	2014		80
	Leuven (BE), Aquafin	2013		50
	Land van Cuijk (NL), Logisticon	2015		150
	Apeldoorn (NL), Vallei & Veluwe	2016		550
	Braunschweig Steinhof (DE), SE|BS / AVB	2018/19		--
NutriTec® (Sustec, DMT)	Zutphen (NL), SaNiPhos® GMB	2010	Struvite & DAS	offline
PEARL®	Tigard, OR (USA), Clean Water Services	2009	Struvite	760
	Suffolk, VA (USA), Hampton Roads Sanit. District	2010		400

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Fosforin talteenotto

Technology	Location and operator	Operational since	Recovered material or product	Qty/a in tons
	Onsite wastewater treatment plants			
(OSTARA)	York, PA (USA), City of York	2010	(Crystal Green®)	270
	Hillsboro, OR (USA), Clean Water Services	2012		1000
	Slough (UK), Thames Water	2012		130
	Saskatoon, SK (CDN), City of Saskatoon	2013		500
	Madison, WI (USA), Madison Metro. Sew. Distr.	2014		1000
	Burford, GA (USA), Gwinnett County	2015		1000
	Amersfoort (NL), Vallei & Veluwe	2015		500
	Edmonton, AB (CDN), EPCOR Water Services	2015		2500
	Stickney, IL (USA), Metro. Water Recl. Chicago	2016		7700
	Reno, NV (USA), Cities of Reno and Sparks	2016		500
	Madrid (ES), Canal de Isabel II	2016		500
	Winchester, VA (USA), F. Winchester Service A.	2016		500
	St. Cloud, MN (USA), City of St. Cloud	2018		500
	Atlanta, GA (USA), City of Atlanta	2018		(1000)
	Jarocin (PL), City of Jarocin	2019		(130)
	Tel Aviv, (IL), Mey Ezor Dan	2020		(5000)
Phosforce (Veolia)	Schönebeck (DE), OEWA Wasser & Abwasser GmbH	2019	Struvite or Brushite (DCP)	n.i.

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Technology	Location and operator	Operational since	Recovered material or product	Qty/a in tons
Onsite wastewater treatment plants				
PHOSNIX® (Hitachi Zosen)	7 plants installed in Japan between 1989 and 2011 with capacities between 80-500 m^3/d	1989	Struvite	n.i.
		1992		n.i.
	--	1995		n.i.
	Lake Shinji-East (JP), Matsue City (1998)	1998		125
	--	2000		n.i.
	--	2009		n.i.
	--	2011		n.i.
	Kinan Environment Improvement Association (JP)	2014		n.i.
PHORWater	Calahorra (ES), El Cidacos	2015 (demo)	Struvite	n.i.
PHOSPAQ™	Olburgen (NL), Waterstromen (municipal & food)	2006	Struvite	400
	Lomm (NL), Waterstromen (food)	2007		260
	China (brewery)	2011		(1100)
	Poland (bio-ethanol)	2011		(500)
	Nottingham (UK), Severn Trent Water	2012		730
	USA (confidential)	2013		(800)
	Hünfeld (DE), BFG-IAR Hünfeld GmbH (dairy)	2014		730
	China (food processing)	2015		(1400)
	China (ethanol)	2016		(90)
	Tilburg (NL), Waterchap de Dommel	2016		340
	UK (municipal)	2017		(600)

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Technology	Location and operator	Operational since	Recovered material or product	Qty/a in tons
Onsite wastewater treatment plants				
PhosphoGREEN (SUEZ)	Aaby (DK), Aarhus Water	2013	Struvite	110
	Herning (DK), Herning Water	2016		106
	Marselisborg (DK), Aarhus Water	2018		302
	Villiers Saint Frederic (FR), SIARNC	2019		43
	Sausheim (FR), Mulhouse	2019		88
REPHOS® (delivered by NuReSys)	Altentreptow (DE), Remondis Aqua (dairy)	2006	Struvite	200
Rintoru®	Mobile unit applying A-CSH to recover P	--	CaP at CSH	--
STRUVIA™	Helsingør Southcoast (DK)	2015	Struvite	40
Stuttgart	Offenburg (DE), AZV	2011 (demo)	Struvite (after acid leaching)	20
	Mobile Pilot – MSE Mobile Schlammentwässerungs GmbH	2015 (mobile)		--
Swing	Higashi-Nada, Kobe City (JP), Swing Corp.	2012	Struvite	130

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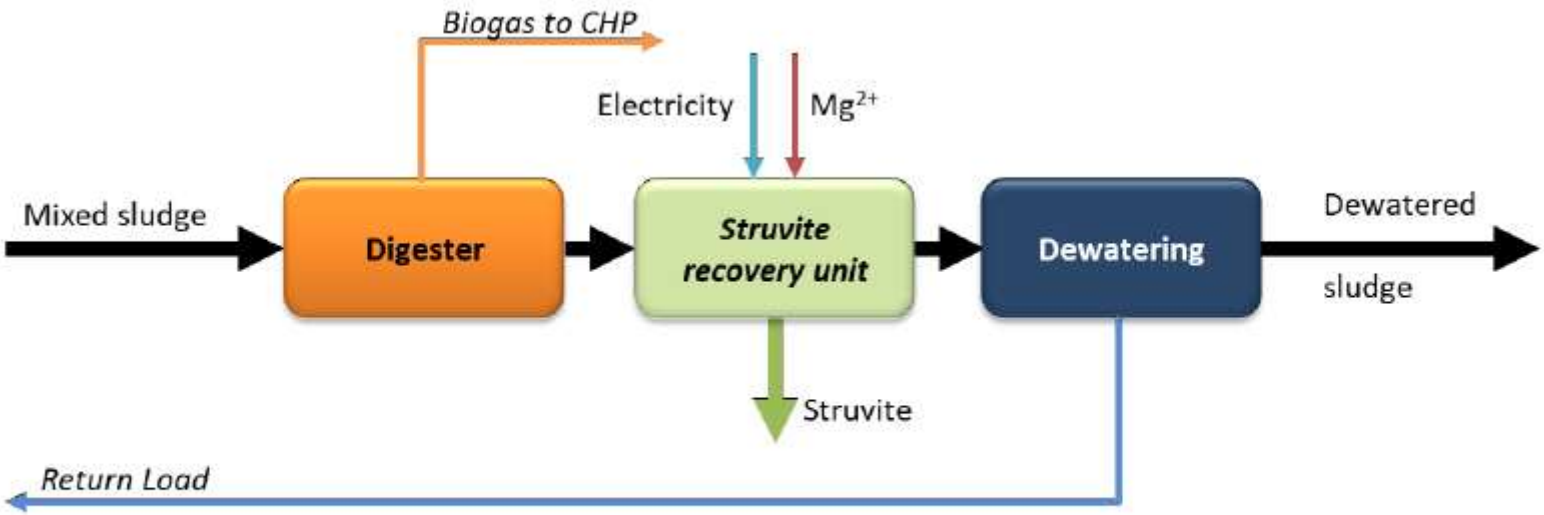

Figure 9: Struvite recovery from digestate with a fluidized bed, aerated reactor like AirPrex using CO_2 stripping for pH adjustment (adapted from Kraus et al., 2018).

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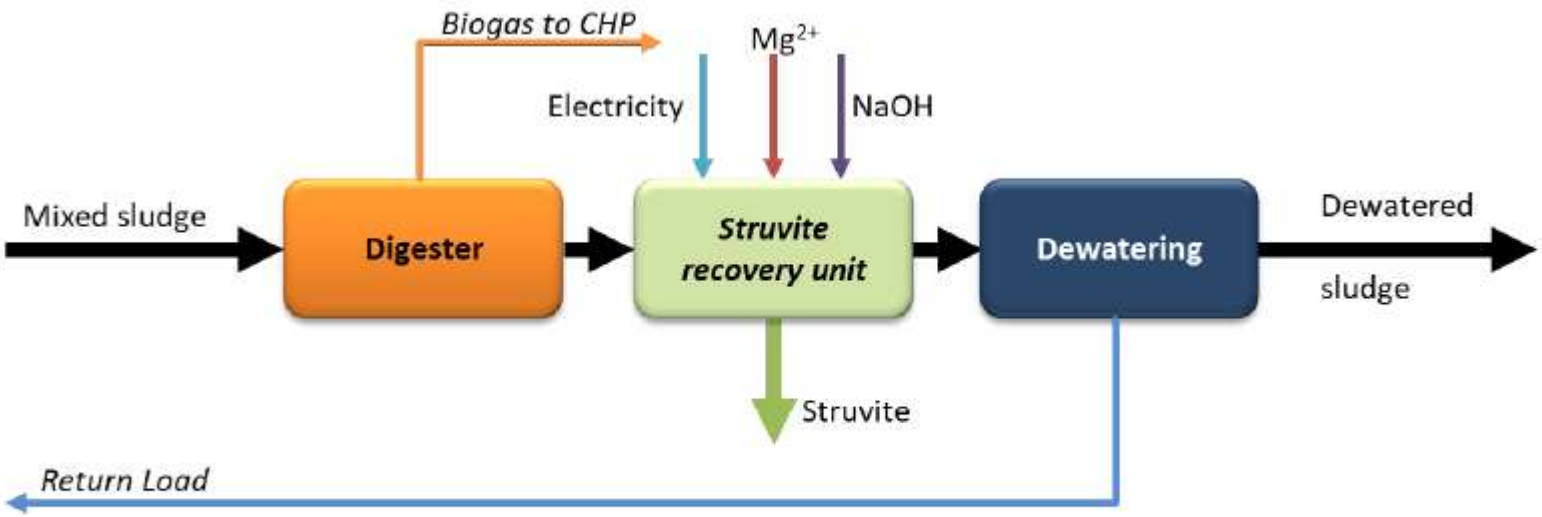

Figure 10: Struvite recovery from digestate with a mixed tank reactor using caustic (i.e. Rephosmaster, Nuresys) or the mixing itself for pH adjustement (Swing Corp.) (adapted from Kraus et al., 2018).

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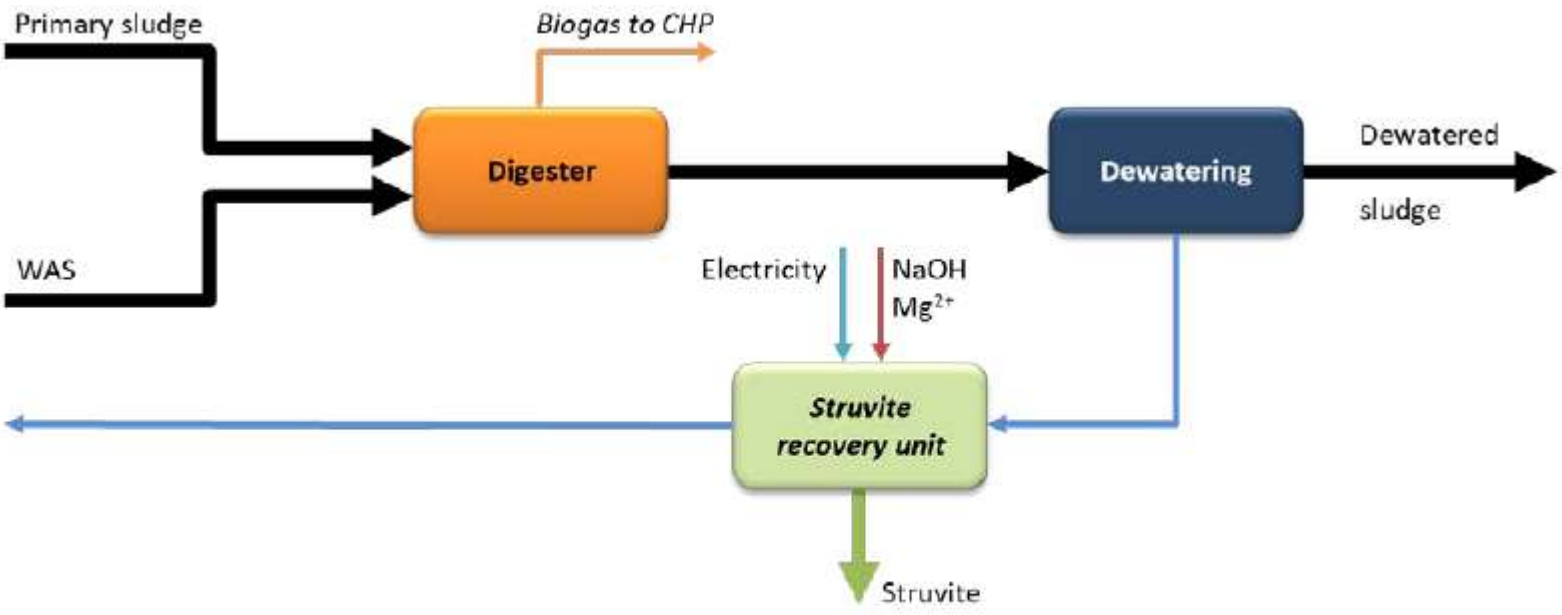

Figure 11: Struvite recovery from sludge liquor/filtrate using caustic soda for pH adjustement i.e. Pearl, Phosnix, Phospaq, Phosphogreen, Nuresys (adapted from Kraus et al., 2018).

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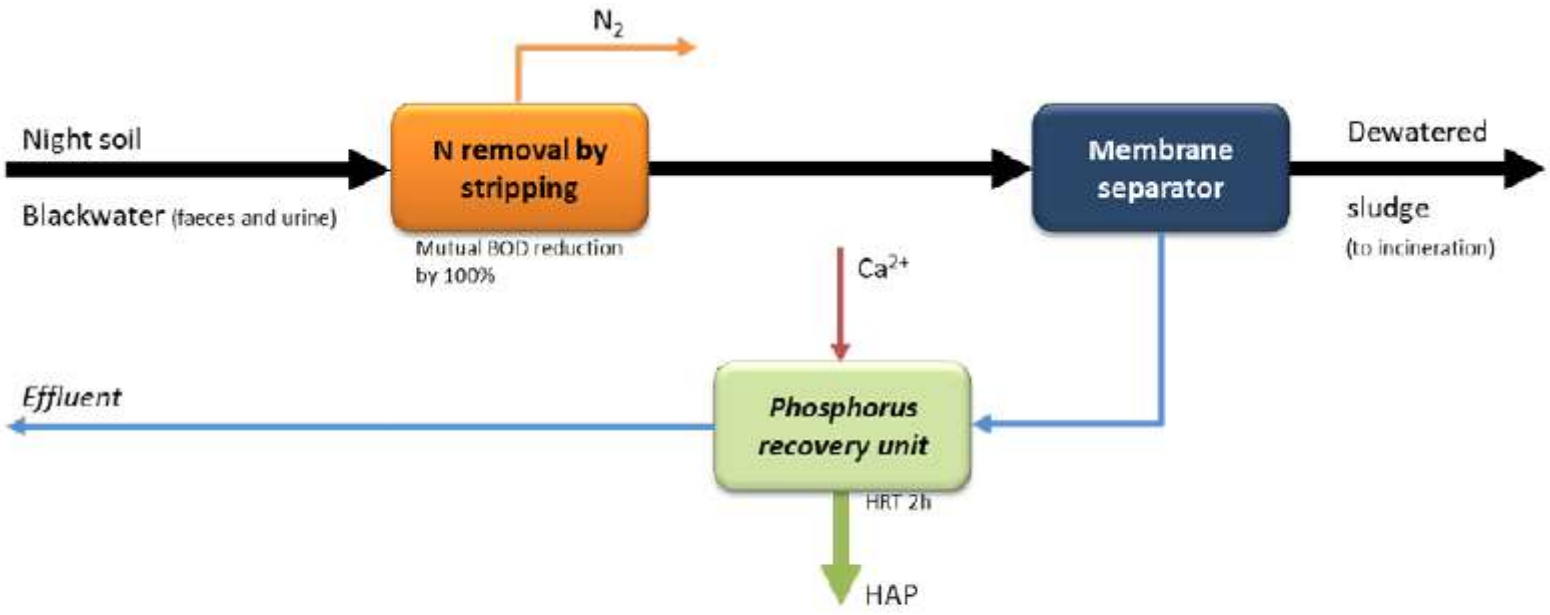

Figure 12: Phosphorus recovery as Calcium hydroxyapatite (HAP) from night soil/blackwater in a continuously stirred tank at blackwater treatment plants in Japan. In Senboku, $CaCl_2$ is dosed as precipitant. Example Technology: AD-HAP

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Fosforin talteenotto

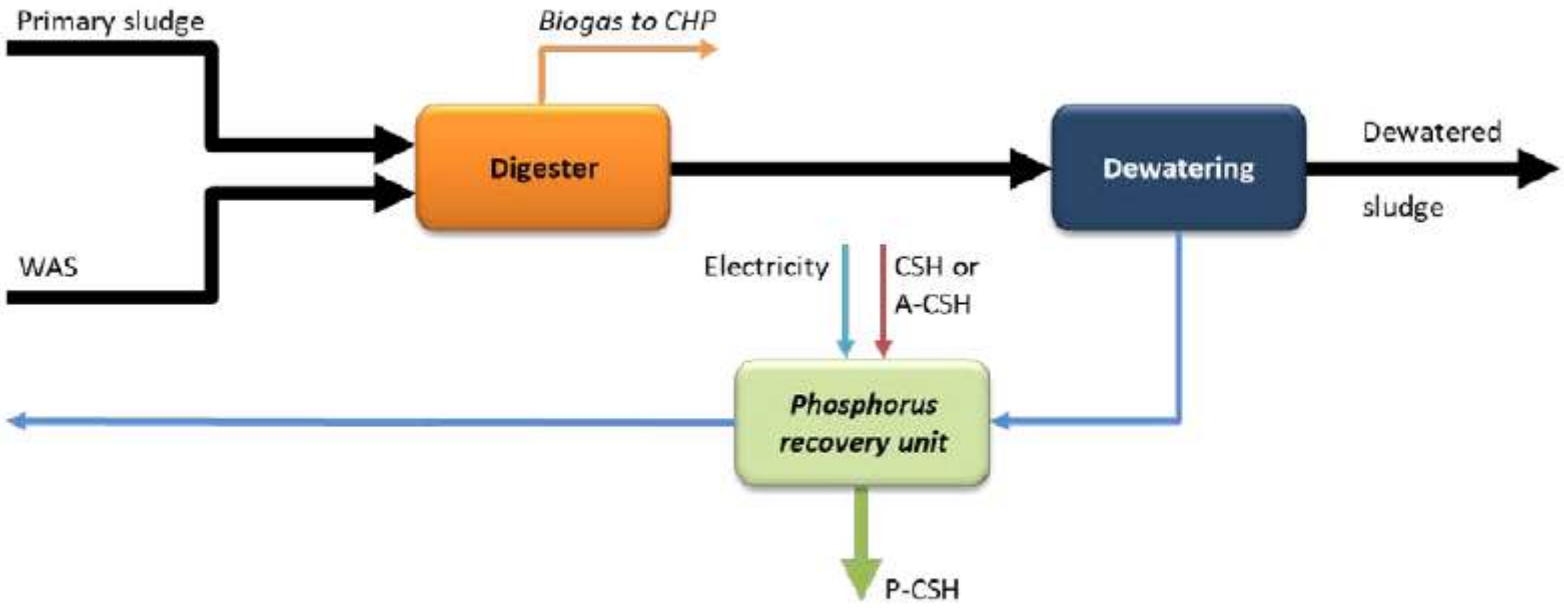

Figure 13: Phosphorus recovery from process waters or sludge liquor by adding Calcium silicate hydrate (CSH) as absorbent.

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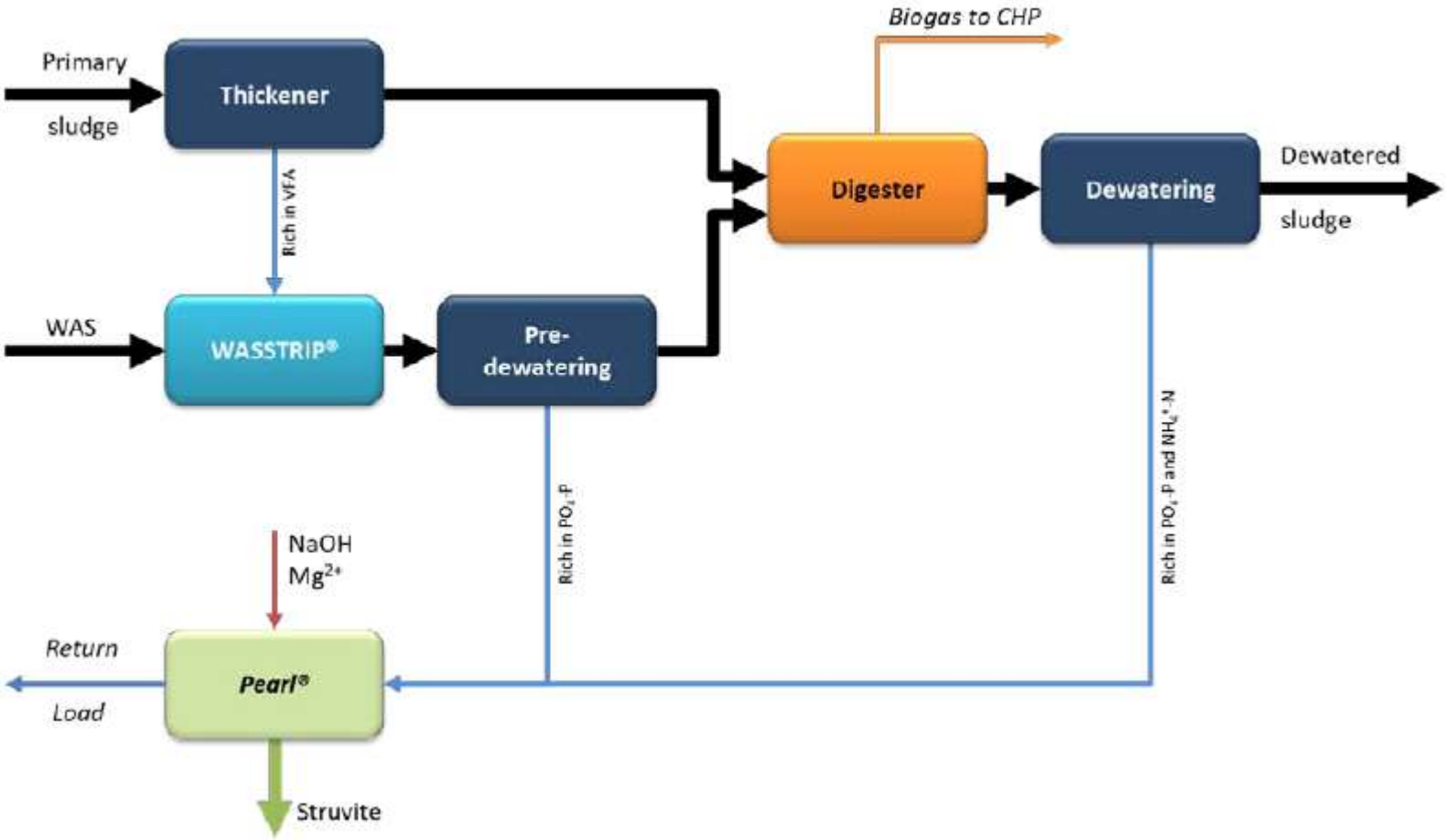

Figure 15: Combination of WAS bio-acidolation (WASSTRIP®) prior digestion and struvite recovery

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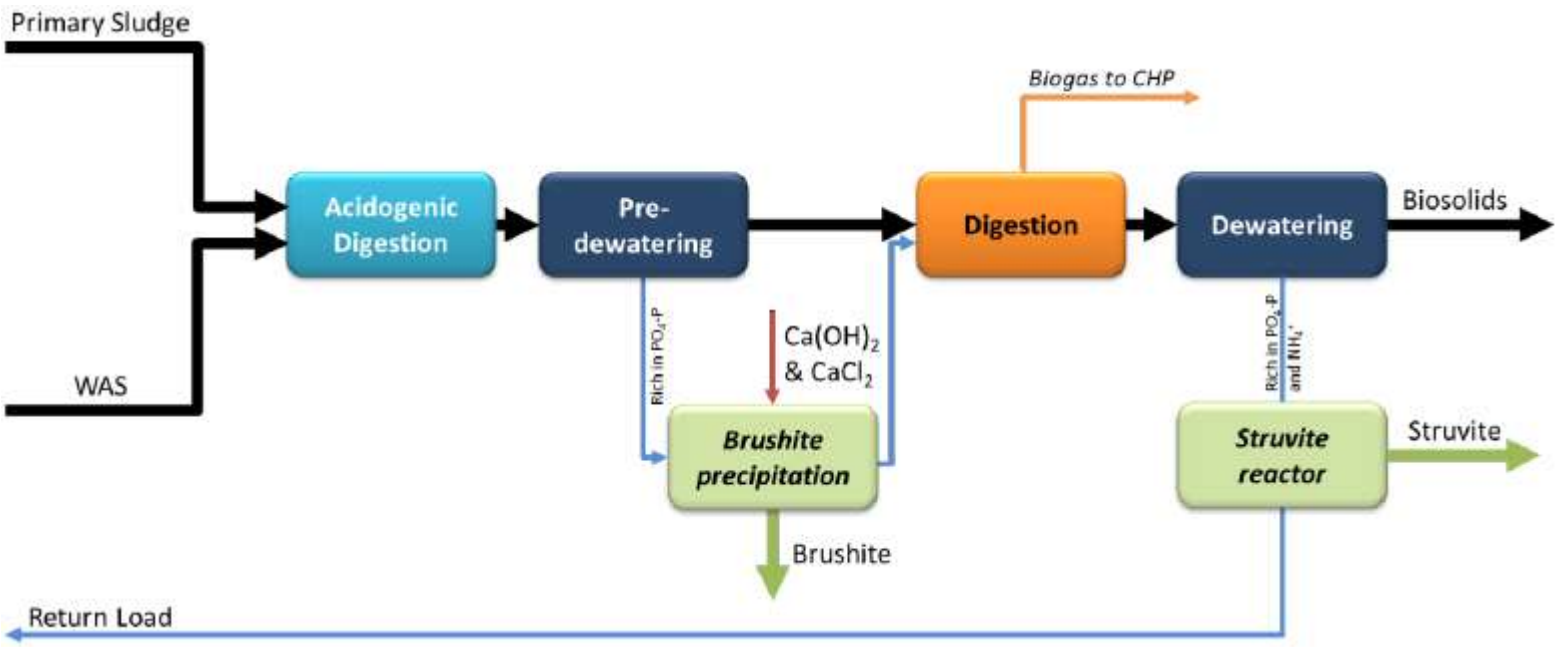

Figure 17: The Phosforce concept promoted by Veolia using a Struvia system for struvite recovery

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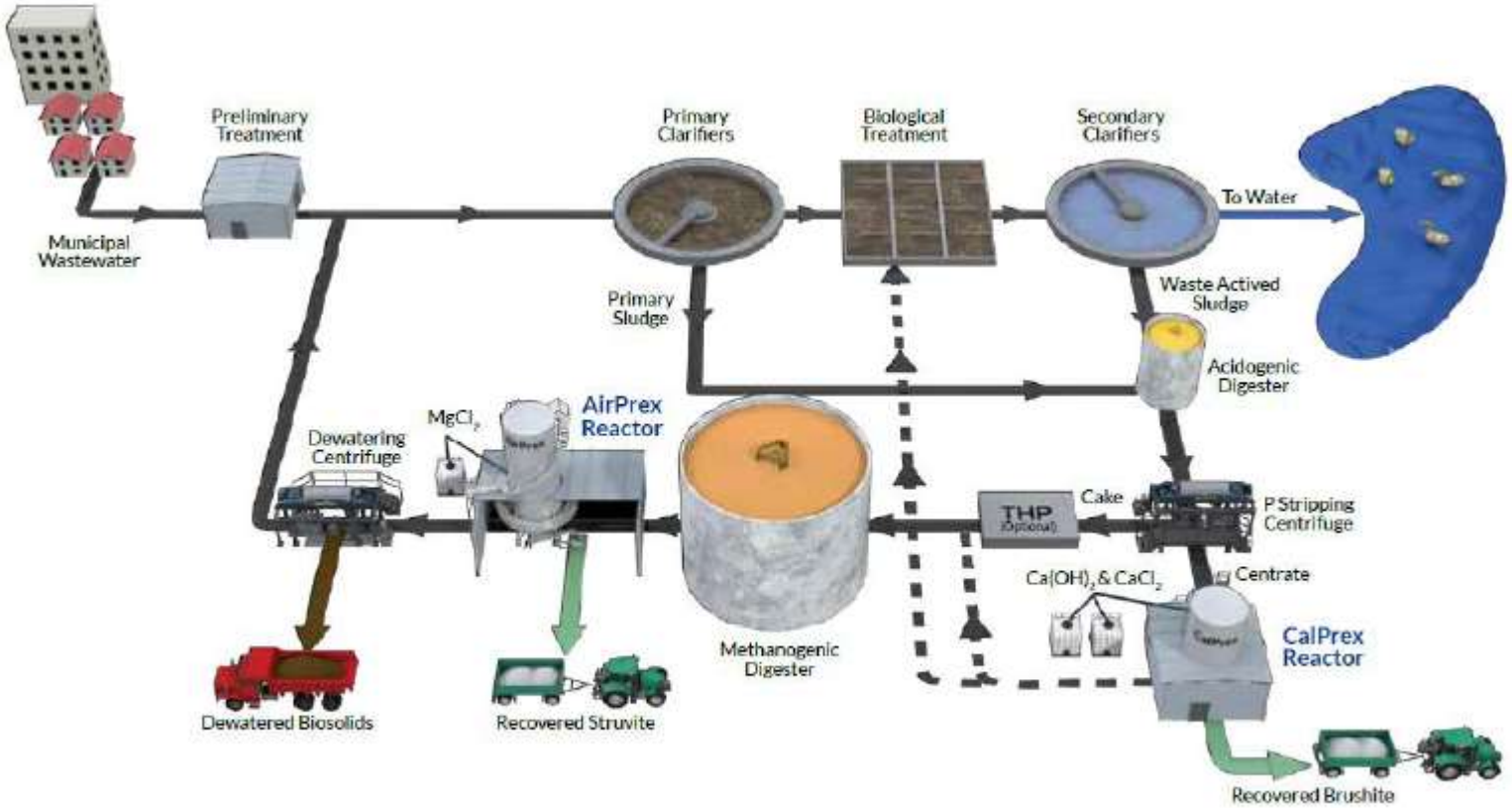

Figure 16: The CalPrex™ concept promoted by CNP (Courtesy of CNP Technology and Biosolids).

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Fosforin talteenotto

Technology	Supplier	Input for recovery step			Recovered Material	TRL
		2a Diges-tate	2b De-watering Liquor	2c WAS Thickening Liquor		
AD-HAP	Hitachi Zosen		X		HAP	9
AirPrex	CNP	X			Struvite	9
Anphos	Colsen		X		Struvite	9
CalPrex	CNP			X	Brushite (DCP)	7
Crystalactor	RoyalhaskoningDHV		X		Struvite	9
EloPhos	Eliquo Stulz	X			Struvite	7
ePhos	Fraunhofer IGB		X		Struvite	7
ExtraPhos*	Budenheim	X			Brushite (DCP)	7
MultiForm + MultiWas	MultiForm Harvest		X		Struvite	9
				X		n.i.
Naskeo	Naskeo		X		Struvite	8
NureSys	NuReSys	X	X	X	Struvite	9

Technology	Supplier	Input for recovery step			Recovered Material	TRL
		2a Diges-tate	2b De-watering Liquor	2c WAS Thickening Liquor		
NutriTec	Sustec DMT		X		Struvite	9
Pearl + WASSTRIP	Ostara		X		Struvite	9
				X		9
Phosnix	Hitachi Zosen		X		Struvite	9
PhosForce	Veolia			X	Brushite (DCP)	7
PhosphoGreen	Suez		X	X	Struvite	9
Phospaq	Paques		X		Struvite	9
P-RoC	CMM		X		Struvite at CSH	7
Rephos	Remondis		X		Struvite	9
Rephosmaster	Swing	X			Struvite	9
Struvia	Veolia		X		Struvite	9
Stuttgart*		X			Struvite	7

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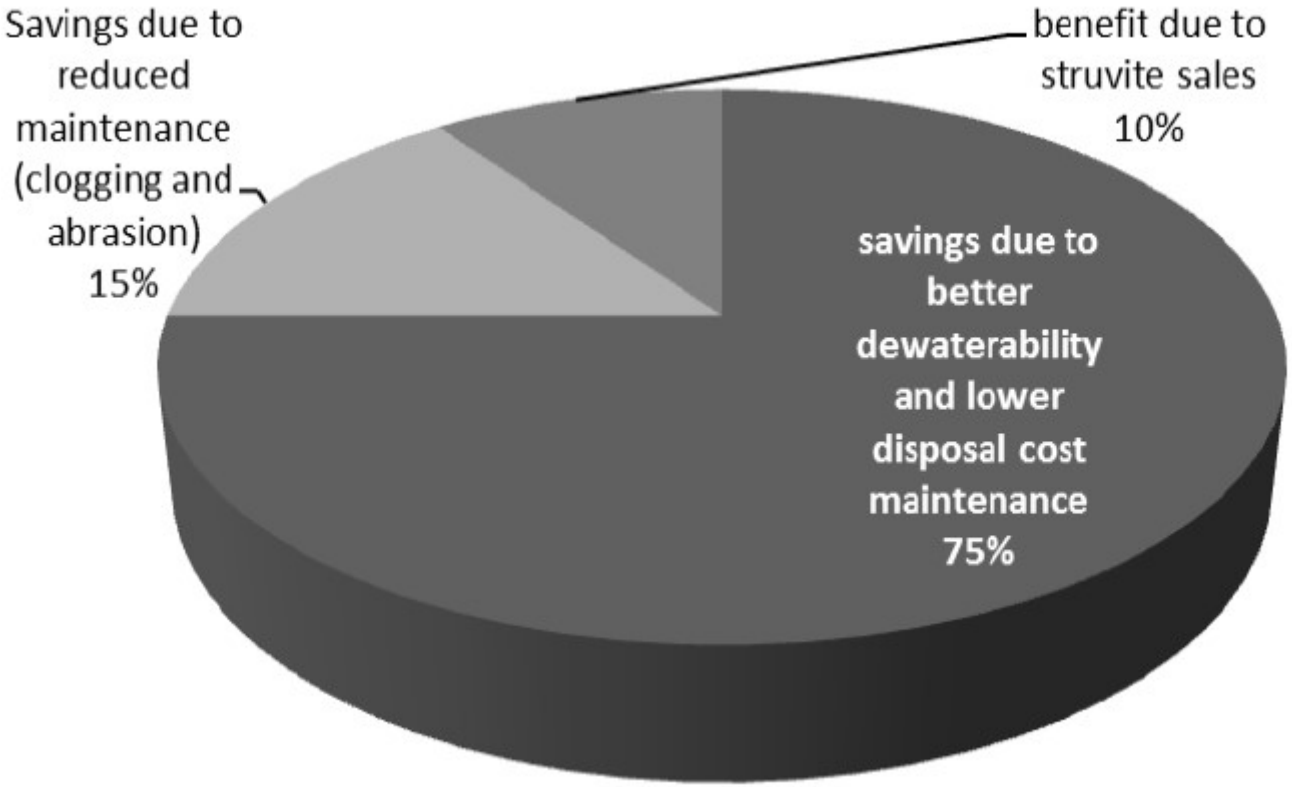
Fosforin talteenotto

Struviitti



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Fosforin talteenotto – lietteen jatkokäsittely

Technology	Location and operator	Operational since	Recovered material or product	Qty/a in tons
	Downstream wastewater treatment plants and ashes			
Ash2®Phos	Helsingborg (SE), EasyMining Sweden AB Bitterfeld (DE), EasyMining & Gelsenwasser	2022 2022	MAP/DCP	-- --
EcoPhos®	Varna (BG), DecaPhos (for testing ashes) Dunkerque (FR), EcoPhos	2016 2020	H_3PO_4/DCP/ MCP	-- --
Fertiliser industry	Various companies already apply or consider use of secondary P sources	tested and intended	Commercial ferti-liser	Mixed in
METAWATER	Gifu North (JP), Gifu City Akisato (JP), Tottori City	2010 2013	HAP	300 150
Nippon PA	Chiba (JP), Nippon Phosphoric Acid	2009	H_3PO_4	n.i.
TetraPhos®	Hamburg (DE), Remondis Aqua	2020	H_3PO_4	--

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Fosforin talteenotto – lietteen hajotus

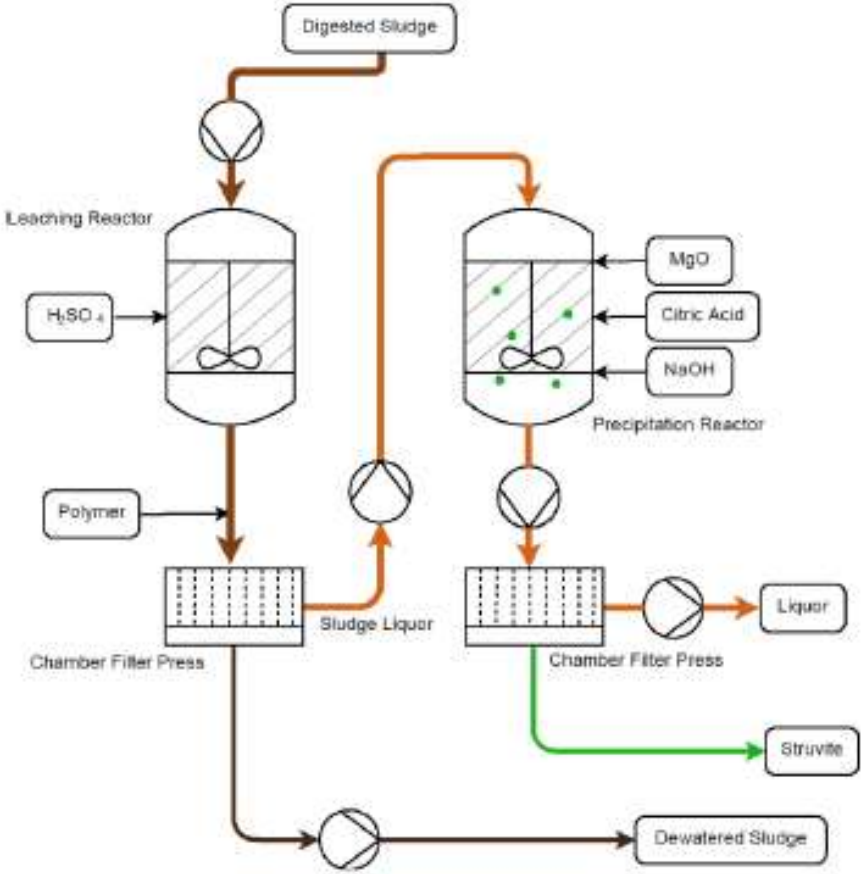

Figure 18: Process scheme of the mineral acid leaching Stuttgart process (P-REX factsheet 2015).

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Fosforin talteenotto – lietteen hajotus

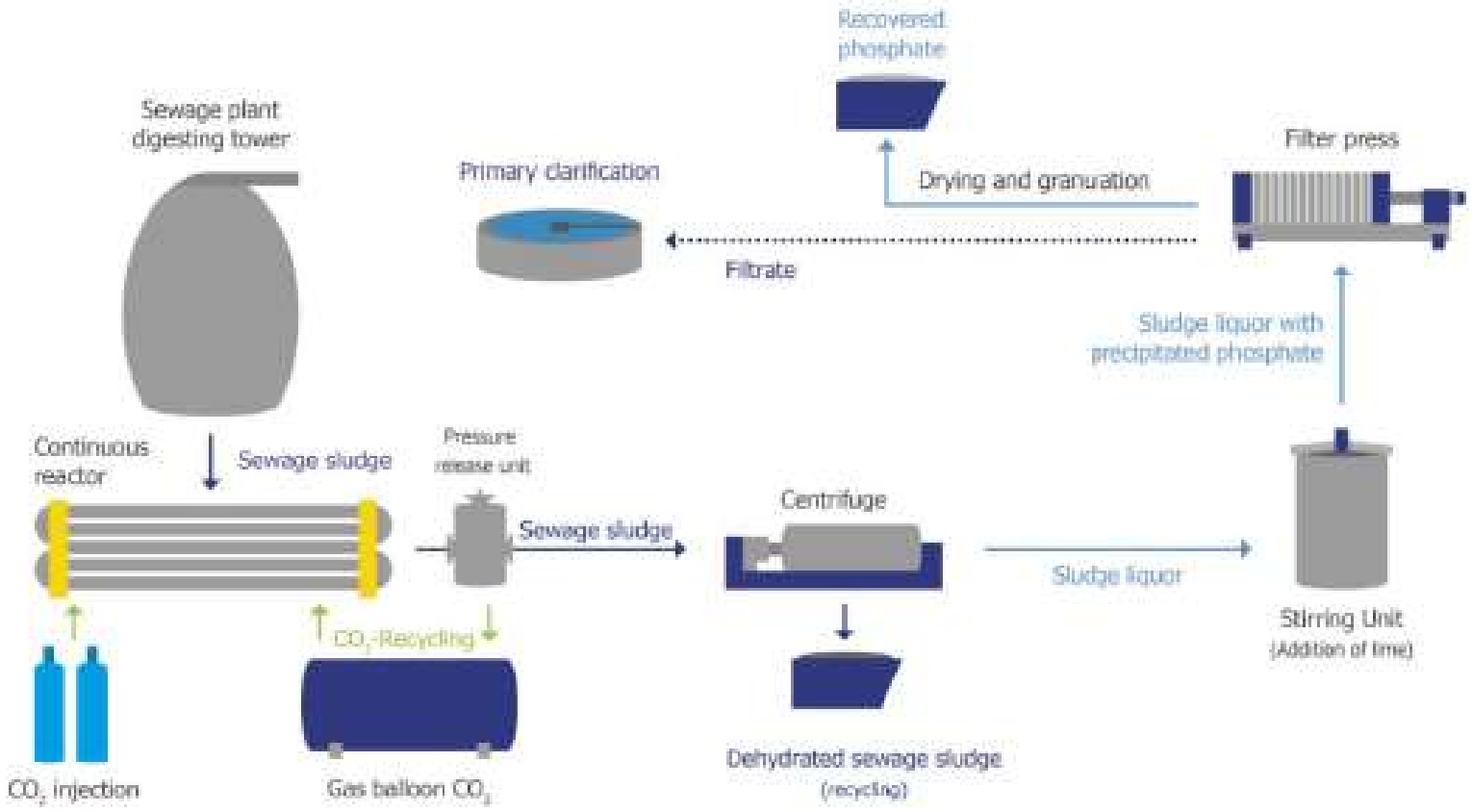

Figure 19: Process scheme of Budenheim's Extraphos® CO_2 P recovery process (courtesy of Budenheim).

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Fosforin talteenotto - tuhkasta

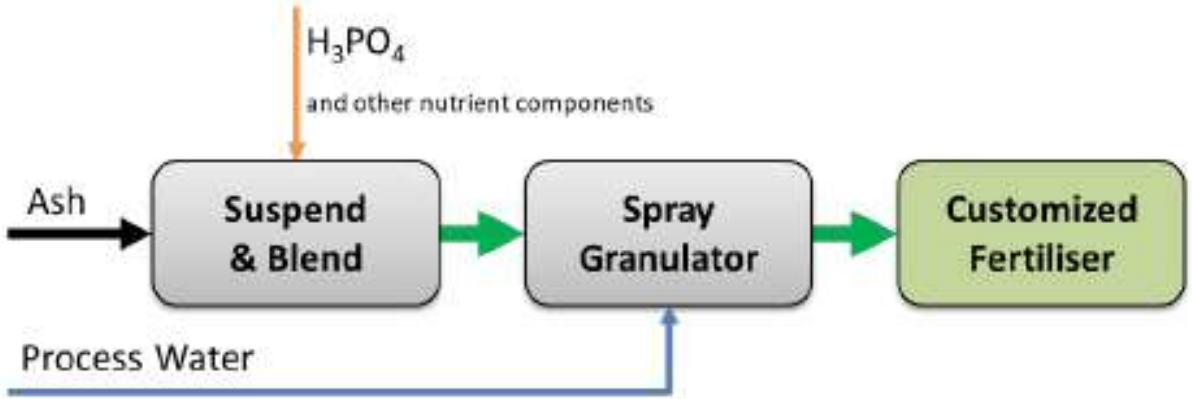

Figure 21: Schematic flow of the Glatt® SeraPlant pocess.

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Fosforin talteenotto - tuhkasta

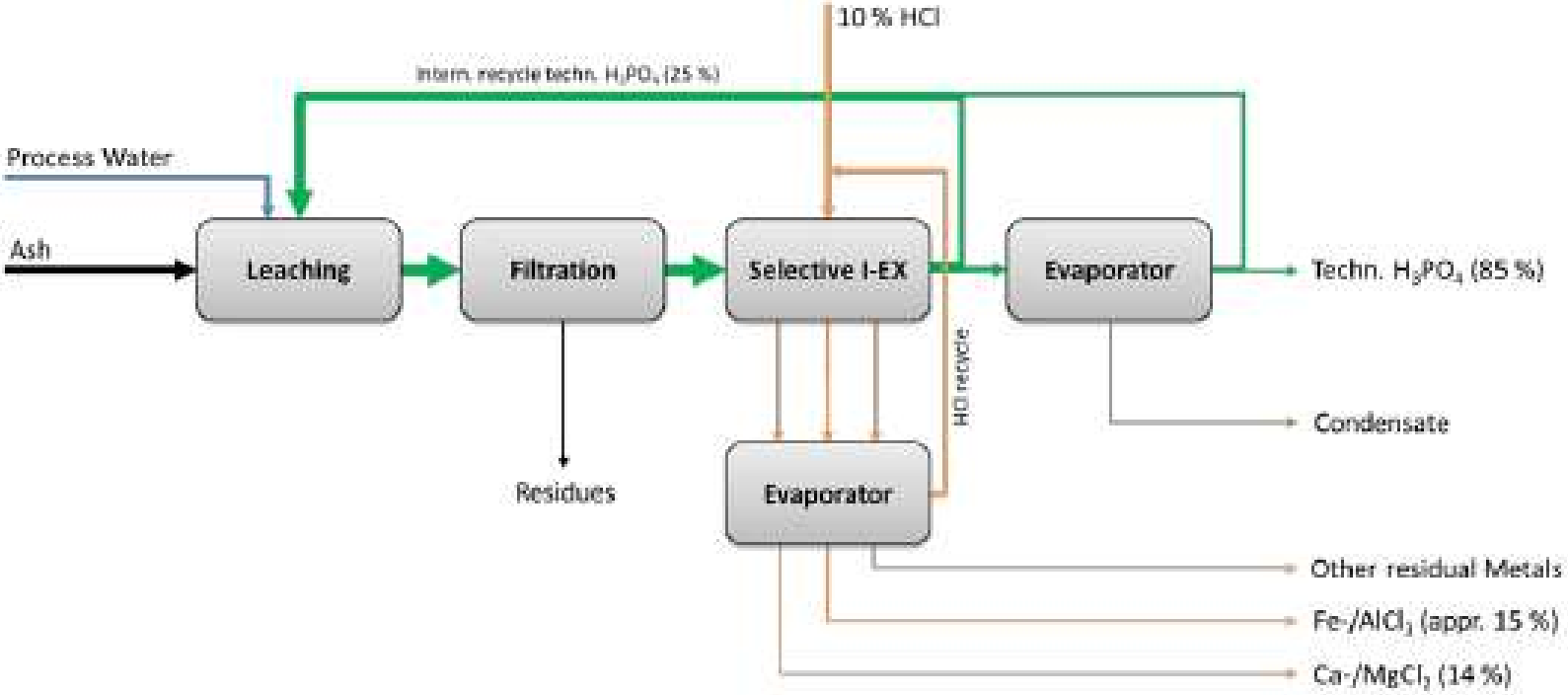

Figure 22: Schematic flow of the ECOPHOS H_3PO_4 process (adapted from Kraus 2018 and Takhim et al., 2018).

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Fosforin talteenotto - tuhkasta

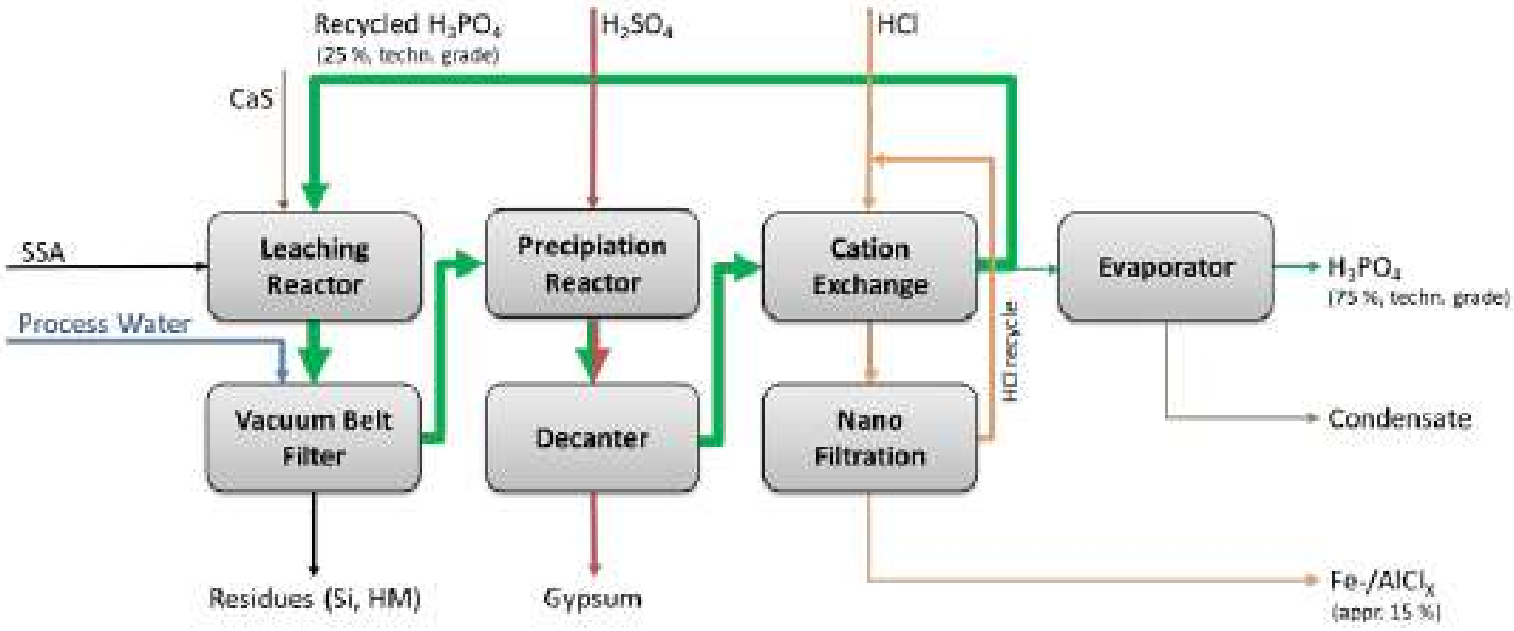

Figure 23: Schematic flow of the TetraPhos® process (adapted from Kraus 2018).

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Fosforin talteenotto - tuhkasta

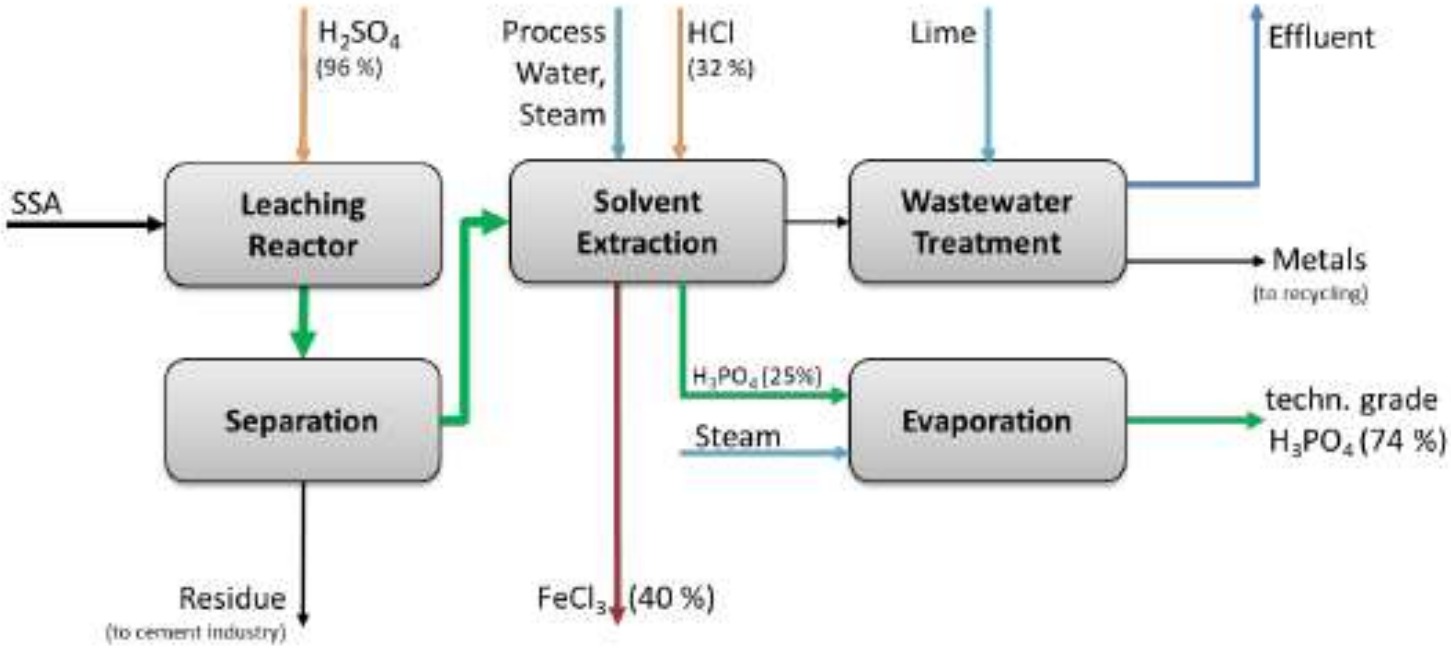

Figure 24: Phos4Life process to produce phosphoric acid from sewage sludge ash.

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Fosforin talteenotto - tuhkasta

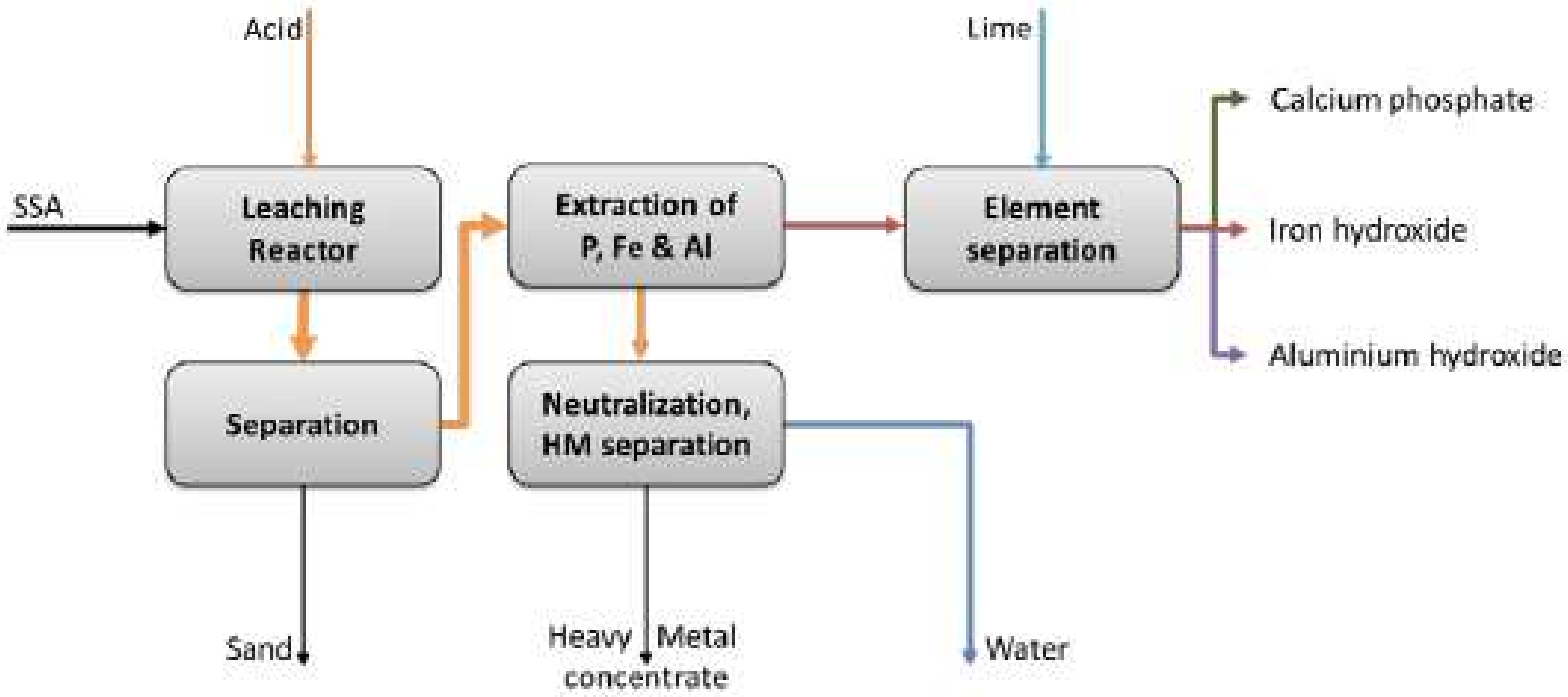

Figure 25: Schematic flow of the Ash2°Phos process (adapted from Kraus et al., 2018).

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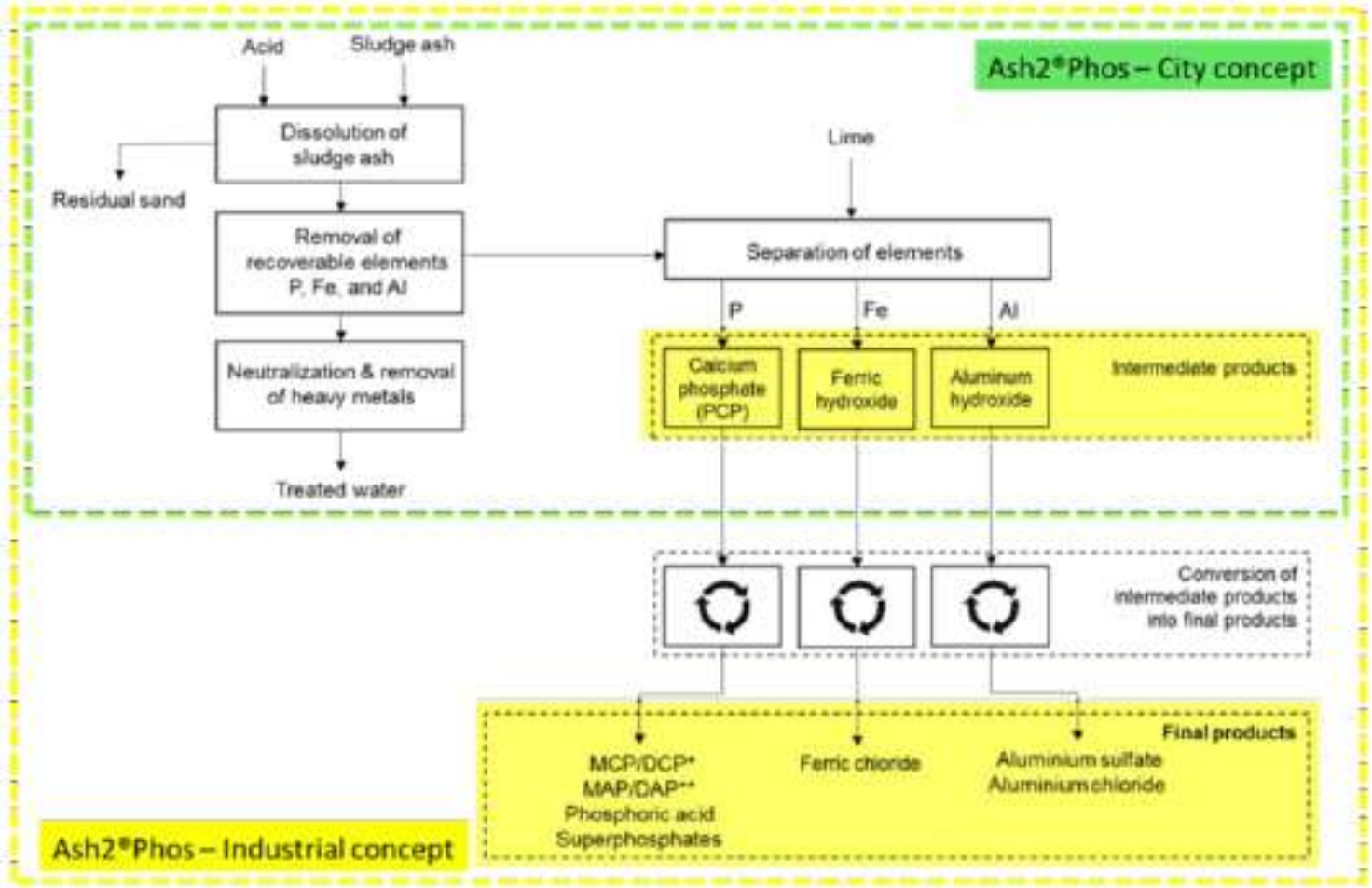
Fosforin talteenotto - tuhkasta



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Fosforin talteenotto - tuhkasta

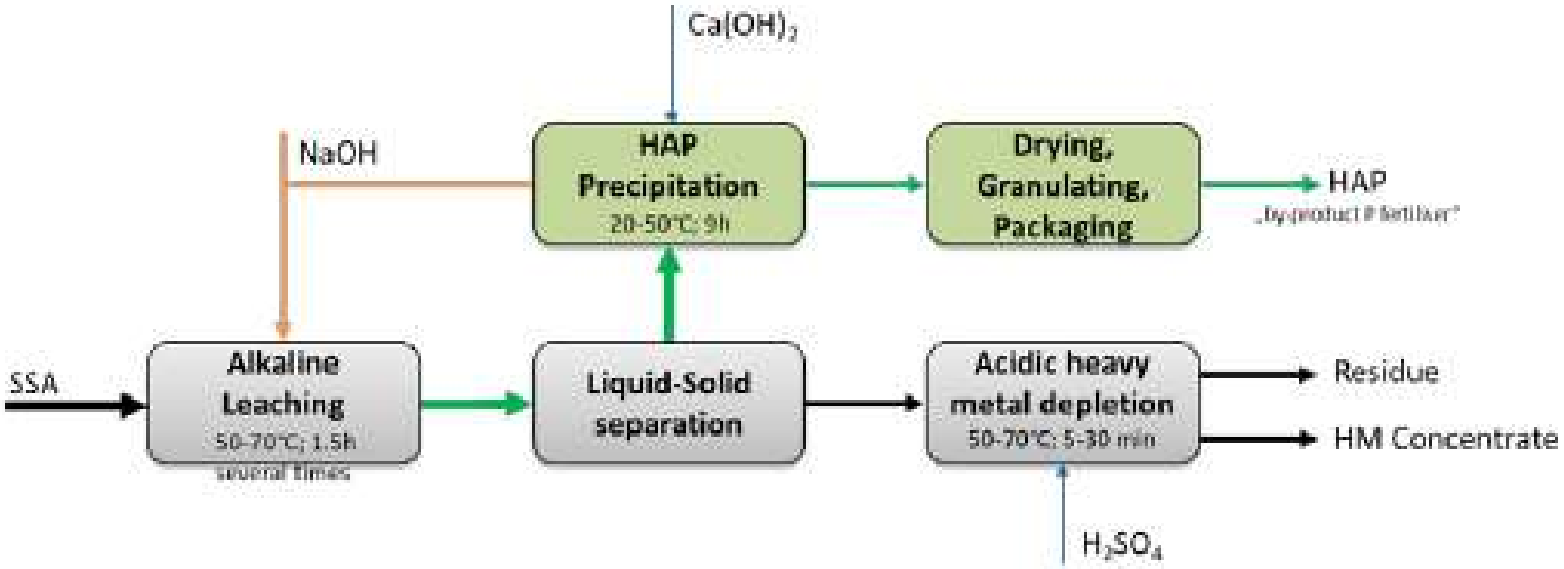

Figure 27: The alkaline ash leaching process as implemented in Gifu and Tottori in Japan (Nakagawa and Ohta, 2018).

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Fosforin talteenotto - tuhkasta

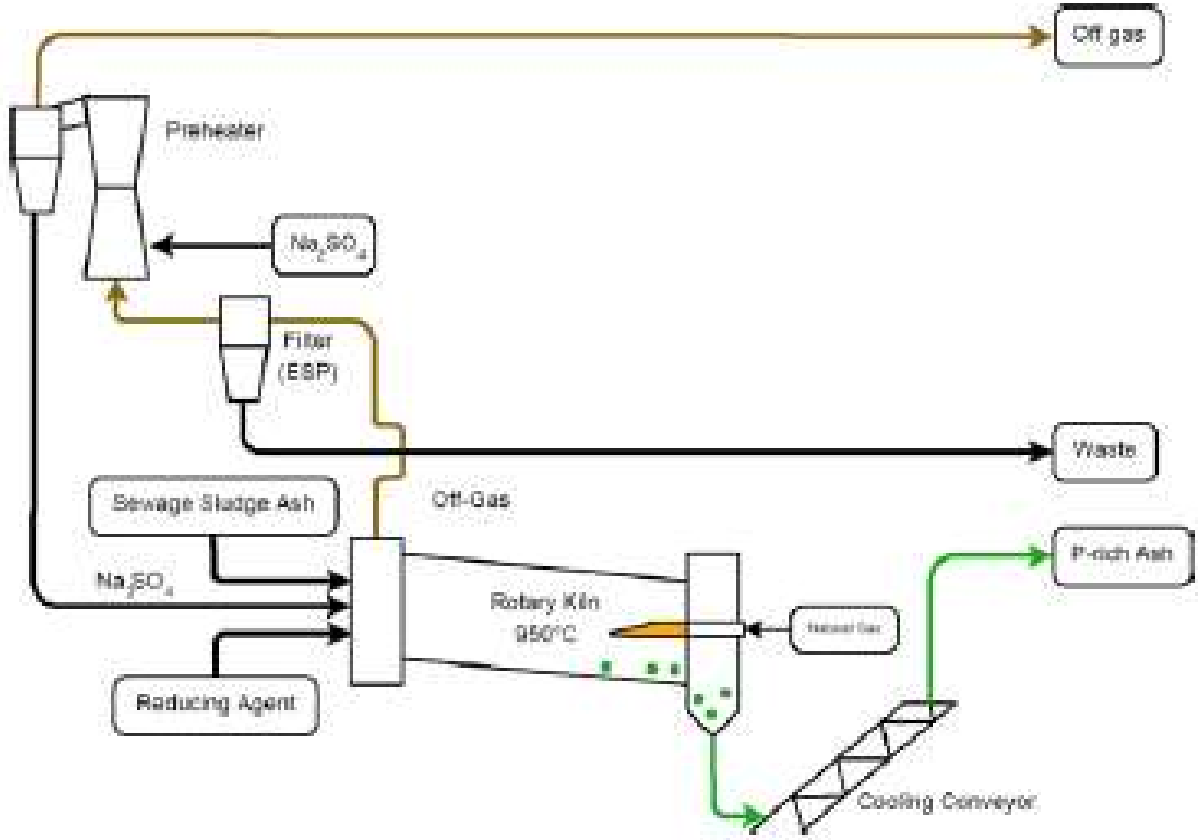

Figure 30: Process scheme of the Ashdec thermo-chemical ash treatment (P-REX Technical Factsheet 2015).

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Fosforin talteenotto - kuonana

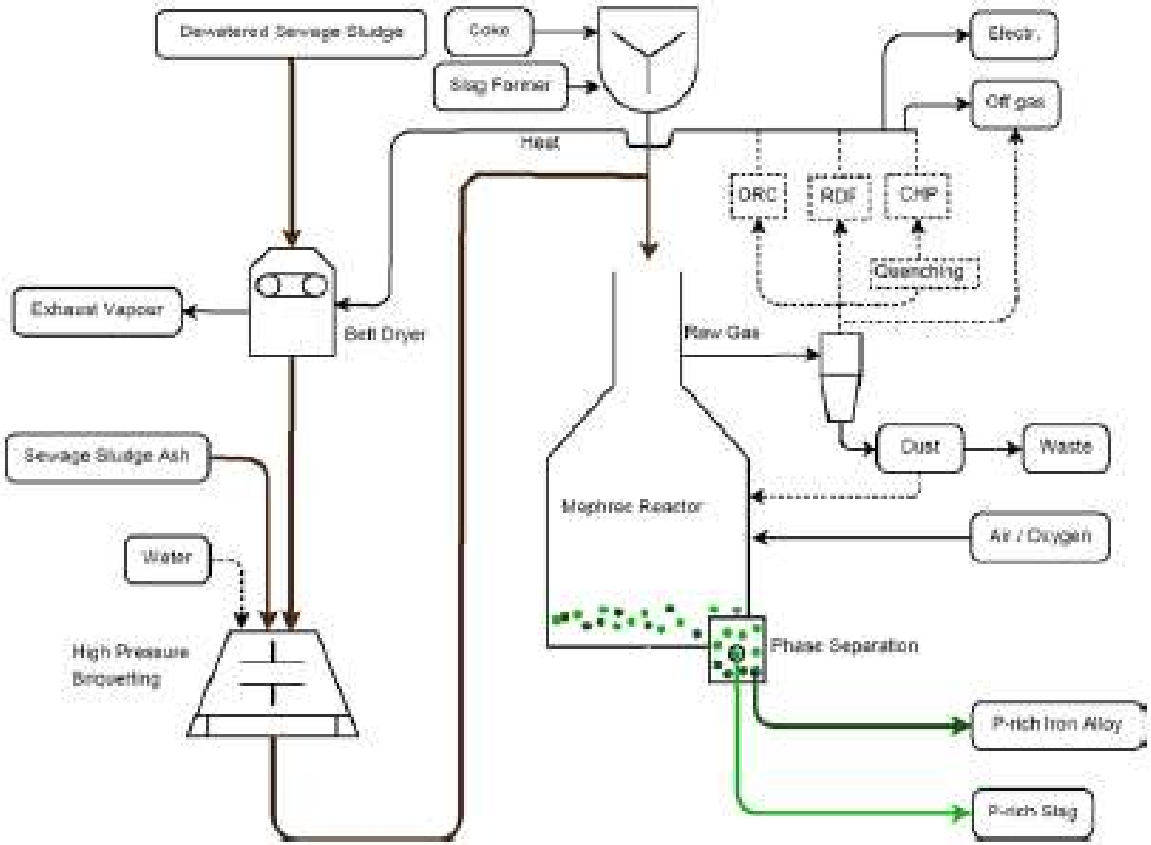

Figure 28: Process scheme of the Mephrec metallurgical sludge or ash treatment (P-REX Technical Factsheet 2015).

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Fosforin talteenotto - kuonana

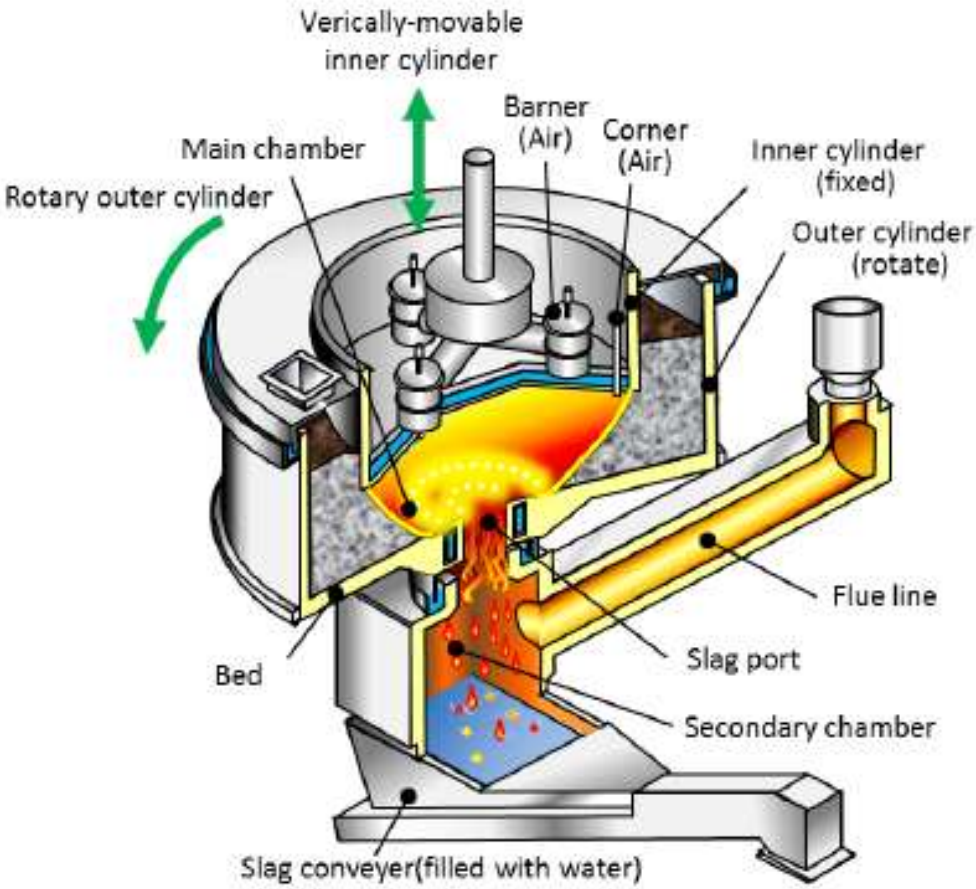

Figure 29: Schematic view of the KUBOTA Surface Melting Furnace (KSMF), (courtesy of KUBOTA Corp. / Hosho, 2018).

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Fosforin talteenotto - termisesti

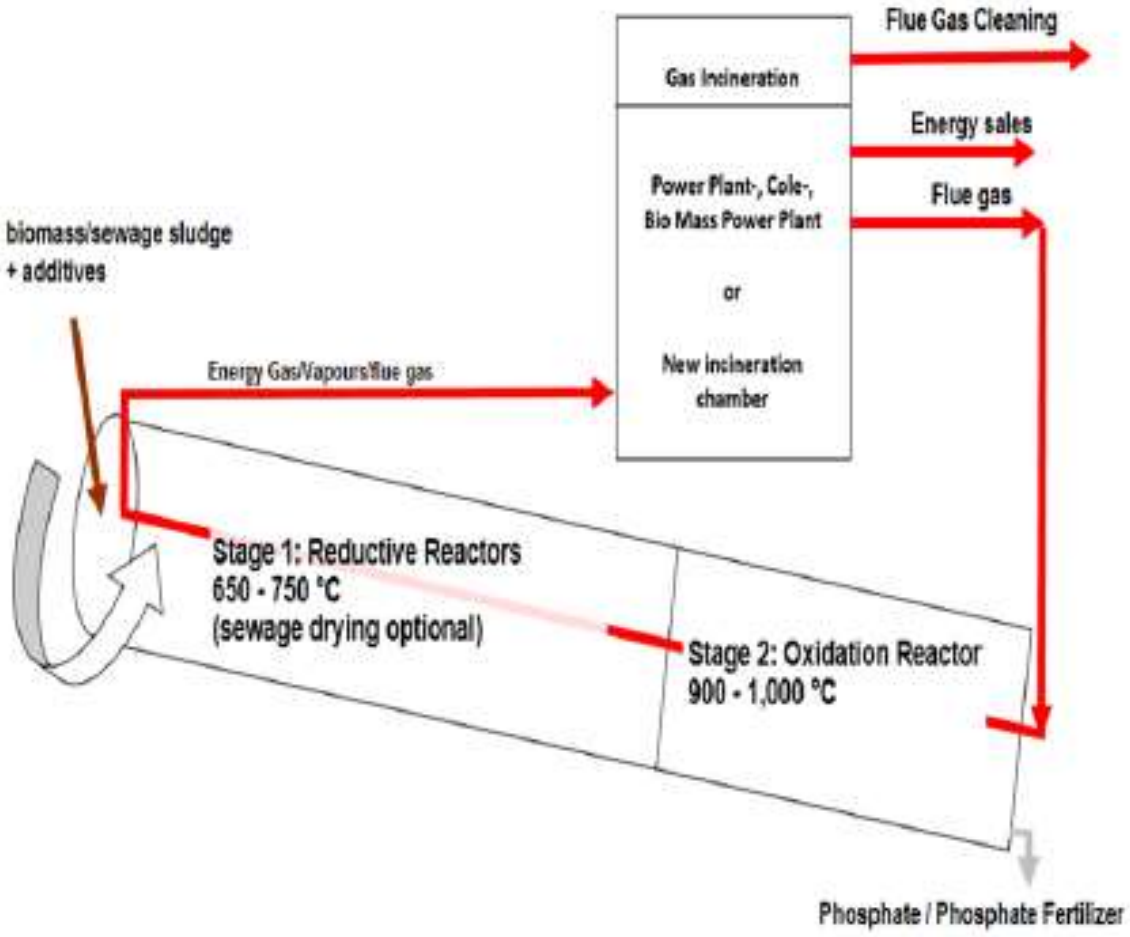

Figure 31: Process scheme of the EUPHORE® RedOx ash treatment (Courtesy of EUPHORE).

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Fosforin talteenotto

Technology	Supplier/User	Input for recovery/recycling step			Recovered Material	TRL
		Sludge	Sludge ash	Intermediates*		
Ash2Phos	EasyMining		X		DCP, Fe/Al hydroxides	6
AshDec	Outotec	X	X		Calcined Intermediates	6
EcoPhos	Ecophos		X		DCP, H_3PO_4, $FeCl_3$	9 (8)
EuPhoRe	EuPhoRe	X			Intermediates Min. Fertiliser	6
CleanMAP	EasyMining			X	MAP, DAP, SSP $FeCl_3$, $Al_2(SO_4)_3$	5
Conventional Fertiliser Manufacturing	Various companies		X	X	Customized fertilisers (SSP, NP, NPK)	9
Glatt SeraPlant	Glatt Seraplant		X		MCP, customised Fertiliser	6
HTC**	Various	X			Carbonisates	7
KUBOTA SMF	Kubota	X			P-slag	9
P.KON	KRN Nuremberg	X	X		H_3PO_4	2
METAWATER	METAWATER		X		HAP	9
Parforce	Parforce		(X)	X	H_3PO_4	6
Phos4Life	Tecnica Reunidas		X		H_3PO_4 $FeCl_3$	6
Pyrolysis**	Various	X			Pyrochar	7
TetraPhos	Remondis Aqua		X		H_3PO_4 $FeCl_3$	6

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Fosforin talteenotto

- **Laitokset puhdistamoilla**
  - **89 struviittilaitosta**
    - **tiedossa oleva tuotanto 36 000 t/a**
  - **9 HAP-laitosta (kalsiumhydroksiapatiitti)**
    - **tiedossa oleva tuotanto 450 t/a**
  - **1 brushiittilaitos (dikalsiumfosfaatti)**
  - **1 CaP-CSH-laitos (kalsiumfosfaatti absorboidaan kalsiumsilikaattihydraattiin)**
- **Laitokset jatkokäsittelyssä**
  - **2 HAP-laitosta (hydroksiapatiitti)**
    - **tiedossa oleva tuotanto 450 t/a**
  - **2 MAP/DCP-laitosta (monoammoniumfosfaatti/dikalsiumfosfaatti)**
  - **2 H_3PO_4/DCP/MCP-laitosta (fosforihappo, mono-/dikalsiumfosfaatti)**
  - **2 H_3PO_4-laitosta (fosforihappo)**
    - **Hampurin laitoksen arvioitu tuotanto 6 400 t/a**

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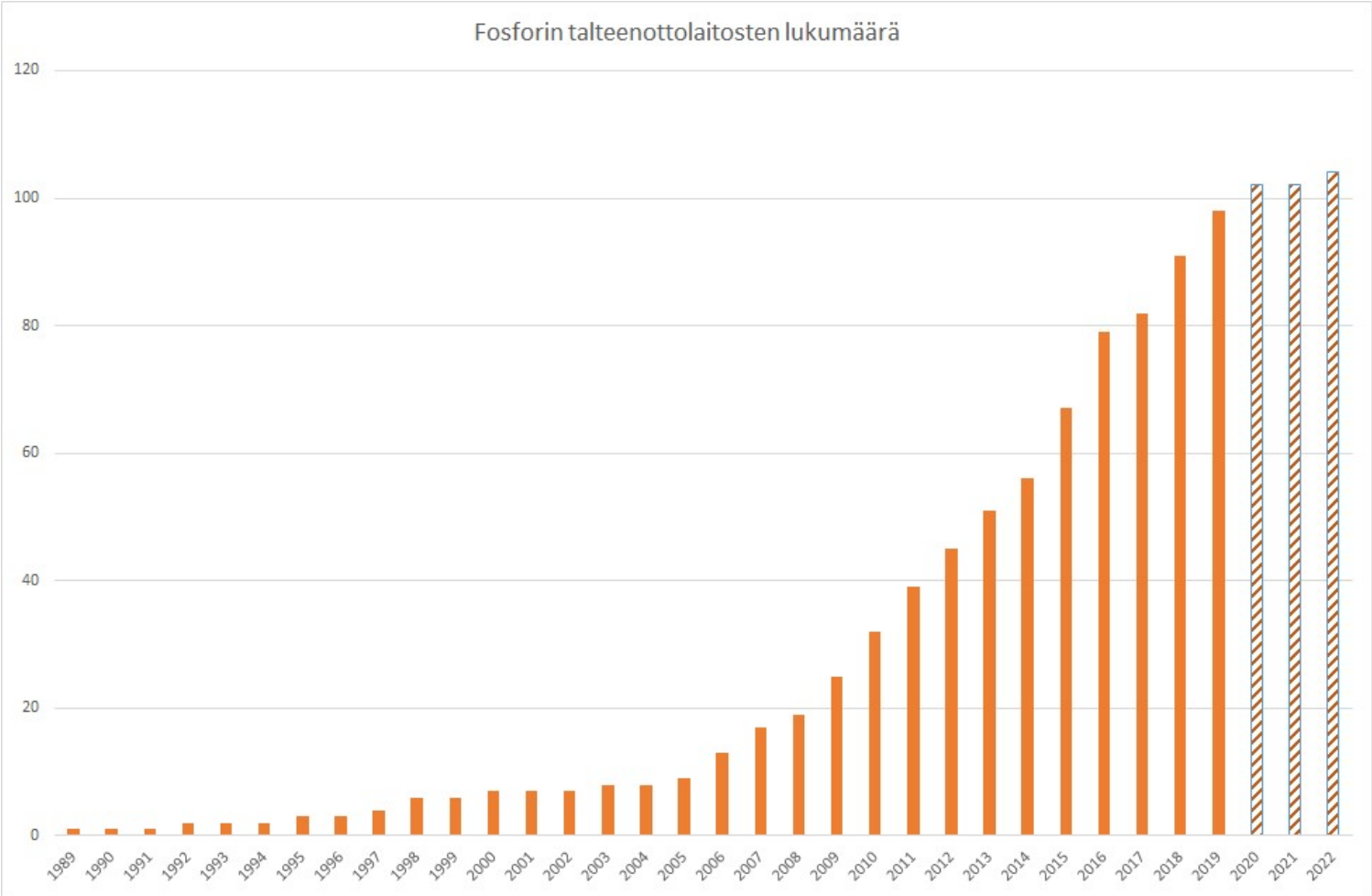
Fosforin talteenotto



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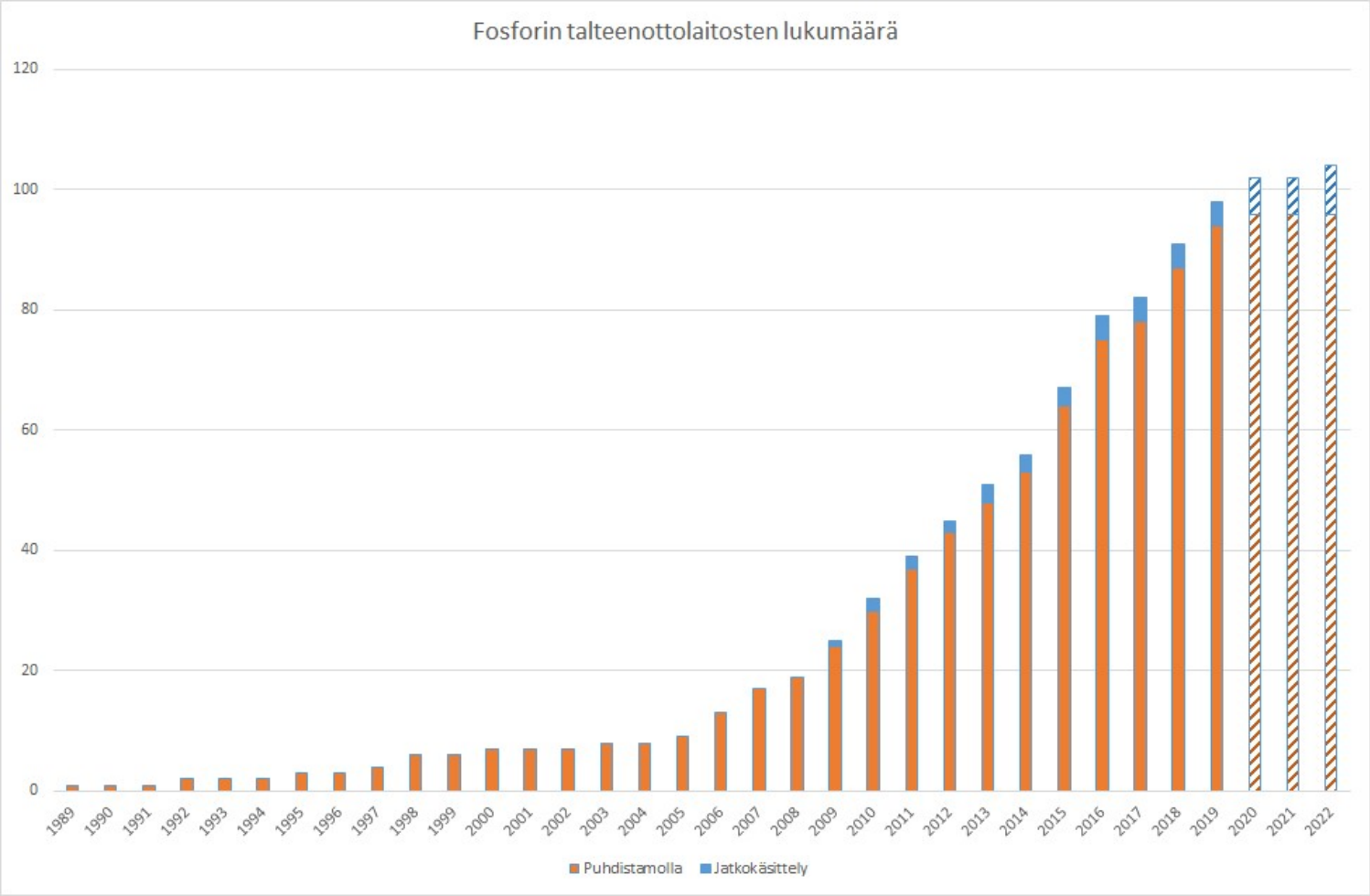

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Typen talteenotto

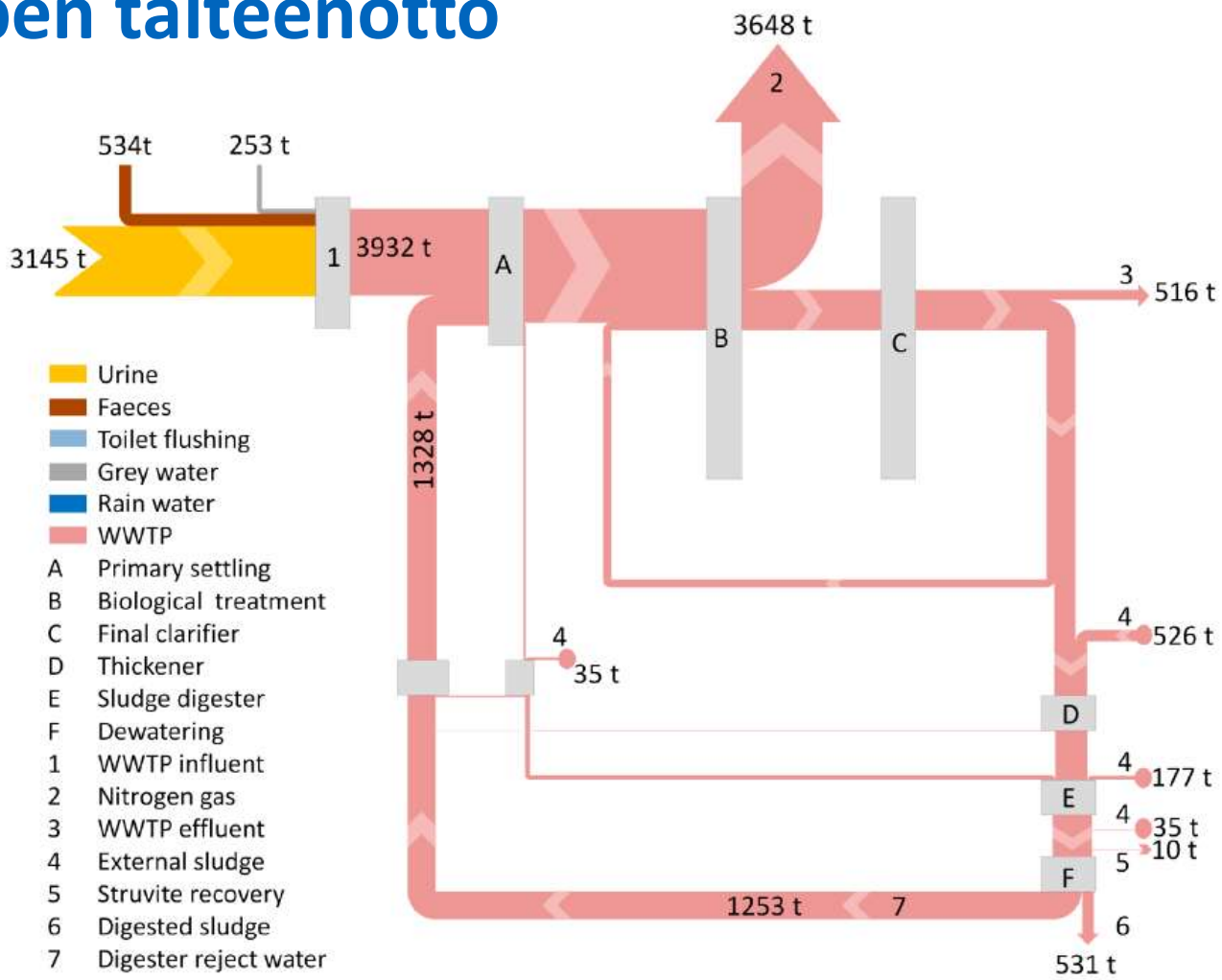

Figure 4. The nitrogen balance of the WWTP Amsterdam-West (mass flow in tons/year).

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Typen talteenotto

Mädättämön rejektivesistä (33 % tulevasta)

Ammonium ammoniakkikaasuksi

- **Strippaus 24 %**
  - **Alkalilisäys**
  - **Höyry**
- **Kalvosuodatus 75 %**

Ammoniumpitoisen rejektin konsentrointi

- **Vakuumihaihdutus 75 %**

Lietteen termisen kuivauksen poistokaasuista 2,1 %

Struviittisaostuksessa 1,1 %

Virtsan erilliskeräys 60 %

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Typen talteenotto

Stripatun ammoniakin sidonta

- **Rikkihappo – ammoniumsulfaatti, $(NH_4)_2SO_4$**
- **Fosforihappo – ammoniumfosfaatti, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$**
- **Suolahappo – ammoniumkloridi, NH_4Cl**
- **Etikkahappo – ammoniumasetaatti, NH_4CH_2COOH**
- **Typpihappo – ammoniumnitraatti, NH_4NO_3**

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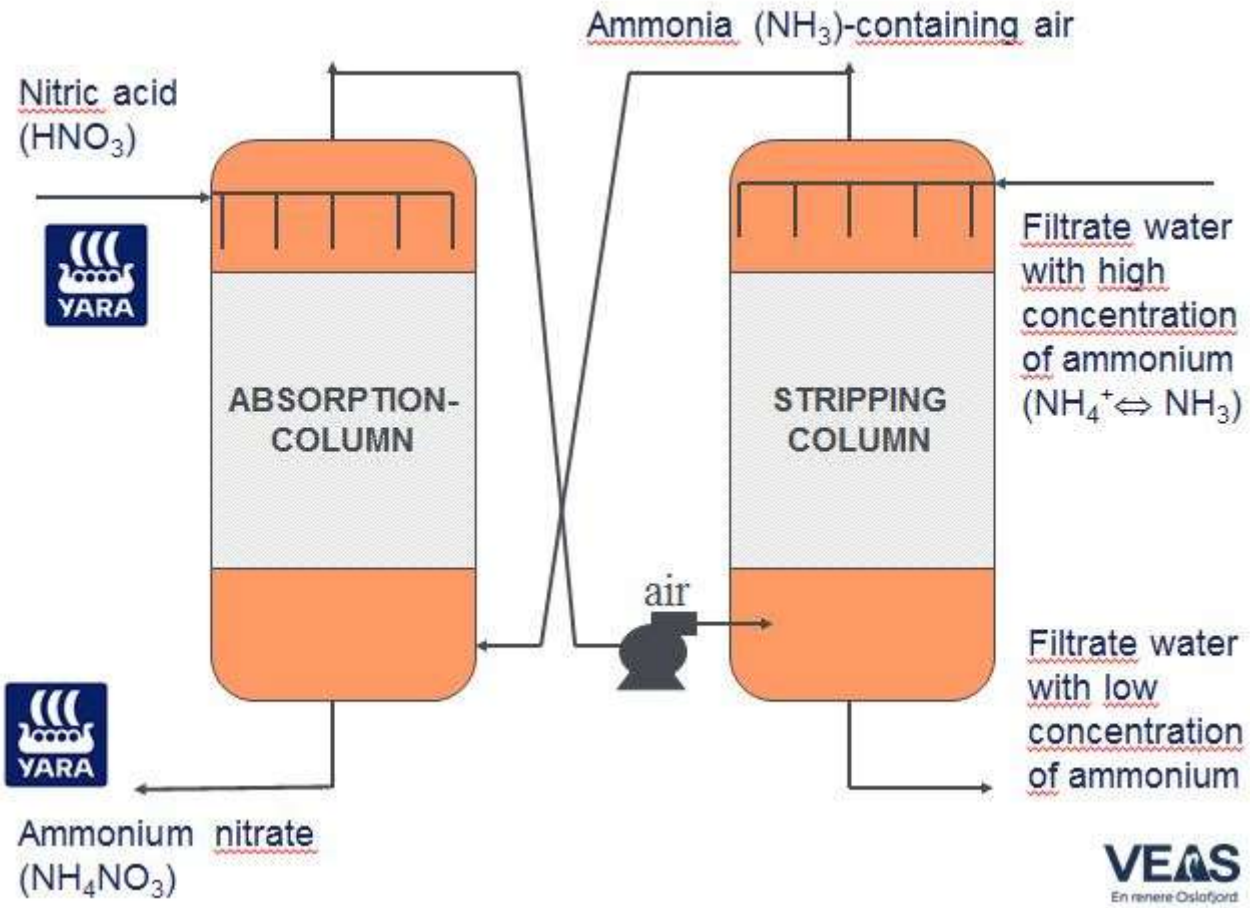
Typen talteenotto



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Typen talteenotto

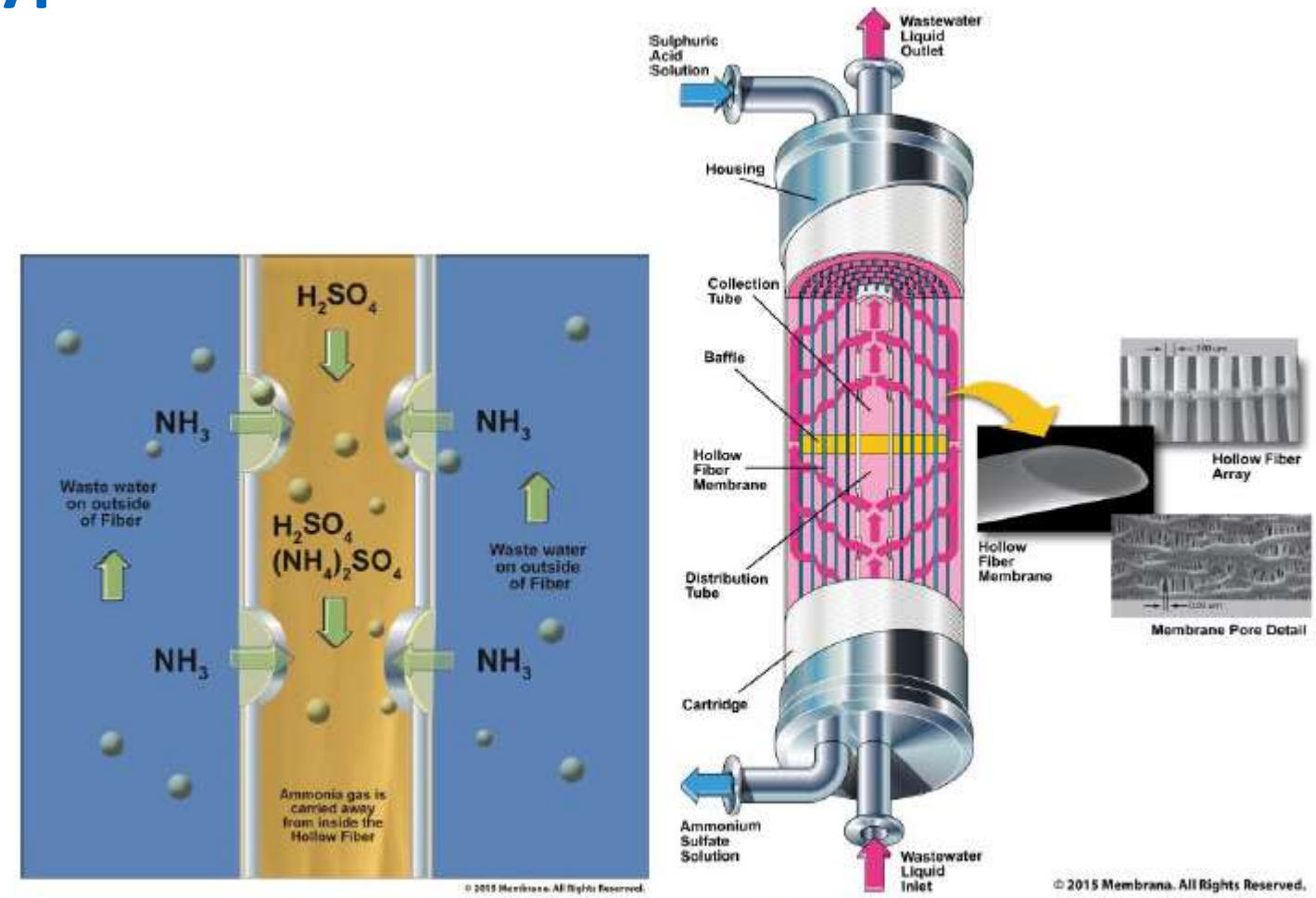

Figure 8-5. Gas Transfer Membrane for the Removal of Ammonia (Membrana Liqui-Cel Membrane Contactor).

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Fosforin ja typen talteenotto

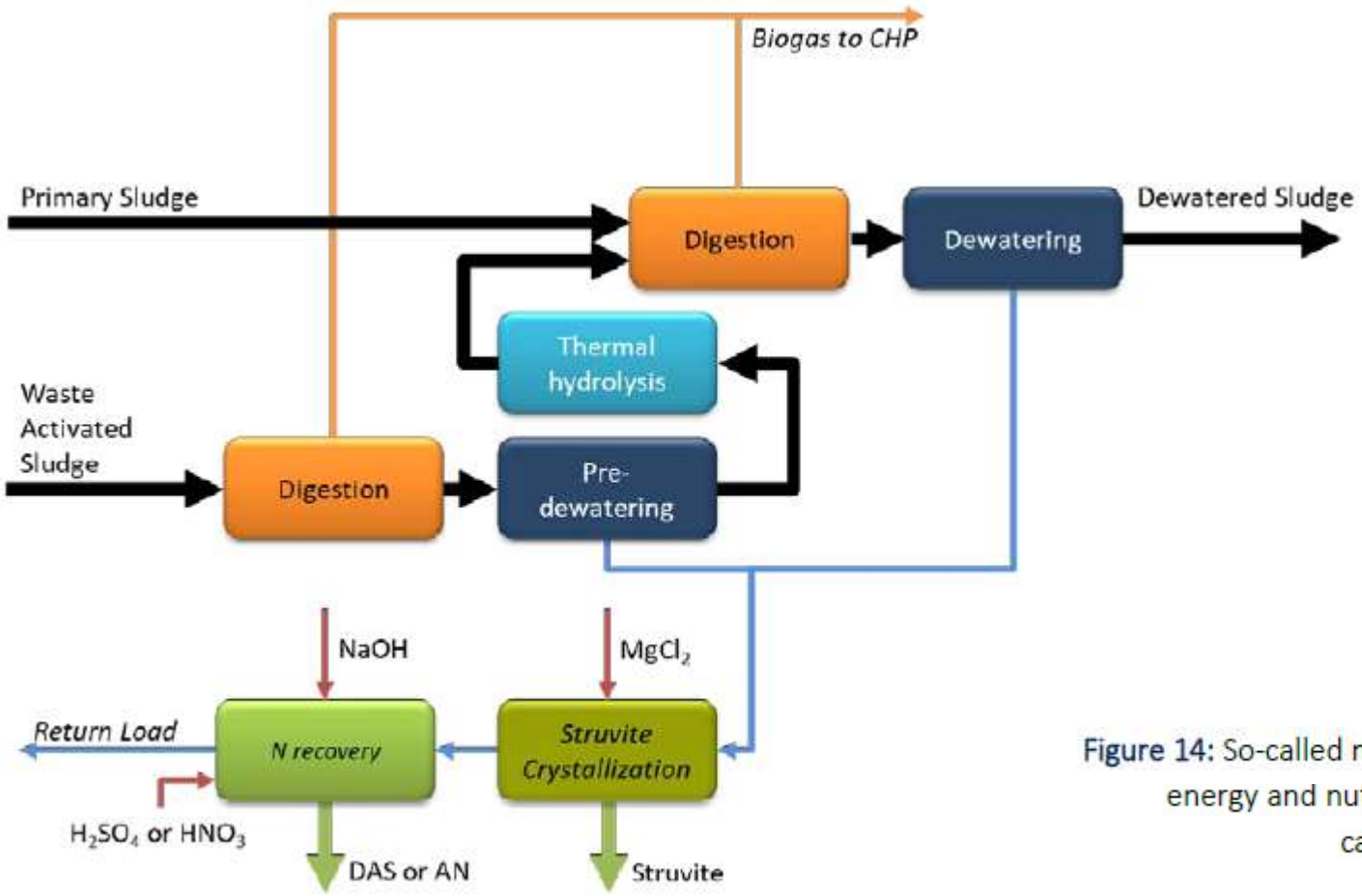

Figure 14: So-called next generation energy and nutrient recovery cascade concept

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Ravinteiden poisto jätevedestä Suomessa

AMBIO 2015, 44(Suppl. 2):S180–S192

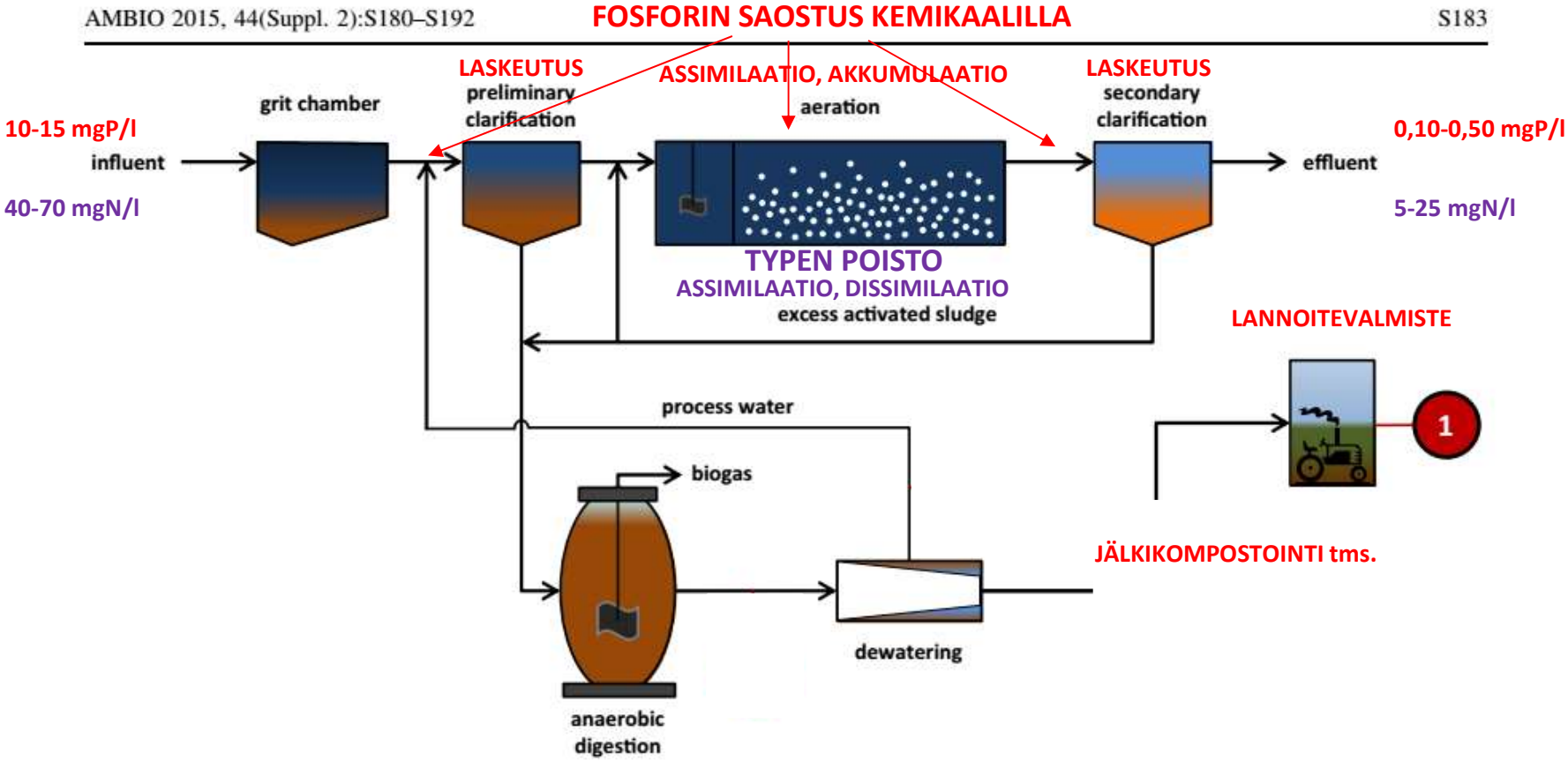

Fig. 2 Hotspots for phosphorus (P) recovery from the wastewater stream (in centralized sanitation systems). *Source* Kabbe (2013). *1* Direct sludge application in agriculture; *2a* P recovery from aqueous sludge phase prior to dewatering; *2b* P recovery from sludge liquor after dewatering; *3* P recovery from mono-incineration ash

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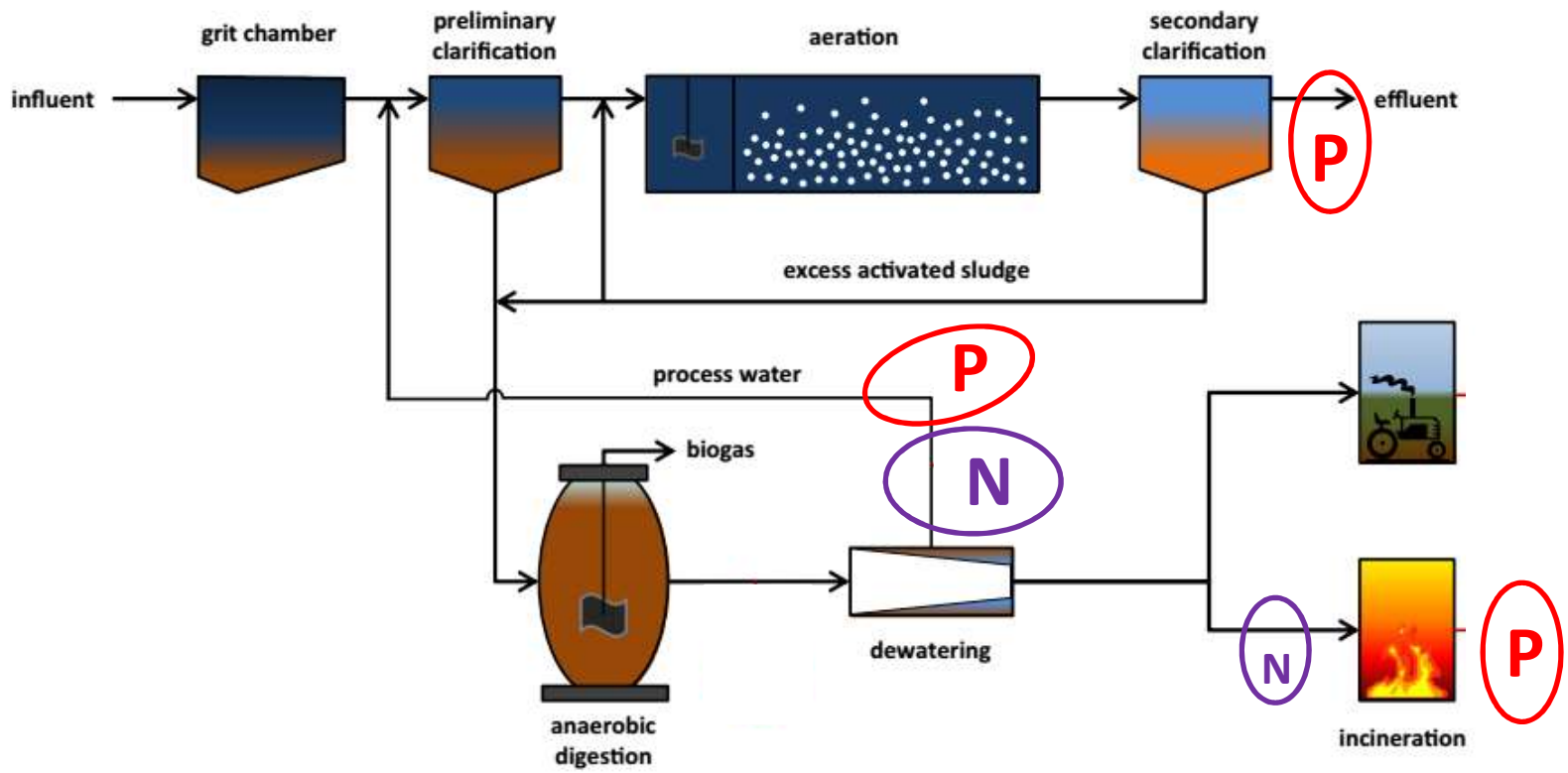
Ravinteiden talteenotto jätevedestä Suomessa?

AMBIO 2015, 44(Suppl. 2):S180–S192 S183



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Ravinteet puhdistamolietteestä

Ravinteiden talteenotto vesistä

- Lietteenkäsittelyn rejektivesistä
- Erillissaostuksella

Poltto

- Tuhkan hyödyntäminen
- Ravinteiden talteenotto tuhkasta / lauhteesta

Ravinteiden rooli kehittyvissä menetelmissä

- Käsittely mikropollutanttien eliminoimiseksi
  - Hapettavat menetelmät
  - Lämpökuivausmenetelmät
- Termiset käsittelymenetelmät
  - Pyrolyysi yms.
  - Biohiili
  - Tisleet, polttoaineet
  - Synteesikaasu

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Kiitos!