ICL Fertilizers
Where needs take us

Realising Phosphorus Recycling

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About Me

UvA UNIVERSITEIT VAN AMSTERDAM

- **Bachelor of Science**:
  - Chemistry at UvA 2013 - 2017

- **Studying:** Chemistry Master (UvA)
  - Track: *‘Science for Energy and Sustainability’*

- **8 month Internship:** ICL Fertilizers Europe in Amsterdam

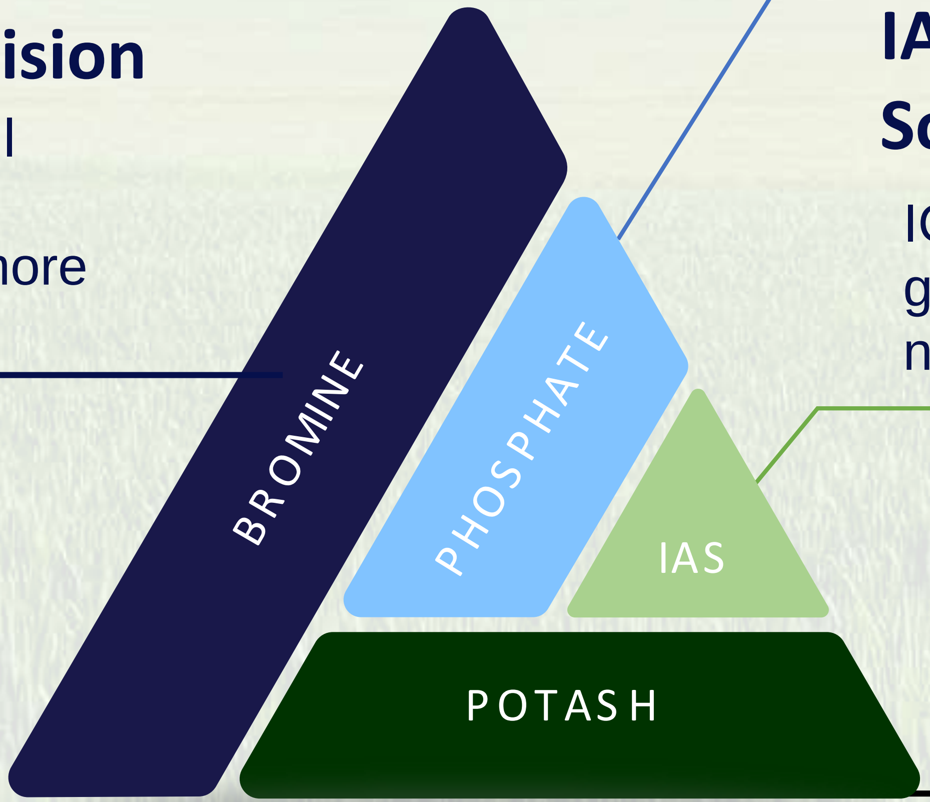
About the ICL – Group

Phosphate Solutions division

ICL provides essential ingredients for various industrial and food applications

Industrial Products division

ICL's bromine solutions are all around us, making consumer goods safer and production more efficient & sustainable



IAS - Innovative Ag Solutions division

ICL specialty fertilizers provide growers with optimal plant nutrition solutions

Potash division

ICL potash helps farmers increase yields and feed the world

ICL- AT A GLANCE

$5.6B
Sales in 2018, with balanced product portfolio

49
Manufacturing plants in 15 countries worldwide

~11,000
Employees worldwide, 4,500 in Israel

TOP 3
Leading supplier across most business lines and target markets

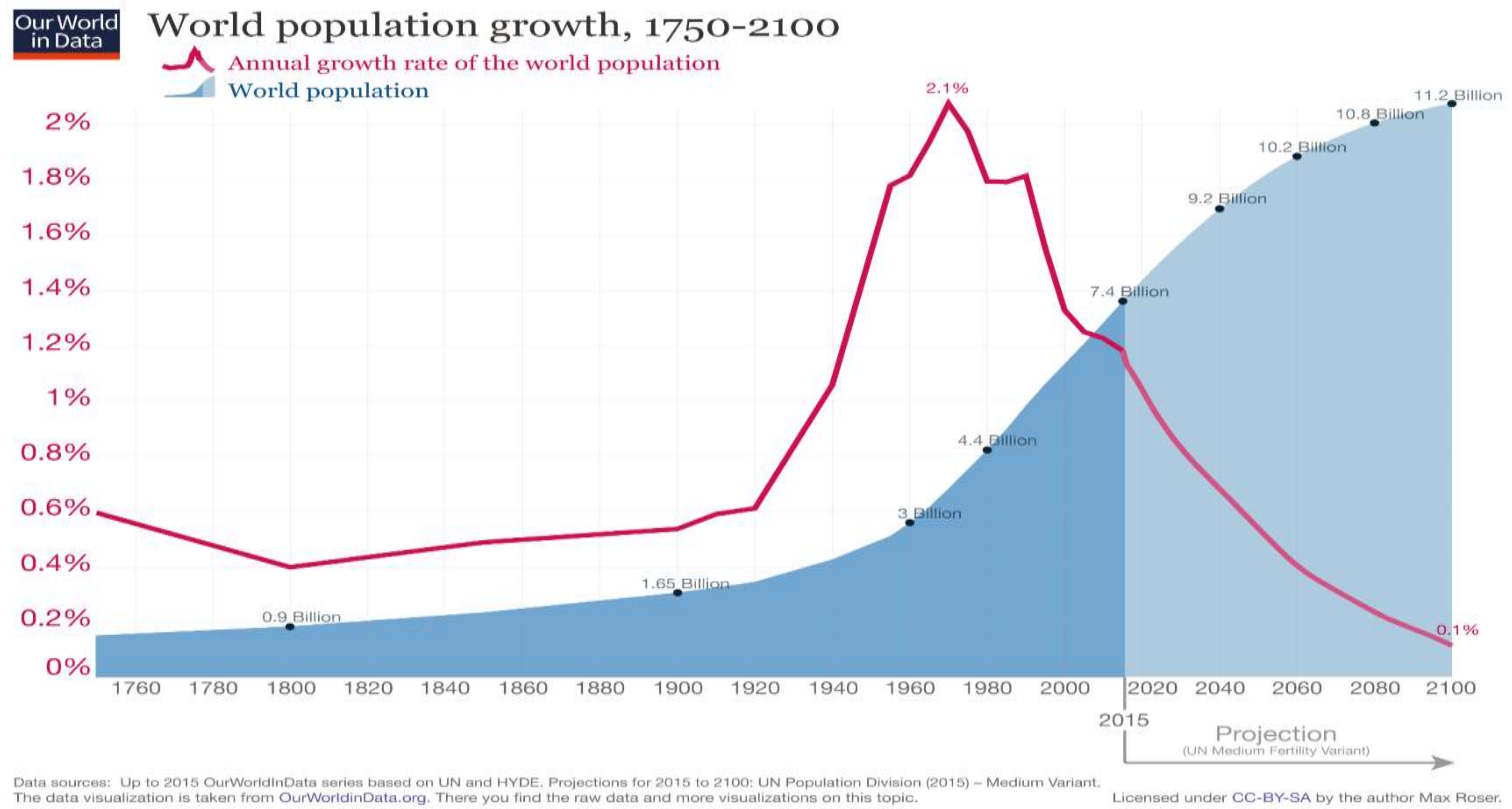
$7.1B
Market Cap as of Feb 28, 2019
Traded on TASE since 1992
Traded on NYSE since 2014

>3%
Industry leading dividend yield

BBB-
Investment grade rating & stable outlook. Net debt to EBITDA reduced from 2.9 as of 2017 year-end to 2.0 as of Sep 30, 2018

#2
Second largest public Israeli company in terms of sales

Global Population



A growing P-Demand

Factors influencing P-demand:

- Food factors:
  - Increasing global population
  - Growing economies that eat more ‘luxurious’ foods

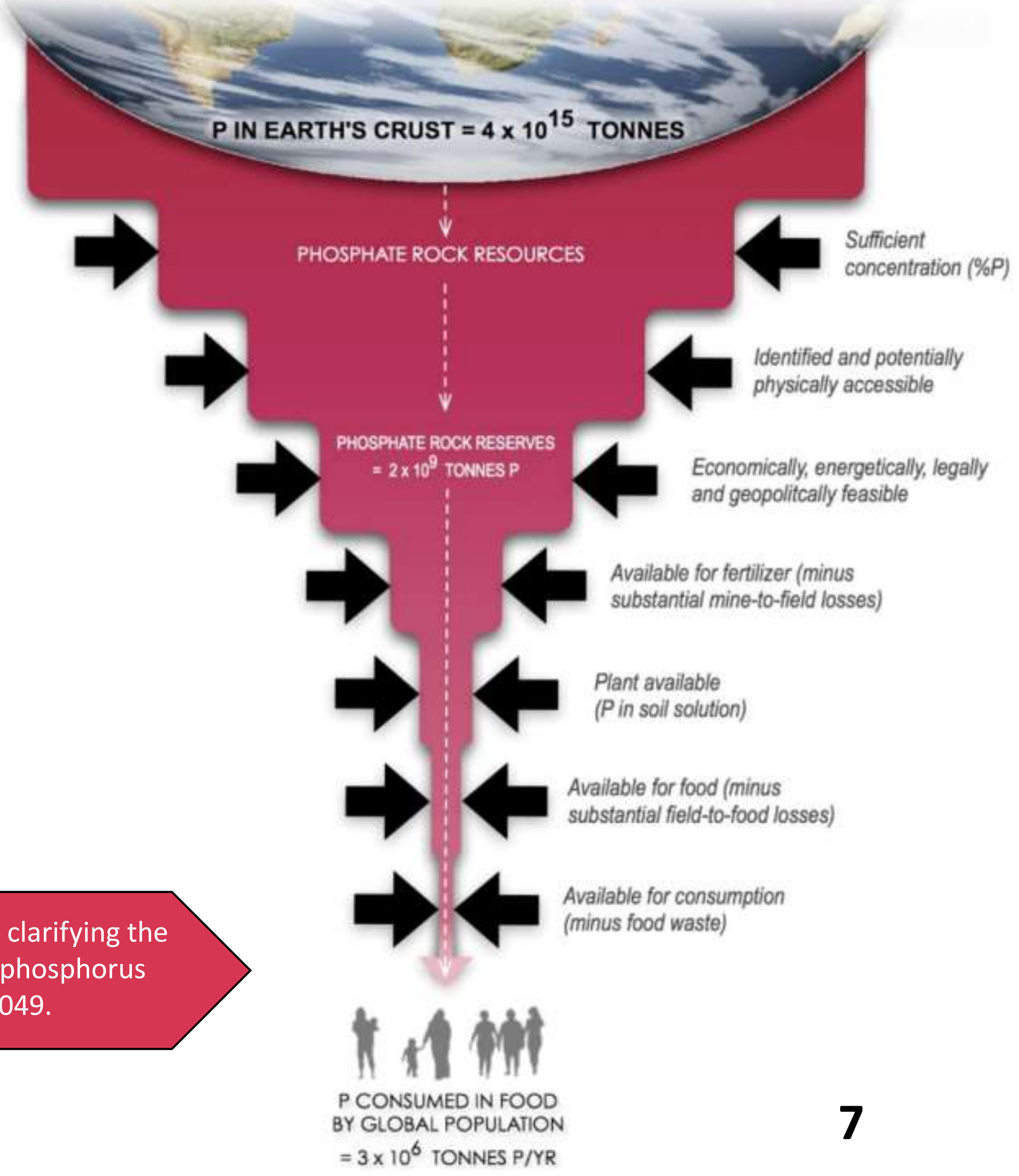
- Energy transition factors:
  - Growing demand for biofules
  - More Li-Fe-P batteries in cars

An electrical vehicle can contain up to 60 kg of P in its battery/batteries

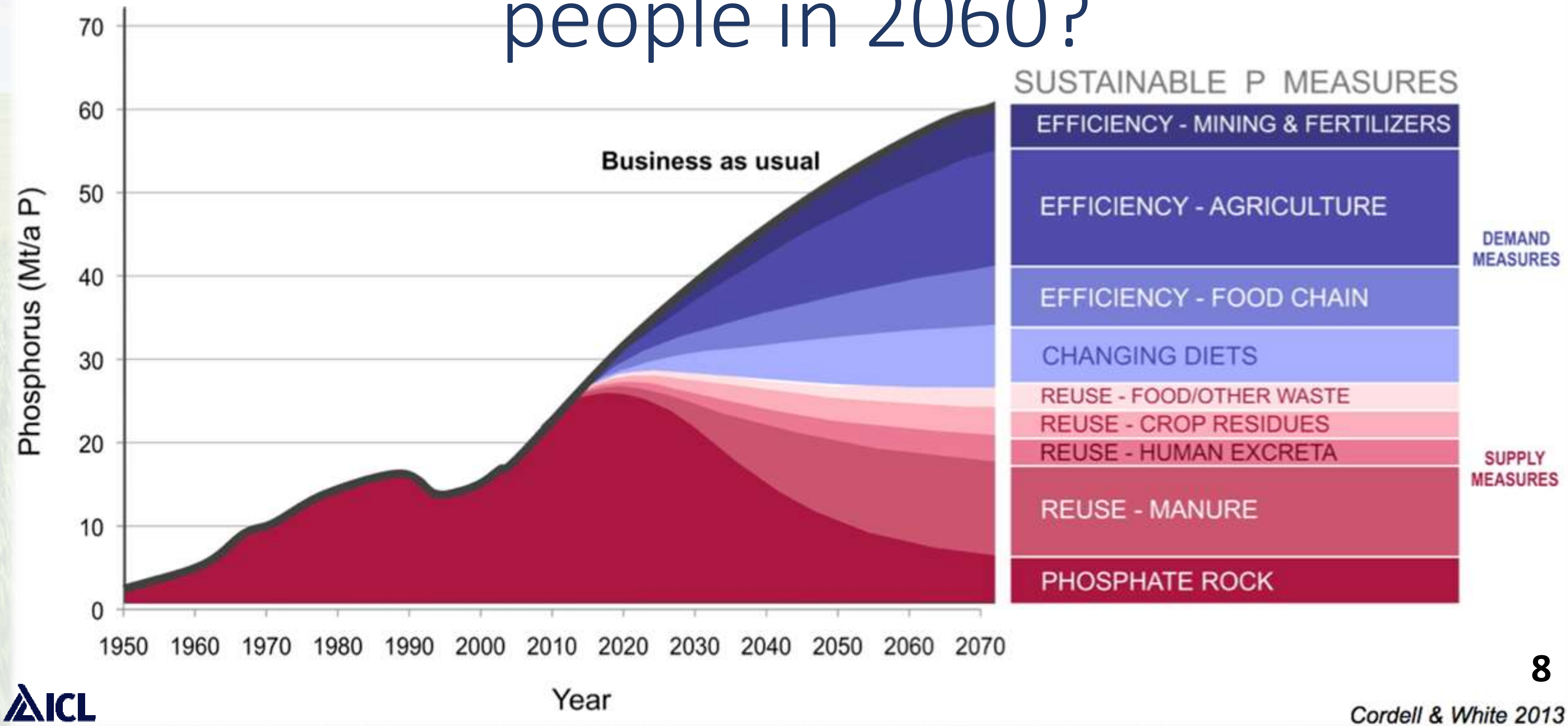
Facts about Phosphorus (P)

- Mining of 0.00005% of all P on the globe is economically feasible.
- **0.15% of mined P is consumed** by the global population.
- PR quality declines
  - Waste from PR mines increases
- PR Accessibility decreases
  - Energy increase for mining/processing
  - Cost increase

Cordell, D. and White, S. (2011). Peak phosphorus: clarifying the key issues of a vigorous debate about long-term phosphorus security. *Sustainability*, **3**(10), pp. 2027-2049.



How will we feed over 10 billion people in 2060?



Cordell & White 2013

From linear to circular

PR Mining

Fertilizer production

Agricultural Application

Consumption

Landfilling

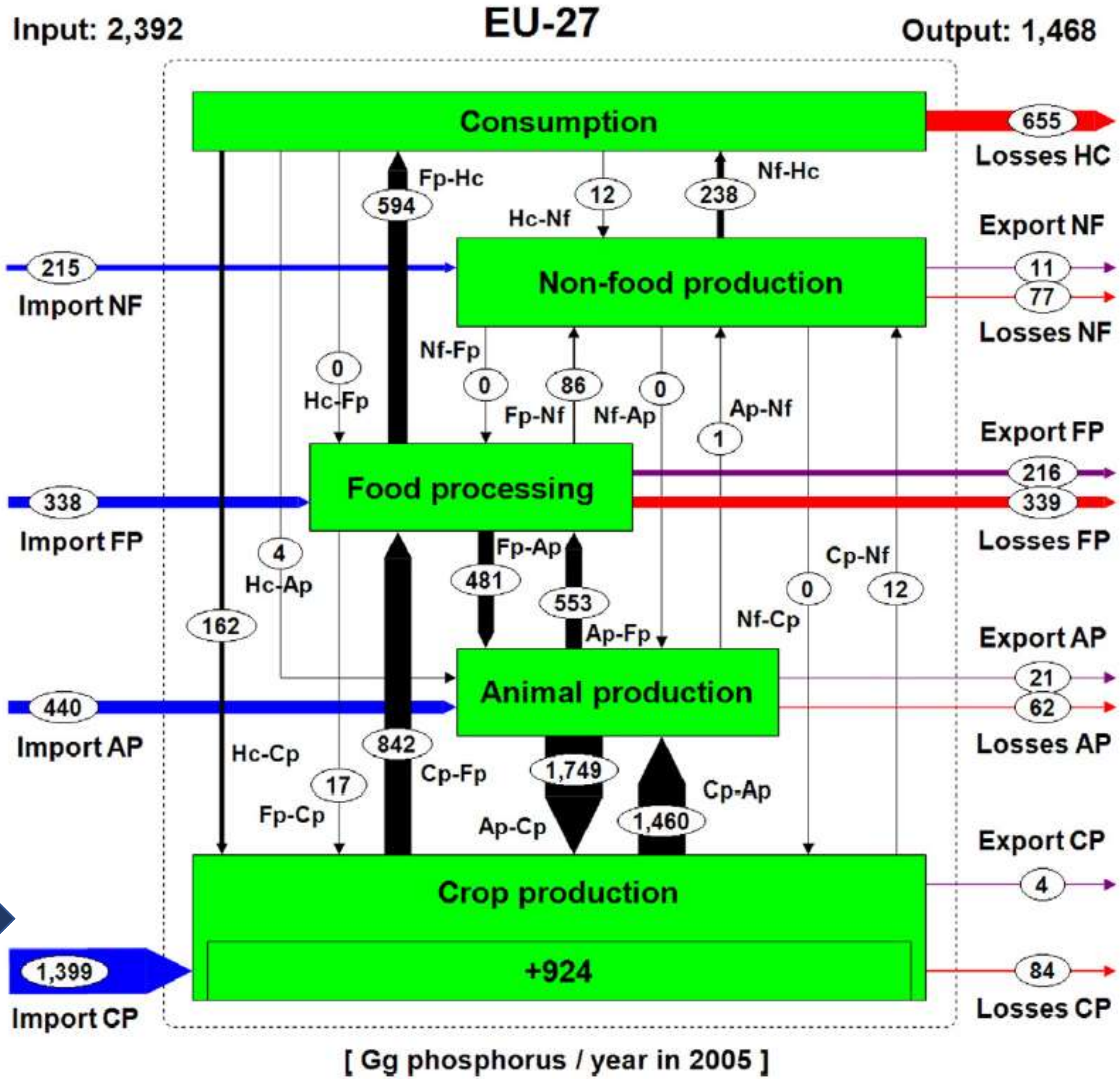
Sludge Incineration

Waste Water Treatment

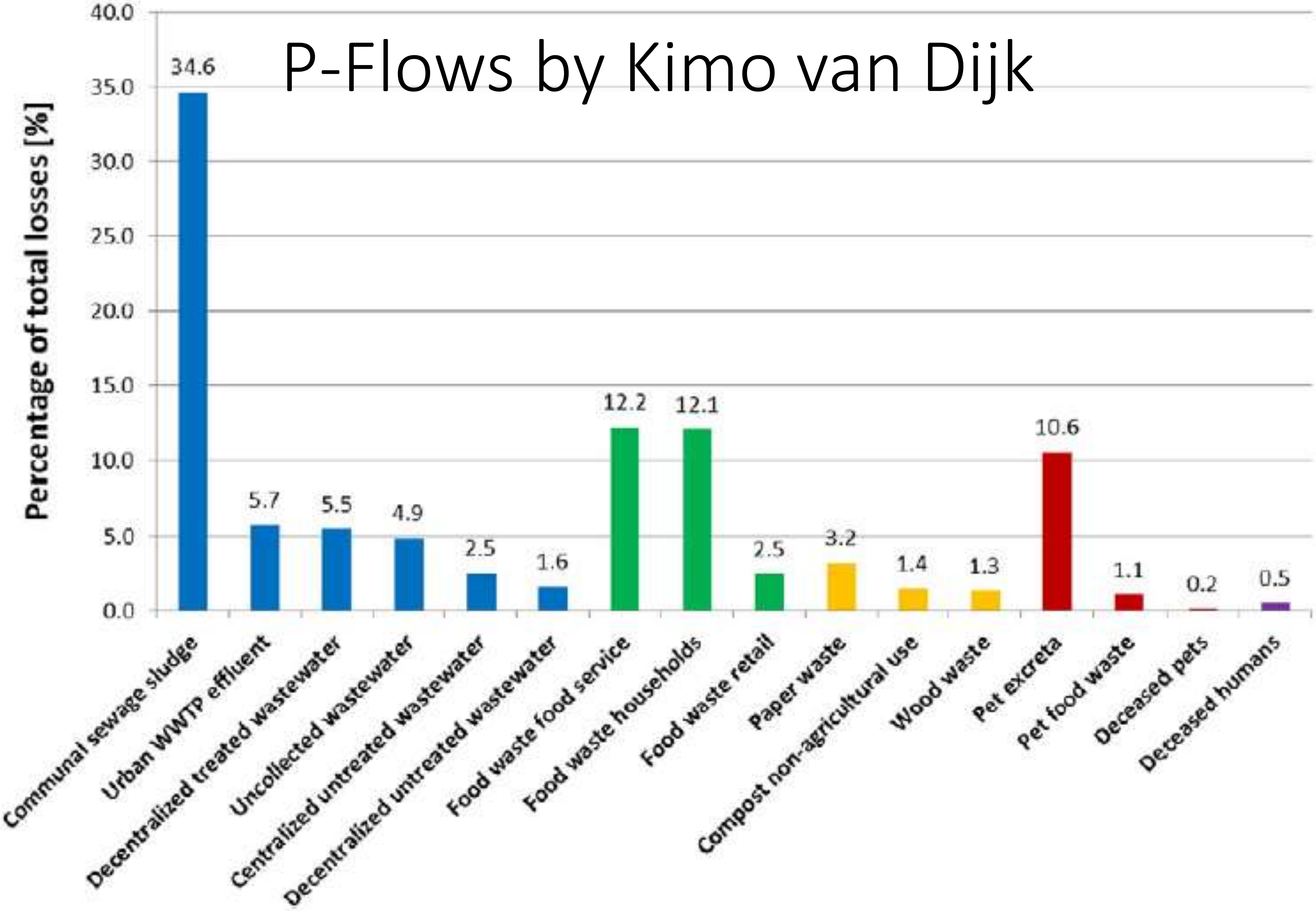
P-Flows by Kimo van Dijk

- **Total input: 2392 Gg P/year**
  - 74% or 1777 Gg P/year imported as PR
    - 78% for mineral fertilizer
    - 22% for animal production
  - 76% (924 Gg P/year) sinks
- **Total output: 1468 Gg P/year**
  - Export: 251 Gg P/year
  - System loss: 1217 Gg P/year

van Dijk, K. C., Lesschen, J. P., & Oenema, O. (2016). Phosphorus flows and balances of the European Union Member States. *Science of the Total Environment*, *542*, 1078-1093.



P-Flows by Kimo van Dijk



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New EU Fertilizer Regulation

Goals of the new fertiliser regulation are to:

- Promote a circular economy
- Maintain European soil qualities to secure the safety of human and animals
- Lowering the EU's dependency on third countries for essential nutrients

Contaminant Limits for Inorganic Compound Fertilizers

	New Regulation (Starting 2022)
Cd when P-content in fertilizer is smaller than 5%:	3 mg/kg dry matter
Cd when P-content in fertilizer is larger than 5%:	**60 mg/kg P2O5**
Hexavalent chromium (Cr)	2 mg/kg dry matter
Mercury (Hg)	1 mg/kg dry matter
Nickel (Ni)	100 mg/kg dry matter
Lead (Pb)	120 mg/kg dry matter
Arsenic (As)	40 mg/kg dry matter
Biuret ($C_2H_5N_3O_2$)	12 g/kg dry matter
Perchlorate (ClO_4^-)	50 mg/kg dry matter
Copper (Cu) *	**600 mg/kg dry matter**
Zinc (Zn)*	**1500 mg/kg dry matter**

* These limits do not apply where Cu or Zn have been added intentionally to correct a soil deficiency of the micronutrient of interest.

mg/kg = ppm

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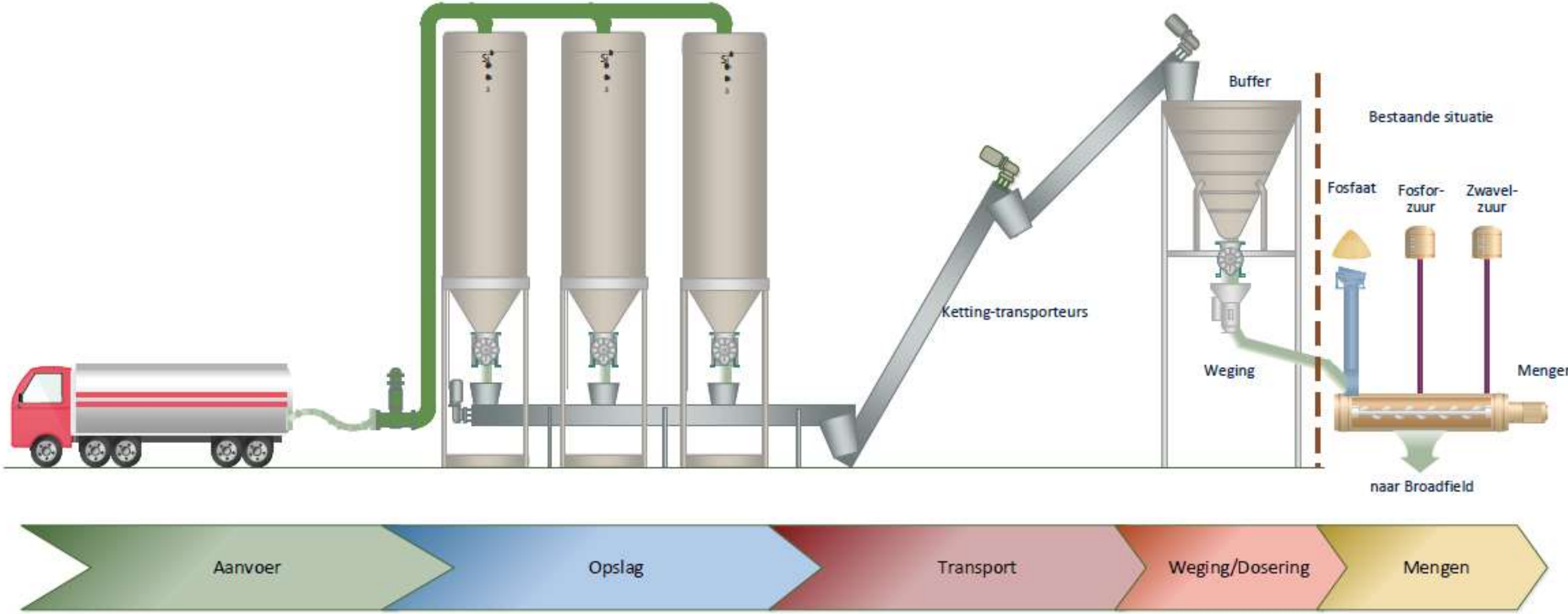
Phosphate Recycling Unit at ICL Fertilizers Europe C.V. in Amsterdam

- **Opening March 7th 2019**

- **Safe & Practical handling of fine ashes**
  - Silos
  - Precise dosing trap
  - Air tight conveyor belt system
  - Loading via cyclones

New Silos in Amsterdam



Recycled P-sources at ICL Amsterdam

- **Struvite crystals**
  - 24% P2O5 slow release
  - 10-15% Mg

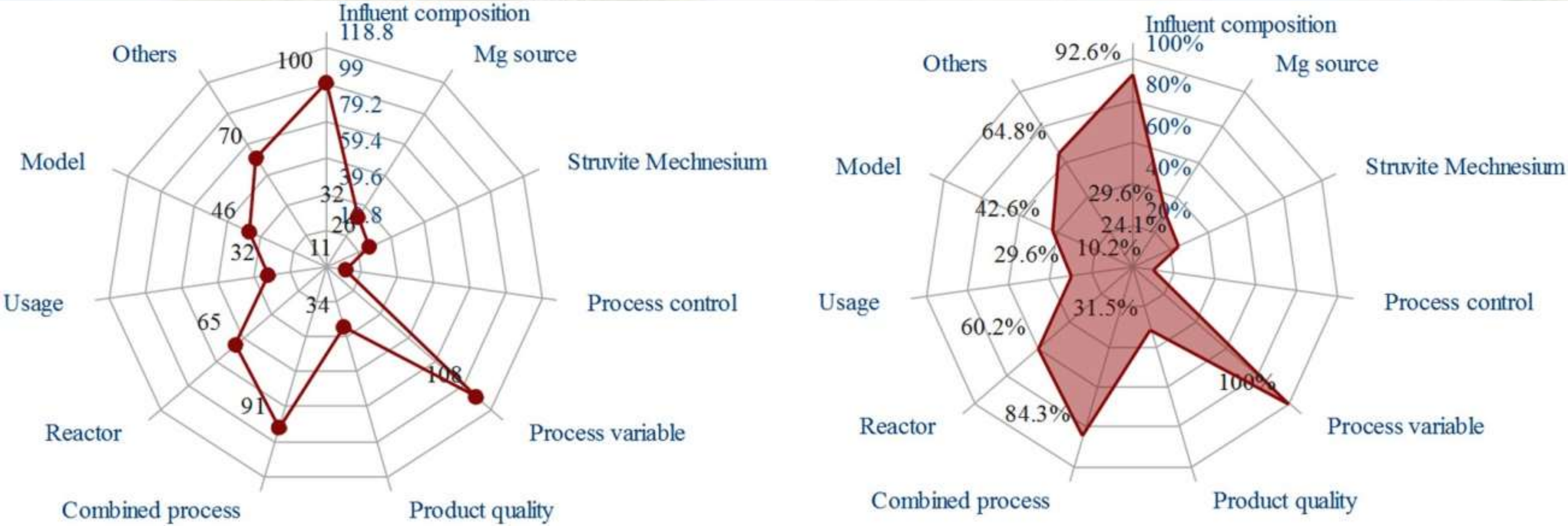
- **Meat and Bone Meal Ashes**
  - 31% P2O5 total
  - Low heavy metal contents

- **Sewage sludge ashes**
  - 21% P2O5 total
  - Low in Cd
  - High in Fe, Al, Cu, Zn, Mn

Struvite Precipitation

- Problematic struvite scaling
- 24% P2O5 *(10.5% P)* slow release
- Multiple benefits from preventing scaling:
  - Less maintenance to remove scaling
  - Lower P-load in discharge
  - Smaller sludge fraction
  - Easier dewatering of sludge (exact reasons are unknown)

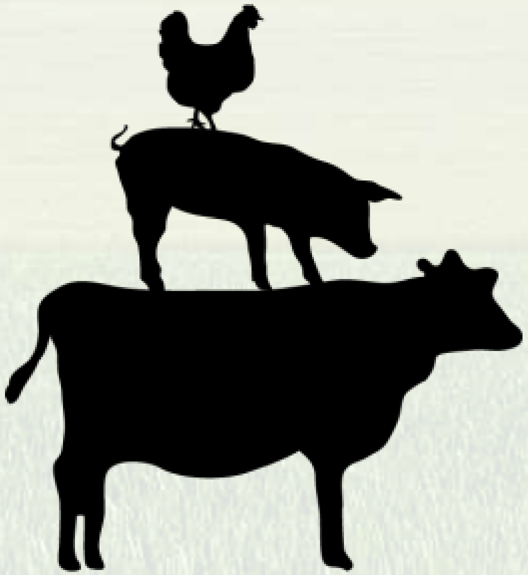
Research activities in different non-medical struvite crystallization fields.



Li, B., Boiarkina, I., Yu, W., Huang, H. M., Munir, T., Wang, G. Q., & Young, B. R. (**2018**). Phosphorous recovery through struvite crystallization: Challenges for future design. *Science of the Total Environment*.

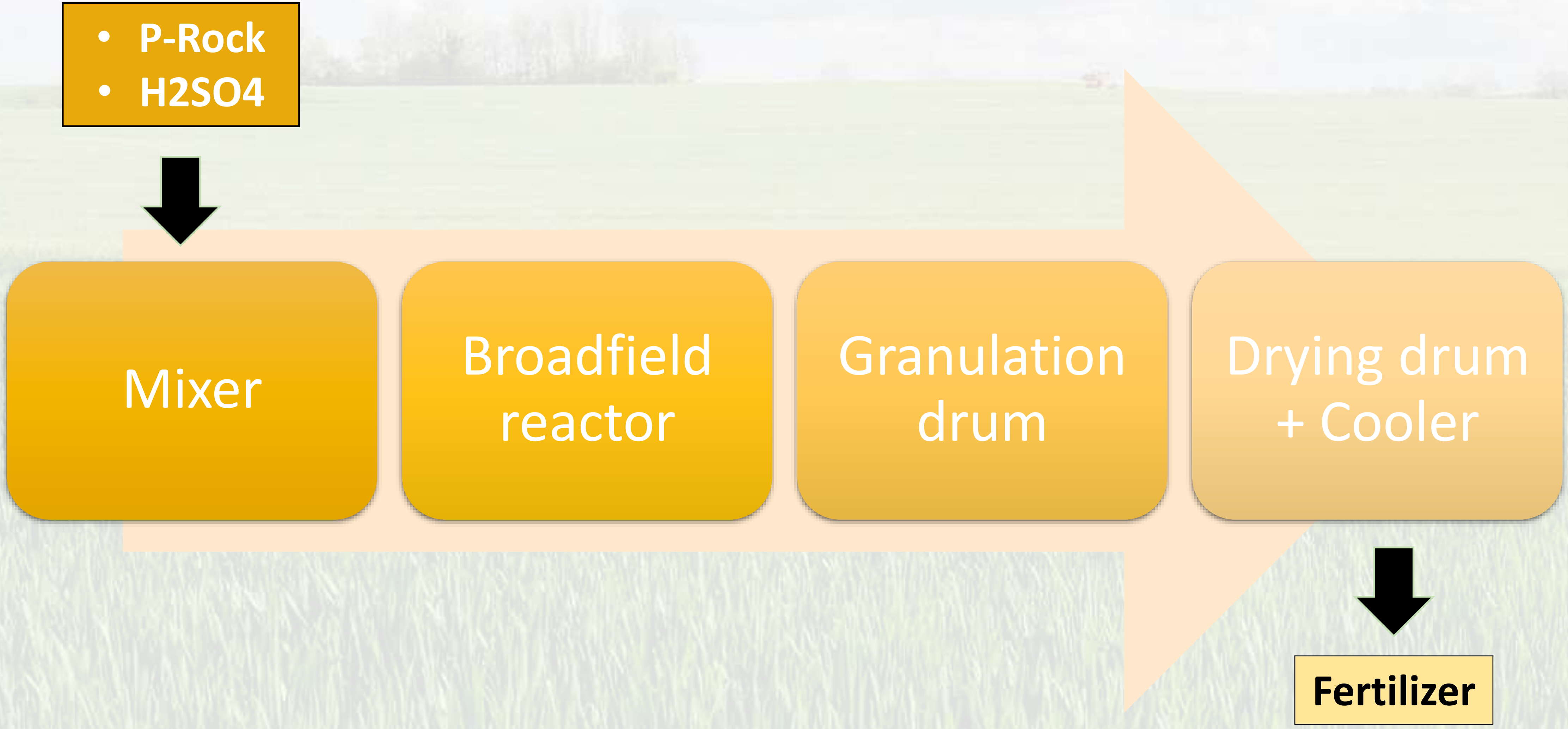
Meat and Bone Meal Ashes

- Produced from the incineration of:
  - hairs,
  - bones,
  - feathers,
  - contaminated meat



- High P-conent: 31% P2O5 (*13,5% P*)
- Meat production stabilized in EU
- **Compatible with existing industrial process for phoshphate rock(!)**

Phosphate Rock Acidulation



Acidulation of Meat and Bone Meal Ash

- MBMA
- H2SO4

Mixer → Broadfield reactor → Granulation drum → Drying drum + Cooler

Fertilizer

Using Sewage Sludge Ashes

Advantages :

- High P_2O_5-content: 21,8%
- Low Cadmium content
- Circular
- Cheap resource

Disadvantages:

- Poorly soluble P_2O_5
- Compromised production process from metal interference

Strategies

Peu de Peu

Adding small volumes of ashes to the main process:

P-Rock
H_2SO_4
Ashes

Separate Processing

Using resources with a different composition:

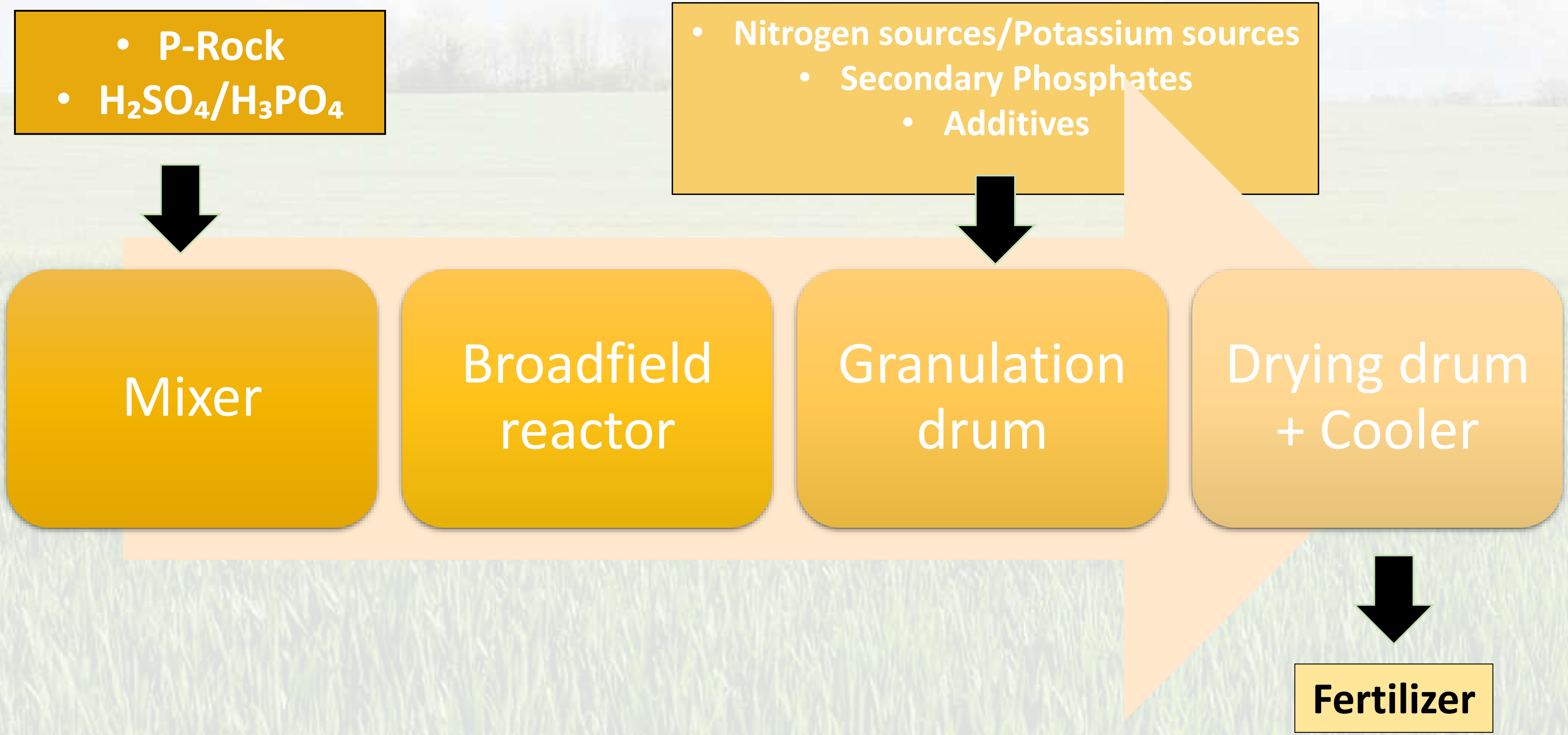
Ashes
H_2SO_4
Additives

Phosphate Extraction

Using new industrial settings:

Ashes
Heat/Solvents
Additives

Phosphate Rock Acidulation



Peu de Peu

- P-Rock
- H_2SO_4/H_3PO_4
- Ashes

Mixer → Broadfield reactor → Granulation drum → Drying drum + Cooler

- Nitrogen sources/Potassium sources
- Secondary Phosphates
- Additives

Fertilizer

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Separate Processing

- H_2SO_4
- Ashes
- Additives

- Nitrogen sources/Potassium sources
- Secondary Phosphates
- Additives

Mixer → Broadfield reactor → Granulation drum → Drying drum + Cooler

100% Recycled P-Fertilizer

- **Reach registration needed!**

P2O5-Sources and Products

(w/w)	PR (resource)	SSP-ROP	TSP-ROP	SSA (resource)	SSA-ROP	MBMA (resource)	MBMA-ROP	Struvite (resource)
Total P2O5 (%)	31.2	17.9	45.2	21.0	10.2	32.7	18.6	24.4
Water soluble P2O5 (%)	0.0	16.5	42.1	0.1	4.9	0.0	14.8	0.8
Fe2O3 (%)	0.07	0.08	0.20	2.17	2.94	0.27	0.25	2.17
Al2O3 (%)	0.06	0.06	0.20	4.41	2.61	0.20	0.13	0.01
MgO (%)	0.26	0.18	0.56	2.66	1.38	1.07	0.69	11.14
As (ppm)	6.98	4.69	6.66	15.73	8.04	2.44	1.73	0
Cd (ppm)	21.91	14.06	18.39	2.50	0.92	0.33	0.24	0.10
Cr (ppm)	38.66	29.40	59.77	20.23	35.30	24.98	20.50	4.753
Cu (ppm)	16.80	14.21	23.24	772.06	487.96	83.16	58.39	19.74
Hg (ppm)	0	0	0	0	0	0	0	0
Mn (ppm)	6.51	5.94	93.21	757.67	449.46	126.57	85.77	449.271
Ni (ppm)	30.02		26.86	27.32	30.64	11.57	11.27	3.95
Pb (ppm)	4.04	2.67	2.06	177.14	91.28	37.78	23.26	11.44
Zn (ppm)	361.22		386.68	1526.30	1018.06	250.46	155.64	66.77

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P-Recovery Technologies using SSA

Ash

Separation Techniques

Thermo-chemical

Acid Leaching

Interfering metals

Steel industry

Calcium Phosphate

Conventional PR processes

P-Extraction

Pros :

- Pure products
- Easy processing of $CaPO_4$ in conventional units
- Higher yield for further processing with P-rock
- Possibility of commercial 'side products'

Cons :

- More research required for process optimisation
- Need for new industrial units/factory
- Possible 'waste products'

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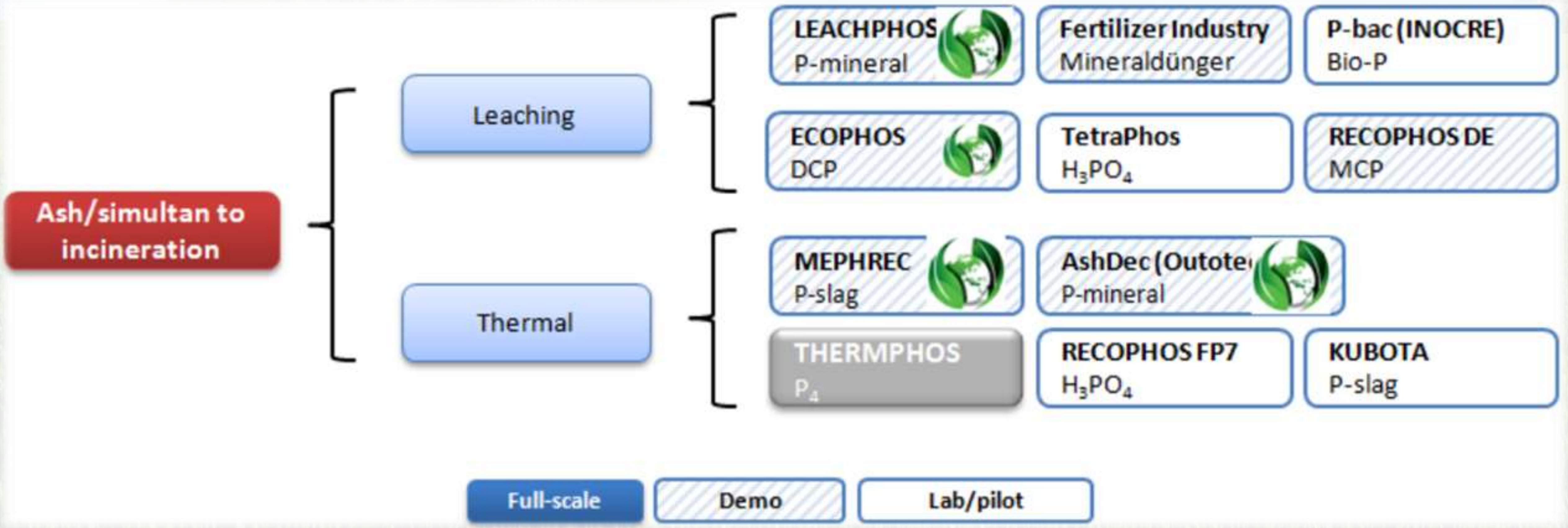
P-Recovery From Ashes

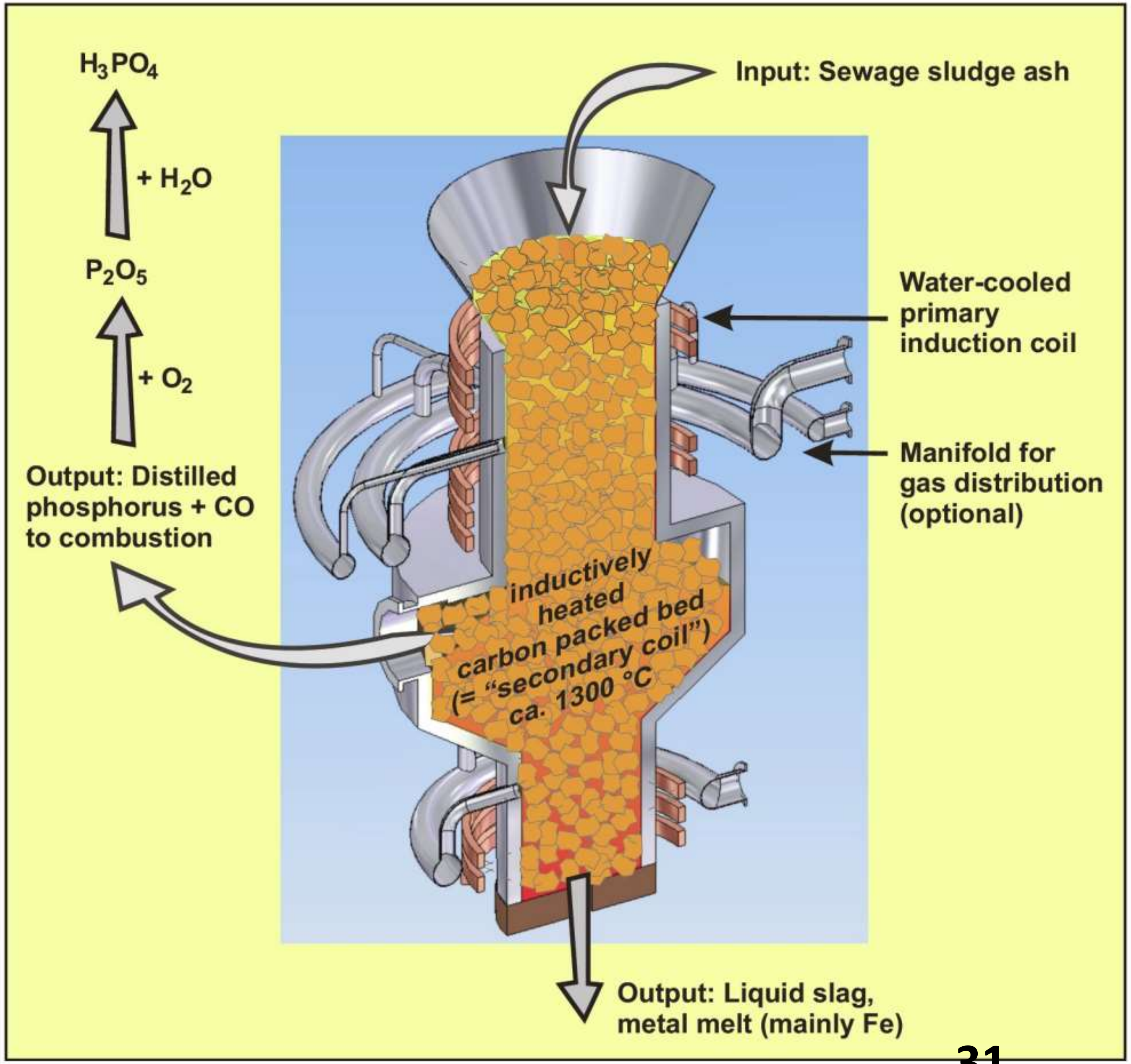


Thermal Treatment

- Improves the bioavailability of ashes
- Removes heavy metals
  - Using additives
- 850 - 1000° Celsius
- P_4/H_3PO_4/P-Rich Slag/P-Mineral
- Gas/Electricity

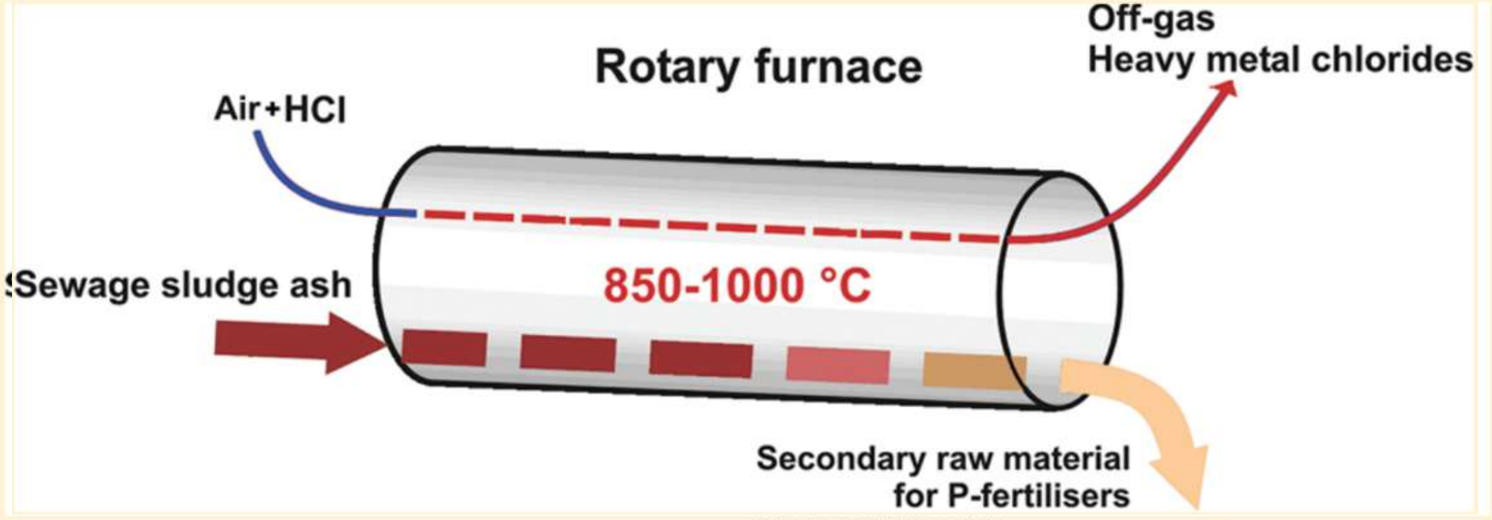
RECOPHOS FP7

- Inductively heated
- 1000° Celsius
- Relatively low amount of additives needed
- Smelting
- P_4/H_3PO_4
- Metal slag
- >90% P-recovery yield
- Metal Slag <0.5% P2O5



Thermo-Chemical Additives

- Solid Chloride donors:
  - $MgCl_2$ (favours Zn over Cu removal)
  - $CaCl_2$
  - KCl (favours Cu over Zn)
  - NaCl
  - PVC (SUSYPHOS)
- Gaseous Chloride donors:
  - Cl_2
  - HCl-gas
- Reductive Conditions:
  - Na_2CO_3
  - Na_2SO_4

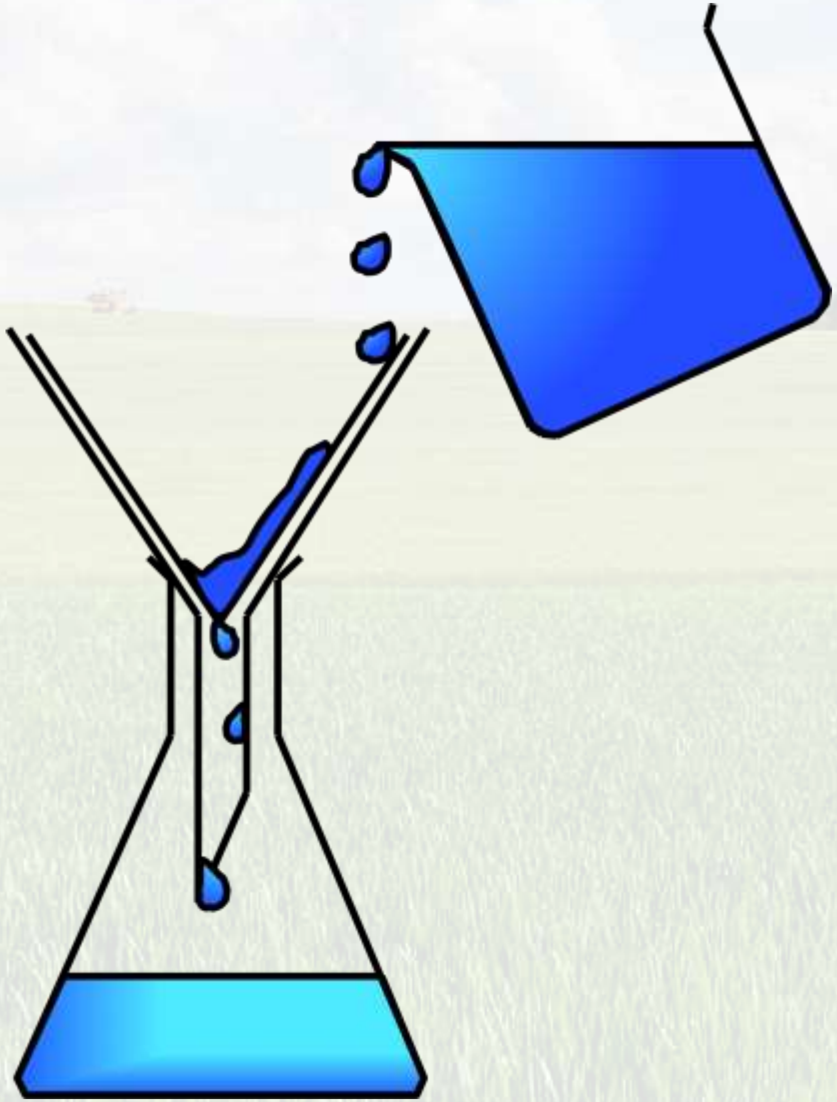


Vogel, C., Exner, R.M. and Adam, C. (2012). Heavy metal removal from sewage sludge ash by thermochemical treatment with polyvinylchloride. *Environmental science & technology*, **47**(1), pp. 563-567.

Acid Leaching

- Heavy metal removal
- Mild temperature
- Solvents
- Acids
- Additives
- Filtration
- H_3PO_4/P2O5-Mineral
- Electricity

- **Acids:**
  - HCl
  - H_2SO_4
  - H_3PO_4
- **Bases:**
  - NaOH
  - Lime (CaO)
  - KOH



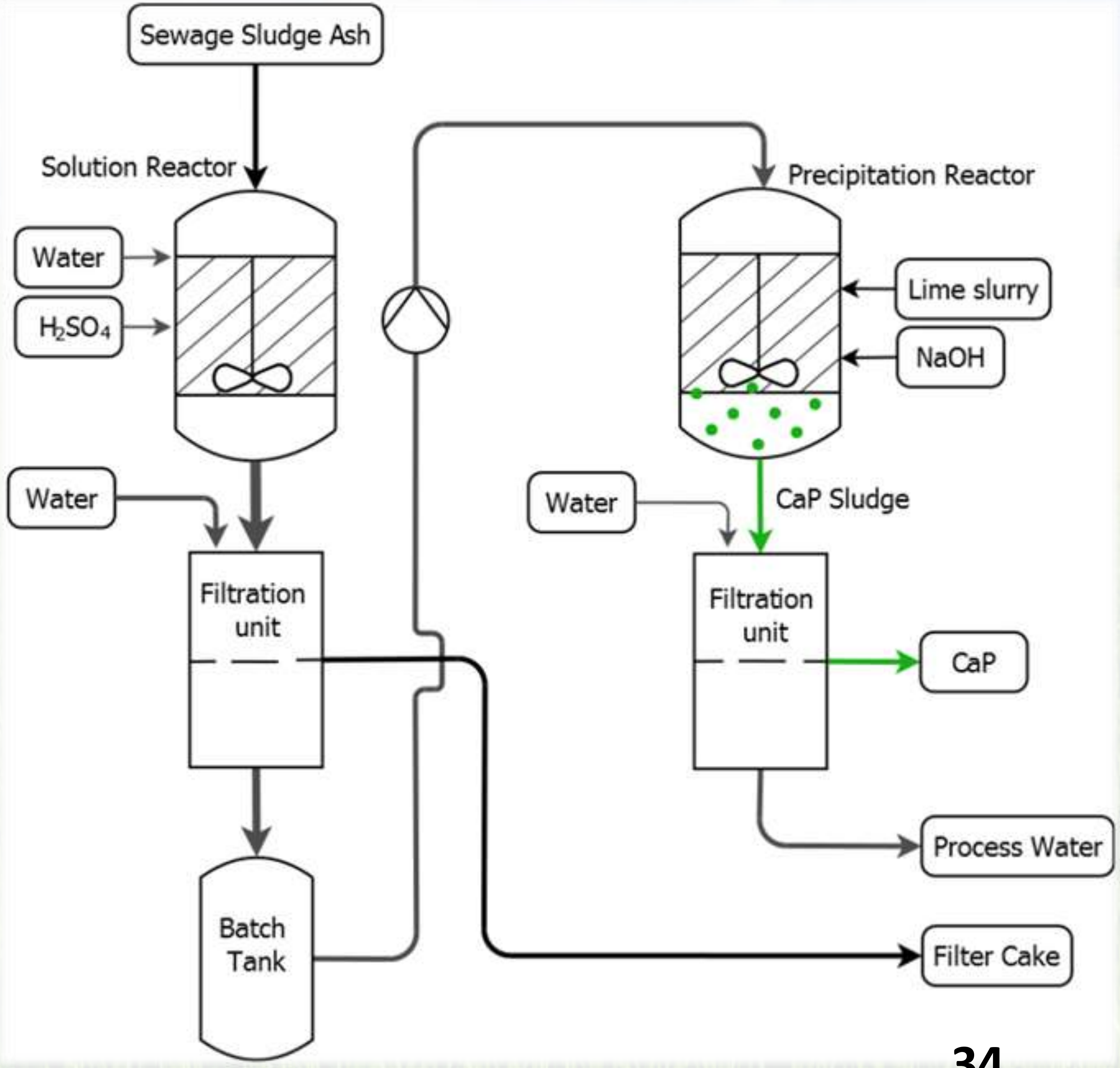
LeachPhos

Used:

- H_2SO_4
- Lime
- NaOH

Produced:

- P2O5-Mineral



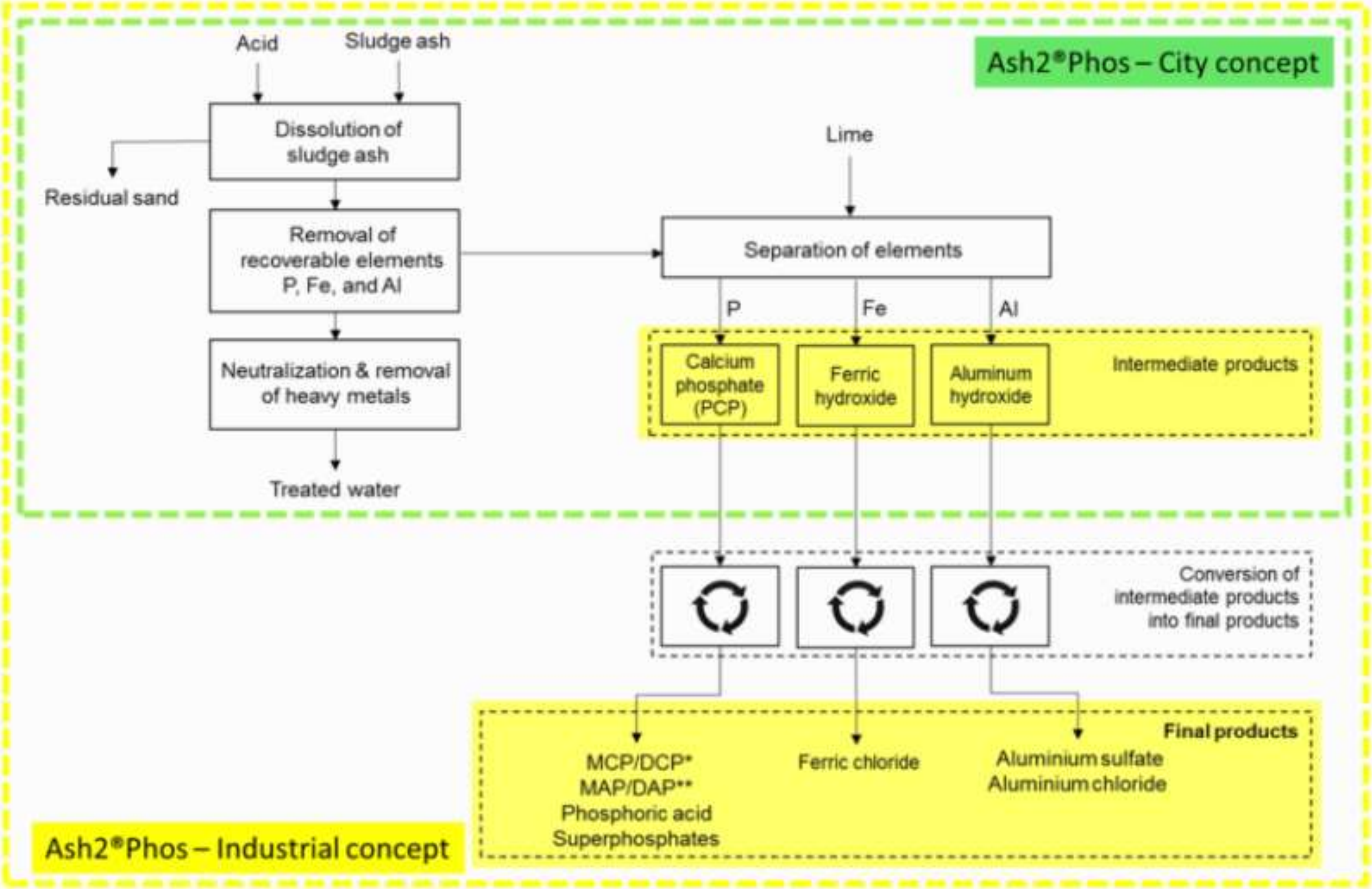
Ash2Phos

Used:

- HCl
- Lime
- Filtration

Produced:

- P-Mineral



* mono/di-calcium phosphate (feed phosphate), mono/di-ammonium phosphate (fertilizer)

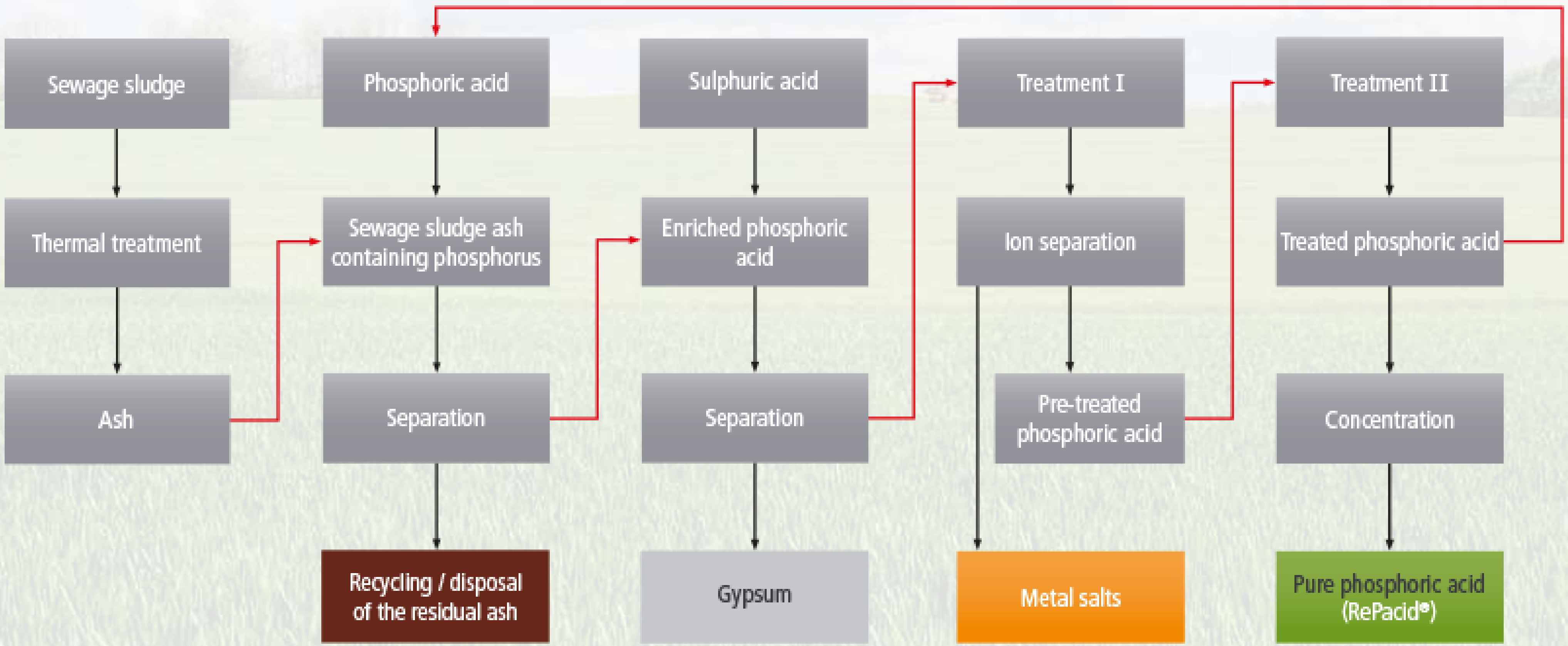
REMONDIS - TETRAPHOS

Used:

- H_3PO_4
- H_2SO_4

Produced:

- H_3PO_4



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Acid Leaching with EDTA Pre-Treatment

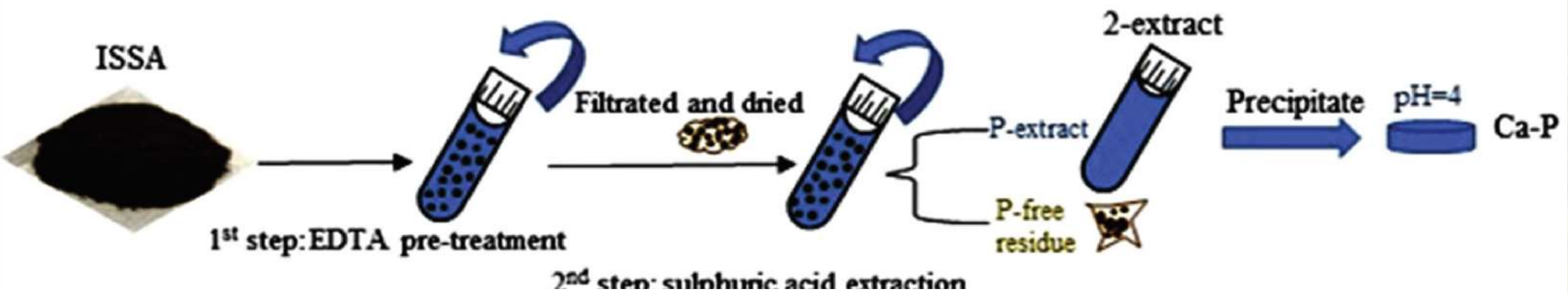
1. EDTA Pre-Treatment
   (for metal removal)
2. Washing
3. Sulfuric Acid Extraction
4. Precipitation

Used:

- EDTA
- H_2SO_4
- NaOH

Produced:

- P2O5-Mineral

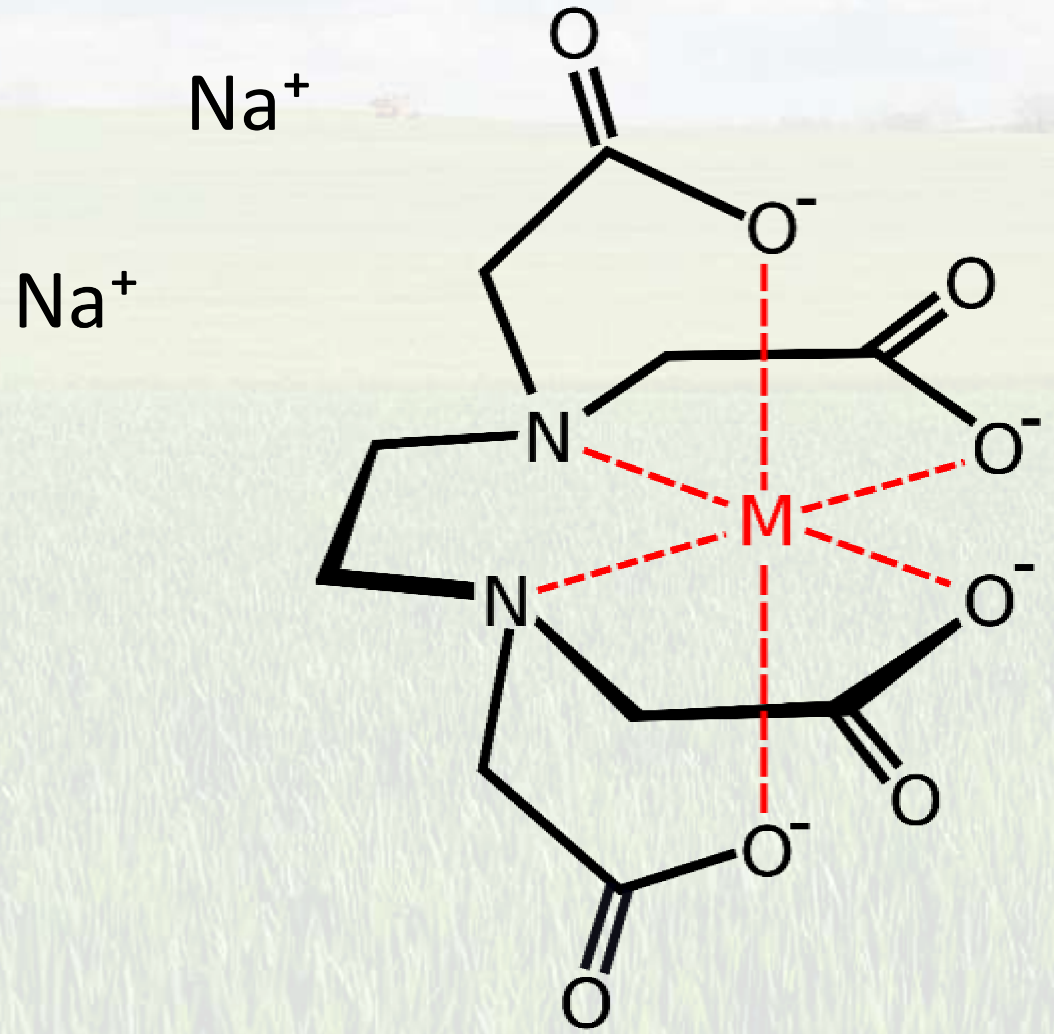


Fang, L., Li, J. S., Donatello, S., Cheeseman, C. R., Wang, Q., Poon, C. S., & Tsang, D. C. (2018). Recovery of phosphorus from incinerated sewage sludge ash by combined two-step extraction and selective precipitation. Chemical Engineering Journal, 348, 74-83.

Acid Leaching with EDTA Pre-Treatment

Disodium-EDTA:

- Non-toxic
- Degrades naturally
- Chelating agent
- Iron EDTA



Acid Leaching with EDTA Pre-Treatment

- 0.075 M EDTA is optimal
  - Slight excess of EDTA relative to iron contentration
- more concentrated EDTA solutions induces dissolution of phosphates as a result of lower pH

- Next steps for research:
  - More concentrated sulfuric acid solution for phosphate extraction step
  - Higher pH value for precipitation
  - Finer SSA powder

EDTA exp	Dry product (g)	P2O5 conc.	P2O5 (g)	Recovery yield P2O5 (%)
0,025 M	2.71	11.56	0.31	12,5
0,050 M	3.19	39.37	1.26	50,2
0,075 M	3.25	40.35	1.31	52,4
0,100 M	3.15	39.21	1.24	49,4
0,125 M	2.76	39.74	1.10	43,8
0,150 M	2.50	40.15	1.00	40,2
0,175 M	2.31	40.68	0.94	37,5
0,200 M	2.16	40.83	0.88	35,2

Acid Leaching with EDTA Pre-Treatment

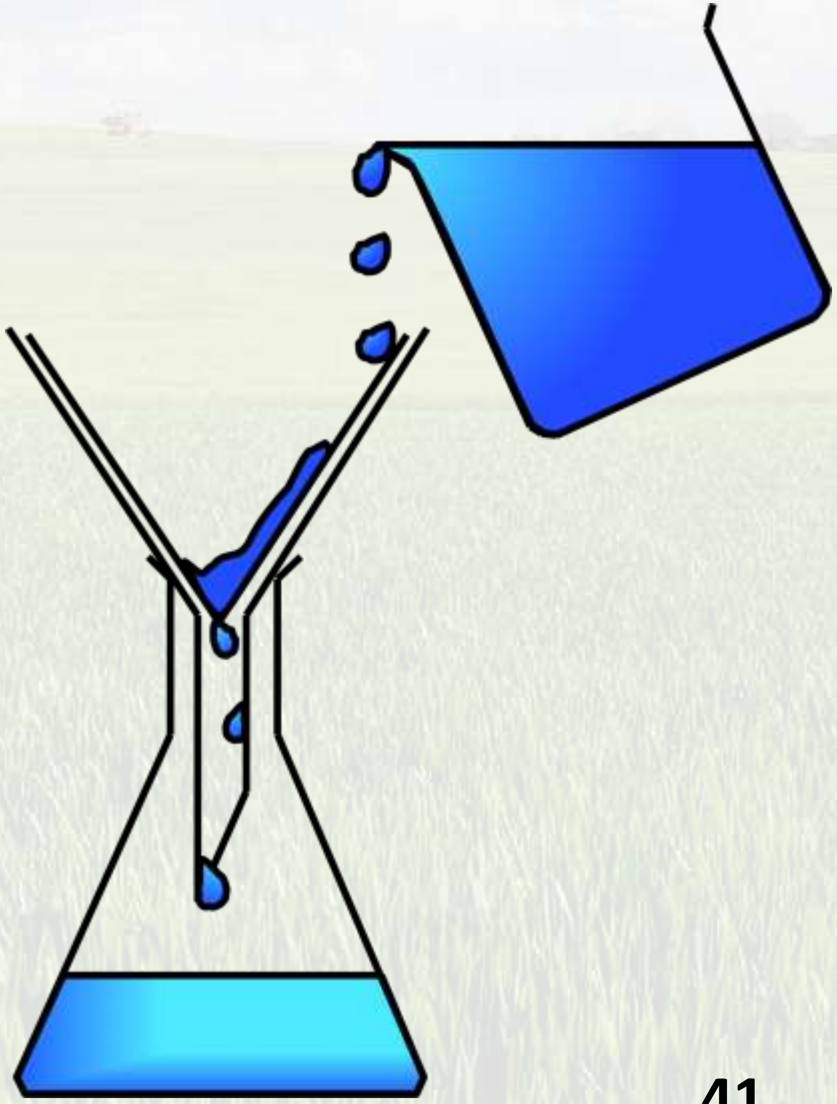
- Fine ashes were used (0.12 micron)
  - No improvement compared to courser ashes
- More concentrated sulfuric acid solutions for phosphate extraction, improve yield
- Optimal pH value for precipitation is somewhere between 4 and 4.5
- Different type of ashes?

Acid conc.	Product (g)	P2O5%	P2O5 (g)	Yield %	Precipitation pH
0,2 M	6.65	38.03	2.53	48.2	4.47
0,2 M	6.85	38.31	2.62	50.0	4.45
0,3 M	8.86	34.20	3.03	57.7	4.59
0,3 M	9.09	33.59	3.05	58.2	4.58
0,4 M	10.37	31.07	3.22	61.4	4.56
0,4 M	10.95	30.69	3.36	64.0	4.46
0.34 M	9.37	37.44	3.51	70.1	4.90
0.38 M	10.62	35.83	3.80	76.1	4.56

Acid Leaching with EDTA Pre-Treatment

Further research:

- Optimising acid concentration
- Using different precipitating agents
  - KOH
  - Lime
- Optimising pH range for precipitation
- Optimising solid to liquid ratio (L:S)
- Minimising reaction time
- **Acidulation of product**



Conclusions

- Techniques for P recovery are available
- Optimisation of P recovery for different waste streams can be very easy

We need to rethink the ethics of discounting sustainability to ensure that we leave behind a liveable earth for future generations.

Davidson, M. D. (2015). Climate change and the ethics of discounting. Wiley Interdisciplinary Reviews: Climate Change, 6(4), 401-412.

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Where needs take us

Thank You

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