

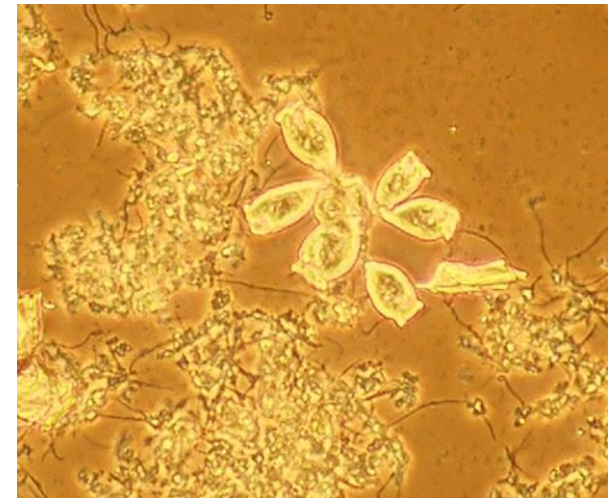
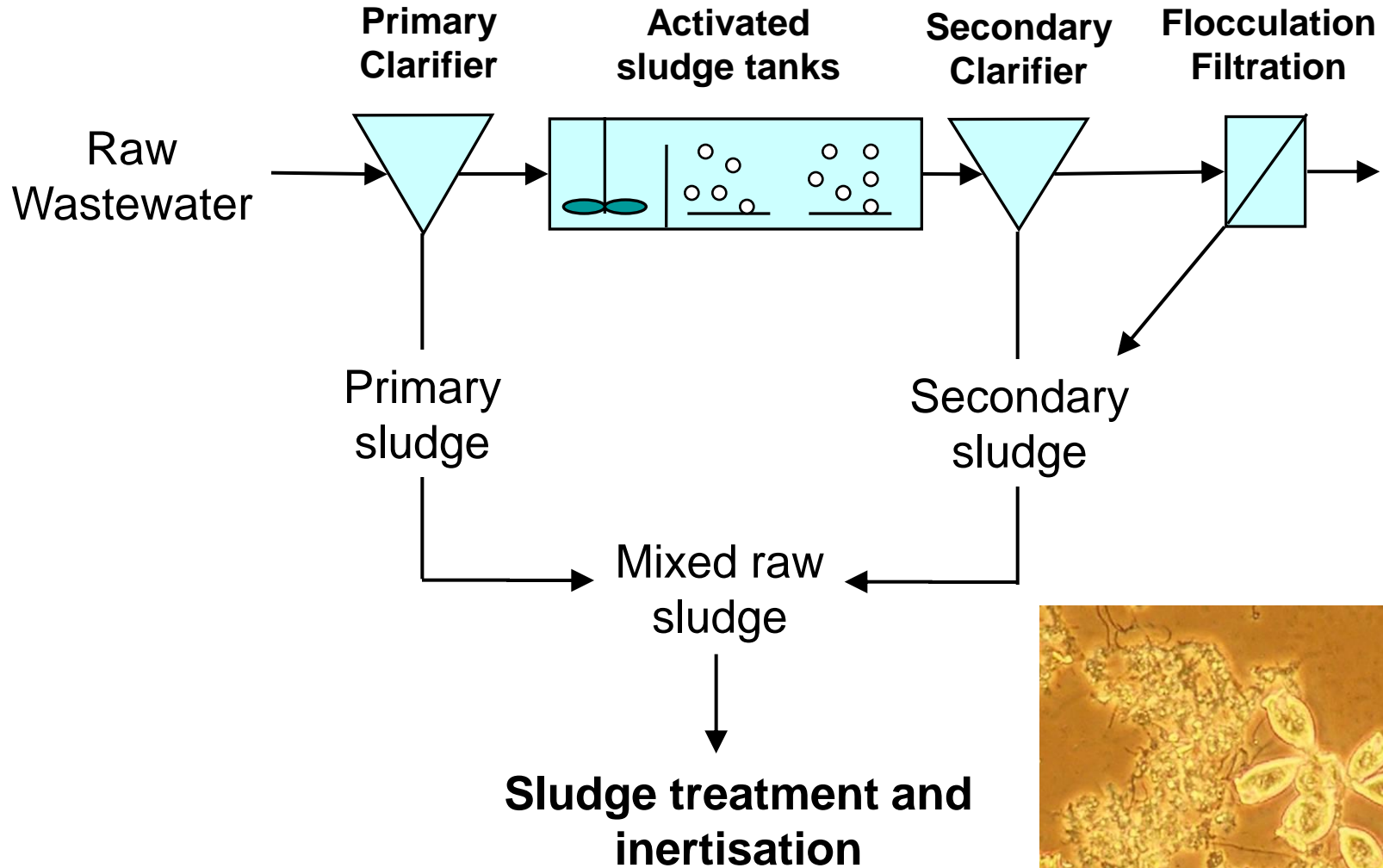
Sewage Sludge Inertisation by Ultrahigh Temperature Pyrolysis

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- Sewage sludge treatment and composition
- Pyrolysis process - potential for energy and P reuse
- LCA results - comparison with incineration

Sludge production in WWTP



- Stabilization (to reduce mass, volume, odor problems and pathogens as well as gaining energy) with anaerobic digestion

For agricultural use:

- Pasteurization (thermophilic pretreatment) or composting
- Lime treatment (if no stabilization step) and
- Long time storage in winter

- Dewatering

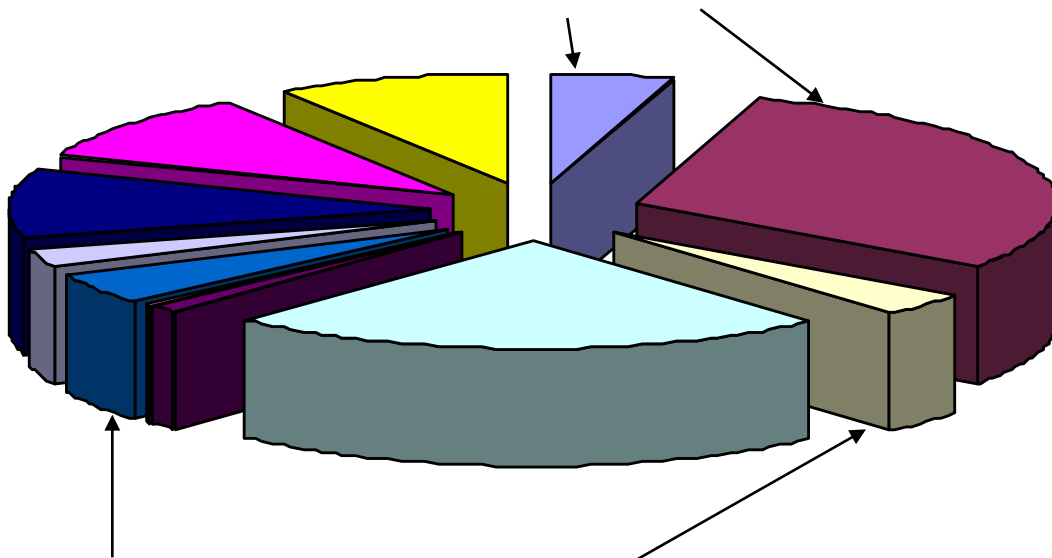
- Drying



Sludge composition (stabilized sludge)

Energy

20-22 MJ/kg orgTS = 8-10 MJ/kgTS



- Hydrogen
- Carbon
- Nitrogen
- Oxygen
- Sulfur
- Chlorine
- Phosphorus
- Ammonium nitrogen
- Calcium
- Iron
- Silicon

Nutrients

Nutrient	Nutrients in WW vs. fertilizer consumption %
Nitrogen	12% - 19%
Phosphorus	8% - 21%
Potassium	11% - 24%

Sludge composition (stabilized sludge)

- Heavy metals

	<i>mg/kg</i>
Cd	0.28-2.66
Cr	11.2-192.5
Cu	27.3-448.7
Hg	0.21-2.1
Ni	6.3-63
Pb	9.1-154.7
Zn	99.4-1400

**) Data are for EU member states,
Source: Disposal and recycling routes
for sewage sludge, Part 3, European
Commission, October 2001*

- Organic contaminants

<i>Polynuclear aromatic hydrocarbons (PAH)</i>	<i>Herbicide residues</i>
<i>Polychlorinated biphenyls (PCB)</i>	<i>Organo-tin compounds</i>
<i>Polychlorinated terphenyls</i>	<i>Phthalate esters</i>
<i>Phenol</i>	<i>Petroleum hydrocarbons</i>
<i>Chlorinated hydrocarbon solvents and phenols</i>	<i>Surfactants</i>
<i>Organochlorine insecticides</i>	<i>Aromatic amines</i>
<i>Organophosphorus compounds</i>	

- Pathogens?

Sludge disposal and recycling

- ~~Ocean dumping~~ 1980's
- ~~Land filling~~ ? In Switzerland since 2000, in Sweeden since 2005
- ~~Agriculture~~ ? Switzerland, Sweeden, The Netherlands...
- Incineration
- Other methods
- P-Recycling



Novel sludge inertisation processes - reuse of sludge and of its resources

Super Critical Water Oxidation

$T > 374^{\circ}\text{C}$; $p = 22\text{MPa} = 220\text{ bar}$

Wet Oxidation

$T = 250\text{-}300^{\circ}\text{C}$; $p = 6\text{-}10\text{MPa}$

Sludge Gasification

$T=850^{\circ}\text{C}$

Ultra High Temperature Pyrolysis

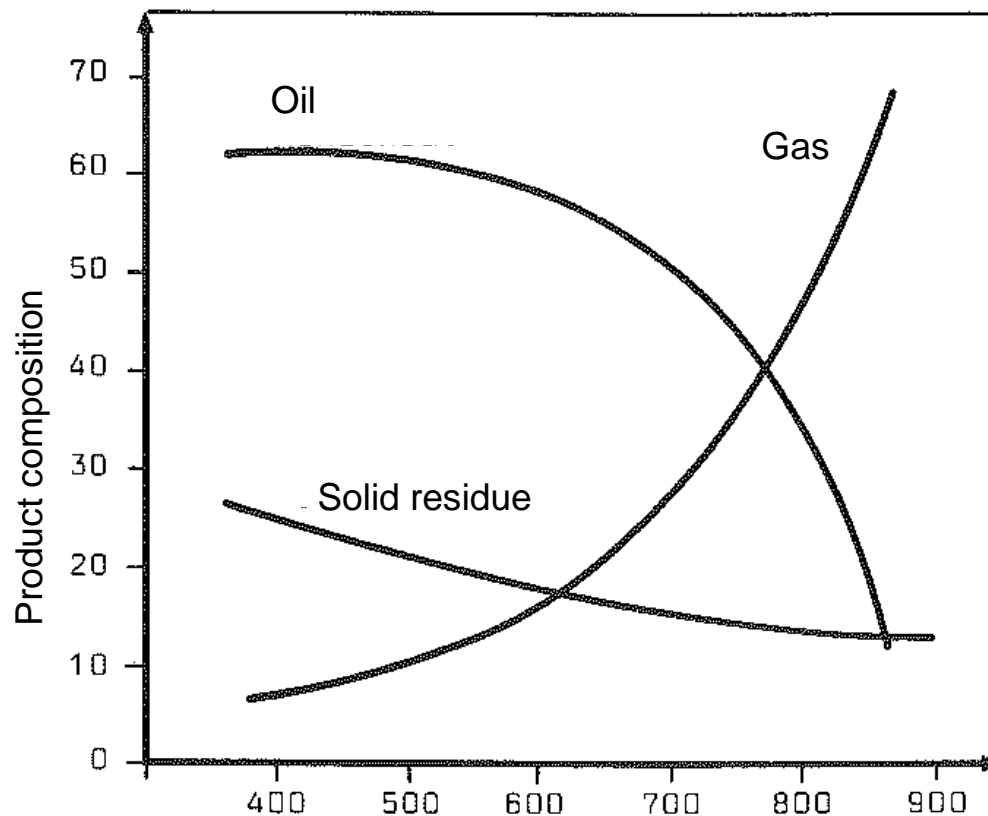
$T=1200\text{-}1400^{\circ}\text{C}$

The final result should be:

- Sludge reduction, Mineralization of organics
- Elimination or fixation of pollutants
- Recovery of nutrients
- Recovery of energy (not only in form of heat)

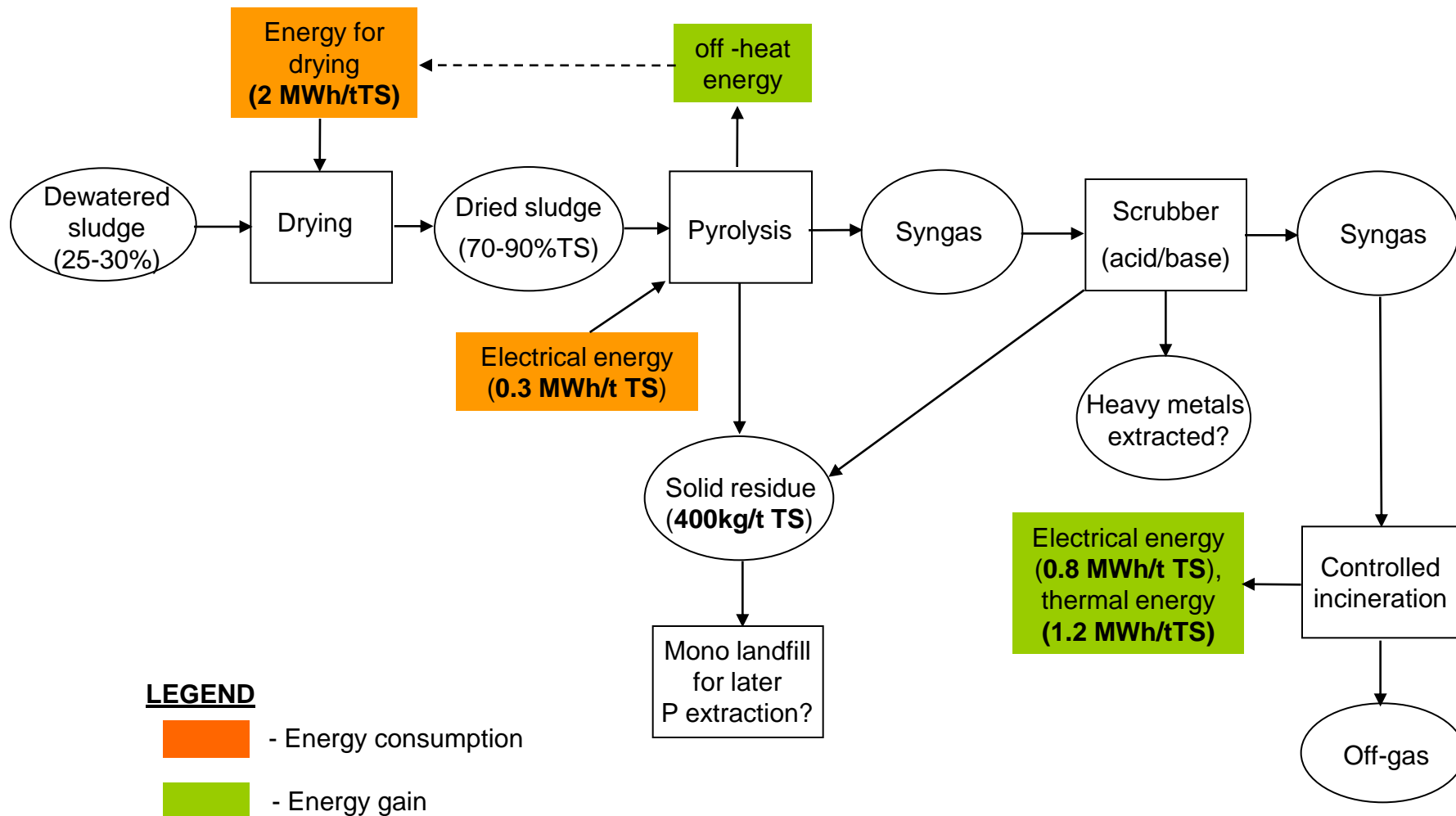


High Temperature Pyrolysis (>1'000°C)

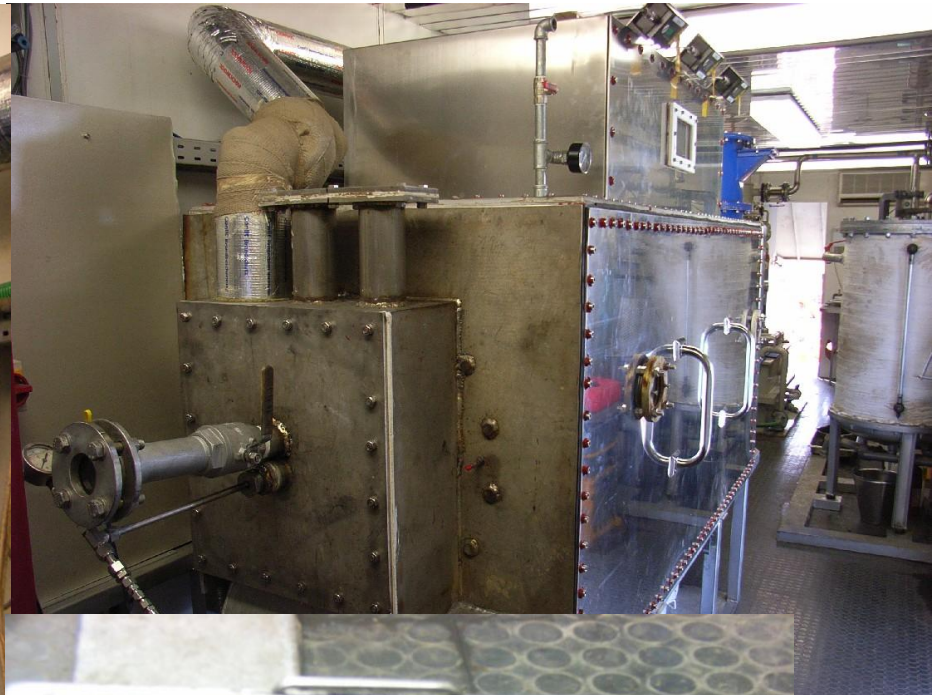
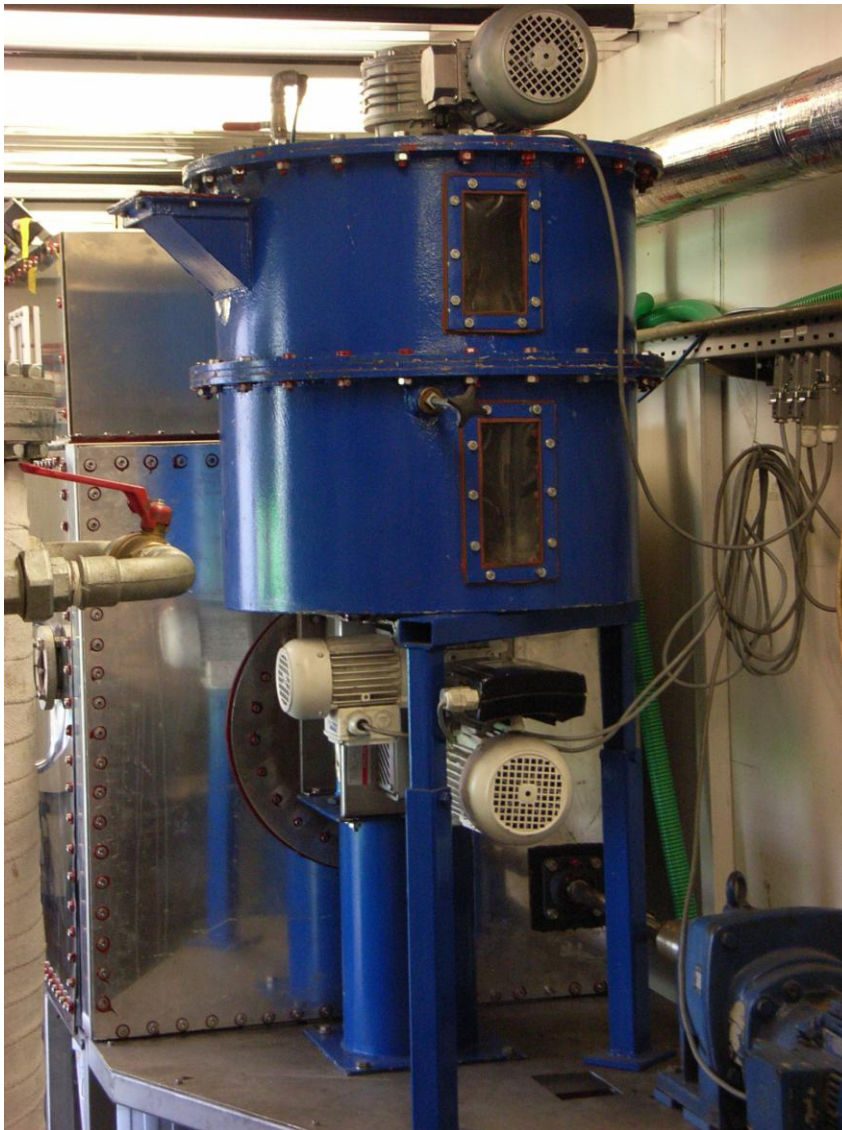


- Only two product (solid residue and gas)
- Gas is free of tar but contains heavy metals (gas cleaning?)
- Organic micropollutants are completely destroyed

High temperature pyrolysis

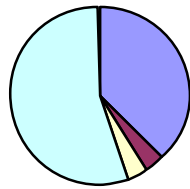


High temperature Pyrolysis, pilot plant Munich

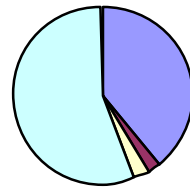


Process gas = Syngas (mainly H₂ and CO)

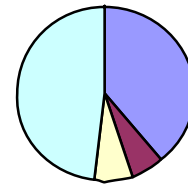
T=1200°C, t=10min



70% TS



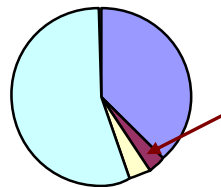
80% TS



90% TS

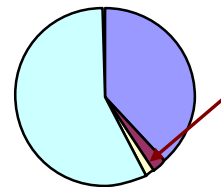
TS = 80%, t = 5min

- CO
- CO₂
- CH₄
- H₂



T=1200°C

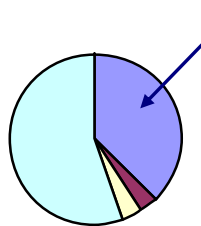
3.3% CO₂



T=1400°C

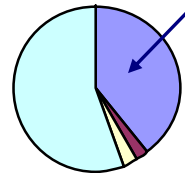
2.8% CO₂

TS = 80%, T = 1200°C



t=5min

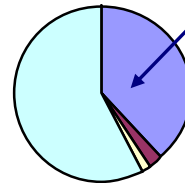
36.1% CO



t=10min

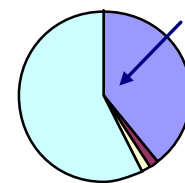
38.6% CO

TS = 80%, T = 1400°C



t=5min

36.4% CO

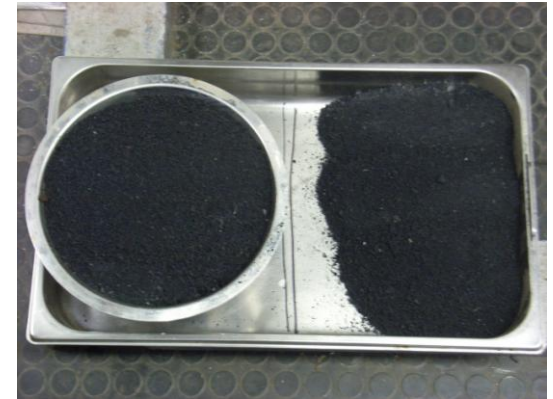


t=10min

37.3% CO

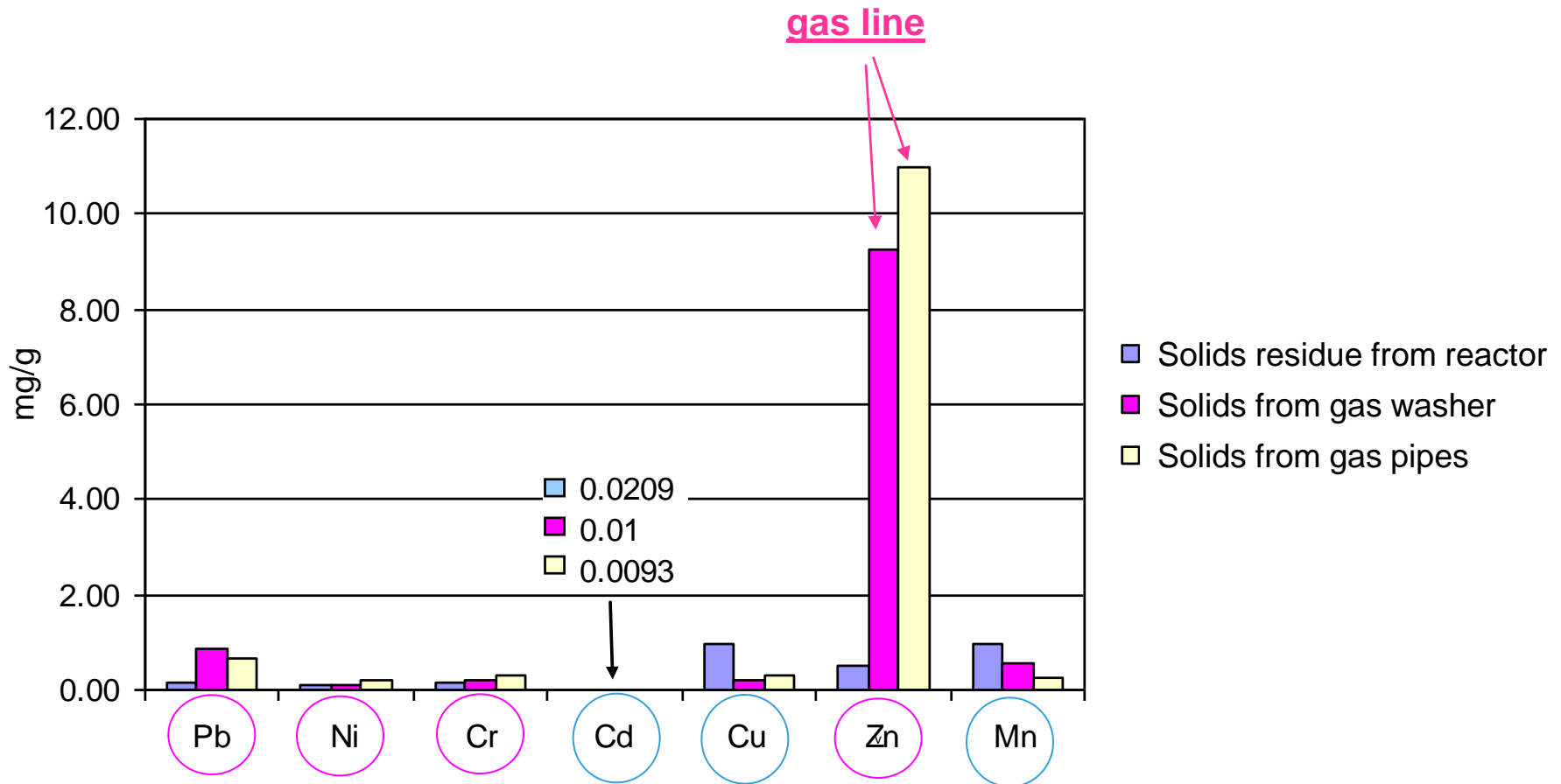
Solid residue in reactor and syngas

- The amount of produced solid residue and syngas depends on process temperature and reaction time
- TS reduction is maximal about 60% (theoretically calculated from the dried sludge composition: Si, Ca, Fe, Al and P oxides)
- TS reduction observed (see Table) was higher probably due to loss in the gas piping system and gas washer (in the reactor 80% of solid residue and in the gas system and washer only 20% was found)

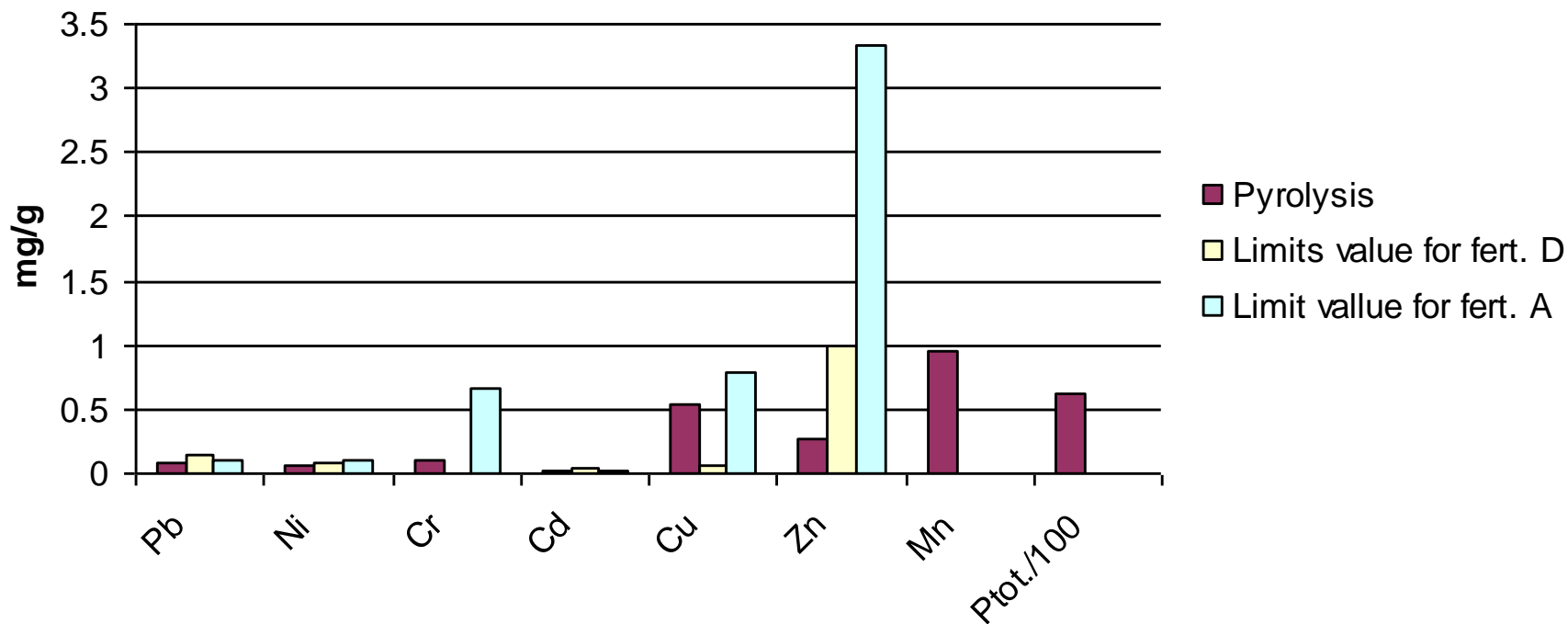


<i>T</i> \ <i>t</i>	5min	10min
1200°C	62%	81%
1400°C	76%	87%

Heavy metals distribution among solids products (90% TS, T=1200°C, t=10min)



Heavy metals content – comparison with EU limits¹⁾ for fertilizers



1) Adam et al., (2007) Materials Transactions, 48 (12): 3056-3061



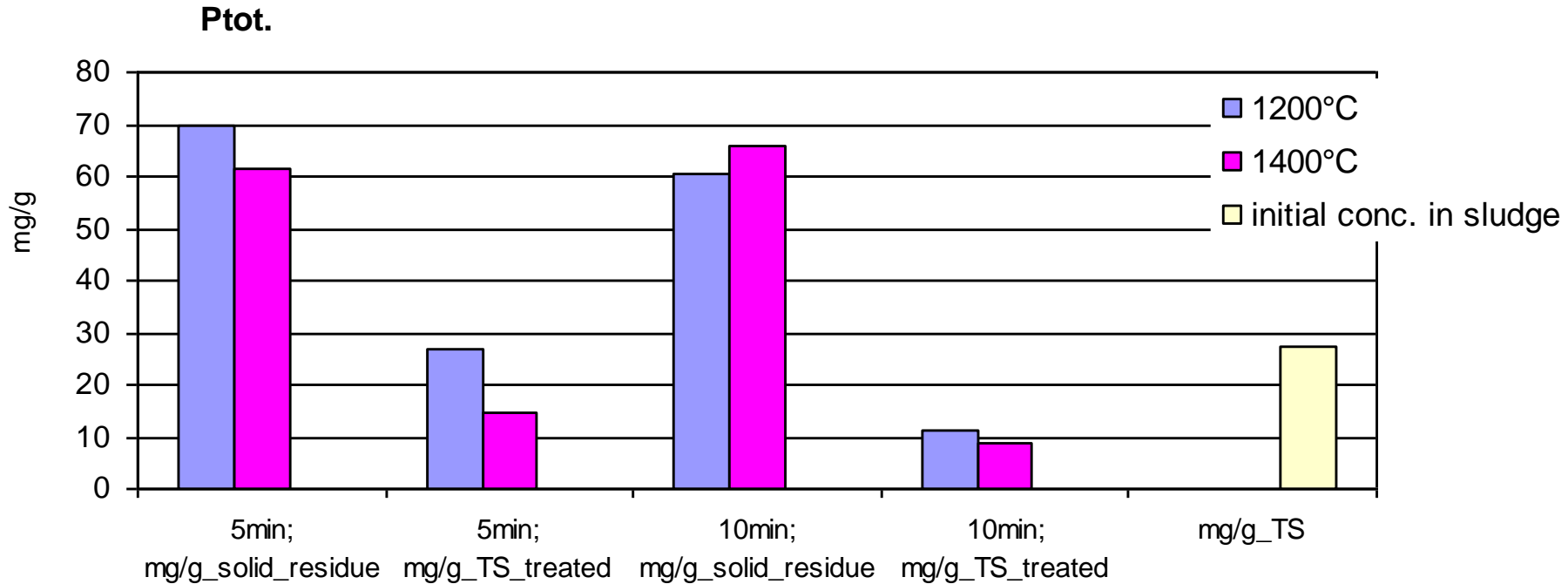
Heavy metals leaching from the solid residue (starting pyrolysis from 80% TS)

- 1g sample was placed in a closed flask suspended in 20ml of deionised water and shaken for 5 days. After filtration the heavy metals content in the liquid was measured and the leached fraction calculated (Table):

<i>T</i>	<i>time</i>	<i>Pb</i>	<i>Ni</i>	<i>Cr</i>	<i>Cd</i>	<i>Cu</i>	<i>Zn</i>	<i>Mn</i>
1200°C	5 min	0.63%	0.15%	0.10%	0.13%	0.04%	0.02%	0.00%
	10 min	1.42%	0.19%	0.13%	0.65%	0.08%	0.05%	0.00%
1400°C	5 min	0.77%	0.16%	0.09%	0.16%	0.04%	0.03%	0.01%
	10 min	0.73%	0.19%	0.10%	0.14%	0.04%	0.03%	0.01%

- Neither the temperature nor the residence time influenced the stability of the heavy metals in the solid residue.

Potential for phosphorus recovery



Commercial fertilizer has about 8% P content

Phosphorus bioavailability, (1g in 20ml of 2% citric acid)

	5min		10min		
	init.conc.in res. (mg/g)	% leached	init.conc.in res. (mg/g)	% leached	
<i>T</i>					
1200°C	69.9	12.6%	60.6	9.9%	27.4
1400°C	61.4	11.9%	65.6	11.8%	

Conclusion:

Phosphorus bioavailability seems not to depend on the reaction temperature but is slightly reduced with the reaction time.

	<i>Ptot. init. (mg/g)</i>	<i>Percentage leached</i>
Incineration ash	58-90	0.07%-0.12%
Wet Oxydation solid residue	81.1	8.9%
Pyrolysis (TS80%, 1200°C, 10min)	60.6	9.9%
Gasification in Balingen	58.6	16.5%



Operating data and costs for full-scale pyrolysis

Pyrolysis process	
Capacity:	7000tTS/year
TS :	70-90%
Electricity consumption:	320kWh/tonTS
Oxygen consumption:	none
Solid mineral out:	250kg/tonTS
Gas out (to the atmosphere)	none
Operato and maintenance:	4men/year
Primary energy gain:	960kWh/tonTS
Investment costs:	9million € (for 25ton/d unit)
Personal costs	200'000€/year

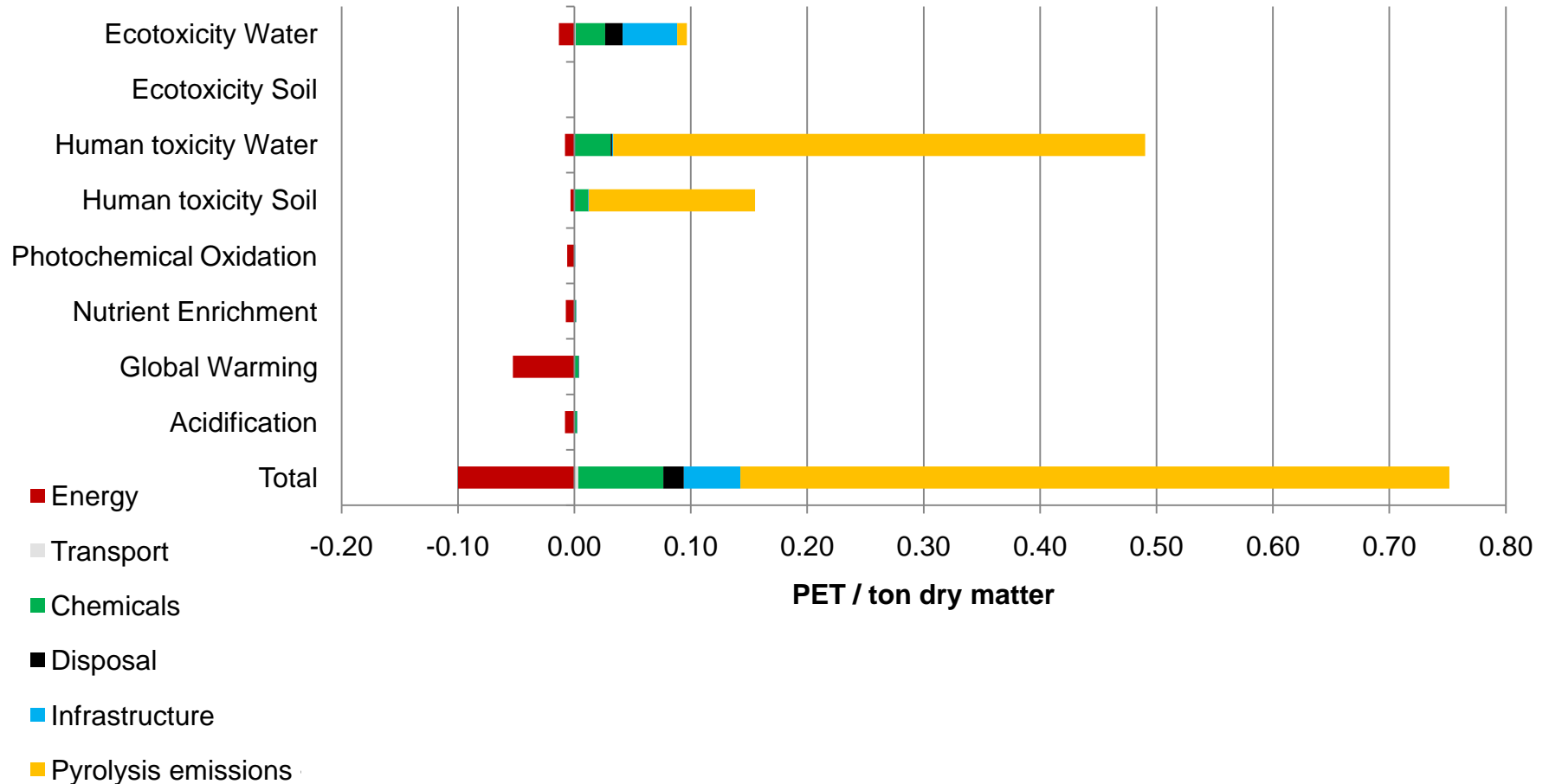
For inventory list of LCA

- Sludge composition of municipal WWTP (European average), thickened to 4% DS, dewatered to 25-30% DM)
- Emissions of heavy metals to air -> *Cd, Cr, Cu, Hg, Ni, Pb, Zn*
- Infrastructure
- Disposal of solid residues
- Chemicals (for off-gas treatment; assumed identical to on-site incineration)
- Transport
- Energy consumption / production

Energy production	Electricity	0.78 MWh/tDM (33% of theoretical yield)
	Heat	1.20 MWht/DM (50% of theoretical yield)
Energy consumption	Electricity	0.34 MWh/tDM (data from Pyromex)
	Heat	1.7-2.2 MWh/tDM (evaporation, 25-30%DM)
Energy balance	Electricity surplus	0.4 - 0.5 MWh/tDM
	Heat missing	0.5 - 1.0 MWh/tDM

LCA: Impact profile; Pyrolysis - heat drying

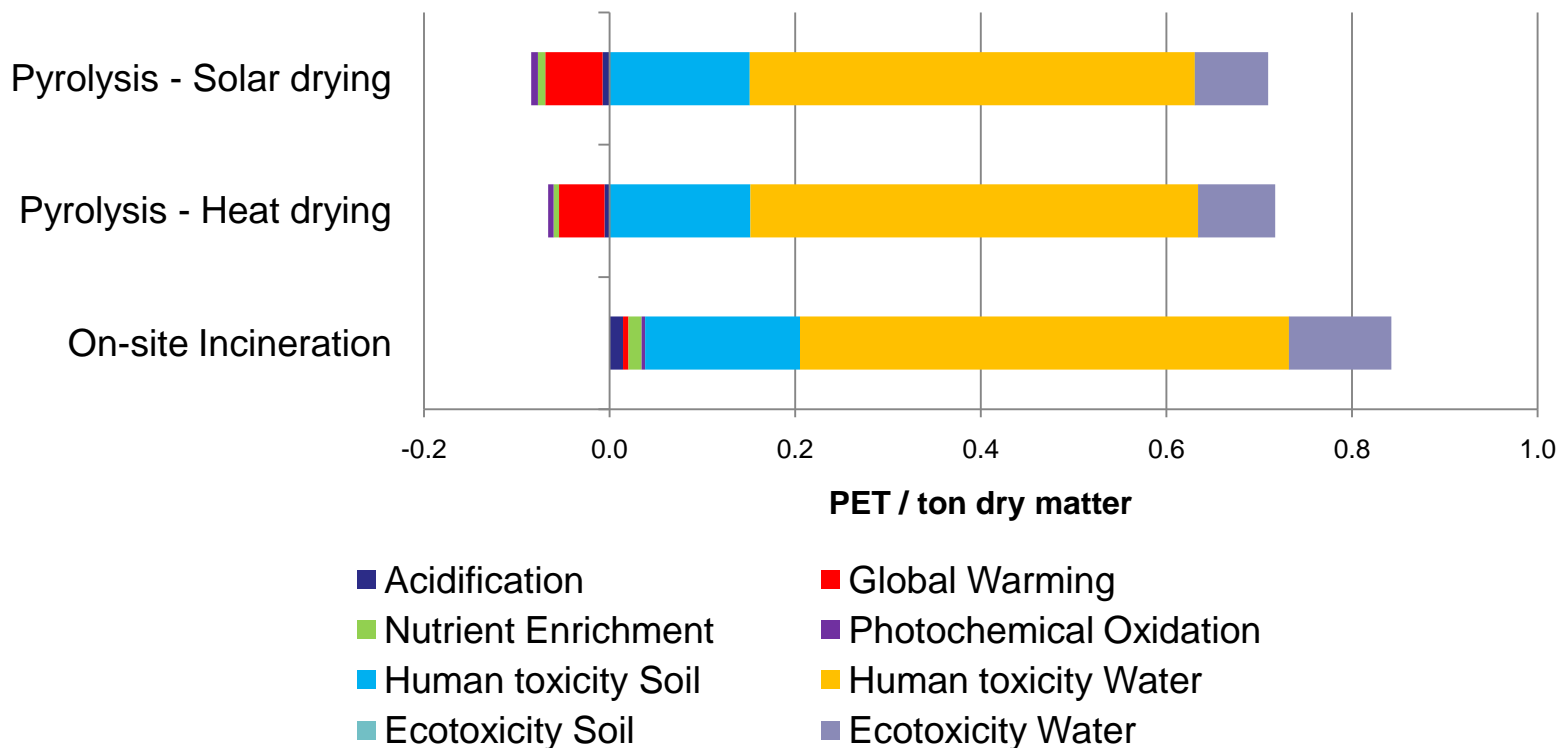
(Normalized and weighted impacts, PET. Weighting factors =1 for all impact categories).



Total (net) = 0,65

The impact of "pyrolysis emissions" is dominated by mercury air emissions

LCA: Comparison of impact profiles; Pyrolysis and on-site incineration



Total (net):

Incineration = 0,84 PET/ton DM
 Pyrolysis – heat drying = 0,65 PET/ton DM
 Pyrolysis – solar drying = 0,63PET/ton DM

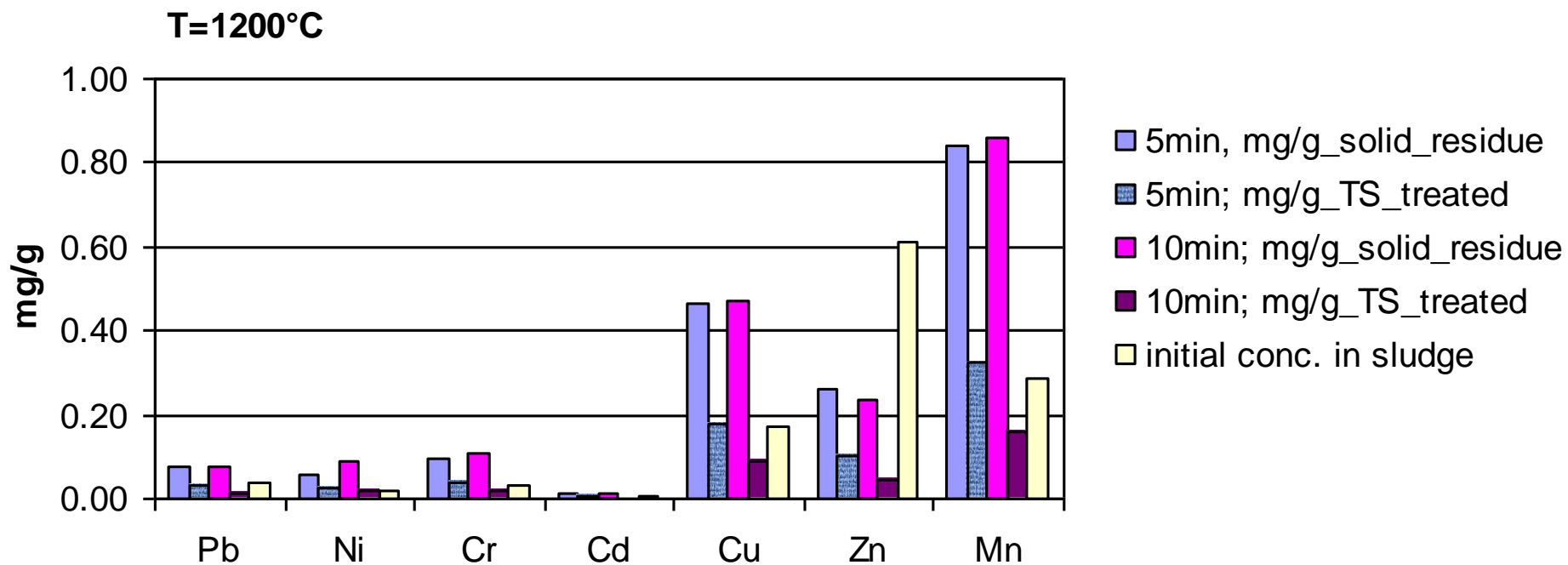
Conclusions

- High temperature pyrolysis avoids oily phase; only solids (free of organics) and syngas.
- Gas is free of tar and expensive cleaning is avoided.
- Solid product in the reactor has low content of heavy metals, ash has probably to be treated to extract heavy metals
- Potential for phosphorus recycling.
- Higher bioavailability than incineration ash
- Heavy metals are well immobilized
- LCA indicates that high temperature pyrolysis might be more sustainable than incineration due to lower air emissions and better energy balance
- However, the LCA is highly sensitive to heavy metal emissions, mainly mercury?



- This study was part of the EU Neptune project (Contract No 036845, SUSTDEV-2005-3.II.3.2), which was financially supported by grants obtained from the EU Commission within the Energy, Global Change and Ecosystems Program of the Sixth Framework (FP6-2005-Global-4

Heavy metals in solids residue of reactor (80% TS, 1200°C, t = 5-10 min)



Heavy metals in solids residue of reactor (80% TS, 1200-1400°C, t = 10 min)

