Retorted Oil Shale In Estonia: An Environmental Audit

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Pollution is in the eyes of the beholder

Is it?

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Background

- 85 years of shale oil production
- two main processes today -
  - •gaseous heat carrier, lumpy oil shale - semicoke
  - •solid heat carrier, fine grained oil shale - coke-ash residue
- 80 years - ca 110 Million tons of spent shale (dw)
- semicoke - 2 bigger deposition areas
- coke-ash residue deposited together with combustion ash until today
- In last 5 years
  - •ca 1 Million tons of semicoke and
  - •1 Million tons of coke-ash residue a year
- till the end of 20th century - “wet deposition method” of semicoke
- since then no extra water used besides water used for cooling the waste
- groundwater around the deposition areas is contaminated with phenols
- deposition areas to be reconstructed as landfills till 2009
- old deposition areas to be closed till 2013
- development of deposition technology - compaction of semicoke for better cementation

Legal

Oil shale semicoke is classified as hazardous waste in the Estonian Waste List.

- The Waste List currently valid in Estonia is based on the EU Waste List.
- According to the general logic of the EU Waste List, wastes that have undergone the process of pyrolysis should be categorized as hazardous waste since they contain **tarry and bituminous substances**.

The solid waste of the solid heat carrier process has no separate number in the Estonian Waste List.

- It is still a pyrolysis waste.

Oil shale combustion ashes are also hazardous wastes.

All together 95% of the hazardous waste in Estonia

Legal II

Environmental impact of semicoke (investigation for Environmental ministry, 2003)

1. high TOC 12…14%
2. phenols
3. sulfides
4. bitumoids
5. high pH of leachates

Requirements for landfills

Waste acceptance criteria for landfills

TOC

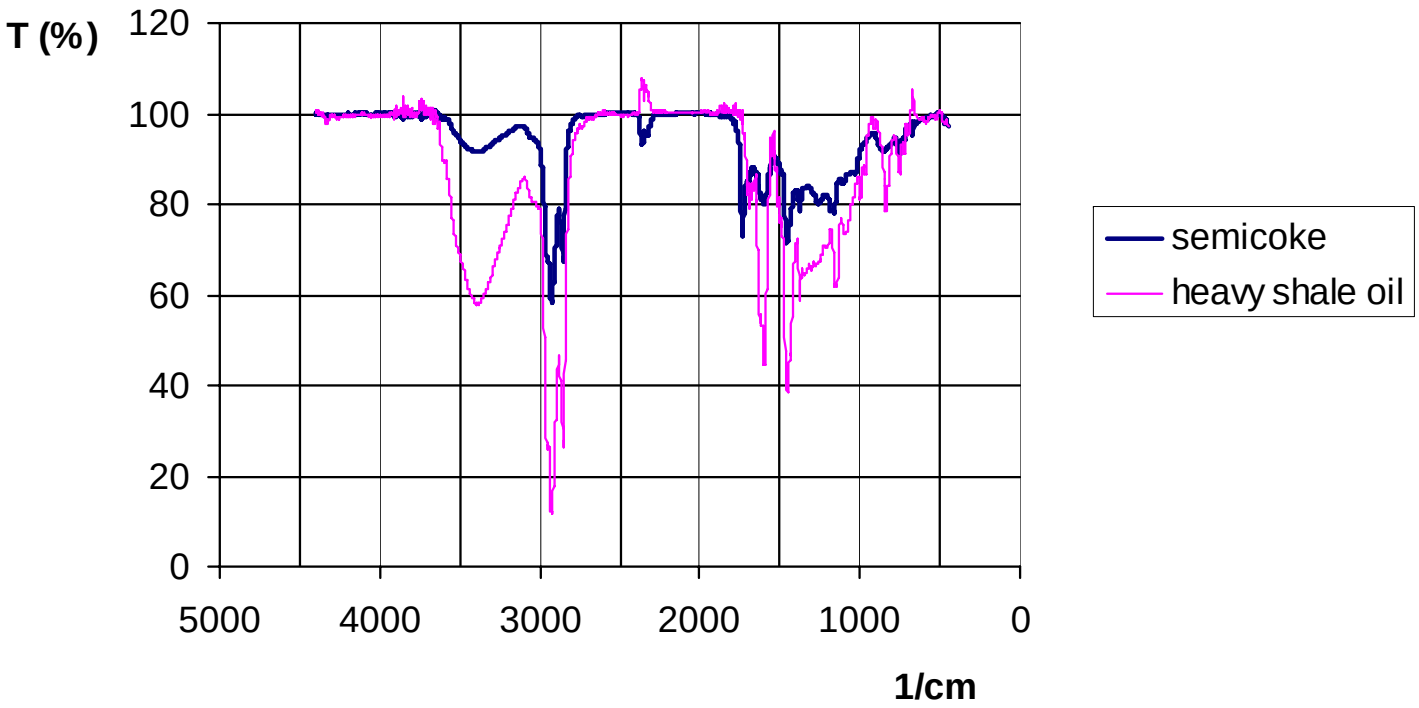
- semicoke 8...14 (LHW limit 6%)
- coke-ash residue <1

Leaching limit values

(DOC)

Bituminous substances

IR Spectra of semicoke soxhlet extract and heavy shale oil



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TOC

Parameter	Values	
	Min	Max
Fischer oil, %	<0,1	3,1
Yield in Soxhlet extraction, g/kg	<1	16
TOC, %	8	11

***Most of TOC originates from pyrolysis char**

***Limit 6% (or less) can be achieved**

1) burning the char

2) using lower calorific value oil shale

LEACHING BEHAVIOUR OF OIL SHALE SEMICOKE

Components	L/S = 10 l/kg				L/S = 2 l/kg			
	Leaching limit values, mg/kg		Amount leached from semi-coke, mg/kg		Leaching limit values, mg/kg		Amount leached from semi-coke, mg/kg	
	Haz	Non-haz	Sample 25	Sample 27	Haz	Non-haz	Sample 25	Sample 27
Ca	-	-	13000	9800	-	-	10000	1500
Mg	-	-	0.22	0.17	-	-	0.2	nd
Fe	-	-	<0.2	<0.2	-	-	nd	<0.02
Na	-	-	150	230	-	-	118	190
K	-	-	550	1700	-	-	820	2700
Al	-	-	0.35	<0.2	-	-	0.062	0.05
As	25	2	<0.1	<0.1	6	0.4	nd	<0.1
Ba	300	100	1.7	3.1	100	30	1.8	1.3
Cd	5	1	nd	nd	3	0.6	nd	nd
Cr (total)	70	10	<0.2	<0.2	25	4	nd	<0.02
Cu	100	50	<0.2	<0.2	50	25	nd	nd
Hg	2	0.2	nd	nd	0.5	0.05	nd	nd
Mn	-	-	<0.2	<0.2	-	-	nd	<0.02
Mo	30	10	0.8	0.44	20	5	0.64	0.12
Ni	40	10	<0.2	<0.2	20	5	nd	< 0.02
Pb	50	10	<0.2	<0.2	25	5	nd	<0.02
Se	7	0.5	nd	<0.5	4	0.3	nd	<0.05
Zn	200	50	<0.2	<0.2	90	25	nd	nd
Sb	5	0.7	nd	<0.5	2	0.2	nd	<0.05
Sr	-	-	nd	51	-	-	nd	35
S_{total}	-	-	11000	4600	-	-	11600	nd
DOC	1000	800	390	40	480	380	450	73
SO_4^{2-}	50000	20000	740	860	25000	10000	260	150
Cl^-	25000	15000	1800	2100	17000	10000	4600	nd
F^-	500	150	<5	nd	200	60	nd	nd
TDS	100000	60000	47500	32000	70000	40000	38000	nd

nd- not determined, elements that were not present in the solid semi-coke samples in amounts exceeding the leaching limits
"-" no leaching limit values set

Oxidation of phenolics

1d/1w/8w

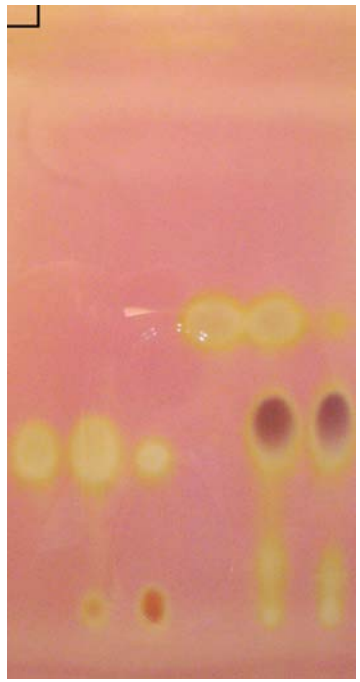
0 2d 7d 0 1d 2d

3h/1d/2d/4d/8d

phenol+cresols

2,5 -dimethyl resorcinol

resorcinol+
5-methyl resorcinol



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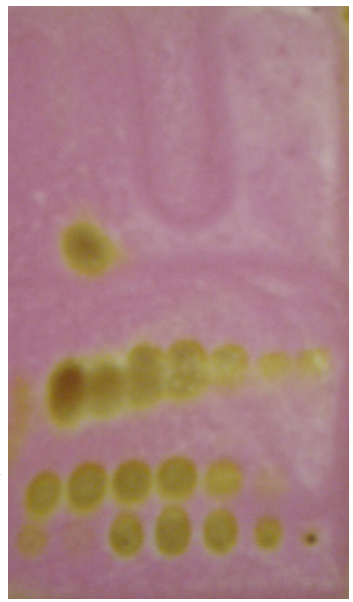

Y

semicoke leachate

5-methyl resorcinol

2,5-dimethyl resorcinol

5-methyl resorcinol +

2,5-dimethyl reorcinol

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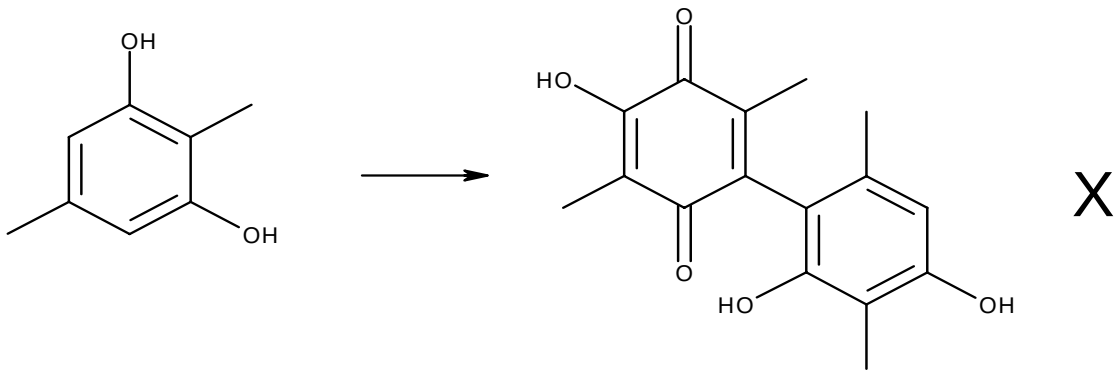
Oxidation of phenolics II



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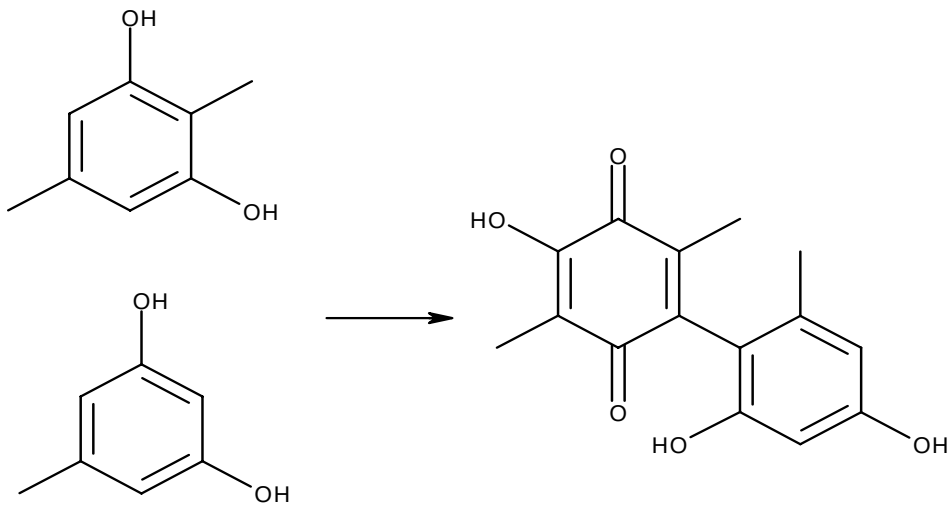

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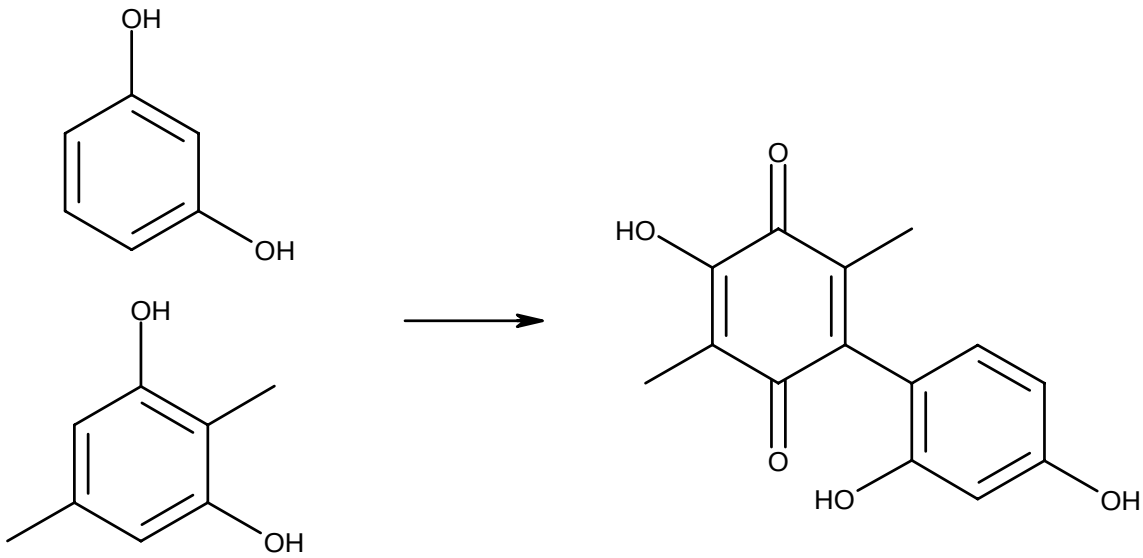
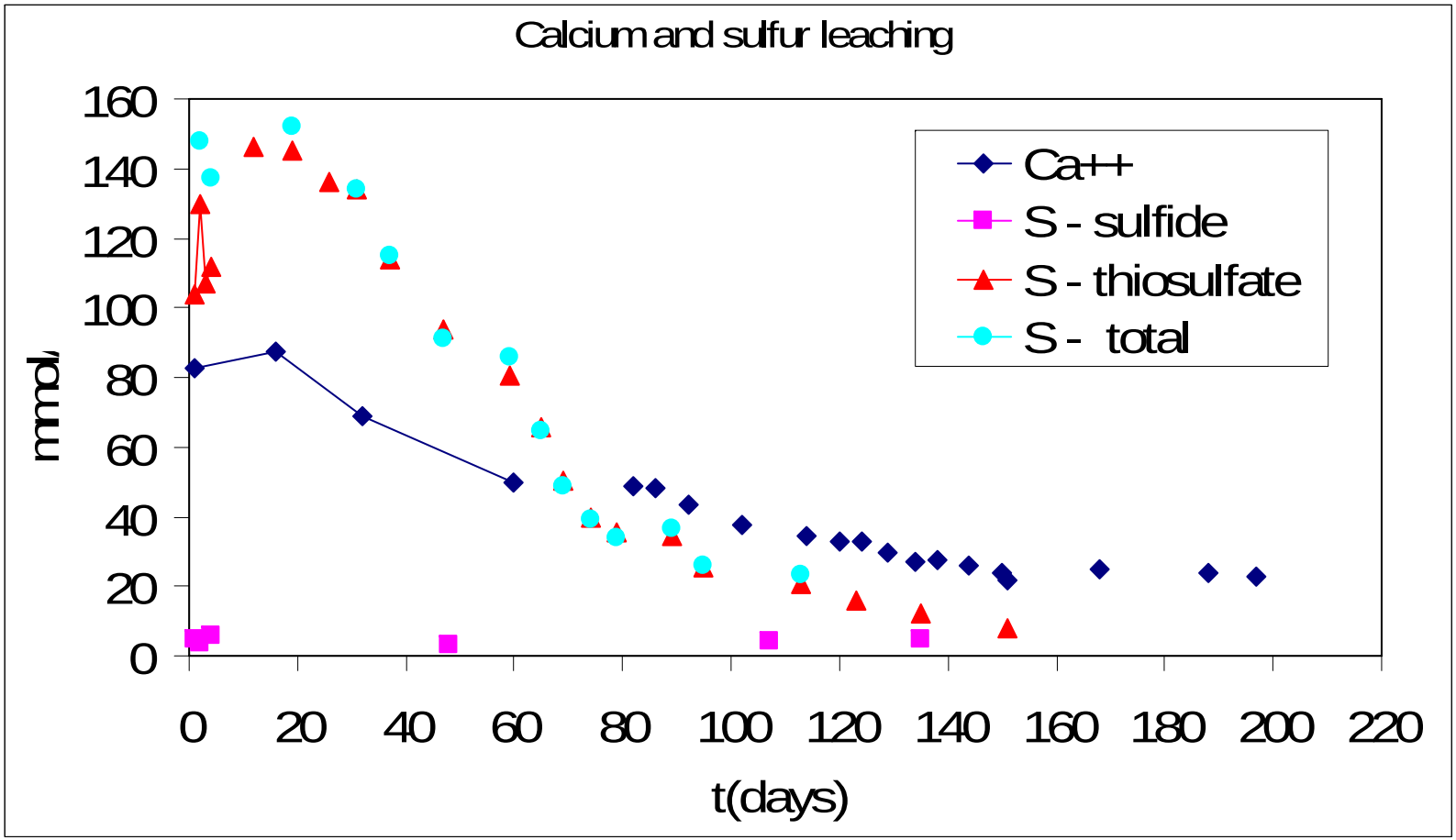
Oxidation of phenolics III



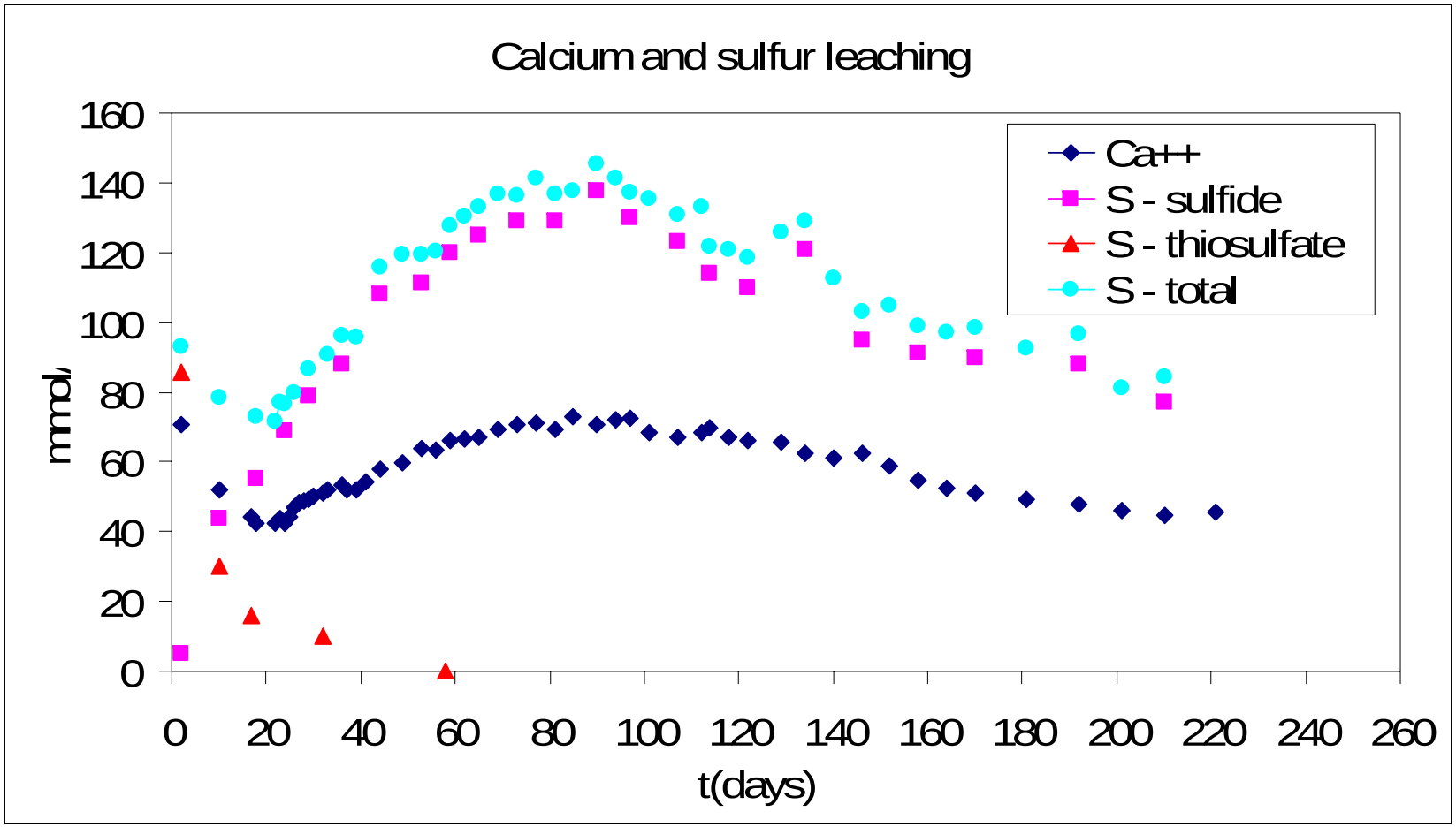
The reaction products shown are all stable intermediates

Leaching of sulfur species

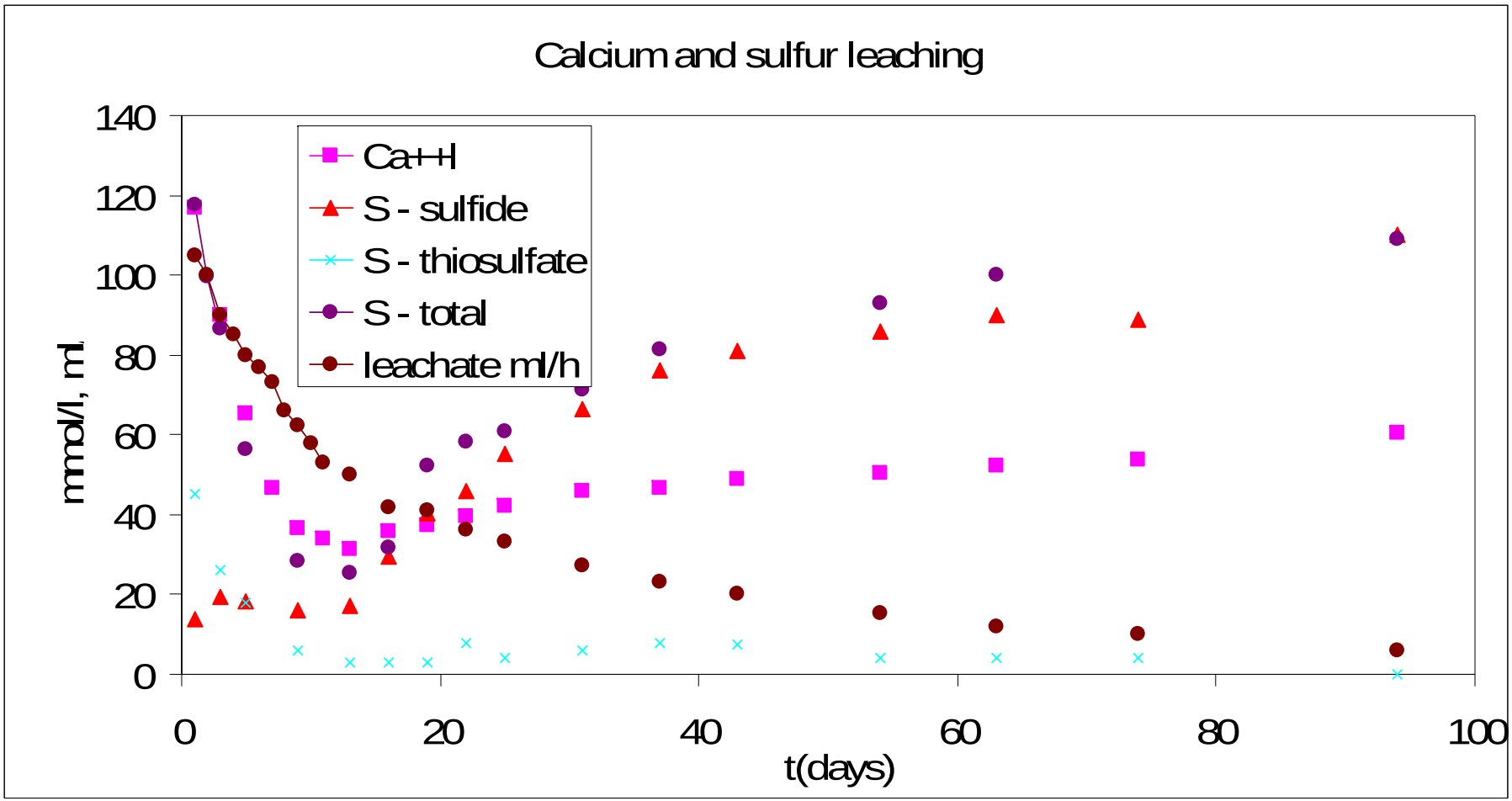
Total sulfur: 2…4%, sulfide sulfur 0,4…0,8%



Leaching of sulfur species II



Leaching of sulfur species III



Conclusions

A few words about sampling

No “new”extractable bituminous substances found

High TOC values do not reflect organic carbon

Phenols, if present, are oxidized

Sulfide leaching, hydrogen sulfide emission

High pH - possibilities of neutralization - P8

References

LEACHING BEHAVIOUR OF OIL SHALE SEMICOKE: COMPLIANCE WITH THE WASTE ACCEPTANCE CRITERIA FOR LANDFILLS Kaja Orupõld, Jaan Habicht, Toomas Tenno Oil Shale, accepted

LEACHING BEHAVIOUR OF OIL SHALE SEMICOKE: SULPHUR SPECIES SPECIATION Hedi Harzia, Kaja Orupõld, Jaan Habicht, Toomas Tenno, Oil Shale, accepted

Aknowledgements

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Thank you!

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