



Solid Wastes of Oil Shale Processing, Environmental Challenges of Disposal and Use

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Introduction I

Oil shale as a fossil fuel

- Huge resources worldwide
- Represent a viable energy alternative for several countries

Why the oil shale shale is not widely used?

- Low calorific value of oil shale that means high mineral content, 60-88%, and vast quantities of solid wastes.



Introduction II

- Geographical, economical and political aspects influence consumption of any fuel, including oil shale.
- As result of changing world, the position of oil shale in global scale at present is changed.
- There are both, economical and ecological needs to convert the enormous quantities of oil shale wastes into a resource.



Exploitation and use

Australia, Brazil, China, Germany, Israel, Russia, ...

... Estonia

- large deposits of commercial significance (since 1916)
- for producing oil (retorting 500-550 °C) and combustion for power generation



Energy generation in Estonia

by

- pulverized firing (PF) technology (from 1963)
- circulating fluidized bed (FBC) combustion (from 2004)

Total in Narva Elektriijaamad AS (www.powerplant.ee) 2380 MWe or 484 MWth

Ash dumps (Estonia)

230 Mt wastes

Alkaline water up to 5 Mm³

Surface area > 20 km², height up to 30-40 m



Spent shale deposits (Estonia)

70-80 Mt of wastes

up to 120 m height and ca 200 ha of land



Five sisters

Spent shale deposits in Scotland
(kindly provided by Dr. Kenneth G. Boyd)



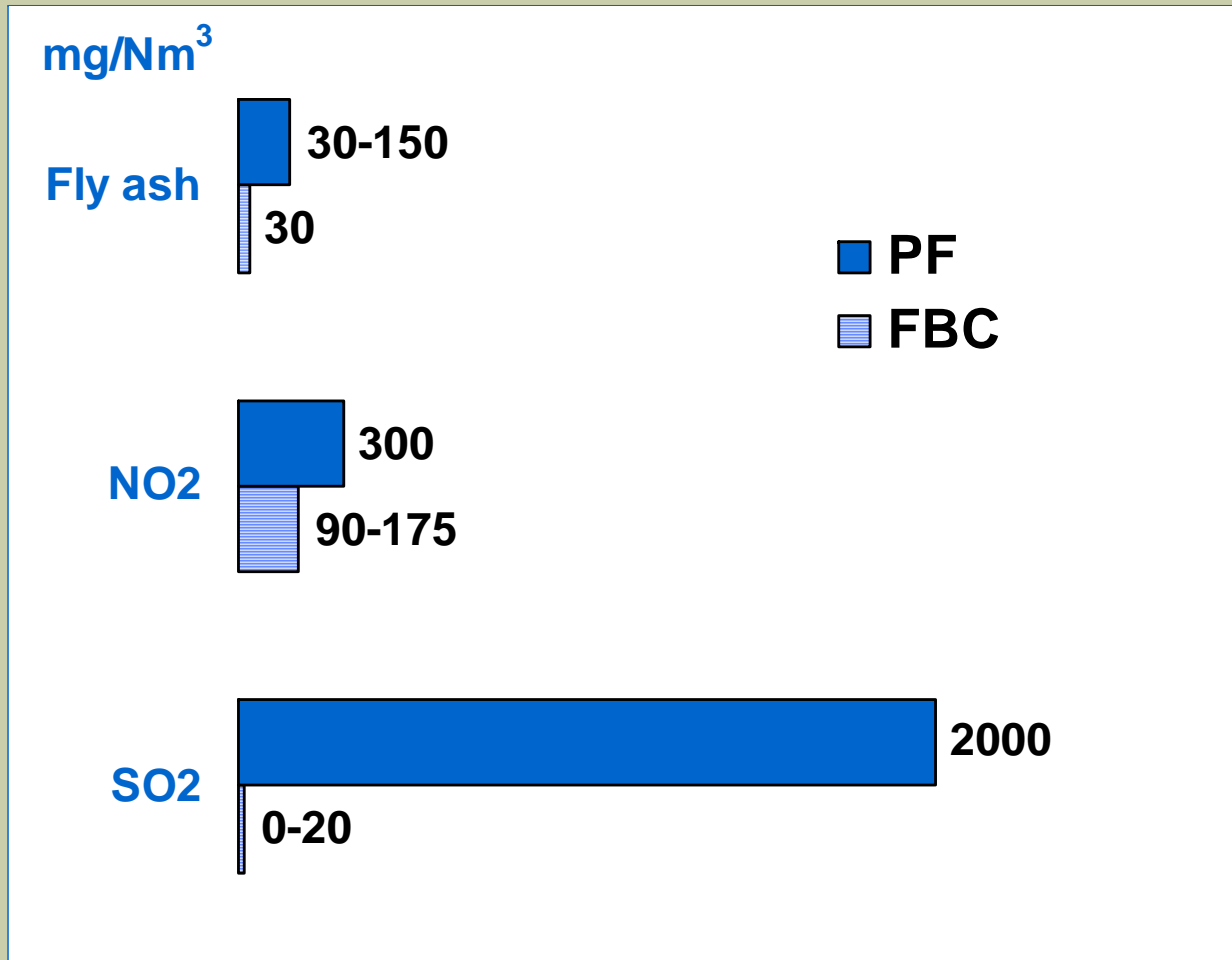


Aim and objectives:

Evaluation of environmental impact
based on practice of current oil shale
processing technology used in Estonia

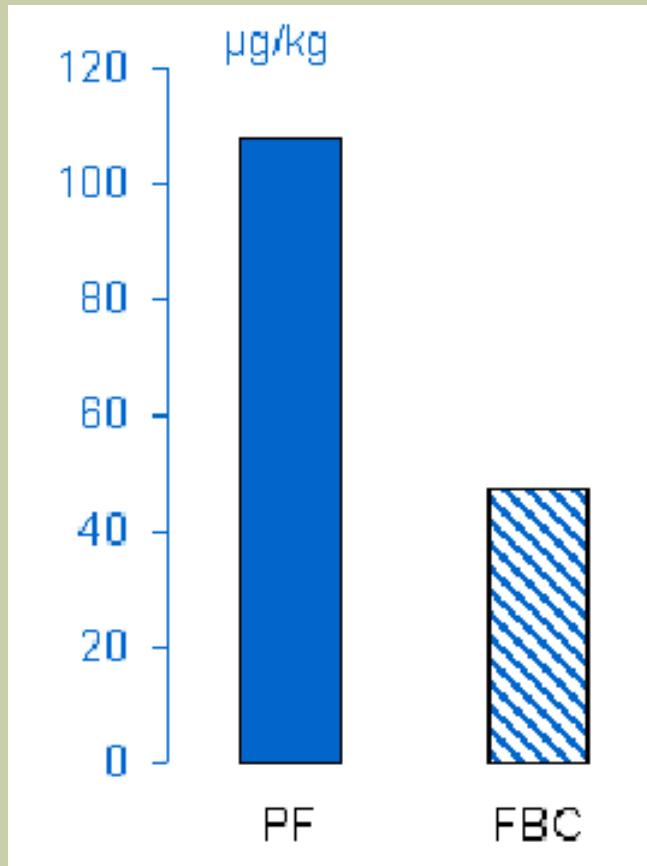
Atmospheric discharge of pollutants

FBC *vers* PF process

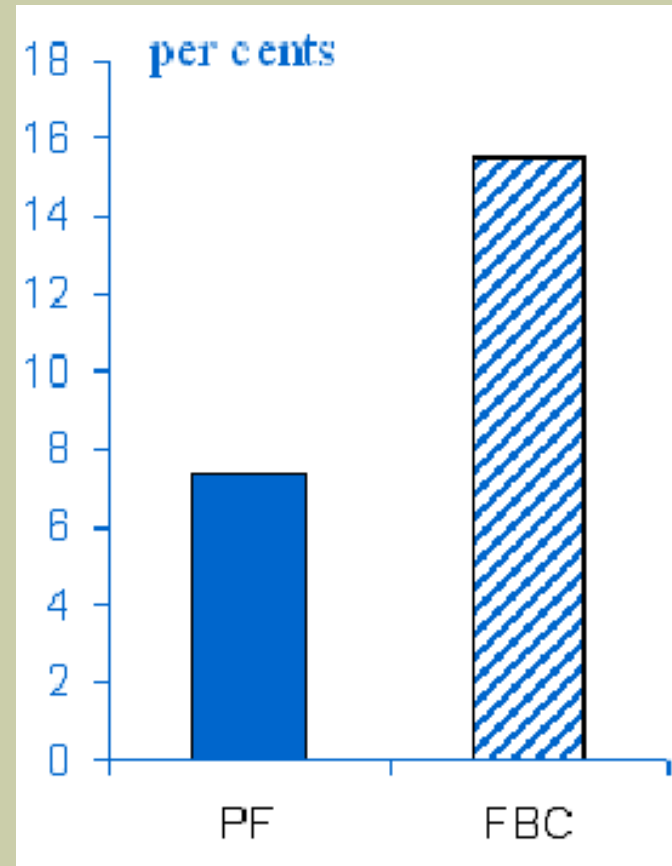


Mobility of PAHs (PF *vers* FBC)

Initial content



Mobile fraction



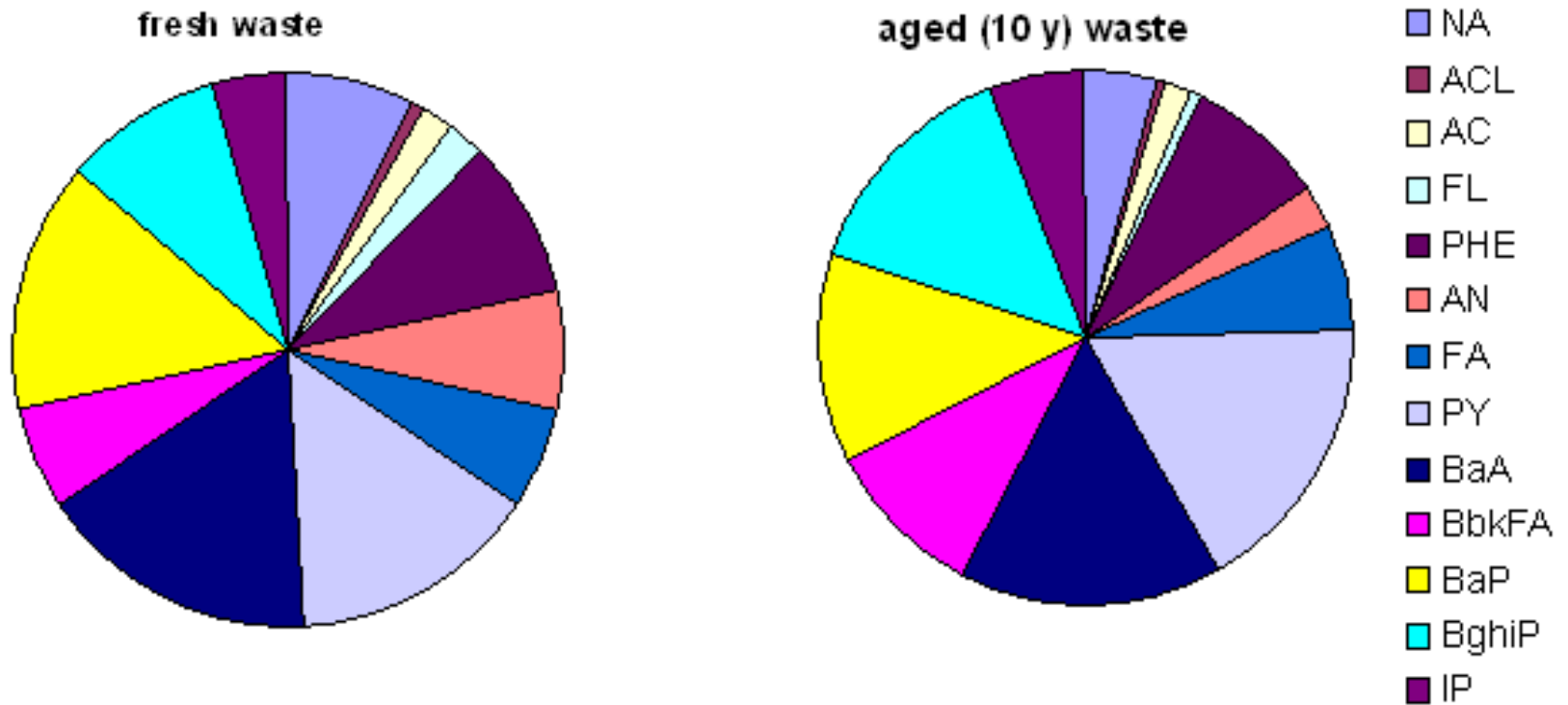


Quantification of toxic compounds in oil shale wastes

The content of toxic trace metals and PAHs was disclosed using ICP-MS and GC/MS in:

- Combustion ash and spent shale samples
- Laboratory and field leachates
- Post-leached solid samples
- Particulate matter of urban aerosols

Distribution of PAH in fresh and old wastes (spent shale)






Conclusions on Environmental impact

Deposition of solid wastes of oil shale processing could continuously generate environmental pollution from past to present

Any possible solution of the problem?

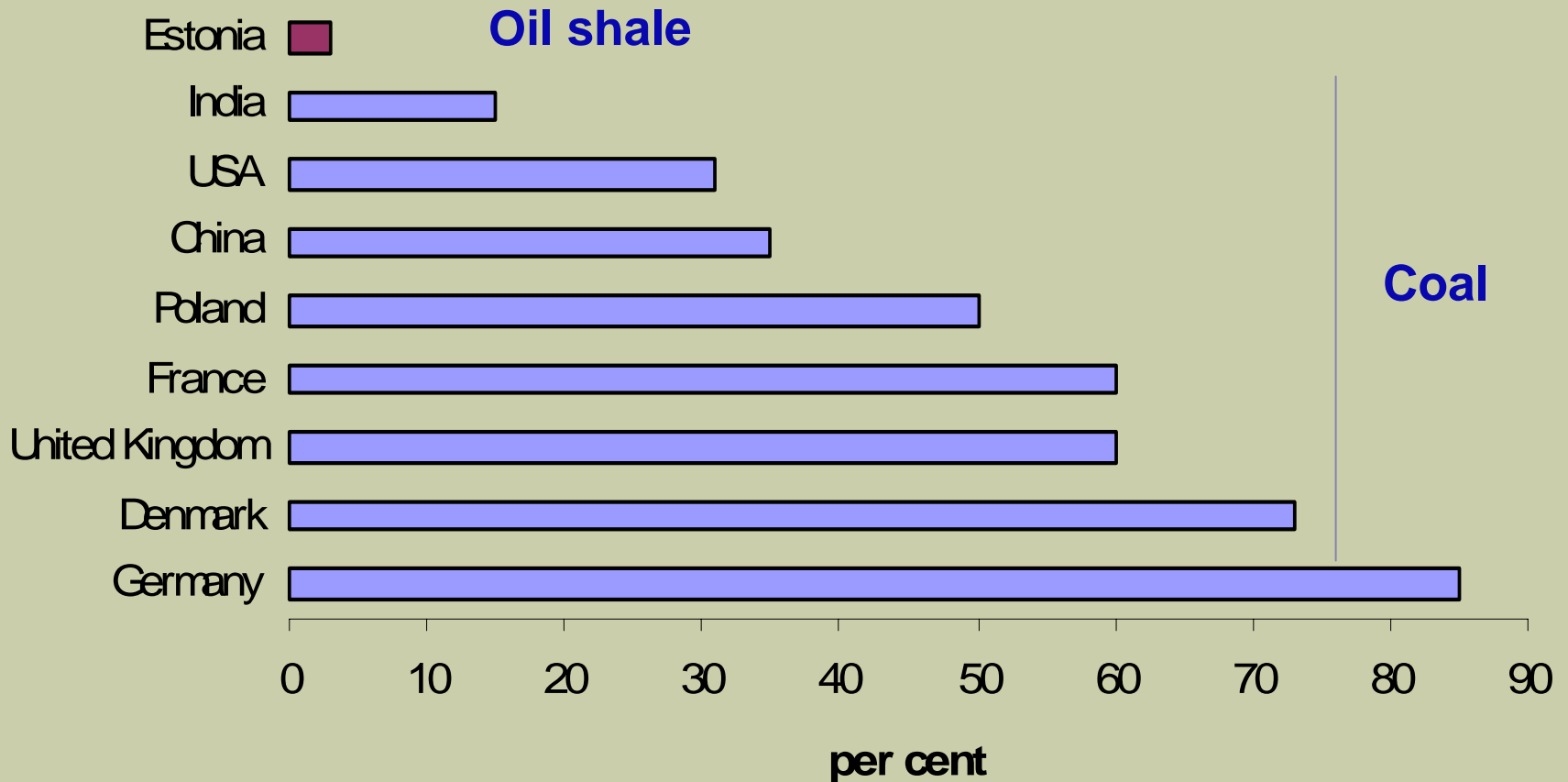



Solving of problems: commercial use of by-products

Overall utilization strategy

- Use of a larger quantity of ash in industry
- Find market applications - the quantity would not be large, but the price would be high
- Minimization of the waste disposal

Percentage ash utilization of the total ash generated in different countries





Promising R&D activity on recycling of oil shale wastes

Australia: spent shale as adsorbent (Zhu et al., 1988).

Brazil: spent shale as fertilizer (Mangrich et al., 2001), for synthesis of zeolites (Machado and Miotto, 2005), as an adsorbent (Pimentel et al., 2008).

China: oil shale ash in building materials (Jiang et al., 2007) for cement (Feng et al., 1997, 2007), for synthesis of silica nanoparticles (Gao et al., 2008).

Israel: oil shale ash in building materials (Bentur et al., 1981; Baum et al., 1985, 1986; Freidin, 1998, 1999, 2002, 2004).

Jordan: oil shale ash in building materials (Khedaywi et al., 1990), in Portland cement concrete (Smadi and Haddad, 2003; Al-Otoom, 2006), for synthesis of zeolites (Shawabkeh et al., 2004), as an adsorbent (Al-Qodah 2000; Al-Qodah et al., 2007).

Russia: oil shale ash in road building, in building materials, as lime fertilizer, in Portland cement (Strizhakova, Usova, 2007) in glass ceramics (Gorokhovskiy et al., 2002).

UK, Scotland: spent oil shale in road construction, in earthwork construction (Winter, 2001).

USA: spent oil shale in road construction materials (Kassim et al., 2005).



General strategy

- Critical evaluation of efforts on recycling of ash fractions from combustion of different types of coal ash.
- Selection of ash fractions from oil shale combustion using ASTM classification for coal fly ash utilization system (class F and C ash).
- Find the ASTM specification prototype that is closest to each shale ash fraction.



Aim and objectives

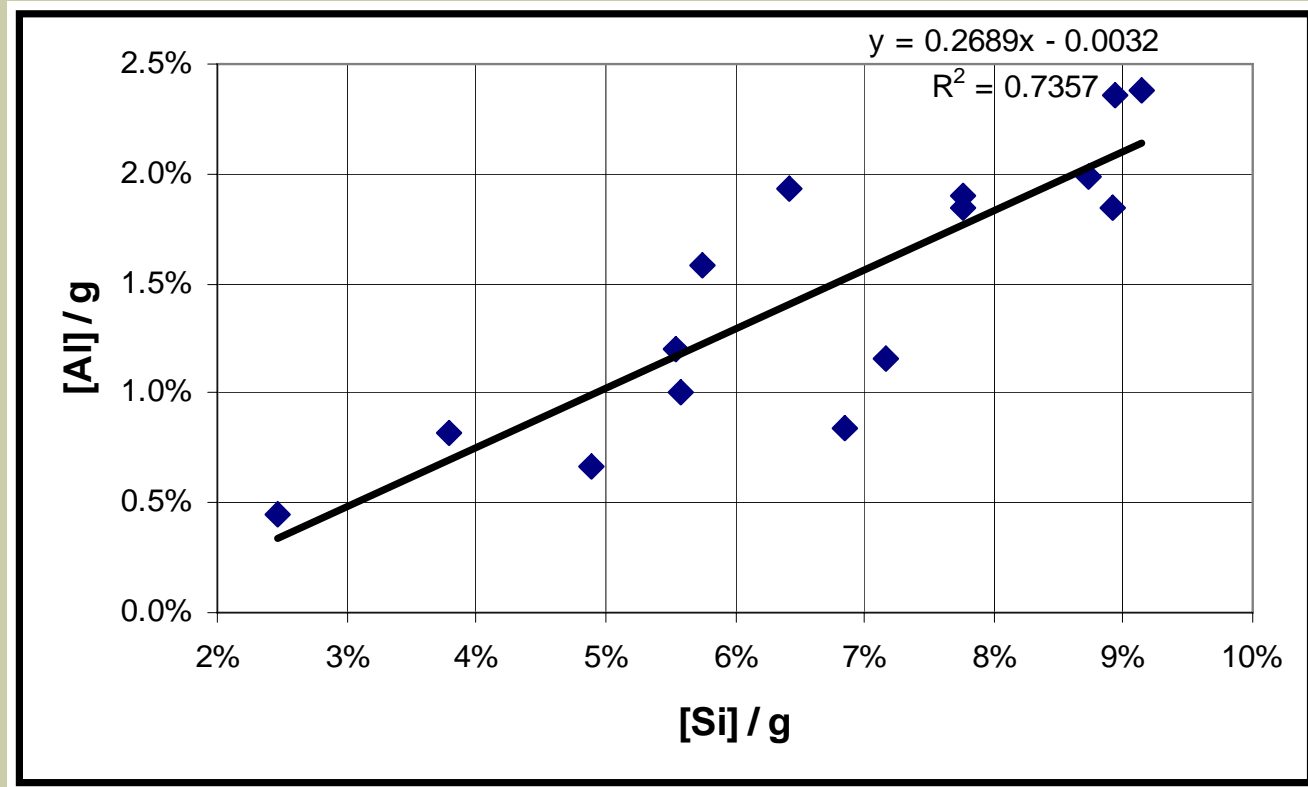
Disclose

- the chemical composition of each ash fraction
- the matrix characteristics of ash material

Find the most appropriate method for treatment the raw material

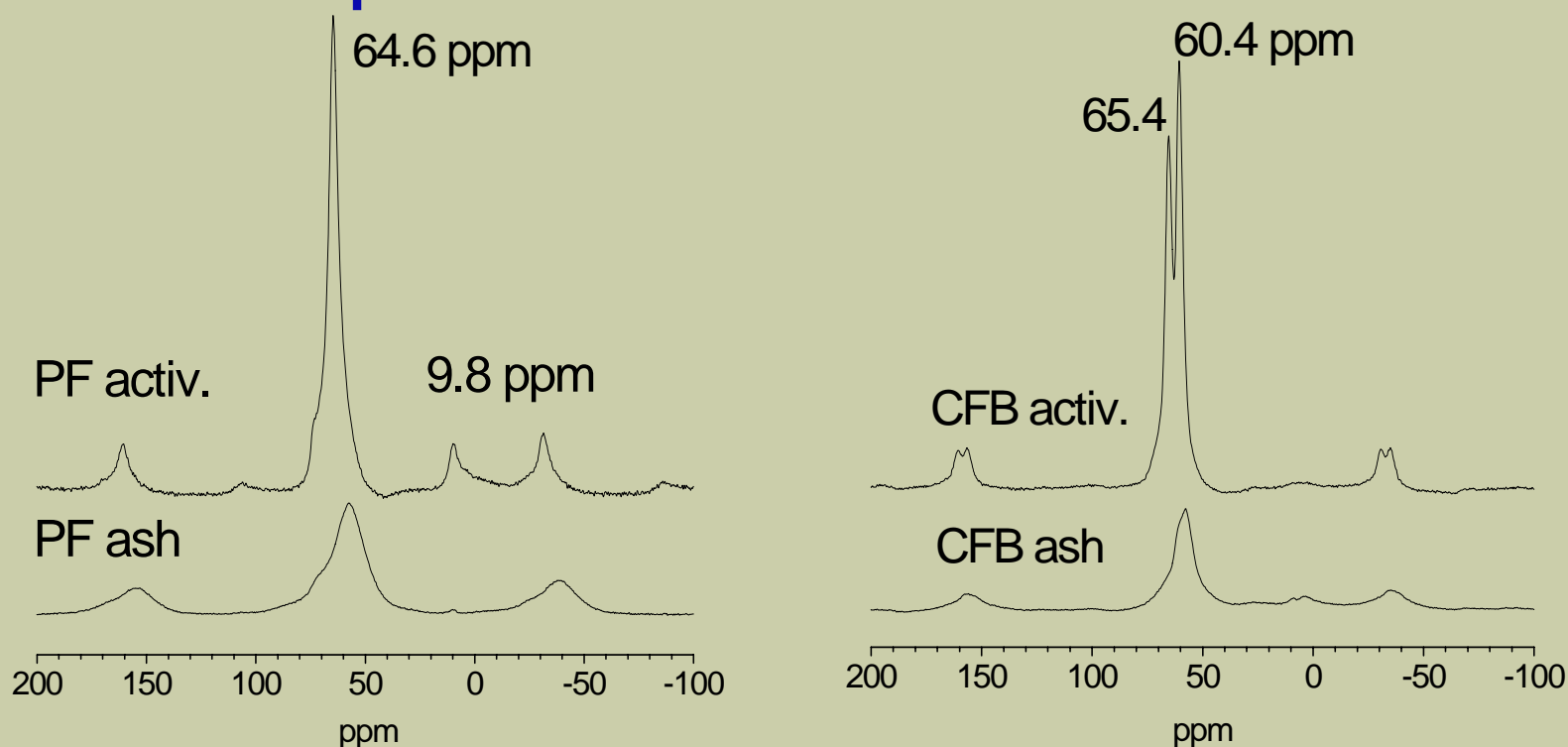
Test the new material obtained

Content of Si and Al in ash fractions



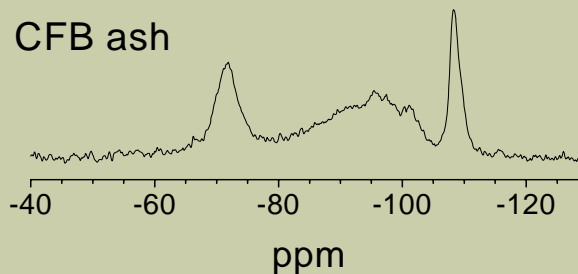
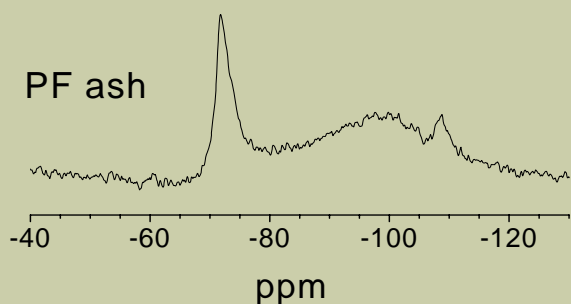
*I. Heinmaa, U. Kirso, T. Joon, J. Reinik, G. Karelson, E. Teinemaa:
Characterization of oil shale ash by solid-state ^{29}Si and ^{27}Al MAS NMR spectra*

^{27}Al MAS-NMR spectra of treated (top) and non-treated (bottom) ash samples from PF and CFB boilers

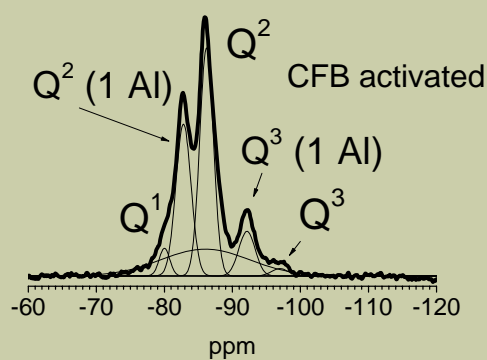
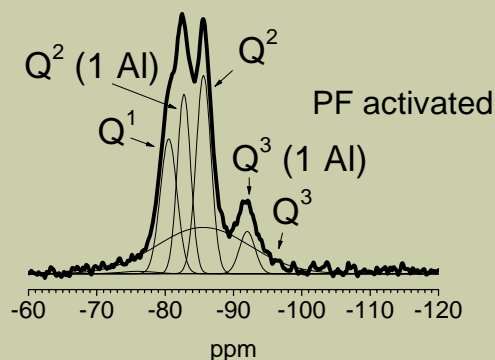


J. Reinik, I. Heinmaa, J.-P. Mikkola and U. Kirso (2007). Hydrothermal alkaline treatment of oil shale ash for synthesis of Tobermorites. Fuel, 86, 5-6, 669-676.

^{29}Si MAS-NMR spectra of treated and non-treated ash samples

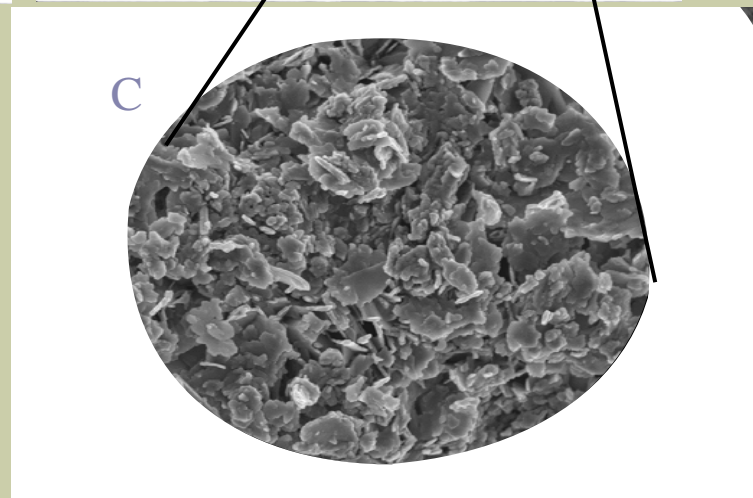
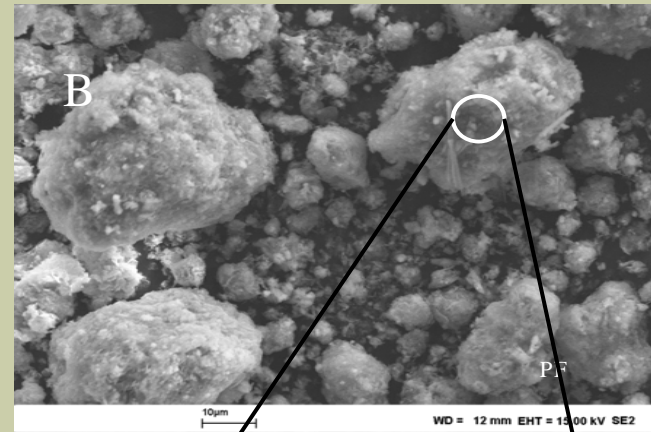
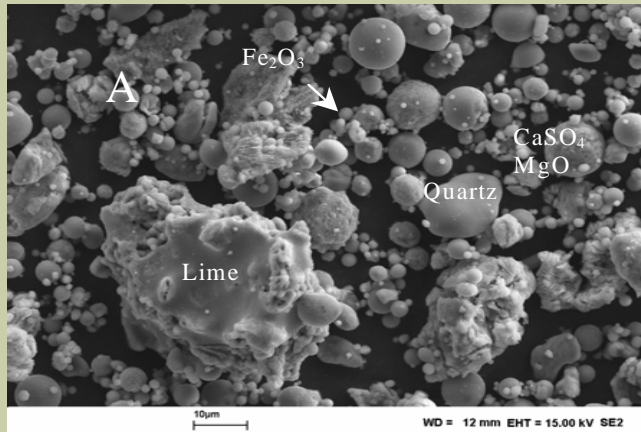


^{29}Si MAS-NMR spectra of non-treated ash from PF and CFB boilers



^{29}Si MAS NMR spectra of treated PF and CFB ash samples (deconvolution of the spectra by Gaussian lines)

SEM photos of non-treated (A) and treated (B,C) oil shale ash



J. Reinik, I. Heinmaa, J.P. Mikkola, U. Kirso (2008). Synthesis and characterization of calcium-alumino-silicate hydrates from oil shale ash – Towards industrial applications. Fuel 87, 1998-2003.



Conclusions

The strategy of any method for utilization of oil shale wastes should include pretreatment of material to eliminate hazardous ingredients or decrease their mobility.



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