Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

CO_2 Conversion

Reduction of CO_2 emissions by production of calcium carbonates from calcium silicates and steelmaking slags

Sebastian Teir[1], Sanni Eloneva[1], Carl-Johan Fogelholm[1],

Ron Zevenhoven[2]

[1]Helsinki University of Technology, [2]Åbo Akademi University, Finland

May 8-11, 2006 • Hilton Alexandria Mark Center • Alexandria, Virginia

---

Outline

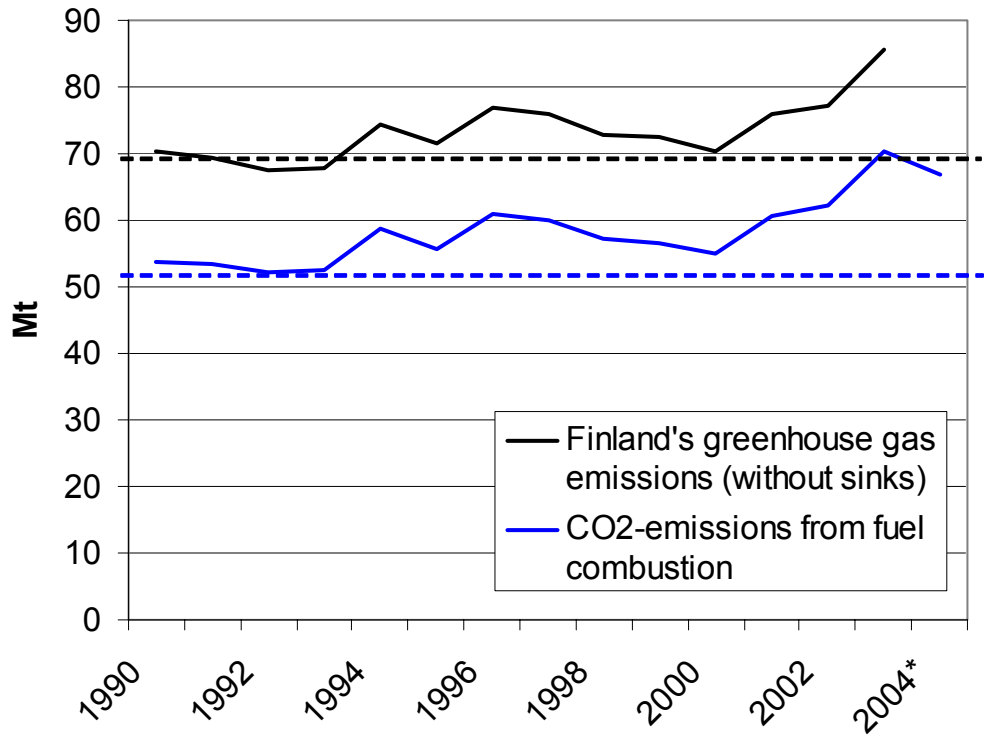
1. Introduction
2. Suitable raw materials and their CO_2 storage potential
3. Process alternatives
4. Thermodynamic calculations
5. Experiments

1. Mineral carbonation research in Finland

- Started in year 2000
- Helsinki University of Technology
  - Laboratory of Energy Engineering and Environmental Protection
- Åbo Akademi University
- Geological Survey of Finland
- Research funded by:
  - Nordic Energy Research
  - National Technology Agency of Finland
  - Rautaruukki
  - UPM
  - Wärtsilä
  - Finnish Recovery Boiler Committee

1. Greenhouse gas emissions in Finland

- Kyoto protocol: GHG reduction to the level of 1990 (70.5 Mt) during 2008 – 2012
  - Approximately 11 Mt per year (13 %)
- No geological reservoirs suitable for CO_2 storage
- Large deposits of natural silicate minerals



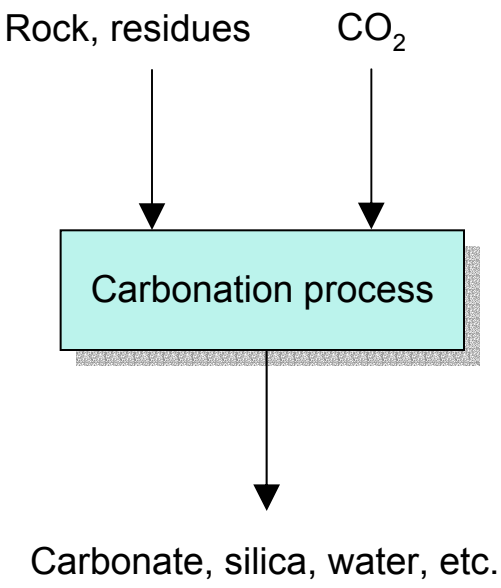
[Figures: Statistics of Finland, 2006]

1. CO_2 storage by production of carbonates

- Carbonation of Mg and Ca silicates is a potential CO_2 storage option by storing carbon dioxide (CO_2) as inert carbonates

  $MO + CO_2 \rightarrow MCO_3 + heat$

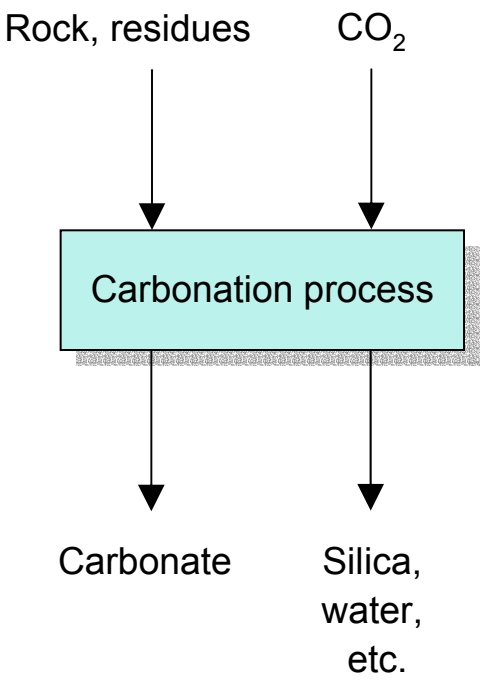
- Advantages: vast storage capacity and permanence
- Drawbacks: process costs
  - Carbonation kinetics
  - Energy and additives requirements
  - Pretreatment requirements
  - CO_2 and mineral requirements
    - Quality and amounts



[Figures: IPCC, 2001]

1. Objectives

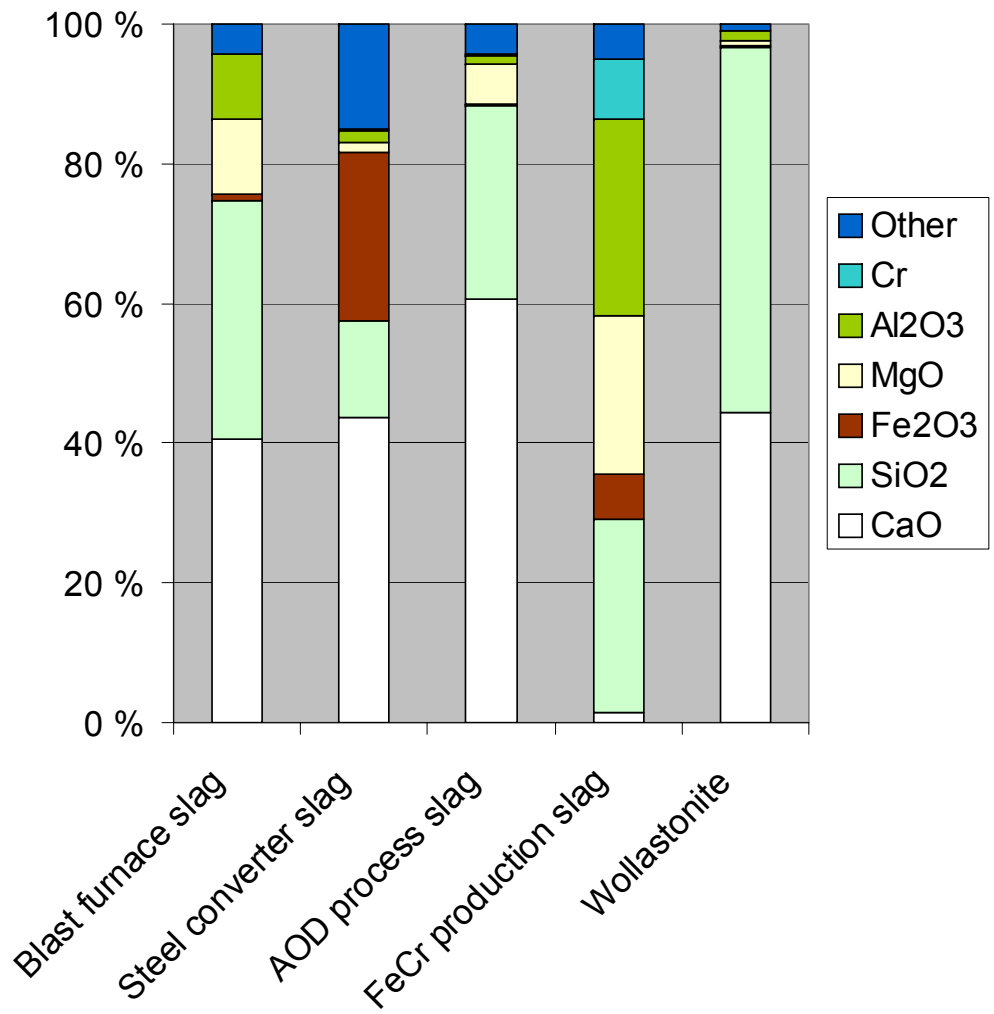
- Investigate and develop multi-step carbonation processes
  - Energy-efficiency
  - Integration with industrial processes / power generation
  - Pure carbonate production for industrial reuse
- Mapping of suitable calcium silicate minerals / calcium-rich residues for carbonation
  - Mainly Finnish resources
- Carbonation of magnesium silicates (see poster)



2. Suitable materials

- Natural calcium silicates
  - Wollastonite (mineral)
    - High CaO-content (44 %)
    - Rare and expensive (200 €/t)
  - Basalt (rock)
    - Low CaO-content 5 – 10 %
- Alkaline industrial by-products
  - Steelmaking slags
    - Readily available and cheap (< 10 €/t)
    - High CaO-content: 39 – 60 %
    - Many impurities
    - Limited but continuous availability
  - Other slags, process ashes and dusts

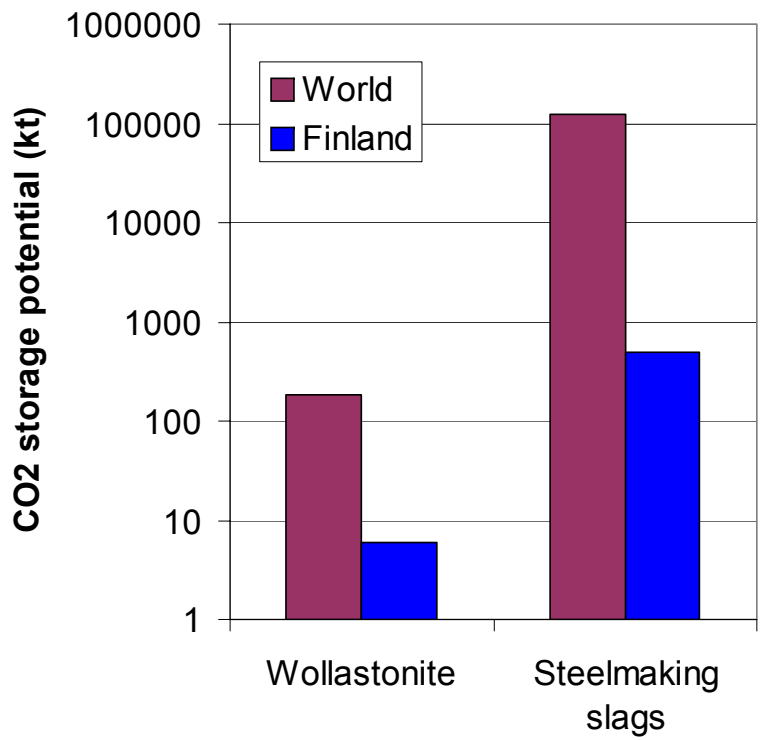
Example of composition of steelmaking slags and wollastonite



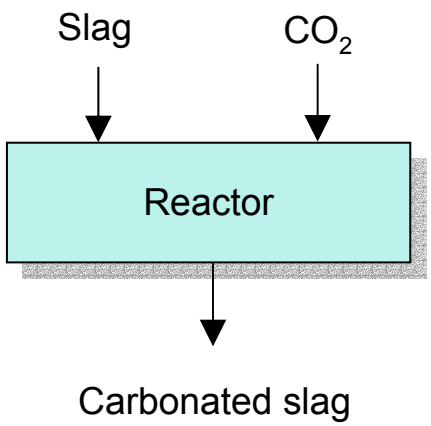
2. CO_2 storage potential by carbonation

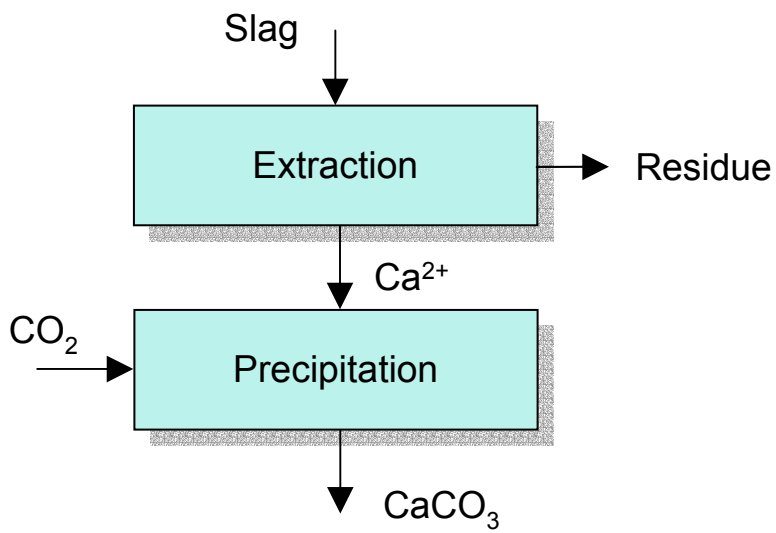
(based on current mineral/residue production numbers by USGS)

- CO_2 storage potential by (Mg and Ca) carbonation of steelmaking slags
  - World: 70 – 180 Mt CO_2 / year
    - 0.3 – 0.7 % of annual anthropogenic CO_2 emissions
  - Finland: 280 – 550 kt CO_2 / year
    - 2 – 21 % of factory specific CO_2 emissions
    - 3 – 5 % of Finland's Kyoto target
- End product may have industrial uses (if pure $CaCO_3$)



3. Process alternatives

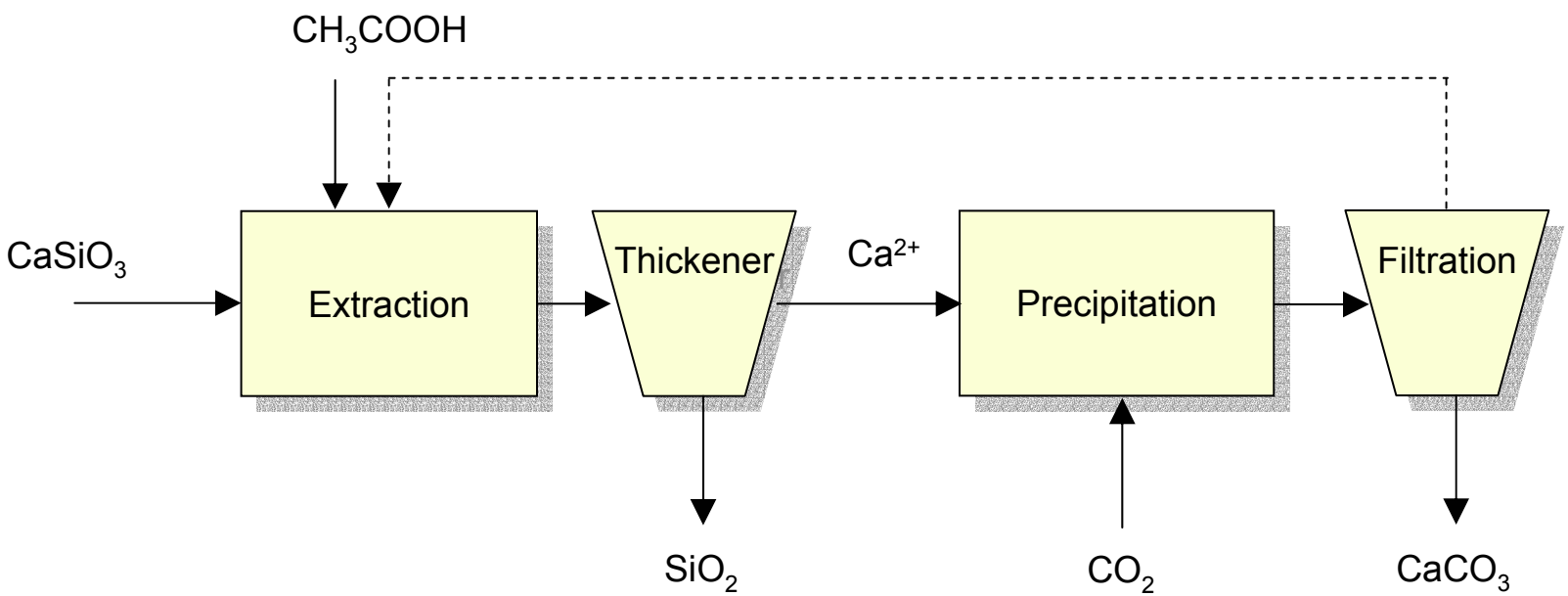




- Direct carbonation of Mg and Ca oxides/silicates in slag can stabilize the slag
- Extraction and precipitation processes can produce pure $CaCO_3$

3. Carbonation of steelmaking slags using acetic acid

- Carbonation process suggested by Kakizawa et al. (2001) studied for implementation with steelmaking slags
  - 50 % Ca extraction efficiency from wollastonite reported
  - 20 % Ca to $CaCO_3$ conversion reported using 30 bar CO_2 pressure

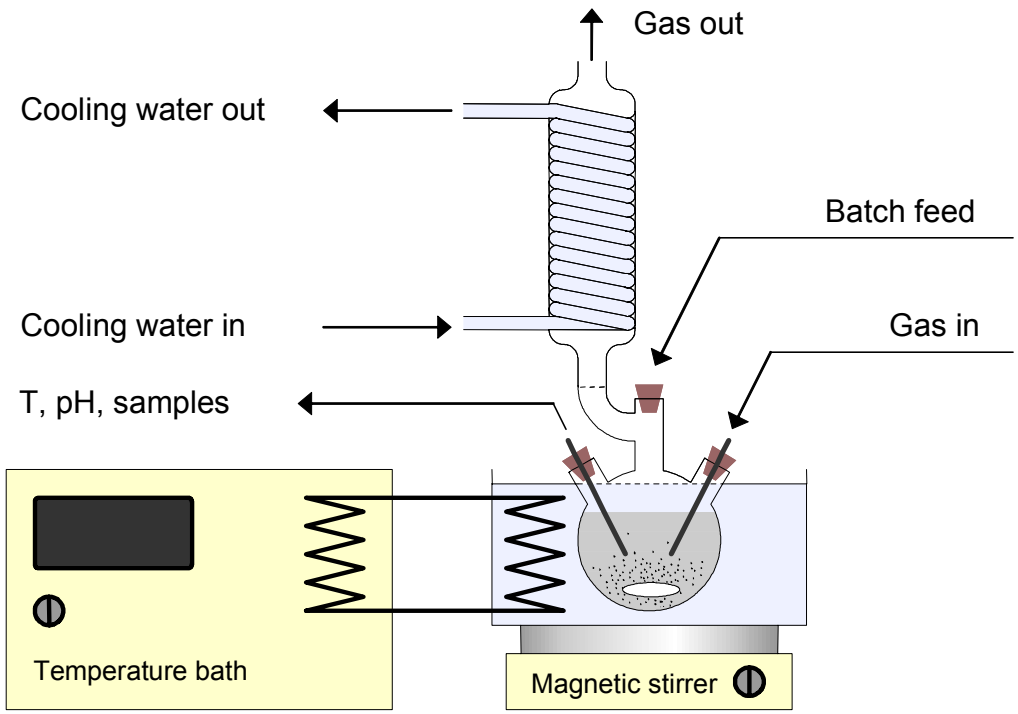


4. Thermodynamic equilibrium calculations

- Performed to determine if there are any thermodynamic restrictions for producing $CaCO_3$ from steelmaking slags using acetic acid
- Extraction of steelmaking slag
  - Input: main species of blast furnace slag
    - Al_2O_3, CaO, Fe, Mg, S, SiO_2, Ti
  - Result: total dissolution of elements regardless of temperature
    - Majority metal-acetate ions, eg. Calcium acetate
    - Minority free metal ions, eg. Ca^{2+}
- Carbonation of calcium-rich acetic acid solutions
  - Surplus of acetic acid prevent calcium carbonate formation
  - Pressurized CO_2 and higher alkalinity promote calcium carbonate formation

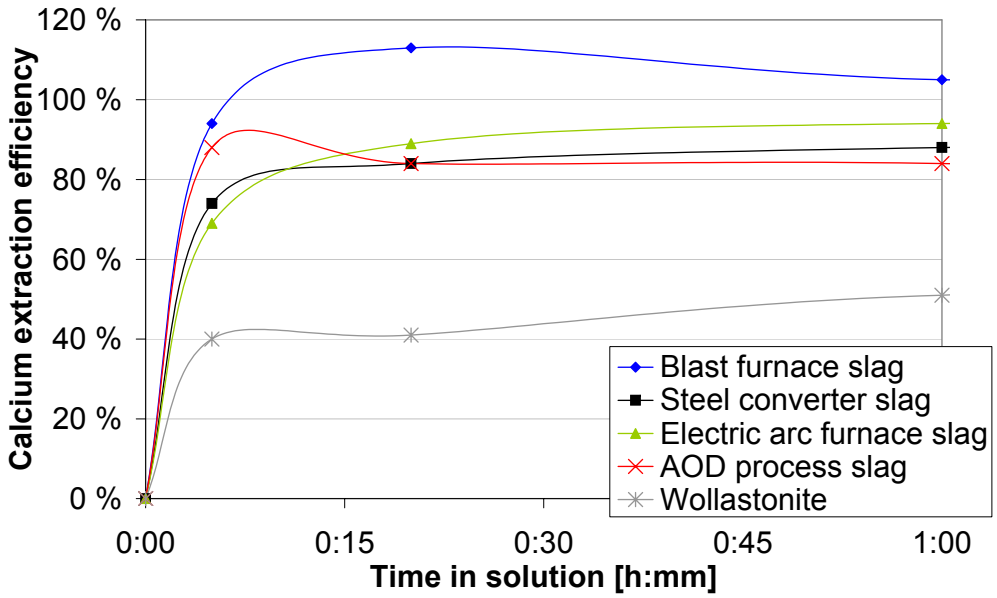
5. Experimental methods

- Experiments with extraction and precipitation performed
- Reactor volume: 250 – 500 ml
- Temperature: 30, 50, 70 °C
- N_2 or CO_2 flow 1 l/min, at 1 bar
- 4 - 50 g of material
  - Blast furnace slag
  - Steel converter slag
  - Argon-oxygen decarburization slag
  - Electric arc furnace slag
  - Wollastonite



5. Extraction experiment results

- Only partial extraction of calcium from wollastonite achieved
  - 51 % in 2 h
- Steelmaking slag dissolve relatively fast in acetic acid
  - Other elements dissolve as well (Mg, Si, Al, Fe etc.)
  - Si can be removed as a gel at 70 °C and 80 °C
  - Higher temperature causes faster dissolution
  - Lower temperature decreases acid requirements
    - ~3 ml CH_3COOH per g slag at 50 °C



5. Precipitation experiment results

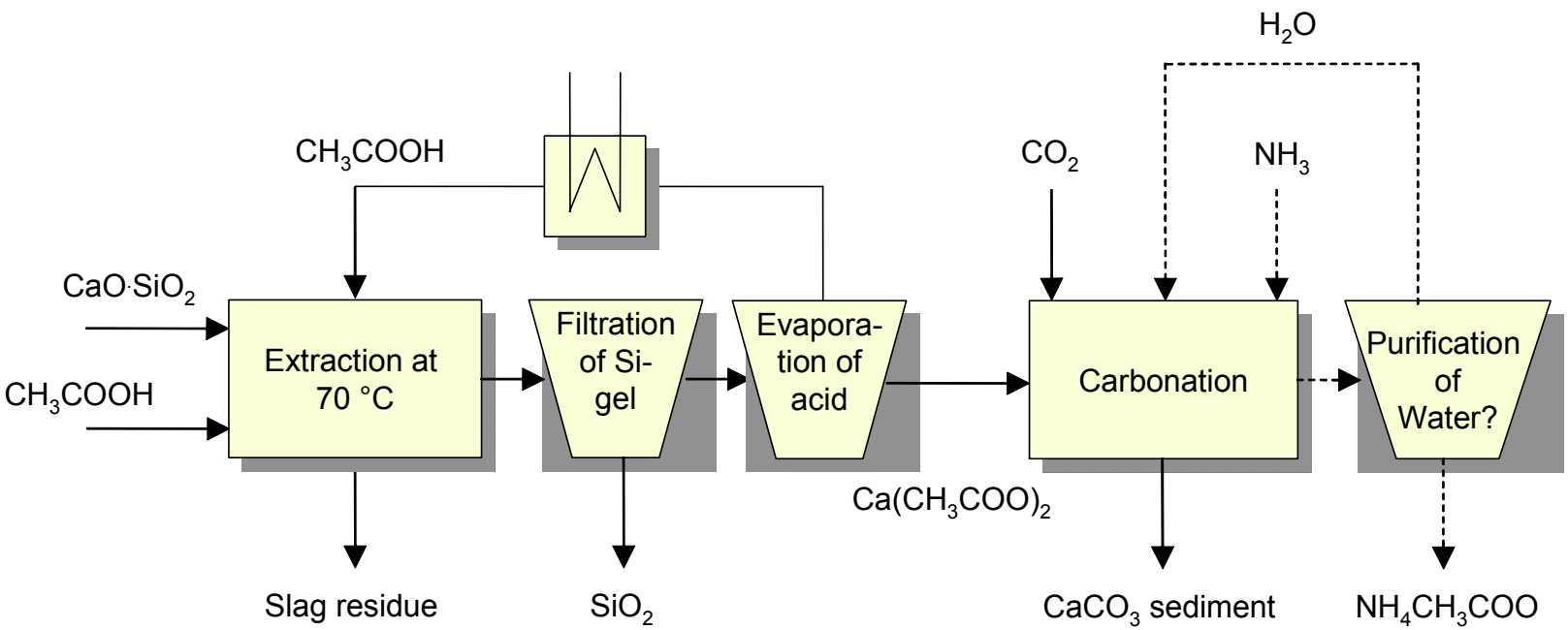
- Precipitation without pH regulation → 0.4 – 1.2 g / l in 4 h
  - Mostly magnesium acetate hydrate and calcium acetate hydrate
- Addition of NaOH for pH regulation resulted in 50 – 130 g / l in 15 min – 1 h
  - pH was raised from 4 to 11 – 12 by adding 85 g NaOH / l
  - $CaCO_3$ precipitated (~50 % calcite, vaterite and antigorite)
  - Contamination of sodium acetate, calcium aluminate and other carbonates of magnesium and calcium

→ Acetic acid prevents precipitation of calcium carbonate

→ Neutralization of acid by NaOH too expensive for a continuous process

Future work

- Precipitation of carbonates from acid – slag solutions
  - Pressurized precipitation of calcium carbonates
  - Precipitation by raised alkalinity
- Investigation of Ca-selective solutions for leaching Ca from slags



Conclusions

- Carbonation of calcium silicate-rich materials allows for simultaneous reduction of CO_2 emissions and refining of industrial by-products
- World potential of CO_2 reduction by steelmaking slag carbonation 70 – 180 Mt CO_2 / year
- Although slags are more reactive than natural silicate minerals, the carbonation process using acetic acid require still development to be economically feasible
  - Steelmaking slags dissolve faster than wollastonite in acetic acid, but require separation of unwanted elements
  - Precipitation of calcium carbonate from solutions of slag and acetic acid requires neutralization of acid
  - The economics of the process mainly depend on acetic acid recovery
- More information and publications: http://eny.tkk.fi/noco2