Aalto University
School of Science
and Technology

Carbon dioxide sequestration using steelmaking slags as raw material

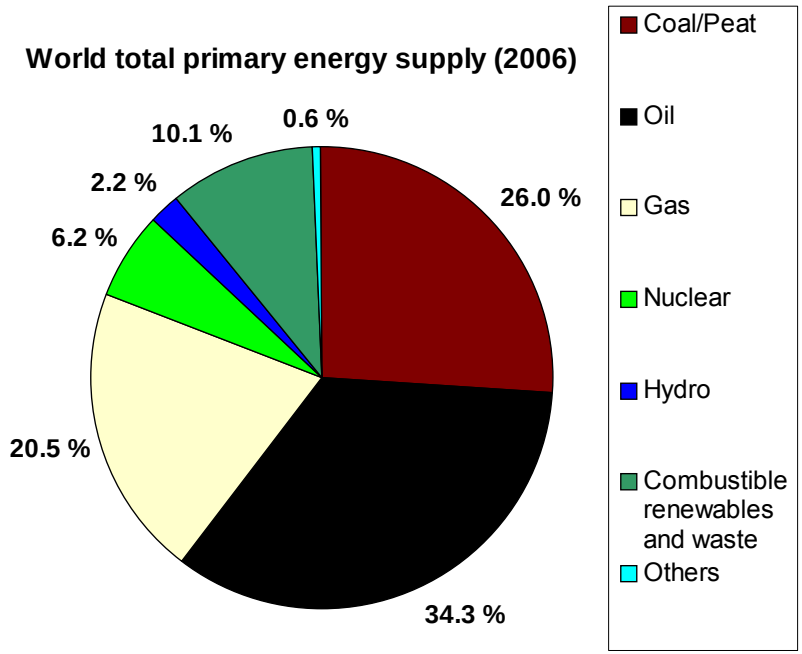
Lic. Sc. (Tech.) Sanni Eloneva

Research group of energy engineering and environmental protection,
Department of Energy Technology, Aalto University School of Science
and Technology

Nordic Recycling Day V, 3-4.2.2010

Means for reducing CO_2 emissions

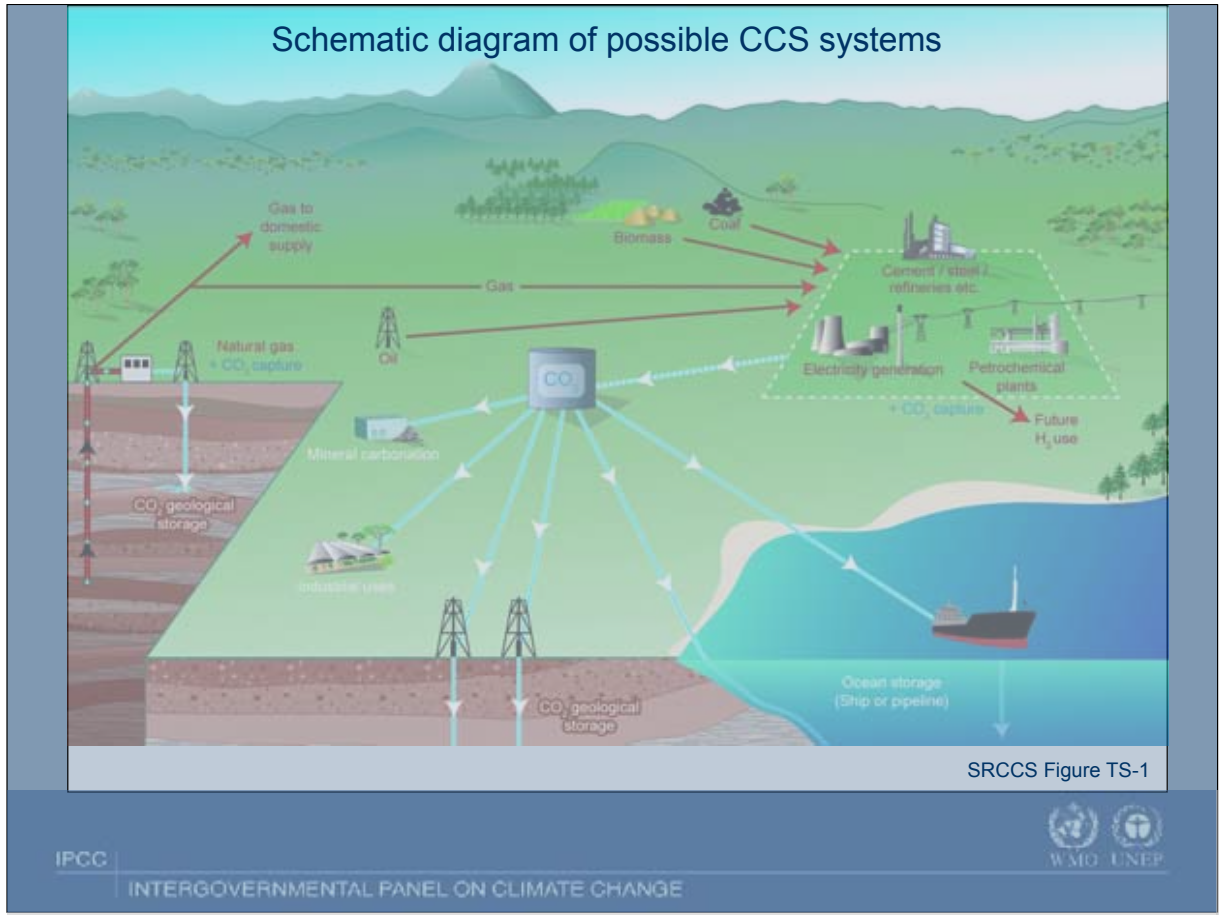
- Reduce utilization of fossil fuels
  - Replace fossil fuels by nuclear power or renewable energy
  - Switch from coal to natural gas
  - Reduce energy consumption
    - Increase energy efficiency
- Reforestation
- Carbon dioxide capture and storage (CCS)



IEA, 2008. Key world energy statistics.

CO_2 Capture and Storage (CCS)

- Capture
  - Concentrated CO_2 stream
  - From a large point source
- & Transport
  - Ship or pipeline
- & Storage
  - Geological formations
  - Ocean
  - Mineral carbonation



IPCC Special Report on Carbon Dioxide Capture and Storage, 2005. (http://www.ipcc.ch/publications_and_data/publications_and_data_reports_carbon_dioxide_graphics.htm)

Mineral carbonation for CO_2 emissions reduction

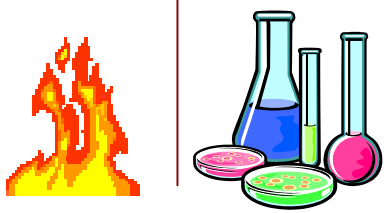
$$(Mg,Ca)_xSi_yO_{x+2y+z}H_{2z}(s)+xCO_2(g)\rightarrow$$

$$x(Mg,Ca)CO_3(s)+ySiO_2(s)+zH_2O$$

Silicate mineral: rock, industrial waste material…

CO_2

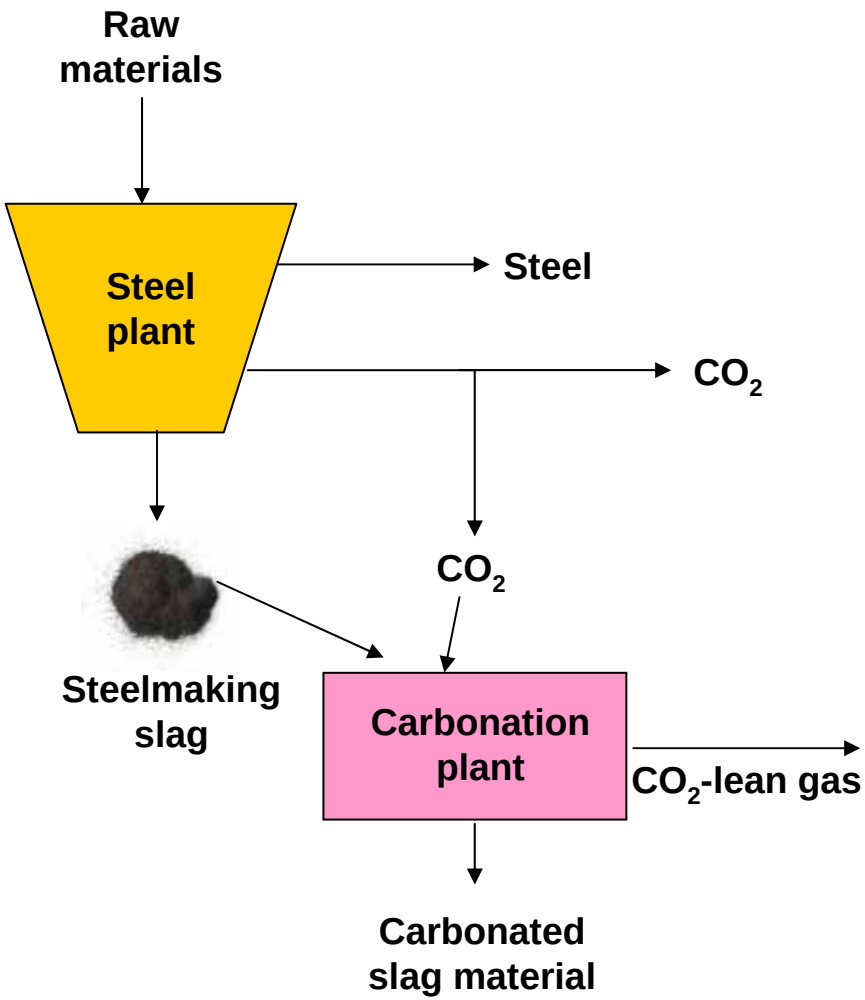
Carbonation process



Energy, chemicals

Carbonate, silica, water, etc.

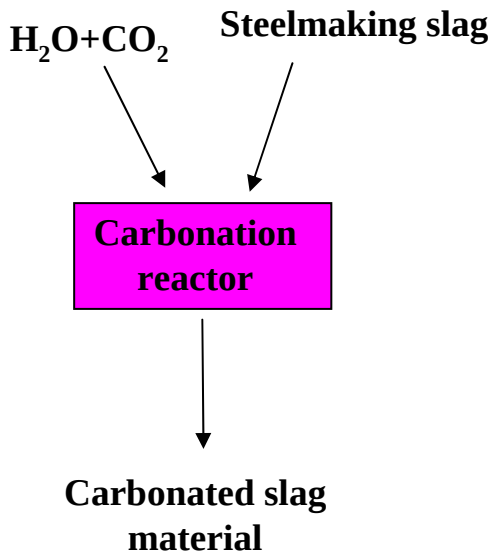
Steelmaking slag carbonation



- World's annual steelmaking slag generation: 220-420 Mt
- CO_2 sequestration potential: 70-130 Mt CO_2/a
- Other Ca/Mg-containing by products/waste materials suitable for CO_2 sequestration by carbonation:
  - Waste cement
  - Ashes
- Finland:
  - Annual CO_2 emissions: 66 000 kt
  - 1 450 kt/a steelmaking slags
  - Sequestration potential: 700 kt CO_2/a
  - Other by products: + 900 ktCO_2/a

Direct aqueous carbonation of steelmaking slags

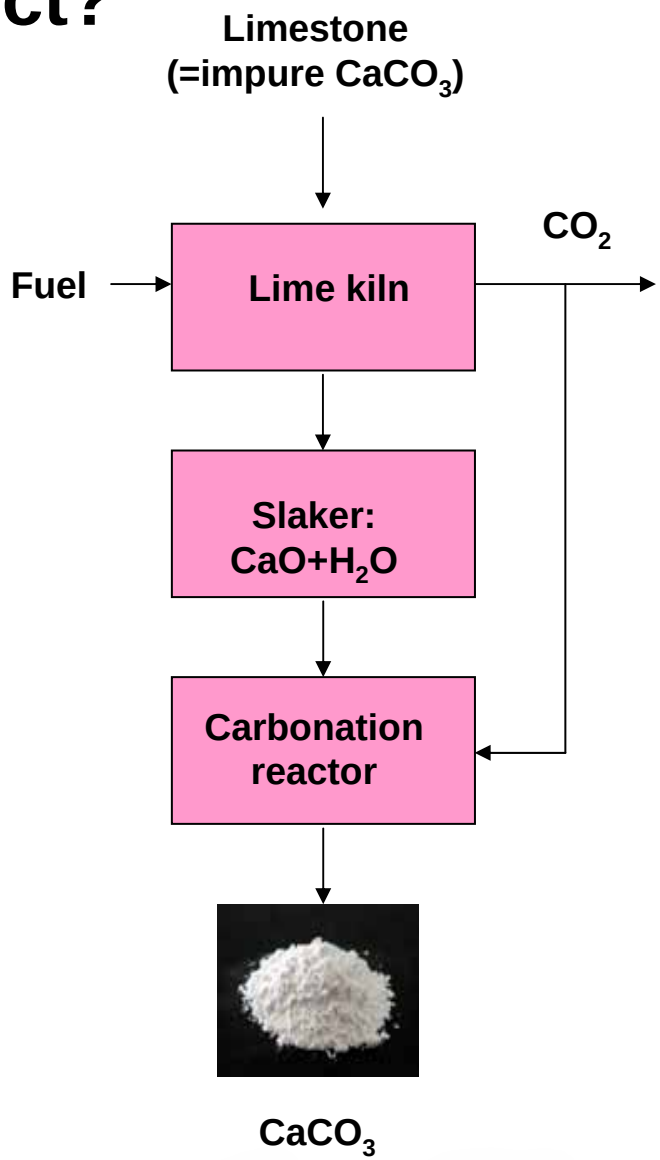
- Imitates and tries to enhance the slow natural carbonation of ultramafic rocks
- Carbonic acid extracts calcium from the slag
  - $CO_2(g)+H_2O(l)\rightarrow H^+(aq)+HCO_3^-(aq)$
  - $CaSiO_3(s)+2\ H^+(aq) \rightarrow Ca^{2+}(aq)+SiO_2(s)+\ H_2O(l)$
- Dissolved calcium reacts with bicarbonate ions forming solid carbonate
  - $Ca^{2+}(aq)+2HCO_3^-(aq) \rightarrow CaCO_3(s)+\ 2\ H^+(aq)$
- Elevated pressures and temperatures
- The maximum carbonation degree of steel slag: 74% of the Ca content (30 min, 19 bar CO_2 pressure, 100 °C, <38 µm) by Huijgen et al.(2005)



Huijgen W. J. J., Witkamp G.-J., Comans R. J., 2005. Mineral CO2 Sequestration by Steel Slag Carbonation. Environ. Sci. Technol., 39,9676-9682

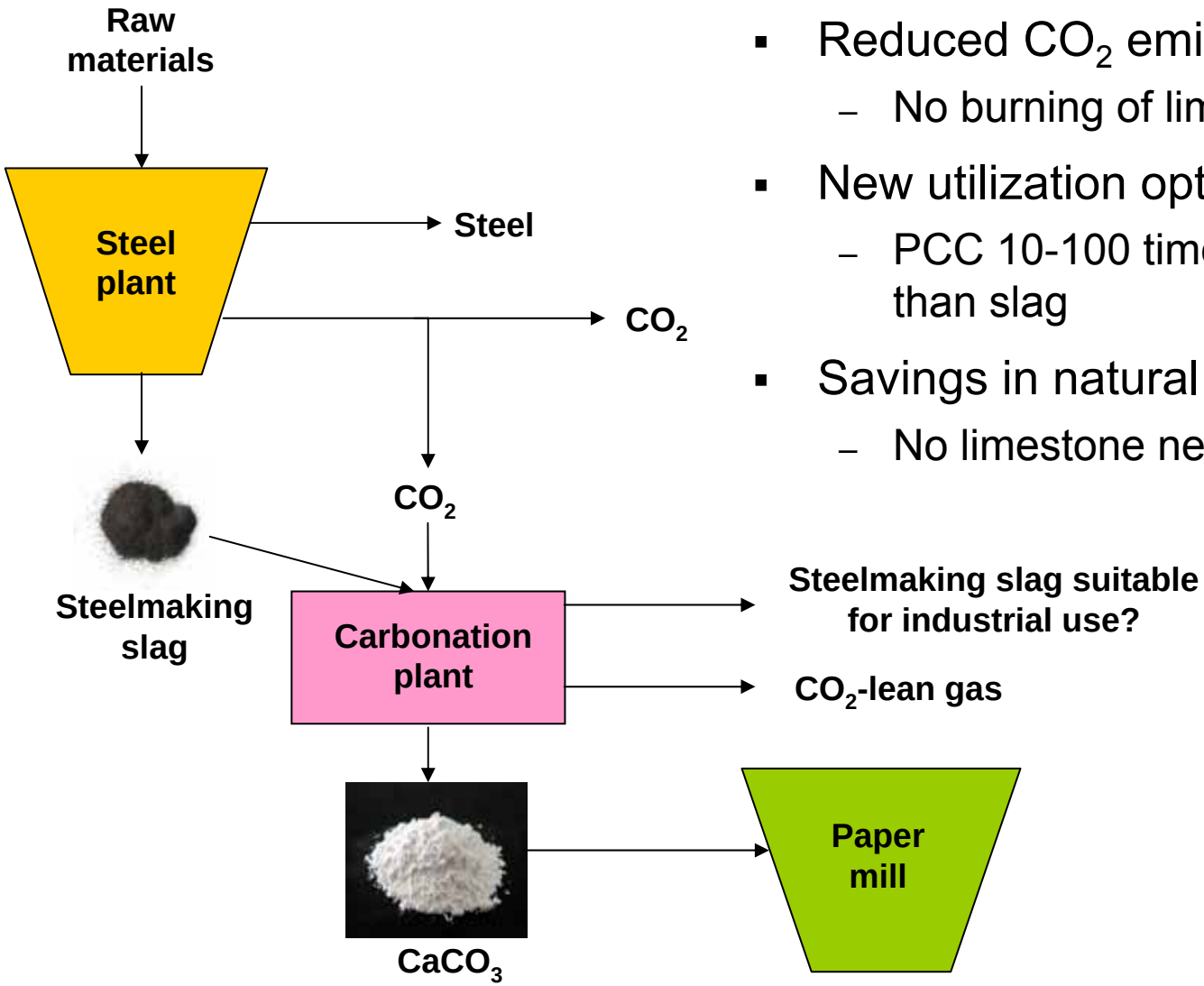
Valuable end product?

- If the calcium is separated from the slag material prior carbonation, the end product should be calcium carbonate ($CaCO_3$)
- $CaCO_3$ is used in various applications
  - Cement manufacture, agricultural use, lime manufacture...
  - Billions of tons mined annually
    - ~1 Gt/a in U.S. alone
    - 1.5 Mt mined annually in Finland
- Pure precipitated calcium carbonate (PCC)
  - >100 €/t
  - Filler and coating material in paper
  - ~13 Mt/a in the world
  - Manufactured from the limestone
    - CO_2 emissions of 0.23 t/t $CaCO_3$



Conventional PCC production process

Advantages of producing PCC from slags

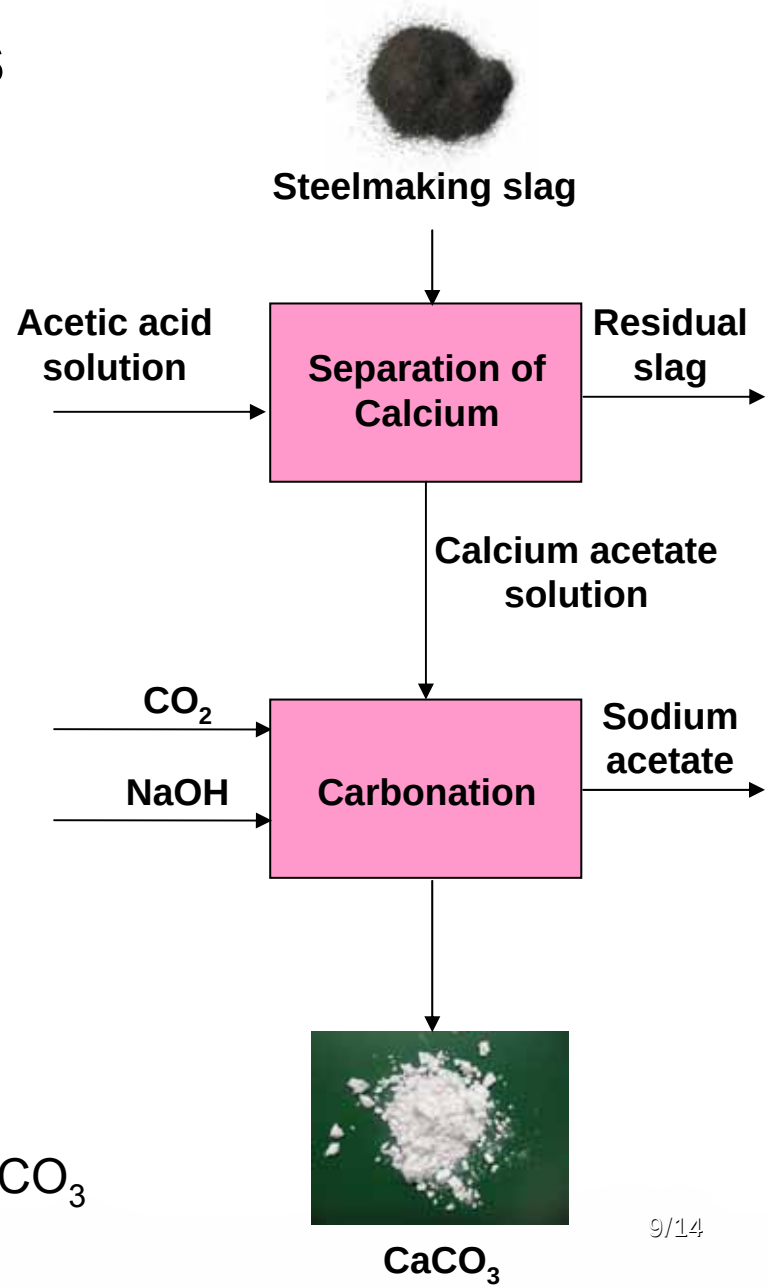


- Reduced CO_2 emissions
  - No burning of limestone
- New utilization option for slags
  - PCC 10-100 times more valuable than slag
- Savings in natural resources
  - No limestone needed

Acetic acid process route and steelmaking slags

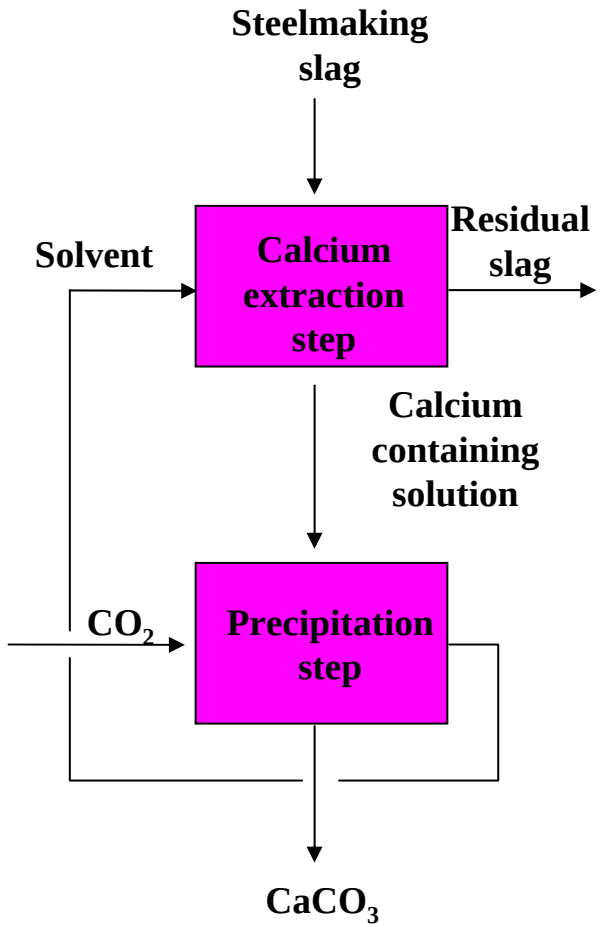
- 440 kg CO_2 reduction per ton of $CaCO_3$ produced
  - Additional 220 kg CO_2 per every conventionally produced PCC replaced
- However, indirect CO_2 emissions from the production of the chemicals used in the process, would most likely exceed these reductions
- The costs of the chemical consumption: > 1000 €/t of $CaCO_3$ produced

$$Ca(CH_3COO)_2+H_2O+CO_2 \rightarrow 2CH_3COOH+CaCO_3$$



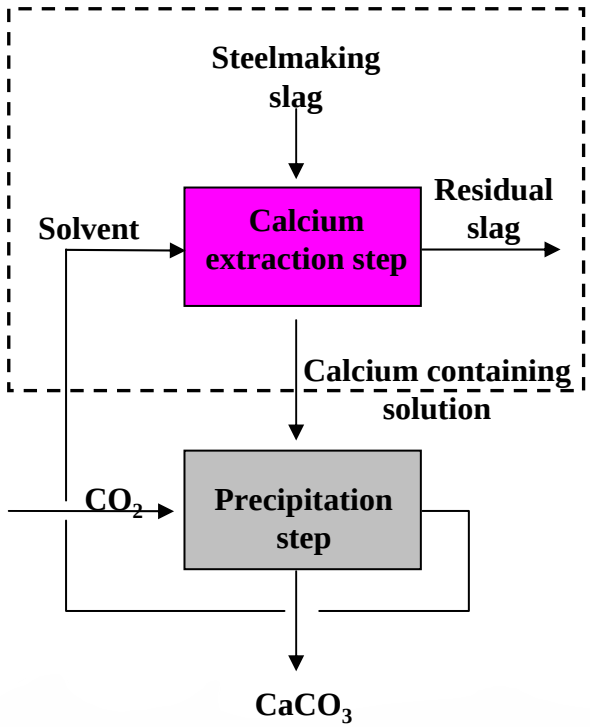
Search for the better solvent:

- Key issue for developing a feasible process for producing pure calcium carbonate from steelmaking slags:
  - To find an effective Ca-selective solvent that at the same time can be fully recovered and reused
- This means that:
  1. Solvent should dissolve calcium selectively from the slag
  2. Calcium carbonate should precipitate from the formed solution without need for additives



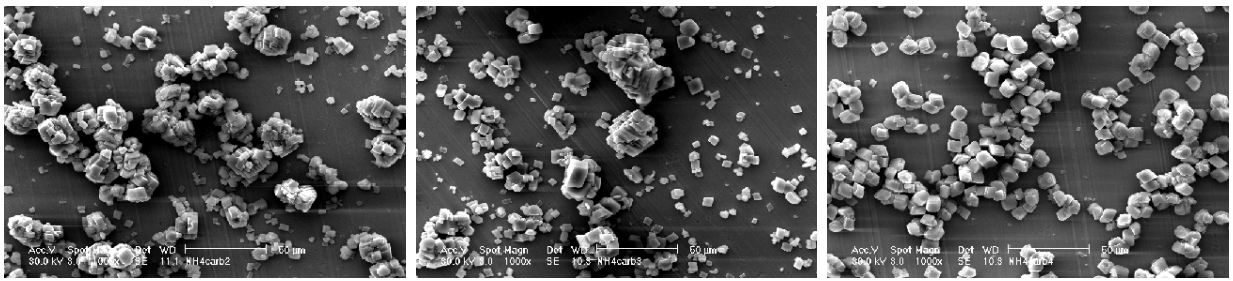
Step 1: Solvent selection

- Solvent selection using various relatively common acids and salts, as well as few other solvents
- Significant amount of the slag's Ca (>50 %) dissolved only in various acids and ammonium salts
- All the ammonium salt solutions dissolved Ca selectively from the slag
  - Also weak concentrations of acetic acid and nitric acid were selective for Ca
- Acids not suitable for precipitation of calcium carbonate → Ammonium salts seem to be the most promising solvents from the tested ones

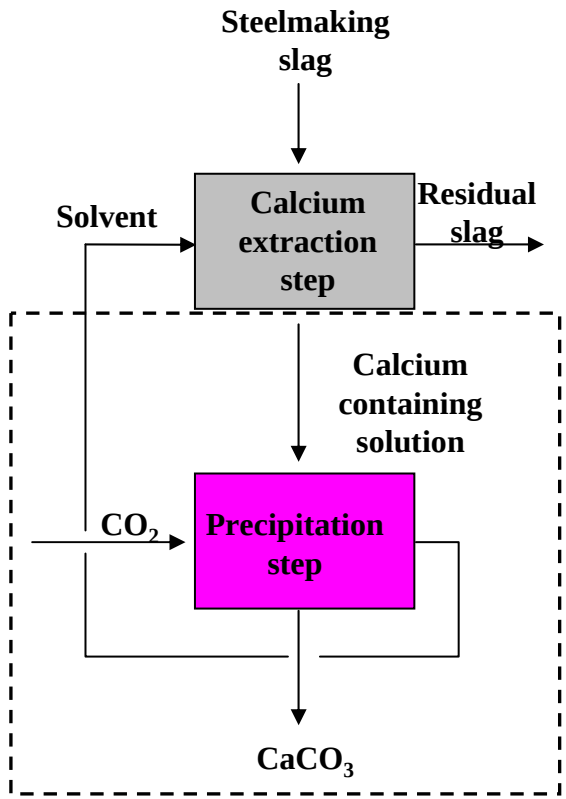


Step 2: Precipitation experiments

- Carbonation of Ca containing ammonium salt solution
- Precipitates consisted of calcium carbonate as rhombohedral calcite
- ~99.8 % $CaCO_3$
- Ca conversion from the solution into the precipitate was ~ 50-70 %
- Solution can be reused



SEM pictures of the precipitates produced from the solution of ammonium salt and steel converter slag



Summary

- Direct aqueous carbonation of steelmaking slags
  - At elevated pressures and temperatures
  - Simpler method
  - But endproduct is carbonated slag material

- Pure $CaCO_3$ can be produced from the steel converter slag by using an aqueous solution of ammonium salt as a solvent
  - At low temperatures and pressures
  - Without additional chemicals i.e. solvent can be recycled
  - Clearly negative CO_2 emissions

- The ammonium salt based process route has economical potential
  - Unfortunately seems to be suitable only for steel converter slag, desulphurization slag and AOD –process slag

Thank you for your attention!

Contact information:

sanni.eloneva@tkk.fi

The Graduate School
for Energy Science
and Technology (EST)