Feasibility study for nuclear heat injection in cement manufacturing: the process dissection.

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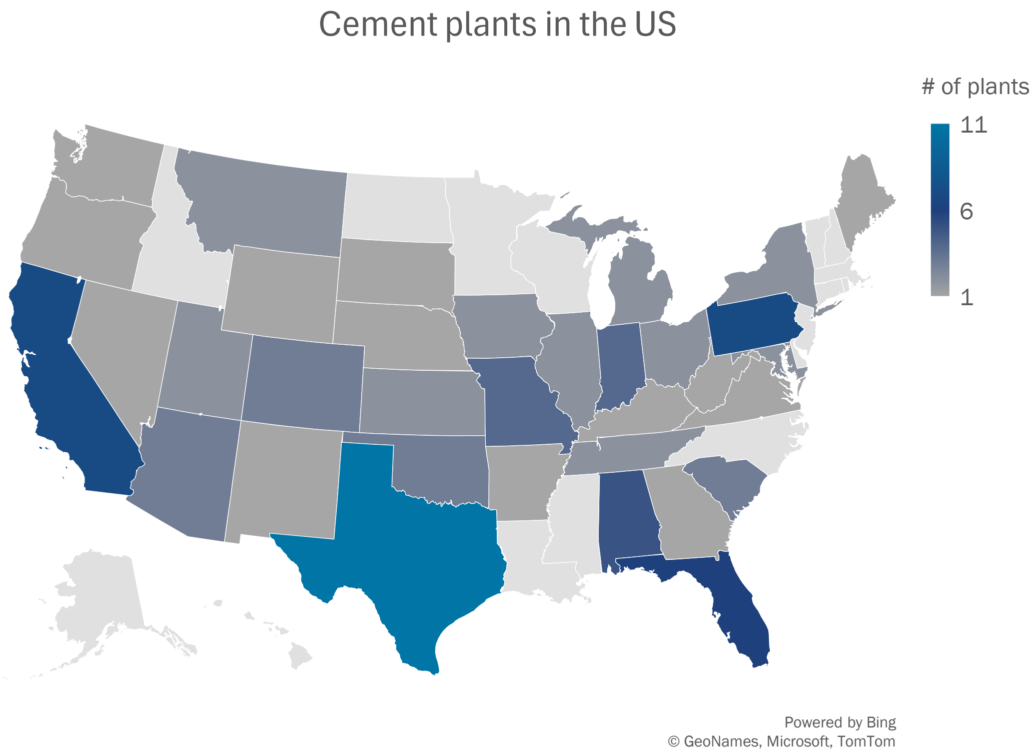
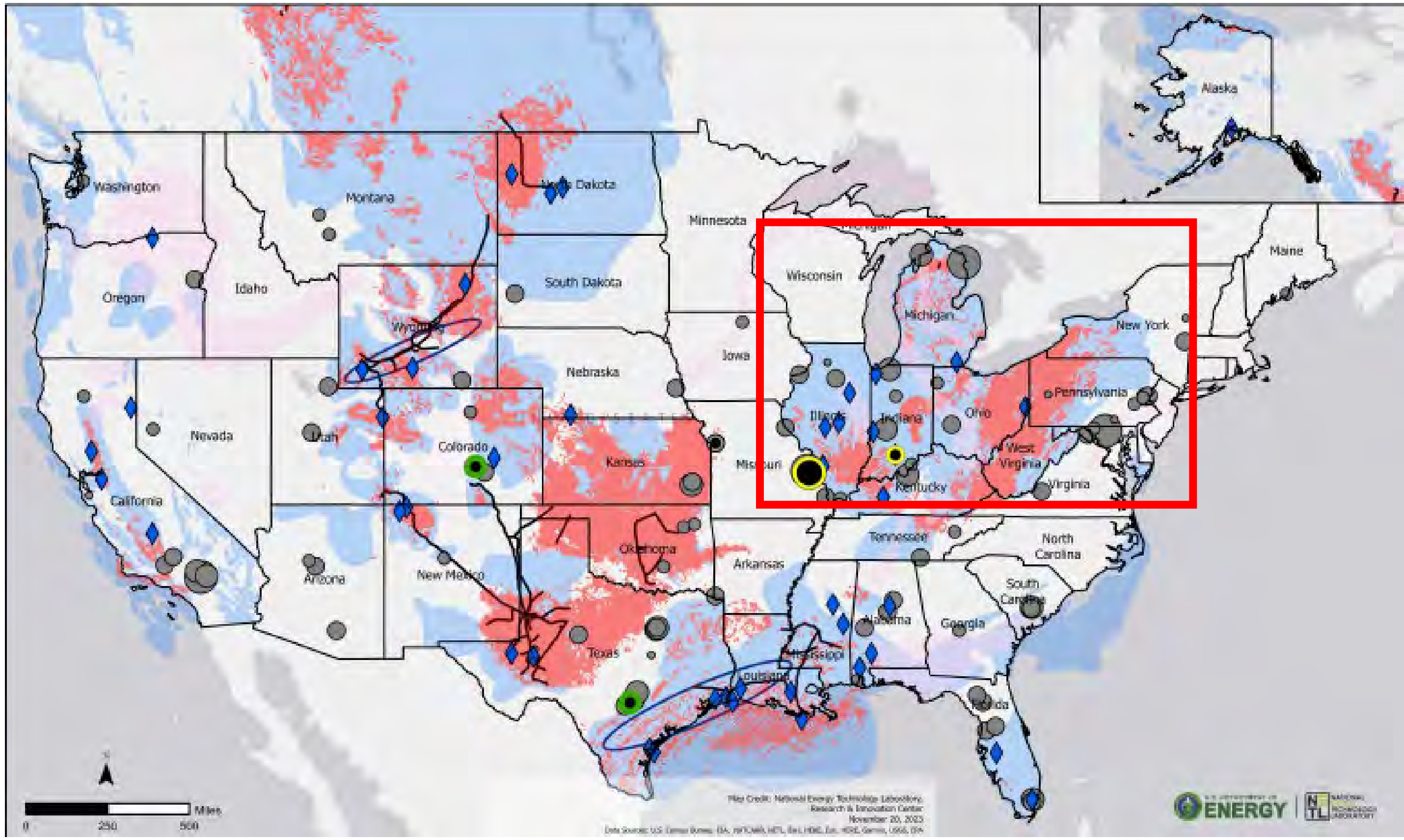
Cement industry in the US

- In 2021, the U.S. cement industry produced approximately **93 million metric tons** (MT) of Portland and masonry cement, with sales at roughly $13.4 billion.
- For the same year, U.S. cement production facilities reported 69 million MT carbon dioxide equivalents (CO2e).
- On average, to produce one ton of cement, **3.4 GJ of thermal energy** (in dry process) and **0.4 GJ of electrical energy** are needed.
- This represents nearly 5% of U.S. industrial sector total greenhouse gas (GHG) emissions and just over 1% of U.S. total GHG emissions.
- By 2050, cement production is expected to increase by more than 10% globally.

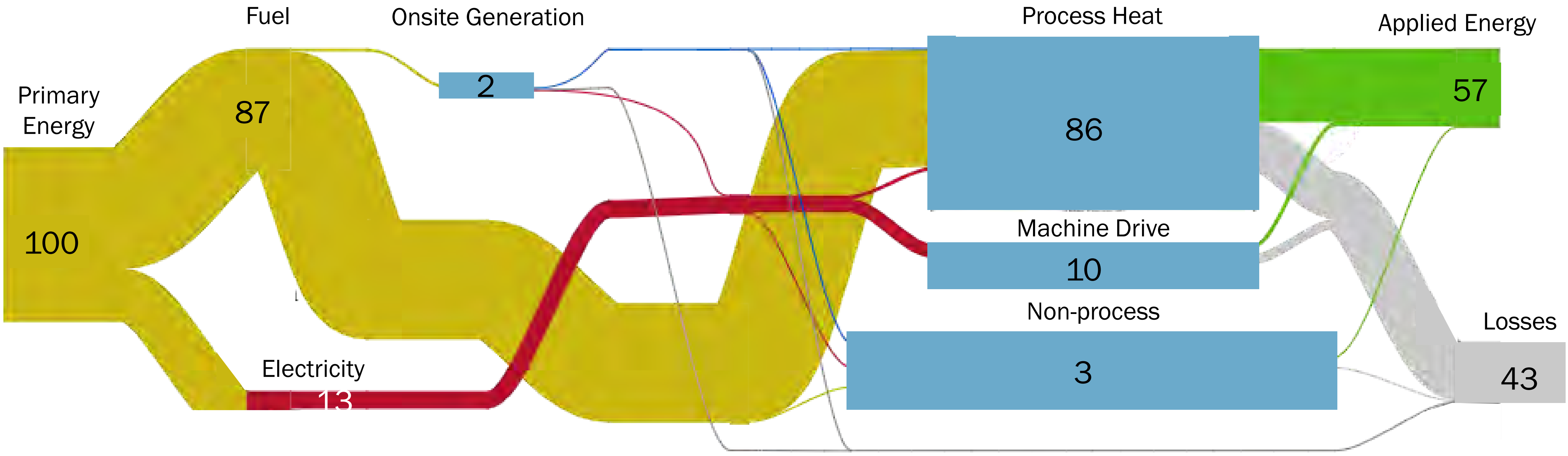
US cement manufacture infrastructure





Cement process energy balance

Primary energy use per ton of cement: 3.2-3.8 GJ



Adapted from DOE energy Sankey tool (https://www.energy.gov/eere/iedo/dynamic-manufacturing-energy-sankey-tool-2010-units-trillion-btu-0)

Cement production energetics

- Three fundamental reactions occur in the cement process:
  - **Reaction 1**: Thermal decomposition of calcium carbonate (limestone) to form calcium oxide (quicklime).

$$CaCO_3 \rightarrow CaO + CO_2$$

  - **Reaction 2:** Synthesis of belite (calcium disilicate) by reacting limestone and sand.

$$2CaCO_3 + SiO_2 \rightarrow Ca_2SiO_4 + CO_2$$

  - **Reaction 3:** Synthesis of alite (calcium trisilicate) by reacting belite and quicklime

$$Ca_2SiO_4 + CaO \rightarrow Ca_3SiO_5$$

Heats of reaction

- Knowing the standard heats of formation ΔH_f of all substances involved, we can estimate the energy release/demand for each reaction (heat of formation of products minus reactants).

Substance	Formula	ΔH_f (kJ/mol)
Limestone	$CaCO_3$	-1207.6[1]
Sand	SiO_2	-910.9[1]
Quicklime (C1)	CaO	-635[1]
Belite (C2)	Ca_2SiO_4	-2317[2]
Alite (C3)	Ca_3SiO_5	-2930[2]
Carbon dioxide	CO_2	-393.5[1]

[1]CRC Handbook of Chemistry and Physics 105th ed. Table data source:
[2]Shetenberg (2107). Russian Journal of Inorganic Chemistry 62(11):1464-1468

$$CaCO_3 \xrightarrow[179.1\frac{\text{kJ}}{\text{mol C1}}]{} CaO + CO_2$$

$$2CaCO_3 + SiO_2 \xrightarrow[592\frac{\text{kJ}}{\text{mol C2}}]{} Ca_2SiO_4 + CO_2$$

$$Ca_2SiO_4 + CaO \xrightarrow[22\frac{\text{kJ}}{\text{mol C3}}]{} Ca_3SiO_5$$

The estimated energy required to produce a mole of alite is 793 kJ/mol, or 3.5 GJ/ton

Fuel demand

- Knowing the energy required to produce alite (the most abundant component in cement clinker), we can obtain the fuel demand.

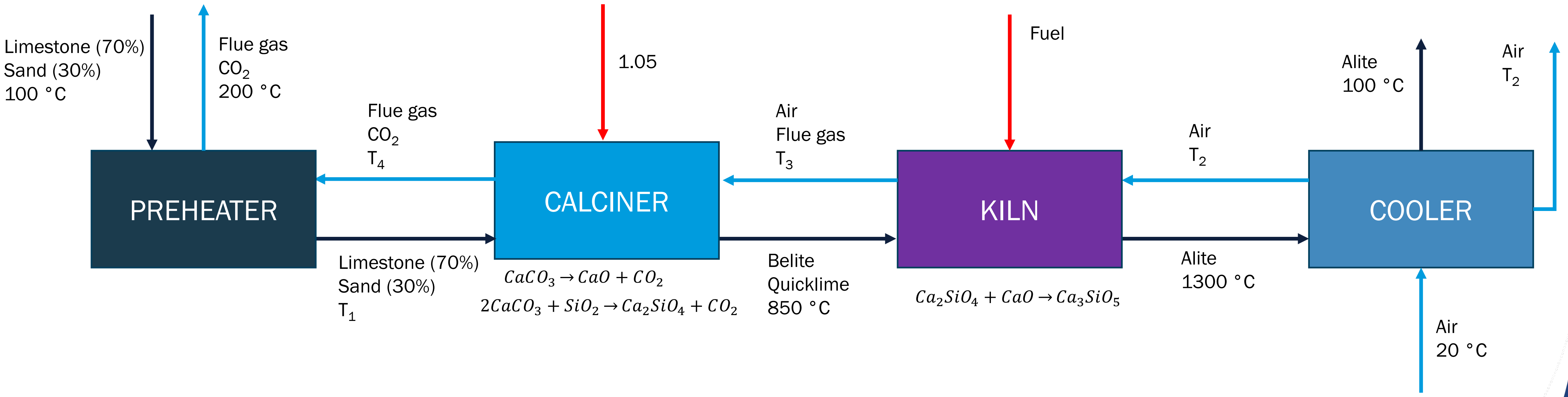
Fuel	LHV (kJ/g)	Fuel Demand (g fuel/mol alite)	CO2 emissions (g CO2/mol alite)
Hydrogen	120	6.6	0
Natural gas	47.1	16.84	44.24
Diesel fuel	42.6	18.61	58.68
LPG	45.5	17.43	52.57
Coal (lignite)	14	56.64	87.86
Coal (anthracite)	32.6	24.32	74.46
Wood	15	52.87	80.9

To obtain values per kg of alite (cement), divide table values by 0.23

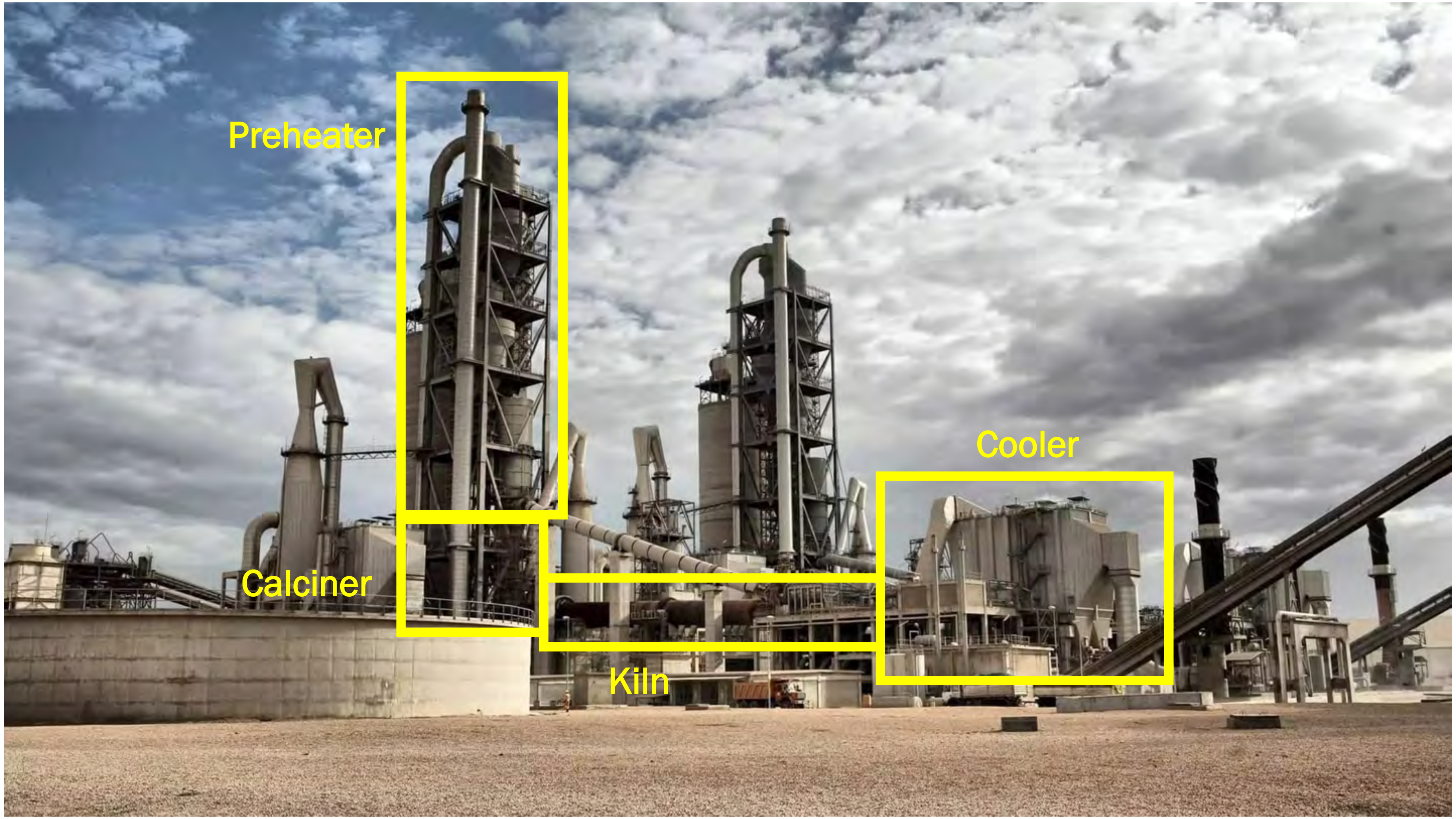
Temperature conditions

- The raw mill typically heats the solid feedstock to 150 °C by using some air leftover from the clinker cooler.
- Calcium carbonate decomposes appreciably above 825 °C.
- Belite forms appreciably around 1000 °C
- Alite is stable once belite is near its melting point, which happens at 1450 °C.
- Clinker must be quenched rapidly to temperatures below 100 °C to avoid alite reverting to belite.

Process flow diagram



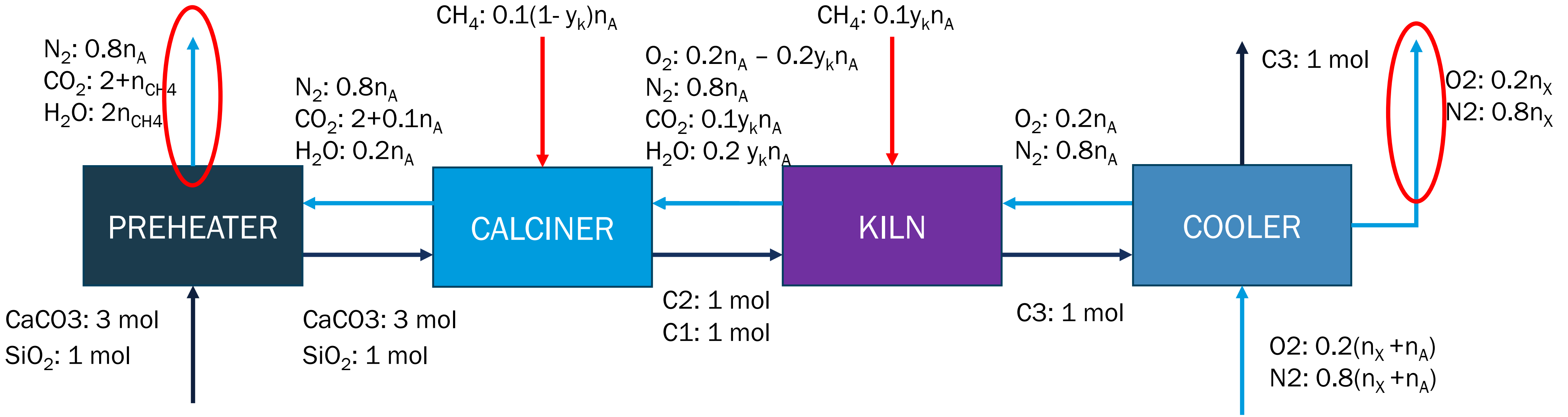
Process buildings



Steps on cement process production

- Preheater
  - Limestone and sand are heated from 100 °C to calciner solids input temperature
  - Gases (CO_2, N_2 and H_2O) cool from calciner gas output temperature to preheater gas output temperature
- Calciner
  - Heat up solids to calcination reaction temperature
  - Gases from the kiln and CO_2 cool down from reaction temperature to calciner gas output temperature, providing heat for the two calcination reactions, producing belite (Ca_2SiO_4) and quicklime (CaO).
  - Natural gas combustion provides supplemental heating
- Kiln
  - Belite and quicklime from the calciner react at 1300 °C to produce molten alite (Ca_3SiO_5).
  - Natural gas combustion heats air from the cooler and solids from the calciner to 1300 °C, as well as melting them at that temperature.
- Cooler
  - Ambient air is drawn to cool the solids to 100 °C. Part of the hot air is sent to the kiln.

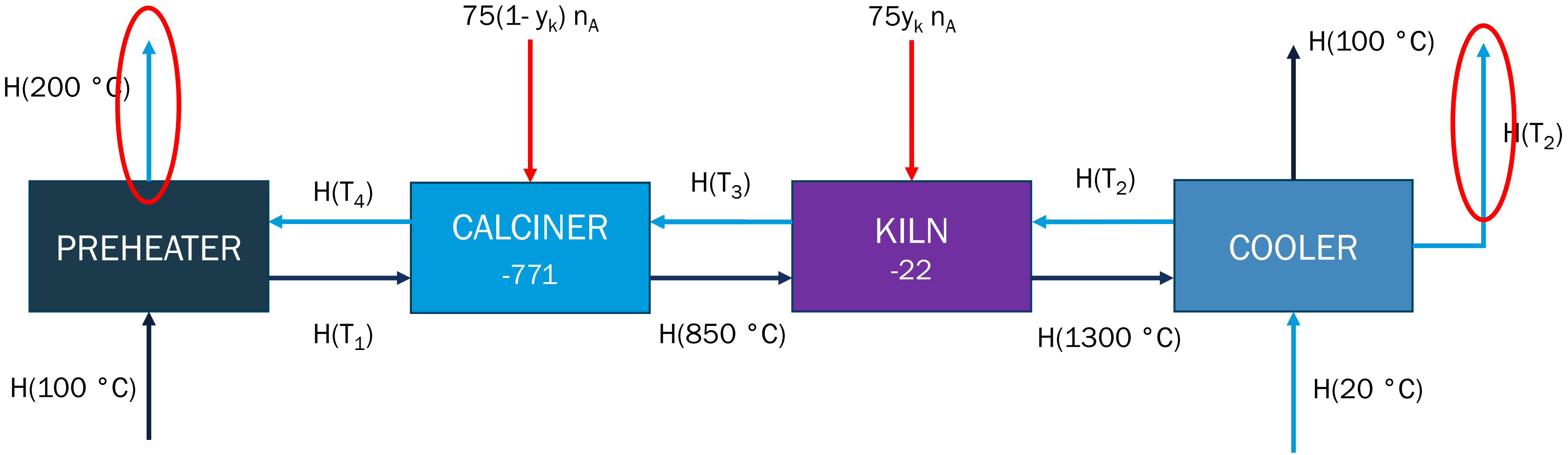
Mass balance of plant



Assumptions:

- No oxygen leftover
- No external fuel leftover
- Complete reactions

Energy balance of plant



Assumptions:

- No additional reactions
- Instantaneous reactions at 850 and 1300 °C
- All gases at 1 atm
- Isentalpic operation

Heating and cooling of solids

- For solid materials, you can use constant values of the heat capacity as a good approximation

Substance	Heat capacity (kJ/mol K)
Calcium carbonate (limestone)	0.082
Silicon oxide (sand)	0.0446
Calcium oxide (quicklime)	0.0423
Dicalcium silicate (belite)	0.1275
Tricalcium silicate (alite)	0.171

$$\Delta H = mC_p\Delta T$$

- Melting of dicalcium silicate requires 18 kJ/mol

Heating and cooling of gases

$$\Delta H = m \int_{T_1}^{T_2} C_p(T)dT$$

$$C_p(T) = \sum_{i=0}^{3} A_i T^i$$ Shomate equation

$$\Delta H = m \int_{T_1}^{T_2} \sum_{i=0}^{3} A_i T^i \, dT = m \sum_{i=0}^{3} A_i \int_{T_1}^{T_2} T^i \, dT = m \sum_{i=0}^{3} A_i \frac{T^{i+1}}{i+1} \Bigg|_{T_1}^{T_2} = mT \sum_{i=0}^{3} A_i \frac{T^i}{i+1} \Bigg|_{T_1}^{T_2}$$

Heat capacities of gases in J/mol/K

	A0	A1	A2	A3
Nitrogen	19.505	1.989e-2	-8.598e-6	1.37e-9
Oxygen	30.032	8.77e-3	-3.998e-6	7.88e-10
Carbon dioxide	24.99	5.518e-2	-3.37e-5	7.95e-9
Water vapor	30.09	6.832e-3	6.793e-6	-2.534e-9

Table data source: NIST chemistry webbook

$$C_p(T) = \sum_{i=0}^{3} A_i T^i$$

Shomate equation

Kiln draft constrain

- The preheater and the calciner require solids fluidization. This is accomplished by the gas exhaust from the kiln (“kiln draft”).
- Typical fluidization speeds fall between 6 and 10 m/s.
- This imposes a restriction in the gas flow coming from the kiln, and gives an additional equation to use in the system.
- Based on literature research and consultation with industry operators, the gas volumetric flow constrain at the kiln output is roughly 0.8 m^3/mol alite.

Equations

Cooler energy balance:

$$\underbrace{1200C_{p,C3}}_{\text{Cooling of solids}} + \underbrace{(n_A+n_X)[0.2h_{O2}(300) + 0.8h_{N2}(300) - 0.2H_O(T_2) - +0.8H_N(T_2)]}_{\text{Air heating}} = 0$$

Kiln energy balance:

$$\underbrace{-22}_{\text{Reaction 3}} + \underbrace{75y_k n_A}_{\text{NG comb. In kiln}} - \underbrace{450\left(C_{p,C2} + C_{p,C1}\right)}_{\text{Heating of solids}} + \underbrace{0.8n_A[h_{N2}(T_2) - h_{N2}(T_3)] + 0.1n_A(2 - y_K)[h_{O2}(T_1) - h_{O2}(T_2)] + 0.1y_K n_A[h_{CO2}(T_1) + 2h_{H2O}(T_1) - h_{CO2}(T_2) - 2h_{H2O}(T_1)]}_{\text{Flue gas and air cooling}} = 0$$

Calciner energy balance:

$$\underbrace{-771}_{\text{Reactions 1 and 2}} + \underbrace{75(1 - y_k)n_A}_{\text{NG comb. In calciner}} + \underbrace{(T_1 - 1123)\left(C_{p,s} + C_{p,l}\right)}_{\text{Heating of solids}} + \underbrace{0.8n_A[h_{N2}(T_3) - h_{N2}(T_4)] + (2 + 0.1n_A)[h_{CO2}(T_3) - h_{CO2}(T_4)] + 0.2n_A[h_{H2O}(T_3) - h_{H2O}(T_4)]}_{\text{Flue gas cooling}} = 0$$

Equations

Preheater energy balance:

$$\underbrace{(373 - T_1)(C_{p,s} + C_{p,l})}_{\text{Heating of solids}} + \underbrace{0.8n_A[h_{N2}(T_4) - h_{N2}(473)] + (2 + 0.1n_A)[h_{CO2}(T_4) - h_{CO2}(473)] + 0.2n_A[h_{H2O}(T_4) - h_{H2O}(473)]}_{\text{Flue gas cooling}} = 0$$

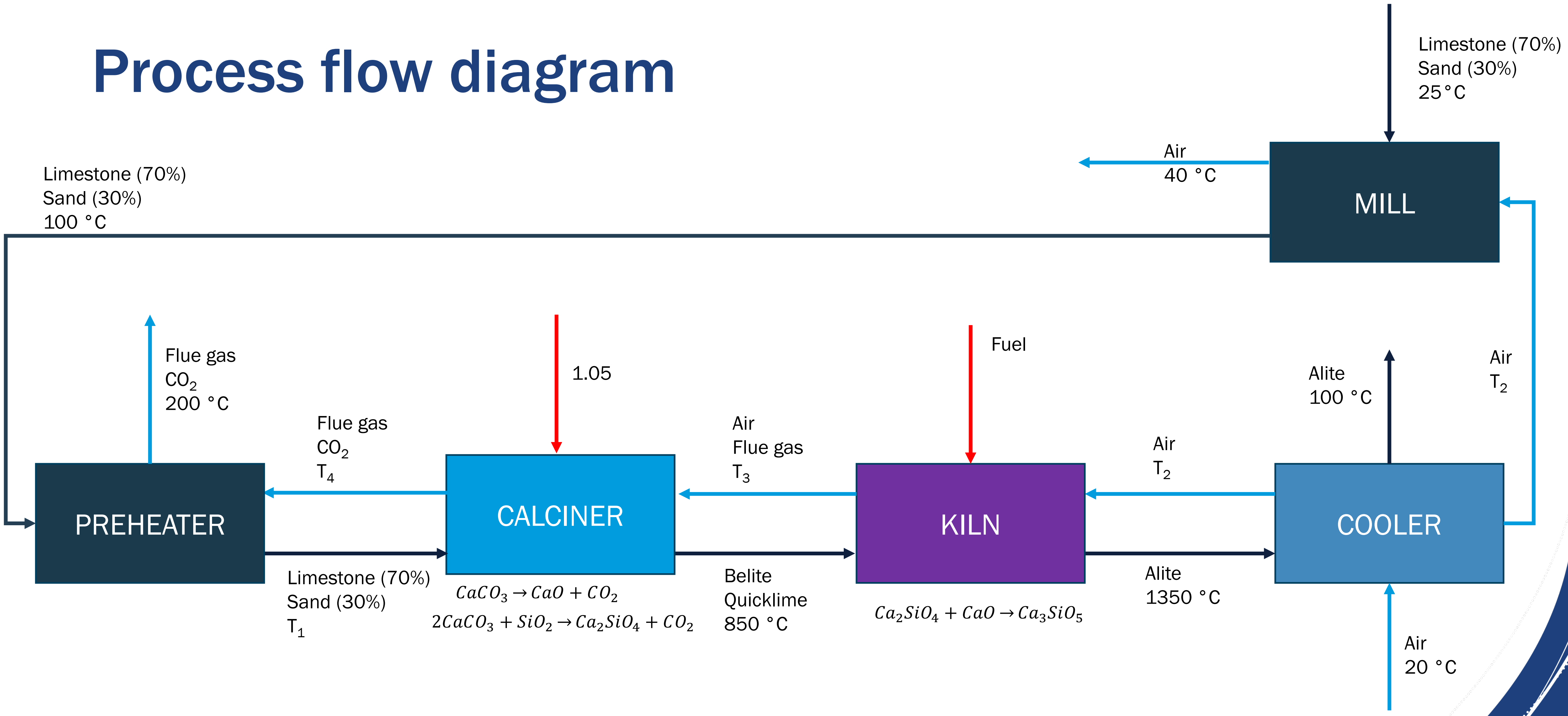
Kiln draft requirement:

$$\underbrace{(101300\ \text{Pa})}_{\text{Atmospheric pressure}}\underbrace{(0.8\ \ \text{m}^3)}_{\text{Volume flow requirement}} = \left(8.314\frac{\text{J}}{\text{mol K}}\right)\underbrace{n_A(1 + 0.1y_K)}_{\text{Molar flow}}\underbrace{T_3}_{\text{Kiln gas exit temperature}}$$

Unknowns

- We have six unknowns:
  - Four temperatures
  - Flow of air into kiln
  - Excess air flow in cooler
- We only have 5 equations! To close the system, we will assume that the excess air flow from the cooler and gases leaving the preheater are used to heat the solid feed during crushing from room temperature to 100 °C, and that air leaves at 40 °C. Therefore, a sixth equation is available:
- This can be modified to allow the preheater exhaust to heat the solids prior to entering the preheater

Process flow diagram



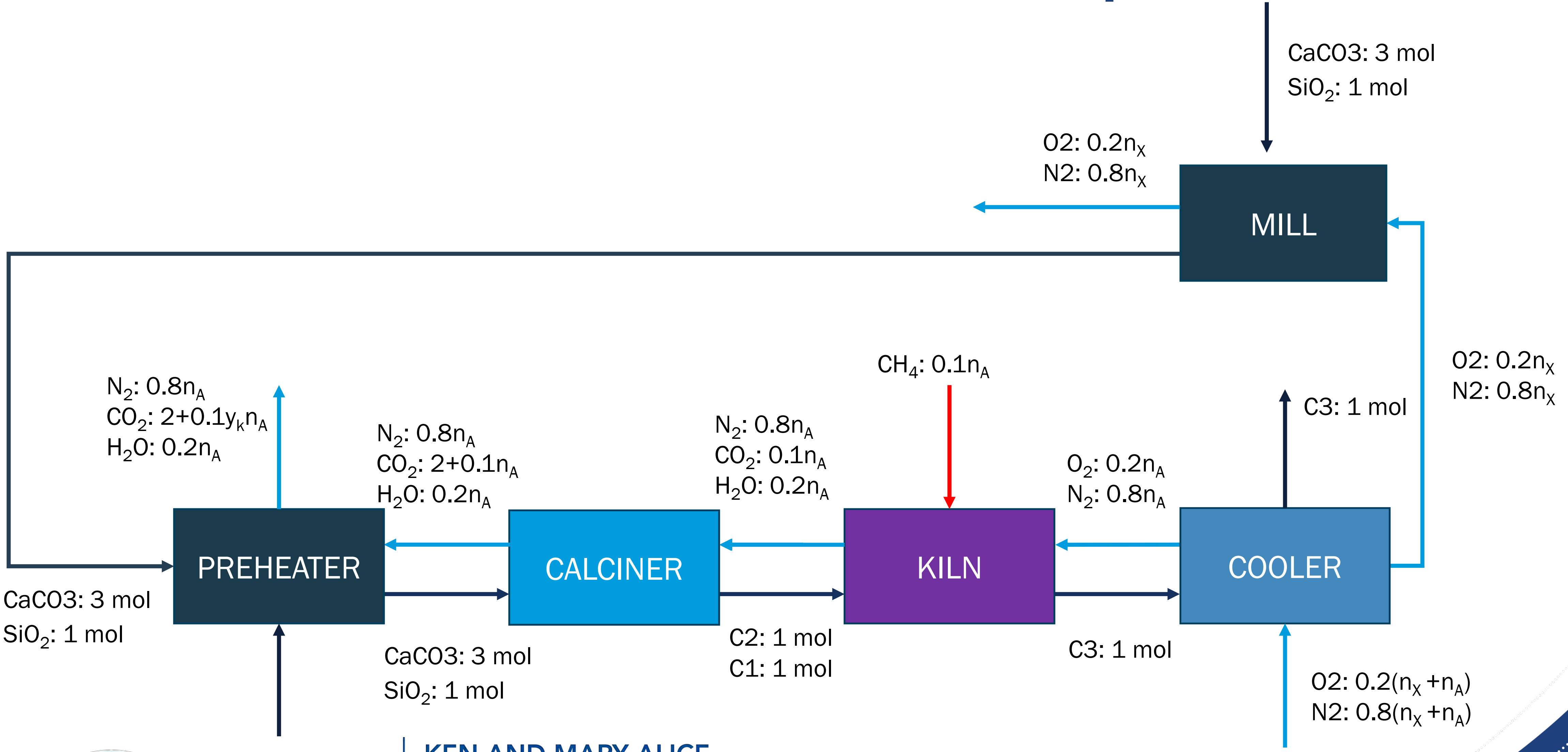
Fixed conditions

- Air enters the cooler at ambient temperature.
- Solids leave the calciner at the onset of carbonate decomposition temperature (800-850 ^{o}C).
- Solids leave the kiln at the alite melting point (1350-1400 ^{o}C)
- Solids are quenched to 100 ^{o}C in the cooler.
- Solids enter the mill at ambient temperature and leave at 100-150 ^{o}C.
- Flue gases leaving the preheater are at 200 ^{o}C.

Nuclear heat insertion

- A nuclear battery (microreactor) can used to partially replace fuel input.
- Replacement in the kiln section is challenging due to the extremely high temperatures required.
- Nuclear heat injection in either the preheater or calciner steps is more feasible.
- For this stage of the analysis, the only relevant feature is the amount of heat that the reactor can supply.

Mass balance with nuclear heat input



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Energy balances

$$-10.35 + n_X[0.2\Delta h_{O2}(T_2, 313) + 0.8\Delta h_{N2}(T_2, 313)] = 0$$ ❶ Mill

$$180 + (n_A + n_X)[0.2\Delta h_{O2}(298, T_2) + 0.8\Delta h_{N2}(298, T_2)] = 0$$ ❷ Cooler

$$-22 + 75n_A - 144 + n_A[0.8\Delta h_{N2}(T_2, T_3) + 0.1\Delta h_{CO2}(T_2, T_3) + 0.2\Delta h_{H2O}(T_2, T_3)] = 0$$ ❸ Kiln

$$-771 + q_{nuc} + 0.1374(T_1 - 1123) + n_A[0.8\Delta h_{N2}(T_3, T_4) + 0.1\Delta h_{CO2}(T_3, T_4) + 0.2\Delta h_{H2O}(T_3, T_4)] + 2\Delta h_{CO2}(T_3, T_4) = 0$$ ❹ Calciner

$$0.1374(373 - T_1) + n_A[0.8\Delta h_{N2}(T_4, 473) + 0.1\Delta h_{CO2}(T_4, 473) + 0.2\Delta h_{H2O}(T_4, 473)] + 2\Delta h_{CO2}(T_4, 473) = 0$$ ❺ Preheater

$$9747.41 = 1.1n_A T_3$$ ❻ Kiln draft

$$180 + \left[\left(n_A + \frac{10.305}{0.2\Delta h_{O2}(T_2, 313) + 0.8\Delta h_{N2}(T_2, 313)}\right)\right][0.2\Delta h_{O2}(298, T_2) + 0.8\Delta h_{N2}(298, T_2)] = 0$$ ❼

$$-771 + q_{nuc} + 0.1374(373 - 1123) + n_A[0.8\Delta h_{N2}(T_3, 473) + 0.1\Delta h_{CO2}(T_3, 473) + 0.2\Delta h_{H2O}(T_3, 473)] + 2\Delta h_{CO2}(T_3, 473) = 0$$ ❽

Solution strategy

- Assume total air flow into the cooler nA
- From eq. ❷, find T_2
- From eq. ❶, find nX, so nA is known
- From eq. ❸, find T3 knowing T2 and nA
- By combining ❹ and ❺, find T1 and T4
- With all temperatures known, calculate the air flow from ❻. If it does not match the assumed value, repeat until convergence is achieved.

- Perform energy balance for a fixed fraction of air going into the kiln

Conclusions

- We have a very good thermodynamic understanding of a simplified cement process.
- Currently working on a numerical tool to automate the mass and energy balances.
- Once the tool is available, it will be used to explore scenarios of nuclear energy insertion for different plant operating conditions.