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Development of Methods to Measure Heat Release from Hydration and Carbonation of Ash in Landfills

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Model to predict temperatures in landfills

- Model simulations and field observations identified <u>ash from coal and MSW</u> combustion as potential sources of heat generation
- ~50 million tons of ash is disposed in surface impoundments and landfills every year

Methods are needed to evaluate the suitability of ash for disposal and to parameterize landfill models of heat accumulation Model results showing accumulation of heat with MSW and ash [*Hao et. al., 2020*]



Ash contents and reactions

- Ash contains varying concentrations of calcium oxide (CaO) and calcium hydroxide Ca(OH)₂ (~5 - 40%)
- Both CaO hydration and Ca(OH)₂ carbonation are exothermic.
- Literature suggests hydration is fast; followed by slower carbonation

CaO hydration reaction

$$CaO_{(s)} + H_2O_{(I)} \rightarrow Ca(OH)_{2(s)} \quad \Delta H = -1164 \frac{kJ}{kg \ CaO}$$



Research objectives

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- Develop laboratory methods to measure the amount and rate of heat release from ash hydration and carbonation
- Objective 1: Method development and validation for an isothermal calorimeter: standard instrument, relatively simple
- Objective 2: Method development and validation for a quasi-adiabatic flow reactor: closer to landfill relevant conditions (abundance of gaseous CO₂), more complex
- Objective 3: Apply methods to coal and MSW ash samples
- Objective 4: Landfill model simulations using the measured heat release and rate of heat generation

Methods to measure heat generation



Objective 1

Method development and validation using an isothermal calorimeter

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Measurement of heat release during hydration and carbonation of ash disposed in landfills using an isothermal calorimeter



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Isothermal calorimeter validation



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- Hydration recovery between 79 and 90%
- Carbonation recovery between 65 and 74%
- Hydration products confirmed using TGA and XRD
- In case of carbonation, additional reactions occurring
- Takeaway:
 - Use <u>KHCO₃</u> in calorimeter system and include carbonation

Objective 2

Method development and validation for a quasi-adiabatic flow reactor under landfill relevant conditions

Reactor setup 9 Data acquisition device PC Water in CO_2 Temp De-Gas out Gastin sensor humidifier sensor Flow Flow sensor meter Vent out Flow sensor Insulation 50/ Stainless steel sample box to hold the • sample 50 Insulated container (dewar flask) and for ٠ insulation to reduce heat loss to the CO_2 Sample environment +Temp $/N_2$ Three channels for gas flow and liquid • sensors water • Two temperature sensors one in the center pH<3 Rubber disl and one outside Dewar Flask

Reactor setup





Stainless steel sample box

Channels for gas, liquid, and temperature sensor



¥ Styrofoam insulation

Dewar flask

Data acquisition <-device



Reactor characterization for heat loss

- Reactor was characterized by supplying a known amount of electrical energy
- With a known amount of electrical energy, at steady state, the heat loss equals the heat supplied which allows determination of ∝ (heat loss coefficient). ∝ was determined at five temperatures
- Rate of temperature decrease after power supply disconnect is used for *C* (reactor thermal capapcity) calculation



Reactor characterization

- \propto was computed to be 105 J·hr⁻¹·K⁻¹ (SD 6)
- Rate of fall of temperature yielded a C of 1200 J·K⁻¹



Reactor hydration validation



- CaO was tested for hydration
- Efficiency was 106 and 103% for duplicate samples
- Efficiency was adjusted for purity of samples using TGA
- We checked the conversion in product samples

Carbonation: $Ca(OH)_{2(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(l)}$

- Tested Ca(OH)₂ carbonation
- Two ways to validate the method
 - 1. CO₂ uptake (direct measure)
 - 2. Temperature measurements (other reactions may contribute)

CO₂ uptake



Objective 3

- Implementation of methods for a 6 coal and 6 MSW ash samples
- Samples from various locations across the country. They were collected at different locations at a power plant or incinerator

Hydration heat for ash samples



- Calorimeter heat is higher in all MSW ash samples and three coal ash samples
- C6 heat is much higher in the calorimeter
- Calorimeter has a lower detection limit than reactor

Time for hydration



- Time for MSW ash is longer compared to coal ash (C6 is an outlier)
- MSW ash has metal in it which can go through corrosion reaction when exposed to water
- We tested potential for corrosion reaction

Ash corrosion



- Serum bottle experiments
- All MSW ash samples produced hydrogen suggesting that the slow heat generation is from metal corrosion
- Leads to rate constants that represent multiple reactions which is not how the model was developed

$$2Al^+ + 3OH^- \rightarrow Al_2O_3 + \frac{3}{2}H_2$$

Carbonation for ash samples



- Heat is calculated from CO₂ uptake with stoichiometry of Ca(OH)₂ carbonation
- We used CO₂ uptake because it is a direct measurement.
- Calorimeter data not comparable because the calorimeter relies on a temperature increase
 - additional reactions (e.g., salt dissolution)
- Coal ash with hydrated lime injection generated most heat (C3 and C6)

Comparison of calorimeter and reactor

- We began with hydration and carbonation, but other reactions are contributing (e.g., salt dissolution, metal corrosion)
- Calorimeter is a standard instrument that measures hydration, carbonation, and dissolution. However, it is an aerobic system and landfills are anaerobic
- CO₂ uptake data from reactor gives carbonation but does not account for other reactions. However, reactor is more complex
- Ideal system would be a calorimeter operated under anaerobic conditions

Objective 4

Landfill model simulation using the measured heat generation for ash

Rate calculations for model simulations



- Rate constant is estimated from fitting the measured data to pseudo first order reaction models
- Heat generation data from calorimeter used for hydration
- CO₂ uptake data used for carbonation

 $Ash + H_2O \rightarrow Products$ $r = k[Ash][H_2O] = k'[Ash]$ $[Ash] = [Ash]_0 * e^{-k't}$

Batch model simulations



- Hydration based on calorimetry (higher)
- Carbonation based on reactor CO₂ uptake (specific)
- 20% ash mixed with MSW (temperature increases at 10% were insignificant)
- Coal ash contributed more towards the landfill temperatures than MSW ash because of higher heat generation
- When rate was 100 times slower, time to reach maximum temp increased
- 5% impact on maximum temperature with slower rate

Conclusions and Implications

- Calorimeter system was developed and validated. ~85% heat was recovered during hydration and ~70% was recovered for carbonation
- Reactor system was developed and validated. 104% heat was recovered during hydration and 106% CO₂ was recovered during carbonation
- Both methods have limitations
- The ideal system to measure all heat sources and sinks is a calorimeter operated under conditions that would allow anaerobic reactions to occur
- Both methods helped measure the heat generation for multiple coal and MSW ash samples
- Heat generation is sample specific, cannot generalize

Conclusions and Implications

- Batch model simulations helped understand the contribution of ash to landfill temperatures
- This work contributed to an improved understanding of heat generation potential and rates from ash disposed in landfills
- Landfill owners and operators can use the developed methods along with a landfill heat accumulation model to estimate the suitable mass of ash that can be safely disposed without excessive heat generation
 - User-friendly model under development in ongoing EREF-funded work

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