Supplementary Information

Recycled cement production, with zero emissions

Tengxiao Ji[1#], Shaoxuan Ren[1#], Yumeng Yang[2], Gaopeng Jiang[1], Giuseppe V. Crescenzo[1], Sabrina S. Scott[1], Yongwook Kim[1], Aubry S.R. Williams[1], Jordan Rumscheidt[1], Monika Stolar[1], and Curtis P. Berlinguette[1,2,3,4,*]

[1]Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, V6T 1Z1, Canada.
[2]Department of Chemical and Biological Engineering, The University of British Columbia, 2360 East Mall, Vancouver, British Columbia, V6T 1Z3, Canada.
[3]Stewart Blusson Quantum Matter Institute, The University of British Columbia, 2355 East Mall, Vancouver, British Columbia, V6T 1Z4, Canada.
[4]Canadian Institute for Advanced Research (CIFAR), 661 University Avenue, Toronto, Ontario, M5G 1M1, Canada.

[#]These authors contributed equally to this work.

Correspondence: cberling@chem.ubc.ca

Materials and Methods

Materials

The materials used for the cement recycler experiments are presented below. The cement electrolyzer was purchased from Dioxide Materials. The bipolar membrane (BPM, Fumasep FBM) was purchased from the Fuel Cell Store. The cation exchange membrane (CEM, Nafion™ N117) was purchased from Ion Power Inc. Nickel foam was purchased from MTI Corporate. White Portland Cement and Natural limestone were purchased from Amazon.ca. St. Marys® Portland Cement and Rapid Set® CEMENT ALL Multi-purpose Concrete were purchased from the Home Depot. Aged waste concrete from building demolition was collected from Riverside Recycling LTD. We primarily removed rebars and large-grained aggregates through grinding and only selected waste cement chips with sizes of 1–5 mm. Pure gasses: N_2 (99.999%), H_2 (99.999%), and Ar (99.999%) gasses were obtained from Linde Canada Inc. KOH (≥85%), KCl (99.0–100.5%), $CaCl_2 \cdot 2H_2O$ (≥99%), and HCl (37%) were purchased from Sigma Aldrich. All materials were used without any further purification. Fumasep FBM was soaked in 1 M KCl for 24 h before use. Nafion™ 117 were soaked in 1 M $CaCl_2$ for 24 h before use.

Other characterization methods

The X-ray diffraction patterns of waste cement and $Ca(OH)_2$ product were obtained on an Empyrean system using Cu Kα radiation (λ = 1.5405 Å) as the X-ray source with a θ−2θ model. Fourier-transform infrared spectra were measured in a Bruker Invenio-R FTIR Spectrometer with RT-DLaTGS detector. The concentration of Ca^{2+} cations in the anolyte and catholyte was measured by inductively-coupled plasma optical emission spectroscopy.

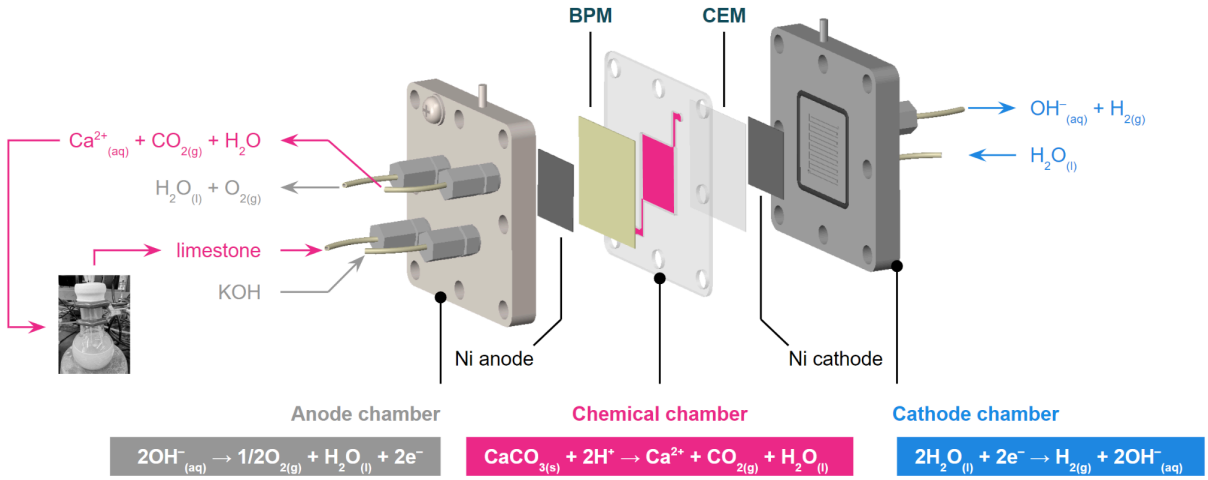
The voltage responses of the electrolyzer using current densities ranging from 100 to 300 mA cm^{-2} were measured using a Keithley 22805-32-6 DC Power Supply. In stability tests, the recording of electrolyzer voltages started after 10 min of stabilization. The voltage stability of the electrolyzer was tracked at a current density of 100 mA cm^{-2}. For the cement recycler, we washed the cathode chamber with 0.5 M HCl for 5 min after every 1 h of electrolysis.

Calculation of reduction in CO_2 emissions by the cement recycler

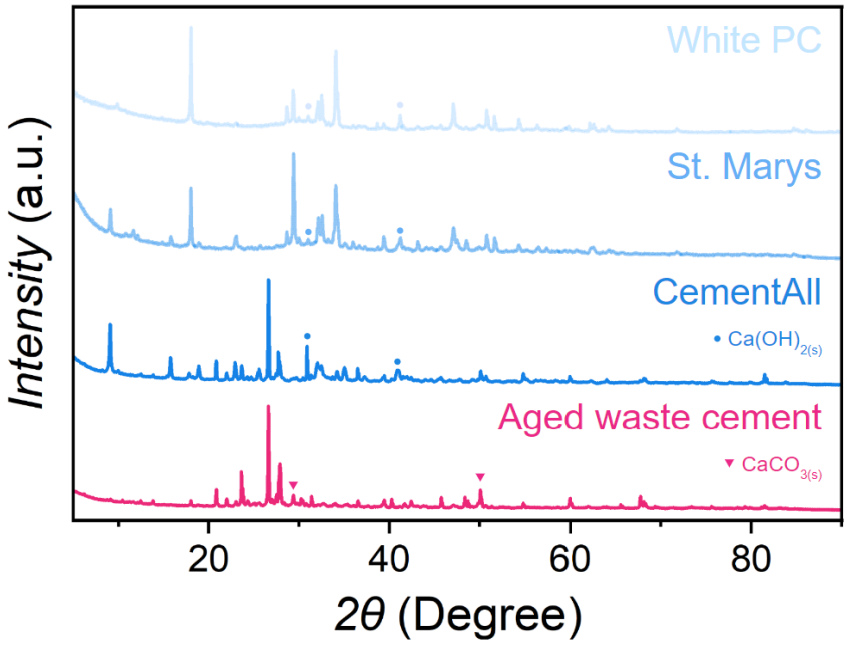
The standard CO_2 emissions from cement production using the traditional thermal method is 688 kg CO_2 t_{cement}^{-1}.[1] According to the experimental gas chromatography results, we achieved a reduction of CO_2 emissions by approximately 75% when converting aged waste cement into $Ca(OH)_2$, and a near 100% reduction in CO_2 emissions when converting fresh waste cement into $Ca(OH)_2$.

We then estimated the CO_2 emissions from the life cycle of converting aged waste cement into $Ca(OH)_2$ using the cement recycler, and subsequently converting it into cement clinker using a kiln. In our calculations, we assume that the electrolyzer is powered by renewable electricity, and the kiln for clinker production is powered by hydrogen combustion (sourcing from H_2 and O_2 produced from the electrolyzer). A combustion efficiency of 88% was determined to be powerful enough to cover the heat requirement for the kiln (Supplementary Fig. 12). Therefore, we conclude that there is no new CO_2 emitted from electricity production and the clinker production process. Rather, it releases the original CO_2 captured by the aged waste cement due to the weathering carbonation in its lifespan. Therefore, this pathway achieves carbon neutrality for cement production. With the above parameters and assumptions,

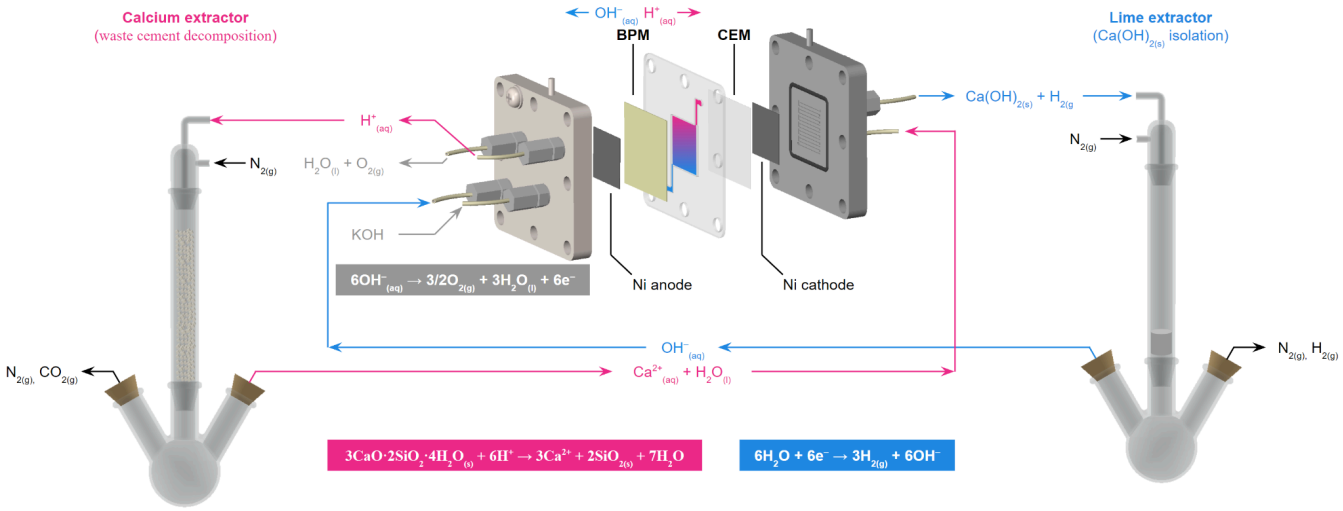
we estimated that by using the electrochemical pathway developed in this work, we can reduce CO_2 emissions by 0.3–0.9 billion tons when compared to the traditional thermal method (Fig. 1).



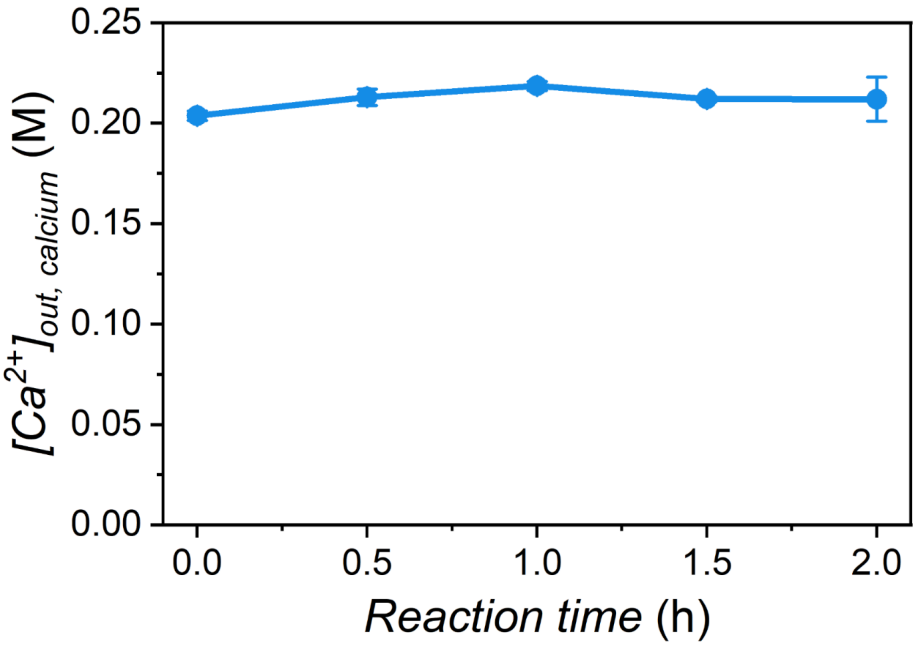
Supplementary Fig. 1: The experimental setup of our previously reported electrolyzer. We used the water splitting reaction to produce H^+ and OH^- for electrolytic production of cement clinker precursor ($Ca(OH)_2$). The source of calcium comes from limestone powder ($CaCO_3$, 20 g L^{-1}) suspended in the electrolyte. The slurry is circulated solely in the chemical chamber. BPM: bipolar membrane; CEM: cation exchange membrane.



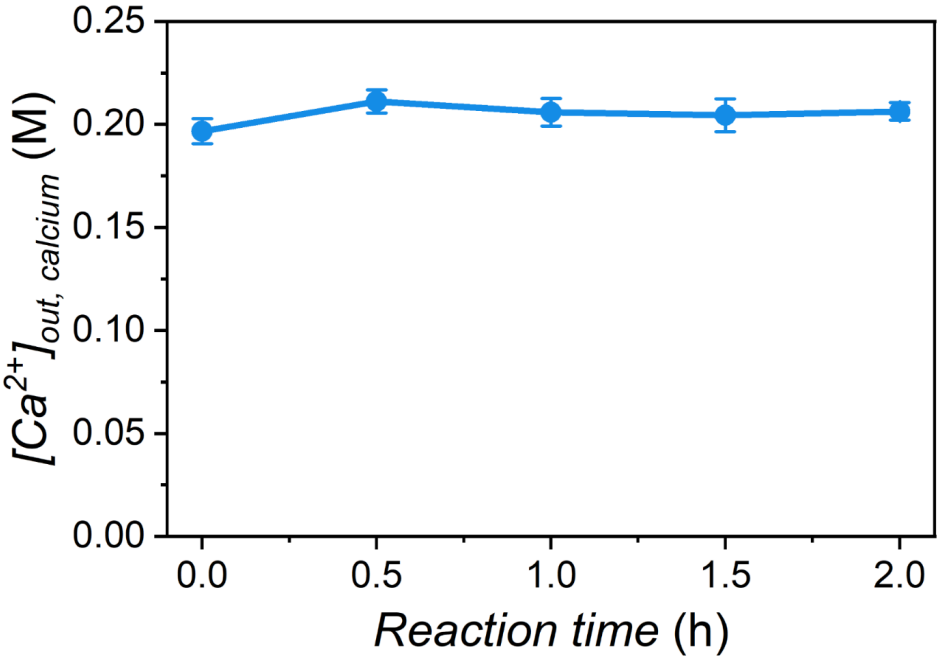
Supplementary Fig. 2: X-ray diffraction patterns of the waste cement used in this study. $Ca(OH)_2$ formed as a byproduct of cement hydration. Results showed that aged waste cement had higher $CaCO_3$ content, because it absorbs CO_2 from weathering calcination during its lifespan. Major components of these waste cement materials are tabulated in Supplementary Table 1.



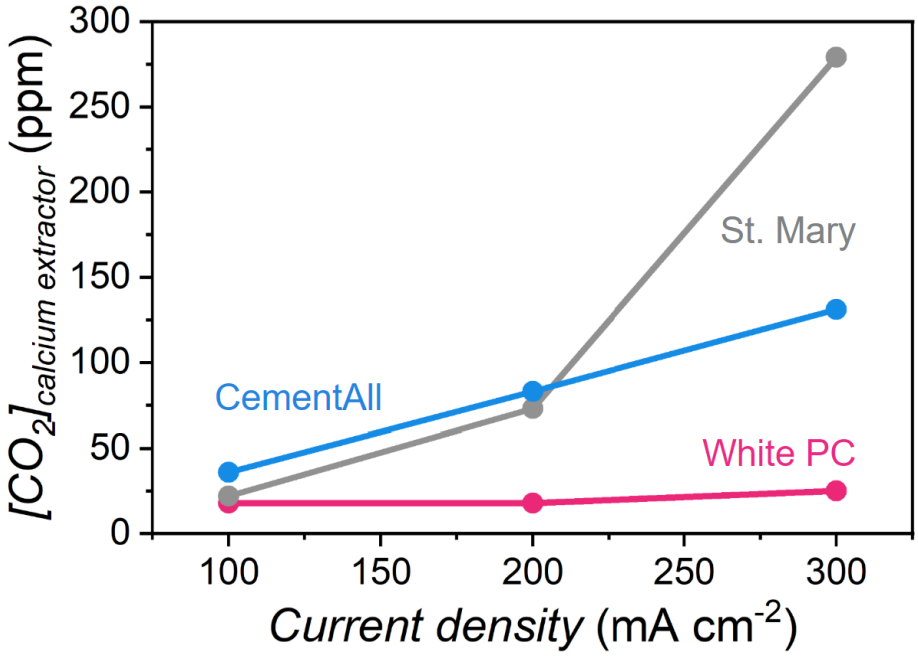
Supplementary Fig. 3: The experimental setup of the cement recycler. We used the water splitting reaction to produce H^+ and OH^- for electrolytic production of cement clinker precursor ($Ca(OH)_2$). While the 3 M KOH electrolyte is circulated solely in the anode chamber, we run a closed-loop electrolyte in the chemical and cathode chambers. H^+ ions generated by the BPM react with waste cement to release Ca^{2+} ions in the calcium extractor. In the cathode chamber, the Ca^{2+} ions react with OH^- ions and form $Ca(OH)_2$. The product is isolated in the lime extractor and the electrolyte ($Ca(OH)_2$ saturated clear solution) is returned to the chemical chamber.



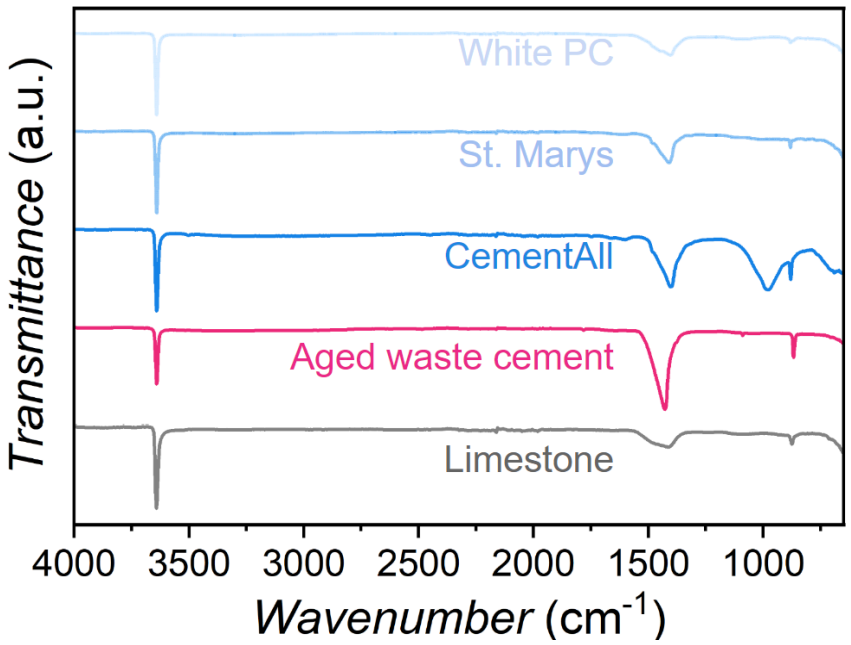
Supplementary Fig. 4: Inductively-coupled plasma optical emission spectroscopy results show the minimal variation of Ca^{2+} concentration in the closed-loop electrolyte during electrolysis at 100 mA cm^{-2} for 2 h.



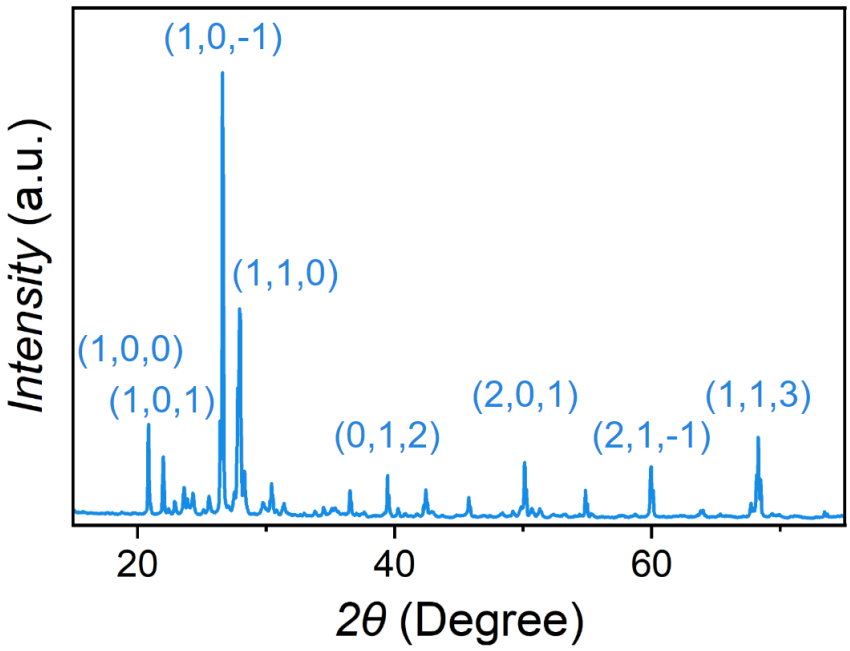
Supplementary Fig. 5: Inductively-coupled plasma optical emission spectroscopy results show the minimal variation of Ca^{2+} concentration in the closed-loop electrolyte during electrolysis at 300 mA cm^{-2} for 2 h.



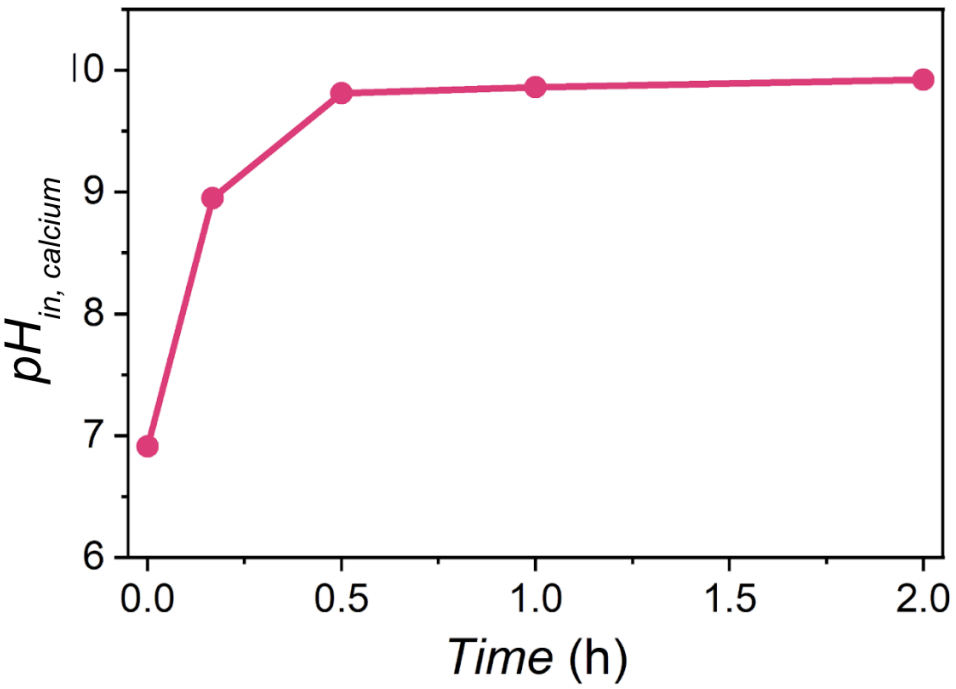
Supplementary Fig. 6: Concentration of $CO_{2(g)}$ emissions ($[CO_2]_{calcium\ extractor}$) from the calcium extractor in the cement recycler during electrolysis at different current densities of 100–300 mA cm^{-2}. Carrier gas: N_2 with a flow rate of 200 sccm.



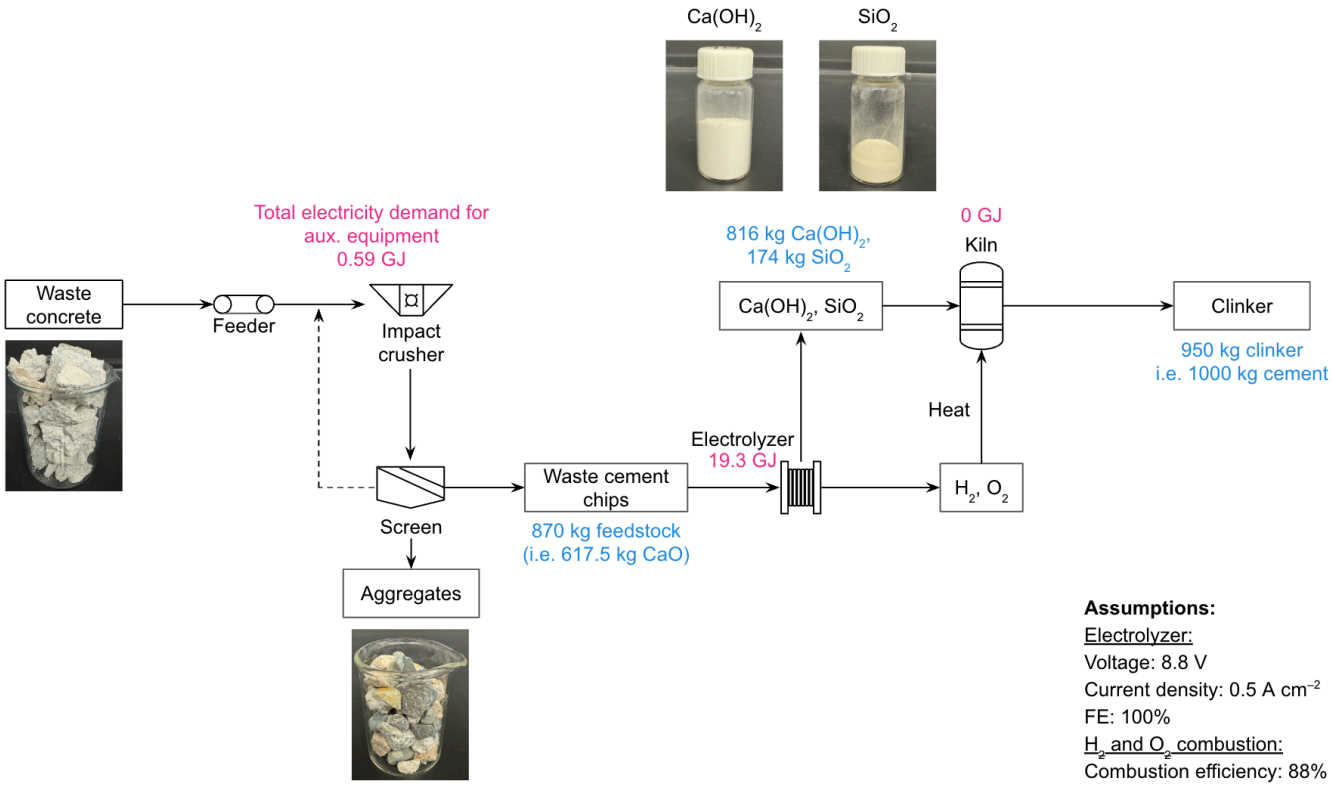
Supplementary Fig. 7: Fourier-transform infrared spectra of the $Ca(OH)_2$ product collected from the lime extractor. $Ca(OH)_2$ was produced from the electrolysis of waste cement. Results were also compared with the $Ca(OH)_2$ product obtained from the electrolysis of natural limestone ($CaCO_3$). All electrochemically synthesized $Ca(OH)_2$ demonstrated good purity (>79%).



Supplementary Fig. 8: X-ray diffraction patterns of the SiO_2 byproduct we collected from the calcium extractor. The byproduct was produced from the electrolysis of aged waste cement. Crystal facet parameters were marked for the major characteristic peaks. The major impurity is Tremolite ($CaMg_{2.5}Fe_{0.5}Si_4O_{12}$, 9%).



Supplementary Fig. 9: The pH_{in} of the closed-loop electrolyte tracked over 2 h of electrolysis at 200 mA cm^{-2} without the initial addition of Ca^{2+} ($CaCl_2$, 0.2 M). The change of $pH_{in,\ calcium}$ from acidic to basic indicated that waste cement decomposition cannot occur in the calcium extractor.



Supplementary Fig. 10: The flow diagram for the electrochemical conversion of waste cement into $Ca(OH)_2$ at an industrial scale. This diagram shows the changes in mass and energy during the manufacturing process. In our previous study, we found that a hydrogen-fed kiln with a combustion efficiency of >88% is able to cover the heat requirement for the clicker formation.[1,2] The whole process does not release additional CO_2 to the atmosphere. Rather, it releases the original CO_2 captured by the aged waste cement due to the weathering carbonation in its lifespan. Therefore, this pathway achieves carbon neutrality for cement production.

Supplementary Table 1. Summary of the major components of waste cement.[a]

Catalog	Raw material	Major components (content from high to low)
Fresh waste cement	White Portland cement	$CaSiO_3$, $Ca(OH)_2$, Alite, $CaSO_4$
	St. Marys	Alite, Belite, $CaSO_4$, $Ca(OH)_2$
	CementAll	$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$,[b] SiO_2, C-S-H, $Ca(OH)_2$
Aged waste cement	Aged waste cement	SiO_2, C-S-H, Alite, $CaCO_3$

[a] Alite: $3CaO{\cdot}SiO_2$; Belite: $2CaO{\cdot}SiO_2$; C-S-H: $3CaO{\cdot}2SiO_2{\cdot}3H_2O$.
[b] Calcium aluminosilicate ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$): Only partially soluble in acid at elevated temperatures (80–100℃). Does not react with acid in ambient conditions. This solid byproduct remains in the calcium extractor after electrolysis, and can be used as a raw material for ceramic and glass industries.

We obtained pure $Ca(OH)_2$ (purity = 79%) from CementAll, an aluminate cement. The reason that we did not detect a high proportion of aluminum-containing impurities in the product (Fig. S3) is because during the hydration of CementAll, calcium aluminosilicate ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$), does not dissolve in or react with acidic solution in ambient conditions,[3,4] and it is only partially soluble in acid at elevated temperatures (80–100℃). This solid byproduct remains in the calcium extractor after electrolysis, and can further serve as an important raw material for the ceramic (accounts for 30% of the total amount of raw materials)[5–7] and glass industries (accounts for 50-60% of the total amount of raw materials).[8–10]

Supplementary Table 2. **Cell voltages required to drive cement electrolysis at 100, 200, and 300 mA cm^{-2} in the cement recycler. All reported voltages are those measured after 10 min of electrolysis.**[a]

J (mA cm^{-2})	Full cell voltage (V)	
	Average	Best cell
100	4.56 ± 0.04	4.51
200	6.26 ± 0.13	6.10
300	7.67 ± 0.18	7.50

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