Supplemental Information

Nickel Extraction from Olivine using Waste Acid from an Electrochemical Marine CO_2 Removal Process

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ICP-MS Sample Preparation and Methodology

All ICP-MS sample dilutions were made in an ISO-5 cleanroom with Optima acid and deionized water to of 18.2 MΩ. Tubes used for dilution were metal free or acid leached before use to minimize contamination. Dilution factors were calculated using gravimetric data to provide accurate mass changes in the sample. The ICP-MS instrument was tuned prior to every analysis conducted and is run with a kinetic energy discriminator to filter out data from polyatomics. Each sample injection is measured 7 times before averaging and each sample is injected 3 times to ensure consistency of the measurement. In between samples, calibration verification measurements are conducted to further ensure the data is reliable. Any data collected that had unreliable data (RSD>20%), such as data obtained for Cr, was not included in the reported results.

Table S1. Particle size distribution statistical analysis for as received olivine powders

Min	D10	D25	D50	D75	D90	Max
1.76 μm	38.26 μm	57.26 μm	82.91 μm	114.2 μm	147.1 μm	312.12 μm

Table S2. pH and composition of major cations present in BPMED acid

pH	Na (mg/L)	Mg (mg/L)	K (mg/L)	Ca (mg/L)
0.4	2,230	3.6	79	3.9

Table S3. Dissolution of olivine in varying ionic strength solutions

NaCl Added (M)	Start Mass (g)	End Mass (g)	Percent Dissolved (%)
0	0.2±.002	0.1628	18.60±0.81
0.1	0.2±.002	0.1553	22.35±0.78
1	0.2±.002	0.1529	23.55±0.76

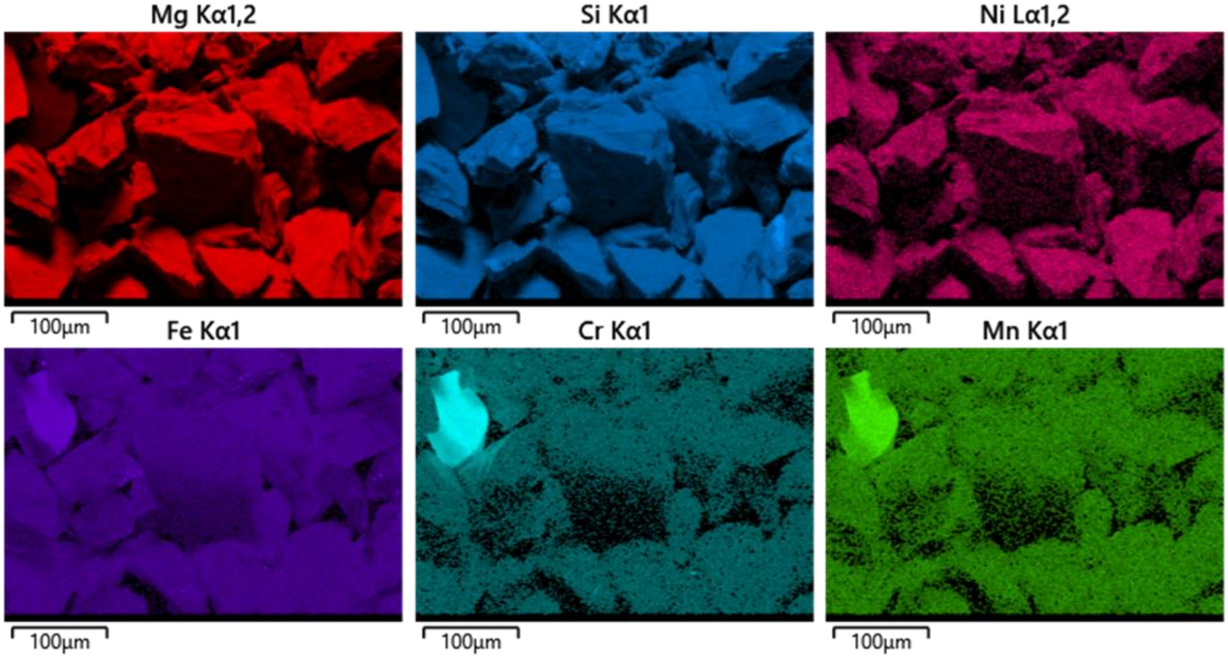

Figure S1. EDS analysis of olivine sample after 24 hours of dissolution in BPMED acid. Bottom row shows hotspots for Fe, Cr, and Mn at the same location, indicating a separate phase heavy in those elements. The likely phase is chromite ($FeCr_2O_4$) that is known to contain Mn impurities. The top row shows the elements present that do not have a heavy presence in this new phase. Mg and Si are deficient in this area compared to the rest of the sample while Ni appears to be equally dispersed within this separate phase with the rest of the sample.

Figure S2. Bulk olivine dissolution experiment of 15 g of olivine in 1 liter of BPMED acid (left). BPMED solution after 2 weeks of dissolution after solid removal (middle). Solid residue collected after exposure to BPMED acid for 2 weeks (right)

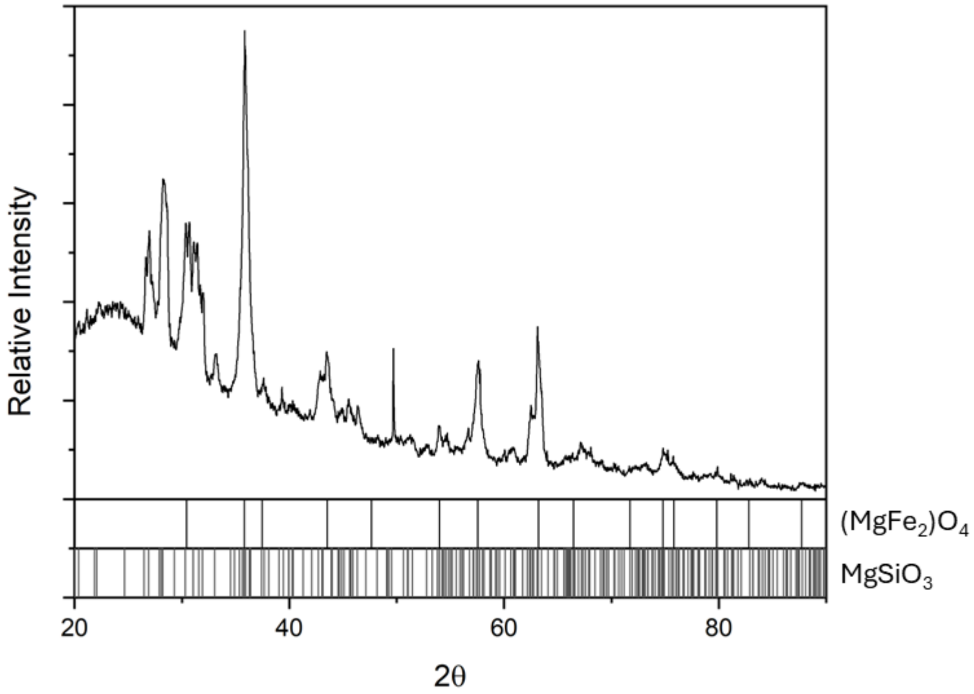

Figure S3. Best fit for the XRD data obtained from the solid residue obtained after digesting olivine in BPMED acid for 2 weeks. Fit suggests the presence of enstatite (PDF# 98-000-02060 and magnesioferrite (PDF# 98-000-4923) with potentially amorphous SiO_2 present as indicated by 'bump' in pattern between 20° and 30°. No $FeCr_2O_4$ or olivine phase detected after the digestion.

Table S4. Measured percent water lost after adjustment to indicated pH threshold

pH	**2**	**3**	**4**	**5**	**6**
% Solution Lost	0.1	0.37	1.8	11.16	13.53

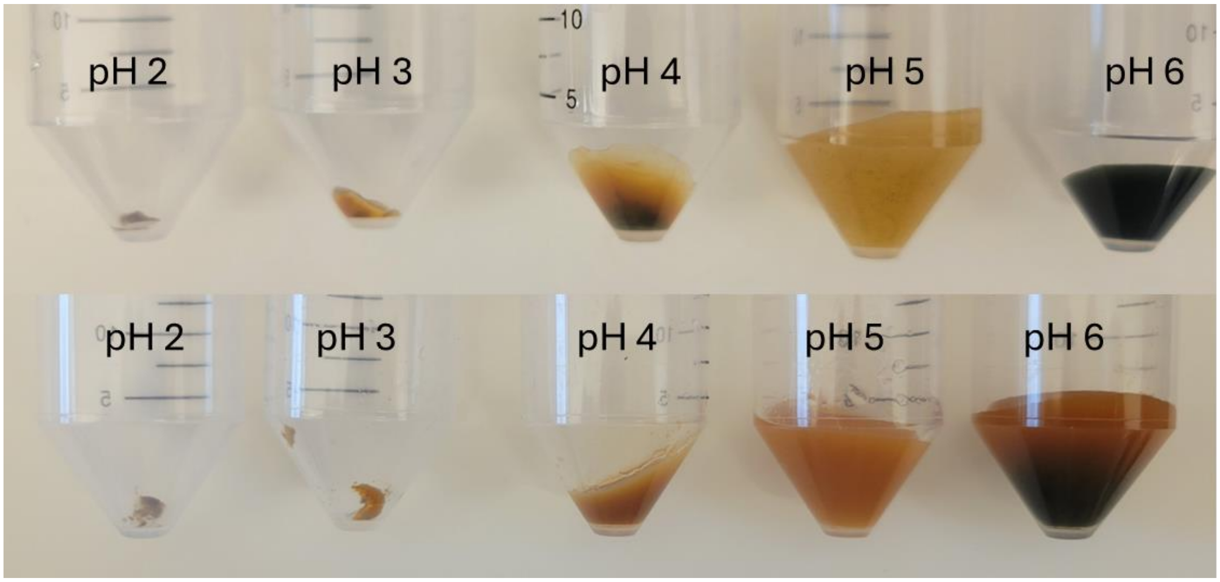

Figure S4. Precipitates formed after pH adjustment to indicated level done sequentially (top) by removing obtained solid at each threshold before adjustment onward or done in bulk (bottom) where all the precipitate was left in the tube for collection at the indicated pH threshold. A gel forms in the tube for both methods at pH 4 and above.

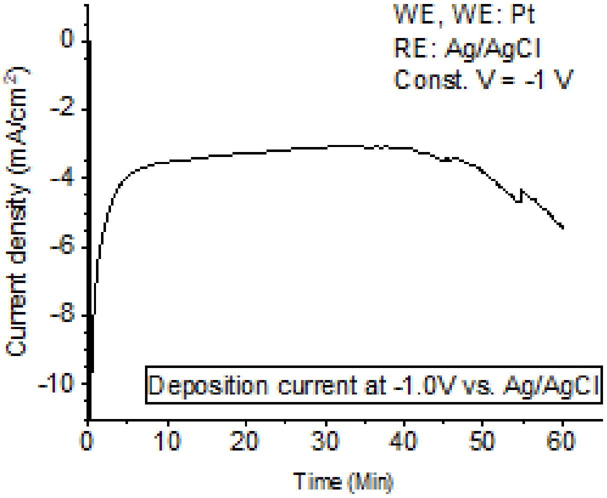

Figure S5. Current profile of Pt electrode during constant voltage deposition at -1 V vs. Ag/AgCl using leachate solution. The electrochemical cell using pt strip as working electrode, Pt wire as counter electrode, and Ag/AgCl reference electrode

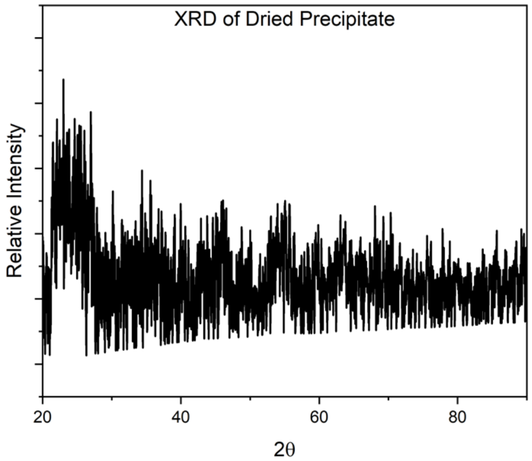

Figure S6. XRD pattern of the dried precipitate obtained after bulk pH adjustment

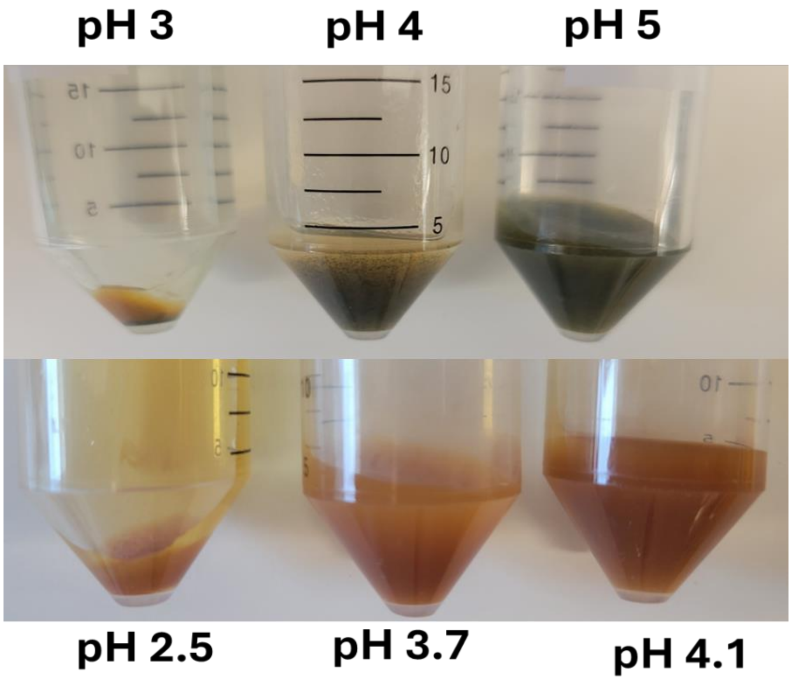

Figure S7. Color of precipitates obtained after pH adjustment of solution to pH 3, 4, and 5 (top) and after thermal treatment at 50°C overnight (bottom). Color change from green to orange indicates a transition from Fe(II) to Fe(III) which is less soluble in water.

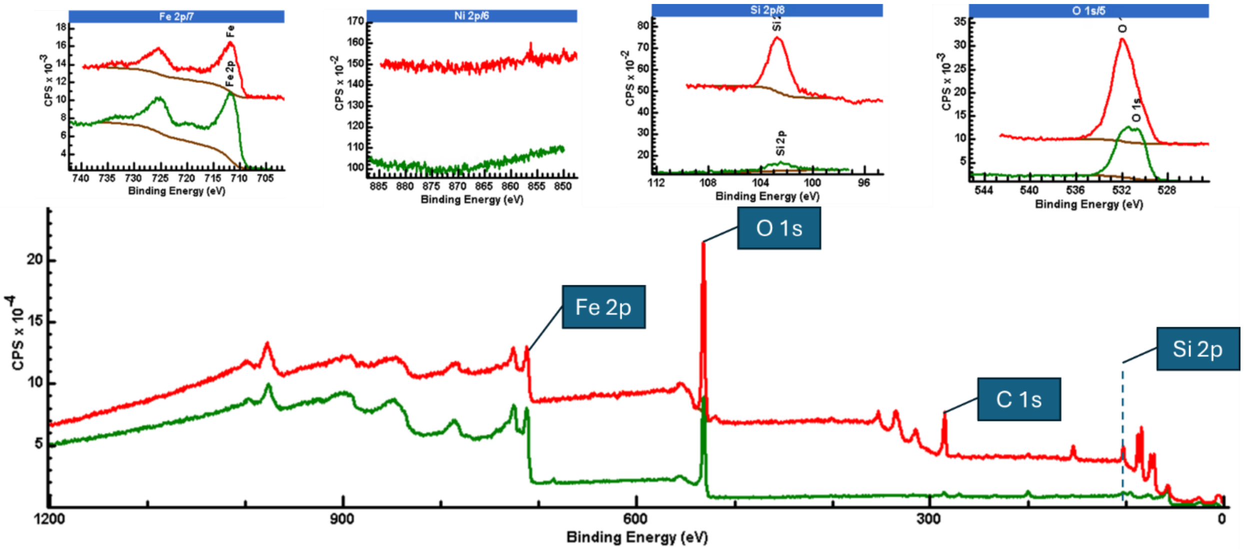

Figure S8. XPS results on an electrodeposit taken before heat treatment of the pH adjusted olivine leachate with binding energies of Fe, Ni, Si, and O shown on the top. The Red line is for experiments done at a constant voltage of -0.8V and the Green line is for experiments done at -1.0V. From the results, the deposit formed had either none or very little incorporation of Ni. The heat treatment used (80°C for 6 hrs) was able to remove enough Fe and Si from the solution to enable detectably higher quantities of Ni to be electroplated (see Figure 5 in Manuscript).

Technoeconomic Analysis

Magmatic ultramafic rocks are 40-100% olivine, which can contain significant (500-5000 ppm) Ni.[1] To estimate the total volume of ultramafic rocks in the United States, the surface area of the ultramafic rocks was taken from the 2009 USGS mineral resource.[2] With estimated average depths, the total volume of the ultramafic rocks in the United States that contain olivine can be estimated to be 32,900 km^3. A simple high-level estimation using conservative values for the key factors, including the olivine concentration in ultramafic rock ore, the Ni concentration in olivine, and the recovery rate of Ni, was done to evaluate the potential impact of Ni extraction from olivine in the United States. Assuming 40% of the ultramafic rock is olivine, the Ni concentration in olivine is 500 ppm.[1, 3] Assuming about 10% of the Ni can be recovered, the total potential amount of Ni from the olivine in the United States can reach 1,908 million t, which can supply the nation for more than 90 years assuming an compound annual growth rate of Ni consumption of 7.3% and 200,000 t/year Ni consumption rate in the United States.[4] Of course, the total amount of Ni obtained from olivine depends on the accessibility of the ultramafic rock ore.

The current efficiency ε of the Ni plating is defined as

$$\varepsilon = m / (M * I * t / (N * F))$$

Where m is the theoretical yield (mass of product produced in grams), M is the molar mass of Ni (58.69 grams/mol), I is the current (Amperes), t is time (seconds), N is number of electrons exchanged per atom (2), and F is Faraday's constant (96,485 C/mol).

Based on the literature information, the current efficiency is 15.5% when applying 3.5V to the Ni plating cell. The energy consumption to produce 1 kg Ni is about 5.36 kWh with a recovery rate of 61.7%.

The major equipment used in this process includes dissolving reactors for olivine, pumps for BPMED acid flow, and electrochemical cells for Ni plating. The process rate for the ultramafic ore is set to 35 t/h, and the corresponding flow rate of the BPMED acid is 1400 m^3/h. Based on the experiment data, it took 2 weeks (336 h) to dissolve the olivine to get the Ni out of the mineral. So the total volume of the reactor equals 336X1400 m^3. For the dissolving reactor, a continuous stirred-tank reactor (CSTR) example from the literature was used as the reference to scale up. The base price for the 10,000 m^3 CSTR reactor (multistage) costs about $1,900,000 (2007). Rough estimates for plant scaling are obtained by relating the capacity increase of equipment to the cost increase by an exponential law.[5] A CSTR (multistage) reactor with a volume of 42,000 m^3 would cost about $6.14 million US (2024), and it will need 12 of these reactors to process 35 t/h of ore. The total cost of the dissolving reactor is about $73.68 million. The annualized cost can be estimated as $2.46 million with a 30-year of operating time. Similarly, the annualized costs of the pump and electrochemical cell were calculated, and the results are shown in the table below. The reference pump was a magnetic drive pump for chemical process with a flow rate of 160 GPM and price $2,300 (https://www.pumpworld.com/products/112982/iwaki-mxm-series-chemical-process-magnetic-drive-pump). The reference electrochemical cell was 1 kW (PEM) cell with an average price of $830 from the literature.[6]

Table S5. Major equipment cost estimation for Ni recovery from olivine.

Equipment	Size	Cost ($ 2024)	Number of equipment	Total cost ($)	Operating life (Year)	Annualized cost ($)	Normalized cost ($/kg Ni)
Dissolving reactor	42,000 m^3	6.14 M	12	73.68 M	30	2.46 M	12.56
Pump	0.8 m^3/s	43 K	168	7.32 M	30	0.24 M	1.23
Electrochemical cell	2300 kW	86 K	168	14.59 M	30	0.48 M	2.44

References

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