Recovery and separation of phosphorus as dicalcium phosphate dihydrate for fertilizer and livestock feed additive production from a low-grade phosphate ore

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Electronic Supplementary Information

Table S1. Comparison of various chelating agents. The complexation formation constants for M + L binding for Fe^{3+} is given for each chelating agent. An indicative price for each agent is also listed for the agents which had a readily available retail price. These prices are only intended to compare the relative cost of the different chelating agents.

Name	**Formula**	**log[K_f]: L + $[Fe]^{3+}$**	**Indicative Price***	**Binding-Cost index**	**Ref**
			$/g	**log[K_f]/($/g)**	
ACAC	$C_5H_8O_2$	9.30	0.48	19.3	[1]
IDA	$C_4H_7NO_4$	10.9	2.06	5.3	[2]
MIDA	$C_5H_9NO_4$	10.99	11.92	0.9	[2]
NTA	$C_6H_9NO_6$	15.9	0.64	24.9	[1]
DHNS	$C_{10}H_8O_5S$	19.84			[1]
CAT	$C_6H_6O_2$	20.4			[1]
EGTA	$C_{14}H_{24}N_2O_{10}$	20.50	4.02	5.1	[1]
EEDTA	$C_{12}H_{20}N_2O_9$	24.7			[1]
EDTA	**$C_{10}H_{16}N_2O_8$**	**25.10**	**0.55**	**46.0**	**[1]**
EDDHA	$C_{18}H_{20}N_2O_6$	25.13			[3]
PDTA	$C_{11}H_{18}N_2O_8$	26.0	44	0.6	[1]
TETA	$C_{18}H_{32}N_4O_8$	26.50			[1]
TTHA	$C_{18}H_{30}N_4O_{12}$	26.80	35	0.8	[1]
TRITA	$C_{17}H_{30}N_4O_8$	27.50			[1]
DTPA	$C_{14}H_{23}N_3O_{10}$	27.8	3.87	7.2	[2]
DMEDTA	$C_{12}H_{20}N_2O_8$	28.05			[1]
NOTA	$C_{12}H_{21}N_3O_6$	28.3			[2]
CDTA	$C_{14}H_{22}N_2O_8$	30.00			[1]
PLED	$C_{22}H_{30}N_4O_8$	30.80			[1]
HBET	$C_{15}H_{20}N_2O_7$	32.02			[1]
EHPG	$C_{18}H_{20}N_2O_6$	35.54			[1]
HBED	$C_{20}H_{24}N_2O_6$	39.01			[1]
DOTA	$C_{16}H_{28}N_4O_8$	39.40	2188	0.0	[1]

*The indicative price was determined by comparing the **retail** price of the various agents (in $CAD) from Sigma-Aldrich Canada (https://www.sigmaaldrich.com/canada-english.html) on 2020-09-14. The product package sizes, grades, and purities varied, but the prices were selected to be as close as possible to 100 g package size, Reagent grade, and 99 % purity. Example: ACS Reagent, 99.4-100.6 % EDTA was $54.60 for 100 g, thus Indicative Price = 0.55 $/g.

[1]: Martell, A. E.; Motekaitis, R. J.; Chen, D.; Hancock, R. D.; McManus, D. Selection of New Fe(III)/Fe(II) Chelating Agents as Catalysts for the Oxidation of Hydrogen Sulfide to Sulfur by Air. Can. J. Chem. 1996, 74 (10), 1872–1879, DOI 10.1139/v96-210.
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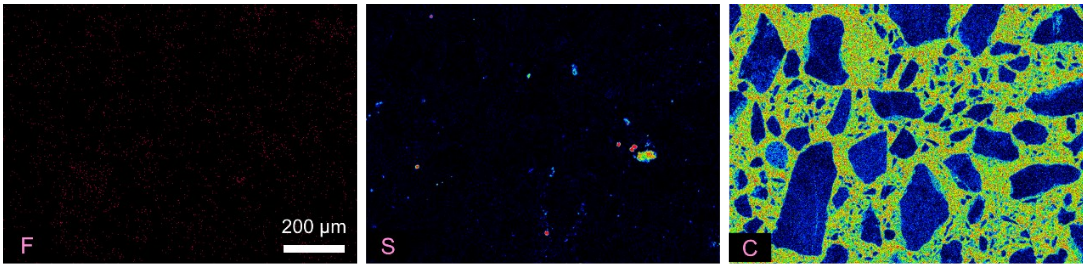

Figure S1. Cross-sectional EPMA elemental mapping of starting ore (additional elements). The starting ore cross section shown in Figure 2c was also analyzed for fluorine, sulfur, and carbon. The primary source of carbon is the epoxy used to fix the ore particles.

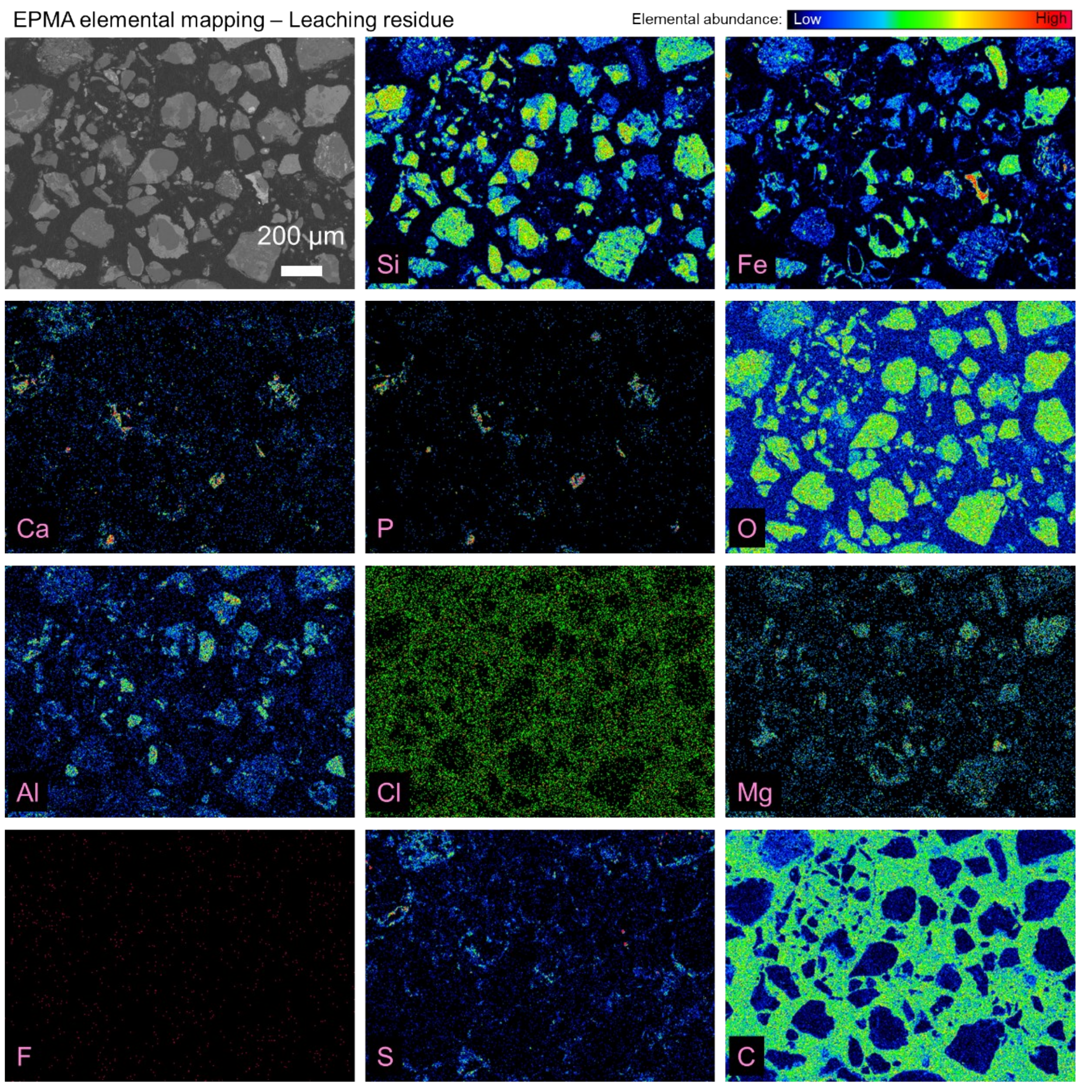

Figure S2. Cross-sectional EPMA elemental mapping of leached ore residue. The primary source of carbon is the epoxy used to fix the ore particles. The color scale for the EPMA maps show the relative elemental abundance, and the scale is unique for each element. Note: the ore particles were fixed in epoxy which contained chlorine and oxygen, leading to a high background reading for Cl and O. The ore was leached for 5 min in 0.29 M H_2SO_4 solution at 25 °C with a solid/liquid ratio of 0.3 g/mL.

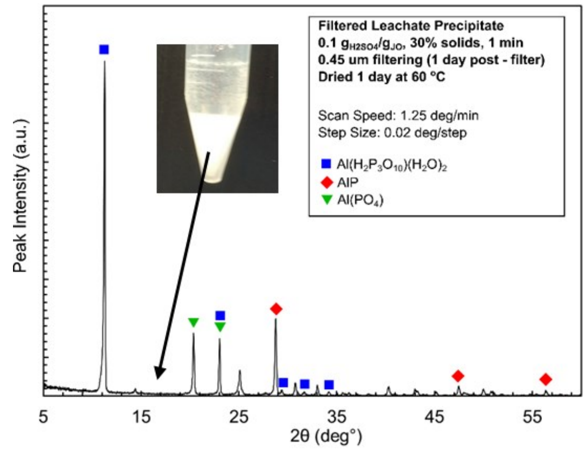

Figure S3. XRD diffractogram of the time-delayed precipitate formed in filtered leachate solution. The ore was leached under standard conditions (0.29 M H_2SO_4, 3 mL/g), sampled after 1 min then filtered with a 0.45 µm nylon syringe filter. The clear filtrate was incubated at room temperature for 24 h, then collected and dried for 24 h at 60 °C.

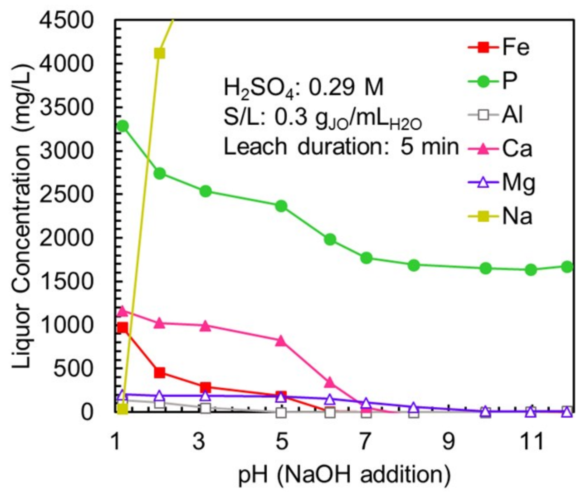

Figure S4. Precipitation of extracted elements from leachate with NaOH. The leached solution was neutralized by adding 0.5 M NaOH solution and the solution was sampled, filtered and analyzed at regular pH intervals.

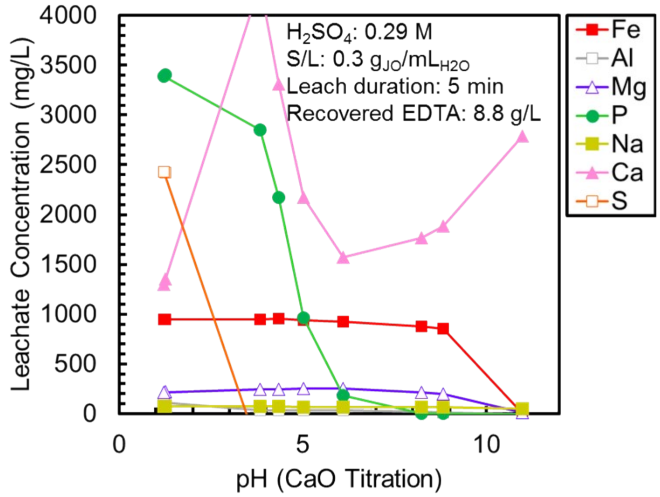

Figure S5. Precipitation of extracted elements from leachate with CaO using recovered H_4EDTA solids as a stabilizing agent. The H_4EDTA solids were recovered from a previous precipitation trial by H_2SO_4 acidification and were used as the only EDTA source. The H_4EDTA solids (8.8 g/L) were added to ore direct leaching solution (DLJO), which was neutralized by addition of CaO solids, and the solution was sampled, filtered and analyzed at regular pH intervals.

Figure S6. Physical appearance of the unfiltered slurries, filtered slurries, and wet filter cakes for each processing step for the simplified selective precipitation process.

Table S2. Economic analysis of the overall leaching, stabilization, precipitation process. The material costs and revenues for the process were estimated from the mass balance flows (Table 3) and estimated industrial costs for the process. The calculations are made on a processing basis of 1 tonne of ore during closed loop operation. The sources of pricing information are given in the table. All costs were corrected to a uniform basis of 2019 USD using price indices as indicated. The estimated industrial costs presented here are approximations based on publicly available pricing information. Note: this estimation does not consider revenue from the iron-magnesium precipitation product

Reagent/ Product	Consumption/ Production rate	Estimated Cost	Cost/ Revenue	Cost/ Revenue Reference
	kg/tonne of ore	USD_{2019}/kg	USD_{2019}/ tonne of ore	
Lime (CaO)	58	0.137	-7.97	[1]
H_2SO_4	112	0.047	-5.31	[2],[3]
Na_2EDTA	4.0	1.34	-5.31	[4],[5]
Deionized Water	725	0.001	-0.75	[2],[6]
DCP	62	0.355	22.14	[4],[5]
Gypsum	89	0.008	0.71	[7]
Total	-	-	3.50	
(no EDTA loss)	-	-	8.81	

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[7]: Statista. Average price of crude gypsum on a free-on board (FOB) mine basis in the U.S. from 2007 to 2019 https://www.statista.com/statistics/219363/wallboard-products-crude-price-in-the-us/; 2020.