

CALCIUM FERRITES FOR PHOSPHATE ADSORPTION AND RECOVERY FROM WASTEWATER

SUPPLEMENTARY MATERIAL:

CALCIUM FERRITES SYNTHESIS

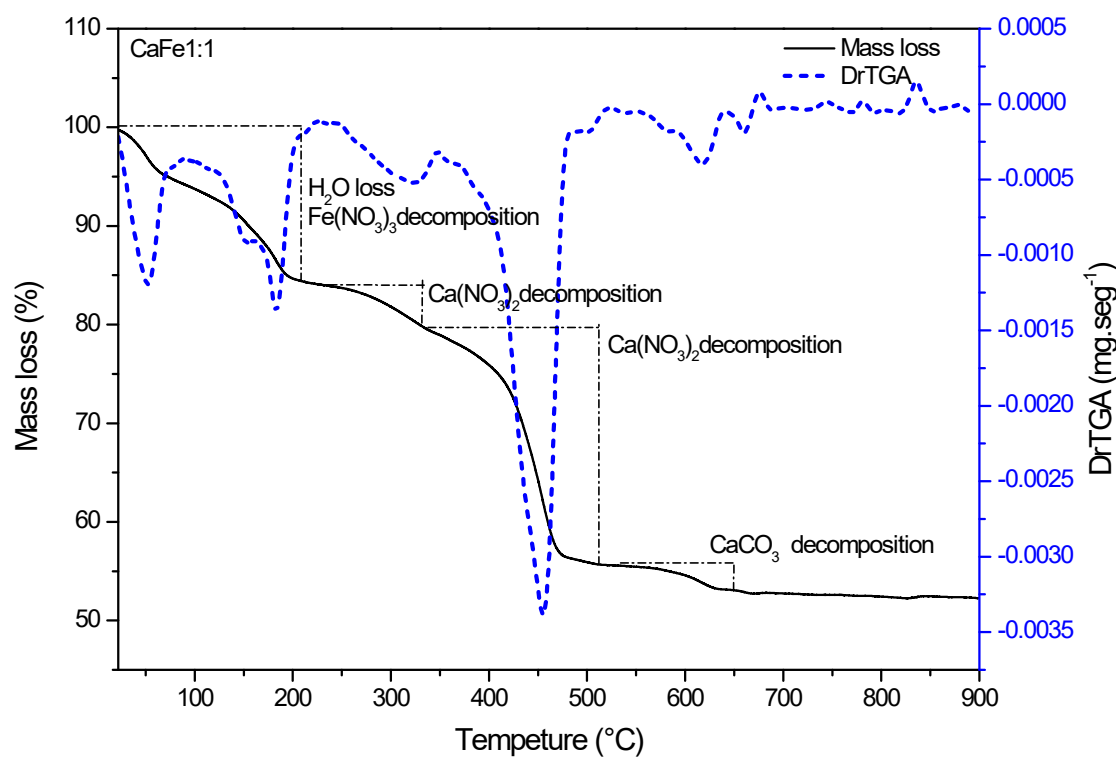
The materials are identified according to the terminology CaFeY:X-R, where Ca (calcium) is the first metal, Fe (iron) is the second metal, Y:X is the molar ratio between the first and second metal and R is the calcination temperature—a total of 20 samples ().

Table S 1: Sample codes.

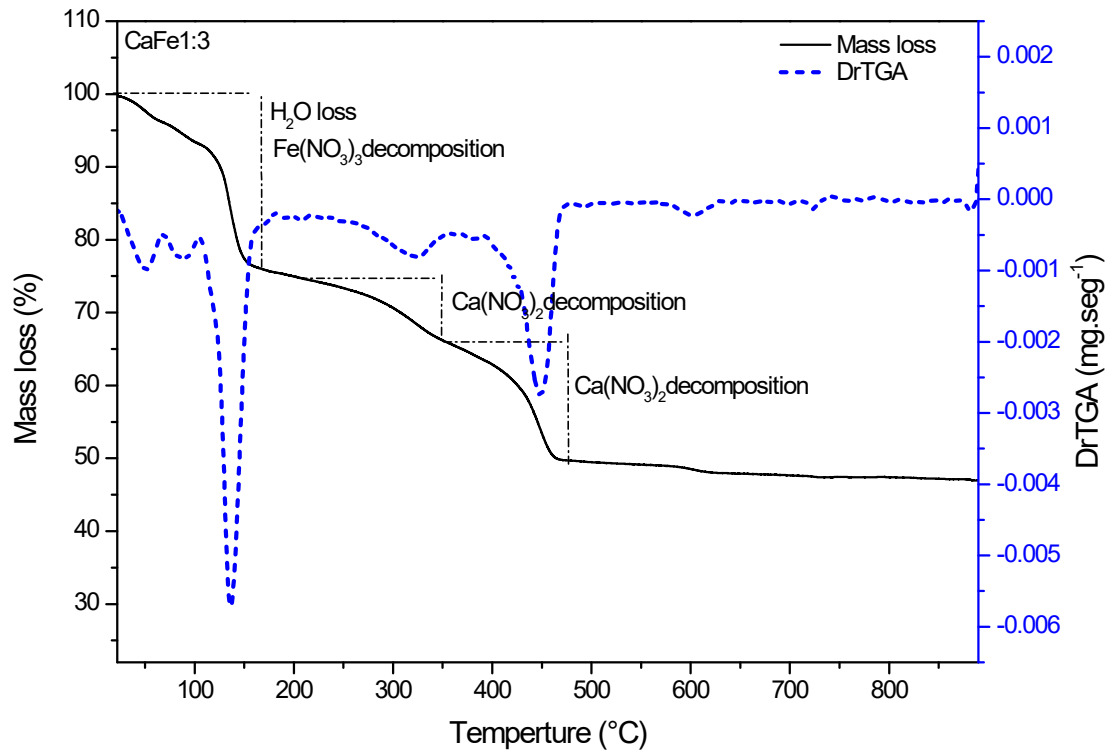
		Temperature			
		RT	300°C	700°C	900°C
Molar Proportion (Ca:Fe)	0:1	Fe	Fe300	Fe700	Fe900
	1:1	CaFe1:1	CaFe1:1-300	CaFe1:1-700	CaFe1:1-900
	1:2	CaFe1:2	CaFe1:-300	CaFe1:2-700	CaFe1:2-900
	1:3	CaFe1:3	CaFe1:3-300	CaFe1:3-700	CaFe1:3-900
	2:1	CaFe2:1	CaFe2:1-300	CaFe2:1-700	CaFe2:1-900

After calcination, the adsorbents were washed with deionized water (GEHAKA) in the water-adsorbent 1:1 (mL:mg). An adsorbent mass was kept under stirring at 200 rpm for 3h and repeated four times. The powder was dried in the incubator and kept at 90 °C for 24 hours. The supernatant was stored in a propylene tube for atomic absorption (AA) measurement in the Varian (AA740 FS) spectrophotometer.

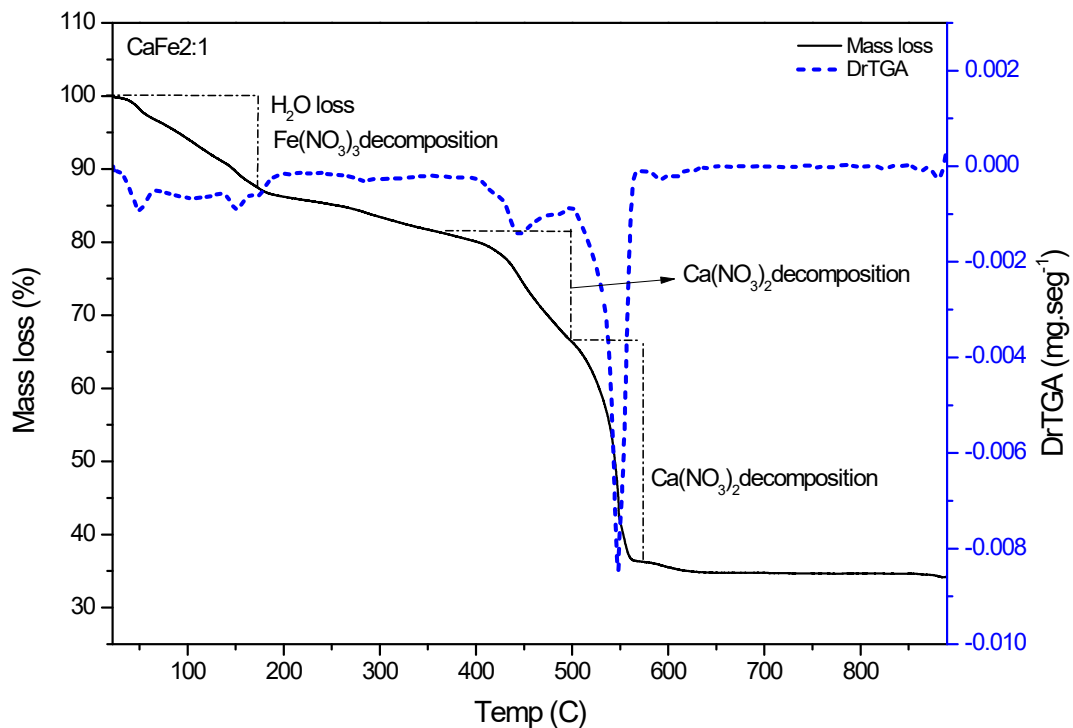
THERMAL DECOMPOSITION (DTG)



S 1: Thermal decomposition curve and DTG for the sample CaFe1:1 at air atmosphere (50 mL min⁻¹) and heating rate of 10 °C min⁻¹.

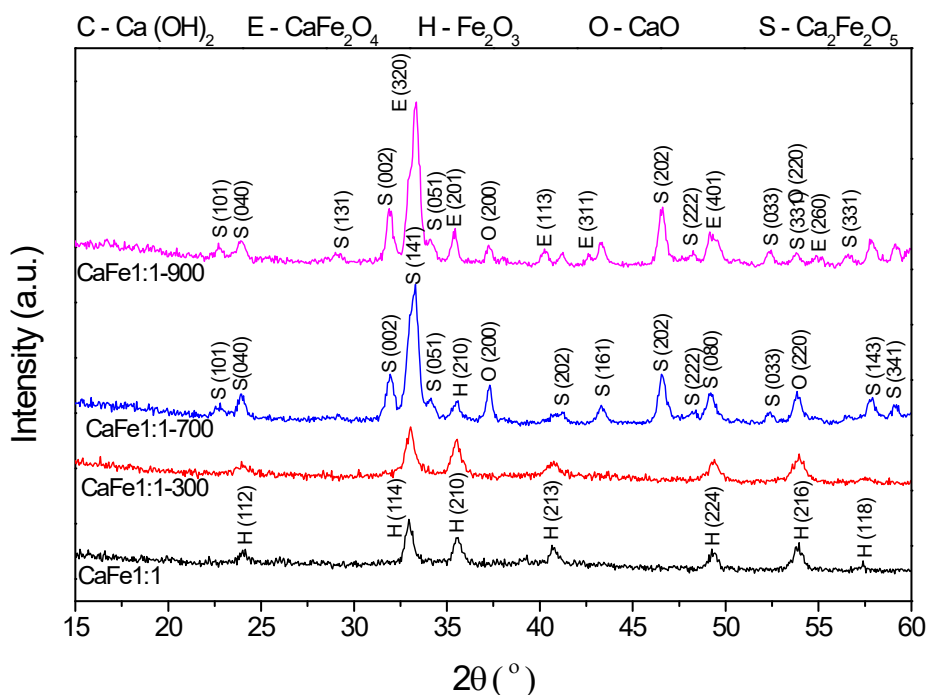


S 2: Thermal decomposition curve and DTG for the sample CaFe1:1 at air atmosphere (50 mL min⁻¹) and heating rate of 10 °C min⁻¹.

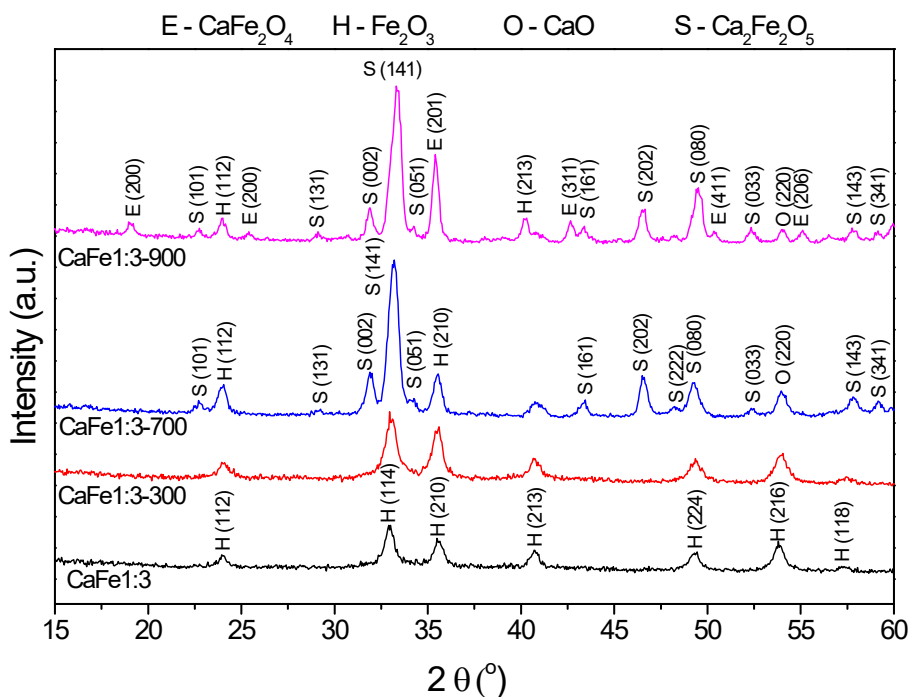


S 3: Thermal decomposition curve and DTG for the sample CaFe2:1 at air atmosphere (50 mL min⁻¹) and heating rate of 10 °C min⁻¹.

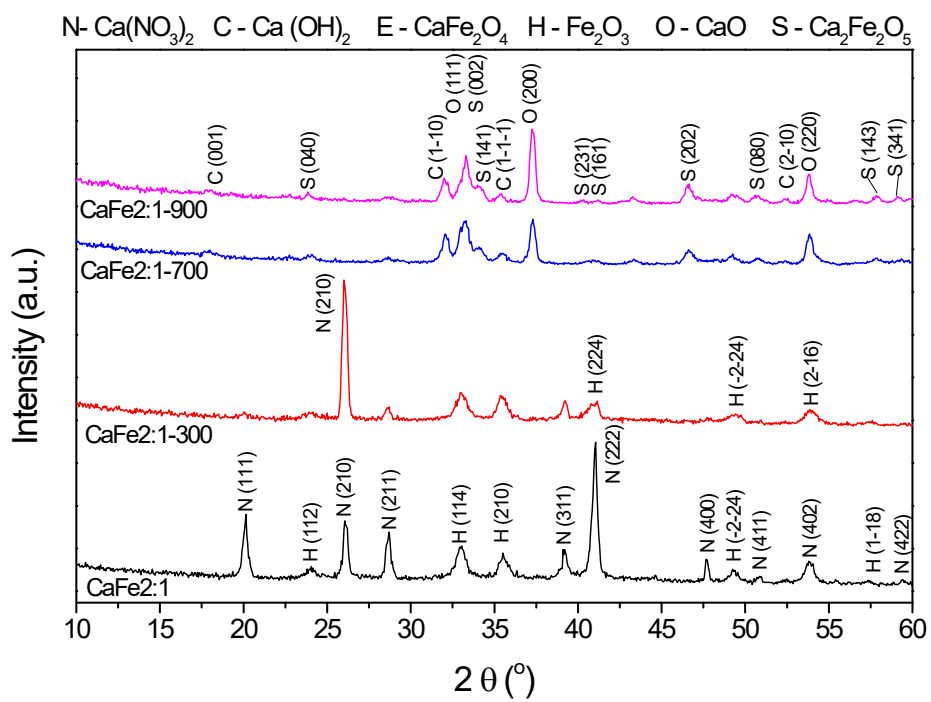
X-RAY DIFFRACTION



S 4: Diffractograms of synthetic adsorbents prepared in the molar ratio Ca:Fe 1:1 calcined at different temperatures (300, 700 and 900 °C for one hour).

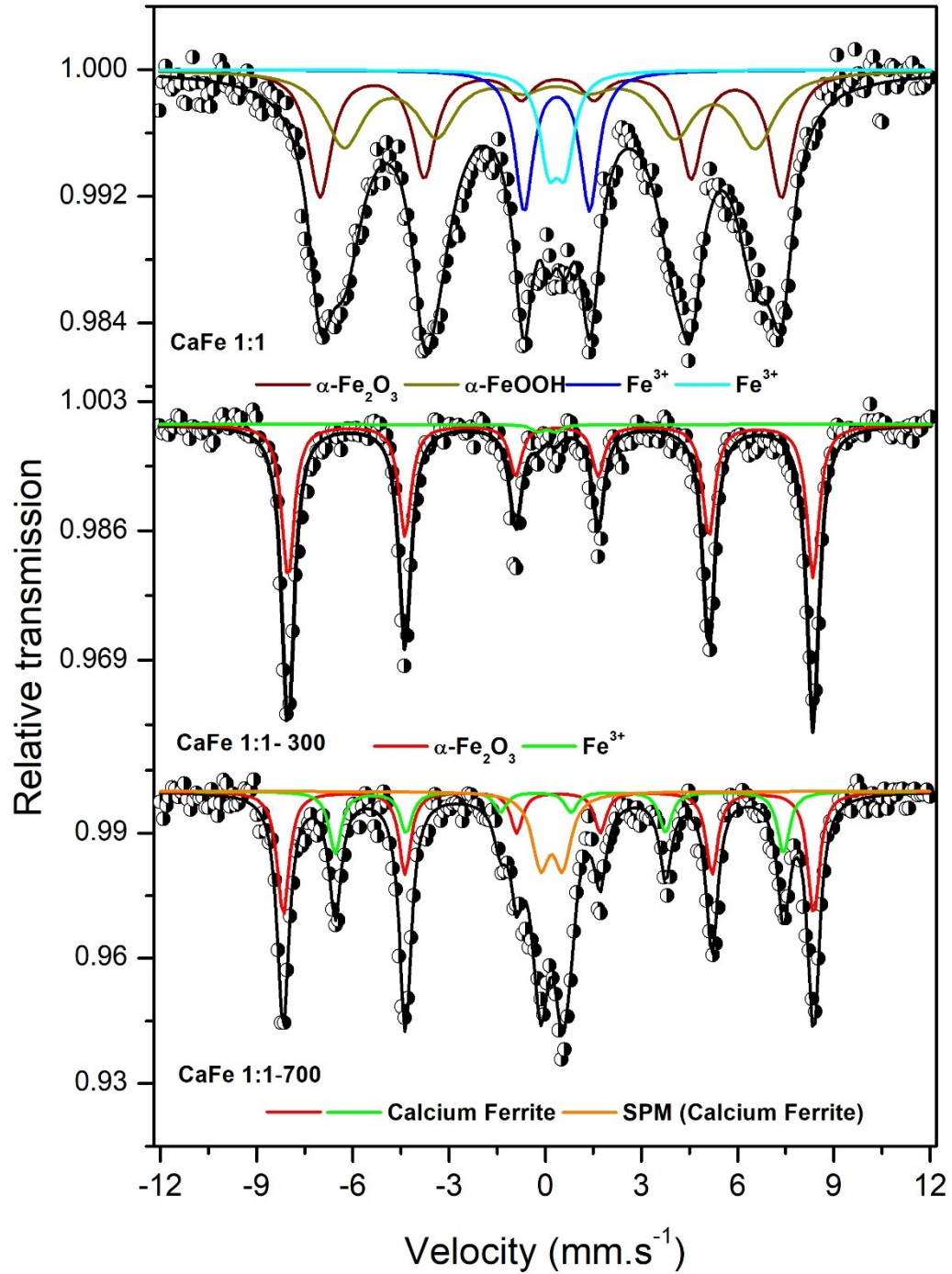


S 5: Diffractograms of synthetic adsorbents prepared in the molar ratio Ca:Fe 1:3 calcined at different temperatures (300, 700 and 900 °C for one hour).



S 6: Diffractograms of synthetic adsorbents prepared in the molar ratio Ca:Fe 2:1 calcined at different temperatures (300, 700 and 900 °C for one hour).

MÖSSBAUER SPECTROSCOPY



S 7: Mössbauer spectra at room temperature to samples in ratio CaFe 1:1 not calcined and calcined at different temperatures (300, 700 e 900 °C for one hour).

Table S 2: Hyperfine parameters obtained from Mössbauer spectra fitted with Normos software at room temperature of samples in the ratio CaFe 1:1 not calcined and calcined at different temperatures (300, 700 and 900 °C for one hour)

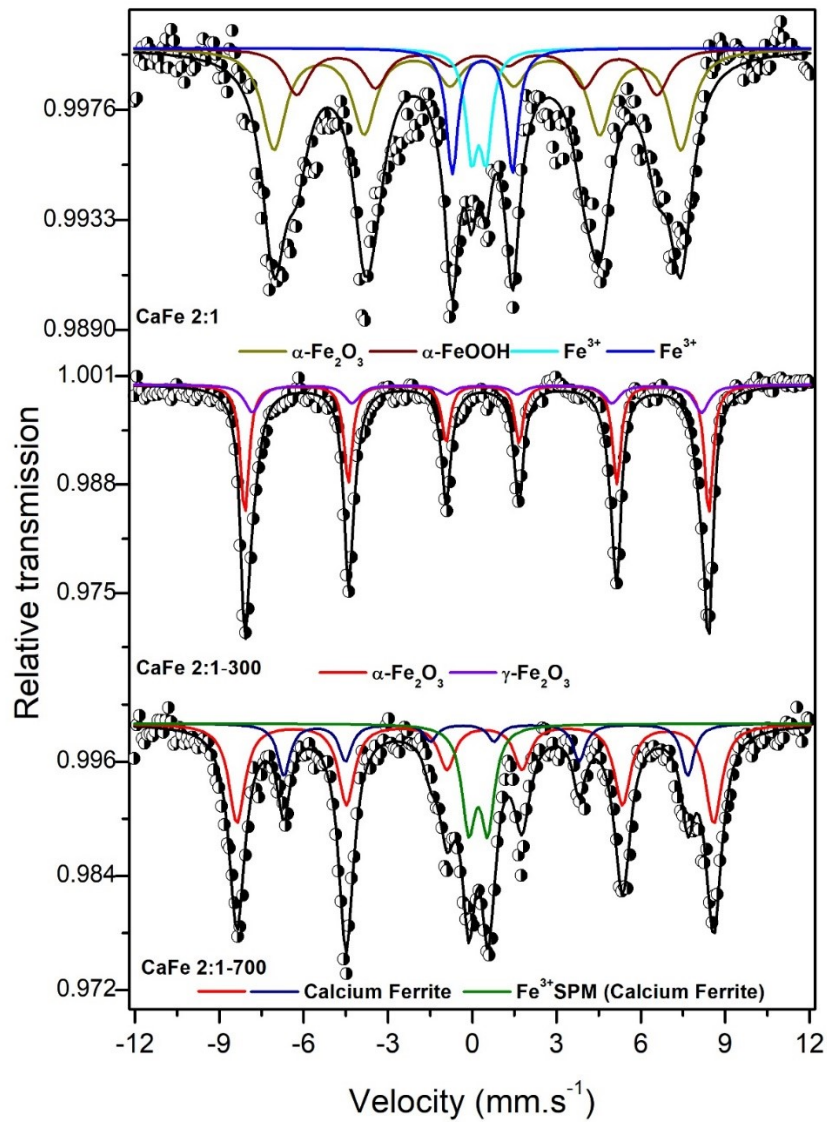
Sample	Site	$\delta (\pm 0.05)$ (mm s ⁻¹)	$\varepsilon (\pm 0.05)$ (mm s ⁻¹)	BHF (± 0.5) (T)	RA (± 1) (%)	
CaFe1:1	α -Fe ₂ O ₃	0.48	-0.21	44.6	31	
	α -FeOOH	0.33	-0.18	39.7	52	
	Fe ³⁺	0.46	2.04		11	
	Fe ³⁺	0.46	0.51		6	
CaFe1:1-300	α -Fe ₂ O ₃	0.36	-0.20	50.7	98	
	Fe ³⁺	0.20	0.55		2	
CaFe1:1-700	Calcium ferrite	Octa	0.36	-0.32	51.2	49
		Tetra	0.25	0.75	43.3	24
	Fe ³⁺ (SPM-ferrite)	0.29	0.69		27	
CaFe1:1-900	Calcium ferrite	Octa	0.21	-0.30	51.5	32
		Tetra	0.08	0.69	43.4	39
	Fe ³⁺ (SPM-ferrite)	0.27	0.51	-	29	

δ = isomer shift para α -Fe; ε = quadrupole splitting; B_{HF} = hyperfine spectra; RA = spectral relative area; octa = octahedral; tetra = tetrahedral

Table S 3: Hyperfine parameters obtained from Mössbauer spectra fitted with Normos software at room temperature of samples in the ratio CaFe 1:2 not calcined and calcined at different temperatures (300, 700 and 900 °C for one hour).

Sample	Site	$\delta (\pm 0.05)$ (mm s ⁻¹)	$\varepsilon (\pm 0.05)$ (mm s ⁻¹)	BHF (± 0.5) (T)	RA (± 1) RA (%)	
CaFe1:2	α -Fe ₂ O ₃	0.38	-0.19	44.8	48	
	α -FeOOH	0.40	-0.09	40.3	37	
	Fe ³⁺	0.48	2.08	-	8	
	Fe ³⁺	0.38	0.47	-	7	
CaFe1:2-300	α -Fe ₂ O ₃	0.36	-0.21	51.0	58	
	γ -Fe ₂ O ₃	0.33	-0.06	48.9	42	
CaFe1:2-700	Calcium ferrite	octa	0.36	-0.21	51.7	64
		tetra	0.31	-0.11	47.2	28
	Fe ³⁺ (SPM-ferrita)	0.36	0.59	-	8	
CaFe1:2-900	Calcium ferrite	Octa	0.25	-0.26	51.3	32
		Tetra	0.07	0.69	43.5	38
	Fe ³⁺ (SPM-ferrite)	0.26	0.50	-	30	

δ = isomer shift para α -Fe; ε = quadrupole splitting; B_{HF} = hyperfine spectra; RA = spectral relative area; octa = octahedral; tetra = tetrahedral

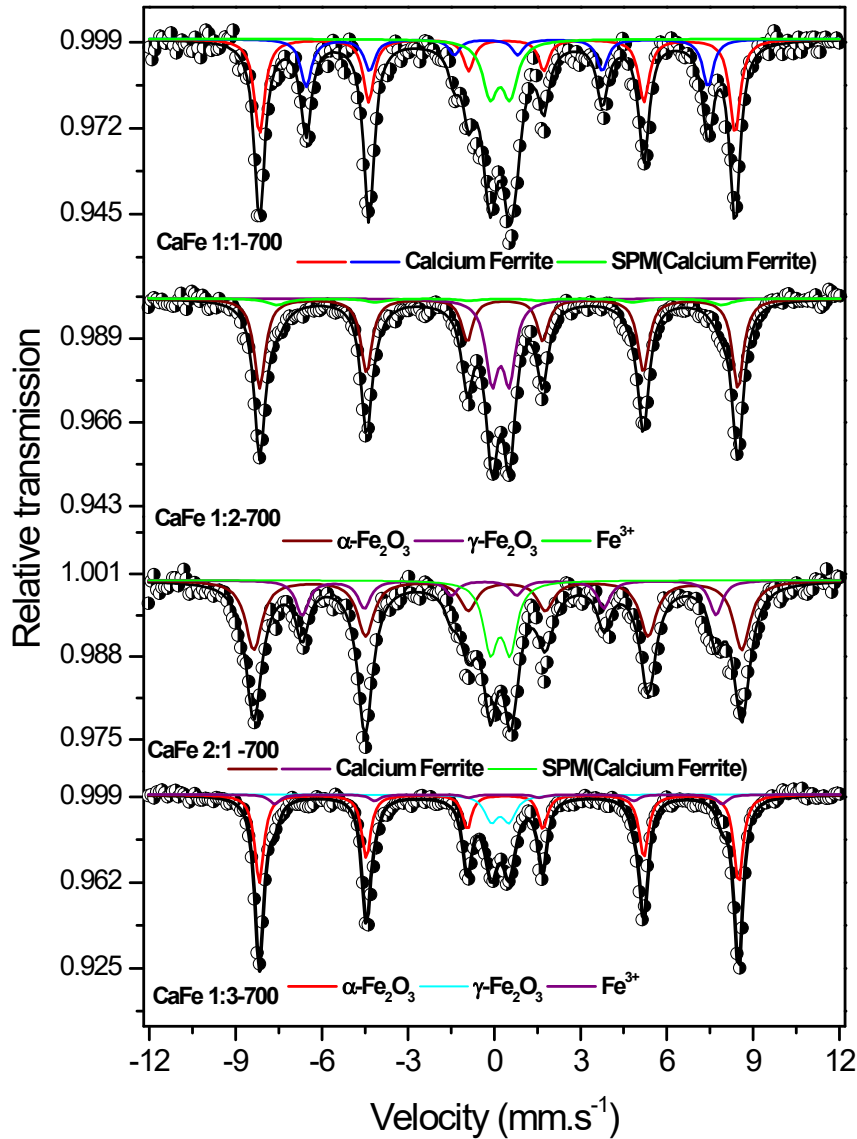


S 8: Mössbauer spectra at room temperature to samples in ratio CaFe 2:1 not calcined and calcined at different temperatures (300, 700 e 900 °C for one hour).

Table S 4: Hyperfine parameters obtained from Mössbauer spectra fitted with Normos software at room temperature of samples in the ratio CaFe 2:1 not calcined and calcined at different temperatures (300, 700 and 900 °C for one hour).

Sample	Site	$\delta (\pm 0.05)$ (mm s ⁻¹)	$\varepsilon (\pm 0.05)$ (mm s ⁻¹)	BHF (± 0.5) (T)	RA (± 1) (%)	
CaFe2:1	α -Fe ₂ O ₃	0.36	-0.15	44.8	58	
	α -FeOOH	0.31	-0.09	39.7	27	
	Fe ³⁺	0.46	2.14	-	8	
	Fe ³⁺	0.43	0.52	-	7	
CaFe2:1-300	α -Fe ₂ O ₃	0.36	-0.20	51.1	61	
	Fe ³⁺	0.350	-0.18	49.5	39	
CaFe2:1-700	Calcium ferrite	octa	0.37	-0.32	51.7	62
		tetra	0.19	0.87	44.4	19
	Fe ³⁺ (SPM-ferrite)	0.30	0.68	-	19	
CaFe2:1-900	Calcium ferrite	Octa	0.20	-0.29	51.0	34
		Tetra	0.10	0.66	43.5	36
	Fe ³⁺ (SPM-ferrite)	0.26	0.50	-	30	

δ = isomer shift para α -Fe; ε = quadrupole splitting; B_{HF} = hyperfine spectra; RA = spectral relative area; octa = octahedral; tetra = tetrahedral

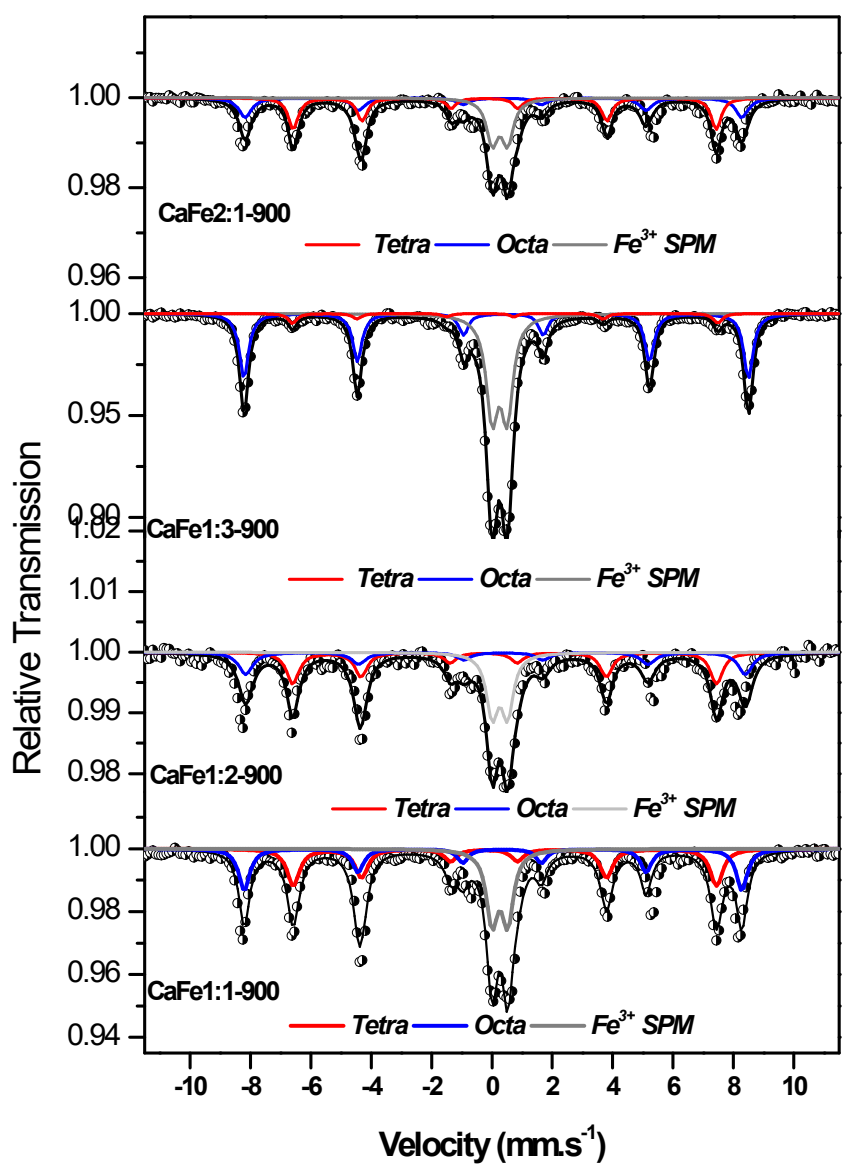


S 9: Mössbauer spectra at room temperature to samples in different ratios CaFe (1:1; 1:2; 2:1 and 1:3) calcined at 700 °C for one hour.

Table S 5: Hyperfine parameters obtained from Mössbauer spectra fitted with Normos software at room temperature of samples in the ratio CaFe 1:3 not calcined and calcined at different temperatures (300, 700 and 900 °C for one hour).

Sample	Site	$\delta (\pm 0.05)$ (mm s ⁻¹)	$\varepsilon (\pm 0.05)$ (mm s ⁻¹)	BHF (± 0.5) (T)	RA (± 1) (%)
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CaFe1:3		Octa	0,26	-0.18	41.7	60
		Tetra	0.27	-0.16	35.9	20
		Fe ³⁺	0.23	1.02	-	20
CaFe1:3- 300		α -Fe ₂ O ₃	0.27	-0.21	51.6	73
		γ -Fe ₂ O ₃	0.25	-0.15	49.8	23
		Fe ³⁺	0.36	2.5	-	4
CaFe1:3- 700	Calcium ferrite	Octa	0.26	-0.26	51.5	76
		Tetra	0.09	0.71	43.4	20
		Fe ³⁺ (SPM-ferrite)	0.49	2.30	-	4
CaFe1:3-900	Calcium ferrite	Octa	0.26	-0.23	51.8	44
		Tetra	0.03	0.81	43.7	5
		Fe ³⁺ (SPM-ferrite)	0.25	0.49	-	51



S 10: Mössbauer spectra at room temperature to samples in different ratio CaFe (1:1; 1:2; 2:1 and 1:3) calcined at 900 °C for one hour .

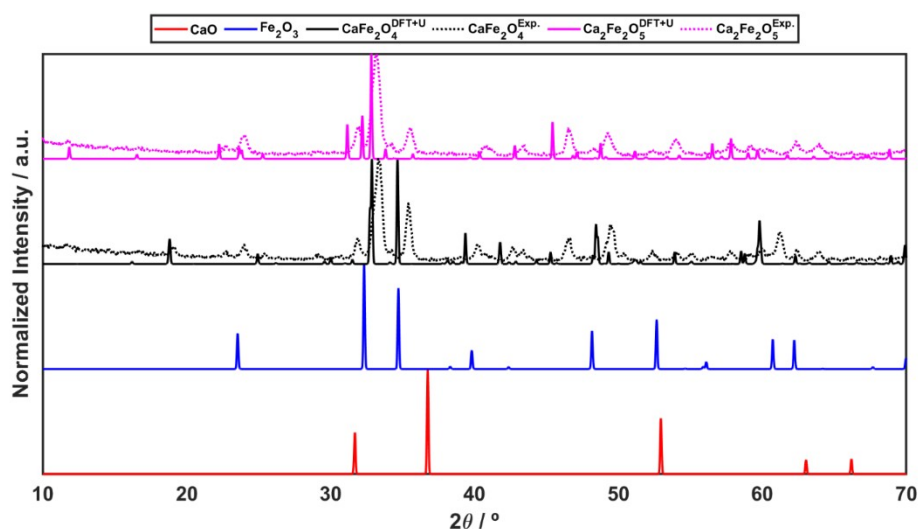
THEORETICAL STUDIES

Structural properties and iron local environments

The structural properties are summarized in Table S 5. Our computed lattice parameters of the orthorhombic unit cell are in reasonably good agreement with the reported experimental values.^{1,2} Consistent with typical GGA functionals, our lattice parameters are slightly overestimated compared to the experimental ones, resulting in about 2% overestimation in volume. Table S 5 also presents the octahedral distortion parameters, such as angles and bond lengths between Fe – O atoms.

Table S 6: Structural properties and iron environment parameters obtained using DFT+U approach: Lattice parameters, volume (V), average distances $\langle \text{Ca} - \text{O} \rangle$, $\langle \text{Fe} - \text{O} \rangle$, and Fe-distortion parameters.

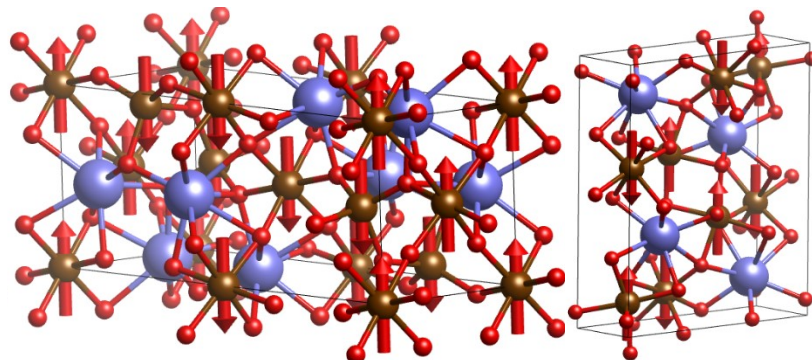
Properties	Systems	
	$\text{Ca}_2\text{Fe}_2\text{O}_5$	CaFeO_4
Lattice Parameter, (Å)	a = 5.55	a = 9.42
	b = 14.93	b = 3.09
	c = 5.73	c = 10.93
Volume, (Å ³)	475.64	318.35
Fe – O, (Å)	Fe _{Oh} 2.17 2.03	2.09
	Fe _{Td} 1.87 1.96	
Ca – O, (Å)	2.51	2.49
O – Fe – O, (°)	Eq. – Ax. 87.7	Eq. – Ax. 91.0
	Ax. – Ax. 92.7	
	Fe _{Td} 108.4	Ax. – Ax. 86.5



S 11: X-Ray diffraction calculated x experimental.

Electronic properties

We determine the lowest energy magnetic structure of systems, we have considered all combinations of magnetic ordering (S 12) the antiferromagnetic ordering, where the coupling between the Fe atoms, both inter and intra-planar, are antiferromagnetic, is the lowest in energy.



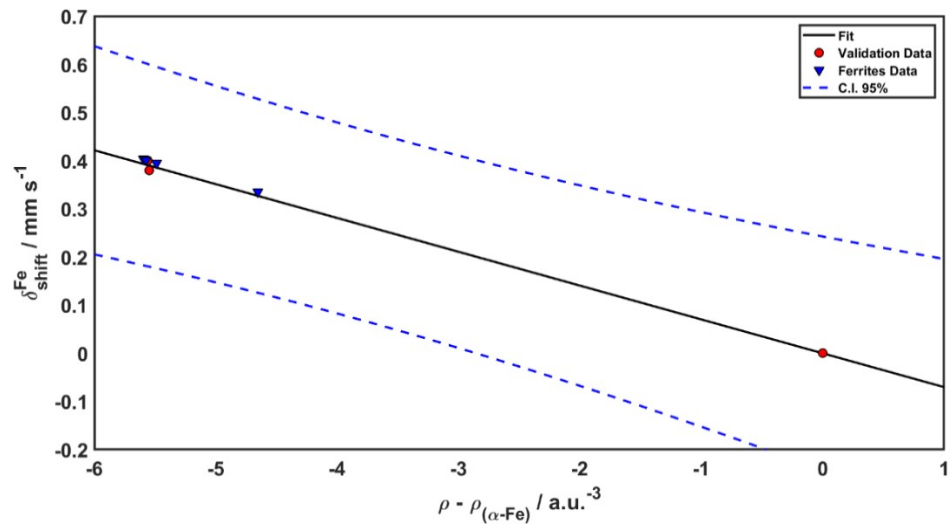
S 12: Spin polarization study to $\text{Ca}_2\text{Fe}_2\text{O}_5$ (left) and CaFeO_4 (right). The arrows represent the spin ordering.

We determined the band gap to the bulk, magnetics local moments, Bader charges and isomer shift (δ) predictions by the DFT+U calculations at each Fe-atomic site (Table S 6).

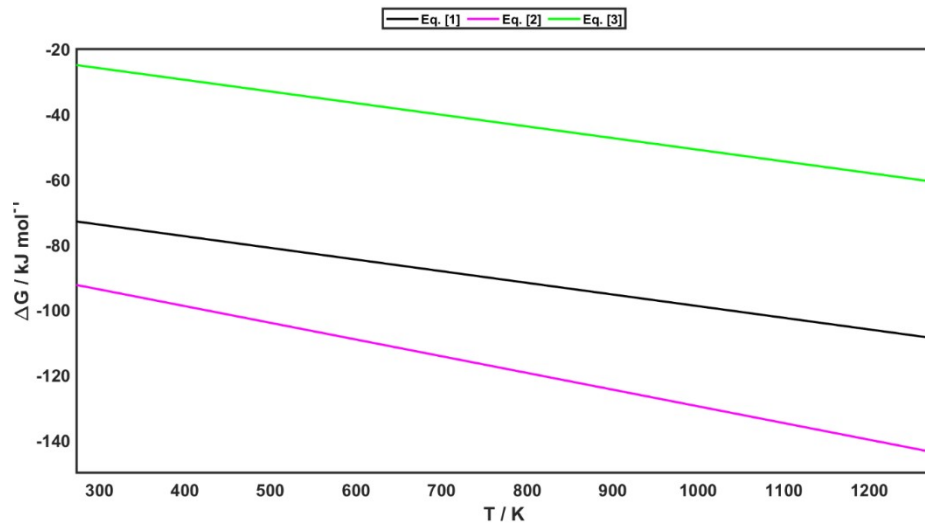
Table S 7: The calculated Fe local magnetic moments (m_s) and the band gap (Δ_g) and comparison of isomer shift (δ) predictions expressed in mm s^{-1} . Fe oxidation state assignment is based on the total magnetization analysis.

Properties	Systems			
	$\text{Ca}_2\text{Fe}_2\text{O}_5$		CaFeO_4	
	DFT+U	Source	DFT+U	Source
m_s , (μ_B)	3.6 (Fe_{Td}) 3.7 (Fe_{Oh})	3.7 – 4.3 ³	3.8	4.1 – 4.3 ^{2,4}
Δ_g , (eV)	1.9	2.0 – 2.2 ⁵	1.8	1.9 ⁶
δ , (mm s^{-1})	0.33 (Fe_{Td}) 0.39 (Fe_{Oh})	0.31 (Fe_{Td}) 0.36 (Fe_{Oh})	0.40	0.07 – 0.25
Bader charges	+1.61 (Fe_{Td}) +1.73 (Fe_{Oh})	+3.00*	+1.75	+3.00*

* Nominal charge.

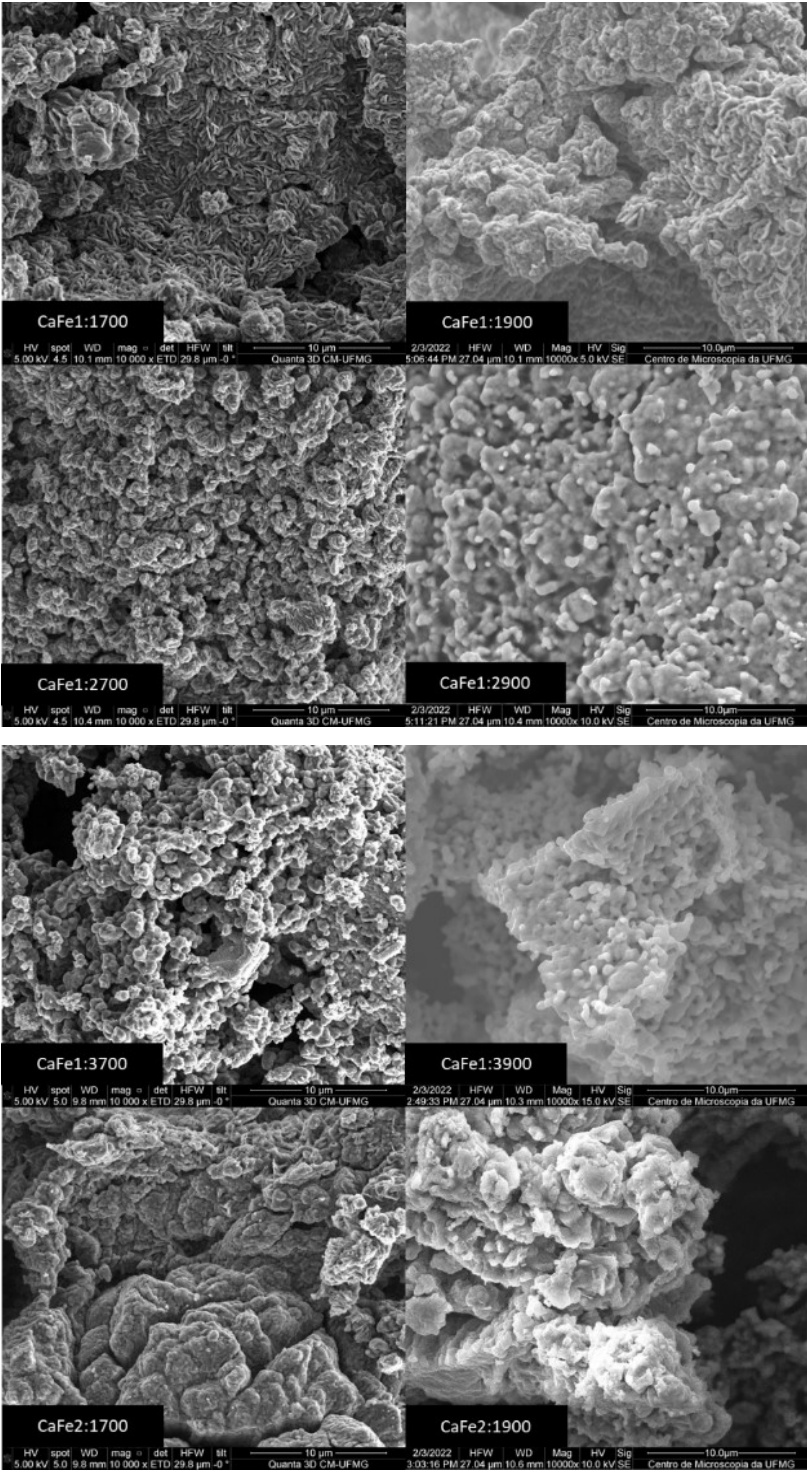


S 13: Mössbauer Calibration.

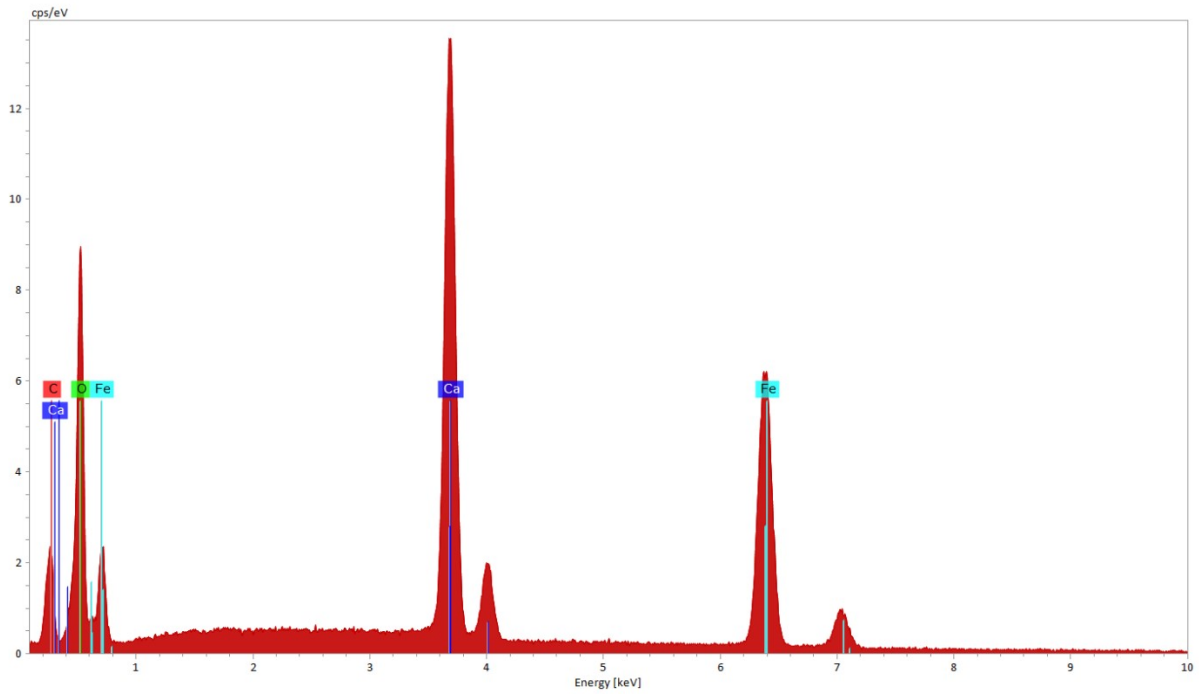


S 14: Phase Transition.

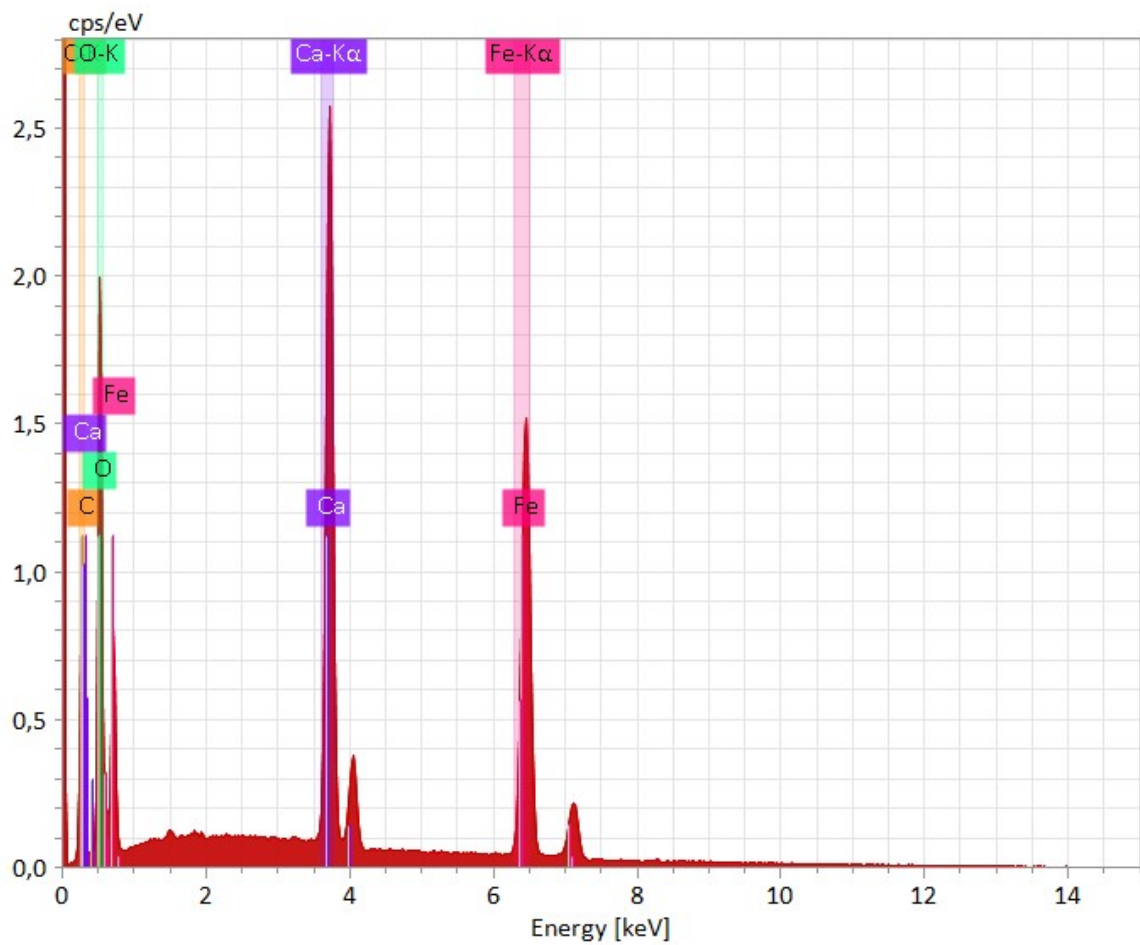
ELECTRON SCANNING MICROSCOPE AND ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (EDS)



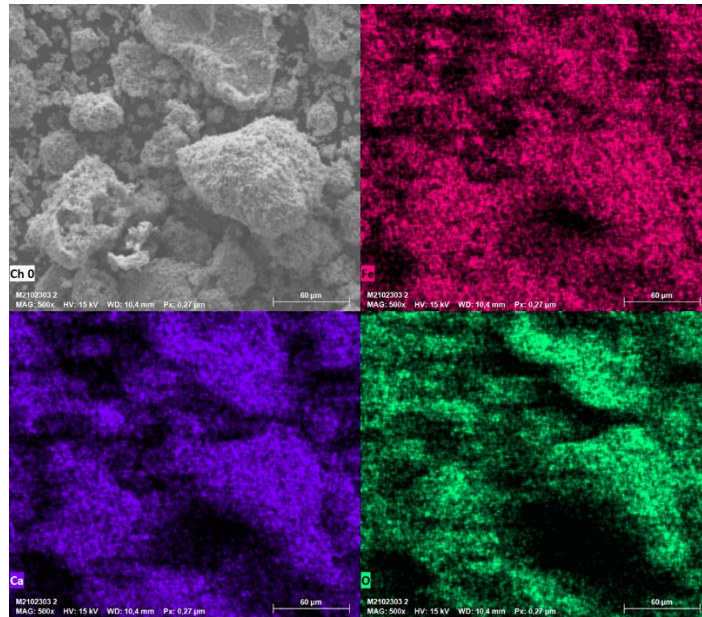
S 15: Adsorbent materials in different proportions Ca:Fe (1:1; 1:2; 1:3 and 2:1) calcined at 700 and 900°C for one hour submitted to morphological analysis at 10000x magnification.



S 16: Energy-Dispersive X-ray Spectroscopy (EDS) spectra for sample CaFe12-700.



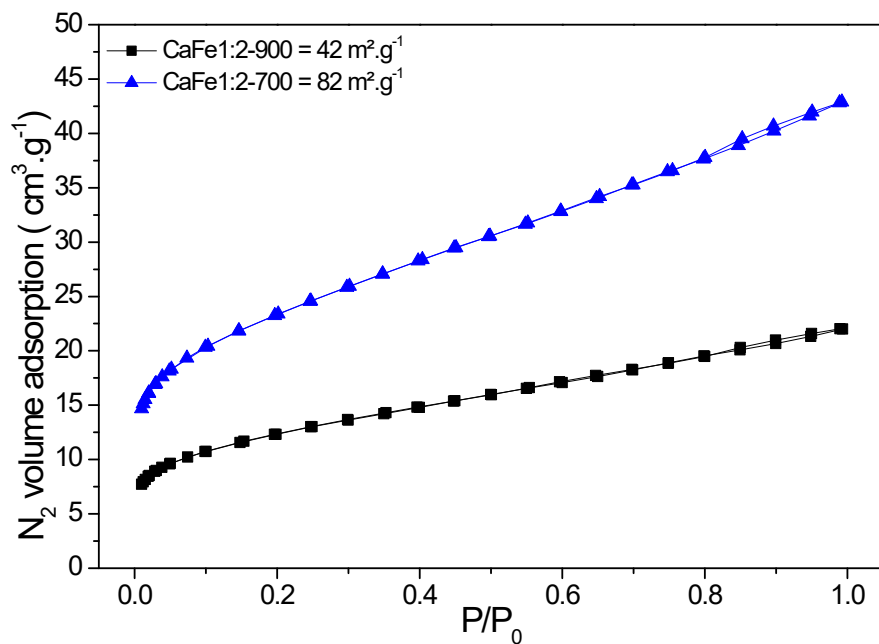
S 17: Energy-Dispersive X-ray Spectroscopy (EDS) spectra for sample CaFe12-900.



S 18: Chemical mapping images for sample CaFe1:2-900.

*The carbon signal indicated by the spectrum refers to the carbon ribbon and carbon deposition in sample preparation.

N₂ ADSORPTION-DESORPTION ISOTHERM AND SUPERFICIAL AREA (BET)

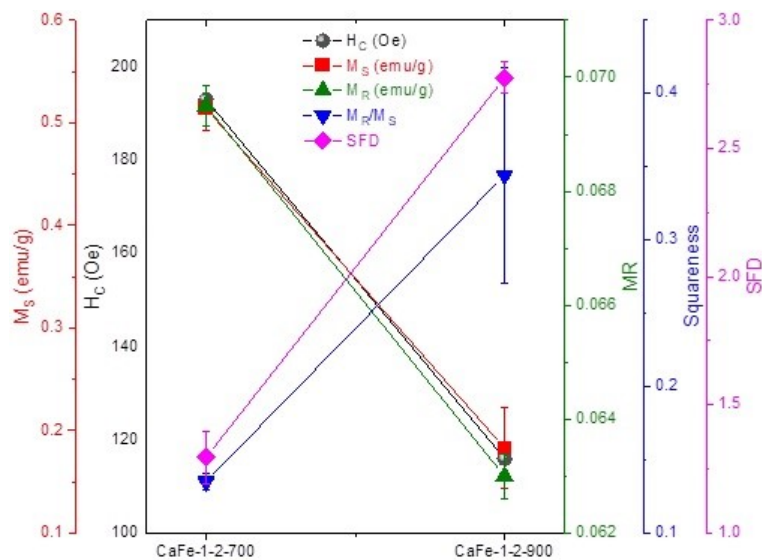


S 19: N₂ adsorption-desorption isotherm and BET surface area for samples CaFe1:2-700 (black) and CaFe1:2-900 (blue).

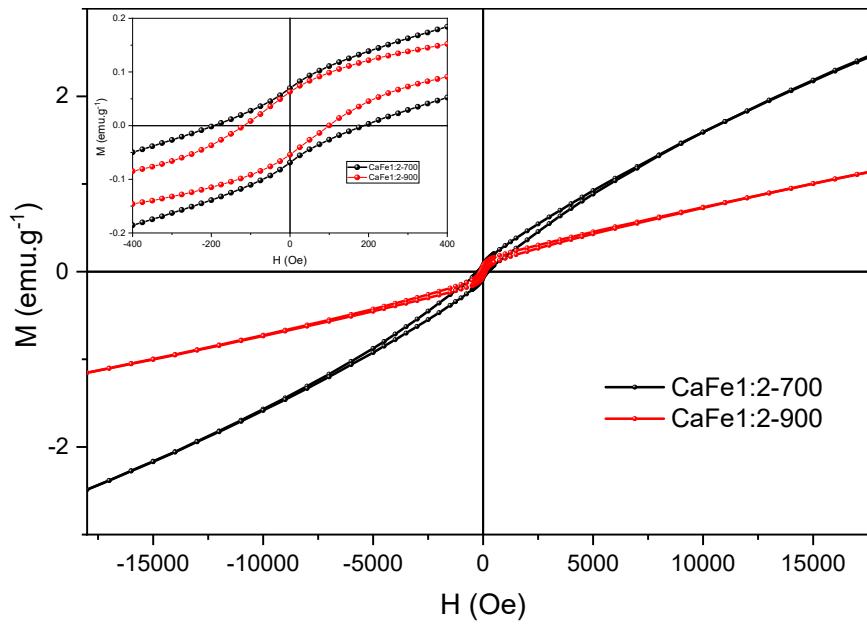
VIBRATING SAMPLE MAGNETOMETER (VSM)

Vibrating Sample Magnetometer (VSM) was used to measure the magnetic properties of different samples. Figure S 17 shows the room temperature field-dependent magnetization curve recorded for CaFe1:2-700 and CaFe1:2-900 samples. The magnetic loop indicates a

ferromagnetic material formed with coercivity and remanent magnetization (M_r) close to zero. The samples show low saturation magnetization (M_s), 2.5 emu g^{-1} for CaFe1:2-700 and 1.25 emu g^{-1} for CaFe1:2-900. As shown, the saturation magnetization of CaFe1:2-900 is half that of CaFe1:2-700. High treatment temperatures increase the grain size, as observed in X-ray diffraction, which can increase the magnetic domain and consequently reduce magnetic interactions, thus decreasing the coercivity and magnetization of the samples. In addition, as observed by Mössbauer spectroscopy, the sample with the highest heat treatment at $900 \text{ }^\circ\text{C}$ has a larger fraction of Fe^{3+} superparamagnetic (SP) phases, which is confirmed by the reduction of the magnetization value of these samples. Thus, when measuring the magnetic hysteresis at ambient temperature, this superparamagnetic phase of Fe^{3+} seen in the Mössbauer overlaps the paramagnetic signal of calcium, effectively reducing the M_s and H_c of the loop.



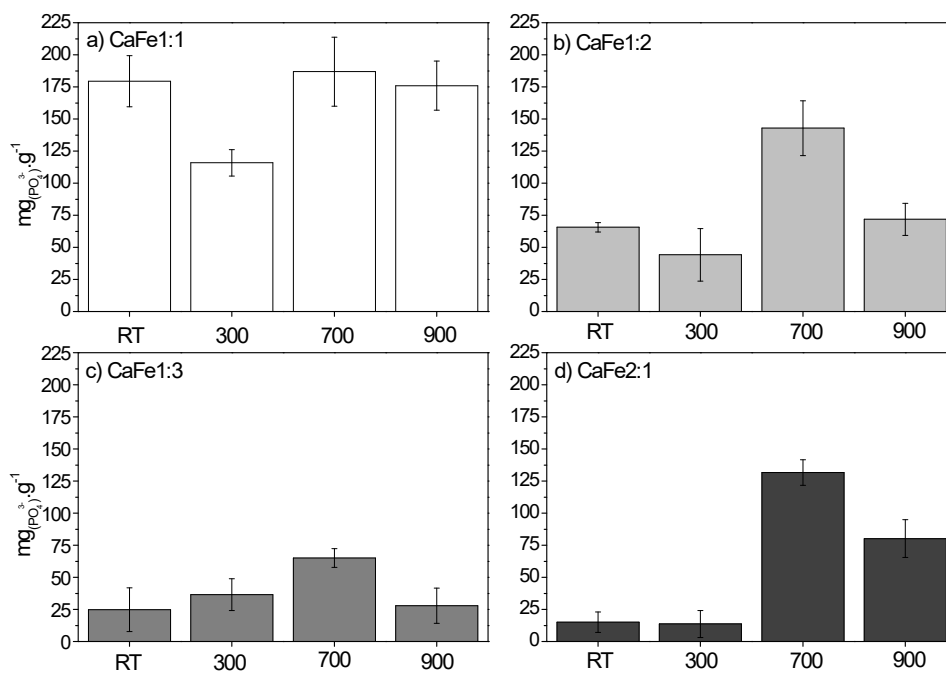
S 20: Values of the magnetic properties of calcium ferrites in the proportion 1:2 at treatment temperatures at $700 \text{ }^\circ\text{C}$ and $900 \text{ }^\circ\text{C}$ obtained from the hysteresis curves. Where H_c , M_r , M_s , Squareness and SFD are respectively the coercive field, remanent magnetization.



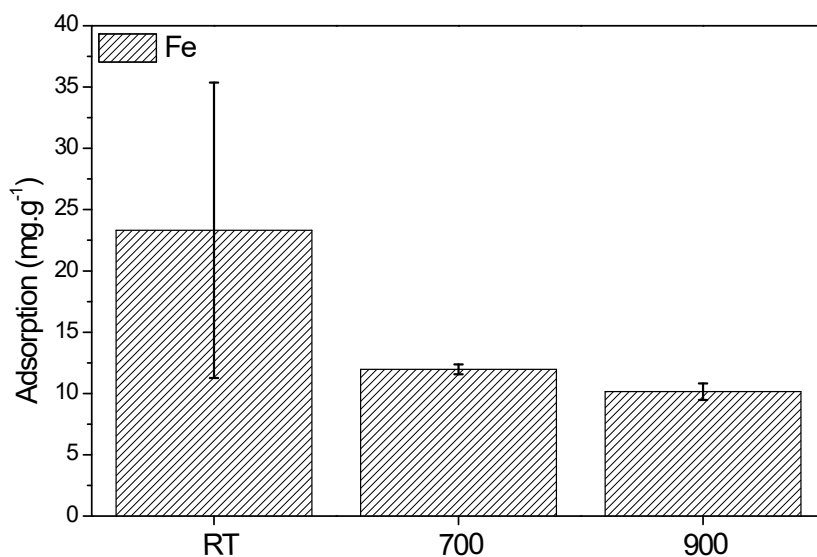
S 21: Hysteresis loops for $\text{CaFe}_{1:2}$ heat treatment samples at 700 °C and 900 °C for one hour.

PRELIMINARY TEST FOR PHOSPHATE REMOVAL CAPACITY FOR UNWASHED MATERIALS

Adsorption tests for unwashed samples are present in **S 19** the removal capacity (from 13.8 mg g⁻¹ for sample CaFe2:1-300 to 187.0 mg g⁻¹ for sample CaFe1:1-700) than washed materials (with a range of 7.8 mg g⁻¹ for sample CaFe1:3-300 to 62.2 mg g⁻¹ for sample CaFe1:2-700). The high adsorption capacity for unwashed samples can occur because of the CaO and Ca(OH)₂ observed by XRD; these materials can promote phosphate precipitations⁷. The Supplementary Material (S 21 and S 22) shows that samples leach Ca²⁺ and Fe³⁺ ions with a phosphate capture capacity. In addition, the unwashed samples uncalcined and calcined at 300°C for one hour show a low phosphate removal capacity compared to 700 and 900°C for one hour of samples unwashed, even presenting a high leach of Ca²⁺ and Fe³⁺.

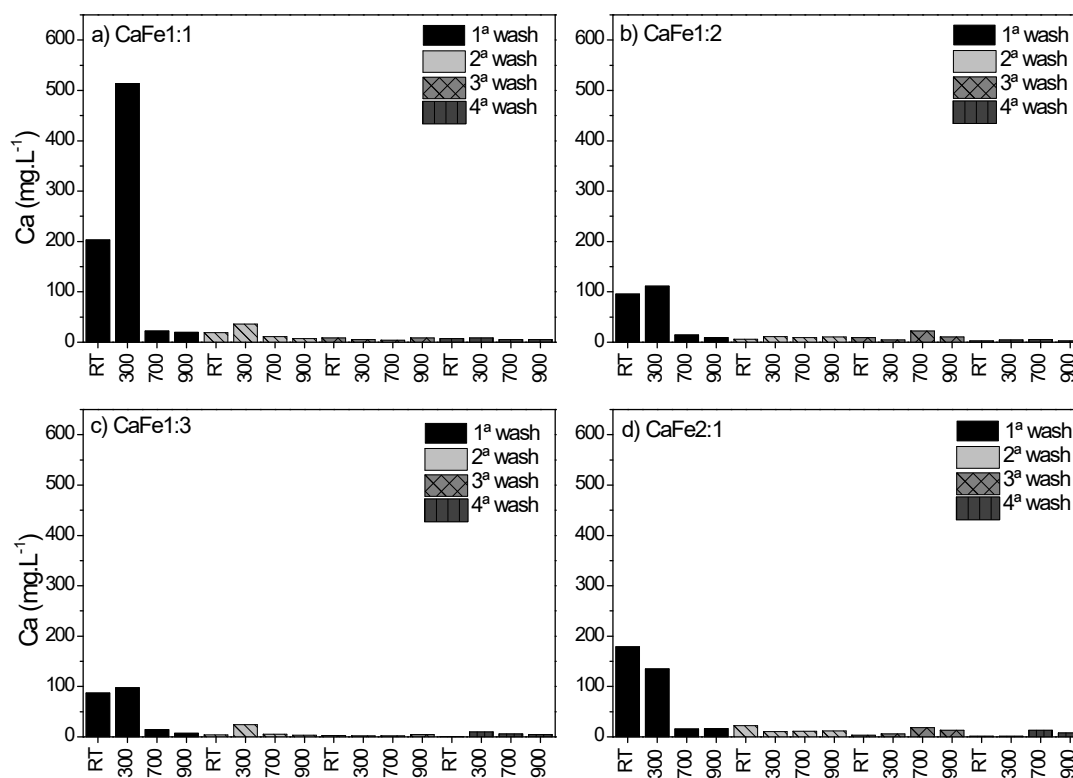


S 22: Preliminary phosphate removal test (100 mg.L⁻¹) results for unwashed samples in Ca:Fe ratios 1:1, 1:2, 1:3 and 2:1 uncalcined (RT) and calcined at 300, 700 and 900 °C for one hour .



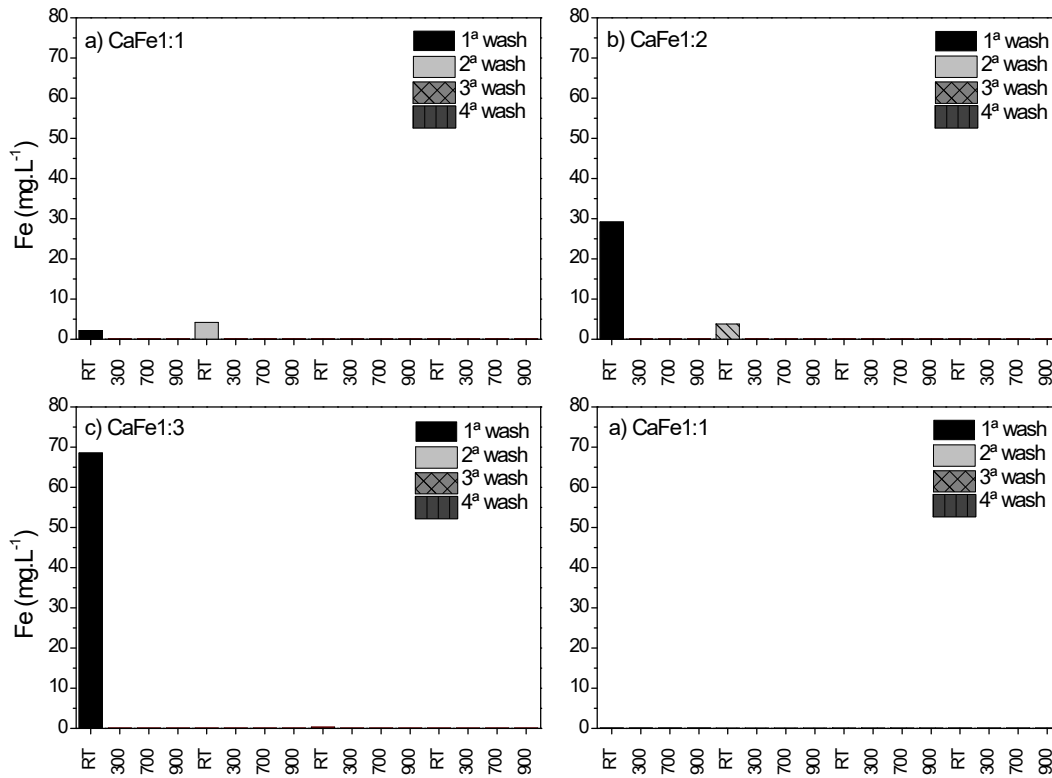
S 23: Preliminary phosphate removal test (100 mg.L^{-1}) results for iron nitrate uncalcined (RT) and calcined at 700 and 900 °C for one hour .

CALCIUM LEACH TEST



S 24: Evaluation of Ca release during 4 washes for the different Ca:Fe ratios (1:1; 1:2; 1:3 and 2:1) uncalcined and calcined at (300, 700 and 900 °C for one hour).

IRON LEACH TEST



S 25: Evaluation of Fe release during 4 washes for the different Ca:Fe ratios (1:1; 1:2; 1:3 and 2:1) uncalcined and calcined at (300, 700 and 900 °C for one hour).

INFLUENCE OF ADSORBATE DOSE – ISOTHERM

Table S 8: Isotherm models

Isotherm model		Equation	Reference
Two parameters isotherm	<i>Langmuir</i>	$q_e = \frac{Q_0 b C_e}{1 + b C_e}$	8-11
	<i>Freundlich</i>	$q_e = K_F C_e^{\frac{1}{n}}$	
	<i>Temkin</i>	$q_e = \frac{RT}{b_T} \ln A_T C_e$	
Tree parameters isotherm	<i>Redlich–Peterson</i>	$q_e = \frac{K_R C_e}{1 + a_R C_e^n}$	

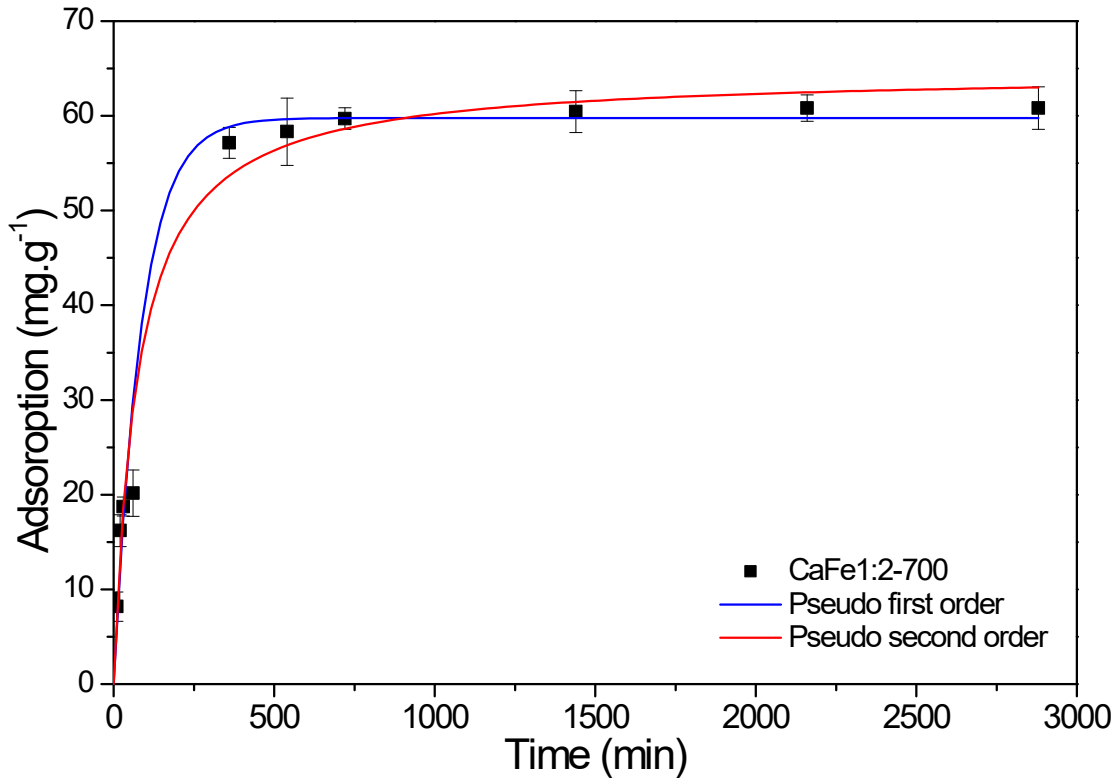
Table S 9: Parameters of the calculated isotherm models for samples CaFe1:2-700 and CaFe1:2-900.

Isotherm model	Parameter	Sample	
		CaFe1:2-700	CaFe1:2-900
Langmuir	k_l	0.1012	6.8576
	q_{max}	78.3	36.44
	R^2	0.9438	0.9231
Freundlich	n	5.5478	48.8128
	K_f	30.0427	32.7470
	R^2	0.8798	0.8867
Temkin	A	3.3151	$2.99868 \cdot 10^{18}$
	b	12.1820	0.7648
	R^2	0.9005	0.8887
Redlich–Peterson	K	4.9901	103.2180
	a	0.0249	1.9223
	n	1.1897	1.0940
	R^2	0.9487	0.9621

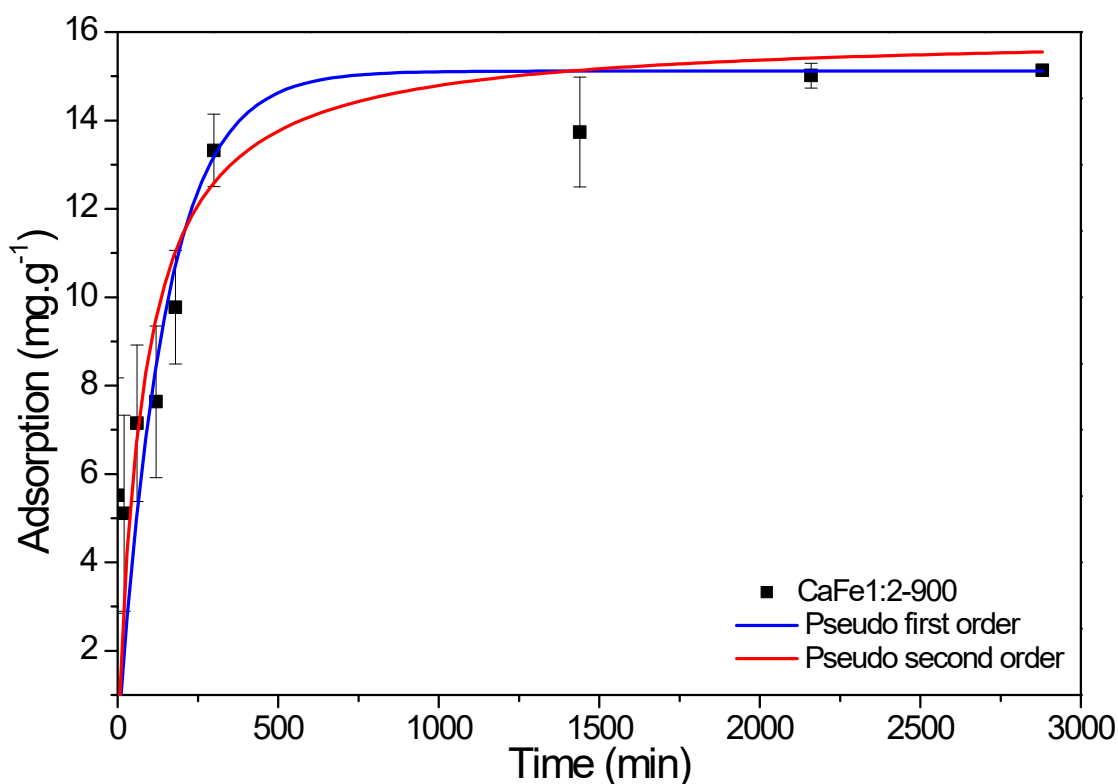
CONTACT TIME INFLUENCE – KINETICS

Contact time adsorbent/adsorbate is critical to understand the adsorption process and applications. Figures **S 26** and **S 27** show the phosphate adsorbed quantity along the contact time to CaFe1:2-700 and CaFe1:2-900. The figures show that adsorption capacity increases with time. Both samples show an adsorption equilibrium near 400 min, suggesting the material is saturated after 6 hours. **S 26** shows that the adsorption process could be divided into two steps to CaFe1:2-700. From 0 to 4 hours, 20.2 mg g⁻¹ (33.4%) of the equilibrium adsorption capacity was achieved in the first and quick step. In the second, after 8 hours, 95% of the maximum adsorption occurred. In the sample CaFe1:2-900, kinetic adsorption reaches 89% (13.4 mg g⁻¹) of the equilibrium adsorption capacity after 6 hours **S 27**.

The results show that the two kinetics models fitted for CaFe1:2-700 have a satisfactory agreement. Pseudo-first-order kinetics with q_e 59.7 mg g⁻¹ and fit of R^2 0.9400 indicates that only one adsorbate ion is adsorbed by the material's surface. The pseudo-second-order shows q_e calculated 64.6 mg g⁻¹ with R^2 0.9409 (**Table S 10**), indicating that the adsorption process is governed by a limiting step controlled by chemisorption. Both kinetic models probably coexist in the sample CaFe1:2-700 adsorption process¹². For the CaFe1:2-900 sample, the pseudo-second-order kinetic model best describes the data, with R^2 0.9583 and q_e 15.1 mg g⁻¹ (**Table S 10**). The pseudo-second-order model indicates that the adsorption process is governed by a limiting step controlled by chemisorption¹².



S 26: Adsorption kinetics for the sample CaFe1:2-700.



S 27: Adsorption kinetics for the sample CaFe1:2-900.

Table S 10: Parameters of kinetic models calculated for samples CaFe1:2-700 and CaFe1:2-900.

Sample	Kinetics Model	k	q _e (calculated)	Q _e (experimental) (mg g ⁻¹)	R ²
CaFe1:2-700	Pseudo 1 ^a order	0.0116	59.7	61.1	0.9400
	Pseudo 2 ^a order	2.1133.10 ⁻⁴	64.6		0.9409
CaFe1:2-900	Pseudo 1 ^a order	0.00686	15.1	15.1	0.8812
	Pseudo 2 ^a order	7.7208.10 ⁻⁴	15.9		0.9583

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