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ARTICLE

Diagnosis of Native Iron Compounds and Some Basrah Soils Fertilized with Iron and Agricultural Sulfur

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ABSTRACT

This study was conducted to diagnose native iron compounds in some selected calcareous soils of Basrah Province, south of Iraq, and evaluate effect of iron and agricultural sulfur fertilization on its chemical reactions under wetting–drying cycles. Ten soil samples were collected from different locations of uncultivated soils, and a laboratory incubation experiments was using with three levels of iron (0, 25, and 50 kg Fe ha^{-1} as $FeSO_4 \cdot 7H_2O$) and three levels of agricultural sulfur (0, 1000, and 2000 kg S ha^{-1}), in the presence of organic matter as cattle manure (2.5%). Soil samples were incubated under two wetting–drying cycles. Chemical and physical properties of soils (pH, electrical conductivity (EC), soluble iron, and sulfate) were measured. The Ion Activity Product (IAP) and Saturation Index (SI) were calculated to identify dominant iron minerals. Results indicated that hematite (½α-Fe_2O_3) was the dominant native iron mineral in all studied soils during the first wetting–drying cycle (SI > 1), while siderite ($FeCO_3$) and Fe $(OH)_3$ were not detected (SI < 1). Application of iron and sulfur fertilizers reduced SI and IAP values, reflecting increased iron availability in soil solution. During the second wetting–drying cycle, mineral composition shifted, with the formation of Fe $(OH)_3$, hematite, and siderite (SI > 1), although hematite remained dominant. The increase in SI and IAP values was associated with enhanced iron activity due to fertilization and sulfur-induced acidification. The study indicates the significant role of agricultural sulfur in improving iron availability in calcareous soils through pH decreasing and mineral transformation, particularly under repeated wetting–drying conditions.

Keywords: *Saturation Index; Calcareous Soils; I on Activity Product; Iron Transformation; Agricultural Sulfur*

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INTRODUCTION

Iron is a major constituent of the lithosphere, comprising approximately 5.1%; its average in soils is estimated at 3.8%. In primary minerals iron occurs largely as ferromagnesium minerals. During weathering these minerals dissolve, and the released iron precipitates as ferric oxides and hydroxides (Lindsay, 1979).

Al-Tamimi (1997) indicated that several factors influence the chemical behavior of iron in soils due to its rapid changes in valence and related with the behavior of other elements (oxygen, Sulphur and carbon) in soils. The activity of iron in soil solutions controlled by several minerals such as pH , electron activity and Redox in soils which is affected by wetting and drying conditions(Lindsay,1979).The application of mineral fertilizers such as ferrous sulfate ($FeSO_4$), and chelated organic forms such as Fe-fulvate (Fe-FA) and Fe-humate (Fe-HA), reduced the presence of iron carbonate based on iron solubility diagrams.

Rasheed (2023) reported that siderite ($FeCO_3$) is the dominant mineral controlling iron solubility in 21 calcareous soils cultivated with vegetables in Sulaymaniyah, Iraq. This agrees with Lindsay and Schwab (1982), who stated that iron availability in calcareous soils is governed by siderite equilibrium. The solubility of siderite is influenced by soil pH, iron content, calcium carbonate

content, and carbon dioxide (CO_2) partial pressure. chemical structure of soil solution affected the solubility and precipitation of iron in soils, especially soil salinity and organic acids (Han *et al*.,2020).

In calcareous soils under dry conditions, iron is subjected to adsorption and precipitation as oxides, carbonates, and hydroxides. Sabagh *et al*. (2014) showed that the application of elemental sulfur at rates of 0, 250, and 500 kg S ha^{-1} increased the solubility of iron compounds in soils. Numerous studies have confirmed that sulfur oxidation produces sulfuric acid, which lowers soil pH, enhances dissolution of minerals, releases exchangeable ions, and increases electrical conductivity (EC) due to both ion displacement and sulfur salinity (Al-Zubaidi, 2015; Kazim, 2016; Hindi, 2017). Shakeri and Saffari (2020) remembered that the status of iron compounds in soils affected by physiochemical and mineralogical properties of soils.The present study aims to diagnose native iron compounds in selected Basrah soils and to evaluate the effect of iron and agricultural sulfur fertilization on iron chemical behavior after one and two wetting–drying cycles.

MATERIALS AND METHODS

Soil Sampling and Preparation

Ten uncultivated agricultural sites were selected across Basrah Governorate, including northern and southern regions (Al-Faw, Al-Seba, Abu Al-Khaseeb, Al-Tanoma, Al-Hartha, Al-Dair, Al-Medina, Al-Qurna, Safwan and Al-Luhais). Soil samples were collected on 18/10/2024 from a depth of 0–30 cm and composited (Figure 1).

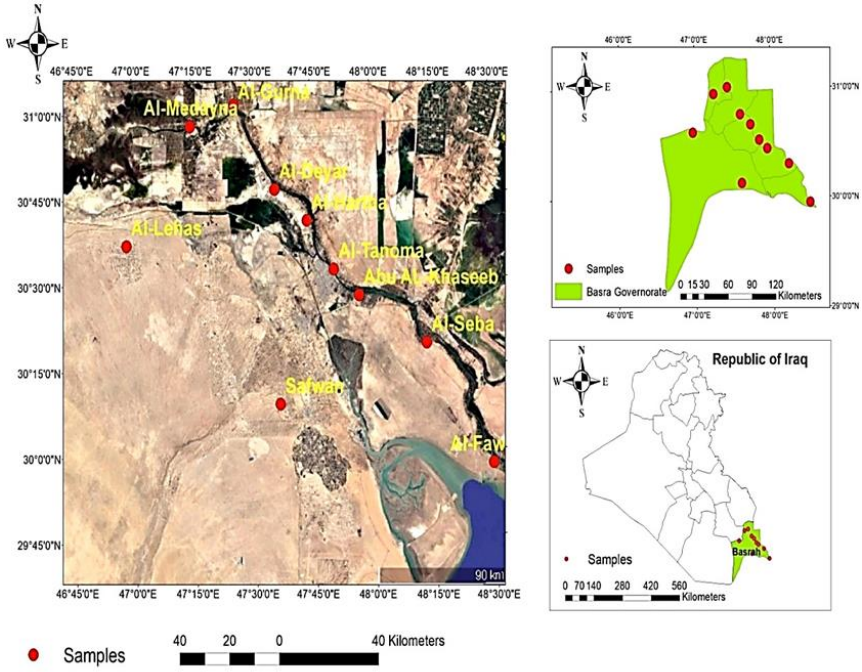

Figure (1) Locations of soil samples from uncultivated agricultural fields in Basrah Governorate.

Samples were air-dried, ground, and sieved through a 2 mm sieve, then stored in plastic containers for physical and chemical analysis according to Black (1965), and Page et al (1982) (Table 1).

Table (1) Physical-chemical properties of soils

Soils	pH 1:1	EC (1:1) dSm1-	CaCO3 gm kg^{-1}	CEC Cmole + kg^{-1}	Organic Matter (gm kg^{-1})	Soil particles (gm kg^{-1})			
						Sand	Silt	Clay	Texture
Al-Faw	7.98	11.60	340	15.80	9.75	185.4	454.3	360.3	Silty Clay
Al-Seba	7.65	6.75	385	25.10	15.85	150.2	485.5	364.3	Silty Clay
Abu AL-Khaseeb	7.94	7.35	315	19.20	12.20	220.6	502.1	227.3	Silty Clay Loam
Al-Tanoma	7.79	4.19	305	22.50	15.65	240.5	485.2	274.3	Silty Clay Loam
Al-Hartha	8.05	5.21	395	21.20	13.10	215.3	510.4	274.3	Silty Clay Loam
Al-Deyar	7.76	7.11	375	22.85	14.50	195.8	525.9	278.3	Silty Clay Loam
Al-Medayna	7.70	10.01	420	21.80	15.80	120.4	475.3	404.3	Silty Clay
Al-Gurna	7.77	4.08	400	19.85	13.20	105.2	490.5	404.3	Silty Clay
Safwan	7.91	7.67	267	4.30	0.43	905.4	54.3	40.3	Sand
Al-Lehas	7.77	5.02	187	2.57	0.32	918.2	45.5	36.3	Sand
Less Value	7.65	4.08	187	2.57	0.32	105.2	45.5	36.3	-
Highest value	8.05	11.60	420	25.10	15.85	918.2	525.9	404.3	-
Mean	7.83	6.90	338.9	17.52	11.08	511.7	285.7	220.3	-

Experimental Design

A laboratory experiment was conducted to identify native iron compounds (Native-Fe) in all soils under:

- Three iron levels: 0, 25, and 50 kg Fe ha^{-1} (as $FeSO_4 \cdot 7H_2O$) (Control, F1, F2)
- Three sulfur levels: 0, 1000, and 2000 kg S ha^{-1} (S1, S2)

Three hundred grams of soil were placed in 500 cm^3 plastic containers. Organic matter (cow manure) was added at 2.5% (Chemical properties of cow manure were determined according to the methods mentioned in Page et al (1982) (Table 2) was added to help agricultural sulfur oxidize and make the culture (soil) acidic. Samples were adjusted to field capacity (20% for coarse soils and 30% for fine soils) In the laboratory, soil samples are air-dried, gently crushed, and passed through a 2 mm sieve. A known weight of soil is placed in suitable containers or filter units. Water is then gradually added until the soil becomes fully saturated without surface ponding. The samples were left to drain under gravity by using filter paper for 24 hours, depending on soil texture. The soil is considered to be at field capacity when free drainage ceases and moisture content stabilizes, after which samples can be weighed to determine field capacity water content and incubated for one week. After drying and grinding, sulfur treatments were added (equivalent to 0.5 and 1.0 g kg^{-1} soil) (Some chemical and physical properties of agricultural sulfur were determined according to methods mentioned in Page et al (1982) and Black (1965), (Table 3). Samples were incubated for: Two weeks and four weeks (one month).

Table (2) some chemical properties of cow manure**.**

pH (1:5)	E.C(1:5) dS m-1	Organic –C gm Kg^{-1}	Organic matter gm Kg^{-1}	Total –N gm kg^{-1}	C:N	Total –Fe mg kg^{-1}
7.07	12.25	313	539.6	22.7	13.79	1500

Table (3) some physiochemical properties of agricultural sulfur.

pH (1:1)	E.C(1:1) (dS m^{-1})	Sulfur (%)	Ca^{2+} (mg kg^{-1})	Gypsum (%)	Calcium carbonate (%)	Clay (%)	Diameter (mesh)
3.7	4.4	95	64	Nil	1	1.5	325

After each incubation period, soil suspensions (1:1) were prepared and shaken for two hours. The following parameters were measured (pH, EC, Soluble iron and soluble sulfate) according to Page et al (1982). The Saturation Index (SI) was used to diagnose iron minerals.

Calculation of Solubility Product and Saturation Index

Due to the formation of ion pairs and complexes, the active iron concentration must be calculated.

Ionic Strength:

I=0.013×EC] ……..….. (1)

Where is I: ionic strength, (Mole l^{-1})

EC: Electrical conductivity (dS m^{-1})

Ion activity coefficient (f) was calculated by using Davies equation (1962), which mentioned in Lindsay (1979).

$$\text{Log } F_{10} = - A Zi^2 \left(\frac{\sqrt{I}}{\sqrt{I} + 1} - 0.3 I \right) \quad \text{…….…….. (2)}$$

Where is:

A: constant its value 0.509

Zi: ion valence

From calculating ion activity coefficient of iron and sulfate, it can be calculated the activity of iron from the relationship below: -

Ion activity (a) = Concentration (c) x F

After that, the **Ion Activity Product (IAP)** was calculated using the following relationship:

Ion Activity Product (IAP) = (activity of products/activity of reactants)…….. (3)

Saturation Index:

Saturation Index (SI) = log IAP calculated/log Ksp …… (4) (standard, from Lindsay,1979)

Based on the calculated values of the **Saturation Index (SI)** for all treatments in the laboratory experiment and for both incubation cycles, and according to the equations presented in the table below (Table 4) as reported by Lindsay (1979):

- If the SI value is equal to or greater than one (SI ≥ 1), this indicates the presence and formation of the mineral.
- If the SI value is less than one (SI < 1), this indicates the absence or non-formation of the mineral in the soil.

Table (4) Equilibrium equations of iron minerals (Lindsay, 1979).

Equation No.	Equilibrium equation	Log K^o
1	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$	2.70
2	$1/2\ \alpha\text{-}\ Fe_2O_3(hematite) + 3H^+ \longleftrightarrow Fe^{3+} + 3/2\ H_2O$	0.09
3	$FeCO_3(siderite) + 2H^+ \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$	7.92

RESULTS AND DISCUSSION

Results presented in Tables 5–14 show the values of the Ion Activity Product (IAP) and Saturation Index (SI) of iron compounds in the native soils and after the application of iron and agricultural sulfur fertilizers during the first and second wetting–drying cycles. The results indicated that the native iron compound (Fe-Native) in all studied soils was identified as hematite (½α-Fe_2O_3), since the SI values were greater than 1. In contrast, ferric hydroxide [$Fe(OH)_3$] and siderite ($FeCO_3$)

were not present as controlling mineral phases because their SI values were less than 1(SI < 1). These findings disagree with those reported by Al-Tamimi (1997), who found that siderite ($FeCO_3$) was the dominant mineral controlling the dissolution of native iron in the sandy loam and silty loam soils of Basrah during the first wetting–drying cycle.

The application of iron and agricultural sulfur fertilizers, as well as their interaction, reduced the values of both the Ion Activity Product and the Saturation Index during the first wetting–drying cycle in all soils. However, hematite remained the dominant mineral controlling iron dissolution because the SI values remained greater than 1(SI > 1) despite decreasing with the addition of iron and sulfur fertilizers. This reduction can be attributed to the increased availability of iron in the soil solution. The decrease in IAP values following fertilizer and sulfur applications further supports this interpretation. This response is considered favorable because it enhances iron availability in the studied calcareous soils, where iron is generally susceptible to precipitation. Although soil properties varied and influenced the chemical behavior of the applied treatments, a similar trend of response was observed across all studied soils.

Table (5) Saturation index (SI) of iron minerals of Al-Faw soil treated with iron and agricultural sulfur for one and two wetting and drying cycles.

Treatments	First Cycle		Second Cycle	
	SI	Log IAP	SI	Log IAP
	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$		$\log K^0 = 2.70$	
Control	0.584	1.016	3.139	3.571
F1	0.536	0.967	3.203	3.634
F2	0.529	0.961	3.277	3.709
S1	0.476	0.908	3.025	3.456
S2	0.426	0.857	3.198	3.629
F1S1	0.381	0.813	3.240	3.671
F1S2	0.422	0.854	3.067	3.498
F2S1	0.349	0.780	3.138	3.570
F2S2	0.240	0.671	3.122	3.553
	$1/2\ \alpha\text{-}Fe_2O_3(hematite) + 3H^+ \longleftrightarrow Fe^{3+} + 3/2\ H_2O$		$\log K^0 = 0.09$	
Control	3.061	1.016	4.616	3.571
F1	2.013	0.967	4.680	3.634
F2	2.006	0.961	4.754	3.709
S1	1.954	0.908	4.502	3.456
S2	1.903	0.857	4.675	3.629
F1S1	1.859	0.813	4.717	3.671
F1S2	1.899	0.854	4.544	3.498
F2S1	1.826	0.780	4.616	3.570
F2S2	1.717	0.671	4.599	3.553
	$FeCO_3(siderite) + 2H^+ \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$		$\log K^0 = 7.92$	
Control	0.663	1.562	3.218	4.117
F1	0.615	1.514	3.282	4.180
F2	0.608	1.507	3.357	4.255
S1	0.556	1.454	3.104	4.003
S2	0.505	1.404	3.277	4.176
F1S1	0.461	1.359	3.319	4.218
F1S2	0.501	1.400	3.146	4.045
F2S1	0.428	1.327	3.218	4.116
F2S2	0.319	1.218	3.201	4.100

Increasing the incubation period of soils with the applied treatments through the second wetting–drying cycle altered the nature of iron mineral formation in the soils. The composition of the native iron minerals (Fe-Native) changed, and hematite [½α-Fe_2O_3], ferric hydroxide [$Fe(OH)_3$], and siderite ($FeCO_3$) were all formed, as indicated by SI values greater than 1. Nevertheless, hematite remained the predominant mineral phase compared with the other two minerals.

The increase in SI values was accompanied by an increase in the Ion Activity Product (IAP) values for all soils and treatments, reflecting the increased activity of iron ions in the soil solution. The addition of iron and agricultural sulfur fertilizers, as well as their interaction, further increased iron ion activity during the second wetting–drying cycle, resulting in higher SI values compared with the first cycle. This behavior can be attributed to enhanced iron solubility and release resulting from oxidation processes mediated by soil microorganisms. The presence of agricultural sulfur further contributed to this effect by lowering soil pH, thereby increasing iron dissolution and availability in the soil solutions.

Rasheed (2023) reported that siderite was the dominant mineral controlling iron dissolution in calcareous soils of northern Iraq (based on 56 soil samples from the Kurdistan Region of Iraq), owing to the high soil pH and elevated calcium carbonate content of those soils.

Table (6): Saturation index (SI) of iron minerals of Al-Seba soil treated with iron and agricultural sulfur for one and two wetting and drying cycles.

Treatments	First Cycle		Second Cycle	
	SI	Log IAP	SI	Log IAP
	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$ $\log K^0=2.70$			
Control	0.224	0.654	2.703	3.134
F1	0.207	0.639	2.852	3.284
F2	0.200	0.632	2.928	3.359
S1	-0.075	0.357	2.480	2.912
S2	-0.102	0.330	2.489	2.921
F1S1	-0.118	0.314	2.563	2.995
F1S2	-0.102	0.330	2.463	2.894
F2S1	-0.137	0.294	2.418	2.850
F2S2	-0.155	0.277	2.429	2.860
	$1/2\ \alpha\text{-}Fe_2O_3(hematite) + 3H^+ \longleftrightarrow Fe^{3+} + 3/2\ H_2O$ $\log K^0= 0.09$			
Control	1.701	0.655	4.180	3.134
F1	1.685	0.639	4.329	3.284
F2	1.677	0.632	4.405	3.359
S1	1.403	0.357	3.958	2.912
S2	1.376	0.330	3.967	2.921
F1S1	1.359	0.314	4.041	2.995
F1S2	1.375	0.330	3.940	2.894
F2S1	1.339	0.294	3.896	2.850
F2S2	1.322	0.277	3.906	2.860
	$FeCO_3(siderite) + 2H^+ \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$ $\log K^0=7.92$			
Control	0.303	1.201	2.782	3.681
F1	0.287	1.185	2.931	3.830
F2	0.280	1.178	3.007	3.906
S1	0.005	0.903	2.560	3.458
S2	-0.023	0.876	2.569	3.467
F1S1	-0.039	0.860	2.643	3.541
F1S2	-0.023	0.876	2.542	3.441
F2S1	-0.059	0.840	2.498	3.396
F2S2	-0.076	0.823	2.508	3.407

Table (7) Saturation index (SI) of iron minerals of Abu AL-Khaseeb soil treated with iron and agricultural sulfur for one and two wetting and drying cycles.

Treatments	First Cycle		Second Cycle	
	SI	Log IAP	SI	Log IAP
	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$ log K^0=2.70			
Control	0.550	0.982	3.137	3.568
F1	0.508	0.939	3.118	3.550
F2	0.484	0.916	3.173	3.604
S1	0.457	0.889	2.639	3.070
S2	0.417	0.848	2.637	3.068
F1S1	0.394	0.826	2.747	3.178
F1S2	0.372	0.804	2.514	2.946
F2S1	0.399	0.830	2.601	3.033
F2S2	0.136	0.568	2.668	3.099
	$1/2\ \alpha\text{-}Fe_2O_3(hematite) + 3H^+ \longleftrightarrow Fe^{3+} + 3/2\ H_2O$ log K^0= 0.09			
Control	2.027	0.982	4.614	3.568
F1	1.985	0.939	4.596	3.550
F2	1.961	0.916	4.650	3.604
S1	1.935	0.889	4.116	3.070
S2	1.894	0.848	4.114	3.068
F1S1	1.872	0.826	4.224	3.178
F1S2	1.849	0.804	3.991	2.946
F2S1	1.876	0.830	4.078	3.033
F2S2	1.613	0.568	4.145	3.099
	$FeCO_3(siderite) + 2H \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$ log K^0=7.92			
Control	0.630	1.528	3.216	4.115
F1	0.587	1.486	3.198	4.096
F2	0.563	1.462	3.252	4.151
S1	0.537	1.435	2.718	3.617
S2	0.496	1.395	2.716	3.615
F1S1	0.474	1.372	2.826	3.725
F1S2	0.452	1.350	2.593	3.492
F2S1	0.478	1.376	2.681	3.579
F2S2	0.215	1.114	2.747	3.646

Table (8): Saturation index (SI) of iron minerals of Al-Tanoma soil treated with iron and agricultural sulfur for one and two wetting and drying cycles.

Treatment	Second Cycle		First Cycle	
	SI	Log IAP	SI	Log IAP
	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$ log K^0=2.70			
Control	0.411	0.842	2.930	3.361
F1	0.306	0.738	2.872	3.304
F2	0.295	0.727	2.952	3.383
S1	-0.156	0.276	2.360	2.791
S2	-0.177	0.255	2.383	2.814
F1S1	-0.180	0.252	2.479	2.910
F1S2	-0.203	0.228	2.318	2.749
F2S1	-0.234	0.197	2.362	2.794
F2S2	-0.195	0.236	2.411	2.843
	$1/2\ \alpha\text{-}Fe_2O_3(hematite) + 3H^+ \longleftrightarrow Fe^{3+} + 3/2\ H_2O$ log K^0= 0.09			
Control	1.888	0.842	4.407	3.361
F1	1.783	0.738	4.349	3.304
F2	1.772	0.727	4.429	3.383
S1	1.321	0.276	3.837	2.791
S2	1.300	0.255	3.860	2.814
F1S1	1.297	0.252	3.956	2.910
F1S2	1.274	0.228	3.795	2.749
F2S1	1.243	0.197	3.839	2.794
F2S2	1.282	0.236	3.888	2.843
	$FeCO_3(siderite) + 2H^+ \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$ log K^0=7.92			
Control	0.490	1.388	3.009	3.908
F1	0.386	1.284	2.951	3.850
F2	0.374	1.273	3.031	3.930
S1	-0.077	0.822	2.439	3.337
S2	-0.097	0.801	2.462	3.361
F1S1	-0.101	0.798	2.558	3.457
F1S2	-0.124	0.775	2.397	3.296
F2S1	-0.155	0.744	2.441	3.340
F2S2	-0.116	0.783	2.490	3.389

Table (9): Saturation index (SI) of iron minerals of Al-Hartha soil treated with iron and agricultural sulfur for one and two wetting and drying cycles.

Treatments	First Cycle		Second Cycle	
	SI	Log IAP	SI	Log IAP
	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$ log K^0=2.70			
Control	0.643	1.074	2.986	3.417
F1	0.607	1.038	3.188	3.620
F2	0.571	1.003	3.166	3.597
S1	0.528	0.960	2.944	3.375
S2	0.517	0.948	3.008	3.439
F1S1	0.491	0.923	3.027	3.458
F1S2	0.309	0.74	2.869	3.301
F2S1	0.334	0.765	2.901	3.332
F2S2	0.320	0.751	2.904	3.335
	$1/2\ \alpha\text{-}Fe_2O_3(hematite) + 3H^+ \longleftrightarrow Fe^{3+} + 3/2\ H_2O$ log K^0= 0.09			
Control	2.120	1.074	4.463	3.417
F1	2.084	1.038	4.665	3.620
F2	2.048	1.003	4.643	3.597
S1	2.006	0.960	4.421	3.375
S2	1.994	0.948	4.485	3.439
F1S1	1.969	0.923	4.504	3.458
F1S2	1.786	0.74	4.346	3.301
F2S1	1.811	0.765	4.378	3.332
F2S2	1.797	0.751	4.381	3.335
	$FeCO_3(siderite) + 2H^+ \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$ log K^0=7.92			
Control	0.722	1.621	3.065	3.964
F1	0.686	1.585	3.267	4.166
F2	0.650	1.549	3.245	4.144
S1	0.608	1.506	3.023	3.922
S2	0.596	1.495	3.087	3.986
F1S1	0.571	1.469	3.106	4.005
F1S2	0.388	1.287	2.949	3.847
F2S1	0.413	1.312	2.980	3.879
F2S2	0.399	1.298	2.983	3.882

Table (10): Saturation index (SI) of iron minerals of Al-Deyar soil treated with iron and agricultural sulfur for one and two wetting and drying cycles.

Treatments	First Cycle		Second Cycle	
	SI	Log IAP	SI	Log IAP
	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$ log K^0=2.70			
Control	0.282	0.713	2.763	3.195
F1	0.267	0.699	2.973	3.405
F2	0.255	0.686	2.991	3.422
S1	0.239	0.670	2.675	3.106
S2	0.225	0.657	2.789	3.221
F1S1	0.210	0.641	2.804	3.236
F1S2	0.196	0.627	2.609	3.040
F2S1	0.131	0.563	2.710	3.141
F2S2	0.127	0.558	2.730	3.161
	$1/2\ \alpha\text{-}Fe_2O_3(hematite) + 3H^+ \longleftrightarrow Fe^{3+} + 3/2\ H_2O$ log K^0= 0.09			
Control	1.759	0.713	4.241	3.195
F1	1.744	0.699	4.451	3.405
F2	1.732	0.686	4.468	3.422
S1	1.716	0.670	4.152	3.106
S2	1.702	0.657	4.266	3.221
F1S1	1.687	0.641	4.282	3.236
F1S2	1.673	0.627	4.086	3.040
F2S1	1.608	0.563	4.187	3.141
F2S2	1.604	0.558	4.207	3.161
	$FeCO_3(siderite) + 2H^+ \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$ log K^0=7.92			
Control	0.361	1.260	2.843	3.741
F1	0.346	1.245	3.053	3.951
F2	0.334	1.233	3.070	3.969
S1	0.318	1.217	2.754	3.653
S2	0.304	1.203	2.869	3.767
F1S1	0.289	1.188	2.884	3.782
F1S2	0.275	1.173	2.688	3.587
F2S1	0.210	1.109	2.789	3.688
F2S2	0.206	1.105	2.809	3.708

Table (11) Saturation index (SI) of iron minerals of Al-Medayna soil treated with iron and agricultural sulfur for one and two wetting and drying cycles.

Treatments	First Cycle		Second Cycle	
	SI	Log IAP	SI	Log IAP
	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$ log K^0=2.70			
Control	0.339	0.771	2.503	2.935
F1	0.310	0.742	2.959	3.391
F2	0.265	0.696	3.087	3.518
S1	0.225	0.656	2.809	3.240
S2	-0.073	0.359	2.907	3.338
F1S1	-0.171	0.261	2.964	3.395
F1S2	-0.189	0.242	2.840	3.271
F2S1	-0.229	0.203	2.934	3.365
F2S2	-0.268	0.164	2.966	3.397
	$1/2\ \alpha\text{-}Fe_2O_3(hematite) + 3H \longleftrightarrow Fe^{3+} + 3/2\ H_2O$ log K^0= 0.09			
Control	1.817	0.771	3.981	2.935
F1	1.787	0.742	4.436	3.391
F2	1.742	0.696	4.564	3.518
S1	1.702	0.656	4.286	3.240
S2	1.404	0.359	4.384	3.338
F1S1	1.307	0.261	4.441	3.395
F1S2	1.288	0.242	4.317	3.271
F2S1	1.249	0.203	4.411	3.365
F2S2	1.209	0.164	4.443	3.397
	$FeCO_3(siderite) + 2H^+ \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$ log K^0=7.92			
Control	0.419	1.317	2.583	3.481
F1	0.390	1.288	3.038	3.937
F2	0.344	1.243	3.166	4.065
S1	0.304	1.203	2.888	3.787
S2	0.006	0.905	2.986	3.884
F1S1	-0.091	0.807	3.043	3.942
F1S2	-0.110	0.789	2.919	3.818
F2S1	-0.149	0.750	3.013	3.912
F2S2	-0.189	0.710	3.045	3.944

Table (12) Saturation index (SI) of iron minerals of Al-Gurna soil treated with iron and agricultural sulfur for one and two wetting and drying cycles.

Treatments	First Cycle		Second Cycle	
	SI	Log IAP	SI	Log IAP
	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$ log K^0=2.70			
Control	0.260	0.691	2.676	3.107
F1	0.253	0.684	2.929	3.360
F2	0.256	0.688	2.971	3.403
S1	0.175	0.606	2.707	3.139
S2	0.158	0.589	2.731	3.162
F1S1	0.142	0.574	2.718	3.150
F1S2	0.132	0.563	2.651	3.083
F2S1	0.116	0.547	2.681	3.113
F2S2	0.069	0.501	2.653	3.085
	$1/2\ \alpha\text{-}Fe_2O_3(hematite) + 3H^+ \longleftrightarrow Fe^{3+} + 3/2\ H_2O$ log K^0= 0.09			
Control	1.737	0.691	4.153	3.107
F1	1.730	0.684	4.406	3.360
F2	1.733	0.688	4.448	3.403
S1	1.652	0.606	4.184	3.139
S2	1.635	0.589	4.208	3.162
F1S1	1.619	0.574	4.196	3.150
F1S2	1.609	0.563	4.128	3.083
F2S1	1.593	0.547	4.159	3.113
F2S2	1.546	0.501	4.131	3.085
	$FeCO_3(siderite) + 2H^+ \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$ log K^0=7.92			
Control	0.339	1.239	2.755	3.654
F1	0.332	1.231	3.008	3.907
F2	0.335	1.234	3.050	3.949
S1	0.254	1.153	2.787	3.685
S2	0.237	1.136	2.810	3.708
F1S1	0.221	1.120	2.798	3.696
F1S2	0.211	1.110	2.730	3.629
F2S1	0.195	1.094	2.761	3.659
F2S2	0.148	1.047	2.733	3.631

Table (13) Saturation index (SI) of iron minerals of Safwan soil treated with iron and agricultural sulfur for one and two wetting and drying cycles.

Treatments	First Cycle		Second Cycle	
	SI	Log IAP	SI	Log IAP
	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$ log K^0=2.70			
Control	0.525	0.957	3.205	3.636
F1	0.499	0.930	3.112	3.543
F2	0.487	0.918	3.107	3.538
S1	0.455	0.886	2.968	3.399
S2	0.453	0.884	3.007	3.439
F1S1	0.451	0.882	2.974	3.405
F1S2	0.369	0.800	2.872	3.304
F2S1	0.357	0.788	2.889	3.321
F2S2	0.337	0.768	2.892	3.323
	$1/2\ \alpha\text{-}Fe_2O_3(hematite) + 3H^+ \longleftrightarrow Fe^{3+} + 3/2\ H_2O$ log K^0= 0.09			
Control	2.002	0.957	4.682	3.636
F1	1.976	0.930	4.590	3.543
F2	1.964	0.918	4.584	3.538
S1	1.932	0.886	4.445	3.399
S2	1.930	0.884	4.484	3.439
F1S1	1.928	0.882	4.451	3.405
F1S2	1.846	0.800	4.350	3.304
F2S1	1.834	0.788	4.367	3.321
F2S2	1.814	0.768	4.369	3.323
	$FeCO_3(siderite) + 2H^+ \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$ log K^0=7.92			
Control	0.604	1.503	3.284	4.183
F1	0.578	1.477	3.191	4.090
F2	0.566	1.465	3.186	4.085
S1	0.534	1.432	3.047	3.946
S2	0.532	1.431	3.086	3.985
F1S1	0.530	1.429	3.053	3.952
F1S2	0.448	1.346	2.951	3.850
F2S1	0.436	1.335	2.969	3.867
F2S2	0.416	1.315	2.971	3.870

Table (14): Saturation index (SI) of iron minerals of Al-Luhas soil treated with iron and agricultural sulfur for one and two wetting and drying cycles.

Treatments	First Cycle		Second Cycle	
	SI	Log IAP	SI	Log IAP
	$Fe(OH)(soil) + 3H^+ \longleftrightarrow Fe^{3+} + 3H_2O$ log K^0=2.70			
Control	0.342	0.773	2.796	3.227
F1	0.331	0.763	2.801	3.233
F2	0.330	0.761	2.892	3.324
S1	0.286	0.717	2.750	3.181
S2	0.106	0.537	2.729	3.160
F1S1	0.096	0.528	2.757	3.189
F1S2	0.064	0.495	2.681	3.112
F2S1	0.013	0.445	2.745	3.176
F2S2	-0.008	0.423	2.826	3.257
	$1/2\ \alpha\text{-}Fe_2O_3(hematite) + 3H^+ \longleftrightarrow Fe^{3+} + 3/2\ H_2O$ log K^0= 0.09			
Control	1.819	0.773	4.273	3.227
F1	1.809	0.763	4.278	3.233
F2	1.807	0.761	4.370	3.324
S1	1.763	0.717	4.227	3.181
S2	1.583	0.537	4.206	3.160
F1S1	1.574	0.528	4.234	3.189
F1S2	1.541	0.495	4.158	3.112
F2S1	1.490	0.445	4.222	3.176
F2S2	1.469	0.423	4.303	3.257
	$FeCO_3(siderite) + 2H^+ \longleftrightarrow Fe^{2+} + CO_2(g) + H_2O$ log K^0=7.92			
Control	0.421	1.320	2.875	3.774
F1	0.411	1.309	2.880	3.779
F2	0.409	1.308	2.972	3.870
S1	0.365	1.263	2.829	3.728
S2	0.185	1.084	2.808	3.707
F1S1	0.176	1.074	2.837	3.735
F1S2	0.143	1.042	2.760	3.659
F2S1	0.093	0.991	2.824	3.723
F2S2	0.071	0.970	2.905	3.804

CONCLUSIONS

This study concluded that hematite (α-Fe_2O_3) is the dominant iron mineral in calcareous soils of Basrah during the initial wetting–drying cycle, while siderite ($FeCO_3$) and Fe $(OH)_3$ were initially unstable (SI < 1). Application of iron fertilizer and agricultural sulfur reduced IAP and SI values, and increasing iron solubility in soil solutions. In the second cycle, iron minerals transformations occurred with the appearance of Fe $(OH)_3$ and siderite alongside hematite, mainly due to sulfur-induced acidification, although hematite remained dominant in most studied soils. Overall, agricultural sulfur effectively increased iron availability through soil acidification and mineral transformations; therefore, its use is recommended in calcareous soils to alleviate iron deficiency especially in arid and semiarid regions, with further field studies needed to optimize its long-term effectiveness.

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