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# Effect of Mineral Sulfur on the Intensity and Capacity Relationship of Copper in Different Calcareous Soils

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**Abstract:** The study aims to evaluate the effect of mineral sulfur on the availability of copper in different calcareous soils by adopting some thermodynamic parameters (capacity and intensity relationships, free energy, Gabon's constant). Three levels of mineral sulfur (1,2,3) g.kg<sup>-1</sup> were adopted. The study showed that the coefficient of statistical determination of the amplitude and intensity equations ranged between (0.82 and 0.99), and the values of the regulatory capacity ranged between (282.58, 574.76) (centimol.kg<sup>-1</sup>), while the values of mobile copper CU-Labile ranged between (0.0093-0.0093). The values of free energy (15.7865, 26.7014) kilojoules.mol<sup>-1</sup>, while the values of the preference coefficient for Gabon ranged (12.7288, 40.2459). These results indicate that all thermodynamic values decrease (increase in copper availability) with increasing levels of added mineral sulfur (1,2,3) g.kg<sup>-1</sup> in the soil.

**Keywords:** Mineral Sulfur, Copper, Calcareous Soils, Capacity, Intensity, Gabon's Constant

## Introduction

Calcium carbonate, CaCO<sub>3</sub>, is considered one of the natural components of soil, especially in arid and semi-arid areas. The content of Iraqi soils of CaCO<sub>3</sub> ranges between 10-45 g.kg<sup>-1</sup> [1]. The soils containing CaCO<sub>3</sub> are characterized by high pH values. (pH) and the high ability to adsorb and precipitate most nutrients, especially the micro-elements necessary for plant growth and production promotion [2], [3]. Recent studies have tended to address the negative impact of calcium carbonate (lime) by adding acidic-impact improvers, including organic matter and mineral sulfur [4], [5]. Where the chain of its interactions in the soil ends with an increase in the concentration of the [H<sup>+</sup>] ion, which leads to a decrease in the value of calcium pH of the soil, which leads to an increase in the availability of most nutrients, including copper. Thus, sulfur is one of the elements capable of finding a solution to pH problems in basic soils and some low-salinity soils [6], [7].

Copper is one of the micro-elements that play an important role in plant nutrition, including photosynthesis, electron transfer, carbohydrate metabolism, and enzymes. The case of copper deficiency in calcareous soils is a common case, as it is believed that this is the result of interactions between the dissolved copper and the solid phase in the soil, which leads to a decrease in its readiness

for the plant, as it is the adsorption or sedimentation reactions on the surface of the solid phase that reduce its concentration in the soil solution and for the characteristics Physical and chemical properties such as pH and the presence of organic or inorganic colloids have a role in increasing the deposition of copper and the formation of low solubility complexes [8] and that the adsorption behavior of copper is important both in terms of fertility and environmental terms, as the availability of copper in the soil depends on the state of its presence in Soil in different states is adsorbed and exchangeable or dissolved in solution, and this readiness is affected by several factors, including calcium carbonate, which plays a negative role in the readiness of many micro-elements, including copper, which leads to its precipitation in the form of  $\text{CuCO}_3$  [9]. Therefore, readiness conditions must be addressed. Microelements in these soils.

It is known that the addition of mineral sulfur leads to an increase in the availability of nutrients. This study aims to evaluate the process of adding mineral sulfur by using some thermodynamic concepts in modern soil chemistry.

## Materials and Methods

### Materials

- Three sites were selected within the northern-eastern administrative borders of Salah al-Din Governorate, whose soil contains different levels of lime: Qadir Karam district  $105 \text{ g.kg}^{-1}$ , Suleiman Bek district  $152 \text{ g.kg}^{-1}$  and Yinkaja district  $202 \text{ g.kg}^{-1}$ .
- Soils were air dried, pulverized, and passed through a sieve with a hole diameter of 2 mm to be used in routine soil analysis to know some of their chemical and physical properties Table (Table 1).
- Study of the copper adsorption process.

Put 2 g of each soil in a test tube of 50 ml capacity, copper was added at levels of (0, 1, 2, 4, 8, 10)  $\text{mg}^{-1}$ . L copper as ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and for a volume of 40 ml, with two repetitions for each concentration.

The equilibrium suspensions were left for two hours on a shaker device. Then they were left for a period of 24 hours to reach a dynamic equilibrium state at a constant [10]. The pH, electrical conductivity,  $E_c$ , calcium, and magnesium were also estimated. The following thermodynamic parameters were calculated.

The ionic strength in aqueous extracts was calculated from the electrical conductivity values and according to the relationship suggested by [11].

$$I = EC \times 0.013 \quad (1)$$

$I$  = ionic strength (mol/L).  $EC$  = electrical conductivity ( $\text{dSm}^{-1}$ ).

The ionic activity ( $a$ ) of copper and other ions was calculated from the concentration values according to the following relationship:

$$a_i = c_i + f_i \quad (2)$$

$a_i$  = expresses the ionic activity ( $\text{mol.L}^{-1}$ ).  $c_i$  = expresses the measured ion concentration ( $\text{mol.L}^{-1}$ ).  $f_i$  = ionic reactivity factor.

The activity coefficient of the copper ion was calculated using the modified (Davies) equation as reported by [12]

$$-\log f_i = \frac{AZ_i^2 \sqrt{I}}{1 + \sqrt{I}} - 0.3I. \quad (3)$$

$-\log f_i$  = The negative logarithm of the ionic reactivity factor.  $Z_i^2 \sqrt{I}$  ion charge box = .square root of ionic strength.  $A$  = constant of 0.509

The capacity of the solid soil phase was calculated from the adsorbed copper (Cu-quantity) according to the following equation [13].

$$q = \frac{(C_{in} - C_{fin})}{w} \times V \quad (4)$$

$q$  = the amount of copper adsorbed on the surface unit in units ( $\text{mg. kg}^{-1}$ ).  $C_{in}$  = the initial copper concentration ( $\text{mg.L}^{-1}$ ).  $C_{fin}$  = the concentration of copper in the equilibrium solution ( $\text{mg.L}^{-1}$ ).

$V$  = the volume of the total extraction solution (liter).  $W$  = weight of soil (g).

As for the relative effectiveness of copper, according to [14], it was calculated from the following equation.

$$ARCu = \frac{a_{Cu}}{\sqrt{a_{Ca} + a_{Mg}}} \quad (5)$$

$ARCu$  = the relative activity of the copper ion.  $a_{Ca}$  = the activity of the calcium ion.  $a_{Mg}$  = the activity of the magnesium ion.

The modified Capon constant was calculated according to the following equation [15],

$$KG = \frac{PBC}{CEC} \quad (6)$$

$KG$  = rate capon constant.  $PBC$  = Potential regulatory capacity of the copper ion.  $CEC$  = The cation exchange capacity of the soil.

As for the substitutive free energy,  $\Delta F$  / the value of the substitutive free energy was calculated using the equation proposed before [16].

$$-\Delta F = 2.303RT \log ARcu \quad (7)$$

$-\Delta F$  = substitution free energy ( $\text{Kilojoules.mol}^{-1}$ ).  $R$  = General constant for gases.  $T$  = absolute temperature.  $\log AR^{\circ}cu$  = The logarithm of the relative activity of copper.

**Table 1.** Some chemical and physical properties of the soil under study.

Texture	Sand Silt clay CaCO <sub>3</sub> O.M					C.E.C C.mole.kg <sup>-1</sup>	E.c ds.m <sup>-1</sup>	PH	Soil
	gm.kg <sup>-1</sup>								
Clay	605	190	205	105	19	22.1	1.38	7.46	First
Clay	520	130	350	152	11	13.7	1.76	7.59	Second
Clay Loam	480	300	220	202	15	18.3	1.07	7.63	Third

## Results and Discussion

### Effect of Mineral Sulfur on the Relationship Between Amplitude and Intensity

Recent studies have adopted the intensity and organizational capacity of the elements in order to obtain a perception that reflects the stored quantities of nutrients in the soil, so these relationships were used to predict the behavior of the copper element and its dynamics, adsorption and liberation, and this is linked with the organizational capacity because it controls the readiness of elements in the soil [17]. The readiness of the elements was expressed by relations called amplitude and intensity curves according to the concept of [14]. The relationship between the capacity and intensity of the studied soils was drawn in such a way that the relationship shows a linear behavior on which most of the points are located, where the slope of the linear relationship represents the regulatory capacity of the copper voltage, and the linear secant represents the moving ion (Labile ion) and the curves were described (I/Q) by many researchers in the field of soil chemistry based on the straight line of these curves as being based on the Gabon exchange equation, which represents the regulatory capacity of the ion [18] and it is clear from Figures (3,2,1) that there is a difference in the slope values The secant of the linear relationship is related to several factors, including soil texture, mineral composition, and soil content of different forms of copper.

The shape of the straight lines of the relationship (I/Q) is a characteristic feature of each soil and describes the behavior of the ion and the dynamics of its adsorption and liberation. These curves also indicate the different ability of soils to prepare the ion. and the need for ions.

### Effect of Metallic Sulfur on Copper Regulatory Capacity Values (PBC<sub>Cu</sub>)

The relationship between the thermodynamic indicators of the factors of capacity (Capacity), which represents the amount of copper adsorbed on the surface of the soil, and the intensity (Intensity),

which represents the effectiveness of copper in the equilibrium solution under different levels of mineral sulfur (0,1,2,3) g.kg<sup>-1</sup> to the regulatory capacity of copper decreases with the increase in the levels of mineral sulfur added to all soils, which leads to an increase in the ability of the soil to process copper (Table 2). The reason for this is due to the ability of mineral sulfur to reduce the degree of soil reaction (pH), which leads to an increase in the solubility of the original copper (Native).

The additive (0,1,2,4,8,10) mg.kg<sup>-1</sup> on one hand, and on the other hand, the mineral sulfur leads to an increase in the ionic strength, which in turn leads to an increase in the available copper in the soil. The addition of mineral sulfur led to a reduction The values of the regulatory capacity of copper by (89.2) (88.2) (82.8) % for the levels (1,2,3) g.kg<sup>-1</sup> compared to the values of the treatment (without addition) that gave the highest value (lower availability of elements) for the first soil and the same behaviors can be obtained On it to the rest of the soil. We conclude from Table 2 that the lowest value of the organizational capacity was obtained at the first soil, and by adding (3 g. kg<sup>-1</sup> of sulfur), and the highest value was obtained when the comparison treatment (without addition). These indicators are very suitable for assessing the readiness of copper by adding mineral sulfur, as it turns out that mineral sulfur plays an important role in reducing the regulatory capacity (increasing the availability of copper), which leads to an increase in the plant's supply of what it needs of this element during the different stages of growth [19].

### **Moving Copper**

Mobile copper is calculated from the extension of the linear relationship of amplitude-intensity (I/Q) through the x-axis at (AR<sub>cu</sub>=0) and ending with the y-axis as shown in Figure (3,2,1). Table 2 indicates the lowest value of mobile copper for the study soils. It was recorded in the first soil (105 g.kg<sup>-1</sup>) CaCO<sub>3</sub> (control) 0.0176 (centimole.kg<sup>-1</sup>), but when adding different levels of mineral sulfate (1,2,3) gm.kg<sup>-1</sup>, we notice a decrease in the mobile copper values ( -0.0079, -0.0093, -0.0046) (centimol.kg<sup>-1</sup>).

The reason for the decrease in the values of the mobile copper ion in the study soil is due to the decrease in the values of the regulatory capacitance of the ion voltage (increasing the availability of copper) and this is due to the ability of mineral sulfur to reduce the temperature of Soil reaction (pH), which leads to an increase in the solubility of the original copper (Native) and the added (0,1,2,4,8,10) mg.kg<sup>-1</sup>, on the one hand, and on the other hand, the mineral sulfur leads to an increase in the ionic strength, which in turn It leads to an increase in the ready copper in the soil, which leads to a decrease in the regulatory capacity and thus a decrease in the values of mobile copper (increasing the availability of elements

### **Effect of Metallic Sulfur Levels on the Substitution Free Energy Values of Copper at Equilibrium (-ΔF)**

The value of the free energy of copper in the soil depends on the values of the ion activity of copper in the equilibrium solution. The higher the value of the free energy, the more it is associated with a deficiency of copper in the soil and indicates a decrease in its availability due to adsorption reactions on the exchange complex. The lower the value, indicates that the soil is well prepared for copper. The results shown in Table (2) indicate the free energy values of copper reactions in the soil, expressed in units of KJ.mole<sup>-1</sup>, that the free energy values decrease with the increase in the levels of added sulfur, meaning that the addition of mineral sulfur led to a decrease in the free energy values of copper in the soil, as it decreased to lower value of free energy at the level of addition (3) g.kg<sup>-1</sup> (15.786) KJ.mol<sup>-1</sup> compared to the value of the coefficient (Control), which gave the highest value of free energy (23.3543) KJ.mol<sup>-1</sup> and this is due to the action of sulfur in increasing.

This solubility of copper, on the one hand, the increase in ionic strength and the decrease in the potential of copper, on the other hand, which reduces the free energy values of copper reactions, in turn, leads to an increase in the activity of copper in the equilibrium solution, and the same behavior can be obtained for sulfur levels in other soils.

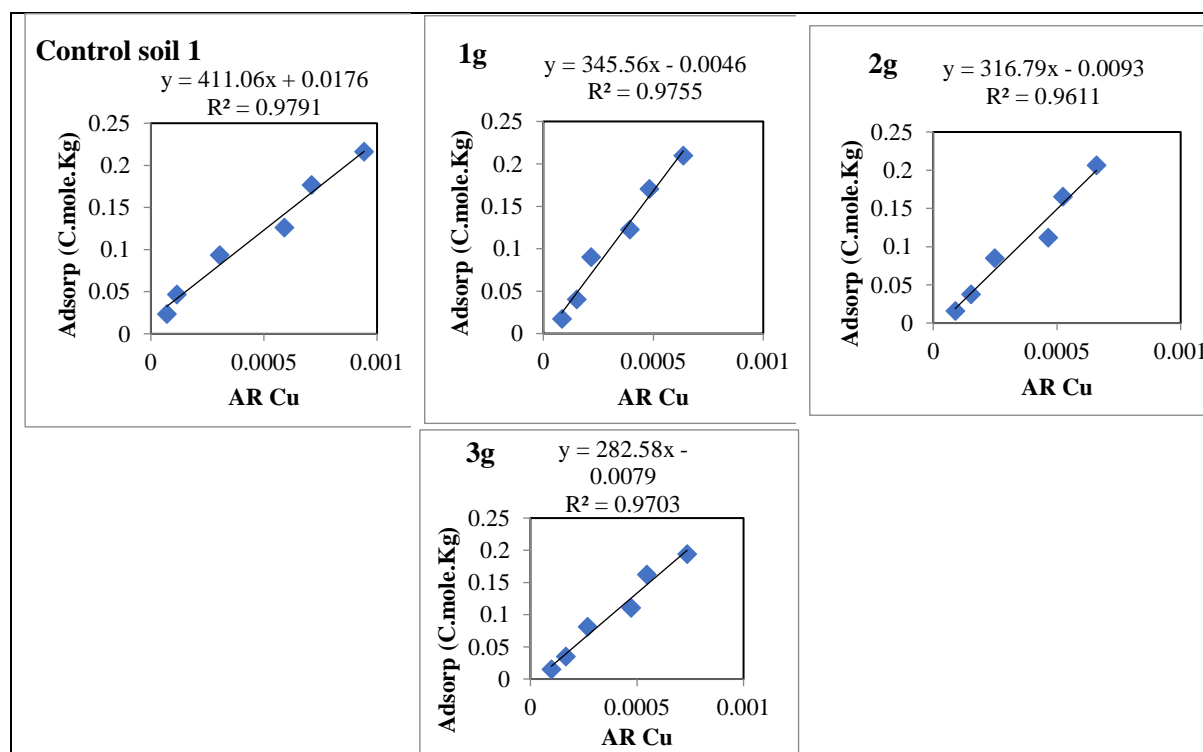
### **Gabon's Preference Coefficient According to the Thermodynamic Input (K<sub>G</sub>)**

The values of the modified Capone constant were calculated from the intensity and amplitude curves I/Q from the differential change of the voltage values of the regulatory capacity of the copper ion, divided by the value of the cation exchange capacity (CEC) [20]. We conclude from Table (2) that

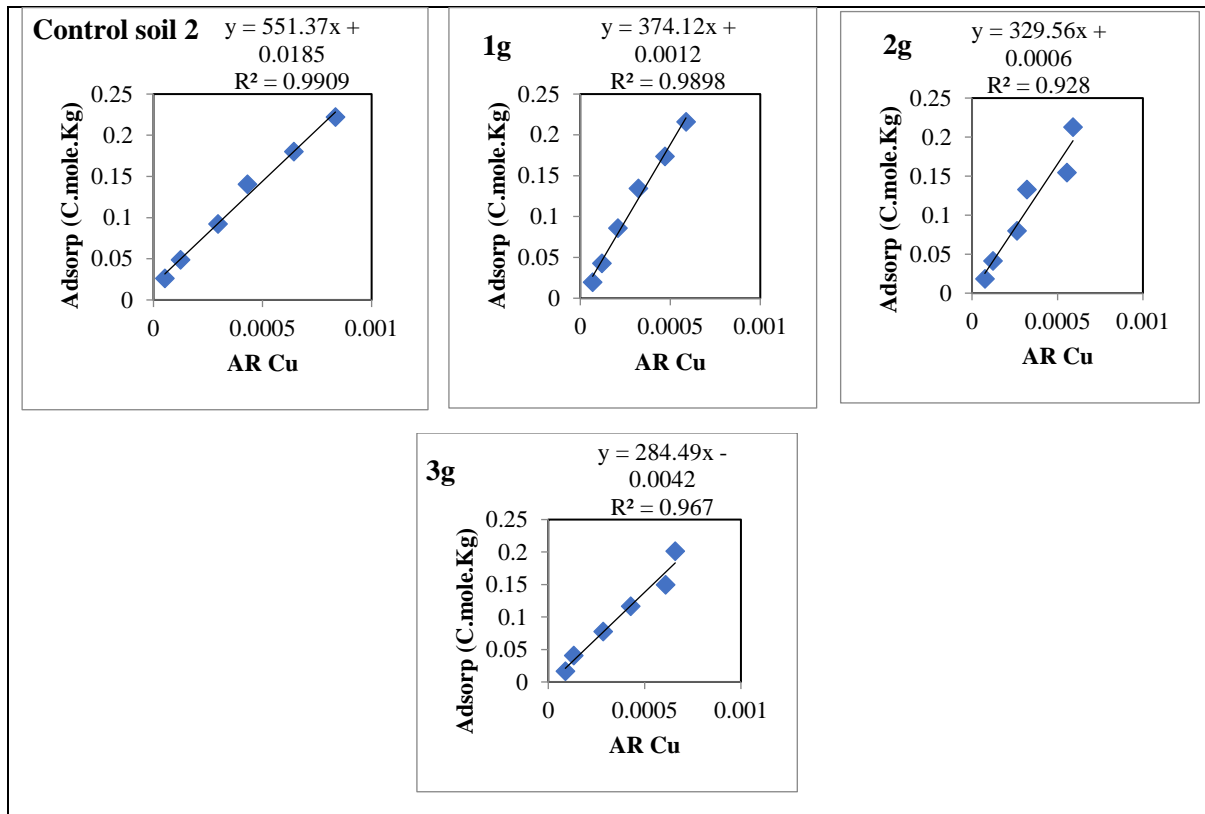
the level of addition (3) g.kg<sup>-1</sup> (12.7288) recorded the lowest value of the Gabon constant compared to the value of the treatment (Control), which gave the highest value of the Gabon constant (18.6), and this is due to the positive role of mineral sulfur in increasing the solubility of copper, therefore, leads to an increase in the activity of copper in the equilibrium solution due to the decrease in the value of the regulatory capacity of copper, and the same behavior of sulfur in the two soils (152 and 202) g.kg<sup>-1</sup> [21]

**Table 2.** values of thermodynamic criteria for study soils.

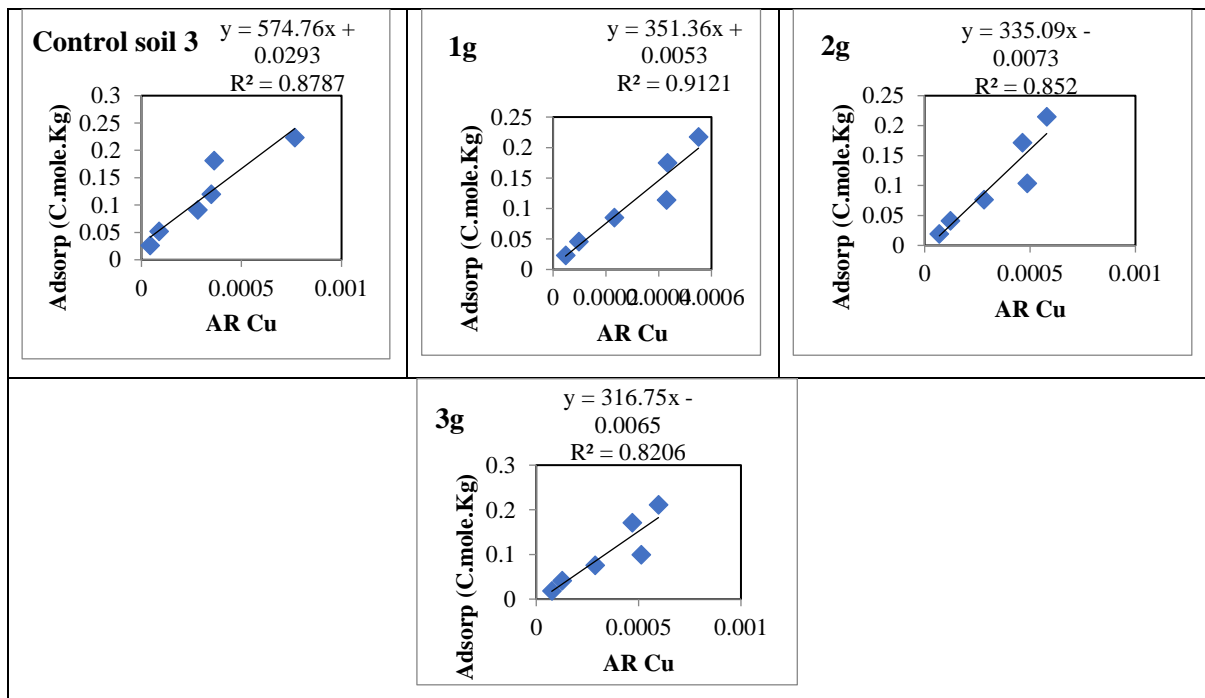
Study Soil	Sulfur g.kg <sup>-1</sup>	PBCCU Cmole.kg <sup>-1</sup>	CU-Labile Cmole.kg <sup>-1</sup>	-ΔF KJ.mole <sup>-1</sup>	K <sub>G</sub>	R <sup>2</sup>
Control		411.06	0.0176	23.3543	18.6	0.97
	(g1)	345.56	0.0046-	20.9439	15.3582	0.97
	(g2)	316.79	0.0093-	19.1993	13.8943	0.96
%10.5 Caco3	(g3)	282.58	0.0079-	15.7865	12.7288	0.97
	Control	551.37	0.0185	24.0990	40.2459	0.99
%15.2 Caco3	1(g)	374.12	0.0012	20.2202	27.9194	0.98
	2(g)	329.56	0.0006	17.5601	24.7789	0.92
	3(3)	284.49	0.0042-	14.8733	21.5522	0.96
%20.2 Caco3	Control	574.76	0.0293	26.7014	31.4076	0.87
	(g1)	351.36	0.0053	22.4226	18.8195	0.91
	(g2)	335.09	0.0073-	20.6842	18.4115	0.85
	(g3)	316.75	-0.0065	19.6619	17.4903	0.82



**Figure 1.** Strength and amplitude curves at different levels of mineral sulfur addition to the soil, 10.2% cal.



**Figure 2.** Strength and amplitude curves at different levels of mineral sulfur addition to the soil, 15.2% cal.



**Figure 3.** Strength and amplitude curves at different levels of mineral sulfur addition to the soil, 20.2% cal.

**Conclusion**

The thermodynamic input for copper adsorption was shown according to the relationships between amplitude and intensity I/Q. The thermodynamic values (regulatory capacitance voltage, moving copper, substitution free energy, and Gabon's constant) all decreased (increase in copper

availability) with increasing levels of added metallic sulfur (1,2,3). (g.kg<sup>-1</sup>), The reason for this is due to the ability of sulfur to reduce the degree of soil reaction (pH), which leads to an increase in the solubility of the original and added copper. In addition to that, mineral sulfur increases the ionic strength, which in turn leads to an increase in copper in the soil. From this, it turns out that the relationship between the thermodynamic indicators was appropriate to increase the effectiveness of copper in the soil with an increase in the level of added sulfur, and then these indicators become very suitable for assessing the readiness of copper by adding metallic sulfur.

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