

SOME CHEMICAL ASPECTS OF SELENIUM IN SOME SOILS OF TOSHKA (EGYPT)

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ABSTRACT

The distribution and chemistry of selenium in Egyptian soils is still unclear. The present work aimed to assess the chemistry of Se in some Toshka soils (Egypt). The results reveal that Se contents in the tested soils ranged from 0.57 to 1.11 ppm with a mean of 0.90 ppm. The AAAC-EDTA extractable -Se in the soils varied widely from 0.107 to 0.472 ppm with a mean of 0.301 ppm. The relation between the total -Se and AAAC-EDTA extractable Se, could be described by the following equation:

$$\text{Total-Se} = -9.3\text{E-}02 + 0.3469 (\text{available-Se}) + 9.75\text{E-}02 (\text{available-Se})^2$$

$$R\text{-sq} = 67.8 \quad (n=35)$$

Among the tested soil properties, only pH and CEC values were related with the AAAC-EDTA extractable -Se. The present data also referred that Se can move downward which in turn may achieve hazardous concentrations in surface ,drainage ,and ground water . Also, The used fractionation scheme has been shown to be satisfactory as indicating from the highly correlation between the total -Se and the sum of Se fractions.

The regression equation is :

$$\text{Tot -Se} = - 8.269 + 16.79 (\text{sum}) - 7.43 (\text{sum})^2$$

$$R\text{-sq} = 88.3\% \quad (n=35).$$

The fractionation results also show that the highly available portion of Se (KCL- extracted) constitutes more than 29% of the sum , followed in decreasing order by Se -associated with oxide mineral , resistance -Se fraction ,sulfide-Se fraction , and specifically adsorbed -Se . Mean while, the Se availability index reveals that unavailable fractions >available fractions >resistance fraction.

Se speciation studies demonstrate that most of Se in some Toshka soils is present as SeO_4^{2-} , followed by HSeO_4^{1-} , ZnSeO_4 , MnSeO_4 and $\text{Zn}(\text{SeO}_4)^{2-}$. The results further reveal that the activity values of Se in the tested soil solutions varied from $3.0199 \text{E-}06$ to $2.2908 \text{E-}06 \text{M L}^{-1}$.

INTRODUCTION

The full extent of Se distribution throughout Egyptian soils is yet unknown FAO(1992).It is also reported that this element need further studies .Furthermore, Sippola, (1979) and Mayland *et al.*(1989) stated that Se studies should not only be directed toward the distribution of Se ,but should include the chemistry behavior of that element in soils

Se is present in almost all rocks and soil . In world soils ,National Academy of Science -National Research Council (1983) found an average Se was 0.09 ppm. Adriano (1986) added that shales rocks seem consistently higher in Se, followed by sandstone and limestone .

In normal soils, Se content ranges from 0.1 to 2 ppm (Swaine, 1955). In Egypt, Elsokkary (1980) reported that Se content in Delta soils ranged from 0.18 to 0.85 ppm, with an average of 0.45 ppm.

Se exists in four oxidation states in normal system; +6 (selenate, Se VI), +4 (selenite, Se IV), 0 (elemental Se), and -2 (Selenide). A balance among these species may be ultimately responsible for the effective behavior of Se in soil and water (Elrashidi et al., 1987).

One of the approaches to study the origin, mode of occurrence of Se is the sequential dissolution technique. Elsokkary (1980) modified the sequential extraction procedure which proposed by Cary *et al.*, (1967) and fractionated Se in some soils at north Egypt. Furthermore, Chao and Sanzolone (1989) sequentially fractionated Se into five fractions and reported that Se tended to be associated with oxides in soil developed through intensive leaching and weathering, whereas in soil with high pH Se presented as mobile form. They also added that the insoluble portion of Se was mainly associated with sulfide minerals.

The aims of this study were ;(i) To elevate the distribution and mobility of Se in some of Toshka soil, (ii) To determine the intrinsic Se pools, and (iii) To predict the dominant species of Se and calculate their activities in the tested Toshka soil solutions.

MATERIALS AND METHODS

Sampling area: Two studied areas of about 220 feddans, in the vicinity of Abou Simbel city, which lies approx. 275 Kms at Southeast corner of Egypt, in the vicinity of Abou Simbel city, approx. 275 kms south of Aswan High Dam.

Soil sampling: A total of thirty-five surface soil samples were taken randomly in two research facilities; namely the National Water Research Center (NWRC) research complex, and the Agricultural Research Center (ARC) research farm.

Also, a soil profile was dug down to a depth of 110cm at ARC farm. The profile was sampled according to its morphological features into four depths; 0-20, 20-40, 40-75 and 75-110 cm.

The collected soil samples were air dried, grounded and passed through a 2 mm sieve and analyzed for pH, organic matter, total calcium carbonate, electrical conductivity and cation exchange capacity according to the conventional analytical methods (Page *et al.* 1982).

Analytical Procedure:

1- Available -Se : Available Se in the tested soils was extracted by AAAC-EDTA solution (0.5M CH₃COONH₄, 0.5 M CH₃COOH, 0.02 M Na₂ EDTA, pH 4.65). as described by Lakanen and Ervio (1971) and modified by Sippola (1979).

2- Se- Fractionation : Se fractionated sequentially into five pools using Chao and Sanzolone (1989) procedure as follows :

- 1- Highly available (0.25 M KCl), denoted as (F1).
- 2- Available (0.1 M K_2HPO_4), denoted as (F2).
- 3- Conditionally available (4.0 M HCl), denoted as (F3).
- 4- Unavailable-Se ($KClO_3$ HCl) denoted as (F4).
- 5- Resistance-Se ($HF + HNO_3 + HClO_4$) denoted as (F5).

After each step, the extraction was centrifuged, filtrated and the clear supernatant was collected for Se determination.

3- Total - Se: A 0.2 g of soil sample was digested with 10 ml concentrated ($HF + HNO_3 + HClO_4$) in Teflon beaker at $220\text{ }^\circ\text{C}$. When the volume of mixture reduced to about 2 ml, 20 ml of 6 M HCl was added and the mixture heated to $95\text{ }^\circ\text{C}$ for 15 min. Then the solution was transferred to 50ml volumetric flask with 4 M HCl and bring to volume for Se determination.

4- Speciation of Se in soil solutions: Speciation of Se was carried out in solutions obtained from saturated soil paste as described by Hirsh and Banin (1990).

5- Data analysis: For computed Se-speciation concentrations of Pb, Ni, Cu, Zn, Fe, Mn, P, NO_3 , SO_4 , Cl were determined by the conventional analytical methods (Page *et al.* 1982), Se determined by hydride generation atomic absorption (Solaar 969 AA Spectrometer). While, the data were analyzed using Chemical Equilibrium Modeling Program (Mineql v2.1) as outlined by Westall *et al.*, (1976).

RESULTS AND DISCUSSION

All the soils under investigation are alkaline in reaction, pH (7.69 - 8.55), having wide variation in salt concentration and calcium carbonate, as shown in Table 1. The soils are also poor in organic matter ($x^- = 0.18\%$). The majority of the tested soils having CEC of about 4.0 meq/100g. Means, standard deviations of the tested soil properties and Se contents are also listed (Table 1).

1-Total Soil -Se:

Se content of the tested soils is listed in Table 1. The data show that Se contents in some Toshka soils (south Egypt), are present at levels range from 0.57 to 1.11 ppm with a mean of 0.9 ppm soil.

The average reported of Se contents for some countries (in ppm) were: Ireland-30, Fleming (1662); Denmark-0.57, Bisberg (1972); Norway-0.53, Lag and Steinnes (1978); Egypt-0.45, Elsokkary (1980); Sweden -0.39, Lindberg and Bingenfors (1970) and USA-0.3, Cary *et al.* (1967).

Furthermore, Adriano (1986) reported that some seleniferous soils in United Kingdom had Se contents of 0.9 to 91.4 ppm, where in normal soils, it ranged from 0.2 to 1.8 ppm. It is obvious from the present data that Se contents in Toshka soils (south Egypt) is much higher than those reported by Elsokkary (1980) for north Egypt soils. This conflicting results may be

attributed to the wide variation between soil Se environment at the two locations(Temperature , precipitation, nature of soil, land use,...). In the same concern ,Rosenfeld and Beath (1964) mentioned that Se can be expected to be present in excessive amounts only in Semi-arid and arid region.

Table 1: Some soil properties and soil –Se of the tested soil samples .

Sample No	Soil properties				Soil-Se(ppm)		
	pH*	EC, mmoh/cm	OM %	CaCO ₃ %	CEC meq/100g soil	AAAc-EDTA ext-Se	Total Se
1	7.79	6.40	0.19	4.02	4.39	0.384	1.05
2	7.83	2.87	0.09	3.89	1.41	0.189	0.57
3	8.01	0.37	0.21	2.61	1.86	0.187	0.64
4	7.81	0.94	0.12	2.31	4.28	0.279	0.87
5	7.80	8.44	0.19	3.08	4.41	0.189	0.68
6	7.81	1.06	0.15	3.50	2.01	0.107	0.63
7	7.75	9.04	0.22	5.00	4.40	0.107	0.82
8	8.01	0.95	0.18	8.00	4.96	0.287	1.05
9	8.04	0.84	0.24	2.80	3.62	0.317	1.04
10	7.69	3.01	0.19	5.38	3.90	0.156	0.68
11	8.00	1.65	0.24	5.77	5.13	0.241	0.83
12	8.11	4.03	0.20	4.26	4.14	0.392	0.84
13	7.89	6.51	0.12	6.92	3.80	0.329	0.92
14	8.00	6.21	0.19	7.80	3.66	0.327	0.91
15	8.37	6.47	0.24	5.61	2.21	0.405	1.03
16	7.74	4.25	0.09	3.60	2.68	0.167	0.70
17	7.80	3.52	0.12	4.00	4.56	0.250	0.76
18	8.14	10.47	0.20	5.60	3.84	0.319	0.82
19	8.45	10.55	0.26	4.80	5.14	0.405	1.01
20	7.90	3.14	0.16	5.42	3.20	0.314	1.03
21	7.75	2.14	0.21	6.41	4.10	0.258	0.87
22	7.94	3.60	0.18	4.98	4.60	0.370	0.97
23	7.96	1.59	0.09	3.97	4.56	0.397	1.07
24	8.10	3.19	0.20	3.56	4.20	0.361	1.01
25	7.90	6.00	0.19	4.20	4.30	0.326	0.97
26	7.74	4.58	0.21	3.05	2.66	0.248	0.95
27	7.83	2.64	0.15	3.14	2.79	0.285	0.90
28	7.92	6.94	0.17	9.75	4.79	0.319	1.04
29	8.01	6.25	0.20	8.26	4.39	0.395	1.05
30	8.15	5.34	0.21	6.37	5.00	0.472	1.09
31	8.29	6.58	0.24	5.32	4.50	0.415	1.11
32	7.80	2.80	0.18	3.60	3.97	0.286	0.84
33	8.14	1.97	0.25	8.54	4.90	0.401	1.00
34	8.12	4.28	0.19	9.84	2.85	0.316	0.87
35	8.15	2.98	0.23	5.30	2.36	0.344	0.92
Mean	7.96	4.33	0.19	5.16	3.82	0.301	0.90
St.Dev.	0.18	2.73	0.04	2.00	1.02	0.091	0.15

* pH determined in (1:2.5 soil suspension).

** EC determined in soil solution paste extract.

The statistical results also show that total Se is highly correlated (r=0.82**) with the AAAC-Ext. –Se),the polynomial fit equation is :

$$(Tot-Se) = -9.3E-02+0.3469 (AAAc-ext-Se) +9.75E-02 (AAAc-ext-Se)^2$$

$$R.sq = 67.8\%$$

AAAc-EDTA extractable –Se (Available) :

As with most trace elements, total –Se is unreliable index of the availability of Se in soils. Consequently ,several extracting solution have been employed to predict potential bioavailability of Se (i.e,NH₄HCO₃-DTPA (Soltanpour and Workman,1980) ;0.02M k₂SO₄ solution (Elsokkary,1980) . The data reported in Table 1 reveal that the available portion of Se in the tested soils varied widely from 0.107 to 0.472 ppm with a mean of 0.301 ppm.

Also, the available portion of Se in the present study are higher than those reported by El-Sokkary (1980) who mentioned that the available portion of Se extracted with 0.02 M K₂SO₄ solution from delta soils, Egypt ranged from 0.05 to 0.24 ppm. Mean while, the data published by FAO (1992) for Egyptian Se ranged from 16.3 ± 16.1 to 16.3 ± 25.0 ug/l were much closer to the present results .

On the other hand , AAAC-EDTA extractable soil Se as a function of some of soil factors was statistically tested,Table(1) . The results show that only pH and CEC values were the significantly contributed ones.The regression equation is

$$\text{AAAc-Edta ext –Se} = - 3.32 + 0.316 \text{ pH} + 0.0288 \text{ CEC}$$
$$\text{R-Sq}=57.8\% \quad \text{n}=35$$

Also, FAO (1990) reported that above pH 7,the AAAC-EDTA extracted Se was directly proportional with pH .In the same connections, Cary et al.,(1967) Greeing et al.,(1968) and Gissel –Nielsen (1971) , their studies concluded that increasing soil pH induced increasing in Se uptake by plants . The highly available portions of Se in the tested soils may attributed to that under ordinary alkaline conditions , Se does not form highly insoluble salts or stable compounds , consequently , the available portion under these circumstance increased (El-rashidi et al ., 1987). It also seems that the employed extract , (AAAC-EDTA) capable to release many pools of Se ,instead to water available portions only.

3- Movement of Se in soil profile:

There is evidence from the Table (2) that appreciable amount of Se can move downward. It also seems that most of Se lost from upper layer is found in the second layer ,20-to 40 cm depth ,although net losses of Se may be expected from whole profile to groundwater .

The movement of Se within the tested soil profile may be attributed to many reasons ; 1) The dominant species of Se in the tested soil solutions is selenate SeO₄²⁻ (as will shown latter) .This species is effectively noncreative with the soil components and thus groundwater would be affected , 2) The area of the selected soil profile was cultivated and daily drip irrigated for many years , consequently an accumulated layer may be formed below root zone and 3) It not need to say that the hydrophysical properties of the tested soils facilitate the downward movement of Se . Similar observations were also observed by Alemi et al.,(1988) .

4-Fractionation of soil –Se :-

It worth to mention here that the extraction scheme used herein acts with soil-Se through several mechanisms; (1) mass action and ion exchange to extract highly available –Se , F1 ; (2) anion competition and ligand exchange mechanism to extract specifically adsorbed–Se ,F2 ; (3)acid dissolution and hydrolysis to extract Se –associated with oxide ,F3 ; (4)oxidative acid dissolution mechanism to extract sulfide –Se ,F4 and (5) acid destruction of mineral lattice structure to release resistance –Se fraction ,F5 .

The fractionation results as shown from Table 2 , reveal that the average of Se recovery (calculated as the sum of the five fractions / total content *100) is up to 92 % , (the Table),indicating satisfactory of the employed scheme. This findings is also confirmed by the results of the statistical studies .

The fit equation between the total –Se content and the sum of the five fractions is :-

$$\text{Total} = - 8.269 + 16.792 \cdot \text{sum} - 7.431 (\text{sum})^2$$

$$R - \text{sq} = 88.3 \% \quad n = 35$$

Also, the statistical results show that the amount of Se extracted by AAAC – EDTA are highly correlated ($r=0.969^{**}$) with the sum and the polynomial fit equation is :-

$$\text{Sum} = 6.843 - 41.56 (\text{available}) + 73.632 (\text{available})^2$$

$$R - \text{sq} = 97.2$$

These results confirmed the previous observations, that AAAC-EDTA extract capable to release Se from many pools.

Table 2 : Se-fractionation of the tested soils expressed as percentages of their sums.

Depth (cm)	Item	Se-fractionation %					Sum (ppm)	AAAc Se (ppm)	Total (ppm)	Sum/ Total %
		(F ₁)	(F ₂)	(F ₃)	(F ₄)	(F ₅)				
0-20	ppm	0.275	0.074	0.245	0.190	0.196				
	%	28.08	7.55	25.0	19.39	19.98	0.98	0.287	1.05	93.33
20-40	ppm	0.342	0.084	0.352	0.089	0.293				
	%	29.48	7.24	30.34	7.67	25.27	1.16	0.336	1.21	95.86
40-75	ppm	0.294	0.109	0.326	0.139	0.220				
	%	26.97	10.09	29.91	12.84	20.19	1.088	0.319	1.24	87.90
75-110	ppm	0.369	0.090	0.308	0.122	0.20				
	%	33.94	8.26	28.26	11.19	18.35	1.089	0.324	1.18	92.37
Mean(x ⁻¹)		0.320	0.089	0.307	0.135	0.227	1.078	0.317	1.17	92.36

Where;

- F1 is the fraction of highly available Se.
- F2 " " " of available Se.
- F3 " " " of conditionally available Se.
- F4 " " " of unavailable –Se .
- F5 " " " of resistance –Se .

Furthermore, the sum of Se fractions are highly correlated with (F₃)fraction, indicating that most of Se in the tested soil occurs mainly associated with oxide minerals and amorphous materials ($r = 0.98^{**}$)
The linear fit equation is:

$$\text{Sum} = 0.589 + 1.605 \text{ oxide minerals .}$$

$$R\text{-sq} = 96.7 \%$$

Also, the present data reveal that most of Se is associated with highly available fraction (29.62% of the sum), followed in decreasing order by Se – associated with oxide minerals (F₃) (28.37) >resistance –Se fraction (20.95%) >sulfide –Se fraction , (F₄) (12.77 %)and specifically adsorbed –Se , F₂ (8.29).

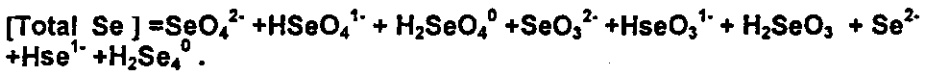
On the other side, the availability index of Several that Se fractions may be arranged as follows:

$$\text{Unavailable (F}_3\text{+F}_4\text{)} > \text{available (F}_1\text{ +F}_2\text{)} > \text{resistance (F}_5\text{)}$$

The data reported by Elsokkary (1980)suggested the highest portion of Se was associated with water soluble fraction (25.4% of the total) followed by NH₄-OH fraction which associated with Se –organically bounded .

5 – Speciation and activity of Se in the tested soil solutions:

El-rashidi *et al.*, (1987) reported that total Se in the tested soil solutions can be written as :



The speciation of Se in the saturated soil extracts were computed by Chemical Equilibrium Model (Mineql v 2.1) . The input data calculated as pM (-log Molar concentration) of the following ions are listed in Table 3.

Table (3): Ionic compositions of the extracted soil solutions:

Depth (cm)	pH	NO ₃ ⁻ *E-03	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻ *E-05	Fe ²⁺ E-05	Zn ²⁺	Mn ²⁺ *E-05	Cu ²⁺ *E-05
0-20	8.31	2.495	0.14	0.07	0.08	8.53	1.29	1.85E-06	1.01	28.8
20-40	8.30	2.111	0.15	0.05	0.09	5.63	5.61	1.51E-05	1.74	2.85
40-75	8.32	1.344	0.09	0.08	0.02	3.83	6.21	6.15E-07	3.81	2.65
75-110	8.27	1.344	0.13	0.05	0.06	5.15	2.80	2.05E-05	0.105	6.19

The results of Se speciation are illustrated in Fig. 1

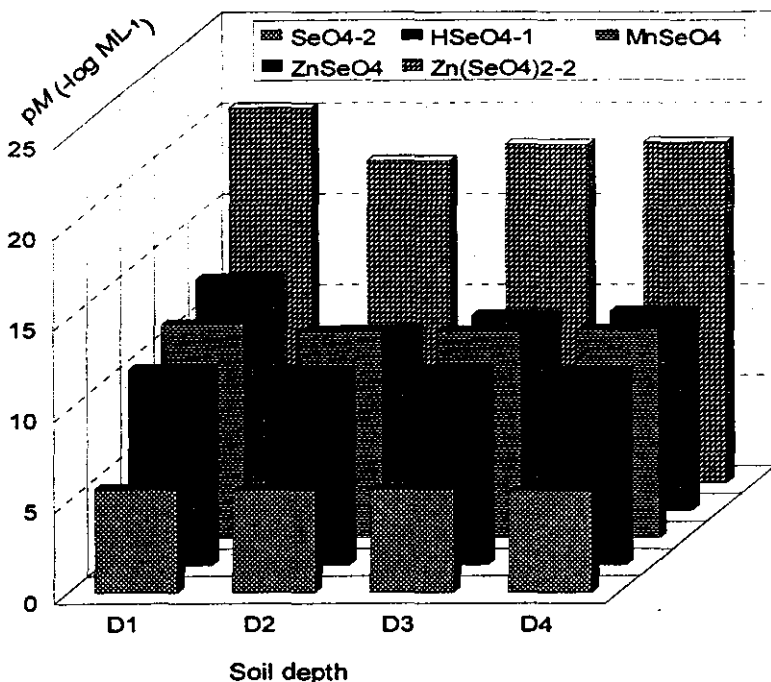


Fig. 1. Speciation of various Se in the tested soil solutions.

The Fig. demonstrated the importance SeO_4^{2-} species in the tested soil solutions, which comprise the majority of Se species. On average basis, the concentrations of the various Se species (expressed as $\text{pM} = -\log \text{M}$) were :

SeO_4^{2-} , (5.58) > HseO_4^{1-} , (10.65) > ZnSeO_4 , (11.04) > MnSeO_4 , (11.43) > $\text{Zn}(\text{SeO}_4)_2^{2-}$, (18.9). These results are in agreement with the findings Elrashidi *et al.* (1987) who mentioned that selenate (SeO_4^{2-}), under oxidizing conditions were the dominant species in soil solutions.

6- Se-activities in the tested soil solutions :

The computed results also reveal that the activity of Se in the tested soil solutions varied between $3.0199\text{E-}06$ to $2.2908\text{E-}06\text{ ML}^{-1}$.

ACKNOWLEDGMENT

The authors wish to express their sincere gratitude and appreciation to Prof .Dr. Ahmed S.Ahmed for his assistance and cooperation as well as introducing all facilities needed for accomplishing this study .

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بعض الاعتبارات الكيميائية لعنصر السيلينيوم في بعض اراضي توشكي (مصر)
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مركز البحوث الزراعية - معهد بحوث الاراضي والمياه والبيئة .

توزيع عنصر السيلينيوم وسلوكه الكيميائي في الاراضي المصرية يحتاج الي المزيد من الدراسات والبحوث (FAO, 1992). ولقد تناولت هذه الدراسة توزيع عنصر السيلينيوم والتعرف علي سلوكه الكيماوي في اراضي توشكا (جنوب مصر). ولقد اوضحت الدراسة ان المحتوي الكلي من عنصر السيلينيوم يتراوح ما بين 0.057 - 1.11 ميكروجرام / جم تربة و كان المتوسط العام 0.09 ميكروجرام/جرام. كذلك اوضحت نتائج السيلينيوم المستخلص بواسطة (AAAc-EDTA) ان الكمية الميسرة من السيلينيوم تتباين بشدة في الارض محل الدراسة حيث تتراوح ما بين 0.107 - 0.472 جزء في المليون بمتوسط قدره 0.301 ملليجرام /لتر. ولقد اوضحت الدراسة وجود علاقة معنوية بين الكمية الكلية من السيلينيوم والكمية المستخلصة بواسطة AAc-EDTA وكانت العلاقة كالآتي:

$$\text{الكمية الكلية من السيلينيوم} = -9.3 * 10^{-2} + 0.3469 (\text{الكمية الميسرة}) + 9.75 (\text{الكمية الميسرة})^2$$

R-sq. = 67.8 (n = 35).

واظهرت النتائج ان من بين خصائص التربة التي تمت دراستها تبين ان قيم درجة الحموضة وكذلك السعة التبادلية الكاتيونية هي الخصائص الوحيدة التي تؤثر علي الكمية الميسرة من السيلينيوم. كذلك تبين امكانية تحرك السيلينيوم داخل القطاع الارضي الامر الذي قد يترتب عليه تلوث الماء سواء كان سطحيا او ماء صرف او ماء جوفي.

اوضحت نتائج طريقة الاستخلاص التتابعي للسيلينيوم انها كانت مقنعة لحد كبير وذلك من خلال الارتباط القوي ما بين الكمية الكلية من السيلينيوم ومجموع المفصولات الكيماوية الخمسة المستخلصة وكلفت معادلة الارتباط كالآتي:

$$\text{الكمية الكلية} = -8.269 + 16.79 (\text{مجموع الصور الخمسة}) - 7.43 (\text{مجموع الصور الخمسة})^2$$

R-sq = 88.3 (n = 35)

وكان ترتيب المفصولات الكيماوية للسيلينيوم كالآتي: اكثر من 29 % من مجموع الصور علي صورة عالية التيسر يليها صور السيلينيوم المرتبط بالاكاسيد < السيلينيوم المرتبط بالتركيب المعنوي < السيلينيوم علي صورة كبريتيدات < السيلينيوم المرتبط ارتباط نوعي.

ولكن تبين من حساب دليل الصلاحية انه يمكن ترتيب تلك المفصولات الكيماوية للسيلينيوم كالآتي : الجزء غير الميسر < الجزء الميسر < الجزء المثبت داخل التركيب المعنوي

اوضحت دراسة الصور الايونية المختلفة للسيلينيوم في المحلول المشبع للاراضي محل الدراسة ان الصورة الايونية سليكات SeO_4^{2-} كانت هي الصورة الايونية السائدة في الاراضي محل الدراسة يليها الصورة HSeO_4^- ثم ZnSeO_4 ثم MnSeO_4 واخيرا $\text{Zn}(\text{SeO}_4)^{2-}$.

ولقد تم حساب معامل نشاط السيلينيوم في المحلول المشبع للاراضي تحت الدراسة وكان يتراوح ما بين 1.0×10^{-1} الي 2.2908×10^{-1} مولر/لتر