

Redox potential E_H [Se(VI)/Se(IV)] of aqueous extract of soils from Yongshou Kaschin-Beck disease region and the influence by humic acid

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Abstract—The relation between E_H [Se(VI)/Se(IV)] and pH of soil aqueous extract in Kaschin-Beck disease region and the effects of natural redox agents, namely humic substances, MnO_2 and Fe^{2+} , on the redox property of the system were studied. The results indicated that both humic acid and Fe^{2+} could enhance the reducibility of Se(VI) and MnO_2 , a limited oxidizability for Se(IV). Fe^{2+} showed a weak reducibility only at low pH value. The reducibilities of three sulfur-containing compounds for Se(VI) were in following order:

thioglycollic acid > L-cysteine > sulfide

Keywords: selenium; redox potential; Kaschin-Beck disease; humic acid.

Selenium exists in the natural environment in the forms with oxidation numbers of -2, 0, +4 and +6. The chemical properties of these forms of selenium determine the chemical behaviors of selenium in the environment (Robberecht, 1982). In natural water, Se(IV) and Se(VI) are two oxidation states of selenium. Dalahay *et al.* (Leutwein, 1977) proposed a pH- E_H diagram to manifest the geochemical properties of selenium in aquatic system, and they pointed out that within a wide range of E_H and pH, selenium exists as several stable +4 forms: H_2SeO_3 , $HSeO_3^-$ and SeO_3^{2-} . Whereas SeO_4^{2-} is present only under extremely oxidative conditions. It has been reported that the Se(IV)/Se(VI) ratio of water samples from different sources is different. It has also been proved by Massee *et al.* (Massee, 1977) that selenite is the principal form in natural water, but in drinking water we can get about 60% Se(VI) of the total selenium determined. Selenate can be easily formed under alkaline and oxidizing conditions. Most of the selenates are soluble and unable to form stable complexes. The transformation of selenate into less soluble selenite is a slow process.

The bioavailability of selenium is closely related to its chemical speciation. Furthermore, the chemical speciation and concentration of selenium in the environment are determined by the relevant dissociation constant, solubility, product and redox potential. Based on several long-term investigations, two hypotheses on the pathogenesis of Kaschin-Beck disease have been proposed, i.e. low selenium content in the environment and high humic acid level in drinking water of epidemic regions. These two pathogenic factors of Kaschin-Beck disease were considered together in our work to reveal the environmental connections between humic acid and selenium. For this purpose we firstly investigated the soils of the typical Kaschin-Beck disease regions at Yongshou County, Shaanxi Province, then studied the E_H [Se(VI)/Se(IV)]-pH relation in soil water and the influence of MnO_2 , Fe^{2+} , humic acid and other natural redox agents on selenium in the environment. Finally, we discussed the actual form of selenium existed in the disease regions and the related influence by its redox interactions. Up to now there is little information concerning the study on the redox properties of selenium in Chinese natural environment. Most of the references on this topic from other countries are just some reports resulted from theoretical calculations. In this sense the experimental results of our work may

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shed light on the understanding of the redox properties of selenium, the interrelation between selenium and humic acid and its role in the cause of Kaschin-Beck disease.

E_H [Se(VI)/Se(IV)]-pH OF THE SOIL AQUEOUS EXTRACT IN KASCHIN-BECK DISEASE REGIONS AND THE INFLUENCE BY HUMIC ACID

Samples and methods

Preparation of soil aqueous extract

To prepare soil water, 100 g of air-dried soil from Guanguan Gou Kaschin-Beck disease regions, Yongping village, Yongshou County, was thoroughly mixed with 1L of distilled water. The supernatant (pH=6.97, E_H =+464mv) was used for the experiments.

Experimental method

Different concentrations of Se(VI)/Se(IV) redox pair solutions were prepared by the soil extract. Humic acid and Fe^{2+} solutions were added. The redox potentials of the solutions were determined at 25°C at various pH values.

Reagents and instrument

Se(VI): $Na_2 SeO_4 \cdot 10H_2O$ (AR Beijing Chemical Plant)

Se(IV): SeO_2 (AR Beijing Chemical Plant)

Fe^{2+} : $FeSO_4 \cdot 7H_2O$ (AR Beijing Chemical Plant)

Humic acid(HA): extracted from the soil of Jiangjia Shan, Yongping village, Yongshou County, Shaanxi Province.

pH values were adjusted with dilute HNO_3 (AR) and $NaOH$ (AR).

Instrument: PHS-3 pH meter, LB-801 Super thermostat.

E_H measurement: Potentiometry, Pt-electrode/saturated calomel electrode as reference.

Calibration of the instrument: Standard Voltmeter.

Buffer solution: standard buffer solution pH=4.01(potassium hydrogen phthalate), 7.02 (disodium hydrogen phosphate).

Standard E_H solution: $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ (226mV, 25°C).

Results and discussion

The results of the E_H [Se(VI)/Se(IV)]-pH studies of the soil solution from Yongshou disease region was shown in Table 1. Table 2 and Figure 2 summarized the influence of the concentration of humic acid on E_H [Se(VI)/Se(IV)]-pH. To compare the effects on E_H [Se(VI)/Se(IV)] by humic acid and Fe^{2+} , E_H [Se(VI)/Se(IV)]- $[Fe^{2+}]$ curves in different pH conditions were presented in Figure 3 and Table 3. Figure 1 is the comparison of E_H -pH relations resulted from our experiments ($[Se(VI)]$, $[Se(IV)]=0.1$ ppm) and reference calculation.

From Table 1 we could see that in each group of selenium solution, the redox potential decreased gradually with increasing pH value. The concentrations of either Se(VI) or Se(IV) had little influences on the redox potentials of selenium except the highest concentration group in which the E_H value decreased slightly. As Figure 1 ($[Se(VI)]$, $[Se(IV)]=0.1$ ppm) shown, the experimental E_H -pH curve was in good correspondence with the theoretical results calculated from standard redox potential, dissociation constants and ionic activity by Lakin (Lakin, 1961), Pearsall *et al.* (Pearsall, 1961). Comparing our results with those from references, the E_H -pH relation was almost the same at pH<7. When pH>7, the experimental E_H value was a little bit higher than the calculated value. Above the SeO_4^{2-}/SeO_3^{2-} curve there should exist O_2/H_2O , MnO_2/Mn^{2+} redox pairs, below the curve SeO_3^{2-}/Se^0 , $Fe(OH)_3/Fe^{2+}$, $Se^0/CuSe$, H^+/H_2 , Se^0/HSe^- and some other related redox pairs. All of these redox pairs could affect the oxidation state of selenium in soil water. Based on Figure 1 and all of the E_H -pH data it becomes possible for us to discuss and divide the regions of actual soil water in which Se(VI), Se(IV) and other forms of selenium existed. It is important to the investigation of selenium in Kaschin-Beck disease regions. For instance, the pH and E_H values in the soil water of Guanguan Gou,

Yongping village were 6.97 and 464 mV we could then assume that the dominant species of selenium in this area was selenite (HSeO_3^-).

Table 1 Relation of pH and E_H of soil solution from Yongzhou County

Se(VI) 0ppm	pH	3.19	4.14	4.98	6.09	6.97	8.07	8.73	10.07	11.08	11.98	13.02
Se(IV) 0ppm	E_H ,mV	797	699	574	490	464	412	387	304	241	184	125
Se(VI) 0.001ppm	pH	3.05	4.05	4.97	6.02	6.95	8.05	9.02	9.76	11.02	11.99	13.02
Se(IV) 0.001ppm	E_H ,mV	845	699	606	550	484	430	374	330	258	197	130
Se(VI) 0.1ppm	pH	2.97	3.99	5.08	5.97	6.95	7.87	9.06	10.05	11.02	12.02	13.11
Se(IV) 0.1ppm	E_H ,mV	817	727	591	529	483	429	365	307	248	191	124
Se(VI) 1ppm	pH	2.96	4.05	4.92	6.05	7.07	8.00	9.03	10.00	11.01	12.02	13.00
Se(IV) 1ppm	E_H ,mV	801	715	594	522	462	410	363	297	238	182	127
Se(VI) 10ppm	pH	3.00	4.25	5.04	6.04	7.05	8.04	9.02	10.03	11.00	11.99	12.98
Se(IV) 10ppm	E_H ,mV	788	673	585	529	471	422	364	299	244	191	133
Se(VI) 100ppm	pH	3.06	4.06	5.06	5.96	7.00	7.94	9.02	10.03	10.99	12.03	13.00
Se(IV) 100ppm	E_H ,mV	684	573	504	481	436	394	347	287	237	184	126

According to Swain (1970), all E_H values were corrected by adding $E_o = +245\text{mV}$

Table 2 Effect of humic acid concentration on the E_H -pH

[HA],ppm	[Se]=0,								
E_H ,mV	[HA]=0	0	10	50	100	200	500	1000	
pH									
1.97	894	848	837	819	805	789	754	518	
3.00	801	739	727	687	645	555	285	217	
4.97	552	674	657	601	510	429	252	217	
7.02	405	644	628	546	428	357	215	182	
9.02	337	619	598	530	422	355	221	185	
12.08	171	183	183	183	183	180	174	168	

Table 3 Effect of Fe^{2+} concentration on the E_H -pH

[Fe ²⁺],ppm	[Se]=0,								
E_H ,mV	[Fe ²⁺]=0	0	10	50	100	200	500	1000	
pH									
2.98	824	744	627	584	565	547	523	507	
4.98	527	635	549	510	487	475	461	453	
6.98	371	628	537	496	479	465	447	437	
9.03	312	563	505	472	458	445	435	429	
11.13	231	390	296	290	290	298	323	348	
12.99	127	137	135	122	77	17	-235	-373	

The concentrations of Se(VI) and Se(IV) in Table 2 and 3 are 100 ppm; concentration ratio: 1:1

Figure 2 and Figure 3 summarized the experimental data in Table 2 and Table 3. The results showed that both humic acid and Fe^{2+} could decrease the Se(VI)/Se(IV) redox potential and their effects are concentration dependent. In other words, natural redox agents humic acid and Fe^{2+} enhanced the reducibility of Se(VI)/Se(IV) system and resulted in the increasing of Se(IV) fraction in total selenium. Relatively, the effect of the concentration of Fe^{2+} on E_H -pH was weak, while humic acid was a better reductant for selenium. The results of E_H -pH relation were repeated in different pH conditions. The concentration dependence of $E_H[\text{Se(VI)/Se(IV)}]$

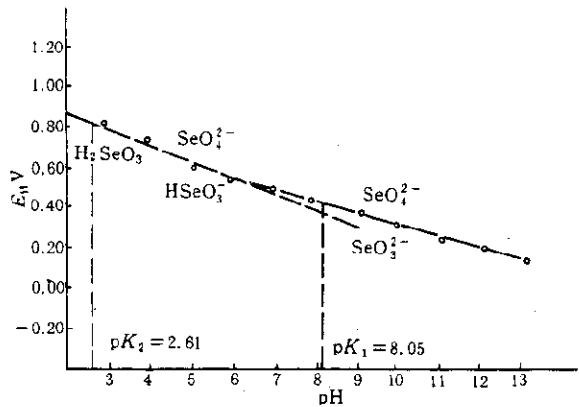


Fig. 1 pH vs E_H in soil solution (25°C) (The solid curve stands for the experimental results)

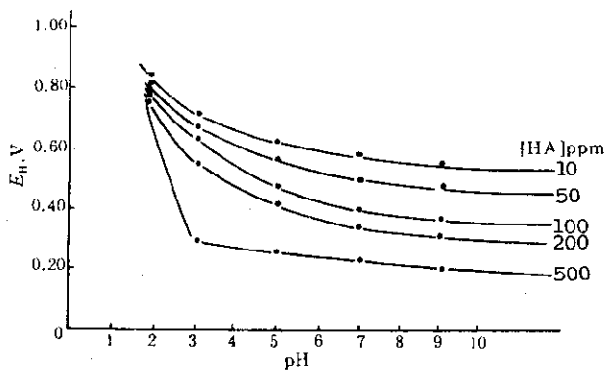


Fig. 2 Effect of humic acid concentration on the E_H -pH(25°C)

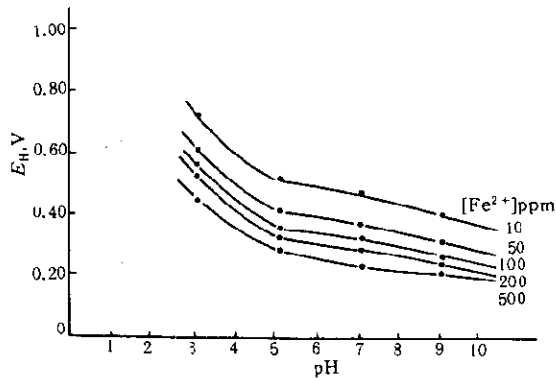


Fig. 3 Effect of Fe^{2+} concentration on the E_H -pH(25°C)

by humic acid was found to be in accordance with that by Fe^{2+} in all groups of experiments.

REDOX OF SELENIUM [Se(VI) / Se(IV)] BY HUMIC ACID, MnO_2 , Fe^{2+} AND OTHER ENVIRONMENTAL SUBSTANCES

Materials and methods

Preparation of soil aqueous extract and experimental procedure

Aqueous extract of soil samples were prepared, following the procedure mentioned above. The redox agents studied were added to the extract, and pH were adjusted with acid or base to achieve various pH values. Standard Se(IV) or Se(VI) solutions were added into these prepared soil extract. Finally, the concentrations of different forms of selenium in the solutions were determined in the presence of various redox agents and pH conditions.

Method of selenium determination

According to reference (Wang, 1981), Se(IV), Se(VI) and total Se were determined by gas chromatographic technique. Standard Se solution was tested in each group of experiment to eliminate determination error.

Sample and instrument

Gas chromatograph: Model SP-501.

Humic acid: fulvic acid (FA) from Songhuajiang, humic acid (HA) from Lianjiang and fulvic acid (FA) from Zhanjiang were all provided by the Institute of Chemistry, Academia Sinica.

MnO_2 : AR Beijing Shuangqiao Chemical Plant.

Fe^{2+} : $FeSO_4 \cdot 7H_2O$, AR Beijing Chemical Plant.

The reagents for determination of selenium including 1,2-diamino-4-nitrobenzene were supplied by the Inorganic Chemical Laboratory of the Research Center for Eco-Environmental Sciences.

Results and discussion

Figure 4 and 5 showed the pH dependence of Se(IV) oxidation with various amounts of MnO_2 . The reductions of Se(VI) with various concentrations of Fe^{2+} under varied pH conditions were summarized in Figure 6 and Figure 7. The pH dependence of Se(VI) (0.1 ppm) reduction by humic acid (5 ppm) was shown in Figure 8, and by sulfide, L-cysteine and thioglycolic acid in Figure 9.

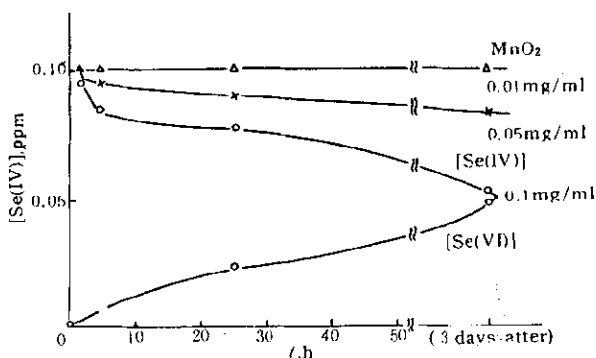


Fig. 4 Oxidation of Se(IV) by MnO_2 (pH=6.5, E_H =473 mV)

It was shown in Figure 4 and 5 that MnO_2 had a limited oxidizability for Se(IV). In neutral solution the rate of transformation of Se(IV) to Se(VI) was proportional to the amount of MnO_2 suspended in the solution. The detection of the oxidation product Se(VI) in solution was an evidence of the proposed oxidation mechanism, it eliminated any other cause of the concentration decrease of Se(IV). In neutral solution, 50% of Se(IV) (0.1 ppm) was oxidized by a high concentration of MnO_2 (0.1 mg/ml). MnO_2 concentration was lower, Se(IV) was

oxidized slowly, under acidic conditions (pH=3). We did not observe any oxidation of Se(IV) at a low concentration of MnO_2 under neutral and alkaline conditions.

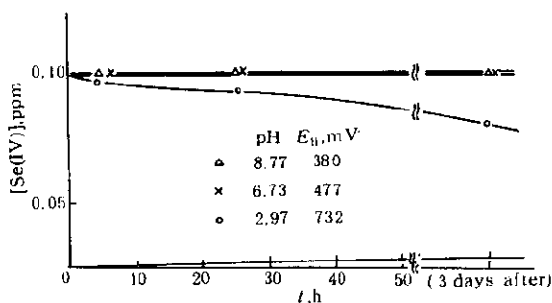


Fig. 5 pH dependence of Se(IV) oxidation by MnO_2 (0.01 mg MnO_2/ml)

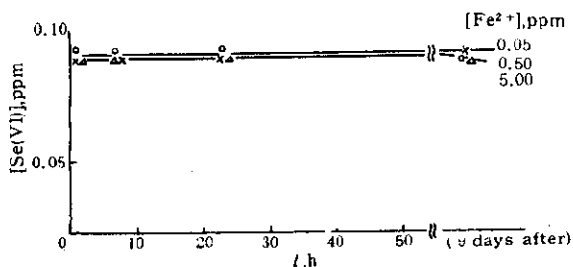


Fig. 6 Reduction of Se(VI) by Fe^{2+} (pH=7, $E_H = 412$ mV)

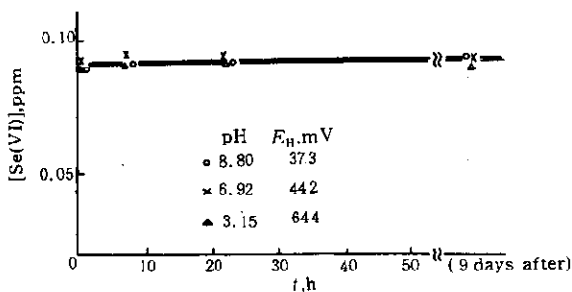


Fig.7 pH dependence of Se(VI) reduction by Fe^{2+} ($\text{Fe}^{2+} = 0.5$ ppm)

Reductions of Se(VI) by Fe^{2+} ion were shown in Figure 6 and 7. The results showed that at various pH and $[\text{Fe}^{2+}]$ concentration, Fe^{2+} could only reduce 10% of Se(VI) to Se(IV) at the beginning of reaction. Then, the reduction proceeded slowly. Only after a few days, a further and weak reduction with a high concentrations of Fe^{2+} (> 0.5 ppm) could be observed under acidic conditions (pH=3).

Similarly, humic acid could only show its weak reducibility for Se(VI) at pH 3 (Fig.8). Under acidic conditions the reducibility of humic acid for Se(VI) was stronger than that of Fe^{2+} . We could see the same trend from previous work (Fig. 2 and Fig.3), at pH 3 the same concentrations of humic acid and Fe^{2+} depressed $E_H[\text{Se(VI)}/\text{Se(IV)}]$ from 0.75V to 0.30V and

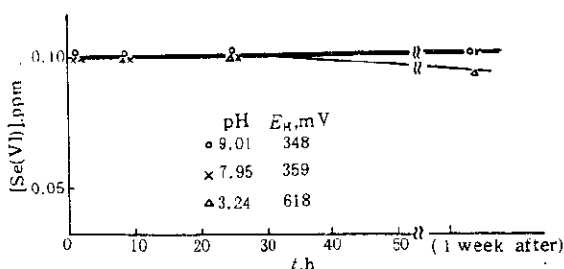


Fig.8 pH dependence of Se(VI) reduction by humic acid (FA extracted from Songhua River sediment = 5 ppm)

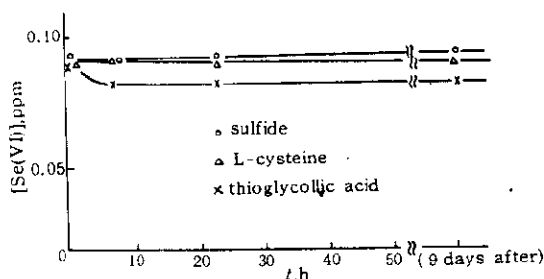


Fig.9 Reduction of Se(VI) by sulfur containing compounds (pH=7, sulfide= 10^{-3} mol/L, L-cysteine and thioglycollic acid = 5ppm)

0.52V respectively. In addition to Yongshou FA, we repeated the same experiments by using Songhuajiang FA, Lianjiang HA and Zhanjiang FA. The results of these experiments were identical. It should be noticed that our results of the reducibility of humic acid for Se(VI) were similar to the results of Cr(VI) reduction by humic acid in soil water (Wang, 1982).

Finally, we compared the reducibilities of three sulfur-containing substances for Se(VI) (Fig.9). The results indicated that in neutral solution thioglycollic acid and L-cysteine showed limited reducibilities for Se(VI), -SH here reacted as the reductant. As for sulfide, it just reduced 8% of Se(VI) to Se(IV) within the first 20 minutes. After that we could not see any reduction in the system. The reducibilities of three sulfur-containing compounds for Se(VI) were in following order:

thioglycollic acid > L-cysteine > sulfide.

Our experimental results showed that humic acid, Fe^{2+} , MnO_2 and other natural redox agents each had a limited redox ability to the Se(VI)/Se(IV) pair. All the reactions were affected by pH. An acidic condition favored the transformation between Se(VI) and Se(IV). Considering the pH condition of soils and water in Kaschin-Beck disease regions of Yongshou County, Shaanxi Province, the influence of humic acid on the major forms of selenium: Se(IV) and Se(VI) was relatively limited. The mutual transformation between Se(VI) and Se(IV) was a long and slow process.

SUMMARY

The relation between E_H [Se(VI)/Se(IV)] and pH in soil water and the effects of humic acid and so forth on the redox properties of Se(VI)/Se(IV) system were studied. Generally speaking, the E_H of Se(VI)/Se(IV) pair decreased as the pH value and the concentration of humic acid increased. The influence of Fe^{2+} was evident only in the low Fe^{2+} concentration,

as the E_H -pH curve declined rapidly. Then the slope of the curve changed less than that of humic acid. The effect of pH on $E_H[\text{Se(VI)}/\text{Se(IV)}]$ was similar to that of humic acid.

The redox reactions between humic acid, MnO_2 , Fe^{2+} and $\text{Se(VI)}/\text{Se(IV)}$ in soil aqueous extract were determined by gas chromatography with an electron-capture detector. The results indicated that under acidic conditions all of the redox agents used in the experiment had limited oxidizabilities or reducibilities for selenium. Among these oxidizing agents, MnO_2 is the strongest oxidant. The redox actions of MnO_2 , humic acid or Fe^{2+} on selenium were stronger in acidic condition than in alkaline condition.

The reducibilities of sulfur-containing compounds for Se(VI) were in following order:

thioglycollic acid > L-cysteine > sulfide.

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