

THE ABSORPTION OF SELENATE AND SELENITE  
SELENIUM BY COLLOIDAL FERRIC HYDROXIDE

Oscar E. Olson and Curtis W. Jensen  
South Dakota State College

It has been shown that selenium in the form of selenates, when added to soils, is more available to plants than selenium added in the form of selenites,<sup>1, 2, 3</sup> selenites being "fixed" by soils.<sup>4, 5</sup> Williams and Byers<sup>6</sup> have published results which indicate that colloidal iron oxide is probably largely responsible for the fixation of selenites. In a study of the absorption of selenite selenium, Olson<sup>7</sup> has shown that of various colloidal materials studied only colloidal aluminum oxide and colloidal iron oxide "fixed" selenites.

Boswell and Dickson<sup>8</sup> studied the adsorption of arsenious acid by ferric hydroxide and concluded that the removal of the arsenious acid from solution by ferric hydroxide was not a case of simple adsorption because their results indicated a

deviation from the simple adsorption equation  $\frac{x}{m} = kc^n$ , where

"x/m" is the concentration of the adsorbed substance in the adsorbing phase, "c" is the concentration of unadsorbed substance in solution at equilibrium, and "k" and "n" are

<sup>1</sup>Hurd-Karrer, A. M. Selenium injury to wheat plants and its inhibition by sulfur. *J. Agr. Res.* 49:343-57 (1934).

<sup>2</sup>Hurd-Karrer, A. M. Factors affecting the absorption of selenium from soils by plants. *J. Agr. Res.* 50:413-27 (1935).

<sup>3</sup>Moxon, A. L., Olson, O. E., and Searight, W. V. Selenium in rocks, soils and plants. *S. Dak. Agr. Expt. Sta. Tech. Bull. No. 2* (1939).

<sup>4</sup>Franke, K. W. and Painter, E. P. Effect of sulfur additions on seleniferous soils. Binding of selenium by soils. *Indus. and Eng. Chem.* 29:591-95 (1937).

<sup>5</sup>Knight, S. H. and Beath, O. A. The occurrence of selenium and seleniferous vegetation in Wyoming. *Why. Agr. Expt. Sta. Bull.* 221 (1937).

<sup>6</sup>Williams, K. T. and Byers, H. G. Selenium compounds in soils. *Indus. and Eng. Chem.* 28:912-14 (1936).

<sup>7</sup>Olson, O. E. The adsorption of selenium by certain inorganic colloids. *Proc. S. Dak. Acad. Sci.* 19:22-24 (1939).

<sup>8</sup>Boswell, M. C. and Dickson, J. V. The adsorption of arsenious acid by ferric hydroxide. *J.A.C.S.*, 40:1793-1801 (1908).

constants. Yoe<sup>9</sup> has shown that the removal of arsenious acid from solution by hydrous aluminum oxide prepared at temperatures below 50° C in a case of simple adsorption when relatively concentrated solutions of arsenious acid are used, and further<sup>10</sup> that the same is true for iron hydroxide, although in the case of aluminum hydroxide he found that after several hours of contact a secondary reaction probably occurred.

The purpose of this investigation was to study further the removal of selenite selenium from solution and to determine whether or not selenate selenium might be adsorbed to some extent by iron colloids.

#### Experimental

The ferric hydroxide was prepared several months before the investigation by precipitating the iron from ferric nitrate with ammonium hydroxide, and washing by decantation until a negative test for ammonia was obtained with Nessler's solution. The ferric hydroxide was used in the form of a colloidal suspension, the concentration of which was determined gravimetrically.

Selenious acid and selenic acid solutions were prepared using Eimer and Amend C.P. salts and distilled water. The selenium content of the two solutions was checked gravimetrically.

In series 1, 75 cc of ferric hydroxide gel was placed in each of twelve 250 cc erlenmeyer flasks, the gel being constantly agitated while measured to insure a homogeneous suspension. Several determinations showed that this amount contained 1.568 grams of ferric hydroxide. To the first flask was added exactly 150 cc of standard selenious acid. 500 cc of the standard was then carefully diluted to twice its volume and a 150 cc portion was added to the second flask. This procedure was carried out throughout the series, so that each succeeding flask contained half as much selenium as the one preceding it in the series. The flasks were tightly stoppered

<sup>9</sup>Yoe, J. H. The adsorption of arsenious acid by hydrous aluminum oxide. J.A.C.S. 46:2390-97 (1924).

<sup>10</sup>Yoe, J. H. The adsorption of arsenious acid by hydrous ferric oxide. J.A.C.S. 52:2785-90 (1930).

and agitated until thoroughly mixed. They were then placed in a constant temperature oven at 0° C for one week, at which time it was assumed that equilibrium had been established. At the end of this time the clear supernatant liquid was drawn off from each flask and each portion was analyzed for selenium. The higher concentrations were determined gravimetrically by taking 50 cc aliquots, adding 25 cc of 40% hydrobromic acid, and reducing to elemental selenium with sulphur dioxide. The precipitated selenium was allowed to stand on a steam bath for one hour and after twelve hours was filtered through a fritted glass crucible, dried and weighed. The lower concentrations were determined colorimetrically.<sup>11</sup> Portions of from 0.5 to 50 cc were used for the colorimetric tests, depending upon the concentration of selenium in the sample. The results obtained are shown in Table 1.

Series 2 was similar to series 1 except that selenic acid was used in place of selenious acid. This series was allowed to stand for three days at 30° C. This time was believed to be sufficient for equilibrium to be attained. The analysis of these samples was also analogous to that of series 1, except that hydroxylamine hydrochloride was used as the reducing agent in place of sulfur dioxide. The results are shown in Table 2.

<sup>11</sup>Moxon, A. L. Alkali disease or selenium poisoning. S. Dak. Agr. Expt. Sta. Tech. Bull. No. 311 (1937).

TABLE I

## The Adsorption of Selenites by Ferric Hydroxide

Flask No.	Millimoles SeO <sub>2</sub> /Flask	Millimoles SeO <sub>2</sub> in soln. c	Millimoles SeO <sub>2</sub> Adsorbed x/m	Log c	Log x/m
1	8.328	6.516	1.812	0.8140	0.2582
2	4.164	2.730	1.434	0.4362	0.1566
3	2.803	0.803	1.279	9.9047-10	0.1069
4	1.041	0.273	0.768	9.4363-10	9.8854-10
5	0.5205	0.0325	0.4880	8.5119-10	9.6884-10
6	0.2603	0.0000	0.2603		
7	0.1302	0.0000	0.2603		
8	0.0651	0.0000	0.0151		
9	0.0325	0.0000	0.0325		
10	0.0162	0.0000	0.0162		
11	0.0081	0.0000	0.0081		
12	0.0041	0.0000	0.0041		

TABLE 2

## The Adsorption of Selenates by Ferric Hydroxide

Flask No.	Millimoles SeO <sub>3</sub> /Flask	Millimoles SeO <sub>3</sub> in Soln. c	Millimoles SeO <sub>3</sub> Adsorbed x/m	Log c	Log x/m
1	7.325	6.885	0.440	0.8379	9.6435-10
2	3.663	3.232	0.431	0.5095	9.6345-10
3	1.831	1.408	0.423	0.1486	9.6263-10
4	0.9156	.5357	4.3799	9.7289-10	9.5797-10
5	0.4578	.1367	0.3211	9.1358-10	9.5066-10
6	0.2289	.0525	0.1769	8.7202-10	9.2477-10
7	0.1145	.0451	0.0694	8.6542-10	8.8414-10
8	0.0573	.0342	0.0231	8.5340-10	8.3636-10

## Discussion of Results

Adsorption isotherms for the two series were plotted and are shown in Figure 1. The curves were obtained by plotting the millimoles of the selenium oxide adsorbed against the millimoles of the oxide remaining in solution at equilibrium.

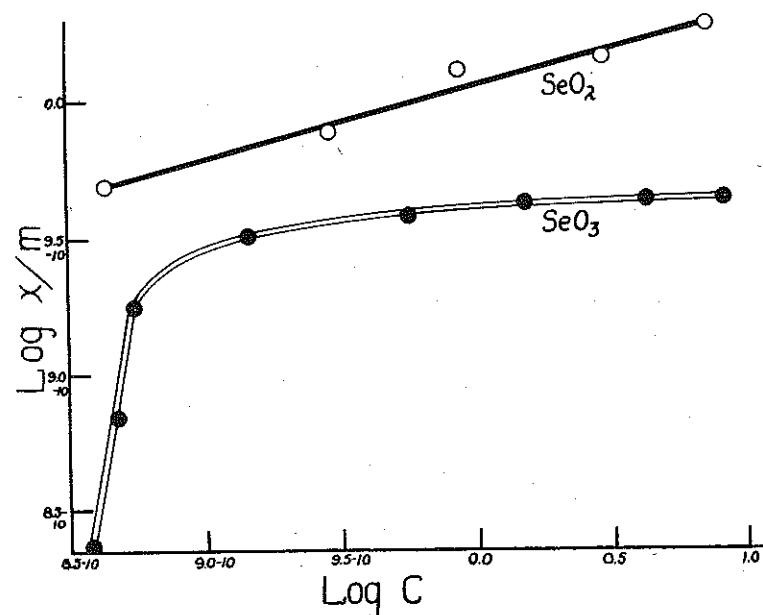


FIGURE I

Adsorption isotherms of selenious and selenic acids on hydrous ferric oxide at 30° C.

As is shown by the adsorption isotherm for selenium dioxide (figure 1), selenite selenium is completely removed by iron hydroxide from dilute solutions. In the case of selenate solutions, however, even in the most dilute solutions the complete removal of selenium by the iron colloid did not occur. These results are in agreement with the work of Williams and Byers,<sup>12</sup> and this phenomenon probably explains the difference in "fixation" of the two forms of selenium when they are added to soils.

<sup>12</sup>Op. cit.

There are least two possible explanations for the complete removal of selenite selenium from solution by colloidal iron. First, it may be due to the formation of a compound such as the basic iron selenite prepared by Williams and Byers. Second, it may be the result of adsorption of the same type as that demonstrated in the case of arsenious acid. When arsenious acid was added to one of the weaker solutions of selenite used in this study, considerable selenium was detected in the solution, whereas before addition of the arsenious acid the removal of selenium from solution had been complete. This phenomenon indicates that some type of adsorption rather than reaction is responsible for the complete removal of the selenite from solution.

Logarithmic curves for the adsorption of the two selenium acids are shown in figure 2.

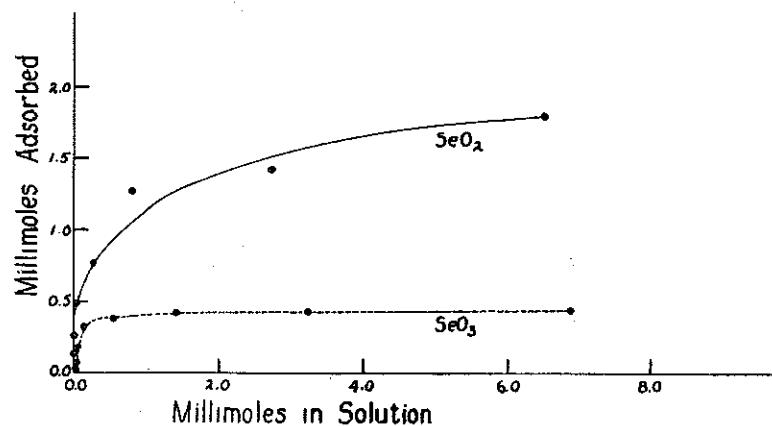


FIGURE II  
Logarithmic plot curves in Figure I

$\frac{x}{m}$  = millimoles adsorbed one iron oxide

$c$  = millimoles in solution at equilibrium.

According to the equation  $\frac{x}{m} = kc^n$  a straight line will result when the data are plotted as they are in figure 2 if a case

of simple adsorption occurs. In plotting the data for selenite selenium, only data were plotted which concerned the solutions from which the iron colloid did not completely remove the selenium. The line thus obtained indicates that, following an initial type of adsorption in which selenite is completely removed from solution, simple adsorption as expressed by Freundlich's equation exists. Further work must be done before the curves obtained for selenate selenium, as shown in figures 1 and 2, can be explained. Obviously simple adsorption does not occur throughout the range of concentrations of selenic acid used.

#### Summary

The adsorption of selenite selenium by colloidal iron hydroxide has been found to differ considerably from the adsorption of selenate selenium by the same colloid.

At low concentrations iron hydroxide completely removes selenite selenium from solution, but at higher concentrations the adsorption can be expressed by the equation  $\frac{x}{m} = kc^n$ .

Selenate selenium was not completely removed from solution even at very low concentrations. Its adsorption could not be expressed by the equation  $\frac{x}{m} = kc^n$  for the whole range of concentrations used in this study.

The results of this investigation offer a possible explanation for the difference in availability to plants of selenites and selenates in the soil.