&EPA   Project Summary

Selenium Oxidation and Removal by Ion Exchange

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Strong-base anion exchange was evaluated as a process for the removal of trace quantities of selenium from groundwater. The efficiency of the process was found to depend on the oxidation state of selenium, with the selenate anion, Se(VI), having a greater affinity for the anion-exchange resin than selenite or biselenite anions, Se(IV). Bench-scale experiments with an ion-exchange column compared the effluent concentration histories for synthetic groundwater solutions contaminated with 100 ppb of either Se(IV) or Se(VI). The resin bed capacity for selenium removal was 55% greater with Se(VI). Since Se(IV) is less preferred than the major groundwater anion, sulfate, it was eluted from the column with a chromatographic concentration peak 5.4 times its feed concentration. Se(VI) concentration in the effluent never exceeded its feed concentration.

An analytical method was developed to measure the concentrations of Se(IV) and Se(VI) (i.e., to determine the speciation of selenium) at trace concentration in groundwater. This method uses anion exchange at pH 1.5 to separate undissociated selenious acid (Se[IV]), which passes through the column, from selenate and biselenate anions (Se[VI]), which are retained by the resin. Graphite furnace atomic absorption spectroscopy (GFAAS) is used to measure total selenium in an aliquot of the original groundwater sample and Se(IV) in the anion-exchange column effluent. Se(VI) is determined by difference.

Using this new analytical method as a tool, the oxidation of Se(IV) to SE(VI) at trace concentration in groundwater was studied. The study found that free chlorine can oxidize Se(IV) to Se(VI) in groundwater. In synthetic groundwater containing sulfate, chloride, and bicarbonate at pH 8.3, the reaction is first order in both Se(IV) and free chlorine concentrations, and it can be described by the following rate expression:

$$-r_{Se} = -dC_{Se}/dt =$$
$$(0.21 \ L/(min\text{-}mg \ Cl_2))(C_{Cl})(C_{Se})$$

The pH dependence of the reaction was examined in the pH range of 5 to 10. A pH optimum exists between 6.5 and 7.5 in which nearly 70% of the Se(IV) is converted to Se(VI) within 5 min with a chlorine dosage of 5 mg/L. Oxygen was completely ineffective as an oxidant for Se(IV), and potassium permanganate and hydrogen peroxide were much less effective than chlorine.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that are fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The U.S. Environmental Protection Agency (EPA) National Primary Drinking Water Regulations of 1976 established maximum contaminant levels (MCL's) for 10 inorganic contaminants: barium, cadmium, chromium, lead, mercury, silver, fluoride, nitrate, arsenic, and selenium. Public drinking water supplies contaminated with any one of these substances in excess of the MCL must be

treated to remove the contaminant or abandoned.

The MCL for selenium was set at a very low level (0.01 mg/L) because of selenium's suspected carcinogenicity. Selenium contamination of groundwater is fairly common in some regions of the United States, but its removal from these water supplies is not yet practiced. Thus a continuing need exists for research to evaluate treatment processes for selenium removal. This study is based on an understanding of selenium chemistry and complements the work of previous researchers. The study focuses on the following two-step process for removal of selenium from groundwater:

1. Oxidation of all aqueous selenium to selenate anion, Se(VI), and

2. Strong-base anion-exchange removal of the selenate anion.

Experimental Details

The study described in this report included three phases: (1) evaluation of anion exchange for removal of both Se(IV) and Se(VI) from groundwater, (2) development of a method for the separate analysis of Se(IV) and Se(VI) at trace concentration in groundwater, and (3) determination of the preferred oxidant and optimum reaction conditions for the oxidation of Se(IV) to Se(VI).

Evaluation of Anion Exchange for Removal of Selenite and Selenate

Ion chromatography (IC) was used to provide a rapid determination of the positions of selenite and selenate anions in the selectivity sequence of a strong-base anion-exchange resin. A Dionex Model 16 Ion Chromatograph * (Dionex Corporation, Sunnyvale, California) was used for all IC work. The eluent used was the standard carbonate buffer consisting of 0.003 N $NaHCO_3$ and 0.0024 N Na_2CO_3 with pH 10.4. Standard anion solutions were prepared from reagent-grade sodium salts of the anions fluoride, chloride, bromide, nitrite, nitrate, phosphate, sulfite, sulfate, selenite, and selenate.

Ion-exchange column runs were used to generate experimental breakthrough curves for selenite and selenate in a background of highly saline synthetic groundwater. Figure 1 shows the ap-
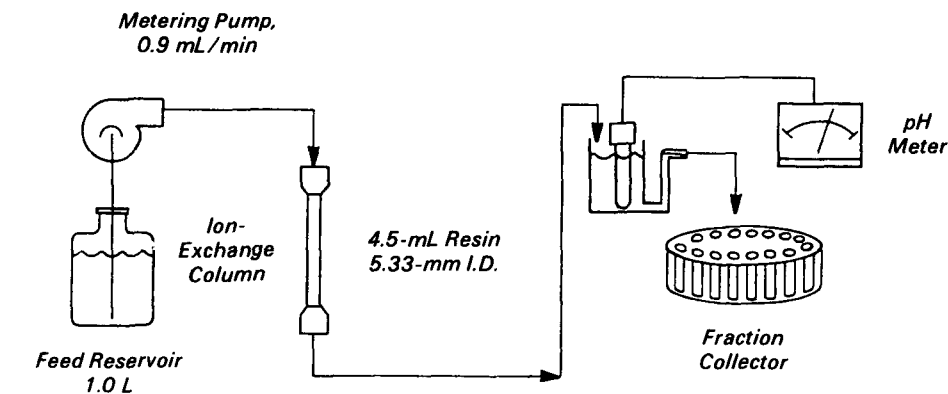
Figure 1.   Experimental set-up for the ion-exchange column runs.

paratus used. A variable-speed positive displacement pump (Milton Roy) was used to pump the feed water at 0.9 mL/min from a glass reservoir bottle through a column packed with Rohm and Haas IRA-458 strong-base, acrylic anion-exchange resin. The column was constructed from 6.35-mm (0.25-in.) O.D. stainless steel tubing with an I.D. of 5.33 mm (0.21 in.). The resin bed volume was 4.5 mL and the empty bed contact time (EBCT) was 5.0 min. Effluent from the column was collected in glass test tubes held in the carousel of an Eldex universal fraction collector.

The multicomponent, ion-exchange column runs required chemical analyses for pH, bicarbonate, chloride, sulfate, selenite, and selenate. Methods used for these analyses were pH electrode, Beckman infrared TOC analyzer (inorganic carbon channel) for bicarbonate, potentiometric titration with $AgNO_3$ for chloride, ion chromatography for sulfate, and GFAAS for both selenite and selenate.

Development of Method for Se(IV)/Se(VI) Separation and Analysis

The method developed to determine the speciation of selenium in groundwater uses ion exchange for the separation of Se(IV) from Se(VI) at low pH and GFAAS for analysis of selenium in both the original sample and the ion-exchange column effluent. Determination of optimum pH for the ion-exchange separation involved a series of separation experiments at different pH's within the range of 0 to 2.5.

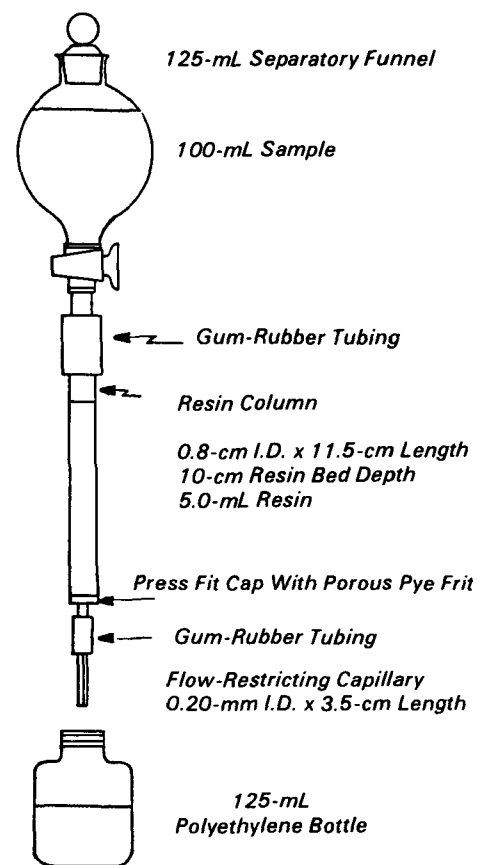Figure 2 shows the apparatus used for ion-exchange separation of Se(IV) and

Figure 2.   Ion-exchange apparatus for separation of Se(IV) from Se(VI).

Se(VI). The ion-exchange separation column was a glass tube filled with 5 mL (wet, settled volume) of IRA-458 anion-exchange resin in chloride form. Before using a fresh or freshly regenerated resin

column, an HCl solution of the desired separation pH was passed through the column at about 10 mL/min to adjust column pH. After each separation test, the column was regenerated with 1.0 N NaCl or 0.5 N HCl.

For each experiment, three 5-mL ion-exchange columns were adjusted to the specified pH, and test solutions (adjusted to the same specified pH by dropwise addition of HCl) were passed through each column. The three test solutions, designated A, B, and C, were standard solutions of selenate or selenite or both in a 383-mg/L TDS synthetic groundwater containing 1 meq/L (58.5 mg/L) sodium chloride, 1 meq/L (72 mg/L) sodium sulfate, and 3 meq/L (252 mg/L) sodium bicarbonate. Test solution A contained 100 ppb Se(IV), B contained 100 ppb Se(VI), and C contained 50 ppb Se(IV) and 50 ppb Se(VI). Column effluents were collected, preserved with 5 mL concentrated nitric acid per 100 mL of sample, and analyzed for selenium by GFAAS.

A Perkin Elmer model 5000 atomic absorption spectrophotometer equipped with a graphite furnace, a model 400 graphite furnace programmer, and Zeeman background correction was used for all selenium analyses. A selenium electrodeless discharge lamp was the light source. Pyrolytically coated graphite tubes with L'vov platforms were used, and all sample injections were 20 μL followed by 20 μL of $NiNO_3$ matrix modifier (1000 ppm Ni).

Study of Se(IV) Oxidation

The test solution for all oxidation experiments was the previously described 383 mg/L TDS synthetic groundwater, with an initial pH of 8.3 and spiked with 100 ppb Se(IV). The Se(IV) stock solution was made up from sodium selenite (99%) from Aldrich Chemical Company. Reagents used for oxidation experiments were sodium hypochlorite solution prepared by dilution of Clorox bleach, oxygen gas, hydrogen peroxide solution prepared by dilution of 30% H_2O_2, potassium permanganate, and ammonium hydroxide. All chemicals were reagent grade unless otherwise noted.

For all oxidation reaction experiments involving liquid-form oxidizing agents, 100-mL aliquots of the test solution were placed in 250-mL Pyrex Erlenmeyer flasks and stirred with Teflon-coated magnetic stirring bars on a six-position stirring plate. A pre-measured aliquot of the oxidant solution was injected into each test solution flask with a graduated glass pipette. Quenching agents were added at predeter-

mined times in the same manner. The new ion-exchange separation/GFAAS method was used to determine the concentration of Se(IV) remaining in solution after each oxidation experiment.

In the test of oxygen as an oxidizing agent for Se(IV), pure oxygen at a supply pressure of 20 psi was bubbled into 200 mL of the test solution in an open 500-mL Erlenmeyer flask through a porous gas-diffusing stone made of fused crystalline alumina with an average pore size of 60 μ.

The temperature was between 21° and 24.5 °C for all tests. For the study of pH dependence of selenium oxidation by free chlorine, the pH of the test solution was adjusted in the range of 5 to 10 by the dropwise addition of either NaOH or HCl.

Results and Discussion

Evaluation of Anion-Exchange Removal of Selenite and Selenate

Figure 3 shows the multicomponent ion chromatogram for a dilute aqueous mixture of anions, including selenate and

selenite. The anion corresponding to each peak is noted on this chromatogram, along with its observed retention time. The least preferred anion has the shortest retention time and appears first in the effluent, whereas the most preferred anion has the longest retention time and is eluted last. The selectivity sequence from most preferred to least preferred at the eluent pH of 10.5 is as follows:

$$SeO_4{}^= > SO_4{}^= > NO_3{}^- > Br^- > HPO_4{}^=$$
$$> SeO_3{}^= > NO_2{}^- > Cl^- > F^-$$
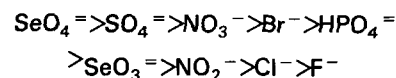
The most-preferred-ion status of selenate is significant in consideration of an ion-exchange process to remove trace amounts of selenium from groundwater containing much larger concentrations of sulfate. Based on this chromatogram, and regardless of their relative concentrations, selenate is expected to break through after sulfate with no chromatographic peak elution of selenate. Furthermore, the breakthrough capacity of the ion-exchange column for selenate is expected to be much greater than it would be if the major
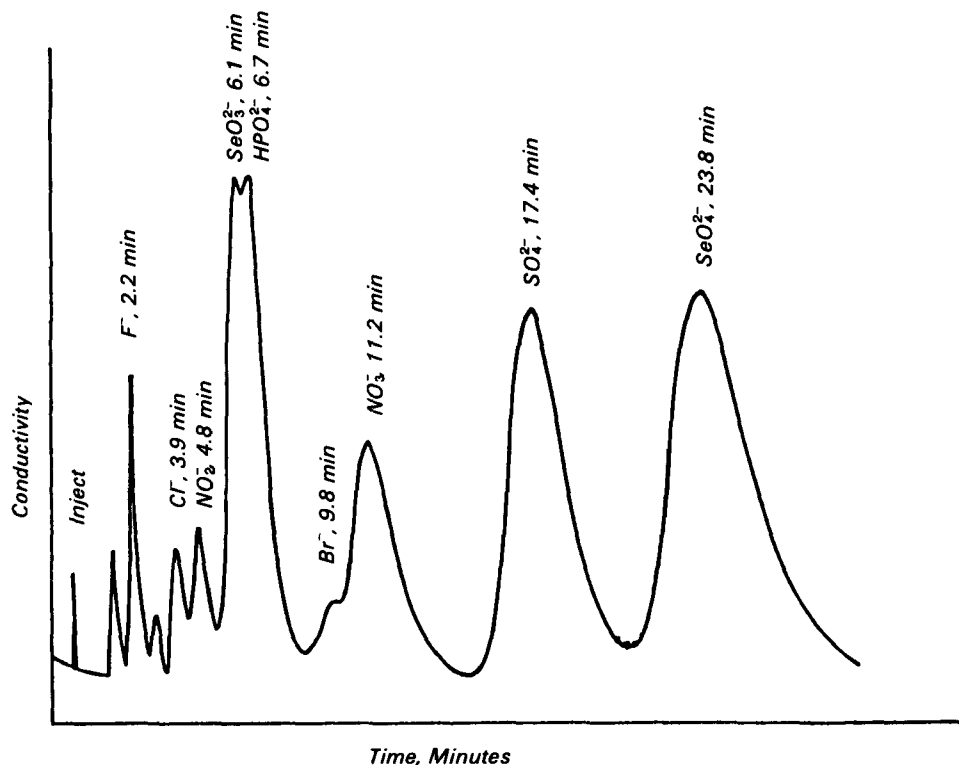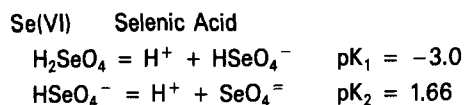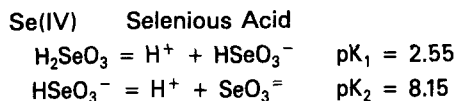

Time, Minutes

Figure 3. *Ion chromatogram for selenium species in the presence of common anions. Eluent = 0.003 M NaHCO₃/0.0024 M Na₂CO₃, pH = 10.5.*

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anion, sulfate, were preferred over selenate. Selenite's low position in the selectivity sequence suggests that ion exchange is unfavorable for the removal of selenium in the +4 oxidation state.

Experimental breakthrough curves for selenite and selenate in a highly mineralized (712 mg/L TDS) synthetic groundwater verified the predictions of the ion chromatogram. Figure 4, the breakthrough curve for Se(IV), shows selenium concentration reaching the 10 ppb MCL at about 152 bed volumes (BV's) throughput and peaking to 540 ppb (5.4 times the feed concentration) at 237 BV's. The column is completely exhausted at 265 BV's, where the most-preferred sulfate anion has reached its influent concentration. Figure 5, the breakthrough curve for Se(VI), shows selenium concentration reaching the MCL at 235 BV's with a gradual, presumably mass-transfer-controlled increase to feed concentration at about 385 BV's. As expected from the IC selectivity sequence, selenate broke through after sulfate, and the Se(VI) concentration in the effluent never exceeded the feed concentration of 100 ppb. A very significant improvement (55% in this case) exists in ion-exchange removal of selenium when it is in the selenate rather than the selenite form. In less saline groundwaters with lower sulfate concentrations (e.g., 50 mg/L sulfate), run lengths exceeding 1000 BV's to Se(VI) breakthrough may be expected.

Method for Se(IV)/Se(VI) Separation and Analysis

The basis for the ion-exchange separation of Se(IV) and Se(VI) is the difference in acid strength of selenious (Se[IV]) and selenic (Se[VI]) acids. The dissociation equations and constants for the two acids are as follows:

Se(IV)   Selenious Acid

$H_2SeO_3 = H^+ + HSeO_3^-$ $pK_1 = 2.55$

$HSeO_3^- = H^+ + SeO_3^=$ $pK_2 = 8.15$

Se(VI)   Selenic Acid

$H_2SeO_4 = H^+ + HSeO_4^-$ $pK_1 = -3.0$

$HSeO_4^- = H^+ + SeO_4^=$ $pK_2 = 1.66$

Below its pK_1 of 2.55, the weaker selenious acid exists predominantly as the undissociated acid that has no charge and therefore no electrostatic attraction to the positively charged quarternary ammonium sites of a strong-base anion-exchange resin. Selenic acid is a much stronger acid, comparable to sulfuric acid. Above a pH of −3, Se(VI) exists predominantly as a
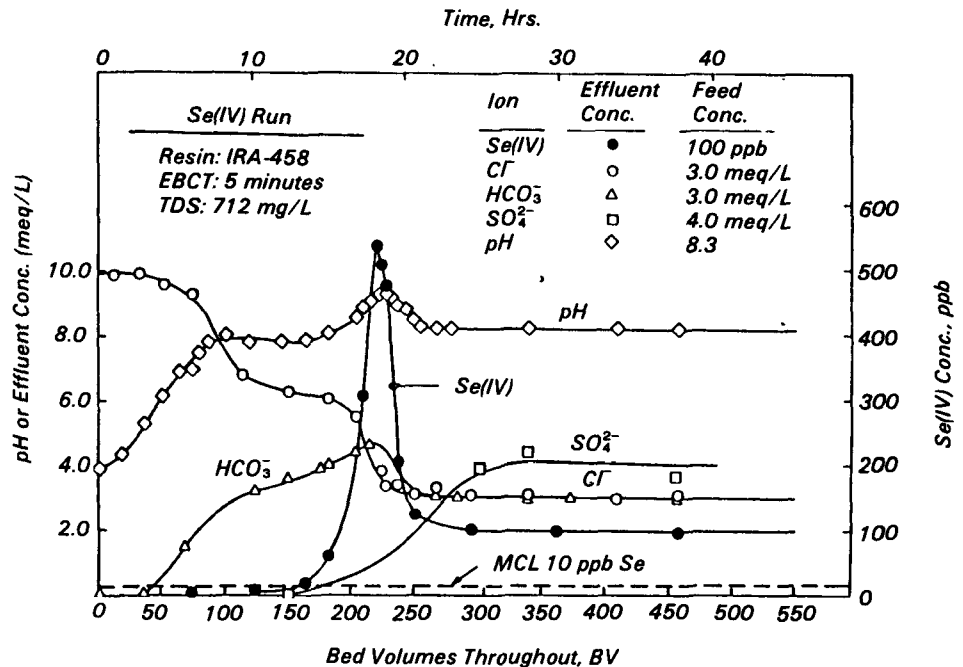

Figure 4.   Breakthrough curves for Run No. 1—synthetic groundwater feed contaminated with 100 ppb Se(IV).
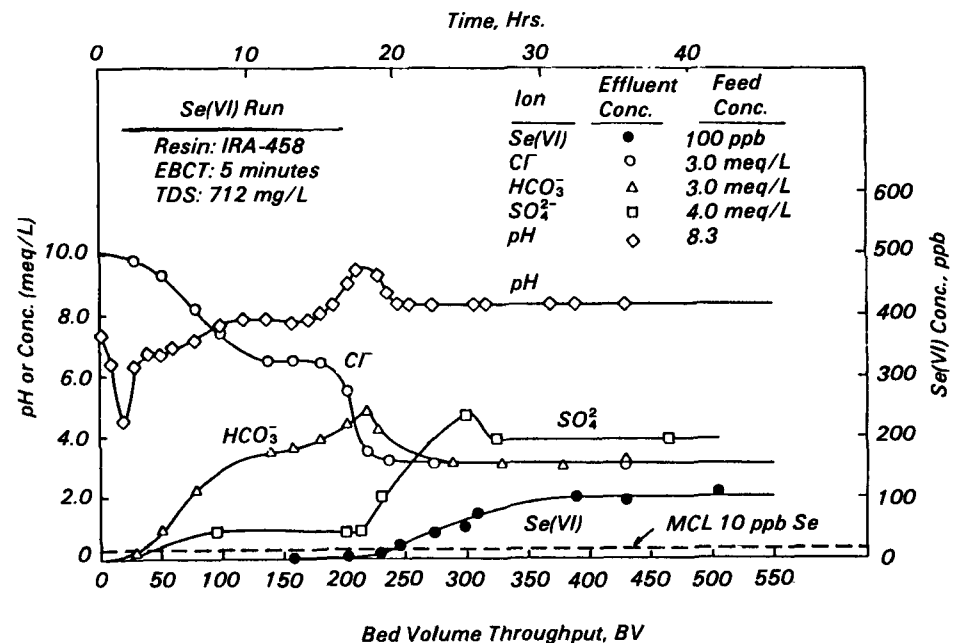

Figure 5.   Breakthrough curves for Run No. 2—synthetic groundwater feed contaminated with 100 ppb Se(VI).

negatively charged ion, and Se(VI) anions will be attracted and held by strong-base anion-exchange resins. Because of their acid dissociation equilibria, most Se (IV) will pass through an ion-exchange column, and most Se (VI) will be retained in the same column at any pH between −3 (pK₁ of selenic acid) and + 2.55 (pK₂ of

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selenious acid). Based on acid dissociation equilibria alone, the optimum separation of Se(IV) and Se(VI) would be expected at the midpoint of this range, pH 0.225.

Table 1 presents results of separation experiments at five pH's: 0.6, 1.0, 1.1, 1.5, and 2.1. Figure 6 plots the percentage of recovery of selenium in the column effluent (i.e., passage of selenium through the column) as a function of separation pH for test solutions A and B, prepared with pure Se(IV) and pure Se(VI), respectively. The experimental passage is compared with that predicted by the acid dissociation constants for Se(IV) and Se(VI). The best correlation of experimental results to predicted % recovery occurred at a pH equal to or greater than 1.5, and the maximum separation of Se(IV) from Se(VI) was observed at pH 1.5.

At lower pH, a very significant, unexpected recovery of Se(VI) occurred in the column effluent. This passage of Se(VI) at low pH could have resulted either from reduction of Se(VI) to Se(IV) in the presence of strong HCl, or unfavorable competition between the low concentrations of Se(VI) anions and the very high chloride concentration, e.g. 8900 mg/L Cl^- at pH 0.6.

Based on the pH screening experiments, an optimum separation pH of 1.5 was identified, and the following procedure was adopted for the analytical technique:

1. Collect a 200-mL water sample.

2. Divide the sample into two 100-mL aliquots — one (A) for total Se analysis and the other (B) for Se (IV) analysis.

3. Adjust pH of sample B to 1.5 by dropwise addition of 1.5 N hydrochloric acid.

4. Pass acidified sample B through a small (5-mL) column of chloride-form, strong-base anion-exchange resin at a flowrate of 1.5 mL/min. Collect the effluent and then pass 25 mL of deionized water through the same column at 10 mL/min and collect the rinse effluent. Theoretically, 91.8% of the Se(IV) and 0% of the Se(VI) from the original sample will be recovered in the effluent and rinse.

5. Preserve all samples with 5 mL concentrated nitric acid per 100 mL of sample.

6. Analyze the original water sample, A, and the IX column effluent and rinse, B, for Se by GFAAS.

Table 1. Results of pH Screening Experiments

pH	Flow Rate (mL/min)	Test Solution*	% Selenium Recovered (% Passage)[+] Predicted	Experimental
0.6	10.3	Se(IV)	96.91	78.7
0.6	9.9	Se(VI)	.02	66.9
0.6	8.5	Se(IV/VI)	48.45	72.9
1.0	1.5	Se(IV)	95.31	97.4
1.0	1.5	Se(VI)	<0.01	40.5
1.0	1.4	Se(IV/VI)	47.65	70.2
1.1	9.1	Se(IV)	94.64	95.5
1.1	11.0	Se(VI)	<0.01	13.1
1.1	9.1	Se(IV/VI)	47.32	48.6
1.5	11.6	Se(IV)	89.98	93.5
1.5	11.9	Se(VI)	<0.01	8.5
1.5	12.6	Se(IV/VI)	44.99	54.9
1.5	1.5	Se(IV)	89.98	85.6
1.5	1.6	Se(VI)	<0.01	2.0
1.5	1.7	Se(IV/VI)	44.99	52.0
2.1	11.0	Se(IV)	72.3	70.3
2.1	11.0	Se(VI)	<0.01	6.8
2.1	11.0	Se(IV/VI)	36.15	36.5

*All test solutions were prepared with synthetic groundwater containing 3 meq/L $NaHCO_3$, 1 meq/L NaCl, and 1 meq/L Na_2SO_4. Test solution Se(IV) contained 100 ppb Se(IV); Se(VI) contained 100 ppb Se(VI); and Se(IV/VI) contained 50 ppb Se(IV) and 50 ppb Se(VI).

[+] The desired selenium passages are Se(IV) = 100%, Se(VI) = 0%, and Se(IV/VI) = 50%.
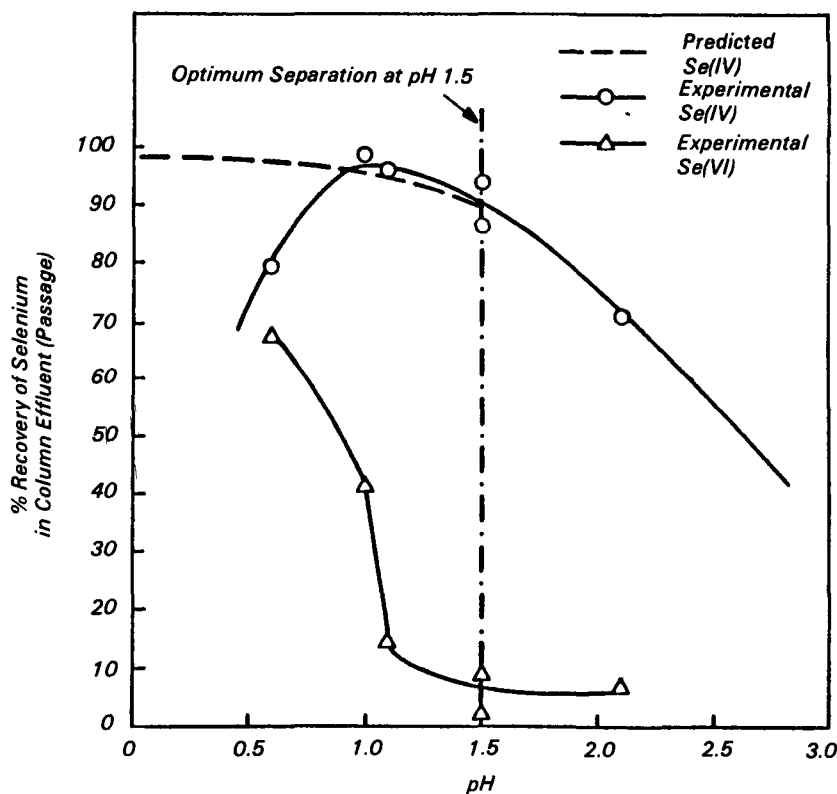
Figure 6. Se(IV) and Se(VI) passage through ion-exchange separation columns as a function of pH.

7. Calculate the concentrations of total Se, Se(IV), and Se(VI) as follows: Total Se (mg/L) is determined directly by GFAAS analysis of sample A. Se(IV) (mg/L) = (1/0.918) × (total mg Se measured in the combined IX column effluent and rinse from sample B)/(0.100 L original sample B). Se(VI) concentration is determined by difference — that is, total Se concentration minus Se(IV) concentration.

The accuracy of this technique with the separation pH of 1.5 is verified in Table 2, which shows a slight tendency toward Se(VI) leakage. This leakage results in slightly high values for the reported Se(IV) concentration. Nevertheless, the method proved to be of adequate precision and accuracy for this research.

Se(IV) Oxidation Study

Experiments proved ammonia to be a satisfactory quenching agent for the oxidation of Se(IV) by free chlorine in synthetic groundwater. When added to a test solution at a dosage 10 times the chlorine dosage, ammonia completely and instantaneously destroyed the free chlorine. The product of this reaction was chloramine, which had no tendency to react with either Se(IV) or Se(VI), and did not interfere with the ion-exchange separation/GFAAS technique used to monitor the progress of the oxidation reaction.

With ammonia as a quenching agent, kinetic data were obtained for the oxidation of Se(IV) by free chlorine. The results are plotted in Figure 7. The experimental rate expression for the reaction is as follows:

$$-r_{Se} = -dC_{Se}/dt =$$
$$(0.21 \ L/(min\text{-}mg \ Cl_2))(C_{Cl})(C_{Se}),$$

where the chlorine concentration is given in mg/L and the Se(IV) concentration, C_{Se}, is arbitrary.

The pH dependence of the oxidation was examined in the range of pH 5 to 10. Results are plotted in Figure 8. The optimum pH is clearly between 6.5 and 7.5. The reaction becomes very slow at both extremes, with less than 10% of the Se(IV) converted to Se(VI) in 5 min at pH 5 and at pH 10.

Experiments were designed to compare the effectiveness of three other oxidizing agents commonly used in water treatment — oxygen, permanganate, and hydrogen peroxide — with that of chlorine. The dosages of permanganate and hydrogen

Table 2. pH 1.5 Ion-Exchange Separation of Se(IV) and Se(VI)

μg Se in Sample		Total μg Se(IV) Passage	μg Se(IV) Reported	Apparent* Se(IV) Recovery(%)	Apparent* Se(VI) Leakage(%)
Se(IV)	Se(VI)				
10.0	0.0	9.27	10.1	101	—
0.0	10.0	0.36	0.4	—	4
5.0	5.0	4.57	5.0	100	0
1.0	2.0	1.04	1.1	110	5
2.0	1.0	1.82	2.0	100	0

*The apparent values are based on the observed total Se passage and a calculation that presumes 91.8% Se(IV) passage.
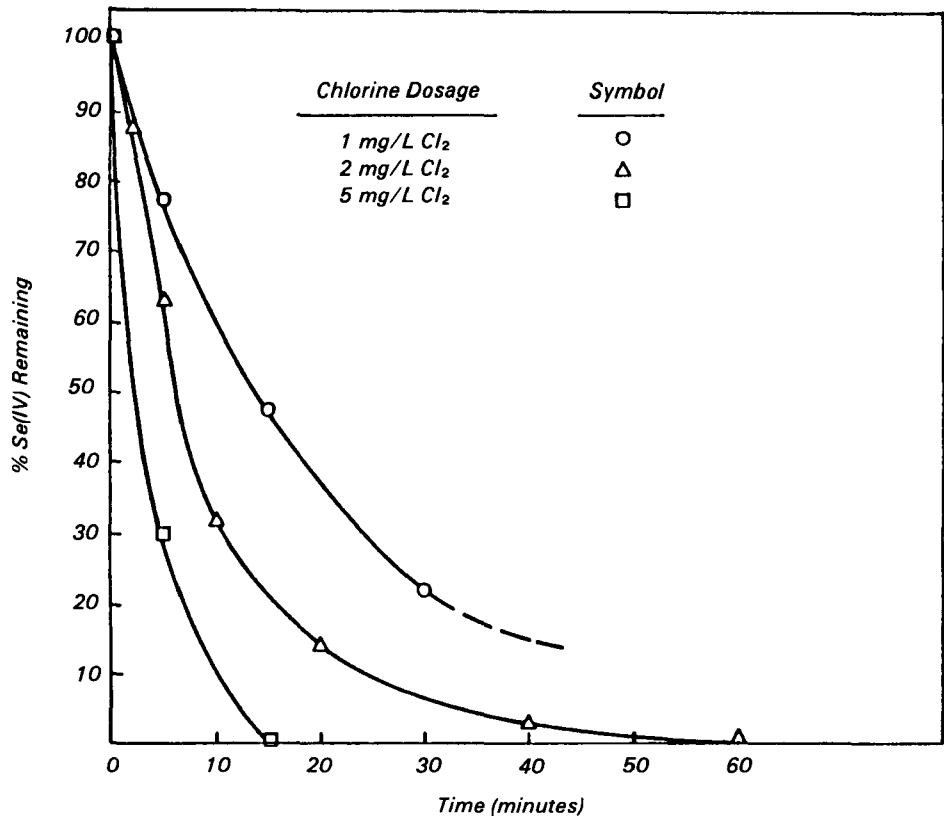

Figure 7. Kinetics of Se(IV) oxidation by free chlorine at pH 8.3 in simulated groundwater.

peroxide were chosen to be equivalent to 2 mg/L free chlorine, a dosage that produced easily measurable Se(IV) remaining after 5- and 30-min contact times. Table 3 lists the experimental results. No quenching other than pH reduction to 1.5 before separation was used in the nonchlorine oxidation experiments. Thus the nonchlorine oxidations indicated in Table 3 may be greater than actually achieved in the indicated contact time. Oxygen appears to be completely ineffective in the oxidation of Se(IV). Neither permanganate nor hydrogen peroxide is as effective as chlorine at near-neutral pH.

Conclusions and Recommendations

The two-step process of oxidation with free chlorine followed by anion exchange appears to be technically feasible and should be considered for removal of selenium to produce potable water from selenium-contaminated groundwater. Further research and development is recommended to develop the optimum process and to adapt the process for optimum operation at specific sites.

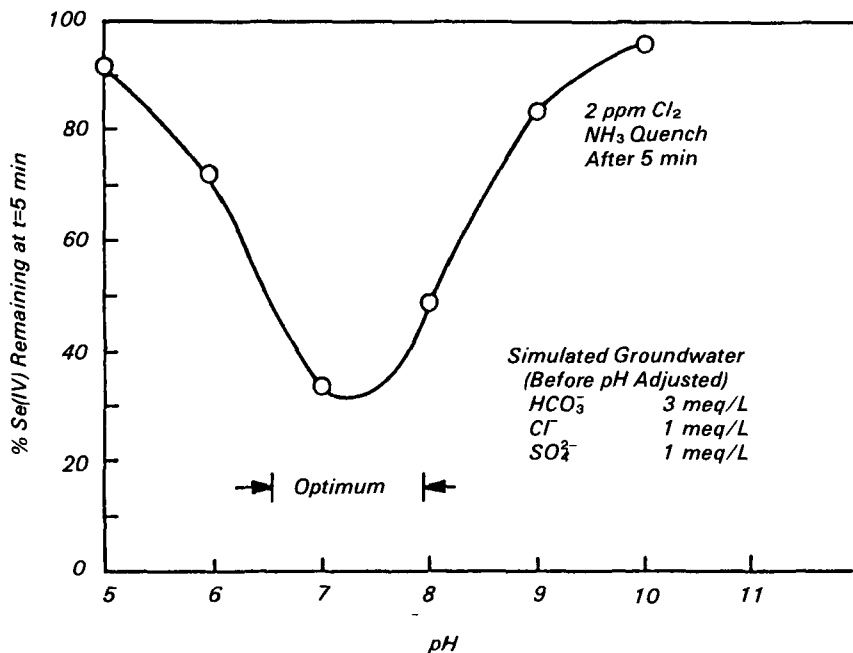Some problems that must be addressed in the next phase of process development

Figure 8. Effect of pH on Se(IV) oxidation at 23°C in pH-adjusted, simulated groundwater.

Annotations in figure:
- y-axis: % Se(IV) Remaining at t=5 min
- x-axis: pH
- 2 ppm Cl_2 / NH_3 Quench / After 5 min
- Simulated Groundwater (Before pH Adjusted)
  - HCO_3^- 3 meq/L
  - Cl^- 1 meq/L
  - SO_4^{2-} 1 meq/L
- Optimum

Table 3. Comparison of Oxidizing Agents*

Oxidizing Agent	pH	Time(min)	Se(IV) Remaining (%)
O_2	8.3	60	101.9
$KMnO_4$	7.5	5	72.1
$KMnO_4$	7.5	30	63.5
H_2O_2	7.5	5	97.4
H_2O_2	7.5	30	89.8
NaOCl	7.5	5	32.0
NaOCl	8.3	5	63.5
NaOCl	8.3	30	7.0

*All oxidant concentrations are equivalent to 2.0 ppm chlorine — that is, a 22-fold stoichiometric excess for the 100 ppb Se(IV) initially present.

include determining the effects of temperature and the presence of other chlorine demands such as TOC, Fe^{2+}, Mn^{2+}, and S^{2-} on oxidation kinetics, countering the effects of residual chlorine from the oxidation process on the anion-exchange resin, determining the optimum anion-exchange resin type and empty bed contact time (EBCT), developing a process control scheme that includes some means (possibly pH changes) of detecting selenium breakthrough, and disposing of spent regenerant.

The analytical method developed to determine the speciation of selenium in groundwater proved to be a useful tool for the study of Se(IV) oxidation and is recommended for measurement of both Se(IV) and Se(VI) in actual groundwaters that are contaminated with selenium. However, the analytical technique should be refined by optimizing the acid used and the sample flow rate.

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