



The elimination of selenium(IV) from aqueous solution by precipitation with sodium sulfide

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ABSTRACT

In this study, the removal/precipitation of selenium with sodium sulfide from initially weakly acidic sulfate solutions containing 300 mg/L of selenium(IV) at 23 °C was studied. The results showed that, below a pH of approximately 7.0, the precipitation reaction was complete at a sulfide to selenium ratio above 1.8 and less than 11 with less than 0.005 mg/L of soluble selenium remaining in solution. When the pH rose between 7.0 and 9.5 the precipitation of selenium was incomplete. Above pH 9.5 the solution turned dark red but no precipitation was apparent. The precipitation reaction started as soon as the sodium sulfide was added in the selenium-bearing solution and was completed in less than 10 min. The orange “selenium sulfide” precipitates, characterized using X-ray diffraction, scanning electron microscopy and chemical analysis, were crystalline in the form of aggregated dense particles with their sulfur/selenium molar ratio varying from 1.7 to 2.3. The precipitate was deduced to be a Se–S solid solution consisting of ring molecules of the following Se_nS_{8-n} formula, where $n=2.5-3$. Long term leachability tests (>2 month equilibration) under ambient conditions at pH 7 showed the produced precipitate to be essentially insoluble (<0.005 mg/L).

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1. Introduction

The medieval physician Paracelsus, sometimes considered the father of toxicology, once said: “All things are poison and nothing is without poison, only the dose permits something not to be poisonous” [1]. Selenium is a particularly good example of this general principle since most living organisms require small amounts of selenium in their food to remain healthy, yet higher intake of this element can cause diseases and even death [2–5]. Because of this effect, a lot of research has been performed on selenium removal techniques to protect the environment and on the positive physiological effect of low selenium levels on humans and animals [6,7]. Interestingly, selenium sulfide (usually described as SeS_2) is of interest in both fields since it is widely used to treat skin diseases while allowing the precipitation and removal of selenium from industrial waste water [8].

Little information is available about the nature and effectiveness of the precipitation reaction involved when selenium sulfide is precipitated, especially in environmental applications. Selenium removal is becoming increasingly important given the fact that this element is a very common impurity in metallurgical feedstocks and

is increasingly regulated. For example copper and zinc refineries generate acidic solution effluents that contain variable amounts of selenium (typically as Se(IV)) ranging from a few to hundreds of mg/L [9]. Lime neutralization, one of the most common acidic solution treatment techniques, is ineffective for selenium since this element does not form insoluble hydroxides. On the other hand, separation techniques such as bacterial reduction, ion exchange membranes, electrocoagulation, and sorption have been investigated but proven either too costly or only suitable for solutions containing low levels of soluble selenium (<5 mg/L) [6,10,11]. For solutions with higher concentrations of selenium use of reductive techniques taking advantage of the favorable Se(IV)/Se reduction potential are employed [12–14].

Sulfur dioxide is commonly used in industry to precipitate and remove selenious ions from aqueous solution. The literature indicates that when dealing with hot and relatively concentrated sulfuric (>1 g/L of soluble Se) or hydrochloric acid solutions (above 80 °C and pH < 1), full selenium reduction to elemental state occurs very rapidly [15]. However, when working with lower concentration Se(IV) dissolved in room temperature solutions, such as those encountered in the zinc industry [9], the reduction of Se(IV) with SO_2 becomes too slow to be of practical interest [16]. As noted earlier several other reagents have been found to reduce selenious ions to elemental state. Sodium dithionite is one of them that has found industrial application as described elsewhere [13] albeit with its own drawbacks, such as relatively poor efficiency, high cost, and

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subsequent redissolution of the selenium [17]. In this work the removal of selenium(IV) by sodium sulfide is described.

The precipitation of selenium by sulfide ions is not a new system as it has been initially mentioned almost two centuries ago. Despite this long history, its chemistry remains poorly understood and far from being optimized in particular as far it concerns its use in industrial effluent treatment. Originally, it was thought that the precipitate was composed of both elemental sulfur and selenium [18,19] or of selenium monosulfide (SeS) [20]. However, the reaction commonly suggested today involves the formation of selenium disulfide [19]:



Selenium disulfide constitutes the main ingredient of different skin care products and was first introduced in the market back in 1951 [21–23]. In the medical field however, selenium disulfide is prepared by fusing selenium and sulfur at a ratio of 1:2 and not from an aqueous route. Medical literature also generally specifies that selenium disulfide is composed of a mixture of selenium monosulfide existing in equilibrium with a sulfur selenium solid solution [24,25]. It is worth noting that while selenium disulfide has been used for decades in the pharmaceutical industry, selenium monosulfide has recently been classified as carcinogenic [26].

Since sulfur and selenium are miscible in all proportions and can form polymer-like molecules of crystalline or amorphous composition, it appears that the sulfur–selenium solid solutions are composed of cyclic Se–S rings containing a variable number of Se and S atoms, most commonly following the general formula $\text{Se}_n\text{S}_{8-n}$ [27–29]. These cyclic molecules have been extensively studied and three different phases (that depend on the sulfur to selenium ratio) have been shown to exist [30]. These ring compounds can exist in the amorphous or crystalline state; and six, seven, ten and twelve member sulfur–selenium molecules have also been observed [31,32]. However, it has proved impossible to isolate with certainty any particular compound because of the plasticity of these molecules [27,31]. Finally, other selenium compounds having the general formula SeS_n (n : 1–7) have been identified in some quartz ores [32,33].

Despite the above described long history of studies involving selenium sulfide compounds essentially no detailed study focusing on the reaction of selenium(IV) species and sulfide ions in an aqueous solution has been previously reported. In addition the effectiveness of this reaction in terms of selenium removal from simulated industrial effluents or long-term stability of the generated precipitate has not been addressed. The previous studies involved selenium sulfide produced by fusion of elemental selenium and sulfur. In this paper the parameters that affect the precipitation reaction are studied; the precipitates formed are characterized; the optimum conditions for conducting the precipitation/removal of selenium(IV) species from aqueous solution by reaction with sulfide ions are determined; and finally its stability is assessed.

2. Experimental

Tests were performed with a synthetic weak sulfuric acid solution containing 300 (mg/L) of Se(IV) at pH 1.3 (adjusted with H_2SO_4). This concentration and pH were chosen as they represent typical conditions encountered in industrial zinc refinery acid effluent solutions [9]. Reagent grade selenium dioxide from Sigma–Aldrich ($\geq 99.5\%$ SeO_2) was used as the source of selenious species. Unless otherwise noted, all the experiments were performed at 23 °C.

The precipitation experiments were performed with freshly prepared sodium sulfide solutions. Typically, different amounts

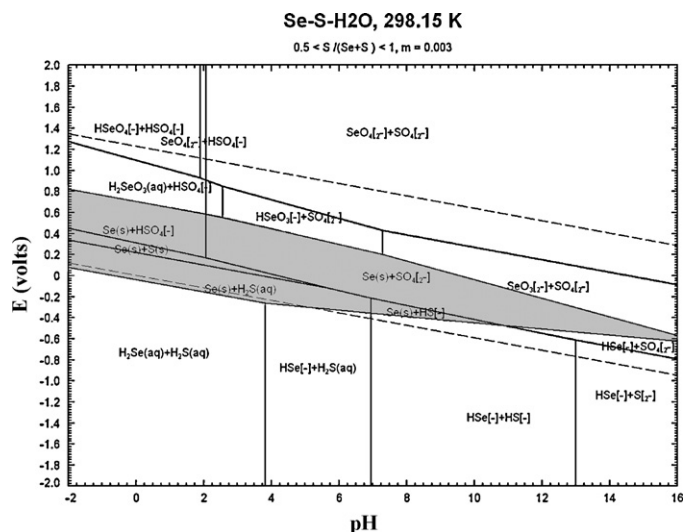


Fig. 1. E_h –pH diagram for the selenium–sulfur–water system (elemental selenium stability region shown in gray) (active soluble species = 0.00379 M, $0 < S/(Se + S) < 1$ and $T = 25^\circ\text{C}$).

of reagent grade sodium sulfide from Sigma–Aldrich ($\geq 98\%$ $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) were dissolved in a volume of deionized water representing a quarter of the weak acid volume. The pH of the sulfide solution varied according to the amount of Na_2S added but was generally around 12. The sulfide solution was always prepared fresh via rapid mixing (a few minutes) hence avoiding oxidation problems. Then the sulfide solution was added at once in the Se(IV) solution and the mixture was agitated with the aid of a magnetic stirrer. At the end of the precipitation test, the slurry was pressure filtered and the precipitate collected for analysis following washing and drying at 30 °C for approximately 24 h until a constant weight was achieved.

The concentration of dissolved selenium in samples containing more than 1 mg/L was measured using regular atomic absorption spectrometry (AAS) with an air/acetylene flame. Samples with less than 1 mg/L Se were analyzed using graphite furnace AAS. This technique, although somewhat less sensitive, was chosen because hydride generation AAS and inductively coupled plasma mass spectrometry (ICP-MS) were found to give erratic and unreliable results especially when dealing with solutions with high sodium concentrations. The oxidation–reduction potential (ORP) and pH of the solution were monitored using a platinum electrode (Cole-Parmer R-05990-55) and a Corning high performance pH electrode (37-476146) respectively. The precipitates were characterized using X-ray diffraction spectroscopy (Philips PW 1710, Cu anode, K-Alpha 1.54060 Å, scan rate: $2^\circ 2\theta/\text{min}$) and electron microscopy (Hitachi S-3000N FEG SEM). The sulfur content of the selenium sulfide precipitates was measured using an ELTRA CS-800 automated sulfur analyzer. On the other hand, the selenium content of the precipitate was determined using chemical digestion in aqua regia followed by AAS analysis.

3. Results and discussion

3.1. Aqueous reaction

The underlying equilibrium chemistry of the reaction system was examined with the aid of an E_h –pH diagram constructed using the FactSage 5.5 software package (Fig. 1) [34]. The diagram, prepared using a selenium and sulfur concentration of 0.003 and 1 m respectively (corresponding to a concentration of approximately 300 mg/L Se), indicates that the predominant Se(IV)

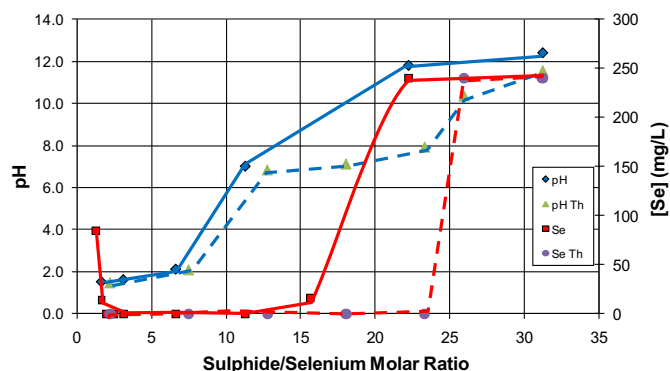


Fig. 2. Effect of the sulfide/selenium molar ratio on the effectiveness of the precipitation reaction and on final pH after 10 min. Solid lines indicate experimental results while the thermodynamic simulation data is shown with dotted lines (conditions: initial $[\text{Se(IV)}] = 300 \text{ mg/L}$, initial $\text{pH} = 1.3$, 23°C).

aqueous species corresponding to the weak acid solution composition (pH 1–1.6) is H_2SeO_3 . It is noteworthy that no sulfur–selenium compound or solid solution is present on the diagram since such solid compounds or solid solutions have not been characterized unequivocally or studied from a thermodynamic point of view and thus are not present in established databases.

The effect of sodium sulfide to selenium molar ratio on the effectiveness of the precipitation reaction is shown in Fig. 2. On the same graph the resultant final pH (initial pH was 1.3) is plotted as well along thermodynamically calculated values. The data indicate that the reaction proceeds to completion (less than $0.5 \mu\text{g/L}$ of selenium remaining in solution) for sulfide/selenium molar ratio between 1.8 and 11.3 and reaction time of 10 min. The precipitation of selenium is accompanied by pH rise and ORP drop. Thus for a selenium/sulfide molar ratio of 11.3 the ORP (vs. SHE) of the solution (data not shown) dropped suddenly from 713 mV to 6.0 and subsequently shifted and stabilized at -110 mV after 10 min reaction. Using similar conditions but without selenious ions present in solution the ORP dropped from 727 mV to -76 mV after 10 min and thereafter remained stable. It is interesting to note that the final ORP value is within the stable region of elemental selenium (refer to Fig. 1).

Large excess of sodium sulfide proved counterproductive. Thus at sulfide to selenium molar ratio from 10 to 25, the precipitation reaction was incomplete and that at higher ratios (>25) the solution turned blood red with no signs of precipitate formation. In order to validate these results, thermodynamic modeling calculations were carried with the aid of FactSage [34] coupled with the OLI database (www.olisystems.com). One must note that, as in the case of the E_h –pH diagram shown previously, thermodynamic databases do not include sulfur–selenium solid solutions. Thus the equilibrium calculations consider pure elemental selenium and sulfur and not Se–S solid solutions. However, as it can be seen on Fig. 2, the two sets of data overlap quite well, indicating that near equilibrium levels have been attained.

Returning to the effect of pH, its observed rise with the addition of sodium sulfide solution may simply reflect the fact that the latter was basic and thus gradually increased the overall pH of the solution. The question that arises though is if the pH has a direct influence on the yield of selenium precipitation or it is only the $\text{S}^{2-}/\text{Se}^{\text{IV}}$ molar ratio that controls the latter. In order to investigate further the effect of pH, a similar Se(IV)-carrying-solution of synthetic weak acid (pH 1.3) was mixed with a sodium sulfide solution to obtain a sulfide/selenium molar ratio of 22.2, i.e. a ratio outside of the complete precipitation region (refer to Fig. 2). After the addition of the sodium sulfide the weak acid solution turned clear dark red but no precipitation was witnessed. After 10 min of reaction the pH

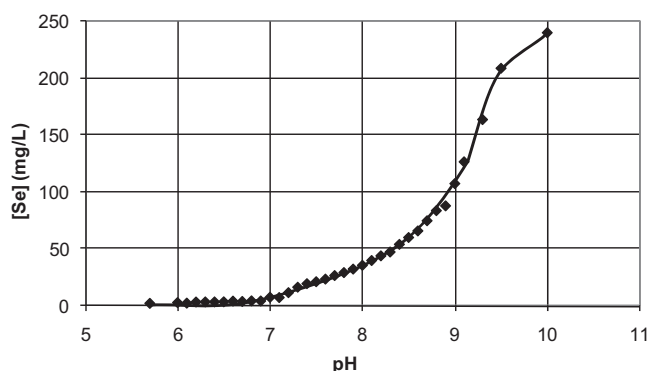


Fig. 3. Effect of pH adjustment (by HCl addition) on selenium precipitation following reaction of selenium(IV) solution with sodium sulfide at high sulfide/selenium molar ratio = 22.2 (conditions: initial $[\text{Se(IV)}] = 300 \text{ mg/L}$, $[\text{Se(IV)}]$ after the addition of Na_2S solution = 240 mg/L , 23°C).

and ORP were found to be stabilized at 11.8 and -633 mV (vs. SHE) respectively. The solution was subsequently slowly acidified with 1 M hydrochloric acid. The effect of this acidification experiment on selenium precipitation is shown in Fig. 3. At pH 9.5 a precipitate started forming and samples were then taken regularly afterwards.

As it can be seen in Fig. 3, while the precipitation reaction started at pH 9.5, it was not complete before reaching approximately pH 7.0. This experiment demonstrates that complete precipitation is possible even at high sulfide/selenium molar ratio (>11) as long as the final pH of the solution is kept between 1.7 and 7.

Interestingly, it was found that as the pH and the concentration of selenium in the solution were lowered in the above experiment (Fig. 3), the solution color went from dark red, to yellow-green before finally becoming totally colorless. It was thus possible to visually monitor the progress of the precipitation reaction; the concentration of selenium remaining in solution was found to be very low (less than 0.5 mg/L of soluble Se remaining) when the solution became colorless.

3.2. Stability of the precipitate

In order to evaluate the stability (in terms of leachability) of the selenium sulfide precipitates, several ageing tests were performed. In the most basic ones, the precipitates were left to agitate in the mother solution for several hours. The results are shown on Fig. 4. It was observed that the precipitate obtained within the optimum range of conditions (Fig. 2) was very stable, releasing only small amounts of soluble selenium ($<0.1 \text{ mg/L}$ – refer to

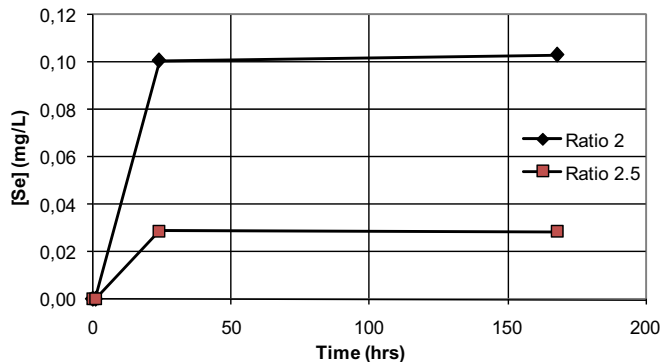


Fig. 4. Stability test for selenium sulfide precipitates in the mother solution (precipitation conditions: initial $[\text{Se(IV)}] = 300 \text{ mg/L}$, $[\text{Se(IV)}]$ after the addition of Na_2S solution = 240 mg/L , initial and final $\text{pH} = 1.3$, sulfide/selenium molar ratio = 2 and 2.5, 23°C).

Table 1

Stability test for selenium bearing solids in 1 N hydrochloric acid (conditions: 100 mL of 1 N HCl, 0.100 g of commercial selenium sulfide or elemental selenium, 0.050 g of experimental selenium sulfide precipitate (precipitation conditions: same as Fig. 4, sulfide/selenium molar ratio = 3.3), 23 °C).

Precipitate	[Se (mg/L)] after 24 h	[Se (mg/L)] after 168 h
Selenium sulfide (experimental)	0.0146	0.0106
Selenium sulfide (commercial)	0.0165	0.0176
Elemental selenium (commercial)	0.0166	0.0170

Fig. 4) back into solution. Also, it was found that only trace amounts of the selenium sulfide precipitate were dissolved after 1 week equilibration in 1 N hydrochloric acid (Table 1). Interestingly, similar results were obtained with commercially available selenium sulfide and elemental selenium. The small difference in solubility between experimental and commercial selenium sulfide probably comes from slightly different sulfur to selenium ratios in the final products.

Finally, in order to evaluate the long-term stability of the precipitate, 0.5 g of the selenium sulfide product (produced at a sulfide/selenium molar ratio of 2.5) was left to agitate with 50 mL of commercial buffer solutions at pH 3, 5, 7 and 10 (produced using potassium biphthalate and hydrochloric acid, potassium biphthalate and sodium hydroxide, potassium phosphate and sodium hydroxide and potassium hydroxide and potassium carbonate respectively). During the tests, the pH of the solutions was measured and found to remain almost perfectly constant. The results, shown in Fig. 5 indicate that the precipitate slowly dissolved at pH 3 and 5, attacked more rapidly at pH 10 but remained perfectly stable (<0.005 mg/L) at pH 7.

At this point it is not clear as to the origin of variation of selenium solubility with pH. While the buffers used introduced small amounts of contaminants to the ageing tests, their very dilute nature makes unlikely to have caused the observed variation of solubility with pH. It is possible that the observed variation relates to selenium(IV) speciation that varies with pH or with the crystallinity and ring structure of the selenium sulfide precipitate as discussed in the following section. Further work would be required to elucidate the true cause behind this behavior.

3.3. Characterization

3.3.1. XRD analysis – selenium sulfide

As discussed earlier, the characterization of the true nature of the various selenium sulfide compounds synthesized by high temperature melting procedures has been the subject of several

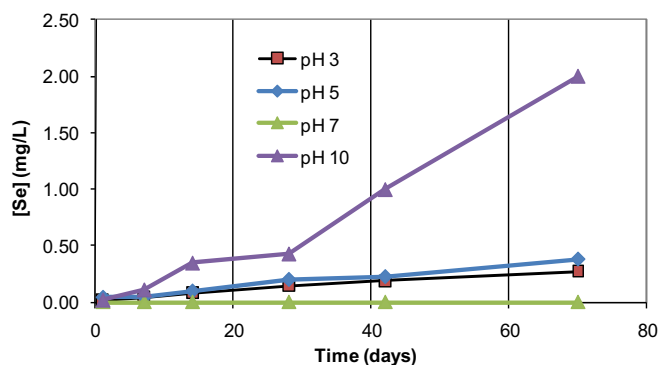


Fig. 5. Long term ageing test for selenium sulfide precipitate in different pH buffered solutions (precipitation conditions: initial [Se(IV)] = 300 mg/L, [Se(IV)] after the addition of Na₂S solution = 240 mg/L, initial pH = 1.3, sulfide/selenium molar ratio = 2.5, 23 °C).

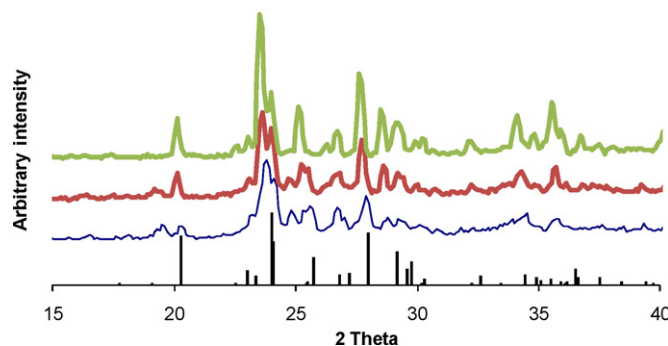


Fig. 6. XRD pattern of two sodium sulfide precipitates (bottom and middle patterns) and one of the commercially available “selenium disulfide” (top pattern) compared to that of Se_{1.09}S_{6.91} (00-041-1317) (vertical lines) (conditions: initial [Se(IV)] = 300 mg/L, [Se(IV)] sulfide/selenium molar ratio: bottom: 1.6, middle: 5.6, 23 °C).

investigations for long time. However characterization of selenium sulfides precipitated out of aqueous solution has hardly been done before. Thus, two selenium sulfide precipitates produced using different selenium–sulfides ratios (one in the full precipitation range ($S^{2-}/Se^{IV} = 5.6$) and the other in the partial precipitation region ($S^{2-}/Se^{IV} = 1.6$) were analyzed using X-ray diffraction (Fig. 6). For comparison, commercially available selenium sulfide (Sigma–Aldrich, no listed purity – described as SeS₂) was also analyzed. The very similar patterns indicate that the structure of the compound formed does not seem to vary significantly when the sulfide to selenium ratio is varied. Interestingly, the spectra matched very well the old XRD pattern from General Electric (International Centre for Diffraction Data (ICDD) number 00-002-0320 – identified as selenium monosulfide) confirming that the aqueous synthesized precipitate is a similar product. It appears that the association of this crystallographic pattern with selenium monosulfide explains why most of the medical literature refers to commercial selenium disulfide as a mixture of selenium monosulfide and a sulfur–selenium solid solution. However, the existence of selenium monosulfide as a discrete compound, although proven in the gaseous state, remains highly questionable when selenium is precipitated from aqueous solutions using sulfide ions [27]. In fact, the most recent characterization studies seem to indicate that cyclic selenium sulfides (Se_{1.09}S_{6.91} and Se_{3.94}S_{4.96}) can have very similar spectra (00-041-1317 and 00-041-1316 respectively [36]) to the one found in this work as it can be seen in Fig. 7 (for clarity only the pattern of Se_{1.09}S_{6.91} is used as a reference on Fig. 7). From this analysis we may deduce that the selenium sulfide precipitate produced

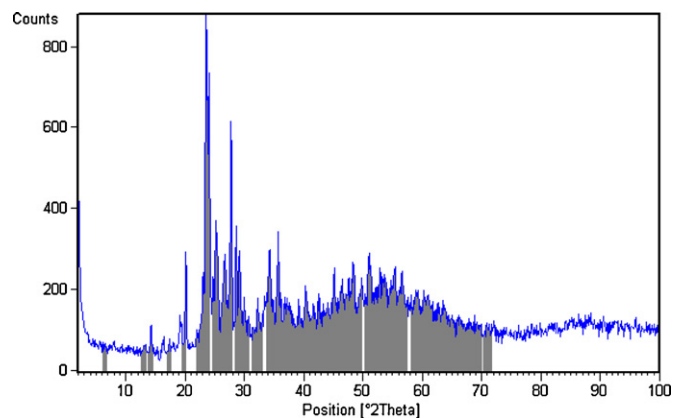


Fig. 7. XRD pattern of the sodium sulfide precipitate compared to that of Se_{1.09}S_{6.91} (00-041-1317) (gray peaks) (precipitate formation conditions: initial [Se(IV)] = 300 mg/L, [Se(IV)] sulfide/selenium molar ratio = 5.6, 23 °C).

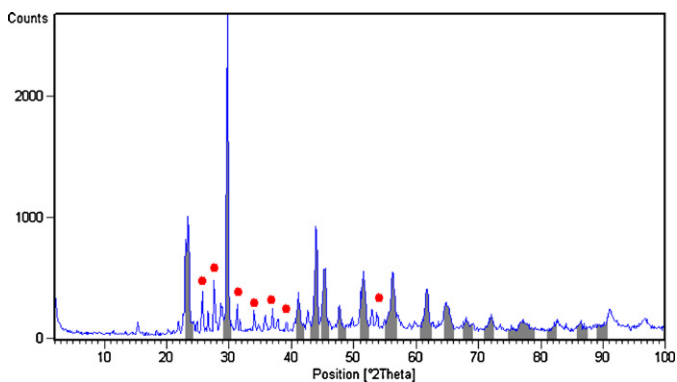


Fig. 8. XRD pattern of the precipitate formed during the acidification of a selenium-sulfide solution compared to that of hexagonal synthetic selenium (00-006-0362) (gray peaks) and orthorhombic sulfur (00-001-0478) (red dots) (conditions: initial [Se(IV)] = 300 mg/L, [Se(IV)] sulfide/selenium molar ratio = 22.2, 23 °C). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in this work is composed of a sulfur-selenium solid solution composed of heterocyclic molecules having the $\text{Se}_n\text{S}_{8-n}$ structure [28]. The reaction leading to the formation of this type of solid solution precipitate can be envisioned to involve electron exchange between the two reacting species (H_2S and HSeO_3^- according to the E_h -pH diagram of Fig. 1) yielding atoms of elemental selenium and sulfur (produced by reduction and oxidation of the respective species) arranged in 8-member rings [33]

In contrast to the selenium sulfide (identified as solid solution) formed within the U-shaped precipitation region of Fig. 2 ($2 < \text{S}^{2-}/\text{Se}^{\text{IV}} < 11$ or $1.7 < \text{pH} < 7$) the precipitate that formed during the acidification reaction described in Fig. 3, was composed of both elemental gray hexagonal selenium and of elemental sulfur (Fig. 8) and not of solid solution in the form of cyclic selenium sulfide ($\text{Se}_n\text{S}_{8-n}$) as shown on Fig. 6. The same precipitate (mixture of elemental Se and S and not solid solution) was observed to form in the partial precipitation region (between approximately pH 7 and 9.5). However, in the latter case, the selenium precipitate was originally composed of red amorphous selenium that rapidly recrystallized into the gray hexagonal allotrope. This seems to indicate that pH has an important effect on the nucleation of sulfur and selenium. At lower pH, nucleation of both species is probably faster and comparable, resulting in the formation of a solid solution

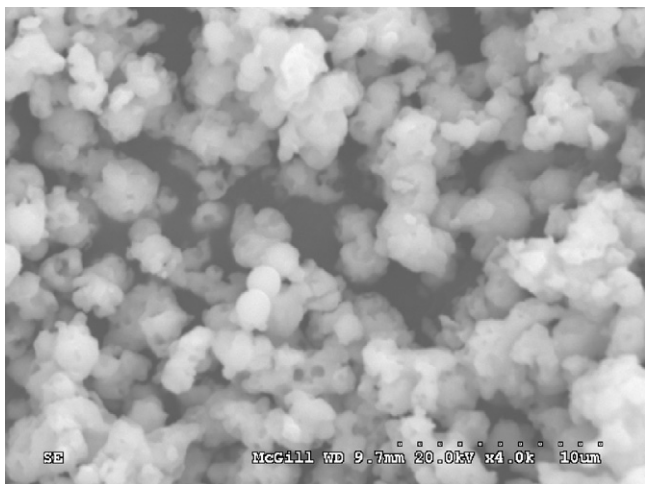


Fig. 9. Scanning electron microscope image of the selenium sulfide precipitate (precipitation conditions: initial [Se(IV)] = 300 mg/L, initial pH = 1.3, sulfide/selenium molar ratio = 5.6, 23 °C).

Table 2

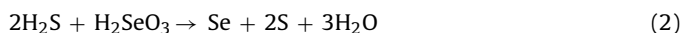
Particle size and BET surface area of selenium sulfide precipitates obtained at different sodium sulfide/selenium molar ratios after a reaction time of 10 min.

Sulfide to selenium molar ratio	Mean particle size (μm)	BET (m^2/g)
6.64	6.53	0.154
11.3	5.48	0.261
13.28	5.44	0.0501

whereas at higher pH, different nucleation rates apparently lead to the formation of distinct elemental particulates.

3.4. Reaction mechanism

As described above it appeared that at very high sulfide to selenium ratios (>25) no precipitate formed. However, it is interesting to note that the color of the solution was deep red as is the case when elemental selenium is dissolved in a strong base. In the latter case it has been demonstrated that selenium is present in a very fine colloidal state [35]. It was suspected this to be the case as well with the high S/Se ratio (>11) system in this work. To confirm this hypothesis, a typical high S/Se solution was evaporated near room temperature; then the obtained residue was redissolved in water where it was noticed to form aggregates (possibly because of the pH be near its isoelectric point). The precipitate after that was boiled in toluene, analyzed under XRD and found to be elemental selenium (results not shown). This indicates that sodium sulfide reduced selenious ions to elemental state via reaction (2) but the formed selenium was colloidal. Apparently upon acidification the colloidal Se/transformed to crystalline selenium (and sulfur) as shown in Fig. 8.



A similar redox reaction is believed to take place in the lower pH region where the solid solution Se-S phase ($\text{Se}_n\text{S}_{8-n}$) (Fig. 7) was found to form. However in this case the selenium and sulfur atoms are organized in 8-member hetero-rings ($\cdots\text{Se}-\text{Se}-\text{S}-\text{Se}-\text{S}-\cdots$) rather than homo-rings or chains of the respective elements.

The zero-valence state of selenium and sulfur in the proposed solid solution structure ($\text{Se}_n\text{S}_{8-n}$) was further confirmed via the following test: selenium sulfide solid solution (with XRD pattern as in Fig. 7) was precipitated using a S/Se ratio of 2.5. After this, strong base was added to raise the pH from 1.8 to 12.2. As a result of this pH adjustment the precipitate transformed to a mixture of elemental Se and S (as per XRD pattern of Fig. 8). No redox reaction was involved in this adjustment. This implies that the solid solution made up of the 8-member heterocycle rings ($\text{Se}_n\text{S}_{8-n}$) becomes unstable in the alkaline region breaking down to its constituent parts: elemental selenium and sulfur. This phenomenon is probably caused by the apparent corrosive effect (although no oxidation-reduction is effectively present) that bases have on selenium [35].

3.5. Precipitate particle properties

A scanning electron microscope (SEM) image of selenium sulfide particles (formed in the optimum precipitation range – no selenium remaining in solution) taken after approximately 2 min of reaction time (Fig. 9) reveals that the precipitate is composed of fine particles slightly agglomerated into larger ones. Results for particle size and BET surface area analysis, shown in Table 2, indicate that the sulfide to selenium ratio has little influence on particle size and that, although more variable, the specific surface remains small in all cases suggesting a rather dense and easily filterable precipitate.

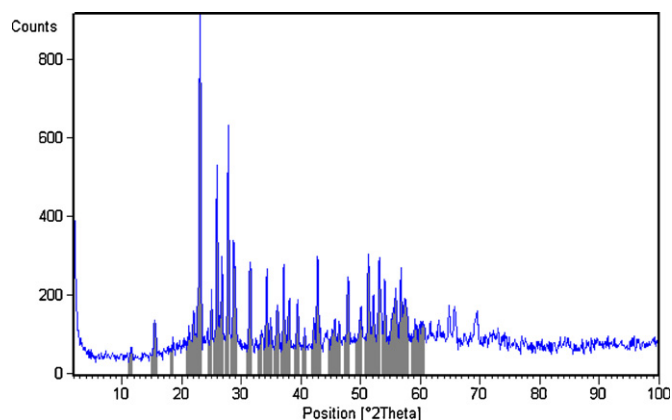


Fig. 10. XRD pattern of the secondary sulfur precipitate compared to that of orthorhombic sulfur (00-001-0478) (gray peaks).

3.6. Precipitate composition

According to the XRD analysis the selenium sulfide precipitate is a solid solution of Se and S consisting of 8-member hetero-rings: $\text{Se}_n\text{S}_{8-n}$. Chemical analysis of several precipitates produced within the complete precipitation zone ($<1.7\text{S}/\text{Se} < 11$ – refer to Fig. 2) yielded a sulfur to selenium ratio between 1.73 and 2.28 independent of the initial S/Se ratio in the solution. This corresponds to the commonly used “selenium disulfide” name. In terms of the $\text{Se}_n\text{S}_{8-n}$ formula this range of values gives a n value between 2.5 and 3: $\text{Se}_{2.5-3}\text{S}_{5-5.5}$. It must be noted, however, that upon prolonged (beyond the standard 10 min duration of the tests) equilibration of the reaction solutions (in the case of solutions with $\text{S}/\text{Se} > 2.3$) secondary precipitation of elemental sulfur was observed to take place apparently due to decomposition/oxidation of the excess sulfide. (It is clarified that the S/Se ratio of the precipitate reported above was determined before secondary sulfur precipitation would start.) The formation of sulfur out of the colorless Se-free solution, following the complete precipitation of selenium, was signaled with an opaque cloudy appearance that turned after several minutes into a light white milky liquid. The sulfur precipitate was extremely fine and difficult to filter at the beginning but it agglomerated into slightly larger particles after a few minutes of agitation. The secondary formed sulfur was found to be stable in the final solution for at least several days and be crystalline (orthorhombic) (Fig. 10).

4. Conclusion

Selenious ions can be effectively precipitated from weak acidic solutions using sodium sulfide. Below a pH of approximately 7.0 and a sulfide/selenium molar ratio of 1.7–11, the precipitation reaction goes to completion with only 0.005 mg/L of soluble selenium remaining in solution after 10 min at ambient temperature. If the pH was allowed to rise between 7.0 and 9.5 the precipitation of selenium was incomplete while above pH 9.5 the solution turned dark red and was determined to contain colloidal selenium. The latter transforms to crystalline selenium aggregates upon acidification (terminal pH < 7). The reaction involves reduction of selenium and oxidation of sulfide to their respective elemental states. In the region of complete precipitation ($1.7 < \text{S}/\text{Se} < 11$ and $1.7 < \text{pH} < 7$) the selenium and sulfur atoms appear to form a solid solution consisting of sulfur–selenium ring molecules having the $\text{Se}_n\text{S}_{8-n}$ formula, with $n = 2.5-3$. Elevation of pH above 7 leads to a breakdown of the $\text{Se}_n\text{S}_{8-n}$ solid solution structure and the formation of individual elemental and selenium colloidal particles. The selenium–sulfur solid solution phase was found to be extremely stable (< 0.005 mg/L Se) when subjected to over 60-day leachability test at pH 7. Following

the precipitation of $\text{Se}_n\text{S}_{8-n}$ secondary sulfur formation occurs via the decomposition of the excess sulfide.

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