Selenium Removal from Aqueous Solutions

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To Mom and Geneviève

Abstract

The aqueous chemistry of the reduction of selenious species by sodium dithionite, sodium sulfide, stannous chloride and sulfur dioxide/sulfite was studied. The resultant precipitates were characterized using different techniques, including scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy.

In the case of sodium dithionite, the research showed that, at initial pH below 1.7 and dithionite stoichiometric excess above three, less than 0.5 μg/L remained in solution less than a minute after the addition of the reagent. However, it was found that the precipitate, mainly composed of red amorphous selenium, was not stable in the presence of the dithionite decomposition by-products and partially redissolved after several hours. In the case of the reaction involving selenious acid and sulfide ions, the results showed that, below a pH of approximately 7.0, the precipitation reaction was complete in less than 10 minutes at a sulfide to selenium ratio above 1.8 with less than 5 μg/L of soluble selenium remaining in solution. The precipitate was deduced to be a Se-S solid solution consisting of ring molecules of the following Se_nS_{8-n} formula.

However, above pH 7 the removal of selenium was incomplete due to formation of a stable colloidal suspension. In the case of industrial solutions, high dissolved sulfur dioxide content (> 5g/L) decreases the effectiveness of the precipitation reaction. Concerning the removal of Se(IV) by tin(II), at an initial pH below 1.3 and molar ratios above two, less than 5 μg/L of selenium(IV) remained in solution after reduction. The

reaction products, were determined to be composed of approximately equal amounts of tin selenide and tin dioxide with a small amount of selenium(IV) being adsorbed on the latter. Finally, it was found that Se(IV) can be reduced quantitatively at ambient temperature via a combination of sulfite reduction and ultra-acidification to a colloidal form that can be determined using turbidimetry. The developed technique was shown to be equally effective with real Se(IV)-bearing industrial solutions generated in a zinc concentrate roasting operation hence making the method particularly useful as on-line process monitoring and control tool.

Résumé

La chimie aqueuse des réactions de réduction entre les ions sélénieux et le dithionite de sodium, le sulfure de sodium et les ions stanneux ont été étudiées. Les précipités résultant de cette réaction ont été caractérisés par différentes techniques comme la microscopie électronique à balayage, la diffraction à rayons X et la spectrométrie de photoélectrons induits par rayons X.

Dans le cas du dithionite de sodium, ce projet a démontré que, pour un pH initial inférieur à 1.7 et un ratio stœchiométrique de dithionite supérieur à trois, moins de 0.5 µg/L de sélénium(IV) restait en solution moins d'une minute après l'addition du réactif. Par contre, le précipité, formé en majorité de sélénium rouge amorphe, n'était pas stable en présence des composés issus de la réaction de décomposition du dithionite et était partiellement re-dissous après quelques heures.

Dans le cas de la réaction entre l'acide sélénieux et le sulfure de sodium, les résultats indiquaient que pour un ratio molaire sulfur/sélénium plus grand que 1.8 et un pH sous 7.0 la réaction de précipitation était complète et moins de 5 µg/L de sélénium (IV) restait en solution. Aucune précipitation n'a été constatée pour un pH plus élevé que 9.5 et la réaction était incomplète pour un pH entre 7 et 9.5. Le précipité semblait être composé d'une solution solide Se-S formé de molécules circulaires répondant à la formule Se_nS_{8-n}. Par contre, pour un pH plus élevé que 7, la précipitation du sélénium était incomplète à cause de la formation d'un précipité de sélénium colloïdal. De plus,

dans le cas des solutions industrielles, de hautes concentrations de dioxyde de souffre dissous (> 5g/L) diminuait l'efficacité de la réaction de précipitation.

En ce qui concerne la réaction entre le sélénium(IV) et l'étain, pour un pH initial sous 1.3 et un ratio molaire étain/sélénium plus grand que deux, moins de 5 μg/L de sélénium restait en solution après la réaction. Les analyses ont révélé que le précipité était composé de parts approximativement égales de séléniure d'étain et de dioxyde d'étain et que ce dernier pouvait adsorber une petite quantité d'ions sélénieux. Finalement, ce projet a démontré que le sélénium(IV) peut être réduit, à la température ambiante, par une solution ultra-acide riche en sulfites. Une fois le sélénium précipité sous forme colloïdale, la concentration originale de celui-ci peut ensuite être déterminée par turbidimétrie. Par ailleurs, cette méthode est aussi efficace sur des solutions industrielles contenant du sélénium(IV) et peut donc être appliquée pour l'analyse en temps réel de cet élément.

Foreword

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Contribution of authors

The following papers, that also constitute chapters in the thesis, have been published or submitted for publication with Prof. G. P. Demopoulos as a co-author:

Chapter 3: Geoffroy, N. and Demopoulos, G.P., 2009. Reductive Precipitation of Elemental Selenium from Selenious Acidic Solutions Using Sodium Dithionite., Industrial & Engineering Chemistry Research, 48(23): 10240-10246.

Chapter 4: Geoffroy, N. and Demopoulos, G.P., 2010 The elimination of selenium (IV) from aqueous solution by precipitation with sodium sulfide., Journal of Hazardous Materials, 185(1): 148-154.

Chapter 5: Geoffroy, N. and Demopoulos, G.P., 2011 Stannous chloride-an effective reducing agent for the removal of selenium (IV) from industrial acidic effluent to less than 5.0 μg/L., Submitted to the Journal of Hazardous Materials.

Chapter 6: Geoffroy, N. and Demopoulos, G.P., 2011 The rapid measurement and monitoring of selenite concentration by turbidimetry following its conversion to colloidal state by sulfite reduction and acidification., Submitted to Hydrometallurgy.

All the research work has been performed by the author of this thesis except for the normal supervision and advices given by the supervisor.

I hereby give copyright clearance for the inclusion of the above papers, of which I am co-author, in the Ph.D dissertation thesis of Nicolas Geoffroy:

Prof. G.P. Demopoulos, Department of Mining and Materials Engineering

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Chapter 1 – Introduction

1.1 Background

Selenium was discovered in 1817 by Jöns Jakob Berzelius in a Swedish sulfuric acid plant. The researcher originally thought that the red powder that he had collected on the lead reactor walls was tellurium but, once burnt, the substance gave off an unusual horseradish odor (caused by H_2Se). Berzelius thus realized that he had discovered a new element and named it after the Greek word σελήνη (selene) meaning Moon. This name was chosen because selenium is often associated with tellurium that, in turn, was named after the Latin word for Earth [1, 2]. In the earth's crust, selenium is widely distributed but is present in small quantities, being approximately as common as silver and platinum. This element is especially common in pyritic ores, thus explaining why it is a common impurity in the copper industry [1].

It is well-known that selenium naturally present in the soil can be concentrated by some plants (up to several thousands mg/kg) and cause a wide range of health problems [3]. While the link between this element and health problems is relatively recent, evidences of selenium intoxication have been described as early as the thirteenth century [4]. For humans, selenium intoxication, known as selenosis, can give rise to symptoms such as gastrointestinal upsets, hair loss, white blotchy nails, garlic breath odor, and nerve damage [5]. Because of this, selenium discharge into the environment must be closely controlled and monitored.

1.2 Industrial application

The dangerous and cumulative consequences of higher concentrations of selenium on wildlife have been well demonstrated [6]. Because of this, industries involved with the processing of selenium-bearing materials are now closely regulated. For example, primary metallurgical industries such as zinc and copper refineries often deal with selenium since this element is a common impurity in mineral concentrates. In zinc smelting operations, part of the selenium is released in the roaster off-gas and is then concentrated in a weak sulfuric acid stream that must be treated and neutralized prior to being released to the environment [7]. Furthermore, mercury, another toxic and volatile element, follows the same path and must also be treated and removed.

Since the aqueous chemistry of mercury has been extensively studied and is well understood, several methods to eliminate this element have been elaborated [1]. One of the most common and efficient removal techniques involves the precipitation of mercury in the form of mercuric sulfide (HgS) [8, 9]. On the other hand, the inorganic chemistry of selenium has not been studied as extensively and the environmental problems associated with this element have only been discovered recently. Because of this, various processes have been proposed in the last twenty years to eliminate selenium from aqueous solutions. These involve techniques such as chemical reduction, ion exchange membranes, electrocoagulation and adsorption [10].

Among these various methods, those that include the reduction and subsequent precipitation of soluble selenium species seem to achieve the best results for relatively concentrated industrial solutions. Furthermore, various reagents have been found to reduce selenium ions in various types of aqueous solutions [1]. A technique involving the reduction of selenious ions by sodium dithionite was patented in 2000 by Noranda Inc. (now absorbed by Xstrata) [11]. This process is presently being used by the Canadian Electrolytic Zinc Company (CEZinc) (Valleyfield, Quebec) in order to meet environmental regulations [7].

The CEZinc process is divided in two steps (Figure 1). In the first one, sodium sulfide is added to the weak acid solution in order to precipitate the soluble mercury (Equation 1). The solution is then treated with sodium dithionite in order to reduce the selenium to elemental form (Equation 2). The precipitate is then filtered and disposed of while the weak acid solution is neutralized before being released in the environment [7].

$$Hg^{2+} + Na_2S \rightarrow HgS(s) + 2Na^+ \qquad (1)$$

$$H_2SeO_3 + 2H_2SO_4 + 2Na_2S_2O_4 \rightarrow Se(s) + 4SO_2 + 2Na_2SO_4 + 3H_2O \qquad (2)$$

The effectiveness of the CEZinc Se and Hg removal process can be evaluated with the typical industrial operating data plotted in Figure 2. While mercury removal has been consistently well below the permissible level of 50 ppb (0.05 mg/L) the control of selenium has shown rather erratic behavior (Figure 2) with values slightly below the target of 3.5 mg/L. In general a large excess of dithionite is commonly used to maintain the soluble selenium content below the 3.5 mg/L limit. Furthermore, the problem of selenium control is complicated by the variation of weak acid solution composition.

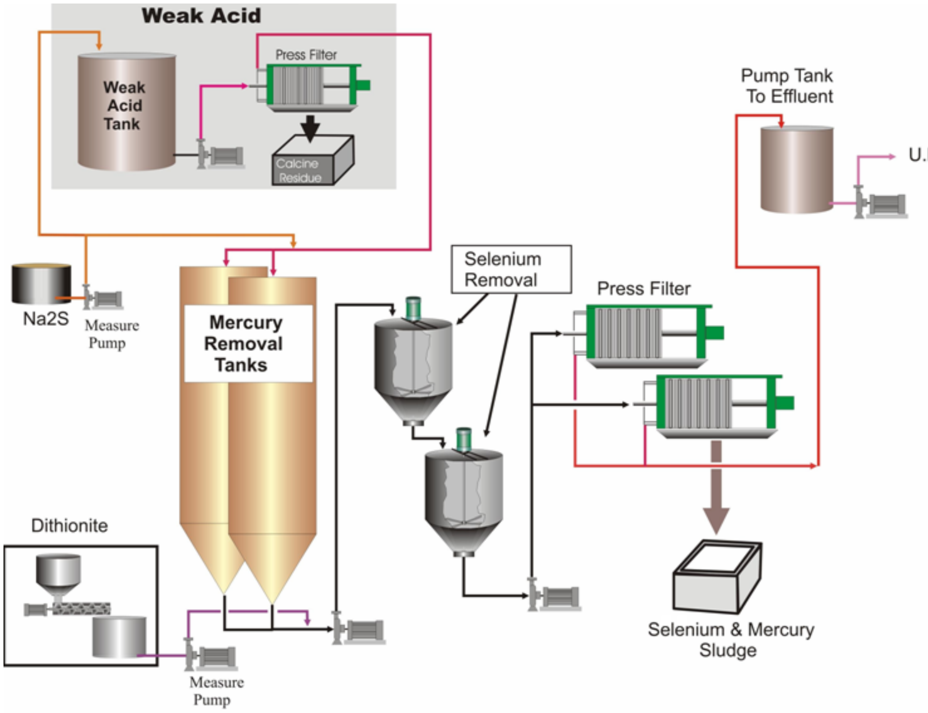

Figure 1 - Flowchart of the CEZinc Selenium and Mercury Removal Process

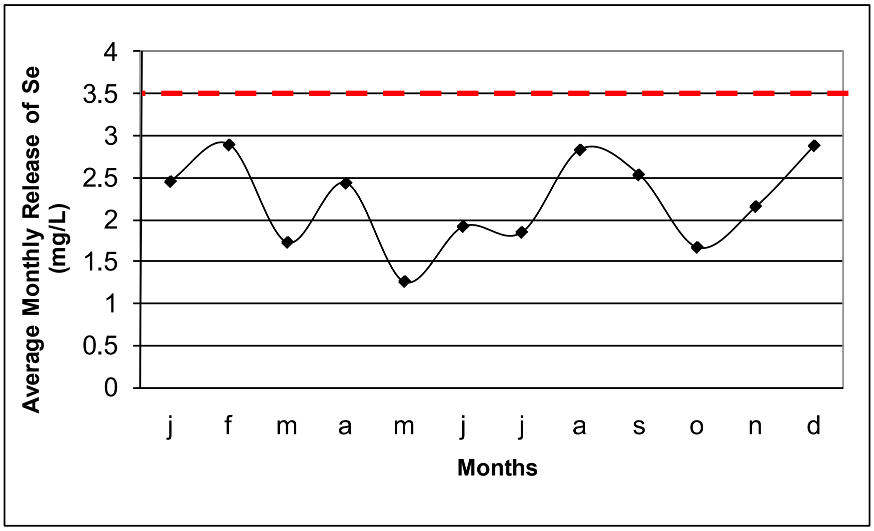

Figure 2 - Concentration of selenium (mg/L) released per month in 2001 with the 3.5 mg/L legal limit indicated by the dashed line

The industrial weak acid solution treated at CEZinc is complex and its composition varies according to the nature of the ore and to smelting operating parameters (more details are given in the appendices):

-5 to 30 g/L H_2SO_4 (pH 1 to 1.6)

-Saturated in SO_2 when fresh

-0.5 to 10 g/L Zn

-0 to 75 mg/L Hg and 10 to 300 mg/L Se

-Varying amounts (a few mg/L to a few g/L) of other elements such as, Al, As, Bi, Ca, Cd, Cu, In, Mn, Mo, Pb, and Sb

Changes in the concentrate feed over the next few years are expected to increase the selenium concentration in the weak acid up to levels as high as 700 mg/L. At the same time a new set of environmental regulations may well reduce the permissible release level below the current 3.5 mg/L limit. As such, there exists a need for the development of more effective removal processes for selenium-bearing industrial process effluents. To this end the current investigation was undertaken that focuses on the study of the elimination chemistry of selenium (mainly as selenite, Se(IV)) from weakly acidic solutions via a number of reducing agents, such as dithionite, sulfide, and stannous.

1.3 Scope of this work

The aim of this project is to evaluate the effectiveness of different reagents to precipitate selenium from aqueous solutions. The first two reagents studied, sodium dithionite and sodium sulfide are presently used at the CEZinc refinery to precipitate selenium and mercury respectively. The third, stannous chloride, does not appear to have been studied or used for selenium removal applications, especially from an industrial point of view. In all cases, the optimal operating parameters were determined and the limitations of each reagent were determined. Also, in order to determine rapidly the selenious acid concentration, especially in an industrial setting, a new analytical technique was also developed and described.

1.4 Organization of the thesis

This thesis has been organized in the following manner: following this introduction, Chapter 2 gives a literature survey of selenium chemistry with particular emphasis on selenium removal by reductive precipitation methods. Chapters 3 to 5 describe the elimination chemistry of selenious species with sodium dithionite, sodium sulfide and stannous chloride respectively. Chapter 6 describes a novel selenious acid analytical method that involves turbidity measurements following formation of colloidal elemental selenium by the combined action of sulfite reduction and ultra-acidification. Chapter 7 summarizes the most important findings and describes the claims to originality. Finally in the Appendix additional information of supplementary value is presented that covers issues relating to selenium analysis, selenate removal, and characterization of the industrial weak acid (CEZinc process) solution.

1.5 Final remarks

The Chapters 3 to 6 of this thesis are based on manuscripts/papers that were published or submitted for publication to scientific journals during the course of this project. As such, a certain overlap in the introduction of these chapters is present in order to make them understandable as stand-alone papers.

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Chapter 2 - Literature Review

2.1 Foreword

In this chapter, a general review of the literature published on selenium removal from aqueous solutions is presented. The review is divided in three main parts: the redox properties of selenium, removal techniques and analytical procedures. Because of important differences in the chemical behaviour of selenite Se(IV) and selenate Se(VI) species, the removal techniques for these species will be discussed separately. Furthermore, an in depth review on the reductive precipitation of selenite by sodium dithionite, sodium sulfide and stannous chloride is presented since this topic constitutes the subject-matter of Chapters 3, 4 and 5 respectively.

2.2 Redox Properties of Selenium

Selenium shares most of its chemical properties with the elements directly below and above it in the periodic table. In other words, selenium is, from a chemical point of view, similar to sulfur and tellurium. This behavior can best be summarized by looking at the most common oxidation states for sulfur and selenium and their associated nomenclature (Table 1). The reduction equilibria and potentials of the different selenium species are represented by equations 1 to 5 [1].

Table 1 - Summary of oxidation states and nomenclature for sulfur and selenium species [2, 3]

Sulfur Species	**Selenium Species**	**Oxidation State**
Sulfate/Bisulfate (SO_4^{2-}/HSO_4^{2-})	Selenate/Biselenate (SeO_4^{2-}/$HSeO_4^{2-}$)	S^{6+}, Se^{6+}
Sulfite/ Bisulfite (SO_3^{2-}/HSO_3^{2-})	Selenite/Biselenite (SeO_3^{2-}/$HSeO_4^{2-}$)	S^{4+}, Se^{4+}
Elemental Sulfur (S)	Elemental Selenium (Se)	S, Se
Sulfide (S^{2-})	Selenide (Se^{2-})	S^{2-}, Se^{2-}

$$Se + 2H^+ + 2e^- \rightarrow H_2Se(aq)\ (E^o = -0.115\ V) \quad (1)$$

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O\ (E^o = 0.739\ V) \quad (2)$$

$$SeO_3^{2-} + 6H^+ + 2e^- \rightarrow Se + 3H_2O\ (E^o = 0.885\ V) \quad (3)$$

$$HSeO_4^{2-} + 3H^+ + 2e^- \rightarrow H_2SeO_3 + H_2O\ (E^o = 1.094\ V) \quad (4)$$

$$SeO_4^{2-} + H_2O + 2e^- \rightarrow SeO_3^{2-} + 2OH^-\ (E^o = 0.031\ V) \quad (5)$$

Elemental selenium is relatively stable, as shown by its high reduction potential between the selenite and elemental states (Equation 2). Thus, the element is not attacked by hydrochloric or sulfuric acid if oxygen or other oxidants are not present [4]. However, if burned in air or dissolved in an oxidizing solution, selenium will be oxidized to the selenite state. Because of this, selenium dioxide (SeO_2), a white, needle-shaped power, is by far the most common compound of selenium. Once dissolved in water selenium(IV) behaves as weak acid (selenious acid, H_2SeO_3), which dissociates according to the prevailing pH [4].

On the other hand, if very strong oxidizing conditions are used selenium may be oxidized to its higher selenate oxidation state. For example the preparation of selenic (Se(VI)) acid (H_2SeO_4) has been reported to be accomplished by anodic (electrolytic) oxidation of a selenious acid solution or the reaction of the latter with hydrogen peroxide. Other oxidizers such as nitric acid, *aqua regia*, mercuric and cupric salts are not able to oxidize selenium past the selenite state [4, 5]. Interestingly, even though it is relatively difficult to produce selenates in the laboratory, it is the most common oxidation state in nature. On the other hand, despite the high reduction potential of selenate (Equation 4), it is very difficult, because of kinetic issues, to reduce it in aqueous solutions hence making its removal from effluent solutions as discussed later quite challenging.

Finally, selenium can also take a negative oxidation number (selenide, -II) and thus form compounds with hydrogen and most transition metals. It is interesting to note here that the element itself was discovered because of the strong horseradish odor of hydrogen selenide (H_2Se). This gas, highly soluble in water, can be formed under strongly reducing conditions and represents a serious safety hazard since it is by far the most toxic selenium compound. On the other hand, most selenium-transition metal compounds are thermodynamically more stable than elemental selenium itself and are almost completely insoluble. In fact, almost all selenium minerals, including the two most common: clausthalite (PbSe) and crookesite ($Cu_7(Tl,Ag)Se_4$) are selenide based [2].

2.3 Selenium removal techniques

It has been known for about seventy years that certain plants can concentrate selenium naturally present in the soil (up to several thousand mg/L) and become toxic to grazing animals. Selenium intoxication, known in the agricultural field as the "alkali disease" can cause hoof deformation, a rough coat and potential death [6]. While the link between this condition and selenium is relatively recent, the disease was documented as early as the 13th century by Marco Polo [7]. In humans, selenium intoxication is known as selenosis and can give rise to symptoms such as gastrointestinal upsets, hair loss, white blotchy nails, garlic breath odour, and nerve damage [8]. Because of this, selenium rapidly developed a reputation that rivalled that of arsenic and thallium.

However, this perception started changing in the 1950s when it was discovered that selenium is also an essential micronutrient and that several diseases associated with malnutrition are actually caused by selenium deficiencies [6]. Furthermore, modern research suggests that certain types of cancers and the rapid propagation of AIDS in Sub-Saharan Africa might be linked to low selenium level in the diet [9]. Because of this, it appears that health problems caused by selenium deficiencies are much more of a threat to human and animal heath than potential selenium intoxication. In fact, rural or industrial cases of irreversible chronic diseases or death caused by selenium appear to be extremely rare [2]. Furthermore, in 1991 the United States Environmental Protection Agency (EPA) increased the maximum selenium level in drinking water from 10 to 50 ppb to account for the potential positive effect this element can have on human health. A summary of selenium regulations in North America is shown in Table 2. It is interesting to note that the selenium intake varies very significantly around the world according to the distribution of this element in the soil.

Thus, while trace amounts of selenium appear to have positive health effects, it is important to note that the environmental discharge limits are very low and that removal techniques are often needed. Because of this, various processes have been recently proposed to eliminate selenium from aqueous solutions. However, this has proved rather challenging. For example, lime neutralization, the most common industrial technique to precipitate heavy elements as hydroxides is ineffective for selenium since it does not form insoluble hydroxides. Overall, selenite ions have been found to be significantly easier to remove than selenate ones because of the poor reduction kinetics of the latter. Because of this behavior, the removal of the two selenium oxidized states will be examined separately.

Table 2 - Summary of Selenium Regulations in North America [10, 11]

Law or Regulation	Max [Se] (ppb)
Safe Drinking Water Act (USA)	0.050
Clean Water Act, acute - 1hr freshwater (USA)	0.020
Clean Water Act, acute - 1hr marine (USA)	0.030
Clean Water Act, chronic - 4hr freshwater (USA)	0.005
Clean Water Act, chronic - 4hr marine (USA)	0.071
Federal Irrigation (USA)	0.020
Quebec Drinking Water Standards (CAN)	0.01

2.3.1 Selenite

While purification techniques such as bacterial reduction, ion exchange membranes, electrocoagulation and adsorption have been investigated, they are either not very effective or only suitable to treat solutions containing low levels of dissolved selenium (< 1 ppm) [12]. Furthermore, these techniques are more appropriate for selenate-bearing solutions since chemical reduction is very difficult for this oxidation state. Thus these techniques will be covered in the selenate removal section. For industrial applications involving selenite species, techniques that involve the reductive precipitation of selenium seem to achieve the best results [13]. Furthermore, because of its high reduction potential, various reagents have been found to reduce selenious ions in different types of aqueous solutions [14, 15].

In analytical chemistry as well as industrially, it appears that sulfur dioxide is by far the preferred reactant to reduce selenium(IV) to elemental state. 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 will occur very rapidly [2, 16, 17]. However, when working with more dilute solutions near room temperature, such as the one processed at CEZinc, the reduction reaction, while still thermodynamically possible, becomes too slow to be of practical interest [18]. In connection to the use of SO_2 to eliminate selenium it is noteworthy to refer to Hamada, who demonstrated that increasing selenium concentration and temperature have a positive effect on the reaction rate but temperature elevation is not feasible for large volumes of dilute solutions. The opposite effect is seen with pH (the reaction rate increases with acidity) and the rate constant is reported to be:

$$k = 2.054 * 10^{15} * [H^+]^2 * e^{\left(\frac{-22500}{RT}\right)} \quad (6)$$

In the case of the CEZinc weak acid (room temperature and pH 1.3) empirical results showed that the reduction of Se(IV) with dissolved sulfur dioxide is too slow to be of any practical use[18].

Metals such as zinc [19], aluminum [18] and copper [20], because of their lower reduction potentials compared to that of selenite, have also been found to reduce selenite ions to elemental state. However, cementation tests performed with aluminum showed the presence of hydrogen selenide, a serious drawback given the toxicity of this compound [18]. The use of copper has been patented in Canada and is presently used to treat mixed selenite/selenate solutions in copper electrorefining operations [20]. However, highly acidic (<< pH 1) solutions and relatively high temperatures (50 to 95°C) are needed to achieve acceptable reaction rates. On the other hand, other reducing agents such as copper (I) chloride [21] and titanium (III) chloride have been successfully used on a lab-scale to reduce selenite ions. Their industrial applicability is nevertheless limited by their high costs and handling problems. Finally, several other reagents such as thiourea [22], glucose [23], hydrazine [15], [24] and stannous chloride [25] have been proposed as quantitative reducing agents for selenium (IV) in acidic solutions. However, issues such as high toxicity (hydrazine and thiourea) or poor efficiency (glucose) seem to have limited the industrial applicability of these reagents while stannous chloride was never considered outside the analytical domain hence its investigation in this work.

2.3.1.1 Dithionite

Dithionite ($H_2S_2O_4$ and its sodium salt), also known as hydrosulfite or, in older texts, as hyposulfite is a well-known reducing agent that is often used as a dying reagent in the textile industry [4]. The reduction potential of dithionite in water had not been determined with certainty but was assumed to be close to zero (0.0 – 0.08 V) [26]. Owing to its strong reducing action dithionite was selected as the preferred reagent for the elimination of selenium from an industrial zinc process acidic effluent. However, the efficiency of this process has not been optimized nor its chemistry been studied in depth before the present project [4, 18].

The dithionite complex is unstable in acidic aqueous solutions, and decomposes into several sulfur species of variable oxidation states. The decomposition of dithionite has been studied and while some controversy remains it appears that the decomposition mechanism can be broken down in two fundamental stages [27-35]: A slow induction reaction (Equation 10, [36]) followed by a faster, autocatalytic one (Equation 11).

$$16H_2S_2O_4 \rightarrow S_8 + 24SO_2 + 16H_2O \qquad (7):$$

$$3H_2S_2O_4 \rightarrow H_2S + 5SO_2 + 3H_2O \qquad (8)$$

The reaction products then react with each other to form other sulfur complexes:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (9)$$

$$xH_2SO_3 + S_x \rightarrow x\ H_2S_2O_3 \qquad (10)$$

$$nH_2S + mSO_2 \rightarrow \text{polythionates} \qquad (11)$$

$$nH_2S + mSx \rightarrow \text{polysulfides} \qquad (12)$$

As seen above, the decomposition is very complex because the reaction products can decompose and interact with each other at various rates, giving rise to a final solution rich in thiosulfates, polysulfides, and polythionates. Furthermore, elemental sulfur can be formed at different stages of the decomposition reaction including various radicals increasing furthermore the complexity of the decomposition process [36].

2.3.1.2 Sulfide

As discussed in Chapter 1, the CEZinc process uses sodium sulfide to precipitate the soluble mercury and sodium dithionite to reduce and precipitate selenium. It is interesting to note that the original CEZinc patent describing the mercury/selenium removal process mentioned that a fraction of the selenious ions could be removed by the sulfide ions used to precipitate mercury [37]. However, no adequate data or explication was given for this phenomenon and it appears to have been seen as an added bonus and not an inherent part of the process. The precipitation of selenium by sulfide ions is not a new system as it has been identified only a few years after the discovery of the element itself. Originally, it was thought that the precipitate was composed of both elemental sulfur and selenium [17-18] or of selenium monosulfide (SeS) [19]. However, the reaction often suggested today involves the formation of selenium disulfide [19]:

$$2H_2S + SeO_2 \rightarrow SeS_2 + 2H_2O \tag{13}$$

This compound, while produced only a few years after the discovery of the element itself, was not used industrially before the 1920s. Around that time, researchers at General Electric realized that the very active sulfur inside the molecule could be used to detect traces of mercury vapor in the air [20]. While this application does not appear to have been successful, it was also tried to treat skin diseases since elemental sulfur was known to be very effective for this purpose. In 1951, after decades of tests, the first selenium sulfide shampoo, “Selsun”, appeared on the market. Interestingly, this drug was originally only available on a physician’s prescription [21]. Today, most of the medical literature refers to commercial selenium disulfide as a mixture of selenium monosulfide and a sulfur-selenium solid solution [38]. 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. Furthermore, several patents (most of them significantly overlapping each other) have been issued in different countries for the production of aqueous selenium sulfide [39-44]. One must note that the reaction shown in Equation 13 has not been studied in detail and no detailed information is available on operating parameters (pH, concentration, temperature) and on the morphology of the product.

On the other hand, more information is available on the so-called “selenium sulfide” produced by fusion. For example, the phase diagram of sulfur and selenium, shown on Figure 3, indicates that selenium and sulfur can both dissolve significant amounts of each other in their structure and can also form intermediate phases. These phases are constituted of polymer-like cyclic Se–S rings containing a variable number of Se and S atoms, most commonly following the general formula Se_nS_{8-n} [45-47]. These 8-member cyclic molecules have been extensively studied and different phases have been described [48]. In addition it is reported that these ring compounds can exist in the amorphous or crystalline state; while six, seven, ten and twelve member sulfur-selenium molecules have also been observed. [49, 50]. However, it has proved impossible to isolate with certainty any particular compound because of the plasticity of these molecules [45, 49]. Finally, some other selenium compounds having the general formula SeS_n (n: 1 to 7) have been identified in certain quartz ores [51, 50].

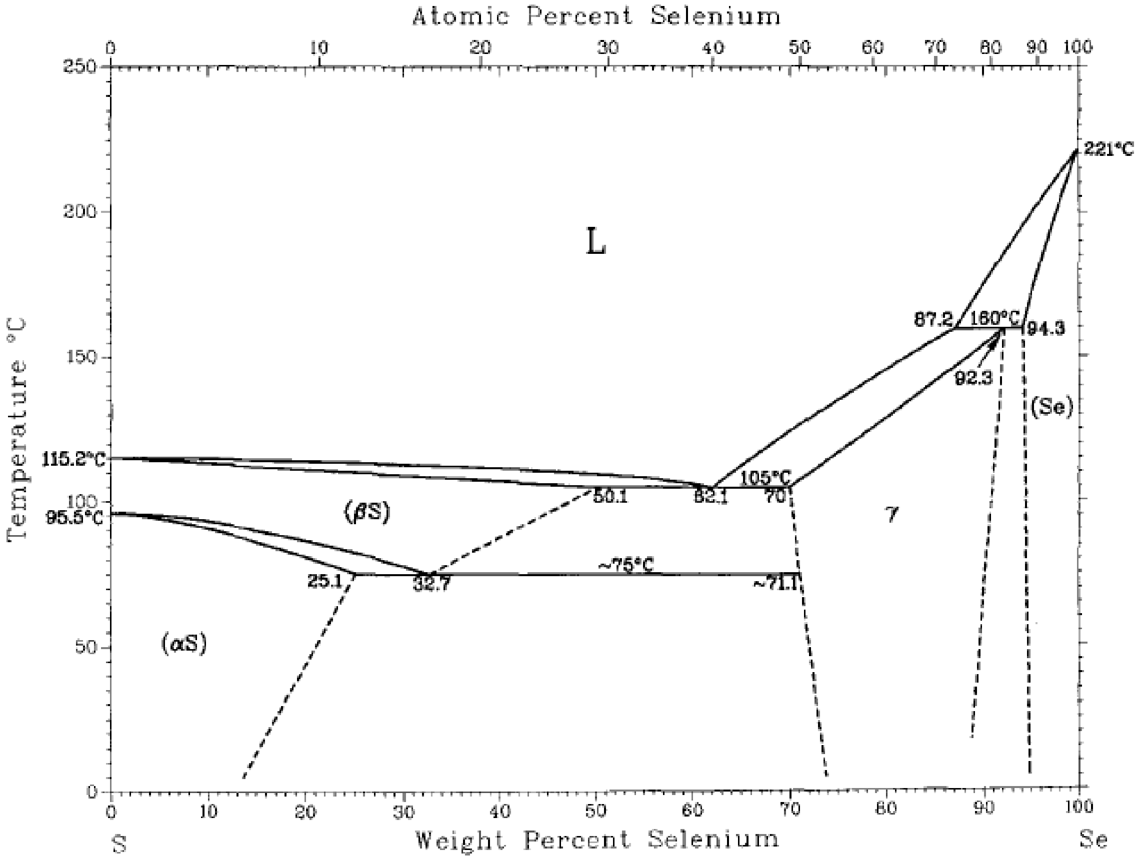

Figure 3 - Sulfur - selenium phase diagram [52]

2.2.1.3 Stannous

Stannous ions (generally available as stannous chloride) have been used for long time as reducing agent because of their favorable reduction potential, low toxicity and high efficiency. However, almost no information is available on the reaction between stannous and selenite ions other than the fact that selenium reduction proceeds to completion in acidic solutions. Furthermore, thermodynamics suggest that stannous ions can reduce selenium to elemental state as shown below [53]:

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \ (E^o = 0.74 \text{ V}) \tag{14}$$

$$SnO_2 + 4H^+ + 2e^- \rightarrow Sn^{2+} + 2H_2O\ (E^o = -0.094\ V) \tag{15}$$

$$SeO_3^{2-} + H_2O + 2Sn^{2+} \rightarrow Se + 2H^+ + 2SnO_2\ (E^o = 0.834\ V) \tag{16}$$

It is also known that weakly acidic stannous chloride solutions have a tendency to hydrolyze and form an insoluble stannous oxychloride (known as abhurite). The exact formula of this compound has been the topic of much work and speculation since its discovery on the surface of tin ingots found in a shipwreck [54]. The original suggested formula was $Sn_3O(OH)_2Cl_2$ but more recent work suggested a larger molecule with similar stoichiometry: $Sn_{21}Cl_{16}(OH)_{14}O_6$. The precipitation of abhurite by the hydrolysis of stannous ions in aqueous solution can be represented by the following reaction [55, 56]:

$$21Sn^{2+} + 16Cl^- + 20H_2O \rightarrow Sn_{21}Cl_{16}(OH)_{14}O_6 + 26H^+ \tag{17}$$

However, it is worth noting that, as abhurite is still partially composed of stannous ions, the stability region of this compound is fairly narrow as shown in Figure 4.

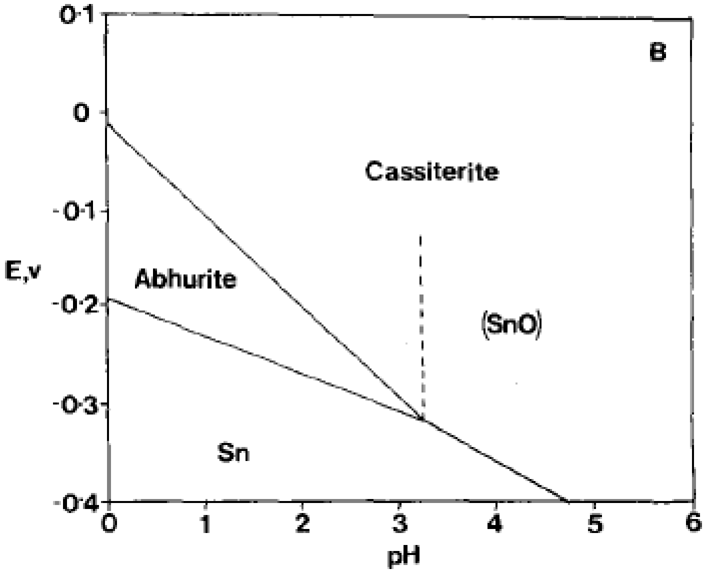

Figure 4 - Pourbaix diagram of abhurite stability [55]

Aqueous stannous solutions are unstable when left in contact with the atmosphere since dissolved oxygen can easily oxidize stannous ions to the stannic state and result in pale yellow gel-like precipitate [4]. As seen on Figure 5, pH is an important factor since highly acidic solutions slow down the oxidation process significantly [57]. Curiously, while the rate of the reaction in various aqueous solutions has been extensively studied, it does not appear that the nature of the stannic precipitate has been conclusively elucidated.

Tin and selenium can form two compounds,: stannous and stannic selenide (SnSe and $SnSe_2$ respectively), as seen on Figure 6 [58]. The existence of another tin selenide (tin sesquiselenide, Sn_2Se_3) has been dismissed by recent work [4, 58]. Stannous selenide has been studied for its electronic properties (especially its potential use in memory switching devices) and has been synthesized using several techniques (including electro and electroless plating, vapor deposition, and solvent-assisted processes) [59-66]. In addition, the vapor pressure and crystallographic structure of SnSe have been studied [67, 60, 68].

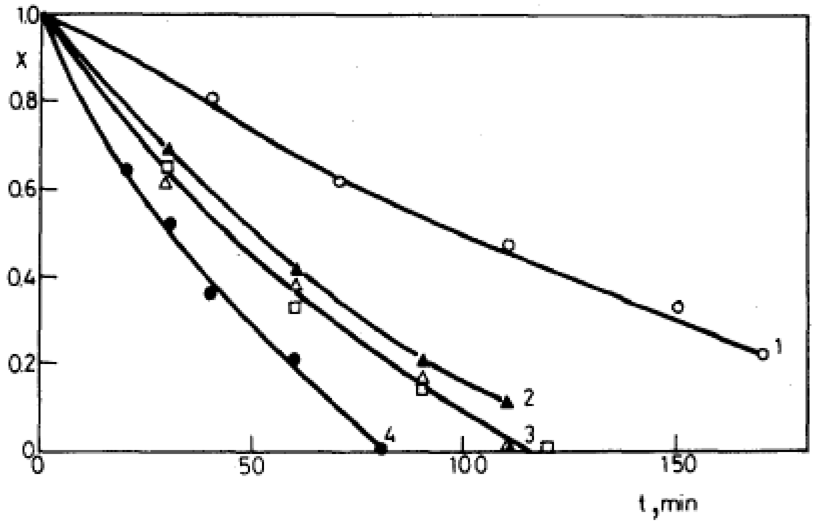

Figure 5 – Stannous concentration as a function of time for different hydrochloric acid concentrations (Conditions: Original [Sn] = 0.06 g/L, [HCl]: (1) 10M, (2) 6M, (3) 1M and 0.1M, (4) 0.01M, stored in open air at room temperature) [57]

While several studies report the formation of tin selenide in aqueous solution, most allegedly achieve this via direct reaction of selenide and stannous ions, i.e. without reduction. In some of these studies, so-called sodium selenosulfate (Na_2SeSO_3) was used as the source of selenide [69, 70],while in other studies selenide ions were claimed to have been obtained by dissolving elemental selenium in hot concentrated sodium hydroxide solution [71, 64, 72]. This is rather surprising as other researchers have demonstrated that elemental selenium boiled in concentrated sodium hydroxide yields a colloidal selenium precipitate [73].

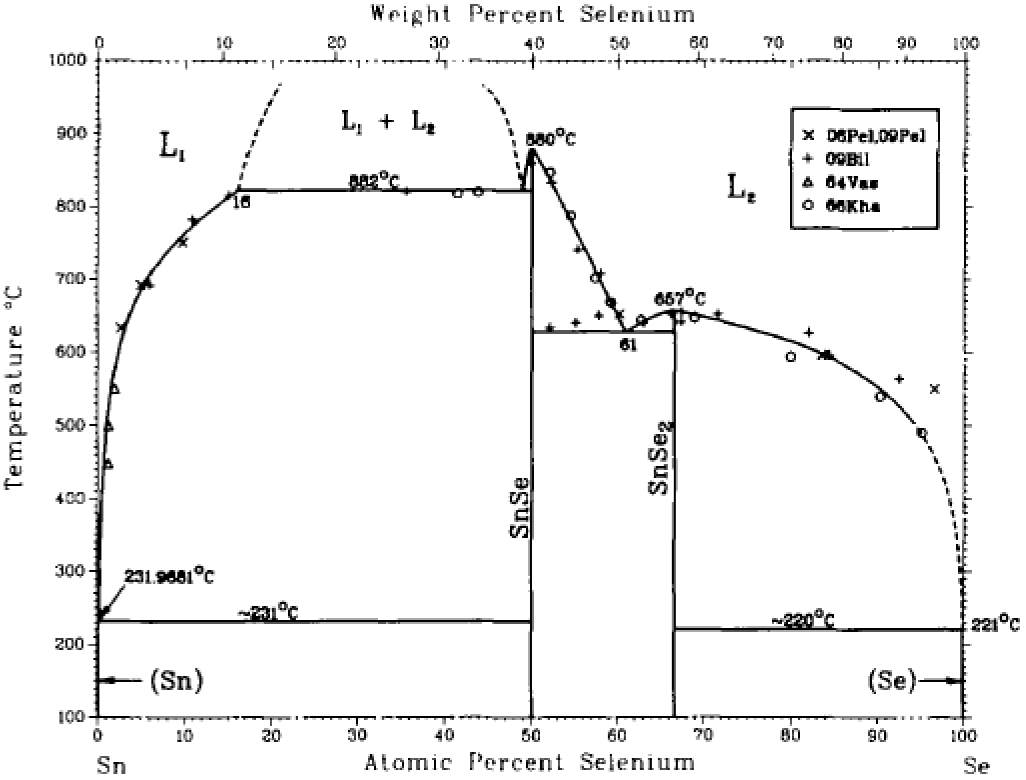

Figure 6 –The tin – selenium phase diagram [58]

With regards to the reaction between selenite and stannous ions, the subject of this work, Engelken reported that when small amounts of selenite ions are gradually added to a solution rich in stannous ions, red amorphous elemental selenium is formed first which gradually transforms to stannous selenide with increasing selenium concentration [74]. With reference to aqueous formation of stannic selenide several researchers have prepared this compound through by using hydrogen selenide as a selenium source [4]. However, these studies are in all cases extremely old and the reliability of the results (especially the identification of the products) can be questioned. On the other hand, the crystallography and crystal growth of this compound has been the topic of several recent studies [75-78].

Finally, while stannous ions have been suggested to measure the amount of soluble selenite ions (or vice versa) no work has been reported concerning the use of tin salts for selenium removal from complex industrial-type effluent solutions [25, 79].

2.3.2 Selenate

Selenate ions have a very high reduction potential but are kinetically inert. In other words, while the reduction of selenate ions to selenite is thermodynamically favorable, the kinetics are very slow. Thus, most if not all reagents found suitable to reduce selenite ions are theoretically effective on selenates but the reaction times are usually unacceptably long. For example, thiourea and sulfur dioxide can be used industrially on selenate solutions but high temperatures and very long reaction times are needed for full reduction (several hours around $100^{o}C$) [2]. The same can be said about sulfide ions but it appears that the reduction reaction is extremely complex and even slower [80, 4]. Because of this, these reagents are difficult to apply to large volumes of dilute solutions such as mine effluents or industrial solutions.

Because of these drawbacks, three approaches have been favored for the removal of selenates from solutions. The first one involves the use of physical removal techniques (i.e.: no redox reactions are involved). For example, reverse osmosis has been used successfully to treat mine effluent and bring the selenium concentration below 5 μg/L. In this method (shown in Figure 7), the water is forced, using high pressure, through an extremely fine filter (pore size < 1.5 nm) and most ions, organic molecules and other contaminants are left behind. However, the cost of this technique is generally very high, pretreatment often required to bring the selenium concentration below 0.1 mg/L, the pH and temperature of the water must often be adjusted to meet the operating requirements of the membrane and the brine solution (effluent) must be also treated using another method [81]. Nanofiltration, a method where filters with slightly larger pore sizes are used, has also achieved some success either alone or in combination with reverse osmosis. However, in both cases, implementation and maintenance costs are high.

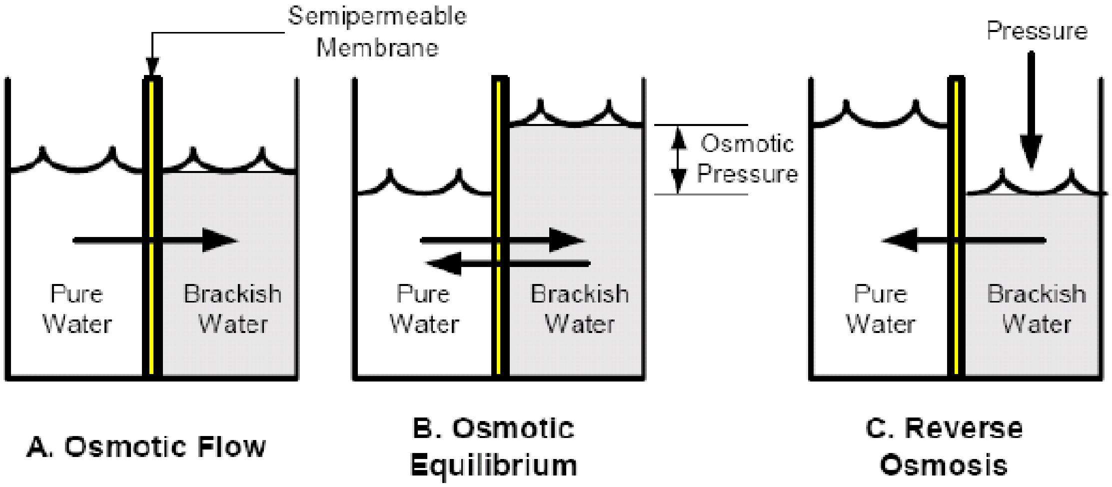

Figure 7 – Schematic principles of reverse osmosis technique [81]

Ion exchange, where a specific contaminant is reversibly exchanged for a similarly charged species attached to a solid surface, has also been successfully investigated on a lab-scale to treat selenate solutions. However, since sulfate and selenate ions have similar structures and charges, competition is often a problem. Furthermore, once spent, the resin must be regenerated and the eluent subsequently treated to remove the selenate. Similar to ion exchange, adsorption on organic substrates (rice hulls, straw etc...) has also been proposed. For example, peanut shells treated with sulfuric acid (to produce a carbonaceous material) have been found to have some limited selenium removal capability [81]. Thus physical treatments are best seen as ways to concentrate the selenium in a solution that is easier to treat and are thus best suited to a final polishing step than to single industrial treatment dealing with concentrated solutions [81].

Another potentially promising way to treat selenate-bearing solutions is the search for catalysts that would speed up the reduction reaction using common reagents. For example, cupric ions have been reported as increasing the reduction rate of selenate ions by sulfur dioxide. However, while two patents have been filed on this application, it does not appear to be used industrially and the precise effect of this catalyst does not appear to have been studied [82, 83]. Alternative removal processes such as bacterial reduction, or a mixture of adsorption and reduction have been studied. In the first case, a lot of work has been devoted on the study of biological systems able to reduce selenite and selenate ions to elemental state in a wide range of aqueous solutions [84-87]. In practice, organic material (molasses, grain, wood chips) is oxidized by the microorganisms and the electrons are transferred to the selenate reducing it to elemental state [81].

The process can be carried out in an active way (using pumps, water heater and several reactors) or in a passive way (in a single reactor and without the need for electricity and constant nutrient inputs). The former technique is more efficient but also more costly. In general however, while competitive treatment costs and good efficiency can be achieved, precise control of the solution being treated is vital to ensure to formation of thriving bacterial colonies. Furthermore, the bacterial reduction rates are often dissimilar for selenate and selenite ions, resulting in accumulation problems when both species are present in the solution being treated [88].

Metallic iron (often referred as zero-valent iron, ZVI) and ferrous salts have also been studied for the removal of selenate ions [89-91]. While the exact removal mechanism is complex and not fully understood, it involves both adsorption on hematite (α-Fe_2O_3), goethite (α-FeOOH), and amorphous iron hydroxide ($Fe(OH)_3$) (all produced in situ by the oxidation of iron) as well as reduction of Se(IV,VI) to elemental state [92, 93]. In other words, elemental iron or ferrous ions can reduce a fraction of the selenate ions to the selenite and elemental forms and the resultant iron oxide/hydroxides can remove the rest (selenate and selenite) by adsorption [91]. Some research projects focused their attention on the reduction of the selenate on the iron surface (and thus tried to limit iron corrosion and passivation) while others went the opposite way and tested the selenate removal capabilities of different iron corrosion products. In all cases however, industrial results have been rather poor and in most cases zero-valent iron alone was unable to meet the 5 μg/L target even when starting with very dilute solutions (< 20 μg/L) [94]. On a laboratory scale however, encouraging results have been obtained by using iron nanoparticles (significantly increasing the surface area and reaction rate) and by employing so-called green rust, a corrosion product composed of mixed ferrous and ferric oxidation states. In the first case, it has been reported that selenate ions are reduced all the way to the selenide state relatively rapidly (> 85% removal in two hours), forming iron selenide in a pH 7 solution [95]. In the case of green rust, the exact removal mechanism is unclear but adsorption seems to dominate with selenate ions becoming part of the rust's complex crystallographic structure [96].

In a similar vein, co-precipitation of selenate with ferrihydrite has also been evaluated and is presently listed as the Best Demonstrated Available Technology (BDAT) for selenium (and not specifically selenate) by the EPA [94]. In this case, ferric chloride is added to the solution which upon in situ hydrolysis removes selenium species by adsorption on the formed ferrihydrite. Industrial tests have shown that this technique is significantly more efficient for selenite ions rather than for selenate ones. Furthermore, the adsorption process is strongly dependant on the pH (ideally between 4 and 6) and composition of the aqueous solutions (competition from sulfate and bicarbonate).

2.4 Analysis techniques

Several techniques have been developed to measure the amount of soluble selenium present in solution. The most common method today for selenium determination in aqueous solution is atomic adsorption spectroscopy (AAS). Interestingly, the most up to date documentation provided by a major instrument manufacturer advises against the use of simple AA spectroscopy because of sensitivity problems and if absolutely needed, suggests the use of a nitrous oxide flame [97]. However, as per established practice in at least one industrial laboratory, by using an air-acetylene flame and a wavelength of 196 nm, the total selenium concentration can be reliably determined with a detection limit of approximately 0.5 mg/L [98]. If a lower concentration is needed to be determined, AAS can be coupled with a hydride generator provided that any selenate ions present have been previously reduced to selenite state by boiling the sample with concentrated hydrochloric acid. In this case, the detection limit can be as low as 0.5 µg/L.

In addition to AAS several other selenium aqueous measurement techniques have been developed over the years to fill niche applications. The earliest ones are gravimetric methods that rely on the precipitation of a compound that can be dried and weighted accurately. In the case of selenium, selenious ions are excellent candidate for this treatment because of their ease of reduction. Sulfur dioxide is commonly used as a reducing agent but hydroxylamine and hydrazine have also been found to be suitable [99]. However, high temperatures are generally needed to obtain fast reaction rates and aggregated precipitates. Also, when selenates are present, as mentioned previously, they have to be reduced previously to the selenite state by boiling the sample in concentrated hydrochloric acid. Nevertheless, because of the extreme care needed during the manipulations and the time required to perform the analysis, gravimetric methods do not appear to be used commonly for selenium analysis [2].

On the other hand, since AAS cannot be used on-line and can only measure the total selenium concentration, other analytical methods have been investigated. For example, ion selective electrodes are fast, inexpensive and target a single ion as opposed to measuring the total concentration of an element in solution. If glass electrodes, which are exclusively used to monitor pH, are exempted, two types of ion selective electrodes are commonly available. The first type, known as solid state electrodes, are commonly used to monitor the concentration of uncomplexed transition metal cations [100]. The second type, known as membrane electrodes are generally used to monitor common anions such as perchlorates, nitrates and carbonates [101]. While commercial selenite electrodes are not available, the literature provides description of several prototypes, of both the membrane and solid-state types [102-111]. The most interesting one involves the use of silver selenide and copper sulfide as the solid-state electrode. The authors report that the response of this electrode is linear in the 10^{-5}–10^{-2} M range and the slope of the linear portion is 28 mV per 10-fold change in selenite concentration. Interference effects are seen with sulfide, cupric and silver ions but not with sulfate, chloride, bromide and iodide ones [107]. However, it does not appear that any selenate ion selective electrode have been developed yet.

Several reagents have been found to form colored complexes with selenious ions, permitting the use of a visible spectrophotometer to directly measure the selenium concentration in solution. By far the most common reagent for this application is 3,3’-diamino-benzidine [112-115]. This chemical binds with selenious acid and forms a yellow colored complex. This complex can then be measured directly or extracted using toluene at a pH above 5. In the latter case, Beer's law is followed for a concentration of $5x10^{-4}$ to $2.5x10^{-3}$ mg/L at a wavelength of 340 to 420 μm. If transition metals are present, the use of ethylenediaminetetraacetic acid (EDTA) reduces the risk of interferences by forming stable complexes [116]. Other reagents such as 2,3-diaminophtalene, 4,5-diamino-6-thiopyrimidine, papaverine and thioglycolic acid also form colored complexes with selenious ions but do not appear to be as commonly used [117-119, 2, 99]. Finally, volumetric and polarographic methods have also been studied. However, it appears that all the above techniques are only used in special circumstances [2].

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Chapter 3 - Reductive Precipitation of Elemental Selenium from Selenious Acidic Solutions Using Sodium Dithionite

3.1 Foreword

Since sodium dithionite is the main reagent used in the CEZinc process to reduce and precipitate selenium(IV) the first part of this research project was dedicated to studying this reaction. Interestingly, while dithionite is a common reducing agent that has several important industrial applications, its reducing effect on selenious ions had never been studied in depth. While this chapter, which has previously been published[1], deals with synthetic selenium(IV) solutions, other results, presented in section 3 of the appendices and in conference papers[2,3], describe the reaction of dithionite with the actual CEZinc industrial solution.

3.1 Abstract

In this work, the batch-reactor reduction of selenious acid (H_2SeO_3) species with sodium dithionite ($Na_2S_2O_4$) from weakly acidic sulfate solutions containing 300 mg/L of selenium at 23^{o}C was studied. The results showed that, at an initial pH below 1.7 and

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dithionite stoichiometric excess above three, less than 0.5 μg/L of selenium(IV) remained in solution after reduction. The reductive precipitation reaction started as soon as dithionite was added in the selenium-bearing solution and was completed in less than a minute. However, it was found that the precipitate was not stable in the presence of the dithionite decomposition by-products and partially redissolved after several hours. The reaction product, characterized using x-ray diffraction, scanning electron microscopy and chemical analysis, was determined to be red amorphous selenium. The precipitate, in addition to elemental selenium was found to contain monoclinic sulfur that was apparently formed via a side reaction pathway involving the decomposition of dithionite.

3.2 Introduction

Zinc and copper concentrates processed in the metallurgical industry commonly contain various impurity elements. These impurities are separated during processing and properly controlled to protect the environment. Among those, selenium is of particular concern because of its high prevalence and toxicity. In zinc smelting operations, selenium is often concentrated in a weak sulfuric acid stream (typically of pH ~1.5) that must be treated and neutralized prior to being released to the environment [1].

However, given the unique chemical properties of selenium, this has proved rather challenging. For example, lime neutralisation, the most common industrial technique to precipitate metal ions as hydroxides, is ineffective for selenium since this element as metalloid does not form insoluble hydroxides. Separation techniques such as bacterial reduction, ion exchange membranes, electrocoagulation and adsorption have been investigated but proven either not very effective or only suitable for solutions containing low levels of dissolved selenium (< 5 mg/L) [2].

For industrial applications involving more concentrated solutions, techniques that involve the precipitation of selenium seem to achieve the best results [3]. Because of the high Se(IV)/Se reduction potential, various reagents have been evaluated and found to reduce selenium(IV) species in different types of aqueous solutions [4, 5].

In industrial applications, it appears that sulfur dioxide is by far the preferred reactant to reduce selenium (IV) to elemental state. The literature indicates that when dealing with hot and relatively concentrated sulfuric (> 1 g/L of soluble Se) or hydrochloric acid solutions (above 80^{o} C and pH < 1), full selenium reduction occurs very rapidly [6-8]. However, when working with lower concentration of Se(IV) solutions near room temperature, such as those encountered in the zinc industry [1], the reduction of Se(IV) with SO_2 becomes apparently ineffective.

Other reactants such as hydrazine [5], zinc powder [9], metallic copper [10], copper (I) chloride [11], thiourea [12], glucose [13], titanium (III) chloride [14] and stannous chloride [15] have been proposed as quantitative reducing agents for selenium (IV) in acidic solutions. However, issues such as high toxicity (hydrazine and thiourea), poor efficiency (zinc, glucose) and high costs (copper(I) chloride, titanium chloride and stannous chloride) seem to have limited the industrial applicability of these reagents.

Sodium dithionite ($Na_2S_2O_4$) is another strong reducing agent of interest because of its fast reaction rate, moderate cost and relatively low toxicity [16]. This chemical, also known as sodium hydrosulfite or, in some older texts as sodium hyposulfite, is a highly-soluble white powder that rapidly reacts with air but also decomposes in solution via disproportionation [17]. The decomposition of dithionite has been studied in the past and proposed to involve a slow induction step followed by faster autocatalytic reactions with its decomposition products [18]. This decomposition depends strongly on the pH and is rapid in the acidic region. The main decomposition reaction leads to production of thiosulfate ($S_2O_3^{2-}$) and sulfite (SO_3^{2-}) species as per Equation 1:

$$2S_2O_4^{2-} + H_2O \rightarrow S_2O_3^{2-} + 2HSO_3^{-} \tag{1}$$

Dithionite subsequently reacts with thiosulfate yielding hydrogen sulfide:

$$S_2O_4^{2-} + S_2O_3^{2-} + 2H_2O + H^{+} \rightarrow H_2S + 3HSO_3^{-} \tag{2}$$

However, the overall decomposition reaction is very complex since the reaction products can decompose and interact with each other at various rates, giving rise to a final solution rich in thiosulfates, polysulfides and polythionates. Furthermore, sulfur can be formed at different stages of the decomposition reaction and be present as a regular or colloidal precipitate [19].

The decomposition behavior of dithionite was studied by Wayman [20] in the pH range 2.5 to 4 as they found the decomposition rate to become too fast in more acidic solution. On the other hand, Cermak [19] reported that the reaction mechanism itself does not change at different pH values except in the case of extremely acidic solutions (boiling 5M HCl). Another complication arising from the decomposition of dithionite is that its standard reduction (dithionite/sulfite) potential has not been determined with certainty. The reported values are nevertheless near zero (0.0 to 0.08V) [21].

Sodium dithionite was tested, patented and applied industrially for the reduction of selenium from weak acidic solutions by the Canadian Electrolytic Zinc Company (CEZinc, Valleyfield, Canada) in order to meet environmental regulations [1, 22].The CEZinc process consists of two steps. In the first one, sodium sulfide is added to the weak acid solution in order to precipitate the soluble mercury as sulfide. The solution is then treated with sodium dithionite in order to reduce the selenium to elemental form. The precipitate following its isolation by filtration is disposed of while the weak acid solution is neutralized before being released in the environment. The reaction can be summarized by [1]:

$$H_2SeO_3 + 2H_2SO_4 + 2Na_2S_2O_4 \rightarrow Se(s) + 4SO_2 + 2Na_2SO_4 + 3H_2O \qquad (3)$$

Despite its industrial significance very little basic data about the reaction between Se(IV) and dithionite is known. This paper analyses the parameters that affect the reduction reaction, characterizes the products and describes the conditions under which the reaction is most efficient.

3.3 Experimental

Tests were performed with a synthetic weak sulfuric acid solution containing 300 (mg/L) of Se(IV). This concentration level was chosen as it represents the upper range of concentrations encountered currently in the CEZinc industrial operation [1]. The initial pH of the solution was fixed to 1.3, the average pH of the solution processed by CEZinc. Reagent grade selenium dioxide from Sigma-Aldrich (≥99.5% SeO_2) was used as the source of selenious species. Unless otherwise noted, all the experiments were performed at 23^{o} C.

Because of the unstable nature of dithionite solutions, the precipitations experiments were performed with freshly prepared dithionite solutions. Typically, different amounts of purified dithionite from Riedel-de Haehn (≥86% $Na_2S_2O_4$) were dissolved in a volume of deionised water representing a tenth of the weak acid volume. As soon as the reagent crystals were completely dissolved, the dithionite solution was added at once in the Se(IV) acidic (pH 1.3) solution and the mixture was agitated with the aid of a magnetic stirrer.

At the end of each precipitation test, the slurry was pressure filtered and the precipitate collected for analysis following washing and drying at 30^{o} C for approximately 24 hours until a constant weight was achieved. In order to facilitate characterization of the reaction product it was found necessary to subject it to a recrystallization-purification procedure. This was done by boiling (at 111 ^{o}C) 1.00 g of the precipitate in 100 mL of toluene. As a result of this treatment any elemental sulfur present dissolved in the toluene solvent while the amorphous red elemental selenium crystallized by the action of heat into the pure gray hexagonal allotrope.

The oxidation reduction potential (ORP) and pH of the solution were monitored using a gold double junction electrode (Cole-Parmer EW-27013-45) and a Corning high performance pH electrode (37-476146) respectively. The concentration of dissolved selenium in the samples was measured, above 1 mg/L, using regular atomic absorption spectrometry (AAS) with an air/acetylene flame and below 1 mg/L using hydride generation AAS. In some cases, the precipitates were characterized using X-ray diffraction spectroscopy (Philips PW 1710, Cu anode, K-Alpha 1.54060 Å, scan rate: 2 °2θ/min) and electron microscopy (Hitachi S-3000N FEG SEM).

3.4 Results and Discussion

3.4.1 The Se-H_2O System

The underlying chemistry of the process can be examined with the aid of an E_h-pH diagram constructed using the FactSage 5.5 thermodynamic software package [23]. The constructed diagram for the selenium-water system is shown in Figure 8. The diagram, prepared using a selenium concentration of 0.003m (corresponding to a concentration of approximately 230 mg/L Se), indicates that the predominant Se(IV) aqueous species corresponding to the weak acid solution composition (pH 1-1.6) is H_2SeO_3. According to the diagram the reduction of the latter is highly favorable with elemental selenium enjoying stability over a wide range of pH and E_h conditions.

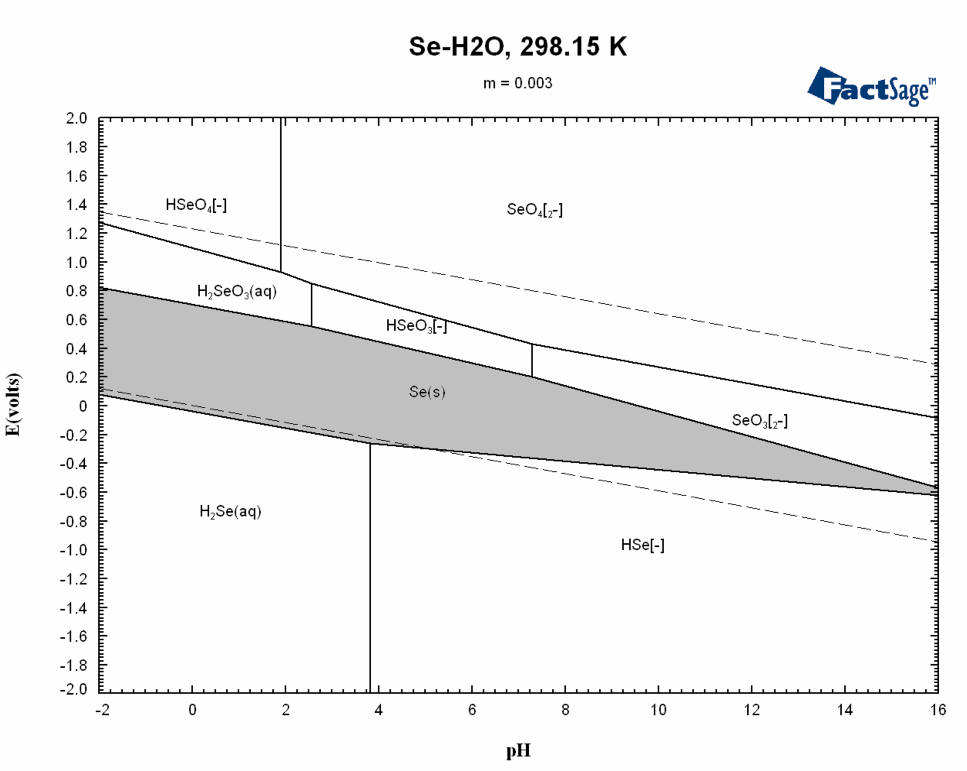


Figure 8 - E_h-pH diagram for the Selenium - Water system (active soluble species = 0.003m and T = 25° C)

3.4.2 Reaction Parameters Effects

3.4.2.1 Stoichiometric Ratio: The effect of the dithionite to selenium stoichiometric ratio on the effectiveness of the precipitation reaction (time = 1 min) at initial pH 1.3 is shown in Figure 9. Here the stoichiometric ratio is defined on the basis of reaction (3). So a stoichiometric ratio of one is equivalent to a molar ratio of $Na_2S_2O_4/H_2SeO_3$ equal to 2. The data indicate that the reaction proceeded very fast to completion (less than 0.5 μg/L of selenium remaining in solution) for ratios above two, i.e. for 100% dithionite excess.

Because of the inherent instability of dithionite that leads to its decomposition a dithionite stoichiometric ratio of ten (molar ratio of dithionite/selenium = 20) was adopted as safe margin. Tests performed at 11 and 42^{o} C (the minimum and maximum temperatures commonly encountered industrially) with initial pH= 1.3 and dithionite/Se stoichiometric ratio = 10 failed to detect any differences in the reaction rate or the precipitation efficiency (data not shown).

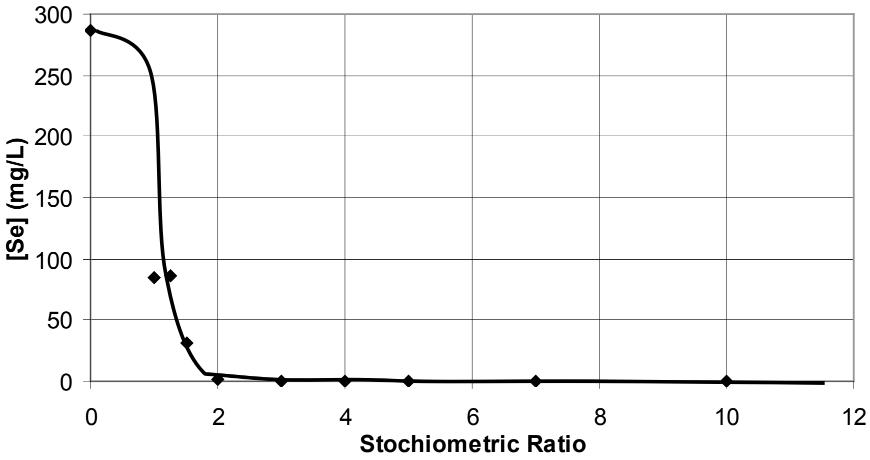
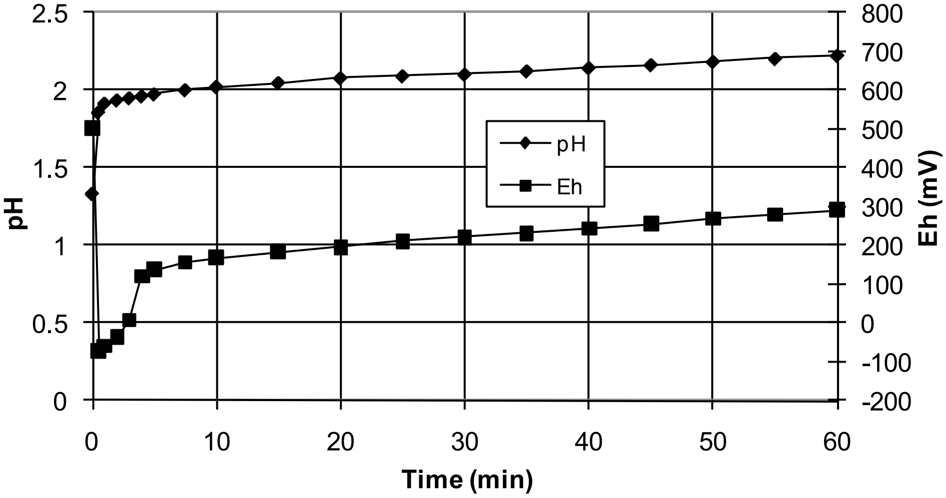


Figure 9 - Effect of the dithionite stoichiometric ratio on the effectiveness of the precipitation reaction at initial pH 1.3 after one minute (Conditions: stoichiometric ratio 10, initial [Se(IV)]= 300mg/L, initial pH=1.3. 23 C)

3.4.2.1 pH and Oxidation-reduction Potential (Eh): The reaction between Se(IV) and dithionite was associated with a pH increase and a complex change of E_h with time (Figure 10). Of interest here are the early stages of the reaction as depicted in the bottom part of the Figure 10. The results indicate that there were three distinct stages: the first one (first 30 s) was characterized by a steep decrease in the potential from ~500 mV down to ~ -80mV and a simultaneous increase in pH from 1.3 to 1.8.



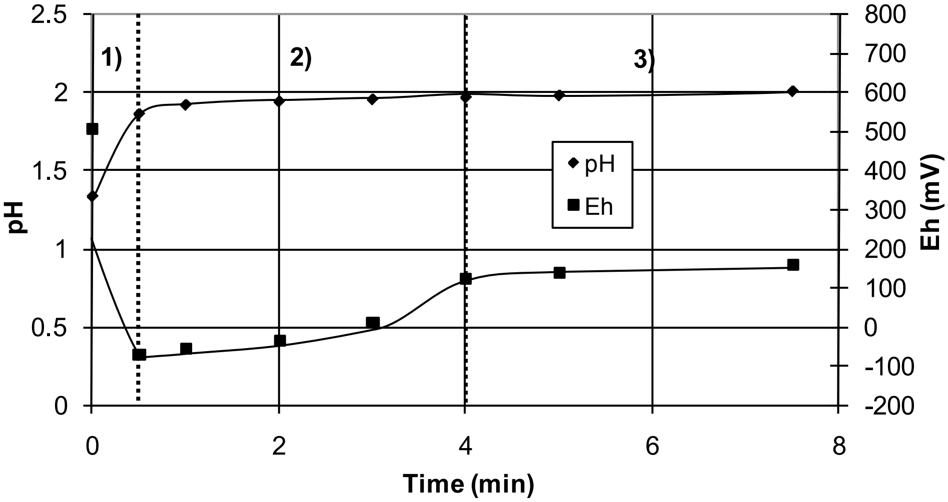


Figure 10 – Oxidation-reduction potential (Eh) and pH as a function of time during reaction of selenium (IV) with dithionite (Conditions: stoichiometric ratio 10, initial [Se(IV)]= 300mg/L, initial pH=1.3. 23 C)

Thereafter (stage 2 between 30 s and 4 min) the pH and potential increased with the latter's increase going through slow/fast/slow pattern. After that (stage 3) both parameters kept increasing at a slow linear rate (0.3 pH units (pH 2—>pH 2.3) and 60 mV (180—>240 mV) over the 50 minutes span).

The initial (stage 1) potential drop from 500 mV down to -80 mV may be understood by referring to the two half reactions of the Se(IV)/Se and S(IV)/S(III) couples. Thus by applying the Nernst equation to the Se(IV)/Se equilibrium (Equation 4) in the initial solution ([Se(IV)]=0.003M and pH=1.5) before the addition of dithionite (taking the standard potential equal to 0.74 V [24] a potential of 500 mV is obtained, which is exactly the value measured. Upon addition of excess dithionite (stoichiometric ratio=10) the potential dropped to -80mV. This potential was compared to the theoretical one for the dithionite/sulfite couple (S_2O_4/SO_3) (Equation 5):

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \tag{4}$$

$$2HSO_3^- + 2H^+ + 2e^- \rightarrow S_2O_4^{2-} + 2H_2O \tag{5}$$

Using the redox potential parameters for equation 5 reported by Mayhew [25] a potential of -95 mV was calculated for pH 1.5 and dithionite concentration 0.070M (corresponding to stoichiometric ratio 10), which is close to the measured one of -80mV (refer to the bottom of Figure 10). In other words the measured potential upon addition of dithionite in the solution is near that of dithionite/sulfite couple because of the large excess used.

By combining equations (4) and (5) the overall reaction becomes:

$$H_2SeO_3 + 2S_2O_4^{2-} + H_2O \rightarrow Se + 4HSO_3^{-} \qquad (6)$$

Since selenium reduction was complete in less than 1 min the subsequent rise in redox potential (and pH) in stages 2 and 3 is considered to reflect the complex decomposition of dithionite via disproportionation (Equations 1 and 2) [18] and the reaction of its decomposition products and dithionite itself with atmospheric oxygen. As described later in the Characterization section elemental sulfur was identified as major dithionite decomposition product.

The effect of initial pH on selenium precipitation was evaluated and the relevant precipitation data are shown in Figure 11. This selenium removal data correspond to 5 min reaction time. As it can be seen the selenium reduction reaction went to completion at initial pH values below approximately 1.7 while being partially effective up to pH 2.5 and stopping completely above pH 3.5 Additional experiments (data not shown) done in basic solutions (pH 5.5, 9 and 12) involving longer reaction times (more than one hour) resulted in no selenium precipitation. This confirms that the reduction reaction occurs only in acidic solutions. Experiments performed at the same conditions (initial pH= 1.3, 23 C and stoichiometric ratio = 10) but this time using hydrochloric or nitric acid showed that the nature of the acid (or anions) do not to have any influence on the efficiency of the reduction reaction. It was thought that the observed pH effect may reflect the involvement of protons in the reaction as shown in equation 4 or alternatively that the selenious acid anion, $HSeO_3$-, which dominates above pH 2.5 (refer to Figure 8), may be non reactive towards dithionite.

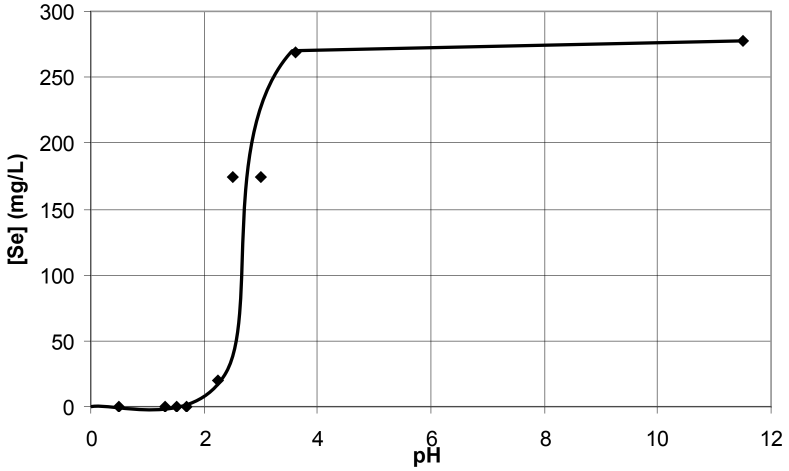


Figure 11 - Effect of initial pH on the effectiveness of selenium precipitation after five minutes reaction with dithionite (conditions: stoichiometric ratio 10, initial [Se(IV)]= 300mg/L, initial pH=1.3. 23 C)

3.4.2.3 Selenium product redissolution: During the pH effect investigation it was observed that in the pH range 2.5-4 there was some precipitation after 1 min reaction but the Se product redissolved quickly. For example at initial pH 3.5 the Se(IV) concentration dropped from 275 mg/L down to 225 mg/L after 1 min reaction but all Se precipitate redissolved thereafter reaching 270 mg/L Se after 5 min and the initial level of 275 mg/L Se after 30 min. This observation prompted further investigation of the stability of elemental selenium product.

It was found that the selenium product is not stable even at the optimum pH (refer to Figure 11) of precipitation if allowed to remain in contact with the mother weak acid solution. This is shown with the data presented in Figure 12. It can be seen that the fresh precipitate produced at an initial pH of 1.3 and a stoichiometric ratio of 10 redissolves partially within a matter of hours. Its redissolution rate slowed down after approximately twenty-four hours. Of interest is the finding that the presence of zinc sulfate slowed down redissolution while not stopping it entirely.

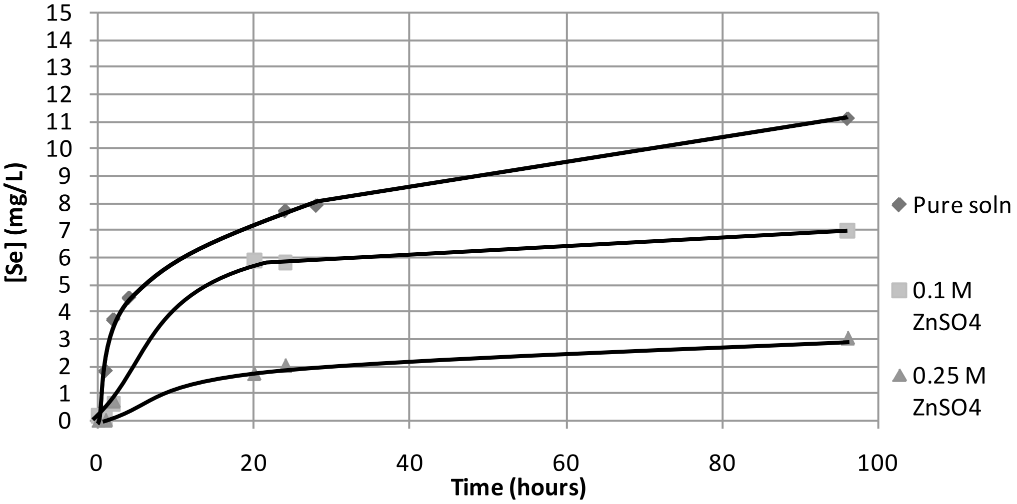


Figure 12 – Redissolution of fresh selenium precipitate as a function of time after reduction with dithionite: the effect of zinc sulfate background concentration (Conditions: selenium stoichiometric ratio 10, initial [Se(IV)] = 300mg/L, initial pH =1.3. 23 C)

The selenium redissolution may be thought to be due to re-oxidation by air as predicted from a thermodynamic point of view (refer to Figure 8). To evaluate the practical feasibility of this reaction a test was carried involving exposure of commercially obtained 99% pure Se powder with an acidic aqueous solution (0.5 g in 0.5 L weak acid-pH 1.3) to air over several hours (without agitation). This test yielded less than 0.02 mg/L of Se(IV) in solution. However, when the test was repeated in the presence added dithionite (0.076 mol/L) significant redissolution took place. The obtained data is shown in Figure 13. It appears, in other words that this phenomenon is caused by one (or a combination) of sulfur species resulting from the dithionite decomposition reaction. While the exact mechanism behind the reaction between selenium and dithionite degradation products is not fully understood, it is postulated that the SO_2^* and $S_2O_4^*$ radicals, generated during dithionite decomposition [26], play a role, by acting as powerful oxidizing agents in combination with oxygen (air). Powerful oxidants are known to bring selenium back into solution [26-30]. Furthermore, it has been known that sulfur dioxide or equivalently sulfites (produced during the dithionite decomposition reaction), while generally used industrially for their reducing properties, can act as very powerful oxidizing agents when mixed with an excess of oxygen because of the formation of sulfite radicals (SO_3^*) [31]. The lowering effect of excess sulfate (added as $ZnSO_4$ - refer to Figure 12) on selenium redissolution may be linked to the reduction in formation of these oxidizing radicals via the minimization of some dithionite reaction pathways (refer to Equations 1, 2 and 6).

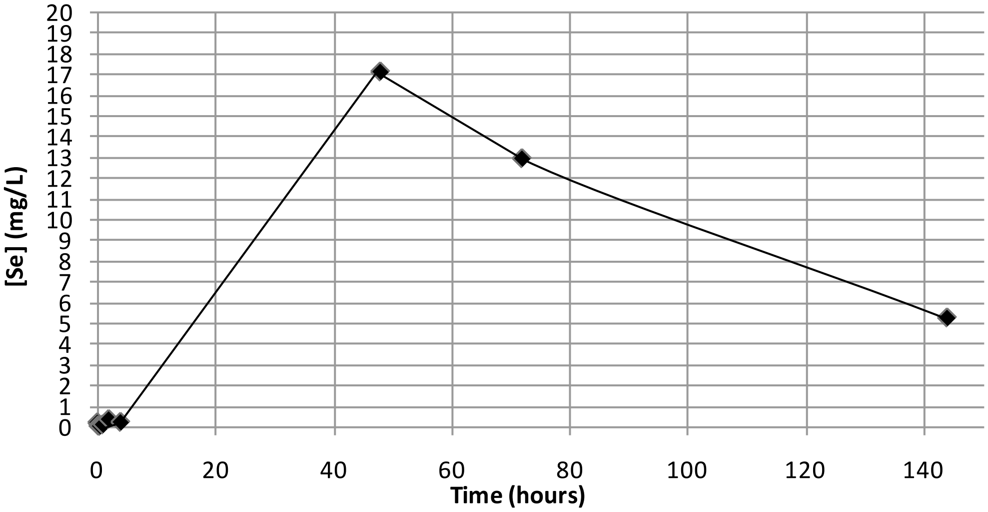


Figure 13 – Dissolution of particulate selenium as a function of time by reaction between elemental selenium and dithionite and air (give all conditions).

3.4.3 Characterization

3.4.3.1 XRD and SEM: Selenium has, like sulfur and tellurium, several allotropes (up to eight), some of which have not been fully investigated [6, 32] Furthermore, even if at room temperature the gray hexagonal phase is the most common and stable, other metastable allotropes can be formed. For example, as described in the literature, the precipitate formed by aqueous reduction near room temperature is composed of red amorphous selenium, as confirmed by the X-ray diffraction (XRD) spectrum shown on Figure 14. One must note that the two broad peaks in the diffraction spectrum are indicative of some degree of crystallinity and that the precipitate could be best described as poorly crystalline.

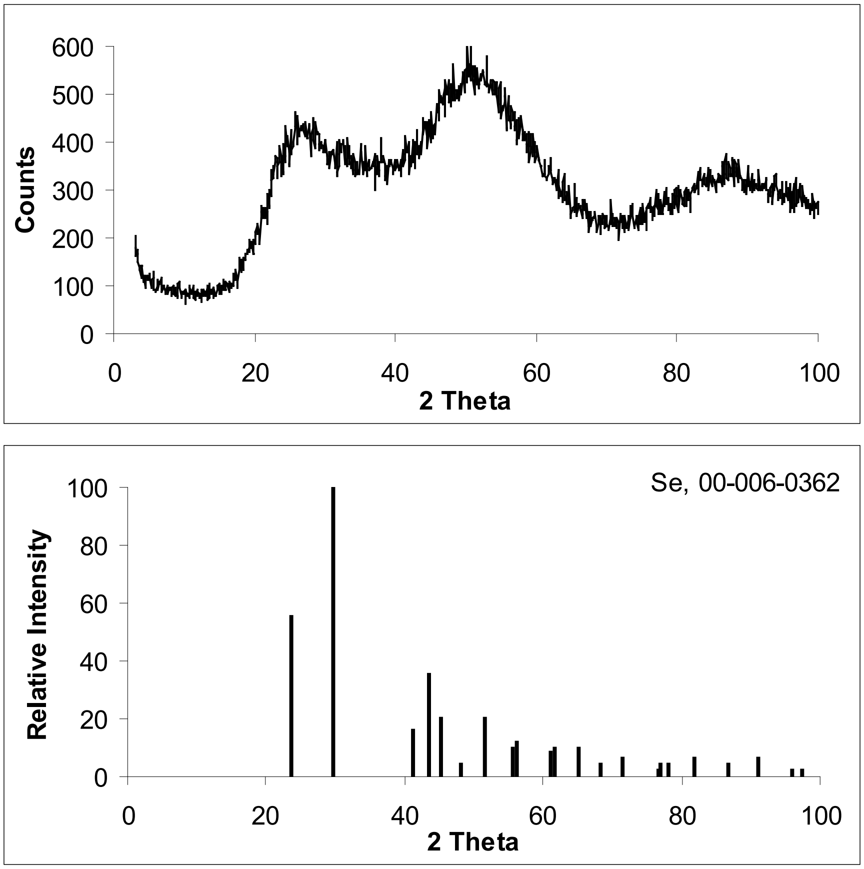


Figure 14 - XRD pattern of the poorly crystalline red selenium precipitate (produced at pH 1.3 and 23 C with dithionite/Se(IV) stoichiometric ratio=10) compared to that of hexagonal synthetic selenium (00-006-0362)

For dithionite stoichiometric ratios above three, the selenium precipitation reaction started essentially instantly after the addition of the reduction agent and analytical data confirmed that the reaction was complete after one minute. At this step, the precipitate was extremely fine and difficult to filter, but as opposed to what is suggested in the literature, aggregated rapidly upon intense agitation [6]. Scanning electron microscope (SEM) images of selenium particles taken after approximately two minutes of reaction time (Figure 15) show that the precipitate is indeed composed of fine primary particles agglomerated into larger ones. Also, it was shown that agitation time has no effect on the size of the primary particles (as opposed to the size of the agglomerates). On average, the aggregated particles had mean size of 15 microns and no significant difference was found between magnetic and mechanical agitation. However, type of agitation and time had a slight effect on the specific surface area (BET) of the precipitate as seen in Table 3.

Table 3 - Specific surface area of the selenium precipitate according to agitation time and type

Type of Agitation	**Time**	**BET (m^2/g)**
Magnetic	20 Minutes	0.3757
	30 Minutes	0.4299
	60 Minutes	0.4842
Mechanical (Impeller)	20 Minutes	0.4008
	30 Minutes	0.5060
	60 Minutes	0.5134

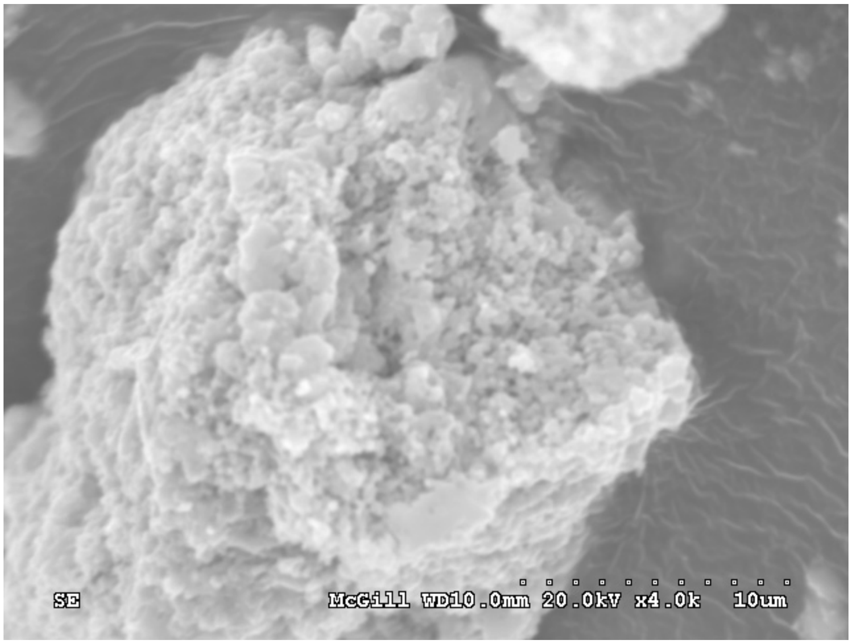


Figure 15 - Scanning electron microscope image of the selenium precipitate (Conditions: stoichiometric ratio 10, initial [Se(IV)]= 300mg/L, initial pH=1.3. 23 C)

3.4.3.2 Sulfur and Selenium: By employing chemical digestion with *aqua regia*, the precipitate was analysed and determined to contain approximately 85% (w/w) of selenium. The main impurity was found to be elemental sulfur and this was confirmed by boiling the precipitate in toluene. As a result of this procedure, the sulfur was dissolved into the toluene. Simultaneously as a result of this procedure the selenium underwent recrystalization turning into gray hexagonal selenium as verified by X-ray diffraction analysis (Figure 16).

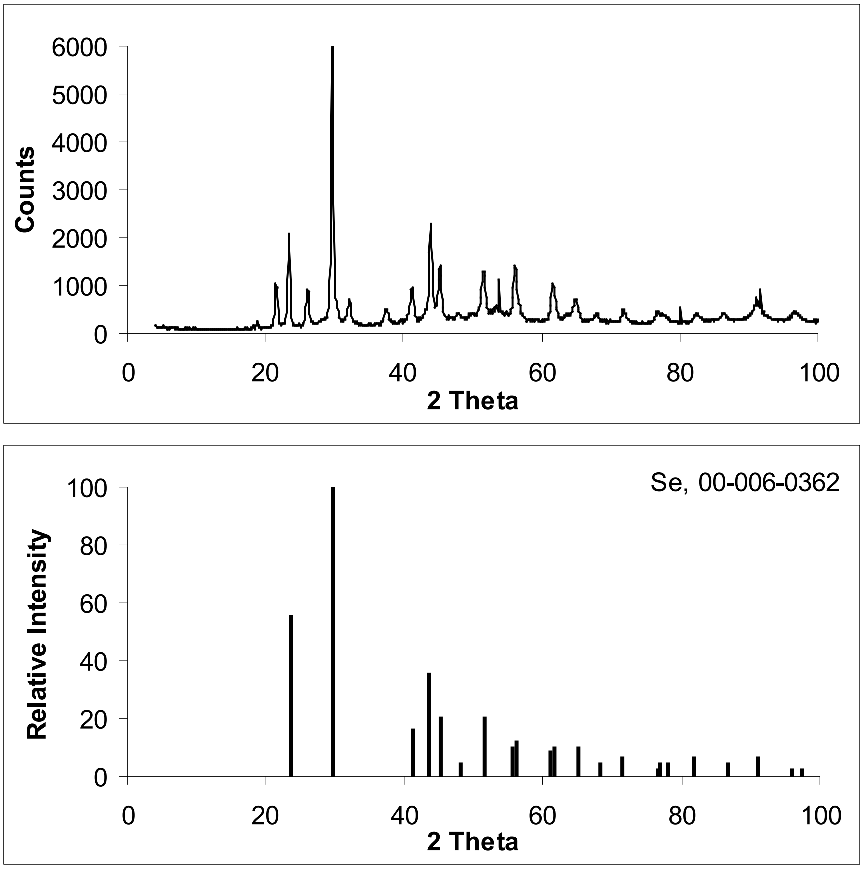


Figure 16 - XRD pattern of the selenium precipitate following separation of elemental sulfur in boiling toluene compared to that of hexagonal synthetic selenium (00-006-0362)

As mentioned earlier, elemental sulfur can be formed at different steps during dithionite decomposition. For example De Carvalho mentioned the following reaction as a possible elemental sulfur formation path [18]:

$$16H_2S + 8HSO_3^- + 8H^+ \rightarrow 3S_8 + 24H_2O \qquad (7)$$

In this work a light yellow precipitate was observed to form indeed several minutes after the start of the reaction. At first, the solution became slightly cloudy and after several minutes turned into a light yellow milky liquid. The sulfur precipitate was extremely fine and difficult to filter at the beginning but, as in the case of elemental selenium, it aggregated into large clusters within about five minutes. The sulfur precipitate, in contrast to what is suggested in the literature, was found to be stable in the final solution for at least several months [33].

The sulfur formed at the end of the selenium-dithionite reaction was amorphous, i.e. not detectable by XRD (refer to Figure 14). However the sulfur collected following its dissolution in toluene and the evaporation of the solvent was composed of pure orthorhombic crystalline sulfur, as shown in Figure 17. Tests performed using hydride generation AAS confirmed that the formation of the sulfur precipitate had no effect on the concentration of soluble selenium remaining in solution following reaction with dithionite. This implies that selenious species do not combine with or adsorb on the amorphous sulfur precipitate.

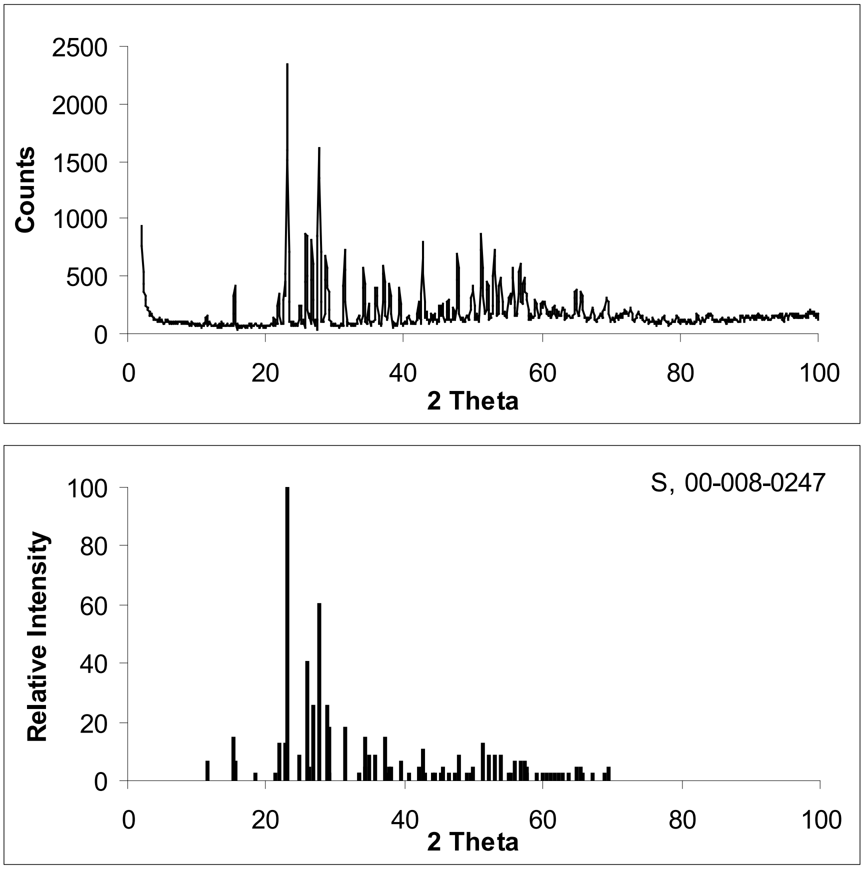


Figure 17 - XRD pattern of the sulfur separated from the selenium precipitate by toluene dissolution and evaporation compared to that of orthorhombic synthetic sulfur (00-008-0247)

3.5 Conclusion

Selenious acid species can be effectively reduced from weak acidic solutions using sodium dithionite. At pH values below 1.7 and dithionite stoichiometric excess above three, the reaction was found to go to completion leaving less than 0.5 µg/L of selenium in solution. The precipitation reaction started right after the dithionite addition and was completed in less than a minute. The precipitate, composed of red amorphous selenium was originally very fine and difficult to filter but agglomerated rapidly upon continuing agitation. However, due to its inherent instability dithionite decomposes producing various intermediate oxidation state sulfur species. Some of these species (radicals like SO_2* and S_2O_4*) are postulated to act as powerful oxidizing agents causing partial redissolution after several hours of the selenium product. Another complication of the decomposition of dithionite is the co-precipitation of amorphous elemental sulfur. Treatment of the precipitate with hot toluene led to separation of the two elements and their recrystallization.

3.6 Acknowledgments

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Chapter 4 - The elimination of selenium (IV) from aqueous solution by precipitation with sodium sulfide

4.1 Foreword

As previously described, sodium dithionite is the reagent used in the CEZinc process to reduced and precipitate selenium. However, in the same process (first step) sodium sulfide is used to precipitate mercury. Since during this step it was observed that some selenium is also removed by sodium sulfide it was decided to study in detail the reaction of sodium sulfide with selenium(IV) in order to elucidate the relevant chemistry and determine if the process can be optimized to allow for a single reagent being used for the removal of both Se and Hg. This chapter, which has already been published[4], focuses on the parameters affecting the reaction between selenious and sulfide ions in simple synthetic solutions. Furthermore, results based on more complex industrial solutions are reported in section 3 of the appendices

4.2 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

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[4] Geoffroy, N. and Demopoulos, G.P., 2010 The elimination of selenium (IV) from aqueous solution by precipitation with sodium sulfide., Journal of Hazardous Materials, 185(1): 148-154.

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 (<0.005mg/L).

4.3 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) [7, 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^{o}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 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]:

$$2H_2S + SeO_2 \rightarrow SeS_2 + 2H_2O \qquad (1)$$

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 Se_nS_{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 to 7) have been identified in some quartz ores [33, 32].

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.

4.4 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 (≥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 of reagent grade sodium sulfide from Sigma Aldrich (≥98% $Na_2S.9H_2O$) 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 hours 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 °2θ/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.

4.5 Results and Discussion

4.5.1 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 (Figure 18) [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) 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 Figure 19. 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 μg/L of selenium remaining in solution) for sulfide/selenium molar ratio between 1.8 and 11.3 and reaction time of ten minutes. 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 minutes reaction. Using similar conditions but without selenious ions present in solution the ORP dropped from 727 mV to -76 mV after 10 minutes and thereafter remained stable. It is interesting to note that the final ORP value is within the stable region of elemental selenium (refer to Figure 18).

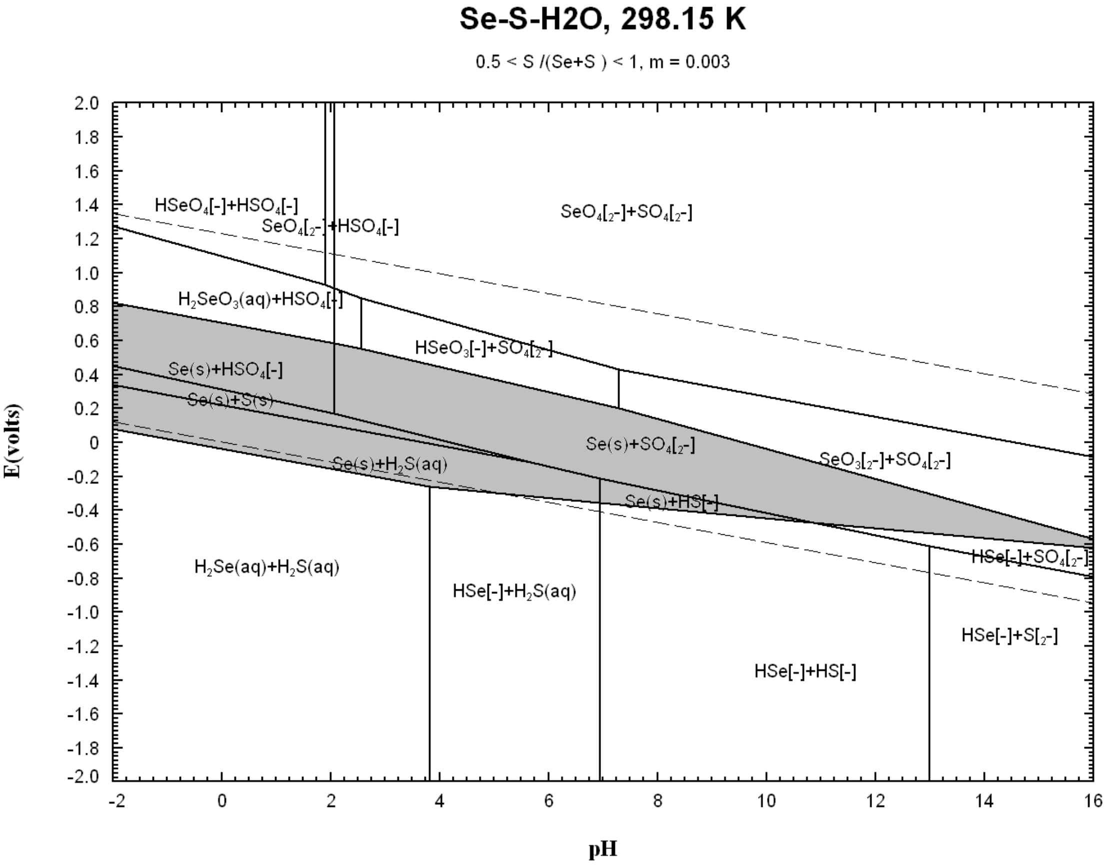

Figure 18 - E_h-pH diagram for the selenium - sulfur - water system (elemental selenium stability region shown in gray) (active soluble species = 0.00379 M, 0<S/(Se+S)<1 and T = 25°C)

Large excess of sodium sulfide proved counterproductive. Thus, at sulfide to selenium molar ratio from of 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 Figure 19, the two sets of data overlap quite well, indicating that near equilibrium levels have been attained.

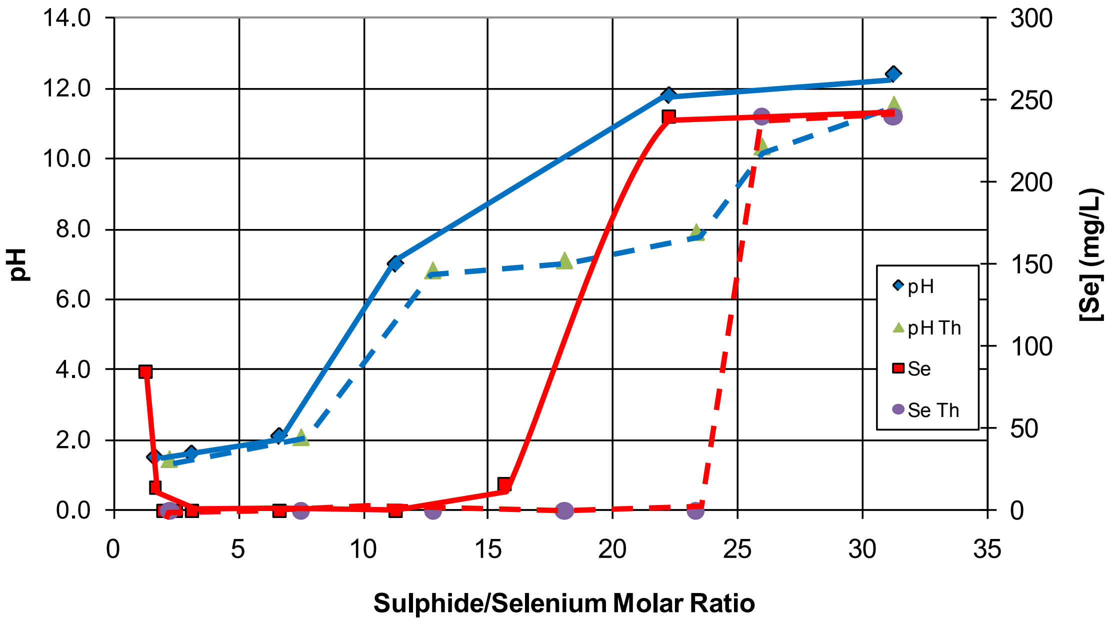

Figure 19 - Effect of the sulfide/selenium molar ratio on the effectiveness of the precipitation reaction and on final pH after ten minutes. Solid lines indicate experimental results while the thermodynamic simulation data is shown with dotted lines (Conditions: initial [Se(IV)]= 300mg/L, initial pH = 1.3, 23°C)

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 S^{2-}/Se^{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 Figure 19). After the addition of the sodium sulfide the weak acid solution turned clear dark red but no precipitation was witnessed. After ten minutes of reaction the pH and ORP were found to be stabilized at 11.8 and -633 mV (vs.SHE) respectively. The solution was subsequently slowly acidified with 1M hydrochloric acid. The effect of this acidification experiment on selenium precipitation is shown in Figure 20. At pH 9.5 a precipitate started forming and samples were then taken regularly afterwards.

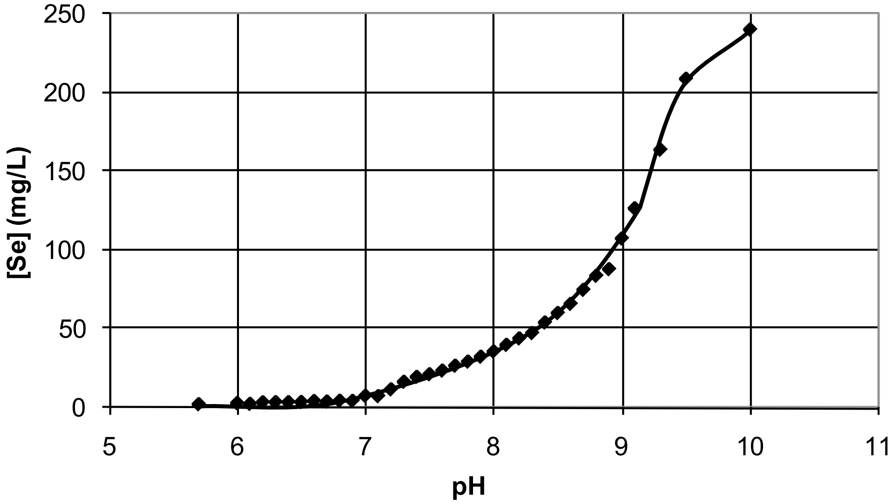

Figure 20 - Effect of pH adjustment (by HCl addition) on selenium precipitation following reaction of selenium (IV) solution with sodium sulfide at high sulfide/selenium molar ratio = 22.2 (Conditions: initial [Se(IV)]= 300mg/L, [Se(IV)] after addition of Na_2S solution = 240mg/L, 23°C)

As it can be seen above, 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 (Figure 20), 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.

4.5.2 Stability of 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 Figure 21. It was observed that the precipitate obtained within the optimum range of conditions (Figure 19) was very stable, releasing only small amounts of soluble selenium (<0.1 mg/L-refer to Figure 21) back into solution. Also, it was found that only trace amounts of the selenium sulfide precipitate was dissolved after one week equilibration in 1N hydrochloric acid (Table 4). 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.

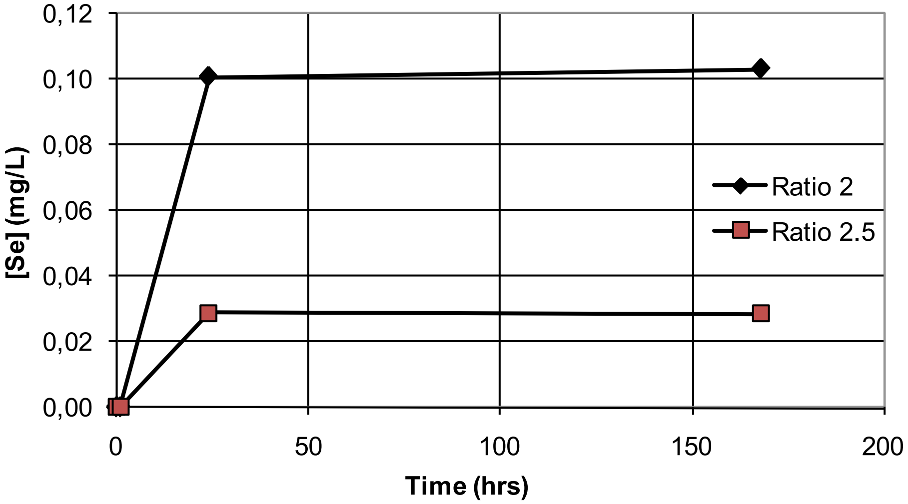

Figure 21 - Stability test for selenium sulfide precipitates in the mother solution (Precipitation conditions: initial [Se(IV)]= 300mg/L, [Se(IV)] after addition of Na_2S solution = 240mg/L, initial and final pH=1.3, sulfide/selenium molar ratio = 2 and 2.5 , 23^{o}C)

Finally, in order to evaluate the long-term stability of the precipitate, 0.5g 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 Figure 22, indicate that the precipitate slowly dissolved at pH 3 and 5, attacked more rapidly at pH 10 but remained perfectly stable (<0.005mg/L) at pH 7.

Table 4 – Stability test for selenium bearing solids in 1 N hydrochloric acid (Conditions: 100 ml of 1N HCl , 0.100 g of commercial selenium sulfide or elemental selenium, 0.050 g of experimental selenium sulfide precipitate (precipitation conditions: Same as Figure 21, sulfide/selenium molar ratio = 3.3), 23^{o}C)

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

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 it 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.

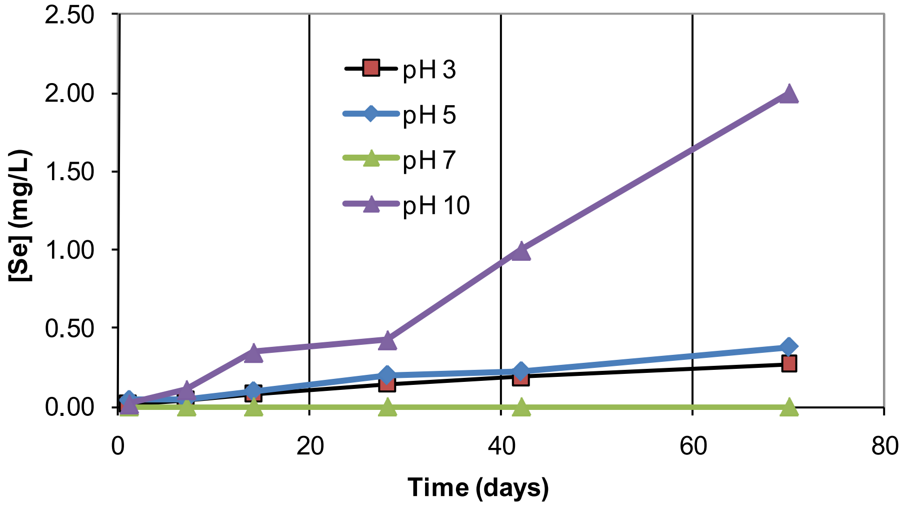

Figure 22 – Long term ageing test for selenium sulfide precipitate in different pH buffered solutions (Precipitation conditions: initial [Se(IV)]= 300mg/L, [Se(IV)] after addition of Na_2S solution = 240mg/L, initial pH=1.3, sulfide/selenium molar ratio = 2.5 , 23°C)

4.5.3 Characterization

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 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 (Figure 23). For comparison, commercially available selenium sulfide (Sigma-Aldrich, no listed purity - described as SeS_2) 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 [35]) to the one found in this work as it can be seen in Figure 24 (for clarity only the pattern of $Se_{1.09}S_{6.91}$ is used as a reference on Figure 24). From this analysis we may deduce that the selenium sulfide precipitate produced in this work is composed of a sulfur-selenium solid solution composed of heterocyclic molecules having the Se_nS_{8-n} structure [29]. 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 Figure 18) yielding atoms of elemental selenium and sulfur (produced by reduction and oxidation of the respective species) arranged in 8-member rings [33].

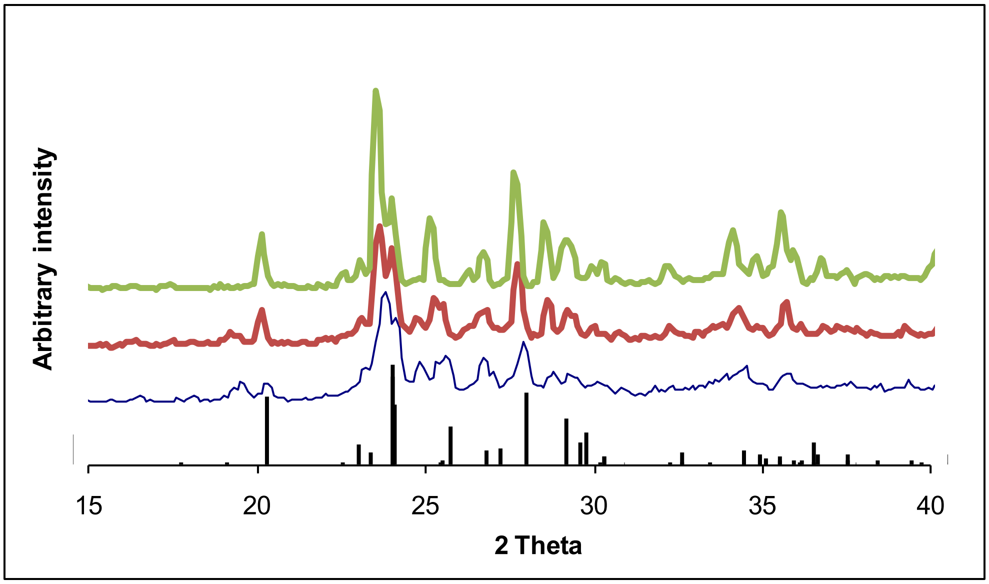

Figure 23 - XRD pattern of two sodium sulfide precipitates (bottom and middle patterns) and one of commercially available “selenium disulfide” (top pattern) compared to that of $Se_{1.09}S_{6.91}$(00-041-1317) (vertical lines) Conditions: initial [Se(IV)]= 300mg/L, [Se(IV)] sulfide/selenium molar ratio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

In contrast to the selenium sulfide (identified as solid solution) formed within the U-shaped precipitation region of Figure 19 ($2<S^{2-}/Se^{IV}<11$ or $1.7<pH<7$) the precipitate that formed during the acidification reaction described in Figure 20, was composed of both elemental gray hexagonal selenium and of elemental sulfur (Figure 25) and not of solid solution in the form of cyclic selenium sulfide (Se_nS_{8-n}) as shown on Figure 23. 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 whereas at higher pH, different nucleation rates apparently lead to the formation of distinct elemental particulates.

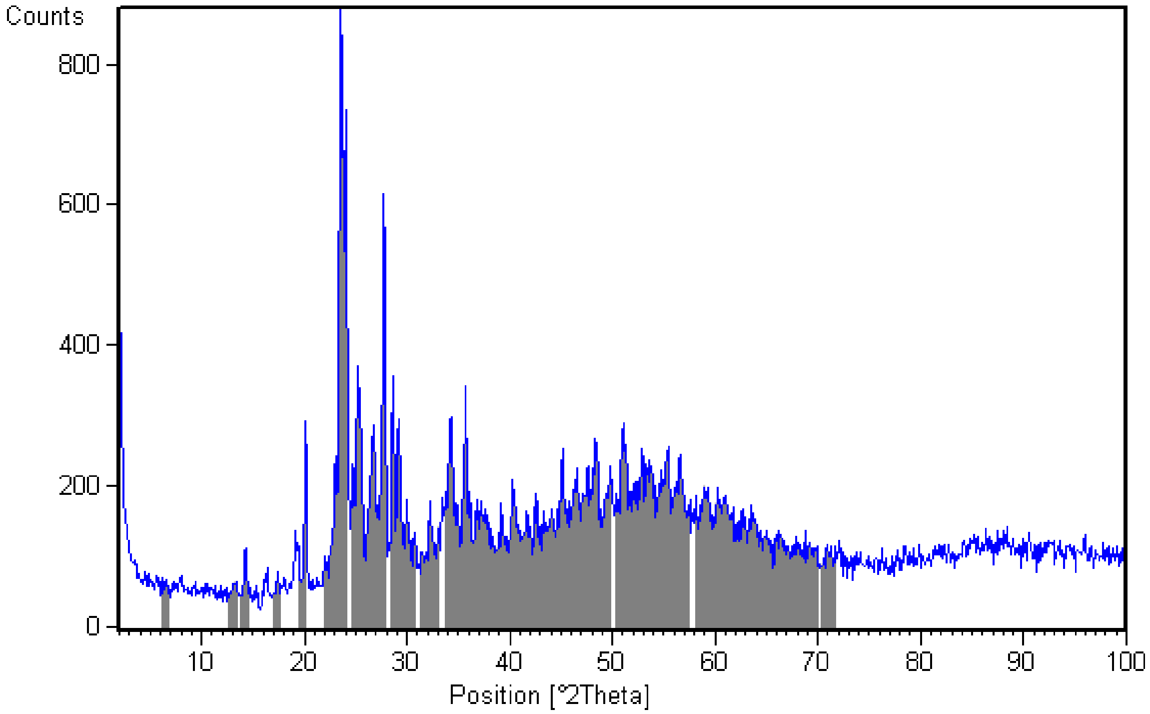

Figure 24 - XRD pattern of the sodium sulfide precipitate compared to that of $Se_{1.09}S_{6.91}$(00-041-1317) (gray peaks) (Precipitate formation conditions: initial [Se(IV)]= 300mg/L, [Se(IV)] sulfide/selenium molar ratio = 5.6 , 23°C)

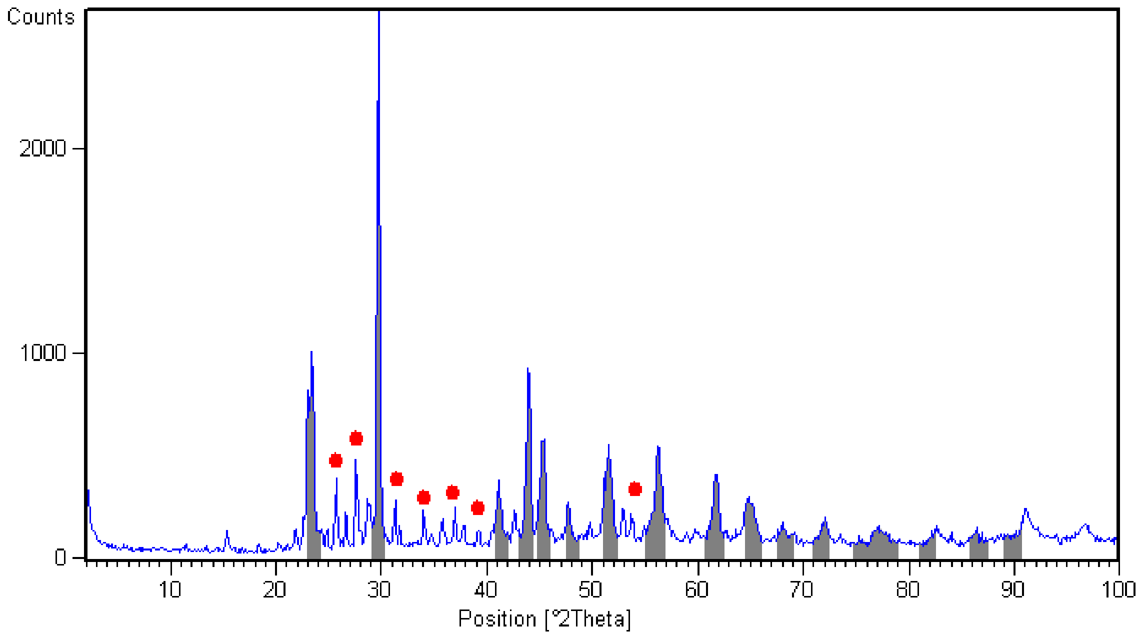

Figure 25 - XRD pattern of the precipitate formed during the acidification of a selenium – sodium sulfide solution compared to that of hexagonal synthetic selenium (00-006-0362) (gray peaks) and orthorhombic sulfur (00-001-0478) (red dots) (Conditions: initial [Se(IV)]= 300mg/L, [Se(IV)] sulfide/selenium molar ratio = 22.2, 23^{o}C)

4.5.4 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 [36]. 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 reddisolved 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 Figure 25.

$$2H_2S + H_2SeO_3 \rightarrow Se + 2S + 3H_2O \tag{2}$$

A similar redox reaction is believed to take place in the lower pH region where the solid solution Se-S phase (Se_nS_{8-n}) (Figure 24) was found to form. However in this case the selenium and sulfur atoms are organized in 8-member hetero-rings (..-Se-Se-S-Se-S-S-..) rather than homo-rings or chains of the respective elements.

The zero-valence state of selenium and sulfur in the proposed solid solution structure (Se_nS_{8-n}) was further confirmed via the following test: selenium sulfide solid solution (with XRD patter as in Figure 24) 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 Figure 25). No redox reaction was involved in this adjustment. This implies that the solid solution made up of the 8-member heterocycle rings (Se_nS_{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 [36].

4.5.5 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 two minutes of reaction time (Figure 26) 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 5, 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.

Table 5 – Particle size and BET surface area of selenium sulfide precipitates obtained at different sodium sulfide/selenium molar ratios after a reaction time of ten minutes

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

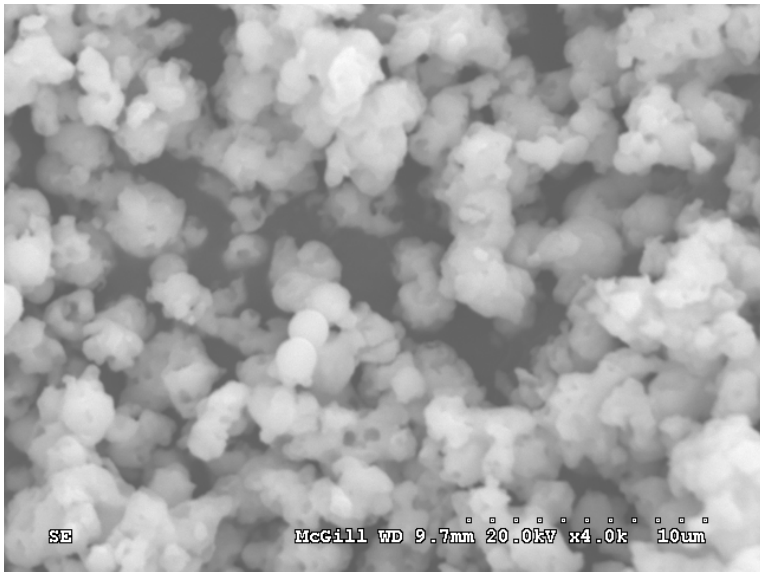

Figure 26 - Scanning electron microscope image of the selenium sulfide precipitate (Precipitation conditions: initial [Se(IV)]= 300mg/L, initial pH=1.3, sulfide/selenium molar ratio = 5.6 , 23^{o}C)

4.5.6 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: Se_nS_{8-n}. Chemical analysis of several precipitates produced within the complete precipitation zone (<1.7S/Se<11 - refer to Figure 19) yielded a sulfur to selenium ratio between 1.73 to 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 Se_nS_{8-n} formula this range of values gives a n value between 2.5 and 3: $Se_{2.5-3}S_{5-5.5}$. 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 S/Se> 2.3) secondary precipitation of elemental sulfur was observed to take place apparently due to decomposition/oxidation of the excess sulfide. (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) (Figure 27).

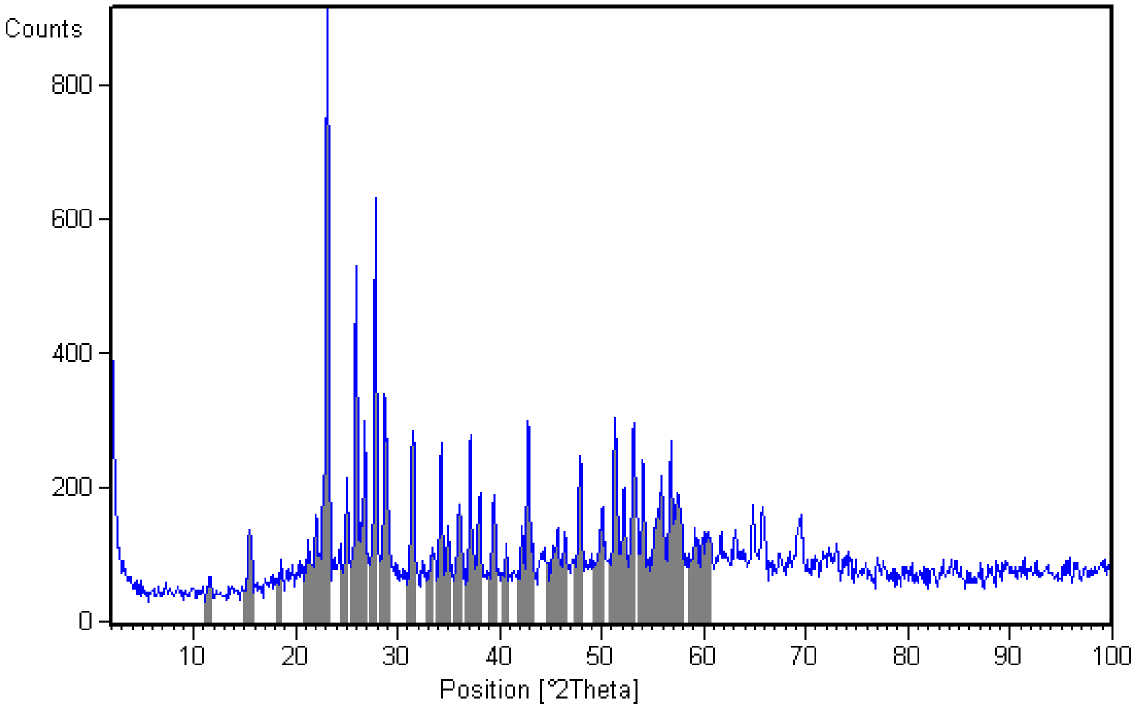

Figure 27 - XRD pattern of the secondary sulfur precipitate compared to that of orthorhombic sulfur (00-001-0478) (gray peaks)

4.5 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<S/Se<11 and 1.7<pH<7) the selenium and sulfur atoms appear to form a solid solution consisting of sulfur-selenium ring molecules having the Se_nS_{8-n} formula, with n=2.5-3. Elevation of pH above 7 leads to a breakdown of the Se_nS_{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 (<0.005mg/L Se) when subjected to over 60-day leachability test at pH 7. Following the precipitation of Se_nS_{8-n} secondary sulfur formation occurs via the decomposition of the excess sulfide.

4.6 Acknowledgements

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Chapter 5 - Stannous chloride-an effective reducing agent for the removal of selenium (IV) from industrial acidic effluent to less than 5.0 µg/L

5.1 Foreword

While sodium dithionite and sodium sulfide can both effectively precipitate selenium(IV) from acidic solutions, they both have important limitations, namely the rapid redissolution of the selenium precipitate in the case of dithionite and the formation of a very stable elemental selenium colloidal suspension in the case of sodium sulfide. In an effort to identify other reagents that potentially offer more reliable performance, stannous chloride was selected for detailed investigation. The results from this investigation are presented in this chapter (also submitted for publication[5]).

5.2 Abstract

In this work, the reduction of selenious acid (H_2SeO_3) species with stannous ions (Sn^{2+}) from weakly acidic sulphate solutions containing 300 mg/L of selenium at 23°C was studied. The results showed that, at initial pH below 1.3and molar ratios ≥ two, less than 0.5 µg/L of selenium (IV) remained in solution after reduction. The reductive precipitation reaction started as soon as the stannous ions were added in the selenium-bearing solution and was completed in less than 5 minutes. The reaction products,

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[5] Geoffroy, N. and Demopoulos, G.P., 2011 Stannous chloride-an effective reducing agent for the removal of selenium (IV) from industrial acidic effluent to less than 5.0 µg/L., Submitted to the Journal of Hazardous Materials.

characterized using X-ray diffraction, X-ray photoelectron spectroscopy and chemical analysis, were determined to be composed of approximately equal amounts of tin selenide and tin dioxide. In addition to tin selenide a minor amount of selenium (IV) was found to be removed via adsorption on the tin dioxide formed in-situ. Tests with a complex industrial solution also resulted in full and stable selenium precipitation.

5.3 Introduction

Selenium is an interesting element both from environmental and technological points of view. First, selenium compounds are toxic, but most living organisms cannot survive without trace amounts of this element in their diet [1, 2]. Selenium is used for several advanced technological applications such as thin film photovoltaics [3, 4]. Its recovery constitutes a by-product of other major extractive metallurgical operations such as copper refineries [5, 6]. In many instances, however it is simply considered an impurity that needs to be controlled. For example, in zinc smelting operations, selenium is often concentrated in a weak sulfuric acid stream (typically of pH ~1.5) that must be treated and decontaminated prior to being released to the environment [7].

Selenium, being a non-metal, has different chemical properties than most other contaminants and must be removed using different techniques. For example, lime neutralisation, the most common industrial technique to precipitate metal ions as hydroxides, is ineffective for selenium since this element as does not form insoluble hydroxides. Other techniques such as bacterial reduction, ion exchange membranes, electrocoagulation and adsorption have been investigated but found to be cumbersome, unreliable or only suitable for solutions containing low levels of dissolved selenium (< 5 mg/L) [8].

For industrial applications involving more concentrated solutions, techniques that involve the precipitation of selenium seem to achieve the best results [9]. Because of the high Se(IV)/Se reduction potential, various reagents have been evaluated and found to reduce selenium(IV)species in different types of aqueous solutions [10-12]. Unfortunately most of the reducing agents had reliability or toxicity problems that prevented them from being used on an industrial scale with the exception of dithionite. The precipitated selenium in the latter case, however, was found, to partially re-solubilize into the solution after a few hours if not filtered right away hence imposing particular engineering challenges in actual practice. Hence, identifying other effective reducing reagents for the elimination of selenite from relatively concentrated (>100 mg/L Se) solutions is of interest [12, 13].

Stannous ions (generally available as stannous chloride or stannous sulfate) are well-known reducing agents that offer a low toxicity, high efficiency, and essentially insoluble character when oxidized to stannic oxide (SnO_2). It thus provides an attractive alternative that has not so far been considered for controlling selenium in industrial effluent treatment. According to thermodynamics stannous ions can reduce selenium(IV) to elemental state as per Equation 1 [14]:

$$H_2SeO_3 + H_2O + 2Sn^{2+} \rightarrow Se + 4H^+ + 2SnO_2 \quad (1)$$

$$E^o = 0.834\ V$$

A possible complication in using stannous chloride is its tendency to partially hydrolyze and form an insoluble stannous oxychloride (also known as abhurite) [15-17]:

$$21Sn^{2+} + 16Cl^- + 20H_2O \rightarrow Sn_{21}Cl_{16}(OH)_{14}O_6 + 26H^+ \quad (2)$$

Tin and selenium can form at least two compounds: stannous and stannic selenide (SnSe and $SnSe_2$ respectively). Stannous selenide has been studied for its electronic properties and has been synthesized using several techniques [18-24]. However, all methods that involve precipitation of stannous selenide from aqueous solutions proceed via direct reaction of selenide and stannous ions (i.e. without changes in oxidation states) [25, 26, 22, 27, 28] or via electrolysis [29-32]. Presently there is no information available on the production of tin selenide directly from aqueous solutions by direct chemical reduction.

Finally, while stannous ions have been suggested in analytical chemistry literature to measure the amount of soluble selenite ions (or vice versa) no work has been reported concerning the use of stannous salts for selenium (IV) removal from industrial effluent solutions.[33, 34]. Thus, this paper analyses the parameters that affect the reduction reaction between selenite species and stannous ions in the acidic pH region at 23°C, characterizes the products, and describes the conditions under which the reaction is most efficient for selenium control purposes.

5.4 Experimental

Tests were performed with a synthetic weak sulfuric acid solution containing 300 (mg/L) of Se(IV). This concentration level was chosen as it represents the upper range of concentrations encountered currently in the CEZinc industrial operation (a zinc extraction plant in Valleyfield, Canada)[7]). The initial pH of the solution was fixed to 1.3, the average pH of the solution processed by CEZinc. Reagent grade selenium dioxide from Sigma-Aldrich (≥99.5% SeO_2) was used as the source of selenious species. Unless otherwise noted, all the experiments were performed at 23^oC.

In order to avoid pre-reaction oxidation of the stannous reagent, the precipitation experiments were performed with freshly prepared tin(II) solutions. Typically, different amounts of stannous chloride dehydrate (≥99% $SnCl_2.2H_2O$, Sigma-Aldrich) were dissolved in a volume of deionised water representing a tenth of the weak acid volume. Since the pH of deionised water is too high to solubilise large amounts of tin chloride, an opaque hydroxide slurry was formed. As soon as the reagent crystals had reacted with the water, forming a white cloudy solution, the latter was added at once in the Se(IV) acidic (pH 1.3) solution and the mixture was agitated with the aid of a magnetic stirrer (or in the case of the long term adsorption tests a shaking table). Because of the hydrolysis reaction shown by Equation 2, a white cloudy precipitate was also observed to form, regardless of the presence of selenium.

At the end of a precipitation test, the slurry was pressure filtered and the precipitate collected for analysis following washing and drying at 25°C for approximately 24 hours until a constant weight was achieved. The oxidation reduction potential (ORP) and pH of the solution were monitored using a gold double junction electrode (Cole-Parmer EW-27013-45) and a Corning high performance pH electrode (37-476146) respectively. The concentration of dissolved selenium and tin in the samples was measured, above 1 mg/L and 2.5 mg/L respectively, using atomic absorption spectrometry (AAS) with an air/acetylene flame. When higher precision was needed at the low concentration range, a graphite furnace AAS was used. Several of the precipitates were characterized using X-ray diffraction spectroscopy (Philips PW 1710, Cu anode, K-Alpha 1.54060 Å, scan rate: 2 °2θ/min), X-ray photoelectron spectroscopy (VG Escalab 3 MKII), electron microscopy (Hitachi S-3000N FEG SEM) particle size (Horiba LA-920) and surface area (Micromeritics TriStar) instruments. In order to recrystallize the amorphous selenium precipitates and avoid air oxidation, some of the precipitates were boiled in toluene according to the following procedure. Approximately one gram of precipitate was mixed with 40 mL of pure toluene, sealed in a 50 mL Teflon pressure vessel and heated to 110°C overnight [35, 12]. The container was then left to cool down slowly, drained, and the excess toluene was left to evaporate at room temperature.

For the adsorption tests the following procedure was followed. Selenious acid solutions of fixed concentration (300 mg/L) were contacted with different amounts of commercially available finely powdered tin dioxide (average particle size: 0.75 μm) in mechanically stirred conical flasks for seven days. At this time near equilibrium was reached. The final slurries were filtered, washed and analyzed.

5.5 Results and Discussion

5.5.1 The Se-Sn-H_2O System

The underlying chemistry of the process can be examined with the aid of E_h-pH diagrams constructed using the FactSage thermodynamic software package [36] (shown below). For the sake of brevity, the basic selenium – water diagrams will not be repeated here [12]. The diagram, prepared using a total selenium and tin concentration of 0.01 M ([Se] + [Sn] =0.01M), indicates that the predominant selenium and tin aqueous species corresponding to the original weak acid solution composition (approximately pH 1.3 and ORP 730 mV) are $H_2SeO_3$and SnO_2 respectively. In slightly more reducing conditions however, elemental selenium becomes thermodynamically stable instead. At even lower potential (~ 0.2 V at pH ~1.5) stannous selenide is shown to be the stable Se-bearing phase. Tin selenide is shown in two stoichiometries $SnSe_2$ and SnSe depending on the potential. On the other hand, with the exception of a limiting low pH window (shown in gray) where soluble Sn^{2+} appears, tin dioxide is the tin phase co-existing with tin selenide.

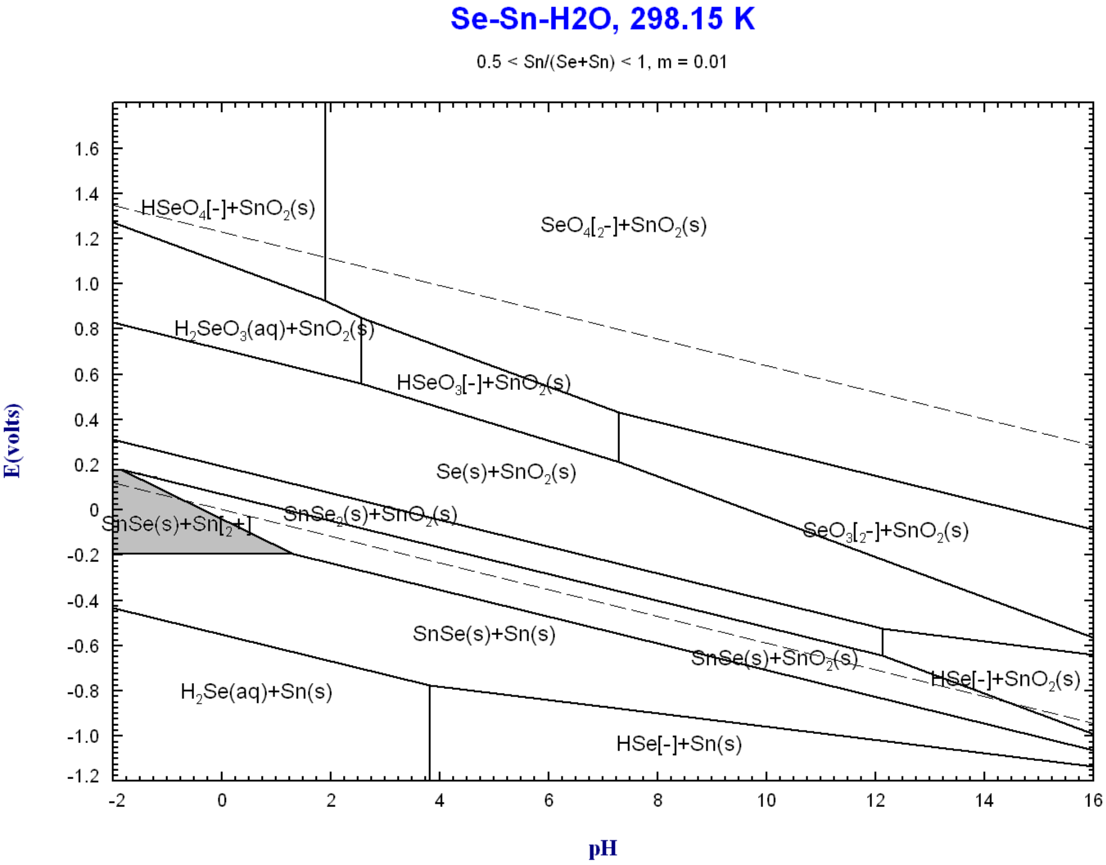


Figure 28 - E_h-pH diagram for the selenium-tin- water system(active soluble species = 0.01M and T = 25^{o}C)

5.5.2 Effects of Reaction Parameters

The data (shown on Figure 29) indicate that the reaction proceeded very fast to completion (less than 0.5 µg/L of selenium remaining in solution after 5 minutes) for tin to selenium molar ratios = 2.0.

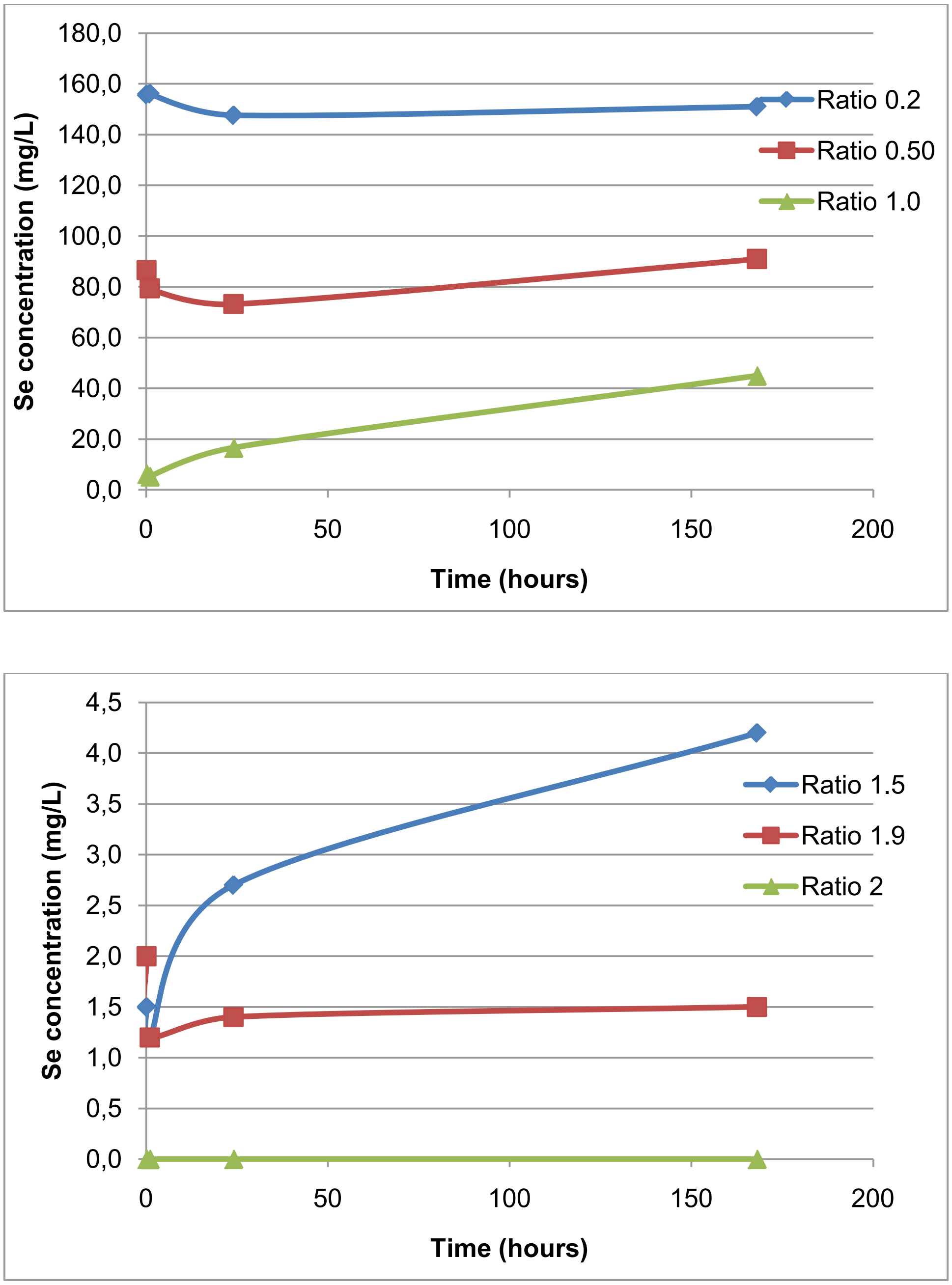


Figure 29 -Soluble selenium concentration as a function of time at different tin(II) to selenium(IV) molar ratio ([Sn]/[Se]) (Conditions: initial [Se(IV)]= 300mg/L, initial pH=1.3. 23°C)

The reaction between Se(IV) and stannous chloride was associated with a drastic potential (E_h) drop but small pH decrease (Figure 30). The potential decreased from the original 734 mV to 523 mV in the first minute or so and stabilized to 433 mV after ten minutes. This decrease was expected since stannous is a well known reducing agent. On the other hand, pH dropped from 1.32 to 1.27 and stayed constant thereafter. With reference to the e_h-pH diagram of Figure 28 under these conditions the products of the reaction are predicted to be elemental selenium and tin dioxide. Characterization of the products is done in the next section.

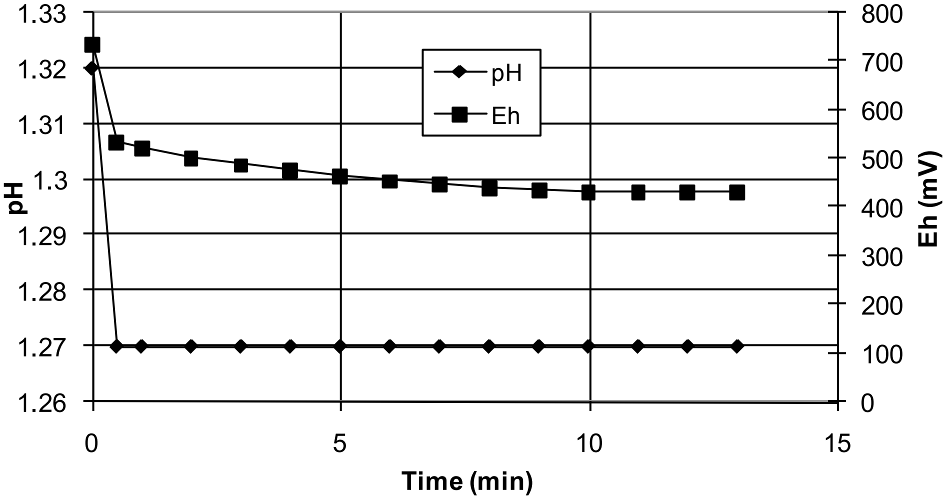


Figure 30 – Oxidation-reduction potential (E_h) and pH variation as a function of time during reaction of selenium (IV) with stannous chloride(Conditions: Sn(II)/Se(IV) molar ratio = 2.1, initial [Se(IV)] = 300mg/L, initial pH=1.3. 23°C)

The effect of initial pH of the solution on the reaction was also investigated (Figure 31). Interestingly, it was found the rate and equilibrium (final) of selenium precipitation to strongly depend on pH. Thus, at initial pH 2.7 the selenium concentration dropped very fast initially down to ~ 2mg/L but thereafter it took over 50 hours for the terminal Se concentration to drop below 0.1 mg/L. As the initial pH was raised to 4.1 and 7.5 the kinetics slowed down significantly with the terminal concentration not decreasing below ~2-3 mg/L. However at initial pH 11 the fastest kinetics and lowest (µg/L range) equilibrium selenium concentration were obtained. Such behaviour suggests a rather complex sequence of reaction steps which are discussed in a later section following the characterization of the products.

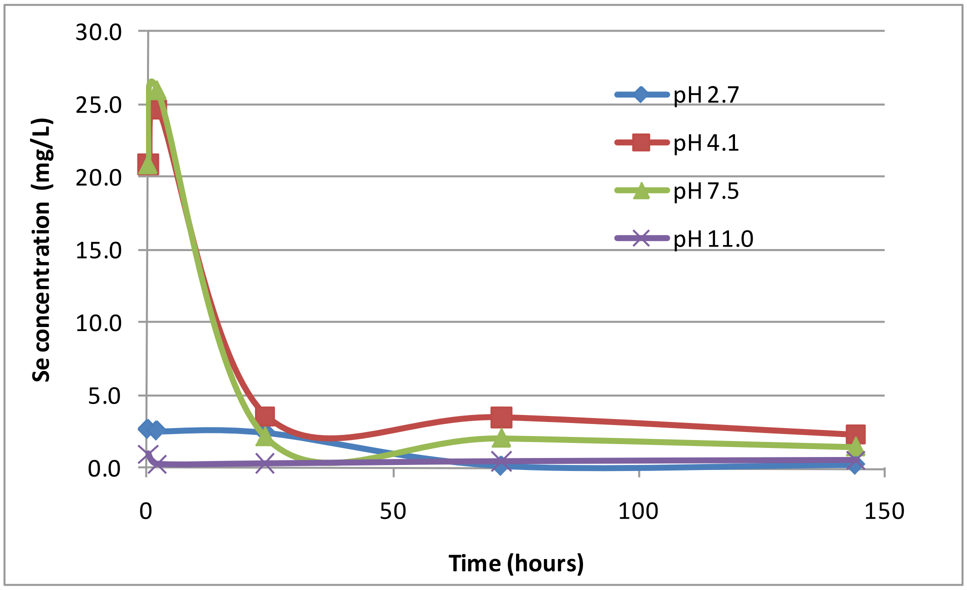


Figure 31 - Soluble selenium concentration as a function of time for solutions at different initial pH values (Conditions: initial [Se(IV)]= 300mg/L, initial pH=1.3. 23°CSn(II)/Se(IV) molar ratio = 2.1)

5.5.3 Characterization

5.5.3.1 XRD: The selenium-bearing precipitates formed at Sn/Se molar ratio of two or lower were deep red in color while at higher tin/selenium ratios they appeared yellow or beige. The red coloured precipitate would suggest that some selenium was reduced to elemental form as amorphous selenium is known to be red [9,32]; it is important to note, however, that SnSe can also take a reddish tint [37]. The X-ray diffraction pattern of the precipitate produced at pH 1.3 is shown in Figure 32. The major peaks were found to correspond to tin dioxide - apparently formed from the oxidation of stannous ions. No selenium phase was detected. This would imply that the selenium is mainly present as the red amorphous allotrope or that is co-precipitated via adsorption on the surface of the tin dioxide.

In order to facilitate characterization of the apparently amorphous Se-bearing phase its recrystallization was sought by boiling the sample (110^{o} C) for approximately twelve hours in toluene. This procedure avoids air oxidation and has been shown to recrystallize red amorphous selenium to the gray hexagonal allotrope, permitting identification by X-ray diffraction [12]. The results of this treatment (shown on Figure 33) indicate that elemental selenium is present in the precipitate. In addition, the possibility that the elemental selenium appeared as a result of decomposition of a different selenium compound during the hot toluene treatment cannot be completely ruled out.

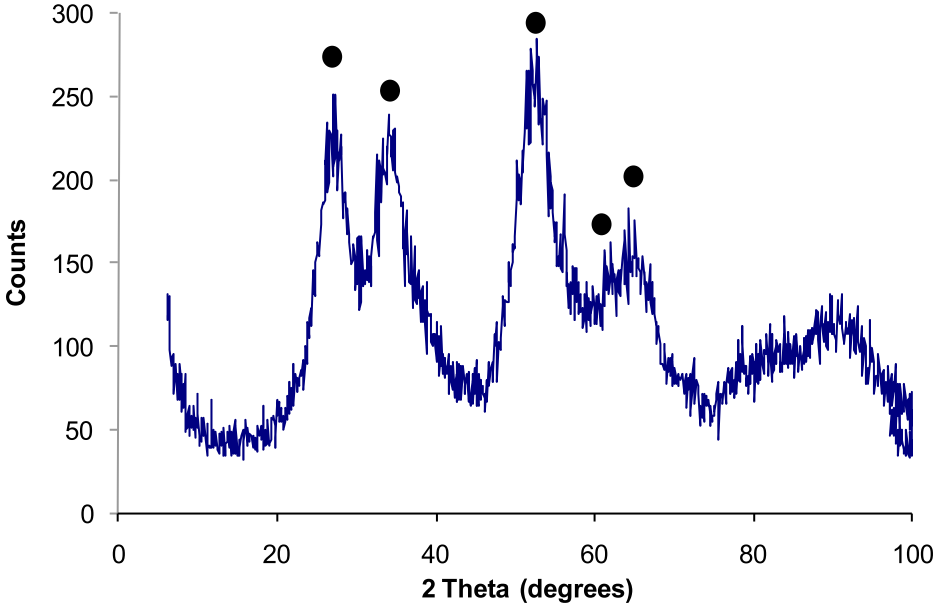


Figure 32 - XRD pattern of the tin - selenium precipitate after 10 min boiling in toluene (produced at pH 1.3 and 23°C with Sn(II)/Se(IV) molar ratio = 2). Black circles indicate tin dioxide peaks (Ref: 00-005-0467)

It is important to note that upon addition of stannous chloride in the solution a white precipitate was observed to form. This was suspected to be tin dioxide. This was confirmed by the addition of stannous ions to a selenium-free weak acid and agitation for 5 min or 24 hours. After five minutes, the broad peaks matched moderately well the tin dioxide pattern but after 24 hours, the crystallinity of the sample had improved significantly, yielding positive identification (refer to Figure 34). No evidence of the formation of abhurite was found.

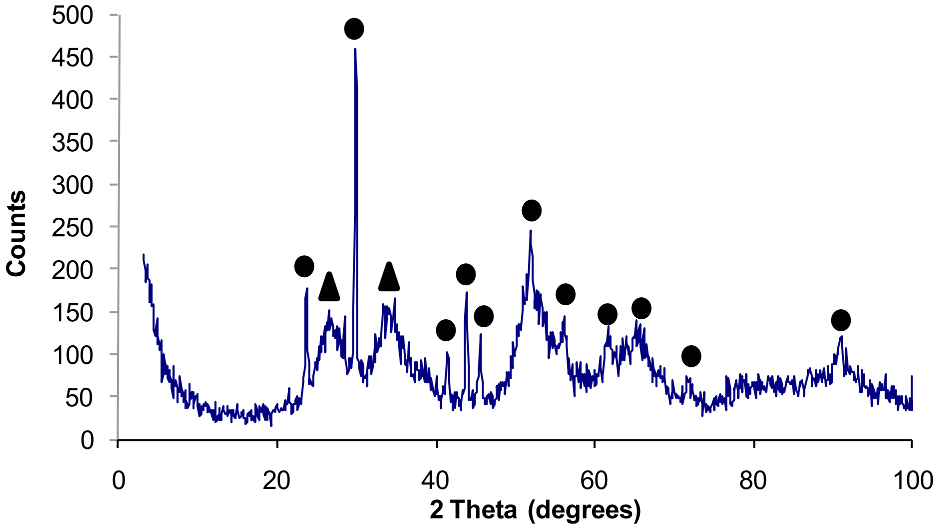
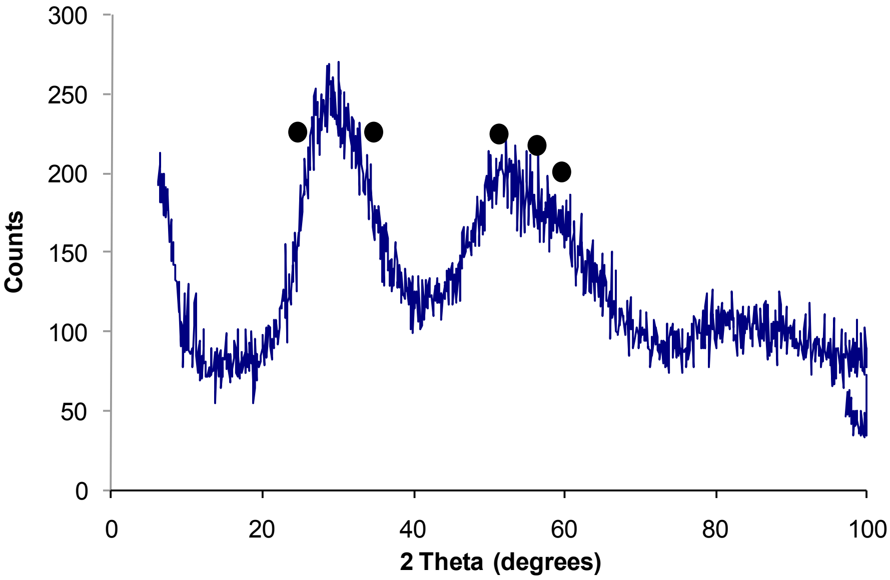


Figure 33 - XRD pattern of the tin - selenium precipitate after being boiled overnight in toluene (produced at pH 1.3 and 23°C with Sn(II)/Se(IV) molar ratio = 2). Black circles indicate gray hexagonal selenium peaks while triangles indicate tin dioxide ones.



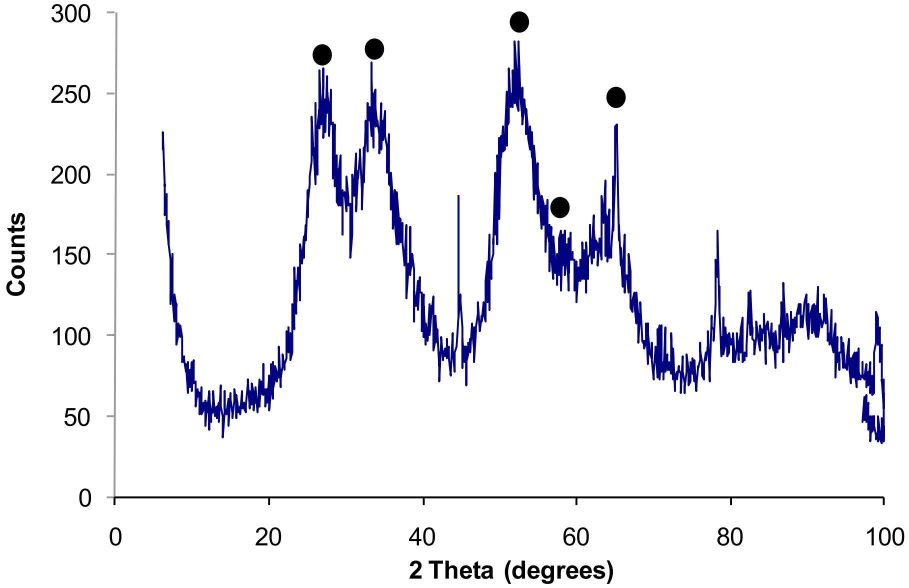


Figure 34 - XRD patterns of the tin precipitate produced after 5 minutes (top) and 24 hours (bottom) of agitation in weak acid without selenium (produced at pH 1.3 and 23°C). Black circles indicate tin dioxide peaks.

5.5.3.2 Particle features and composition: Samples of the precipitates were also examined using scanning electron microscopy. Overall, it was found that the precipitate consisted of very fine particles (around 200 nm in diameter) aggregated into much larger fragments in the order of 50-80 microns as determined by particle size analysis (Table 6). These aggregates were characterized by a large specific surface area in the order of 10-30 m2/g. However, by contrast the tin dioxide that precipitated in the absence of selenium had much lower specific surface area (about 5-10 times lower) indicating denser and better grown primary crystallites. Apparently in the presence of selenium the growth of the tin dioxide primary crystallites was blocked due to adsorption on them of selenite species. This aspect is discussed in section 5.5.4.

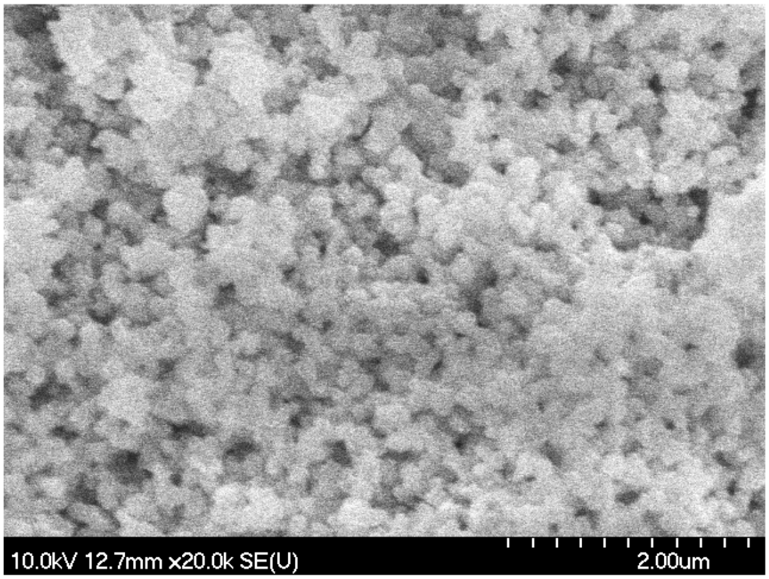


Figure 35 – SEM image of the tin-selenium precipitate (produced at pH 1.3 and 23^{o}C with Sn(II)/Se(IV) stoichiometric ratio = 5)

Once precipitated, filtered and dried at near room temperature, some of the precipitates were analysed for tin and selenium using aqua regia digestion and AAS analysis. The results are summarized in Table 7.

As the data in the table indicates, the tin to selenium ratio measured in the precipitates tends to increase with increased agitation time for Sn/Se ratios above two. This is obviously caused by the reaction of the excess tin in solution that is slowly oxidized into tin dioxide.

Table 6 – Particle size and specific area measurements of tin-selenium precipitates, commercial tin dioxide and tin dioxide precipitated in weak acid (Sample 444)

Sample	Time	Molar ratio (Sn/Se) added	Se left in solution (mg/L)	Average particle size (μm)	Specific area (BET - m^2/g)
312	10 min	1	12.0	72.08	19.82
313	24 hrs	1	10.9	81.55	30.67
314	24 hrs	2	< 0.0005	76.60	30.32
315	10 min	2	< 0.0005	60.20	14.07
316	10 min	5	< 0.0005	58.15	11.03
317	24 hrs	5	< 0.0005	54.44	13.70
Commercial SnO_2	N/A	N/A	N/A	1.04	7.11
444	24 hrs	N/A	N/A	13.31	2.46

Table 7 – Elemental tin and selenium analysis of precipitates

Sample	Time	Molar ratio (Sn/Se) added	Se left in solution (mg/L)	Se (molar %)	Sn (molar %)	Molar ratio (Sn/Se) measured in solids
312	10 min	1	12.0	37.4	30.8	0.82
313	24 hrs	1	10.9	48.0	30.3	0.63
314	24 hrs	2	< 0.0005	22.1	35.1	1.59
315	10 min	2	< 0.0005	25.6	36.7	1.43
316	10 min	5	< 0.0005	18.2	33.6	1.84
317	24 hrs	5	< 0.0005	13.9	43.2	3.10

5.5.3.3 XPS analysis: While chemical analysis was helpful in determining the elemental composition of the precipitate it could not reveal the oxidation states of tin and selenium. Furthermore, the XRD results were only partially revealing due to the presence of poorly crystalline and overlapping selenium and tin compounds. Thus, the same precipitates were also characterized using X-ray photoelectron spectroscopy. A typical XPS spectrum is shown in Figure 36.

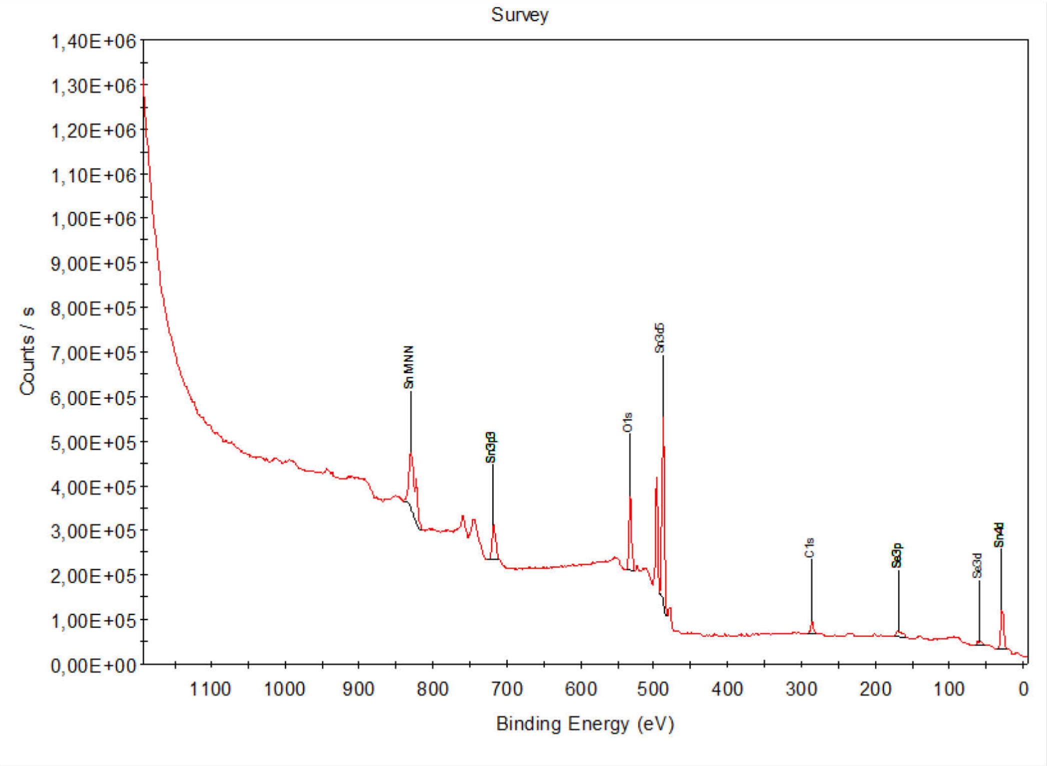


Figure 36 – XPS spectra for sample 315 (produced at pH 1.3 and 23°C with Sn(II)/Se(IV) molar ratio = 2 and agitation time of 10 min)[6]

If we neglect the presence of adsorbed carbon dioxide from the atmosphere, the analysis of the spectra (shown Table 8) determined that the solids were composed of four compounds: tin (II) selenide (SnSe), tin selenide oxide ($SnSeO_x$), tin oxide (SnO_x), and selenium (II) oxide (SeO_2).The tin selenide oxide ($SnSeO_x$), based on previous studies [39], is assumed to have resulted from the oxidation of part of SnSe during the handling of the sample prior to analysis. So the total tin selenide is the sum of the two compounds, SnSe and $SnSeO_x$,. which is about half of the total precipitate (Table 8). In the case of tin

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[6] Analysis performed on a VG Escalab 3 MKII, source: Mg Kα, power: 300 W (15 kV, 20 mA), area: 2 mm x 3 mm, depth 50-100 Å, high resolution spectrum: 0.05 eV and 20 eV, noise correction: Shirley's Method.

oxide, overlapping peaks made the tin oxidation state impossible to determine. However, given the thermodynamic stability of stannic oxide (SnO_2), it appears safe to assume that SnO_x is essentially tin dioxide. Finally, approximately 10% of the precipitate was determined to be selenium dioxide. Given that this compound is highly water soluble, it is considered instead to represent selenite anions adsorbed on the stannic oxide. This effect is studied in the next section.

Table 8 – Relative atomic percentage of selenium dioxide, tin dioxide and tin selenide in tin-selenium precipitates (refer to Table 7 for precipitation conditions)

	Relative Atomic Percentage				
Sample	SeO_2[1]	SnO_x	$SnSeO_x$[2]	SnSe	Total Tin Selenide
312	13.17	41.28	41.02	4.53	45.55
313	7.49	33.91	42.85	7.42	50.27
314	10.85	38.65	41.13	9.37	50.50
315	9.76	46.61	39.53	4.09	43.62
316	9.73	45.34	38.46	6.47	44.93
317	12.35	44.76	38.82	4.13	42.95

[1] Selenite adsorbed on tin dioxide

[2] Signifies oxidized tin selenide [39]

5.5.4 Selenium Adsorption on Tin Dioxide

Assuming Equation 1 is correct, the data shown on Figure 29 would indicate that all stannous ions have reacted with selenite in a very short period of time. This appears unlikely, especially because of the formation of a small amount of tin precipitate right after the addition of stannous ions. Because of this, it was hypothesised that some of the selenious ions could have adsorbed on the tin dioxide formed in situ. Furthermore, tests performed at tin to selenium ratios below two showed larger decreases in soluble selenium concentrations than what were predicted by Equation 1 alone. In order to substantiate the hypothesis of adsorption, five tests were performed at different tin dioxide to selenium ratios. The results yielded the adsorption isotherm shown in Figure 37.

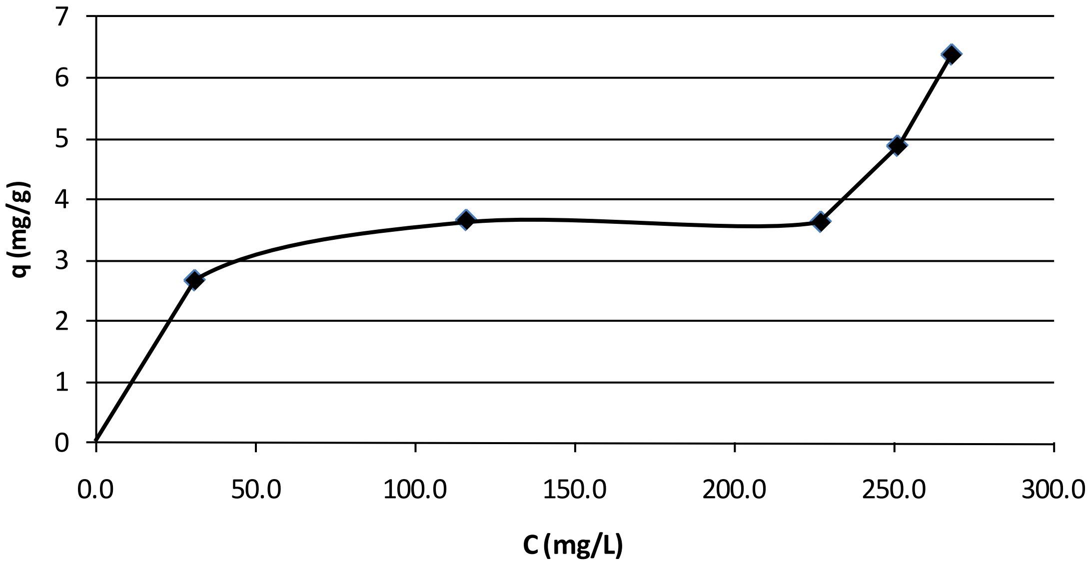

Figure 37 - Adsorption isotherm for the tin dioxide - selenite system (produced at pH 1.3 and 23°C with 100mL of 300 mg/L of Se(IV) and 0.5 to 10g of tin dioxide (average particle size: 0.75 μm))

The results shown above were then verified against three common adsorption models [38-40], Langmuir, Fruendlich, and BET. Of the three, Langmuir (Equation 3b) offered the best fit of data (R^2=0.74vs. 0.689 and 0.555 for the Fruendlich and BET respectively).

$$\text{Langmuir Original: } q = \frac{q_{m*}K_L*C}{1+K_L*C} \tag{3a}$$

$$\text{Langmuir Linearized: } \frac{C}{q} = \frac{1}{K_L*q_m} + \frac{1}{q_m} * C \tag{3b}$$

Where:

-q is the amount of metal ions adsorbed per specific amount of adsorbent (mg/g),
-C is the equilibrium concentration (mg/L),
-q_m is amount of metal ions required to form a monolayer (mg/g),
-K_L is Langmuir equilibrium constant,
-C_s is solute concentration at saturation.

The linearized Langmuir model plot is shown in Figure 38.

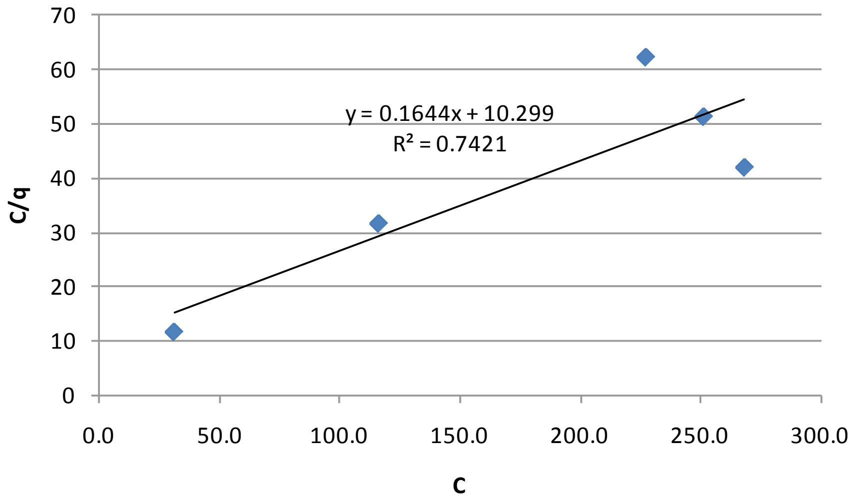

Figure 38 -Linearized form of the Langmuir model for the adsorption of selenious ions on tin dioxide.

It is interesting to note that even the correlation coefficient for the best model (Langmuir) was not very high. Given that the deviation from the model occurs as surface saturation is approached it is suggested that another reaction, most likely oxidation-reduction occurs, causing surface accumulation of selenium. This was evident indirectly, since during the adsorption procedure, the tin dioxide powder progressively took a slight pink color. This could indicate the presence of selenium complexes on the surface of the adsorbent and/or the presence of tin-selenide compounds. In order to verify this possibility, a tin dioxide sample was also analyzed using XPS. The results indicated that approximately 2% of the precipitate was selenium, split equally between tin selenide and an unidentified selenium compound (most likely an adsorbed selenium complex).

5.5.5 Mechanism

Based on the results presented the following reaction sequence is proposed as possible mechanism to account for the reductive precipitation of selenium (IV) by stannous ions:

$$SeO_3^{2-} + H_2O + 2Sn^{2+} \rightarrow Se + 2H^+ + 2SnO_2 \qquad (4a)$$

$$Se + Sn^{2+} + 2H_2O \rightarrow Se^{2-} + 4H^+ + SnO_2 \qquad (4b)$$

$$Se^{2-} + Sn^{2+} \rightarrow SnSe \qquad (4c)$$

Or overall:

$$SeO_3^{2-} + 3H_2O + 4Sn^{2+} \rightarrow 6H^+ + 3SnO_2 + SnSe \qquad (4d)$$

At the same time some of the selenite ions may be removed via adsorption onto tin dioxide:

$$SeO_3^{2-} + SnO\text{-}O_{(surf)} + 2H^+ \rightarrow SnO\text{-}SeO_{3(surf)} + H_2O \quad (5)$$

As already mentioned, under conditions of near surface saturation, some tin-selenium compound appeared to form which suggests that adsorption may constitute an intermediate step facilitating the subsequent formation of tin selenide. This then raises the question as to how Se(IV) adsorbed on SnO_2 was reduced when no reducing agent was present. To account for behavior it is postulated that adsorbed selenious ions underwent disproportionation into selenide and selenate ions according to:

$$4SeO_3^{2-} \rightarrow 3SeO_4^{2-} + Se^{2-} \quad (6)$$

5.5.6 Industrial solution

While most of this research was performed with synthetic solutions, the ultimate aim is to remove selenium from industrial solutions. Because of this, several tests were also performed with an industrial weak acid solution originating from the zinc refinery of CEZinc (Valleyfield, Canada). The composition of this acid is complex and varies according to the nature of the ore and roasting operating parameters:

-5 to 30 g/L H_2SO_4

-Saturated in SO_2

-0.5 to 10 g/L Zn

-0.1 to 1 g/L Fe (as Fe^{2+})

-0 to 75 mg/L Hg and 10 to 300 mg/L Se

-A small amount (generally < 25 mg/L) of other trace elements: Al, As, Bi, Ca, Cd, Cu, In, Mn, Mo, Pb, Sb

Tests performed with stannous chloride at room temperature gave consistently <5.0 μg/L selenium remaining in solution as long as the tin to selenium molar ratio was three or higher. The higher molar ratio (three versus two for synthetic tests) was most likely needed because of the numerous impurities in the industrial acid. Also, at a tin to selenium molar ratio of two the remaining selenium concentration was barely higher (<20.0 μg/L) Furthermore, the precipitate was found to be very stable not showing any signs of redissolution for at least seven days, in contrast to precipitates produced by other reducing reagents [12, 13]. Thus, it may be concluded that stannous chloride is highly effective in removing selenious ions from complex matrix industrial solutions. Considering furthermore its essentially stoichiometric (Sn/Se=2)usage and that tin does not cause secondary contamination of the effluent due to its complete precipitation as tin dioxide and the adsorption properties of the latter makes stannous a very attractive environmental reagent.

5.6 Conclusion

Stannous chloride proved very effective reagent in eliminating selenious acid species from both synthetic and industrial acidic effluent solutions. At pH values below 1.3 and Sn/Se ratios two or higher, the reaction was found to go to completion leaving less than 0.5 μg/L of selenium in solution. The precipitation reaction started right after tin addition and was completed in less than five minutes. The precipitate was found to be composed of tin selenide and tin dioxide with the latter carrying a small fraction of adsorbed selenite. There was evidence that some of the adsorbed selenite is further reduced to selenide causing deviation from Langmuir adsorption behaviour. The mixed tin-selenium precipitate was found to be stable for at least seven days when left in the reaction liquor. Tests with industrial solutions yielded similar results, confirming the industrial applicability and effectiveness of this technique.

5.7 Acknowledgments

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5.8 Literature Cited

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Chapter 6 - The rapid measurement and monitoring of selenite concentration by turbidimetry following its conversion to colloidal state by sulfite reduction and acidification

6.1 Foreword

While the previous chapters dealt with reducing agents able to precipitate selenium(IV) from aqueous solutions, it is also important to note that, from an industrial point of view, there exists a need for a quick and reliable method of analysis of the selenium content. By knowing in advance the selenium concentration before its removal, the wasting of expensive reagents and the undesirable redissolution of the precipitate in the case of dithionite use can be avoided. In this chapter, a novel technique is described for the rapid determination of Se(IV) and its application to synthetic and industrial solutions is demonstrated. This chapter has also been submitted for publication[7].

6.2 Abstract

In this study, the rapid reduction of selenious ions using sulfite species at negative pH is described and its use as analytical technique in combination with turbidimetry is proposed. It was found that Se(IV) can be reduced quantitatively at ambient temperature

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[7] Geoffroy, N. and Demopoulos, G.P., 2011 The rapid measurement and monitoring of selenite concentration by turbidimetry following its conversion to colloidal state by sulfite reduction and acidification., Submitted to Hydrometallurgy.

via a combination of sulfite reduction and ultra-acidification with sulfuric acid to a colloidal form that can be determined using turbidimetry. The developed analytical procedure can accurately and reproducibly measure Se(IV) concentrations down to 1 mg/L. For concentrations above 20 mg/L dilution is necessary. Common transition metal ions such as iron(II), copper(II) or zinc(II) up to 10 g/L concentration were found not to have noticeable influence on the precision of the method. Finally the developed technique was shown to be equally effective with real Se(IV)-bearing industrial solutions generated in a zinc concentrate roasting operation hence making the method particularly useful as on-line process monitoring and control tool.

6.3 Introduction

Some extractive metallurgical industries generate dilute effluent sulfuric acid solutions coming from scrubber off-gases [1, 2]. These solutions generally contain small concentrations of various impurity elements and are also saturated with sulfur dioxide coming from the roasting process. One such impurity element is selenium, the removal of which from acidic effluents may be accomplished via a variety of technologies [3]. For acidic effluents generated in the zinc industry selenium tends to be present as selenite in complex matrix solutions and at relatively high concentrations, more than 10 mg/L. For this type of solutions chemical reduction appears to be the preferred method to eliminate selenium [4].

An industrial reduction process that is based on sodium dithionite (a powerful reducing agent) is employed by the Canadian Electrolytic Zinc Company (CEZinc, Valleyfield, Canada) [1, 2]. The chemistry of this process was described in a recent publication by the present authors [5]. In this case, selenium(IV) is reduced to elemental form. The precipitate, once filtered, is disposed of while the weak acid solution is neutralized before being released in the environment. The selenium precipitation reaction can be summarized by:

$$H_2SeO_3 + 2H_2SO_4 + 2Na_2S_2O_4 \rightarrow Se(s) + 4SO_2 + 2Na_2SO_4 + 3H_2O \qquad (1)$$

While the dithionite reduction process for selenium-bearing acidic effluents has many advantages such as very fast reaction rates, high efficiency and low toxicity, it also has a few drawbacks. The two main ones are the relatively high cost of sodium dithionite and the subsequent partial redissolution of the selenium precipitate. During an investigation on the later problem, the authors of this work discovered that the redissolution phenomenon is caused by dithionite decomposition by-products and that high concentrations of the reducing agent worsen the problem [6]. In other words, if large excess dithionite is used (and this happens commonly because of the variable selenium loads), this constitutes significant economic losses but also complicates compliance with environmental regulations because of the ensued rapid selenium redissolution. In order to avoid these problems, the selenium concentration in the weak acid must be known before the dithionite treatment so the appropriate amount of dithionite reagent can be administered. This is accomplished currently via inefficient and time consuming manual sampling and analysis using standard analytical methods such as atomic absorption spectroscopy (AAS) - a method that cannot be used on-line. Because of this problem a project was launched into the development of a fast and easy to implement technique for on-line monitoring of the selenite concentration in weak acid solutions of industrial interest.

The first trials involved the use of ion selective electrodes, well known analytical tools that have been developed for the most common anions and cations. Two types of ion selective electrodes are commonly available. The first one, know as solid state electrodes, are commonly used to monitor the concentration of (uncomplexed) transition metal cations. The second type, known as membrane electrodes are generally used to monitor common anions such as perchlorates, nitrates and carbonates [7]. While commercial selenite electrodes were not available, the literature provided the description of several prototypes, of both the membrane and solid-state types [8-16]. After thorough screening in the context of the intended application that involves a complex corrosive industrial weak acid most of them were found unsuitable because of efficiency, durability or interference issues. A potentially promising design involved the use of silver selenide and copper sulfide as the solid-state electrode [14]. But despite following the same procedure to prepare the electrodes and consulting with the original authors, the obtained results were found to be extremely erratic and unreliable. Hence, no further work with ion selective electrodes was pursued.

The other method selected for evaluation was UV-Visible spectrophotometry involving the use of 3-3 diaminobenzidine and papaverine, two reagents known to react with selenious ions to produce colored complexes (orange and blue respectively) [17-21]. However, the complex nature of the industrial weak acid, especially the high amount of dissolved sulfur dioxide, caused interactions with both reagents, preventing the formation of colored complexes. Visible spectroscopy has also been used quantitatively on colloidal selenium precipitates formed by reduction by stannous chloride. However, it has been reported that the Beer-Lambert law was only followed for 1 to 10 mg/L selenium concentrations; a low and narrow range for industrial applications [22].

Interestingly, during these investigations, it was noticed that the industrial weak acid, when mixed with large amounts of concentrated mineral acids, formed also a red colloidal precipitate. Subsequent analysis showed that no selenium remained in solution after the acid treatment and that the precipitate was too coarse to be measured directly with visible spectroscopy. However, the turbidity of the solution was found to vary linearly with the amount of selenium originally present in solution. It thus became possible to develop the present selenium determination method for industrial weak acid solutions using a simple turbidimeter.

6.4 Experimental

The majority of tests was performed with a synthetic weak sulfuric acid solution containing between $1.27*10^{-5}$ and 0.00633 mol/L (1 and 500 mg/L) of Se(IV) at pH 1.3 (adjusted with H_2SO_4). This range of concentration and pH were chosen as they represent typical conditions encountered in industrial zinc refinery acid effluent solutions [1].

Reagent grade selenium dioxide from Sigma-Aldrich (≥99.5% SeO_2) was used as the source of selenious species. Unless otherwise noted, all the experiments were performed at 23°C.

The turbidity of the final solution was measured using a HF Scientific Micro 1000 turbidimeter equipped with an infrared lamp. The pH of the solution was monitored using a Thermo Scientific Orion Sure-Flow pH glass electrode (EW-05718-55). The concentration of dissolved selenium in the samples was measured using regular atomic absorption spectrometry (AAS) with an air/acetylene flame. The precipitates were characterized using X-ray diffraction spectroscopy (Filips PW 1710, Cu anode, K-Alpha 1.54060 Å, scan rate: 2 °2θ/min and electron microscopy (Hitachi S-3000N FEG SEM).

6.5 Results and Discussion

6.5.1 Background

As mentioned in the introduction, the ultra-acidification of the Se(IV)-bearing CEZinc weak acid solution resulted in the formation of colloidal selenium. The reducing agent involved here was apparently, given the roasting gas origin of the acid, sulfur dioxide (SO_2). The latter is a well-known reducing agent with a standard reduction potential equal to 0.16 V. The relevant reduction reaction of selenium (IV) by SO2 is given by Equation 1. By employing the Nernst equation (Equation 2) to the typical industrial solution parameters (25^{o}C, [H2SO4] = 0.1 M, [SO2] = 0.1 M, [Se] = 0.003 M (230 ppm)) it is determined the above reduction reaction to be thermodynamically feasible (E = 0.54 V).

$$H_2SeO_3(aq) + 2SO_2(aq) + H_2O \rightarrow 2H_2SO_4 + Se(s) \qquad (1)$$

$$E = E^{\circ} - \frac{RT}{nF}\ln\frac{[H_2SO_4]^2}{[H_2SeO_3][SO_2]^2} = 0.54 > 0.0 \qquad (2)$$

However, in practice, the above reaction only occurs to a limited extent this being so due to unfavorable kinetics. It has now been discovered that ultra-acidification accelerates the reaction leading to colloidal selenium formation-a phenomenon exploited in developing the analytical procedure described in this paper. Before the demonstration/application of this new procedure to the actual industrial solution (described section 3.7) results are presented involving synthetic solutions.

6.5.2 Results

The synthetic weak acid solution was composed of selenious ions $1.27*10^{-5}$ and 0.00633 mol/L (1 and 500 mg/L) of selenium and dilute sulfuric acid (pH 1.3). In this solution 0.156 M (10g/L) of anhydrous sodium sulfite ($Na2SO_3$) was added as reducing agent. Since this compound is very soluble in water (> 2.5 kg/L of solution), its dissolution was fast and easy. Once the salt was totally dissolved the solution was ultra-acidified with the addition of concentrated acid causing an immediate reaction. It was found that to obtain full and almost instantaneous reduction of Se(IV) to Se(0), a volume of concentrated mineral acid equal to that of the test solution was needed. Concentrated sulfuric (ACS grade, 98% w/w) and hydrochloric acid (ACS grade, > 36% w/w) were both tested and found to be equally efficient to convert all the selenium(IV) in colloidal form. The colloidal Se produced with hydrochloric acid aggregated and settled faster than that produced with sulfuric acid (an hour or two hours as opposed to more than twelve). Thus, if hydrochloric acid is used, the turbidimetry measurements will need to be performed more quickly since, once the selenium precipitate has settled, no reliable turbidity measurement can be made.

6.5.3 Discussion

Here the beneficial effect of ultra-acidification in accelerating the reductive production of colloidal selenium precipitate is discussed on the basis of the relevant sulfur dioxide/sulfite/acid equilibrium expressed by Equation 3.

$$SO_{2(aq)} + 2H_2O \leftrightarrow HSO_3^- + H_3O^+ \tag{3}$$

Undissociated sulfurous acid (H_2SO_3) and sulfite ions (SO_3^{2-}) can be neglected from this analysis since the former species does not appear to exist in aqueous solutions and the latter is only present in negligible amounts because of the very low second dissociation constant of sulfurous acid (6.24x 10^{-8}) [23]. The equilibrium amount of aqueous sulfur dioxide can be determined using Equation 4 [28]. At 25° C the reaction constant (K) is equal to 1.28 x 10^{2}. Moreover, according to literature, the constant decreases with temperature elevation due to the exothermic nature of the reaction [24].

$$\mathrm{K} = \frac{\gamma[HSO_3^-]*\gamma[H_3O^+]}{([Total\ dissolved\ SO_2]-[HSO_3^-])} \tag{4}$$

Upon addition of sulfuric acid addition the SO_2/HSO_3^- equilibrium (Equation 3) shifts towards the formation of aqueous sulfur dioxide because of the combined effect of proton activity/concentration effect and temperature elevation. This was confirmed quantitatively by performing thermodynamic calculations with the aid of the OLI Analyzer Studio 3.1 software. The results, shown below, indicate that after mixing with pure sulfuric acid, the sulfite/sulfur dioxide equilibrium is totally shifted towards the formation of the latter and all the selenium present is reduced to elemental state. The above analysis suggests that the abundance of $SO_{2(aq)}$ promotes the fast and complete reduction of Se(IV) to elemental selenium. Further work is required to reveal the true mechanism by which the rate of the reaction is accelerated.

Table 9 – Thermodynamic equilibrium results for the following feed: 0.555 mol (10 mL) water, 0.188 mol (10 mL) sulfuric acid, 7.933e-4 mol (0.1g) sodium sulfite and 3.80321e-4 mol (0.0422 g or 300 mg/L of soluble Se) of selenium dioxide.

	Total	**Aqueous**	**Solid**
	mol	mol	mol
Water	0.555115	0.555115	0.0
Sulfuric acid	1.98015e-5	1.98015e-5	0.0
Sulfur trioxide	2.75907e-8	2.75907e-8	0.0
Sulfur dioxide	**3.27301e-5**	**3.27301e-5**	**0.0**
Sodium bisulfate	1.2557e-3	0.0	1.2557e-3
Selenium	**3.80321e-4**	**0.0**	**3.80321e-4**
Bisulfate(VI) ion (-1)	0.184908	0.184908	0.0
Sulfate ion(-2)	2.15071e-3	2.15071e-3	0.0
Hydrogen ion(+1)	0.188937	0.188937	0.0
Sodium sulfate ion(-1)	2.93523e-5	2.93523e-5	0.0
pH		**-3.53**	
ORP (hydrogen electrode)		0.658 V	
Total solution volume		20.68 mL	

6.5.4 Colloidal Selenium Precipitate

In order to characterize the elemental selenium precipitate formed during the reduction reaction, 100 mL of a 1 g/L Se(IV) solution with 10 g/L (0.156 M) of dissolved sodium sulfite was mixed with 100 mL of concentrated (36% w/w) hydrochloric acid. The solution immediately turned brick red and the precipitate was separated (following its apparent aggregation) using a 0.2 µm filter. Interestingly, some selenium colloidal nanoparticles remained in solution since the filtrate exhibited a light yellow-green color [25]. The precipitate was then washed, dried and observed using scanning electron microscopy. The pictures shown in Figure 40, reveal that the precipitate is made of spongy aggregates of sub-micron (200-300 nm) elongated primary particles. The as-produced precipitate was visibly composed of red amorphous selenium. This was confirmed (see XRD pattern in Figure 39) via its recrystallization in boiling toluene solution [26, 5].

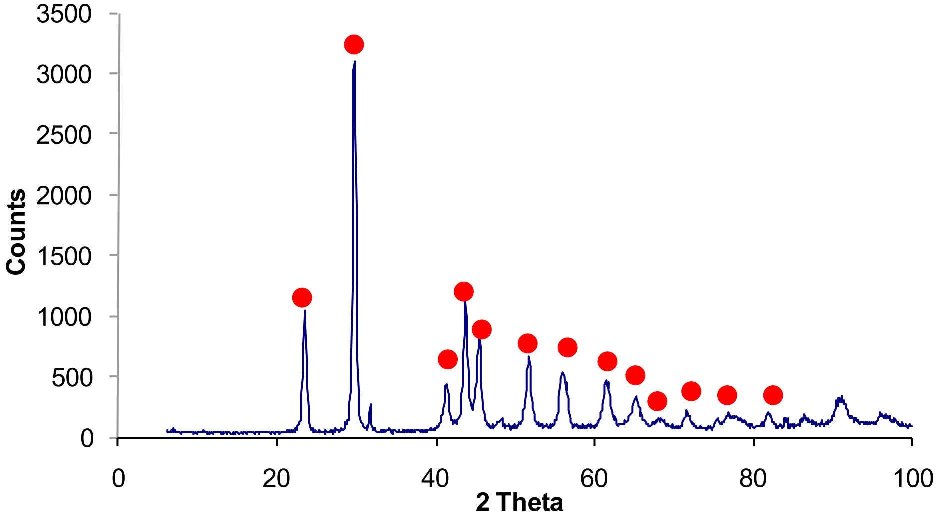


Figure 39 - XRD pattern of the selenium precipitate after toluene treatment, compared to that of hexagonal synthetic selenium (red dots, ICDS: 00-006-0362).

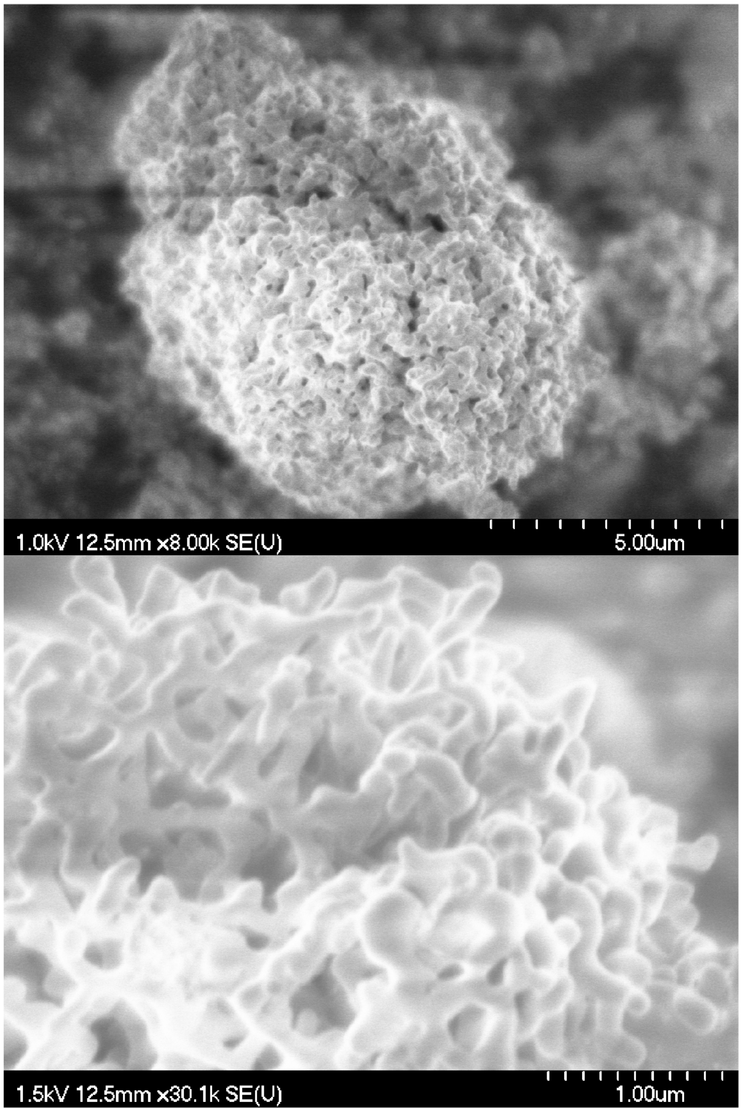
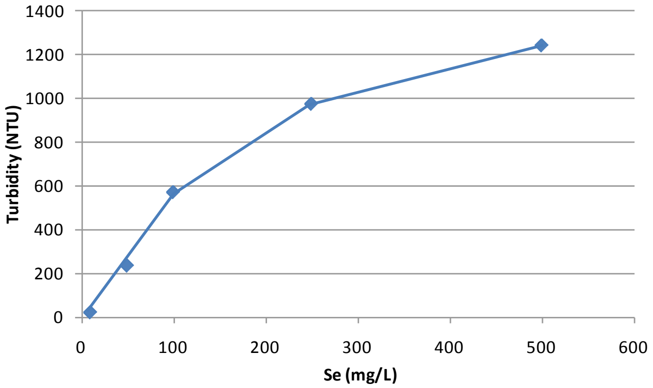


Figure 40 – Scanning electron microscope image of the colloidal selenium precipitate (following drying)

6.6.5 Turbidimetry

Following the conversion of selenite to colloidal selenium via the combined action of sulfite reduction and ultra-acidification tests were performed to determine the optimum set of conditions for conducting the turbidity measurements. Among the parameters tested were the range of selenium concentration that provides a linear range of turbidity, the effect of sulfite concentration and the possible interference by third ions.

6.6.5.1 Linear Concentration Range: It was found that for test solutions containing more than 12.5 mg/L of soluble selenite ions the turbidity to be rather high making the measurements prone to error (deviation from linearity). It is thus necessary to dilute the solution, after the reduction procedure, in order to lower the selenium concentration within the linear range of turbidity measurements. To determine the most suitable dilution ratio (linear range), two sets of tests were performed. In these tests, 5 and 10 mL samples were mixed with the same volume of concentrated sulfuric acid and diluted to 100 mL using volumetric flasks. The results are shown in Figure 41 and Figure 42 and Table 10 and Table 11. Also in Figure 43 a picture of the variable concentration colored solutions is provided.



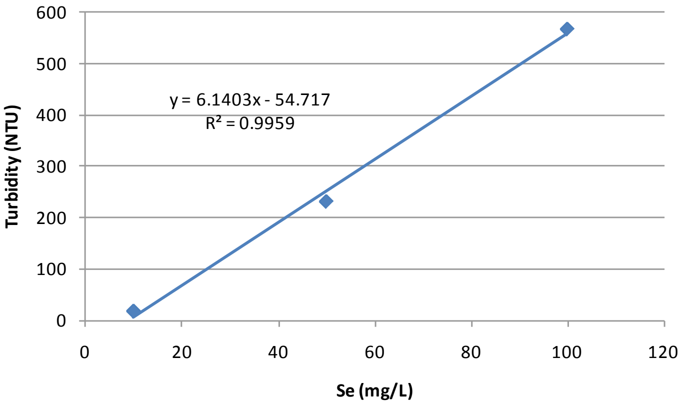


Figure 41 - Turbidity as function of initial selenium concentration for a dilution factor of ten (Conditions: 10 mL of sample, 0.1g of Na_2SO_3, 10 mL of 98% w/w sulfuric acid, mixed for a few seconds and diluted to 100 mL using deionized water, average of five tests; standard deviations given in Table 10)

Table 10 - Turbidity results for a dilution factor of ten (as a function of initial selenium concentration)

	10 mg/L Se	50 mg/L Se	100 mg/L Se	250 mg/L Se	500 mg/L Se
Average (NTU)	18.1	231.8	578.4	972.6	1240.2
Standard deviation (NTU)	2.2	12.9	24.8	64.8	39.2

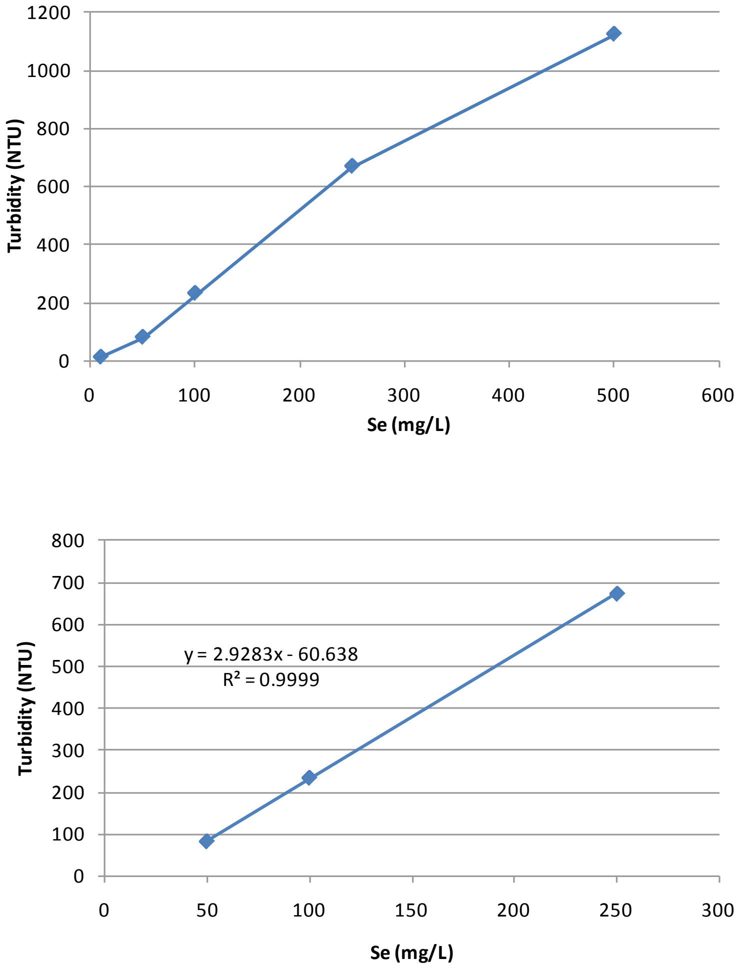


Figure 42 - Turbidity as function of initial selenium concentration for a dilution factor of twenty (Conditions: 5 mL of sample, 0.05g of Na_2SO_3, 5 mL of 98% w/w sulfuric acid, mixed for a few seconds and diluted to 100 mL using deionized water, average of five tests; standard deviations given in Table 11)

Table 11 - Turbidity results for a dilution factor of twenty (as a function of initial selenium concentration)

	10 mg/L Se	50 mg/L Se	100 mg/L Se	250 mg/L Se	500 mg/L Se
Average (NTU)	15.6	83.9	234.7	670.8	1124.4
Standard deviation (NTU)	7.8	2.7	4.8	14.5	37.2

Figure 43 – Color variation of solutions of different turbidity following 20x dilution (from left to right 50, 100, 250 and 500 mg/L initial selenium concentration)

As it can be seen, both sets of results are linear up to a certain concentration (100 and 250 mg/L for the ten and twenty dilution factors respectively) and start leveling off after that point. The upper limit of linear response is 15 mg/L Se. Thus, the dilution ratio has to be adjusted to lower the selenium concentration within the 1-15 mg/L linear range.

6.6.5.2 Spectator-ion Effects: Tests were also performed to evaluate possible interference effects from transition metal ions commonly found in industrial solutions, like Zn(II), Fe(II) and Cu(II). These metal ions were added into the solution at 1g/L for cupric ions and 10 g/L for the ferrous and zinc ions (the maximum concentration encountered in industrial acid effluent solutions). No reaction between sulfite and these ions took place nor interference with the turbidity measurements was encountered. In addition selenate-bearing solutions in lieu of selenite were tested but proved not suitable for application of the reduction/acidification/turbidimetry method because of selenate's resistance to reduction.

6.6.5.3 Sulfite Concentration Effect: To evaluate the effect of the sulfite/sulfur dioxide concentration on the turbidity results, 5 mL samples containing 100 mg/L of selenium (IV) and different concentrations of sodium sulfite were mixed with the same volume of concentrated sulfuric acid and diluted to 100 mL with deionized water. The results, shown in Figure 44, indicate that sulfite concentration can have a significant effect on the turbidity of the final solution. Thus, care should be taken to use the same sulfite concentration and preferably between 0.16 and 0.32 M (20 and 40 g/L) Na_2SO_3 to minimize any interference with selenium concentration determination.

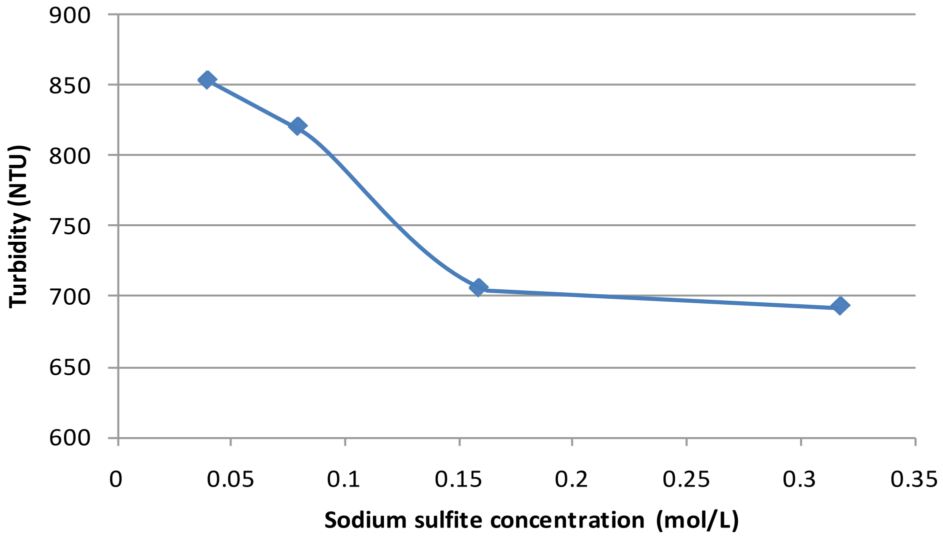


Figure 44 - Turbidity as function of sodium sulfite concentration for a dilution factor of twenty (Conditions: 5 mL of sample, 0.040, 0.079, 0.159 or 0.317 mol/L of Na_2SO_3, 5 mL of 98% w/w sulfuric acid, mixed for a few seconds and diluted to 100 mL using deionized water)

6.6.6 Application to SO_2-containing Industrial Solution

For solutions that already contain sulfites because of SO_2 dissolution as is the industrial acid effluent generated from the roasting of zinc sulfide concentrates there is no need for addition of sodium sulfite. Here the application of the turbidity technique to industrial solutions containing SO_2 (CEZinc plant, Valleyfield, Canada) is described.

Tests performed on industrial weak acid showed that the amount of dissolved sulfur dioxide (the method of determination is described in the Appendix) can vary widely according to various parameters, such as storage time and exposure to air, agitation, and temperature. It was determined generally to be between 5 and 25 g/L of total dissolved SO_2 corresponding to 0.08 and 0.40 M sulfite. In order to compensate for this effect, it is possible to add sulfite ions or to use a higher dilution factor. For example, complex industrial samples taken at several weeks of interval were tested using the turbidimetry method. It was found that using a dilution factor of 40 compensated for variations in the sulfite effect and allowed accurate measurements to be performed. The obtained results are presented in Figure 45.

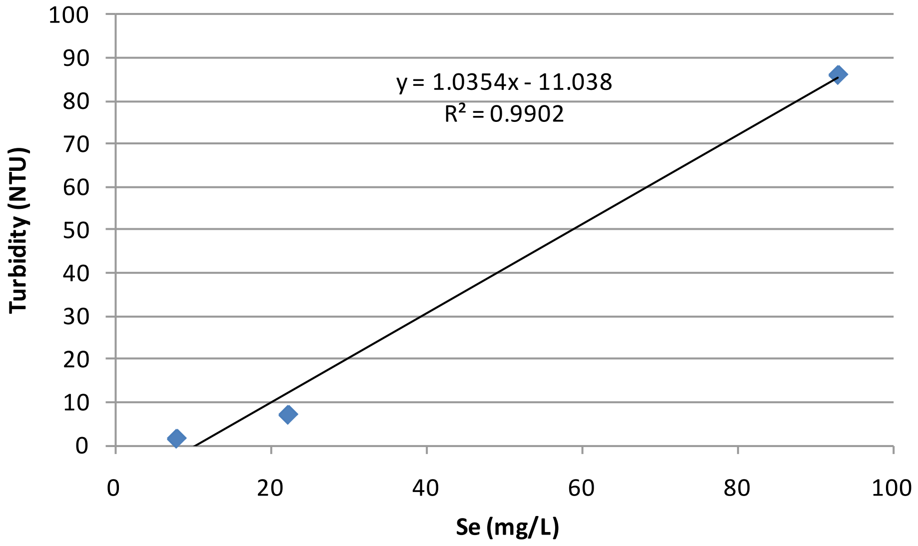


Figure 45 - Turbidity as function of initial selenium concentration for a dilution factor of forty (conditions: 5 mL of industrial weak acid sample, 5 mL of 98% w/w sulfuric acid, mixed for a few seconds and diluted to 200 mL using deionized water)

6.6.7 Analytical Flowchart

Based on the work reported above, turbidimetry can be applied to selenium (IV) concentration analysis as per the flowchart of Figure 46. Thus typically sodium sulfite of at least 0.160 M concentration is added (if not already present) to the weak acid solution containing Se(IV) anywhere between a few to several hundreds mg/L of selenite. After that an equal volume of 98% sulfuric acid is added to produce the colloidal selenium. Prior to turbidity, measurement the appropriate dilution is required to operate within the linear turbidity vs concentration range.

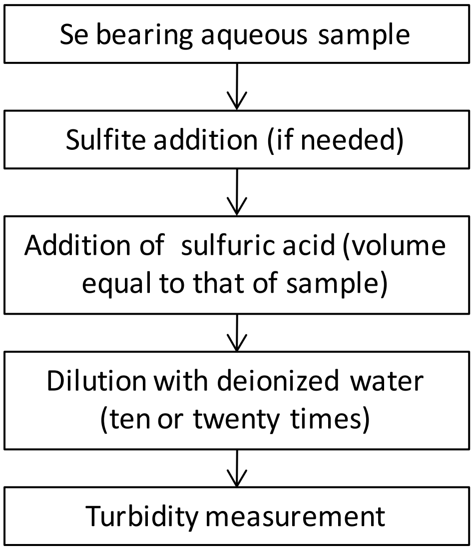


Figure 46 – Flowchart of the selenium(IV) measurement technique (in order to obtain a linear concentration range, dilution factor of ten should be used for selenium concentrations below 50 mg/L and twenty up to 250 mg/L. A sodium sulfite concentration above 0.160 mol/L is recommended in all cases)

6.7 Conclusion

Selenite ions can be almost instantaneously reduced to a colloidal form using dissolved sulfur dioxide/sulfite salt (above 0.1M of dissolved SO_2) if the solution is ultra-acidified using a strong mineral acid. The turbidity of the colloidal solution, once properly diluted, can be measured and related with excellent precision to the original selenium concentration. This analytical procedure is very fast, simple, and cost-effective that renders itself amenable to on-line implementation. The method is free of interference effects by transition metal ions such as iron(II), copper(II) or zinc(II). The method is not applicable to selenate analysis.

6.8 Acknowledgments

The authors would like to thank Dr. Elyse Benguerel of CEZinc and Monique Riendeau of McGill for their invaluable help. NSERC (Natural Sciences and Engineering Research Council of Canada), FQRNT (Fonds québécois de la recherche sur la nature et les technologies) and CEZinc are acknowledged for funding this research.

6.9 Appendix-Determination of dissolved sulfur dioxide

In order to measure the concentration of dissolved sulfur dioxide/sulfite in the industrial solution, sodium permanganate can be used according to:

$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+ \qquad (6)$$

The reaction can be monitored because of the color difference between Mn^{7+} (purple) and Mn^{2+} (light green) ions. When a slight purple color remains in solution for more than a few seconds, the titration is complete, the volume of permanganate solution used is recorded and the amount of dissolved sulfur dioxide is determined. A drawback of this technique is that the ferrous salts present in solution can also be oxidized by the permanganate ions according to:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe(SO_4)_3 + 8H_2O \quad (7)$$

If the concentration of ferrous ions is known, it is possible to account for it when calculating the dissolved sulfur dioxide concentration. Based on Equations 6 and 7, 0.57g of dissolved sulfur dioxide is overestimated for every g/L of iron present in solution. While it is also possible to remove the iron using a cationic ion exchange resin (such as Dowex G-26H), experience has shown that a significant fraction of dissolved sulfur dioxide is lost when the acid is agitated and passed through the resin.

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Chapter 7 - Synopsis

7.1 Conclusions

Findings deduced from the different parts of this work have already been outlined at the end of each chapter. Thus, only the general conclusions of the overall research are given here.

1) Selenious ions can be effectively precipitated from aqueous solutions to <0.5 µg/L using sodium dithionite provided that the initial pH of the solution is below 1.7 and a dithionite stoichiometric excess of three is used. The precipitate is made of red amorphous selenium and some elemental sulfur resulting from the decomposition of sodium dithionite.

2) The dithionite decomposition products were found to “catalyse” the oxidation of the elemental selenium precipitate, thus causing its redissolution if left for several hours in contact with the mother liquor.

3) Sodium sulfide can also fully precipitate selenious ions (< 5 µg/L) if the pH of the solution is maintained below 7 and a sulfide to selenium ratio above 1.8 is used. Starting at pH 7, a fraction of the selenium reduced by sodium sulfide is present in a colloidal form. The whole precipitate was found to form a stable colloidal suspension above pH 9.5, effectively making selenium removal impossible in basic solutions.

4) The precipitate obtained by the reduction of Se(IV) species with sulfide ions was found to be composed of a Se-S solid solution consisting of ring molecules apparently having the Se_nS_{8-n} formula.

5) Stannous chloride can reduce selenious ions to less than 5 µg/L provided that the pH is below 1.3 and molar ratios above two.

6) Characterization of the precipitate obtained by the reduction of Se(IV) by Sn(II) showed that it is composed of tin selenide and tin dioxide with a small amount of selenium (IV) being adsorbed on the later.

7) Selenious ions can be analytically reduced via a combination of sulfite reduction and ultra-acidification with H_2SO_4 or HCl acids to a colloidal form that can be determined using turbidimetry.

8) This procedure can accurately and reproducibly measure Se(IV) concentrations down to 1 mg/L and there is no limit to the upper concentration if proper dilution is used. It can be used on complex industrial solutions since other ions have little to no effect.

7.2 Claims to Originality

Several aspects of the work constitute, in the opinion of the author, original contributions to knowledge. The most important ones are listed below:

1) The effect of pH and stoichiometry on the reduction of selenious ions by sodium dithionite was investigated in depth for the first time. Furthermore, the dissolution effect of the dithionite decomposition products on elemental selenium had also never been reported previously.

2) The nature of the sulfur-selenium precipitate formed by aqueous reduction of selenious ions by sodium sulfide had not been analyzed using modern analytical methods. The formation, in basic conditions, of a colloidal selenium precipitate had also never been reported for this system and helped confirm the ability of elemental selenium to form very stable colloidal suspensions.

3) The composition of the precipitate formed by the reduction of selenium (IV) by stannous ions had never been investigated. The adsorption of selenious ions on tin dioxide had also never been reported or studied.

4) The new turbidity-based analytical technique for selenium (IV)-bearing aqueous solutions is totally novel. The reducing effect of dissolved sulfur dioxide on selenious ions in extremely acidic conditions is reported for the first time as well.

Chapter 8 - Appendices

In addition to the main body of research investigations conducted and described in the previous chapters, supplementary work was undertaken dealing with the analytical determination of soluble selenium. Also the characterization and analysis of the selenium-bearing industrial weak acid generated at CEZinc's roasting facility in Valleyfield, QC was performed.

A.1 Analytical determination of total soluble selenium concentration

This section deals with the challenges encountered with the total aqueous selenium concentration measurements using atomic adsorption spectroscopy and with the methods that were found to be most suitable to measure this element.

While several experimental techniques to measure selenium concentration in aqueous solutions have been developed, atomic adsorption spectroscopy (AAS) is by far the most common for routine measurements. However, there have been disagreements on the optimal operating conditions, especially when dealing with dilute solutions. Varian, the manufacturer of the instrument available in our departmental analytical laboratory (Varian AA240FS) suggested two procedures (shown in Table A.12) that both involved the use of a nitrous oxide - acetylene flame. However, the operating guide also warned that selenium measurements using AAS were difficult [1]. This was confirmed via a private communication with a Varian application specialist [2].

Table A.12 – Selenium AAS operating conditions suggested by Varian (nitrous oxide - acetylene flame)

Wavelength (nm)	Slit width (nm)	Optimum working range (mg/L)
196.0	1.0	5 – 250
204.0	0.5	90 - 1200

During the early phase of this project, the 196.0 nm nitrous oxide – acetylene flame procedure was tested but it was found to be unreliable and subject to numerous interferences. Furthermore, the procedures suggested by Varian were contradicted by other sources that suggested that nitrous oxide – acetylene flames are totally inappropriate to analyze selenium [3]. Interestingly, at CEZinc, in order to analyze the selenium concentration in the weak acid, they used the 196.0 nm wavelength and an air – acetylene flame [4]. The optimum working range for this procedure was reported to be 0.5 to 10 mg/L. For the needs of the present project, this method was found to be indeed reliable and was used when ultra-low concentration analysis (µg/L range) was not needed. It was also found that above 10 mg/L, the absorption curve became non-linear but that relatively good accuracy could be maintained up to 150 mg/L. A typical calibration curve is shown in Figure A.47. Tests performed with various solutions showed that this method was not subject to significant interferences from common ions such as sodium and sulfates when a background corrector (deuterium lamp) was used.

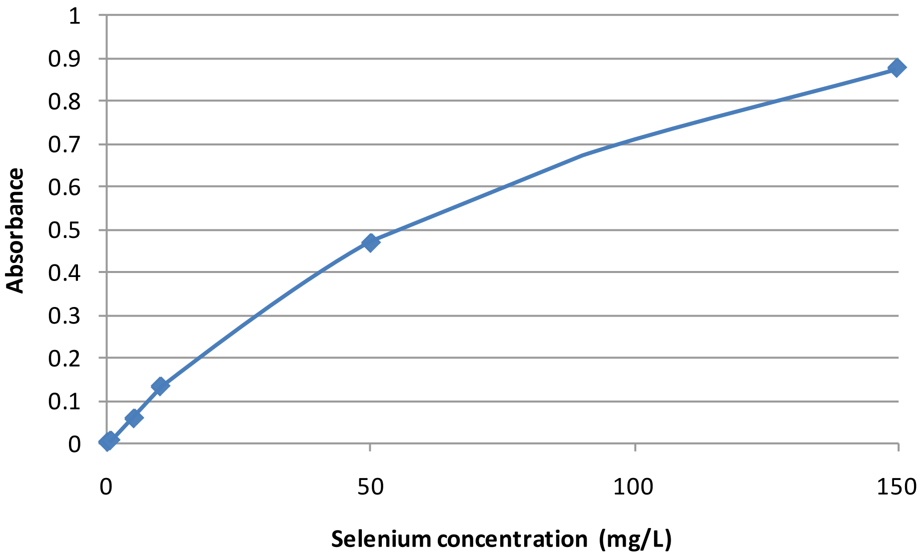

Figure A.47 – Typical calibration curve for the 196.0 nm air – acetylene flame selenium AAS analysis method

When very low concentration analysis was required (< 0.5 mg/L), the first method used was hydride generation AAS. In this technique, various elements in the sample are converted to volatile hydrides before being vaporized for analysis in a regular AAS. While this technique is both significantly more sensitive (detection limit of 0.5 µg/L for selenium) and more tolerant to interferences it also has drawbacks such as significantly increased complexity and higher cost [5]. Furthermore, since samples tested during this project often contained very large sodium to selenium molar ratios (> 1000 times) interferences still proved to be a problem when dealing with very concentrated solution where almost full selenium precipitation had been achieved. Inductively-coupled plasma atomic emission spectrometry (ICP-AES) was also rejected for the same reason.

Thus, for low selenium concentration (5 to 500 μg/L) determination eventually, graphite furnace AAS (GFAAS) was selected and used with excellent precision (Perkin Elmer AAnalyst 800 atomic absorption spectrometer with longitudinal Zeeman graphite furnace). During this procedure, the sample is vaporized and deposited on graphite surfaces where the atomic adsorption can be measured [6]. Although the precision of this technique is one order of magnitude lower than that of hydride generation AAS (5 versus 0.5 μg/L), it nevertheless enabled the direct analysis of samples without the need for complex and possibly unreliable purification steps.

A.2 Industrial Weak Acid Characterization

This section describes the characterization work that was performed on the CEZinc industrial acid and gives its average composition during the period this project was performed.

The previous chapters dealt with the reductive precipitation of selenious ions using mostly synthetic acid solutions and not the industrial acid itself. Since one of the goals of this project was not only to understand the relevant solution and precipitation chemistry of selenium removal but also its relation to the performance of the actual industrial process practiced at CEZinc, it was important to properly characterize the industrial acid. This is not an easy task since this solution, produced from scrubber off-gases, can contain all kind of metallic and non-metallic impurities whose concentration can vary according to operating parameters and the precise blend of zinc concentrate being processed that day. Its major components, other than water, are sulfuric acid, sulfur dioxide and zinc sulfate. In the last five years the average, minimum and maximum concentration of these components (and of chloride, cadmium, mercury and selenium) in the weak acid (based on daily measurements performed at CEZinc) are as shown in Table A.13 and Figure A.48.

Table A.13 – Results of five years of daily measurements (May 12 2005 to November 2nd 2010) for total zinc, chloride, mercury, cadmium, selenium and free sulfuric acid in the CEZinc industrial weak acid.

	Zn (g/L)	H_2SO_4 (g/L)	Cl^- (g/L)	Hg (mg/L)	Cd (mg/L)	Se (mg/L)
Average	**5.48**	**13.51**	**0.78**	**21.05**	**30.05**	**82.73**
Minimum	0.0	0.6	0.1	0.1	0	1
Maximum	50	95.9	5.3	640	139	580
Minimum target	N/A	>=5	N/A	N/A	N/A	N/A
Maximum target	<=4	<=30	<3	<1	<100	<=1200

As the results above and below indicate, because of a change in the main type of concentrate treated at CEZinc (from the Persévérance mine in Matagami, QC), the selenium concentration increased fivefold starting from the middle of 2008 and has remained relatively high since then (average before Persévérance: 18.3 mg/L, average after 96.8 mg/L). This increase has thus put much more pressure on the selenium removal process, especially since several concentration peaks above 300 mg/L have been witnessed.

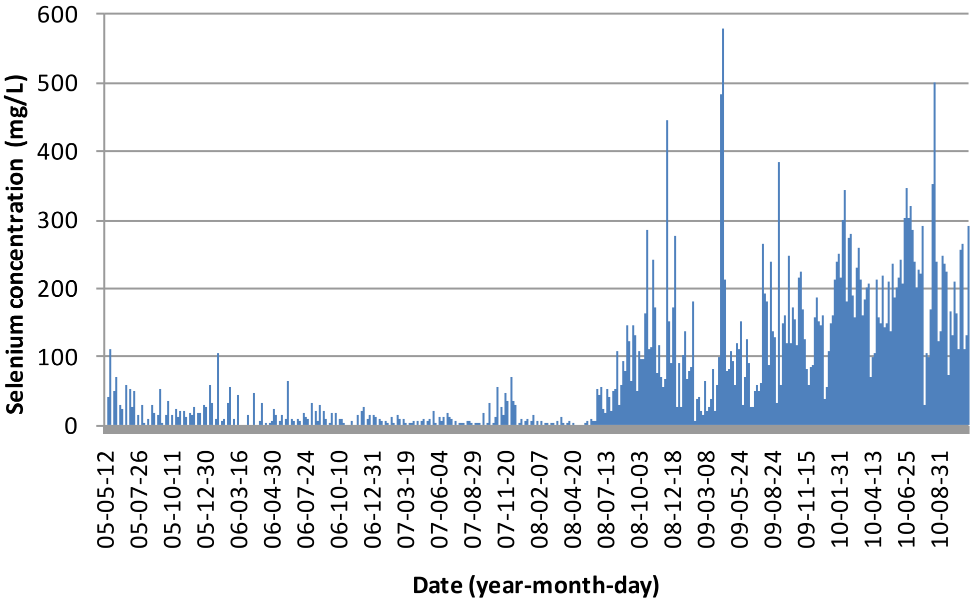

Figure A.48 – Selenium concentration in CEZinc industrial weak acid between May 12 2005 and November 2nd 2010

While it is not commonly measured by CEZinc and thus not present in Table A.13, it is important to note that the fresh CEZinc acid is saturated by sulfur dioxide. Sulfur dioxide molecules are solubilized in aqueous solution according to the following equilibria:

$$SO_{2(g)} \leftrightarrow SO_2(aq) \qquad (A.1)$$

$$SO_{2(aq)} + 2H_2O \leftrightarrow HSO_3^- + H_3O^+ \qquad (A.2)$$

Undissociated sulfurous acid and sulfite ions can be neglected from the analysis since the former species does not appear to exist in aqueous solutions and the latter is only present in very small amounts because of the low second dissociation constant ($6.24\text{x } 10^{-8}$). While in acidic solutions the equilibrium is heavily shifted toward the formation of bisulfites, the exact amount of aqueous sulfur dioxide remaining in solution can be determined using the following equation [7]:

$$K_1 = \frac{\gamma[HSO_3^-]*\gamma[H_3O^+]}{([Total\ dissolved\ SO_2]-[HSO_3^-])} \quad (A.3)$$

Thermodynamic modeling performed with the OLI thermodynamic software package (Analyzer Studio version 3.1) showed that in a 13.51 g/L sulfuric acid solution (the average CEZinc concentration) up to 1.31 mol/L of sulfur dioxide (83.9 g/L) can be dissolved. In practice however, as Henry's law indicates the solubility of sulfur dioxide in the weak acid is a function of the partial pressure of this gas over the liquid and experience has shown that storage and handling of the acid in open containers (including its oxidation by air) can significantly reduce its concentration. In order to measure the actual concentration of dissolved sulfur dioxide, sodium permanganate can be used according to:

$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+ \quad (A.4)$$

The reaction can be monitored because of the color difference between Mn^{7+} (purple) and Mn^{2+} (light green) ions. When a slight purple color remains in solution for more than a few seconds, the titration is complete, the volume of permanganate solution used is recorded and the amount of dissolved sulfur dioxide can be determined. A drawback of this technique is that the ferrous salts present in solution can also be oxidized by the permanganate ions according to:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O \quad (A.5)$$

If the concentration of ferrous ions is known, it is possible to account for it when calculating the dissolved sulfur dioxide concentration. Based on Equation 1 and 2, 0.57g of dissolved sulfur dioxide is overestimated for every g/L of iron(II) present in solution. Although it is also possible to remove the iron using a cationic ion exchange resin (such as the Dowex G-26H), experience has shown that a significant fraction of dissolved sulfur dioxide is lost when the acid is agitated and passed through the resin.

Tests performed on industrial weak acid showed that while it is initially (when fresh) saturated, the amount of dissolved sulfur dioxide can vary tremendously according to various parameters (storage time and conditions, agitation, temperature). Samples tested (after considerable time following their collection at the plant) at McGill however were between 5 and 25 g/L of total dissolved SO_2. In order to preserve as much sulfur dioxide as possible, the acid was kept in small and tightly closed containers.

In addition to the chemical components discussed above, a whole range of other elements are present in solution: aluminum, arsenic, beryllium, bismuth, copper, cadmium, cobalt, chromium, iron, germanium, indium, magnesium, manganese, molybdenum, sodium, nickel, lead, antimony, silicon, strontium, tellurium, thallium and vanadium. Of those, only arsenic, calcium, cadmium, copper, lead, iron, magnesium, mercury, sodium and silicon are generally present in significant amounts (> 10 mg/L). The results, shown on Table A.14, indicate that, of those elements, iron is present in the greatest amount and can thus possibly influence the selenium precipitation reaction. Fair amounts of sodium and silicon are also detected (> 100 mg/L) but these elements are much less likely to interact with the reducing reagents studies such as sodium sulfide or dithionite.

Table A.14 – Average concentration of several elements in CEZinc weak acid (based on eleven random samples taken between June 2008 and November 2010)

	As (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	Mg (mg/L)	Na (mg/L)	Pb (mg/L)	Si (mg/L)
Average	10.33	31.10	10.76	639.79	13.46	118.23	27.07	136.24

Finally, the pH and ORP of the industrial acid was also measured. The average pH was found to be 1.4 with peaks up to 1.7. The ORP (vs, standard hydrogen electrode) varied from approximately 170 to 500 mV with an average of 320 mV. Also, since the industrial solution contains large amounts of dissolved sulfur dioxide that partially reacts to form the hydrosulfite ion, it can be considered as buffer solution hence its relatively stable pH.

A.3 Evaluation of the presence and removal of selenate from synthetic solution and the industrial weak acid

This section examines the effect of sodium dithionite and sodium sulfide on selenate-containing solutions, both synthetic ones and the actual industrial weak acid.

As discussed in Chapter 3, the erratic selenium precipitation results obtained using dithionite were determined to arise from the relatively rapid redissolution of the elemental selenium precipitate when left in contact with the dithionite decomposition products. As a result of this discovery the CEZinc process was modified to promptly filter the selenium precipitate and thus avoid leaving it in contact with the mother liquor for several hours. This simple modification effectively solved the selenium removal problems and resulted in a significant reduction in dithionite use.

On another front, when the CEZinc process was implemented, a reduction in soluble selenium levels had been noticed when high amounts of sodium sulfide were used for the removal of mercury but this effect had not been studied. During the course of this work (Chapter 4) it was determined that the effectiveness of sulfide ions to precipitate selenium depends on the applied sulfide/selenium ratio. Thus it was found that all selenium (IV) could be precipitated if the sulfur to selenium molar ratio was above 2 and the pH of the final solution was kept below 7. In industrial solutions however, even if these parameters were met, it was found that approximately 10 to 50% of the soluble selenium was left in solution several minutes after the sodium sulfide addition.

One of the theories that was put forward (Dr. Bryn Harris' comments during preliminary PhD thesis proposal examination) to explain this phenomenon was that a fraction of the soluble selenium was present as selenate ions (as opposed to being only as selenite ones). As discussed in the Literature Review chapter, the reduction of selenate ions to elemental state is kinetically very unfavorable Furthermore, it has been shown that sulfide ions have barely any effect on selenates [8, 9]. Thus, it was hypothesized that sodium dithionite could remove selenate ions from a mixed selenate/selenite solution while sodium sulfide could only remove selenite ions. In order to verify the validity of this hypothesis a series of tests was conducted the results of which are presented in this section.

9.3.1 Selenate removal from synthetic solutions

The first step of this study was to simply try to precipitate selenium from pure selenate-bearing synthetic solutions using sodium dithionite. This test proved particularly difficult by the fact that a clear orange-red solution was generated as soon as the dithionite was added to the weak acid solution (with or without selenium present). Attempts to filter the solution with 0.02 μm pore size filters were unsuccessful. Interestingly, the color tended to fade with time, becoming colorless after a few minutes. Thus it was concluded that dithionite was not effective on selenate notwithstanding any minor effects from the complex dithionite decomposition reactions [10, 11].

However, since selenate ions are never present alone in the industrial acid, tests involving selenite/selenate samples were used to evaluate the effectiveness of dithionite on mixed solutions. Various solutions containing different selenite/selenate fractions (295 mg/L Se(IV)/5 mg/L Se(VI), 275/25, 250/50, 200/100 and 150/150) were treated using sodium dithionite. The results are shown below:

Table A.15 – Selenium precipitation results from mixed selenite/selenate synthetic solutions using sodium dithionite (initial pH of 1.3 and 23°C; 1.323g of sodium dithionite in 10 mLof deionized water, 10 min)

Sample	295/5	275/25	250/50	200/100	150/150
Final [Se] (mg/L)	<0.5	21.2	42.3	82.6	126.0
[Se(VI)] precipitated (mg)	>4.5	1.5	3.2	8.3	10.4
% of [Se(VI)] precipitated	100%	6.0%	6.4%	8.3%	6.9%

The results above indicate that when selenite ions are present, full precipitation of Se(VI) is achieved up to 5 mg/L of selenate ions but that above this; only approximately 7% of the selenate ions are removed. However, it is unclear if the selenium removal effect is caused by a partial reduction of the selenate ions or by adsorption of the selenate on the red amorphous elemental selenium precipitate formed by the reduction of selenious acid.

The same experiment was also conducted with sodium sulfide. The results are shown below:

Table A.16 – Selenium precipitation results for mixed selenite/selenate solutions using sodium sulfide (initial pH of 1.3 and 23°C; 0.667g of sodium sulfide in 25 mL of deionized water, 10 min)

Sample	295/5	275/25	250/50	200/100	150/150
Final [Se] (mg/L)	4.1	17.2	37.5	77.5	117.2
[Se(VI)] precipitated (mg)	0.0	2.8	2.5	2.5	2.8
% of [Se(VI)] precipitated	0.0%	11.2%	5.0%	2.5%	1.9%

In this case, the results are quite different since the highest removal percentage was achieved at the 25 mg/L selenate concentration and decreased steadily after that. Also, no selenate removal was measured at the 5 mg/L concentration. The reduced selenate removal percentage at higher selenate concentration is quite normal if adsorption is assumed to be the only removal mechanism.

9.3.2 Analysis of industrial solution for selenate

In order to validate/quantify the possible presence of selenate ions in the industrial acid, several samples were analyzed using high performance ion chromatography. The results showed that trace amounts of selenate ions may be present in the industrial acid but that their concentration was always well below 1 mg/L and thus if indeed present at that range they are probably removed (via co-precipitation) by sodium dithionite as per data of Table A.15. In the case of sodium sulfide, the results shown in Table A.16 suggest that Se(VI) ions might remain in solution following a sodium sulfide treatment but the fact that they were found to be < 1 mg/L in the industrial solution implies that the high amounts of soluble selenium is due to other factors as discussed in Chapter 4.

9.3.3 Evaluation of the possible interference of iron, zinc and sulfites during selenium (IV) removal by sodium sulfide

This section considers the possible interference of zinc, iron as well as sulfites on the effectiveness of the selenious ion precipitation reaction with sodium sulfide.

Since the industrial acid has a very complex chemistry and contains varying amounts of several transitions metals plus dissolved sulfur dioxide, it appeared plausible that these might affect the selenium precipitation reaction and lower its efficiency. For example, it was hypothesized that zinc and iron, present in relatively large amounts in the weak acid may form insoluble precipitates (ZnS and FeS respectively) with sulfide ions and thus interfere with the selenium removal reaction. Because of this possibility, great care was also taken during the practice of selenium removal in the plant to avoid the use of large amounts of sodium sulfide that could lead, when added to industrial weak acid, to the formation of black zinc and ferrous sulfide amorphous precipitates that are virtually unfilterable.

In order to clarify this issue, two sets of tests were performed. In the first place, synthetic weak acid solutions (4.5g/L of H_2SO_4, 300 mg/L Se(IV)) containing 10g/L of Zn^{2+} and 1.5 g/L of Fe^{2+} ions-close to the maximum concentration of Zn and Fe commonly encountered in the industrial weak acid) were treated with varying amounts of sodium sulfide corresponding to S/Se molar ratios of 2.5 to 7.25. In all cases, less than 0.5 mg/L of soluble selenium remained in solution. Similar tests were also performed with the actual industrial acid. The results, shown in Table A.17, indicate that this time selenium removal was not as effective despite the fact that all the S/Se ratios used were above the minimum required to achieve full precipitation (i.e. S/Se > 2.0 as per results presented in Chapter 4). Only at ratio, S/Se, 7 and 10 the removal of selenium(IV) was satisfactory (< 1 mg/L remaining Se in solution).

Table A.17 – Selenium (IV) precipitation results for industrial CEZinc solution using sodium sulfide (conditions: original pH of 1.3, 100 mg/L of Se(IV), 7.5 g/L of Zn and 1.25 g/L. The sodium sulfide was dissolved in 10 ml of deionized water, agitated for ten minutes, at 23^{o}C)

S/Se ratio	2.5	5.0	7.0	10.0
Final [Se] (mg/L)	16.1	1.73	0.11	0.00
[Se(IV)] precipitated (mg)	282.29	298.10	299.88	100.00
% of [Se(IV)] precipitated	94.1	99.4	99.9	100

Furthermore, analysis performed before and after the sodium sulfide addition showed that the iron and zinc concentrations had remained constant for all the samples. In other words, little to no zinc and iron had been precipitated at the sulfide concentrations used. Because of these results, another set of experiment was performed to evaluate the effect of dissolved sulfur dioxide/sulfites (simulating the presence of dissolved SO_2 in the industrial solution) on the effectiveness of the sulfide precipitation reaction. In this case, various amounts of sodium sulfite were added to synthetic weak acid samples, the pH was adjusted to 1.3 and an S/Se molar ratio of 12 was used. The results, shown in Figure A.49, indicate that the selenium concentration left in solution after the sulfide addition increases with the dissolved amount of sodium sulfite. Thus, if full selenite precipitation using sulfide ions is desired, dissolved sulfur dioxide levels should be kept to a minimum. This could be done by oxidizing the dissolved sulfur dioxide to the sulfate state or by simply agitating the acid to free the gas. In practice, both effects could be reached by sparging air into the solution before sodium sulfide addition.

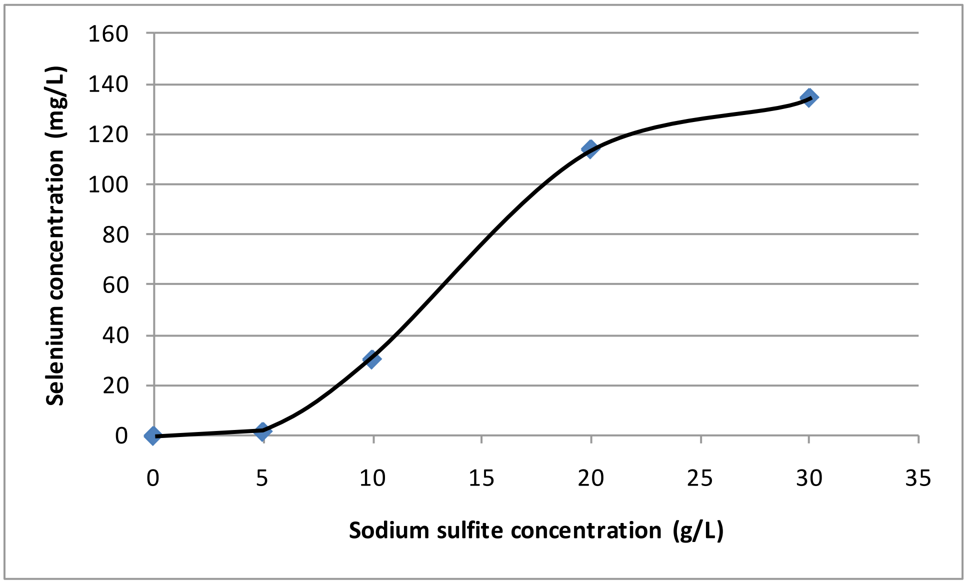

Figure A.49 - Selenium precipitation results, using sodium sulfide, for synthetic selenite weak solutions containing dissolved sodium sulfite (initial pH of 1.3 and 23^{o}C; 0.728g of sodium sulfide in 25 ml of deionized water, 10 min)

A.4 Literature cited

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