Speciation Analysis of Colloidal Silica in Acidic Conditions

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Abstract

Dissolved silica speciation is of great importance in mining as it interferes in the various metals extraction/removal processes especially in electro-winning. Analytical methods have been devised to identify species in colloidal silica in acidic conditions. Total silica was determined after microwave acid digestion by ICP-AES. Monosilicic acid was determined using molybdic method; alpha and beta isomers were quantified. Silicon dioxide was determined after precipitation as potassium fluorosilicate by titrimetric method. Various interfering ion species which can co-precipitate with silicon dioxide were investigated.

Keywords: colloidal silica, acidic conditions, speciation

Introduction

Silicon is the second most common element found in the earths crust and mantle. It is most abundant in the form of silicates and occurs throughout the mineral realm complexed to metals such as magnesium, calcium, iron and aluminium (Ning 2002; Holleman-Wiberg 1995).

Many different techniques have been adapted to extract minerals from ores. The first step of processes is the milling or crushing of ores followed by a dissolution step. A method of metal extraction is electro-winning, once the sample is completely dissolved.

Silica dissolves from the ore samples, both under acidic or alkali conditions. Various species of silica and its complexes undergo polymerization to form colloidal suspensions. The colloidal silica then interferes with electrodes, complexes with metal ions and metal extraction processes cannot occur (Ning 2002).

There are two types of colloidal systems formed by silica. Silica sols are poly-silicic acids in spheroid, amorphous forms. When sodium silicate (Na_4SiO_4) is acidified a sol is formed. Addition of a base causes deprotonation and a negative overall charge of the molecules that prevent bonding and results in a sol. Under very specific conditions, a sol can convert itself to a gel (Holleman-Wiberg 1995; Govett 1961). If the pH is acidic or if a base does not stabilize the silica, the subunits fuse to form interlinking chains. The aggregation of subunits due to van der Waals forces results in a soft then hard gel.

Most literature on silica analysis focus on the determination of monomeric form of silica using colorimetric technique where a molybdate solution reacts with monomeric silicic acid to produce silicomolybdic acid as proposed by Dienert and Wandenbulkcke (Govett 1961; Roa 1992).

Silicic acid is a tetravalent weak acid with a strong tendency to eliminate water during condensation reactions with other silicic acid molecules (Ning 2002; Holleman-Wiberg 1995). The acid is most stable at a low pH of 1 - 3 and least stable at pH 5 - 6. The solubility of silicic acid increases in the presence of acids such as hydrofluoric acid (HF) and reacts with it to form silicoflouride anions (Govett 1961). Polymerization of silicic acid results in large polymers that form a colloidal solution. The molecules condense to produce a Si-O-Si bond between two molecules. Silicic acid polymerization is strongly dependant on pH (Ning 2002). Below pH 3.2, the polymerization reactions result in linear or openly branched polysilicic acids. Above pH 3.2, the polymerization results in cyclic or cross-linked polymer arrangements. Polymerization is rapid in alkaline or neutral environments and in acidic pH it is much slower. The condensations eventually result in a 3-D structure with the repeating units of $(SiO_2)n$.

Monomeric as well as polymeric silica species exists in dissolved ore samples. It is imperative that their concentration is determined. It is therefore not substantial to just know the total concentrations of silica but more importantly, its speciation (Holleman-Wiberg 1995).

The objective of this study was to develop methods for the analysis of various silica species in colloidal matrix under acidic conditions and to apply the developed methods to carry out silica speciation in electro-winning processes.

Experimental

Determination of silica in this study followed the following procedure: standard sample preparation, determination of total silica content (ICP-AES), monomeric silica determination (Molybdate reagent) and SiO_2 determination by titrimetric method.

Preparation of colloidal silica standard samples

Analytical grade silica gel was milled to a fine powder using Fritsch Planetary mono mill GmbH 'Pulverisette 6' at a speed of 130 rpm for 6 hours, sulphuric acid solution of known pH was added and the mixture shaken for 16 hours to prepare colloidal solutions of known concentration (Saccone et al. 2006) .

Acid digestion and determination of total silica by ICP-AES

Acid digestion was used to convert samples into solution for determination of total silica (Multiwave 3000 digestion Anton Paar GmbH). 0.1 g of ground sample masses were weighed into reaction vessels and 5 mL HNO_3, 5 mL HF and 0.5 mL HCl added. The digested samples are then placed in a 100 mL volumetric flask and mixed with boric acid in the ration of 6 mL : 1 mL of hydrofluoric acid [Roa 1992; May and Rowe (1965). Total silica was determined by spectral analysis using Spectro ICP-AES Genesis.

Determination of soluble silica (monosilicic acid complexation).

Preparation of a stable solution of ammonium molybdate. 100 g of $(NH_4)6Mo_7O_{24}.4H_2O$ and 47 g of concentrated (28% NH_3) ammonium hydroxide was dissolved in 1 L of deionised water.

Preparation of molybdate acidic reagent. A mixture of 100 mL of ammonium molybdate solution, 500 mL of deionised water and 200 mL of 1.5% ($H2SO4$) were mixed to give a concentration of 0.0707M $MoO4-2$, 0.375M $SO4-2$ and 0.148M $NH+4$, with a pH of 1.2.

Alpha Monosilicic acid analysis

A mixture of 20 mL of molybdate acidic reagent with no more than 5 mL of sample solution was prepared containing about 0.01 to 1.0 mg of SiO_2 and the total volume was then diluted to 25 mL with deionised water. The absorption was measured at a wavelength of 410 nm. Fresh reagent mixtures were made daily (Govett 1961).

Beta Monosilicic acid analysis

Sample solution was diluted to silica concentration of between 0.5 - 4 mg/L. All dilutions preformed were with 1.5 % $H2_SO_4$. 10 mL of each sample was then into 50 mL flasks. 2 mL of a 10% w/v solution of ammonium molybdate was added. The solutions were mixed and allowed to react for 20 minutes. 2 mL of 8% w/v solution of tartaric acid was added to the reagent mixture to prevent ferric (III) ion reduction, followed by 1 mL of reducing agent (4-amino-3-hydroxy-1-naphthalene-sulfonic acid/sodium metabisulfite/sodium sulfite solution). The sample was allowed to stand for 20 minutes to react before reading the absorbance on a UV-Vis spectrometer ((UV- 1201) at 820 nm).

Determination of silica dioxide (SiO_2)

To a 1 mL of sample, 5 mL of 20% calcium chloride and 1 g of sodium fluoride was added; the solution was stirred. Solid potassium chloride was added until an excess of 2 - 3 g over saturation point was attained. The precipitate was filtered and washed with a solution containing 70 g of potassium chloride in 1 L of 1:1 ethanol-water to ensured effective removal of excess acid. The washed precipitate, filter paper were transferred to a 1 L beaker containing 500 mL of boiled deionised water. The solution was titrated with 0.15M sodium hydroxide and 1% phenolphthalein (Lewis-Russ A, Ranville J and Kashuba AT (1991).

Results and discussion

Total silica

The concentration of Si determined for the prepared colloidal solution is shown in table 1. The measurements were done in triplicate and taken at a wavelength of 251.612 nm.

Percentage of silica in the solution was determined as 99.4% with a good precision of 0.15 % RSD.

Monomeric silicates

Monomeric silicates were quantified using UV-Vis spectroscopy. The acidic molybdate reagent forms two compounds when reacting with the Monosilicic acid; Molybdenum heteropolyacid (MHA) $(SiMo_{12}O_{40})^{-4}$ and heteropoly anion $(SiMo_{12}O_{40})^{-5}$ complexes. These ions are commonly known as the alpha (MHA) and beta (anion) forms. The alpha form is the most stable while the beta form converts spontaneously to the alpha form at pH above 2.5. The MHA complex forms a yellow solution that was measured at 410 nm while the reduced beta species forms a blue complex that was measured at a wavelength of 815 nm. The alpha isomer is very stable at pH 3.5 - 4.5 while beta formation occurs more readily at pH 0.8 - 2.5. When the environment is at a low pH the conversion of the beta form is very slow (Govett 1961; Maybodi and Atashbozorg (2006). If the reduction of beta molybdosilicic acid occurs at a low pH of 1.2 the heteropoly blue anion (beta- $(SiMo_{12}O_{40})^{-5}$) results.

Three colloidal solutions were prepared of pH ranges of between 0.8 – 1.0, 1.2 – 1.4 and 1.8 -2.0. They were left to stand and sampled at the top, middle and bottom for analysis to assess the stability of the colloidal solutions and to get a representative fraction of the colloid samples. The means and percentages of monosilicic acids were calculated (table 2) for beta and alpha monosilicic acid values, respectively.

The values obtained are all time dependant as the beta isomer is continually converting into the stable alpha isomer. The two silicic acids differ due to variation in their ionic charges.

Beta molybdosilicic acid predominates during maximum colour formation at pH 1.2 -1.4 and below. Both beta and alpha acids are formed at pH 1.8 − 2.0. The absorbance of alpha acid increases with time at any pH value. The time dependence is minimized under strongly acidic conditions. Therefore the results obtained in acidic media are accurate.

Above a pH value of 3.6 the alpha form dominates and can be purely alpha. The alpha molybdosilicic acid absorbance increases with time at any given pH. This occurs due to the conversion of the unstable beta monomer to it.

The precision of the process is indicated by the RSD values. Generally the higher the pH of the system the lower the RSD value and the greater the precision. The rate of conversion of the beta isomer to the alpha isomer is greatly reduced due to the acidic medium and the ROOM temperatures in which the experiments were done.

Table 1. Concentration of total silica by ICP-AES

Solution #	Concentration of silica (ppm)
1	0.994
2	0.993
3	0.996
Mean	0.994
SD	0.002
RSD (%)	0.15

Table 2. Beta and alpha monosilicic acid concentration in µg L^{-1} determined by UV-vis spectroscopy at different acidic pH ranges

Sampled region of colloidal solution	pH range of the solution analyzed		
	0.8 - 1.0	1.2 - 1.4	1.8 - 2.0
Beta monosilicic acid			
Top	47.4	43.8	39
Middle	48.6	49.2	37.8
Bottom	50.4	52.8	38.4
X (mean)	48.8	48.6	38.4
SD	1.5	4.5	0.6
RSD	1.2	3.7	0.5
Total Beta %	87.1	86.8	68.6
Alpha monosilicic acid			
Top	3.4	5.45	14
Middle	8.0	8.5	11.9
Bottom	6.6	6.8	13.4
X (mean)	6.0	6.8	13.0
SD	2.4	1.6	1.2
RSD	1.9	1.3	0.9
Total Alpha %	10.7	12.2	23.3

Table 3. SiO$_2$ (%) in colloidal solution determined by precipitation and titration method (titre volumes are given in mL)

Sampled region of colloidal solution	pH range of the solution analyzed		
	0.8 - 1.0	1.2 - 1.4	1.8 - 2.0
Top	1.4	1.6	0.4
Middle	1.5	1.8	0.7
Bottom	1.6	1.4	4.1
X (mL)	1.5	1.6	1.7
SD	0.1	0.2	2.1
% SiO$_2$	80.4	85.7	92.9

Silica dioxide (SiO$_2$)

Titrimetric method was used to determine the amount of silica dioxide by alkaline fusion. The titrimetric values were multiplied by a fraction that is dependant on the experimental conditions to determine percentage. The experiment must be done as quick as possible as the longer it takes the more errors occur due to co-precipitation by other metal species Glaso O and Patzauver G (1961).

Three colloidal solutions were prepared in pH ranges of between 0.8 – 1.0, 1.2 – 1.4 and 1.8 – 2.0. They were left to stand and sampled at the top, middle and bottom and analysed for SiO$_2$ by precipitating it out of solution then titrating with NaOH.

Percentage of SiO$_2$ in solution was calculated as follows: % SiO$_2$ = 0.150 × mL NaOH/g of sample

Hence for the top sample: 1.4 mL NaOH titre, (Dilution factor × 500) % SiO$_2$ = (0.015 × 1.4/1.4) = 105/1.4 = 74%.

The stability of a system greatly affects the accuracy of the results obtained. For the pH region of 1.8 - 2.0 silica stability in solution reduces and the percentage of the compound increases. Therefore, the system exists at a meta-stable equilibrium with its monomer.
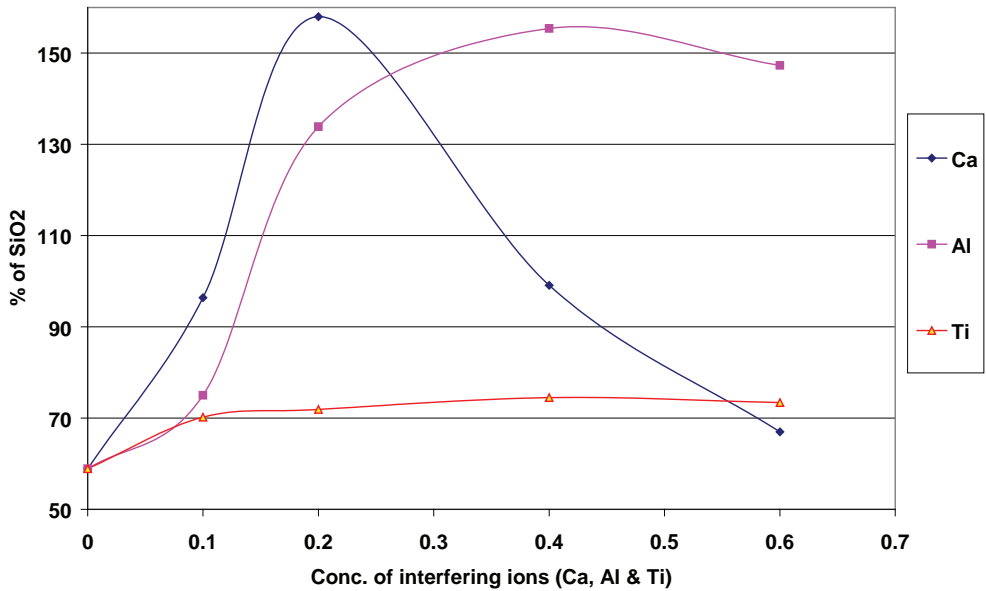
Figure 2 *Change in SiO2 percentage with increasing interfering ions concentrations*

Interferences

Metal ions present in solutions can cause interferences as they complex with silica dioxide and precipitate out as colloid. The positively charged ions electro-statically interact with the negatively charged surface of the colloid. Once the metal co-precipitates with silica it is incorporated into the colloidal structure and becomes difficult to extract during mining.

Silica solutions were spiked with various concentrations of interfering ions and then analysed. Calcium aluminium and titanium exhibited different trends as shown in fig. 2.

Calcium: Calcium causes an immediate exponential increase in the silica dioxide concentrations right from the start. It is the most reactive interfering ion. It appears that in any competition for fluoride ions, calcium is stronger than aluminium and titanium (fig. 2). There is a drastic decrease in % SiO_2 after 0.2 ppm for the calcium curve and this could be due to reversible attachment.

Aluminium: Initially aluminium causes a small increase in percentage silica dioxide but exponentially shots up at a concentration of about 0.1 ppm. At a slightly higher Al ion concentration of 0.2 ppm, % SiO_2 approaches a maximum value and stays constant with continued increase concentration.

Titanium: Of all the three metal ions investigated, titanium has the least influence in increasing silica dioxide concentration by co-precipitation. Initially there is a gradual increase in % SiO_2 and a maximum is rapidly reached. % SiO_2 stays relatively constant after an increase in titanium ion concentration of about 0.15 ppm.

Co-precipitation of SiO_2 occurs with calcium, aluminium and titanium in solution. This is due to the solubility constants of these compounds that are minimal. Calcium ions suppress the co-precipitation of aluminium and titanium. The lowest complexation occurs with titanium.

All the graphs show an increase the colloidal silica percentage to a maximum value and then decreases gradually as no more metal ions can complex by binding due to saturation of the binding sites. The calcium interference reached a maximum value and then decreased which indicates a reversible attachment to the colloidal silica.

Table 4. *Mean, standard deviation and relative standard deviation for various species analysed in the Skorpion leachate samples*

Sample	pH	Alpha	Beta	Silica ioxide (mg/L) dioxide	*Total Si (ICP-AES) (mg/L)
T1 Mean					
SD		0	0	0.26	0.27
RSD		0	0	0.21	1.26
T2 Mean					
SD		0	0	0.45	0.34
RSD		0	0	0.37	1.96
T3 Mean					
SD		0	0	0	0.31
RSD		0	0	0	1.77

Percentages (%) given in parenthesis, * Total Si after acid digestion

Silica speciation in leachate samples

Acid leachates of Skorpion samples at different pH values ranging from 0.8 – 2.0 obtained from Anglo Research Lab. were analyzed for alpha, beta and total silica, table 4.

Conclusions

Speciation of colloidal silica in acidic conditions was successfully achieved in this study. Various interfering ion species that co-precipitate with the silicon dioxide and increase the titrimetric values such as Ca (II), Ti (II) and Al (III) were assessed.

Good percentage recoveries, accuracy and precision were obtained for the methods used and they were applied to analyze leachates from acid leaching of silica at different pH values.

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