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Separation of Selenium from Sulfide Leach Liquors

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NOTE

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Abstract

Five different methods, namely, the extraction of selenium as the thiol complex, isolation as cuprous selenide, coprecipitation as lead selenite with lead sulfate, coprecipitation with arsenic as the collector, and cation exchange chromatographic method for the separation of selenium from sulfide leach liquors and discharge solution, were studied. Of the methods studied, cation exchange chromatography proved to be the most suitable method for the separation of selenium from leach liquors and discharge solutions.

INTRODUCTION

Many rare minerals containing selenium exist in the form of selenides which are analogous in composition to the sulfides. Also, selenium occurs as an impurity in many sulfide ores such as those of bismuth, copper, lead, mercury, and silver. Selenium is extracted along with other metals such as copper, nickel, and iron during the leaching of the sulfide ores. Usually one finds about 100 ppm of selenium in leach liquors as well as in metal-barren discharge solutions.

It is a well-known fact that selenium and its various compounds are extremely toxic and carcinogenic. The toxic symptoms produced by selenium in man and animals include depression, nervousness, giddiness, extreme fatigue, dermatitis, garlic odor of breath and sweat, and gastrointestinal disturbances (*1*). Therefore selenium should be separated almost completely from leach liquors and metal-barren effluents before discharging into the natural waterways.

A survey of the literature shows that methods such as the distillation of selenium as selenium tetrabromide, coprecipitation of selenous acid using ferric hydroxide, electrolytic deposition, and chelation using cupferron have been used for the separation of selenium from solutions of complex composition (*2*). These methods aside, Yoshino (*3*) used a cation exchange resin to separate the selenite ion from some metal ions present at low concentrations. The leach liquors containing Cu^{2+}, Fe^{3+}, and Ni^{2+} at considerably high concentrations present difficulty in the separation of low concentrations of selenium from the interfering metallic ions, and so far no method of separation of selenium has been applied to leach liquors. Hence a systematic study was undertaken on the separation of selenium from leach solutions, and the results are reported in this paper.

EXPERIMENTAL

Separation of Selenium as the Thiol Complex

The procedure described by Kovalskii (*4*) was followed to separate selenium as the dithiol complex. This method was applied for the separation of selenium from metal ions such as Cu^{2+}, Ni^{2+}, Fe^{3+}, and Co^{2+} present in leach liquors.

Separation as Cuprous Selenide

To each 10 mL of neutral Se(IV) solution add 5 mL of buffer solution (5 g of citric acid and 400 mg of $CuSO_4 \cdot 5H_2O$ adjusted to pH 4.5 and to 100 mL with aqueous ammonia) and 1 mL of 10% aqueous hydroxylamine sulfate solution and place a small funnel in the neck of the flask. Boil for 3 min, cool, and rinse the funnel and the walls of the flask with a few milliliters of methanol. Filler the contents through a microfilter stick (porosity 4). Wash the flask and the filter stick with 3 mL of water, then several times with methanol, and finally with 1 to 3 mL of water. This method separates selenium as cuprous selenide (*5*).

Return the filter stick to the flask, warm with 1 mL of nitric acid (d = 1.4), remove the stick, and wash it with water into the flask; the final volume of the solution should be $\nless 25$ mL. Shake the solution with 25 mL of diethyl ammonium diethyl dithiocarbamate solution (0.04% in CCl_4) and filter the organic phase through a dry filter paper into a 1-cm cell and measure the absorbance at 436 nm with CCl_4 as the blank.

Separation of Selenium as Lead Selenite

The procedure described by Jachwerth (*6*) was followed. The principle of the method of separation consists of coprecipitation of selenite as lead selenite with lead sulfate which is subsequently dissolved in ammonium tartrate solution and the solution analyzed for selenium by a modified spectrophotometric method using 3,3′-diaminobenzidine as the organic complexing reagent (*7*).

Separation of Selenium by Coprecipitation with Arsenic

To a suitable aliquot of selenium solution add 50 to 60 mL of 12 *M* HCl followed by 5 mL of sodium arsenite solution (0.5 g of As_2O_3 and 4 g of NaOH in 400 mL water) and 20 mL of hypophosphorus acid. Heat the solution to boiling and let it boil for 5 to 10 min. Cool and filter the solution through Whatman 42 filter paper and wash the precipitate with 6 *M* HCl for 6 to 8 times. This procedure separates the selenium from other ions. The selenium in the precipitate is determined by the modified spectrophotometric method with 3,3′-diaminobenzidine as the organic complexing reagent.

Cation Exchange Separation of Selenium

Fill an ion-exchange column 30 cm long and 2 cm in diameter with cation exchange resin Dowex-50 × 8 of 20–50 mesh. Pass the solution containing selenite, Cu^{2+}, Ni^{2+}, Fe^{3+}, and Co^{2+} through the ion-exchange column at a flow rate of 1 mL/min. Collect the effluent (75 mL) and analyze for selenium by the modified spectrophotometric method using 3,3′-diaminobenzidine as the organic complexing agent, as described below. Both the sulfide leach liquors and the discharge solutions were subjected to this ion-exchange procedure for the separation of selenium.

Place an aliquot of the sample solution containing 5 to 20 μg of selenium in a beaker and add 2 mL of 2.5 *M* formic acid followed by 10 mL of masking solution [0.1 *M* in EDTA, $(NH_4)_2C_2O_4$ and NH_4F] and 20 mL of water. Adjust the pH to 0.8 to 1.0. Add 2 mL of 0.5% diaminobenzidine solution and allow the solution to stand in the dark for about 2 hr. Then adjust the pH of the solution to 8.0 with ammonia and transfer the solution to a 125-mL separatory funnel. Add 10 to 12 mL of toluene (or benzene) and shake vigorously for a minute. After phase separation, discard the aqueous layer and transfer the organic layer into a 25-mL volumetric flask and make up the solution to the mark. Measure the absorbance of the toluene extract at 420.5 nm using a reagent blank subjected to the same procedure as the sample solution. Beer's law was found to hold good between 0 to 25 μg of selenium.

RESULTS AND DISCUSSION

Data obtained on the separation of selenium from synthetic solutions by separation methods such as the extraction as the thiol complex, isolation as the cuprous selenide, coprecipitation of lead selenite with lead sulfate, coprecipitation of selenium with arsenic as the collector, and cation exchange chromatographic method are presented in Table 1. Of the methods studied for the separation of selenium, the cation exchange chromatographic method gave the best separation (cf. Table 1) Coprecipitation of selenium with arsenic as the collector gave very low separation. In the case of separation of selenium as cuprous selenide, high recoveries of selenium were obtained. This may be due to the fact that the species isolated may be a mixture of cuprous selenide and some copper-bearing

TABLE 1

Data on the Separation of Selenium by Different Methods

Method	Recovery of selenium (%)
As thiol complex	85.8
As cuprous selenide	(143.0)
As lead selenite	87.3
Coprecipitation with arsenic	65.0
Cation exchange	98.1

TABLE 2

Data on the Cation Exchange Separation of Selenium

Composition of the solution		Recovery of selenium (%)
Leach liquor:		
Ni	4.1 g/L	98.0
Cu	3.9 g/L	
Co	0.2 g/L	
Fe	4.3 g/L	
Se	0.1 g/L	
Discharge solutions:		
Fe	0.1 g/L	102.0
SO_4^{2-}	7.0 g/L	
Se	0.1 g/L	

contaminants instead of pure cuprous selenide. Separation of selenium as the thiol complex and lead selenite gave recoveries of 85.8 and 87.3%, respectively, and no further improvements in the results could be obtained in repeated trials.

Experimental data on the separation of selenium in sulfide leach liquors and metal-barren discharge solutions using cation exchange chromatography are presented in Table 2. Although the separation of selenium as the thiol complex and coprecipitation of lead selenite with lead sulfate gave low recoveries of 85.8 and 87.3%, respectively (Table 1), these methods were applied to the problem of separation of selenium from sulfide leach liquors and metal-barren discharge solutions. These two methods gave poor separations and thus proved inadequate for the separation of selenium from leach liquors and discharge solutions. Cation exchange chromatography gave the best results for the separation of selenium from leach liquors and discharge solutions (Table 2), and the quality of the water obtained meets enviromental quality requirements.

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