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ANALYTICAL METHODS FOR THE DETERMINATION OF
SOME ELEMENTS AND Fe^{+2} TO Fe^{+3} RATIO IN
SIMULATED SLUDGES AND SYNROC FORMULATIONS

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ANALYTICAL METHODS FOR THE DETERMINATION OF SOME ELEMENTS AND Fe^{+2} TO Fe^{+3} RATIO IN SIMULATED SLUDGES AND SYNROC FORMULATIONS

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Abstract

Analytical methods for the determination of Fe, Al, Mn, Ca, Ni, Na, Sr, Cs, Ti, and Ba in simulated sludges and Synroc formulations are discussed. These are the elements that may be completed by atomic absorption spectroscopy, AAS. AAS methods are complicated by the dissolution methods used. These problems are discussed. In addition, the method used for the determination of Fe^{+2} to Fe^{+3} ratio is presented.

INTRODUCTION

The Synroc process proposes to immobilize high level wastes in a synthetic rock formed from a mixture of oxides, principally, TiO_2 , BaO , ZrO_2 , Al_2O_3 , and CaO .^{1,2} The high level waste species will be incorporated as components of dilute solid solutions in the crystal lattices of the constituent minerals, hollandite, zirconolite, and perovskite. In the development of the Synroc process, calculated amounts of TiO_2 , ZrO_2 , CaO , SiO_2 and BaO will be added to simulated sludges to form the desired mineral assemblage.^{3,4} Analysis of the simulated sludges is necessary to establish the required amounts of Synroc additives to form the desired mineral phases. The final product is also analyzed to insure a good mass balance and redox control of our process.

Dissolution of Sample

The SRP simulated sludge is composed of Fe, Al, Mn, Ca Ni, Na hydroxides, SiO_2 , and Na_2SO_4 that are easily dissolved with dilute HCl and small amounts of HNO_3 . SiO_2 does not dissolve and it may be determined by carefully evaporating the solution to dryness twice then redissolving with HCl and filtering the insoluble silicic acid. The other cations may then be analyzed in the filtrate.

DISCLAIMER

This course will examine the development of international law as a branch of the United States Government. To begin the study of international law, the student should be familiar with the history of the United States, including its political, economic, and social development, and its role in the world. The student should also be familiar with the history of the United States Government, including its political, economic, and social development, and its role in the world. The student should also be familiar with the history of the United States Government, including its political, economic, and social development, and its role in the world.

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The Synroc samples that are received for analysis are usually either calcined powders or crushed material from a hot pressing. These are usually very difficult to dissolve. These formulations usually contain Fe, Al, Mn, U, Ca, Ni, Si, Na, Sr, Cs, Ce, Nd, Ba, Ti, Zr oxides and Na_2SO_4 . We have found that a hot solution of H_2SO_4 with the addition of HF to be the most effective solvent. However, the fluorides of Ca, Sr, and Ba are not very soluble.

When the H_2SO_4 is taken to fumes to expel the HF, the titanium tends to hydrolyze, thus giving low titanium results. Even after expelling the HF, Ba and Sr sulfate are still insoluble. Therefore, we found that it is best to just take this solution to light fumes of H_2SO_4 , cool and carefully add water dropwise. HCl is then added to help keep the titanium in solution. This solution is then used to determine Fe, Al, Mn, Ni, Na, Cs, and Ti by AAS.

Ca, Sr, and Ba may be determined in Synroc calcined powders by treating another portion of the sample with a mixture of HCl and HNO_3 at least overnight. Titanium and zirconium oxide will not dissolve but the elements of interest will be in solution. Samples of hot pressed Synroc can not be treated in this manner because the mineral phases will have been formed and the individual oxides cannot be preferentially dissolved.

Synroc calcined powders and hot pressed and grounded material may also be dissolved with HCl, HNO_3 , and HF. This mixture requires a long digestion period to complete the dissolution.

Dissolution Procedure for SRP Simulated Sludge

1. Weigh about a 5 g sample into a 150 ml beaker.
2. Add 30 ml of deionized water and then add slowly 20 ml of concentrated HCl.
3. Add 2 ml of concentrated HNO_3 .
4. Evaporate to dryness overnight on a hot plate set at 100°C or on a steam bath.
5. Wet the residue with 5 ml of concentrated HCl and 15 ml of deionized water.

6. Evaporate to dryness again.
7. Wet the residue with 5 ml of concentrated HCl and 25 ml of deionized water.
8. Heat the solution to near boiling to dissolve all the salts.
9. Filter the insoluble silicic acid through fine filter paper (Whatman 42 or equivalent).
10. Receive the filtrate in a 200 ml volumetric flask and dilute to volume with deionized water.

Dissolution Procedure for Snroc Samples

1. Weigh about a 1-2 g sample into a 100 ml Teflon beaker fitted with a Teflon cover.
2. Add 20 ml of 1:1 H_2SO_4 .
3. Heat the solution to $100^{\circ}C$.
4. Carefully add 10 ml of concentrated HF with stirring.
5. Cover and digest at approximately $100^{\circ}C$ for about 3-4 hours.
6. Remove cover and continue heating until light fumes of H_2SO_4 appear or approximately $200^{\circ}C$.
7. Cool and add 10 ml of deionized water dropwise.
8. Add 10 ml of concentrated HCl.
9. Transfer to 100 ml volumetric flask and dilute to volume with deionized water.

Dissolution Procedure for Ca, Sr, and Ba Determination

1. Weigh about a 1-2 g sample into a 150 ml beaker.
2. Add 15 ml of concentrated HCl and 5 ml of concentrated HNO_3 .
3. Cover with watch glass and allow to digest overnight on a hot plate set at $70-80^{\circ}C$.
4. Then add 20 ml of deionized water and allow to warm for 2-3 hours more at the same temperature.
5. Transfer to a 100 ml volumetric and dilute to volume with deionized water.

Analytical Method for the Elements

Iron: AAS

Wavelength - 2483 Å

Light Source - Hollow cathode lamp

Flame Type - Air-acetylene flame, oxidizing (lean, blue)

Sensitivity - 0.1 µg Fe/ml for 1% absorption

Linear Working Range - The working range for Fe is linear up to concentrations of approximately 5 µg Fe/ml in aqueous solution.

Comments - The concentration of acid in the final dilution of sample should be matched as closely as possible in the standards. Normally there is a large quantity of iron to work with and a large dilution will have to be made for the iron determination. Thus it is convenient to make dilutions and standards in 1% HCl by volume, then the acid contributed by the sample solution may be neglected. The HF concentration in the sample solution should be low for the iron determination to avoid the formation of iron fluoride which might complicate the determination. Boric acid may be used to eliminate this problem. To eliminate this problem, 50 ml of saturated boric acid may be used in the original solution.

Aluminum: AAS

Wavelength: 3093 Å

Light Source: Hollow cathode lamp

Flame Type: Nitrous oxide - acetylene flame reducing (rich, red).

Sensitivity: 1 µg Al/ml for 1% absorption.

Linear Working Range: The working range for Al is linear up to concentrations of approximately 50 µg Al/ml in aqueous solution.

Comments: If the sample solution contains unknown concentrations of HF, it is best to make dilutions in a known excess of HF, such as 4% by volume. This is necessary because HF enhances the Al sensitivity. Aluminum is partially ionized in the nitrous oxide - acetylene flame. The ionization may be controlled by addition of alkali metal salts (1000-2000 µg/ml) to sample and standard solutions.

Manganese: AAS

Wavelength: 2795 Å

Light Source: Hollow cathode lamp

Flame Type: Air - acetylene flame, oxidizing (lean, blue).

Sensitivity: 0.06 µg Mn/ml for 1% absorption

Linear Working Range: The working range for Mn is linear up to concentrations of approximately 3 µg Mn/ml in aqueous solution.

Comments: The analysis of Mn by AAS appears to be interference free.

Calcium: AAS

Wavelength: 4227 Å

Light Source: Hollow cathode lamp

Flame Type: Nitrous oxide - acetylene flame reducing (rich, red).

Sensitivity: 0.05 µg Ca/ml for 1% absorption

Linear Working Range: The working range for Ca is linear up to concentrations of approximately 6 µg Ca/ml in aqueous solution.

Comments: The sample solution used for determining Ca should not contain any F^- . Calcium fluoride is only slightly soluble, and low results will be obtained in the presence of fluoride. Best results may be obtained by adding 0.5% La to sample and standards to control interferences and ionization of the calcium in the nitrous oxide - acetylene flame. Acid concentration of the standards should be matched with that of the samples.

Nickel: AAS

Wavelength: 2320 Å

Light Source: Hollow cathode lamp

Flame Type: Air-acetylene flame oxidizing (lean, blue)

Sensitivity: 0.2 µg Ni/ml for 1% absorption

Linear Working Range: The working range for Ni is linear up to concentrations of approximately 5 µg Ni/ml in aqueous solution.

Comments: Spectral interference may occur when using the 2320 Å nickel line. This may be minimized by closing the slits down as much as possible.

Sodium: AAS

Wavelength: 3302 Å

Light Source: Hollow cathode lamp

Flame Type: Air-acetylene flame oxidizing (lean, blue)

Sensitivity: 3 µg Na/ml for 1% absorption

Linear Working Range: The working range for Na is linear up to concentrations of approximately 200 µg Na/ml in aqueous solution.

Comments: The effects of ionization is reduced by the use of the secondary line, 3302 Å, so that the matching of ionization buffers in the standards is not necessary.

Strontium: AAS

Wavelength: 4607 Å

Light Source: Hollow cathode lamp

Flame Type: Nitrous oxide: acetylene flame reducing (rich, red).

Sensitivity: 0.1 µg Sr/ml for 1% absorption

Linear Working Range: The working range for Sr is linear up to concentrations of approximately 10 µg Sr/ml in aqueous solution.

Comments: The sample solution used for determining Sr should not contain any F^- nor SO_4^{2-} . Strontium fluoride and sulfate are only slightly soluble, and low results may be obtained in the presence of these ions. The addition of 0.5% La will control chemical interference from Si and Al and the use of the nitrous oxide flame will control chemical interferences even more.

Cesium: AAS

Wavelength: 8521 Å

Light Source: Hollow cathode lamp

Flame Type: Air-acetylene flame oxidizing (lean, blue)

Sensitivity: 1 µg Cs/ml for 1% absorption

Linear Working Range: The working range for Cs is linear up to concentrations of approximately 20 µg Cs/ml in aqueous solution.

Comments: Best results may be obtained by optimizing the instrument for the near infrared wavelengths, namely a grating more suitably blazed and a detector more responsive to the longer wavelengths. If this is

not possible, the use of an electrodeless discharge lamp may be necessary. Cesium has the lowest ionization potential of all the alkali metal. Thus, 1-2 mg/ml of another alkali metal salt, such as potassium chloride, should be added to both standards and samples to obtain accurate results.

Titanium: AAS

Wavelength: 3643 Å

Light Source: Hollow cathode lamp

Flame Type: Nitrous oxide-acetylene flame reducing (rich red)

Sensitivity: 2 µg Ti/ml for 1% absorption

Linear Working Range: The working range for Ti is linear up to concentrations of 200 µg Ti/ml in aqueous solution.

Comments: Titanium sensitivity is increased by many other cations, and the addition of 1-2 mg/ml of potassium chloride is often recommended. However, to ensure that all the titanium in the sample is dissolved the use of HF is recommended. Fluoride has also been noted to enhance titanium sensitivity. Therefore, we recommend making all solutions to contain 4% by volume HF as a means of correcting for this and other interferences.

Barium: AAS

Wavelength: 5535 Å

Light Source: Hollow cathode lamp

Flame Type: Nitrous oxide-acetylene flame reducing (rich, red).

Sensitivity: 0.5 µg Ba/ml for 1% absorption

Linear Working Range: The working range for Ba is linear up to concentrations of 30 µg Ba/ml in aqueous solution.

Comments: As discussed in the dissolution of samples, a HCl and HNO₃ leach of the sample will have to be used for the determination of Ba. An ionization buffer, such as 1-2 mg/ml of potassium chloride will have to be added to all the solutions to control ionization of the barium in the nitrous oxide flame.

DISCUSSION

Due to the differing chemistry of the elements in the Synroc formulation, a single true solution for all the elements was difficult to obtain. We did not resort to fusion methods of dissolution because the excess alkali metal introduced will complicate the subsequent AAS determinations. Using the above mentioned techniques, we were able to determine most of the elements in Synroc formulations.

The remaining refractory elements such as U, rare earths, and Zr were completed by X-ray fluorescence analyses. A description of this method is beyond the scope of this paper.

Determination of Iron⁺² to Iron⁺³ Ratio

The Fe⁺² to Fe⁺³ ratio is determined by a controlled - potential coulometric method.⁵ This analysis is necessary to determine the redox state of the calcined powders as well as the final hot-pressed Synroc sample.

Dissolution Procedure:

1. Place approximately 150 mg of grounded sample into a Teflon FEP bottle, fitted with an inlet purge gas tube, addition of reagent device, and gas exit hole. Purge with nitrogen.
2. Place 15 ml of water in with the sample and then carefully add 5 ml of concentrated H₂SO₄.
3. Bring mixture to a boil with an oil bath.
4. Then add 3 ml of concentrated HF.
5. After the sample appears to be dissolved (in about 15 minutes), add 3 g of H₃BO₃ dissolved in 60 ml of boiling water.
6. Cool the solution, turn off purge gas, and dilute to 100 ml with deionized water.

Controlled-Potential Coulometric Procedure:

1. Deoxygenate 0.5 M H₂SO₄ supporting electrolyte solution for 10 min. before carrying out electrolyses of Fe⁺³ or Fe⁺².
2. Precondition the Pt electrode at + 0.23 V vs SCE until the background current is less than 25 μ m.
3. Transfer a 10 ml aliquot of the sample solution into the platinum electrolysis cell and deoxygenate 5 min. more.

4. Determine the Fe^{+3} by reduction at + 0.23 V and terminate the electrolysis when the current reaches 25 μA .
5. Total Fe and/or Fe^{+2} can be determined by reoxidation at + 0.65 V.
6. This determination can also be carried out in 0.5 M HCl or HClO_4 with the reduction and oxidation potentials being + 0.30 and + 0.70 V vs SCE, respectively.

DISCUSSION

The sample redox condition may be determined by the Fe^{+2} to Fe^{+3} ratio. Therefore, complete dissolution of an exact amount of sample is not necessary for this analysis. Care must be taken during the grinding of the sample to avoid air oxidation of ferrous iron. Extreme fineness is not necessary and prolonged grinding should be avoided. Mesh size about 60 should be sufficient.

A more serious error is the possible oxidation of ferrous iron during the dissolution with HF. Fluorides form very slightly ionized complex ferric fluorides, and in the presence of excess fluoride the oxidation potential of the ferrous-ferric iron system is lowered to such an extent that air oxidation is very easy. Therefore, care must be taken to exclude oxygen during the dissolution with HF. After the sample is mostly dissolved, fluoride can be made harmless by the addition of boric acid, which forms fluoboric acid, thereby eliminating the possibility of air oxidation during the subsequent steps. The boric acid also prevents any possible interference of manganous salts, by preventing the formation of slightly ionized manganic fluoride.

Uranium does not interfere with the controlled-potential coulometric method. U^{+4} and U^{+6} are not reduced during the reduction of Fe^{+3} . Au^{+3} , Ag^{+1} , and Pt metals will interfere with this method.

Other classical oxidation-reduction titrations may also be used to complete the determination of Fe^{+2} . These are the titrations using cerium (IV),⁶ potassium dichromate,⁷ or potassium permanganate.⁸ However, all these titrations methods also oxidizes any U^{+4} that may be present. A correction for the uranium content will have to be made.

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