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REMOVAL OF SILICA FROM SOLUTIONS OF NUCLEAR FUELS

by

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ABSTRACT

By the addition of gelatin, small amounts of silica present in nitric acid solutions of metals can be flocculated for ready removal by filtration or centrifugation. In the processing of nuclear reactor fuels by solvent extraction, the prior removal of silica by gelatin reduces emulsification and solids accumulation without complicating product recovery, fission product removal, or waste disposal.

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INTRODUCTION

When reactor fuel is dissolved in acid, the solution contains varying amounts of dissolved and suspended silica that was originally present as impurities in the metals or as silicon in bonding alloys. Silica causes stable emulsions to form and solids to accumulate in the contacting equipment of the solvent extraction process.

In the course of development of a solvent extraction process at the Savannah River Laboratory, a precipitating agent was sought which would remove dissolved silicates or silicic acid, as well as colloidal silica, from aluminum nitrate - nitric acid feed solutions. It was necessary that the treatment be simple and economical and that it not interfere with product recovery, fission product behavior, or waste disposal.

SUMMARY

The introduction of gelatin to the extent of about 100 ppm of feed solution effectively flocculated the silica and facilitated its removal by centrifugation. Other soluble proteins reacted similarly, whereas their constituent amino acids did not. The flocculation probably involves hydrogen bonding between the silica and the peptide linkages of the proteins. The treatment with gelatin had no adverse effect on fission product behavior or uranium recovery. Conventional methods of feed clarification, including precipitation of MnO_2 and the use of synthetic polymeric flocculating agents, were found to be ineffective in removing the silica.

DISCUSSION

BEHAVIOR OF SILICA IN SOLVENT EXTRACTION

The occurrence of traces of solid materials in aqueous process solutions is a common problem in the recovery of irradiated nuclear fuels by solvent extraction. The magnitude of the problem depends on the nature and the amount of solid impurities present. Some of the difficulties which solids cause are:

1. The formation of emulsions in the liquid-liquid contacting equipment, limiting throughput rates and contactor efficiency.
2. The accumulation of solids, or "cruds," in the contacting equipment. These accumulations frequently absorb fission products and become highly radioactive. The increased radiation level accelerates the radiolysis of the solvent.
3. Limitation of the decontamination achieved in the process. This may result from the solvent degradation or breakthrough of radioactive particles into product streams.

To avoid or lessen these interferences, solvent extraction processes usually include a preliminary step for feed clarification. Digestion, filtration, centrifugation, scavenger precipitation, or a combination of these operations are customarily used in a "head-end" step to remove suspended solids.

One of the most troublesome impurities encountered in acidic systems is silica. Silica arises from impurities in the core or cladding metals, and from silicon in bonding alloys. For example, 2S aluminum, which contains about 0.1% silicon, is frequently used as a cladding material for uranium or thorium; aluminum-silicon alloy is commonly used to bond the cladding to the core. Although elemental silicon is ordinarily thought to be insoluble in concentrated sulfuric or nitric acids, it does dissolve slowly in boiling nitric acid. Prolonged exposure to acid conditions leads to polymerization and coagulation of the silica. Thus, a feed solution from which the solids have been removed may at a later time form a precipitate of silica, due to slow conversion of soluble silicic acid to insoluble silica polymer. Another troublesome property of silica and silicic acid is their tendency to form organic complexes. Preparations of complexes between silicic acid and polar organic compounds, such as triethyl phosphate and tributyl phosphate, have been described⁽¹⁾. This property accounts for the tendency of silica to seek the organic-aqueous interface in tributyl phosphate extraction systems, and thereby to induce the formation of emulsions or "cruds." The ability of silica particles to absorb fission product zirconium and niobium is well known. Silica has been mentioned in connection with a number of processes as an impurity which interfered seriously with process performance⁽²⁾.

EXPERIMENTAL PROCEDURE

Potential treatments for removing silica were screened by a series of laboratory tests with nonradioactive solutions. The behavior of the more promising candidates was then observed in a miniature mixer-settler. Those treatments that gave solutions that mixed and settled satisfactorily were tested finally by application to radioactive dissolver solution being used as feed to a cascade of miniature mixer-settlers.

The preliminary tests used in screening reagents were the following:

1. The treated solutions were examined under a strong light beam. A distinct Tyndall effect was observable from the colloidal silica. Changes in particle size induced by a given treatment were readily detected.
2. The total silica content of a sample was determined. The solution was acidified to 3N HNO₃ and boiled under reflux for 24 hours. This digestion was shown to precipitate all of the suspended, as well as dissolved, silica.
3. An emulsification test was made with the TBP-kerosene solvent and the treated solution.

RESULTS AND CONCLUSIONS

A large variability in the behavior of silica was encountered in different batches of feed solution. Samples of feed solution were made by dissolving U-Al alloy in 6N HNO_3 containing 0.005M $\text{Hg}(\text{NO}_3)_2$ to produce a solution with the approximate composition: 1.2M $\text{Al}(\text{NO}_3)_3$, 0.5N HNO_3 , 0.01M $\text{UO}_2(\text{NO}_3)_2$. The fuel elements contained between 0.5 and 1% Si. The feed solutions were found to contain between 10 and 100 ppm of SiO_2 . In addition to variations in the total silica content, changes in the ratio of dissolved silica to colloidal or polymerized silica were found to be important in determining the behavior of solutions in solvent extraction. Thus, a feed solution containing silica which was largely present as particles of filterable size was successfully clarified by passage through a bed of diatomaceous earth; whereas a solution in which the silicon was present largely in solution as polysilicic acid performed badly in solvent extraction after passage through the same filter bed. This variability was also shown by the fact that it was impossible to classify sample quality by a photonephelometer; a measure of suspended silica gave no indication of total silica content. Some of the factors which affect the distribution of silica species are the dissolution conditions, the composition of the dissolver solution, and the age of the solution.

The materials tested for silica removal are listed in Table I. Electrolytes, complexing agents, adsorbents, scavenging precipitates, flocculating agents, resins, and gums were tested. In addition, silica itself was added in various forms to saturate the solution and to encourage the growth of large particles. Included in the tests of scavenging agents were conventional "head-end" precipitations of manganese dioxide. This treatment was ineffective in removing silica⁽³⁾. The only successful additives found were sodium fluosilicate, fluosilicic acid, and gelatin. The fluosilicate was introduced as a soluble salt or acid and was subsequently hydrolyzed to silica, which was removed by centrifugation. The formation of one gram of silica per liter of feed was sufficient to clarify the feed. This clarification procedure required the complete destruction of the fluosilicate ion since excess reagent was shown to be detrimental in subsequent process steps. The objectionable feature of this treatment is that complete hydrolysis of the fluosilicate required as much as an 8-hour digestion at the boiling point at fairly high acidities.

Gelatin was the most efficient flocculating agent found. It was introduced as a 1% aqueous solution to the extent of about 100 mg of gelatin per liter of feed. Flocculation of the silica occurred at room temperature; it was accelerated by a brief period of heating and gentle agitation. Vigorous stirring and prolonged boiling of the solution dispersed the floc, but it readily coagulated again on standing. The resulting precipitate was readily filtered or centrifuged from the solution. Excess gelatin left in solution had no detrimental effect on the performance of subsequent solvent extraction steps. Tests with radioactive feed solutions showed that the excess gelatin remaining also had no adverse effect on fission product behavior. The silica-gelatin precipitate scavenged up to 50% of the zirconium-niobium from solution, providing a useful decontamination. Uranium absorbed on the precipitate was quantitatively removed by washing with dilute acid.

The photographs in Figure 1 show the progress of a typical gelatin treatment. The beaker in the first picture contains 300 ml of untreated feed

solution. The second exposure shows the same solution 90 seconds after stirring 2 ml of 1% gelatin solution into the feed (gelatin concentration in feed, 70 ppm); the third 5 minutes later; the fourth 30 minutes later. The solution used for this demonstration contained about 250 ppm silica, which was somewhat more than that in the average solution tested.

The photographs in Figure 2 show the improvement in the emulsifying behavior of a solution treated with gelatin. The bottle on the left in each pair contains the solution clarified by gelatin treatment, the one on the right contains untreated feed. The exposures were made 20 seconds, 90 seconds, and 3-1/2 minutes after vigorous agitation with an equal volume of 30% tributyl phosphate in dodecane.

The reaction between gelatin and polysilicic acid to form an insoluble complex probably involves hydrogen bonding between the peptide nitrogens of the gelatin and the siloxane oxygens of the polysilicic acid, or the silonal groups on the surface of colloidal silica particles⁽⁴⁾. These two bonds are illustrated in the following diagram.

The formation of a multiplicity of such bonds between the relatively large molecules of gelatin and polysilicic acids leads to a mixed network of these molecules, and eventual separation of the aggregates from solution. The conditions that are required for complete flocculation in a given solution will depend on the average initial molecular weights of both the polysilicic acid and the gelatin. The acidic and highly salted solutions considered in this work probably were especially suited to form complexes between silica and gelatin, because the high acidity favored polymerization of the silicic acid to units of high molecular weight, and the high salt content tended to dehydrate the gelatin, allowing silica to compete more favorably with water for the reactive sites.

A variety of soluble proteins in addition to gelatin were tested for flocculating activity with silica. In addition, several simple amino acids were tested. These are listed in Table II. None of the amino acids showed any tendency to precipitate the silica from the feed solutions. On the other hand, all of the proteins did form precipitates which removed silica from the solutions to a greater or less extent. The amino acids, glycine, proline, and hydroxyproline are the predominant constituents of gelatin. Leucine was chosen as a neutral amino acid of relatively high molecular weight; arginine as a basic

amino acid; and aspartic and glutamic as acidic amino acids. If there was any reaction between the amino acids and the polysilicic acid or the silica colloid, it did not yield insoluble products. It is thus necessary for the constituent amino acids to be linked as polypeptides of relatively high molecular weights. None of the proteins tested reacted with the silica colloid as rapidly as gelatin. In most cases it was necessary to heat the solutions to boiling to effect precipitation.

The failure of the commercial polymeric flocculating agents (listed in Table I) to remove silica from the feed solutions is consistent with the negative results obtained by LaMer⁽⁵⁾ and co-workers. They reported that otherwise superior flocculating agents, made by cross-linking polyacrylamide with formaldehyde, were ineffective when applied to silica slimes. The use of gelatin as a flocculating agent may have application to various industrial filtering and settling operations involving siliceous slimes.

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TABLE I

MATERIALS TESTED FOR SILICA REMOVAL

Electrolytes

Calcium Nitrate
Barium Nitrate
Dibasic Sodium Phosphate

Complexing Agents

Potassium Fluoride
Ammonium Molybdate
Sodium Tungstate
Silicotungstic Acid

Coagulants

Gelatin
Gum Arabic
"Separan" 2610 (Dow Chemical Co.)
"Aerofloc" 552, 3000, S-3100, S-3019 (American Cyanamid Co.)
"Span" 20, 80, 85 (Atlas Powder Co.)
"Nopco JMY" (Nopco Chemical Co., Inc.)
"Jaguar" A-20-A (Stein-Hal & Co., Inc.)
Mini Guar Gum (Morningstar-Nicol, Inc.)

Silica

"Celite" Diatomaceous Earth (Johns-Manville)
Silicic Acid
Silica Gel
Sodium Metasilicate
Sodium Fluosilicate
Fluosilicic Acid
"Santocel" (Monsanto Chemical Company)
"Ludox" (du Pont Co.)

Adsorbents or Scavengers

Aluminum Oxide
Aluminum Hydroxide
Colloidal Zirconia
Manganese Dioxide

Resins

"Duolite" A-102 (Chemical Process Co.)
"Geon" Resins (B. F. Goodrich Chemical Co.)

TABLE II

TEST OF SUBSTANCES RELATED TO GELATIN

<u>Amino Acids</u>	<u>Proteins</u>
Glycine	Egg Albumin
Leucine	Casein
Proline	Lactalbumin
Hydroxyproline	Rennin
Arginine	Pepsin
Aspartic Acid	
Glutamic Acid	

FIGURE 1

0 SECONDS

90 SECONDS

5 MINUTES

30 MINUTES

TYPICAL FLOCCULATION OF COLLOIDAL SILICA WITH GELATIN

FIGURE 2

20 SECONDS
AFTER SHAKING

90 SECONDS
AFTER SHAKING

3.5 MINUTES
AFTER SHAKING

EFFECT OF GELATIN TREATMENT ON THE EMULSIFICATION BEHAVIOR