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REMOVAL OF SILICA FROM DAREX DISSOLVER SOLUTIONS

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ABSTRACT

The nature and behavior of silica in Darex dissolver solutions were found to be dependent on solution temperature, the length of time the solution was maintained at temperature, and the concentration of fluoride in the solution. A fluoride-gelatin treatment essentially completely precipitated silica from the dissolver solution, but the precipitate packed on the filter surface and greatly decreased the solution filtration rate.

CONTENTS

1.0 INTRODUCTION

This report is a summary of work on removal of silica from Darex (dilute aqua regia dissolvent) solution immediately after dissolution of stainless steel—uranium or stainless steel—UO_2 fuels. The silica must be removed[2] to prevent formation of emulsions at the organic interface in the subsequent solvent extraction process. The chloride must also be removed, and in other proposed[1] methods the chloride is removed first. However, during chloride removal the silica is converted from a fine granular material of 50% SiO_2 to a gel of 3% SiO_2 with a large increase in solids volume. Prior silica removal therefore could have several advantages.

The nature of the silica and the effect of digestion temperature and time and fluoride concentration on its behavior in Darex solutions were studied. Various reported[3-9] reagents and methods of solution treatment for converting silicious material to an easily removed form were investigated.

The authors acknowledge the assistance of E. R. Johns with the laboratory experiments and are indebted to G. R. Wilson and staff of the ORNL Analytical Chemistry Division for analyses performed.

2.0 EXPERIMENTAL STUDIES

The most effective method of silica removal from Darex dissolver solutions and the one that shows the most promise combines a fluoride and gelatin treatment. A 15-min digestion at 95-100°C with 0.01 M fluoride followed by cooling to 80°C and addition of 0.15 g of gelatin per liter resulted in complete and immediate separation of silica from solution in a form that was removed on a 30-70 mesh graded sand filter. Though the volume of the solid was roughly 5% of that obtained after chloride removal, it was very difficult to filter. Further study of filtration methods is needed. The rate of hydration and growth of SiO_2 particles was directly dependent on the temperature of the solution, the length of time the solution was at this temperature, the concentration of fluoride in the solution, and apparently the concentration of chloride in the solution. During removal of chloride from a dissolver solution, the silica was converted from <14-μ-dia particles of 50% SiO_2 content to large particles of 3% SiO_2 gel with a 15- to 30-fold increase in the occupied volume of solids. Approximately 98% of this silica was removed on a 30-mesh sand filter. If a Darex dissolver solution is digested 3 hr at 95-100°C with no fluoride added, 96% of the silica is removed as 12% SiO_2 particles by filtration through a filter with an effective pore size of 14 μ. The volume of the precipitate produced by this treatment was only 25% of that obtained when the filtration was performed after the chloride removal step.

2.1 Conditions Affecting Silica Behavior in Darex Dissolver Solutions

The percentage of the total silica present in Darex dissolver solutions retained by a Corning medium glass-frit filter and the percentage of SiO_2 in the undried retained particles was dependent on the fluoride concentration and the time and temperature of solution digestion.

In solutions digested 2 hr at 80-85°C, increasing the fluoride concentration from 0 to 0.008 M increased the silica removal from 55 to 98% and decreased the SiO_2 content of the retained solids from 80 to 11% (Table 2.1, Fig. 2.1). At 95-100°C, increasing the fluoride from 0 to 0.004 M increased the removal of silica from 90 to 97% and decreased the SiO_2 content of the solids from 14 to 9%.

Table 2.1 Effect of Fluoride Concentration on Silica in Darex Dissolver Solutions

Digestion time: 2 hr
Composition: 1.17 M HNO_3, 1.75 M HCl, 60 g of APPR fuel and 1.8 g of SiO_2 per liter

Temperature, °C	Fluoride Concentration, M	Silica Removal, %	Precipitate Composition, % SiO_2
80-85	0.000	55	80
	0.002	69	70
	0.004	73	50
	0.006	93	13
	0.008	98	11
95-100	0.000	90	14
	0.001	92	15
	0.002	94	12
	0.004	97	9

With a digestion time of 2 hr and no fluoride present, as the temperature increased from 80 to 100°C, silica removal increased from 55 to 90% and the SiO_2 content of the solids decreased from 80 to 14%. With 0.004 M fluoride present, as the temperature varied from 60 to 100°C, silica removal increased from 40 to 97% and the SiO_2 content of the solids decreased from 88 to 9% (Table 2.2, Fig. 2.2).

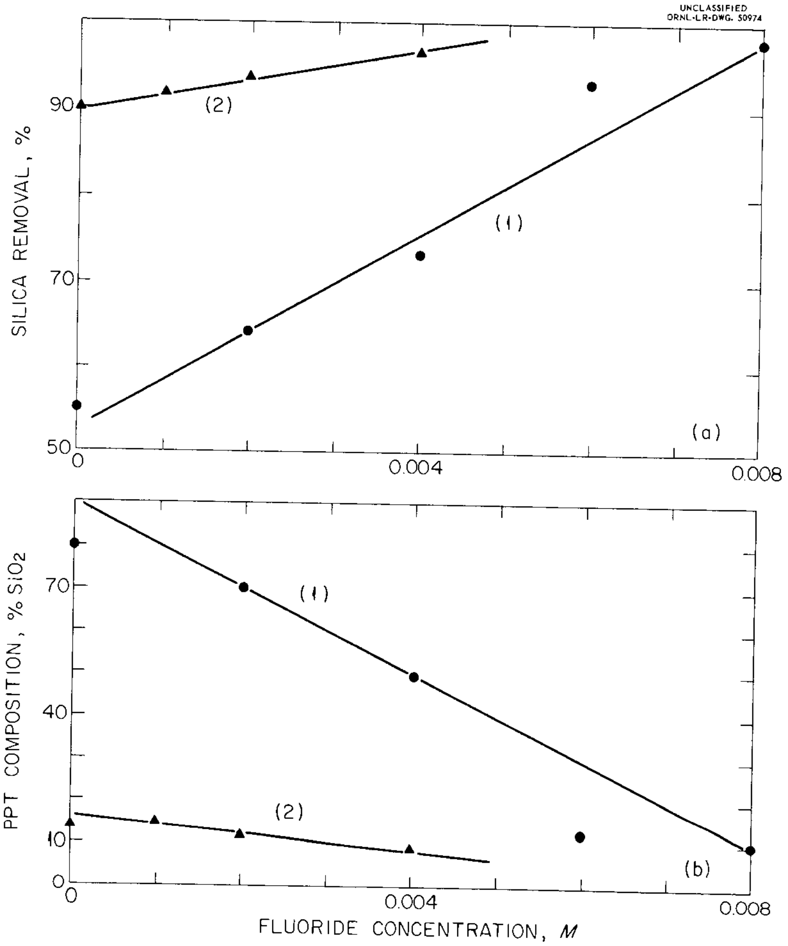

Fig. 2.1. Effect of fluoride concentration on (a) silica removal from fuel solution and (b) composition of silica precipitate. Solution: 1.17 M HNO_3, 1.75 M HCl, and 1.8 g of SiO_2 and 60 g of APPR prototype fuel per liter plus fluoride; digested 2 hr at (1) 80-85°C and (2) 95-100°C and then filtered through Corning medium glass-frit filter.

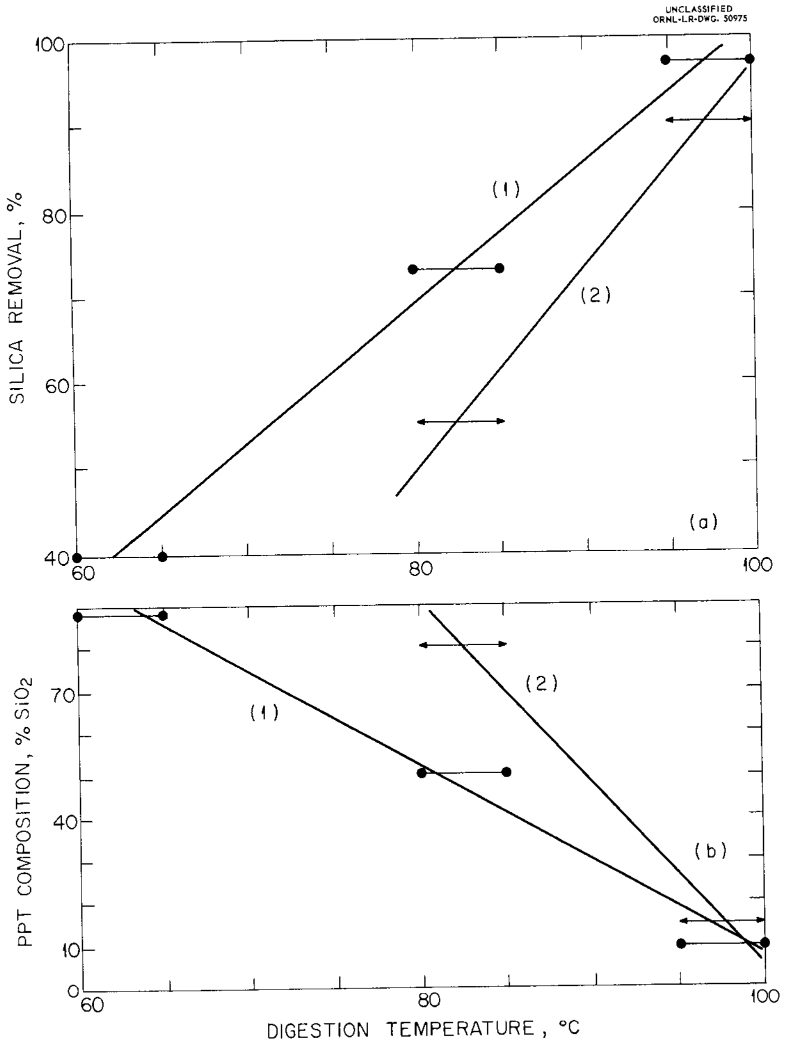

Fig. 2.2. Effect of digestion temperature on (a) silica removal from fuel solution and (b) composition of silica precipitate. Solution: 1.17 M HNO_3, 1.75 M HCl, and 1.8 g of SiO_2 and 60 g of APPR prototype fuel per liter plus 0.004 M fluoride for curves 1; and no fluoride on curves 2. Solution digested 2 hr and then filtered through Corning medium glass-frit filter.

At 95-100°C with no fluoride present, as digestion time was varied from 0.75 to 2 hr, silica removal increased from 66 to 90% and the SiO_2 content of the solids decreased from 53 to 14% (Table 2.3, Fig. 2.3). With 0.004 M fluoride, as the digestion time was varied from 0.5 to 2 hr, SiO_2 removal increased from 70 to 97% and the SiO_2 content of the solids decreased from 80 to 9%.

Table 2.2 Effect of Temperature on Silica in Darex Solutions

Digestion time: 2 hr
Composition: 1.17 M HNO_3, 1.75 M HCl, 60 g of APPR fuel and 1.8 g of SiO_2 per liter

Fluoride Concentration, M	Digestion Temperature, °C	Silica Removal, %	Precipitate Composition, % SiO_2
0.000	80-85	55	80
	95-100	90	14
0.004	60-65	40	88
	80-85	73	50
	95-100	97	9

Table 2.3 Effect of Digestion Time on Silica in Darex Solutions

Digestion temperature: 95-100°C
Composition: 1.17 M HNO_3, 1.75 M HCl, 60 g of APPR fuel and 1.8 g of SiO_2 per liter

Fluoride Concentration, M	Digestion Time, hr	Silica Removal, %	Precipitate Composition, % SiO_2
0.000	0.75	66	53
	1.50	81	22
	2.00	90	14
	3.00	96	12
0.004	0.50	71	80
	1.00	79	65
	1.50	88	15
	2.00	97	9

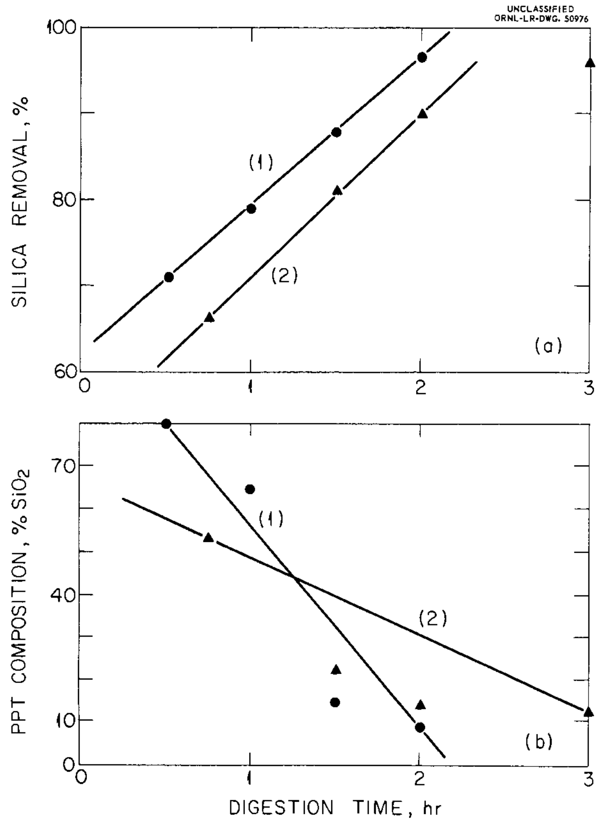

Fig. 2.3. Effect of digestion time on (a) silica removal from fuel solution and (b) composition of silica precipitate. Solution: 1.17 M HNO_3, 1.75 M HCl, and 1.8 g of SiO_2 and 60 g of APPR prototype fuel per liter plus 0.004 M fluoride for curves 1 and no fluoride for curves 2. Solution digested at 95-100°C and then filtered through Corning medium glass-frit filter.

2.2 Silica Removal from Darex Dissolver Solutions

Of the reagents and methods investigated, treatment with fluoride in conjunction with gelatin addition was the most effective for removing silica from solution. Other reagents were ineffective and/or impractical. Gelatin and fluoride used separately removed only about 60% of the silica from solution after 2 hr. Additives (2-4 g/liter), added to the solution as a filter aid or to the filter as a precoat, e.g., Cellite-545, alumina, aluminum nitrate, and silica gel, were all ineffective in removing silica, as was freezing the solution. As a result of three scouting experiments, the use of ammonium molybdate and ammonium tungstate was judged impractical because of the quantities of reagent required and the bulk of precipitate generated.

Three 250-ml samples of a fresh Darex dissolver solution were digested 15 min at 95-100°C in the presence of 0.01 M fluoride. After the digestion, 0.15 g of gelatin and 6.0 g of Cellite-545 per liter were added (a) immediately, (b) after cooling the solution to 90°C, and (c) after cooling to 80°C. The solution was then filtered through 30-70 mesh graded sand, precoated with Cellite-545 and having a surface area of 2.8 cm^2. Approximately 6 min, 1 hr, and 5 hr were required for the respective filtrations with corresponding silica removals of 90, 95, and 98%. The SiO_2 content of the solid was not determined.

Fluoride ion was the most effective single agent for silica coagulation and removal from freshly prepared Darex solutions. With a fluoride concentration of 0.01 M, after 15 min digestion and cooling to 40°C, 98% of the silica was retained on a 30-mesh sand bed as a 4% SiO_2 gel. With a fluoride concentration of 0.004 M, approximately 35% of the silica was removed on a Cellite-precoated sand bed while about 60% of the silica was removed from a similar solution on a Corning medium glass-frit filter as a 50% SiO_2 material. Refiltering the latter filtrate after 1 day removed the remaining silica as a 9% SiO_2 gel.

Gelatin alone was only partially effective in removing silica from solution. When 0.4 g of gelatin per liter of solution was added to the hot fuel solution and the solution was cooled to 40°C, approximately 50% of the silica was removed on a Cellite-precoated sand bed as a 23% SiO_2 precipitate. Filtration of a similarly prepared solution through a Corning medium glass-frit filter removed about 60%. No further silica was removed after 24 hr aging at room temperature.

2.3 Nature of Silica in Darex Solutions Before and After Chloride Removal

When freshly prepared, the silica particles in Darex dissolver solutions ranged in size from <5 to >14 μ and are essentially anhydrous. Immediately after dissolution ~40% was retained on a Corning medium glass-frit filter (14 μ effective pore diameter), and the remainder passed through a Corning fine glass-frit filter (5 μ effective pore diameter). From the time of dissolution an action that increases particle size, probably hydration, proceeds slowly at room temperature. When the solution was allowed to stand

24 hr at room temperature, 97% of the silica settled out as a solid of 50% SiO_2 content, and the percentage retained by a medium filter was increased from 40 to 60.

Particle growth (or hydration) rate is increased by digestion of the solution at increased temperature by the presence of fluoride ions (Sects. 2.1, 2.2, and 2.3) and apparently by the chloride ion. In the Darex process, during chloride removal by evaporation the silica is converted from small particles of 50% SiO_2 content to large gel particles of 3% SiO_2. Prior to chloride removal, with no digestion, more than 90% of the silica passed through a 30-mesh sand filter, and the amount was not significantly decreased by the addition of 2-4 g of Cellite-545 per liter to the solution as a filter aid or to the filter as a precoat.

3.0 EQUIPMENT AND PROCEDURE

3.1 Equipment

All-glass equipment was used in this study. Dissolutions were performed in a 1-liter 3-neck flask surrounded by a Glas-Col heater. The top of the flask was fitted with a reflux condenser, a mechanical stirrer, and a thermowell. Solution was removed through a short length of glass tubing and a stopcock on the flask bottom. Solution temperature was maintained by a thermocouple and a Wheelco controller.

Two filters were used in the study. The first was a vacuum flask equipped with a Corning fritted glass filter. The second was a 4-in. sand bed (30-mesh or 30- to 70-mesh graded sand) contained in a 12-in. thistle tube 2.8 cm^2 in cross section.

3.2 Procedure

The normal procedure followed in this study was dissolution of a 15-g sample of a prototype APPR fuel element in 260 ml of 5 $\underline{M}$ HNO_3-2 $\underline{M}$ HCl at 100°C. Approximately 15 min was required for complete dissolution of the sample. When used, fluoride was added as an aqueous solution of NaF and digestion was then carried out at the desired temperature for the desired length of time. Except where otherwise stated, filtrations were made at the temperature of digestion. When the rate of filtration through sand was determined, a 6-in. head was maintained above the sand bed. In all filtrations solids were held in suspension by mechanical stirring.

The composition of the initial Darex dissolver solutions used was approximately the same as that recommended for the Darex-APPR flowsheet: 55 g/liter 304 stainless steel, 4.3 g/liter uranium, 1.17 $\underline{M}$ HNO_3, 1.75 $\underline{M}$ HCl, and 1.8 g/liter SiO_2.

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