THE EFFECT OF SILICON IN THE REPROCESSING OF A URANIUM ALUMINUM ALLOY

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Date Report Written

May 10, 1958

Chemical Development Section
CPP Technical Branch

PHILLIPS PETROLEUM COMPANY
Atomic Energy Division
AT (10-1) -205

IDAHO OPERATIONS OFFICE
U. S. ATOMIC ENERGY COMMISSION

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A B S T R A C T

The insoluble residues produced during the reprocessing of certain nuclear fuel elements containing aluminum, silicon, and uranium were investigated with respect to particle size, shape and distribution, composition, and surface active tendencies.

w/o The fuel material samples studied contained from 0.4 to 7.0 percent silicon by weight (the high analysis represents a cast base AlSi alloy). The fuel materials were dissolved in mercury-catalyzed nitric acid. Two types of solid residue were produced by actual fuel dissolution. One was a finely divided material, brown in color and the other was black, crystalline material relatively large in size. Only the black crystalline material was obtained when cast AlSi was dissolved in nitric acid. Spectrographic analysis of the residues showed that silicon and aluminum were the major constituents. X-ray Diffraction analysis of each type indicated the presence of elemental silicon only. The x-ray pattern obtained with the brown material showed lower intensities indicating the presence of amorphous material. Under a magnification of 970 diameters, the crystals observed appeared to be non-uniform, shallow platelets of irregular shape. The bulk of the residue is removed by a 10-micron filter; however, the resulting filtration rates are very low, (2.0 gallons per hour per square foot). Sedimentation data of typical dissolver solution showed that about 20 percent of the silicon particles have equivalent diameters of 20 microns or greater, that 25 percent have equivalent diameters between 10 and 20 microns and the remaining have equivalent diameters of less than 10 microns. Dispersion-coalescence data disclosed minor surface active tendencies which appear to be insufficient to cause unusual extraction column operation. The particle size, distribution, and surface active tendencies were not affected by aging.

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I. INTRODUCTION

The excellent bonding characteristics of alloys containing silicon have led to their increased usage in aluminum-uranium fuel fabrication and have necessitated a determination of the effect of silicon on the uranium recovery process. When fuel elements containing aluminum, silicon and uranium are dissolved in nitric acid, the silicon remains as an insoluble residue. Because of its potentially abrasive characteristics and bulk, this residue could be very detrimental to any system incorporating moving parts. If this silicon is surface active, it could limit the proper functioning of an extraction column by causing flooding or by forming a stable interface which could absorb fission products. The actual occurrence or severity of these effects in the process will be due, primarily, to the silicon concentration in the fuel, the particle size, the frequency at which the system is flushed or the column interfaces jetted, the presence of organic materials which would serve to bond the particles; and secondarily, by the operating conditions, flow rates and shut down periods which would control sedimentation time and aging periods.

II. SILICON CONTENT CONTROL OF PROCESS SOLUTIONS

Certain fuel elements may be fabricated by inclosing a uranium-aluminum alloy in aluminum cladding and using an aluminum-silicon alloy (for bonding or sealing purposes either as a film or in bulk). Additionally, silicon may be incorporated in aluminum either as a natural result of the manufacturing process or deliberately in larger amounts to control workability and strength. Typical over all contents may range in different areas from 0.4 percent by weight to 4.0 percent by weight. The silicon concentration that could be attained in the dissolution process of an entire fuel element of such varying composition would be intermediate in this range. It was conceived that such amounts could give rise to the problems mentioned in the introduction. However, the silicon concentration in the process solutions might be significantly reduced by cutting off high silicon areas to the dissolution. However, to avoid possible loss of minor amounts of uranium it might be desirable to process the high silicon areas separately. Consequently, it was deemed

necessary to investigate the effect of a wide range of silicon concentrations.

It would also be feasible to use filters after dissolution in order to remove part or all of the silicon from the feed stream. Filtration would prolong process cycle times and reduce production capacity.

III. METHODS OF INVESTIGATION

In order to exaggerate the potential process problems, the high silicon areas were chosen as the fuel source for the investigation because they represented the extreme condition.

The silicon content of this portion of the fuel element was computed from geometric measurements and these results were verified by the analysis of the fuel dissolver solutions. Microscopic and macroscopic observations and spectrographic and X-ray diffraction analyses were made of the solid residues. Particle size distribution was investigated by filtration experiments and sedimentation studies. The surface active tendencies of the solid residue were investigated by means of dispersion-coalescence experiments and fission product adsorption studies.

A. Fuel Analysis

By using the manufacturer's specifications and the geometry of the fuel elements, the silicon content of the high silicon areas was found to be 4.14 percent by weight. Gravimetric analysis of two coupons showed the silicon content to be 4.15 percent by weight. This percentage of silicon in the fuel would lead to a dissolver solution having 2.99 milligrams of silicon per milliliter of solution. Spectrographic analysis of ashed samples of actual fuel pieces dissolver solutions gave an average silicon concentration of 2.9 milligrams per milliliter. Among eight samples tested the concentration varied, however, from 5.2 to 1.6 milligram per milliliter with a mean deviation of 0.69.

B. Dissolution

The dissolution of the high silicon areas of the fuel element was conducted by cutting coupons from five different elements. Each coupon weighed approximately 56 grams, contained approximately two moles of aluminum, and by flowsheet proportions produced approximately two liters of dissolver solution. The dissolutions were made using a 4.4 nitric acid-to-fuel mole ratio and were conducted at 100° C. A typical dissolver solution composition was 1.20M aluminum nitrate, 0.98M nitric acid and .009M mercuric nitrate. D2 and D3 were coupon dissolutions of fuel element number one; D4, D5, and D6 of element number two; D7, D8, and D9 were of elements number three, four, and five, respectively. Each coupon had approximately the same surface area. Coupons from the same element were adjacent sections taken either parallel or normal to the direction of the extrusion.

The solid particles produced by these dissolutions were of two distinct types and occurred in varying amounts. One was composed of relatively large grayish-black particles while the other was composed of very small brown particles. Spectrographic analysis of the solid residues showed greater than 80 weight percent silicon with the remainder aluminum. X-ray diffraction showed more evidence of crystalline elemental silicon in the grayish-black particles than in brown particles.

Dissolutions were also made of the cast AlSi alloy which is used in fuel fabrication (7 percent Si). The rate of dissolution of AlSi was very slow compared to the dissolution rate of the actual fuel in the same dissolving medium. The solid particles obtained were of only one type, the grayish-black variety. By heating the cast AlSi beyond its annealing temperature and then rolling, the material was given extruded characteristics. This treatment did increase the dissolution rate but the solid particles produced were still of only the grayish-black type. It was concluded that neither the cast nor rolled AlSi was representative of the silicon in the actual fuel element.

C. Microscopic Study

When viewed under the microscope with a magnification of 970 diameters, the solids appeared to be non-uniform shallow platelets of irregular shape. The very small crystals are often transparent and light orange in color.

D. X-ray Diffraction Analysis

An effort was made to distinguish the chemical natures of the two solid residues. The literature revealed that elemental silicon can exist in either crystalline or amorphous forms.* The crystalline form has a modified diamond structure. The black type of solid was considered to be essentially crystalline silicon and the brown solid to be a mixture of amorphous silicon, crystalline silicon, and some form of alumina because x-ray diffraction patterns showed only elemental silicon to be present when either solid was analyzed.

D7 dissolver solution was used for the analysis because it contained both types of solids. The dissolver solution of the cast AlSi, D10, was used as the source for the purer crystalline silicon. Each sample was calcined at 800° C to transform the small amounts of aluminum nitrate present to alumina. Each sample was then subjected to X-ray diffraction analysis and the resulting patterns were compared. The interpretations are presented in Table 1.

* In this report an amorphous form is defined as one in which no crystalline structure is detected by X-ray.

TABLE 1
INTERPRETATION OF
X-RAY DIFFRACTION PATTERNS

SAMPLE NUMBER	NAME	SOURCE	RATIO Si TO Al BY WEIGHT	RELATIVE CRYSTALLINE SILICON PEAK HEIGHT AT 47.3°	PRESENCE OF ALUMINA PEAKS IN SCAN
1	D ₁₀	Solid residue from cast AlSi dissolution considered to be the purest sample of crystalline silicon	9/1	considered as 100	None
2	D ₇ C	D ₇ centrifuged at 10,000 RPM for 15 minutes	4/1	81	None
3	D ₇ M	Mixture of solid obtained by allowing D ₇ to settle for 24 hours.	4/1	89	None
4	*D ₇ B	D ₇ C supernate centrifuged at 20,000 RPM for 15 minutes	4/1	13	None
5	D ₁₀ + Al ₂ O ₃	10% by weight aluminum added in the form of Al ₂ O ₃ to D ₁₀	4/1	82	Yes
6	D ₁₀ + Al ₂ O ₃ + D ₇ B	1 part D ₁₀ Al ₂ O ₃ was added to one part D ₇ B	4/1	22	None
<p>* In the diffraction patterns obtained from this sample, the base line increased five units indicating the possible presence of amorphous materials.</p>					

From these data it was concluded that elemental crystalline silicon is present in the solid material. Also, since the alumina present in all the samples is of sufficient quantities to produce observable peaks and since such peaks were not observed, it must either be of an amorphous type or another amorphous material is present acting as a diluent. The diffraction patterns obtained with the simulated samples, numbers 5 and 6 (see Table 1), and the physical properties of this material suggest that amorphous silicon is probably the diluent.

E. Crystal Size Production

Since the solid residues are thought to be silicon in two forms, crystalline and amorphous, an explanation for their coexistence was sought. Both forms of silicon can be produced by dissolving the silicon in molten metals and by varying the quenching methods.⁽¹⁾ The black crystalline type is obtained when the melt is slowly cooled while the brown amorphous type will be produced if the melt is quenched rapidly. It is possible that if a large variance in the temperature is allowed to occur in a given piece of fuel during its fabrication, both types of silicon could occur in that element.

Extrusion processes may be employed in the fabrication of fuel elements. Since this implies that varying degrees of pressure or working could be experienced throughout the fuel element, it is thought that this process would also be a determining factor in the crystal sizes produced.

F. Filtration

The solution prepared in the dissolution section were used in the filtration experiments to determine the most effective filter for silicon, that could be used in conjunction with the plant batch dissolution equipment.

Four stainless steel sintered filters and one wire mesh were used in the experiment. These have been designated as H, G, F, E, and M, and were stated to have porosities of 5, 10, 20, 35, and approximately 40 microns, respectively. The filter areas were limited by sealing teflon washers to the filter surfaces. This was done to define the equivalent volume needed to correspond to plant flow-sheet volumes and plant filter areas. A volume of 100 milliliters was determined equivalent to one batch run through the plant. The filtration was performed using a vacuum of a 20 inch of mercury at 23° C.

The wire mesh was found to have too large a pore size to secure effective silicon removal and the five micron filter was too small for reasonable filtration. The particle size distribution was found to differ among solutions from different coupons tested even though they were cut from adjacent sections of a fuel element. This difference can readily be seen on Figures 1 through 6. In Figure 1

(1) Manchot, W., and Funk H., Zietchriffit Fur Anorganische Und Allgeneine Chemic, Volume 120, Page 277-299, 1922.

the percentages of gross silicon removed is plotted against the filter pore size. In Figures 2, 3, and 4 the cumulative volume of filtrate is plotted against time for each filter. Figures 5 and 6 represent average silicon removal efficiency and average filtration rate. The mean deviation is shown in each case.

On the basis of the filtration experiments two conclusions were made. One, that the coupons used were too small a unit to give reproducible particle size and distribution data in the region larger than 10 microns. Second, the 10 micron filter was the most effective of those tested with respect to silicon removal efficiency. A silicon removal efficiency of 90 percent is obtained. However, the filtration rate is low, 2 gallons per hour per square foot. In fact, even with the maximum variance taken into consideration the average cumulative volume obtained in an eight-hour period is not equal to the plant batch equivalent (Figure 6). However, the rate of the next larger sized filter, 20 microns, is no better and the feed solutions of D6 and D7 went through that sized filter with as low as a 46 percent removal. (Figures 1 and 3).

G. Sedimentation

Particle size and distribution can be determined from sedimentation data and the application of Stoke's law. Two methods were used to obtain sedimentation data. One employed a cumulative weight while the other utilized concentration change. D4 was chosen as the most representative dissolver solution because of its middle positioning on the filter efficiency curve and because the silicon concentration of D4 was low compared to the average concentration thus reducing interference between particles during settling.

The testing apparatus of the cumulative weight method consisted of a pan suspended in a homogeneous solution. The pan is attached to a balance so that a weight increase with time can be determined. By introducing a bouyancy correction factor, the actual weight can be determined. The height that a particle in the solution can fall in a time period can be measured and directly applied to Stoke's law as the velocity. Having determined the viscosity of the system, the specific gravity of the liquid and using the specific gravity of the solid as that of elemental silicon, Stoke's law can then be solved for the equivalent diameter.

Since Stoke's law requires spherical shaped particles for absolute validity and since the examination of the particles under the microscope disclosed them to be platelets and not spheres, the term equivalent diameter is used instead of the apparent diameter. As a result, the equivalent diameters obtained in a sedimentation test will differ from the apparent diameters obtained from the filtration. Further, the particle size distribution obtained from the application of Stoke's law cannot be used in the prediction of filter efficiencies, and the apparent diameters obtained from the filter efficiency curves are not applicable to Stoke's law for determining sedimentation rates.

The fraction of solid particles that settle in a particular time can be divided into two portions using Oden's method of tangential intercepts. (2) In Figure 7 the percentage of the total weight settled is plotted against time. One fraction, s, consists of coarse particles whose settling time for the distance, h, is greater or equal to the time, t. The remaining portion, $t \, dp/dt$ are the fines or smaller particles that settled because of their position or close proximity to the pan. This division can be made by drawing tangents to the percentage settled versus time curve.

An Andreason pipette was used in the concentration change method. Samples were taken periodically and were ashed and analyzed by emission spectroscopy for silicon concentration. The weight of each increment having a particular velocity can be determined by the following calculations.

Let:

C_0 = the concentration of silicon in the sample at t_0 - mg/ml.

C_{t1} = the observed concentration of silicon in sample at time t_1 - mg/ml.

C_1 = the calculated silicon concentration in the original sample having a settling time equal to t_1 - mg/ml.

Since the settling time, t_1 , is over a distance, h_1 , the velocity, h_1/t_1 can be substituted into Stoke's law from which the equivalent diameter can be determined. The observed change in concentration from t_0 to t_1 is

$$C_0 - C_{t1} = t_1 \frac{C_1}{t_1} + t_1 \frac{C_2}{t_2} + t_1 \frac{C_3}{t_3} + \dots + t_1 \frac{C_n}{t_n} \quad (1)$$

and from t_0 to t_2 is

$$C_0 - C_{t2} = t_1 \frac{C_1}{t_1} + t_2 \frac{C_2}{t_2} + t_2 \frac{C_3}{t_3} + \dots + t_2 \frac{C_n}{t_n} \quad (2)$$

Subtracting equation (1) from equation (2) one can solve for C_2 which is the amount of silicon that settled in time interval t_1 to t_2 .

Then

$$C_2 = t_2 \left[\left(\frac{C_{t1} - C_{t2}}{t_2 - t_1} \right) - \left(\frac{C_3}{t_3} + \dots + \frac{C_n}{t_n} \right) \right] \quad (3)$$

This equation in the general form is

(2) Symposium of New Methods for Particles Size Determination in the Subsieve Range, 4 March, 1941, Page 67, Washington Spring Meeting American Society for Testing Materials.

$$C_{n-3} = t_{n-3} \left[\left(\frac{C_{t_{n-4}} - C_{t_{n-3}}}{t_{n-3} - t_{n-4}} \right) - \frac{C_{n-2}}{t_{n-2}} + \dots + \frac{C_n}{t_n} \right] \quad (4)$$

The equivalent diameters obtained with the two methods are given in Table 2 and shown graphically in Figures 8 and 9.

TABLE 2

Equivalent Diameters (Micron)	Percentages	
	Oden's Method	Andreasson's Method
< 10	51	62
10 - 15	14	17
15 - 20	9	7
20 - 25	16	12
> 25	10	2

From these data it was concluded that about 20 percent by weight of the total silicon particles present in D4 have an equivalent diameter of 20 microns or greater, 25 percent have equivalent diameters between 10 and 20 microns, and the remaining have equivalent diameters of less than 10 microns.

H. Surface Active Tendencies

a. Dispersion-Coalescence Test

The effect of silicon in the extraction column process was investigated by means of a dispersion-coalescence rate test using the equipment and techniques described in the literature.⁽³⁾

A standard aluminum nitrate-nitric acid feed solution was used in the test with 3.25 volume percent TBP in Amsco. This standard solution gave a 64-second initial dispersion time, a 7-second equilibrium dispersion time, and an 89-second coalescence time. When the silicon-containing dissolution solutions and their filtrates were tested the results showed a slightly reduced initial dispersion time, a normal equilibrium dispersion time, and a 20 to 40 percent increase in the coalescence time.

(3) Hill, O. F., HW-26104, Quarterly Report, Chemical Research, Nov. 3, 1952, (Secret.)
Hill, O. F., HW-26937, Quarterly Report, Chemical Research, Jan. 26, 1953, (Secret.)

The dispersion-coalescence reruns using filtrates showed that the above results were not changed after filtration. Therefore, these effects are presumably due to small particles which have an apparent diameter of less than 10 microns, or about 10 weight percent of the total particles present.

From these results and previous experience it was concluded that the silicon present in the extraction process should not lead to unusual operating conditions even though the solid particles do seem to be somewhat surface active. The larger particles may settle on surfaces, or in quiescent zones of the process equipment, and physically obstruct flow. However pilot plant studies of the extraction process with similar solutions have not indicated the likelihood that this will occur to a serious extent.

b. Fission Product Adsorption

On the basis of this surface active tendency, fission product adsorption was investigated using as a criterion the coprecipitation tendency that zirconium has for silica or silicic acid. This coprecipitation experiment was done also in order to supplement the indication of the presence of silica or silicic acid in the system. A colormetric method employing molybdate ion had failed to prove the presence of silica because of instability of the color complex.

Zirconium tracer was introduced into equal volumes of 3.25 percent TBP in Amsco and dissolver solutions in a graduated container. The phases were dispersed until a stable interface was produced. The individual phases were separated by pipetting, leaving the interface in the original container. Each phase, that is, the organic, aqueous, and interface was counted separately. No concentration of zirconium at the interface was noted and it was concluded that such contamination would not be experienced in the process.

IV. AGING EFFECTS

The effect of aging upon these solutions; that is, changes in the particle size and their distribution, was investigated using the filtration and dispersion-coalescence tests (since it was assumed that any aggregation or change in the particle size and distribution would affect the filtration rates and the dispersion-coalescence times).

The effect of three months aging at 23° C on the filtration rate of D3 feed solution is shown in Figure 9. Here the original filtration rate curves are compared with those of the rerun. The dispersion-coalescence test rerun after 3 months aging further evidenced that any aging effect was negligible.

Therefore, it was concluded that aging will have little or no effect upon operating conditions of the plant extraction columns.

V. CONCLUSIONS

The refractory residue resulting after the dissolution of certain uranium-aluminum fuel elements was found to be composed principally of silicon with a small amount of aluminum. It was observed in two forms; one, grey-black irregular platelets having metallic luster and giving a relatively sharp X-ray pattern for silicon; the second, small, brown particles which gave a weaker X-ray pattern for silicon. The particle size distribution, Stoke's law "equivalent" diameters, and settling characteristics of the residue were defined by two sedimentation methods. Quenching and the extrusion process employed in the fuel fabrication may be responsible for the crystalline form and particle size distribution of the silicon residues. Removal of the residue from process solutions with sintered stainless steel filters was possible but 90 percent removal of the silicon required a 10 micron porosity filter. This filtration rate was only 2 gallons per hour per square foot at 20 inches mercury vacuum.

Dispersion-coalescence tests showed some minor surface activity but in general the adsorptive and emulsification properties frequently associated with silica and other extraction system residues were not detected. Further, three months aging at 23° C of one dissolver solution sample yielded essentially no difference in either the filtration characteristics or the dispersion-coalescence rate tests. It was concluded that the residue is essentially stable in the process dissolver solutions.

VI. ACKNOWLEDGMENT

The extensive X-ray diffraction and spectrographic analyses, which were a part of this study, were performed and interpreted by G. V. Wheeler, Kenneth Arnold, and Walter Ryder of the CPP Analytical Section.

Figure 2

FILTRATION RATES FOR SILICON
REMOVAL (35 MICRON FILTER)

FILTER AREA RATIO

$$\frac{\text{PLANT}}{\text{Lab}} = \frac{476 \text{ in}^2}{.111} = 4,288.9$$

SOLUTION VOLUME RATIO

$$\frac{\text{PLANT}}{\text{Lab}} = \frac{508}{.100} = 5080$$

VACUUM = 20 inches MERCURY

TEMPERATURE = 25°C

Figure 3

FILTRATION RATES FOR SILICON
REMOVAL (20 MICRON FILTER)

FILTER AREA RATIO

$$\frac{\text{PLANT}}{\text{Tab}} = \frac{476\text{m}^2}{.111} = 4,288.9$$

SOLUTION VOLUME RATIO

$$\frac{\text{PLANT}}{\text{Tab}} = \frac{508}{.100} = 5080$$

VACUUM = 20 inches MERCURY
TEMPERATURE = 23° C

Figure 4

Figure 5

AVERAGE SILICON REMOVAL EFFICIENCY
FILTRATION THROUGH STAINLESS STEEL FILTERS

Figure 6

Figure 7

SETTLING RATES OF SILICON PARTICLES
ODEN'S METHOD

CPP-S-835

Figure 8

SETTLING RATES OF SILICON PARTICLES
ANDREASON'S METHOD

THE EFFECT OF AGING ON FILTRATION RATES
DISSOLVER SOLUTION NUMBER 3-AGED 3 MONTHS