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AEC RESEARCH AND DEVELOPMENT REPORT

IMPREGNATION OF GRAPHITE WITH URANIUM COMPOUNDS FOR USE AS FUEL ROD MATERIALS

Chemistry Division, Section C-II

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0 ABSTRACT

A process has been developed for impregnating graphite with U_3O_8 in connection with the proposed use of such material for fuel rod elements in the Daniels' High Temperature Pile. The process as developed consists of five steps: 1. Fabrication of the graphite in the desired shape.

2. Pretreatment of the graphite by boiling in water and then firing in helium at 800°C.

3. Impregnating the graphite by first evacuating the pretreated material and then admitting an aqueous uranyl nitrate solution whose concentration is determined by the final uranium content desired in the graphite.

4. Drying the impregnated graphite slowly under equilibrium conditions.

5. Conversion of the uranyl nitrate to U_3O_8 by firing in helium at 800°C.

By this process fuel rod elements have been made which contain as much as 19% U_3O_8 distributed uniformly throughout the graphite. The considerations leading to the choice of this process are discussed in this report, together with the alternate procedures which were investigated.

1 INTRODUCTION

Preliminary tests of beryllia fuel rods (i.e., rods hot-pressed out of mixed beryllium and uranium oxides) for the Daniels' Power Pile indicated that such material was especially susceptible to thermal crackup, due to the low resistance of fabricated beryllia to thermal stresses. This thermal cracking of such fuel tubes would probably be the limiting factor in operating the pile at high energy levels (greater than 4000 kw). The use of graphite was therefore suggested as a replacement for beryllia in the fuel rod because of its plasticity at high temperatures, its mechanical strength, its relatively low cost and its availability. Also it seemed likely that the chemical processing of spent fuel rods would be easier when made of graphite rather than beryllia. Furthermore, a great deal of experience had been obtained with graphite as a pile material.(1) The program described herein was undertaken to develop a method for incorporating uranium into a graphite fuel rod.

Two approaches to the problem were suggested: (1) that uranium oxide be mixed with coke flour and the mixture graphitized, and (2) that the uranium be incorporated into the fabricated graphite rods. Since no high temperature facilities were available for graphitization at this laboratory, attention was focused on the second approach.* The Argonne National Laboratory has, however, interested the Norton Company, the Battelle Memorial Institute, and the National Carbon Company in the graphitization approach.

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(1) CL-FD-4 by F. Daniels, August 4, 1946.

* A preliminary experiment was carried out at the Argonne National Laboratory before abandoning the first approach. Powdered graphite was added to a solution of uranyl nitrate hexahydrate and the mixture was evaporated to a thick paste. This was packed into a beryllia tube and baked over night at 400°C, whereby the remaining water was removed and the nitrate decomposed. The temperature of the oven was then raised to 1450°C and held there for a few hours. When the sample was removed from the furnace it was found to be in the form of a fine powder and it was obvious that to produce coherent material, it would be necessary to mix the powders in pitch and actually regraphitize at very high temperatures.

Since graphite is quite porous, it was believed that the pores could be filled with a solution of a uranium salt which could then be changed to a form stable under pile conditions. Uranyl nitrate was the salt chosen because it has a high solubility and is easily converted to an oxide stable at the proposed pile temperatures. Early estimates of the amount of uranium in the Daniels' pile showed that approximately 0.04 g of U_3O_8 (enriched in the 235 isotope) per cubic centimeter of graphite would be required.(1) On a weight basis, the fuel elements would have to have 2 - 3% U_3O_8, depending on the density of the graphite. Hence the primary requirement of the process was that it should produce fuel rods containing 2 - 3% U_3O_8, preferably by one impregnation, with as little variation in uranium content as was possible. The process selection was also guided by the fact that the uranium should be deposited uniformly throughout the fuel element.

This report describes a process for making fuel rods by impregnation with uranyl nitrate and gives a summary of the experimental work leading to this process.

2 THE IMPREGNATION PROCESS

2.1 Types of Graphite Used

Three types of graphite, all products of the National Carbon Company, have been used. They are:

(1) AGOT-K, which has a density varying from 1.60 to 1.72 g cm^{-3} ,

(2) AGR graphite, a "high purity" graphite whose density averages 1.4 to 1.5 g cm^{-3} , and

(3) B-1508-A, a low density graphite made to be essentially uniform in its porosity.(2) It has a density of 1.36 g cm^{-3}.

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(1) CL-FD-19 by F. Daniels (October 6, 1946).

(2) The use of this graphite was suggested by V. C. Hamister and H. G. MacPherson of the National Carbon Company.

On the basis of the reproducibility of its properties, type B-1508-A seems to be the best graphite for fuel rod material of the three types tested.

The process itself consists of five steps:

(1) Fabrication of a fuel rod blank from graphite stock

(2) Pretreatment

(3) Impregnation

(4) Drying

(5) Conversion to a stable uranium compound

2.2 Fabrication of the Graphite

Design requirements for the fuel rods called for a hollow cylinder, 6 inches in length, 1.500 inches OD and 0.875 inches ID. The large graphite bars were cut into small blocks slightly larger than the outside dimensions of the fuel rods. They were then cut down on a lathe to the outer diameter and the inner dimension was obtained by drilling and reaming.

2.3 Pretreatment

The graphite fuel rods were boiled in water for 30 minutes to remove loose graphite powder remaining from the machining operations. They were then fired in helium at 800°C for 30 minutes to remove water and any volatile substances present. About 0.1% by weight of the graphite was burned off in this step since no effort was made to purify the helium.

2.4 Impregnation

The fuel rod was placed in a vessel which was subsequently evacuated. The pressure was maintained below 1 mm of mercury for about 10 minutes, following which an aqueous solution of uranyl nitrate was admitted to the vessel to cover

the fuel rod. (The concentration of this solution was adjusted to give the desired uranium content according to the relationship shown in Figure 1.) After approximately five minutes, the system was opened to the atmosphere and the fuel rod was allowed to stand in the impregnating solution for five minutes more. Thus atmospheric pressure served to drive the solution into the pores of the graphite, approximately 97% of the void volume being filled.

2.5 Drying

The fuel rod was removed from the impregnating bath and allowed to drain. The sample was allowed to stand over a $CaSO_4$ desiccant for 40 - 50 hours or alternately it was dried by passing helium over it at room temperature for 4 - 5 hours.

2.6 Conversion to a Stable Uranium Compound

To convert the uranyl nitrate to U_3O_8, the fuel rod was fired to 800°C in helium for 15 minutes. Small oxidation losses due to water and oxygen from the decomposition of the uranyl nitrate plus that traceable to the free oxygen content of the helium were noted.

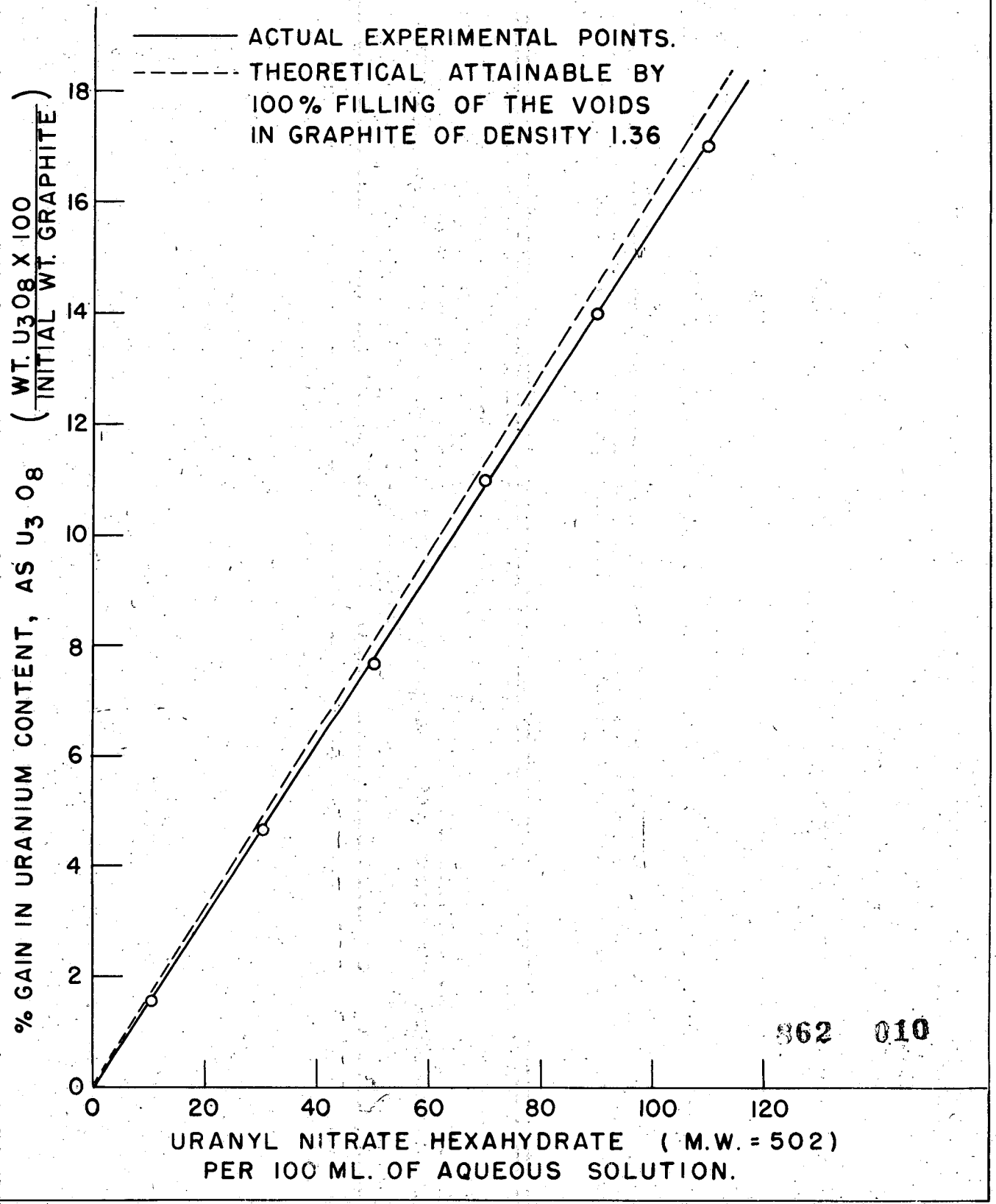
3 DISCUSSION OF THE CHOICE OF PROCESS

The process for impregnating graphite fuel rods given in Section 2 was chosen with two chief considerations in mind: reproducibility of the uranium content from one fuel rod to another, and uniformity of the uranium distribution throughout each fuel rod. In the following paragraphs the five steps are taken up with the considerations leading to their choice and the alternative steps investigated are discussed.

3.1 Fabrication

All the graphite used in this work was in the form of extruded bars in

FIG.1 URANIUM CONTENT ATTAINED IN THE IMPREGNATION OF B-1508-A GRAPHITE BY THE EVACUATION TECHNIQUE (PERCENT GAIN IN URANIUM CONTENT VS. CONCENTRATION OF IMPREGNATING SOLUTION.)



two sizes, 3 inch diameter round bars, and 4 inch x 4 inch square bars. The machining operations were quite standard and required little attention. However, it was noted that reaming the inner hole in the fuel rod was necessary to keep the inner dimensions to a tolerance of ± 0.001 inches. The tolerances obtained in these dimensions give a variation in volume of 0.2%.

The possibility of fabricating the fuel rod by extrusion of the graphite in the required shape and size has been suggested[1] but no impregnations have been carried out with samples of such type.

3.2 Pretreatment

The pretreatment step was deemed necessary in the early part of the experimental work in order to obtain a reasonably comparable initial weight for the graphite. The quantitative removal of loose particles remaining from the fabrication of the fuel rods could be accomplished by wiping, brushing, or vacuum cleaning; however, immersion in boiling water appeared to be satisfactory. Then to dry the sample thoroughly, it was fired at 800°C in helium. The high temperature was used to drive out volatile matter although 800°C was chosen chiefly because a furnace operating at that temperature was available.

When impregnation using the evacuation technique given in Section 2.4 was used, the pretreatment, or lack of it, had no measurable effect on the uranium content of the final fuel rod. However, with no pretreatment, graphite particles accumulated in the impregnating solution, a factor which would hinder any re-use of the impregnating solution. Consequently, the pretreatment step was retained.

When the impregnation was carried out by refluxing the solution with the graphite, the pretreatment did have some effect. The firing at the high

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(1) Personal Communication, V. C. Hamister of the National Carbon Company.

temperature appeared to activate the graphite so that greater pickup of solution was attained on impregnation. Detailed data on these experiments are given in Section 4.3.

3.3 Impregnation

Impregnation by the evacuation technique described in Section 2.4 seemed to be the most satisfactory process. By this process, the voids in the graphite are almost completely filled with uranyl nitrate (97%). The degree of impregnation was found to be constant with respect to limited variations in process time, evacuation pressure, solution concentration, hydrogen ion concentration, and degree of activation of the graphite. From preliminary experiments it was found unnecessary to control these variables. Hence the variation in uranium content obtained by this technique is determined chiefly by the constancy of the graphite porosity.

Impregnation by the following refluxing technique was also studied. The fuel rod was pretreated as in Section 2.3 and then allowed to reflux for 30 minutes in a boiling solution of uranyl nitrate. It was then removed from the solution, dried and fired. The degree of impregnation by this method was dependent on the pretreatment of the graphite as well as on the solvent employed for the uranyl nitrate. Using an aqueous solution of uranyl nitrate, only some 65% of the voids could be filled whereas with ether, acetone, and hexone solutions, 88 - 90% were filled. Addition of wetting agents to the aqueous solutions gave no increase in the uranium content over that attained with pure water.

The uranium content and the limits to which it can be held seem to be prime considerations upon which the choice of impregnating technique depends. Table I gives a comparison of the uranium contents attainable with graphite of different densities when impregnated by the evacuation and by the refluxing

techniques. The data are for an impregnating solution of 1 M aqueous uranyl nitrate. Other concentrations would give uranium contents in direct proportion.

Table I
Comparison of the Uranium Content Attainable by Impregnation of Various Graphites by the Evacuation and Refluxing Techniques

Type of Graphite	Percent Gain in Uranium Content $\left(\frac{\text{Wt. } U_3O_8 \times 100}{\text{Initial Wt. of Graphite}}\right)$	
	Evacuation Technique*	Refluxing Technique*
B-1508-A (density = 1.36 g cm^{-3})	7.7	6.4
AGOT-K (density = 1.67 g cm^{-3})	3.1	1.8
AGR (density = 1.42 g cm^{-3})	- -	5.5

*The impregnating solution was 1 M aqueous uranyl nitrate.

It can be seen that the reproducibility in the U_3O_8 content of the fuel elements will depend chiefly on the constancy of the graphite porosity and the efficiency of the impregnation. In this work only a rather rough estimate of these factors could be made because the uncertainty in the one limited an estimate of the other. However, it is believed that the efficiency of impregnation by the evacuation techniques is constant to something under 1%. Section 4.4 gives data on one series of tests correlating the uranium content after impregnation with the graphite porosity.

Table II gives a resume of the reproducibility obtained with the two

impregnating techniques. These data are limited to a rather small number of samples. The B-1508-A data are based on twenty fuel elements cut from four different bars received in two shipments. The AGR data are based on thirty samples from four different bars received in three shipments, and the AGOT-K data on some twenty samples taken from two bars whose history is not known. No correlation from bar to bar was recorded. These tolerances should be interpreted as being limited since no effort was made to sample the total supply of any of these types of graphite.

Table II
Variation of Uranium Content Observed in the Impregnation of the Different Types of Graphite

Type of Graphite	Number of Samples	Percent Variation in Uranium Content $\left(\frac{\text{Greatest Deviation} \times 100}{\text{Average Value}}\right)$	
		Evacuation Technique	Refluxing Technique
B-1508-A	20	±2%	±5%
AGOT-K	30	±4%	±13%
AGR	20	- -	±25%

3.4 Drying

Uniform distribution of uranium is the critical requirement which determines the choice of the drying procedure. It was determined that there is uniformity of impregnation before the sample is removed from solution (Section 4.2). A number of drying methods were tested in terms of the resultant uranium distribution and those methods which approximated equilibrium drying conditions gave good results. The procedures in Section 2.5 were satisfactory for full size fuel rods dried individually in laboratory apparatus but it is

to be remembered that the exact conditions would depend on the type and size dryer being used.

3.5 Firing

Conversion of the uranyl nitrate in the pores of the graphite to U_3O_8 was effected by firing in helium at 800°C for thirty minutes. A quartz tube heated with a Burrell furnace was used. Work reported by Malm and Mason(1) showed that the U_3O_8 in impregnated graphite changes successively to UO_2 and UC_2 as the temperature is raised from 800°C to 1400°C but upon re-exposure to air U_3O_8 is again formed. Hence it would seem that the preferred form of uranium in graphite would be U_3O_8 if the fuel elements were not to be used immediately.

3.6 Type of Graphite

Tables I and II show the variations in uranium content using the three graphite types. No attempt has been made here to consider any other properties of graphite, but, on the basis of the behavior in impregnation, B-1508-A seems best suited for fuel rod material.

4 SUMMARY OF THE EXPERIMENTAL WORK

The experimental work in the development of the process described in the preceding sections was largely a series of trials of various procedures to see what uranium content or what type of uranium distribution could be obtained. Some of the preliminary work was done using small cylindrical graphite samples but all final conclusions were based on full size fuel element sections. The uranium content was measured in most of the work by taking the gain in weight of the graphite sample after impregnating and firing. It was known that this quantity did not represent the true amount of uranium present

(1) J. G. Malm and G. Mason, ANL-4003, Section 1.5 and ANL-4090, Section 1.5.

due to the loss of graphite by oxidation, but, for experiments in which comparative results were most important, it proved sufficient. In cases where it was necessary to obtain the actual uranium content, this was done by firing the graphite in a platinum crucible at 800°C and weighing the residue as U_3O_8 after correcting for the ash content of the graphite.

The determination of the uranium distribution was done either by direct analysis or by x-ray shadowgraph. For direct analysis, the samples were set up on a bench lathe, successive layers were turned down, and the turnings from each layer analyzed for uranium by ignition as above. For x-ray shadowgraphs, a transverse slice was taken from the sample, placed on a sheet of film and exposed to x-ray.* It was found rather difficult to get absolute values of uranium content because of the difficulty of securing adequate control of exposure time and sample thickness, but the method did indicate whether any irregularity existed.

Some of the work described herein is not too relevant to the process discussed under Section 2, but is grouped with that portion of the work to which it most nearly applies. Work was done on several methods of impregnation, the use of various solvents for impregnating solutions, on several methods of pretreatment, drying and firing. The nature of the uranium in the finished fuel element, the causes of the non-uniform distribution, and the choice of the graphite type were also investigated.

4.1 Impregnation Techniques

The first approach to the problem of impregnating graphite was based on preparing an impregnating medium containing the required amount of uranium and then getting all of this uranium into the sample. The method involved considerable recycling and resulted in badly coated samples so it was soon discarded.

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* The x-ray shadowgraph technique was developed with the advice and assistance of Miss A. Smigelskas.

4.1.1 Refluxing

The general method used for impregnation consisted of refluxing the sample in a solution containing uranyl nitrate at the boiling point at atmospheric pressure. Various solvents were used as discussed in Section 4.1.4.

Changing the time of refluxing showed that there was no appreciable pickup of uranium after 15 minutes for samples of thickness comparable to that of fuel tubes. Therefore a refluxing time of 30 minutes was taken for all subsequent work. This conclusion is based on the data shown in Tables III and IV. Table III gives the weight gain after firing for samples of AGOT-K graphite after refluxing in an acetone solution of uranyl nitrate hexahydrate (UNH) for varying lengths of time.

Table III
Effect of Time of Refluxing on Uranium Content of Standard Graphite Samples*

Time of Refluxing (minutes)	Percent Weight Increase
10	2.78 3.79 2.90
30	3.37 3.26 2.86
60	3.20 3.38 3.20
120	3.66 3.22 3.14

* AGOT-K graphite samples (1 cm in diameter x 2 cm in length) refluxed with an acetone solution of uranyl nitrate (44 g of UNH/100 ml of solution).

Table IV gives the percent weight increase after firing for fuel tube sections of AGOT-K refluxed for various times in an acetone solution of uranyl nitrate hexahydrate.

Table IV
Effect of Time of Refluxing on Uranium Content of Fuel Tube Sections*

Time of Refluxing (minutes)	Percent Weight Increase
30	1.98
60	2.05
90	1.97
120	1.93
150	1.89
180	2.03

* AGOT-K fuel tube sections refluxed with an acetone solution of uranyl nitrate (40 g UNH/100 ml of solution).

While these results show some variations, it would seem that a refluxing period of 30 minutes is sufficient to attain virtually maximum impregnation.

One experiment was done which confirmed this conclusion in a more fundamental manner. A fuel tube section was boiled in distilled water and hydrostatic measurements of its weight immersed in water were taken at various times. Each weighing was made after allowing the sample to cool below the boiling point momentarily so that an accurate weighing could be made. Here too it was shown that after ten minutes no measurable amount of water was absorbed.

As the original specification for uranium content of the fuel tubes was higher than could be obtained by a single impregnation, tests were made to determine the effect of repeated impregnations on the same sample. In these runs each sample was first pretreated by boiling in water and then firing in helium at 800°C. Following this it was impregnated by refluxing in the uranium solution for 30 minutes; finally the sample was dried and fired in helium. The refluxing and firing cycle was then repeated. The data in Table V show the relationship between the number of impregnations and the weight gain for three cylinders of AGOT-K graphite impregnated in an ether solution of uranyl nitrate hexahydrate.

Table V
Effect of Repeated Impregnations by the Refluxing Technique on the Uranium Content of Graphite Samples

Number of Impregnations	Percent Weight Gain*		
	#1	#2	#3
1	4.0	2.7	3.1
2	7.1	5.4	6.1
3	10.8	8.6	9.3
4	13.8	11.0	12.1
5	16.8	13.1	14.5

* AGOT-K samples 1 cm in diameter and 2 cm long refluxed with an ether solution containing 39% uranyl nitrate hexahydrate.

The data indicate that the gain in weight per impregnation decreases as the uranium content of the samples increases. It was also noted that the variations in the results were such that each sample deviated from the other two samples by about the same amount, indicating that the irreproducibility

was largely due to the graphite.

Impregnations were carried out using fuel tube sections of B-1808-A graphite to check the reproducibility of the impregnation by refluxing. The solution used was 28 g of UNH per 100 ml of aqueous solution. The gain in weight for five sections ranged from 3.14% to 3.46% which was a spread of approximately 10% around the average value.

4.1.2 Evacuation

Very early in the program evacuation was suggested as a possible means for impregnation. The procedure used consisted of placing the pretreated samples in a vessel which was evacuated to a pressure of about 1 mm of mercury. The impregnating solution was then admitted to the sample without breaking the vacuum and allowed to stand until most of the gas bubbles had boiled out. The system was then opened to the atmosphere.

This technique was tried with the usual pretreatment procedure using ether solutions of uranyl nitrate as the impregnating solutions. One set of tests was concerned with the effect of the number of impregnations on the uranium content. The tests were stopped at 13 impregnations because the graphite samples were becoming badly coated with a surface layer of green uranium oxide. These data are shown in Table VI.

Here as in the case of simple refluxing the weight increase per impregnation gradually became smaller as the uranium content of the graphite increased. Comparison of these results with those obtained on recycling by the refluxing technique (Table V) showed that with ether solutions a greater weight gain was obtained by refluxing than by evacuation. This was assumed to be due to the high vapor pressure of ether at room temperature.

However, with aqueous solutions a greater weight gain was obtained by the evacuation than by the refluxing technique as is shown in Table VII.

Table VI
Effect of Repeated Impregnations by the Evacuation Technique on the Uranium Content of Graphite Samples

Number of Impregnations	Percent Weight Gain*	
1	2.7	2.6
2	5.1	4.7
3	8.4	7.9
4	10.9	10.4
5	12.8	12.8
6	15.2	15.1
7	16.0	15.9
8	18.0	18.3
9	19.0	19.0
10	21.4	21.6
11	22.4	23.0
12	24.7	25.1
13	26.7	26.3

* Small cylinders of AGOT-K graphite impregnated by the evacuation technique using an ether solution containing 39% of UNH.

Table VII
Comparison of the Impregnation of B-1508-A Graphite by the Evacuation and by the Refluxing Techniques

Percent Gain in Weight* $\left(\frac{\text{Increase in Wt x 100}}{\text{Initial Wt}}\right)$	
Evacuation Technique	Refluxing Technique
3.83	3.25
3.88	3.46
3.93	3.29
3.91	3.14
3.99	3.35
3.81	
3.91	

* Fuel tube sections of B-1508-A graphite impregnated from an aqueous solution containing 28 g UNH/100 ml of solution.

The data are for fuel tube sections of B-1508-A graphite impregnated from an aqueous solution of UNH. Some idea of the comparative reproducibilities of the two techniques can also be obtained from this table.

4.1.3 Immersion

One of the more important disadvantages of using organic solvents as the impregnating medium with the refluxing technique was the reaction with uranyl nitrate at elevated temperatures. Several tests of impregnation by simply immersing the graphite samples in the solution were made for different lengths of time and for different types of agitation. Table VIII gives the results of tests on three samples and compares them with the refluxing technique.

Table VIII
Impregnation of Graphite by Immersion in a Hexone Solution of Uranyl Nitrate

Type of Treatment	Time of Treatment (hours)	Percent Weight Gain*		
Refluxing	0.5	3.43	3.81	3.74
Immersion without agitation	1	2.49	2.51	2.47
	15	3.47	3.55	3.47
	20	2.49	2.56	2.43
Immersion with vibratory agitation	1	1.20	1.07	1.26
	20	3.08	3.26	3.18

* Small cylinders of AGOT-K graphite impregnated from a hexone solution containing 44 g of UNH/100 ml and which was ca. 0.1 M in nitric acid.

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It was noted that immersion did not give as great a weight gain as did refluxing, although some of the long time runs were comparable. The discrepancy between the 15 and 20 hour runs without agitation was taken to indicate the inherent irreproducibility of the process. Agitation decreased the weight gain on impregnation. However, it was noted that the solutions from these runs showed loose graphite particles and this may account for the lower gain in weight.

4.1.4 Use of Solvents Other than Water

Ether, acetone, hexone, and water were the solvents studied as a medium for impregnation by the refluxing technique. Impregnations were carried out after the usual pretreatment of the graphite by maintaining a solution of uranyl nitrate hexahydrate in the particular solvent at reflux over the graphite. The samples were then dried and fired to 800°C. It is presumed that the uranium in these samples was distributed non-uniformly, but the total content was not affected. The gain in weight was taken, corrected for oxidation losses, and the percentage of the voids filled was calculated from the final uranium content. The results are compared on this basis in Table IX.

Table IX
Comparison of the Efficiency of Impregnation of AGOT-K Graphite by Refluxing in a Solution of Uranyl Nitrate in Various Solvents

Solvent for UNH	Percentage of Voids Filled
Ether	90
Acetone	88
Hexone	90
Water	65

The increased efficiency of impregnation obtained by the use of organic solvents in refluxing was offset by the difficulty in handling the solvents at the elevated temperatures. Ether, acetone, and hexone all gave precipitates which were found to be organic compounds of uranium. A few preliminary experiments on varying the acidity of the solutions produced no appreciable inhibition of these reactions.

4.2 Drying and Firing Procedure

The work on drying and firing is combined because these steps were investigated together in many cases. The investigation of the distribution of uranium in the resultant samples was the most significant portion of this work.

4.2.1 Effect of Drying and Firing on the Uranium Distribution

The following experiment was done to determine the distribution existing in the fuel element before it was removed from the impregnating bath. A glass vessel was prepared which had as its lower portion two parallel sides about 5 mm apart. The top was a tapered glass joint which allowed the vessel to be used in the same impregnation equipment used for other runs. A transverse slice cut from a graphite fuel tube was coated on its faces with a silicone resin to make these faces impervious so that water would penetrate only from the edges in a manner similar to the penetration of the impregnating solution in a whole fuel rod. The thickness of this sample was such that it just fitted between the parallel faces of the vessel described above. The sample was then impregnated with an aqueous solution of uranyl nitrate and shadowgraphed by x-ray while in the impregnating solution. The film gave a clear picture of the uranium distribution, showing that it was essentially uniform. This is contrary to an earlier conclusion reached in this laboratory based on an experiment in which the fuel element was quickly removed

from the impregnating bath, frozen in liquid nitrogen, and analyses made of the uranium distribution by means of successive turnings of the frozen rod. These analyses showed a very non-uniform distribution. (See ANL-OCS-93, 12/12/46.) The present x-ray evidence of an initial uniform distribution appears unquestionable, however, since new methods of drying have yielded a fuel rod with a final uranium distribution which is uniform.

A large number of small graphite cylinders were then dried by different methods and the distribution was determined by x-ray shadowgraphs of sectional slices from these cylinders. The results of these experiments are listed in Table X and the x-ray shadowgraphs are shown in Figure 2.* Figure 3 shows graphs of uranium distributions as determined by chemical analysis of the layers for a sample typical of those designated by the terms uniform, almost uniform, and non-uniform.

From the data shown in Figure X it is apparent that uniform uranium distribution may be obtained by drying the impregnated sample under essentially equilibrium conditions. Thus either prolonged desiccation over $CaSO_4$ (Table X, sample numbers 2, 3, 4, and 11) or else a four hour drying period in a stream of helium at room temperature (Table X, sample number 10) led to uniform uranium distribution.

For samples impregnated by the refluxing technique, removal of the graphite sample from the boiling solution resulted in a non-uniform distribution in all cases, irrespective of the treatment used thereafter.

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* The x-ray shadowgraphs in Figure 2 are prints made from the originals, hence the uranium appears as the darker portions.

Since the x-ray source available for this work was of very high intensity the exposure time was of the order of a second or less. Consequently, due to the difficulty of controlling the exposure time, no attempt was made to reach uniform exposures. For this reason the shadowgraphs were interpreted only as to variation in density for each individual sample. No comparison of total uranium content from one sample to another can be made on the basis of these shadowgraphs. (Several of the shadowgraphs were omitted from Figure 2 because of the difficulty of reproduction in cases where over-exposure occurred.)

Table X
Effect of Drying and Firing Procedures on the Distribution of Uranium in Graphite Samples*

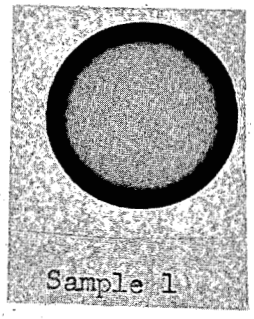
Sample No.**	Drying and Firing Technique Used	Resulting Uranium Distribution (by x-ray shadowgraph)
1	No drying; placed immediately in furnace at 800°C.	Non-uniform
2	Dried in desiccator 24 hours.	Uniform
3	Dried in desiccator 24 hours; inserted in furnace at room temperature, and heated to 800°C in two hours.	Uniform
4	Dried in desiccator 24 hours; inserted in furnace at room temperature, and heated to 800°C in 1 hour.	Almost uniform
5	Dipped in NH_4OH; dried in desiccator 24 hours; inserted in furnace at room temperature, and heated to 800°C in 2 hours.	Non-uniform
6	Kept at a pressure of 0.1 mm of mercury 1 hour; heated to 275°C under vacuum in 1 hour; fired in helium furnace at 800°C.	Uniform except for a thin outer rim of high uranium content.
7	As above with a nitric acid dip after firing.	Outer portion of sample badly depleted in uranium
8	Inserted in furnace at room temperature; heated to 800°C in 4 hours.	Fairly uniform
9	As above but heated to 800°C in 2 hours.	Non-uniform
10	Inserted in furnace at room temperature; allowed to remain in the helium stream at room temperature for 4 hours, and then brought up to 800°C in 1 hour.	Uniform
11	Dried in desiccator for 48 hours; placed in furnace at 800°C.	Uniform

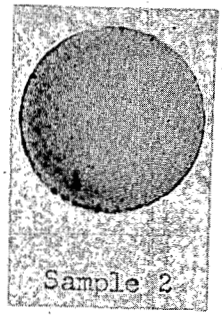
* Samples B-1508-A graphite impregnated with an aqueous solution of UNH.

** X-ray shadowgraphs for these samples are shown in Figure 2.

Figure 2

X-ray Shadowgraphs Showing Uranium Distribution Obtained by the Various Drying and Firing Procedures Described in Table X


Sample 1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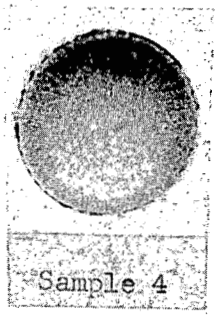
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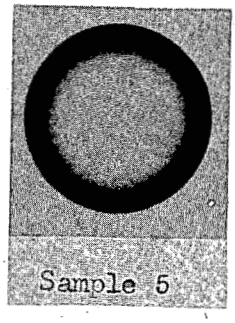
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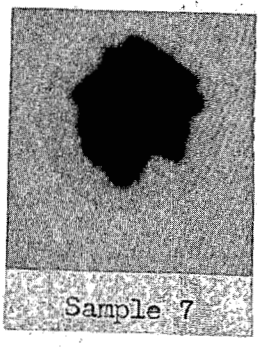
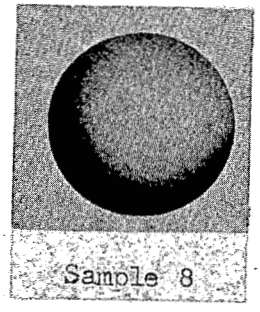
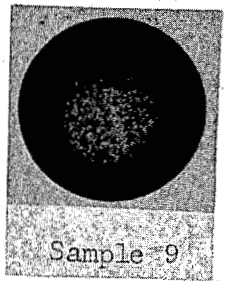

Sample 7


Sample 8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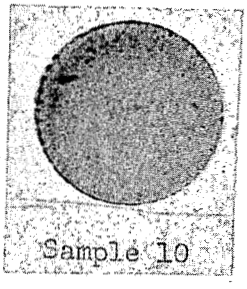
Sample 10

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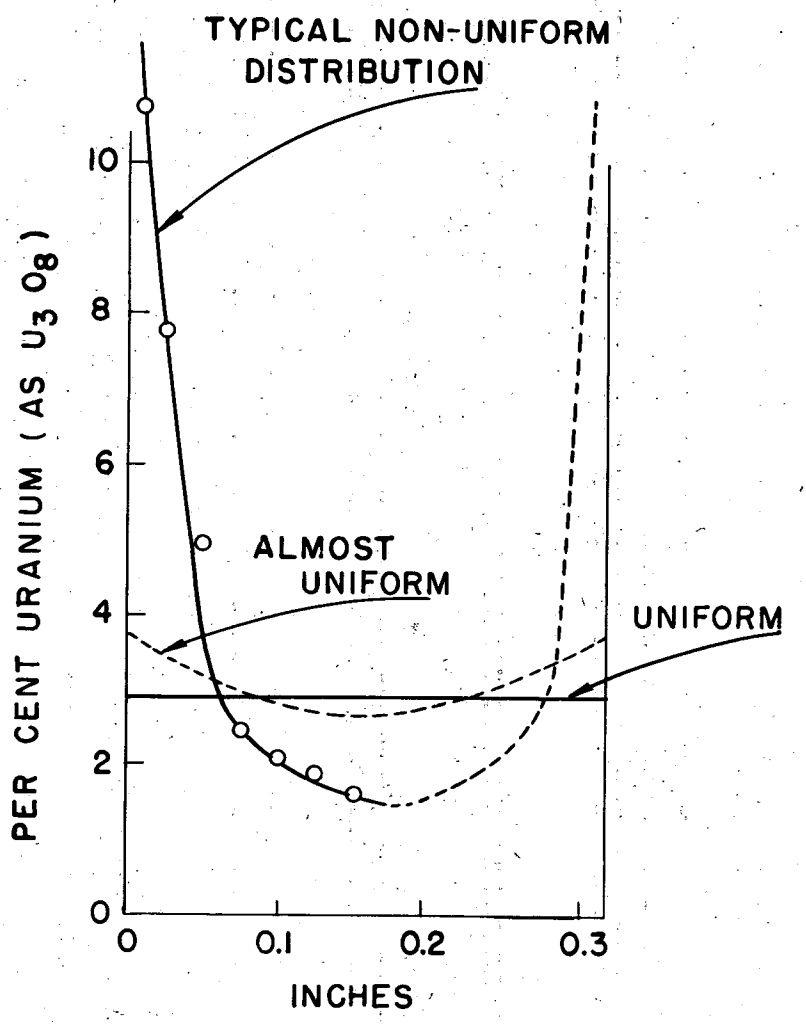
FIG. 3 TYPICAL URANIUM DISTRIBUTIONS OBTAINED BY VARIOUS DRYING AND FIRING TECHNIQUES IN B-1508-A GRAPHITE FUEL RODS.



4.2.2 Graphite Losses on Firing

The firing step in this process was carried out in a tube furnace which was continually swept with commercial tank helium. It was found that graphite losses due to oxidation (oxygen content of the helium averaged about 0.05%) amounted to not more than 0.06% by weight at 800°C. This was not considered serious enough to warrant gas purification. Determination of the carbon burnt off in the decomposition of uranyl nitrate hexahydrate showed that the amount was approximately equal to 2% of the weight of U_3O_8 in the graphite.

4.3 Pretreatment Procedure

For the most part the pretreatment used in this work was done to remove loose graphite particles remaining from the machining operations and to obtain a dry sample free from volatile matter for the impregnation. While working with the refluxing technique, it was thought that the efficiency of the impregnation could be increased if the porosity of the graphite could be increased. A pre-treatment step consisting of boiling in concentrated nitric acid followed by firing at 800°C was therefore investigated. The effect of this pretreatment was measured by impregnating the resultant graphite with water, weighing the immersed sample, and then calculating the percentage of the voids filled. It was found that such pretreatment with nitric acid increased the amount of water which could penetrate into the graphite. Each such treatment increased this effect up to the third treatment, where it became obvious that the increase in water pickup was about equivalent to the volume of graphite lost by oxidation. Data for these experiments are given in Table XI. It was found on comparing the nitric acid pretreatment with a corresponding water pretreatment, that the water pretreatment also had an activation effect although this was not as great as for the nitric acid.

Data for one experiment of this nature are given in Table XII.

Table XI
Effect of Nitric Acid Pretreatment of AGR Graphite
on the Resultant Water Absorption

Pretreatment	Percent Voids Filled with Water			
	#1	#2	#3	#4
Before Treatment	75.6	68.8	82.0	81.8
After one HNO_3 treatment	89.9	86.5	91.1	89.5
After two HNO_3 treatments	93.0	87.8	94.3	93.7
After three HNO_3 treatments	94.3	90.4	96.1	95.9

Table XII
Effect of Water Pretreatment of AGR Graphite
on the Resultant Water Absorption

Number of Pretreatments	Percent Voids Filled with Water
0	80.7
1	82.5
2	87.6
3	91.7
4	92.6
5	93.0
6	93.4
7	93.7
8	93.9
9	94.0
10	94.0

With impregnation by the evacuation technique, the efficiency of impregnation was not substantially improved by a nitric acid pretreatment since activation of the graphite is not necessary to complete filling of the voids.

4.4 Correlation of Irreproducibility of Impregnation by Refluxing with Graphite Density

Impregnations were carried out with 25 fuel rod sections of AGR graphite

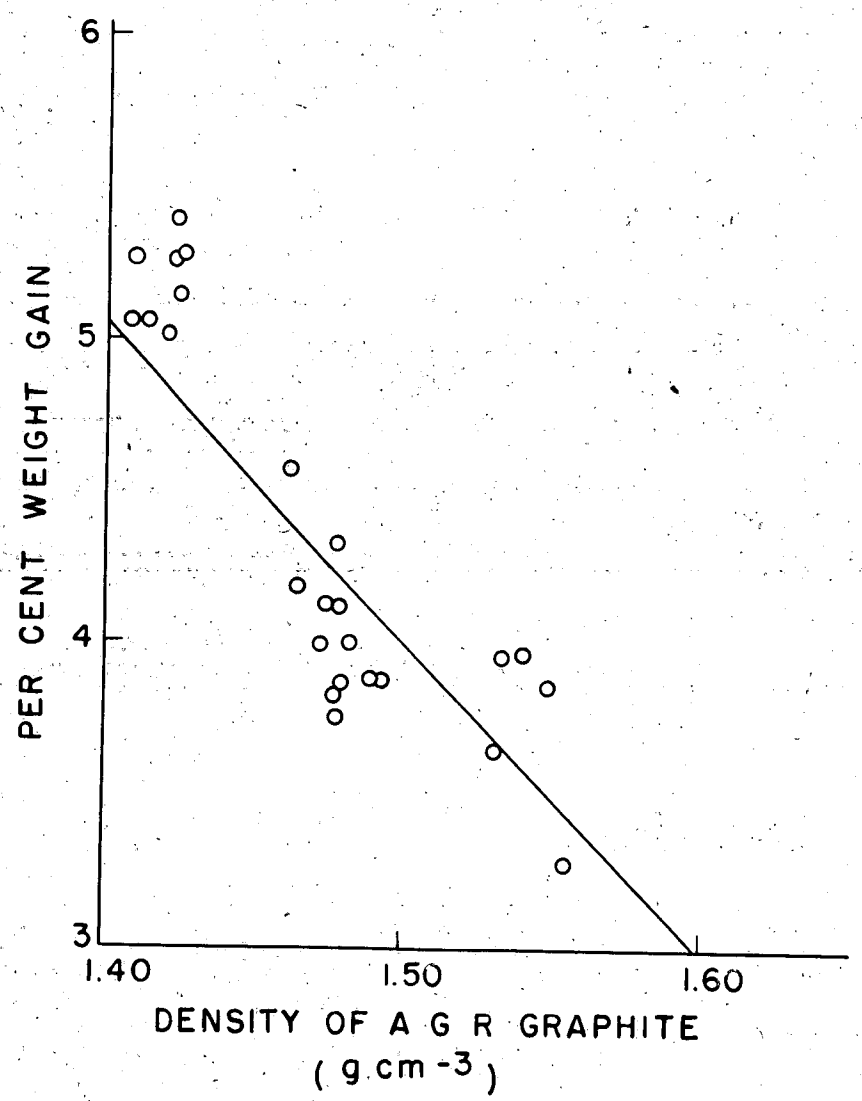
in order to estimate how much of the irreproducibility in the uranium content (as shown in Table II) was due to the graphite and how much to the process. The volume and initial weight of the sample were taken, following which it was boiled in water for 30 minutes, and then fired in helium at 800°C. Impregnation by refluxing in a 1.2 M aqueous solution of uranyl nitrate hexahydrate was carried out, followed by conversion to U_3O_8 in helium at 800°C. The density (as calculated from weight and volume measurements) and the gain in weight on impregnation were compared as shown in Figure 4. A rough approximation of the inherent irreproducibility of the refluxing process was obtained by applying the method of least squares to the data. Assuming that the variations in density of the graphite are accounted for by these calculations, the remaining deviations can be assumed to be the variations introduced with experimental technique. The maximum deviation shown on the graph is ±12%. Impregnations with B-1508-A graphite using the same refluxing technique have shown no variation above 5%. Only 5 samples were used in this case, however, so the data may not be complete.

5 SUMMARY

Graphite containing U_3O_8 distributed uniformly throughout the cross-section was made by impregnation with uranyl nitrate and subsequent firing at 800°C in helium. Samples as large as the fuel rods for the Daniels' High Temperature Pile were processed to contain up to 19% U_3O_8 by weight in a single impregnation and it was shown that higher percentages could be attained by repeating the process one or more times.

The process as developed consisted of five steps. (1) The graphite was fabricated in the desired shape. (2) It was boiled in water for 30 minutes and fired in a helium atmosphere for 30 more minutes. (3) The actual impregnation step was carried out by first evacuating the graphite

FIG. 4 VARIATION OF URANIUM CONTENT WITH THE DENSITY OF A G R GRAPHITE ON IMPREGNATION BY THE REFLUXING TECHNIQUE.



sample and then admitting an aqueous uranyl nitrate solution whose concentration was determined by the final U_3O_8 content desired. (4) It was then dried slowly at room temperature over a desiccant and (5) fired in helium at 800°C.

The reproducibility of the process seemed to be chiefly dependent on the porosity of the graphite. AGR, AGOT-K, and B-1508-A graphites (products of the National Carbon Company) were used and a rather definite correlation between the uranium content and the porosity was found. On the basis of limited sampling, B-1508-A graphite was found to be the most constant with respect to porosity.

Only one critical step was found in the experimental work, the drying step. In order to obtain uniformity of the uranium distribution within the graphite it was necessary to dry the sample in a manner which did not cause the aqueous solution to flow in the pores of the graphite but rather to allow the water to evaporate slowly enough to maintain equilibrium within the sample at all times.

Impregnation by refluxing and by simple immersion, use of non-aqueous solutions or uranyl nitrate, and other pretreatment procedures were also investigated but were found to be less advantageous.