PARTICLE SIZE DISTRIBUTIONS OF U_3O_8 PRODUCED BY OXIDATION IN AIR AT 300-900°C

by

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ABSTRACT

Both unirradiated and irradiated UO_2 fuels were isothermally oxidized in air at temperatures between 300 and 900°C. During oxidation, the UO_2 samples fragmented and formed U_3O_8 particles. Sieving and sedimentation techniques were used to measure the size distribution of the particles. The median particle sizes of the unirradiated samples oxidized at 900, 700, 500 and 300°C were 600, 80, 16 and 7.5 μm, respectively. The relative humidity of the environment during sieving did not affect the size distributions of particles from 900, 700 or 500°C oxidation. For the 300°C sample, increasing the humidity from 11% to 50% did not influence its size distribution, but when the humidity was increased to 98%, its median size increased from 7.5 μm to about 100 μm. The size distributions of the irradiated fuel (burnup 457 MW·h/kgU) were similar to those of the unirradiated fuel.

1.0 INTRODUCTION

During an accident scenario, when fuel is exposed to steam or air at high temperatures, UO_2 may be oxidized and fission products released [1, 2]. When UO_2 is oxidized in air at temperatures below 1550°C, the equilibrium product is U_3O_8. The transformation of UO_2 to U_3O_8 is accompanied by a 32% volume increase. The volume expansion results in fragmentation of the UO_2 at low temperatures, where U_3O_8 is brittle [3]. The resulting particle size may be very fine and such particles might become airborne during some accident scenarios. Particle size distribution after oxidation is therefore a key factor for predicting the possibility of release of active airborne particles from fuel [4].

As part of the Reactor Safety Research programs at AECL, studies on the oxidation behaviour of UO_2 in air and steam have been conducted to determine the influence of fuel oxidation on fission-product release during postulated accident conditions. These studies have shown that the oxidation of fuel has the potential to increase the activity released to containment [5, 6]. Four processes have been identified that contribute to increased fission-product release as a consequence of UO_2 oxidation: enhanced fission-product diffusion in the oxidized fuel, increased volatility of some fission products, volatilization of the UO_2 with associated fission-product

release, and release of fine oxide particles containing all of the retained fission products [7]. The principal objective of the experiments reported here was to investigate some of the parameters that increase the latter process. In these tests, the effect of the oxidation temperature on particle size distribution was measured. Also, since postulated accident atmospheres are unlikely to be dry, and humidity is known to influence the agglomeration of fine particles, the effect of humidity on the oxidized particle size distribution was investigated.

2.0 EXPERIMENTAL

2.1 Samples

Both unirradiated and irradiated fuels were used in the experiments, to compare the influence of irradiation. The enrichment of ^{235}U of the unirradiated fuel was natural (0.72%), and the irradiated fuel was 1.38% enriched. The unirradiated UO_2 cylinders, 12.15 mm diameter and about 10 mm long, weighed about 10 g, and were cut from sintered pellets with a density of 10.7 Mg/m^3. The average grain size was 9 μm. The irradiated samples were UO_2 fragments, about 10 g for each sample, obtained by cutting a CANDU fuel element irradiated in the NRU reactor (element AC-19 from bundle XM). The fuel density before irradiation was 10.6 Mg/m^3. The burnup of AC-19 was 457 MW·h/kgU and the end-of-life power was 32 kW/m. After irradiation, the grain size ranged from about 8 to 25 μm, between the periphery and the centre of the fuel element.

2.2 Oxidation

The oxidation conditions are listed in Table 1. Tube furnaces with environmental control were used to oxidize the UO_2 samples. The samples were put into a quartz boat and pushed into the furnace. When the samples reached the test temperature, air was introduced. The unirradiated samples were isothermally oxidized

Table 1
Oxidation Conditions

Sample	Temperature (°C)	Time (h)
Unirradiated	900	21
Unirradiated	700	21
Unirradiated	500	5
Unirradiated	300	94
Irradiated	900	61
Irradiated	700	40
Irradiated	500	3

at 300, 500, 700 and 900°C in the laboratory. The irradiated samples were isothermally oxidized at 500, 700 and 900°C in a hot-cell. The air flow rates were 50 STP mL/min in the laboratory tests and 100 STP mL/min for the hot-cell tests.

The weight gains of the samples were measured using a top-loading digital balance with a resolution of 10^{-5} g. After oxidation, sieving and sedimentation techniques were used to determine the size distribution of the particles.

2.3 Sieving

Sieving was used to determine the size distribution of particles larger than 53 μm. The mesh sizes of the sieves were 2000, 1000, 500, 250, 125, 75 and 53 μm. The sieving was carried out in a sealed box in which the humidity was controlled and monitored. The samples were stored in the box at a given humidity for at least 12 hours before they were sieved for 1 hour in the box. The sieves were grounded to avoid the possible influence of static electricity.

The unirradiated samples were sieved at 11%, 50% and 98% relative humidity. After each sieving, the samples were recombined and sieved again at a higher humidity. Finally, the samples were recombined and sieved at 22% humidity, and the particles smaller than 53 μm were measured with a sedimentation technique.

The irradiated samples were sieved in 11% and 78% relative humidity. The sedimentation technique was not applied to the irradiated samples.

2.4 Sedimentation

The size distribution of the unirradiated particles that passed through the 53 μm sieve was measured by sedimentation, using a SediGraph™ machine. The samples were mixed with a Sedisperse™ solution with 8.512 mPa·s viscosity and 0.827 g/mL density. A magnetic stirrer, instead of the usual blender, was used to mix the samples with the solution, in order to avoid further mechanical breakup of the particles.

2.5 Morphology

The samples were photographed before and after oxidation. The unirradiated particles that passed through the 53 μm sieve were examined using a JEOL™ JSM-T330 Scanning electron microscope (SEM).

3.0 RESULTS AND DISCUSSION

The photographs in Figure 1 show the unirradiated UO_2 samples before and after oxidation. After oxidation at 900 or 700°C, the U_3O_8 particles were much coarser than those at 500 or 300°C. Due to the much smaller particle sizes, the apparent volumes of the samples that were oxidized at 500 or 300°C appeared to be larger than those oxidized at 900 or 700°C.

The weight gains of the samples were used to calculate the percentages of the UO_2 oxidized (see Table 2), assuming the initial samples were pure UO_2 and the oxidation product was U_3O_8. At 900, 700 and 500°C, the samples were fully oxidized. After 94 hours at 300°C, the sample was 70% oxidized. The un-oxidized 30% of the 300°C sample likely comprised the largest pieces. If the particles larger than 250 μm were assumed to be still UO_2, and considering only the particles smaller than 250 μm, recalculation from the same weight gain suggested that 99% of this fraction of the UO_2 was oxidized. In the rest of this paper the particles larger than 250 μm from the 300°C sample will be assumed to be UO_2 and therefore will not be included in the analysis.

Table 2
Percent of UO_2 Oxidized

Sample	Temperature (°C)	% UO_2 Oxidized
Unirradiated	900	98
Unirradiated	700	100
Unirradiated	500	96
Unirradiated	300	70(99*)

* Calculated assuming particles larger than 250 μm were unoxidized.

Figure 2 shows the percent of the unirradiated particles smaller than a given size, determined by sieving at room temperature at 11%, 50% or 98% relative humidity. These plots indicate that the higher the oxidation temperature, the coarser the particle sizes. This is due to an increase in the U_3O_8 plasticity with increasing temperature, which allows oxidation-induced stresses to be relaxed. The relative humidity did not affect the particle size distributions for samples oxidized at 900, 700 or 500°C. For the finer particles produced at 300°C, increasing the humidity from 11% to 50% did not affect their size distribution. But when the humidity was increased to 98%, the particle size was increased (see Figure 2(c)). This is probably due to the agglomeration of the fine particles in the humid condition, or the adhesion of the fine particles to the sieves.

Figure 3 shows the results of the unirradiated sample determined by sieving and sedimentation. The percentage of particles larger than 53 μm was measured by sieving at 22% relative humidity, and the remainder was measured by sedimentation. The figure shows that the higher the temperature of oxidation, the coarser the U_3O_8 particles. For the oxidation temperatures of 900, 700, 500 and 300°C, the median particle sizes were about 600, 80, 16 and 7.5 μm, respectively. These median sizes were much larger than the results reported by Iwasaki et al [8]. Of their samples, with an original grain size of 9 μm, oxidized at 700 and 500°C, the median sizes were 30 and 7 μm, respectively. The difference between their results and our work is not understood. They sieved the samples by a 44 μm sieve and used sedimentation to measure the size distribution of the particles smaller than 44 μm. They did not identify their method of mixing the particles with the sedimentation solution. In preliminary trials for our tests, we observed a breakup of the particles when a blender was used to mix the powder and Sedisperse solution. Mixing by a blender shifted the median size of a sample from 7.6 μm to 3.6 μm. This effect may explain the differences between our results and those of Iwasaki.

A comparison of Figure 3 with Figure 2(c) shows that for the 300°C sample, when the humidity was increased to 98%, the median particle size increased from 7.5 μm to 100 μm.

The size distributions of the irradiated samples are shown in Figure 4. The size distribution of the unirradiated samples shown in Figure 2 are re-plotted for comparison. The particles produced at 500°C, for both irradiated and unirradiated fuels, were very fine, mostly smaller than 53 μm. For the 700°C samples, the particle size distributions of the irradiated and unirradiated fuels were very similar, except that the irradiated sample did not have particles larger than 1 mm. This was likely due to a difference in the size of the initial UO_2 pieces. The irradiated UO_2 fragments were typically a few millimetres across, while the unirradiated UO_2 was a cylinder (ϕ12×10 mm). At 900°C, the irradiated sample had more particles larger than 1 mm; otherwise, its size distribution would be very similar to that of the unirradiated sample. This difference may be caused by the sintering of fine particles for a long time (61 hours) at 900°C.

The SEM photographs in Figure 5 show the morphology of the unirradiated particles that passed through the 53 μm sieve. At 300°C, the size of the particles was close to the original UO_2 grain size. The particle size increased with increasing oxidation temperature, as shown in Figure 5(b) through (d). At 900°C, some columnar U_3O_8 grains were observed. In all the samples, considerable secondary cracking was observed.

The test results indicate that the oxidation temperature is the most important factor determining the particle size distribution. In the 300 to 500°C range, UO_2 is oxidized to very fine powders

and a significant amount would be capable of becoming airborne. This is consistent with the analysis of the Chernobyl accident by Hunt et al [9]. After the initial fission-product release on the first day of the Chernobyl accident, the effective temperature of the fuel was estimated to be reduced to about 500°C, and it remained at that temperature for about 5 days. Oxidation of UO_2 in air at this period was very rapid and resulted in very fine particles. These particles probably became airborne later in the accident and contributed to the fission-product releases, which reached about 30 times that of the initial release.

4.0 CONCLUSIONS

When oxidized in air at temperatures between 300 and 900°C, UO_2 samples were fractured and U_3O_8 powders were obtained. At 900 or 700°C, the particles formed were much coarser than those at 500 or 300°C. The median particle sizes were 600, 80, 16 and 7.5 μm, respectively. The oxidation rate at 300°C was much slower than that at 500°C and above.

Humidity did not affect the measured size distributions of the particles from oxidation at 900, 700 or 500°C. For the sample oxidized at 300°C, increasing the relative humidity from 11% to 50% did not influence the size distribution. However, when the humidity was increased to 98%, the sample's median size increased from 7.5 μm to about 100 μm, likely due to agglomeration or adhesion.

The size distributions of the irradiated samples were similar to those of the unirradiated fuel. Some small differences, possibly caused by parameters other than the oxidation temperature or humidity, were observed. A greater fraction of particles larger than 1 mm were measured for the irradiated fuel oxidized at 900°C, possibly due to re-sintering. Also, no particles greater than 1 mm were measured for the irradiated fuel oxidized at 700°C, possibly due to the small size of the initial UO_2 fragments.

The results of this study could be used to assess the potential consequences of fuel oxidation with U_3O_8 formation for various accident scenarios, if a limiting size could be defined below which the fine powders were assumed to become airborne. Since high relative humidity affects the results for the fine powders produced at 300°C, it may be necessary to quantify the humidity threshold in future experiments. Also, the effect of re-sintering at high temperatures may warrant further investigation.

5.0 ACKNOWLEDGEMENT

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work. The staff of the Building 234 hot-cells are acknowledged for their important contributions during the experiments.

6.0 REFERENCES

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Figure 1 The UO_2 samples before and after oxidation: (a) before oxidation; (b) 300°C for 94 hours; (c) 500°C for 5 hours; (d) 700°C for 21 hours and (e) 900°C for 21 hours.

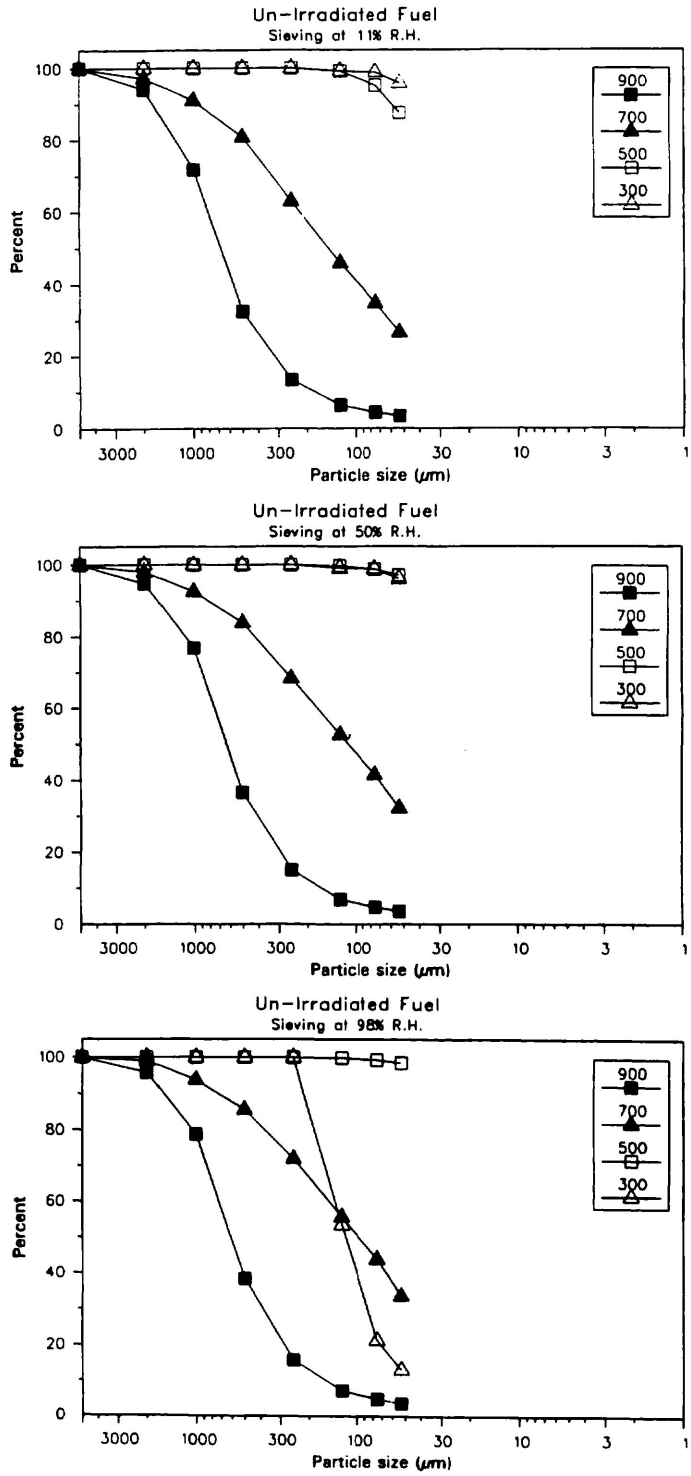


Figure 2 The weight percent of particles smaller than a given size. The unirradiated samples were sieved at different relative humidity: (a) 11%, (b) 50%, and (c) 98%.

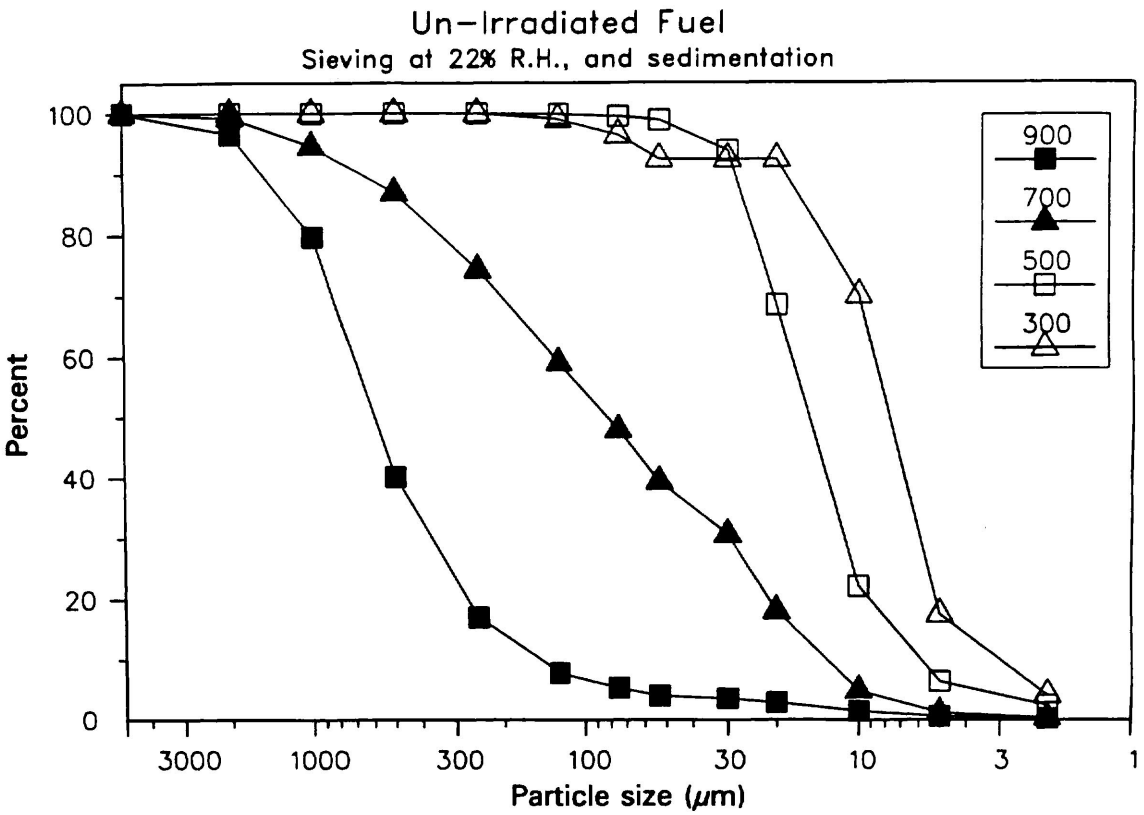


Figure 3 The percent of particles smaller than a given size for unirradiated UO_2, sieved at 22% R.H. The particles smaller than 53 μm were measured by sedimentation.

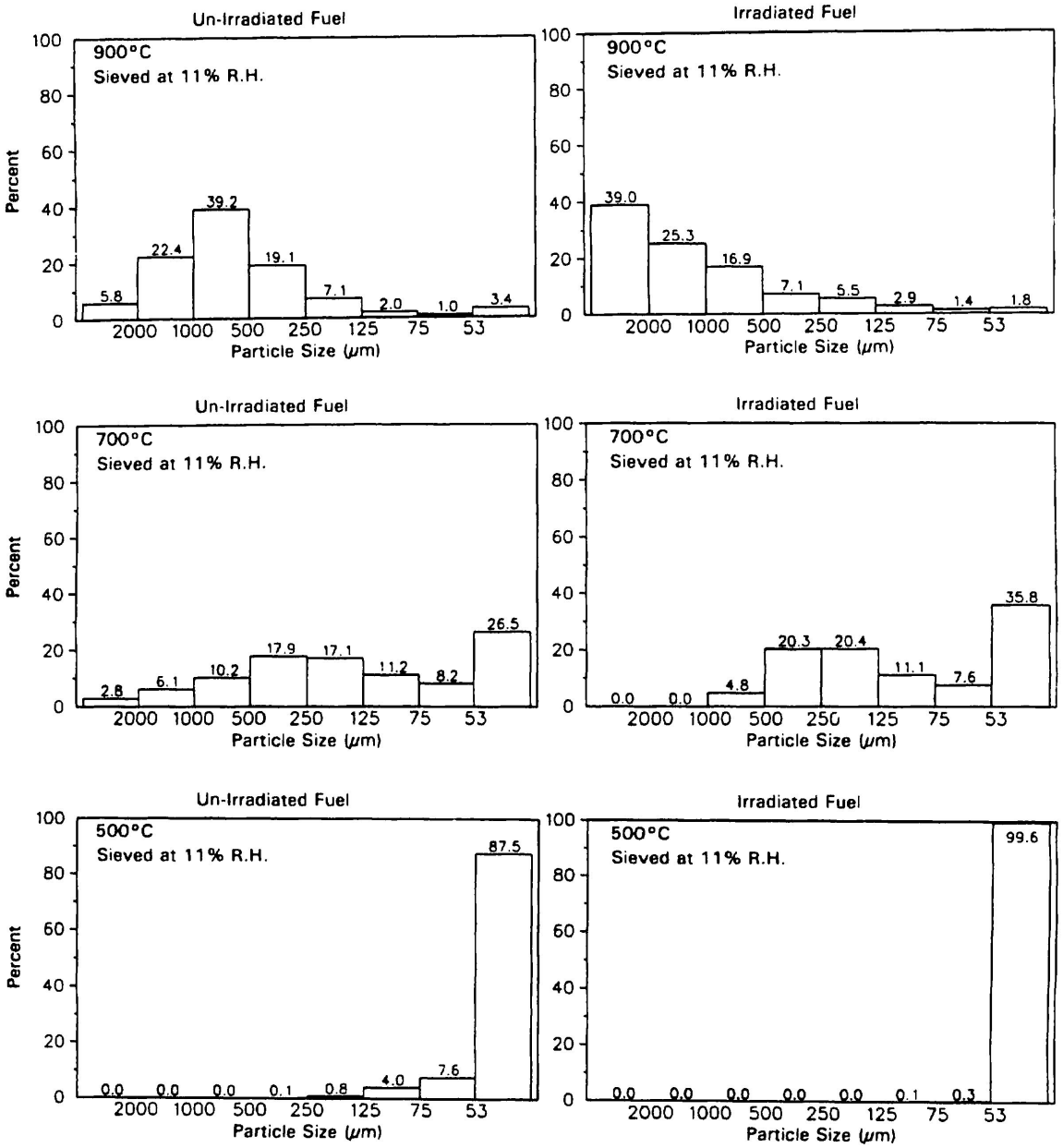


Figure 4 The size distribution of unirradiated and irradiated samples determined by sieving at relative humidity of 11%.

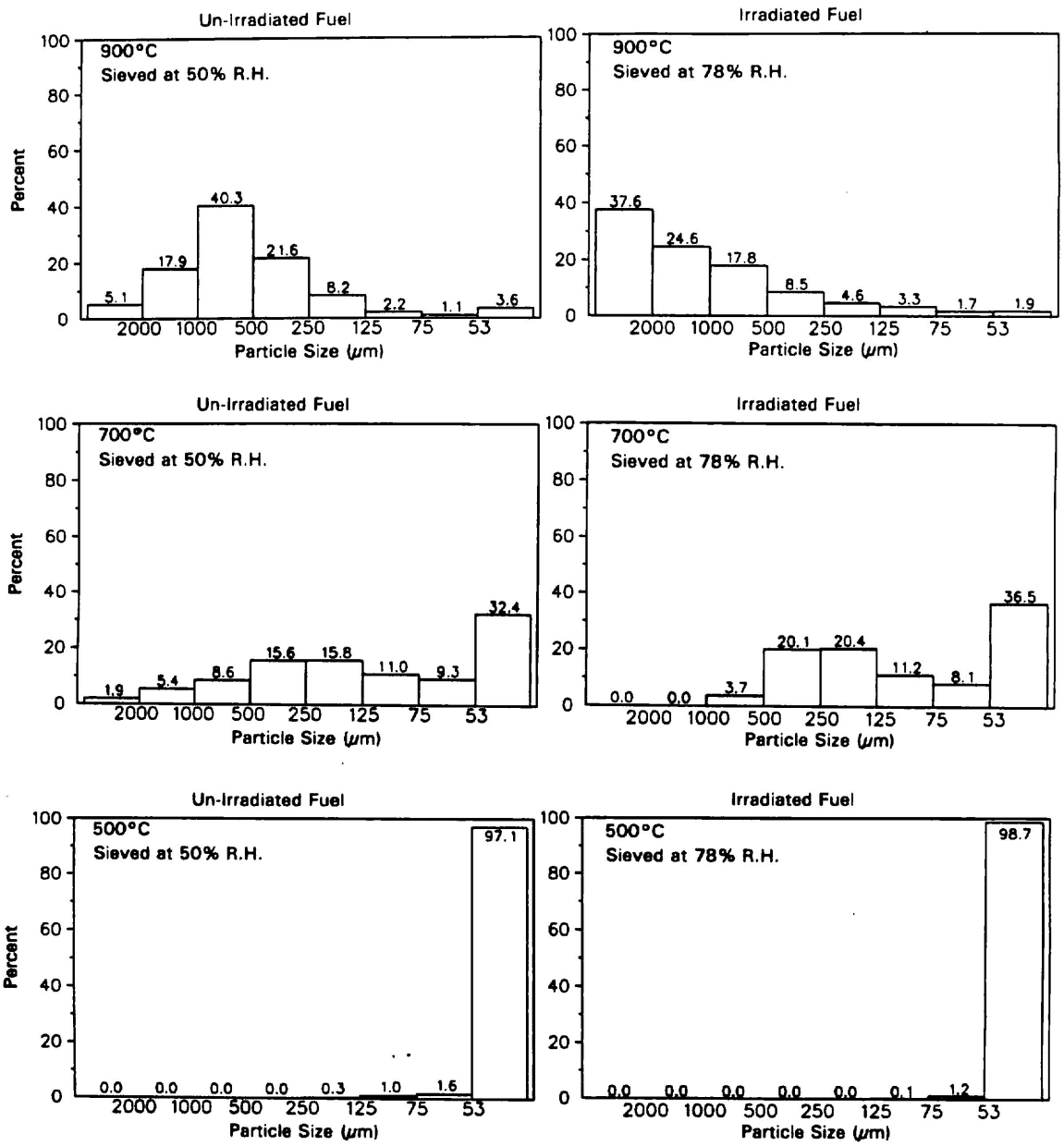
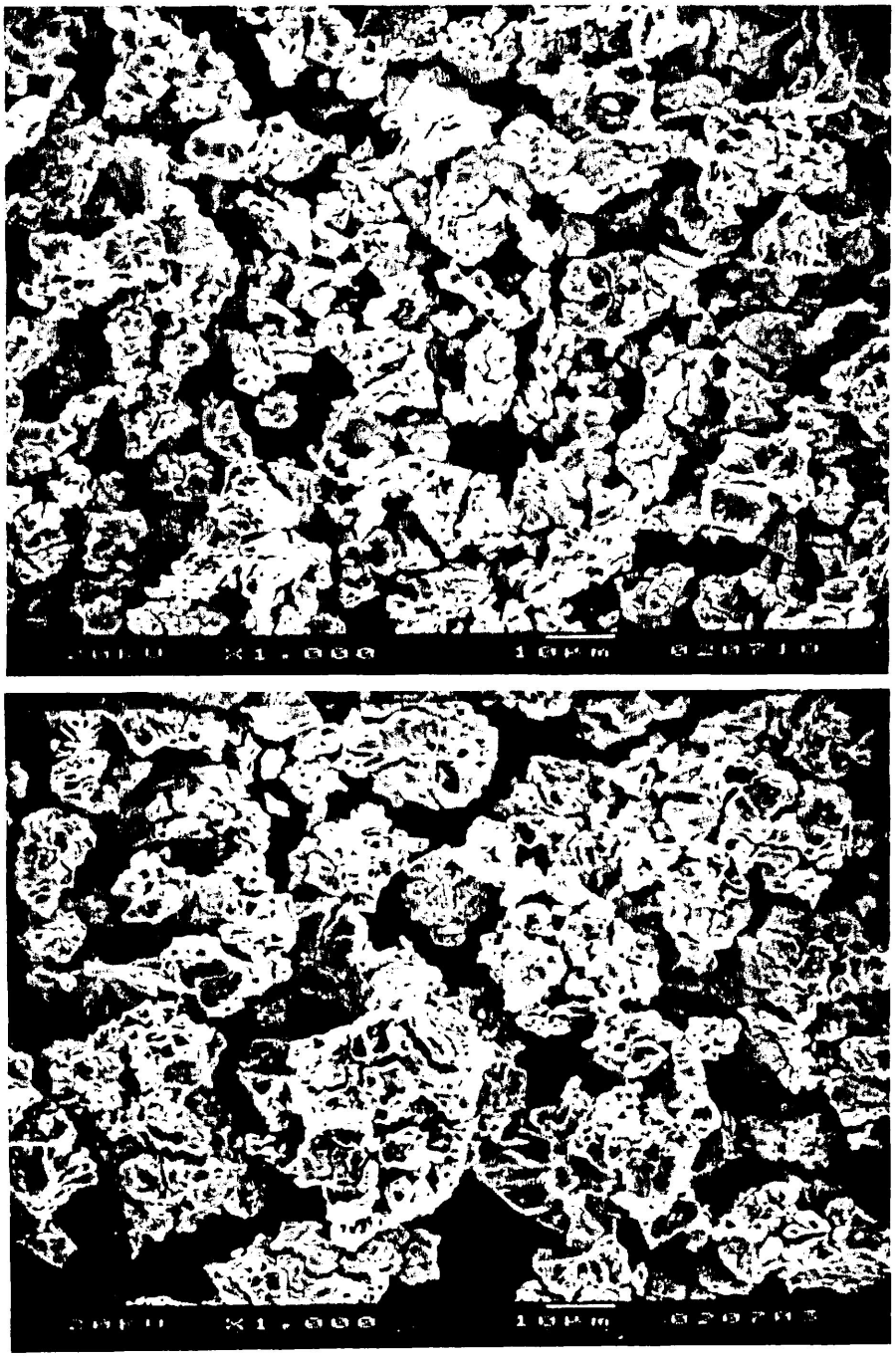


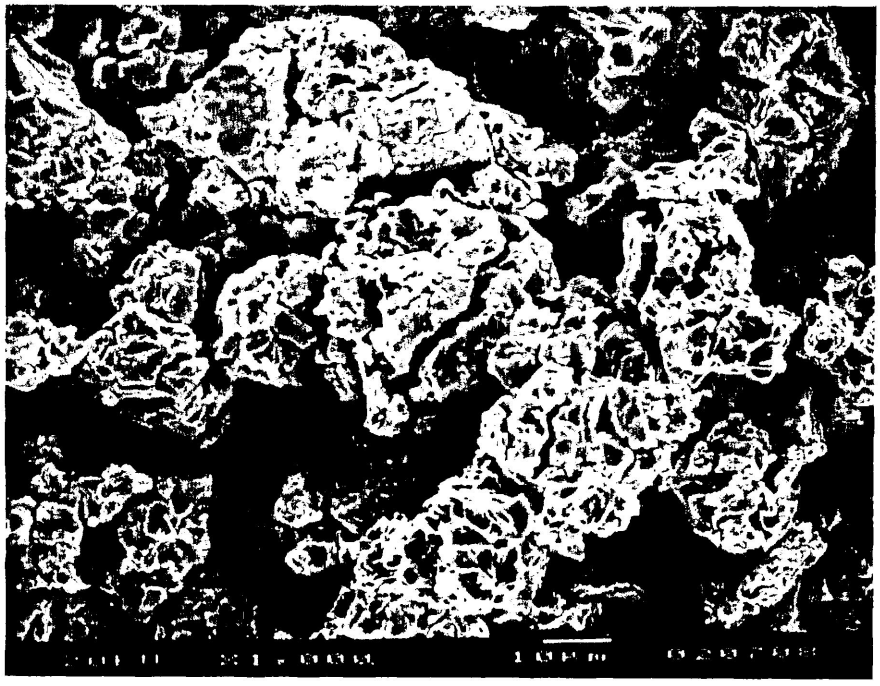
Figure 4 (continued) The size distribution of unirradiated and irradiated samples determined by sieving at relative humidity of 50% and 78%, respectively.



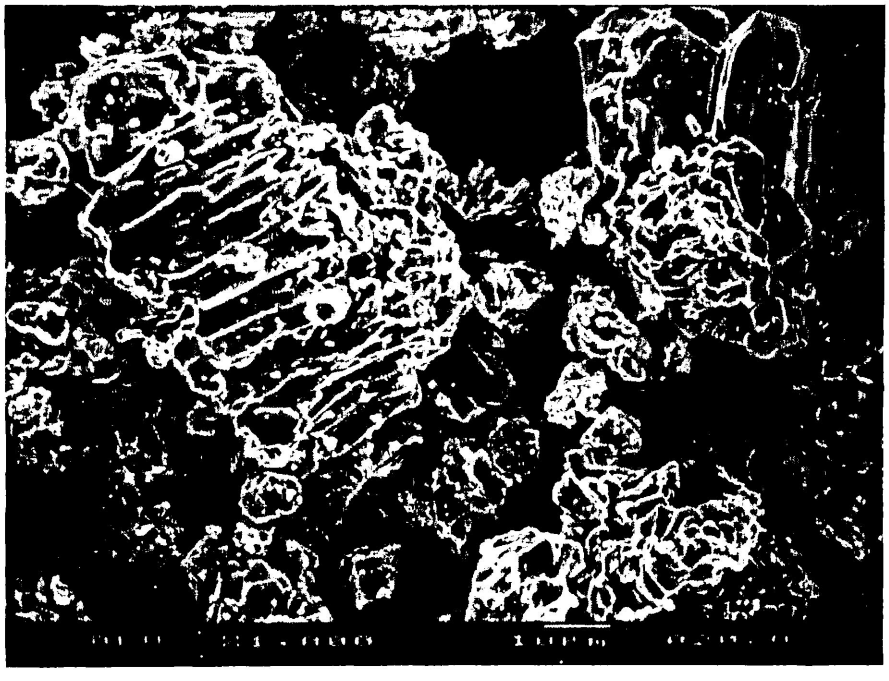
(a)

(b)

Figure 5 The morphology of the particles which passed through the 53 μm sieve. The oxidation temperatures were: (a) 300°C for 94 hours; (b) 500°C for 5 hours.

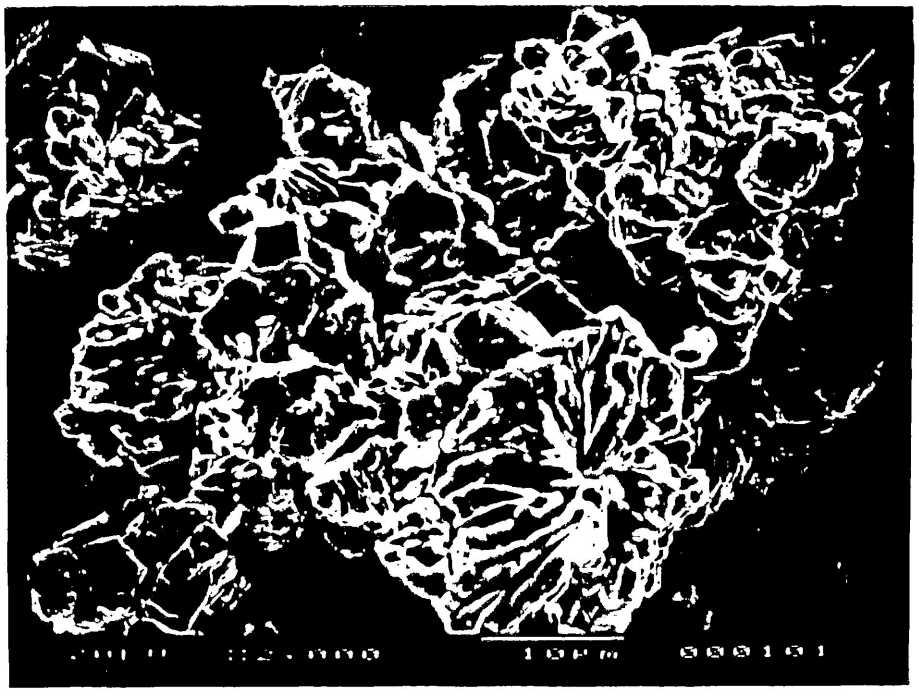


(c)



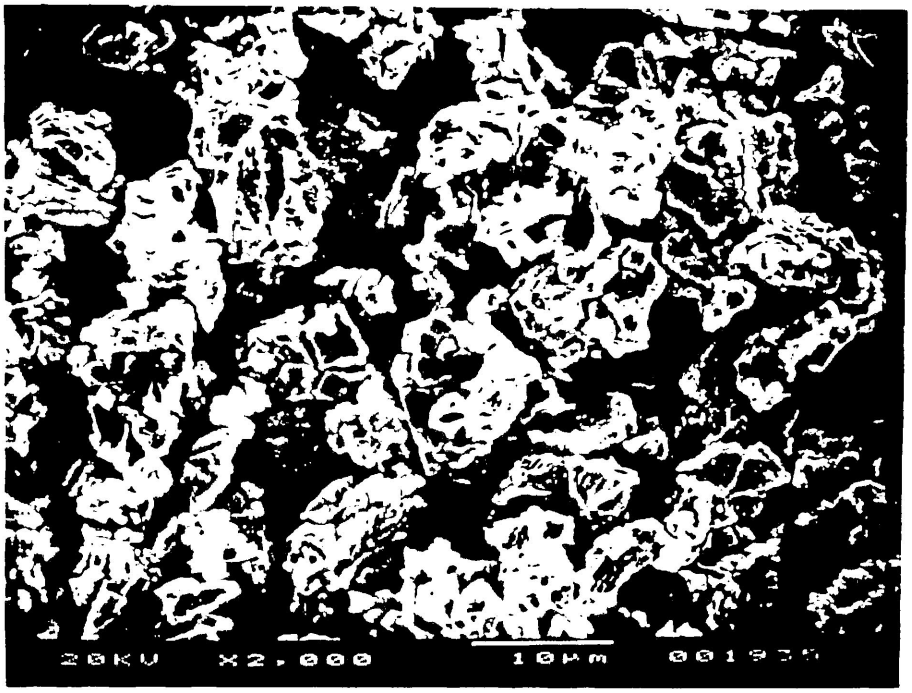
(d)

Figure 5 (continued) The oxidation temperatures were: (c) 700°C for 21 hours; (d) 900°C for 21 hours.

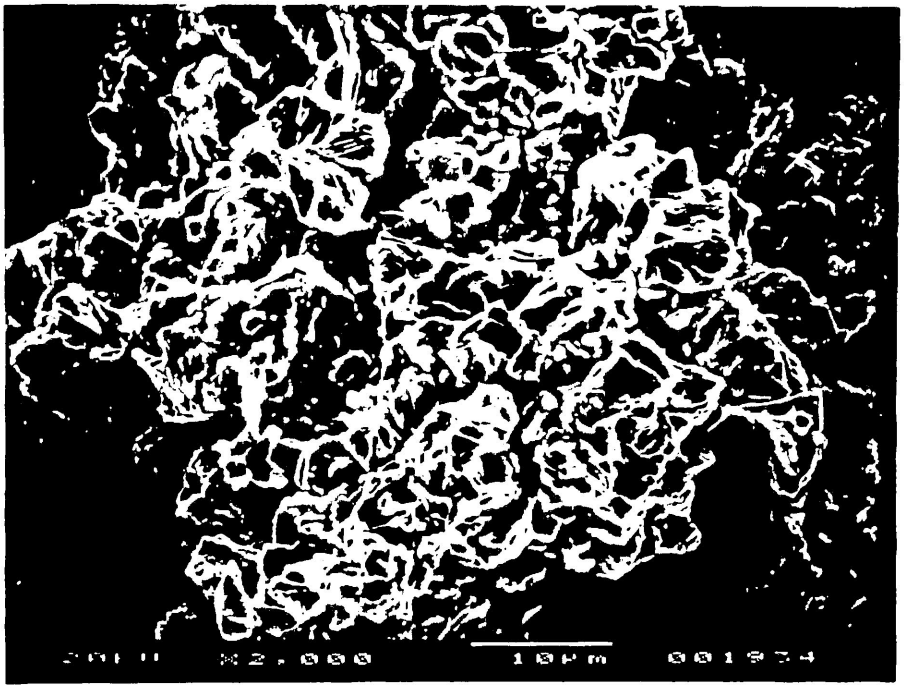


(c)

(d)



(a)



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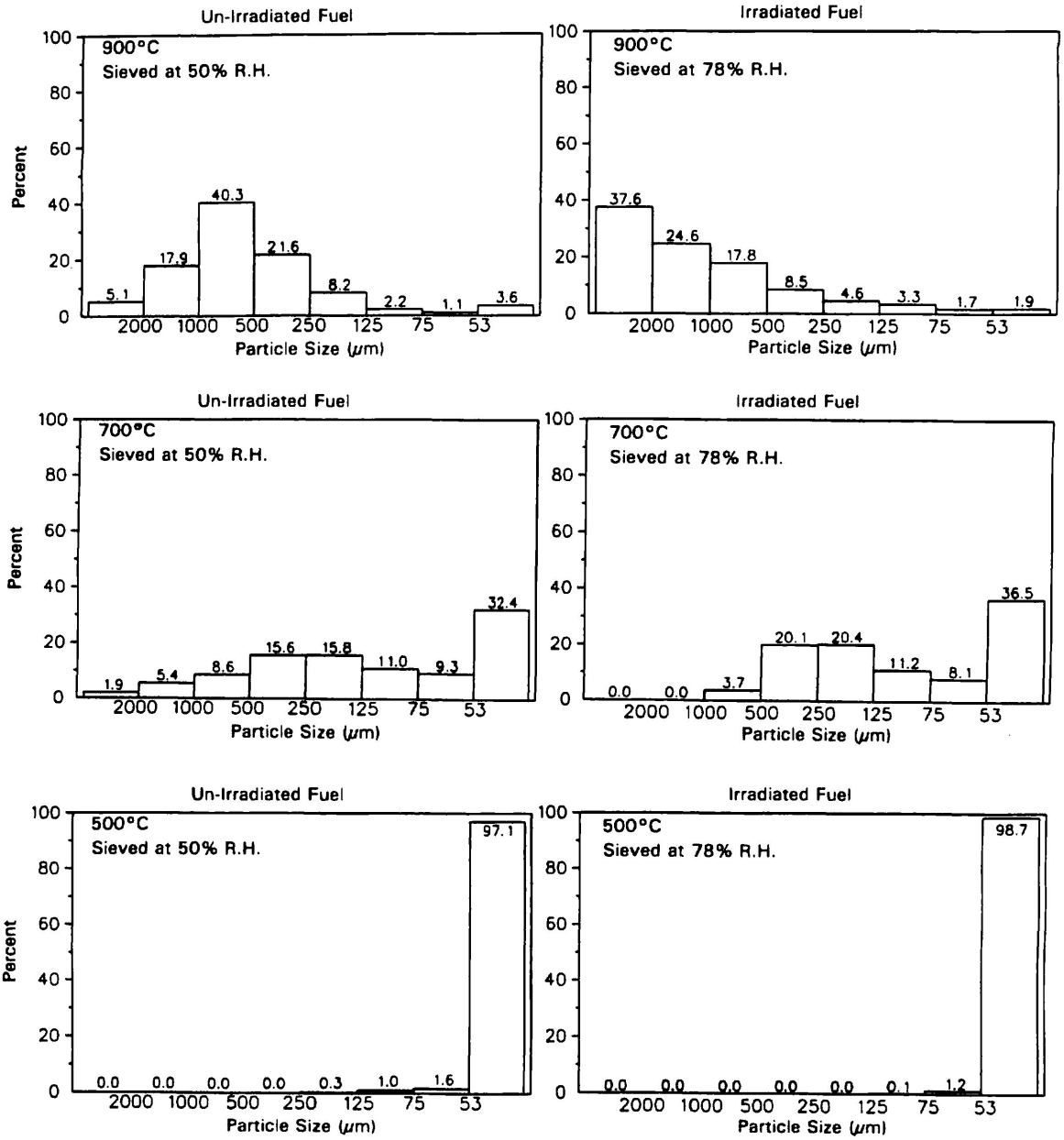
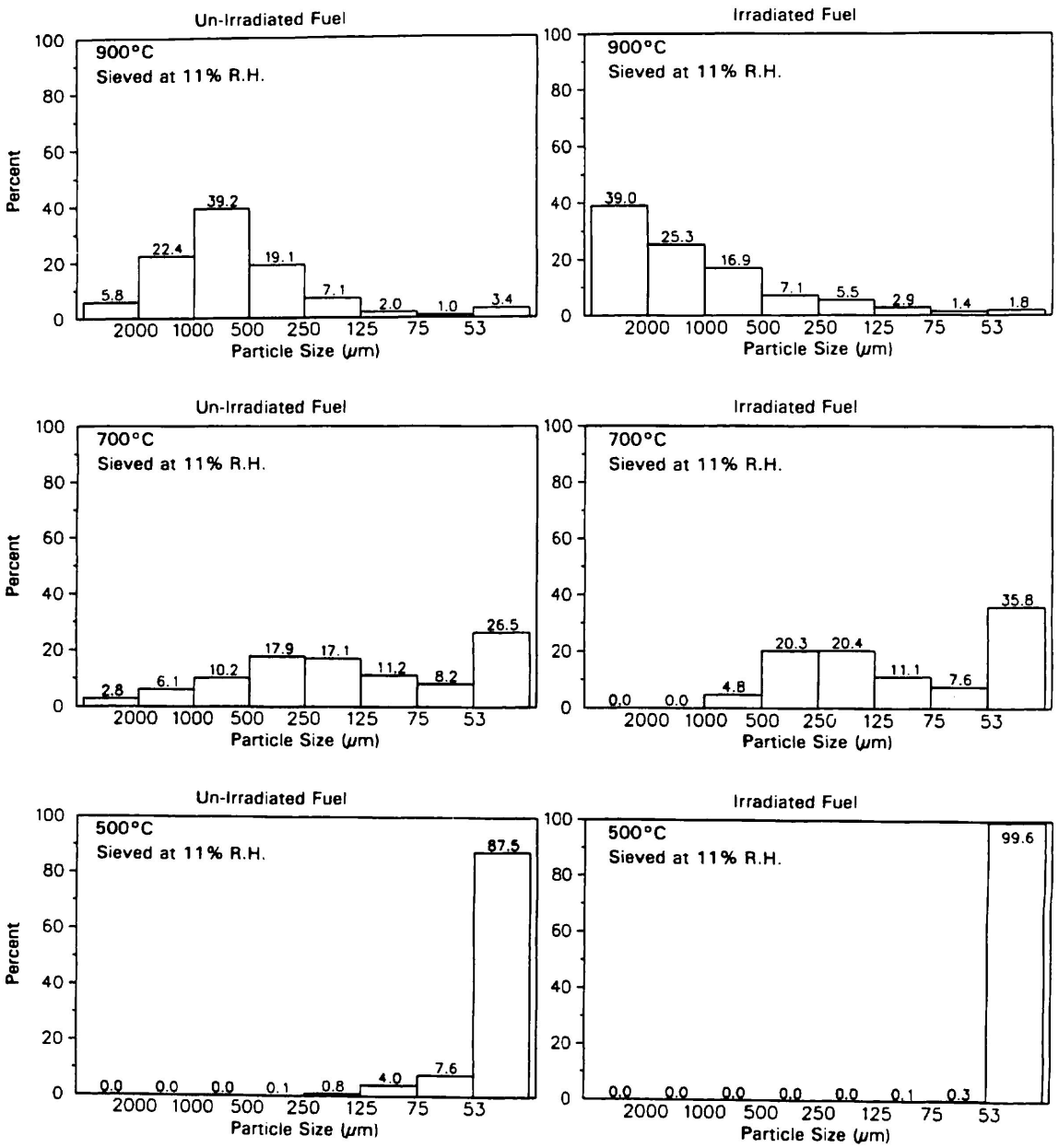
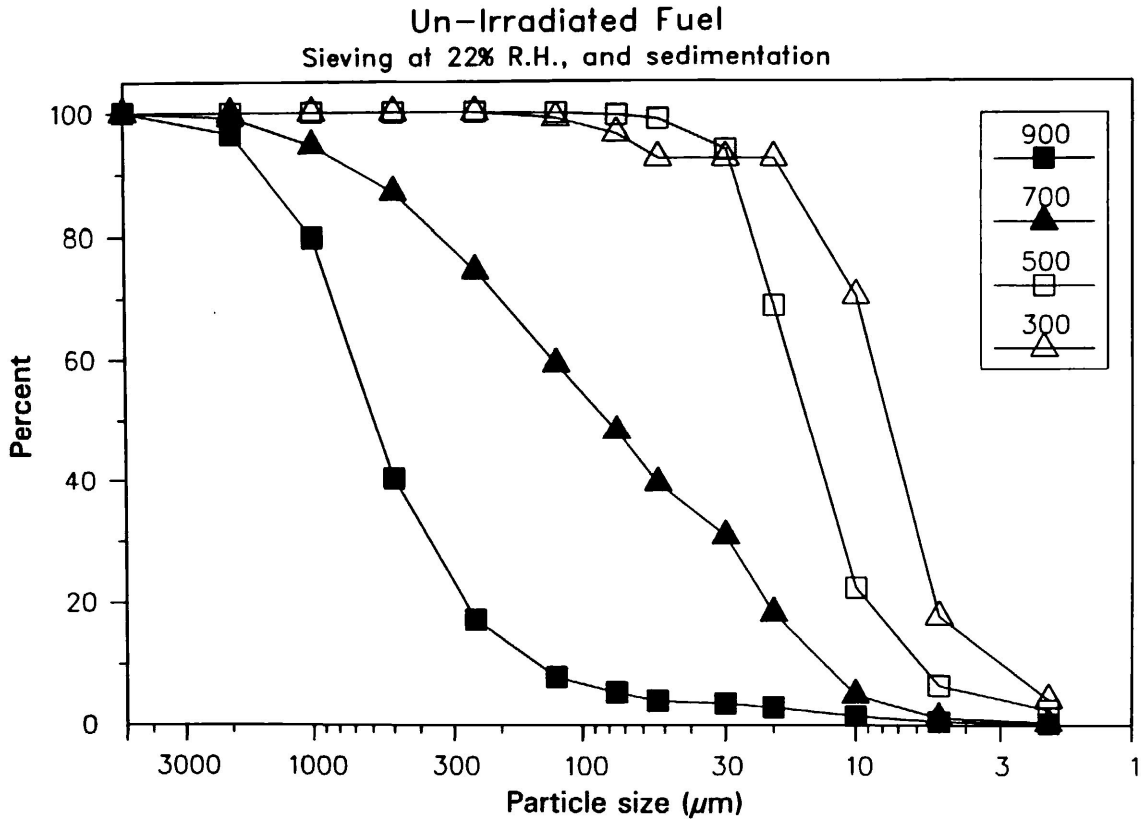
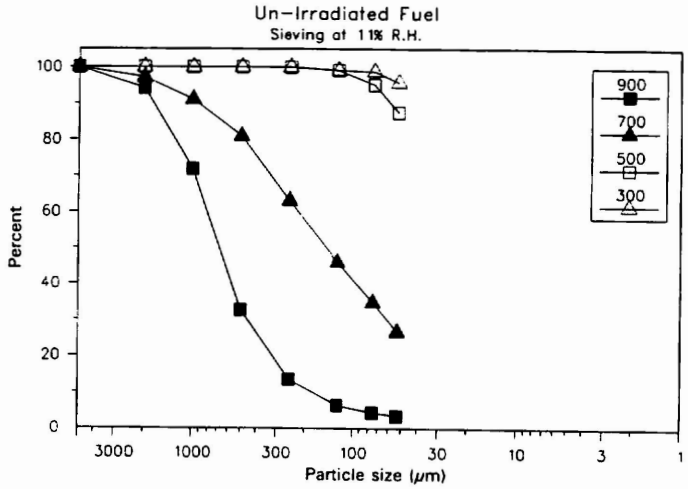
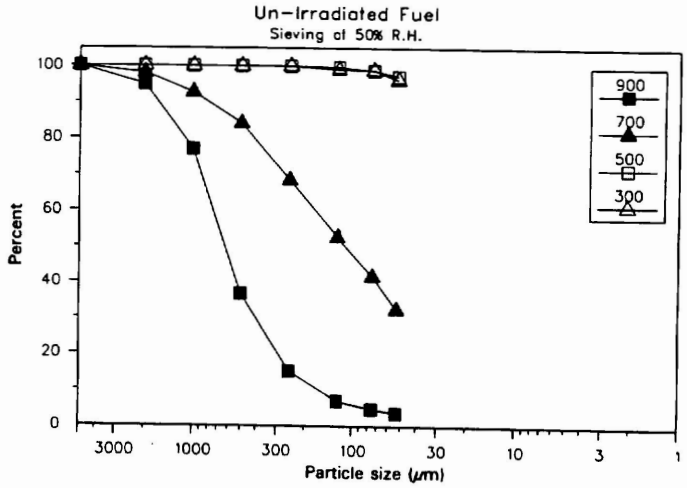
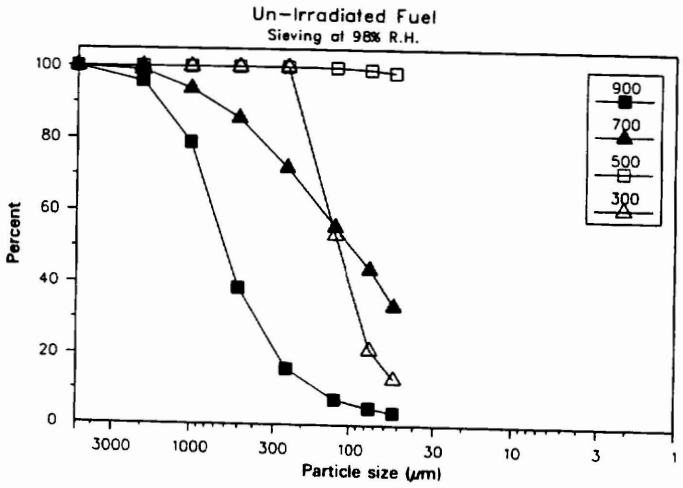

Un-Irradiated Fuel
900°C
Sieved at 50% R.H.
Percent
100
80
60
40
20
0
5.1
17.9
40.3
21.6
8.2
2.2
1.1
3.6
2000 1000 500 250 125 75 53
Particle Size (μm)
Irradiated Fuel
900°C
Sieved at 78% R.H.
37.6
24.6
17.8
8.5
4.6
3.3
1.7
1.9
2000 1000 500 250 125 75 53
Particle Size (μm)
Un-Irradiated Fuel
700°C
Sieved at 50% R.H.
Percent
1.9
5.4
8.6
15.6
15.8
11.0
9.3
32.4
2000 1000 500 250 125 75 53
Particle Size (μm)
Irradiated Fuel
700°C
Sieved at 78% R.H.
0.0
0.0
3.7
20.1
20.4
11.2
8.1
36.5
2000 1000 500 250 125 75 53
Particle Size (μm)
Un-Irradiated Fuel
500°C
Sieved at 50% R.H.
Percent
0.0
0.0
0.0
0.0
0.3
1.0
1.6
97.1
2000 1000 500 250 125 75 53
Particle Size (μm)
Irradiated Fuel
500°C
Sieved at 78% R.H.
0.0
0.0
0.0
0.0
0.0
0.1
1.2
98.7
2000 1000 500 250 125 75 53
Particle Size (μm)


Un-Irradiated Fuel
900°C
Sieved at 11% R.H.
Percent
Particle Size (μm)
2000 1000 500 250 125 75 53
5.8
22.4
39.2
19.1
7.1
2.0
1.0
3.4
Irradiated Fuel
900°C
Sieved at 11% R.H.
39.0
25.3
16.9
7.1
5.5
2.9
1.4
1.8
Un-Irradiated Fuel
700°C
Sieved at 11% R.H.
2.8
6.1
10.2
17.9
17.1
11.2
8.2
26.5
Irradiated Fuel
700°C
Sieved at 11% R.H.
0.0
0.0
4.8
20.3
20.4
11.1
7.6
35.8
Un-Irradiated Fuel
500°C
Sieved at 11% R.H.
0.0
0.0
0.0
0.1
0.8
4.0
7.6
87.5
Irradiated Fuel
500°C
Sieved at 11% R.H.
0.0
0.0
0.0
0.0
0.0
0.1
0.3
99.6

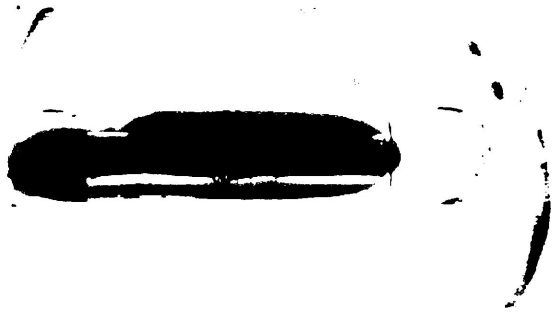

Un-Irradiated Fuel
Sieving at 22% R.H., and sedimentation
Percent
100
80
60
40
20
0
3000
1000
300
100
30
10
3
1
Particle size (μm)
900
700
500
300


Un-Irradiated Fuel
Sieving at 11% R.H.
Percent
Particle size (μm)
900
700
500
300


Un-Irradiated Fuel
Sieving at 50% R.H.
Percent
Particle size (μm)
900
700
500
300


Un-Irradiated Fuel
Sieving at 98% R.H.
Percent
Particle size (μm)
900
700
500
300

(a)



(b)

(c)

(d)

(e)