ELECTRON-BEAM PROCESSING OF POWDERED MATERIAL

Thesis for the Degree of M. S.

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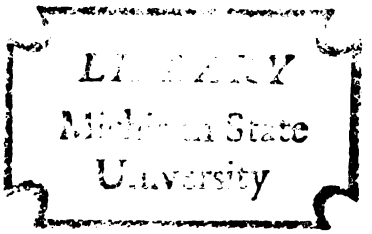

ABSTRACT

ELECTRON-BEAM PROCESSING OF POWDERED MATERIAL

by Wayne H. Clifford

As the use of ionizing radiation to induce chemical changes increases, it is natural that more efficient ways be sought to utilize such radiation. The characteristic of an electron beam is very high power delivery to a very small volume of material compared to other kinds of radiation.

For irradiation of powdered materials on a conveyor belt--the method now commonly used--this means that, for uniform irradiation, a thin sample must be used, resulting in much of the beam being absorbed in the belt. If a thick enough layer is irradiated to utilize the whole beam, there will be an extreme dose variation.

The purpose of this research was to demonstrate how these problems might be overcome by the use of a fluidized bed. In this case a pulsed fluidized bed (since pulsing enables the fluidization of a greater variety of particle sizes and densities) was used. The bed was two feet high by one foot in diameter and was filled with approximately twenty-five pounds of methylcellulose powder. The fluidizing gas was nitrogen from a forty-five gallon surge tank which was filled to ten or fifteen pounds per square inch

gage pressure. A solenoid valve in the line from the surge tank to the fluidized bed was generally open for one second and then closed for one second.

Fourteen different batch runs were made, of which half gave good product uniformity as determined by the viscosity of a two per cent aqueous solution at twenty degrees Celcius. The other runs involved poor fluidization and the presence of a "dead spot" in the bed.

A continuous feed and drawoff mixing run (without radiation) was made where the bed was filled with previously irradiated methylcellulose and fresh material was fed. The results of this run corresponded to a perfectly backmixed model of the system.

A continuous feed and drawoff irradiation run was made starting at approximately steady-state conditions. In spite of difficulties in maintaining the feed and drawoff mechanism a relatively uniform product was obtained.

In an effort to estimate the efficiency of utilization of the electron beam, thin-layer samples of methylcellulose were irradiated to various doses. A comparison of the dose and resulting viscosity for the batch fluidized bed material and the thin layer material showed that less dose was required in the fluidized bed (half as much in some cases), to achieve the same viscosity as in the thin layer samples.

ELECTRON-BEAM PROCESSING OF POWDERED MATERIAL

By

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1. INTRODUCTION

The application of high energy radiation to the processing of plastics, chemicals, medical products and food has been investigated extensively in the last two decades. This field of research was initiated by the availability of significant quantities of radioactive isotopes resulting from the preparation of nuclear weapons materials. Once the idea of desirable radiation-induced reactions had been raised, the field was broadened to include the effects of high energy particulate radiation (principally electrons) as produced by accelerators. The use of electron beams has been demonstrated with regard to film irradiation (preparation of cross-linked polyethylene film which has higher temperature stability); electrical insulation (cross-linked wire coating materials); irradiation of food materials for sprout-inhibition, pasteurization or sterilization; and several other fields. Similarly, radiation from radioisotopes has been demonstrated to be applicable for the catalysis of various chemical reactions as well as several of the processes listed above with regard to electron beam processing.

In the design of irradiation experiments as well as the design of irradiation production facilities, one of the problems encountered in the technique to be used is

to attain uniform radiation exposure to the entire mass being processed. The problem applies to both electron beam and radioisotope radiation (generally gamma rays) but is particularly severe with electron beams.

In the electron beam radiation processing of powdered materials, the common technique involves spreading the powder in a thin film on a suitable conveyor belt. The belt then carries the powder beneath the electron beam at a rate suitable to achieve the proper radiation dose. The permissible depth of material on the belt is controlled by the absorption characteristics of the material and the electron beam available. For a monoenergetic beam of electrons, the typical variation of radiation dose with sample depth may be seen in Figure 1. If, as is the usual case, it is desired to expose the entire sample being processed to a relatively uniform radiation dose, a problem is encountered. A variation of radiation exposure or dose from 60 to 100% of the maximum is observed in the top layers of material (near the radiation source). Likewise, an even wider variation in absorbed dose is encountered as the sample depth is increased beyond the peak dose. Thus, in order to achieve relatively uniform doses, it is necessary to limit the depth of material being irradiated, as shown in Figure 2. Obviously, this reduces the efficiency of radiation utilization since the radiation falling outside the chosen depth is wasted. Furthermore, if the

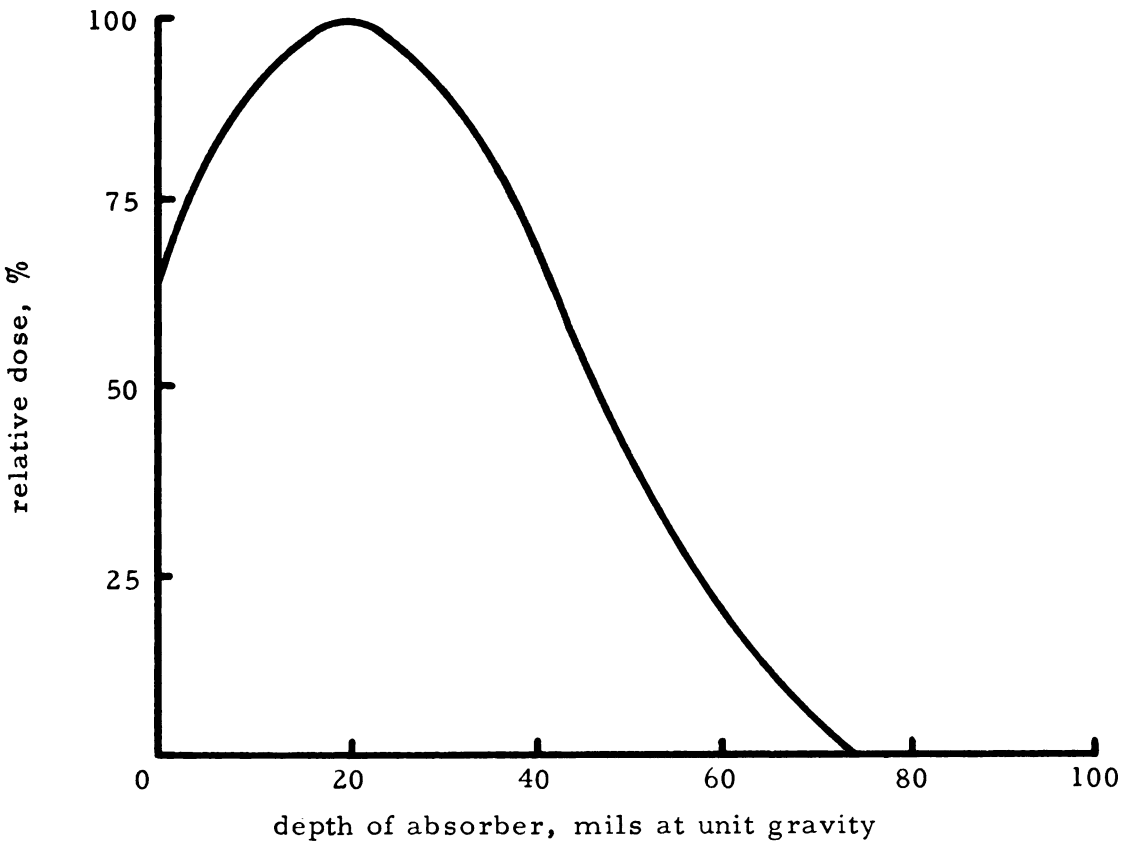

Figure 1. Depth-Dose Profile for 500 Kilovolt Electrons

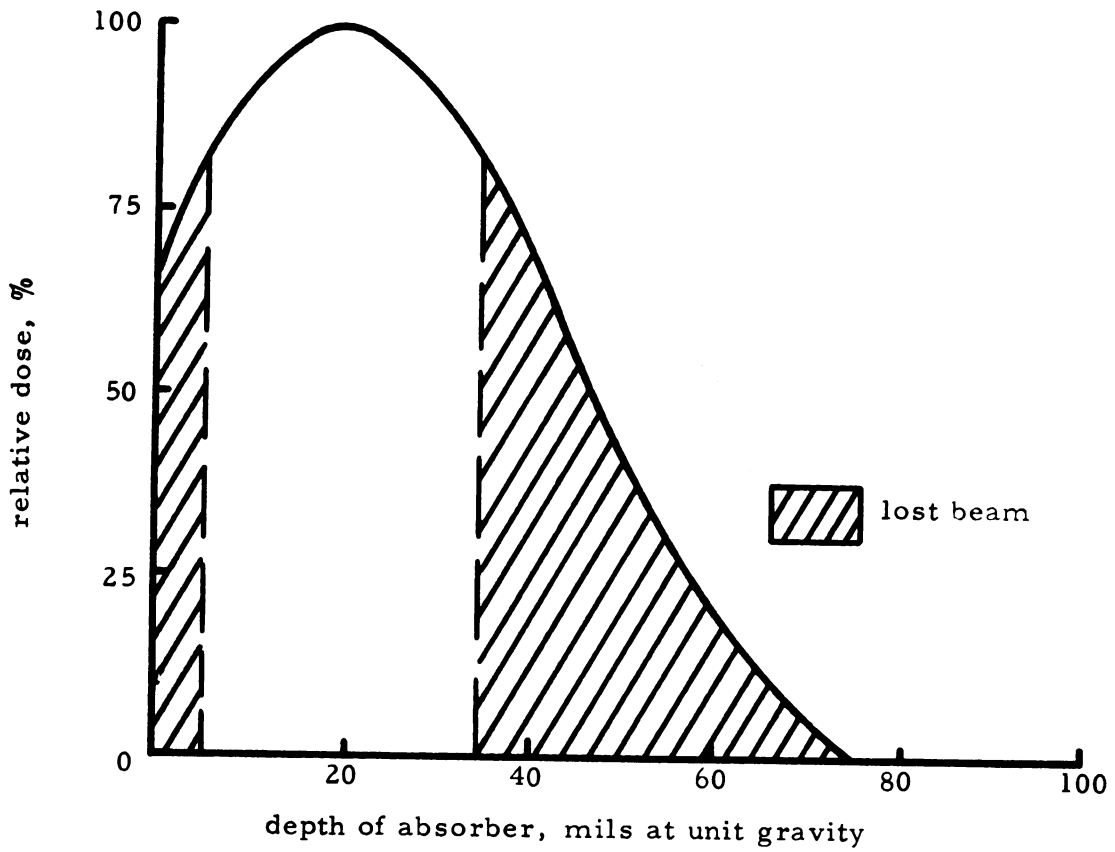

Figure 2. Depth-Dose Profile for ± 10 Percent Dose Variation Using 500 Kilovolt Electrons

depth of sample is not carefully controlled, product will be produced which has somewhat lower radiation dose than desired. Conversely, too thin a layer of sample reduces the efficiency of radiation processing by wasting a larger portion of the beam. Another solution applicable to particles which are small in relation to the depth of penetration of the electron beam is to use a very deep bed of the material and to keep the particles in constant motion in and out of the electron beam--a fluidized bed. It has been found[1,2,3] that, for fine particles, there is a tendency for caking in a continuously fluidized bed. This tendency is overcome with pulsing: i.e., a period of high flow of the fluidizing gas followed by a period of no or low flow.

A deep fluidized bed ensures that all of the beam striking it will be absorbed in the material. Presumably, as the fluidized material moves into and out of the beam region, it experiences a radiation exposure equal to the average exposure of the fluidized bed. Of course, it is possible that uniform irradiation is not achieved, but,

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[1]R. P. Levey, Jr., "Gas-Solids Contacting Method," United States Patent #3,164,440, January 5, 1965.

[2]L. Massimilla, G. Volpicelli, and G. Raso, "A Study of Pulsing Gas Fluidization of Beds of Particles," Chemical Engineering Progress Symposium Series 62, 62, 63 (1966).

[3]F. A. Zenz, and D. F. Othmer, Fluidization and Fluid-Particle Systems (New York: Reinhold Publishing Co., 1960).

rather, non-uniform irradiation followed by intimate mixing of the fluidized material is experienced. The purpose of the present work was to show the degree of uniformity of the final material and to relate the chemical effect to the average dose to the bed.

A fluidized bed capable of pulsed flow of the fluidizing gas was constructed. Several samples of Methocel, a particular methyl cellulose product of The Dow Chemical Company, were irradiated in it on a batch basis to demonstrate the degree of uniformity of the final product. The bed was then modified for continuous feed and drawoff. An unsteady-state run was made without the electron beam where unirradiated Methocel was continuously fed to a bed of previously irradiated Methocel. This test was used to demonstrate the applicability of modeling the fluidized bed as a perfectly stirred backmix reactor. Finally, a continuous feed and drawoff irradiation run was made starting near steady-state conditions.

The uniformity of exposure of the Methocel was determined by measuring the resulting 2% solution viscosity at 20.0°C. The radiation absorbed causes chain scission in the methyl cellulose molecule and thus quantitatively lowers the molecular weight (and solution viscosity) of the material. In addition, the approximate molecular weight distribution of irradiated material was determined in an effort to ascertain the radiation exposure homogeneity.

2. DESCRIPTION OF THE PULSED FLUIDIZED BED REACTOR

The fluidized bed reactor used in these experiments was built, tested for proper fluidization by visual examination and dynamic pressure measurements, and modified until apparently satisfactory results were obtained. Then, after the batch experiments were completed, it was modified for continuous feed and drawoff. Figures 3 and 4 are a photograph and a schematic diagram of the batch fluidized bed reactor.

The bed of powdered material was contained in a vertical thick-walled glass cylinder 12 inches in diameter and 24 inches high. The bed was supported at the bottom by a fine mesh stainless steel screen. The nitrogen distributor under the screen was a conical section 6 inches high, 12 inches in diameter at the top, connected to a 1-inch by 3/4 inch reducing tee at the bottom. A second stainless steel screen was placed inside the nitrogen distributor about 4 inches below the bed support screen just before batch run number 10. One of the horizontal 3/4 inch ends of the copper tee led to a 10 psi safety relief valve while the other led to the nitrogen supply. Eight inches from the tee on the supply side was a 3/4 inch copper tee with its center connected to a pressure

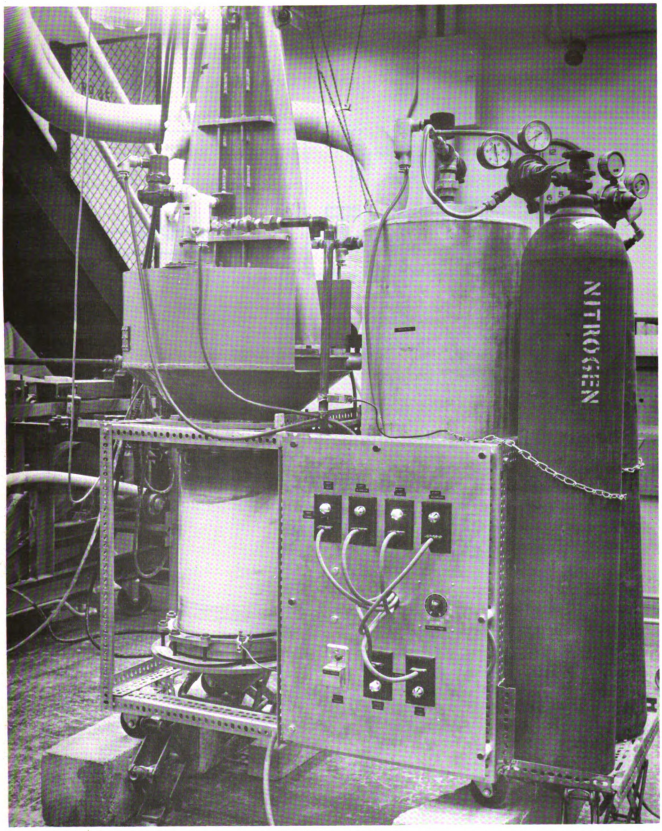

Figure 3. Photograph of Pulsed Fluidized Bed Reactor Set Up for Batch Processing

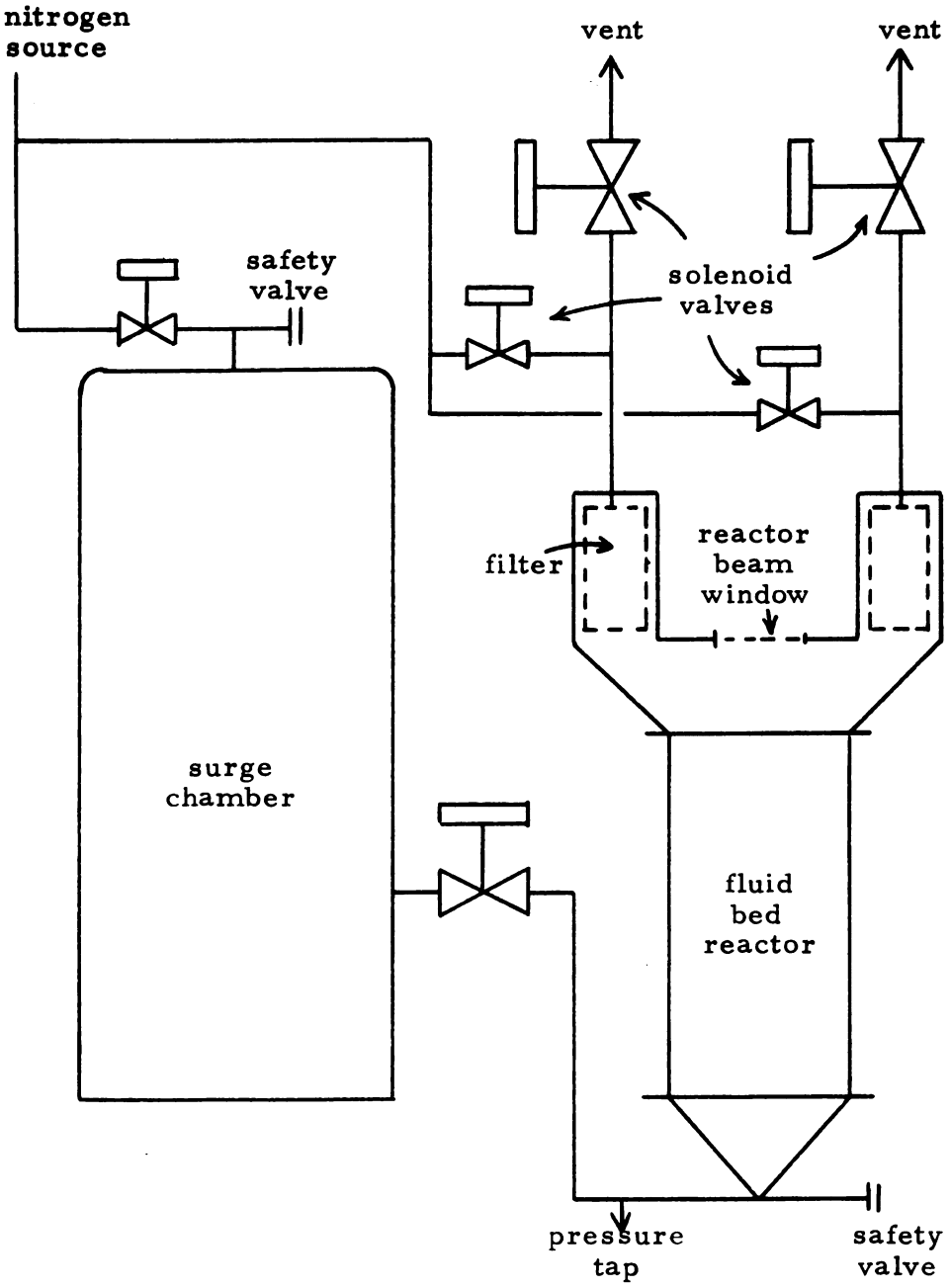

Figure 4. Schematic Diagram of the Batch Pulsed Fluidized Bed Reactor

transducer (which allowed the measurement of the pressure pulse-time characteristics). The line continued through the second tee for another 2 inches to a 90 degree elbow and 18 inches of vertical 3/4-inch rubber hose. A 1-inch 90 degree elbow led to one of the large solenoid valves and through it to the surge tank. The solenoid valve used was of type JJ from the Atkomatic Valve Company, and had 1-inch fittings and a 1-inch port.

The surge tank was a galvanized steel tank 4 feet high and 20 inches in diameter and had a capacity of about 45 gallons. A 30 psi safety valve was connected to the surge tank. A small solenoid valve served to control the nitrogen feed to the surge tank. This valve was type S115 made by the Alco Valve Company. The feed to the solenoid was made through 3/4 inch copper pipe, which led to 3/8 inch flexible copper tubing and then to the nitrogen regulators. The recorded pressures were read from the downstream gauge on the regulators during dynamic flow conditions.

The bottom part of the filter housing, located just above the reactor, was a conical steel section 12 inches in diameter at the bottom, 24 inches in diameter at the top, and 6 inches high. The top part of the filter housing was a right circular cylinder 24 inches in diameter by 10 inches high, with a 13 inch wide cutout through the center. Two filters were supported inside the two

remaining 10 inch high chambers. They were Cuno No. 52045-1-41-C4 filters with a 10 micron maximum pass dimension. The reactor electron beam port was located in the center of the cutout part of the filter housing. It was 6 inches in diameter, covered by aluminum foil and a wire support screen. The latter was a square grid with two .042 inch diameter wires per inch. There was a pressure gauge on the outside of one filter chamber.

The control system for the filters included a large solenoid valve exiting to the air, and a small solenoid valve connected to 3/4 inch copper lines from the nitrogen supply for each filter. The large solenoid was open and the small one closed for 174 seconds for normal filtering followed by a flow reversal for 6 seconds to achieve filter blowback in the 180 second period. The blowback times for the two filters were 87 seconds apart. The bed gas pulse control system was on a variable period (normally 2 seconds was used) with the large solenoid valve between the surge tank and reactor open and the small feed valve closed for half the period.

A single rubber gasket served to seal the filter housing and the glass cylinder, and two more gaskets, one on either side of the bed support screen, sealed the bottom of the reactor. A vibrator was used on the sloping part of the filter housing for some of the runs. There was never more than a half pound of Methocel on the sloping

part of the filter housing. An external air blast past the reactor window was provided to assure that overheating of the window did not take place. Care was taken that all parts of the equipment were grounded during operation. The reactor, surge tank, and timers were supported on a steel support frame which was on wheels for mobility.

The bed sampling device was a 3 foot long plastic tube fitted with an internal piston. The piston was held in place while the tube was thrust into the bed of Methocel through the opened reactor beam port. In this manner, it was possible to "core" the bed and thus sample it vertically.

It was observed that a "dead spot" existed at times in the bed at the bottom of the side nearest the surge tank. This was thought to be a result from the nitrogen flow which was horizontal and away from the surge tank for 10 inches before it reached the nitrogen distribution cone. Had there been room under the resonant transformer, the line leading to the distribution come would have been modified to give 6 or 8 inches of vertical flow before reaching the distribution cone. In this manner, it is believed that the bed would have been more uniformly fluidized.

There were several changes in the reactor for continuous processing (see Figures 5 and 6). The small solenoid valve feeding the surge tank was removed to

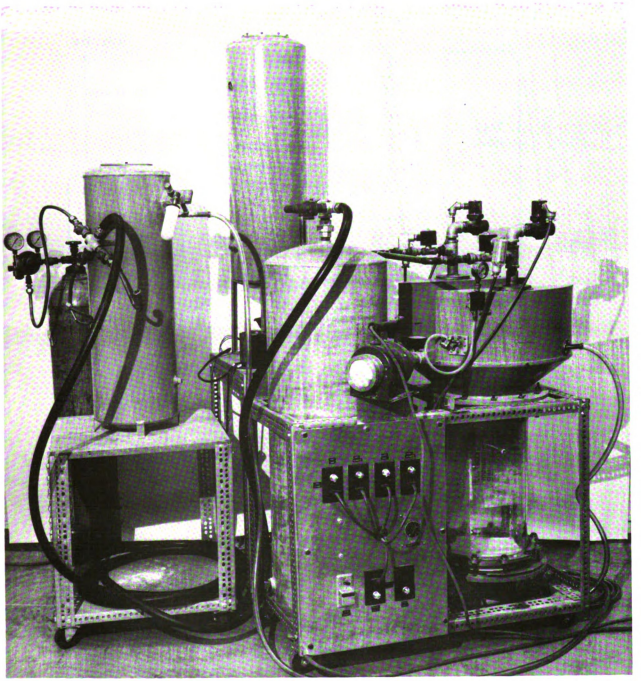

Figure 5. Photograph of Pulsed Fluidized Bed Reactor with Continuous Feed and Drawoff

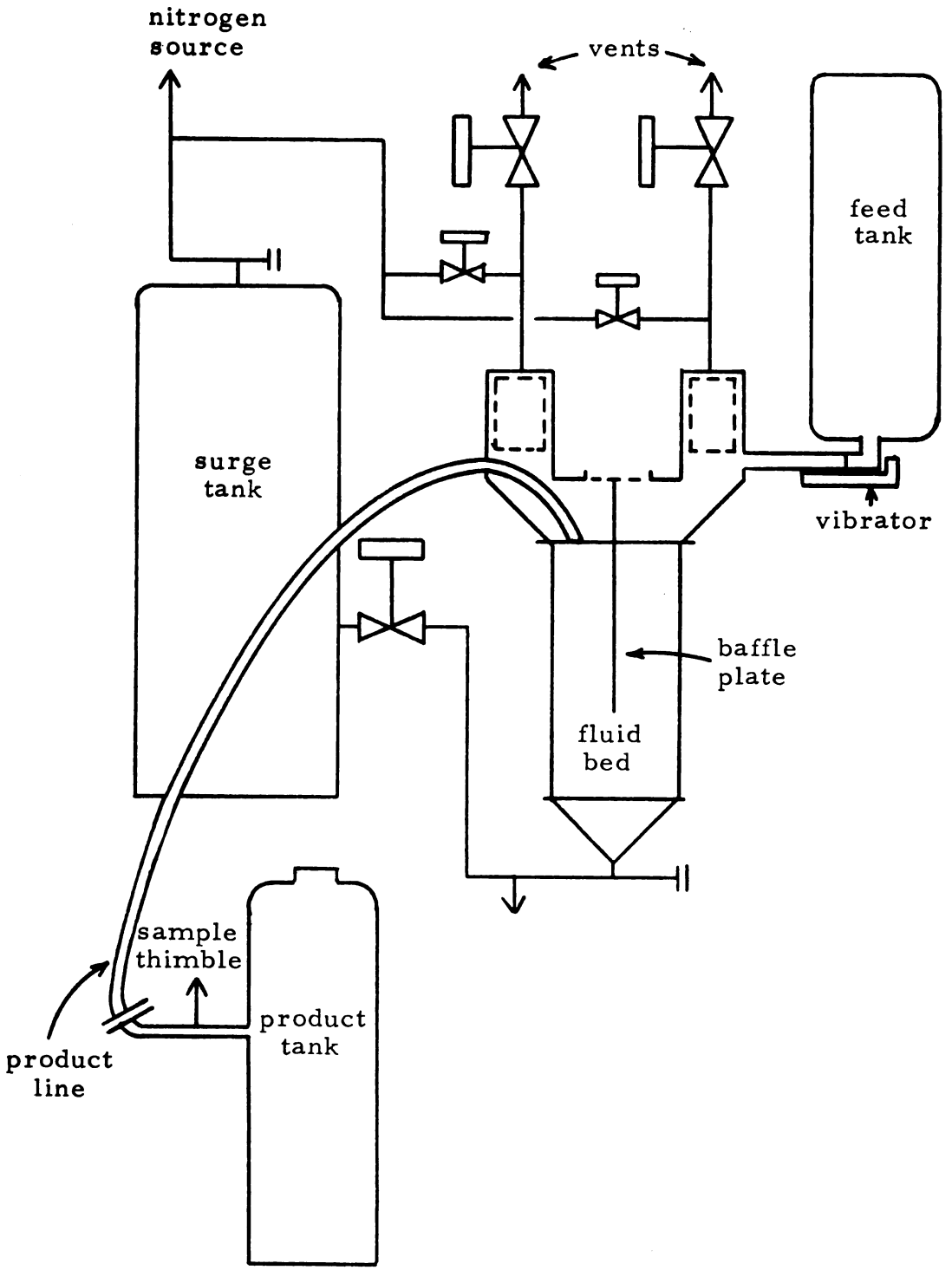

Figure 6. Schematic Diagram of Pulsed Fluidized Bed Reactor with Continuous Feed and Drawoff

reduce the resistance in the line. Methocel feed to the reactor was made from a tank 35 inches high by 12 inches in diameter emptying into a 2-inch aluminum pipe with a 90 degree elbow. There was a thin aluminum dam covering all but the bottom half inch of this pipe. The pipe was sealed to the bottom of the feed tank and the side of the filter housing with large thin-walled rubber tubing which allowed the pipe to vibrate freely. A vibrator was used on the feed pipe to control the flow rate of powder. It was a Syntron Company VibraFlow feeder model FTO with an electric voltage controller model FCTO by the same company, with a 0 to 100 scale of settings.

In the center of the reactor, a thin vertical galvanized steel plate was installed in three hinged sections so it could be removed through the beam port. This plate came to within 3/4 inch of the beam port and the bottom was 7-1/2 inches above the bed support screen. The Methocel thus had to travel down the sloping part of the filter housing, down one side of the reactor, under the dividing plate, and up the other side to the exit port. The powder exit port was a 1/2 inch hard copper tube which protruded inside the reactor to the bottom of the filter housing. Thus, unless it was overloaded and blocked off, the exit port maintained the bed height at the top of the glass cylinder.

The line leading to the product tank was clear plastic tubing 1/2 inch inside diameter, 30 feet long (so the product

tank could be located outside the radiation room). The product sampling device was located just before the product tank. It was a hard copper 3/8 inch tee, with normal horizontal flow straight through to the product tank. The center of the tee led up 5 inches on a 45 degree angle to a movable steel cut-off plate. The plate had a 3/8 inch hole leading to a 90 degree elbow and back down at a 45 degree angle to a paper thimble. For sampling, the plate was moved so the holes matched for a few seconds and then moved back.

An automotive air filter on top of the product tank was provided so there would be less resistance to flow out through the product tank than through the reactor filters.

The nitrogen feed manifold was installed so that three tanks could be used at a time and independently removed and replaced. The nitrogen tanks were mounted on the stand for the product tank, with 30 feet of 3/4 inch hose leading from the nitrogen manifold to the surge tank and filter blowback lines.

3. BATCH IRRADIATION EXPERIMENTS

Fourteen batch irradiation runs were made, eight of these using the 1 Mev (peak) Michigan State University Resonant Transformer located in room 105 of the Agricultural Engineering Building, and six using the 2 Mev Van de Graaff Accelerator in the Radiochemistry Laboratory of the Dow Chemical Company in Midland.

In order to eliminate variations between batches of Methocel, a large quantity of a single batch was acquired. Since the effect of radiation is most striking for high viscosity materials, it was decided to use 4000 centipoise material. Thus, the Methocel used in all but two runs was 65 HG Standard Methocel of 4000 centipoise nominal viscosity (lot number 060262-T). This was found to have an actual viscosity (as determined by the procedure described in Appendix C) of about 4500 centipoise. One of the other two runs used granular Methocel of 5800 centipoise viscosity, and the other used 10 centipoise nominal viscosity MC Standard (lot number 021074).

Tables 1 and 2 summarize the data for the batch runs. The Methocel used in Runs 1 and 2 had been in the reactor for some time before the irradiation run. It was used to determine good fluidization conditions from the standpoint of visual observation. The fluidization was still good at

TABLE 1

Data for Batch Irradiation Runs Made on the MSU Resonant Transformer

Run no. and date	Pulse cycle time, sec.	Irradiation time, min.	Average dose to bed, megarads	Starting material	2% aqueous solution viscosity data and position in the bed					
1 Jan. 4	2	5	0.25	25 lb 65 HG 4000	TC 1170	MC 1170	BC 1260	TS 1150	MS 1180	BS 1270
2 Jan. 4	2	5	0.25	product of run no. 1	TC 646	MC 632	BC 659	TS 643	MS 632	BS 647
3 Jan. 22	2	10	0.62	20.0 lb 65 HG 4000	TC 461	MC 457	BC 494	TX 528	MS 1020	BS 4780
4 Jan. 22	continuous fluidization	5	0.31	product of run 3 after mixing	TC 227	MC 232		TS 224	MS 344	BS 396
5 Jan. 25	2	7.5	0.37	25.1 lb 65 HG 4000		MC 632	MF 629	BF 620	MR 630	BR 614
6 Feb. 8	5	5	0.27	22.8 lb 65 HG 4000		MC 1240	TF 1080	BF 2730		MR 1270
7 Feb. 8	continuous fluidization	3	0.16	product of run 6 after mixing		MC 778	TF 786	BF 1270		MR 749
14 May 15	2	15	0.53	35 lb 65 HG 10 (11.2 cps)		MC 8.2	BC 8.6	TF 8.6		BF 8.9

TABLE 2

Data for Batch Irradiation Runs Made with the Dow Van de Graaff Generator

Run no. and date	Pulse cycle time, sec.	Irradiation time, min.	Average dose to bed, megarads	Starting material	2% aqueous solution viscosity data and position in the bed*					
8 Feb. 14	2	4.5	0.84	25.0 lb 65 HG 4000	MC 500	BC 554	MF 497	BF 4520	TR 495	BR 501
9 Feb. 14	2	6.38	1.2	25.0 lb 65 HG 4000	MC 228	BC 351	MF 494	BF 3310	TR 366	BR 1380
10 Feb. 28	2	1.0	0.19	25.0 lb 65 HG 4000	MC 2210	BC 2190		TF 2180	BF 2250	
11 Feb. 28	2	1.0	0.19	Run 10 product	MC 1240	BC 1250		TF 1250	FB 2400	
12 Feb. 28	2	2.0	0.37	25 lb 65 HG 4000	MC 1210	BC 1240		TF 1220	BF 2250	
13 Feb. 28	2	0.67	0.19	16 lb 5780 cp granular	MC 3130	BC 4110		TF 2840	BF 4830	

*First letter stands for T = top, M = middle, B = bottom.
Second letter stands for C = center axis, S = side of bed, F = front end of bed (side nearest the surge tank), R = rear of bed (side away from the surge tank).

the end of Run 1. There was no buildup of Methocel on the reactor walls, the slanting filter housing walls, or the underside of the beam window. At the end of Run 2, the fluidization was observed for 1 minute before sampling, and found to be less than the best.

Runs 3 and 4 were segmented into two 5 minute periods. In between the two periods the fluidization was observed to be poor. In an effort to remedy this, a large pulse of nitrogen was sent through the bed by allowing the surge tank to fill for about 15 seconds with the timer off. The extra blast of nitrogen thus produced helped to break up the bed and improve the fluidization. The nitrogen pressure was 30 psig for the runs as compared to 20 psig for runs 1 and 2. Run 4 was made on the same Methocel after fluidizing it for 10 minutes. The nitrogen pressure was 15 psig for this case.

Run 5 was segmented into 3 periods of 2, 3, and 2-1/2 minutes with examination of the reactor in between. The nitrogen pressure was 30 psig. After 2 minutes the fluidization was good, but after 5 minutes some stagnation was evident, so a large pulse was used to break it up.

Run 6, with the slower pulse time, showed less bed expansion than the previous runs. There was evidence of dead areas in the bed and some buildup of Methocel on the slanting walls of the filter housing. At the end of the run (after sampling) the bed was mixed with pulsing for several minutes, but the fluidization was poor. This was

perhaps due to lower tank nitrogen pressure since the flow of nitrogen to the system was controlled in part by critical flow through the pressure regulator on the cylinder. Run 7 was then made on the mixed bed. The nitrogen pressure used was 30 psig for this continuous run. The fluidization was still satisfactory at the end.

Run 8 was somewhat unfortunate in that the air blower used to cool the beam window was not used. The window thus overheated and failed. Run 9 was essentially a repeat of 8 with the blower on. The nitrogen pressure was 30 psig. The irradiation was stopped in the middle of the run so the reactor could be examined. The fluidization was found to be poor, so a large pulse was sent through the bed. A significant discoloration of the glass reactor wall was observed. Thus, a part of the radiation was missing the bed (the bed was lower than expected). It was theorized that the poor fluidization might be due to low tank pressure since both runs used the same tanks.

Runs 10 and 11 used fresh nitrogen tanks with the nitrogen pressure again set at 30 psig. The fluidization appeared good throughout both runs, although some Methocel collected on the slanted side of the filter housing. Run 12 was a duplicate of the above runs, except that no samples were taken in the middle.

Run 13 was made using granular Methocel. With each pulse the whole bed moved up and down with relatively little

mixing. The reactor and the method of operating it were not optimized for the granular material.

Run 14 was made on 10 centipoise feed to provide material for molecular weight distribution testing at the Dow Chemical Company. Similar material was also irradiated in a thin layer so that there was only a small dose variation similar to methods used in Appendix D. The molecular weight distributions and average data are given in Table 3.

TABLE 3

Molecular Weight Data for 10 cps Starting Material

Sample treatment method	Thin layer, MSU	Plused fluidized bed, location MC	Pulsed bed, location BF	No dose	Thin layer Dow, ± 1.5% dose variation	Thick layer Dow, ± 50% dose variation
Viscosity, centipoise	5.5	8.4	8.6	11.5	3.7	4.1
weight percent* in mw range 5000	2.9	3.3	4.4	0		
14000	13.6	11.7	10.9	4.0		
45000	38.6	34.2	34.6	12.2		
120000	33.0	35.4	39.6	37.4		
	11.9	15.4	10.5	46.4		
number average mw*	10,5000	15,500	16,000	15,500	11,500	10,000

*These data were taken by I. T. Takahashi of the Dow Chemical Company.

4. CONTINUOUS FEED AND DRAWOFF EXPERIMENTS

There were two continuous feed and drawoff experiments. The first did not involve irradiation, but simply mixing previously irradiated Methocel with an unirradiated batch. The object in the second was the steady state continuous processing of Methocel. Thus, the bed was filled with irradiated material and fed unirradiated Methocel while under irradiation.

For the mixing run, the bed was charged with 21 pounds of previously irradiated Methocel and the feeder was filled with the unirradiated 65 HG 4000. The nitrogen pressure was 10 psig, and the feeder was set at 60. Table 4 shows the weight of product with time and the average drawoff rate for the first 20 minutes operation. At 16-1/2 minutes into the run the product line became plugged, so the run was temporarily interrupted.

Next, the feeder was set at 80, and the operation continued for 15 minutes, at the end of which a cumulative total of 12.06 pounds of product had been collected (for 35 minutes operation). Then the nitrogen pressure was gradually increased to 15 psig with the feeder off to partially empty the bed. In this way an additional 2.69 pounds of Methocel were emptied from the bed to the product

TABLE 4

Amounts of Methocel Product Obtained for the First 20 Minutes of the Continuous Mixing Run

Run Time, Minutes	Cumulative Total pounds of Methocel	Average Exit Flow Rate, lb/min
5	1.5	0.30
10	2.94	0.29
15	4.81	0.32
20	6.81	0.34

tank. Next, the feeder was set at 100 and started, and the mixing continued for 30 minutes more, during which 13.06 pounds of additional product were collected. In the whole run, about 28 pounds of product were collected. Thus, the bed was changed 1.4 times.

The viscosity data, along with the values derived from the viscosity which were used in the discussion, may be seen in Table 5.

The continuous feed and drawoff irradiation run started with 20 pounds of 770 centipoise Methocel which had been irradiated previously. The nitrogen pressure was 15 psig and the feeder was set at 100. The Resonant Transformer beam out current was set at 0.1 milliamperes instead of 1.0 as had been used before, because the feed and drawoff

TABLE 5

Data From the Continuous Feed and Drawoff Mixing Study

Time, min.	μ_p, cp	$\mu_p^{1/8}$	$\log (\mu_B^{1/8} - \mu_P^{1/8})$
0	323	2.059	0.0035
2	316	2.053	0.0060
4	395	2.111	- 0.0195
6	420	2.128	- 0.0273
8	480	2.164	- 0.0443
10	518	2.185	- 0.0540
12	584	2.217	- 0.0706
14	659	2.251	- 0.0883
16*	678	2.259	- 0.0926
	643	2.244	- 0.0846
18*	774	2.297	- 0.1249
	729	2.280	- 0.1040
20*	836	2.319	- 0.1261
	801	2.306	- 0.1192
25	938	2.352	- 0.1457
30	1157	2.421	- 0.1898
35	1274	2.444	- 0.1986
40	1499	2.494	- 0.2418
45	1636	2.522	- 0.2636
50	1866	2.564	- 0.2984
55	2287	2.630	- 0.3595
60	2164	2.612	- 0.3420

*Two viscosimeters were used on these samples.

rates were so low. The feed was 65 HG 4000, as usual. Table 6 shows the product rates and exit viscosities as a function of time during the run.

During this run, the bed level in the reactor dropped somewhat. This caused the drawoff rate to be higher than the feed rate. It is thought that the feed rate to the bed was probably continuous at about 0.12 pounds per minute. This was much smaller than planned.

TABLE 6

Continuous Operation of the Pulsed Fluidized Bed

Run time, min.	Exit viscosity, centipoise	Total drawoff, lbs.	Rate of drawoff, lb/min
0	770		
5	583		
10	550		
15	624	4.5	0.30
20	667		
25	639		
30	623	7.06	0.17
35	678		
40	645		
45	662	8.69	0.11
50	838		
55	802		
60	691		
61.5		10.81	0.13

5. DISCUSSION AND CONCLUSIONS

5.1. Radiation Effects

The mechanism of breakdown of methyl cellulose and cellulose when irradiated in the dry state has been shown to involve a free radical chain reaction where the rate of degradation is proportional to the concentration of free radicals.[1,2] The free radicals are destroyed by two mechanisms. Bimolecular termination involves the combination of two free radicals to make a stable molecule. Alternatively, free radical scavengers such as molecular oxygen (meaning O_2) may result in the destruction of radicals. The fact that free radical loss is nearly second order to cellulose[2] shows that the bimolecular termination is the most important destruction mechanism. It was also found that free radicals could exist for several days in dry irradiated cellulose in an inert gas, and that their destruction was about 10 times as fast in air.[2]

In thin layer electron beam processing where a single particle sees the beam continuously while it is being

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[1] F. A. Blouin, et al., "The Effect of Gamma Radiation on the Chemical Properties of Methyl Cellulose," Textile Research Journal 34, 153-158, February, 1964.

[2] R. E. Florin, and L. A. Wall, "Electron Spin Resonance of Gamma-Irradiated Cellulose," Journal of Polymer Science Part A, 1, 1163-1173 (1963).

processed, the concentration of free radicals builds quickly to a steady state concentration where the rate of production due to the radiation is equal to the rate of termination. For the same total dose, then, a lower dose rate generally results in a steady state free radical concentration which is not as much lower as the dose rate. Thus, the resulting radiation effect is greater. In the pulsed fluidized bed, a particle "sees" the beam for a short time before moving away. Thus, it gets irradiated in short pulses. If it spent the same amount of time in the beam as the thin layer particle, it would experience a much more effective exposure to free radicals because it would see the concentration while they were dying out many times instead of just once.

Table 7 is a summary of the four best batch irradiation runs showing the dose, resulting viscosity, and thin layer dose for the same viscosity taken from Figure 18. It shows, at least in a qualitative way, the effect of using the Van de Graaff generator versus the Resonant Transformer. As may be seen, the Van de Graaff beam spot is smaller and the resultant average dose rate higher. This means that an individual particle will "see" about three times as much dose rate while in the beam.

If, in fact, the bimolecular termination process does predominate, this higher dose rate should more nearly approximate the thin layer work and the amount of radiation required to achieve a given degree of degradation

TABLE 7

Relative Dose Rates for the Three Methods of Irradiation of Methocel and Their Effectivenesses

Radiation Source	MSU Resonant Transformer			Dow Van de Graaff	MSU R. T.
Run No.	1	2	5	10	thin layer
Surface dose rate (spot) krads/sec	96.0	96.0	96.0	300	55.5
Average dose rate, Megarads per minute	0.049	0.049	0.049	0.150	3.34
Average total dose, Megarads	0.25	0.50	0.37	0.19	0.67
Resultant viscosity, centipoise	1180	645	630	2200	1000
Thin-layer dose for the same viscosity, Megarads	0.57	1.01	1.04	0.23	0.67
Area of beam delivering at least 80% of maximum dose, square inches	62	62	62	approx. 6	--
Ratio of thin layer dose to dose used	2.3	2.0	2.8	1.2	1.0

should be higher than with the resonant transformer results. A comparison of the last row on Table 7 would indicate just such an effect. The ratio of thin layer radiation dose required to achieve an equivalent degradation of the solution viscosity is considerably higher with the resonant transformer fluid bed experiments than with the Dow fluid bed experiments which are, in turn roughly equivalent to the thin layer experiments.

This effect may be due to any of several causes:

First is the instantaneous radiation intensity effect. The fact that the dose rate with the fluid bed tests was higher than in the thin film work would imply that the total dose requirements would be higher with these cases as compared to the thin film work. In fact, however, the converse was true with the fluid bed work always using less radiation. Further, since the dose rate with the Van de Graaff is the highest of the three cases, it should be the poorest with regard to radiation efficiency. Again, this was not observed.

The second is the pulse or "shutter" effect. In the case of the fluid bed work, the particle of Methocel is exposed to "pulses" of radiation as the result of its movement into and out of the beam. In such a case, the average free radical concentration would be lower and thus the radiation would be used more efficiently. This is consistent with the data reported. The effect is apparently

much less pronounced with the Van de Graaff and this is perhaps due to the effect of higher radiation intensity with this machine.

The third is oxygen radical scavenging. The pulsed bed work was conducted in an atmosphere of nitrogen whereas the thin layer work was done in air. It is possible that sufficient oxygen was present in the thin layer work to destroy a significant amount of the free radicals. If such were the case, it is difficult to rationalize why the effect was not observed with the Van de Graaff runs.

Finally, one might suspect the dosimetry calculations used for Table 7. Below 10 centimeters from the Resonant Transformer beam window the surface dose rate on the beam axis follows the inverse square decrease law.[1] The axial surface dose rate for the bed, at 35 centimeters below the beam window, was 96.0 kilorads per second, while the like value for the thin layer runs, at 47 centimeters, was 55.5 kilorads per second, in very good agreement with the inverse square law. On the other hand, inherent in the calculations involving the Van de Graaff was the assumption that all of the radiation emitted from the accelerator was absorbed in the bed. The error in this assumption is demonstrated (at least qualitatively) by the

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[1] R. C. Nicholas, "The Application of High-Energy Electrons to Some Grain-Infesting Pests" (unpublished Ph.D. thesis, Department of Agricultural Engineering, Michigan State University, 1958).

discoloration observed in the reactor glass walls. Thus it is likely that, if anything, the radiation dose reported for these runs is too high and this would tend to bring the results more nearly into agreement with the resonant transformer results.

In conclusion, then, one might state that the radiation required to achieve a given degree of product degradation is apparently less with the nitrogen pulsed fluid bed operation than with thin film irradiation in air. The reason for the lower dose requirements may be due either to lower effective radiation intensity (and free radical concentration) with the fluid bed or to the oxygen scavenging in the thin film work.

5.2. Fluid Bed Uniformity Studies

Results have been obtained to indicate that it is possible to achieve good product uniformity within a fluidized bed. Within the experimental apparatus used, a localized "dead spot" of material was often observed. The tendency of the bed toward having a dead spot at the bottom on the side of the reactor next to the surge tank was so strong that only two samples were really necessary to determine the uniformity of the product of a run--one from that position and the other from the center of the bed. This dead spot is probably not critical in constant feed and drawoff work since it will only decrease the effective size of the reactor. The significance of this would

be that a normal free particle will spend a larger fraction of the time in the beam, on the average, since it cannot use the dead volume.

The simplest model of the continuous feed and drawoff pulsed fluidized bed is a perfect backmix reactor, where the reaction is the mixing of Methocel samples of different viscosities. The composition of the misture leaving the reactor, for pure component A in the reactor at first and pure component B entering may be found from the model by making a differential balance on component B in the reactor:

$$\begin{array}{ccccc} \text{(Input)} & - & \text{(Output)} & = & \text{Rate of Accumulation} \\ F & - & F \cdot X_B & = & d(W \cdot X_B)/dt \end{array}$$

where F is the constant feed and drawoff rate, W is the constant amount of material in the bed, and X_B is the weight fraction of component B in the bed.

Rearranging and integrating gives:

$$\int_o^{X_B} \frac{W}{F} \frac{dX_B}{(1 - X_B)} = \int_o^t dt$$

$$X_B = 1 - e^{-(E/W)t}$$

From the Appendix one finds

$$\mu_p^{1/8} = X_A \mu_A^{1/8} + X_B \mu_B^{1/8}$$

and since

$$X_A = 1 - X_B = e^{-(F/W)t}$$

$$\mu_p^{1/8} = e^{-(F/W)t} \mu_A^{1/8} + \mu_B^{1/8} - \mu_B^{1/8} e^{-(F/W)t}$$

$$\mu_B^{1/8} - \mu_P^{1/8} = (\mu_B^{1/8} - \mu_A^{1/8}) e^{-(F/W)t}$$

$$\log_{10} (\mu_B^{1/8} - \mu_p^{1/8}) = \log_{10} (\mu_B^{1/8} - \mu_p^{1/8}) - \frac{.434 F}{W} t$$

so a plot of $\log_{10} (\mu_B^{1/8} - \mu_p^{1/8})$ versus t should be a straight line of slope -.434 F/W.

Table 5 gives the viscosity data from the continuous run along with the calculations for the theoretical straight line plot, which is shown in Figure 7. The slope from the plot was -0.0061/minute, and, with the input and output at about .3 lb/min, and 21 pounds in the bed, -.434 F/W is calculated to be -.0062.

The continuous feed and drawoff mixing run shows that the perfect backmix reactor model is close to the actual physical situation, as evidenced by the straightness of the plot in Figure 7. The continuous radiation run was not absolutely necessary, since the method had been shown

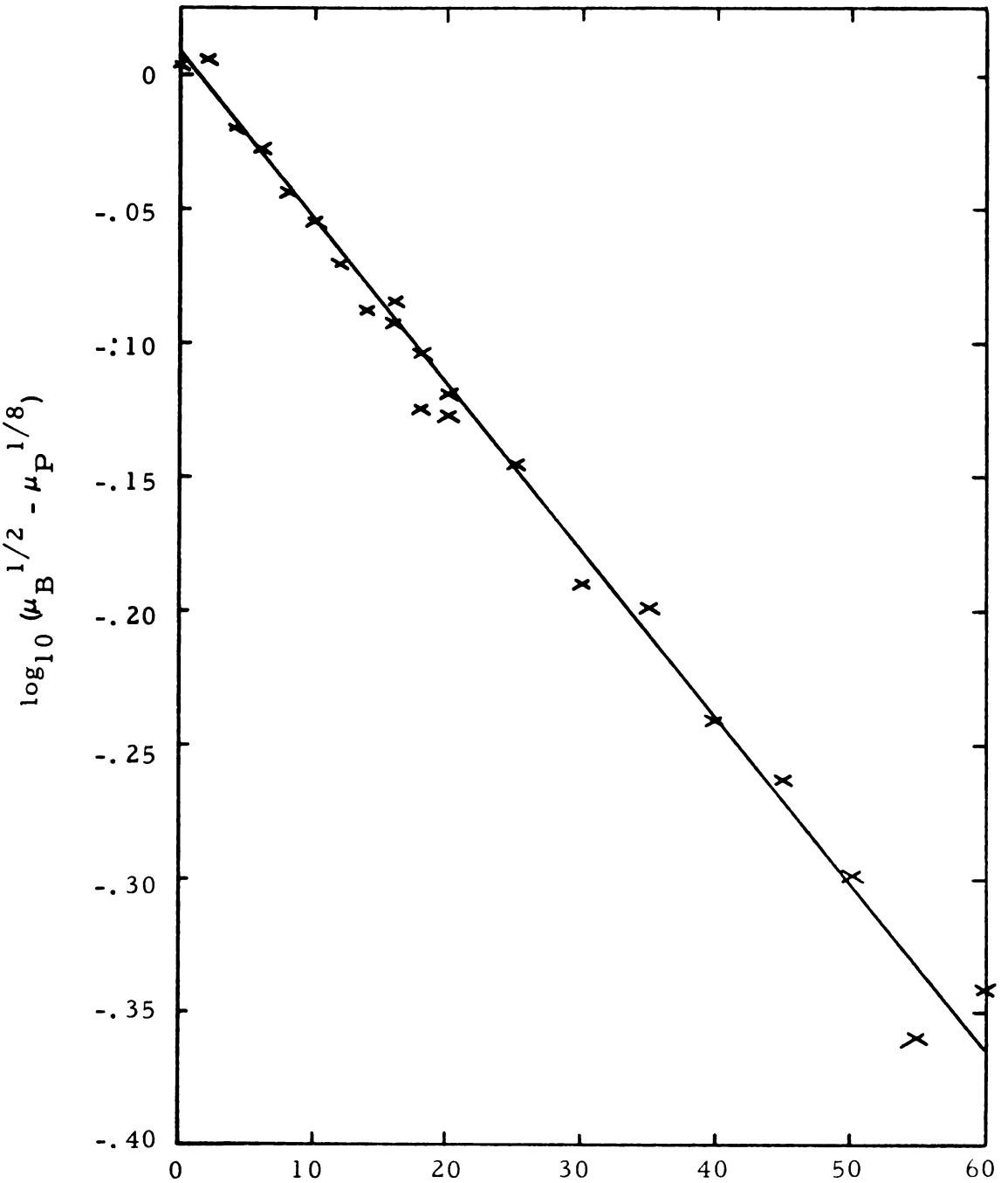

Figure 7. Plot of the Continuous Feed and Drawoff Mixing Run Using the Perfectly Backmixed Model

in the mixing run. Of course, it is possible that the feeder difficulties were due somehow to the radiation, but the problem was not in the fluidized bed.

The best fluidization conditions, which were found by visual observation and demonstrated in batch irradiation runs and the continuous mixing run, were a 2 second pulsing period and 15 psig nitrogen pressure, with 20 to 25 pounds of Methocel in the reactor. This provides a very efficient utilization of the radiation because each particle moves in and out of the beam to extend the utilization of free radicals while they are dying out.

The question of whether the material is actually receiving uniform irradiation or just being well mixed is not as easily resolved, however. A review of Table 3 would indicate that the thin layer irradiation material has experienced a marked decrease in the number average molecular weight whereas the fluid bed irradiation material shows little or no change. This might be explained on the basis that the thin layer material has experienced a rather consistent destruction of the molecules due to the irradiation. An analysis of the molecular weight distributions as shown in Figure 8 indicates very little difference in distribution between the fluid bed and thin film samples. If anything, it would appear that the fluid bed samples experienced a somewhat less uniform exposure than the thin film materials since the former shows a slightly larger

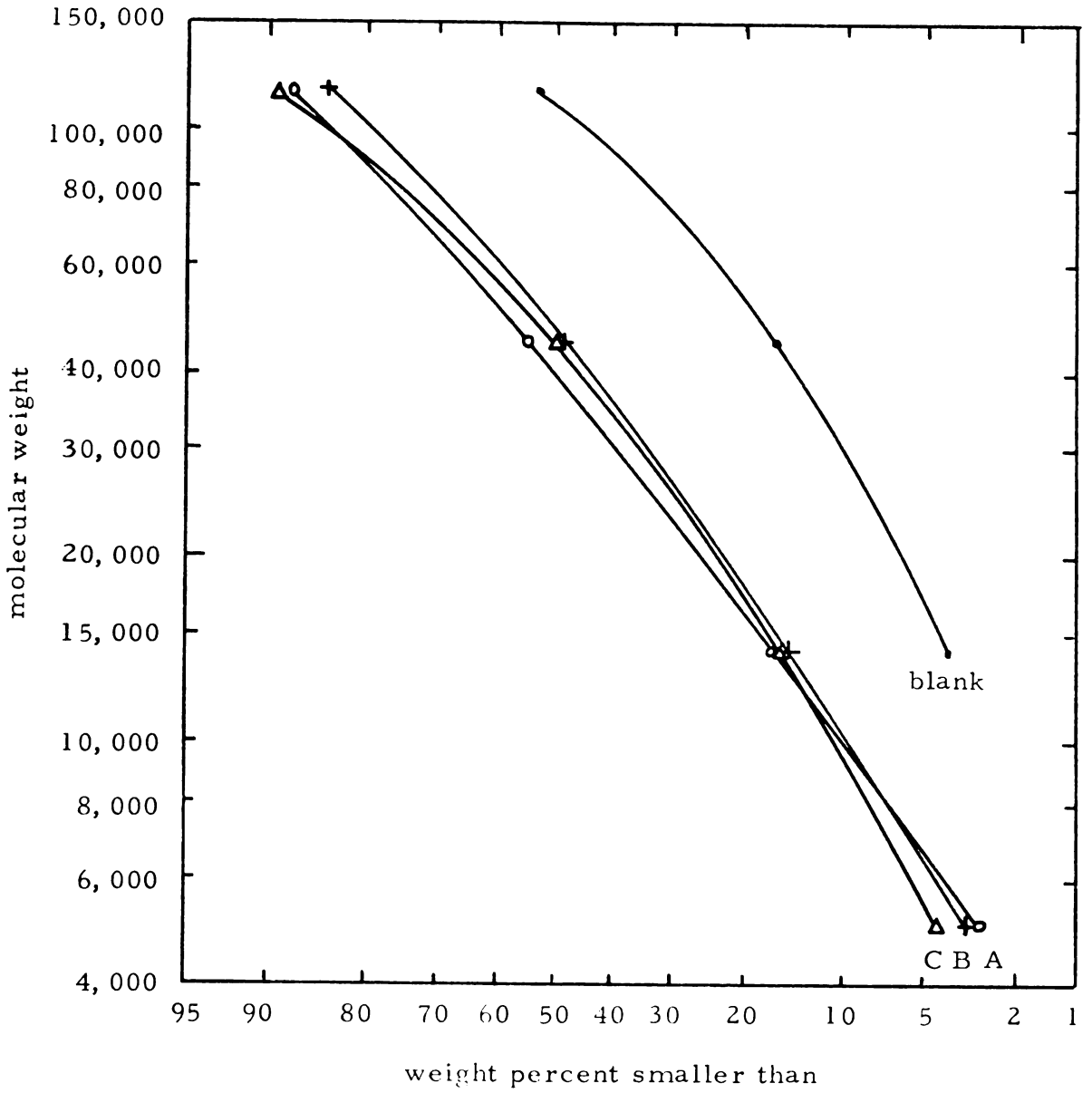

Figure 8. Molecular Weight Distributions for Unirradiated Methocel HC 10 and Three Irradiated Samples. B and C were irradiated in the fluidized bed at HC and FB, while sample A was irradiated in a thin layer.

fraction of low molecular weight material. Further, the sample taken from the relatively stagnant (BF) region of the bed appears to be slightly poorer than the other fluid bed samples. The difference between the samples is small, however, compared to the deviation from the unirradiated sample.

An alternative technique of analyzing the uniformity of irradiation revolved about the total dose required to give a certain degree of molecular weight degradation. If the bed had resulted from a physical mixture of high and low viscosity materials, the total dose requirements would have been higher than if a uniformly average viscosity had been used. Unfortunately, the discrepancy between fluid bed and batch samples with regard to radiation requirements (see above) has masked this effect.

Therefore, although it has not been possible to prove that the bed had, in fact, achieved uniform irradiation, it would appear that the product produced (as characterized by the molecular weight distributions) by the two irradiation schemes is very similar. Thus, the irradiation by fluid bed does not give a grossly nonuniform irradiation.

6. RECOMMENDATIONS FOR FUTURE WORK

Future work with batch irradiation in the pulsed fluidized bed should be directed to the following areas:

1. The "dead" spot should be eliminated. This can perhaps be done by redirecting the nitrogen stream as it enters the distribution cone.

2. The apparently lower radiation dose requirement for fluid bed work needs to be confirmed. Batch thin film irradiations in a nitrogen atmosphere would be helpful as would the irradiation of batch samples beneath a rotating shutter to give a pulsed effect.

3. A more rigorous technique of comparing the radiation homogeneity is required. It is possible that better molecular weight determinations would be helpful and, further, the results of number 2 above would permit the application of the mixing technique discussed in the results.

4. Fluidization conditions need further optimization. The optimum pulse size and frequency might improve the fluidization conditions while minimizing the gas requirements.

Future work on continuous pulsed fluidized bed irradiation must start with finding a more reliable feed and drawoff system. Once this is done the dose uniformity

should be investigated, either with molecular weight distribution studies on a material such as Methocel or perhaps with a microbiological technique where bacteria or spores can be mixed in with the material to be processed. The average dose means nothing to a single bacterium if it has not been hit with radiation, and, if uniformity of microbial kill can be shown this method of processing could be applied to food materials.

It is also suggested that a smaller fluid bed be made (say, 6 inches in diameter by 18 inches high). With this, all the handling difficulties would be lessened as would be the amount of nitrogen used. This would also open the possibility of operating closer to the generator beam window and putting in a length of vertical pipe just below the nitrogen distribution cone. It would also decrease the amount of material needed for a run. This might be important for continuous runs.

APPENDICES

APPENDIX A

RADIATION DOSE CALCULATIONS

Three methods of determining high radiation doses (the Fricke Ferrous Sulfate dosimeter, a Faraday cup, and a small ionization chamber) were tested with the conclusion that the ionization chamber is of most value. A photograph of the ionization chamber used is shown in Figure 9, and a cut away diagram is shown in Figure 10. The starting point of the design was that of Lawton,[1] with the addition of a thermocouple well.

The ionization chamber consists of two 5 inch by 1/8 inch thick aluminum plates, with a 1 inch hole in their centers. As can be seen in the diagram, the hole is not cut off straight, but the last sixteenth of an inch slants out for a quarter inch, so the hole is 1-1/2 inches in diameter at the top or bottom. This is to prevent distortion of the beam due to scattering off the plate or the attraction the grounded plate would have for electrons. The two quartz disks were .044 inches thick, with a one inch hole and big enough to fit snugly in position. A notch was cut in the top of the lower disk to permit the

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[1] E. J. Lawton, and J. S. Balwit, "Ionization Chambers for Measuring Cathode-Ray Dose Rate," General Electric Report No. RL-618, November, 1951.

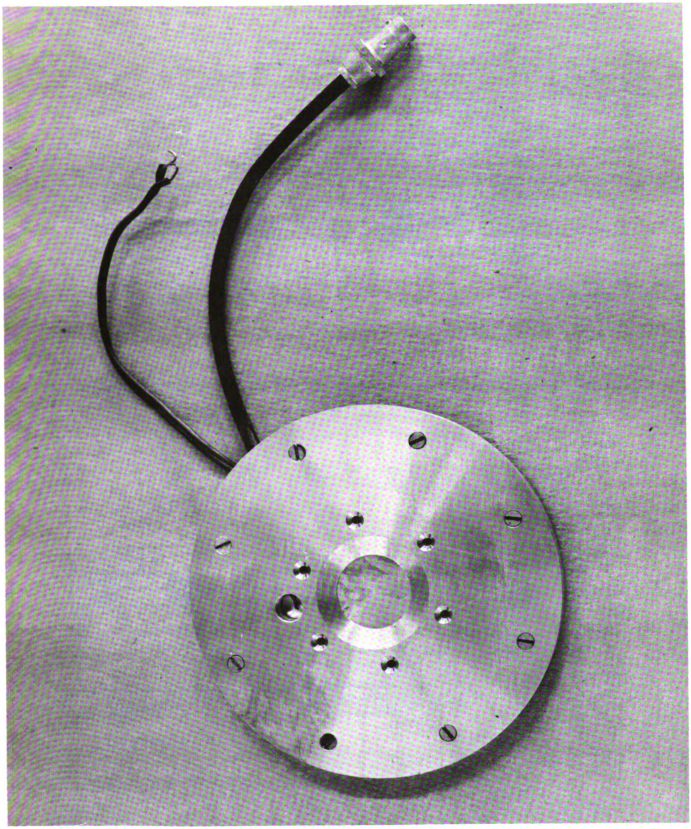

Figure 9. Photograph of Ionization Chamber

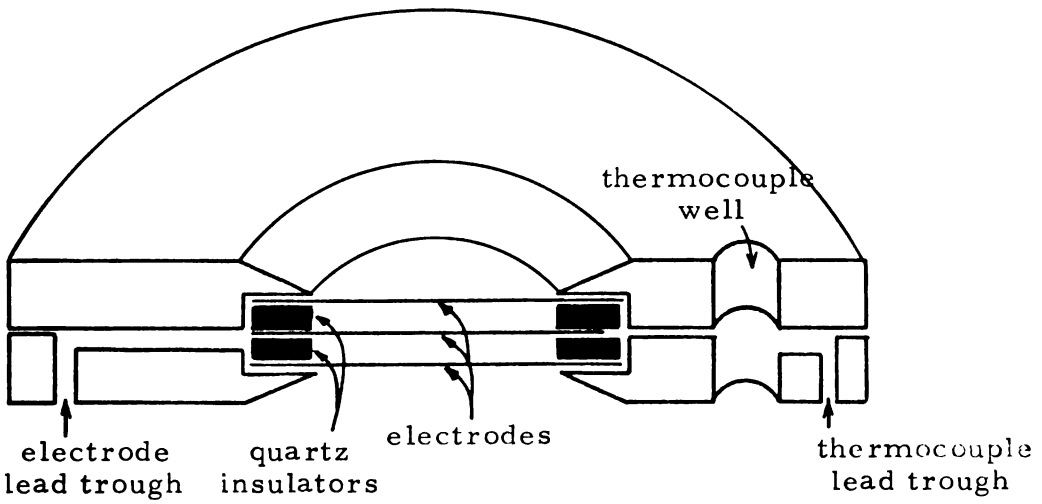

Figure 10. Cutaway Diagram of the Ionization Chamber

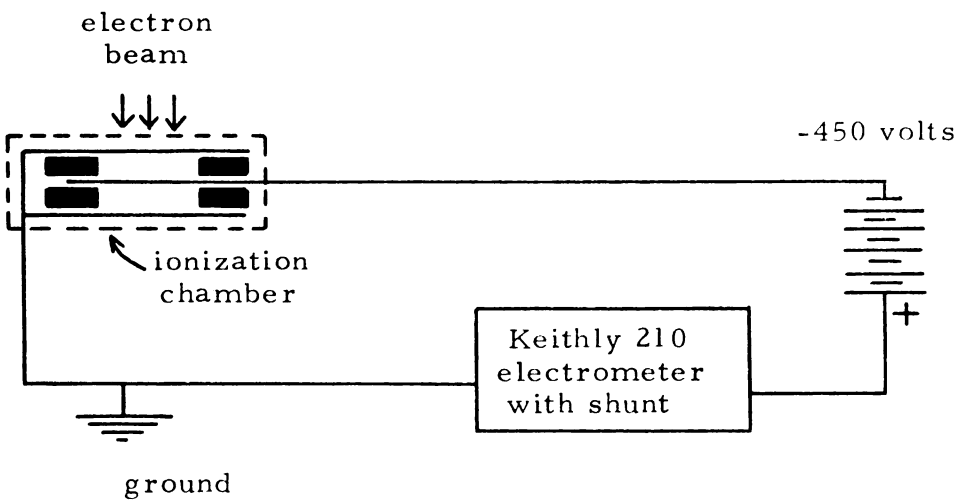

Figure 11. Circuit Schematic for the Ionization Chamber

electrical contact with the center electrode. Contact with the outer electrodes was made through the aluminum plates, since they were in contact and grounded. Figure 11 shows the circuit schematic used for radiation measurements.

In the calculation of the cell constant, the conversion factor which relates the current measured to the dose in the chamber, use is made of the fact that it takes 34.0 electron volts of energy absorbed in the chamber. The chamber constant, c, is given as follows:

$$c = \left(\frac{34.0 \text{ ev}}{\text{electron}}\right)\left(\frac{\text{electron}}{1.602\text{x}10^{-19} \text{ coulomb}}\right)\left(\frac{1.602\text{x}10^{-12} \text{ erg}}{\text{ev}}\right)$$

$$\left(\frac{10^{-6} \text{ coulomb}}{\text{sec. } \mu\text{-amp}}\right) = \frac{340 \text{ erg}}{\text{sec. } \mu\text{-amp}}$$

To get c in terms of rads, the mass of air in the chamber must be calculated. Under these conditions air is essentially a perfect gas, so the perfect gas law will be used.

$$m = \frac{PVM}{RT} = \frac{P}{T}\left(\frac{.088\pi}{4} \text{ in}^3\right)\left(\frac{28.8 \text{g/g mole}}{2113 \text{ in}^3\text{-mmHg/}^\circ\text{R/g mole}}\right)$$

$$m = \frac{P}{T} 9.42\text{x}10^{-4} \text{ grams},$$

and since

1.0 rad = 100 ergs/gram then

$$c = \frac{340 \text{ erg}}{\text{sec. } \mu\text{amp}} \cdot \left(\frac{10^4}{9.42} \cdot \frac{T}{P}\right)\left(\frac{\text{gram rad}}{100 \text{ ergs}}\right)$$

$$c = \frac{T}{P}(3610) \frac{\text{rad}}{\text{sec. } \mu\text{amp}}$$

where T is in degrees Rankine and P is in millimeters of mercury. Under typical conditions of 90°F (549.7°R) and 740 millimeters pressure, the constant is 2680 rads per second per microampere.

Irradiation of Methocel was carried out in three different ways. The first was in thin layers with the Michigan State University Resonant Transformer; the second was in the fluidized bed with the same source; and the last was at the Dow Chemical Company in Midland, Michigan, with the Van de Graaff generator. For the fluidization runs at Michigan State University the ionization chamber was supported at various points in a plane 35 centimeters below the accelerator window. This corresponded approximately to the top of the bed during fluidization. Figure 12 shows the results of that work, along with the fitted parabola used to approximate the curve for integration. The parabola is $D = 96.0 - .984r^2$ kilorads per second when r is in inches. To get the average dose, one simply integrates the dose over the area of the bed and divides by the area.

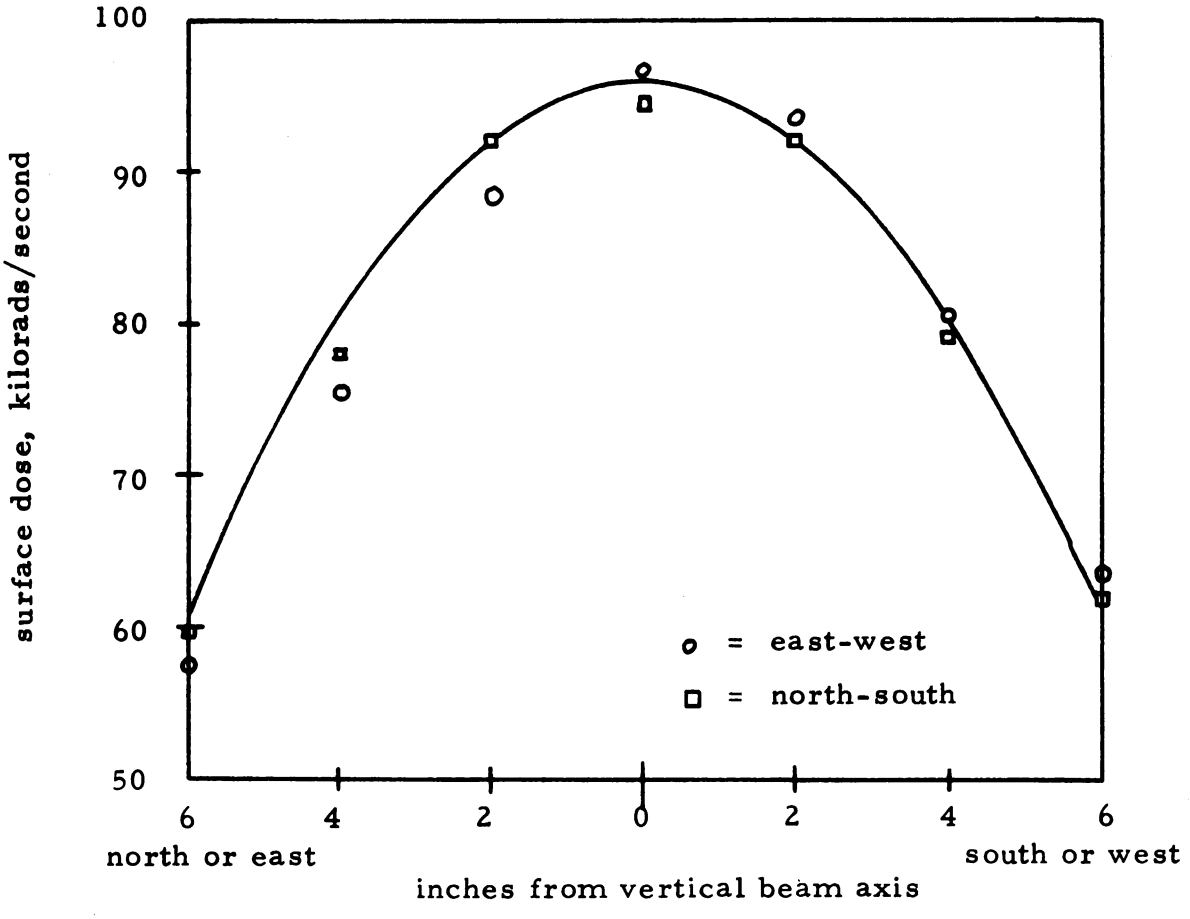

Figure 12. Surface Dose Rate in the Plane 35 Centimeters below the Beam Window at 1000 Kilovolts Peak and 1.0 Milliampere Beam Current for the Michigan State University Resonant Transformer

$$\bar{D} = \frac{1}{A}\int_0^6 D \cdot 2\pi r \cdot dr = \frac{1}{36\pi}\int_0^6 2\pi r\,(96.0-.984r^2)\,dr$$

$$= \frac{1}{18}\left[\frac{96.0r^2}{2} - \frac{.984r^4}{4}\right]_0^6 = \frac{96.0(36)}{36} - \frac{.984(36)^2}{72}$$

$\bar{D}$ = 78.3 Krads/second at the surface at 1 Mev, 100 μamp beam.

To go from the surface dose to the average total dose, use is made of a depth-dose curve, such as the one shown in Figure 10. This curve was made by placing aluminum absorbers of various thicknesses over the ionization chamber and measuring the resulting dose. From this one can determine the average dose to any depth of graphically integrating the cruve. This is shown in Figure 14. From Figure 13 one observes that the whole beam will be absorbed in the first 0.3 grams per square centimeter of material, and from Figure 14 one sees that the average dose to that depth is 66.4% of the surface dose. Since the area considered here is a circle one foot in diameter (or 730 square centimeters) the top 219 grams of material will receive an average of 66.4% of the surface dose. Then the total beam is given by:

$$B = (\text{dose})(\text{mass}) = 78.3\ \frac{\text{Krads}}{\text{sec}}\ (.664)(219\ \text{grams})$$

$$= 11.38 \times 10^6\ \frac{\text{gram-rads}}{\text{second}}$$

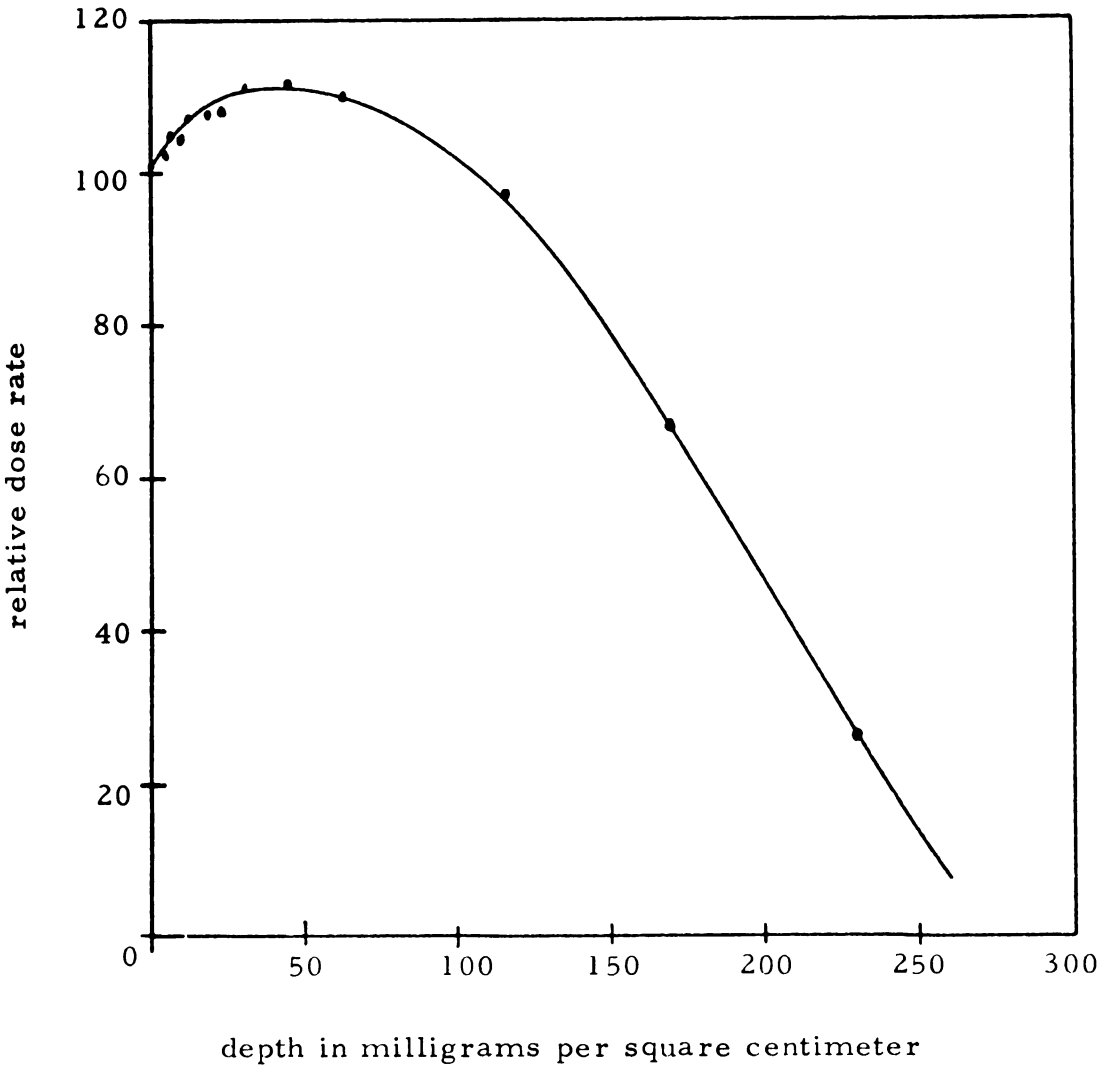

Figure 13. Depth-Dose Curve at 35 Centimeters below the Beam Window of the Resonant Transformer on the Beam Axis at 1000 Kilovolts Peak

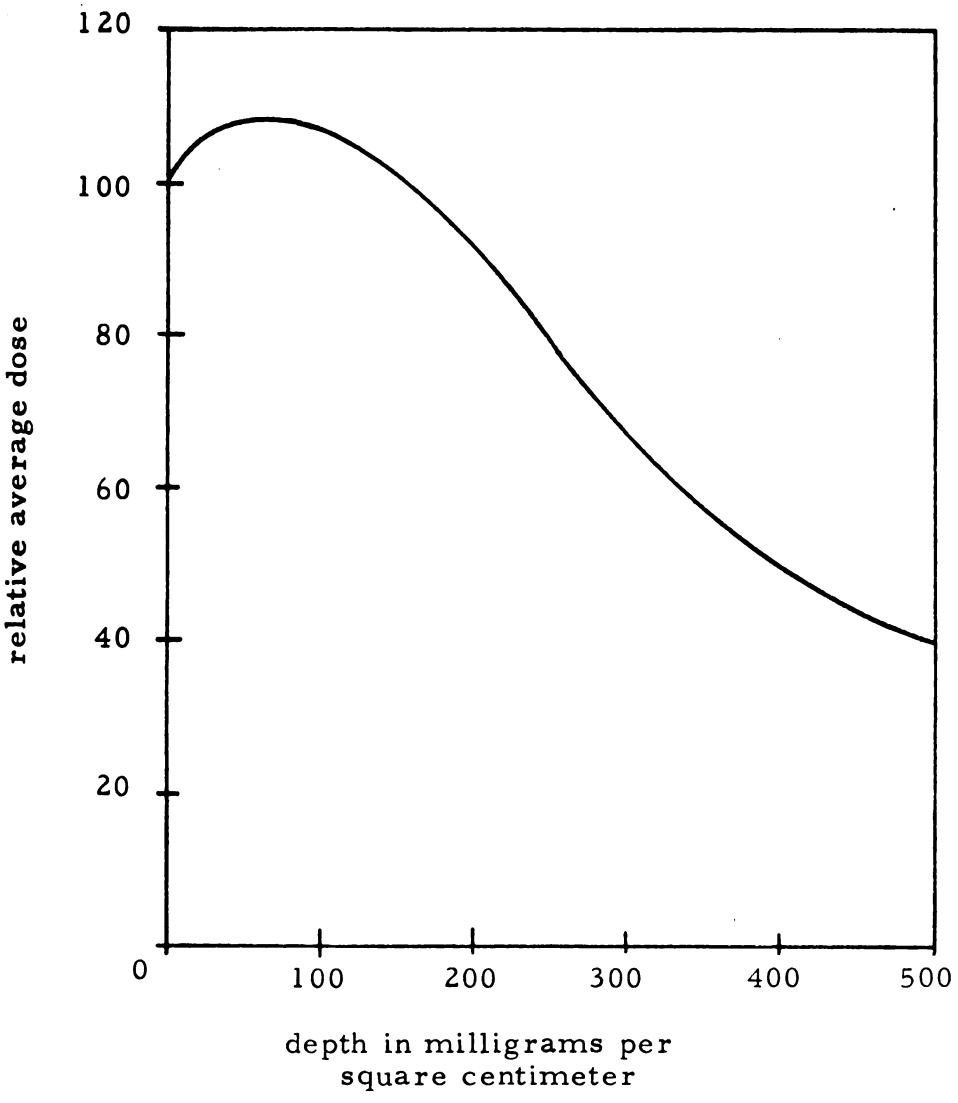

Figure 14. Plot of the Average Dose to a Given Depth of Material at 35 Centimeters below the Resonant Transformer Beam Window on the Beam Axes at 1000 Kilovolts Peak

The beam window on top of the fluidized bed was found to have a thickness of 4 milligrams per square centimeter, so one may calculate the energy absorbed in it in a like manner. The weight would be 3 grams, and from Figure 14 the average dose in the first 4 milligrams is 101.5% of the surface dose, so the beam absorbed in the fluidized bed window is:

$$B = (\text{dose})(\text{mass}) = 78.3 \frac{\text{Krads}}{\text{sec}} (1.015)(3)$$

$$= .24 \times 10^6 \text{ gram-rads/sec.}$$

As will be shown later, the wire support grid lets 83.9 per cent of the beam striking it through. Then the Methocel will receive 11.14 times 0.839, or $9.34 \times (10)^6$ gram rads per second. As an example, the average dose for a 5 minute irradiation of a 25 pound sample of Methocel under these conditions would give:

$$D = 9.34 \times 10^6 \frac{\text{g-rads}}{\text{sec}} \left(\frac{300 \text{ sec}}{5 \text{ min}}\right)\left(\frac{1}{25 \text{ lb}}\right)\left(\frac{16}{453.6 \text{ g}}\right)$$

$$= 247{,}000 \text{ rads in 5 minutes}$$

The total power generated by the Resonant Transformer, converted to dose rate units, may be calculated from the root mean square voltage and beam out current:

$$(707\times10^{3}\ \text{v})(10^{-3}\ \text{amp})\left(\frac{10^{7}\ \text{ergs}}{\text{watt.sec}}\right)\left(\frac{\text{gram-rad}}{100\ \text{ergs}}\right)$$

$$= 7.07\times10^{7}\ \frac{\text{gram rads}}{\text{sec}}$$

This compares with 9.31×10^{6} gram rads per second net power delivered to the fluidized bed, as calculated above, which is 13.2% of the total power. To determine if this is reasonable, the losses from the initial beam will be calculated.

Just before the beam leaves the accelerator it is a rectified sine wave.[1] The losses include absorption in the .0075 inch titanium accelerator beam window, 35 centimeters of air, the iron wire support screen for the reactor window, and the aluminum foil reactor window. In addition, the beam tends to spread out after it leaves the accelerator, so the fraction lost in the reactor walls must be estimated.

Since titanium has a density of 4.5 grams per cubic centimeter, the .0075 inch accelerator window has a face density of 85.8 milligrams per square centimeter. The average dE/dx for electrons in this energy range is 1.6 Mev square centimeter per gram. The loss in the titanium would then be $(85.8\ \text{mg/cm}^2) \cdot (1.6\ \text{Mev cm}^2/\text{g})$ or .137 Mev.

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[1] J. A. Knowlton, G. R. Mahn, and J. W. Ranftl, "The Resonant Transformer: A Source of High-Energy Electrons," Nucleonics 11-11 64-65, 1953.

The beam out current is that which actually leaves the accelerator window, but the root mean square voltage will now be 0.570 Mev instead of .707 Mev.

At 70°F and 740 millimeters of mercury pressure the density of air is 1.16 milligrams per cubic centimeter, so the 35 centimeters of air represents 40.7 milligrams per square centimeter thickness. Since air is a slightly better absorber of electrons than aluminum (by about 19%) and the depth-dose curve was made for aluminum, this is equivalent to 48.3 milligrams per square centimeter of aluminum. The reactor window is aluminum foil 4 milligrams per square centimeter. The average dose to this depth is found to be 1.08 D_o, so the air and window together absorb 56.5 D_o. The average dose to 300 milligrams per square centimeter is 0.664 D_o, so the total available is 199.2 D_o. Then the air and window take out 28.4% of the beam, so the fraction transmitted is 0.716.

The iron wire in the reactor window support screen is .042 inches thick, with a distance of 0.458 inches between adjacent strands. It was assumed that the wire, although round, absorbed all the beam which struck it, because the amount of beam transmitted through the thin parts is offset by the amount absorbed by the solder at the corners and along some parts of the wire. The ratio of the area taken up by the wire to the total area is .161, so the screen will transmit 0.839 of the beam striking it.

It has been reported[1] that in a horizontal plane the variation of dose with radial distance from the center of the beam is described by the error function:

$$D = D_o \cdot \exp(-r^2/2a^2)$$

where r is the radial distance from the vertical axis of the beam, D_o is the dose at the vertical axis, and a is the equivalent of the statistical standard deviation. A weighted average of the data from Figure 12 was used to compute a, which was 6.38 inches. To find the total beam, the product of the differential area, $2\pi r\ dr$, and the dose at r is integrated from r = 0 to infinity

$$D_t = \int_o^\infty 2\pi r \cdot D_c \cdot \exp(-r^2/2a^2)\ dr = 2\pi a^2 D_c$$

For the amount of the beam falling inside the reactor, the integration is carried out from r = 0 to 6 inches.

$$D_i = \int_o^6 2\pi r \cdot D_c \exp(-r^2/2a^2)\ dr = 2\pi a^2 D_o$$

$$(1 - e^{-6^2/2(6.38)^2})$$

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[1] R. C. Nicholas, "The Application of High-Energy Electrons to Some Grain-Infesting Pests" (Ph.D. Thesis, Department of Agricultural Engineering, Michigan State University, 1958).

$$D_i = 2\pi a^2 D_c(1 - .642) = .358\ D_t$$

Then the fraction of the beam which is absorbed in the Methocel is 0.358 of that which enters the reactor.

Then the net beam striking the Methocel will be the root mean square voltage of the electrons leaving the accelerator multiplied by the beam out current and the fractions transmitted by air and the aluminum reactor window, the wire support screen, and the fraction which falls inside the reactor.

$$(270 \times 10^3\ \text{v})(10^{-3}\ \text{amp})(.716)(.839)(.358) = 122\ \text{watts}$$

Converted to dose rate units, this is 12.2×10^6 gram rads per second as compared with 9.31×10^6 actually measured by the ion chamber.

Figure 15 (which was provided by the Dow Chemical Company) was used to calculate the dose to the bed for the irradiation work performed on the Dow Van de Graaff generator. First, the curve was integrated numerically in the same way as was done previously to determine the total power delivered to the plane of the fluidized bed.

$$P = \int_0^\infty 2\ r\pi p(r)\ dr = \Sigma\ 2\pi r\ p(r)\ \Delta r$$

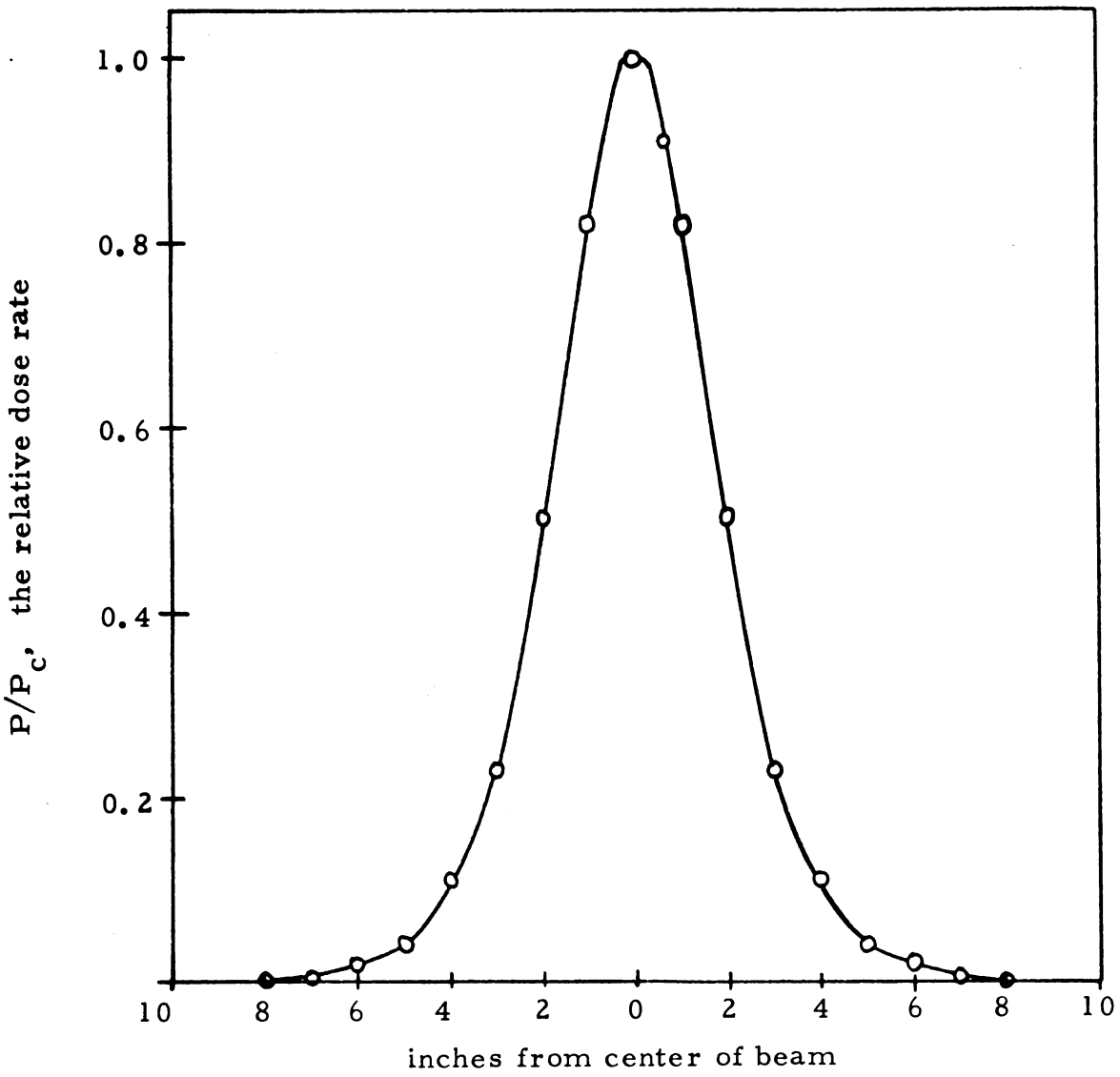

Figure 15. The Variation of Dose Rate with Distance from the Vertical Beam Axis for the Dow Chemical Company Van de Graaff Generator in a plane 12 Inches below the Accelerator Window

where p(r) is p_c multiplied by the value found in Figure 15. p_c was 3.13×10^{-5} watts/cm^2, according to information from the Dow Chemical Company, at 250 microamperes of beam current (the current used for these irradiations). The resulting total power was 425 watts, corresponding to 1.7 Mev or a loss of 0.3 Mev in the accelerator window and intervening air.

At 1.7 Mev the dE/dx in aluminum is 1.47 Mev cm^2/gram, so the 4 milligram per cm^2 reactor window would decrease the beam energy by .006 Mev. Then the reactor window would transmit 0.997 of the energy striking it. As discussed above the wire support screen transmits 0.839 of the beam striking it.

It was also found that the beam used, which had a three-inch scan, was 97.3% inside the reactor. The technique for determining this was to take the integrated power curve calculated from Figure 15, and find the fraction of the total power falling outside the reactor as the center of the curve was moved from the center of the reactor to 1.5 inches from the center of the reactor (a 3 inch beam scan). At the center 98.0% of the beam was inside the reactor, while at 1.5 inches from the center 96.4% of the beam fell inside.

The total dose rate for the Midland irradiations was:

$$425 \text{ watts } (.839)(.974)(.997)\left(\frac{10^7 \text{ erg}}{\text{watt sec}}\right)\left(\frac{\text{g rad}}{100 \text{ erg}}\right)$$

$$= 3.46 \times 10^7 \frac{\text{g rad}}{\text{sec}}$$

For a 1 minute irradiation of 25 pounds of material this gives a dose of

$$3.46 \times 10^7 \frac{\text{g rad}}{\text{sec}} \left(\frac{60 \text{ sec}}{\text{min}}\right)\left(\frac{\text{lb}}{453.6\text{g}}\right)\left(\frac{1}{25 \text{ lb}}\right) = .183 \frac{\text{M-rad}}{\text{min}}$$

Dose calculations for the thin layer samples involve a set of calculations similar to those for the fluidized bed above but with the additional determination of the amount of backscatter from the glass holding the sample. The average atomic number for pyrex is 9.4, so the backscatter will be 19.5% of the radiation incident to the pyrex.[1] Table 8 shows the calculations used for the thin layer samples. The average surface dose over the area was found from ionization chamber measurements 55.6 kilorads per second at 1.0 milliamp beam out current. The calculations were made on a per square centimeter basis, so the total beam is:

$$B = 55.5 \frac{\text{K-rad}}{\text{sec}} (.664)\ 0.3 \frac{\text{grams}}{\text{cm}^2} = 9050 \frac{\text{gram rads}}{\text{sec cm}^2}$$

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[1] R. C. Nicholas, "The Application of High-Energy Electrons to Some Grain-Infesting Pests" (Ph.D. Thesis, Department of Agricultural Engineering, Michigan State University, 1958).

TABLE 8

Dosage Calculations for the Thin-Layer Samples Based on One Square Centimeter of Dish Area

Sample weight, grams	6.36	9.54
Dish area, cm^2	63.6	63.6
Simple thickness, mg/cm^2	100	150
Foil thickness, mg/cm^2	none	5
D_o, surface dose rate, Krads/sec	55.55	55.5
Sample plus foil thickness, mg/cm^2	100	155
Average dose to that depth from Figure	1.072 D_o	1.007 D_o
Total forward energy absorbed, gram-rads/sec	5950	8660
Total beam (from text) gram-rads/sec	9050	9050
Energy striking glass, g-rads/sec	5100	2390
Backscatter fraction for pyrex	0.195	0.195
Backscatter energy to sample g-rads/sec	1000	460
Energy absorbed in foil per D_o	0	1.019 · 0.005
Energy absorbed in foil in g-rads/sec	0	220
Energy absorbed in sample, g-rads/sec	6950	9120
Dose rate to sample,* Krads/sec	69.5	59.0

*At 1000 Kv peak energy and 11.0 μa beam current.

In the same way the amount of forward beam energy absorbed in the sample and foil covering were calculated. The difference between the energy absorbed by the sample and foil and the total beam is the amount of beam striking the pyrex dish, and 19.5% of this is backscattered to the sample.

APPENDIX B

PHYSICAL PROPERTIES OF METHOCEL

The bulk density of Methocel varies from about 0.3 to 0.5 grams per cubic centimeter,[1] and is affected by the amount of packing. The particle density was determined with a pycnometer (using heptane as a wetting agent), and found to be 1.28 grams per cubic centimeter. An analysis of the particle-size distribution was made down to 44 microns least dimension with a set of sieves and down to 7 microns equivalent spherical diameter with a Roller particle-size analyzer.[2]

Sieve and roller analysis data are comparable only for spherical particles. As may be seen in Figure 17 (a photomicrograph of Methocel particles) Methocel can hardly be considered spherical. In order to compare the two sets of data, it was assumed that the particles were right circular cylinders where the length is 4 times the diameter, D_c. The equivalent spherical diameter, D_s, which is the diameter of a sphere of equal volume, can be easily calculated by equating the volumes:

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[1] Methocel, The Dow Chemical Company, 1962.

[2] Roller, United States Bureau of Mines, Technical Publication 490, 1931.

$$\frac{\pi D_c^2}{4}(4\ D_c) = \frac{1}{6}\pi D_s^3 \quad \text{or} \quad D_s = \sqrt[3]{6}\ D_c$$

The sphericity, ψ, of an object is the surface area of a sphere of equal volume divided by the surface area of the object, so:

$$\psi = \frac{\pi\ D_s}{2(\frac{\pi D_c^2}{4}) + \pi D_c(4\ D_c)} = \frac{\pi\ D_c^2\ (6)^{2/3}}{\pi\ D_c^2\ (0.5+4)} = \frac{6^{2/3}}{4.5} = .734$$

From Perry,[1] pages 5-59, it may be seen that:

$$D_s = \sqrt{\frac{18\ \mu u}{g(\rho_p-\rho}}\ \sqrt{\frac{1}{K_1}} \quad \text{where } K_1 = .843 \log \frac{\psi}{.065}$$

for conditions in the Stokes-law region. The roller analysis yields D_s^o,

$$D_s^o = \sqrt{\frac{18\ \mu u}{g(\rho_p-\rho)}} \quad \text{so that} \quad D_s = D_s^o\ \sqrt{\frac{1}{K_1}} = D_c\ \sqrt[3]{6}$$

From the above formula, K_1 is .887 and:

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[1] R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, eds., Chemical Engineers' Handbook, 4th ed., (New York: McGraw-Hill, Inc., 1963).

$$D_c = D_s^o \sqrt{\frac{1}{.887}} \sqrt[3]{\frac{1}{6}} = D_s^o (1.062)/(1.817) = .584\ D_s^o$$

Thus, this correction was applied to the roller data. The results are plotted in Figure 16.

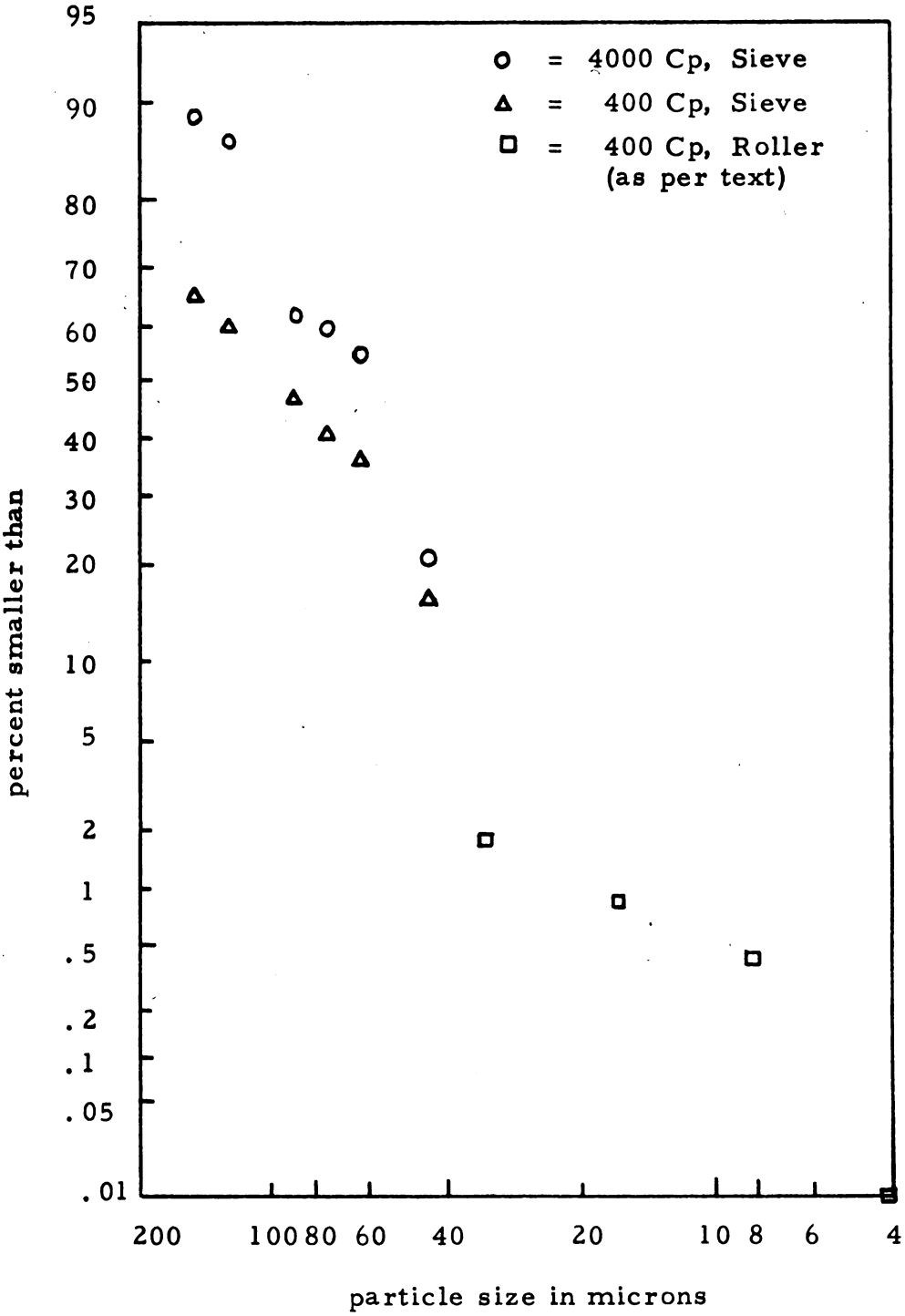
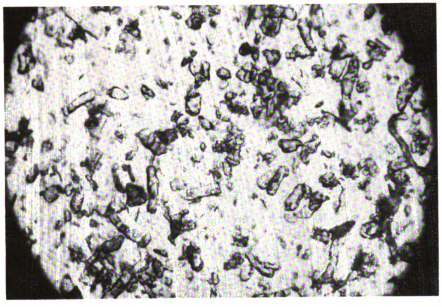


Figure 16. Particle Size Distribution for Methocel



scale → | | ← 50μ

Figure 17. Photomicrograph of 4000 Centipoise Methocel 60 HG, Premium Grade

APPENDIX C

METHOCEL VISCOSITY DETERMINATION

The 2 per cent solution viscosities of Methocel were determined according to the ASTM designation D 1347-64.[1] A moisture determination was made on each sample and sufficient Methocel was weighed out to give 2.00 grams of dry material. This was placed in a tall 8 ounce jar with 98 grams of 90°C water. The jar was covered and the mixture was stirred with a mechanical stirrer for 35 minutes. During the final 25 minutes the jar was in an ice bath. The solution was then spun in a clinical centrifuge for 15 minutes to remove all bubbles and finally placed in a viscometer in a 20.0° Celsius water bath for 30 minutes. At least 4 determinations of the flow time were made. The viscometer was chosen so that the flow time was between 30 and 150 seconds to minimize non-Newtonian behavior. The densities of all solutions were assumed to be 1.00 grams per cubic centimeter.

Except for the low viscosity samples, all viscometers were calibrated with standard viscosity oils as

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[1] "Standard Methods of Testing Methylcellulose," A.S.T.M. Designation D-1347-64, 1964.

called for in the ASTM procedure for testing methylcellulose. The Methocel 10 HG samples were related to the assumed viscosity of the unirradiated material which had been determined by the Dow Chemical Company.

In many cases the viscosity tended to drift downward while the readings were being taken. This was especially true for irradiated samples. A five minute time lag between readings might produce a 0.2 or 0.3 second difference in flow time. Most of the final average values, therefore, represented about 10 minutes standing in the water bath after the flow time determinations had begun. This error, which was less than 1.5% in all cases, was not significant for the use to which the data were put because the change for a sample was always small compared to the viscosity differences between samples.

APPENDIX D

THIN-LAYER IRRADIATION OF METHOCEL

In order to determine the relationship of absorbed radiation dose and resulting 2 per cent solution viscosities, 9 samples of the 4000 centipoise material were irradiated in thin layers. Six 9.64 gram samples were placed in 9-centimeter glass dishes to make an even layer 150 milligrams per square centimeter deep. They were covered with aluminum foil 5 milligrams per square centimeter thick. Three other samples of 6.36 grams each were placed in similar dishes with no foil covering, making a layer 100 milligrams per square centimeter deep.

The samples were irradiated 47 centimeters below the accelerator window for various times and beam currents and at 1000 kilovolts peak energy. The calculations of the dose rate at 1.0 milliampere beam current are shown in Table 8. Table 9 shows the beam current, irradiation time, average dose, and resulting 2 per cent solution viscosities for the nine samples and two controls. The dose-viscosity results are plotted in Figure 18.

Several attempts to find a simple two or three factor analytical function to fit the curve in Figure 18 were made. However, no such function was found, so the points were taken off the curve where dose-viscosity data are needed.

TABLE 9

Dose-Viscosity Data for 4000 Centipoise Methocel Irradiated in Thin Layers

Exposure time, seconds	Beam current, ma	Dose rate at 1.0 ma beam current Krad/sec	Total dose, Krads	2% solution viscosities, centipoise
0	--	--	0	4446
24	0.2	47.2	230	1930
36	0.4	47.2	680	790
70	0.4	47.2	1320	337
120	0.4	47.2	2270	144
240	0.4	47.2	4530	37.8
360	0.4	47.2	6800	16.3
0	--	--	0	4260
24	0.4	55.6	530	1010
48	0.4	55.6	1070	416
96	0.4	55.6	2140	143

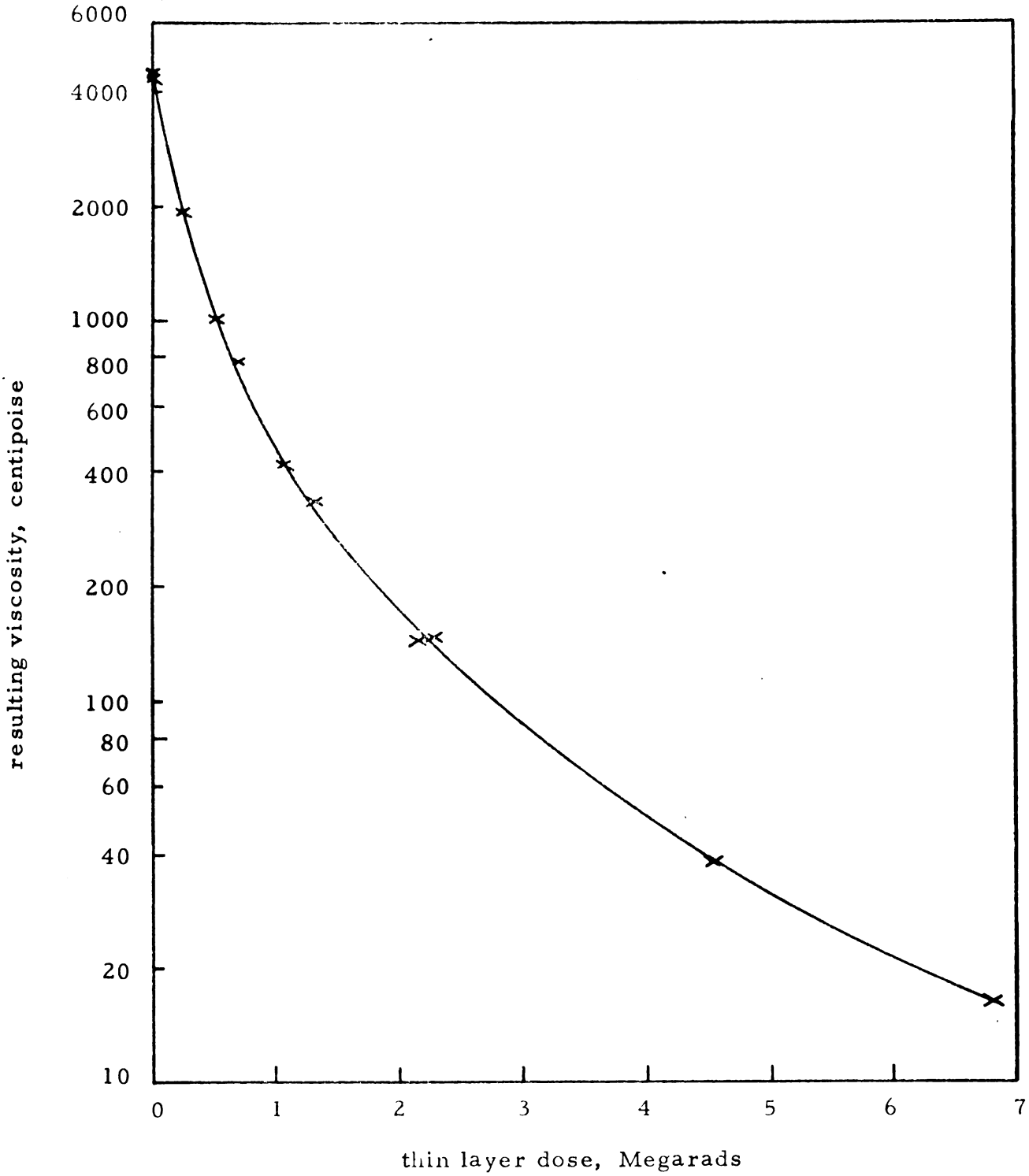

Figure 18. Viscosity Resulting from Various Radiation Doses Applied to Thin Layer Samples of Methocel

APPENDIX E

VISCOSITIES OF MIXTURES OF METHOCEL

The viscosity resulting from a mixture of two different viscosity samples of Methocel was needed to demonstrate the efficiency of fluidization in the continuous mixing experiment. In addition, such information would be helpful in differentiating between uniform irradiation and nonuniform irradiation followed by good mixing in the bed.

Three sets of binary mistures of Methocel were made using 4500, 433, and 49.9 centipose 2% solution viscosity material. Four mixtures were in each set, 80:20, 60:40, 40:60, and 20:80 ratios of the components. The mixture compositions and resulting viscosities are given in Table 10. Several attempts were made to fit the data accurately to a simple mathematical formula. The information given in Methocel showed that, for a single component, the eighth root of viscosity should be a linear function of Methocel concentration. If one assumes that each part of the mixture exhibits its own viscosity independently in this manner, the resulting 2% solution viscosity of the mixture should be the eighth power of the weighted average of the eighth roots of the 2% solution viscosities of the

TABLE 10

Viscosity Resulting from Mixtures of Methocel

Composition	2% solution viscosity
80% 4500 cp, 20% 433 cp	3070 cp
60% 4500 cp, 40% 433 cp	2020 cp
40% 4500 cp, 60% 433 cp	1290 cp
20% 4500 cp, 80% 433 cp	738 cp
80% 4500 cp, 20% 49.9 cp	2340 cp
60% 4500 cp, 40% 49.9 cp	1100 cp
40% 4500 cp, 60% 49.9 cp	471 cp
20% 4500 cp, 80% 49.9 cp	163 cp
80% 433 cp, 20% 49.9 cp	277 cp
60% 433 cp, 40% 49.9 cp	187 cp
40% 433 cp, 60% 49.9 cp	123 cp
20% 433 cp, 80% 49.9 cp	78 cp

components. Mathematically, for N components, the formula is:

$$\mu_R = \left(\sum_{i=1}^{N} x_i \, \mu_i^{1/8} \right)$$

which could be called the "eighth-root rule."

Figure 19 shows this eighth-root rule drawn in as solid lines, and the experimental data shown as points. While the agreement is not perfect, it is sufficiently good for the uses to which it will be put. For a better formula, one would have to make a great many runs. The results indicate that the formula might be an "N-th root rule" where N depends on the component viscosities, since each of the three experimental curves could be fit very closely by allowing N to change.

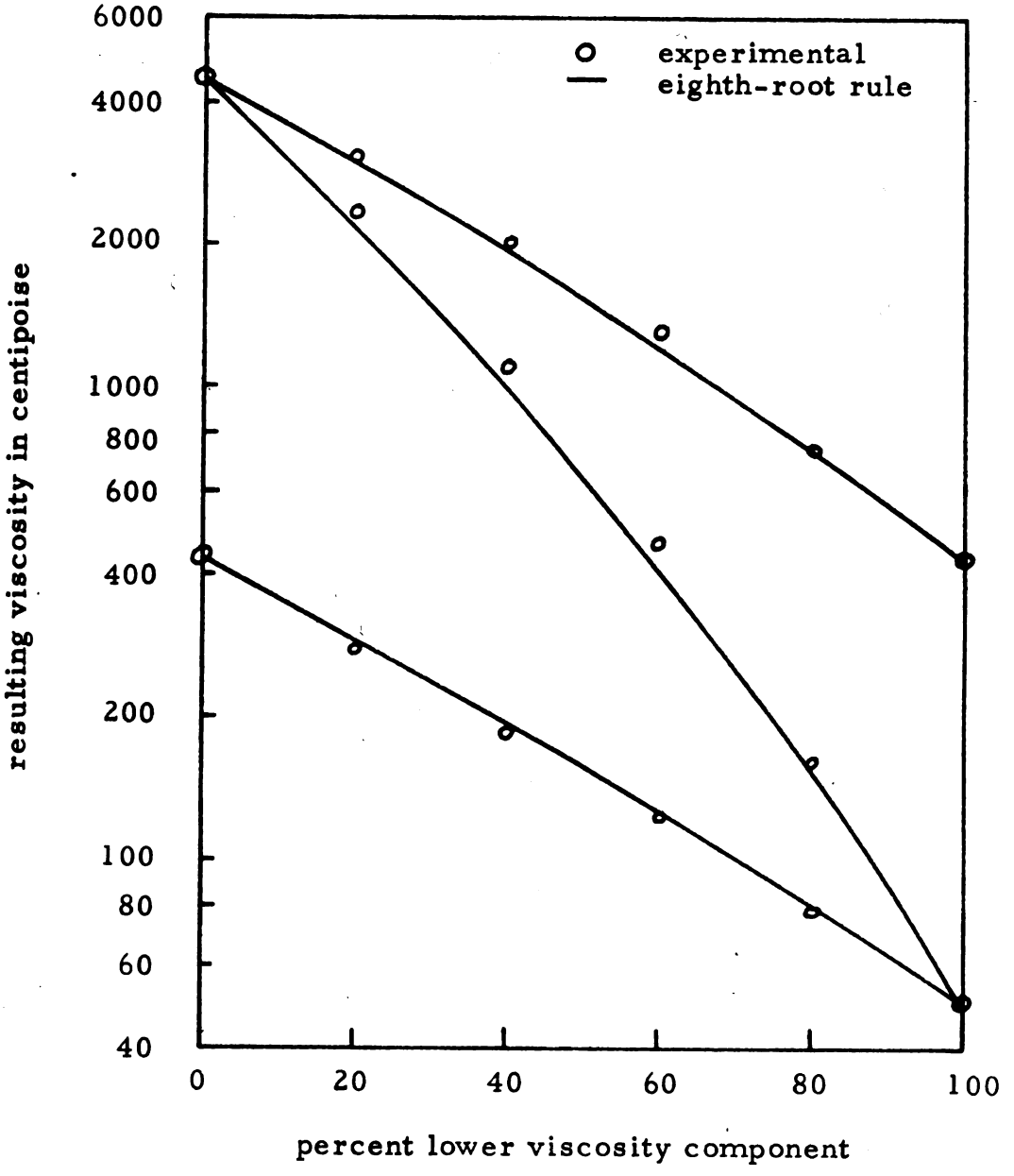

Figure 19. Theoretical and Experimental Viscosities Resulting from Mixtures of Methocel

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