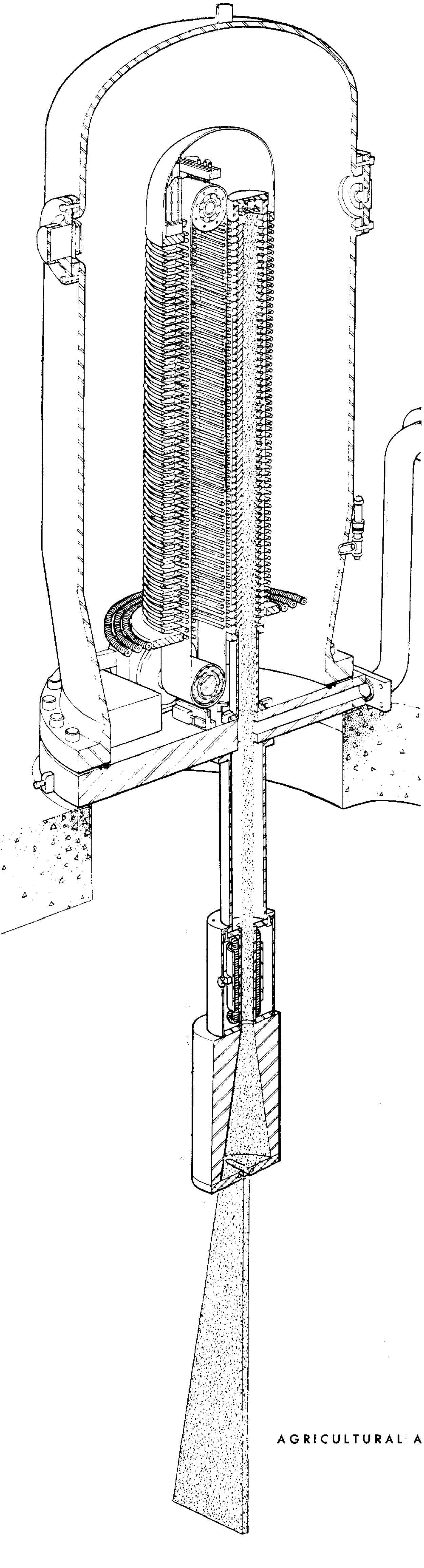


RADIATION STERILIZATIO

OF FOODS

Side effects, chemical reactions resulting in off-flavor and off-odor are principal obstacles to commercial application

THE ERA OF RADIATION STERILIZATION is not yet here, contrary to the optimistic predictions flourishing several years ago. Possibilities for the future are encouraging, but much more research must be completed before radiation sterilization brings about a new era for the food industry.

To those interested in food processing, radiation suggests the possibility of a revolution in food preservation. And in an industry as highly competitive as food processing is in the U. S., no manufacturer can afford to be left out. On the other hand, advances in the food industry must be based on careful scientific research and development. It is for these reasons that the prospect of radiation processing has caused both optimism and confusion among some responsible for the direction food processing will take in the future.

The basic method for sterilization of foods has remained the same for the last 150 years. (Canning and heat sterilization were discovered by Nicholas Appert in 1809). Since that time the basic process has remained the same despite the fact there has been a search for some heatless method of food sterilization.

Destruction of bacteria by ionizing radiation appears as the most promising potential method for sterilization of food without heat. Although preservation of fresh food, maintaining the qualities of freshness—the dream of the food industry—has not yet been realized, there are other, more limited hopes which may be realized in the near future. And in the long run, radiation processing could bring on a radical revolution in the food industry.

Of the numerous electromagnetic phenomena and particularly radiation in the arsenal of the modern physicists, cathode rays and x-rays or gamma radiation are the only ones seriously considered for practical radiation sterilization applications. Cathode rays are electrons from the atomic shell which are artificially accelerated and directed. Particle accelerators such as van de Graff generators and resonance transformers produce cathode rays.

Cathode rays are man-made radiation in that they are produced by man-made machines by imparting additional electrical energy to electrons and projecting these accelerated electrons in a beam path. Machines capable of producing cathode rays with energies of 1 to 3 m.e.v. are now available and 10- to 20-m.e.v. devices could be built.

Major disadvantage of cathode rays is their relatively shallow penetration—maximum range of penetration of 4-m.e.v. cathode rays is about 1 inch of water. Cathode rays of 2 m.e.v. have a maximum penetration of about 0.5 inches of water. On the other hand, gamma radiation with an energy of 1 m.e.v. will penetrate about 10 inches of water.

If the cathode rays produced in a particle accelerator are directed on a metal target, x-rays are produced. X-rays have the same physical characteristics as gamma rays, but x-rays are produced by machines while gamma rays are emitted from the atomic nucleus during radioactive decay. X-rays and gamma rays are true electromagnetic radiation and are not usually considered as particles.

Beta particles are similar to cathode rays but are high energy electrons emitted from atomic nuclei produced during radioactive decay.

Bactericidal Effects

The fact that radiations of the type discovered by Becquerel and Roentgen would destroy microörganisms was announced about 1905. Until recently the general explanation of this killing effect has been that the ionizing particles killed by colliding with the bacteria. The particles hitting the bacterial cell produce free radicals of both oxidative and reductive types which kill the cell either through alteration of its surface chemistry or a destruction of the internal biochemical equilibrium. The direct-hit theory, which probably accounts for most of the destruction of bacteria implies as a corollary that the medium in which the bacteria are suspended should have no effect on the rate of destruction by radiation. Recent work has indicated that this may not be entirely correct.

Reports by Procter and Goldblith indicate that some bacteria are killed by indirect action of the ionizing radiations on the medium. They reported that by the addition of radiosensitive compounds to the bacterial medium, the destruction of bacteria by radiation was decreased. In a simple medium perhaps some bacteria are killed by free radicals produced outside the bacterial cell which react chemically with the bacterial surface, thus bringing about death of the organism by radiation of its environment. Some of these components may infuse into the cell and alter the survival rate. As the complexity of the medium is increased, the free radicals produced have a better chance of reacting with other components of the medium and are "captured" before they can react with the bacteria.

Additional evidence for the so-called indirect effect has been obtained by a somewhat different approach. A greater destruction of bacteria has been reported following irradiation at 40–45° F than if the milk is irradiated in the frozen state. Decrease of bacteria destruction following irradiation in the frozen state is considered additional evidence of importance of free radicals in destruction of bacteria by the indirect effect. Mobility of the free radicals is believed to be greatly reduced if the irradiated medium is in the frozen state.

Other workers (Hollender and associates at Oak Ridge) have reported that *E. coli* bacteria are more sensitive to radiation in the presence of oxygen than in its absence. The radiosensitivity of *E. coli* is also reported to be affected by environmental conditions during development and growth of the bacteria prior to radiation

The potential implications of the so-called "indirect effect" of radiation of the medium on the bacteria have prompted intensified experimental investigations on the effects of environmental conditions on radiation sensitivity of bacteria. Environmental factors, such as temperature, pH, and chemical additives to the bacterial medium are now regarded as of great importance in destruction of bacteria by radiation.

Recent studies emphasize the point that the action of ionizing radiation on bacteria is dependent upon the species and also the medium in which the bacteria are being irradiated. More exact studies of effects of environment on radiation sensitivity might result in techniques for radiation sterilization with considerably lower radiation requirements.

Effects of Ionizing Radiations

The chemical reactions responsible for alteration of flavor and odor in irradiated foods are thought to be oxidative in character, involving OH and HO_2 radicals and possibly hydrogen peroxide. Examples of four of these more simple reactions are shown in Figure I.

Some effects of irradiation on vitamins normally present in food have been reported by James F. Mead, University of California. The work on radiation effects on vitamins is of twofold interest. Analytical studies give general information on the effects of irradiation on relatively complex molecules. Other assay procedures and techniques give more specific information on what effects irradiation will have on the nutrients present in foods.

To understand the basic reactions of vitamins to radiation it has been necessary to irradiate solutions of the vitamins containing known concentrations suspended in various media. However, when the vitamins are present in relatively complex mixtures, such as food, the problems of ascertaining the reactions involved become much more complicated.

The protective effect of other compounds present in food mixtures or the protective effect of materials deliberately added to foods, is not completely understood. The destructive effects of ionizing radiation of vitamins and other complex molecules in foods is believed to be due to oxidative action.

Niacin seems to be the vitamin most resistant to the effects of radiation.

Vitamin B_{12} on the other hand is relatively sensitive to radiation. At a concentration of 10 μg per ml., 80% of it is destroyed by radiation with 10^4 R.e.p. of 3-m.e.v. cathode rays. However, vitamin B_{12} in milk is relatively insensitive, another example of the protective effect.

All the vitamins seem to be sensitive, in some degree, to oxidation when exposed to ionizing radiation and the loss of some vitamins in any radiation processing seems certain. However, another question which arises is that of toxic by-products resulting from radiation of vitamins. Much of the current work on effects of radiation in vitamins is aimed at identification of the oxidative products resulting from this radiation. As yet there has been no evidence that any toxic substances are produced by irradiation of the vitamins.

Particle accelerators have been developed for production line sterilization of packaged materials. The High Voltage Engineering Co. manufactures machines which can be incorporated into existing food processing lines. Here a 2 m.e.v. machine is sterilizing vials of pharmaceuticals

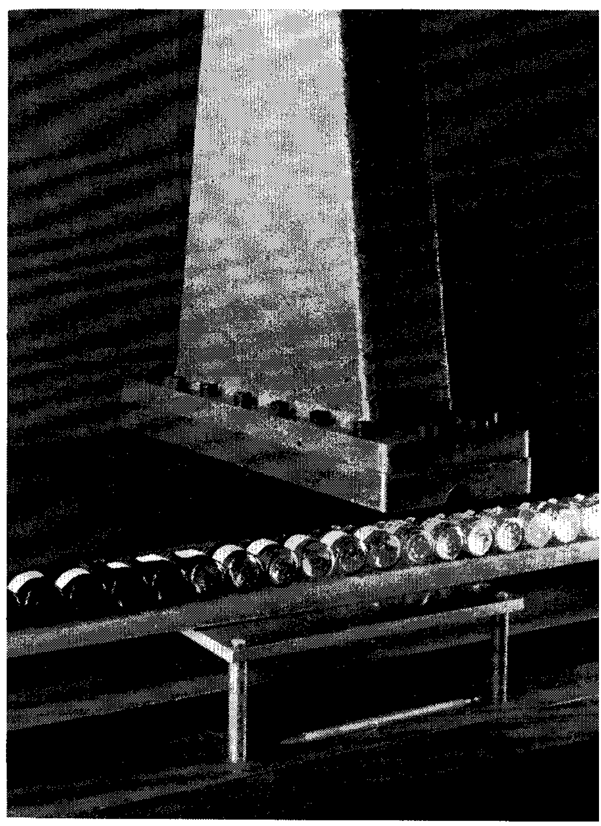
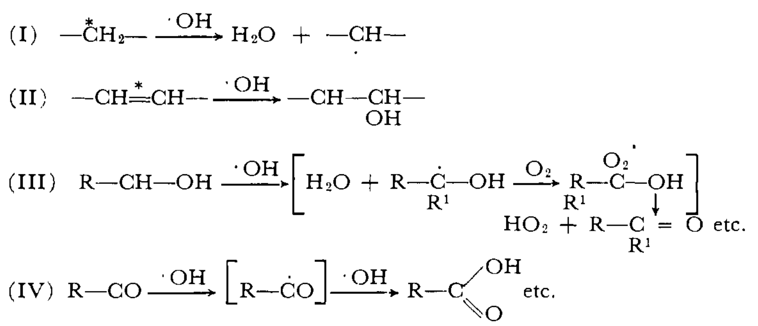


Figure 1

(I) represents the attack of a radical on an active methylene with removal of a hydrogen atom and production of an alkyl radical. (II) shows the addition of a radical to an active double bond accompanied by opening of the bond and production of an alkyl radical. (III) and (IV) represent the oxidation of an alcohol to a carbonyl compound and further reaction to form a carboxylic acid.

These simplified reactions are presented as examples or models of the reactions thought to be responsible for the chemical modification of the complicated molecules present in foods. Consideration of the complexity of the molecules in food products might make the above simplification seem foolhardy. However, even in vast number of giant molecules present in foods, especially those responsible for odor and flavor of food, there are susceptible or labile groupings which are believed to be more sensitive to the oxidative action of ions produced by radiation



Indirect Effects

By their nature, radiations cause ionization while traversing any medium. The object of radiation food processing is ionization and eradication of bacteria. The majority of the free radicals so produced will remain in the food medium, thus perhaps affecting the material being processed. The effects of these ions on the chemistry of the food molecules are called indirect effects, because they are due to reactions between the free radicals produced by radiation and the molecules of the medium. Indirect effects can be classified as: (1) the dilution effect, (2) the temperature effect, (3) the protection effect.

The dilution effect is observed in irradiation of solutions of varying concentrations of radiosensitive compounds. The more a given compound is diluted, the greater the percentage destruction by irradiation. This effect is typified in irradiation of vitamins. The quantity of radiation required to destroy 63% of the molecules of a vitamin at a specified concentration is referred to as the "inactivation dose" (D_0). If the inactivation dose is divided by the concentration of the vitamin (D_0/C) the value obtained is a constant for the given compound. The constants are used to compare radiosensitivities of different compounds.

The temperature effect is also based on the premise that radiation exerts its influence on the solutes by the free radicals produced when the solvent medium is irradiated. If the medium is frozen, mobility of the free radicals is reduced and side effects decrease.

The protection effect is observed when mixtures of different molecules are irradiated and the results obtained following irradiation of the mixture are compared with those obtained by irradiating each component individually. If a mixture of two compounds, one radiosensitive and the other resistant to radiation, is irradiated, one solute will be preferentially destroyed and the other is, therefore, "protected" by the resistant. The protection effect is an illustration of competition between compounds for the free radicals produced in the solvent or medium; since a finite number of free radicals are produced, a certain number of them will react with one solute which, by combining with the free radicals, protects the molecules of the other solute.

The protection effect becomes especially apparent in food materials, where the distribution of various molecules and compounds is extremely complex. The inactivation dosage for ascorbic acid in food materials is about 10 times that required to inactivate the same quantity of ascorbic acid in a simple solution. About 100 times the specific inactivation dosage for a riboflavin solution is required to inactivate the same quantity of the vitamin in milk. The radiosensitive nutrients present in natural foodstuffs are already protected to a significant degree against radiation.

The effects of dilution, temperature, and protection on inactivation of radiosensitive materials in solution are all cited as evidence for the theory that the primary chemical results of radiation are due not to direct collision of radiation particles with the molecules of the radiosensitive material, but rather due to the chemical reactions between the radiosensitive molecules and the free radicals produced in the solvent or suspending medium by the radiation.

The theory of indirect action, which seems well substantiated, implies that chemical techniques can be developed to cut down on destruction of radiosensitive compounds by radiation.

Side Reactions

The largest single problem to be surmounted before radiation techniques can be used in food processing is the production of undesirable side reactions. These side reactions result in off-flavor and off-odor and other properties which detract from consumer acceptability.

In a food the competition among the various molecules present for the free radicals produced by radiation is so complex that quantitative predictions of the reactions appear impossible. In some cases the results of these reactions may be of interest only as an analytical chemical exercise. In other cases the new compounds produced in only the most minute quantities are of great importance for they are thought to be components of off-flavor and off-odor.

Recent research reports indicate that there is little or no loss of essential nutrients in some foods subjected to sterilizing levels of irradiation. There are large differences in flavor, odor, and sometimes color and texture of foods irradiated at levels below those necessary for sterilization. In some cases the changes produced by radiation, although at the bottom limits of analytical chemical detection, are of sufficient intensity to be detected by the human taste system.

Theoretical consideration of the small degree of change occurring in irradiated foods has been made. Assuming that about 25 electron volts is needed to break one CH_2 bond, a sterilizing dose of 2×10^6 R. would break only about 0.003% of the total number of CH_2 bonds present in the foodstuff. When one considers that there are often only a few micrograms of a given nutrient in a foodstuff, the minute quantities of material involved in a change of 0.003% of these nutrients can be understood.

Despite the fact that these changes are quantitatively very small, they are of great qualitative importance, not only with regard to flavor and odor but also in considering the possibilities of a toxic product resulting from modification of a nutrient or vitamin.

Thus far, research workers have not obtained any evidence of a toxic product resulting from irradiation of foodstuffs but the question has not been completely settled.

Reduction of Side Reactions

At present three potential methods have been developed for reducing or offsetting undesirable side reactions: irradiation in the frozen state; irradiation in an inert atmosphere, devoid of oxygen; and addition of free radical acceptors.

Freezing decreases the diffusion rate of most chemical components in the food material. Thus, the free radicals produced by radiation do not have as wide a choice of combination with other molecular components.

In an inert atmosphere, the amount of dissolved oxygen in the material is less and the number of HO_2 and other oxidizing radicals produced is less. Fewer of these radicals in the inert atmosphere lowers the number of undesirable side reactions.

Free radical acceptor chemicals can be added to the material before radiation to combine with the free radicals produced during irradiation and protect naturally occurring components which have less affinity for free radicals than the free radical acceptors.

The theory behind the use of free radical acceptors is that they will capture and combine with more free radicals than the flavor molecules, thus preserving flavors or other natural quality components.

A free radical acceptor, in addition to having a great affinity for the free radicals, must also be a compound of known safety, for these compound materials must often be added to the material in considerable quantities.

Attitude of FDA

The question of harmful products arising in irradiated foods brings the Food and Drug Administration into the picture. The present attitude of FDA is that irradiated foods, like all other foods, will be considered harmful until proved safe. FDA, recognizing that the number of molecules altered by radiation is extremely small, has recommended a schedule of extensive animal feeding tests which would eventually determine some upper toxic limit for radiated foods or conclusively prove that no upper toxic limit can be reached. FDA recommendations call for research workers to find some level of irradiation treatment resulting in unfavorable changes in the food which can be determined by feeding tests. The implication is that some level of radiation, probably many times the dosage required for commercial sterilization, might result in formation of toxic products in the foods. FDA recommends that this radiation level, if found, be established and the toxic products produced at that level be identified. At present no one has reported the identification of any toxic products produced at high radiation levels.

Long range feeding trials with animals are now under way to determine what, if any, effects can be produced by feeding animals irradiated foods for a two-year period. Two types of animals are being recommended in these tests: normal animals and animals in a state of stress, such as that brought on by impaired liver function.

Although there appear to be several obstacles to be overcome before commercial radiation sterilization of consumer foods, there are a number of other applications of radiation to food processing which appear to offer potentialities for the more immediate future.

Surface sterilization, peaches irradiated with 800 m.e.v. for destruction of surface mold then stored for 30 days. Irradiation with relatively low voltages destroys the bacteria and mold on the surface of food extending the shelf life but does not result in complete preservation

Surface Sterilization of Meats

Use of relatively low energy electrons for the surface sterilization of foodstuffs to extend shelf life appears possible in the near future. For some materials such as frankfurters, radiation which would kill off the majority of the bacteria and mold on the surface of the commodity would probably not result in any significant flavor change and yet increase the shelf life of the commodity several-fold. The use of radiation for surface sterilization of fresh fruits and vegetables has also been discussed. The relatively shallow penetration of low-energy cathode rays produced by the particle accelerators would be an advantage in an application of this type.

Doty and research workers at the American Meat Institute have reported on the possible application of gamma radiation to extend the shelf life of refrigerated meats. This application of radiation to decrease, though not eliminate, bacteria is sometimes referred to as "cold pasteurization." The dosage required for sterilization of meat is about 1.5×10^6 r.e.p. and up while radiation dosages of from 6 to 7×10^4 r.e.p. were sufficient to kill the major spoilage organisms in fresh meat. The bacteria primarily responsible for spoilage of fresh meat are members of the genus *Pseudomonas*, which are capable of growing at refrigerator temperatures. Pseudomonas bacteria can, according to Doty, be eradicated by these lower level radiation dosages. The refrigerated storage life of meat irradiated by the lower dosages has been extended about 5 times the normal shelf life of nonirradiated meat. At this lower radiation level no undesirable odors, flavors, or discolorations of the meat are found.

The research workers at the American Meat Institute believe that the use of these low level "pasteurization" dosages may offer considerably more promise for early commercial application of radiation than that anticipated for radiation sterilization.

Radiation pasteurization could be a valuable technique for the meat industry if it could be developed as a practical method for extending the shelf life of prepackaged meat cuts on the refrigerated shelves of self-served supermarkets. Whether or not it can be developed could be determined by extension of Doty's experiments to the experimental pilot plant stage where meat cuts could be irradiated on a semicommercial scale.

The bacteria responsible for food spoilage can be killed by ionizing radiations at the level of from 10^5 to 3×10^6 r.e.p. However, radiation at this level also results in undesirable changes in color or odor. Some method must be developed for preventing these undesirable side effects before radiation can be used for commercial food sterilization.

Much of the current research on off-odor and off-flavor phenomena is concerned with quantitative studies of the chemical changes of the foods responsible for these side reactions. According to Doty and his coworkers the chemical changes occurring in irradiated meat can be characterized as: the formation of odiferous sulfur-containing compounds; a reduction in the total proteolytic enzyme activity; destruction or chemical modification of tyrosine, and conversion of the red pigment of meat, myoglobin. Research workers at the MIT's food technology department report that they have increased the pasteurization dosage to 8×10^5 r.e.p. by addition of free radical acceptors. Chopped meat, hamburger, can be irradiated at this level with no detectable side reactions, off odor, and the refrigerated shelf life of the meat is extended from the normal 5 to 7 days to several months.

Grain Insects

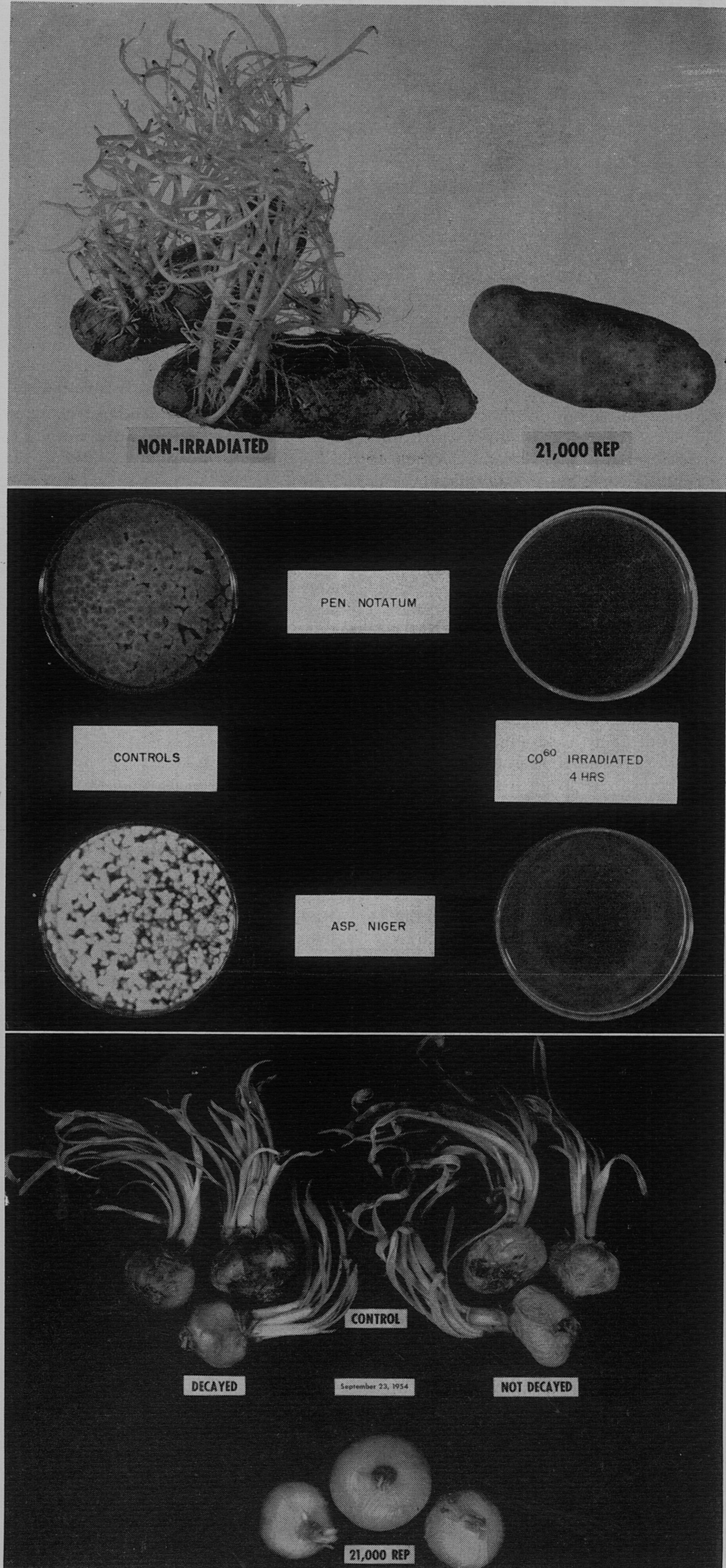
Another possible application of radiation is the eradication of insect infestation from grains. Damage to grain by insects is now estimated in the millions of dollars. Recent extensive studies at MIT have indicated that relatively low dosages of radiation will completely destroy the insects reponsible for this damage to stored grain. Tentative cost estimates indicate that the process might be economically feasible, especially when compared with the costs for fumigation of stored grain.

Potato Sprouting

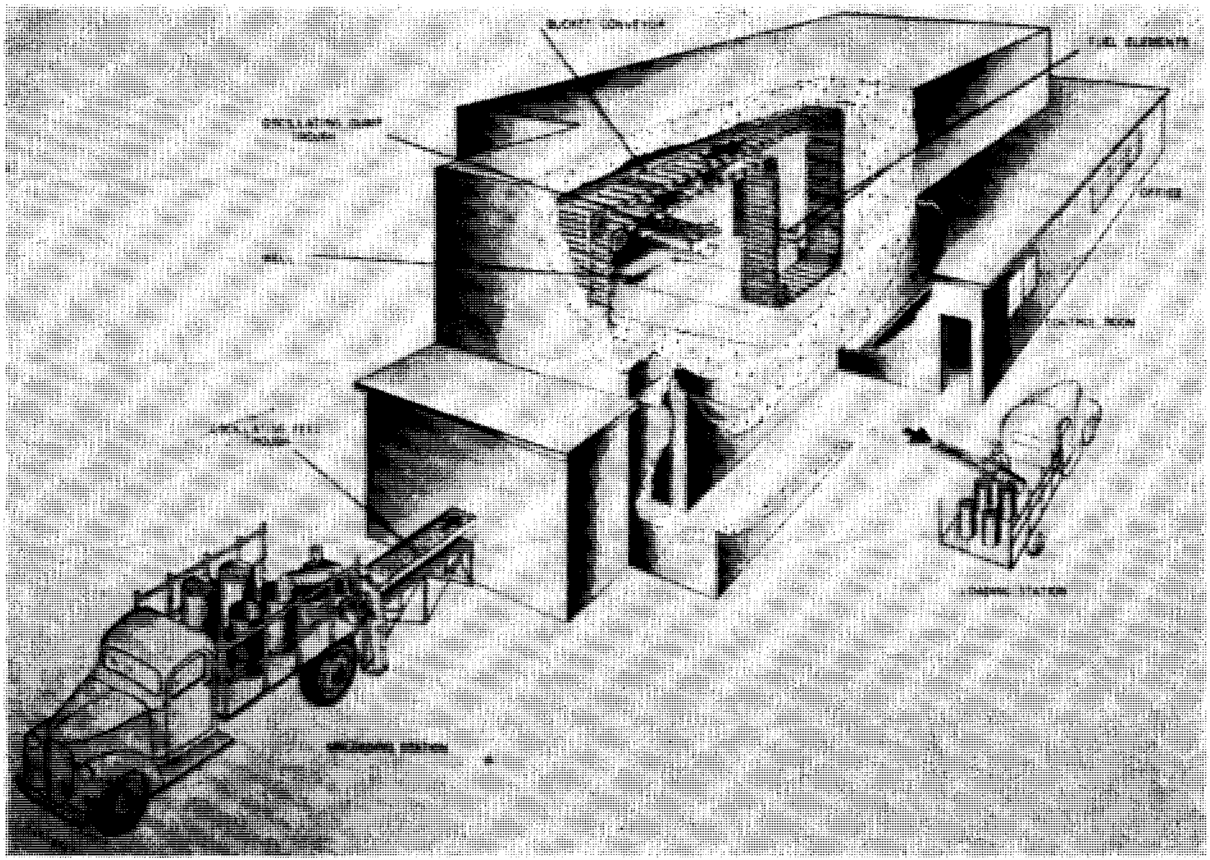
Recent work at Brookhaven and the University of Michigan indicates that the storage life of potatoes can be greatly increased by exposure to gamma radiation. Following dosages of from 5,000 to 20,000 r.e.p., potatoes were stored for up to 18 months with little or no loss in quality. Under normal storage conditions potatoes cannot be kept for more than about 4 months without some sprouting or internal softening.

On a weight basis the potato remains the most important single vegetable in the domestic diet, annual production is about 415 million bushels valued at more than half a billion dollars.

About 75% of the U. S. potato crop is harvested in the fall and cannot be held in unrefrigerated storage later than early spring. With refrigeration potatoes can be held in storage for a maximum of



More applications of radiation to extend storage life of foods. The storage life of onions and potatoes can be greatly extended by radiation treatment. Radiation with from 5000 to 20,000 m.e.v. kills the cells responsible for sprouting in potatoes and onions resulting in products which can be stored up to a year with no loss in quality. The Petri dishes, center, contain two types of common mold, responsible for surface spoilage of food products. Low level irradiation of foods destroys these surface spoilage organisms



Processing plant for irradiation of potatoes designed at the University of Michigan for utilization of the radioactive waste products from the Atomic Energy Commission's reactors. Design study was supported by AEC

Potato Irradiation Facility

THE PLANT pictured would be capable of irradiating 250 bushels of potatoes an hour for a cost of about 0.7 cent per bushel. Building costs are estimated at about $500,000 with yearly operating cost about $40,000 a year including rental of the radioactive source from AEC.

Potatoes would be brought from storage in sacks or barrels and unloaded into the oscillating feed trough. The feed trough would carry the potatoes to the bucket conveyor within the radiation chamber. The bucket conveyor would carry the potatoes around the fuel elements, the source of radiation, then dump the potatoes into trough.

While the potatoes are going through the plant at a rate of about 14 tons per hour, the truck which had unloaded at the loading station would drive around the building to the loading station and fill up with irradiated potatoes which could be returned to storage. The conveyor belt trip through the plant would take about 10 minutes.

Irradiated potatoes could then be stored for a year or more with no danger of rotting or sprouting.

The designers believe that three employees would be capable of operating the plant on a 40-hour week basis.

Based on a radiation dosage of 10,000 r.e.p. and year round operation, estimated costs for irradiation of potatoes range from $3.60 to about $5.00 per ton. These costs would include amortization of plant, rental of radioactive source, and wages for employees. On a 6-month operation per year minimum costs would be about $3.80 per ton of potatoes.

Radiation Sources

Three different radiation sources could be used for a food processing plant of this type: refined cesium-137; concentrated mixed fission products; or cooling reactor fuel elements. Radioactive cesium can be refined from the by-products of AEC nuclear reactors. Both cesium and concentrated mixed products have longer half lives than the cooling reactor fuel elements. Purchase costs for these materials are unknown.

The reactor fuel elements could be rented from AEC and would be the most economical source of radiation for a plant designed to run six months of the year. These highly radioactive sources are normally stored under water to "cool down" after being withdrawn from a nuclear reactor. After cooling for several weeks, radioactivity decreases and the fuel elements can then be processed for isotopes.

A limited number of radiation plants might be built in the vicinity of AEC's nuclear reactors to utilize this radiation during the "cooling off" period of the fuel elements.

For a plant operating at a full year schedule refined fission products or cesium-137 would be the most economical source of radiation. As the activity of the radioactive sources decayed, more rods would be added. Over a five-year period the total number of rods would be increased about 10% to maintain a steady radiation strength.

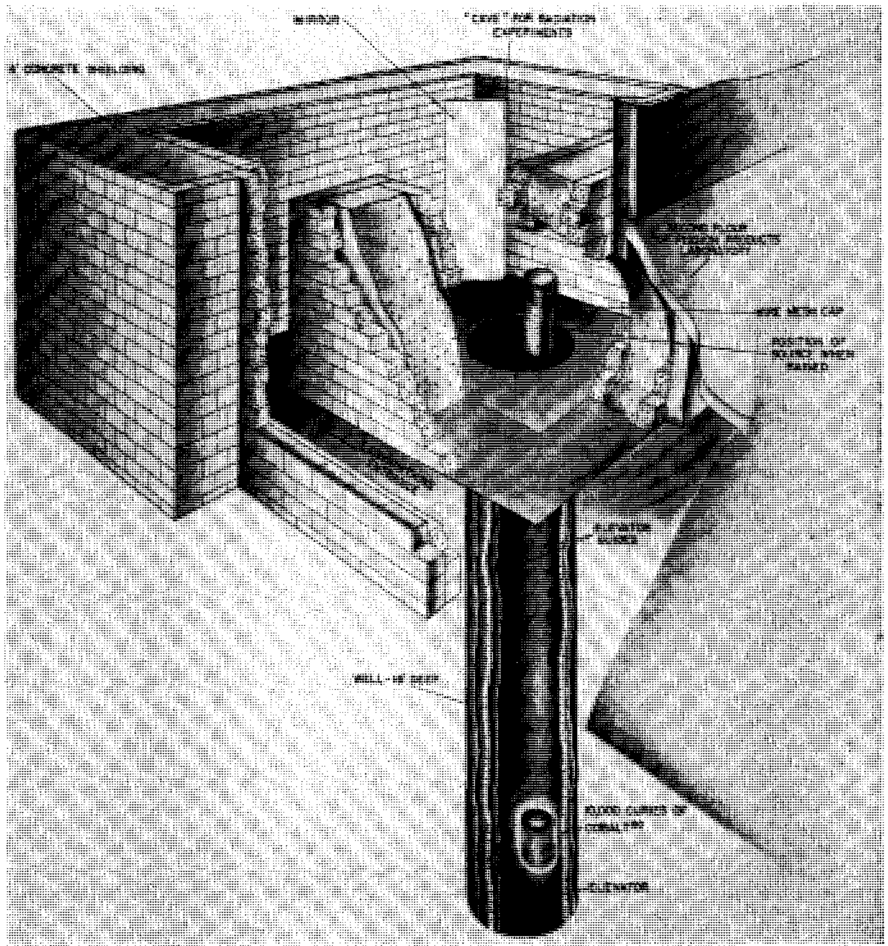
A plant similar to the potato radiation facility outlined above has been designed by the Michigan engineers for radiation pasteurization of meat.

about eight months. Proposed designs for a commercial plant to irradiate potatoes utilizing reactor by-products have been developed by the University of Michigan. Costs for irradiating a bushel of potatoes are estimated at less than the cost of shipping from southern or far western states.

In addition to the difficult and relatively basic research problems, off-flavor and odor, there are still formidable engineering problems to be solved before radiation processing becomes a general commercial reality. Tentative pilot plant schemes for radiation processing of foods and pharmaceuticals have been drawn up but thus far the cost predictions have never been put to practical test.

The Atomic Energy Commission has sponsored a variety of research products to find commercial applications for the radioactive fuel wastes produced as by-products of its atomic reactors. The AEC plans eventual release of these radioactive materials for commercial applications such as radiation sterilization. The advantages of the atomic fuel wastes as a source of radiation are that the gamma radiation given off has a much greater penetration than the cathode rays produced by particle accelerators. Also atomic wastes *theoretically* offer a cheap source of radiation energy.

Despite the fact that the radiation source is potentially cheap, cost factors mount when the problems of utilizing these waste products are considered. The installation of a radiation source, such as cobalt-60 requires extensive shielding and safety precautions. The waste products from the atomic reactors would also have to be concentrated and refined to some degree before they could be installed in a food processing plant; these radiation sources would also have to be replaced or replenished periodically and the partially depleted sources, which had decreased in intensity but would still be extremely dangerous, would have to be disposed of.



Radiation Engineering Laboratory and Stanford Research Institute. The cobalt-60 source is stored in the well in the floor of the pool; when irradiation experiments are underway the radioactive source is raised to the bottom of the water filled pool and materials to be irradiated are lowered into the pool. The radiation from the Stanford source is greater than that given off by 2 kg. of radium

On The Cover

Self Portrait of Radioactive Cobalt

THIS PICTURE was taken without the usual electrical illumination required for pictures—source of light was the glow of the radiation source. The camera is looking down into the storage well at a rod of cobalt-60. Radiation sterilization of foods is just one of the many possible applications of the radiation emitted by sources such as this. Radioactive cobalt is an ideal research source because of its long half life. However, cost of preparation of sources, such as this one at Stanford Research Institute, is probably too great for any commercial application. Research with the cobalt sources is being pushed to find applications for the radioactive by-products produced in the nuclear reactors of the Atomic Energy Commission.

Photo, Courtesy Stanford Research Institute

Particle accelerators, on the other hand, are machines for producing radiation which can be turned on and off. When the radiation source is not needed no radiation is produced. The beams produced by the machines can be directed to specific areas and installed in existing production lines. However, the cathode rays produced by these machines do not have nearly the penetration ability of gamma rays from fission products. Prototypes of microwave linear accelerators, in the range from 6 to 10 m.e.v., for sterilization purposes, will have a maximum penetration of about 2 inches and can produce sterilizing dosages in matter of seconds. Some fission products may take hours to build up sterilizing dosages depending on the concentration of active isotopes. The fact that these machines are rapid might mean that they could find effective usage for surface sterilization and also for sterilization of relatively thin products.

Costs

Based on present facilities the cost for drug sterilization using particle accelerators is estimated at about 3 to 5 cents per pound. Short term preservation of refrigerated foods probably could be obtained for 0.25 to 0.16 cent per pound. With fission waste products, the AEC estimates, 10,000 hams could be processed per day and sterilized for from 3 to 7 cents per pound. The food processing industry now spends about 0.1 cent per pound for steam for ham-canning operations.

When radiation processing is applied industrially to food processing, it seems inevitable that capital investment costs will have to be vastly increased and probably processing costs will go up.

Food industry spokesmen seem to believe that when research has developed practical techniques for radiation processing, production cost factors may be of not too great importance, for if the product is better there will be a market for it. And the market for food is immense.