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《Special Review》

Radiation Processing with Special Emphasis to Food Preservation*

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Besides the huge and impressive establishments of Nuclear Energy it is often overlooked that there is another broad field of Nuclear Technology, which is based on the application of radiation and isotopes. Though much less money for investments is involved in these activities the number of trained people working in radiation and isotope application is considerably higher than those employed in nuclear energy. At the IAEA the number of staff in the corresponding departments (technical operations and research on isotopes) as well as the budgets of these departments are rather equal.

The broadest application of isotope and radiation technology has always been in medicine but industrial applications are keeping up. The production of Cobalt 60, the most favourite source of Gammaradiation has been increased worldwide by a factor of 10 since 1975. Actually it is mostly Radiation Processing, which is going to play an increasing role in many different fields of industry.

1. Physical Base of Radiation Processing

Physicochemical reactions cannot only be initiated by other chemicals but also by heat and electromagnetic or particle radiation. Basic differences do exist between Photochemistry and Radiation Chemistry. Due to the low energy of quanta photochemical reactions are very specific. Ionizing radiation is highly unspecific. Electrons e.g. from gammarays can deliver any part of their maximum energy, which is about $10^3 \sim 10^4$ times higher than chemical binding energies in any reaction with molecules. One of the main advantages is the fact that after treatment with ionizing radiation no residues can be found in the treated material besides the reaction products, which are often called Radiolytic products.

These final Radiolytic products coming out from Radiation processing are very often not identical with the products of the primary reaction between radiation and matter. There can be a number of chain reactions developing after the first event. The G-factor which is defined by

$$G = \frac{N_x}{100\text{eV}}$$

N_x number of changed molecules

can be used for defining any intermediate product of the reaction as well as a final product. Within a wide dose range there is proportionality between the amount of radiation product and radiation dose

$$m_x = 1.04 \times 10^{-7} \times G \times M \times D$$

m_x radiation product (g/kg)
D radiation dose (kGy)
M molecular weight of the irradiated material

This is normally no more valid for rather high dose values as then saturation effects are to be

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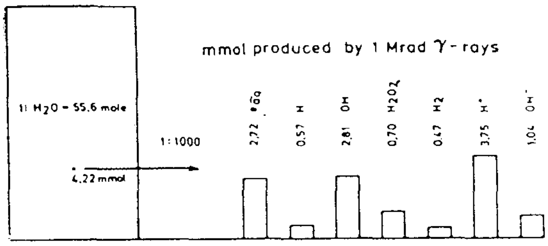

Fig. 1. Radiolytic Products in H_2O after Irradiation with 10kGy (from [1])

expected. The proportionality between the amount of Radiolytic Product and the molecular weight of the substance is easily to be understood.

G-values are normally in the order of $1 \sim 10$. They can be considerably higher for reactions, which do not effect valence bonds e.g. if polymerization takes place.

A famous example is radiolysis of water, which leads to a number of products, many of them having only a short life-time. The average *G*-value is 3, 6. The yield after radiation with 10 kGy is in the order of 0. 01% as to be seen from figure 1.

Besides the very low concentration of radiolytic products in water at this radiation dose level it has to be taken into consideration that the most active products like the radicals H and OH as well as a hydrated electron have a very short lifetime. The only longer lasting oxidizing product H_2O_2 is formed in a very low concentration namely 23. 8mg per litre of water.

Therefore it makes little sense, if some people state that the effect of radiation in water-containing samples is mainly due to the H_2O_2-formation. It is only in living systems that primarily the radicals mentioned above can lead to visible effects as it is well known from Radiation Biology.

10kGy (1 Mrad) is normally considered as a rather high dose, but of course it is a low value from the point of view of energy. If this radiation energy would be completely transferred to thermal energy it would increase the temperature of water by only 0. 24°C.

Most practical applications of radiation processing in industry with one exception of food preservation are performed with radiation doses higher than 10kGy.

All applications of radiation processing are performed with gammarays$<$5MeV or electrons $<$10MeV. Within these energy range—according to laws of nuclear physics—no radioactivity will be produced in the irradiated material. If radiation with higher energies, especialle neutrons, are applied the situation would be different.

2. Industrial Applications of Radiation Processing

2.1. Polymerization, Grafting and chemical reactions

In 1985 133 irradiators have been in operation in 41 countries (2). Meanwhile the number of such facilities has increased and is going to increase further. Some of the applications which are going to be successfully applied in industry should be mentioned here shortly.

Ionizing radition can modify polymers by crosslinking, i.e. by inducing chemical bonds between individual macromolecules. This reaction is one of the chainreactions mentioned above and can be performed with radiation doses between 1 and 100kGy. The polymer gets in this way two important characteristics

a) it does not flow at elevated temperature

b) above the melting point rubberlike properties are developed.

In this way the insulation of wires and cables can be improved. It is also applied to produce heat shrinkable materials and polymerfoam. The method has considerable advantages as compared to chemical methods of crosslinking in polymers. It is more cost-effective and less energyintensive. Further a higher degree of homogenity can be achieved and no additional material is needed.

Another application is curing of surfacelayers of videotapes, paper, woodpanels etc. by production of radicals. In this technology the coating materials (Urethane, Epoxy, Acrylate o.o.) are applied to the surface of the material and then cured by exposure to electrons in the energy range of 1.5~0.3MeV. This method is very fast as compared to thermal curing. Band material with a width of 2m can be treated with the speed of some hundreds of meters per minute. One advantage of using electrons of not to high energy is the very low amount of shielding material to be used.

The surface of polymers can also be modified by radiation grafting. Monomers which have been brought to the surface of a polymer can be bonded chemically to the surface in this way. This method has been used to produce special ion-exchange membranes and also to modify the surface of frying-pans to make it resistant and biocompatible.

Under suitable environmental conditions radiation can also degrade polymers by breaking the long molecular chains. At the end the product can be transformed into fine powder. This process has been used for making special heatresistant lubricants, e.g. from teflon waste.

A very efficient method is the production of wood-plastic composits by impregnating the wood with monomers which are then formed into polymers by radiation. In this way the wood even if it is of low quality can obtain excellent mechanical properties which have been applied not only for production of highly resistant wooden material, but also for preservation of art objects made of wood.

All the methods mentioned here can be achieved with radiation doses$<$100kGy. Chemical changes that means producing different chemical compounds from a given mateial need normally higher doses. Nevertheless, one process might become more important in the future namely the irradiation of stack gases to remove SO_2 and nitric oxides from combustion gases from burning of coal. If Ammonia is added to the stack gase electron irradiation can form Ammonium sulphates and Ammonium nitrates. These salts will fall out as a sediment and can even be used as fertilizers. Unfortunately this method needs rather high beampower between 500 to 1,000kW and is therefore rather expensive.

All the processes mentioned here are going to be developed further and might become even more reasonable if radiation sources are produced in a larger extent.

2.2. Sterilization

The most successful application of radiation processing up to now is the sterilization of medical supplies. This procedure has been introduced first in the early 1950s and is now used in more than 40 countries in about 150 installations. In most developed countries more than 50% of medical gloves, syringes, catheters and surgical instruments are treated in this way, replacing the former methods of sterilization by heat or by ethylene oxide.

Sterilization means to inactivate infectious materials like bacteria, protozoa, fungi and in some cases also insects including their eggs and larvae. The reason why this sterilization method is so efficient lies in a very basic effect. If we consider figure 2, which summarizes the dose ranges for inactivation of different living systems in comarison to the doses needed for real radiochemical processes one can easily see, that a living organism is the more radiation-sensitive the more complex it is. This is a well known basic finding of Radiation. Biology. To change a considerable amount of a substance all or most of the molecules have to be affected. In a living organism only a small disturbance of a few or even in some cases of one molecule can lead to inactivation of the whole system. In this case destruction is effected by the ongoing but now misleaded metabolic activities of the cells. It is the hierarchic system of the living cell which makes it so sensitive to ionizing radiation, if this hits one of the molecular centres which control the metabolic activities. In the model drawing of figure 3 such centres are indicated by somewhat larger circles. primary effects of radiation in less important molecules will be negligible as compared to the effect in the one important target molecule, which could be e.g. a DNA-molecule. Nonliving material irradiated with the same dose would only have effects in a relatively low number of molecules. Therefore the methods mentioned in the former paragraphs and especially real radiochemical processes need higher dose to give a reasonable yield.

Radiation sterilization of medical products is mostly performed at radiation doses of about 50 KGy and with gammarays to penetrate also bulky packed material. The fact that these products can be sterilized by ionizing radiation after packaging is of special importance for the fast growing application of the method as reconta-

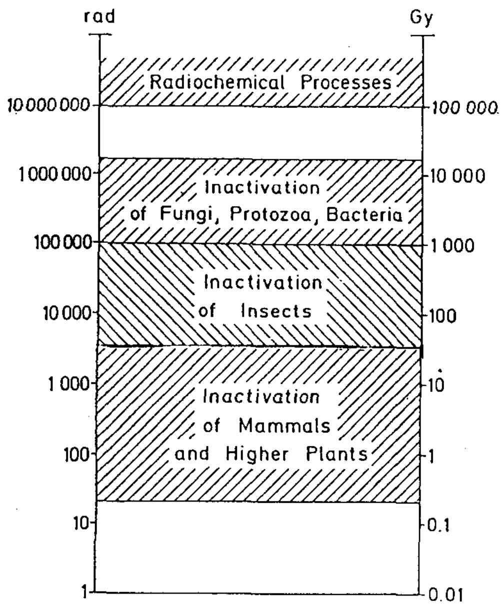

Fig. 2. Does Ranges of Radiation Effects

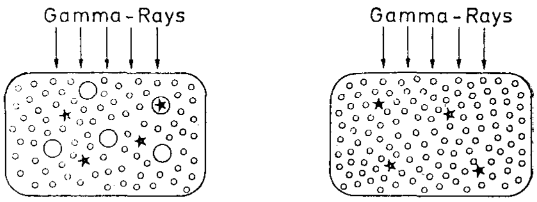

Fig 3. Stochastic Radiation Effects in a Living Cell Nonliving Material

mination can be avoided in this way. In addition radiation sterilization is much less energy-intensive than heat treatment and does not give any residues like chemicals which are also dangerous in handling for the working personal. Especially complete homogenity of treatment is guaranteed with ionizing radiation in contrast to the older ways of sterlilizatio.

Also other industrial materials which can easily be contaminated by microorganisms e.g. paints and liquid soap can be sterilized in the same way. In the technics of leather fabrication fresh hides were preserved up to now mainly by salting, which can easily damage the material and produces a lot of wastewater after washing. Also here radiation sterilization mainly by using Beta-rays has been introduced and proved to be superior to salting. More and more attention is also devoted to the sterilization of sludge and sewage to make it usable for fertilizer purposes.

2. 3. Food preservation

Also since the 1950s experiments have been started to preserve food by treatment with ionizing radiation. This application of radiation processing looks very reasonable. Nearly all food we use to eat has been produced by living organisms but when we eat it, mitotic activity and most metabolic processes in this material have ceased. On the other hand spoilage of food is caused mainly by active living organisms like bacteria, fungi, protozoa and insects with their

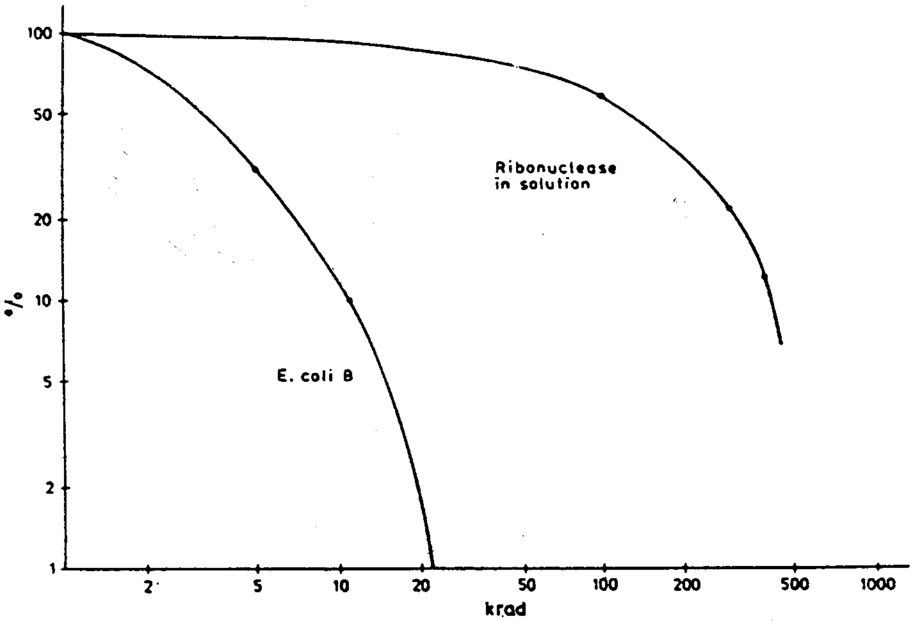

Fig. 4. Inactivation of a Bacterium (E. coli B) and an Enzyme (ribonuclease) by ^{60}Co-Gammarays.

eggs and larvae. Some food items also suffer from mitotically active aprouts which develop themselves by deteriorating the tubers or bulbs we wish to eat like in the case of potatoes, onions, garlic, carrots etc.

Therefore it could be expected that at least a number of food items might be protected against spoilage for some period of time and improved in its hygienic quality by treatment with ionizing radiation. The difference in radiation sensitivity between a living organism and even enzymatic macromolecules can be seen from Fig. 4. The figure also shows that the spoilage by enzymes can only partially prevented by ionizing radiation in the dose range below 10 kGy (1000 krad)

Any way radiation preservation of food is a matter which critically depends on the doses to be applied. By scientific work within the last four decades which has been performed in more than hundred laboratories througout the world optimal doses for special purposes of food preservation have been defined. Table 1 gives an overview on those results which can now be used.

Nobody has ever questioned that additional methods of food preservation have to be developed and applied in view of the terrible food losses especially in the Third World Countries which may go up sometimes to nearly 50% of the food produced. Heating and cooking needs additional energy and cannot be applied to all food items at least not before storage. Deep freezing is even more energy intensive and needs a sophisticated infrastructure. It should also be kept in mind that deep-freezing does not eliminate microbial infections, but can only keep them in a dormant stage until the food is thawed before consumption. Chemicals finally which have been used for food preservation have been found to be toxic or even cancerogenic or mutagenic in many cases and the application of a considerable number of such products is now prohibited by law.

Drying finally which is used in the open air in many developing countries leads to additional infection and dried food therefore needs additional treatment to make it hygienic.

Of course they have also been suspicions that treatment of food by ionzing radiation may affect

Table 1.

LOW DOSE(up to 1 kGy)	kGy	Products
(a) Inhibition of sprouting	0.05~0.15	Potatoes, onions garlic, gingerroot etc.
(b) Insect disinfestation and parasite disinfection	0.15~0.50	Cereals and pulses, fresh and dried fruits, dried fish and meat, fresh pork etc.
(c) Delay of physiological processes	0.50~1.0	Fresh fruits and vegetables(man go, papaya, mushrooms. etc.
MEDIUM DOSE (1~10 kGy)	kGy	Products
(a) Extension of food shelf-life	1.5~3.0	Fresh fish, strawberries etc.
(b) Decontamination of spoilage and pathogenic microorganisms	2.0~5.0	Fresh and frozen seafood, poultry and meat in raw or frozen state, etc.
(c) Improving technological properties in food	2.7~7.0	Grapes (increasing juice yield), dehydrated vegetables (reduced cooking time) etc.
HIGH DOSE (10~50 kGy)	kGy	Products
(a) Commercialsterilization (in combination with mild heat)	30~50	Meat Poultry, seafood, prepared foods, sterilized hospitals diets
(b) Decontamination of certain food additives and ingredients	10~50	Spices, enzyme preparations, Ginseng etc.

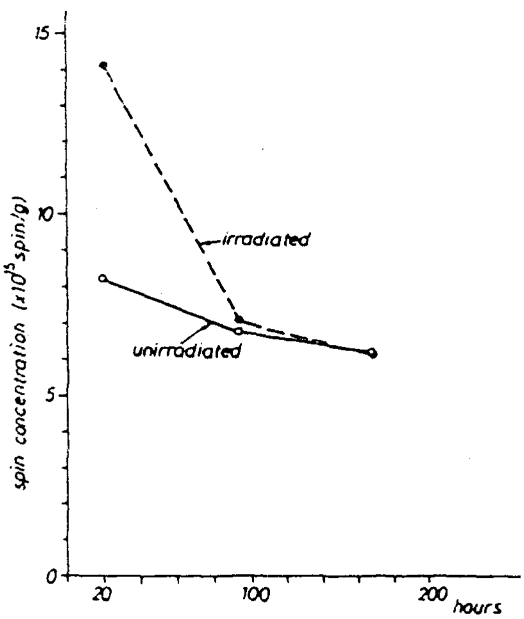

Fig. 5. Concentration of Free Radicals in the Dry outer Scales of Onions after Irradiation with ^{60}Co-Gammarays (50Gy) and during Room-temperature Storage [3]).

the wholesomeness. As mentioned early in this paper radioactivity can not be produced in any product which is treated only with Gamma-rays <5 MeV or electrons<10 Mev. But of course radiochemical reactions will occur and produce changes in molecules. The question is what type of radiation products can be produced and what is the quantitiy to be expected.

Research on this matter has been performed during more than 40 years in many laboratories throughout the world. That means, that research on preservation of food by ionizing radiation has been by far more comprehensive than research on any other food treatment or food additive which has already been introduced into practice. One of the reasons for this careful studies was of course the far spread general fear of major parts of the public everything related to nuclear techniques.

Though it was easy to show that food preservation was a special application of radiation processing and had nothing to do with nuclear energy and of course not at all with military misuse of nuclear reactions, the scientists working in this field felt obliged to demonstrate very clearly that food preserved by ionizing radiation was wholesome.

The experiments performed covered a wide range of studies starting with in vitro radiochemical experiments including individual research on all food items mentioned in Table 1 and finally proving evidence of the results obtained by feeding studies. Only a few typical results of this research can be given here. Fig. 5 gives an impression of the amount of radicals produced by radiation in onions and measured by electron-spinresonance. The natural content of unpaired electrons is nearly doubled immediately after radiation but reaches the normal value after about 4 days. That means, that onions preserved by radiation in this way should be stored before consumption at least 4 days and that after this time irradiated onions can no more be distinguished from non-treated onions by ESR. But of course storage could now last for many more weeks or even months longer than storage of non-treated onions.

Sterlilization of meat needs relatively high doses especially if also inactivation of virus should be achieved. Sensitive methods like Gel Permeation Chromatography show that even at extremely high doses only very small changes can be observed (Figure 6). The small peak to be seen in the lower curve of Figure 5 could

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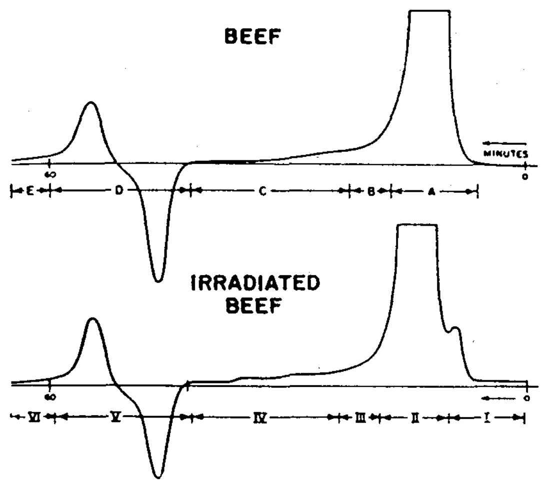


Fig, 6. Gel Permeation Chromatography of Fat extracts from Beef Irradiated with 500 **KGy (from** [4])

be identified to stem from some larger triglycerides produced by recombination of free radicals. Also these compounds are not toxic but anyway the doses applied in meat sterilization are about hundred times smaller.

It has been mentioned very often that also at lower doses volatile components are produced in irradiated meat which are responsible for a special unpleasant flavour. This effect can be strongly reduced if irradiation is performed at low temperatures which can be a little bit above 0°C if oxygen is excluded. The amount of such volatile compounds produced in air but at very low temperature can be seen from Figure 7. Concentration up to 60 kGy are below 1 ppm.

Thousands of data like this have been measured within the last 30 years. They have been the base of consideration of joint experts committees organized by the World Health Organization(WHO) in cooperation with the Food and Agriculture Organization (FAO) and the International Atomic Energy Agency (IAEA) (For details see [6]).

The first expert-meeting took place in 1964. It discussed an experimental programme to ascertain the wholesomeness of irradiated food. The second expert committee was convened 1969.

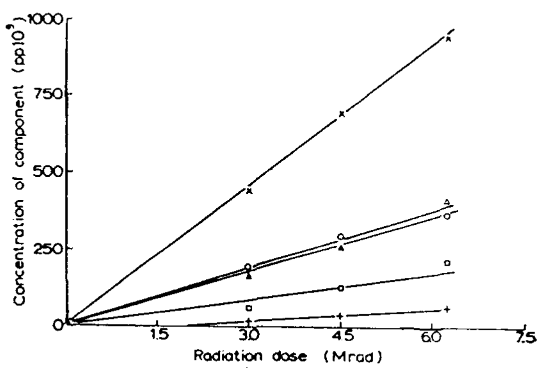


Fig. 7. Relative Concentrations of Volatile Components Produced as a Function of Radiation Dose in Beef Irradiated a-185°C,
× total; 0 sulfur compounds,
□ hydrocarbons; △ carbonyes;
+ alkylbenzenes (from [5] p. 103)

It recommended a temporary acceptance of wheat and wheat products as well as of irradiated potatoes and specified further studies to be performed. The break through came at the third expert meeting at 1976 which recommended *unconditional* acceptance of radiation preservation of six food items and asked the Codex Alimentarius in Rome the highest competent body of UN in all matters of food treatment, to discuss this proposal in its various sub-commissions to recommend it to its 122 member-states.

This request was broadened at the expert committee 1980 when the statement was made "that the irradiation of any food commodity up to an over all average dose of 10 kGy present no toxicological hazard and the toxicological testing of foods so treated is no longer required." The report of the committee also states that "irradiation of food up to an over all average dose of 10 kGy introduces no special nutritional or microbiological problems."

The Codex Food Additive committee developed an international general standard and an international code of practice for irradiates food [7, 8]. The Codex Alimentarius Commission accepted these documents at its 15th Session in July 1983. Since that time preservation of food by ionizing radiation in the limit of the two standards is recommended by the highest competent international institutions. The importance of this decision becomes clear if one considers three facts

1. The increasing food losses especially in Third World Countries
2. The more and more recognized toxicity of chemicals used up to now for food preservation
3. The need of improved food hygiene (e.g. to avoid Salmonellosis Trichinosis etc.)

Meanwhiles food irradiation has been commercialized in 19 countries, 30 facilities for these techniques are now working or under construction [9, 10]. In spite of the clear statements of the competent international organizations criticism of the method is going on. In a few papers published in Japan, USSR and India results were reported which indicated adverse effects of consumption of irradiated food in animals. Each of this publications has been checked and controlled by experienced groups of researchers in other institutions mostly within the same country, and the data were found to be incorrect mainly due to bad experimental practice. Though it should be reasonable to base a judgement not on one special paper which could not withstand the critical review by other authors, the authors of the apparently incorrect experiments are quoted again and again. In addition nutrition scientists who are completely unexperienced in methods of radiation biology or radiation chemistry like to make statements which must be considered as nonsens from scientific point of view. Very often the comment is made that the microbic flora would be changed by irradiation and especially dangerous mutants of bacteria could be produced. This matter has then been investigated by the International Union of Microbiological Societies for 2 years with the result that the statement of the Codex Alimentarius Commission was confirmed. It was also claimed that vitamins would be destroyed or inactivated by radiation, but as a matter of fact the losses in vitamins after radiation treatment are by far lower than e.g. by heattreatment or deep freezing. Finally comments were made on the economic aspect of food irradiation. Actually the costs for the various treatments for food preservation and better hygiene by ionizing radiation are below 1% of the price of the food items itself, in some rare cases e.g. at staple food it might come up to 3 or 4%.

The most unusual comments and discussions were related to the labelling of irradiated food. Some people were worried on the fact that there is no routine method to identify irradiated food in comparison to non-irradiated one as molecular changes which of course will be introduced are extremely small. But also with most sensitive laboratory methods no radiolytic product was found which was not already well-known from other food treatments especially from heating and cooking. Their only clear difference in comparison to non-irradiated food is better hygienic quality and/or longer shelf-life. Nevertheless it might be reasonable to introduce labelling to indicate a better quality of food treated by radiation according to the standards mentioned above, to make sure that the standards are fulfilled. Radiation treatment of foods should be carried out in facilities licenced and registered for this purpose by competent national authorities.

A real problem especially in developing countries might be inadequate competence of people responsible for applying the techniques. Very reliable dosimetry is a pre-requisit of good success by food irradiation but also careful pretreatment and post-treatment have to be considered as an extremely important sector. Therefore just Third World Countries should seek the advice by experienced scientists from other parts of the world before embarking food irradiation[11].

3. Technical Installations for Radiation Processing.

The technical handling of a food irradiation facilities does not offer more or other safety problems than that of the irradiation sources used for other techniques of radiation processing mentioned in the first part of this paper. Long lasting experience is now available and plants with a high standard of safety can be constructed by various industries throughout the world.

Fig. 8 shows a rather simple system to expose the foods to be irradiated to a gamma-source by means of a conveyor system. To achieve a good homogeneity of dose distribution in the material it is passed two times through the circle and in between turned around by 180 degrees. This system is foreseen for a facility using ^{137}Cs as a gamma-source. As radiation of this radionuclide has only half the energy of ^{60}Co the simple turn around the source might be sufficient. In the case of ^{60}Co one is used to have a more complicated guidance of the containers to be exposed to radiation.

Fig. 9 shows an example of a so called Pallet Irradiator which has an advantage that goods can already be packed readily for being sent to

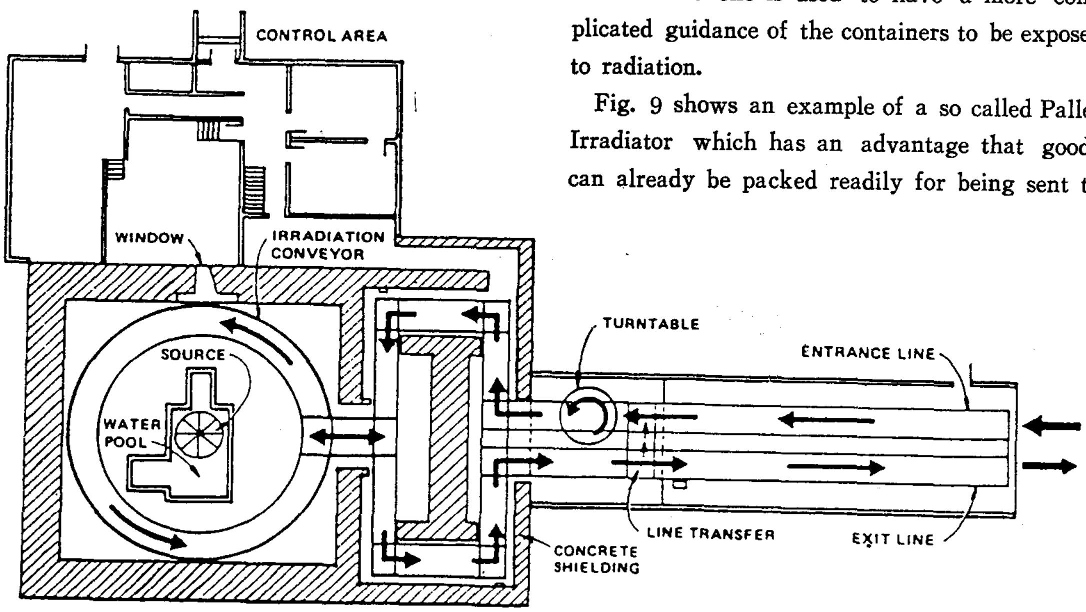
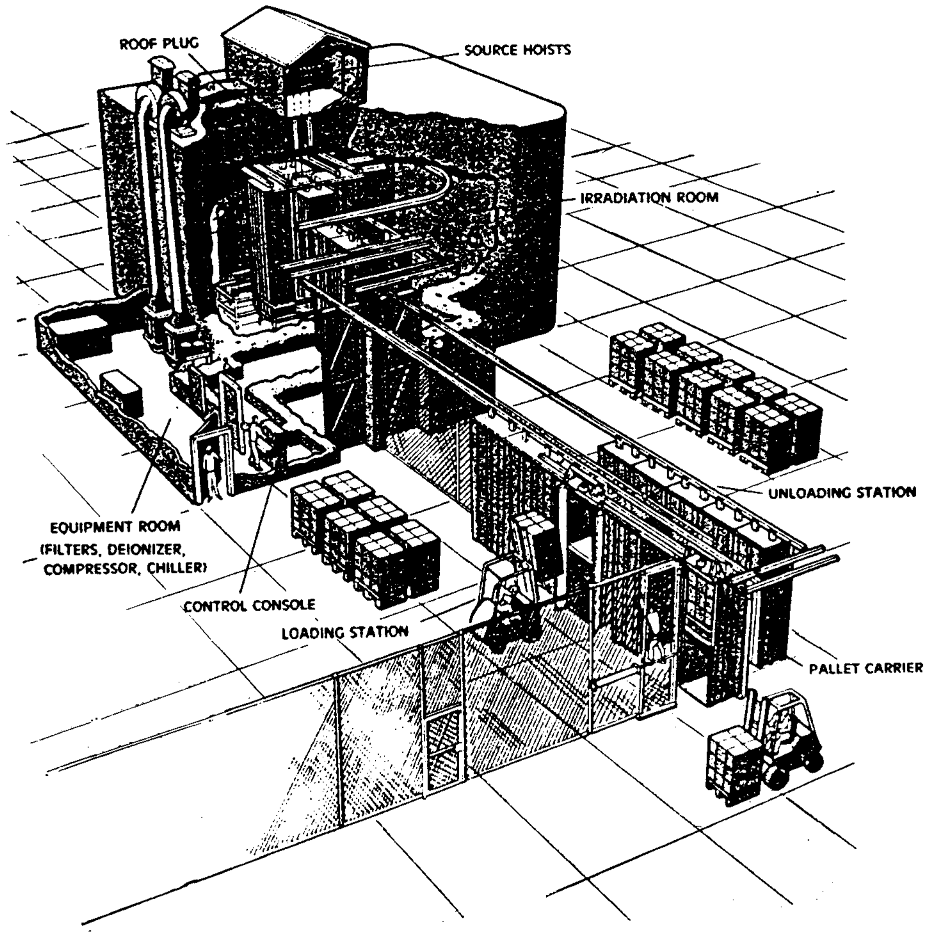


Fig. 8. Basic Schedule of an Irradiation Plant with ^{137}Cs-or ^{60}Co Source



Eig. 9 Pallet-Irradiator (AECL)

the consumer after irradiation. In this case every pallet passes first the radiation source in somewhat more distance and then it is guided backwards to a closer approach. Therefore also radiation which has already passed one pallet is used in addition when new pallets come from the outer part of the conveyor. Perhaps the most perfect system has been developed recently[12] and is demonstrated in Figures 10 and 11.

In this construction the containers which might have different shape at different facilities can be moved in three dimensions. They come in at a lower level and are then transported vertically upwards and leave at the higher level, but when circulating around the source each container is circulated by itself and is in this way exposed to radiation in a very homogeneous way.

Figure 11 shows a device with 8 rotating columns but of course this can be increased. The system also permits to bring individual containers into the irradiation chamber and take it off if the dose is high enough, that means that items can be irradiated at the same time which need rather different dose values. Such a somewhat more complicated construction will be reasonable as the price of the gammasource is considerably high for such a facility and therefore is it reasonable to make use of the emitted radiation as far as possible.

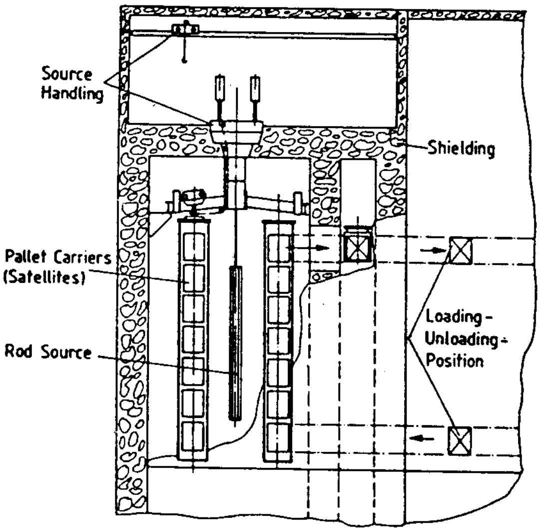


Fig. 10. M4p-Irradiator, Vertical Section (from [12])

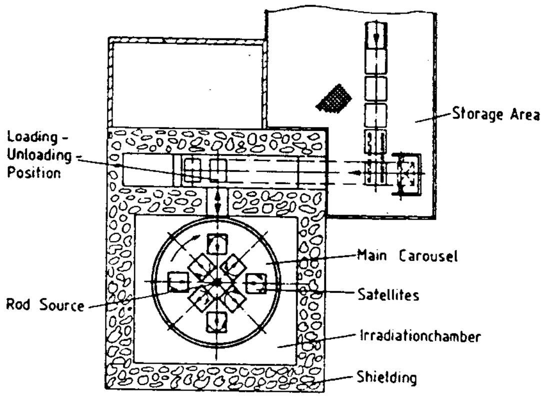


Fig. 11. M4p-Irradiator, Cross-Section(from [13])

Conclusion.

It might have become evident that food preservation by radiation could become the most important application of radiation processing especially in view of the increasing world population and the need to preserve as much of produced food as possible. Recently WHO has summarized its position to this special area of radiation processing in the following way "WHO is concerned that rejection of the process essentially base on emotional or ideological influences may hamper its use in those countries which may benefit the most" but at the same time there is also a warning: "Food radiation has a potential to increase safe food supplies thus contributing to primary health care. It has the advantage of reducing dependce on food treated with chemical substances however food radiation is not a miracle process that can convert spoiled food into high quality food or be suitably applied on all food stuffs."

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