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FNCA Guideline on Development of Hydrogel and Oligosaccharides by Radiation Processing

(Eds.) Hisaaki KUDO, Fumio YOSHII and Tamikazu KUME

Environmental and Industrial Materials Research Division
Quantum Beam Science Directorate

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This report summarizes the current status of development of hydrogel and oligosaccharides by radiation (electron beams and gamma rays) processing in Asian countries, as an outcome of activities of the FNCA (Forum for Nuclear Co-operation in Asia)-industry group during the phase 2 (2006-2008), as one of FNCA Guidelines.

The nine countries, Bangladesh (since 2007), China, Indonesia, Japan, Korea, Malaysia, Philippines Thailand and Vietnam, participates in the phase 2 of the FNCA-industry group, focusing on radiation processing of natural polymers.

Participating countries have been studying radiation processing of natural polymers such as chitosan from shrimp/crab shells and carrageenan taken from seaweeds, in terms of cross-linking for gel and degradation for oligosaccharides.

The former obtains hydrogel which can absorb a lot of water, and application for wound dressing and super water absorbent in the fields of medical and environmental conservation are expected.

The latter obtained oligosaccharides have functions as growth promoter and elicitor activator of plants, sea-creatures and livestocks etc., and application in the fields of agri- and aqua- cultures are expected.

This Guideline consists of 3 parts; part 1 describes the outline of radiation chemistry of polymers; part 2 compiles the protocols of versatile applications; part 3 refers the examples of cost analysis and current status of the technology.

This Guideline would facilitate development, commercialization and technical transfer to end-users of radiation processing of natural polymers.

Keywords: FNCA, Radiation Processing, Hydrogel, Oligosaccharides

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放射線加工によるハイドロゲルとオリゴ糖類の開発に関する FNCA ガイドライン

日本原子力研究開発機構量子ビーム応用研究部門環境・産業応用研究開発ユニット
（編）工藤　久明*、吉井　文男、久米　民和

（2009 年 8 月 3 日受理）

本報告は、FNCA（Forum for Nuclear Co-operation in Asia；アジア地域における原子力協力フォーラム）工業利用グループの第 2 期（2006 年度—2008 年度）活動の一環として、電子線またはガンマ線による、ハイドロゲルとオリゴ糖類の開発について、参加各国の現状をガイドラインとしてとりまとめたものである。

工業利用グループでは、第 2 期は天然高分子の放射線加工に焦点をあてており、バングラデシュ（2007 年度より）、中国、インドネシア、日本、韓国、マレーシア、フィリピン、タイ、ベトナムの計 9 か国が参加している。各国は、天然に産生する高分子化合物（甲殻類由来のキトサンや、海藻由来のカラギーナン等）に対し、放射線加工を行い、架橋によるゲル化や、分解によるオリゴ化を研究している。前者により開発されたハイドロゲルは、優れた吸水性を持ち、それを活用して、創傷被覆材や超吸水材などの医療・環境分野への応用展開が図られている。後者により開発されたオリゴ糖類は、植物や水産物・畜産物の成長促進作用や抗菌・免疫活性作用を持ち、それを活用して、農業（漁業・畜産業を含む）分野への応用展開が図られている。

本ガイドラインは、3 部からなり、第 1 部では高分子の放射線化学の概要を、第 2 部では天然高分子の放射線加工の各論についてプロトコルを、第 3 部ではコスト評価や技術の現状などを、それぞれとりまとめたものである。これらを踏まえて、放射線加工技術およびその製品の、実用化やエンドユーザーへの技術移転が、一層促進されることが期待される。

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FOREWORDS

Radiation processing has been widely used in variety of industries, such as automobile tires, wires and cables, heat shrinkable sheets and tubes, foamed plastics, and medical supplies. Technologies for radiation facilities and processing have been well established.

In the past several years research on radiation processing of natural polymers including starch, chitosan and carageenan to produce value added products, such as plant growth promoter (PGP), super water absorbent (SWA) and medical and cosmetic supplies have been carried out in several FNCA and RCA countries.

Radiation degradation of chitosan can produce oligo-chitosan which is an effective elicitor for plant growth promotion and plant disease resistance, as demonstrated in Vietnam and Indonesia. In China oligo-chitosan is used for aquaculture to increase of fish production. Malaysia has just started large scale field test of oligo-chitosan for rice germination and growth promotion. Hydrogel produced by using electron accelerator are commercially used for wound dressing in Japan and Korea, and for face mask in Malaysia.

This guide book is edited by Dr. H. Kudo with the excellent contribution of project leaders of FNCA countries. I am confident that the FNCA countries will have benefits of learning from the book the manual or know-how to process natural polymers by radiation to produce value added products to meet their needs.

The book should be up-dated regularly according to the improvement of process technology and development of new applications of products.

In conclusion I would highly appreciate Dr. Kudo for his tireless effort of editing the book, and project leaders for elaborated contribution for their respective technologies and applications. I wish FNCA member countries use the guidelines for effective development of radiation processing of natural polymers contributing national socio-economic development.

Sueo Machi
FNCA Coordinator of Japan
Advisor to the MEXT, Japan

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FOREWORDS

The FNCA project on application of electron accelerator was established in 2001 as a first project in the field of industry. The project aims at wider application of electron accelerator and also aims at implementation of practical application that will bring benefits for participating countries. The application of EB system has been implemented and demonstrated in various fields for liquid (degradation of polysaccharides for plant growth promotion, waste water treatment), solid (curing and cross-linking of films, surface irradiation for sterilization/pasteurization of spices, seeds, etc.) and gas (flue gas treatment, degradation of dioxins).Through the activities in phase 1 (2001-2005), it was decided to continue the project as phase 2 for 3 more years focusing on radiation processing of natural polymers.

Since the 1970's, the upgrading of polysaccharides such as starch, cellulose, chitosan, alginate and carrageenan by radiation degradation has been investigated at JAEA (JAERI)-Takasaki[*1]. Following the obtained results, the IAEA Coordinated Research Programme (CRP) on radiation processing of natural polymers was proposed and implemented as a UNDP/RCA/IAEA project. On the other hand, Dr. Hien of VAEC found the activity for plant growth using radiation degraded alginate[*2]. With combination of these experiences, JAEA-Takasaki and VAEC established the bilateral cooperation on radiation processing of marine polysaccharides in 2000.

For wound dressing, radiation cross-linking of synthetic polymers has been studied and Prof. Rosiak of Technical University of Lodz, Poland, succeeded in commercializing the PVP hydrogel in 1992. JAEA-Takasaki also developed the technique of radiation cross-linked PVA for wound dressing and it was transferred to Nichiban Company in 1996. In addition, JAEA-Takasaki found the radiation cross-linking of carboxymethyl-cellulose (CMC) and CM-chitosan by irradiation in solution with high concentration like paste condition[*3]. The RCA project on radiation processing of natural polymers with adding the cross-linking for hydrogel was proposed in 1999 and has been implemented under the RCA program.

From 2006, FNCA EB application in phase 2 focused on radiation degradation for plant growth and radiation cross-linking for hydrogel with the cooperation of RCA. Through the activities, the project discussed and agreed to prepare the guideline to harmonize the materials and methods and to prepare the protocol of successful techniques.

I am confident that this guideline will be useful to transport the techniques to end users as well as to upgrade various natural polymers abundantly available in the region. I expect that this guideline can contribute to convert them into useful value-added products while conserving the environment.

Tamikazu Kume
Project Leader of Japan

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1. Introduction, General description and note

1.1 Preface and scope

This guideline is an outcome of a trial to prepare a "manual" on development of hydrogel and oligosaccharides by radiation processing through a co-work in FNCA electron accelerator application working group, as a part of FNCA guidelines series.

1.1.1. Introduction

Not less researchers and scientists may have experienced that one can not reproduce results that had been reported, or not reproduce even their own past results. It is apparent that this would come from the (potential) differences in procedures. Such cases would lead to loss or damage of properties and, personnel, in the worst case, accidents. Therefore documentation is desirable. Tentatively the written material shall be called "manual". This concept is almost equivalent to "standard (standardization)".

1.1.2. Function of the "manual"

The "manual" would facilitate expansion of knowledge/technique from a researcher to another, stimulate technology-transfer from the academia to the industry, and assure quality of the products. The "manual" would be published as a written material, for example, in the form of a booklet or as a PDF file available at FNCA web site. However, the "manual" will not be affirmative, will not regulate any activity, and will not guarantee any outcome.

1.1.3. Title of the "manual"

In the connection with other activities under FNCA framework, the "manual" of this kind shall be called as a "guideline". Therefore this written material is named "FNCA Guidelines on development of hydrogel and oligosaccharides by radiation processing".

1.1.4. Contents and structure of the guideline

The general structure of this guideline is shown in Appendix 1. This guideline has two PARTs; one has general description on natural polymers and radiation processing, and the other has specific description on each natural polymer. The latter part has two CHAPTERs; one is cross-linked hydrogel and the other is degradation for plant growth. Each chapter has SUB-CHAPTERs; the chapter of cross-linking has sub-chapters of hydrogel wound dressing (HWD) and super water absorbent (SWA), and the chapter of degradation has sub-chapters of plant growth promoter (PGP) and aquaculture. Each sub-chapter has SECTIONs for specific natural polymers. These sections will be attributed to each participating country. Each section has SUB-SECTIONs from raw materials to pre-treatment, irradiation, post treatment, products, and strategies for commercialization, etc. The structure of each SUB-SECTION is shown in Appendix 2. These sub-sections have ITEMs of details and can be modified depending on the specific characteristics of each material.

1.1.5. Method to collect the information for the guideline

The editors of this guideline sent a questionnaire on technical details for standardized experimental procedures, as listed in Appendix 2, to the project leader of FNCA participating countries. The sub-chapters of HWD, SWA, PGP and aquaculture, and sections of respective natural polymer in Part 2, are compilations of the responses from the project leaders.

The editors also queried the cost analysis and current status of the technology and the responses are compiled in Part 3

Note - The idea to prepare a guideline was proposed and agreed at the FNCA workshop in December 2006 in Kuala Lumpur, Malaysia, and then the draft was prepared by editors and each participating countries.

1.2 Natural polymers and radiation processing

1.2.1 Radiation and materials

The definition of radiation is, typically, electro-magnetic waves or corpuscular beams that can ionize material (in a typical case, air), that is, eject of an electron.

The examples of radiation include, alpha-ray (nucleus of helium He from heavier radioisotope), beta-ray (electron from radio-isotope), gamma-ray (electro-magnetic wave resulted from transition between energy-levels of a nucleus), X-ray (electro-magnetic wave resulted from transition between energy-levels of an atom), neutron beam typically upon fission, electron beam (accelerated with a particle-accelerator), ion beam (such as proton, helium and other heavier nuclei accelerated with a particle-accelerator), etc. Among them, from the viewpoint of radiation application (radiation processing), the most widely used radiations are gamma-ray and electron beam.

(1) Gamma-ray source

Among many gamma-ray emitting radio-isotopes, Co-60 gamma ray source is most widely used, followed by Cs-137 gamma ray source, but the share of Co-60 is dominant in quantity. Co-60 has the half-life of 5.27 years, and upon disintegration it emits two photons of energies of 1.17 and 1.33 MeV. The pellets of Co-60 are sealed in a metal rod and the rods are arranged in a plane or cylindrical shape. The sources are stored in a pool and it needs an irradiation room having thick shielding. Typical illustration of the Co-60 gamma rays irradiation facility is given in Fig. 1-1 with courtesy of JAEA.

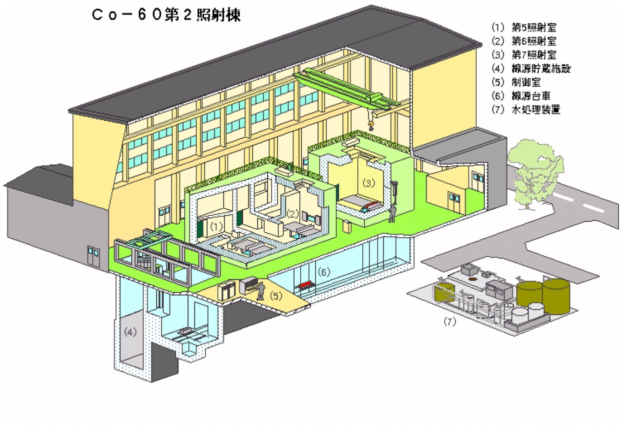


Fig. 1-1. Co-60 gamma-ray irradiation facility at JAEA Takasaki

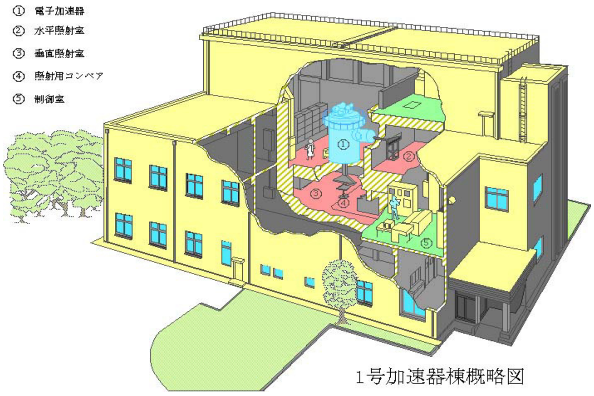


Fig. 1-2. Electron beam accelerator at JAEA Takasaki

(2) Electron beam accelerator

In radiation processing, electron beam in the energy-range of 300 keV-5 MeV is widely used. Electron beam can be generated with electron beam accelerator. At present, various types of accelerating procedures are commercially available; the examples are electro-static type and high-frequency (radio-frequency) type. In electro-static accelerating system, thermo-electron emitted from a cathode and the emitted electron is accelerated with high voltage applied between electrodes. Electron beams are scanned in scanning horn and taken out from the window (typically Titanium foil). Typical photograph of the electron beam irradiation facility is given in Fig. 1-2 with courtesy of JAEA. The operation of electron accelerators is simple and safe, that is, radiation does not come out if the switch is put off, compared to Co-60 gamma irradiation facility. If the energy of electron is not set very-high, besides that thick shielding is not necessary, the initial investment and running cost may not be very heavy task to (potential) owners. These make this system economically competitive.

(3) Radiation sources and current status

Depending on the purpose, the capacity (the amount of radioactivity of Co-60 source; applied voltage, ampere; area of beam scanning, conveyor speed etc.) and geometric arrangement between source or beam-outlet and materials to irradiate), the absorbed dose rate and the total absorbed dose can vary and should be selected or optimized. The typical dose rate varies in the order of kGy/h for Co-60 gamma rays source and in the order of kGy/s in electron beam accelerator. The total absorbed dose can be widely changed based on the sensitivity of the system towards radiation (yield) etc.

The number of irradiation facilities in FNCA participating countries, including both for research and development, and commercial purposes, is tabulated in the FNCA web site (http://www.fnca.mext.go.jp/english/eb/e_gamma.html for gamma-rays facilities and http://www.fnca.mext.go.jp/english/eb/e_institution.html for electron beam accelerators).

(4) Interaction of radiation with materials

Depending on the energy of radiation, the interaction scheme varies from implantation (when the energy of incident electro-magnetic wave / particle is low), sputtering, excitation, ionization, and nuclear reaction (when the energy of incident radiation is sufficiently high). In radiation processing, ionization and excitation are most fundamental events. In the case of Co-60 gamma-ray irradiation, secondary electrons are ejected through Compton effect, and these scattered secondary electrons can interact with material. In the case of electron beam irradiation, the incident electrons can interact with material directly. High energetic (incident and secondary) electrons interact directly or indirectly with electrons of irradiated material through Coulomb interaction, and results in ionization and excitation. Ionized or excited species can form the radical, chemically reactive atoms or molecules having an unpaired electron, and the radicals induce subsequent reactions. Such series of radiation-induced chemical reactions construct the field of so-called "radiation chemistry". In the case of polymer, the final events are cross-linking (new bond formation between two polymer chains), degradation (fragmentation into two or more smaller pieces, denoted as scission as well), un-saturation (formation of double bond, other functional bonds etc), graft-polymerization. This scheme is illustrated in Figure 1-3. In this guideline on radiation processing, only cross-linking and degradation are of interest among them.

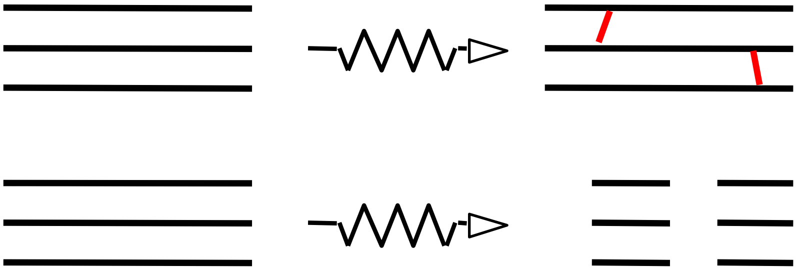


Figure 1-3. Scheme of radiation effects of polymers; cross-linking (top), degradation (bottom)

(5) Radiation chemistry and irradiation effects on polymeric compounds

Not only for scientific but also for practical, the yield is of interest. The radiation chemical yield is often discussed through G values. The G-value denotes the number of events per energy absorption of 100 eV. In SI unit system, G-value in J/mol is recently recommended. The conversion from one to another is that, if $G=1$ per 100eV then $G=0.104$ μmol/J, by considering the Avogadro's number 6.02×10^{23} per mol and the charge of an electron 1.60×10^{-19} C.

Typical G-values (in the traditional definition) vary in the range of, very roughly in most cases, 0.1-10 (in recent definition in 0.01-1 μmol/J), though it depends on factors such as dose rate, the presence/absence of oxygen, temperature during irradiation, etc. In the literatures of radiation chemistry, G-values of events and final products can be found, and sometimes they are tabulated. The G-value means, for example, if the $G=1$, the concentration of the products is 1 mmol/liter at the absorbed dose of 1 kGy. Such rough estimation is necessary to design the radiation processing.

(a) Cross-linking can be brought about by the encounter of two polymer radicals, of which hydrogen was abstracted by the ionized or excited species etc. Cross-linking can be recognized macroscopically by, for example and most typically, formation of the insoluble fraction (to the solvent which initially dissolves the polymer), gel. In the reality, cross-linking and degradation takes place simultaneously. In the case of the polymer where the cross-linking is well dominant over degradation, gel formation is observed. The most important parameters would be swelling ratio and gel fraction.

Swelling ratio (sometimes denoted as solvent uptake) is defined as W_s/W_d or $(W_s-W_d)/W_d$, and gel fraction is defined as W_d/W_0, where W_s denotes the weight of polymer in swollen state, W_d the weight after drying, and W_0 the initial weight, respectively. In general, swelling ratio decreases with dose, while gel fraction increases with dose, and levels off or reaches the unity.

Charelesby-Pinner equation has been well used to evaluate the G-values of cross-linking and degradation, if the initial molecular weight distribution is assumed to be a random (Poission-like, or most probable) distribution;

$$s+\sqrt{s}=\frac{G(S)}{2G(X)}+\frac{4.82\times10^{6}}{G(X)M_nD}$$

Here *s, G(X), G(S), M_n,* and *D* denote the *sol* fraction (the unity minus *gel* fraction), G-values of cross-linking and degradation, number average molecular weight and absorbed dose in kGy, respectively. In the reality, the initial molecular weight distribution may not be random. The modifications of the relationship have been tried by many researchers. Charelesby-Rosiak equation is recently often used in this filed, where D_v is the virtual dose, a dose required for changing the molecular weight distribution to random and D_g is gel formation dose;

$$s+\sqrt{s}=\frac{G(S)}{2G(X)}+\left(2-\frac{G(S)}{2G(X)}\right)\frac{D_v+D_g}{D_v+D}$$

(b) Degradation may be brought about directly (direct action of radiation) in part, and indirectly in another part, by the attack of radicals. Degradation can be recognized macroscopically by the fact that, for example, the solid polymer becomes soft or the solution of the polymer loses its viscosity.

Viscosity (intrinsic) of the polymer solution, η, and the molecular weight (viscosity average molecular weight, M_v) have the relation as

$$[\eta]=K(M_v)^a$$

which is named as Mark-Houwink equation, where *K* and *a* are parameters depending on the system, and tabulated for many combinations of polymers and solvents.

Upon degradation (and simultaneous cross-linking, where degradation is dominant over cross-linking), the number average molecular weight (M_n) changes as

$$\left(\frac{1}{M_n}\right)_D=\left(\frac{1}{M_n}\right)_0+1.04\times10^{-7}\left[G(S)-G(X)\right]D$$

The weight average number molecular weight (M_w) changes as, if the initial molecular weight distribution is assumed to be a random (Poission-like, or most probable) distribution,

$$\left(\frac{1}{M_w}\right)_D=\left(\frac{1}{M_w}\right)_0+1.04\times10^{-7}\left[\frac{1}{2}G(S)-G(X)\right]D$$

where the suffix *0* and *D* mean the initial and at the absorbed dose of *D*, respectively. By following changes of molecular weights by means of, for example, gel permeation chromatography (GPC), as a function of absorbed dose, the G-values can be evaluated.

1.2.2 Radiation chemistry of natural polymers

Natural polymers are defined as polymer (polymeric compounds) that naturally exists in the biological bodies/system, sea-water, soil (ground) etc. This concept is the opposite of artificially-synthesized polymers such as polyethylene.

Examples of natural polymers include polysaccharide, protein, fat, carbohydrate, DNA, etc. Similarly to other polymers, natural polymers undergo, based on their nature, cross-linking or degradation upon irradiation. Its radiation chemical scheme, however, can vary based on various factors such as phase (solid or liquid) of pristine material (especially in the case of aqueous solution, the OH radical, formed upon radiolysis of water, would play a significant role in polymer-radical formation and enhanced degradation compared to solid state), temperature during irradiation, dose rate, (total) dosage, and, especially in the case of solution, on concentration, viscosity, pH, etc. Moreover, pre- and/or post- conditionings of the materials can influence the irradiation effect. On the contrary, if one can control these factors and the final events, one may find a new paradigm of the radiation chemistry.

1.2.3 Radiation processing of natural polymers by radiation technology.

Based on the irradiation effects, modification and functionalization of polymer materials (radiation processing) have been extensively and intensively studied. A lot of experiences and findings are accumulated in the society of radiation application.

(a) **Radiation induced cross-linking** can improve, for example, heat resistance, mechanical properties, etc. For natural polymers, the cross-linking can form "gel" that can absorb solvent, such as water, to a high ratio in weight to the polymer. Such gel are sometimes called as "hydrogel" and its application covers medical, healthcare, agricultural field, for example, as wound-dressing (WD), bed-sore modifying mat, beauty face mask, bio-degradable packaging materials, super water absorbent (SWA) for excrement of livestock, alcoholic processing waste and irrigation of desert land.

The general protocol of radiation processing may be like as Appendix 2 or Table 1-1. Starting from raw material, the material will be conditioned prior to irradiation. After irradiation, gel fraction is measured after immersion in water at ambient temperature for hours, and swelling is measured after drying during hours to days at an elevated temperature. They should be optimized regarding with dose, pre- and post- treatment conditions. The gel product should possess sufficient mechanical properties such as shape stability, tensile strength, peel strength etc., so that it is acceptable as dressing or absorbent etc, not only its originally intended function.

(b) **Radiation induced degradation** can improve solubility to solvent, softness, lubricant etc. For natural polymers, especially polysaccharides such as cellulose, starch, chitin and chitosan which are indigenous resources in south-eastern and eastern Asian countries, the degraded polymer, including oligomer, can promote plant growth, anti-bacterial- or elicitor- activity, etc. Such modified poly- and oligo- saccharides are well applied in agricultural and aqua-cultural (including poultry and livestock) feed.

The general protocol of radiation processing may be like as, Appendix 2 and Table 1-1. Starting from raw material, the material will be conditioned prior to irradiation. After irradiation, viscosity (molecular weight) will be measured with a viscometer such as Ubbelhode, or mixing-rotor type. The degraded product in aqueous solution will be sprayed on plants or added to feeds and the growth will be observed, though this is a rather time-consuming work. The growth should be optimized regarding with dose (molecular weight, viscosity or solubility), pre- and post- treatment conditions, frequency and concentration of spray or feed-additives etc.

Table 1-1. An example of general scheme of development of radiation processing

Stage	Step (Sub-section in Appendix 2)	Items in Appendix 2 and other factors to consider
Laboratory	Raw Material	Grade (purity), molecular weight, history etc
	Pre-treatment	Phase; Solid-size or Liquid-concentration, pH
	Irradiation	Source, Co-60 or EB
		Dose rate, depending on source
		Dose, depending on yield of CL and DG
		Temperature, atmosphere
	Post treatment	
	Products	
	Evaluation/Test	HWD: healing and mechanical
		SWA: swelling, gel fraction
		PGP: plant growth enhancement or acceleration
		AQC: creatures growth enhancement
Developing	Is performance acceptable?	No
	⬇ Yes	
Commercializing	Strategies	Safety: personnel, public and environmental Regulations: domestic and international
		Publications/Patent
		Cost analysis
		Comparison with other method
		Advertisement
		Technology transfer
		Marketing

1.3 Consideration on Intellectual properties and Patents

It is to note that the technical details (protocols) described in this guideline hereafter were already published somewhere. The original references are listed.

However, as a general caution on affairs on intellectual properties, this guideline would like to point out the following.

A typical evolution process of research and development is, starting from laboratory stage, followed by developing stage and reaching eventually commercialized stage, though the project can be suspended or withdrawn by various reasons including financial, technical or personnel reasons. The successful results can be made available through presentations at conferences, publications in scientific journals, including international or domestic ones.

The industry group is rather application or commercialization-oriented, compared to other groups in FNCA, and it is encouraged to apply and obtain patents as a more successful and reputational outcome than a publication. It is also intended to protect the own-developed technology or products from the insensible utilization by other bodies, and to keep the technological advantages against the potential competitors in the same field of business.

However, it is to be noted that unfortunately, the difference in legal system on intellectual properties and patents (including the case that such legal system is not well established), and difference in culture and customs among different countries could cause unexpected cases. Moreover, it needs a special attention when a technology or product developed in certain single country is applied for patents in another country.

This guideline would like to point out that the similar cases potentially may happen. This issue includes complicated and intricate matters, and the industry group wishes the senior level of FNCA to discuss this matter and reach a reasonable decision to deal with intellectual properties.

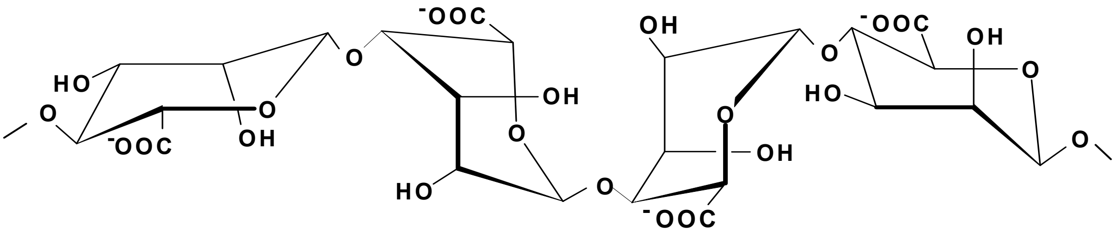
1.4 Abbreviations

Abbreviations in alphabetical order	Classification (Institutional or Technical)	Spelling-out of the abbreviation
AA, AAc, ACA	T	Acrylic Acid
AG, ALG	T	Alginate
AQC	T	Aquaculture
ARTI	T	Advanced Radiation Technology Institute (KAERI)
BATAN	I	Badan Tenaga Nuklir Nasional/ National Nuclear Energy Agency (Indonesia)
CARG, CRG	T	Carrageenan
CAS	I	Chinese Academy of Science
CASV	T	Cassava
CD	I	Coordinator
CDM	I	Coordinators Meeting
CHN	I	China
CHT, CT	T	Chitin
CHTS, CTS	T	Chitosan
CL	T	Cross-linking
CNY	I	Chinese Renminbi Yuan
CMC	T	Carboxyl Methyl Cellulose
CMS	T	Carboxy Methyl Starch
CRP	I	Coordinated Research Programme (IAEA)
Da	T	Dalton
DG	T	Degradation
DOST	I	Department of Science and Technology (Philippines)
EB	T	Electron Beam
EBA	T	Electron Beam Accelerator
FNCA	I	Forum for Nuclear Co-operation in Asia
GL	I	Guideline
HDG	T	Hydrogel
HWD	T	Hydrogel Wound Dressing
IAEA	I	International Atomic Energy Agency
INA	I	Indonesia
KAERI	I	Korea Atomic Energy Research Institute
KOR	I	Korea, Republic of
KOW	I	Korean Won
JAEA	I	Japan Atomic Energy Agency

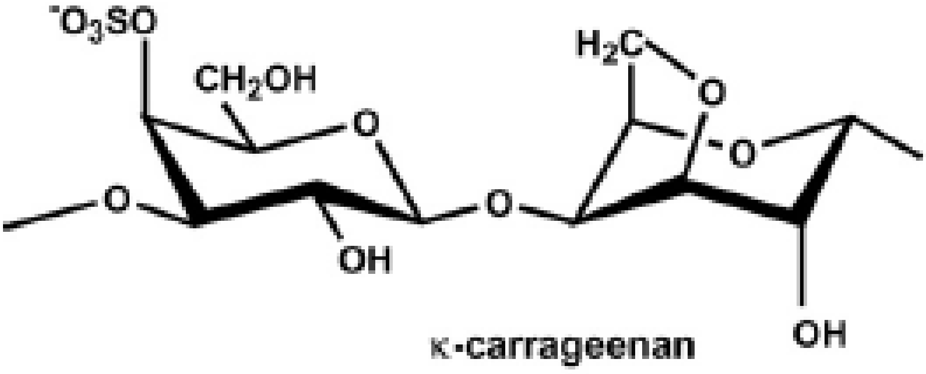
JAERI	I	Japan Atomic Energy Research Institute
JAIF	I	Japan Atomic Industry Forum
JPN	I	Japan
JPY	I	Japanese Yen
MAS	I	Malaysia
MEXT	I	Ministry of Education, Culture, Sports, Science and Technology (Japan)
MINT	I	Malaysia Institute of Nuclear Technology
MOST	I	Ministry of Science and Technology (Korea, Malaysia)
MW	T	Molecular Weight
NSRA	I	Nuclear Safety Research Association (Japan)
PAA	T	Poly Acrylic Acid
PHI	I	Philippines
PHP	I	Philippine Peso
PGP	T	Plant Growth Promoter
PL	I	Project Leader
PNRI	I	Philippine Nuclear Research Institute
PRC	I	People's Republic of China
PVP	T	Poly Vinyl Pyrrolidone
QuBS	I	Quantum Beam Science Directorate (JAEA)
RCA	I	Regional Cooperative Agreement
RI	T	Radio Isotope
RM	I	Ringitto Malaysia
RP	I	Indonesian Rupiah
SAP	T	Super Absorbent Polymer
SINAP	I	Shanghai Institute for Applied Science (China)
ST	T	Starch
SWA	T	Super Water Absorbent
THA	I	Thailand
THB	I	Thai Baht
TINT	I	Thailand Institute of Nuclear Technology
TRCRE	I	Takasaki Radiation Chemistry Research Establishment
TARRI	I	Takasaki Advanced Radiation Research Institute
WS	I	Workshop
VAEC	I	Vietnam Atomic Energy Commission
VIE	I	Vietnam
VND	I	Vietnamese Donh

1.5 Chemical structures of materials

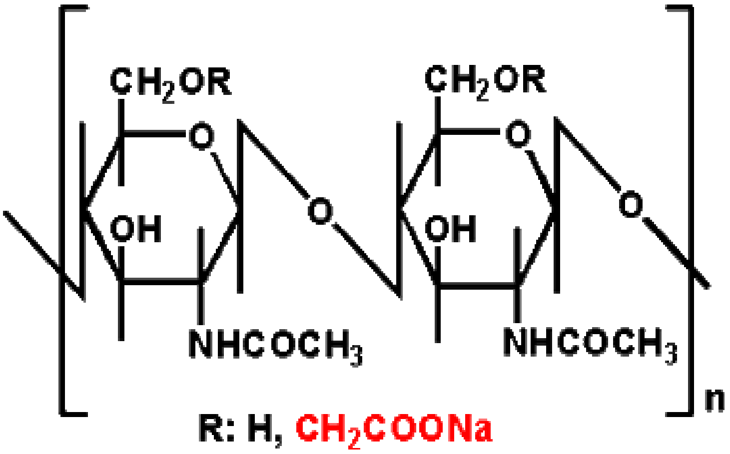
Alginate



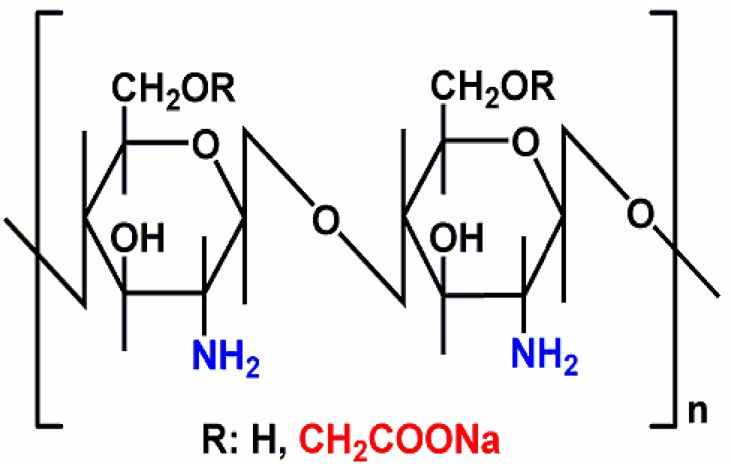
Carrageenan (kappa-carrageenan)



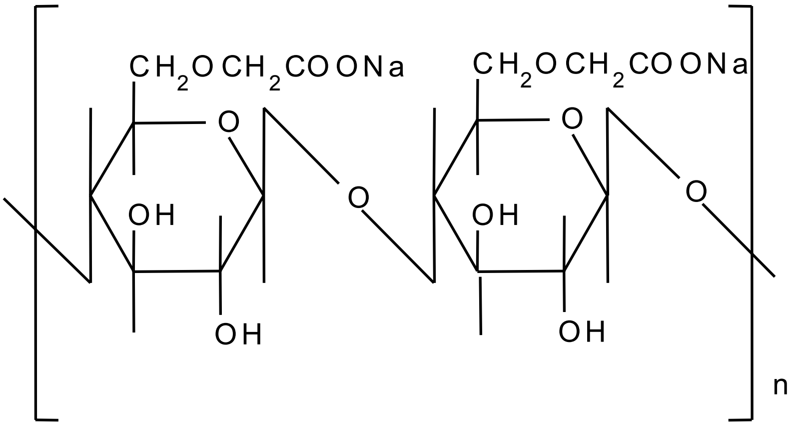
Chitin and CM-Chitin



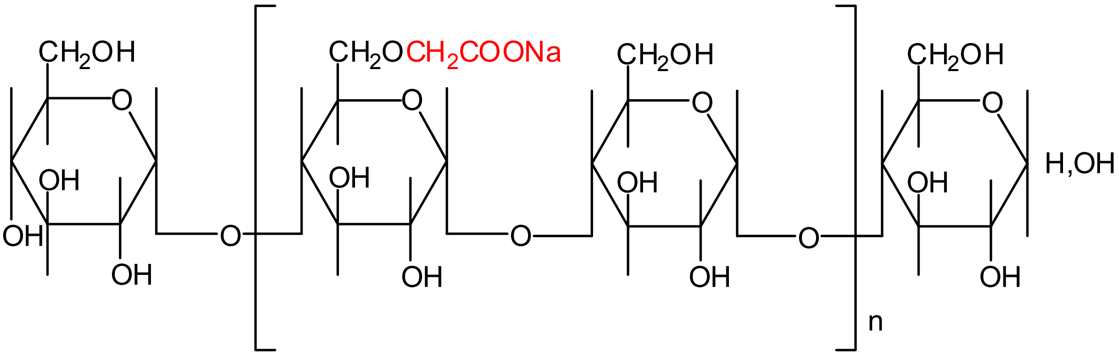
Chitosan and CM-Chitosan



CMC



Starch (CM-Starch)



2. Specific, Technical matters for each material

This part 2 describes specific or technical matters for each material. This part 2 consists of two chapters of cross-linking and degradation as the sub-structure. Each of them has further sub-structures (sub-chapters) of hydrogel wound dressing (HWD) and super water absorbent (SWA) for the former, and plant growth promoter (PGP) and aquaculture for the latter. Each sub-chapter has further sub-structures (sections) for various materials. See Appendix 1 for this hierarchy structure.

As mentioned in **1.1.5,** the editors of this guideline sent a questionnaire on technical details for standardized-experimental procedures, as listed in Appendix 2, to the project leader of FNCA participating countries. The sub-chapters and items of respective natural polymers are compilations of the responses from the project leaders.

Some items are un-answered; being information not available. In the cases the items are made blank.

2.1. Radiation cross-linked hydrogel for healthcare and environment

This chapter of 2.1 is dedicated for Radiation cross-linked hydrogel for healthcare and environment. Hydrogel, as demonstrated in Fig. 2-1 (with courtesy of JAEA), absorbs (several) hundreds of gram-water per gram-polymer. The application of hydrogel, has been extensively tried, especially in the medical and/or healthcare field, such as would-dressing, face/mask, bed-sore modifying mat, ice-bag-like cooler, etc. Also, in the field of environmental conservation, this would be applied for bio-degradable packaging materials for fruits and vegetables, and water absorbent for excrement of livestock, waste from alcoholic process and irrigation of desert land. Many of them have been commercialized in some countries including FNCA participating countries.

Fig. 2-1. Photograph of hydrogel

Some technical aspect and experiences are presented in the later sections and sub-sections. Many examples of successes are introduced, and some of ceased projects are disclosed.

2.1.1. Hydrogel for Wound Dressing (HWD)

It has been believed for a long time that dry curing is appropriate for wound treatment. Recently however, it was found that the wet curing is more effective than dry curing. This is because the liquid from the dermis layer can cure the wound well in the wet environment while the dried scab can cause the new wound in the course of curing. An example reported that the wet curing remedied the wound of the same degree faster than conventional dry curing by a factor of 2.

The HWD, having hydrogel as substrate and medical drug inside or on the surface, has been adopted in the medical field because, besides fast curing, it is transparent so that the medical doctors/nurses can well observe the course of curing.

This application was initially invented and commercialized in the (East) Europe, and soon expanded through the world including North America and Asian region. Various formulations of the base polymer (including both synthetic and natural polymers, and polymer blends) of the HWD have been tried in different countries/institutes or companies.

Examples of natural polymer based HWD are shown in Fig. 2-2 (with courtesy of KAERI and PNRI), which is successfully commercialized as Cligel$^{\mathrm{TM}}$, and Skin-up$^{\mathrm{TM}}$ respectively, both based on polv-inylpyrrolidone (PVP) - carrageenan hydrogel.

A similar application has been successfully carried out in the field of healthcare/cosmetic treatment. An example of beauty face mask to treat acne, based on Sago-starch hydrogel is shown in Fig. 2-3 (with courtesy of Nuclear Malaysia).

Fig. 2-2. Hydrogel wound dressing

Fig. 2-3. Beauty face mask made of hydrogel

2.1.1.1. CM-Chitosan-hydrogel (Korea)

1. Raw material
    - 1.1. Suppliers, grade and material history
        - Suppliers Chito123:
        - Grade: MW. 300K
        - Material history:
    - 1.2. Visual examination:
    - 1.3. Compositional analysis:
    - 1.4. Others:
2. Pre-treatment
    - 2.1. Grinding or pulverization
        - Grinding: Not necessary
        - Pulverization: Not necessary
    - 2.2. Dissolution: 10 wt% aq. solution
    - 2.3. Others: Carboxymethylation and Packaging
3. Irradiation
    - 3.1. Irradiators/Facilities: Co-60 at ARTi, KAERI, KOREA
    - 3.2. Packaging: Prepackaged
    - 3.3. Dose rate: 10 kGy/h
    - 3.4. Dose: 25 kGy
    - 3.5. Temperature: Room Temp.
    - 3.6. Others:
4. Post treatment
    - 4.1. Visual examination:
    - 4.2. Compositional analysis:
    - 4.3. Product performance evaluation:
    - 4.4. Others:
5. Products
    - 5.1. Grinding or pulverization:
        - Grinding: Not Applicable
        - Pulverization: Not Applicable
    - 5.2. Dissolution: Not Applicable
    - 5.3. Packaging: Not Applicable
    - 5.4. Description:
    - 5.5. Instruction manual:
    - 5.6. Others:
6. Strategies
    - 6.1. Safety considerations: Non toxic
    - 6.2. Environmental considerations:
    - 6.3. Cost analysis: 4.7USD/kg Gel Product
    - 6.4. Comparison with other procedures/products:

6.5. Publications/Patents:
6.6. Advertisement for end-users:
6.7. Technology transfer: In progress
6.8. Marketing: Not Applicable
6.9. Others:

2.1.1.2. Sago-starch-hydrogel (Malaysia)

1. Raw material
   - 1.1. Suppliers, grade and material history
     - Suppliers: Songiing Holding Sdn. Bhd.
     - Grade: Food grade
     - Material history: Extract from palm tree
   - 1.2. Visual examination: White powder
   - 1.3. Compositional analysis: Moisture content less than 12%
   - 1.4. Others:
2. Pre-treatment
   - 2.1. Grinding or pulverization
     - Grinding: no need
     - Pulverization: no need
   - 2 2. Dissolution: Mixing in water and gelation process
   - 2.3. Others:
3. Irradiation
   - 3.1. Irradiators/Facilities: 3MeV 30mA EBM/ EBM, Nuclear Malaysia
   - 3.2. Packaging: Vacuum seal
   - 3.3. Dose rate: 1.99 Gy/min (conveyor speed: 3.56m/min)
   - 3.4. Dose: 25kGy
   - 3.5. Temperature: Room Temperature
   - 3.6. Others:
4. Post treatment:
   - 4.1. Visual examination: tackiness
   - 4.2. Compositional analysis:
   - 4.3. Product performance evaluation: cooling effect
   - 4.4. Others: water evaporation
5. Products
   - 5.1. Grinding or pulverization
     - Grinding: no
     - Pulverization: no
   - 5.2. Dissolution: no
   - 5.3. Packaging: Aluminum packing, 5 pieces per box
   - 5.4. Description: outside box
   - 5.5. Instruction manual: Described by company
   - 5.6. Others:
6. Strategies
   - 6.1. Safety considerations: Single use only
   - 6.2. Environmental considerations: Biodegradable
   - 6.3. Cost analysis: Cheap (0.173 RM/g) (1USD = ca.4 RM)
   - 6.4. Comparison with other procedures/products: Sterilized by radiation

6.5. Publications/Patents: Patent Filing, PI 20022825

6.6. Advertisement for end-users: Conference, technology show-case and direct contact

6.7. Technology transfer: Rumbia Bio-Tech Sdn. Bhd.

6.8. Marketing: By company

6.9. Others :

7. Publications

7.1 "Radiation Crosslinking of Starch/Water-soluble Polymers Blends for Hydrogel" K. Hashim, N. Mohid, K. Bahari and K.Z. Mohd Dahlan, Takasaki Workshop on Bilateral Cooperations, 1-2 Nov. 1999

7.2 "Development of sago Starch Hydrogel for Wound", K. Hashim, K.Z. Mohd Dahlan, K. Bahari, F. Yoshii and T. Kume, Takasaki Symposium on Radiation Processing of Natural Polymers, 23-24 Oct. 2000

7.3 "Hydrogel of Sago Starch/Water-soluble Polymers by Electron Beam Irradiation Technique", K. Hashim, K. Z. Mohd Dahlan, N. M. Noordin and F. Yoshii, International Symposium on Radaition Technology in Emerging Industrial Applications, 79-80, 6-10 Nov. 2000, IAEA-SM-365

7.4 "PVA Sago Starch Hydrogel and the Preliminary Clinical Animal Study of the Hydrogel", K. Hashim, A. S. Halim, M. T. Md Nor, K. Z. Mohd Dahlan and F. Yoshii, Takasaki Symposium on Radiation Processing of Natural Polymers, 1-2 Oct. 2001

7.5 "Sago Hydrogel as Dressing for Partial Wound in Rabbits", M. N. M. Tarmizi, A. S. Halim, K. Hashim, J. M. Radzi, G. Kaur and S. A. B. Afifi, Proceeding in CSAMM AGM/ASM 2002, 16-18 May 2002

7.6 "Syntheses of PVA/Starch grafted hydrogels by irradiation", Maolin Zhai, Fumio Yoshii, Tamikazu Kume, Kamaruddin Hashim, Carbohydrate Polymer, 50, 295-303, 2002

7.7 "Radiation Processing of Sago Hydrogel Thin Film", K. Hashim and N. Yacob, Proceeding of the FNCA 2003 Workshop on Application of Electron Accelerator, 92-103, 18 –22 August 2003

7.8 "Review of Radiation Processing of Natural Polymer", Khairul Zaman, Proceeding of the FNCA 2006 Workshop, 12-16 December 2006

7.9 "A Review on Radiation Processing of Polysaccharides", Khairul Zaman Hj Mohd Dahlan, IAEA Report of the Consultants Meeting on Radiation Processing of Natural Polymers for Development of Finished Products for Health Care, Agriculture and Environment, 81-88, 26-30 Mac 2007

2.1.2. Super Water Absorbent (SWA)

Hydrogel can absorb very high amount of water compared to its original weight of polymer gel. It can reach the magnitude of several hundreds. By utilizing this unique property, extensive applications are tried. Drying the excrement of livestock for field disposal, in order to reduce the fermentation and the odor and keep the hygiene, has been tried as shown in Fig. 2-4 (with courtesy of JAEA). Another example of drying gel is treatment of alcoholic waste disposal. The conventional disposal method has been the sea-disposal but this method is being regulated to reduce pollution. Treatment of alcoholic waste by drying gel can reduce the mass of waste.

Moreover, enhanced growth of vegetables and fruits by containing the hydrogel (as SWA) into the soil is observed. The SWA works to help to control soil erosion, limit loss of nutrients and silt for plants. The photograph of the commercialized fertilizer is shown in Fig. 2-5 with courtesy of VAEC.

Another application of SWA is greening of desert land. Spreading SWA having massive amount of moisture over the desert will mediate the dry land. This technology is being intensively investigated especially in the west Asian and African countries, though this is out of the scope of FNCA framework.

Fig. 2-4. Hydrogel as dry gel to treat excrement of livestock.

Fig. 2-5. Hydrogel for soil burial for plant growth.

2.1.2.1. Cassava starch-acrylic acid -hydrogel (Vietnam)

1. Raw material
    1.1. Suppliers, grade and material history:
    Cassava starch (tapioca starch) supplied by Bidofood Co. Ltd, Vietnam, starch content more than 85%
    Glacial acrylic acid (AAc), by BASF, German (manufactured in Malaysia)
    90% flake of KOH, methanol in analytical grade from South Korea
    1.2. Visual examination:
    1.3. Compositional analysis:
    1.4. Others:
2. Pre-treatment
    2.1. Grinding or pulverization
    2.2. Dissolution: Paste starch was formed when 20% KOH aqueous solution was added into starch powder while stirring. Acrylic acid was poured into the mixture slightly, regularly agitating for 30 min. The mixing ratio of starch to acrylic acid monomer is 1 to 1.
    2.3. Others: The well-blended mixture was packed in the polypropylene bags of 10kg.
3. Irradiation
    3.1. Irradiators/Facilities: Gamma irradiator, SV-ST Co-60/B type, made in Hungary installed at VINAGAMMA
    3.2. Packaging: Poured into polyethylene/polypropylene packages and sealed tightly
    3.3. Dose rate: 1.6kGy/h
    3.4. Dose: 4.5-15 kGy
    3.5. Temperature: 12 degree Celsius
    3.6. Others: Gamma irradiation was made in the presence of oxygen. The temperature of irradiated bags was increased to at least 50 degree Celsius as an exothermic process.
4. Post treatment
    4.1. Visual examination: Confirmation of dense, durable, elastic and brownish.
    4.2. Compositional analysis:
    4.3. Product performance evaluation: Swelling ratio larger than 200, and weight loss of 85 % after 9months in soil burial.
    4.4. Others: After visual examination, the block mixture was extruded, cut, anti-stuck and dried at 70 degree Celsius for 10 hours in air prior to test of product performance.
5. Products
    5.1. Grinding or pulverization: Grounded through a sieve of 1-3 mm, and polished.
    5.2. Dissolution: pH 6.8 at equilibrium swelling
    5.3. Packaging: Packed in the 1 kg jars or 5kg polyethylene bags.
    5.4. Description: On the package of the product attached the label, often printed with

the clear direction for use.

5.5. Instruction manual: attached on the label.

5.6. Others:

6. Strategies

6.1. Safety considerations: Non-detective toxicity when rabbits orally administered.

6.2. Environmental considerations: Irradiated wet product has ca. 54ppm of acrylic acid monomer, which is considered safety for human and environment. Dried gel has traceable amount of acrylic acid.

6.3. Cost analysis: 2.95USD/kg

6.4. Comparison with other procedures/products: Imported from US costs 8.90 USD/kg, and from China 5.10 USD/kg.

6.5. Publications/Patents: Patented since 2007. The Ministry of Agriculture and Rural Development allows producing GAN-Sorb S product as a soil conditioner in Vietnam according to the decision No. of 1247 QD/BNN-KHCN dated 28 April 2006.

6.6. Advertisement for end-users:

6.7. Technology transfer:

6.8. Marketing:

6.9. Others: The product is commercialized on the pilot-scale production line with the throughput of 30 tons /month in the VINAGAMMA, Vietnam.

7. Publications

7.1. "Pilot production of water super absorbent gel", D. Binh, Proceedings of 6th National Conference on Nuclear Science and Technology, 26-27 October 2005, Dalat, Vietnam.

7.2. Report on results of field test of Gam-Sorb S gel for conditioning the soil. Institute for the Southern Agricultural Science and Techniques, Ho Chi Minh City, Vietnam, March 2006.

7.3. "The swelling and desorption rate of water superabsorbent gel (GAM-Sorb) under free-substrate condition", D. Binh, Proceedings of the 7th National Conference on Nuclear Science and Technology, 30-31 August 2007, Danag, Vietnam.

2.1.2.2. CM-Cassava-starch-hydrogel (Thailand)

1. Raw material
    1.1. Suppliers, grade and material history
        Suppliers: Synthesis in lab from original cassava starch
        Grade:
        Material history: Synthesis in lab from original cassava starch supplied by Siam Quality Starch Co; Ltd.
    1.2. Visual examination: Yellowish granule
    1.3. Compositional analysis:
    1.4. Others: Degree of substitution = 0.14
2. Pre-treatment
    2.1. Grinding or pulverization: Undone
    2.2. Dissolution: Aqueous solution of 50 wt%
    2.3. Others:
3. Irradiation
    3.1. Irradiators/Facilities: Co-60 gamma rays, OAP Bangkok
    3.2. Packaging: In air
    3.3. Dose rate: 0.17 kGy/h
    3.4. Dose: 2 kGy
    3.5. Temperature: RT
    3.6. Others:
4. Post treatment
    4.1. Visual examination: Examined
    4.2. Compositional analysis:
    4.3. Product performance evaluation: Swelling ratio, gel strength, and gel fraction were tested during developing process
    4.4. Others: Drying at 60 degree C for 12 h
5. Products
    5.1. Grinding or pulverization
        Grinding:
        Pulverization: Pulverized into 5 mm diameter particles (CMS dry gel)
    5.2. Dissolution:
    5.3. Packaging:
    5.4. Description:
    5.5. Instruction manual:
    5.6. Others:
6. Strategies
    6.1. Safety considerations: Material Safety Qualification Tests Required
    6.2. Environmental considerations: Biodegradablity
    6.3. Cost analysis: 455 baht/1kg Product
    6.4. Comparison with other procedures/products: Non-radiation-method (PAAc)

products/ Radiation method is expensive

6.5. Publications/Patents: 31st and 32nd Congress on Science and technology of Thailand

6.6. Advertisement for end-users: Exhibitions

6.7. Technology transfer:

6.8. Marketing:

6.9. Others:

7. Publications

7.1 "Hydrogel Prepared from Radiation-Induced Crosslinking of Carboxymethyl Starch", Kasinee Hemvichian, Phiriyatorn Suwanmala, Wannee Srinuttrakul, Manit Sonsuk, 32nd Congress on Science and technology of Thailand, 229, 2006

7.2 "Preparation of Cross-linked Carboxymethyl Cassava Starch for the Adsorption of Heavy Metal Ions", Phiriyatorn Suwanmala, Kasinee Hemvichian, Wannee Srinuttrakul, Manit Sonsuk, 31st Congress on Science and technology of Thailand, 221, 2005

2.1.2.3. CMC-dry gel (Japan)

1. Raw material
   - 1.1. Suppliers, grade and material history
     - Suppliers: From Daicel Co. Ltd.
     - Grade: Analytical grade
     - Material history: As received
   - 1.2. Visual examination: Examined
   - 1.3. Compositional analysis:
   - 1.4. Others: Degree of Substitution (DS) is 1.3-1.4
2. Pre-treatment
   - 2.1. Grinding or pulverization
     - Grinding:
     - Pulverization: As received
   - 2.2. Dissolution: Aqueous solution of 20wt% is prepared.
   - 2.3. Others: Nothing special
3. Irradiation
   - 3.1. Irradiators/Facilities: Co-60 gamma rays at JAEA Takasaki
   - 3.2. Packaging: In air
   - 3.3. Dose rate: 10kGy/h
   - 3.4. Dose: 5kGy
   - 3.5. Temperature: Room Temperature
   - 3.6. Others: Electron beam (1mA at 1MeV) is also appropriate for irradiation.
4. Post treatment
   - 4.1. Visual examination: Examined
   - 4.2. Compositional analysis:
   - 4.3. Product performance evaluation: Undone, but swelling ratio etc. was tested during developing process.
   - 4.4. Others: Sliced, and drying below 80degree Celsius for 3-24h (depending on thickness) in air, for example, 3h for 1mm-thikness, 24h for 1cm-thickness
5. Products
   - 5.1. Grinding or pulverization
     - Grinding:
     - Pulverization: Pulverized into 1-3mm diameter particles (CMC dry gel)
   - 5.2. Dissolution:
   - 5.3. Packaging:
   - 5.4. Description:
   - 5.5. Instruction manual: Manufacturer had prepared
   - 5.6. Others:
6. Strategies
   - 6.1. Safety considerations: Material Safety Qualification Tests Required
   - 6.2. Environmental considerations: Biodegradability

6.3. Cost analysis: 100 Japanese Yen (JPY)/100g-piece (1 USD=ca.110JPY)
6.4. Comparison with other procedures/products: Non-radiation-method (PAAc) products/ Radiation method is expensive
6.5. Publications/Patents: Scientific Publications and Patents (in United States and Japan)
6.6. Advertisement for end-users: Exhibitions, Techno-information events
6.7. Technology transfer: JAEA made technology-transfer to end-users
6.8. Marketing: Exhibitions, Techno-information events, Consultations
6.9. Others:

7. Publications

7.1. "Hydoregel of Biodegradable Cellulose Derivatives. I. Radiation-Induced Crosslinking of CMC", Bin Fei, Radoslaw A. Wach, Hiroshi Mitomo, Fumio Yoshii, Tamikazu Kume, J. Appl. Polym. Sci., 78, 278-283, 2000
7.2. "Hydrogel of Biodegrdable Cellulose Derivatives. II. Effect of Some Factors on Radiation-Induced Crosslinking of CMC", Radslaw A. Wach, Hiroshi Mitomo, Fumio Yoshii, Tamikazu Kume, J. Appl. Polym. Sci., 81, 3030-3037, 2001
7.3. "Radiation crosslinkimg of carboxymethylcellulose of various degree of substitution at high concentration in aqueous solutions of natural pH", Radslaw A. Wach, Hiroshi Mitomo, Naotsugu Nagasawa, Fumio Yoshii, Radiat. Phys. Chem., 68, 771-779, 2003
7.4. "Hydrogel of polysaccharide derivatives crosslinked with irradiation at paste-like condition", Fumio Yoshii, Long Zhao, Radoslaw A. Wach, Naotsugu Nagasawa, Hiroshi Mitomo, Tamikazu Kume, Nucl. Instr. Methods in Phys. Res. B, 208, 320-324, 2003
7.5. "Self-cross-linked alkyl cellulose", Fumio Yoshii, Tamikazu Kume, Tadashi Murakami, United States Patent: No. US 7,208,593 B2, 2007 April 24

2.2. Radiation degradation for oligosaccharide

This chapter of 2.2 is dedicated for radiation degradation for plant growth. The radiation-induced degradation (scission) causes lowering of molecular weight, and result in solubility into solvent, such as water. The applications of degraded- or oligo-saccharides have been tried in agricultural and aqua-cultural field as PGP, anti-bacterial coating on fruits, and feed-additive for aquatic farms etc. Some of them have been succeeded in FNCA participating countries. The example of such commercial product is demonstrated in Fig. 2-6 with a courtesy of VAEC .

Some technical aspect and experiences are presented in the later sections and sub-sections. Many examples of successes are introduced, and some of ceased projects are disclosed.

Fig. 2-6. Photograph of oligo- chitosan-product

2.2.1. Plant Growth Promoter (PGP)

It was found that radiation degraded natural polymer, or, oligosaccharides increase solubility into water due to its lowered molecular weight and that the aqueous solution can accelerate the growth of some plants such as rice, vegetables, and fruits.

The first finding and trial were made with degraded alginate as shown in Figure 2-7 (with courtesy of VAEC). Soon this technique spread to other oligosaccharides.

Fig. 2-7. Degraded alginate and demonstration of enhanced growth.

Figure 2-8 shows an example in Indonesia (with courtesy of BATAN) which uses radiation degraded chitosan. The optimum molecular weight (depending on the initial molecular weight, probability of degradation and the absorbed dose), concentration in the aqueous solution, spray amount and frequency, etc. were variously tried.

The similar trial has been extensively investigated in the Philippines for degraded carrageenan.

Fig. 2-8. Oligo-chitosan product and demonstration of enhanced growth.

2.2.1.1. Aliginate (Vietnam)

1. Raw material
   - 1.1. Suppliers, grade and material history: From local market. Brown Seaweed should be better
   - 1.2. Visual examination:
   - 1.3. Compositional analysis:
   - 1.4. Others: Brown Seaweed should be better
2. Pre-treatment
   - 2.1. Grinding or pulverization: Cut and grinding
   - 2.2. Dissolution: Dissolve into 5wt% sol. in Na_2CO_3 at RT for 1h for extraction
   - 2.3. Others : Filtration to remove other additives
3. Irradiation
   - 3.1. Irradiators/Facilities: Co-60 at VINAGAMMA
   - 3.2. Packaging: In plastic tank (30 L)
   - 3.3. Dose rate: arbitrary
   - 3.4. Dose: 40kGy
   - 3.5. Temperature: RT
   - 3.6. Others: Liquid form is better for higher yield of degradation
4. Post treatment
   - 4.1. Visual examination:
   - 4.2. Compositional analysis:
   - 4.3. Product performance evaluation:
   - 4.4. Others: Check the concentration of degraded alginates, and add $NaMoO_4$ (micro-element) to add the essential element for plants
5. Products
   - 5.1. Grinding or pulverization:
   - 5.2. Dissolution: Liquid, commercial name of T&D
   - 5.3. Packaging: In plastic bottle (500-1000 mL/bottle)
   - 5.4. Description: Labeled as Dissolve in water 100cc-product/10L-water
   - 5.5. Instruction manual: Attached as Sprayed on the leaves, branches and roots
   - 5.6. Others: Warning as Cationic products, do not mix with anionic solution
6. Strategies
   - 6.1. Safety considerations: Not mix with anionic solutions etc.
   - 6.2. Environmental considerations: (Not necessary, environmental friendly)
   - 6.3. Cost analysis: 330 KVND/kg-polymer
   - 6.4. Comparison with other procedures/products: Chemical method by H_2O_2 (ca. 300 KVND/kg-Polymer); Radiation method is expensive
   - 6.5. Publications/Patents: Publications in Scientific Journals and Patents in US filed
   - 6.6. Advertisement for end-users: Demonstration at the Technological Market Exhibitions biennially
   - 6.7. Technology transfer: Not yet

6.8. Marketing: Demonstration at the Technological Market Exhibitions biennially
6.9. Others: Supply degraded alginate products to fertilizer-factory to produce new high-quality product

7. Publications
7.1. "Plant growth promoter", US Patent Number: 6,117,815; Date of Patent: September 12, 2000.
7.2. Hien N. Q., Le Hai, Dang, Yoshii, F., Kume Y., et al., Rad. Phys. Chem., vol. 59, pp. 97-101, 2000.

2.2.1.2. Carrageenan (Philippines)

1. Raw material
   1.1. Suppliers, grade and material history
      Suppliers: Shemberg Corp.
      Grade: Refined
      Material History: As received
   1.2. Visual examination: Examined
   1.3. Compositional analysis:
   1.4. Others: Compositional certification provided by the supplier
2. Pre-treatment
   2.1. Grinding or pulverization
      Grinding:
      Pulverization:
   2.2. Dissolution: 1wt% aqueous solution
   2.3. Others: Nothing special
3. Irradiation
   3.1. Irradiators/Facilities: Co-60 gamma rays at PNRI
   3.2. Packaging: Poly ethylene bottle/25 Liter Carboy
   3.3. Dose rate: 2kGy/h
   3.4. Dose: 30kGy
   3.5. Temperature: RT
   3.6. Others:
4. Post treatment
   4.1. Visual examination: Done
   4.2. Compositional analysis: Sulfur contents were analyzed.
   4.3. Product performance evaluation: Plant growth was tested under hydroponic condition.
   4.4. Others: 1wt% aqueous solution is concentrated to 4wt% aqueous solution.
5. Products
   5.1. Grinding or pulverization
      Grinding:
      Pulverization:
   5.2. Dissolution: 1wt% aqueous solution is Concentrated to 4wt% aqueous solution.
   5.3. Packaging: No packaging.
   5.4. Description:
   5.5. Instruction manual:
   5.6. Others: Because carrageenan as PGP is under laboratory stage, this item may not be applicable.
6. Strategies
   6.1. Safety considerations: Cytoxicity test was made
   6.2. Environmental considerations: Cytoxicity test was made

6.3. Cost analysis: Not available in PHP/kg (1 USD=ca. 40 PHP)

6.4. Comparison with other procedures/products: Various Fertilizer or Nutrients exist; radiation method is expensive than the other procedures/products.

6.5. Publications/Patents: Scientific Publications were made.

6.6. Advertisement for end-users: Exhibitions

6.7. Technology transfer: Collaboration between International Rice Research Institute (e.g.) is necessary for bio-efficacy.

6.8. Marketing: Not yet

6.9. Others: Because carrageenan as PGP is under laboratory stage, this item may not be applicable.

7. Publications

7.1. "Degradation of carrageenan by radiation", Relleve, L. S., Nagasawa, N., Luan, L. Q., Yagi, T., Aranilla, C. T., Abad, L. V., Kume, T., Yoshii, F., Dela Rosa, A. M., Polym. Deg. Stab., 87, 3, 403-410, 2005

2.2.1.3. Chitosan (Indonesia)

1. Raw material
   - 1.1. Suppliers, grade and material history:
     - Suppliers:
     - Grade: DD=78-80%
     - Material history:
   - 1.2. Visual examination: Powder
   - 1.3. Compositional analysis:
   - 1.4. Others:
2. Pre-treatment
   - 2.1. Grinding or pulverization:
   - 2.2. Dissolution:
   - 2.3. Others:
3. Irradiation
   - 3.1. Irradiators/Facilities: Co-60 gamma rays irradiator installed at BATAN
   - 3.2. Packaging: Treated by 10kg powder
   - 3.3. Dose rate: 9.8 kGy/hr
   - 3.4. Dose: 75-100 kGy
   - 3.5. Temperature: 27degree centigrade
   - 3.6. Others:
4. Post treatment
   - 4.1. Visual examination:
   - 4.2. Compositional analysis:
   - 4.3. Product performance evaluation: Excellent for growth promoters, increasing yield of crops 50-60%
   - 4.4. Others:
5. Products
   - 5.1. Grinding or pulverization:
   - 5.2. Dissolution: To 5% concentration of oligo-chitosan
   - 5.3. Packaging: 10L/package
   - 5.4. Description:
   - 5.5. Instruction manual:
   - 5.6. Others:
6. Strategies
   - 6.1. Safety considerations:
   - 6.2. Environmental considerations:
   - 6.3. Cost analysis: 300,000Rp/10L (1USD=ca. 9,200Rp)
   - 6.4. Comparison with other procedures/products: Super fertilizer; radiation method has early harvest than using super fertilizer,
   - 6.5. Publications/Patents: see item 7
   - 6.6. Advertisement for end-users: Developing stage

6.7. Technology transfer: Developing stage
6.8. Marketing: Developing stage
6.9. Others:

7. Publications

7.1. "Study on irradiation grafting of hydrophilic monomer onto chitin for ion exchange application", Gatot Trimulyadi Rekso, N. M Surdia, Cynthia L. Radiman and Sadijah Achmad, Advances in Chitin Science, V, 333-338, 2002

7.2. "Study on irradiation of condition chitosan for growth promoter of red chili (*Capcinum Annum*) plant", Gatot Trimulyadi Rekso, Kadariah, Anik Sunarni, Isni Marlianti, Dian Iramani and Sri Susilawati, Proceeding of The 6th ITB-UKM Joint Seminar on Chemistry, vol. VI, 328-332, 2005 (In Indonesian)

7.3. "Irradiated chitosan as growth promotes for potato plants *(Corleus Tuberosus Renth*)", Gatot Trimulyadi Rekso, Kadariah, Anik Sunarni, Isni Marlianti, Dian Iramani and Sri Susilawati, Proceeding of PATIR-BATAN, 165-168, 2005 (In Indonesian)

7.4. "The influence of irradiation on seaweed (*Eucheuma Alvarezii*) on the properties of carrageenan product", Gatot Trimulyadi Rekso, Anik Sunarni, Isni Marlianti and Dian Iramani, Proceeding of The 4th National Seminar on Chemistry and Environmental, 140-146, 2005 (In Indonesian)

7.5. "The influence of irradiation on chitin on the deacetylation degree and solubility of chitosan product", Gatot Trimulyadi Rekso, Anik Sunarni, Isni Marlianti and Dian Iramani, Proceeding of The 4th National Seminar on Chemistry and Environmental, 147-153, 2005 (In Indonesian)

7.6. "The preparation of environmental friendly viscose rayon by irradiation", Gatot Trimulyadi Rekso, Made Sumarti and Marsongko, The Proceeding of EBM Application, 104-109, 2007 (In Indonesian)

2.2.1.4. Demonstration study

During Phase 2, a collaborative work has been done at BATAN in Indonesia; the below is the protocol in the degradation of chitosan for PGP.

A. Materials

1. Chitosan (DDA~65-75%, Mw~100-200 kDa, (100 – 200 cPs))* : 10 kg
2. Lactic acid (98 %) : 10 liters
3. Silver nitrate ($AgNO_3$) : 17 g
4. Sodium hydroxide solution (NaOH 2M) : 5 liters
5. Deionized (DI) water : 500 liters

* If chitosan viscosity larger than 100-200 cPs, reduce the viscosity by irradiation, oxidation and others method.

B. Procedures

B1. Preparation of chitosan and irradiation

1. Pouring 200 liters water in the mixing tank
2. Adding 10 kg irradiated chitosan
3. Pouring 100 liters water
4. Stirring at 25 rpm for 1 hour for swelling of chitosan
5. Adding 10 liters lactic acid and stirring for 1 hour
6. Adding 200 liters water and stirring for 2 hours
7. Filtering chitosan solution through 20-50 mesh stainless steel net (if needed)
8. Pumping chitosan solution to irradiation tank
9. Irradiation while stirring at 50 rpm up to 35 kGy
10. Adjusting pH by adding 5 liters NaOH 2M solution while stirring

B2. Preparation of Ag-nano/chitosan for utilization as preservative

1. Take 10 liters of chitosan solution prepared by above mention procedure
2. Adding 17 g $AgNO_3$ (dissolved in small volume of water) into chitosan solution
3. Stirring about 15 minutes
4. Putting prepared Ag^+/chitosan solution into plastic container
5. Irradiated with a dose of 35 kGy
6. Ag-nano/chitosan colloid with concentration of 1.000 ppm Ag

B3. Preservation of oligochitosan with Ag-nano of 20 ppm

1. Taking 49 L oligochitosan solution prepared in B1
2. Adding 1 L Ag-nano/chitosan into oligochitosan solution while stirring
3. Stirring about 30 minutes
4. Store oligochitosan preserved with Ag-nano in cool place

C. Field Applications

1. For rice:
   - 1.1 Rice plant: Dilution 1000 times with water (20 ppm), spraying 3 times (20, 30 and 40 days after sowing), 500 L water diluted oligochitosan/ha it means 1.5 L (2% of original oligo chitosan)/ha
   - 1.2 Rice seed: For rice seed treatment, dilution 100 times with water (1/100). Rice seed are dipped in oligo chitosan solution about 30 min
2. For other plants: such as tea, potato, cabbage, sugarcane, carrot, red pepper, tomato and any kind flower : Dilution 500 times with water (40 ppm), spraying 3 time up to haverst

2.2.2. Aquaculture and stock feeding

Similarly to PGP, the radiation-treated low molecular weight oligosaccharides such as Chitosan can be supplied as nutrition for aquacultural creatures (such as fishes, shrimps, crabs etc.) and chicken feeding as additives. The enhanced growth in weight was observed.

In China, utilization of Chitosan has been extremely investigated. The example of successfully commercialized additives (liquid containing radiation degraded oligo-chitosan) is shown in Fig. 2-9 (with courtesy of SINAP) .

This field may be categorized into rather new application compared to others, but its application is further spreading.

Fig. 2-9. Oligo-Chitosan product.

2.2.2.1. Chitosan (China)

1. Raw material
   - 1.1. Suppliers, grade and material history
     - Suppliers: Chinese domestic suppliers
     - Grade: Industrial/food grade
     - Material history:
   - 1.2. Visual examination: White powder
   - 1.3. Compositional analysis: Mw > 300kD
   - 1.4. Others:
2. Pre-treatment
   - 2.1. Grinding or pulverization
     - Grinding: Yes
     - Pulverization: Yes
   - 2.2. Dissolution: Yes
   - 2.3. Others:
3. Irradiation
   - 3.1. Irradiators/Facilities: Gamma rays at Shanghai Institute of Applied Physics
   - 3.2. Packaging: 20kg/package
   - 3.3. Dose rate: 10kGy/h
   - 3.4. Dose: 10-400kGy
   - 3.5. Temperature: room temperature
   - 3.6. Others:
4. Post treatment
   - 4.1. Visual examination: Yellow powder
   - 4.2. Compositional analysis: Molecular weight decreased
   - 4.3. Product performance evaluation: Good
   - 4.4. Others:
5. Products
   - 5.1. Grinding or pulverization
     - Grinding: No
     - Pulverization: No
   - 5.2. Dissolution: Yes
   - 5.3. Packaging: 1000ml/bottle
   - 5.4. Description: Use for aquaculture
   - 5.5. Instruction manual: Chitosan 5wt%, spraying on water area every 10-15 day
   - 5.6. Others:
6. Strategies
   - 6.1. Safety considerations: Very nice
   - 6.2. Environmental considerations: Nice
   - 6.3. Cost analysis: Relative high but acceptable by users
   - 6.4. Comparison with other procedures/products: Cost is lower

6.5. Publications/Patents: one Chinese patent is already approved, No.ZL 2004 1 0089449.6

6.6. Advertisement for end-users: High safety and good immunity,

6.7. Technology transfer: Already transferred to 4 Chinese companies

6.8. Marketing: 100 tons in 2007 and the market is growing

6.9. Others:

7. Publications

7.1. "Preparation, characterization and antibacterial activity of chitosan – Ca3V10O28 complex membrane", Shuiping Chen, Guozhong Wu, Dewu Long, Carbohydrate Polymers, 64, 92-97, 2006

7.2. "High Efficient Fabrication of Chitosan micropowder by combination of gamma radiation and jet pulverization", Guozhong Wu, Dewu Long, Shuiping Chen, Side Yao, Carbohydrate Polymers, 60, 61-65, 2005

7.3. "Preparation of High antimicrobial activity Chiourea chitosan-Ag^+ complex", Shuiping Chen, Guozhong Wu, Hongyan Zeng, Carbohydrate Polymers, 60, 33-38, 2005

2.3. Other applications

The radiation processing to develop hydrogel and oligosacchrides is continuously improving and expanding. Not only presented in previous sections, but also there are other new findings and applications developed and reported during the phase 2; some of them are presented below.

2.3.1. PVP-Chitosan hydrogel

This PVP-Chitosan hydrogel is used as Bio-implant, and efficient to prevent VUR (vesico-ureteral reflux, abnormal flow of urine from the bladder to the kidneys). The material has enough viscosity to pass through a medical needle (as shown in Fig. 2-10, with courtesy of PNRI) while maintaining its stability with very minimal changes in volume after six months. The implant can be considered biocompatible and non-migratory with minimal inflammatory reaction. The PVP-Chitosan hydrogel has properties of a good tissue augmenting implant comparable to that of the conventional Dextranormer/Hyaluronic acid copolymer (Deflux^{TM})

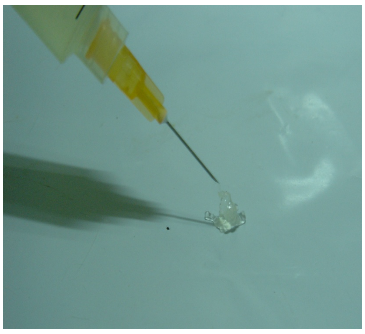


Fig. 2-10. Bio-implant made of PVP-Chitosan hydrogel product.

2.3.2. CM-Chitosan hydrogel

CM-Chitosan hydrogel can collect substantial amount of metal ions dissolved in aqueous solution. An example shows that cross-linked CM-Chitosan gel aqueous solution well adsorbs Cu^{2+} ion in hours to reach equilibrium, as shown in Fig. 2-11 (with courtesy of JAEA). This application can be tried to collect the noble or rare metals such as, Au, Pd, Sc, etc., especially from the hot-spring water.

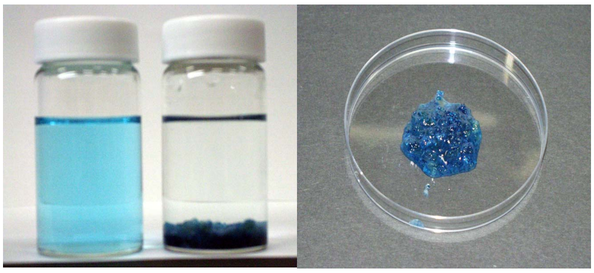


Fig. 2-11. Cu-containing solutions (left, without or with CM-Chitosan hydrogel) and retrieved hydrogel (right).

2.3.3. CM-Carrageenan hydrogel

Recently it was found that CM-carrageenan can be cross-linked upon irradiation, though the pristine polymer undergoes degradation similarly to other natural polymers. This is a new and interesting finding but still under laboratory stage. The expected application of this new hydrogel material includes medical and cosmetic fields.

3. Concluding Remarks

3.1. Cost analysis

Once a technical protocol is established, the cost is the most important factor to compete with other existent non-radiation-technologies. Cost analysis of some applications was tried. Cost analysis should be carried out comprehensively throughout the process, namely, from raw materials, via pre-treatment and irradiation (or other non-radiation treatment), to post treatment.

Tables 3-1 and 3-2 show a summary of cost analysis of the applications presented in the previous part (Table 3-1 is for cross-linking and Table 3-2 is for degradation, respectively, and Table 3-1 annex is a comparison for the same product between countries), though applications in laboratory or developing stages may not be appropriate at this moment. Here the editors draw special attention of the readers so that figures in the Tables should not be over-trusted, because technologies are being continuously improved, and that currency rate is also changing rapidly. Cost for irradiation may be crucial, to cover the initial investment and the running cost during operational period of the irradiation system, and to reduce the irradiation cost/charge will be the key-point.

Another important point is to pay attention to environmentally friendliness; radiation method can reduce usage of (hazardous) chemicals, carbon dioxide emission, etc. By considering these characteristics, radiation method can be a well-competing method.

3.2. Current status

There are many examples of applications; some of them are commercial stage while some of them are developing or laboratory stage. Even if a radiation application is technically established, from the viewpoint of cost etc., it has to be admitted that some of them are suspended or withdrawn. Table 3-3 summarizes the current status and the state of the art during this phase 2.

3.3. Final remarks

This guideline is an outcome of three-year project (2006-2008) of radiation application on natural polymers under the framework of FNCA. The list of proceedings of workshops during phase 1 and phase 2 are given in the following page. If one has interest in the application of radiation to natural polymers, it is recommended to refer them; they are available at the given URL.

If this guideline can be of help for any of researchers, manufacturers and end-users (including potential ones), it is a pleasure for all contributors and editors.

The coordinator, project leaders of participating countries, and the editors and the contributors of this guideline, unanimously wish to launch a new project since the fiscal year of 2009.

REFERENCES

Proceedings of the FNCA Workshop on Application of Electron Accelerator
(Available at http://jolissrch-inter.tokai-sc.jaea.go.jp/abstracts/seika/en/toppage.html)

1) January 28 - February 1, 2002, JAERI, Takasaki, Japan
JAERI-Conf 2002-013; Feb. 2003, 187p.
http://jolissrch-inter.tokai-sc.jaea.go.jp/pdfdata/JAERI-Conf-2002-013.pdf

2) 16-20 December 2002, JAERI, Takasaki, Japan
JAERI-Conf 2003-016; Oct. 2003, 185p.
http://jolissrch-inter.tokai-sc.jaea.go.jp/pdfdata/JAERI-Conf-2003-016.pdf

3) 18-22 August 2003, Kuala Lumpur, Malaysia
JAERI-Conf 2004-007; Jun. 2004, 216p.
http://jolissrch-inter.tokai-sc.jaea.go.jp/pdfdata/JAERI-Conf-2004-007.pdf

4) 6-10 September 2004, Beijing, China
JAERI-Conf 2005-005; Jun. 2005, 178p.
http://jolissrch-inter.tokai-sc.jaea.go.jp/pdfdata/JAERI-Conf-2005-005.pdf

5) 14-18 November 2005, Daejeon, Korea
JAEA-Conf 2006-006; Aug. 2006, 144p.
http://jolissrch-inter.tokai-sc.jaea.go.jp/pdfdata/JAEA-Conf-2006-006.pdf

6) 12-16 December 2006, Kuala Lumpur, Malaysia
JAEA-Conf 2007-007, Aug. 2007, 154p
http://jolissrch-inter.tokai-sc.jaea.go.jp/pdfdata/JAEA-Conf-2007-007.pdf

7) 22-26 October, Ho Chi Minh City, Vietnam
JAEA-Conf 2008-009, Dec. 2008, 219p
http://jolissrch-inter.tokai-sc.jaea.go.jp/pdfdata/JAEA-Conf-2008-009.pdf

8) 27-31 October, Shanghai, China
To be published

Table 3-1 Cost analysis for cross-linking, as of date listed

Radiation effects		Cross-linking		
Material		CM-CTS	PVP-CARG	Sago-starch
Responsible country		KOR	KOR	MAS
Applications		Postsurgical anti-adhesion barrier	HWD	Face Mask HWD
Raw Material		20USD/kg(CTS) 2.2USD/kg in 10% aq. solution	63,000KOW/kgPolm	1.60RM/kg for Sago starch, 18.0RM for PVA
Pre-treatment	Method	Carboxymethylation + 10% aq. solution + processing costs	8wt% aq. sol.	Mixing and Heating
	Cost	20USD/kg	2,780KOW/kgPolym	Not available
	Unit cost	2.2USD/kg aq. CM-CTS solution		
Irradiation	Dose	25kGy	25kGy	25kGy
	Cost	0.3USD/kg Gel	400KOW/kg	0.25RM for face mask, 0.10RM for HWD
	Unit cost	0.3USD/kg Gel		
Post-treatment	Method	None		Coating, packaging and sealing
	Cost	None		Not available
	Unit cost	None		
Total cost of radiation method*1		4.7USD/kg Gel Products	26,000 KOW/kgProduct	0.173RM/g of sago hydrogel face mask
Product Performance		Reduced postsurgical adhesions	Wound healing	Acne treatment and wound healing
Other Method	Method			Nil
	Cost			
Stage of radiation method (L/D/C/S/W)*2		D	C	C (Face Mask) D (HWD)
Other remarks				
Currency rate		1USD=ca.1000KOW	1USD=ca.1000KOW	1USD=ca.3.7RM
Data as of		2007 October	2008 November	2008 June

*1 Transportation, packaging etc are excluded

*2 L: Laboratory, D: Developing, C: Commercialized, S: Suspended, W: Withdrawn

Table 3-1 Cost analysis for cross-linking, as of date listed (Continued)

Radiation effects		Cross-linking		
Material		CMC	CM-cassava-starch	PVP-CTS
Responsible country		JPN	THA	PHI
Applications		Dry gel	CMS dry gel	Bio implant
Raw Material		600JPY/kgPolym	434THB/kgPolym	1100PHP/kgPVP 1000PHP/kgCTS
Pre-treatment	Method	20wt% aq. soln.	50%aq. sol.	7% total polymer in dilute acetic acid
	Cost	0.4JPY/kgPolm	1THB/kgPolm	500PHP/L acetic acid, 1.50PHP/L water
	Unit cost	0.1JPY/kgWater		
Irradiation	Dose	5kGy	2kGy	15kGy
	Cost	400JPY/5kgPaste	15THB/2kgPaste	15 PHP/kgGel
	Unit cost	80JPY/kgPaste	7.5 THB/kg	15PHP/kgGel
Post-treatment	Method	Slice and Dry	Dry	Neutralization, homogenization, packaging, gamma-ray sterilization
	Cost	Not available	Not available	Not available
	Unit cost	Not available		Not available
Total cost of radiation method*1		1000JPY/kgProduct	455 THB/kgProduct	
Product Performance		Excellent water absorbent	Excellent water absorbent	Implant for VUR treatment
Other method	Method	PAAc 350JPY/kgProduct	PAAc 120THB/kgProduct	Hyaluronic acid copolymer, 37,000 PHP/mL- Product
	Cost	Radiation-method is expensive	Radiation method is expensive	
Stage of radiation method (L/D/C/S/W)*2		C/S	D	L/D
Other remarks				
Currency rate		1USD=ca.110JPY	1USD=ca.33THB	1USD=ca 49 PHP
Data as of		2007 August	2008 February	2008 November

*1 Transportation, packaging etc are excluded

*2 L: Laboratory, D: Developing,, C: Commercialized, S: Suspended, W: Withdrawn

Table 3-1(Annex) Comparative cost analysis for cross-linking of PVP-carrageenan

Radiation effects		Cross-linking	
Material		PVP-CARG	PVP-CARG
Responsible country		KOR	PHI
Applications		HWD	HWD
Raw Material		63,000KOW/kgPolm	1,100PHP/kgPVP 600PHP/kgCARG 200PHP/kgPEG
Pre-treatment	Method	8wt% aq. sol.	9% total polymer aqueous solution, heating, moulding, packaging
	Cost	2,780KOW/kgPolym	
	Unit cost		
Irradiation	Dose	25kGy	25kGy
	Cost	400KOW/kg	30PHP/kgHWD
	Unit cost		
Post-treatment	Method		
	Cost		
	Unit cost		
Total cost of radiation method*[1]		26,000 KOW/kgProduct	
Product Performance		Wound healing	Burn and ulcer treatment
Other Method	Method		Hydrocolloid
	Cost		267PHP/20gProduct
Stage of radiation method (L/D/C/S/W)*[2]		C	D/C
Other remarks			
Currency rate		1USD=ca.1000KOW	1USD=ca.49PHP
Data as of		2008 November	2008 November

*1 Transportation, packaging etc are excluded

*2 L: Laboratory, D: Developing, C: Commercialized, S: Suspended, W: Withdrawn

Table 3-2 Cost analysis for degradation, as of date listed

Radiation effects		Degradation		
Material		ALG	CTS	CARG
Responsible country		VIE	VIE	PHI
Applications		PGP	PGP+Elicitor	PGP
Raw Material		100 KVND/kg	20USD/kg	600PHP/kg
Pre-treatment	Method	Chemical extraction		1wt% aq. Soln.
	Cost	100 KVND/kg		750PHP/kgPolm
	Unit cost			7.5PHP/kgWater
Irradiation	Dose	40 kGy	50kGy	30kGy
	Cost	30 KVND/kg	2USD/kg	Not available
	Unit cost			
Post-treatment	Method	Filtration, and add micro-element ($NaMoO_4$)	Dissolve in dilute organic acids (acetic or lactic acids)	Concentrate to 4% by evaporation
	Cost	100 KVND/kg		Not available
	Unit cost			
Total cost of radiation method*[1]		330KVND/kg	22 USD/kg	
Product Performance		Plant Growth Promoter	Liquid, Olicide 9DDA, Fungicide and PGP	PGP
Other method	Method	Chemical (e.g. H_2O_2)		Fertilizer
	Cost	Radiation method is expensive		Radiation-method is expensive
Stage of radiation method (L/D/C/S/W)*[2]		C/W, 15 ton was produced in 2007.	C	L
Other remarks		Demand is high, cost less competitive.	EB irradiation may be cheaper than gamma	
Currency rate		1USD=ca.15000VND	1USD=ca.15000VND	1USD=ca.40PHP
Data as of		2008 November	2008 June	2008 January

*1 Transportation, packaging etc are excluded

*2 L: Laboratory, D: Developing, C: Commercialized, S: Suspended, W: Withdrawn

Table 3-2 Cost analysis for degradation, as of date listed (Continued)

Radiation effects		Degradation		
Material		CTS	CTS	CTS
Responsible country		INA	THA	CHN
Applications		PGP	PGP, Fungicide	Feed Additive
Raw Material		600,000Rp/kgPowder	1200THB/kgPolymer	16USD/kg high MW CTS
Pre-treatment	Method	None	5wt% H_2O_2 at 2% concentration	Milling
	Cost	None	1 THB/kg Polymer	1USD/kg
	Unit cost	None	1 THB/kgPolymer	
Irradiation	Dose	75-100kGy	10kGy	300kGy
	Cost	50,000Rp/10kgPowder	4725THB/5kg moisten chitosan	7USD/kg
	Unit cost	5000Rp/kgPowder	945THB/kg	
Post-treatment	Method	Dilute to 5% concentration of oligo-chitosan	$HOAc/H_2O_2$	Milling
	Cost	AAc 2% Rp5000/L 10,000Rp/10Lpackage	600THB/5kg moisten chitosan	1.5USD/kg
	Unit cost		120THB/kg	
Total cost of radiation method *[1]		300,000Rp/10L	1496THB/10L Product (10% oligochitosan)	25.5USD/kg
Product Performance		Excellent for PGP, increasing yield of 50-60%	Noticeable effects on plant growth rate	
Other method	Method	Super fertilizer	Ozonization	
	Cost		No data	
Stage of radiation method (L/D/C/S/W)*[2]		D	S	D/C
Other remarks				
Currency rate		1USD=ca.9200Rp	1USD=ca.33THB	1USD=ca.7CHY
Data as of		2007 October	2008 August	2008 June

*1 Transportation, packaging etc are excluded

*2 L: Laboratory, D: Developing, C: Commercialized, S: Suspended, W: Withdrawn

Table 3-3 Current status of the technology during phase 2 (2006-2008)

	Cross-linking					
	CARG	CASV-ST	CMC	CM-CTS	Sago-ST	ST-AAc
CHN				HWD/D		
INA	HWD/L					
JPN			*Bedsore mat/C* *Coolant/C* *Dry gel/C*			
KOR	HWD/C			*HWD/L*		
MAS				HWD/L	*Face Mask/C* *HWD/D* *Bio-Film, Foam/D*	
PHI	*HWD/D* *HDG/L*			Bio-implant/D		
THA		*HWD/L*				
VIE				W cream /L HWD/L		*Absorbent/L*

Italic means the leading country of the material.

Table 3-3 Current status of the technology during phase 2 (2006-2008)(Continued)

	Degradation		
	ALG	CARG	CTS
CHN			*Aquaculture/C* *Plant Elicitor*
INA			PGP/D
JPN			
KOR			
MAS			
PHI		*PGP/L*	
THA			PGP/D
VIE	*PGP/C*		Plant Elicitor/C&D

Italic means the leading country of the material.

Acknowledgements

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Editor, Hisaaki Kudo
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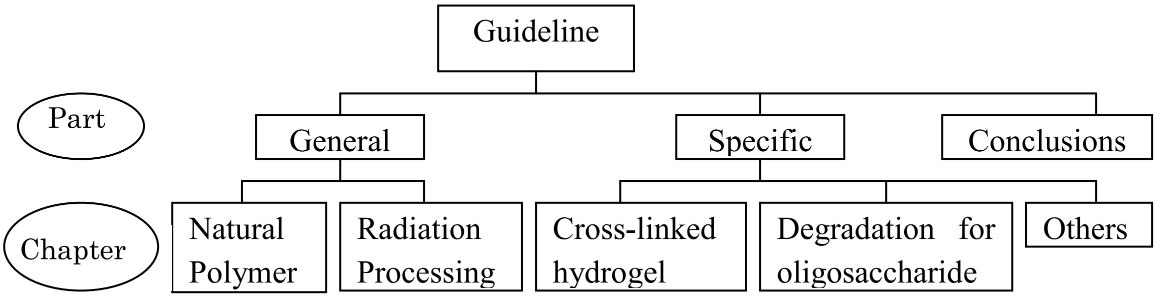
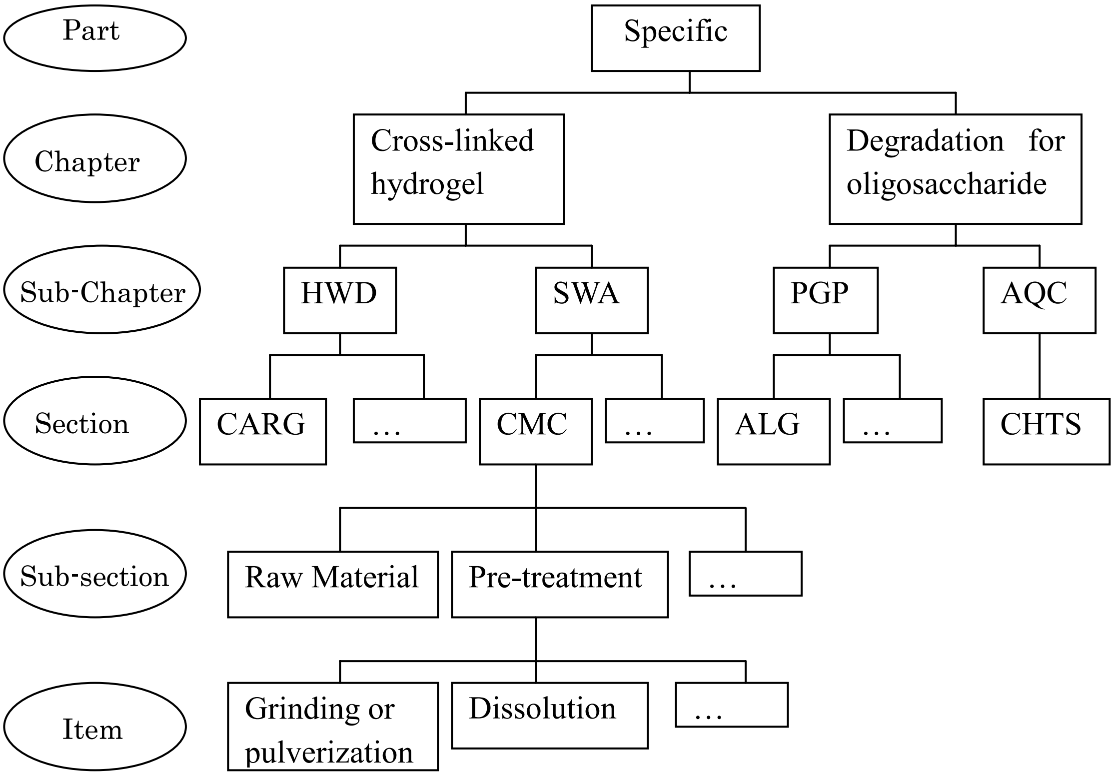
Tamikazu Kume

Appendix 1. General Structure of Guideline

(General structure)



(Detailed structure for the specific part)



(For abbreviations refer chapter 1.4.)

Appedix 2. Structure (Sub-section) of Each Section

1. Raw material
    1.1. Suppliers, grade and material history
    1.2. Visual examination
    1.3. Compositional analysis
    1.4. Others
2. Pre-treatment
    2.1. Grinding or pulverization
    2.2. Dissolution
    2.3. Others
3. Irradiation
    3.1. Irradiators/Facilities
    3.2. Packaging
    3.3. Dose rate
    3.4. Dose
    3.5. Temperature
    3.6. Others
4. Post treatment
    4.1. Visual examination
    4.2. Compositional analysis
    4.3. Product performance evaluation
    4.4. Others
5. Products
    5.1. Grinding or pulverization
    5.2. Dissolution
    5.3. Packaging
    5.4. Description
    5.5. Instruction manual
    5.6. Others
6. Strategies
    6.1. Safety considerations
    6.2. Environmental considerations
    6.3. Cost analysis
    6.4. Comparison with other procedures/products
    6.5. Publications/Patents
    6.6. Advertisement for end-users
    6.7. Technology transfer
    6.8. Marketing
    6.9. Others…

Appendix 3. Workshops

This guideline was proposed, and the draft was discussed and approved at the following workshops of FNCA electron beam industry group phase 2 (2006-2008).

2006 December 12-16, in Kuala Lumpur, Malaysia
2007 October 22-26, in Ho Chi Minh City, Vietnam
2008 October 27-31, in Shanghai, China

Appendix 4. Contributors

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国際単位系（SI）

表１．SI 基本単位

基本量	SI 基本単位	
	名称	記号
長さ	メートル	m
質量	キログラム	kg
時間	秒	s
電流	アンペア	A
熱力学温度	ケルビン	K
物質量	モル	mol
光度	カンデラ	cd

表２．基本単位を用いて表されるSI組立単位の例

組立量	SI 基本単位	
	名称	記号
面積	平方メートル	m^2
体積	立法メートル	m^3
速さ，速度	メートル毎秒	m/s
加速度	メートル毎秒毎秒	m/s^2
波数	毎メートル	m^{-1}
密度，質量密度	キログラム毎立方メートル	kg/m^3
面積密度	キログラム毎平方メートル	kg/m^2
比体積	立方メートル毎キログラム	m^3/kg
電流密度	アンペア毎平方メートル	A/m^2
磁界の強さ	アンペア毎メートル	A/m
量濃度(a)，濃度	モル毎立方メートル	mol/m^3
質量濃度	キログラム毎立法メートル	kg/m^3
輝度	カンデラ毎平方メートル	cd/m^2
屈折率(b)	（数字の）　1	1
比透磁率(b)	（数字の）　1	1

(a)　量濃度（amount concentration）は臨床化学の分野では物質濃度（substance concentration）ともよばれる。

(b)　これらは無次元量あるいは次元１をもつ量であるが、そのことを表す単位記号である数字の１は通常は表記しない。

表３．固有の名称と記号で表されるSI組立単位

組立量	SI 組立単位			
	名称	記号	他のSI単位による表し方	SI基本単位による表し方
平面角	ラジアン(b)	rad	1 (b)	m/m
立体角	ステラジアン(b)	sr(c)	1 (b)	m$^{2/}$m^2
周波数	ヘルツ(d)	Hz		s^{-1}
力	ニュートン	N		m kg s^{-2}
圧力，応力	パスカル	Pa	N/m^2	m^{-1} kg s^{-2}
エネルギー，仕事，熱量	ジュール	J	N m	m^2 kg s^{-2}
仕事率，工率，放射束	ワット	W	J/s	m^2 kg s^{-3}
電荷，電気量	クーロン	C		s A
電位差（電圧），起電力	ボルト	V	W/A	m^2 kg s^{-3} A^{-1}
静電容量	ファラド	F	C/V	m^{-2} kg^{-1} s^4 A^2
電気抵抗	オーム	Ω	V/A	m^2 kg s^{-3} A^{-2}
コンダクタンス	ジーメンス	S	A/V	m^{-2} kg^{-1} s^3 A^2
磁束	ウエーバ	Wb	Vs	m^2 kg s^{-2} A^{-1}
磁束密度	テスラ	T	Wb/m^2	kg s^{-2} A^{-1}
インダクタンス	ヘンリー	H	Wb/A	m^2 kg s^{-2} A^{-2}
セルシウス温度	セルシウス度(e)	℃		K
光束	ルーメン	lm	cd sr(c)	cd
照度	ルクス	lx	lm/m^2	m^{-2} cd
放射性核種の放射能(f)	ベクレル(d)	Bq		s^{-1}
吸収線量, 比エネルギー分与, カーマ	グレイ	Gy	J/kg	m^2 s^{-2}
線量当量, 周辺線量当量, 方向性線量当量, 個人線量当量	シーベルト(g)	Sv	J/kg	m^2 s^{-2}
酸素活性	カタール	kat		s^{-1} mol

(a)SI接頭語は固有の名称と記号を持つ組立単位と組み合わせても使用できる。しかし接頭語を付した単位はもはやコヒーレントではない。

(b)ラジアンとステラジアンは数字の１に対する単位の特別な名称で、量についての情報をつたえるために使われる。実際には、使用する時には記号rad及びsrが用いられるが、習慣として組立単位としての記号である数字の１は明示されない。

(c)測光学ではステラジアンという名称と記号srを単位の表し方の中に、そのまま維持している。

(d)ヘルツは周期現象についてのみ、ベクレルは放射性核種の統計的過程についてのみ使用される。

(e)セルシウス度はケルビンの特別な名称で、セルシウス温度を表すために使用される。セルシウス度とケルビンの単位の大きさは同一である。したがって、温度差や温度間隔を表す数値はどちらの単位で表しても同じである。

(f)放射性核種の放射能（activity referred to a radionuclide）は、しばしば誤った用語で”radioactivity”と記される。

(g)単位シーベルト（PV,2002,70,205）についてはCIPM勧告2（CI-2002）を参照。

表４．単位の中に固有の名称と記号を含むSI組立単位の例

組立量	SI 組立単位		
	名称	記号	SI 基本単位による表し方
粘度	パスカル秒	Pa s	m^{-1} kg s^{-1}
力のモーメント	ニュートンメートル	N m	m^2 kg s^{-2}
表面張力	ニュートン毎メートル	N/m	kg s^{-2}
角速度	ラジアン毎秒	rad/s	m m^{-1} s^{-1}=s^{-1}
角加速度	ラジアン毎秒毎秒	rad/s^2	m m^{-1} s^{-2}=s^{-2}
熱流密度，放射照度	ワット毎平方メートル	W/m^2	kg s^{-3}
熱容量，エントロピー	ジュール毎ケルビン	J/K	m^2 kg s^{-2} K^{-1}
比熱容量，比エントロピー	ジュール毎キログラム毎ケルビン	J/(kg K)	m^2 s^{-2} K^{-1}
比エネルギー	ジュール毎キログラム	J/kg	m^2 s^{-2}
熱伝導率	ワット毎メートル毎ケルビン	W/(m K)	m kg s^{-3} K^{-1}
体積エネルギー	ジュール毎立方メートル	J/m^3	m^{-1} kg s^{-2}
電界の強さ	ボルト毎メートル	V/m	m kg s^{-3} A^{-1}
電荷密度	クーロン毎立方メートル	C/m^3	m^{-3} sA
表面電荷	クーロン毎平方メートル	C/m^2	m^{-2} sA
電束密度，電気変位	クーロン毎平方メートル	C/m^2	m^{-2} sA
誘電率	ファラド毎メートル	F/m	m^{-3} kg^{-1} s^4 A^2
透磁率	ヘンリー毎メートル	H/m	m kg s^{-2} A^{-2}
モルエネルギー	ジュール毎モル	J/mol	m^2 kg s^{-2} mol^{-1}
モルエントロピー, モル熱容量	ジュール毎モル毎ケルビン	J/(mol K)	m^2 kg s^{-2} K^{-1} mol^{-1}
照射線量（Ｘ線及びγ線）	クーロン毎キログラム	C/kg	kg^{-1} sA
吸収線量率	グレイ毎秒	Gy/s	m^2 s^{-3}
放射強度	ワット毎ステラジアン	W/sr	m^4 m^{-2} kg s^{-3}=m^2 kg s^{-3}
放射輝度	ワット毎平方メートル毎ステラジアン	W/(m^2 sr)	m^2 m^{-2} kg s^{-3}=kg s^{-3}
酵素活性濃度	カタール毎立方メートル	kat/m^3	m^{-3} s^{-1} mol

表５．SI 接頭語

乗数	接頭語	記号	乗数	接頭語	記号
10^{24}	ヨタ	Y	10^{-1}	デシ	d
10^{21}	ゼタ	Z	10^{-2}	センチ	c
10^{18}	エクサ	E	10^{-3}	ミリ	m
10^{15}	ペタ	P	10^{-6}	マイクロ	µ
10^{12}	テラ	T	10^{-9}	ナノ	n
10^{9}	ギガ	G	10^{-12}	ピコ	p
10^{6}	メガ	M	10^{-15}	フェムト	f
10^{3}	キロ	k	10^{-18}	アト	a
10^{2}	ヘクト	h	10^{-21}	ゼプト	z
10^{1}	デカ	da	10^{-24}	ヨクト	y

表６．SIに属さないが、SIと併用される単位

名称	記号	SI 単位による値
分	min	1 min=60s
時	h	1h =60 min=3600 s
日	d	1 d=24 h=86 400 s
度	°	1°=(π/180) rad
分	’	1’=(1/60)°=(π/10800) rad
秒	”	1”=(1/60)’=(π/648000) rad
ヘクタール	ha	1ha=1hm^2=10^{4}m^2
リットル	L，l	1L=11=1dm^3=10^{3}cm^3=10^{-3}m^3
トン	t	1t=10^3 kg

表７．SIに属さないが、SIと併用される単位で、SI単位で表される数値が実験的に得られるもの

名称	記号	SI 単位で表される数値
電子ボルト	eV	1eV=1.602 176 53(14)×10^{-19}J
ダルトン	Da	1Da=1.660 538 86(28)×10^{-27}kg
統一原子質量単位	u	1u=1 Da
天文単位	ua	1ua=1.495 978 706 91(6)×10^{11}m

表８．SIに属さないが、SIと併用されるその他の単位

名称	記号	SI 単位で表される数値
バール	bar	1 bar=0.1MPa=100kPa=10^{5}Pa
水銀柱ミリメートル	mmHg	1mmHg=133.322Pa
オングストローム	Å	1 Å=0.1nm=100pm=10^{-10}m
海里	M	1 M=1852m
バーン	b	1 b=100fm^2=(10^{-12}cm)2=10^{-28}m^2
ノット	kn	1 kn=(1852/3600)m/s
ネーパ	Np	SI単位との数値的な関係は、対数量の定義に依存。
ベル	B	
デジベル	dB	

表９．固有の名称をもつCGS組立単位

名称	記号	SI 単位で表される数値
エルグ	erg	1 erg=10^{-7} J
ダイン	dyn	1 dyn=10^{-5}N
ポアズ	P	1 P=1 dyn s cm^{-2}=0.1Pa s
ストークス	St	1 St =1cm^2 s^{-1}=10^{-4}m^2 s^{-1}
スチルブ	sb	1 sb =1cd cm^{-2}=10^{4}cd m^{-2}
フォト	ph	1 ph=1cd sr cm^{-2} 10^{4}lx
ガル	Gal	1 Gal =1cm s^{-2}=10^{-2}ms^{-2}
マクスウェル	Mx	1 Mx = 1G cm^2=10^{-8}Wb
ガウス	G	1 G =1Mx cm^{-2} =10^{-4}T
エルステッド(c)	Oe	1 Oe ≙ (10^3/4π)A m^{-1}

(c)　３元系のCGS単位系とSIでは直接比較できないため、等号「 ≙ 」は対応関係を示すものである。

表10．SIに属さないその他の単位の例

名称	記号	SI 単位で表される数値
キュリー	Ci	1 Ci=3.7×10^{10}Bq
レントゲン	R	1 R = 2.58×10^{-4}C/kg
ラド	rad	1 rad=1cGy=10^{-2}Gy
レム	rem	1 rem=1 cSv=10^{-2}Sv
ガンマ	γ	1 γ =1 nT=10-9T
フェルミ		1フェルミ=1 fm=10-15m
メートル系カラット		1メートル系カラット = 200 mg = 2×10-4kg
トル	Torr	1 Torr = (101 325/760) Pa
標準大気圧	atm	1 atm = 101 325 Pa
カロリー	cal	1cal=4.1858J（「15℃」カロリー），4.1868J（「IT」カロリー）4.184J（「熱化学」カロリー）
ミクロン	µ	1 µ =1µm=10^{-6}m

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