ceramics

Article

Iron (III) Oxide-Based Ceramic Material for Radiation Shielding

Hiroyuki Mori [1,*], Yohei Oku [2], Yudo Mannami [1] and Takahiro Kunisada [3,*]

1 Mitsuishi Refractory Brick Co., Ltd., 868, Mitsuishi, Bizen-shi, Okayama 705-0132, Japan; mtaika-mori@abelia.ocn.ne.jp
2 Ofuna Chuo Hospital, Kamakura 247-0056, Japan; okuoku159@msn.com
3 Graduate School of Medicine, Gifu University, 1-1 Yanagido, Gifu 501-1194, Japan
* Correspondence: mori4x@gmail.com (H.M.); tkunisad@gifu-u.ac.jp (T.K.)

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Abstract: We developed a new ceramic from raw material mainly composed of iron (III) oxide. The measured attenuation coefficient of the ceramic for high-energy gamma rays was in the range 0.268–0.355, which is approximately 40% of that of lead and twice that of concrete. The measured penetrating dose of the ceramic is half of that of concrete. Thus, the novel ceramic material named RASHIX may serve as a novel ceramic alternative for the wide variety of radiation shielding materials used in construction.

Keywords: ceramic; brick; radiation shielding; iron (III) oxide; Fe_2O_3

1. Introduction

Shielding from radiation is key for personnel working in the field of medical radiation, such as clinical radiotherapy and radiophysics, as well as for those in industrial radiation [1]. Lead is highly effective for this purpose [2] and has been commonly used for local shielding, but its use is restricted by the RoHS (Restriction of Hazardous Substance) directive due to its toxicity [3]. Hence, concrete, being far less toxic, is the first choice in the construction of walls and flooring of radiation facilities. Although other materials such as ceramic (brick) [4] and granite [5] have been tested for their usefulness as shielding materials, their linear attenuation coefficient μ is 0.08 to 0.13 cm^{-1} for the ^{60}Co gamma ray source, which is even lower than those of the various heavyweight concrete mixtures (0.15–0.19) [6]. Hence, radioprotective shields for medical radiation facilities such as linear accelerators and for industrial gamma ray sterilization systems are constructed of concrete or concrete with an inserted iron plate.

In this study, we developed a new ceramic material with a high shielding capacity against the high-energy gamma radiation from ^{137}Cs and ^{60}Co sources. As we experienced difficulties during the reconstruction of the concrete shielding wall of the linac room, brick type of shielding material which can be fast assembled in situ, with a flexibility to be shaped any form was expected to replace the conventional concrete shielding. Although the material containing 65% Fe (Fe_3O_4 and Fe_2O_3) has been used for the production of bricks [7], we were not sure that nearly 99% Fe_2O_3 (Iron (III) oxide) purified from the waste material of steel sheet production could be sintered into brick. Unexpectedly, we successfully burned raw material containing iron (III) oxide into a hard-ceramic brick that showed a shielding capacity of 0.278 μ (cm^{-1}) for the ^{60}Co gamma ray source, which is twice that of the bricks commonly used for construction. It was comparable to that of the heavy concrete specifically designed for radiation shielding as well.

2. Experimantal

2.1. Raw Material and Preparation of Ceramic Specimens

A powder containing 99% iron oxide used in this study was provided by TETSUGEN Co. Ltd., Japan. The mean diameter of the powder measured by laser diffraction was approximately 1 mm. The chemical composition of the raw materials is listed in Table 1.

Table 1. Chemical composition of raw material used for ceramic fabrication.

H_2O/mass %	Ig. Loss/mass %	Fe_2O_3/mass %	$ClSO_4$/mass %	MnO/mass %	SiO_2/mass %	CaO/mass %
0.06	0.17	99.08	0.054	0.52	0.019	0.012

The powder was fabricated into specimens by pressing gently into an iron mold. After most of the air was removed, the pressure was increased up to 3 MPa/cm^2. The powder was then subjected to a firing process up to 1320 °C and cooled to room temperature, and allowed to rest for 10 days. Four kinds of the samples with thicknesses of 20, 30, 40, and 50 mm were prepared for the accurate measurement of the radiation shielding.

The physical properties of the samples were analyzed at the Okayama Ceramics Center, Japan. The specific gravity and apparent porosity were measured according to Japanese Industrial Standards (JIS R2205). The cold compressive strength, modulus of rupture, and refractoriness were measured based on the standards JIS 2206, JIS R2213, and JIS R2204, respectively. The thermal conductivity was measured by the laser flash method. The coefficient of linear expansion was measured at a heating rate of 4 °C/min from 990 °C to 1000 °C.

To determine the chemical properties of the sample, X-ray diffraction analysis was performed at the Tokyo Metropolitan Industrial Technology Research Institute, Japan. Y.MG452 generator and Y.TU 450-D02 X-ray tube (Yxlon International GmbH, Hamburg, Germany) were used as X-ray source, and diffracted X-rays were measured by the RAMTEC-1000D ionization chamber irradiation dosimeter (TOYO MEDIC Co. Ltd., Tokyo, Japan). The lead equivalent of each sample was determined on the attenuation rate curve created from four different standard lead plates.

The microstructure of the sample was observed with the help of field-emission scanning electron microscopy (FE-SEM, JSM-6490, JEOL Co. Ltd., Tokyo, Japan) at the Okayama Ceramics Center, Japan. Prior to observation, the samples were polished to a mirror-finish and etched by 5% hydrofluoric acid solution for 30 s.

2.2. Gamma Radiation Spectroscopy of the Iron (III) Oxide Ceramic

A narrow beam of gamma rays from 3.66×10^7 Bq Cs-137 or 1.63×10^6 Bq Co-60 sealed radionuclide sources was irradiated onto the ceramic samples and the high-resolution gamma spectra were measured by Falcon 5000TM detector (Mirion Technologies Inc., San Ramon, CA, USA). The calibrated detector was programmed to record the spectra for 300 s for each measurement. Detailed measurement procedures and apparatus used have been described in the official report of Savannah River National Laboratory (SRNL-TR-2015-00244).

The linear attenuation coefficients were determined by the following equation:

$$I = I_0 e^{-x}$$

where μ is the linear attenuation coefficient (cm^{-1}) and I is the number of uncollided photons detected when a sample of thickness x cm was placed in front of the detector. I_0 is the number of photons without any sample.

2.3. Dosimetry of The Iron (III) Oxide Ceramic by a Low Scatter Irradiator

The penetrating dose through the sample was measured by a low-scatter irradiator (LSI: Model N40, Hopewell Designs Inc., USA). Sealed 2.62 × 10^{12} Bq Cs-137 and 6.03 × 1010 Bq ^{60}Co were used as photon sources, and 8.51 × 109 Bq Cf-252 was used as a spontaneous fission neutron source. A RO-20 ion chamber survey meter (Thermo Fisher Scientific Inc., Waltham, MA, USA) was used for measuring the photon dose rate. The Rem500 neutron survey meter (Far West Technology Inc., Goleta, CA, USA) was used for neutron detection. Detectors were placed at a distance of 74 cm from the radiation sources. Detailed dosimetry procedures and the apparatus used have been described in the official report of Savannah River National Laboratory (SRNL-TR-2015-00244).

3. Result and Discussion

3.1. Fabrication of Novel Iron (III) Oxide-Based Brick and Analysis of its Physical Properties

Although we first intended to manufacture bricks capable of radiation shielding, it is equally important that their physical properties are suitable for use as regular building materials, to avoid the cumbersome preparation and brittleness of concrete or concrete with an inserted iron plate. As previously mentioned, common ceramic bricks have a poor radiation shielding capacity as compared with that of concrete [4]. Hence, we aimed to produce ceramic material from raw materials containing a considerable amount of iron, which is cheap and is expected to be an effective radiation shielding material.

As magnetite (Fe_3O_4) and hematite (Fe_2O_3) have been used in the past for the production of bricks suitable for heat storage with sufficient bending strength [7], we used nearly 99% Fe_2O_3 (Iron (III) oxide) purified from the waste material of steel sheet production. The precise chemical composition of the raw materials is shown in Table 1. X-ray diffraction analysis (Figure 1) revealed that the peak positions (sensor angle of the detector) from the main ingredient Iron (III) oxide did not change after firing, indicating that the micro crystal structure of Iron (III) oxide was maintained even after firing. The field-emission scanning electron microscopy shows that the fibrous structures composed of small particles in raw Iron (III) oxide materials (Figure 2A) develop into large, smooth pebbles similar to a stone wall (Figure 2B). The uniform size of these pebbles in the ceramic indicates a normal grain growth during heat treatment [8]. Table 2 presents the physical properties of the resultant ceramic material. It is seen that the ceramic has a physical strength exceeding that of concrete and a high bulk density close to the true specific gravity of Iron (III) oxide (5.24). These physical properties attest to the suitability of the ceramic to be used as a basic building material.

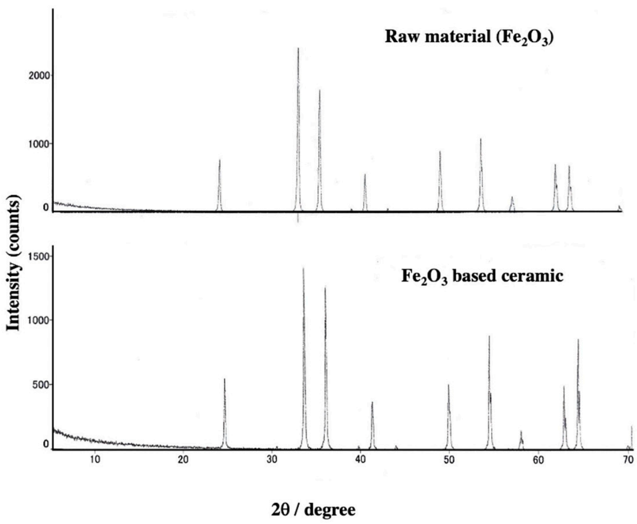

Figure 1. X-ray diffraction profiles of Iron (III) oxide raw material and fired ceramic.

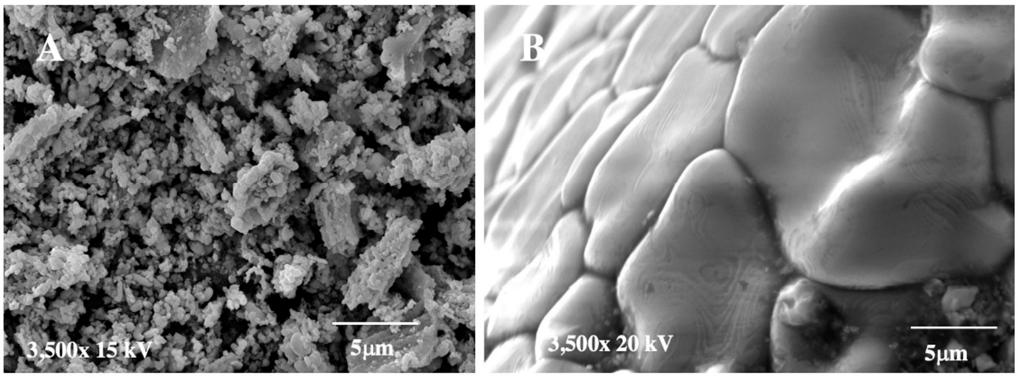

Figure 2. Scanning electron micrographs of Iron (III) oxide raw material (**A**) and fired ceramic (**B**).

Table 2. General physical properties of the Iron (III) oxide-based ceramic.

Physical Property	Typical Value
Specific gravity	4.9
Apparent porosity	1.0%
Cold compressive strength	200 MPa (2000 kg f/cm^2)
Modulus of rupture	20 MPa (200 kg f/cm^2)
Thermal conductivity	4.26 W/(m K)
Coefficient of linear expansion	1.14% (1000 °C)
Refractoriness	SK26

3.2. Radiation Shielding Performance of the Iron (III) Oxide-Based Brick

Peak energy counts representing the total energy of the uncollided photons through the various thicknesses of the ceramic samples are shown in Table 3. The attenuation coefficients were calculated from these raw integral counts (bottom of Table 3). The μ values of the samples for ^{60}Co photons are approximately 40% of those of lead [2], 60% of that of stainless steel [2], twice that of concrete [6] and almost the same as those of the heavy concrete specifically made for radiation shielding [6,9]. Commonly used bricks mostly show a μ of approximately 0.1 [4], indicating the superior radiation shielding capacity performance of this iron (III) oxide-based brick.

Table 3. Peak energy counts and the calculated linear attenuation coefficients of the Iron (III) oxide-based ceramic.

Thickness of Sample (cm)	Raw Counts and the Calculated Linear Attenuation Coefficients		
	1332 keV (^{60}Co)	1173 keV (^{60}Co)	662 keV (^{137}Cs)
0	4.11×10^3	4.63×10^3	3.02×10^5
2.0	2.34×10^3 (0.282) *	2.62×10^3 (0.285)	1.44×10^5 (0.370)
3.0	1.82×10^3 (0.272)	1.97×10^3 (0.285)	9.86×10^4 (0.373)
4.0	1.49×10^3 (0.254)	1.56×10^3 (0.272)	7.30×10^4 (0.349)
5.0	1.11×10^3 (0.262)	1.18×10^3 (0.273)	4.91×10^4 (0.329)

* Linear attenuation coefficient (μ) calculated by the equation in section 2.2 is indicated in parentheses. Mean values of μ for 1332 keV, 1173 keV, and 662 keV are 0.268, 0.279, and 0.355, respectively. The calculated HVL values for these mean μ values are 2.58, 2.48, and 1.95, respectively.

Penetrating doses were measured in an irradiation chamber designed to minimize the scattered radiation from any other material placed between the radiation source and the survey meter. The measured gamma dose rates are indicated in Table 4 along with those of the comparator materials. For the gamma rays from 0.6 to 1.3 MeV emitted from ^{60}Co and ^{137}Cs, the ceramic showed expected and sufficient reduction of the penetrating dose in comparison with that of stainless steel of same thickness. It was twice as effective as concrete. However, the dose rate for neutrons through the ceramic was comparable with that of concrete (Table 4). High-energy electron linac greater than 10 MeV is known to emit photoneutrons and this may occasionally affect the radioprotection of the linac facility [10]. Therefore, the shielding capacity of the iron (III) oxide-based ceramic against neutrons is an additional merit.

Table 4. Dose rate measurement of the Iron (III) oxide-based ceramic for gamma ray and neutron from the indicated radiation sources.

Material	Thickness (cm)	^{60}Co (mSv/h)	^{137}Cs (mSv/h)	^{232}Cf (mSv/h)
Bare	0	3.5	43.5	1.55
Fe_2O_3 based ceramic	2.0	2.5	29	2.4
Fe_2O_3 based ceramic	3.0	2.1	22.5	2.2
Fe_2O_3 based ceramic	4.0	1.7	17.5	2.0
Fe_2O_3 based ceramic	5.0	1.4	13.9	1.7
Stainless steel	5.08	0.7	5.0	1.05
Lead	5.08	0.2	0.7	1.35
Concrete	4.75	2.4	27.0	1.55

3.3. Use of The Iron (III) Oxide-Based Brick as A Construction Material for Clinical Radiotherapy Facility

The use of this iron (III) oxide-based brick as a building material for the shielding wall of the linac room of a hospital is illustrated in Figure 3A. Instead of the ordinally wall made by driving concrete into formwork lined with iron plate, the bricks (Figure 3B) were piled up along with iron plate. The leakage dose rate measured at point A in Figure 3A (distance from the electron target is 1.9 m, including the 60.1 cm wall of the brick) is 314 µSv/3 months, less than the prescribed limit (1.3 mSv/3 months) of the controlled area boundary. The highest leakage dose rate recorded was 999 µSv/3 months at point B in Figure 3A. In this case, the bricks were piled up as in Figure 3C to form a rigid shielding wall. The construction was carried out just by manual stacking of the bricks, which was ideal for the hospital with limited space and a short construction period as shown in Figure 3D. In particular, the seismic strength of the iron (III) oxide-based brick (200 MPa) measured by the JIS R2206-1method exceed that of concrete (20–30 MPa).

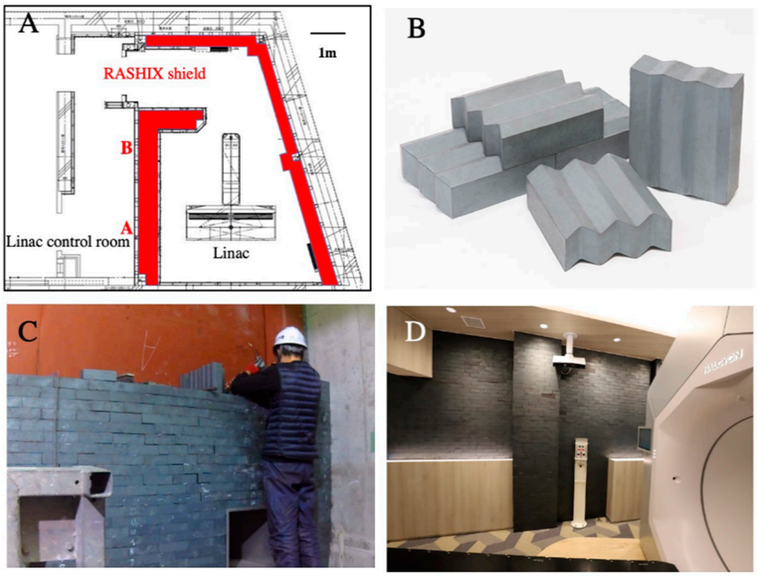

Figure 3. Visual images of Fe_2O_3 based ceramic bricks used for protection shield in linac room. Shields constructed by the Iron (III) oxide-based ceramic bricks were shown in red.

Th iron (III) oxide-based ceramic could be formed into thinner tiles, which were used for the radioprotection of the disaster restoration office of the town hall. Tiles set into the iron frame opened when used. These ceramic shadings are expected to reduce the ^{137}Cs derived gamma rays in the event of a radiation accident of the nuclear power plant.

4. Conclusions

We developed a ceramic product made mainly from iron (III) oxide (Fe_2O_3). The μ values of the ceramic for ^{60}Co photons are approximately 40% of that of the μ of lead and twice that of concrete. The penetrating dose of the ceramic is approximately twice of that of stainless steel and half of concrete. These data suggest that this ceramic material, with a thickness half of that of concrete, will be as efficient. This was confirmed by using this brick as a building material for the shielding wall of the linac room. Although the shielding effect of the iron (III) oxide-based ceramic brick is less than that of lead, the material is non-toxic, very stable and non-rusting, sufficiently hard even at a high temperature, and easy to fabricate into various forms. We named this novel ceramic material RASHIX (RAdiation SHIelding ceramiX) and all these features indicate the possibility of a wide use of RASHIX as construction or shading materials for any protection purposes from radiation.

Author Contributions: H.M. and Y.M. provided the experimental platform and prepared all the materials and equipment. Y.O. set up plans to measure radioactivity and analyzed the related data. H.M. and T.K. analyzed all the experimental data and wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the present work.

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