

Microwave decomposition in the recycling of gadolinium from waste contrast agents

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Unconsumed gadolinium-based contrast agents used in magnetic resonance imaging become medical waste after application. Such a waste is a mixture of plastic, glass, and the contrast agent itself and is usually burned in a hospital incinerator. Due to this, further recyclable materials are lost, as well as gadolinium, which is a valuable industrial commodity. This work is focused on the possibilities of recycling waste containing gadolinium, when seeking optimum conditions for converting the gadolinium complex into the nitrate form applicable to further processing. The respective procedure is compared with the commonly used incineration of medical waste in terms of environmental impacts. An LCA study comparing such ecologic aspects of these two product systems was developed. The current predominance of fossil sources in the composition of the energy mix in the Czech Republic is the reason for the less favorable assessment of the newly proposed procedure.

Keywords: Contrast agents; Gadolinium; Microwave digestion, ICP-OES; LCA study

Introduction

In the last 40 years, there has been considerable technological progress in the field of medical imaging technologies. In particular, magnetic resonance imaging (MRI) has become a widespread tool for the early diagnosis of various diseases. In order to increase the resolution of magnetic resonance images, so-called contrast agents (GBCA) using specific, paramagnetic properties of gadolinium were introduced into medical practice at the end of the 1980s. However, their use has

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led to an increase in anthropogenic pollution of the environment with this metal, as patients excrete the administered contrast material from their bodies and conventional wastewater treatment technologies are unable to effectively capture these substances. In the 1990s, gadolinium of anthropogenic origin had first been detected in the surface water in Berlin and linked to wastewater discharged from medical facilities with magnetic resonance imaging. GBCAs enter the aquatic environment in an unmetabolized form in the urine of patients with hospital wastewater [1,2]. The decontamination processes used in wastewater treatment plants are practically ineffective in degrading GBCA and the result is the presence of these substances in surface, underground and drinking water. The toxicity of the Gd^{3+} ion is generally known, the possible risks of GBCA are currently being discussed and compared with the actual benefit to society (health care). The accumulation of GBCAs or their transformed forms in aquatic organisms represents their entry gate into the food chain with the final consumer – a man [3,4].

Since 1988, when gadolinium-based contrast agents debuted in magnetic resonance imaging, by 2020, more than 450 million doses of GBCA have been administered worldwide. The conducted studies work with the assumption that an average of 1.2 g of Gd is consumed per dose. Taking into account the number of MRI examinations performed with GBCA, 540 tons of Gd were used for medical purposes only in 30 years. This amount converted to one year represents 5 % of the annual world production of Gd (400 tons/year). Since the beginning of the new millennium, the number of MRI examinations performed with GBCA has increased almost exponentially (Figure 1) [5–8].

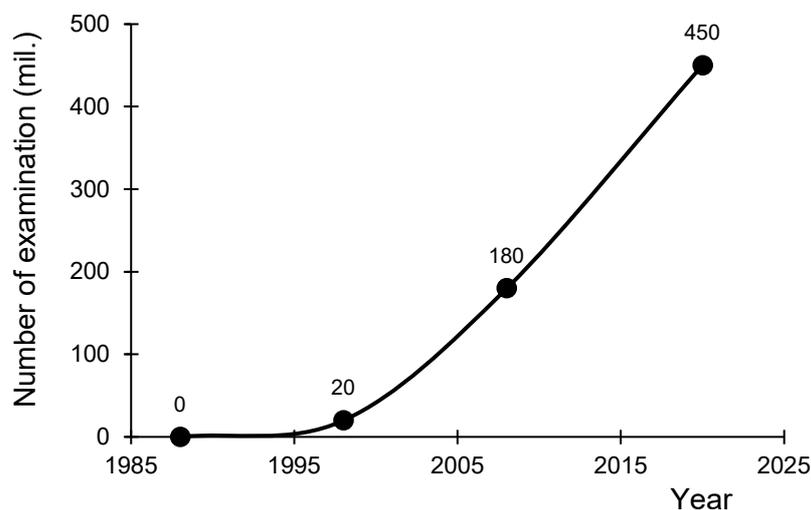


Fig. 1 Consumption of contrast agents for magnetic resonance imaging [5,7]

Ognard et al. (2021) in their research involving 18 MRI facilities in France, USA and Singapore found that 5.98–14.65 % of GBCA remains unused (around 11 % on average) depending on the package volume and especially upon the individual dosing for each patient.

A part of the GBCA enters the sewers via urine and then into the city's WWTPs, where it is removed with a very low efficiency. Packaging materials are incinerated in hospital installations after the GBCA application, even with unconsumed contents [6,7]. It is reported that 250–350 kg of ash, ash and slag remain from 1 ton of incinerated medical waste. In particular, fly ash, which represents about 10 % of the total amount of solid flue gas, is dangerous because it contains heavy metals and solid products of incomplete combustion [9–11]. Gadolinium is partly contained in fly ash, partly in the melt of glass and other medical equipment (so-called clinker), from which it is not possible to further recycle it due to technical and economic difficulties [6].

The incineration of hospital waste containing GDCA irreversibly loses a large quantity of gadolinium every year that could be recycled using alternative methods of handling unused contrast agents. The recovery of gadolinium and other rare earth elements (REEs) present in fly ash by electro dialysis was of interest by Couto et al. The whole process consisted of three steps: (i) the conversion of REEs from the solid matrix to the liquid phase, (ii) the transfer of REEs to the cathode through the cathexis membrane, and finally (iii) the isolation of REEs from the cathodic area. The experiment was carried out on bituminous and anthracite ash with a Gd content of 3.9; respectively, 9.4 mg/kg with efficiency for light REE 70–99 % and for heavy REE (Gd) 17–88 % [12].

A possible procedure for obtaining Gd from waste contrast agents is to convert it to the inorganic form, which is a product of the processing of mined raw materials and then used technologically. For the decomposition of organic substances, microwave mineralization is commonly used, in combination with acid hydrolysis and the subsequent oxidation of intermediate products. The speed of the decomposition reaction is mainly dependent on the temperature ensured by microwave heating. The microwave electromagnetic radiation generated by the magnetron causes heating of the material via the vibrations of the molecules, movement of the ions, and the rotation of the dipoles. Mineral acids, namely HNO_3 , HCl , HClO_4 , HClO_3 , HF , and H_2SO_4 or their mixtures, respectively, can be used as decomposition agents, when the whole disintegration process can be supported by the addition of a small amount of H_2O_2 . For safety and economic reasons, HNO_3 is most often used as a decomposition agent, or a mixture of HNO_3 and H_2O_2 . The resulting products are CO_2 , H_2O and, depending on the choice of decomposition agent, the relevant dissolved salts of the metals present and gaseous oxides, such as NO_x or SO_2 . The advantage of microwave decomposition compared to conventional heating methods is an increase in economic efficiency due to a significantly shorter decomposition time, saving acids and reducing pollution of the material by the external environment [13,14]. To date, no studies have been published dealing with the microwave decomposition of GBCA into basic inorganic compounds for Gd reuse. Thus, there is no generalized methodology for microwave wet decomposition due to a wide variety of matrices.

However, there is considerable space for innovation and further exploration. Microwave mineralization may represent an interesting alternative to conventional GBCA waste management techniques (incineration, gasification) [15].

The aim of this study was to optimize the method of microwave decomposition of contrast agents and its use in the processing of real samples of rinse water containing contrast agents. The data obtained were the basis for the construction of models within the framework of a life-cycle assessment study that compared alternative and conventional methods of handling contrast agents in terms of their impact on the environment.

Materials and methods

Reagents, standards, samples

Ultrapure water produced by Ultra Clear GP TWF UV UFTM (with conductivity 0.07 $\mu\text{S}/\text{cm}$; Evoqua Water Technologies, Günzburg, Germany) was used for all the experiments. Working solutions were prepared from $\text{Gd}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ (p.a. grade; Sigma Aldrich, Co., St. Louis, MO, USA), Gadovist® contrast agent injection solution, Gadobutrolum 1 mmol/mL (604.72 mg/mL), lot number: KT0934P (Bayer Pharma AG, Berlin, Germany) and 65% HNO_3 (special grade "p.p." (for semiconductors); PENTA s.r.o., Prague, Czech Republic). Acetone was used to dry the containers for microwave mineralization. (p.a.; Lach-Ner, Neratovice, Czech Republic) and 96% (v/v) ethanol (p.a.; Lech-Ner).

Urea PND 31-762-64 (p.a.; Lachema, o.p., Brno, Czech Republic) and single-element certified standard solution $\text{Gd} 999 \pm 4 \mu\text{g}/\text{mL}$, 4 % HNO_3 , 140-051-645 (PlasmaCAL, SCP Science, Baie-D'Urfe, Quebec, Canada) were used to prepare the calibration standards. The calibration series for ICP-OES determination of gadolinium was prepared by diluting a standard Gd solution with a concentration of 1 g/L to solutions with a content of 10; 5; 1; 0.5 and 0.1 mg/L. To stabilize the Gd standards, depending on the volume of the volumetric flasks used for the preparation of the calibration series, 1% HNO_3 was used. The calibration series for the use for inductively coupled plasma emission spectrometry (ICP-OES) determination of carbon (100, 50 and 10 mg/L) was prepared from a solution of concentration of 1 g/L carbon (by dissolving 1.25 g of urea in 250 mL of demineralized water). Due to an instability, calibration solutions of desired concentration were prepared before each analysis.

During the proper work, water from the rinsing of used GBCAs packages supplied by three radiological departments (Faculty Hospital in Hradec Králové, Pardubice Hospital and private clinics Multiscan s.r.o., Pardubice, Czech Republic) was processed. Samples of waste GBCAs were obtained as a part of bachelor thesis [16] and used for the purposes of this work as real samples with the permission by the author.

10 vials representing 4 different GBCAs Gadovist®, ProHance®, Dotarem® and Clariscan® were selected from the sample pool (see Table 1). The rinse waters were concentrated from the original volume of 50 mL by evaporation on a hot plate to a half in the volume before further use.

Table 1 Rinse water samples with GBCA [16]

	GBCA	Original packaging		type*	Rinse
		V [mL]	c [mol/L]		c [mol/L]
1	Gadovist®	30	1	B	5.446
2		7.5		S	5.331
3	ProHance®	17	0.5	S	12.47
4				S	9.584
5	Clariscan®	15	0.5	S	6.371
6				S	2.065
7	Dotarem®	10	0.5	B	3.554
8				B	5.744
9				B	4.598
10				B	4.101

Legend: * S – syringe, B – bottle

Instrumentation

In the work, equipment for the preparation of ultra-pure water Ultra Clear GP TWF UV UF TM (Evoqua Water Technologies, Germany) plus laboratory dryer UM 400 (Mettler, Schwabach, Germany), and heating plate Stuart CB300 (BioCote, Coventry, UK) were used. The default operating conditions for the SpeedWave MWS-2 microwave digester (Berghof Products + Instruments GmbH, Eningen, Germany) were as follows: 1st step temperature 170 °C for 15 min at 80 % power, 2nd step 200 °C, 20 min, 80 %, 3rd step 50 °C, 25 min, 40 %. Determination of carbon and gadolinium was performed using an Integra 6000 inductively coupled plasma optical emission spectrometer (ICP-OES, GBC Scientific Equipment Pty. Ltd., Keysborough, Australia) under the conditions: auxiliary gas flow, 0.4 L/min; plasma gas, 10 L/min; carrier gas, flow 0.52 L/min; power, 1000 W; observation height, 5 mm; signal reading, 1s; background correction at a fixed point, pump speed, 10 rpm; signal measurements in 3 replicates. Spectral line of 336.223 nm, background correction at –0.045 nm, photomultiplier voltage of 560 V were used to determine gadolinium, spectral line of 193.032 nm, background correction at 0.018 nm, photomultiplier voltage of 600 V were the parameters of choice for carbon determination.

Detection limit expressed as a concentration corresponding to three times the standard deviation (criterion 3σ) of noise at the background correction site was 0.045 mg/L for gadolinium, 0.15 mg/L for carbon.

Data were processed using Microsoft Apps for large organizations (Microsoft Corporation, Redmond, WA, USA) and GaBi Professional software package version 10.7.0.183 (Sphera®, Berlin, Germany).

Results and discussion

Gadolinium-based contrast agents represent a significant part of Gd use on a global scale. The recycling of waste GBCAs can be an economically interesting secondary source of Gd, which would reduce the demand for mining REE ores. At the same, the introduction of anthropogenic gadolinium into the environment through the incineration of hazardous waste would be limited. Inorganic gadolinium salts are the result of processing ores containing gadolinium and other REE. In this form, REE are ready for further use in a wide range of industry or high-tech production and are currently referred to as "vitamins of industry". The presumed product of the conversion of Gd from contrast agents to an inorganic form by means of nitric acid under the support of a microwave (MW) field is gadolinium trinitrate hexahydrate (Figure 2).

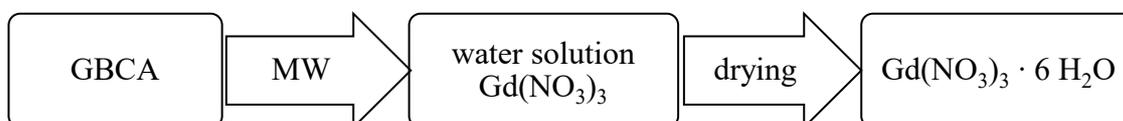


Fig. 2 Scheme of the conversion of Gd from GBCAs to a simpler inorganic form

The resulting optimization data together with the data from Kubitová [16] is used in the modelling of product systems of MW decomposition and conventional combustion in GaBi software (Sphera®) with the aim of comparing them in terms of life-cycle assessment. The main outputs of the experimental part are: optimization of MW decomposition, discussion on the effectiveness of the method for processing real samples of rinse water and Life Cycle Assessment Study (LCA) by comparing the current management of GBCA with recycling of Gd and when using MW decomposition in terms of environmental impacts.

Optimization and efficiency of microwave decomposition

During the microwave decomposition of organic substances, an exothermic reaction occurs often in the temperature range of 130–150 °C, depending on the amount of decomposition agent and the chemical structure of the decomposed substance.

The amount of decomposed organic matter and thus the amount of carbon are also important. The formation of reaction gases, especially CO₂ and NO_x from the decomposition agent, also contributes to the increase in vapor pressure inside the container. As a part of the work, the quantity of decomposition agents, decomposition temperature, decomposition time were optimized with the aim of the least possible consumption of energy and decomposition agents and with nitric acid as test reagent.

The efficiency of the procedure, i.e. the degree of conversion of the organic matter to the inorganic form, was controlled by analyzing the amount of carbon in the digested sample, when, after successful decomposition, the organic matrix is converted to carbon dioxide, released in the gaseous form. The residual carbon content was monitored using ICP-OES, which determined the total carbon and cannot distinguish the degree of conversion from organic to inorganic forms. Due to the use of model samples containing only the selected contrast agent alone, it was assumed that this procedure would be satisfactory. To confirm this assumption, the organic carbon content of some samples was checked (FormacsHT/TN, Q-Skalar Analytical B.V., Breda, The Netherlands). The dependence of the carbon content determined by ICP-OES on the standard determination of organic carbon content (TOC) is expressed by the relation: $c_{\text{ICP-OES}} = 0.806 c_{\text{TOC}} + 0.0851$ ($R^2 = 0.9802$). Carbon determination using ICP-OES can be performed together with gadolinium determination and represents a time and material savings. A possible systematic error in the ICP-OES determination of carbon could be caused by the dissolution of atmospheric CO₂ in the water used.

To optimize the process of microwave decomposition, an injection solution of Gadovist® with a concentration of 1 mol/L was used in an amount of 222 µL, which theoretically corresponds to 100 mg of gadolinium nitrate hexahydrate. The decomposing agent was 65% nitric acid in amounts of 5, 4, 3, 2, 1, 0.8; 0.6; 0.4 and 0.2 mL. The decomposed samples were dried for 10–20 hours at a temperature of 110 °C, then the product was weighed and subsequently dissolved in a defined volume of demineralized water to prepare a sample for the determination of carbon and gadolinium. The influence of the amount of nitric acid used on the efficiency of the conversion of the organic form of GBCA into an inorganic one was evaluated based on the determination of carbon. This is documented in Figure 3, from which it can be seen that, for a reliable course of the process, it is advisable to use a volume of acid larger than 0.4 mL. The break in the curve occurred around 0.6–1 mL of 65% HNO₃.

The volume of 0.6 mL, at which the efficiency of decomposition of Gadovist® reached more than 96 %, was then further used for optimization of the working conditions. The yield of the ICP-OES determination of carbon is presented in Table 2 together with the recovery for gadolinium and based on this it has been possible to evaluate the losses of the entire process. More specifically, by weighing the product, one could estimate the amount of water in the resulting form of gadolinium nitrate (see again Table 2).

Table 2 Evaluation of microwave decomposition efficiency in optimization procedure

Optimization conditions			Recovery [%]			
			Carbon	Gadolinium	Gd(NO ₃) ₃ · 6 H ₂ O	
Volume 65% HNO ₃ [mL]		5	99.0	94.5	91.2	
		4	99.6	95.8	93.0	
		3	98.7	92.6	95.8	
		2	99.8	100	92.2	
		1	99.8	97.1	78.6	
		0.8	96.5	88.0	69.8	
		0.6	96.1	89.3	77.2	
		0.4	88.35	91.32	76.0	
T [°C] Steps I., II., III.*	0.6 mL 65% HNO ₃	I. 130, II. 160, III. 50	95.4	95.2	83.4	
		I. 150, II. 180, III. 50	98.4	89.0	86.2	
		I. 170, II. 200, III. 50	99.1	83.1	91.0	
		I. 190, II. 220, III. 50	100	85.6	86.2	
Time [min] Steps I., II., III.	0.6 mL 65% HNO ₃	I. 5, II. 10, III. 15	98.6	92.3	89.3	
		I. 10, II. 10, III. 30	99.4	83.6	99.4	
		T [°C]: I.190, II.220, III.50	I. 15, II. 15, III. 20	99.8	79.8	86.6
		I. 15, II. 20, III. 25	100	85.6	86.2	

*I., II., III. – Steps of the decomposition MW procedure

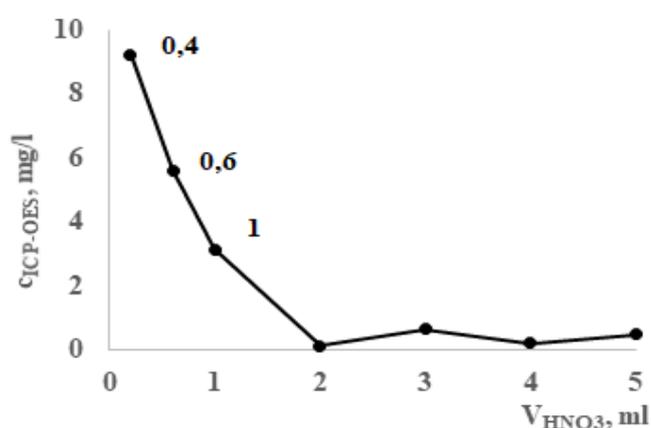


Fig. 3 Effect of the amount of nitric acid on the efficiency of GBCA decomposition

The temperature conditions of the individual phases of microwave decomposition (indicated by Roman numerals, dosed with 0.6 mL of 65% HNO₃) are also summarized in Table 2, along with the recoveries for the parameters monitored. The first and second temperature sequences were particularly important, i.e. the heating and decomposition phases, during which one could attain the complete decomposition of the sample. It is obvious that the best results were achieved with the temperature program I 190 °C, II 220 °C, III 50 °C, which was due to the decomposition temperature of 220 °C, at which the maximal pressure inside the decomposition vessel could be reached when nitric acid had been used as the decomposition agent.

The decomposition time was evaluated for the optimal amount of acid and for optimal decomposition temperatures (given also in Table 2). The time program with the duration of three successive steps, $\tau(\text{I}) = 15$ min., $\tau(\text{II}) = 20$ min., and $\tau(\text{III}) = 25$ min appeared to be the most effective, resulting in an efficiency of organic carbon decomposition close to 100 % and gadolinium recovery above 85 %. In shorter programs, the device was not able to raise the temperature of the given steps in time, so the samples had to be exposed to the decomposition temperature for a shorter time than that originally programmed.

Decomposition and analysis of rinse waters

Selected samples of rinse water (in a volume of 50 mL) were concentrated on a ceramic hotplate to a half of volume and 20 mL used for MW digestion. The effectiveness of the decomposition of contrast agents were monitored as a carbon content (ranged between 60–90 %) and for gadolinium content (ranged between 30–99 %). The main reason was the use of a decomposition program optimized for the Gadovist® solution.

The lower yield was probably due to the insufficient amount of nitric acid used for decomposing other GBCAs. For Gadovist waste samples, the recovery rate for carbon was 74–92 %, for gadolinium 79–100 %. Thus, the conditions should be adjusted with regard to the GBCA requiring the highest content of the decomposition agent.

Environmental impacts of GBCA waste disposal

To compare conventional and alternative treatment with GBCAs in terms of environmental effects, an LCA study was developed using the software GaBi Professional version 10.7.0.183 (Sphera®).

Objectives and scope of the LCA study

GBCAs used in radiological examinations for enhancing the MRI resolution consume approximately 5 % of global gadolinium production and, due to their stability, pose a burden on the environment with the risk of bioaccumulation in aquatic biota and transport through the food chain. The released gadolinium ion is highly toxic to the human organism. GBCAs are sold and distributed to healthcare facilities in one-off packaging. The entire amount of GBCA is not used due to the individual dosage according to the patient's body weight. Unused medicine cannot be used any further and, together with the packaging, it becomes hazardous waste that is incinerated and then landfilled in special locations and must be disposed of in accordance with Czech Act No. 541/2020 Coll. about waste. A comparison of conventional incineration disposal and alternative microwave decomposition of rinse water with possible subsequent recycling of gadolinium in terms of environmental impacts provides a valuable information especially for specialists dealing with the recycling of economically interesting chemical elements and substances.

The functional unit of the LCA analysis is **GBCA-containing waste**, which includes the unused contrast agents and clear glass and packaging plastic. The reference flow is **1 kg** of this waste, which can be quantified on the basis of data from three MRI workplaces in the East Bohemian region [16]. The boundary of the system is determined "from the gate to the grave". Since both GBCA management models operate with 1 kg of GBCA-containing wastes as the main and only input, possible joint steps (extraction, leaching, Gd refining, transport, pretreatment and synthesis of contrast agents) are not included in the product systems. The syntheses of the individual types of GBCA are protected by trade secrets or are part of patents unavailable to the wider public. Figure 4 illustrates an alternative procedure for handling waste GBCAs.

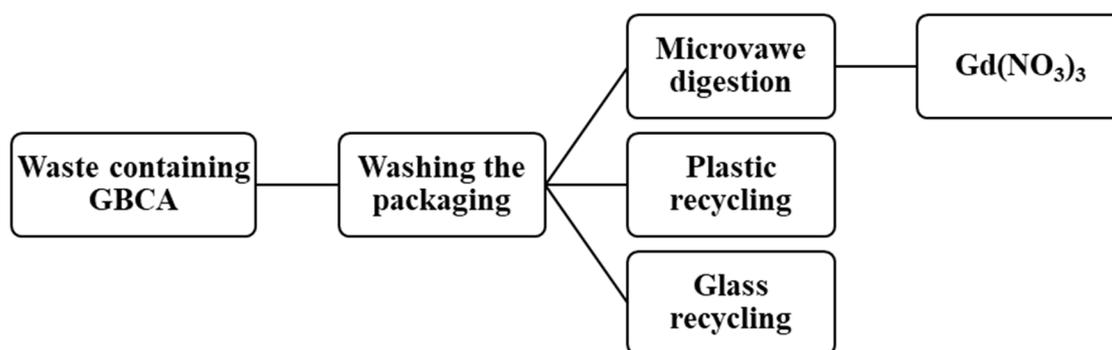


Fig. 4 Alternative treatment of GBCA waste

By rinsing the unused content of contrast agents from the original packaging, their very diluted solution is usually being obtained. It is then concentrated and decomposed in the presence of nitric acid in a microwave device to produce water

vapor, carbon dioxide, nitrogen oxides and gadolinium nitrate, which can be considered to be the basic form of gadolinium suitable for reuse. Washed packaging cannot be reused for legislative reasons (pollution with biological material); however, it is possible to sort out glass and plastic with subsequent recycling of these commodities after removal of residual contrast agents, when considering them as secondary sources of raw materials. With the conventional method of disposal by incineration, no secondary product or raw material is created, only a large amount of flue gas, ash, and slag are released and must be landfilled.

The diagram of the life cycle of gadolinium used for GBCA is illustrated in Figure 5 as a combination of a linear chain for incineration of waste substances (black part of the diagram) and a recycling loop of reuse (white blocks). The greyed-out steps from "Gd(NO₃)₃" to "unused GBCA" and "accumulation in the environment" are common to both of these waste management practices.

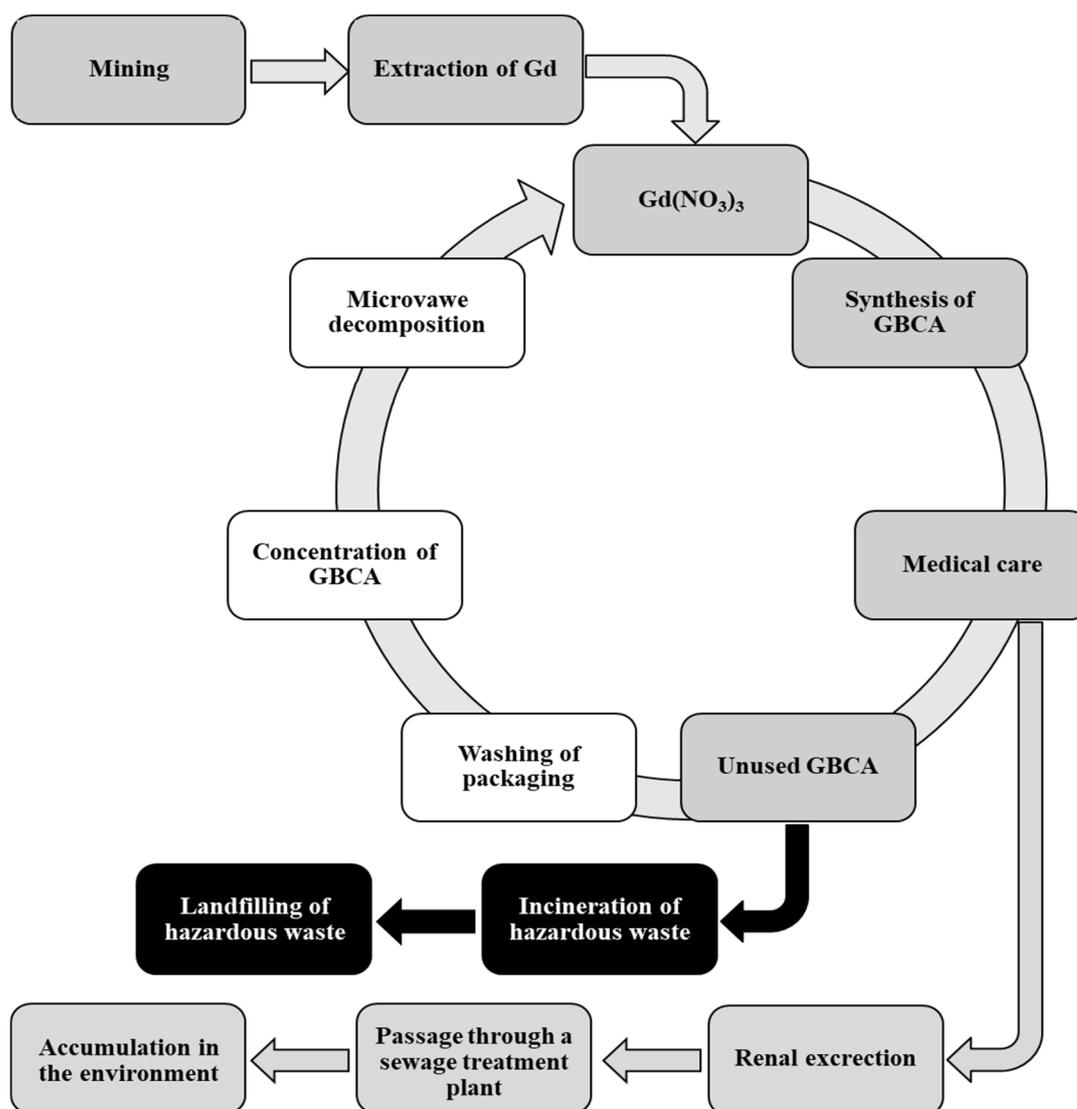


Fig. 5 Life cycle of gadolinium used in GBCAs

Inventory control of product systems

The aim of the inventory phase is the enumeration of all elementary flows of the modelled product systems. Both product systems (Figure 6 and 7 taken from the GaBi software) are dimensioned in such a way as to eliminate steps potentially disturbing the comparability of the final categories of impact according to the methodology chosen or steps being the same for both systems that could be neglected during eventual simplification.

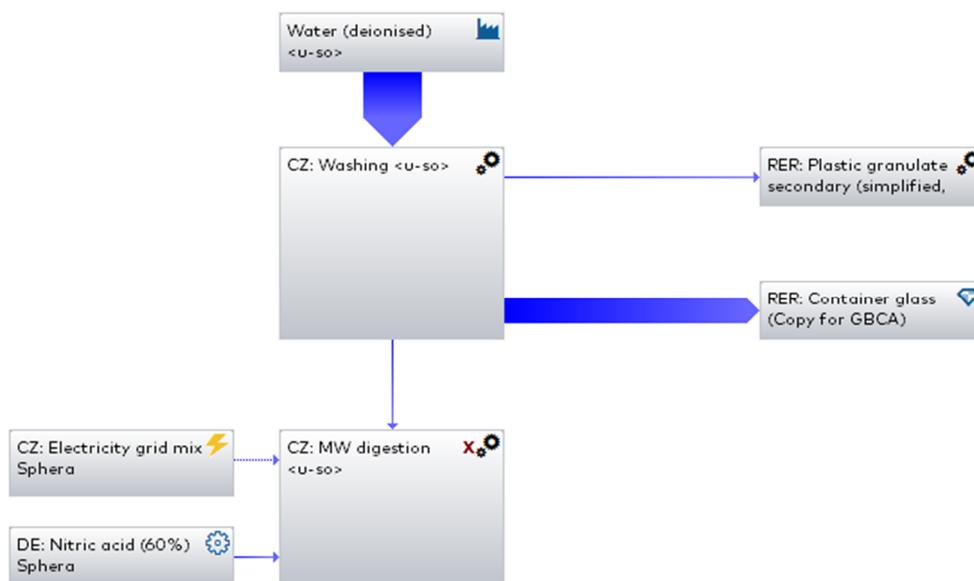


Fig. 6 The product system of MW decomposition of GBCAs

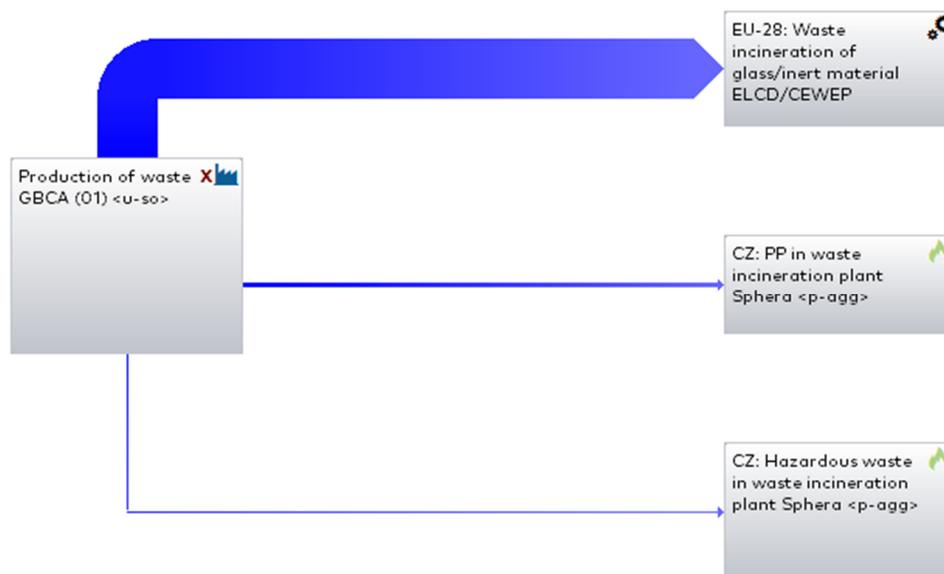


Fig. 7 Product system of GBCA combustion

On the basis of the study [16], the average weight of the packaging was determined to be 25.2 g; therefore, there were approximately 40 pieces per functional unit of 1 kg of the waste with GBCA. 50 mL of distilled water was used

to rinse one used package, i.e. 2 liters of rinsing water per functional unit. The amount of waste gadolinium corresponding to the functional unit was determined based on the knowledge of the concentration in the rinse [16], and its amount, namely 1.9 g on average, a minimum of 0.05 g and a maximum of 5.2 g. The main part of the weight of the packaging is made up in clear inert glass. A small part is plastic, especially the pistons and thumb support, which are made of polypropylene (Table 3). These components are present only in syringes and, due to the demanding process of disassembling the syringe, without the risk of injury or damage to the plastic parts, the syringe was not disassembled, but the ratio of polypropylene to glass was chosen as a qualified estimate, plastic-to-glass = 1 : 9.

The amount of demineralized water, 65% nitric acid, and energy were determined during the optimization of the microwave digestion process. The total weight of demineralized water was defined by the sum of the water consumed during the washing of 40 bottles (2000 g) and the water required for microwave decomposition (238 g). The 65% nitric acid used during the digestions was converted to a mass flow of 60% HNO₃ by the GaBi software database. The energy required for one decomposition cycle was calculated with knowledge of the device's power input (1000 W), the set efficiency, and the time of the individual steps of microwave decomposition (I heating, II decomposition, III cooling).

Table 3 Results of inventory control – conversion of inputs to functional unit

Product system	Gd [g]	Glass [g]	PP* [g]	H ₂ O [g]	60% HNO ₃ [g]	Energy [kWh]
MW decomposition	1.9	900	98.1	4238	53	34.23
Incineration	1.9	900	98.1	0	0	0

*PP polypropylen

Impact assessment

The goal of the third LCA phase is to measurably compare the environmental impacts of product systems and to compare their significance using the impact categories that quantify specific environmental damage based on the elementary flows of the product system. The evaluation of the environmental impacts of both product systems is carried out using the TRACI 2.1 methodology and the impact categories are listed in Table 4. In particular, the midpoint indicators of the impact category are chosen, thus representing equivalent measurable quantities that characterize the potential to cause damage to a certain part of the environment or the entire ecosystem. The degree of damage is calculated by the equivalent of a reference substance or by a special unit defined for these purposes, such as CTUh or PM_{2.5}. The environmental profile of both evaluated product systems was characterized by a set of indicator results of selected impact categories.

Table 4 Survey of results for selected impact categories

Impact category	Unit	Microwave digestion				Incineration			Microwave digestion: NO energy mix	
		CZ: energy mix	DE: 60% HNO ₃	RER: packaging glass	RER: Plastic granulate	total	CZ: hazardous waste in the incinerator	CZ: PP in the waste incinerator		EU-28: incineration of glass
Global warming air	kg CO ₂ ekv	2,04E+01	2,44E-02	1,38E+00	1,23E-02	4,13E-01	2,62E-03	2,95E-01	1,15E-01	2,66E+00
Acidification	kg SO ₂ ekv	4,83E-02	5,95E-05	8,16E-03	2,75E-05	5,87E-04	1,13E-05	4,22E-05	5,33E-04	9,54E-03
Eutrophication	kg N ekv	3,87E-03	1,39E-04	4,09E-04	2,80E-06	1,98E-05	2,06E-07	2,70E-06	1,69E-05	6,30E-04
Stratospheric ozone depletion	kg CFC-11 ekv ³	3,41E-12	1,15E-15	6,48E-14	4,79E-15	8,48E-09	4,04E-17	3,24E-16	8,48E-09	3,13E-13
Fine particulate matter	kg PM _{2.5} ekv ¹	2,67E-03	2,38E-03	8,01E-07	2,92E-04	3,35E-05	8,39E-08	1,40E-06	3,20E-05	3,76E-04
Human toxicity, cancer	CTUh ²	6,82E-09	6,04E-12	6,04E-10	6,18E-12	9,30E-11	3,37E-13	6,24E-12	8,64E-11	4,06E-09
Smog air	kg O ₃ ekv	6,37E-01	9,74E-04	1,20E-01	3,56E-04	9,19E-03	8,95E-05	5,87E-04	8,52E-03	1,42E-01

Legend: ¹ PM_{2.5}, Dust particles with a diameter of less than 2.5 μm;

² CTUh, Comparative Toxic Unit for Human;

³ CFC-11, Trichloro-fluoromethane (chlorofluorocarbons)

Normalization, grouping and weighting steps were not addressed for the purposes of the LCA study. Only the effects of the individual processes of the product systems on the environment were evaluated and compared with each other.

Interpretation

The product systems "Microwave Decomposition of GBCA" and "Combustion of GBCA" were compared and evaluated using a septet of environmental impact categories. Six of the seven impact categories performed worse for the MW decomposition. The main part is the process of electricity production and the "Energy mix" of the Czech Republic. It is generally known that more than 55 % of the Czech energy mix consists of the production of electricity from fossil fuels, mainly brown coal. About further 40 % is a contribution from Dukovany and Temelín nuclear power plants, whereas renewable energy sources occupy only 5–6 % of the total production in the Czech Republic [17].

For the product system of classic waste incineration, the biggest impact was on the incineration of polypropylene. Due to its very small share of the functional unit (98.1 g), it is clear that this is a process with significant impact on the environment. From the point of view of this category, the use of glass as a packaging material is markedly more advantageous in the current method of handling waste containing gadolinium.

Acidification of the soil or water environment turned out to be more disadvantageous for the MW decomposition model, by several orders of magnitude. Again, the effect of the consumed energy in the MW decomposition is crucial. When comparing the impacts of the individual processes, it is interesting to note that the impact of glass recycling is higher than the overall impact on acidification of the conventional waste incineration model.

The rate of ozone depletion based on an equivalent amount of trichlorofluoromethane was higher in the case of conventional combustion, up to a value of 1000 times higher than that of the MW decomposition. The vast majority is occupied by the process of burning glass waste. When considering the 90 % representation of glass in the total amount of waste, this is quite a logical conclusion.

MW decomposition also has a greater impact on the category of dust particles; the largest amount of the fraction with a diameter less than 2.5 μm was created during the production of the electrical energy needed for microwave decomposition. The amount of dust particles in MW decomposition was 100 times larger than that of the incineration of waste containing GBCA.

One of the few categories where the results for both product systems were very similar was the impact category "Human toxicity" in terms of cancer risk. Then, "Comparative Toxicity Unit for Human" (CTUh) expresses the estimated

increase in morbidity in the total human population per unit mass of emitted chemical substance (cases of disease per kilogram of substance), in our case per 1 kg of GBCA waste.

Although MW decomposition was again evaluated more negatively, the CTUh values are so small that 1 kg of waste would result in 1 person suffering from cancer from the total human population in the worst possible scenario.

The last selected impact category "Smog", where the reference substance was the equivalent amount of ground ozone O₃, fared worse again for the MW decomposition model. The processes with the greatest impact on the environment were the production of electricity and recycling of packaging glass for MW decomposition, and the incineration of waste glass for the conventional combustion model.

The product systems "Microwave Decomposition of GBCA" and "Combustion of GBCA" were compared and evaluated using seven environmental impact categories. For six out of this septet, the process of microwave decomposition of contrast agents (MW decomposition) had the greatest impact on the environment. Only in the case of the category of damage to the ozone layer, the impacts were worse for the classic incineration of hazardous waste. Dominance analysis showed that in six out of seven impact categories, the "Energy Mix" process had the greatest impact for MW decomposition. The reason was the high energy demand of microwave equipment and the fact that, in the Czech Republic, the production of electricity is more than 50 % dependent on the burning of brown coal and natural gas, whereas renewable energy sources represent only 5–6 %. If the energy supplied from the Czech distribution network contained more energy from renewable sources, the negative effects of this process on the environment would be dramatically reduced. Furthermore, the process of recycling packaging glass and burning waste from glass and inert material had a relatively high impact. Here, the reason was the large mass proportion of glass per 1 kg of the functional unit (900 g per 1 kg f.u.). The least impact was the hazardous waste incineration process from the GBCA product combustion system, where gadolinium alone (1.89 g Gd) was the mass flow. Due to a very small amount of Gd per functional unit, the environmental impacts of this process were practically negligible. If the energy mix of Norway was used as the model, the results for microwave decomposition were significantly better than for the energy mix of the Czech Republic, due to the greater proportion of the renewable sources of electricity.

Conclusions

It must be stated that the assumption of a smaller environmental impact of microwave decomposition compared to conventional incineration of hazardous waste containing GBCA has not been confirmed and the results turned out to an opposite side. The sensitivity analysis performed did not find inputs in both

product systems, where a small change in the input data would cause a large change in the formulation of significant findings. In the future, it would be advisable to carry out a variation analysis and test a hypothetical scenario where only renewable sources are used as sources of electricity and the new model is compared with the current MW decomposition model. In order to increase the robustness of the study and its completeness, the impacts on the environment can be supplemented in the future by weighting, i.e. by expressing the significance of the impact categories with regard to economic and social aspects. Quantification of the economic and social importance of recycling gadolinium, glass and polypropylene can also be part of the weighing. Such a data could provide a new insight on the problem and initiate a discussion whether an economically interesting model with worse impact results it is more suitable or not for the environment than a model whose output has no source of secondary raw materials, but it is more environmentally friendly. MW decomposition was performed for small volumes of GBCA. If being hypothetically carried out at an operational scale (MW plant for larger volumes), the comparison would probably come out better in favor of MW decomposition.

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