

**Practical Issues for the Description of Chemical Constituents
in Radioactive Waste Packages - 11556**

D. Gründler¹, W. Boetsch¹, C. Haider¹, K. Kugel², P. Brennecke², S. Steyer²

¹Institut für Sicherheitstechnologie (ISTec), P.O. Box 101564, D-50455 Köln, Germany

²Bundesamt für Strahlenschutz (BfS), P.O. Box 100149, D-38201 Salzgitter, Germany

ABSTRACT

In addition to the KONRAD license, which considers mainly radiological risks, a water law permit was issued in order to prevent the pollution of the near surface groundwater. The water law permit stipulates limitations for 10 radionuclides, 2 groups of radionuclides and 94 substances and materials relevant for water protection issues. Two collateral clauses include demands on the monitoring, registering and monitoring of the harmful substances and materials imposed by the licensing authority.

In order to implement the requirements of the water law permit the German Federal Office for Radiation Protection (BfS) as operator of the Konrad repository has developed a procedure, which ensures that all requirements of the water law permit are met and which provides a standardized, easy manageable guidance for the waste producers to describe their wastes.

Principal item of this procedure is a material list, which comprises three types of materials or material vectors together with relevant information and various parameters. The three types of materials or material vectors are basic materials, modules and waste producer specific material vectors. The basic materials are the materials and substances listed in the water law permit and related chemical compounds. Modules are common materials such as concrete or ashes, which are essential waste components. Modules are break down into their basic materials. Waste producer specific material vectors are vectors of modules, which describe main waste streams or batches of waste packages. A particular problem is the treatment of trace impurities. For this, inter alia, the so called declaration threshold values were computed, which allow the distinction between waste component and trace impurity. Another threshold is a lower concentration limit. If this value is not exceeded, the occurrence of harmful materials can be excluded. For the preparation of waste producer specific material vectors BfS has provided a guidance to be applied by the waste producers, which summarizes the necessary information for the application of a waste producer specific material vector. Following this guidance such vector can be prepared in a simple way.

The procedure developed by BfS for the implementation of the water law permit is currently under review by the competent water authority. After getting the approval a manageable procedure will be available allowing the implementation of the procedure to realize the collateral clauses given in the Konrad water law permit at a reasonable level of expenditure.

INTRODUCTION

Based on the Council Directive 80/688/EEC on the protection of groundwater against pollution caused by certain dangerous substances [1] the German Federal Ministry for Justice issued the Groundwater Ordinance [2], which requires a permit for the disposal of waste which may contain materials harmful to the near surface groundwater. Accordingly the licence of the KONRAD repository for radioactive waste with negligible heat generation under the atomic energy act is supplemented by the permit for the emplacement of non-radioactive harmful substances contained in the radioactive waste packages ("water law permit") [3].

In this water law permit limitations for 10 radionuclides, 2 groups of radionuclides and 94 substances and materials relevant for water protection issues are stipulated. In order to examine these limitations two collateral clauses have been stated leading to tasks and responsibilities for the operator of the site (The German federal office for radiation protection, BfS). E. g. the operator has to fulfill the following:

- Monitoring the composition of the wastes to be disposed of.
- Monitoring and recording of all non-radioactive hazardous substances being harmful for the ground water.
- Estimation and recording of waste composition of already existing waste packages.
- Verification of the inventory of harmful substances declared by the waste producers.
- 4 weeks before the disposal of the waste has to be announced to the responsible regulatory authority.
- Annual reports about the non-radioactive hazardous waste contents being disposed of at the KONRAD site.

For more details refer to [4].

The identification of harmful portions of radioactive wastes is an ambitious challenge considering the fact that complete analysis of waste packages should be avoided as far as possible. For this reason a standardized procedure of waste description and declaration was developed. At first the waste producer has to describe his waste in a standard-

ized way. Following this, the operator of the repository has to check this description and to register and balance the materials and substances harmful to water. This procedure is based on a standardized list of materials and a list of containers.

In this contribution practical issues are dealt with on the development and implementation of this standardized procedure for the chemical characterization of radioactive waste to be disposed of in the Konrad repository.

LIST OF MATERIALS FOR THE DESCRIPTION OF THE WASTE

Main issue for the standardized procedure of waste description, declaration and balancing is the list of materials, i.e. a data bank provided by the operator of the repository. This list contains all materials which may occur in the radioactive waste with all their characteristic properties related to the water law permit. Each entry of the list is sought by the operator with the competent water authority and must be approved by this authority from a water law point of view.

The main information and quantities in the list are summarized in table I. The first column gives the name of the respective information, the second column an extensive description.

Table I. Summary of Specific Information and Quantities Given in the Material List

Name	Description
Code	Unique code for the data set entry. This code has to be used for the description of the material composition by the waste producer
Material/ material group	Common name for a material or for a material group (such as fluorides)
Elementary composition, formula, name, material number	This information gives further notations for the material such as chemical formulas, trade names, material numbers or codes from national or international standards
Approval status	Indicator for the status of the approval procedure. Approved data set entries are marked with "g", and only these entries may be applied for further use.
Command variable	Characteristic quantity for the assignment of a material to a waste component, e. g. pH-value, solid fraction of liquid concentrates etc.
Declaration threshold value	Fraction of the material in the waste, from which the respective material is considered to be harmful to the near surface groundwater. The declaration threshold values are computed on the base of solubility and other specific material properties. A value of 101 % is assigned to materials not harmful to the near surface groundwater.
Description threshold value	Fraction of the material in the waste, from which the respective material has to be considered in the material description of the waste
Solubility	Solubility of the material in pure water at 20 °C
References	Documents for the proof of the information
Validity range	Potential restrictions for the use of a data set entry
Composition of the material	Fractions of materials, of which the respective material consists. All materials of this vector must be part of the material list
Specificity fraction	Fraction of specific chemical forms to the whole group, e.g. fraction of calcium fluoride to the whole fluoride group
Balancing parameter	Parameter for balancing the respective constituents of a material
Occurrence probability	Fraction of a waste package or a charge of waste packages in which the respective material may occur

The material list is a living document which will continuously be updated to the demands of the waste producers. It will be published soon (after termination of the approval procedure) in Germany.

The data set entries in the material list can be subdivided into three groups:

- Basic materials:
These materials consist of the materials given in the water law permit and of materials not explicitly mentioned but belonging to material groups of the water law permit.
- Modules
Modules are superior materials needed by the waste producers for the definition of waste producer specific materials or material vectors

- Waste producer specific materials or material vectors

Basic Materials

The water law permit stipulates limitations for 94 substances and materials relevant for water protection issues. Together with the derived materials more than 150 materials are categorized as basic materials, for which the inclusion in the material list is applied for up to date. Table II gives an exemplary choice of these materials together with their computed declaration thresholds.

Table II. Exemplary Choice of Basic Materials with Declaration Threshold Values

Material	declaration threshold	Material	declaration threshold
Vanadium	101,00	Nitrites	5,00
Cobalt	101,00	Natriumphosphonat	2,5
Chrome	101,00	Trimethylphosphate	60,00
Chrome (VI)	2,30	Na ₂ -Oxalate	25,00
Nickel	101,00	Hexamethylphosphoric acid triamide	0,20
Lead	101,00	Hexachlorobenzene	0,10
Gold	25,00	Boric acid	25,00
Mercury	1,00	Ammonia	1,00
Thallium	1,00	EDTA	0,29
Aluminium	101,00	Na-EDTA	0,10
Barium	0,40	Iron	101,00
Beryllium	0,10	Iron phosphat	25,00
Caesium	5,00	Thorium dioxide	3,00
Lithium	1,00	Thorium oxalate	0,01
Rubidium	5,00	Biocides, Microbiocides	0,09
Strontium	25,00	Halogenated phenols	0,10
Fluorides (inorganic)	3,00	anionic surfactants	0,40
Lead (II) carbonate	1,00	Hexacyanoferrate	2,50
Cyanides	1,00	Halogenated naphthalenes	0,10
Uranium	101,00	Biphenyls	0,010

Modules for the Application for Waste producer specific Material Vectors

Modules are typical materials waste streams or complete waste packages consist of such as container materials, shielding materials, filling material, constituents of mixed waste etc. Up to now some 180 materials are predefined for inclusion in the material list (model data). 20 module materials are prepared so far that the inclusion in the material list immediately will be requested after the reception of the approval of the above mentioned basic materials. Table III lists these 20 modules.

Table III. List of Modules Prepared for Inclusion in the Material List

Portland cement	Nonferrous metals
Earth	Galvanized steel
Ashes	Building rubble

slag	Insulation material
Concrete/ crushed concrete	Without PVC plastic
Construction steel	Ion exchange resins
Steel shot	Paper
Tool steel	Textiles
Stainless Steel	Glass
Base metals	Wood

For inclusion in the material list each module has to be degraded in its constituents regarding the approved basic materials as mentioned above. Constituents not included in the list have to be added (using the standard approval procedure). Of particular difficulty here is to determine the correct chemical form of the constituent, as in general the determination of the chemical form in solids is impossible. An analysis of chemical elements, which is the usual case for solids, is of little use because it provides no information on the solubility of the constituents. E. g., instead indicate sodium in concrete in elemental form, it must be specified as silicate. Information on the chemical form comes from waste producers' information, literature, and studies of similar wastes and from chemical considerations. Shares not identifiable are to estimate as non specifiable rest (nsr). For the nsr, the exclusion of harmful substances is qualitatively to make plausible.

From the individual declaration thresholds of the constituents the declaration threshold of the module is calculated. In the same way, the balancing parameters of the module are to determine. For the application of entry in the material list, all computation procedures, data, information etc. are to present clearly.

Waste producer specific Material Vectors

For the description of their main waste streams the waste producers shall use waste producer specific material vectors. The main waste streams can refer either to waste products or to lots of waste packages, such as evaporator concentrates or construction waste in containers. All components of a main waste stream have to be indicated with their mass fractions using the material list, if they are above their description thresholds. This means, that only entries of the material list can be used for the definition of an waste producer specific material vector. Waste components not included in the material list have to be requested for inclusion in the material list. The non specifiable rest has to be described qualitatively.

Up to now, the waste producer specific material vectors in Table IV are announced to describe a significant proportion of the waste planned for disposal in the Konrad repository.

Table IV. Waste Producer Specific Material Vectors Announced at the BFS

Evaporator concentrates from decommissioning projects	Batch of containers from decommissioning of a nuclear fuel fabrication plant(1)
Evaporator concentrates from research centers	Waste producer specific construction waste (1)
Evaporator concentrates from npp operation	Waste producer specific cemented waste (1)
Reinforced concrete	Batch of containers from operation of a nuclear fuel fabrication plant(2)
Ion exchange resins	Waste producer specific bulk waste
Compactable mixed waste	Waste producer specific compacted waste
Filter concentrate	Construction waste with lime sludge
Core components	Solidified solutions from fuel reprocessing
Mixed waste from public waste producers	Incinerator ashes

The waste producer specific material vectors listed in Table IV cover a large proportion of the German radioactive wastes intended for disposal in the Konrad repository. Regarding the application procedure for inclusion in the material list waste producer specific material vectors are dealt with the same way as modules, see above.

TRACE IMPURITIES

The above description of the procedure for describing the material composition neglects the problem of harmful trace impurities in the waste or in modules or waste producer specific material vectors. Regarding trace impurities the water law permit points out:

"For the determination of the amount and for the balancing such substances must not be taken into account, which only occur in small fractions as trace impurities in waste packages or in batches of waste. ... Trace impurities may occur only in quantities, that harmful change of the near surface groundwater is safely excluded".

The latter phrase is used for the definition and assessment of declaration thresholds, see table II. If these declaration thresholds – that means mass fraction of the waste package- are not exceeded, the respective material is considered as a trace impurity. A harmful change of the near surface groundwater caused by a material *i* is defined as exceeding of a concentration limits c_i stated in the German Drinking Water Ordinance" [5] or appropriate guidelines.

The maximum allowable concentration in the deep groundwater is the product of the maximum allowed concentration in the near surface groundwater and the dilution factor, which is set to 10^{-4} in the water law permit.

$$C_{\max, idgw} \leq C_{i, nsgw} \times f \quad (\text{Eq. 1})$$

with

$C_{\max, idgw}$	maximum concentration in the deep groundwater of material <i>i</i>
$C_{i, nsgw}$	maximum concentration in the near surface groundwater of material <i>i</i>
f	dilution factor

If the concentration in the deep groundwater resulting from the declaration threshold value and the solubility of the material doesn't exceed the maximum value from eq. (1), the requirement of the water law permit is met. For the determination of the maximum mass of material *i* its solubility has to be taken into account. For

$$C_{i, nsgw} \times f \geq S_i \quad \Rightarrow m_{i\max} = 0 \quad (\text{Eq. 2})$$

with

S_i	solubility of material <i>i</i>
$m_{i\max}$	maximum mass of material <i>i</i> in the repository

For materials with higher solubility the maximum mass is

$$m_{i\max} = C_{i, nsgw} \times f \times V_{dgw} \quad (\text{Eq. 3})$$

with

V_{dgw}	total dilution volume (1.000.000 m ³)
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The maximum mass of material *i* is the sum of the maximum mass according to the water law permit and the maximum mass caused by trace impurities.

$$m_{iTI} = m_{i\max} - m_{iWLP} \quad (\text{Eq. 4})$$

with

m_{iWLP}	maximum allowable mass of material <i>i</i> according to the water law permit
m_{iTI}	maximum mass caused by trace impurities of material <i>i</i> , the so called slip

The declaration threshold depends on the maximum mass caused by trace impurities:

$$DT_i = \frac{m_{iTI}}{m_{tot}} \quad (\text{Eq. 5})$$

with

m_{tot} total waste mass in repository (606.000 Mg)

(note: the described derivation for the declaration threshold is simplified and neglects chemical forms)

As some calculated maximum masses caused by impurities are very low the resulting declaration thresholds are so low, too, that they are difficult to handle in practice. For this reason it was investigated whether these materials occur in every waste package. As a result it was found that the occurrence of the relevant materials in the waste packages is rather unlikely, however without being able to quantify this. Therefore the occurrence probabilities were estimated in a first step. In a second step these estimates has to be validated during and before the operation of the repository. Central problem for this validation is defining a lower limit at which the occurrence of a material can be excluded (the proportion of this material in the waste package is considered to be zero).

The overriding principle for the validation is that no harmful change in the near surface groundwater occurs. First it has to be determined to which extend the maximum mass caused by trace impurities is exhausted in reality. The result is a new realistic mass.

So that the above mentioned principle is respected the sum of the realistic mass and the and the additional mass by traces of the material below the lower limit in the remaining waste packages must not be greater than the maximum mass caused by impurities as calculated in equation (4). With this the maximum cumulative mass of material i below the lower limit (which is considered to be zero) can be computed.

$$m_{iZero} \leq m_{iTI} - m_{iTrealistic} \quad (\text{Eq. 6})$$

with

m_{iZero} maximum mass of material i below the lower limit in waste packages, which are considered to be free of material i

$m_{iTrealistic}$ realistic mass of material i below the declaration threshold in waste packages, which are considered to contain material i

From this the lower limit results:

$$LL_i = \frac{m_{iZero}}{(1-n) \times m_{tot}} \quad (\text{Eq. 7})$$

with

LL_i lower limit of material i which is considered to be zero

n occurrence probability of material i

If the realistic mass for a material can not be determined, the declaration threshold must be lowered by some percent, e. g. 10 to 50%. By this a lower limit can be computed in a similar way as described above.

For all waste packages, batches of waste packages or waste producer specific material vectors and all materials with lowered occurrence probabilities it have to be examined whether the lower limits are met or not. First practicability checks show, that the lower limits are in the range of 10^{-3} % to 10^{-7} %. Although these lower limits seem to be very low they come to considerable masses when they are applied to gross masses of waste packages or waste streams. E. g., for Cyanides the lower limit can be calculated to 10^{-4} %. This means 1 to 2 kg in a waste package, a mass, that can easily excluded due to balances or origin of the waste.

So with the procedure described, the validation of the occurrence can be rather easily dealt with.

GUIDANCE FOR THE WASTE PRODUCER FOR THE APPLICATION FOR WASTE PRODUCER SPECIFIC MATERIAL VECTORS

For the inclusion of a waste producer specific material vector or a module in the material list the waste producer has to submit an appropriate application at the BfS. The BfS processes this application and forwards it to the competent authority for examination and approval from a water law point of view. After receiving the approval BfS enters the material vector in the material list and informs the applicant, i.e. the waste producer.

The processing of an application by BfS comprises

- examination, whether a comparable application is in processing
- control the correct use of entries in the material list
- prepare necessary modules and forward them to the authority
- Assign a material code
- compute declaration thresholds and balancing parameters
- determine the occurrence of materials with restricted occurrence probability in the material vector
- formatting the application for forwarding it to the authority

Lacking clarity or deficits for the processing by BfS have to be clarified before forwarding the application to the competent water authority. The application of a waste producer specific material vector in the material list by the waste producer is informal. However, to facilitate the processing by BfS, the following guidance should be adhered to.

The application must necessarily include the following information:

- Material/ material group (see table I)
- Elementary composition, formula, name, material number (see table I)
- Command variable (see table I)
- References (see table I)
- date of application
- Validity range (see table I)
- Composition of the material (with ranges of the fractions of the respective components) using the entries of the material list (see table I)
- information on the non specifiable rest
- Information on the occurrence of materials with lowered occurrence probabilities

The upper and lower limits of the composition define the range, in which the material vector may be applied.

This will be determined either on the basis of actual knowledge of the waste or on the basis of assumptions. Thereby the potential harmful influence of the respective component on the near surface groundwater has to be taken into account. (Quantity for this is the declaration threshold; the smaller the declaration threshold is, the smaller is the allowed range.)

For the non specifiable rest qualitative information on the composition is required. This addresses both probable and sure information on the respective components.

All information provided has to be justified or has to be derived. Possible procedures for determining the composition are balances of input or output masses of treatment processes, chemical analyses of conventional disposed wastes, material descriptions or assumptions. In all cases the procedure of determining the information has to be reproducibly described. The data basis for all considerations has to be clearly presented.

The applications for waste producer specific material vectors, see table IV, represent a benchmark for the applicability of the described procedure for the waste producers. They demonstrate that the procedure can be implemented by the waste producers at a reasonable level of expenditure.

PERSPECTIVE

According to the requirements imposed in the water law permit (Annex 4 to the Konrad license) BfS has developed a procedure to implement its clauses and collateral clauses. Objectives of this procedure are:

- the proof, that all requirements of the water law permit are met and
- the provision of a standardized, easy manageable guidance for the waste producers to describe their wastes.

The complete procedure with all parameters, assumptions, calculations and entries in the material list is currently under review by the competent water authority and its experts. In the meantime both BfS and the German waste producers are preparing further material vectors, in order to submit the respective applications as soon as possible.

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The experiences, gained in the preparation of waste producer specific material vectors and modules, suggest, that most of the wastes considered comply with the requirements of the water law permit and thus can be disposed of in the Konrad repository.

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