

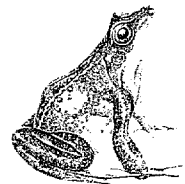
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Improved Material Testing Procedures (DWE 9007)

***Progress Report to the Department of the Environment
- January to June 1991***

DoE 2835-M
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IMPROVED MATERIAL TESTING PROCEDURES

Progress report to the Department of Environment -
January to June 1991

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SUMMARY

I OBJECTIVES

This report summarises the progress made during the period under review in a DoE funded project which has the following objectives:

- i) to assess the approval systems used in EC and other countries and identify features which should be incorporated into UK scheme;
- ii) to establish testing needs, devise, validate and recommend modified testing procedures.

II REASONS

Organic and inorganic impurities from materials and products in contact with water supplies can leach into water and pose a threat to consumers and impair water quality generally. Data from laboratory tests are used to assess whether any such adverse effects resulting from the use of a product would be acceptable. It is therefore important that, for a range of different materials and products and for various usage, appropriate test conditions are devised, validated and well documented and that the quality and quantity of the data obtained from the tests are adequate to allow realistic assessment.

III RESUME OF CONTENTS

Work done during this period of review was largely concerned with gathering and evaluating information on major assessment and approval systems in Europe and USA. The report summarises the main features of systems in Netherlands, Germany, France and USA, in particular their organisation, information required from applicants, the use of 'positive lists', basis of test procedures, criteria for assessments and published information and listing, and compares them with the current UK system.

At present, committees in Europe (CEN) are putting together a new scheme that will in due course apply to all EC countries. Developments in drafting new standards related to the effects of materials on water quality are outlined.

1. OBJECTIVES

The aims of the project are:

1. To assess the approval schemes used in EC and other countries and identify features which should be incorporated into a UK scheme.
2. To establish testing needs, devise, validate and recommend modified testing procedures.

2. INTRODUCTION

Leaching of organic and inorganic impurities from materials and products used in water supplies can pose a threat to consumers and impair water quality generally. The Water Act 1989 gave the Secretary of State powers to make regulations controlling the use of substances, products and processes in the treatment and provision of water supplies. The relevant provisions are given in The Water Supply (Water Quality) Regulations 1989 and came into force on 1 September 1989. The current approvals by the Secretary of State who is advised by the Committee on Chemicals and Materials of Construction for Use in Public Water Supply and Swimming Pools (CCM) are stricter than most in Europe and consequently have many advantages. At present, committees in Europe (CEN) are putting together a new scheme that will in due course apply to all EC countries. It was important that other schemes in Europe were assessed, particularly those which were likely to influence the formation of the new EC standards, and any useful features were considered for inclusion in the UK system. The practicalities and values of positive lists and TOC determinations needed to be investigated. Experimental validation of any proposed modified procedures needs to be carried out and the work needs to be synchronised with developments within CEN.

3. PROGRESS

3.1 Review of current approval systems

Several European countries, particularly Netherlands, Germany and France have established and routinely operate systems for approvals of products for use in contact with drinking water. The three above countries together with the UK, Denmark and Sweden are also the main participants in CEN preparing new standards for product testing, specification and approvals. Leading approval/testing laboratories in Netherlands (KIWA), Germany (Engler-Bunte-Institut, Karlsruhe) and France (CRECEP) have therefore been visited and their current approval systems discussed. Some information on practices of assessment of the effects of materials on water quality in Denmark and Sweden have also been received. In addition details have been gathered on testing methods and a new third party certification scheme introduced in USA recently. Main features of the respective approval systems are summarised and compared with UK systems in the following subsections:

3.1.1 Approval systems in Netherlands

Organisation

In 1986 the Chief Inspector of Public Health and Environmental Protection issued a directive (Inspectorate of Public Health and Environmental Protection 1986) defining the health related requirements for materials and chemicals used for the production of drinking water and outlining the underlying principles of their assessment. The directive was based on recommendations of the Committee on Health Aspects of Chemicals and Materials for Water Supplies (CGCMD). This committee, which is assisted by groups of experts from KIWA, industry and central government, also advises the Chief Inspector on "positive lists" and on assessments of chemicals and materials not included in the positive lists.

The implementation of the directive is the responsibility of the Netherlands Testing and Research Institute KIWA N.V. They issue ATA certificates (Assessment of Toxicological Aspects) as an evidence that the products meet the

requirements of the relevant positive lists or that, after individual assessment, the Chief Inspector found them to be admissible. KIWA also periodically checks products holding ATA to establish whether they still meet the requirements.

For a product containing one or more substances not included on a positive list the applicant can either request an addition to the positive list or can request an individual assessment. In either case relevant toxicological data obtained under GLP in accordance with OECD Guidelines needs to be provided by the applicant.

Informations required from applicants

All applications with details on the product, its chemical composition, specifications of starting materials, outline of manufacturing processes and field of application are submitted in confidence to KIWA. Applications for the assessment of new substances are also submitted to KIWA, together with the required toxicological data and method(s) of analysis, but the applications are then submitted to the CGCMD for assessment. Guidelines on what toxicological data is needed in each case are given in the directive (1).

Positive lists

The system is based on the use of positive lists. Positive lists for several types of material (e.g. polyethylene, PVC, etc.) and chemicals have been published and their number is gradually been extended. Each positive list for a material states the following:

- a) description of the material, i.e. its chemical characteristics;
- b) rules governing manufacturers - which lists monomers and additives which may be used for the production and processing of the material (without specifying any limits on amounts used); and
- c) demands to be satisfied by the final product, listing substances and their migration values which must not be exceeded in standard migration (leaching) tests. A limit value for overall migration/TOC is set in the positive lists for all materials.

Test procedures

The products/materials are subjected to migration/leaching tests where test samples are in contact with test water at set temperature over periods of time. The tests for cold water systems are based on three 72-hours sequential leaching periods and leachates from each of the three periods are analysed for the substances specified in a positive list. GC-MS scans of the leachates and the identification of unsuspected organic compounds are not required. Migration rates from the third period, expressed as mg/dm² 24 hrs, are then converted to mg/l using a complex system of conversion and correction factors. The values are then compared with the acceptable limits in a relevant positive list. Products to be used both in cold and hot water systems are tested and assessed under this approval system.

Criteria for assessments

KIWA issue an ATA certificate when the product is in accordance with the relevant positive list (i.e. all the components are listed and results of specified test do not exceed set values), or when the Chief Inspector considers the product acceptable following an individual assessment.

When setting up acceptable limits in positive lists or when assessing substances not included in a positive list the CGCMD uses the following criteria:

- a) 'no effect level' observed in toxicological assays serves as a basis for setting toxicological standards;
- b) maximum of 10% of the toxicologically acceptable quantity for daily consumption may be ingested via drinking water;
- c) drinking water standards as laid down in the Dutch Water Supply Decree should not be exceeded;

- d) human exposure to substances should be avoided as far as possible, even if below the maximum acceptable concentration, i.e. additives should not be used in greater quantities than strictly necessary and should be of good technical quality;
- e) for chemicals for water supplies no account is taken of the removal of a contaminant during the treatment process; and
- f) an impurity from a treatment chemical may not, in principle, contribute more than 10% of the standard specified in the Water Supply Decree.

Published information/listings

Once a year KIWA published a list of all products for which an ATA has been issued. Issues of and/or amendments to positive lists are announced in the Netherlands Official Journal.

Updated guidelines on quality of materials and chemicals for drinking water supplies are expected to be issued during the Summer 1991.

3.1.2 Approval systems in Germany

Organisation

The hygienic assessment of non-metallic products for use in contact with drinking water is the responsibility of the Working Group 'Drinking Water Affairs of the Commission for Plastics' of the Federal Health Office (BGA). Members of the Working Group are representatives of independent institutes, industry and the Federal Health Office. The Working Group issues recommendations for plastic and other non-metallic materials which can be used in contact with drinking water (KTW-recommendations), i.e. positive lists.

KTW-recommendations are valid for distribution systems up to the free outlet in the house installations and for mobile units for drinking water supplies. The recommendations or certification are not statutory requirements. Materials used in water treatment installations and treatment chemicals are tested and assessed under separate regulations.

DVGW Deutscher Verein des Gas- und Wasserfaches E.V. (German Association of Gas- and Waterworks) issues regulatory and testing requirements for different types of products for gas and water installations. Apart from technical specifications KTW-recommendations have to be satisfied for products to be used in contact with drinking water. So far three testing laboratories have been approved to issue certificates that the product satisfies the conditions of KTW-recommendations. Of these the DVGW-Forschungsstelle at the Engler-Bunte-Institut in Karlsruhe carries out the largest proportion of the tests.

For a product containing one or more substances not included in the KTW-recommendations the applicant has to apply to the BGA for its/their inclusion in the KTW-recommendations. An individual assessment of a material or product is not available.

Informations required from applicants

The producer of the finished product provides the testing laboratory in confidence the chemical composition of the material or declares to the testing laboratory that the product composition is in accordance with the relevant KTW-recommendations.

When applying to BGA for inclusion of a substance to the KTW-recommendations required toxicological data has to be provided.

Positive lists

The KTW-recommendations are based on the recommendations of the BGA for plastics in contact with food. Over 50 positive lists for materials in contact with food are now available. KTW-recommendations have been published for a range of materials, such as PVC, polyethylene, rubber etc. and their number is gradually being extended. Each KTW-recommendation for a material lists the following:

- a) description of the material(s), i.e. their chemical characteristics, for which the particular recommendations apply;

- b) a list of substances including monomers and additives which may be present in the material and, where relevant, their maximum permissible levels therein; and
- c) a list of maximum acceptable values for results from specified tests. Five different values are listed for most parameters depending on the range of the material use (e.g. A - pipes, B - reservoirs, C - fittings, connecting pipes, D1 - gaskets with larger surface, D2 - other gaskets, glues, etc.). Values for organoleptic properties, TOC leaching and chlorine demand are specified for all non-metallic materials. For some materials concentrations of specified substances in the final product have to be checked, e.g. Zinc and Lead in rubbers. Maximum acceptable leaching rates (MALR) (mg/m^2 24 hrs) obtained from standard tests are given for some specific compounds, depending on the material. For example MALRs are specified for Lead in PVCs, and for aromatic amines, phenols and formaldehyde in rubbers.

Test procedures

The migration/leaching tests for cold water systems are based on three 72-hours sequential leaching periods and leachates from each of the three periods are analysed for the substances specified in a positive list. GC-MS scans of the leachates and the identification of unsuspected organic compounds are not required. Migration rates from the third period, expressed as mg/dm^2 24 hrs, are then compared with the appropriate MALR (A to D2) in the relevant positive list. Products to be used in cold, warm and hot water systems are tested and assessed under this certification system.

Criteria for assessments

A product is entitled to bear a DVGW/DIN logo when the specified regulatory and testing requirements, both technical and hygienic, are satisfied. Products are retested after one to five years, depending on the type of the product.

Criteria used by the BGA for inclusion of a new substance/material in KTW-recommendations and the toxicity data to be provided for the assessment are not known.

Published information/listing

KTW-recommendations are published in the 'Bundesgesundheitsblatt'.

3.1.3 Approval systems in France

Organisation

Under the French Regulations on Water Quality (Ministere de la Solidarite, de la Sante et de la Protection Sociale 1989) materials in contact with drinking water in treatment plants and distribution systems must not affect water quality. Though there is no well defined or statutory approval system water undertakers expect suppliers to provide satisfactory reports from a testing laboratory on tests of 'inertness' of the products carried out in accordance with AFFNOR standard procedure (AFNOR 1989).

The Ministry of Health sets limits for substances which are likely to leach from the material into water but which are not included in the Regulations. The Ministry also specifies non-standard analytical methods to be used during the leaching tests.

Assessments of treatment chemicals are dealt with separately. The Ministry of Health decides on specifications for the products and any tests required.

The testing laboratories send all results of the the standard tests on materials to the French Higher Committee on Public Health (Conseil superior d'hygiene publique de France). The Committee, advised by a group of experts, makes rulings on products for which test results exceed the standard values.

The standard testing procedures apply to materials used in public and private distribution networks. For private networks the tests cover only pipes and fittings and storage elements.

At present there are two laboratories which test materials and issue reports in accordance with the AFNOR standard, namely CRESEP in Paris and LHRSP in Nancy.

Informations required from applicants

Applications from manufacturers or suppliers with details on the product, its chemical composition, specifications of starting materials, and fields of application are submitted in confidence to the testing laboratory.

Positive lists

Substances listed in the composition of the product must be listed in a relevant positive list issued in France for materials in contact with foods. The positive lists do not specify quantitative limits for amounts of the ingredients in the product or their leaching rates into water.

Test procedures

The tests of inertness consist of the three following stages:

- 1) Quick screening tests based on one or more 24-hrs stagnation periods in deionised, mineralised or chlorinated waters after which taste, chlorine consumption. TOC and other general parameters (conductivity, pH, ammonium, nitrite, Kjeldahl nitrogen and permanganate value) are determined.
- 2) If the results of the quick tests are satisfactory cytotoxicity tests are performed.
- 3) Finally specific inorganic and organic substances are determined in leachates of chlorinated deionised water after one or two 24-hrs leaching periods. GC-MS scanning of the leachates is also carried out and the compounds identified are determined semi-quantitatively.

For each product a standard set of metals as well as a standard set of organic compounds (PAHs, PCBs, VOCs and unchlorinated solvents) are determined in the third stage using standard AFNOR analytical methods where available, or those specified by the Ministry of Health. Analytical determinations may be required for other inorganic or organic substances (e.g. monomers and additives) depending on the material under test.

The standard (3) specifies different surface area to volume ratios to be tested depending on the intended use of the product. The ratios range from 3 cm²/l of test water for seals in public distribution to 240 cm²/l for pipes in residential dwellings.

Criteria for assessments

A report from the testing laboratory considers the material to be inert if all the components of the product are listed in the relevant positive list for foodstuff and the results from the tests do not exceed values set in the standard (AFNOR 1989).

Criteria of assessment are not known either for setting limits by the Ministry of Health for non-regulatory substances or for the rulings by the Committee on products for which the set values have been exceeded.

Published information/listings

Results of the tests are confidential. Though the Committee receives all the reports no lists of complying materials are issued.

3.1.4 Approval systems in USA

Under The Safe Drinking Water Act [SDWA] the Environmental Protection Agency (EPA) has the primary responsibility for establishing drinking water regulations and the States have the primary responsibility for enforcing such regulations. EPA does not currently regulate the levels of additives in drinking water except for those for which maximum contaminant levels (MCLs) are set in the regulations.

In 1985, in response to a competitive request for proposals from the EPA, a Consortium lead by the National Sanitation Foundation (NSF) agreed to develop voluntary third-party consensus standards and a certification program for all direct and indirect drinking water additives. (Direct additives are defined as contaminants added to water in the production of drinking water and indirect

additives as contaminants that are introduced to drinking water through contact with surfaces of materials or products used for its treatment, storage, transmission, and/or distribution.)

NSF Standards 60 and 61 were published in 1988 and 1990, respectively (ANSI/NSF Standard 60, 1988) (ANSI/NSF Standard 61, 1990). The Standards have been developed to establish minimum requirements for the control of potential adverse human health effects, from products added to water for its treatment (60) and from products which contact drinking water (61). The Standards were written and reviewed by committees composed of representatives from industry, government, and product users, such as water utilities and represent the most detailed and systematic description of data requirements, test conditions and evaluation procedures.

NSF is offering an evaluation and Listing program under the provisions of Standards 60 and 61. However the Standards allow for entities other than NSF to be evaluators of products. It is up to the State and utilities to determine the suitability of any third party certification.

The Listing program includes provisions for a formulation review, in-plant quality control and records audit, laboratory testing, toxicological evaluation and risk assessment and periodic retesting of Listed products.

Information required from applicants

All applications with details on the product, its chemical composition, specifications of starting materials, manufacturing processes and fields of application are submitted in confidence to NSF. Toxicological information in accordance with the Standard also has to be provided. NSF will not share toxicological data. Manufacturers wishing to share such data may mutually arrange to do so, but without the direct involvement of NSF. NSF' records cannot be accessed by other parties, even through 'Freedom of Information'.

Positive lists

Positive lists are not used.

Test procedures

Different conditions of sample preparation, preconditioning, and test procedures (S/V ratio, exposure sequence, temperature) are specified for each group of products, i.e., pipes, protective materials, joining and sealing products, process media and mechanical devices.

Regulated metals are determined in the leachates of all materials. Microbiological growth support tests are required for ductile iron and all plastics except PVCs. Some other determinands such as VOCs and phenolics are specified for ductile iron and all plastics. Neither TOC determinations nor GC-MS scans are specified for any materials. For each material type the leachates are also tested for substances specified by NSF, depending on product formulation.

Concentrations determined in the tests are normalised to 'at the tap' levels using specified complex Normalisation Factors. The normalised concentrations are then compared with calculated Maximum Allowable Levels (MALs). For regulated contaminants MAL should not exceed 10% of the EPA final MCL. For unregulated contaminants MAL should not exceed 10% of The Maximum Drinking Water Level (MDWL) which is calculated from toxicological data using formulae specified in the Standard.

Criteria for assessments

Listing will be authorised if the product fully complies with the Standard which basically means that MALs for all the prescribed tests will not be exceeded. Various factors are taken into account for the calculation of MDWLs and of normalised concentrations, e.g. whether the substance is classified as noncarcinogen or carcinogen, from which toxicology tests the data was obtained, product dimensions, where it would be used etc. Although there is no blanket acceptance of previously accepted products, health effects data and prior regulatory acceptance may be considered in the evaluation.

Published information/Listings

Three complete Listing books are issued by NSF per year for products that have demonstrated conformance with NSF standards and are authorised for Listing. The Listing is also available in NSF's on-line database.

3.1.5 Comparisons with UK approval systems

Under the current statutory UK approval system the approved products have, in general, satisfied a wider range of tests. All materials had to pass tests in accordance with BS6920 (organoleptic, cytotoxicity, microbiological growth and metal leaching tests). Formulation of the product, its method of manufacture and intended use have been assessed individually by the CCM and the Committee had to be satisfied that no substance originating from the product would leach into drinking water at concentrations posing a health risk. Such evaluation is based on concentrations found in leaching tests for substances specified by the Committee or identified by GC-MS scans in the leachates and on toxicity data provided by the applicant when necessary.

Two factors common to all the European systems reviewed are not part of the UK approval procedure, i.e. the determination of TOC in all leachates of non-metallic materials and, more importantly, the use of positive lists as the basis of product assessment.

TOC is a useful, inexpensive determinand, which could be primarily used to detect an unsuspected major leaching which might not be detected by the other tests. Little or no validation of test methods would be necessary before the parameter could be included in testing requirements.

For well established materials the use of positive lists results in shorter approval procedures which can be undertaken by authorised testing laboratories without further reference to groups of experts. In addition, positive lists offer the manufacturer better information, when the product is being developed, on the requirements to be met. The establishment of a well founded positive list, relevant to drinking water consumption is, however, a long term and costly task involving experts in toxicology, chemistry and other fields.

France, Germany and Netherlands, each uses their positive lists differently. Some other countries, such as Denmark and Austria use the German positive list. The system as practised in Netherlands appears to be, in general, most compatible with the current UK system, because it specifies limits of migration values for the widest range of substances which could leach from the material into water. The system also allows individual assessment and approval of a product containing unlisted substances while maintaining confidentiality of the toxicological data. Whether the conversion and correction factors are realistic and whether the derivation of the limits for migration rates would be acceptable would still have to be assessed by experts.

3.2 Monitoring of CEN progress

Working Group 3 of CEN Technical Committee TC164 (Water Supply) is preparing standards relating to effects of materials on water quality. Four Ad Hoc Groups have been set up to draft standards for organoleptic and microbiological tests, for procedures for testing migration/leaching from non-metallic and metallic materials and one to prepare a standard dealing with positive lists. Over the past six months WRC have been involved particularly with AHG2 in drafting standard procedures for the testing of non-metallic materials. The current situation is summarised in the following subsection.

3.2.1 Leaching test procedures

These standard procedures, when accepted, will also become national standards in the UK. Approvals granted in other countries for materials to be used in contact with drinking water will most likely also have to be accepted in the UK as long as the materials were tested and assessed in accordance with CEN standards by an accredited laboratory. It is therefore important that the test procedures should provide data on the basis of which realistic assessments of possible effects on water quality and human health could be made.

The basic protocol of the draft standard is written for factory-made or applied products, samples of which can be simply immersed in the test water. There is a broad agreement on the conditions of such tests. For cold water systems the

proposed test is based on three successive periods of 72-hours stagnation in unchlorinated and chlorinated test waters. At present the suggested S/V ratio is 1 cm²/ml or that corresponding to the smallest pipe diameter to be manufactured. The specification of a standard S/V ratio is, however, less important since the leaching rates will be expressed per unit area per day, i.e. mg/dm² 24 hrs.

Initially the draft proposed inadequate testing of site-applied products. WRc, after consultation with CCM Committee members, have proposed modified test conditions more in line with those specified by the CCM for the assessment of such products. At the last meeting of AHG2 these proposals have been largely accepted. Some validation of the test procedure will, however, still be needed before the conditions can be finalised.

Other products for which more information is required before standard test procedures can be specified are cementitious products, adsorption resins, and membrane filters.

Interlaboratory studies on test procedures for factory applied products have been proposed and they are likely to take place towards the end of this year. WRc has played a major role in defining objectives of the studies and in discussions on appropriate experimental designs and determinands to be measured.

3.2.2 Positive lists

At present it is not yet clear on what principles determinands to be measured in the leachates are to be specified, at what levels they should be measured and even which Group is to decide. Most likely this most important task will be the responsibility of TC164/WG3/AHG4 which deals with matters related to positive lists. This Group met only once over the past six months, at a short notice.

4. FUTURE WORK

Gathering of informations on other approval systems and testing procedures will continue. More details is needed on approval systems in Scandinavia and the other approval systems in France and Germany. The situation in other European countries on the use and testing of materials in contact with drinking water will be reviewed.

Test procedures proposed by WRc to TC164/WG3/AHG2 for site-applied products will be investigated further to enable to finalise the conditions. In particular, more data is needed for two-parts products for pipes re-lining and reservoir coatings and for solvent cements.

Monitoring of and participation in in the development of CEN standards for material testing will continue. WRc will take part in the interlaboratory study for testing factory made or applied products, which is planned to start towards the end of this year.

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AFNOR Standard CF T 90/M Doc.8, June 1989.

ANSI/NSF Standard 60-1988. Drinking Water Treatment Chemicals - Health Effects.

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Inspectorate of Public Health and Environmental Protection (1986) Guideline quality of materials and chemicals for drinking water supplies. Ministry of Housing, Physical Planning and Environment of the Netherlands, Publication 86-01.

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