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Improved Material Testing Procedures (DWQ 9007)

Progress Report to the Department of the Environment - July to December 1991

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SUMMARY

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 or field 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. It has been recognised that any proposed improvements in testing procedures need to be synchronised with developments within committees in Europe (CEN).

Work done during this period of review was focusing on the three following areas:

* Participating in drafting CEN standards on testing the effects of materials on water quality due to migration of chemicals (leaching tests) in order to champion UK views.

* Preparations for a CEN interlaboratory study to assess the suitability of the proposed standard migration test procedure for factory-made or factory-applied products.

* Gathering of data from different laboratory and field leaching tests on site-applied epoxy resin lining systems to assess their comparability and relevance to real situations.

Report No: DoE 3004

1. INTRODUCTION

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

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.

Major approval schemes in Europe were assessed earlier and the findings were reported in the last Progress report (DoE 2835-M, June 1991). It has been recognised that any proposed improvements in testing procedures need to be synchronised with developments within committees in Europe (CEN).

Working Group 3 of the 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.

Ad Hoc Group 2 (AHG2) of the above Working Group (TC164/WG3) is drafting standard procedures for the testing of leaching from non-metallic materials. Experimental validation of any proposed draft standard procedure needs to be carried out. As a part of this project WRc is taking part in an international interlaboratory study on testing products for which drafting of the test conditions has been completed.

For some products, for which the test conditions for an EC Standard are still under discussion, such as site applied epoxy lining, more extensive testing is required for an approval in the UK than most in Europe. It is, therefore, important to provide experimental evidence to support the UK proposal to CEN for more extensive testing of such products.

2. PROGRESS

2.1 Developments in drafting CEN standards for tests on the effects of materials on water quality

2.1.1 Basic standard conditions of leaching/migration tests

CEN TC 164/WG3/AHG2 has now finalised the part of the draft Standard dealing with basic conditions of the migration/leaching test, which would be applicable to a wide range of factory made and factory applied products, such as plastic pipes, coatings, rubber, etc.

WG2 of the CEN TC 155 (Plastic Pipes) is also drafting a Standard for a test to assess the migration from plastic pipes. The draft may be accepted as an EC Standard before the Standard from the TC 164/WG3 is completed, but would be superseded by the latter when that is finally accepted. Regretfully, the two proposed test methods differ in some important areas, because of lack of collaboration between the two Technical Committees. Table 2.1 lists the basic test conditions for the two draft test methods and compares them with those for tests currently used in the UK.

Table 2.1 Basic conditions of leaching tests as proposed by CEN and as used in the UK

	CEN TC164 WG3/AHG2	CEN TC155 WG2	CCM-general (BS6920)	CCM-PVC pipes	BS6920-metals
Stagnation periods (hours):	1) 72 2) 72 3) 72	1) 72 2) 72 3) 72	1) 24 2) 48 3) 72	1) 24 2) 5x24 7) 24	1) 24 2) 5x24 7) 24
Overall duration:	9 days	9 days	6 days	7 days	7 days
Analysis of leachates after periods:	1),2),3)	1),2),3)	1),2),3)	1),7)	1),7)
Number of replicate test samples:	2	3	1	1	1
Type of extraction water:	1) unCl 2) Cl	1) unCl 2) Cl 3) Cl,pH 4.5 4) unCl,pH 4.5 5) unCl,pH 9	1) unCl 2) Cl	1) unCl 2) Cl	1) unCl 2) Cl
Test temperature:	23 ± 2 °C 60 ± 2 °C* 85 ± 2 °C*	23 ± 2 °C 70 ± 1 °C* 90 ± 1 °C*	25 ± 1 °C	Ambient	25 ± 1 °C
S/V ratio:	1 cm^2ml^{-1}+	0.1 cm^2ml^{-1}+	0.15 cm^2ml^{-1}	min i.d.	0.15 cm^2ml^{-1}

* - For products coming in contact with warm or hot water.
\+ - Only a recommendation, results expressed per unit surface area. Pipe testing by filling an appropriate length of a pipe of the smallest diameter with test water is recommended by both the CEN draft methods and required by the CCM protocol for PVC pipes. The CCM usually requires plastic pipes from other materials also to be tested at the highest surface area to volume ratio.

2.1.2 Progress with drafting other standards relevant to the assessment of effects of materials on water quality

At the insistence of WRc and other CEN participants the TC 164/WG3 and TC 155/WG2 are now collaborating in drafting a method for organoleptic assessment.

At present the TC 155/WG2 is discussing a method of use of "conversion factors". This involves defining a systematic approach to converting the migration value (daily leaching rate per unit of material surface), calculated from the results of the migration test, to a likely concentration at a consumer tap. This concentration would then be compared to a prescribed value in a "positive list". These aspects have not yet been addressed by the TC 164/WG3. Participants in this Working Group and its Ad Hoc Groups are mainly representatives of regulatory bodies unlike as in the TC 155/WG2, where the majority of participants are pipe manufacturers. Consequently, the TC 164/WG3 may have different views and, there again, two different methods could be produced for the same products.

The progress in the work of AHG4 of the TC 164/WG3, which is preparing positive lists, is very slow. This could be a major problem in the near future.

2.1.3 Modifications of standard migration test conditions for specific products

From discussions in AHG2 of the TC164/WG3 it has become apparent that specific test conditions would have to be defined for a number of products, such as site applied two-part coatings and linings, cement and concrete products, site applied modified or impregnated cementitious products, jointing compounds, ion exchange resins, filter materials and others.

In the current draft specific requirements are listed as subsections in Section 9 of the draft Standard. WRc has proposed that complete test procedures for individual products should be drafted separately as parts of the Standard. Such procedures would be easier to follow and would eliminate some

ambiguities. Future updating of the Standard for new products would also be simpler. Other participants supported these views, but it may be too late for major redrafting.

There is still a number of outstanding issues, which may take some time before an agreement is reached, in particular the following:

* The nature of test water for concrete/cement and modified or impregnated cementitious products and the implications for use of the products, when approved on the basis of tests with non-aggressive water.

* The extent of testing site-applied two-parts linings and coatings to provide adequate data at reasonable cost to assess the full extent of their possible effects on water quality.

* Suitable procedures and the extent of testing ion exchange resins.

* Whether filter membranes and similar products should be tested under static or dynamic conditions.

2.2 CEN TC 164/WG3/AHG2 interlaboratory study

Within the AHG2 a standard migration test for the majority of factory-made or factory-applied products has been drafted. To be accepted as an EC Standard the proposed test method needs to be validated. The AHG2 has organised Part 1 of an interlaboratory study to test the standard procedure for four products, namely PVC and glass-reinforced polyester (GRP) pipes, epoxy coating, and rubber.

Eight laboratories are participating in the study, from Denmark, Finland, Germany, The Netherlands, three from France and WRc. The participation of WRc as a part of this contract will have the following benefits:

* Playing an active part in the CEN work will provide more influence to promote UK views on testing the effects of materials on water quality.

* A substantial volume of leaching data will be obtained, which will allow comparisons with results available from tests currently used in the UK to provide data to the CCM in support of applications for approval.

* Results of the study will provide some information on the relative performance of the participating laboratories, which are likely to become the testing/accreditation laboratories for EC approvals.

The tests will be performed in accordance with the draft standard but only with one type of test water (unchlorinated) and at one temperature (23 °C). The leachates will be analysed for TOC and compounds specific to each product, and a general GC-MS scan will also be performed. The determinands and the required limits of detection are listed in Table 2.2. The determination of bisphenyls A and F diglycidyl ethers (DGBEA and DGEBF) in epoxy coatings and GC-MS scans have been included at WRc's request. It was therefore necessary to prepare and distribute to the other participating laboratories the appropriate analytical methods, samples of pure DGEBA and DGEBF and solutions of deuterated internal standards for GC-MS analysis.

Other preparative work is in progress to set up suitable test conditions and analytical methods to be be able to commence testing, when the test samples are delivered in January.

Table 2.2 Products, determinands and required limits of detection for Part 1 of the CEN interlaboratory study

Material	Determinand	Limit of detection ($\mu g l^{-1}$)
uPVC pipe (32 and 75 mm)	TOC	200
	Lead	1
	GC-MS	1
Glass-reinforced polyester pipe	TOC	200
	Styrene	1
	Dimethyl phthalate	2
	Cobalt	1
	GC-MS	1
Epoxy coating (free of solvent)	TOC	200
	Sec. aliphatic amines	50
	Alkylbenzenes*	1
	DGEBA/DGEBF	1
	GC-MS	1
Rubber (EPDM)	TOC	200
	phenols (non-specific)	50
	primary aromatic amines (non-specific)	5
	GC-MS	1

2.3 Assessment of test conditions for epoxy lining products

2.3.1 Variations in results from laboratory plate tests and field trials

At present, any applicant for approval of a two-part epoxy resin system for re-lining of mains, has to submit to the CCM leaching data from field trials conducted under conditions resembling real situation.

Three 100-meters lengths of 100-mm diameter main which are either abandoned or dead ends and which can be isolated from supply are lined by a competent contractor. After curing period of 16 hours each lined pipe is disinfected for

30 minutes (50 mgl^{-1} of free chlorine residual) and then flushed for one hour. Flow is then imposed on the pipe to give a retention time of approximately one hour during first 24 hours and ten hours subsequently. Samples for analysis are taken after one hour, 24 hours, 48 hours, 72 hours, one week, two weeks and four weeks.

Any new CEN standard for testing such products will be based on laboratory leaching tests conducted under conditions as close as possible to those for the basic standard procedure. WRc, after consultation with the CCM Committee members, have proposed to the CEN TC164/WG3/AHG2 modified laboratory test conditions more in line with the current UK requirements. AHG2 is now in a broad agreement that the preparation of site applied products is usually subject to larger variation in conditions of applications and, therefore, the tolerances of leaching rates to the variations should be measured for individual products by more extensive testing.

To provide some guidance on the possible variations of the leaching rates, available data from laboratory plate tests and field trials on leaching rates of components originating from the resin and the hardener have been assessed. The data is given in Tables 2.3 to 2.5.

Table 2.3 gives the results of a laboratory test on Product X which was tested at the optimum mix of resin and hardener (R:H), with excess hardener (0.9R:1.1H) and with excess of resin (1.1R:0.9H). One test sample was tested at each mix ratio. Three subsequent leachates were analysed, i.e. after 24-hours, 48-hours and 72-hours stagnation periods.

Similarly, Table 2.4 gives the results of a laboratory test on Product Y, except that no analysis was carried out after the second (48-hours) period and triplicate test samples were tested at each mix ratio.

In both tests the surface to volume ratio (S/V) was 0.4 cm^2ml^{-1} which corresponds to that in a 100-mm i.d. pipe.

Concentrations detected in the extracts of the optimum mix sample are always expressed as 100%. The corresponding concentrations in the excess resin and

excess hardener samples are then calculated relative to the concentration in the optimum mix sample.

Table 2.5 gives relative standard deviations of concentrations found during field trials on three different products. Three linings were tested in each field trial which run for four weeks but for comparison only the periods corresponding to the laboratory tests are considered in Table 2.5, i.e. ~ 144 hours.

The data in Tables 2.2 to 2.5 indicate the following:

a) The concentrations in the extracts will vary depending on the resin/hardener mix ratios, sometimes substantially (five times the concentration for the optimum mix ratio). The effects of mix ratio variations are likely to be different for different products. Any standard test procedure should, therefore, provide data to be able to assess the tolerances of the leaching rates to variations in mix ratios.

b) Relative standard deviations for the triplicate samples were around 25%. Replicate test samples should therefore be tested to differentiate between the test errors and the effects of mix ratios.

c) Relative standard deviations from the field trials carried out under controlled conditions were higher than those from laboratory tests, often around 50% or more. This should be taken into account when drafting the standard test procedure or, alternately when assessing the results.

2.3.2 Laboratory leaching test on epoxy lined pipe

The draft CEN Standard for testing site-applied two-part organic re-lining systems for pipes is most likely to be based on testing samples cut from pipes of the smallest diameter and maximum recommended length to be coated which were lined by competent contractors under supervision of the testing laboratory. Test pieces would be cut, as soon as practicable, from the beginning, the

middle, and the end of the freshly lined pipe and delivered to the laboratory for testing. The test would start immediately when the curing period, recommended by the supplier, was completed. Test conditions would then be the same as for the basic standard test as outlined in Section 2.1.

A laboratory test on pipe segments of a pipe lined with an epoxy resin by a contractor has been undertaken to obtain data allowing to make comparisons between results obtained from laboratory plate tests, laboratory tests on lined pipes and field trials. The test was carried out in accordance with the draft CEN standard using unchlorinated water. The leachates after the three stagnation periods were submitted for analysis to determine the concentrations of total organic carbon (TOC), total nitrogen (TN), two compounds originating from the resin part and two from the hardener.

The analyses have been completed but the evaluation of the analytical results is still in progress. Conclusions reached from the results will be summarised in the next quarterly progress report.

Table 2.3 Laboratory leaching test - epoxy resin - product X

Concentrations in extracts relative to those from optimum mix sample (%)

	Resin components					
Component:	RA			RB		
Period :	I	II	III	I	II	III
Optimum mix	100	100	100	100	100	100
Excess hardener	52	26	41	48	37	55
Excess resin	111	200	501	108	210	404

	Hardener components					
Component:	HA			HB		
Period :	I	II	III	I	II	III
Optimum mix	100	100	100	100	<loD	<loD
Excess hardener	106	207	232	77	<loD	<loD
Excess resin	109	67	25	127	<loD	<loD

Periods: After 30 minutes washing there were 3 successive leaching periods : I - 24 hours, II - 48 hours, and III - 72 hours, i.e. the duration of the test was 144 hours.

Table 2.4 Laboratory leaching test - epoxy resin - product Y

Concentrations in extracts relative to those from optimum mix sample (%)

	Resin components		
Component:		RA	
Period :	I	II	III
Optimum mix	100 (43)*	-	<loD
Excess hardener	57 (88)	-	<loD
Excess resin	357 (94)	-	<loD

	Hardener components								
Component:		HC			HD			HE	
Period :	I	II	III	I	II	III	I	II	III
Optimum mix	100 (25)*	-	100 (21)	100 (0)	-	100 (7)	100 (26)	-	100 (13)
Excess hardener	122 (17)	-	148 (26)	96 (5)	-	141 (26)	73 (27)	-	147 (20)
Excess resin	60 (27)	-	103 (10)	37 (53)	-	103 (34)	27 (57)	-	98 (24)

Periods: After 30 minutes washing there were 3 successive leaching periods : I - 24 hours, II - 48 hours, and III - 72 hours, i.e the duration of the test was 144 hours. Analyses were carried out after periods I and III only.

* The figures in brackets are the relative standard deviations for triplicate test samples.

Table 2.5 Leaching data variation from field trials on epoxy lined mains

	Relative standard deviations of concentrations in water from three linings (%)					
	Resin components					
Component:		RA			RB	
Period :	I	II	III	I	II	III
Product A	48	99	0	<LoD	<LoD	<LoD
Product B	28	6	41	<LoD	<LoD	<LoD
Product C	73	30	47	<LoD	<LoD	<LoD
	Hardener components					
Component:		HX			HY	
Period :	I	II	III	I	II	III
Product A	20	54	64	41	29	78
Product B	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD
Product C	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD

3. FUTURE WORK

* WRc will test distributed samples of PVC and GRP pipes, epoxy coating and rubber for the interlaboratory study for testing factory made and applied products to validate the CEN draft test method. The plan was to report the results to the TC 164/WG3/AHG2 convenor by the end of February 1992. However, because of delays in distributing the test samples, it is unlikely the outcome of the study would be discussed at the next meeting of AHG2 in March.

* Monitoring of and participation in the development of CEN standards for material testing will continue. WRc will consult the CCM for their views on the outstanding issues (as described in Section 2.1.3) before the AHG2 meeting in March.

* Comparisons of leaching rates, obtained for site-applied epoxy lining from laboratory plate and pipe tests and from field trials, will be made when all analytical results are available.

* A study of conditions for leaching tests on solvent cements will be undertaken to asses their validity for real situations and to provide supporting data for the conditions in the CEN draft Standard as proposed by WRC in line with CCM views.

* Gathering of informations on other approval systems and testing procedures will continue. Additional important information will be obtained on approval systems in The Netherlands, Scandinavia, France and Germany. A review will be prepared on the situation in other European countries and major countries outside Europe on the use and testing of materials in contact with drinking water.