

Considerations on the discrimination of “solubility” versus “diffusion” control in renewal time schedules of the tank test (TS2)

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The report is a summary of ECN contributions that used for discussions on technical issues around the standardization of release tests in the EU standardization committee CEN TC 351.

Abstract

Presently the European test is in the phase of “robustness testing” (to investigate potential variability in outcome, as a function of certain test parameters). A focal point is the discrimination between “solubility” and “diffusion” processes by which substances are released. This report is used for technical discussions (2012) on the discrimination between these processes in tank tests as a function of amount and duration of renewal times.

The report reviews current approaches on discrimination between the different release processes, both theoretical and by using actual measurement data. The report is written for a technical / scientific audience involved in standardization of release tests.

The main conclusion is that too much detail in interpretation and assessment of possible solubility/diffusion mechanisms is not justified by the large uncertainties and conditionality in identifying such mechanisms, and their expected limited meaning for scenarios in practice. Based on these considerations, improved assessment methods are proposed, and the time schedule of the current NEN 7375 test method is recommended.

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Summary

European regulations on CE marking of construction products are presently harmonized with respect to requirements on the potential release of “dangerous substances” to the environment. In order to judge the potential release of dangerous substances, laboratory tests are developed and standardized. In the EU standardization committee TC 351, a harmonized test method is developed and standardized for the release of substances from “monolithic” construction products (e.g., concrete) to water (e.g., rainwater). This test method is called a “tank test” as it is based on a vessel (“ tank”) with water, in which a product is submersed for a certain time period to allow diffusion from the substances to the water phase. After this time period, the concentration of released substances is measured in the water (“leachant”). This procedure is repeated a number of times (“leachant renewals”), after which the total release of a substance is determined. Similar procedures are already used on national level in EU member states and implemented in environmental legislation (e.g., the Dutch tank test NEN7375).

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1

Introduction

European regulations on CE marking of construction products are presently harmonized with respect to requirements on the potential release of “dangerous substances” to the environment. In order to judge the potential release of dangerous substances, laboratory tests are developed and standardized. In the standardization committee TC 351, a harmonized test method is developed and standardized for the release of substances from “monolithic” products (e.g., concrete) to water (e.g., rainwater). This test method is called a “tank test” as it is based on a vessel (“ tank”) with water, in which a product is submersed for a certain time period, after which the concentration of released substances is measured in the water. This procedure is repeated a couple of times (“leachant renewals”) after which the total release of a substance is determined. Similar procedures are already used on national level in EU member states and implemented in environmental legislation (e.g., the Dutch tank test NEN7375). Presently the European test is in the phase of “robustness testing” (to investigate potential variability in outcome, as a function of certain test parameters). A focal point is the discrimination between “ solubility” and “diffusion” processes by which substances are released. This report is used for a technical discussion on the discrimination between these processes in tank tests as a function of amount and duration of renewal times. The report reviews current approaches on discrimination between the different release processes, both theoretical and by using actual measurement data.

For the robustness testing of the TS2 tank test (also known as the Dynamic Surface Leaching Test, DSLT) in CEN TC 351, two different time schedules for leachant renewal are under consideration. One is similar to that of NEN7375 (hereafter “ NEN7375” scheme), the other (hereafter “the Alternative” scheme) has different time steps up to 36 days. The European tank test for waste materials, developed in CEN TC292 (TS15863), is based on the “alternative” scheme for leachant renewal. US-EPA also has standardized a tank test, method 1314, which has time steps that are different from both these tests.

The main reason for considering two time schedules in the robustness testing is to investigate which time schedule is more suitable to make a distinction between “solubility of a substance” and “diffusion”. These mechanisms would have

consequences for the extrapolation of test results to long term practice: a solubility controlled substance would - in theory- release at constant concentrations, while diffusion controlled release results in continuously decreasing concentrations. The idea of the Alternative time schedule is to introduce alternating short and long time periods, which would better show the “fingerprint” of diffusion over solubility control than would be possible with the NEN7375 scheme.

On the following pages, technical issues around time schedules are outlined, both theoretically and substantiated with experimental data (supplied by industry and ECN). The focus of this report is merely on the possible discrimination between solubility and diffusion mechanisms, as a decision between the two proposed time schedules depends on this critical possibility. The following time schedules are discussed in this paper:

Table 1: Time schedules for leachant renewal discussed in this paper.

“NEN 7375” scheme	“Alternative” scheme
Duration from the start of the test (t0), in days	Duration from the start of the test (t0), in days
0.25	0.083
1.00	1.00
2.25	2.25
4.00	8.00
9.00	14.0
16.0	15.0
36.0	28.0
64.0	36.0

2

Theoretical considerations

- When a component is released purely by diffusion, the release after a certain time period (e.g., 36 days) can be mathematically shown to be identical regardless the number, duration and amount of time steps (renewals of solution) , based on analytical expressions for 3D-release (Crank, Mathematics of Diffusion, 1979), shown in Figure 1.
- In case the release of a substance is controlled purely by solubility instead of diffusion, a constant concentration would be found in each fraction, provided that saturation is reached and influencing factors such as pH remain invariable. The theoretical concentration patterns in all three cases (diffusion in the NEN7375 scheme, diffusion in the Alternative scheme, solubility in both schemes) is shown in Figure 2, expressed as relative concentration (=concentration in fraction / average concentration in all fractions, C/C-average).
- An analysis of the slope of the cumulative release curve in different trajectories, as is presently prescribed in the NEN7375 standard, is not suitable to distinguish diffusion from solubility, as both solubility and diffusion lead to slopes of 1:0.5 in the initial stages of the test given the currently prescribed renewal times. In case of solubility control, the slope is initially 1:0.5 and levels off suggesting depletion (Figure 3).
- The assumption that solubility control would lead to a slope of 1:1 in the cumulative release curve of NEN7375 is erroneous. This slope will only be achieved for solubility control when time periods of each renewal are equal.¹ This is illustrated in Figure 4 both theoretically (left diagram) and supported with data (right diagram).
- In the results of the present NEN7375, slopes that approach 1:1 or higher are quite common, but these are not indicative for a specific process. It can be observed in case of 1) when pH changes during the test, which influences both diffusion and/or solubility mechanisms; 2) a dissolving mineral phase that has not yet reached saturation within the time period(s) of the test; 3) heterogeneous distribution of a substance in the product; 4) a combination of factors or other factors..

¹ The possible reason why equal time steps were departed during the development of the tank test in the 1970' and 1980's was most likely that concentrations decrease in each consecutive fraction, to levels below detection limits. To prevent that, a different time schedule was developed, that led to constant and slightly increasing concentrations, now known as NEN7375. However, a consequence that might have been overlooked, was that diffusion and solubility were no longer separable based on the cumulative slope.

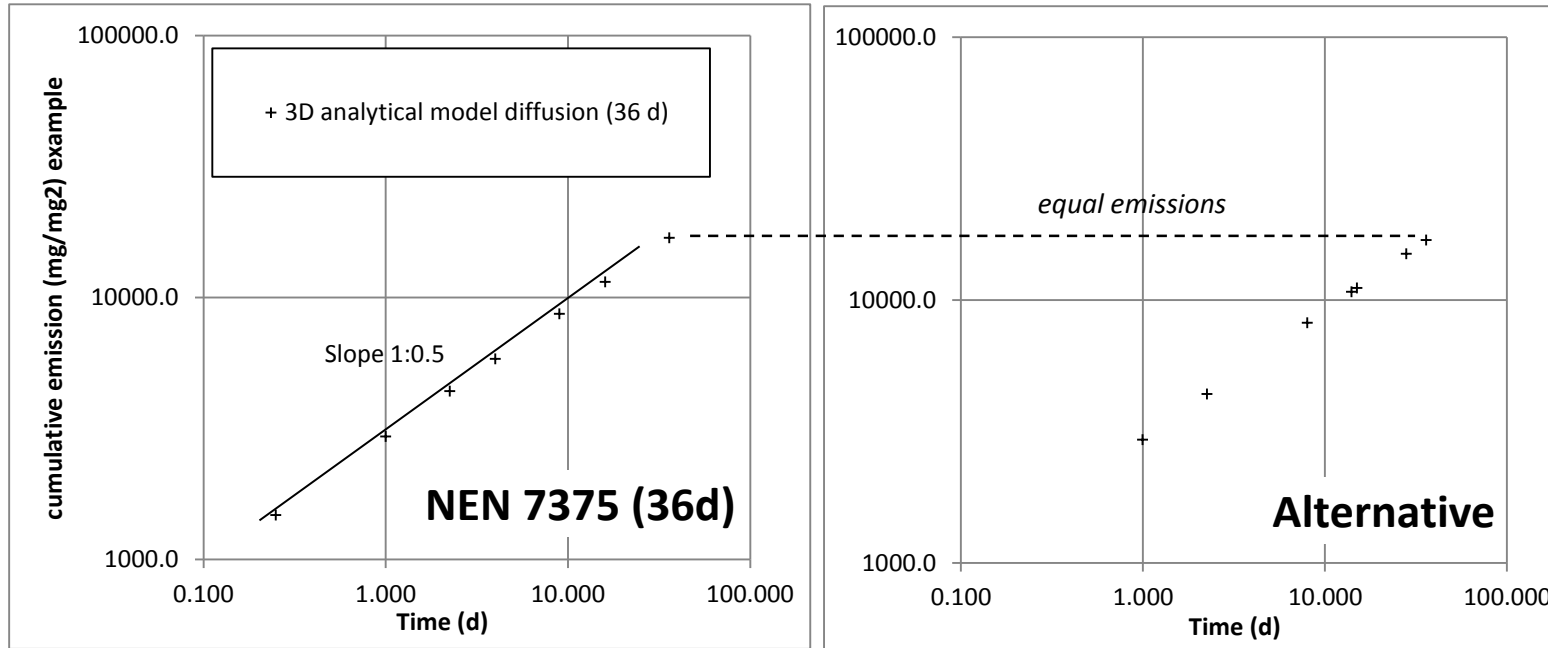


Figure 1: 3D-calculated release in a tank test with different time schedules, calculated with expressions of Crank (1979). The slope of the cumulative curves (mg/m²) is 1:0.5 in both situations, and the release is equal after an equal time period. Amounts on the Y-axis are not absolute values for a specific substance or product.

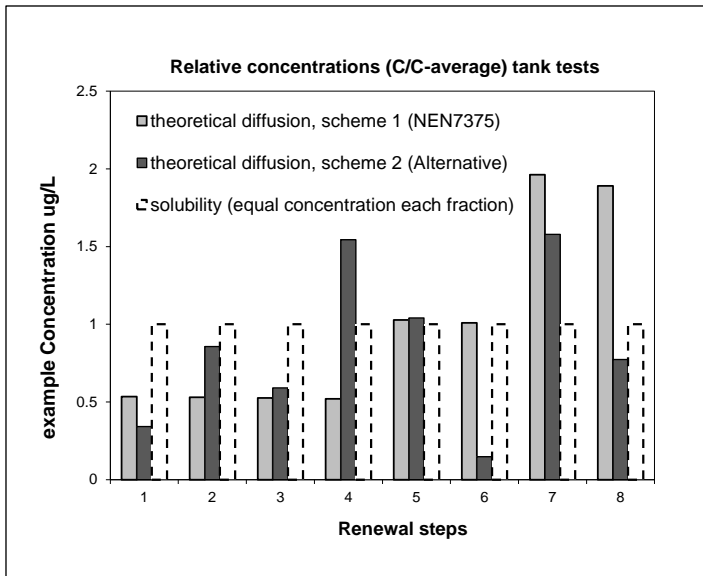


Figure 2: Theoretical concentrations found for a substance controlled by diffusion in a tank test in each time step (8 steps in each time schedule, calculated with 3D analytical model of Crank, 1979) and the concentration pattern expected for solubility control (applicable when saturation is reached in each fraction, and influencing factors such as pH are invariable).

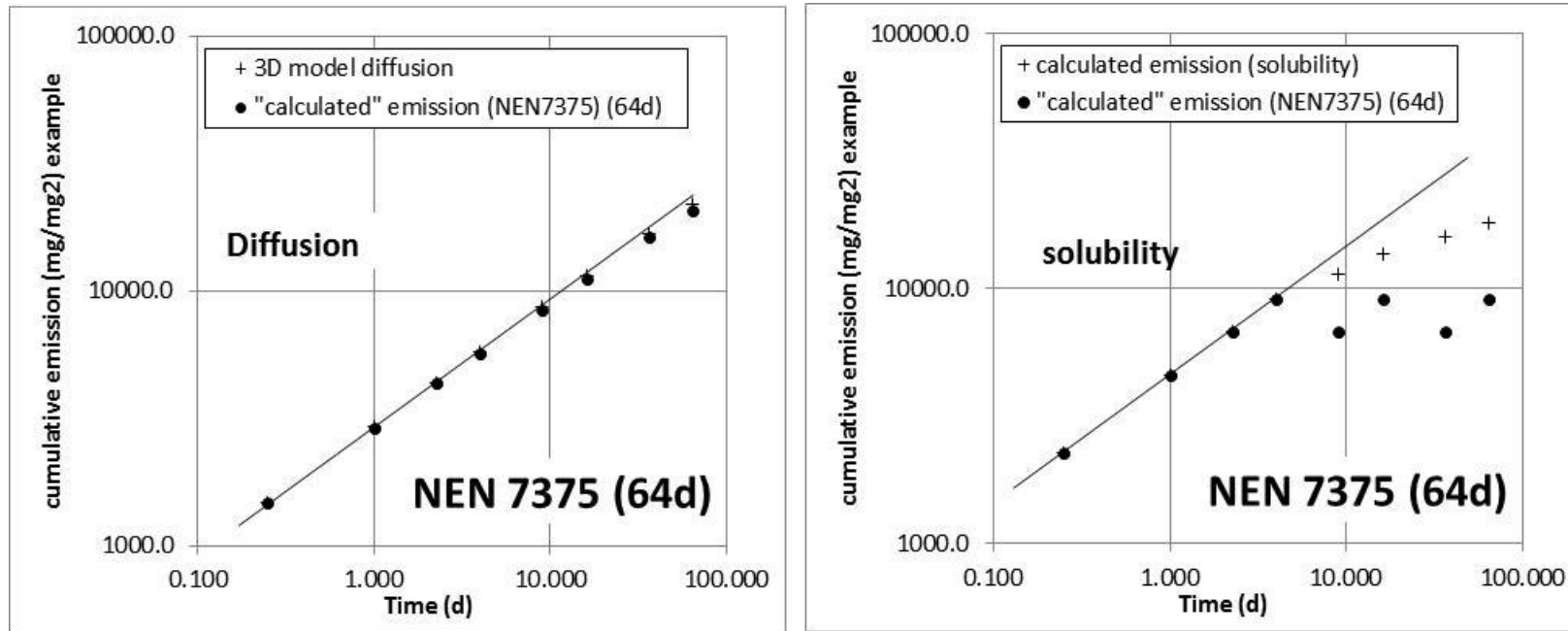


Figure 3: Illustration that the slope of a cumulative release curve (mg/m²) leads to similar slopes for diffusion and solubility control. The measured cumulative emission (+ marks) in case of solubility suggests diffusion (fraction 1-4) followed by depletion (leveling off of concentrations in fraction 5-8). Also shown is the "calculated" emission according to NEN7375 (i.e., a correction formula) which also leads to misinterpretations in identification of mechanism in case of solubility control.

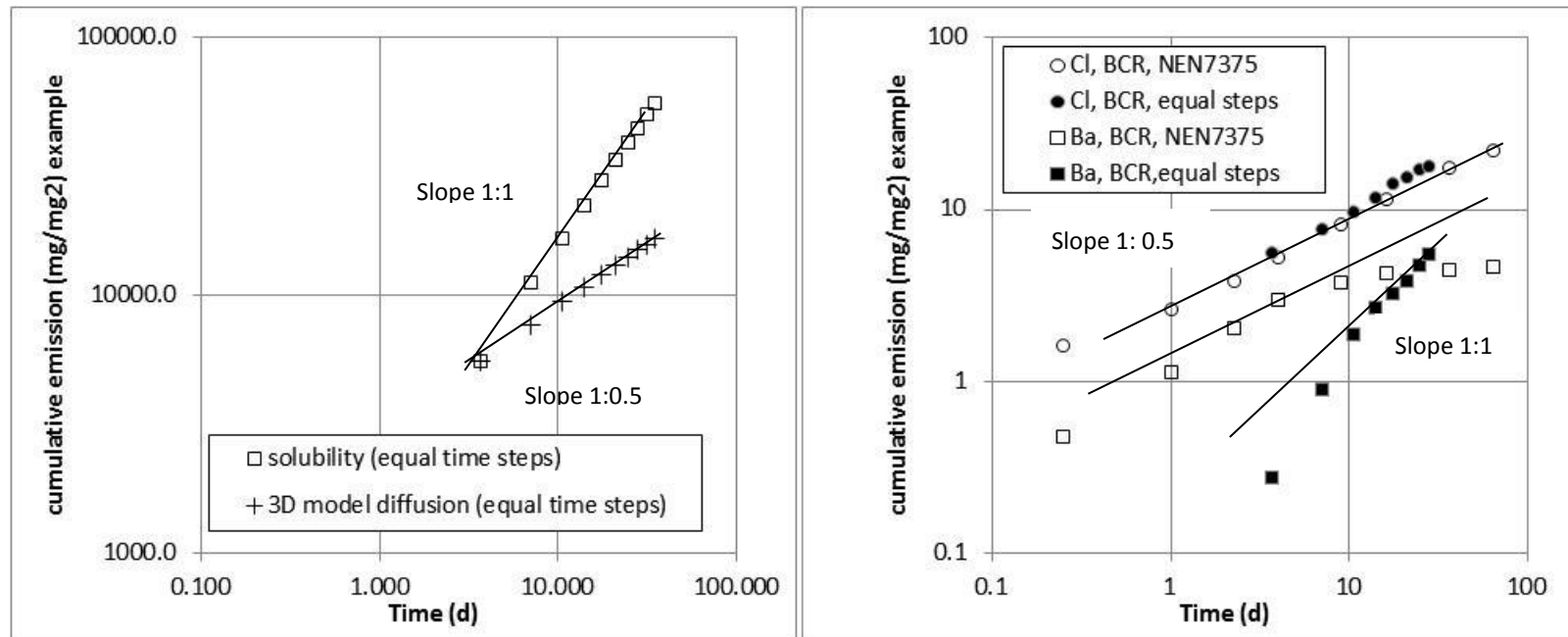


Figure 4: Illustration that equal renewal time steps in the test lead to different slopes for diffusion and solubility. Left diagram: Theoretical cumulative release curve for a time schedule with equal time steps. The situation for diffusion leads to a slope of 1: 0.5, the situation for solubility control (equal concentrations) to a slope of 1:1. The right diagram shows data from a stabilized waste (BCR; data ECN) data that confirms this hypothesis. Barium shows in the NEN7375 test behavior that is similar to that in Figure 2 for a solubility controlled substance and has an initial slope of 1:0.5, while a slope of 1:1 is found when equal time steps are used. Chloride, which is controlled by diffusion, shows a slope of 1:0.5 in both time schedules.

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Alternative ways of assessing different mechanisms in the tank test

- A different and more straightforward assessment of the dominant mechanisms based on concentration patterns is described in the NL contribution “Normative annex to TS-2 INTERPRETATION OF DSL TEST RESULTS” of May 2012. Solubility control (i.e. behavior other than diffusion) could be identified when the following two criteria are met:

$$0.7 \leq \frac{\text{average concentration in fractions 7 and 8}}{\text{average concentration in fractions 5 and 6}} \leq 1.3$$

$$0.7 \leq \frac{\text{average concentration in fractions 2 to 4}}{\text{average concentration in fractions 5 and 6}} \leq 1.3$$

An illustration of the principle is provided in Figure 5 and 6 for NEN7375 schedule, similar principles for the Alternative schedule in Figure 7.

- Similar to above, concentration differences can be used to identify initial washoff (concentration in the first fraction(s) being significantly higher than the average concentrations in the remaining fractions):

$$\frac{\text{concentration in fraction 1}}{\text{average concentration in fractions 2 to 7}} > 2.0$$

And depletion (concentration in the last fraction(s) being significantly lower than the preceding fraction):

$$\frac{\text{concentration in fraction 7}}{\text{concentration in fraction 8}} > 1.5$$

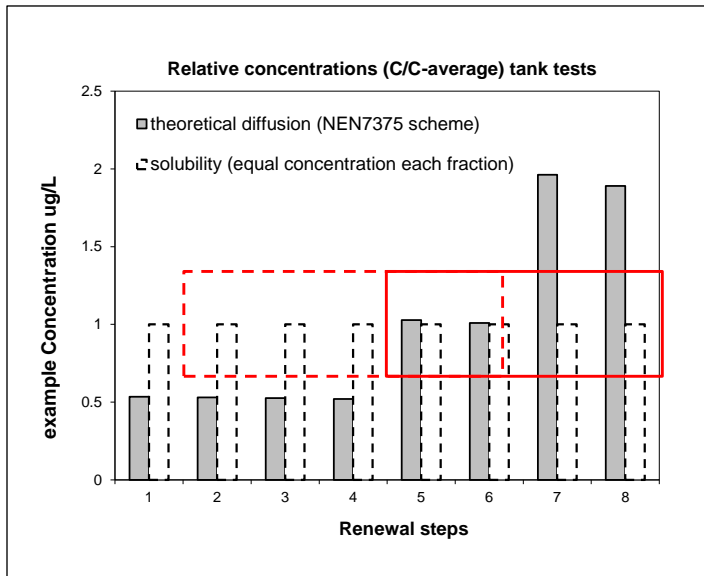


Figure 5: Principle by which solubility can be distinguished from diffusion in the NEN7375 scheme: comparison of average concentrations of different fractions. The solid red box indicates solubility control between fractions 5-6-7-8 (tolerance set at 0.7 and 1.3), dashed red box indicates solubility between fractions 2 and 6.

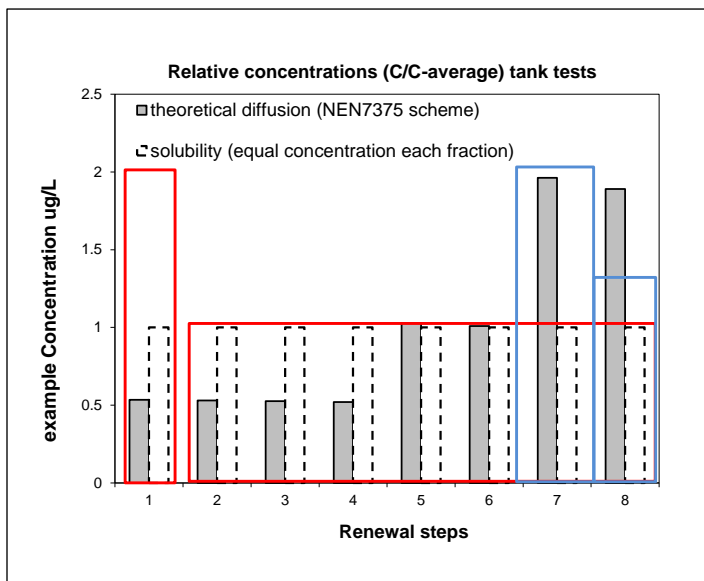


Figure 6: Principles by which surface wash-off (red boxes) and depletion (blue boxes) can be identified from concentration patterns in NEN7375.

- In using the above criteria, one should be careful that “depletion” and “surface wash-off” can only be identified with certainty in case “diffusion” is established as being the dominant release process in the remaining fractions.
- A similar simple approach for a simple identification of mechanisms based on concentration patterns could be followed for the Alternative time schedule. In the Alternative scheme it would be possible to use the differences between theoretical

concentrations in the short and long time steps to identify diffusion or solubility. However, *because* of the variation in time steps and concentration in consecutive fractions, this simple approach is less suitable for the alternative scheme.

- Fraction 6 in the Alternative schedule should in case of diffusion be much lower than fractions 5 and 7, so a simple criterion to identify solubility control could be as below (factor 18 based on theoretical diffusion pattern). An illustration is provided in Figure 6.

$$\frac{\text{concentration in fractions 5 + concentration in fraction 7}}{\text{concentration in fraction 6}} \leq 18$$

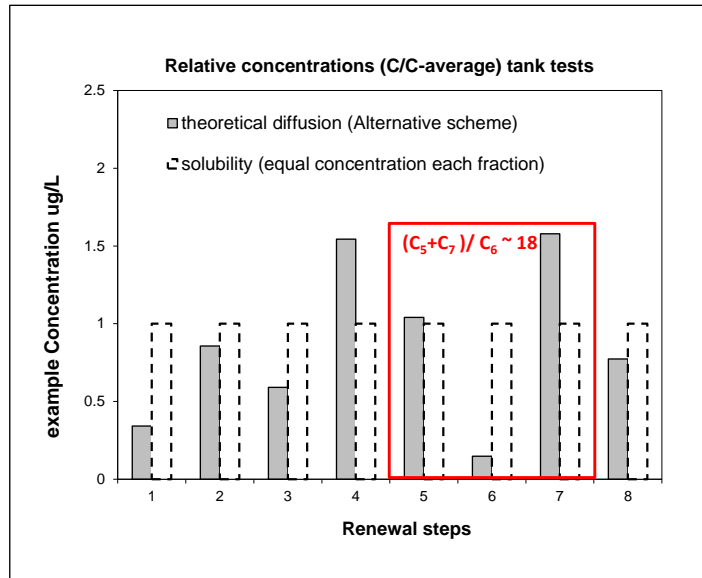


Figure 7: Principle by which solubility can be distinguished from diffusion in the Alternative scheme: comparison of concentrations in different fractions.

- A more rigorous way to separate diffusion and solubility in the NEN7375 and the Alternative schemes would be to calculate the agreement between theoretical and measured relative concentrations based on square-root of errors (see also appendix A):

Table 2: Agreement between theoretical and measured relative concentration (example)

Fraction	Theoretical relative concentration (C/Caverage)	Measured relative concentration (C/Caverage)	'Error' (data-model)
2	0.53	0.63	0.10
3	0.53	0.39	-0.14
4	0.53	0.42	-0.11

Next, calculate the Root Mean Square Error (RMSE) and set constraints to what is “agreement” or not (criteria to be decided). The *lower* the RMSE, the *closer* is the correspondence between observations and theoretical diffusion, the *higher* the RMSE, the *weaker* is the correspondence between observations and theoretical diffusion.

The “RMSE approach” might be more discriminative, because solubility does not by definition result in constant concentrations in the test due to variations in factors such as pH. In example 3 (see below and Appendix A) the RMSE approach is worked out and tested further.

A combination of the straightforward identification rules and the RMSE approach is also possible (e.g., RMSE approach on fractions 2-7, prior to quantifying wash-off and depletion in fractions 1 and 8, respectively).

The conclusions from this theoretical assessment are in summary:

- An assessment of the slope of the cumulative leaching curve (expressed in mg/m²) is not discriminative for identification of diffusion or solubility processes. To make a distinction, the concentration-time patterns should be used, instead of the cumulative slope.
- Both the NEN7375 and the Alternative time schedules are about equally suitable to discriminate “diffusion” from “other processes”, such as solubility of a substance, with simple and straightforward approaches. For the NEN7375 schedule, a simple calculation is possible to compare the data with theoretical diffusion patterns; however, this approach is less suitable for the Alternative scheme. For both NEN7375 and the Alternative scheme, a more rigorous approach is also possible, which is based on the statistical agreement between theoretical and measured relative concentrations, expressed in RMSE (Root Mean Squared Error). A combination of both approaches is also possible.

4

Examples

On the following pages, data is summarized in which NEN7375 and the Alternative scheme are directly compared for the same samples.

Data is shortly discussed with respect to the possibilities for discrimination between solubility and diffusion mechanisms.

Other features (e.g., similarity/dissimilarity between cumulative emissions in both schedules, possibilities for short tests, translation between historic data on NEN7375 and an Alternative schedule) are outside the scope of this paper, because the discrimination between solubility and diffusion is the main technical/scientific reason for considering the two time schedules in the robustness work, and a decision between the two time schedules depends on this critical possibility.

Although there may more data available, in this paper only data is used that is available at the time of writing (June 2012) is used. A selection is made of data of extremely high quality with respect to number of replicates, careful sampling strategies, test execution, and analytical measurability. The data is partly collected by ECN and partly supplied by the Industry. Data from US-EPA and UBA will be considered in the future.

Data are presented all in the form of relative concentrations (actual concentration in fraction / average concentration of all fractions) in combination with theoretical diffusion patterns.

EXAMPLE 1.

COMPARISON NEN7375 and the Alternative for AAC (data on courtesy of the industry) .

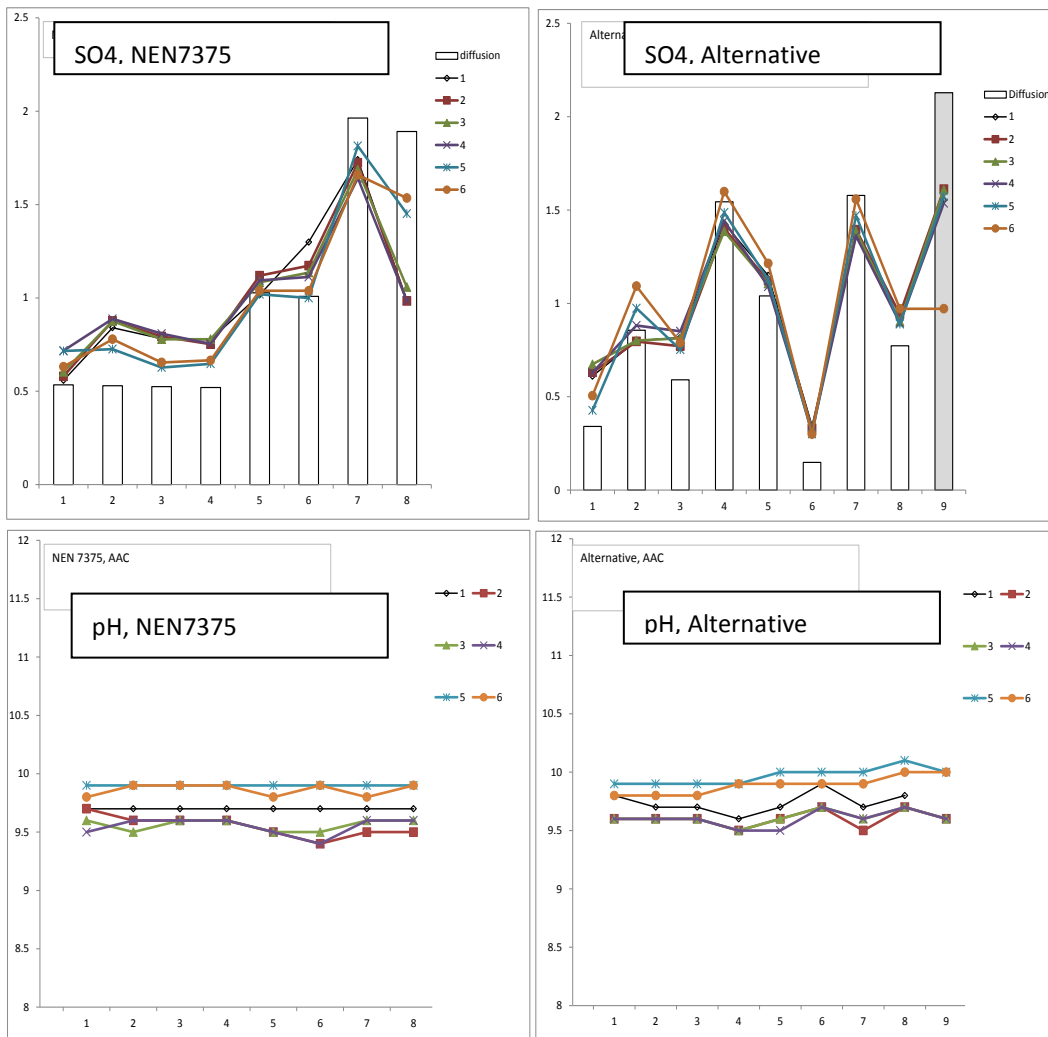


Figure 8: Relative concentrations data for AAC in NEN7375 (left) and the Alternative (right) time schedules (n=6). The Alternative scheme is extended with one step from 36 days to 64 days (grey shaded). Explanation see text.

The figure shows relative concentrations data for AAC in NEN7375 (left) and the Alternative (right) time schedules (n=6). The Alternative scheme is extended with one step from 36 days to 64 days (grey shaded). Both concentration patterns perform equally well in the ability to recognize “diffusion” over other processes, and possibly show some depletion (seen as relatively low concentrations in the final fractions relative to theoretical concentrations in NEN7375 and the Alternative scheme). Even in this case the concentrations do not follow the diffusion pattern ideally. The pH in the alternative scheme is slightly more variable than in NEN7375. Other substances than sulphate were not measured.

- Conclusion: both time schedules perform equally well in the ability to recognize “diffusion” over other processes.

EXAMPLE 2.

NEN7375 and the Alternative for ceramics (data on courtesy of the industry).

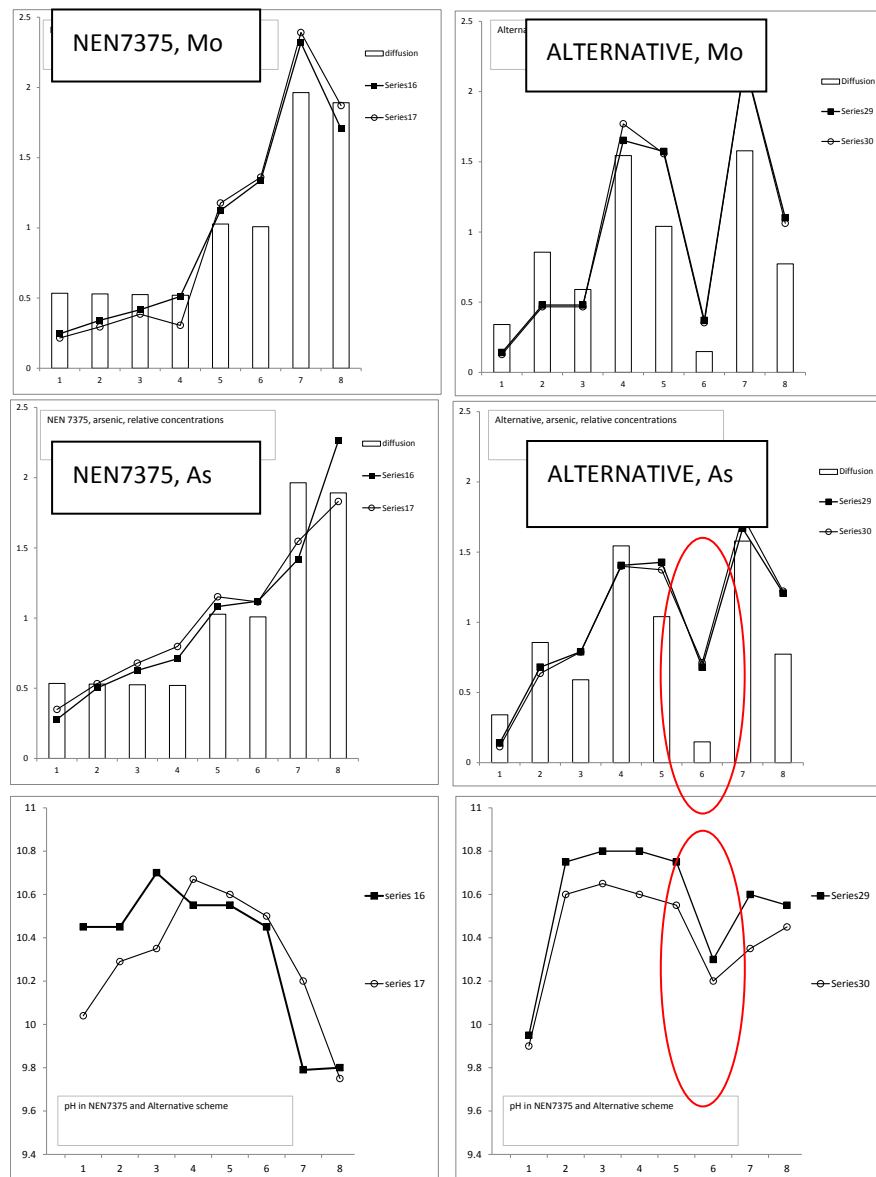


Figure 9: Relative concentrations of ceramics in NEN7375 and the Alternative time schedules, duplicate measurements. Explanation see text.

In case of Mo in example 2, concentrations follow the diffusion pattern (Mo at high pH is almost inert). Arsenic (not inert at high pH) is influenced by diffusion, but interpretation in both tests becomes complicated due to pH effects. This is the case in particular in the short fraction 6 (the Alternative scheme). Note that the pH development shows clear differences in both tests. Substances that clearly show solubility control were not found in the dataset.

- Conclusion: variation in pH (in particular in the Alternative scheme) could have an influence on the concentration pattern for elements that are chemically reactive and sensitive to pH, such as As. This complicates the interpretation of mechanisms.

EXAMPLE 3.

NEN7375 and the Alternative for BCR (cement stabilized waste) (data ECN).

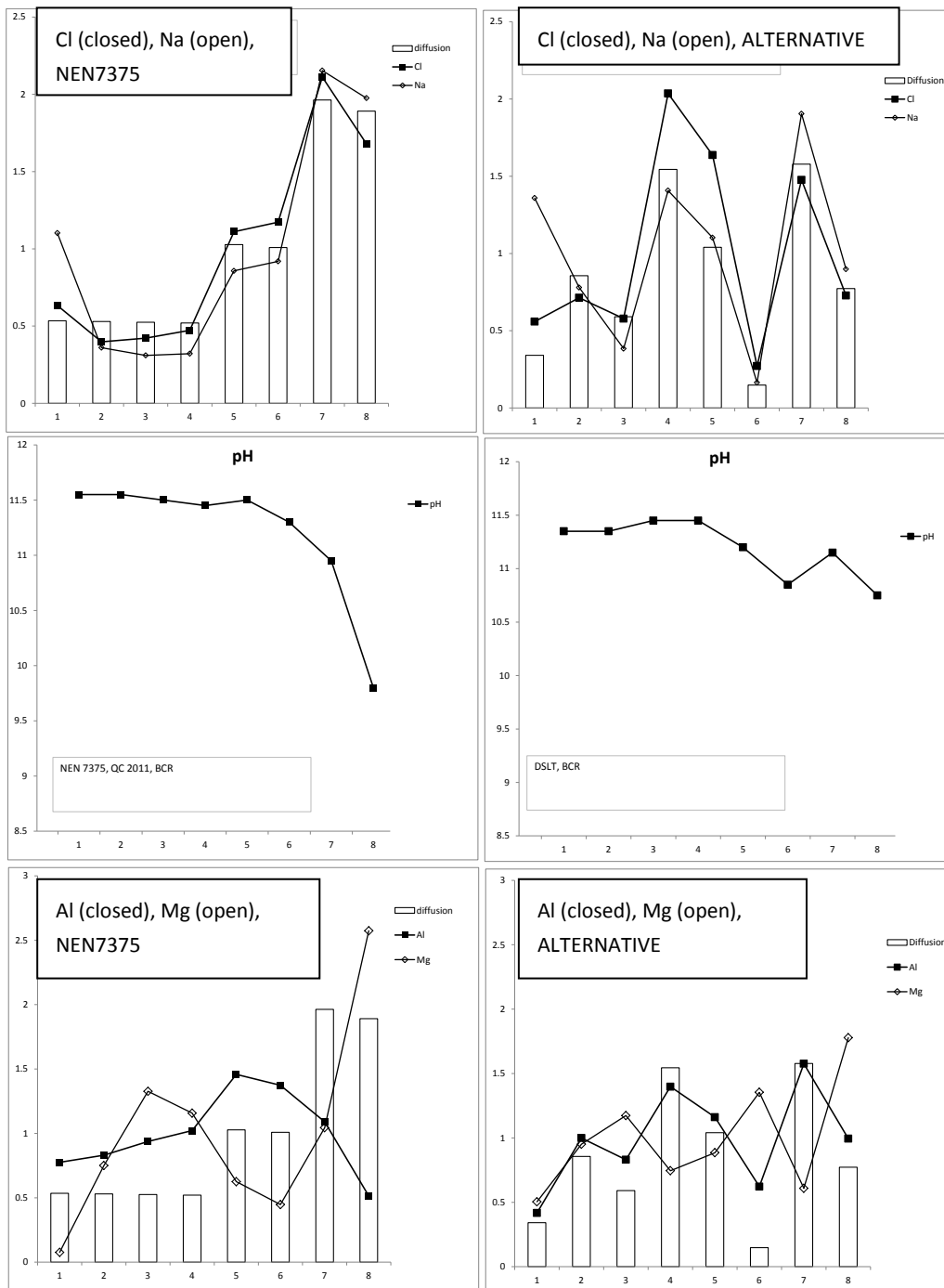


Figure 10: Data for BCR (cement stabilized waste) for Na and Cl (inert substances), and Al and Mg (strongly pH- sensitive substances).

In example 3, Na and Cl show equally clear signs of diffusion behavior in both time schedules. Note that Na and Cl will not be influenced by pH, so their behavior is purely caused by diffusion.

The pH in NEN 7375 gradually decreases, in the Alternative scheme the pH is quite constant but with variation in particular in the short fraction 6.

The interpretation of the behavior of reactive, pH- sensitive substances such as Mg and Al in the same tests is extremely complicated as it is a mixture between chemistry and diffusion. In the BCR sample, heavy metals were partially below detection limit. Therefore in the example we look at Al and Mg, representative for amphoteric metals (such as Cu, Pb, Cd, Zn).

In the NEN7375 scheme, it can be observed from the figure that Al and Mg show behavior that contradicts to “diffusion” .

In the Alternative scheme, Al shows behavior that corresponds with diffusion rather well, but Mg shows almost exactly opposite behavior. We have to look closer, with help of other methods, to find out what are the “real” controlling processes for these substances.

Both Al and Mg appear to be largely, if not completely, influenced by pH dependent solubility as shown in the Figure below, in which the NEN7375 and Alternative scheme data is plotted in terms of actual concentration (mg/l) together with data collected using pH dependence test on the same (crushed) sample:

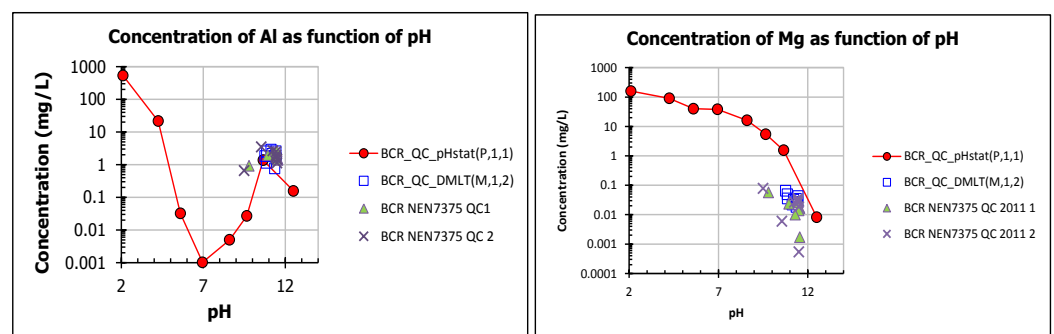


Figure 11: The NEN7375 and Alternative scheme data from the previous figure is plotted in terms of actual concentration (mg/l) together with data collected using pH dependence test on the same (crushed) sample.

Both concentrations of Al and (to a lesser extent) Mg in NEN7375 and the Alternative scheme are close to the pH dependence test curve, indicating potentially solubility control.

According to the observed pH dependency, upon a pH decrease, Al should decrease in concentration while Mg should increase (opposite behavior). Indeed, Al and Mg respond (oppositely) to pH changes in the tank tests, confirming solubility control, rather than that one or both of these substances are controlled by diffusion/depletion. In fact it is likely that the behavior will be a mixture between diffusion and solubility, as also the pH itself is subject to diffusion and solubility (diffusion of alkalinity!).

Hence, the patterns for reactive elements that are sensitive to pH in *both* NEN7375 and the Alternative scheme could erroneously be identified as caused by

diffusion/depletion. This cannot be solved or improved without additional information such as a pH dependence test.

- What would happen when the “identification rules” outlined in this document are applied to these BCR data?
 1. The NEN7375-schedule results, interpreted with the identification rules from the document “Normative annex to TS-2 INTERPRETATION OF DSL TEST RESULTS” of May 2012, lead to Cl and Na being controlled by diffusion, which is justified given their chemical non-reactivity. However, Al would be identified as diffusion followed by depletion, Mg (that follows opposite behavior) as diffusion. The conclusions for Al and Mg are largely erroneous, which is mainly because “solubility” in this case does not lead to constant concentrations, but a complex concentration pattern as a result of pH changes in the test.
 2. The above approach applied to the Alternative scheme is not very feasible, as it would depend strongly on only the 6th fraction (see identification rules previously). Al would, depending on the criteria set, probably be seen as diffusion, Mg as solubility. These conclusions are at least partially erroneous.
- The more rigorous “RMSE approach” outlined on page 8 consists of calculating the statistical agreement between theoretical diffusion and data over the complete experiment and express it in a single number, the Root Mean Square Error (for example calculation see appendix A):

$$\text{RMSE} = \sqrt{1/n (\sum (\text{data-model})^2)}$$

For Cl, Na, Al and Mg this results in (first time steps omitted, to eliminate wash-off effects; details see appendix A):

Table 3: Statistical agreement between theoretical diffusion and data over the complete experiment and expressed in a single number, the Root Mean Square Error.

Root Mean Square Error				
	Cl- relative	Na- relative	Al- relative	Mg- relative
NEN7375	0.14	0.17	0.71	0.64
Alternative	0.30	0.17	0.24	0.79

The *lower* the RMSE, the *closer* the correspondence with theoretical diffusion. The *higher* the RMSE, the *weaker* the correspondence with the diffusion concentration pattern. An unambiguous criterion cannot be given at this point, but as a start one could compare the outcome for different substances with that of little reactive substances such as sodium or chloride, assumed to be representative for “ideal” diffusion- controlled release.

1. In the NEN7375 scheme, both Na and Cl show good correspondence with a diffusion pattern. The resulting RMSE is 0.14 and 0.17 respectively. Al and Mg show much weaker correspondence with diffusion (RMSE 0.71 and 0.64,

respectively). This is an expected outcome since we now know that Al and Mg are controlled by (a mixture of diffusion and) pH dependent solubility.

2. In the Alternative scheme, the interpretation is more complex. Due to the alternating long and short periods, and resulting small pH effects, differences caused by pH dependent solubility and possibly kinetics get exaggerated. Aluminum seems to correspond to “diffusion” behavior, and the RMSE (0.24) is even better than that of chloride (0.30). Sodium corresponds the strongest with diffusion (RMSE 0.17) and Mg, showing behavior opposite to diffusion, scores a high RMSE (0.79). We know, however, that Al and Mg obey pH dependent solubility, with only a small influence of diffusion.

The conclusions from the examples are:

- Both time schedules perform equally well in the ability to recognize “diffusion”, based on comparison of theoretical and measured concentration patterns. For chemically reactive substances, however, unambiguous separation of diffusion and solubility processes may be extremely difficult in both test schemes without additional information.
- An approach based on correspondence between a theoretical diffusion pattern and data (preferably the RMSE approach) would work best for the NEN7375 scheme. The reason for this may be that time steps and theoretical diffusion patterns concentrations are less variable than in the Alternative scheme, where alternating short/long periods may lead to variability in pH and, hence, variation in concentration for elements that are sensitive to pH.

5

Potential uncertainties associated with identification of diffusion/solubility control

Both theory and practice (see the examples) indicate that there are a number of fundamental issues that prevent a clear and useful discrimination of these two processes in a tank test. A few important of these are:

- Diffusion and solubility are for most reactive substances *not* separate processes. Instead, in most cases both processes play a role simultaneously. The chemistry dictates the concentration level, the diffusion determines the transport rate. For chemically reactive elements, influence of chemistry becomes visible when the pH changes slightly during the test. Only for chemically inert substances (chloride; some oxyanions at high pH) chemistry is unimportant.
- Whether solubility control or diffusion is marked “dominant” in a test, is dependent on the conditions of the test itself. It is not exclusively an “intrinsic” property of the material under study. For instance, the time step duration and L/A ratio have an influence on which process is observed to be “dominant”. Longer time steps and/or lower L/A ratio may more quickly lead to solubility equilibrium in the test. This means that even within a single test, conclusions on mechanisms may turn out to be different in different trajectories as a result of time steps of different length.
- Also dissolution kinetics (slow dissolution of a mineral phase) can “disguise” as diffusion (square-root of time behavior) as this can be a surface-related process. Depending on the length of the time steps, dissolved concentrations may reach solubility equilibrium or not. Also here, only for chemically inert substances (chloride; some oxyanions at high pH) chemistry is unimportant.

- The pH in both time schedules for alkaline products (cementitious, $\text{pH} > 10$) will be different from the pH found in practice at the interface product/air after even short time periods ($\text{pH} 8$), which has an considerable influence on release behavior for most reactive elements. Hence, it cannot be by default assumed that "solubility control" in the test would lead to higher or lower release than diffusion, when test results are to be extrapolated to practice on the long term. Instead, the release could become lower or higher (relative to the test results), depending on the pH dependency of the substance. Information from pH dependence tests would be a step forward to allow estimates of such changes. Possibly there is already sufficient data available to come up with "generic" estimates for alkaline products.

6

Conclusions

- Too much detail in interpretation and assessment of possible solubility/diffusion mechanisms in different trajectories is not justified by the large uncertainties and conditionality in identifying such mechanisms, and their expected limited meaning for many scenarios in practice.
- The added value of a simple, straightforward approach based on correspondence between diffusion patterns and data may be:
 1. When a substance is shown to obey to diffusion in the test, the “initial washoff” and “depletion” can be quantified with more certainty. These parameters are less conditional, and may be useful for translation of test results to practice. When instead of diffusion “other processes” are identified to control the release, “washoff” and “depletion” cannot be quantified with certainty and have only limited meaning.
 2. It is important that technical experts know what they are measuring in the test. For that reason alone, it would be of added value to give some guidance on interpretation of test results.
- When it comes to interpretation of tank test data with respect to identification of solubility/diffusion in the test, both the NEN7375 and the Alternative time schedules are about equally suitable to discriminate “diffusion” from “other processes” in the test. To make a distinction, the concentration-time patterns are used instead of the cumulative slope. The NEN7375 scheme would have a slight preference over the Alternative scheme as the identification can be done more simple, and also more rigorous approaches based on statistical agreement between data and theoretical diffusion seem to work better for the NEN7375 scheme.
- If the NEN7375 schedule would become the final time schedule for TS2, the final time step of 64 days is recommended to be able to better quantify “depletion”.
- Observations indicate that the pH in the short fractions of the Alternative scheme (fraction 1 and 6) may differ rather sharply from the pH in the other fractions. In

NEN7375, pH is also subject to large changes during the test, but these are more gradual.

- Although not scope of this study, the variations as a function of amounts, position and duration of renewal times lead to the *expectation* that the alternative scheme could, for some products that are weakly buffered and some chemically reactive substances, lead to different and more variable cumulative emissions than the NEN7375 scheme. This is due to observed sharper deviations in pH as a result of more variable time steps (alternating short/long periods). These potential effects should be evaluated against the need for an alternative test scheme.
- Differences as meant above are also of relevance for comparison of cumulative emissions from the tank test developed in TC 292 (TS15863), the Dutch tank test NEN7375 and the upcoming TS2 depending on the chosen renewal times schedule.

Appendix A. Calculation of Root Mean Square Error

The RMSE can be used to quantify the agreement between “ model” and “ observation” , in this case the “ theoretical diffusion pattern” and the “data”. All concentrations are expressed as relative concentrations (C/C-average). Below the full calculation is given of the table in the main text. The lower left RMSE is explained in detail. The lower the RMSE, the better agreement between diffusion pattern and the actual measurements.

NEN7375

<i>time</i>	Cl-relative	model	data-model	Na-relative	model	data-model	Al-relative	theoretical	data-model	Mg-relative	theoretical	diff
1.00	0.40	0.53	-0.13	0.36	0.53	-0.17	0.83	0.53	0.30	0.75	0.53	0.22
2.25	0.42	0.53	-0.10	0.31	0.53	-0.21	0.94	0.53	0.41	1.33	0.53	0.80
4.00	0.47	0.52	-0.05	0.32	0.52	-0.20	1.02	0.52	0.50	1.16	0.52	0.64
9.00	1.11	1.03	0.08	0.86	1.03	-0.17	1.46	1.03	0.43	0.63	1.03	-0.40
16.0	1.17	1.01	0.16	0.92	1.01	-0.09	1.37	1.01	0.37	0.45	1.01	-0.56
36.0	2.11	1.96	0.15	2.15	1.96	0.19	1.09	1.96	-0.87	1.04	1.96	-0.92
64.0	1.68	1.89	-0.21	1.98	1.89	0.08	0.51	1.89	-1.38	2.57	1.89	0.68
RMSE			0.14			0.17			0.71			0.64

Alternative	Cl-relative			Na-relative			Al-relative			Mg-relative		
<i>time</i>	model	data-model	theoretical	model	data-model	theoretical	model	data-model	theoretical	model	data-model	theoretical
1.00	0.71	0.86	-0.14	0.78	0.86	-0.08	1.00	0.86	0.14	0.95	0.86	0.09
2.25	0.58	0.59	-0.01	0.38	0.59	-0.21	0.83	0.59	0.24	1.17	0.59	0.58
8.00	2.04	1.54	0.49	1.41	1.54	-0.14	1.40	1.54	-0.15	0.75	1.54	-0.80
14.0	1.64	1.04	0.60	1.10	1.04	0.06	1.16	1.04	0.12	0.89	1.04	-0.16
15.0	0.27	0.15	0.12	0.16	0.15	0.02	0.62	0.15	0.47	1.35	0.15	1.21
28.0	1.48	1.58	-0.10	1.90	1.58	0.33	1.58	1.58	0.00	0.61	1.58	-0.97
36.0	0.73	0.77	-0.04	0.90	0.77	0.13	0.99	0.77	0.22	1.78	0.77	1.01
RMSE*			0.30			0.17			0.24			0.79

*sum of squared residuals (SUMSQ): 0.645107
number of observations (n) 7
 $[\text{SUMSQ}/n]^{0.5}$ 0.30

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