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EVALUATION OF HOMOGENEITY OF RADIOACTIVE WASTE FORMS: STATISTICAL CRITERIA

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ABSTRACT. A set of statistical tests is proposed to evaluate the homogeneity of radioactive waste forms. These criteria were applied to cemented wastes forms by using natural thorium and uranium compounds as tracers simulating insoluble and soluble wastes, to evaluate the chemical homogeneity of the final product. The concentration of tracers in the samples were measured by using the delayed neutron counting technique which allows for the determination of uranium and thorium simultaneously. The same set of statistical tests can be applied to evaluate the homogeneity of all chemical and physical quantities necessary to characterize the waste forms (e.g., compressive strength, density, permeability, porosity, leaching rate, thermal conductivity, etc.). the possible influence of the water to cement ratio, (W/C), and salt contents in the waste stream was also investigated. The mixing technique used to produce the cemented waste forms proved to be good enough as a standard method to obtain a homogeneous product.

INTRODUCTION

The objective of waste solidification is to convert it into a stable monolithic form which minimizes the probability of radionuclide release to the environment during interim storage, transportation, and final disposal. The solidified waste should be of such chemical, mechanical, thermal, and radiolytic stability that its integrity can be assured over the time required for the decay of contained radionuclides to an acceptable level.

One of the most fundamental physical properties required for any kind of immobilized waste form is the homogeneity. This property is important in the solidification process and during long-term storage. Furthermore, chemical and physical properties of immobilized waste such as density, porosity, leaching rate, matrix degradation, permeability, compression strength, radiation damage, thermal conductivity, etc. can not be easily understood if the matrix is not homogeneous. Often during waste immobilization in laboratory scale the homogeneity condition can be assumed. However, in the scale up of the immobilization process this condition is mandatory and cannot necessarily be assumed.

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In laboratory scale procedures, emphasis is given to the necessity of well homogenizing the mixture in order to obtain a uniform and reproducible product.

In certain cases compression tests are conducted in samples taken from the real size product. However, a reliable, statistical test is seldom applied to them.

All physical, chemical, physico-chemical and radio-chemical properties have to be uniform throughout the waste form in such a way that it can be considered homogeneous. Of course, if the waste form is homogeneous with respect to a certain property, it does not mean necessarily that it is homogeneous with respect to some other properties. On the other hand, it is known that some properties do correlate in the sense that if one observes homogeneity for one probably, the behavior of the other will also be homogeneous. So a careful selection of a set of properties have to be made in order to assure that once acceptable levels of homogeneity hold for this set, then all relevant properties can be considered homogeneous.

No matter what set of properties is considered, these properties have to be measured according to statistical criteria.

In order to evaluate the degree of homogeneity of simulated wastes immobilized in cement matrices, by using a planetary paddle mixer the delayed neutrons counting technique (1) can be used to measure the distribution of small quantities of soluble uranium salt or insoluble thorium oxide, in powder form. This procedure was applied in this work, and the distribution of uranium and thorium measured throughout the waste form was confirmed to be homogeneous by the application of appropriate statistical tests.

EXPERIMENTAL PROCEDURES

Ordinary Portland cement 320 was used in sample preparation. The cement pastes were prepared using a mixture of cement and simulated neutralized nitric wastes containing two types of tracers: uranil nitrate, $UO_2(NO_3)_2$, used to simulate the soluble radioactive wastes and thorium oxide, ThO_2, used to simulate all insoluble materials which could be present as precipitates or suspension solids. The mixing of all components was done using standard procedure (2) and a planetary paddle mixer.

The metallic can used as a mold for the samples had a cylindrical shape with 165 mm diameter and was 180 mm in height. After the cure time the blocks were disassembled and cut into five parts, as shown in Fig. 1. From each slice ten samples, in powder form, were extracted, with the help of a carbide drill and then, for each sample, uranium and thorium concentrations were determined (1).

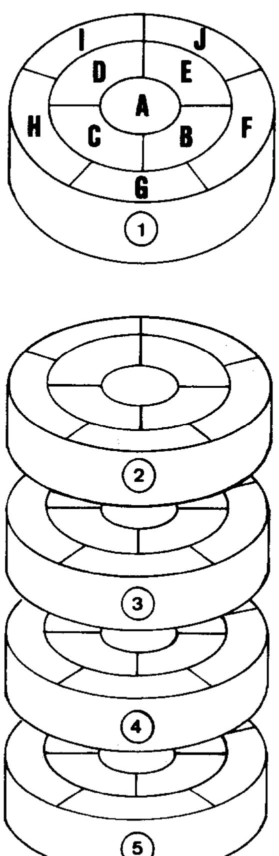

FIGURE 1. Cutted cement block showing the slices and sectors used for homogeneity tests.

In one of the experiments the blocks were contaminated with both uranium and thorium compounds and in the other the blocks were contaminated with the uranium salt only. In those experiments for which the water to cement ratio, as well as the salt contents varied, only the uranium tracer was used. Because the sensitivity of the measurement method is higher for uranium than for thorium, due to its higher cross section, it was necessary to increase the thorium content for those samples where both tracers were used.

Furthermore, it was investigated a possible influence of the water to cement ratio as well as the salt contents of the waste stream on the homogeneity property. Water to cement ratios varied from 0.30 to 0.40 while the assayed salt contents were 3.6 and 7.5% in weight.

METHOD OF ANALYSIS

The procedure utilized to verify the uniformity of uranium and thorium distribution in cement matrices is the same utilized to test the uniformity of pseudorandom numbers generated by special algorithms used in computers. The objectives are similar since both measure the goodness of fit to flat distributions either for the uranium or thorium concentrations along the waste form or for the random numbers in a given interval.

At least three statistical tests are recommended to apply on the data in order to certify their homogeneity (3). For that purpose χ^2, were applied to the Kolmogorov and Smirnov-Crámer-Von Mises tests.

When there are few number of events to analyze the application of goodness of fit tests are restricted to those class of tests for unbinned data. This occurs because by combining events into histogram bins some information is lost, like the position of each event inside the bin. Consequently, one must expect tests on binned data to be inferior to tests on individual events. Despite the fact the χ^2 test is binned, it is generally accepted as good when the expected number of events, per bin, is greater than 5, or if not, when more than 20% of the bins have an expectation between 1 and 5 (4).

The hypothesis of uniform distribution of experimental values of a given quantity must be rejected if the χ^2_{exp} value, calculated out of the experimental values, is larger than the critical value of χ^2 for a given significance level α (5).

The χ^2_{exp} value is calculated from the experimental values by the expression:

$$\chi^2_{exp} = \sum_{i}^{\nu} \frac{(f_i - e_i)^2}{e_i}$$

where f_i and e_i are the observed and expected frequencies for the ν bins where the experimental data

TABLE 1
Homogeneity Statistic Tests For Hydrated Cement Blocks[a] With Uranium and Thorium Tracers

Hydrated Cement Block[a]	Average ± Standard Deviation ($\overline{X} \pm \sigma$) mg/kg	χ^2 Test χ^2 (A)	$\chi^2(95\%)$ (B)	Kolmogorov Test $\sqrt{N}\,D_N$ (A)	$\sqrt{N}\,D_N(95\%)$ (B)	Von Mises Test Nw^2 (A)	$Nw(95\%)$ (B)
With U	106.8 ± 5.7	1.23	5.99	0.47	1.33	0.08	0.46
With U and Th	$(68.5 \pm 5.8)_U$	1.07	3.84	0.63	1.33	0.04	0.46
	$(1237) \pm 101)_{Th}$	0.40	3.84	0.58	1.33	0.05	0.46

(A) Experimental.
(B) Theoretical upper limit.
[a]W/C (wt %) = 0.35; $NaNO_3$ (wt %) = 4; number of concentration analysis per block = 50.

are distributed. This quantity has an approximate χ^2 distribution with $\nu - 3$ degrees of freedom if the hypothesis of uniform distribution is correct. The degree of freedom has decreased from ν because three values have to be estimated to evaluate the $\chi^2_{\rm exp}$. Namely, the $\chi^2_{\rm exp}$ itself, μ and σ^2 where μ is the expected value and σ^2 is the variance of the distribution.

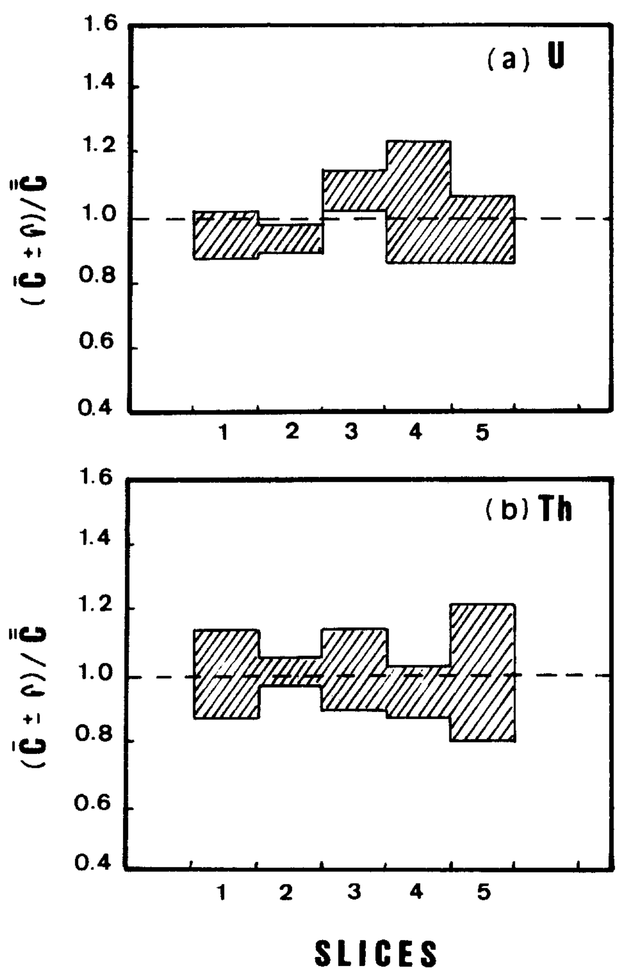

FIGURE 2. Normalized concentration distribution along the slices of the hydrated cement block, with W/C = 0.35; $NaNO_3$ (wt %) = 4, for (a) uranium and (b) thorium tracers.
*($\overline{C}$ = slice average; σ = standard deviation; $\overline{\overline{C}}$ = full matrix average.)

The more successful tests free of binning are based on comparing the cumulative distribution function $F(x)$ under the hypothesis of normality with the equivalent distribution of the data. Here those statistical tests are represented by the Smirnov-Crámer-Von Mises and Kolmogorov tests which measure the "distance" between the experimental and the hypothetical distribution function (6).

The cumulative distribution function is given by:

$$F(x) = \int_{x_{\min}}^{x} f(x')\,dx'$$

where $f(x)$ is the probability density function which for the normal one-dimensional distribution is expressed by:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2}\frac{(x-\mu)^2}{\sigma^2}\right)$$

where μ is the expected value and σ^2 is the variance of the distribution.

The cumulative distribution of the experimental data is obtained by the so called order statistics $X_{(i)}$. Given N independent observations $X_1, X_2, \ldots, X_N$, of the random variable X, reorder the observations in ascending order, so that $X_1 < X_2 < \cdots < X_N$. The ordered observations X_i are called the order statistics and their cumulative distribution function is defined by:

$$S_N(x) = \begin{cases} O & \text{when } x < x_i \\ i/N & \text{when } x_i < x < x_i + 1 \\ 1 & \text{when } x_N < x \end{cases}$$

$$i = 1, \ldots, N-1$$

Thus, by definition of the cumulative distribution function $F(x)$ and from the law of large numbers,

$$\lim_{N\to\infty} \{P[S_N(x) = F(x)]\} = 1.$$

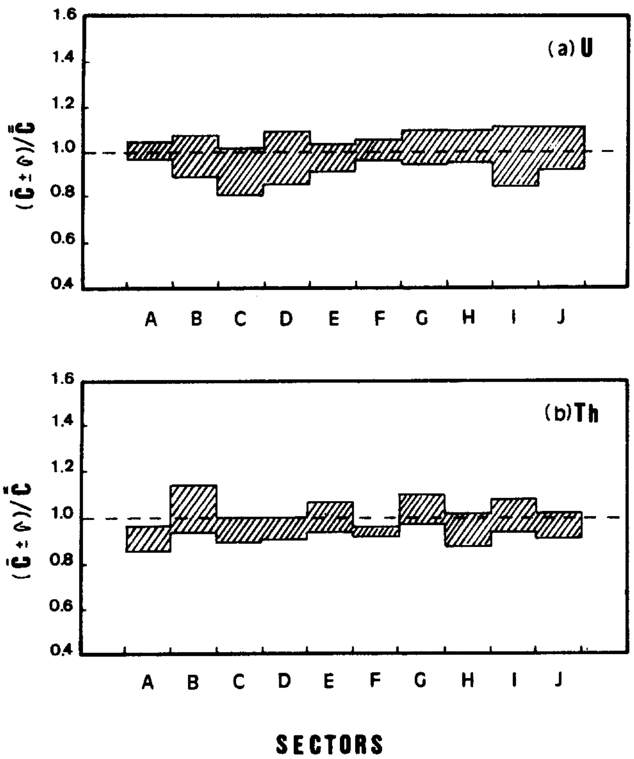

FIGURE 3. Normalized concentration distribution along the sectors of the hydrated cement block, with W/C = 0.35; $NaNO_3$ (wt %) = 4, for (a) uranium and (b) thorium tracers.
*($\bar{C}$ = sector average; σ = standard deviation; $\bar{\bar{C}}$ = full matrix average.)

The Smirnov-Crámer-Von Mises test gives the average square difference between the cumulative distribution function $F(x)$ and the cumulative order statistics $S_N(x)$. Usually, it is expressed as follows:

$$\omega^2 = \int_{-\infty}^{+\infty} [S_N(x) - F(x)]^2 \, dF(x).$$

By inserting the respective expressions of $S_N(x)$ and $F(x)$ one can obtain:

$$N\omega^2 = \frac{1}{12N} + \sum_{i=1}^{N} \left(F(x_i) - \frac{2i - 1}{2N} \right)^2.$$

The value of $N\omega^2$ has to be evaluated out of the experimental data and compared with the critical value for the Smirnov statistical at a chosen level of significance α.

In the Kolmogorov test observed is the maximum deviation of the observed distribution $S_N(x)$ from the distribution $F(x)$ expected value under, the hypothesis of normality. This is defined as:

$$D_N = \max |S_N(x) - F(x)| \text{ for all } x.$$

Analogously, as in the Smirnov statistics, the D_N value has to be evaluated out of the experimental data and compared with the critical value for the Kolmogorov statistics at a chosen level of significance α.

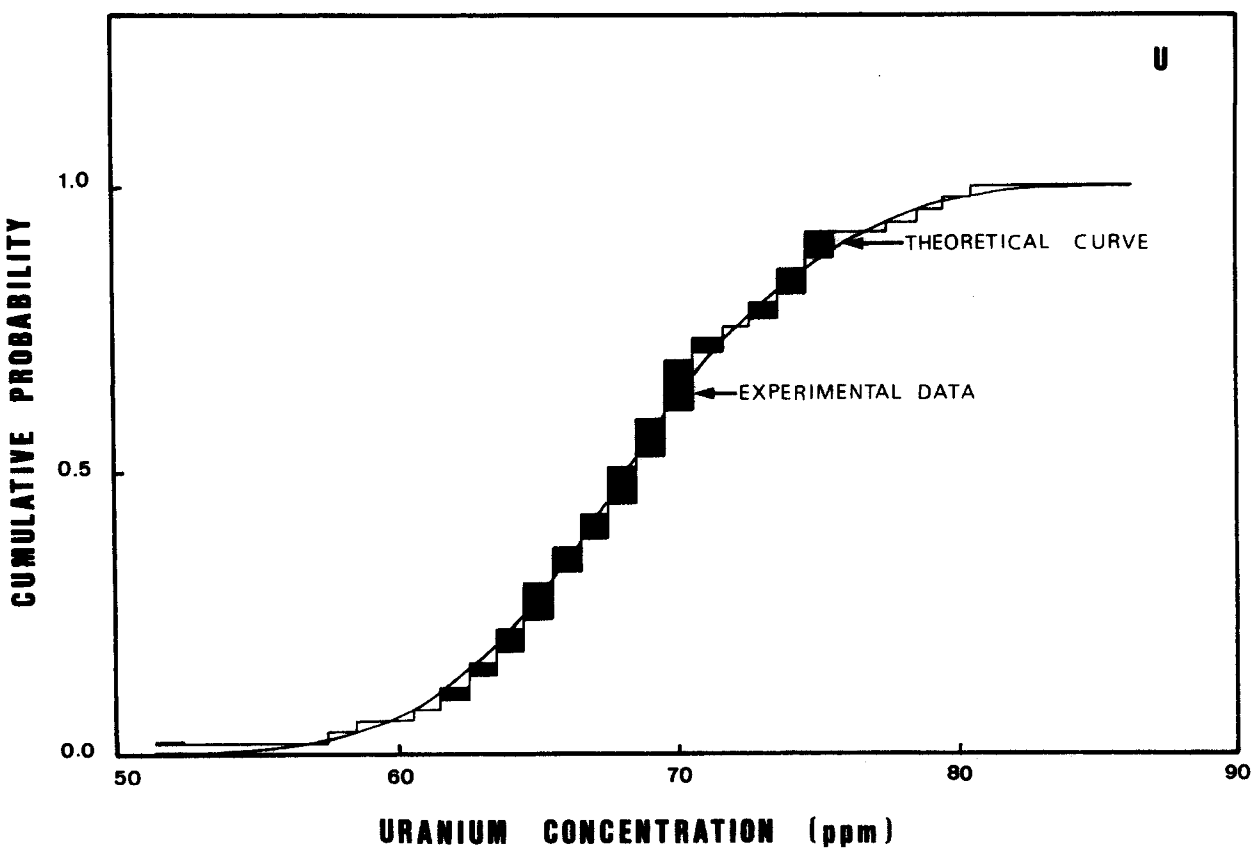

FIGURE 4. Theoretical and experimental cumulative distributions of uranium concentration in the hydrated cement block, with W/C = 0.35, $NaNO_3$ (wt %) = 4, where uranium and thorium tracers were used.

TABLE 2
Homogeneity Statistic Tests For Hydrated Cement Blocks[a], With Different W/C and $NaNO_3$ Concentrations, Where Uranium Tracer Was Used

Hydrated Cement Block[a]	Water/Cement	Salt Content (wt %)	Average ± Standard Deviation ($\bar{X} + \sigma$) mg/kg	χ^2 Test: χ^2 (A)	χ^2 Test: $\chi^2(95\%)$ (B)	Kolmogorov Test: $\sqrt{N}\,D_N$ (A)	Kolmogorov Test: $\sqrt{N}\,D_N(95\%)$ (B)	Von Mises Test: Nw^2 (A)	Von Mises Test: $Nw(95\%)$ (B)
2	0.30	3.6	106.7 ± 5.9	0.33	5.99	0.52	1.36	0.04	0.46
3	0.30	7.5	124.3 ± 9.4	6.32	7.82	0.52	1.36	0.06	0.46
5	0.35	3.6	101.5 ± 6.5	1.73	5.99	0.83	1.36	0.14	0.46
6	0.35	7.5	95.6 ± 4.9	2.12	7.82	0.56	1.36	0.04	0.46
8	0.40	3.6	99.0 ± 6.5	0.27	5.99	0.51	1.36	0.02	0.46
9	0.40	7.5	110.1 ± 6.1	1.27	5.99	0.64	1.36	0.07	0.46

(A) Experimental.
(B) Theoretical upper limit.
[a]Number of concentration analysis for each block = 50.

The hypothesis of normality is then accepted at the α level of significance if the computed values for the statistics do not exceed the critical values for the chosen statistics tests.

RESULTS AND DISCUSSION

The results obtained for the homogeneity tests on the blocks contaminated, one with uranium and the other with both uranium and thorium are reported in Table 1.

It can be seen that both tested blocks satisfied all the applied statistical tests, that is, no computed value of the statistics was higher than the critical value for the chosen statistical test. Therefore, the hypothesis can not be rejected that the observations came from a normal population with an average concentration value $\bar{c}$ and a standard deviation σ within a confidence level of 95%.

The distributions of the relative concentrations of tracers throughout the slices and sectors of the sample matrix are shown in Fig. 2 and Fig. 3. The agreement between the experimental and theoretical cumulative distributions shown in Fig. 4 demonstrate the correctness of the normality hypothesis.

All those results obtained from the experiments performed to observe the possible influence of the water to cement ratio and salt contents are shown in Table 2. It is possible to observe that within the range of parameters assayed, there is no statistical evidence of inhomogeneities in those simulated waste forms.

CONCLUSIONS

Delayed neutron counting technique was applied to determine the chemical concentration of uranium and thorium tracers mixed in cement pastes by using a planetary paddle mixer. According to that process and the used statistical tests one can consider that the resulting product is homogeneous in terms of tracers distribution. Inhomogeneities were not observed in the simulated waste forms assayed even varying the water to cement ratio and salt contents.

For a product to be accepted as homogeneous for waste form evaluation, it is suggested that it has to fulfill a complete set of tests where chemical and physical quantities have to be evaluated and to which should be applied rigorous statistical criteria as used here.

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