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STATISTICAL CRITERIA TO EVALUATE HOMOGENEITY OF RADIOACTIVE WASTE FORMS

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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 waste forms by using natural thorium and uranium compounds as tracers to evaluate the chemical homogeneity of the final product. The mixing technique used to produce the cemented waste forms proved to be good enough as a standard method to obtain a homogeneous product.

CRITÉRIOS ESTATÍSTICOS PARA AVALIAR A HOMOGENEIDADE
DE REJEITOS RADIOATIVOS IMOBILIZADOS

RESUMO

Um conjunto de testes estatísticos é proposto para avaliar a homogeneidade de rejeitos radioativos imobilizados. Os critérios foram aplicados a rejeitos imobilizados em cimento, usando compostos de tório e urânio naturais, como traçadores, para avaliar a homogeneidade química do produto final. A técnica de mistura utilizada na imobilização dos rejeitos em cimento provou ser adequada e é proposta como padrão de misturas homogêneas.

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 property required for any kind of immobilized waste form is the homogeneity which is quite important in the solidification process and during long-term storage. It is the starting point to specify and define the other physical properties and also some chemical one as density, porosity, leaching rate, degradation, permeability, compression strength, radiation damage, thermal conductivity etc which can not be studied if the matrix is not homogeneous.

Usually this property is not considered, except for a qualitative statement, where there is a gross phase separation. Particulary in the setting up of receipts for waste immobilization in laboratory scale the homogeneity condition is assumed without objection. However, in the scale up of the immobilization

process this condition is mandatory.

In laboratory scale procedure, emphasis is given to the necessity of well homogenize the mixture in order to obtain an uniform and reproducible product. In counterpart this is not always done in the process itself. It is assumed that the process will delivers a homogeneous product and a simple visual inspection is enough to assure it.

In some few cases compressive tests are realized in samples taken from the real size product. Nevertheless, none reliable statistical test is usually applied to them.

Many physical, chemical, physico-chemical and radiological properties have to be considered in order to establish the homogeneity of a waste form. As is not possible to satisfy all requirements at same time or to achieve all the specified tests, a small group of properties is required to be fullfilled.

The selection of that group of properties has to be made carefully in order that each selected property stands for a class of correlate properties. For instance, it is well known that the porosity affects mechanical strength as well the leach rate. No matter which property be considered it has to be uniform along the waste form. The selected group of properties have to be measured along the waste form following statistical criteria and afterwards analysed properly. Once those statistical criteria be satisfied the waste form can be considered homogeneous with regard to the selected properties.

Thus in order to evaluate the degree of homogeneity of simulated waste immobilized in cement matrices by using a planetary paddle mixer it was used the high sensibility of the delayed neutrons detection technique to measure the distribution of very small quantities of a soluble uranium salt or insoluble thorium oxide in powder form. With this procedure it was verified the uranium and thorium distribution along the waste form with its homogeneous distribution confirmed by the application of appropriated statistical tests.

The advantages of this method are the fast response and high sensibility associate with the neec lessness of using radioactive tracers which could increase the waste generation.

EXPERIMENTAL PROCEDURES

The cement pastes were prepared using common Portland cement, to which was added 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 the insolubies which could be present as precipitates or suspension solids.

The mixture of all components was done by following the standard procedure given by ABNT-MB-1/79[1] and for this purpose it was employed a planetary paddle mixer.

The metallic can used as mould of the blocks for the cement matrix had cylindrical shape with diameter of 165 mm and 180 mm height.

After the cure time those blocks were disassembled and cutted into five parts, as shown in figure 1. From each of them were extracted, with the help of a carbide drill, around ten samples from which uranium and thorium concentrations were determined. Each sample contained about 2 g of cement paste in powder form.

Those concentrations were measured by using the delayed neutron counting facility existing at the Radiochemistry Division of IPEN-CNEN/SP[2].
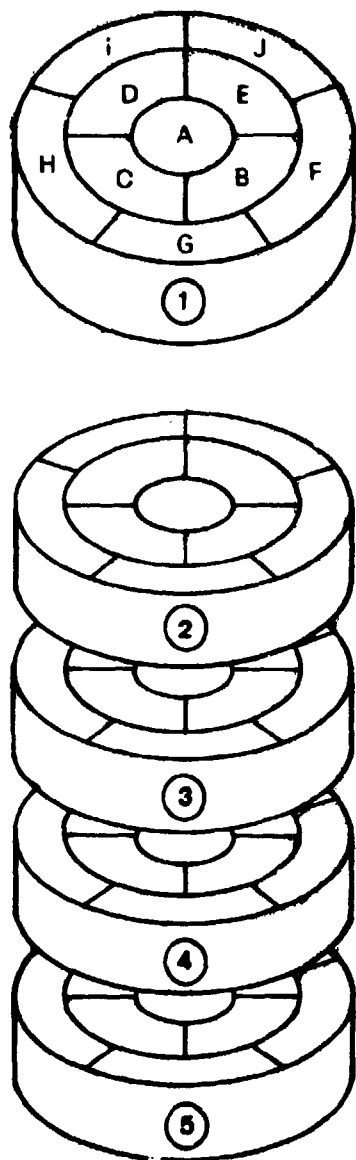
Figure 1 — Cutted cement blocks showing the slices and sectors used for homogeneity tests.

RESULTS AND DISCUSSIONS

The uniformity of the U and Th distribution in cement matrices was verified using the same statistical criteria employed to test the uniformity of pseudo-random number generators utilized in computers. The objectives are quite similar. The former aims to obtain a flat distribution for the U or Th concentrations along the waste form while the latter intend to evaluate the performance of an algorithm to produce random numbers in a given interval. For this purpose is applied more than one statistical test. Usually are employed the χ^2, Kolmogorov and Smirnov-Crámer-Von Mises tests[3].

When the number of events to be analysed is low 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: the position of each event inside the bin. Consequently one must expect tests on binned data 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 numbers of events per bin are greater than 5 or if not when more than 20 % of the bins have 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 value calculated out of the experimental values exceeds the upper limit $\chi^2_{\ell-1}$ (p) of the confidence interval, where p is the assigned confidence probability and $(\ell - 1)$ is the number of degrees of freedom.

Confidence probability p means a probability close to 1 such that, if the hypothesis of uniform distribution is correct, the probability is p that the value obtained for χ^2 will not exceed χ^2 (p). If however the confidence limit is exceeded, this means that the measure of discrepancy, χ^2, indicates a significant departure, and the hypothesis of uniform distribution must be rejected.

On the other hand, extremely small values of χ^2 must be considered an indication of failure of randomness, since in the case of correctness of the hypothesis the probability for a random quantity to assume too small values is extremely small.

The χ^2 value is calculated from experimental values by the expression:

$$\chi^2 = \sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{\bar{x}}$$

where $\bar{x}$ is the expected value and x_i are the observations of the variable x.

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-Cramér-Von Mises and Kolmogorov tests which measure the "distance" between the experimental and hypothetical distribution function.

The cumulative distribution function $F(x)$ 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-dimentional 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, let reorder the observations in ascending order, so that $X_1 < X_2 < \ldots < X_N$. The ordered observations X_i are called the order statistics and their cumulative distribution function is defined by:

$$S_N(X) \;=\; \begin{cases} 0 & X < X_i \\[2mm] i/N \;\text{for} & X_i < X < X_{i+1} \qquad i = 1,\ldots\ldots, N-1 \\[2mm] 1 & X_N < X \end{cases}$$

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

$$\lim_{N \to \infty} \;\{P\,[\,S_N(X) = F(X)\,]\,\} \;=\; 1$$

The Smirnov-Cramér-Von Mises test is the average square difference between the cumulative distribution function F(X) and the cumulative order statistics $S_N(X)$. Usually it is expressed by

$$w^2 \;=\; \int_{-\infty}^{\infty} [\,S_N(X) \cdot F(X)\,]^2 \; d\,F(X)$$

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

$$Nw^2 \;=\; \frac{1}{12N} \;+\; \sum_{i=1}^{N} [\,F(X_i) \cdot \frac{2i-1}{2N}\,]^2$$

The Kolmogorov test is the maximum deviation of the observed distribution $S_N(X)$ from the distribution F(X) expected under the hypothesis of normality. This is defined as

$$D_N \;=\; \max\,[\,S_N(X) \cdot F(X)\,] \qquad \text{for all } X$$

The hypothesis of normality is accepted at 100 p % level of significance if the computed value of the statistic don't exceeds the critical value for the statistic test chosen.

For this paper the homogeneity tests were realized in two ways: in one experiment the blocks were contaminated with uranium salt only while in the other the blocks were contaminated with both uranium and thorium compounds.

As the determination method is more sensitive to uranium due to its higher cross-section, for those samples where both tracers were used it was necessary to increase the thorium content.

In table I is shown the results obtained for the homogeneity tests for block contaminated with uranium alone and both uranium and thorium. As can be seen in this table, both tested blocks satisfied all applied statistical tests. Therefore cannot be rejected the hypothesis that the observations come from a normal population with average concentration value $\bar{C}$ and variance σ^2 within a confidence level of 95%.

Table I

Homogeneity statistic tests for samples* with U and Th tracers

Sample	Average ± standard deviation $(\bar{X} \pm \sigma)$ (ppm)	χ^2 test		Kolmogorov test		Von - Mises test	
		χ^2 experimental	χ^2 (95%) theoretical limit	$\sqrt{N}\ D_N$ experimental	$\sqrt{N}\ D_N$ (95%) theoretical limit	Nw^2 experimental	Nw^2 (95%) theoretical limit
with U	106.8 ± 5.7	1.225	5.991	0.47	1.33	0.08	0.46
with U and Th	$(68.5 \pm 5.8)_U$	1.068	3.841	0.63	1.33	0.04	0.46
	$(1237 \pm 101)_{Th}$	0.404	3.841	0.58	1.33	0.05	0.46

* water-cement ratio, by weight = 0.35 $NaNO_3$ (% by weight) = 4%   Number of samples = 50

From figures 2 and 3 it is possible to visualize the distribution of the relative concentrations of tracers along the slices and sectors of the sample matrix prepared by using a planetary paddle mixer.
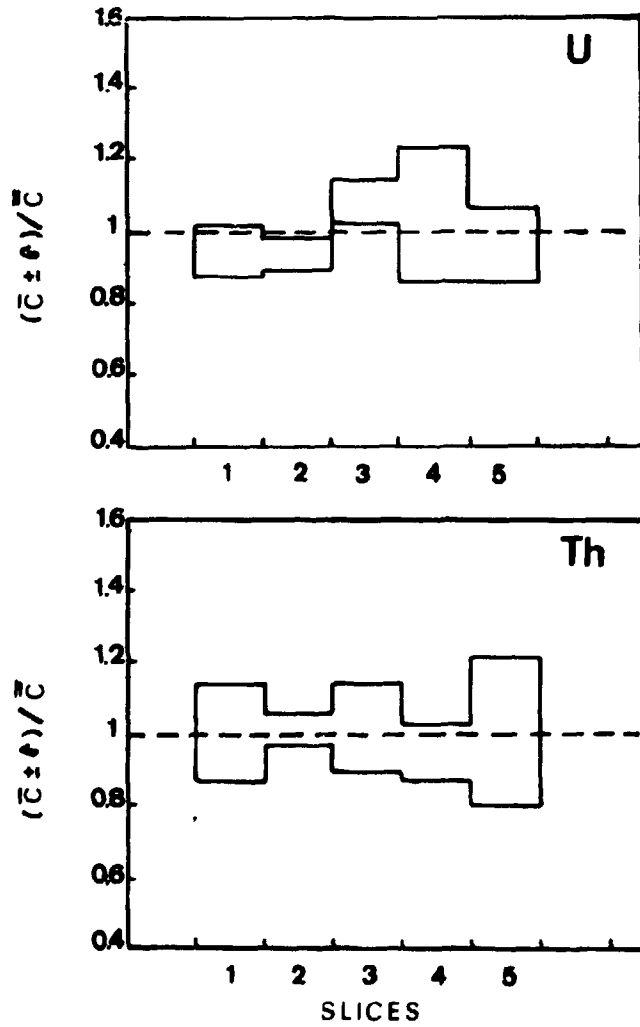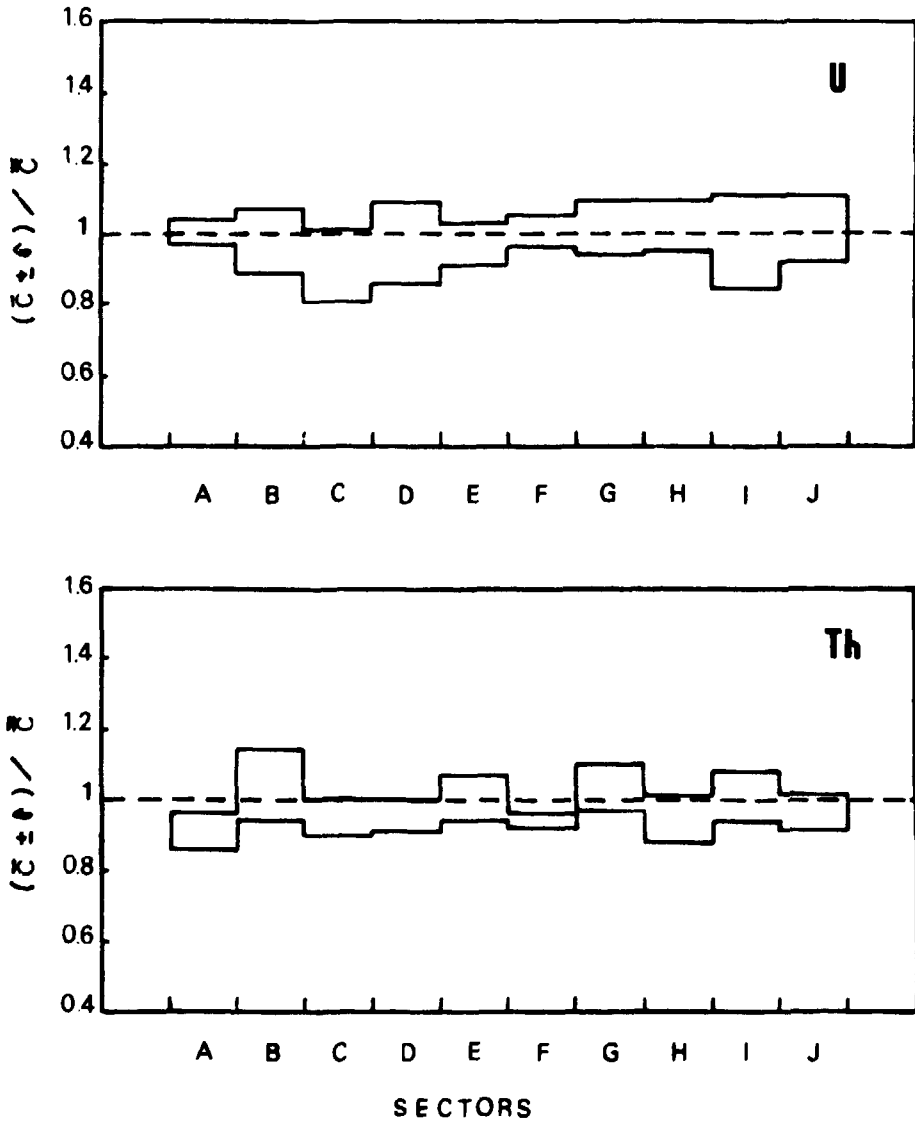

Figure 2 — Normalized concentration distribution along the slices of the cemented matrix prepared by using a planetary paddle mixer. (a) uranium and (b) thorium.

* ($\bar{C}$ = slice average; σ = standard deviation; $\bar{\bar{C}}$ = full matrix average)

Figure 3 – Normalized concentration distribution along the sectors of the cemented matrix prepared by using a planetary paddle mixer (a) uranium and (b) thorium.

* ($\bar{C}$ = sector average; $\bar{\sigma}$ = standard deviation; $\bar{\bar{C}}$ full matrix average)

In figure 4 is shown the experimental and theoretical cumulative distributions which also show correctness of the normality hypothesis.
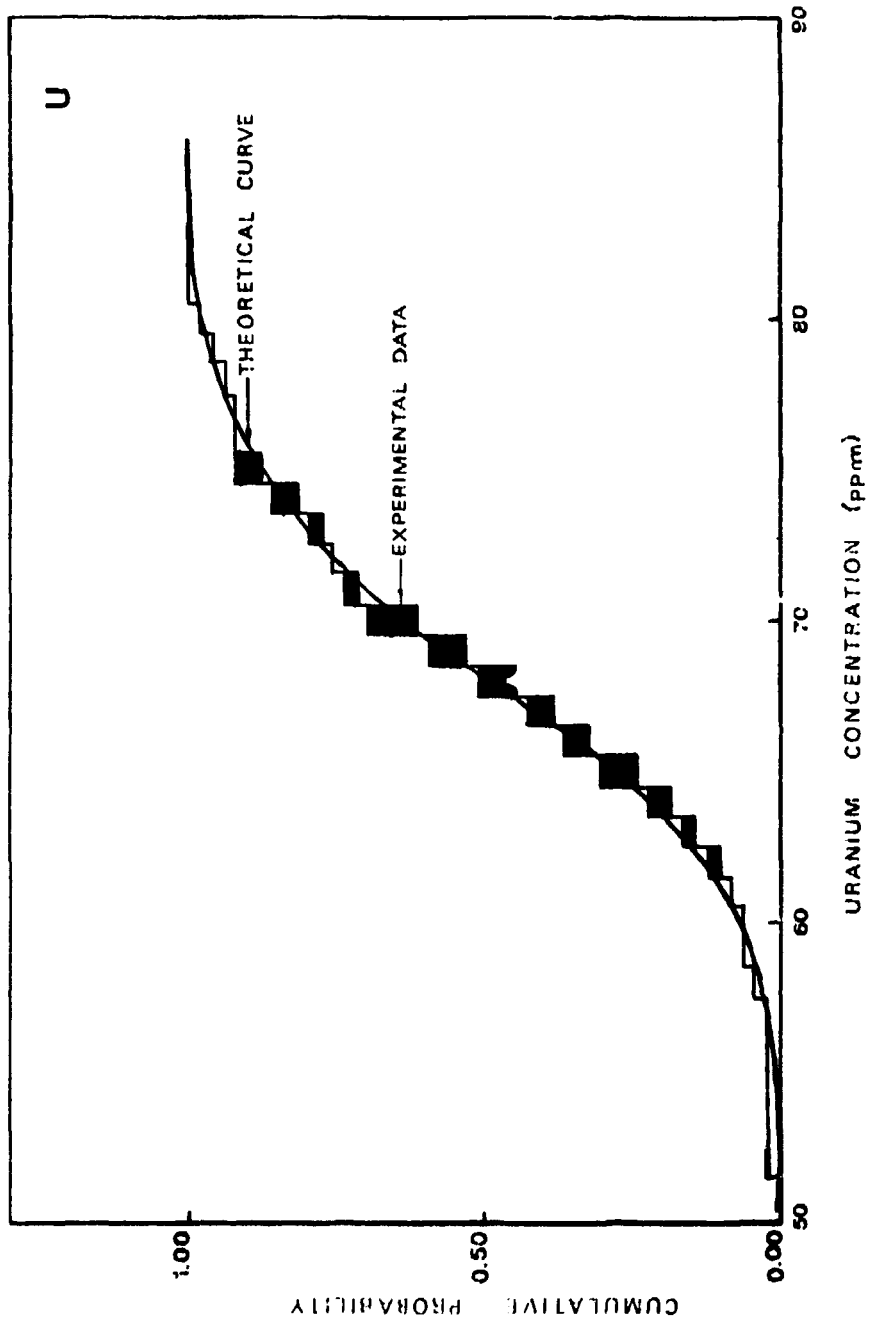
Figure 4 — Theoretical and experimental cumulative distributions of uranium concentration in cement matrix.

CONCLUSIONS

It was applied the delayed neutron counting technique to determine the chemical concentrations of U and Th tracers in cement pastes prepared by using a planetary paddle mixer. According to that process and the statistical tests used one can consider that the resulting product is homogeneous in terms of the tracers distribution and also the mixing procedure can be used as a standard one. Of course to accept the product as homogeneous for waste form purposes it has to fullfill a complete set of tests to which should be applied also the statistical tests used here.

REFERENCES

1. ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. *Ensaio de cimento Portland.* 1979. (ABNT-MB-1/79)

2. ARMELIN, M. J. A. & VASCONCELOS, M. B. A. An evaluation of the delayed neutron counting method for simultaneous analysis of uranium and thorium and for $^{235}U/^{238}U$ isotopic ratio determination. *J. Radioanal. Nucl. Chem., Articles,* 100(1): 37-47, 1986.

3. SHREIDER, Yu. A. *Method of statistical testing - Monte Carlo Method.* Amsterdam, Elsevier, 1964.

4. COCHRAM, W. G. Some methods for strengthening the common chi-squared tests. *Biometrics,* 10: 417-   , 1954.