

XRF APPLICATION FOR DIFFUSION STUDIES
IN RADIOACTIVE WASTE CEMENTED MATRIX★

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The aim of this work is the XRF application for the qualitative identification and relative concentrations determination of the elements Co, Sr, Cs and La on matrix that simulates the conditioned radioactive waste.

The first three elements are the chemical carrier of some important radionuclides in the radioactive waste management. La was introduced to replace Eu which partially simulates the chemical behaviour of Am.

For the spectral analysis of the samples a X-rays, Si-detector was used, due to the fact that it has better efficiency and resolution compared to a Ge-detector. In order to obtain the fluorescence spectrum a Am^{241} inelar source ($\Lambda = 20$ mCi), was used.

The selected matrices for the study are normal cement and concrete compositions with and without mineral additives (bentonite and volcanic tuff).

The results obtained by this analysis give useful information about the XRF application on the diffusion depth and concentrations profiles for each element.

Key words: radioactive waste, X-rays fluorescence, mineral additives, concrete, conditioning matrix.

1. INTRODUCTION

The management of radioactive waste implies the conditioning in a concrete as an embedding stable matrix. In the study of concrete matrix different nondestructive analysis methods were used as: X-ray diffraction analysis, Mossbauer Spectroscopy and Inelastic slow neutron scattering [8–10].

To improve the quality of the conditioning matrix of radioactive waste by the cementation technology, are used mineral additives, which are diminishing the leaching rate of the radionuclides in the disposal environment [6]. An additive is a material that is intergrained or blended in limited amounts into a hydraulic cement during manufacture either as a “processing addition” to aid in manufacturing and handling the cement or as a “functional addition” to modify the properties of the finished product [1, 2].

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It is of importance to choose some indigene sorts of natural ion changers that can be used as effective barriers against the migration of radionuclides deposited in natural geological formations. In this respect, the volcanic tuff and bentonite existent in a series of ore deposits from Romania were studied and have been used [9].

The underlying mechanism by which the combination of pozzolanic and cementitious materials with Portland cement influences the engineering behaviour of the product are not significantly affected by the way in which these by-products are incorporated into concrete [2].

Mathematical modeling of the radioactivity dissemination on the site of the final disposed radionuclides, require a large volume of experimental data concerning the behaviour of the ultimate form of conditioning matrix. In addition, the experimental data are offering informations regarding the interaction between the radionuclides different chemical forms (which are important for radiological safety) with: the major components of the matrix; the package material; the engineering barrier material of disposal site; the host rock in the given hydrogeology conditions [6].

Initial step in the radioactivity spreading is the diffusion of main radionuclides in the conditioning matrix. The diffusion rate can be determined by the concentration profiles of each element.

In order to obtain an important part of this large volume of experimental data some rapid and precise chemical and physical analysis methods are needed suited to a big number of samples with varied composition.

The rapidity of analysis method will be greater as the advanced chemical processing is avoided (for the separation and purification of the interest elements). The radiometric application methods with radioactive tracers simplifies to a great extent the relative and/or absolute determination of the concentration profiles, but it impose very strict work conditions which can be respect on small samples and volumes and generally at radioactive tracers scale.

An "in situ" physical determination method of a large number of chemical elements is X-Ray Fluorescence (XRF) [7]. Although it has a large application area, in the radioactive waste management domain it didn't find an adequate use.

The present paper is the results of the XRF method application in the study regarding the behaviour chemical carrier of some important radionuclides in the radioactive waste management [3, 4].

2. EXPERIMENTAL PART

The purpose of X-ray fluorescence spectrometry is the qualitative and quantitative determination of the elements in a sample by measuring their characteristic radiation [7].

In order to obtain the fluorescence spectrum, a ^{241}Am inelar source ($\Lambda = 20 \text{ mCi}$) was used. The ^{241}Am source besides characteristic gamma ray of 59,54 keV, contain a gamma ray of 26,35 keV. Furthermore the X lines of Np (11,89; 13,95; 13,76; 16,84; 17,74 and 20,8 keV) appear.

The X-ray fluorescence spectrum with this source will contain the lines of diffusion Rayleigh or Compton, which will complicate the interpretation of the obtained data. A first example can be the overlap of characteristic X-ray of Sr (14,164 keV) with the X-ray line of Np (13,95 keV).

The detection system is composed of Si(Li) detector for X-rays with the follows characteristics: active diameter of 4,3 mm; internal collimator of 4,0 mm thickness; the sensible depth of detector of 4,2 mm; the window of Be of 25 μ ; the distance between window and detector of 8 mm; the energy resolution for K_{α} line of Mn (5,898 keV) is 220 eV. The Si(Li)-detector was used due to the fact that it has better efficiency and resolution compared to a Ge-detector.

The selected matrices for the study are normal cement and concrete compositions with and without mineral additives (bentonite and volcanic tuff). Mineral admixtures are finely divided solids added to cement mixes to improve their workability or durability, or to provide additional cementing properties. On the basis of this studies for confinement of nuclear wastes were selected the volcanic tuff with 65% zeolites from Salaj region and bentonites from Valea Chioarului. Possible technological benefits from the use of mineral admixtures in concrete include enhancement of impermeability and chemical durability improved resistance to thermal cracking and increases in final strength [4].

The plasticity of the concrete and its freedom from segregation and bleeding, at any slump, are usually much improved, and this is particularly notable in lean mixes.

The use of pozzolans also improves the impermeability and durability of hardened concrete.

Because the continuing formation of hydrates fills the pores and because there is no free lime that could be leached out, partial replacement of portland cement by a pozzolan reduces the permeability of concrete [2].

The samples were prepared as follows:

- samples of reference: cement – water = 1:0,5
cement – sand – water = 1:1:0,5
- samples with mineral additives: cement – bentonite – water = 1:0,1:0,5
cement – volcanic tuff – water = 1:0,1:0,5

The cement pastes of normally consistency were prepared. The pastes were revolved in cubes of $20 \times 20 \times 20 \text{ mm}$. After the preparation, the samples were kept 24 hours in pattern, then in tight plastic purse for minimum 28 days for reinforcement. After this period on a side were dropped the volume of 30, 90 and

150 μL from a solution which contains 1 mg/ml of element Co, Cs, Sr and La. This solution is a soluble form of chloride or nitrate.

The samples thus prepared were kept in normally conditions of temperature and humidity for 14 days. After 14 days the samples were analyzed by XRF.

The identification of the interest elements of the matrix that simulates the conditioned radioactive waste matrix is based on the characteristic X lines. Besides these lines appear and the X lines of the constitution elements of the matrix.

The characteristic X lines of the important present elements in system are presented in Table 1. In the case of the four interest elements, the elements existence from matrix (Ca, Fe and Ba) leads to the interferential of the spectral lines, respectively the K_{α} line – Co (6,93 keV) and the K_{β} line – Fe (7,05 keV). The same thing become of the X line of Np(13,94keV) and the K_{α} line of Sr (14,164 keV). In order to avoid these problems is measure a sample of cement as reference which will represent the background. This background will be automatically subtracted from the spectrum of the analyzed sample.

The measurements will be carried out in the same conditions of geometry and acquisition time of the spectral data.

Table 1

The characteristic lines of the important present elements in system

	$K_{\alpha 1}$	$K_{\alpha 2}$	$K_{\beta 1}$	$K_{\beta 2}$
K	3.313		3.589	
Ca	3.691		4.012	
Fe	6.403		7.057	
Co	6.930		7.649	
Sr	14.164		15.838	
Cs	30.970	30.623	34.984	35.819
Ba	32.191	31.815	36.376	37.225
La	33.440	33.033	37.799	38.728
Ce	34.717	34.276	39.225	40.231

3. RESULTS AND DISCUSSIONS

The X-Ray Fluorescence analysis is the most suitable analytical technique to handle all the different kind of material, no matter if they are solids, sludge, filters, liquids, powders. For every material type a fast and simple sample preparation technique can be applied. For higher accuracy powdered samples are prepared as pressed pellets or glass discs (3–5 cm in diameter and 0.5–2 cm in

thickness). XRF supports the different application types providing instant answers about element concentration in a dynamic range from ppm to 100%.

The X-rays penetration in sample depends by the mass absorption coefficient. The X-rays penetration depth is ranging from 1 to 50 μm , the form and size of the sample are critical in the light elements analysis. In this work the cubes of 20 mm were used, the penetration depth for the elements of interest is considered in the middle of the interval.

The cement matrix contains the elements Ca, Al, Si, O as major components and small concentrations of Fe, K, Mg and Na. All these elements have small Z and therefore the penetration depth is a few μm .

The elements of interest (Co, Sr and La) in generally have a higher Z excepting Co which is closer to Fe. Thus, it can be considered that the matrix influence on the XRF spectra is insignificant for Sr, Cs and La. The first stage of the study consisted in the experimental determinations of the reference spectra for the pure elements that are presented in Figs. 1–4.

In the case of the concrete sample on which the solution with the elements of interest was dropped, the XRF spectrum presented in Fig. 5 identifies the K_{α} lines of Co, Sr, Cs and La as well as the K_{α} lines of Ca and Fe. Also, the K_{α} line of Ba is present and its intensity is compared with the intensity of the La line. In order to obtain a semi-quantitative determination the correction of the background due to the cement matrix is necessary. The XRF spectrum of the cement matrix is presented in Fig. 6 and its complexity is observed.

After the correction (through the computational program processing of the spectral data) the XRF spectrum of interest for Co, Sr, Cs and La was obtained. This XRF spectrum is presented in Fig. 7.

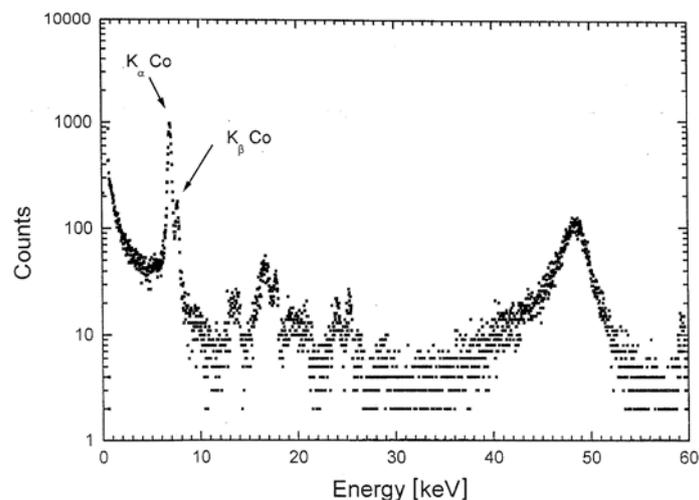


Fig. 1 – The XRF spectrum of Co etalon.

4. CONCLUDING REMARKS

The experimental results of the XRF application tests in the qualitative and relative semi-quantitative determination of the elements Co, Sr, Cs and La on concrete matrix that simulates the conditioned radioactive waste by cemented, allow emphasis the follows conclusion:

- All the five Portland cement matrix have a composition that is seen in the XRF spectra by the elements Ca, Fe and Ba;
- The composition of different matrix types are not presenting big differences in the main components ratios;
- The chosen experimental system based on the Si detector has a good energetic resolution and it allows us the separation of K_{α} and usually K_{β} lines for the interest elements;
- The XRF spectra processing for the samples used in the tests with the automatic background correction will allow in the future high sensitivity analysis;
- The XRF method will be used at the determination of concentrations gradient and their correlation with the diffusion front profile of the carrier agent (water) in cubic concrete samples (having the side length 20 mm).

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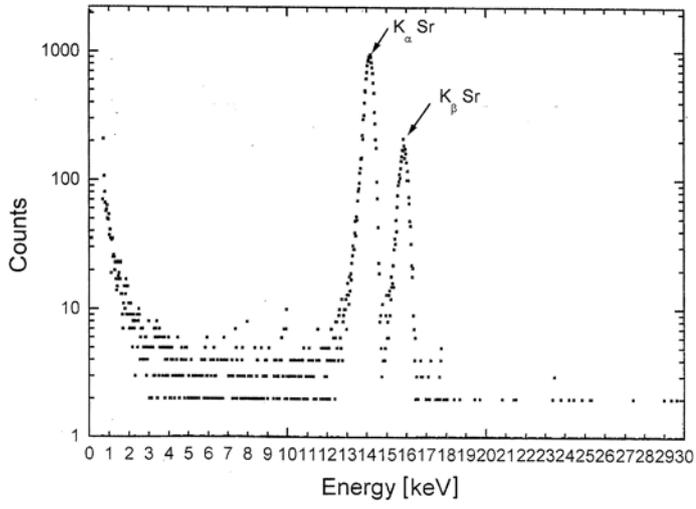


Fig. 2 – The XRF spectrum of Sr etalon.

Fig. 3 – The XRF spectrum of Cs etalon.

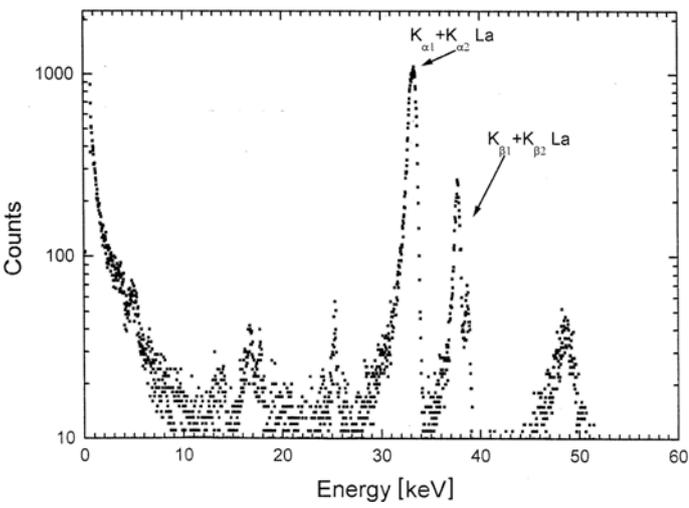
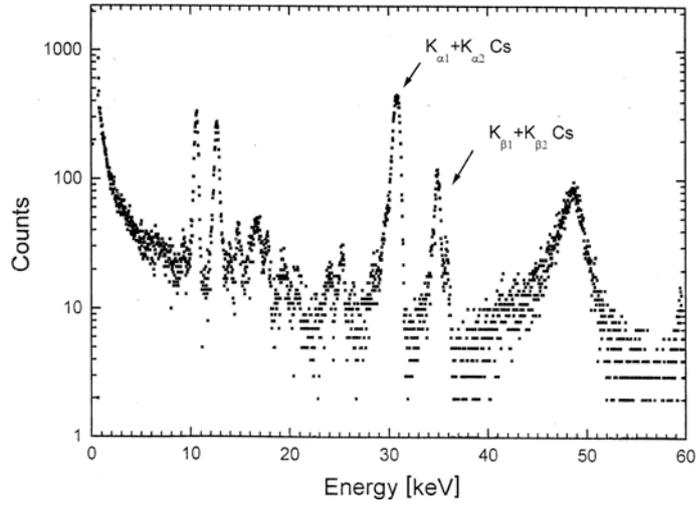


Fig. 4 – The XRF spectrum of La etalon.

Fig. 5 – The XRF spectrum of concrete sample with Co, Sr, Cs and La.

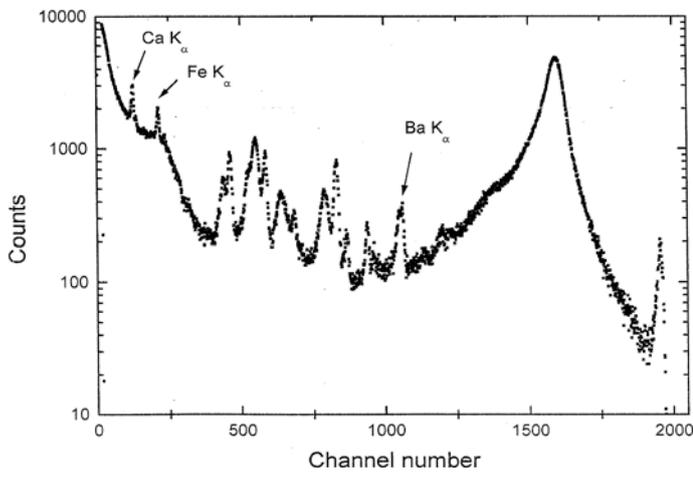
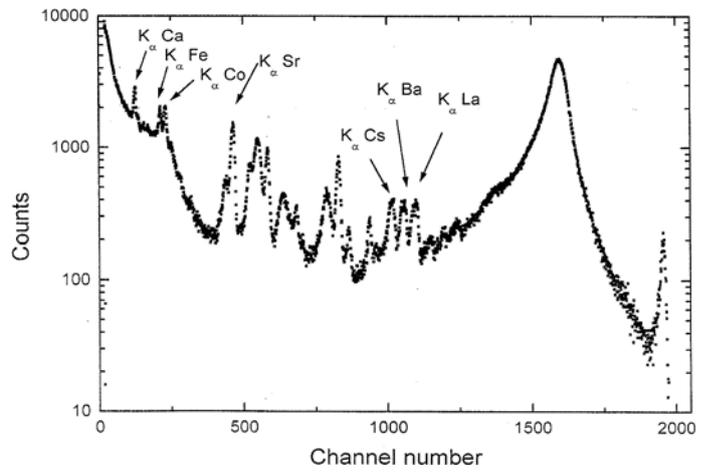


Fig. 6 – The XRF spectrum of concrete sample.

Fig. 7 – XRF spectrum obtained for Co, Cs, Sr and La.

