

THE INFLUENCE OF THE COMPLEXING AGENTS ON THE CONCRETE MATRIX STUDIED BY XRD*

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Radioactive effluents containing complexing agents as oxalic, tartaric and citric acids are generated during the radioactive decontamination operation using chemical methods. The conditioning of these wastes by cementation process imposed the structural investigation by X-ray diffraction (XRD) on the samples prepared with cement and complexing agents at different concentrations.

The results presented in this paper give useful information about the influence of complexing agents on damaged of concrete microstructures. The information obtained will be used further as a data basis for establishing the conditions in which the cement conditioning process will take place and the upper permissible level of complexing agent concentration.

Key words: radioactive waste, X-rays diffraction (XRD), complexing agents, concrete, conditioning matrix.

1. INTRODUCTION

The management of radioactive waste implies the conditioning in concrete as an embedding stable matrix. The study of embedding matrix of radioactive waste is extremely important concerning the request to assure radiological safety for the final disposal of conditioned radioactive waste. The matrix is the most important confinement barrier of radionuclide migration's point of view in the environment [1].

Radioactive effluents containing complexing agents as oxalic, citric and tartaric acids are generated during the radioactive decontamination operation using chemical methods.

The radioactive decontamination has as consequences other wastes named secondary which contain totally or partially the contaminants banished from the contaminated surface and also the chemical or mechanical agents used for the decontamination processes.

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The chemical decontamination techniques use a great variety of mixing reactive. All these chemical decontamination processes use one or more complexing agents which may include oxalic acid, citric acid, EDTA, pycolinic acid in order to obtain the radionuclides complex. Complexing agents form complex combinations of chelat type of iron, nickel, cobalt which are soluble in the water. Because these complexes are stable in the solution, they are not affected by repetitive dilutions and reabsorbed on the surface during the decontamination.

From the radioactive waste conditioning's point of view it is necessary to study certain factors such as: the contamination nature, the contamination mechanism, the decontamination reactive type and their influence on the cement matrix. Although the complexing agents give good results within the decontamination processes, it could appear difficulties in the treatment process of the secondary waste resulted from the decontamination.

This study proposes to establish the influence of the complexing agents on the chemical resistance of the cement-conditioned matrix, and mechanical performances as ultimate form of conditioning matrix. In addition, the experimental data are offering structural information regarding the interaction between the different decontamination agents used with the major components of the matrix.

The work plan included: the preparation of the samples cement-complexing agents (oxalic, citric and tartaric acids) by different concentrations; the micro-structure characterization by X-ray diffraction of these samples; the emphasizing of the influences provided by different complexing agents and by their concentration for the cement paste.

The information obtained within this paper will be used further as data basis for the conditions settlement in which the conditioning process by cementation and the limits of the complexing agents concentrations accepted in matrix will carry out.

The paper has the purpose the study of the structural characterization by X-ray diffraction of the radioactive waste cemented matrix containing complexing agents at different concentrations.

In all solidified systems types, the sensitiveness of the cementation process as for the change of the waste composition, the mixing proportion and the variations within any other chemical pretreatment should be known. This affects the measure and control degree demanded within the alimentation system for the cement, waste and other components of the mixing. The knowledge about the mixture effect of the cement with certain radioactive waste are limited and the experimental works are necessary for the cement-waste matrix optimization [2–4].

The cases in which the cement is used for the solidification of the organic waste are more complex because these affect the hydration degree of the mineralogical compounds of cement and thus affecting the matrix cemented structure [1, 5].

2. EXPERIMENTAL PART

The experimental works consisted in the preparation of the samples obtained through different recipes of preparation changing the concentration of the organic acid solution used, concerning the microstructural characterization by XRD which allows the obtaining of structural information of the cement matrix.

The samples with the complexing organic acids (oxalic, citric and tartaric acids) were prepared using Portland cement and a solution of the organic acid with the water/cement ratio = 0.3.

The following samples were prepared:

- cement – solution of the oxalic acid 0.5%, 1.25%, 2.5% and 5%;
- cement – solution of the citric acid 0.25%, 0.5% and 1%;
- cement – solution of the tartaric acid 0.25%.

(i) The samples as it concerns the upper mentioned recipes were kept in normally conditions of temperature and humidity for 28 days as is usually for the cement paste hardening. After this period the samples were fine milling obtaining the powder with the grain size of 30–40 μm . The big particles give a spreading effect of the diffracted radiation and as for the little particles it is felt amorphous by the reticular structure damage. These samples were investigated by X-rays diffraction an appropriate method for investigation of the influence of complexing agents on the cement mixture.

The present experimental data are references for the determination structural changes after 1, 3, 5, 7 and 10 years and extrapolate these data for 100 years storage period of radioactive waste cemented matrix.

(ii) The X-rays investigation was performed with a diffractometer, using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), for diffraction angles 2θ ranged between 5 and 65° . The computer was connected for data computerized analysis. Calculating “d” parameters for all diffraction maxims which appears in the polycrystalline mixture spectrum and comparing with “d” values from ASTM (American Society for Testing Materials) cards can be obtained a qualitative analysis for crystalline phases. Bibliography “d” \AA parameter is interplanar distance resulting from Bragg relation:

$$d = n\lambda / 2\sin\theta.$$

For each phase there is a certain minimal proportion of it in a mixture in order to be identified and this minimal proportion depends both on the particular phase nature and on the other present phases nature. In the same time with the growth of the phase content in mixture, the intensity of specific lines increases.

X-rays diffraction measurements of dry and hydrated cement were presented in a previous paper [6]. The obtained results gave us more information about physic-chemical processes, which are the basic processes for the cement hardening

and the formation of concrete resistance structures [7]. Based on these results, the samples with cement and complexing agents can be investigated by XRD.

In another study [8] were prepared a lot of samples too, containing cement and complexing agents solutions of different concentrations and then mechanical tested in order to obtain a very good value of the acid concentration which must not influence negatively the matrix structure.

So, after this information obtained concerning the limits of the concentrations belonging to the complexing agents which are introduced in the cement matrix were prepared the samples presented above.

3. EXPERIMENTAL RESULTS

The results obtained before through X-rays diffraction on the hydrated cement are presented in a previous paper [6] (Fig. 1).

(iii) The aim of this analysis is to obtain useful information about structural modification induced by some complexing agents on the cement matrix. With the help of these data and with the diffraction spectrum obtained on the samples: cement – citric acid (Figs. 2, 3 and 4), the cement – oxalic acid (Figs. 5, 6 and 7) and the cement – tartaric acid (Fig. 8), it could be obtained an image concerning the changes which appear in embedding of the complexing organic acids solutions in cement, among the cement basis components and the addition ones.

(iv) The diluted acid solutions has an important influence on Ca(OH)_2 which results from the Portland cement hydration, Ca(OH)_2 being the most soluble. Through the lowering of Ca(OH)_2 concentration carry out the furthering hydrolysis of the other hydro compounds with the damaging consequences on the concrete.

4. DISCUSSION OF RESULTS

The XRD spectrum of the hydrated cement (Fig. 1) emphasizes crystalline hydrated compounds such as: tricalcium hydroasulfataluminate similar to the natural ettringite (d: 5.61; 4.61; 4.08; 2.56; 2.20), calcium hydroxide well crystallized from the intergranular solution (d: 4.92; 2.62; 1.92; 1.80; 1.68), the hexagonal calcium hydroaluminate (d: 7.64; 2.66; 2.49). There are also identified tricalcium silicate (d: 3.02; 2.77; 1.76), dicalcium silicate (d: 3.02; 2.79; 2.77; 2.18) and tricalcium aluminate which remain unreacted (d: 4.08; 2.79) [9].

In the XRD diffractograms obtained on the sample cement – citric acid 1%, it is noticed that the characteristics peaks of Ca(OH)_2 become low in intensity but the acid solution concentration doesn't affect too much the growing of the

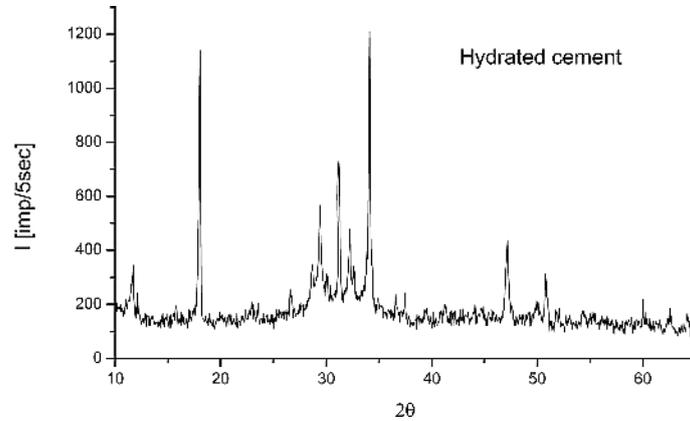


Fig. 1 – The diffraction spectrum of hydrated cement.

cement hydration products and especially of $\text{Ca}(\text{OH})_2$ which gives to cement matrix a higher mechanical resistance.

The diffraction spectra from pictures 2, 3 and 4 obtained on the citric acid – cement samples emphasize that its embedding in the lower concentrations doesn't bring important changes in the cement hardening structure so it has no negative consequences on the products which result through cement hydration.

XRD spectra of the samples with cement and citric acid (Fig. 2, 3 and 4) emphasize crystalline hydrated compounds (which are presented in Fig. 1) and new crystalline compounds such as: calcium carbonate (d: 3.035; 2.28; 2.095; 1.88), calcium silicate hydrate (3.04; 4.83; 2.79; 3.65; 3.23; 2.04; 1.95; 1.88) [9, 10].

From the presented diffraction spectra both in the case of citric acid and also in the case of oxalic acid no matter of the above concentration one can

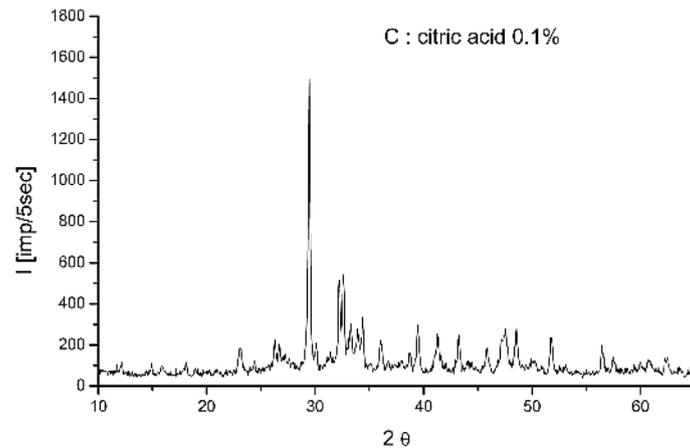


Fig. 2 – The diffraction spectrum of cement-citric acid 0.1%.

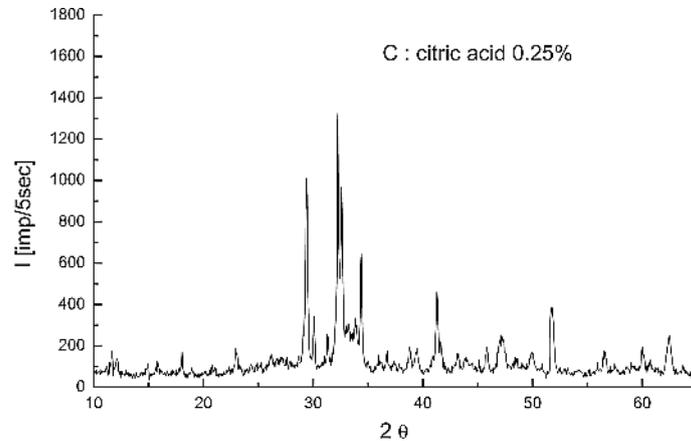


Fig. 3 – The diffraction spectrum of cement-citric acid 0.25%.

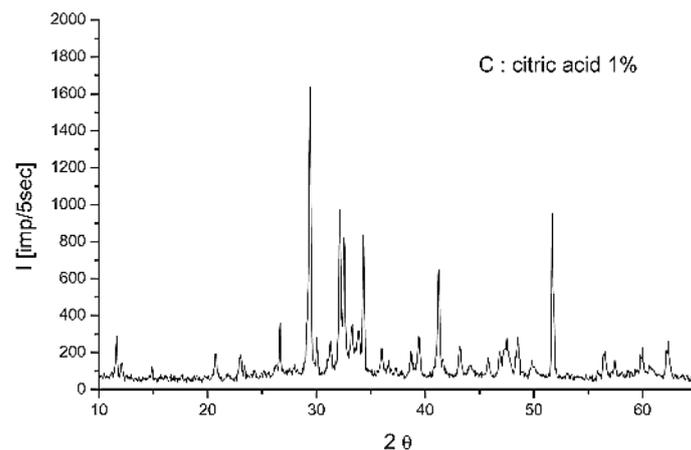


Fig. 4 – The diffraction spectrum of cement-citric acid 1%.

notice that the specific peaks intensities of the anhydride cement components (tricalcium silicate C_3S and dicalcium silicate C_2S) don't get low and also the hydro silicates of calcium which are formed through the cement hydration is lower than in the sample of the cement without addition.

As it concerns the oxalic acid can be noticed an increase of negative influence on the calcium hydro silicates on the calcium hydro aluminates and on the calcium hydroxide format which are vital for the cement matrix hardening.

The $Ca(OH)_2$ concentration gets low due to the calcium oxalate format. Similarly the ferrite and aluminated hydro compounds can decompose and resulting as final products the iron hydroxide and the aluminum hydroxide gels.

The most unstable hydration compounds are in lowering order: $Ca(OH)_2$, tobermorite and calcium hydroaluminated.

XRD spectra of the samples with cement and oxalic acid (Figs. 5, 6 and 7) emphasize crystalline hydrated compounds (which are presented in Fig. 1) and new crystalline compounds such as: calcium carbonate (d: 3.035; 2.28; 2.095; 1.88), calcium oxalate (d: 5.981; 3.645; 2.99), calcium silicate hydrate (3.04; 4.83; 2.79; 3.65; 3.23; 2.04; 1.95; 1.88), iron hydroxide (d: 2.42; 4.61; 2.82) [9–11].

The diffraction spectrum obtained on the tartaric acid – cement sample shows important changes within the concrete structures. These changes are underlined through the important decreasing of the characteristic lines intensity of the cement hydration products (calcium silicate hydrate, tricalcium hydro-sulfataluminate, the hexagonal calcium hydroaluminate) [9].

The complexing agents modify the hydration formation morphology and their structure. They influence both the developing kinetic and the type of the new formations with the consequences on the matrix structure.

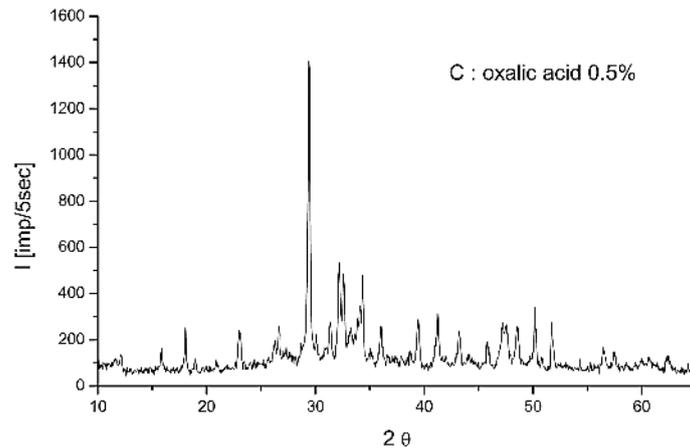


Fig. 5 – The diffraction spectrum of cement-oxalic acid 0.5%.

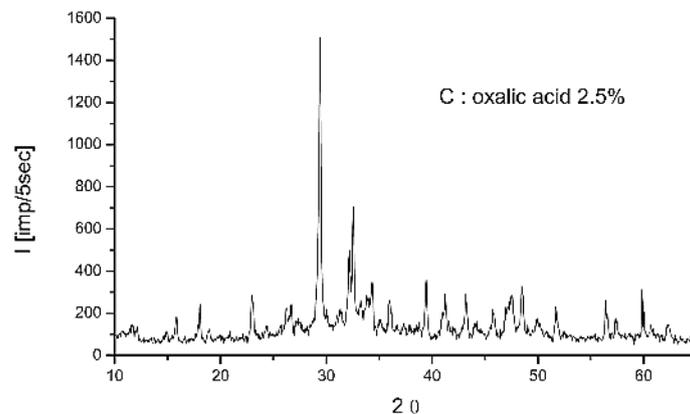


Fig. 6 – The diffraction spectrum of cement-oxalic acid 2.5%.

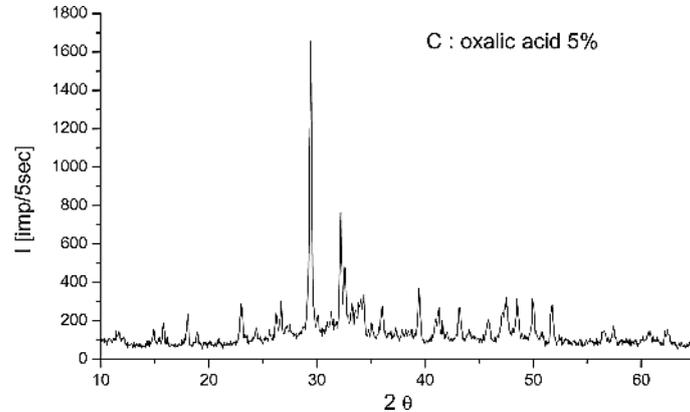


Fig. 7 – The diffraction spectrum of cement-oxalic acid 5%.

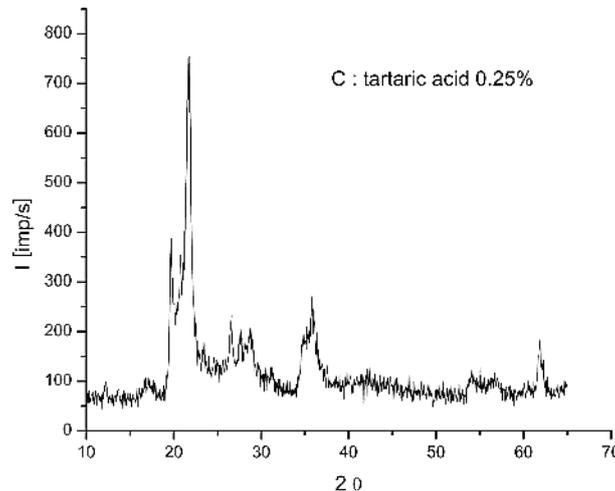


Fig. 8 – The diffraction spectrum of cement-tartaric acid 0.25%.

They can interfere in the ionic equilibrium change of the system influencing the fastening process of coagulation and crystallizing of the hydrated products. Through chemical type interactions they can determine the forming of complex combinations with influence on the kinetic hardening process.

They can also influence the structural characteristics after some surface phenomenon or due to the forming of hydro compounds with big volume (resulted through chemical reactions with the cement hydrolysis – hydration products).

The types of the complexing agent solution influences through the chemical interaction with the cement hydration products in tighten correlation with the properties of the resultative products.

The organic components used in this paper can be considered as promoters or inhibitors of the Portland cement hydration degree. The citric (less) and

tartaric acids can be considered inhibitors of the conditioning process while oxalic acid as a good promoter. The structural modifications in the case of tartaric acid are correlated with the results obtained by mechanical tests. With the growth of concentration over 0,5% values for tartaric acid, the mechanical strength became smaller.

As it concerns the oxalic acid (a bigger than 1% concentration) one can notice a bigger negative influence on the calcium hydro silicates, on the calcium hydro aluminates and on the calcium hydroxide format which are the basis of the cement matrix hardening.

The differences in XRD for the acids can be explained by the differences in the structures, as an effect of alcoholic OH group number. Oxalic acid has not, citric acid has one group and tartaric acid has two. The negative influence on the mechanical performances can be correlated with the decreasing of the compounds revealed in pure cement paste diffraction.

Oxalic acid: HOOC-COOH

Citric acid: $\text{HOOC-CH}_2\text{-COH(COOH)-CH}_2\text{-COOH}$

Tartaric acid: $\text{HOOC-CHOH-CHOH-COOH}$

4. CONCLUSIONS

Within this paper were prepared the cement samples with complexing organic acid solutions (oxalic acid, citric acid and tartaric acid) and then the microstructural characterization by X-rays diffraction.

The experimental results of the XRD application tests allow emphasis the follows conclusion:

- The complexing agents modify the hydration formation morphology and their structure. They influence both the developing kinetic and the type of the new formations with the consequences on the matrix structure.
- The oxalic acid determines the concrete impermeable growth after chemical reactions with the cement hydration products resulting insoluble compounds (calcium oxalate) which fill the concrete pores and fissures.
- The diffraction spectrum obtained on the cement – citric acid samples emphasize that its embedding in lower concentration (till 1%) doesn't bring important changes in the cement hardening structure and thus doesn't have negative consequences on the products which appear by the cement hydration.
- Tartaric acid is an inhibitor of the cement hydration products, the diffraction spectrum for this sample showing important changes concerning the specific lines of the hydration formations.

- In the future these data will be the reference data for structural and mechanical characterization of the long term behavior of these matrices kept in condition simulating the final disposal as part of a long term research program.

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