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STUDY OF RADIOACTIVE PRECIPITATES CEMENTED MATRIX BY THE XRD PHASE IDENTIFICATION*

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Abstract. The aim of this work is the XRD application for the phase identification of matrix that simulates the conditioned radioactive waste. The selected matrices for the study are Ordinary Portland Cement with iron precipitates. The results obtained by this analysis give information about the chemical reactions between the radioactive precipitates and the hydrates, hydrolysis products of the cement. The structural stability of conditioned radioactive waste is the main request because a structural stable waste form will maintain the geometrical dimensions during the disposal, including factors as weight of material, water presence and internal factors as radiation and chemical reactions. The obtained data, by structural analysis, are necessary to follow the modification appearing in the conditioning matrix as a result of radioactive precipitates embedding.

Key words: radioactive waste, cemented matrix, X-ray diffraction.

1. INTRODUCTION

Radioactive wastes are generated in a variety of physical and chemical forms, including gases, liquids and solids. The radioactive wastes must be immobilized in a form that is physically and chemically stable, the most known method being the cementation and hydraulic Portland cement. In the case of cementation, the chemical nature and proportion of the precipitation products affect both the hydrolysis of the initial cement components and the reactions of metastable hydration constituents as well as the mechanical strength and the chemical resistance of the hardened cement system.

The product of this immobilization process should be a monolith with acceptable mechanical, chemical and physical properties that are maintained over

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an appropriate time such that the release of radioactivity from the waste form in the environment is minimized [1].

The knowledge about the mixture effect of the cement with certain radioactive waste is limited and the experimental works are necessary for the cement-waste matrix optimization [2]. Optimal formulations should consider each waste individually because of possible interactions between the constituents of the waste and the cement. Because of the complexity of the system, optimization of this process in terms of its efficacy and safety represents a serious practical problem, even in treatment of the monocomponent radioactive waste. The hydration of Portland cement may be regarded as a series of interrelated consecutive exothermic chemical reactions. These reactions are modified by the introduction of radioactive waste [3]. The aim of the analysis by X-ray diffraction is to obtain information about structural modification induced by some iron compounds, which are the main components of the radioactive sludge. As a result of X-ray diffraction analysis on the samples: cement – iron precipitates (iron hydroxides and iron phosphates) conditioned by cementation, was obtained x-ray diffractogram.

2. EXPERIMENTAL PART

Precipitation of the insoluble compounds is an usual process for the treatment of low level aqueous radioactive wastes (LLAW) having iron hydroxides and iron phosphates as main components in Radioactive Waste Treatment Plant – Magurele, whereas the cementation is the most used process for the final conditioning of the sludge.

The work consists of the microstructural analysis of some samples obtained through methods that simulate the conditioning of iron hydroxide and iron phosphate precipitates.

There were prepared two types of iron precipitates:

– the addition of the neutralization agents NaOH concentrated to the diluted solution of $FeCl_3$;

– the Na_3PO_4 addition to the diluted solution of $FeCl_3$.

The precipitates obtained were conditioned through cementation as it follows:

– cement + iron hydroxide (5g cement + 2.5g wet precipitate);

– cement + iron phosphate (5g cement + 2.5g wet precipitate).

The samples were kept under normal conditions of temperature and humidity (20ºC ± 1ºC) for 28 days, by the same period for the cement paste hardening. After this period the samples were fine milled obtaining powders with the grain size of 30-40μm. The big particles give a spreading effect of the diffracted radiation. The little particles become amorphous by the reticular structure damage. These samples were analyzed through XRD.

The X-ray investigation was performed with a Dron 2 diffractometer (made in Soviet Union), using Ni-filtered Cu-Kα radiation (λ=1.5418 Å), for diffraction angles 2 theta ranged between 5 and 65˚.

Calculating interplanar distance *d* parameters for all diffraction maxima 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. *d* [Å] 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. This minimal proportion depends on the particular phase nature and also 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-ray diffraction measurements of dry and hydrated cement were presented in a previous paper [4]. 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 [5]. Based on these results, the samples with cement and iron precipitates can be investigated by XRD.

3. DISCUSSION OF RESULTS

With the help of the information resulted from the X-ray diffractogram obtained on the samples (hydrated cement, iron hydroxide, iron phosphate, cement – iron hydroxide, cement – iron phosphate) could be obtained an image concerning the chemical reactions, the changes which appear in embedding of the iron compounds in cement, among the cement basis components and the addition ones.

The data presented in the technical literature, as well as the results themselves show that the conditioning matrix of radioactive waste through cementation represent a physical-chemical system which is very complex concerning the structure and its composition far from the chemical balance of the implied subsystems and which suffers some changes. These affect the physical-chemical and mechanical performances during the intermediate stored and the disposal.

The XRD diffractogram of the hydrated cement emphasizes crystalline hydrated compounds as: tricalcium hydrosulfataluminate similar to the natural ettringite – $Ca_3Al_2O_6{\cdot}3CaSO_4{\cdot}31H_2O$ (2θ: 15.8; 19.2; 21.8; 35; 41), calcium hydroxide – $Ca(OH)_2$ well crystallized from the intergranular solution (2θ: 18; 34.2; 47.2; 50.6; 54.6), the hexagonal calcium hydroaluminate – $Ca_4Al_2O_7{\cdot}13H_2O$ (2θ: 11.6; 33.6; 36). We also identified tricalcium silicate – Ca_3SiO_5 (2θ: 29.5; 32.3; 51.8), dicalcium silicate – Ca_2SiO_4 (2θ: 29.5; 32; 32.3) and tricalcium aluminate – $Ca_3Al_2O_6$ which remain unreacted (2θ: 21.8; 32) [6].

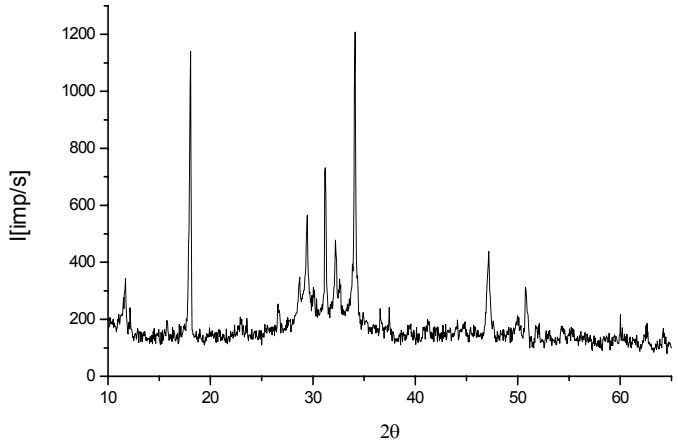

Fig. 1 – The X-ray diffractogram of hydrated cement.

The iron precipitates: $Fe(OH)_3$ and $FePO_4$.

Due to the precipitates low crystallized, a part of the iron compounds present low and large lines. The measurement done through XRD on the iron precipitate $Fe(OH)_3$ confirmed the existence of two types spinelic structures corresponding to magnetite (Fe_3O_4) and γ Fe_2O_3 as well as to β $Fe_2O_3 \cdot H_2O$ and αFe_2O_3 compounds. From the $Fe(OH)_3$ X-ray diffractogram one can notice the appearance of a crystallized phase being present through well underlined peaks and of a amorphous phase presenting very large and low peaks.

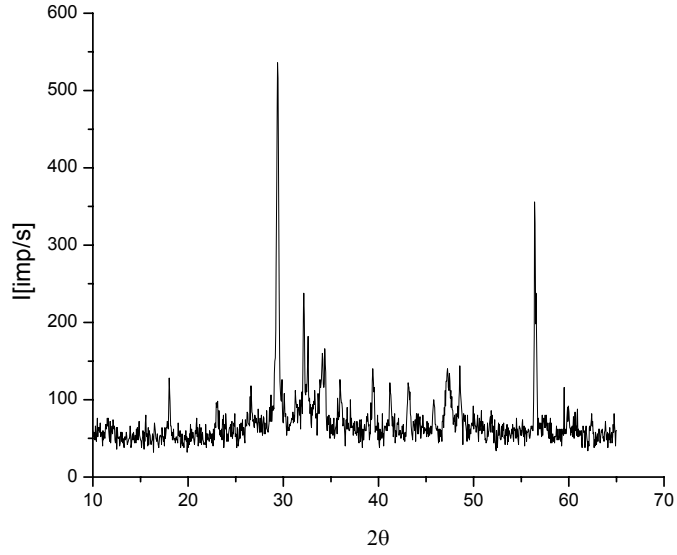

Fig. 2 – The X-ray diffractogram of iron hydroxide.

At the precipitate $FePO_4$ X-ray diffractogram one can notice that the iron phases present a better crystalline namely there are presented more sharped peaks and with the higher intensities especially: iron hydrate orthophosphate – $FePO_4 \cdot 2H_2O$, iron metaphosphate – $Fe(PO_2)_2$ and iron hydrate phosphate – $Fe_4(PO_4)_2(OH)_6 \cdot H_2O$. In the case of this iron precipitate can be noticed in the X-ray diffractogram the appearance of amorphous phase.

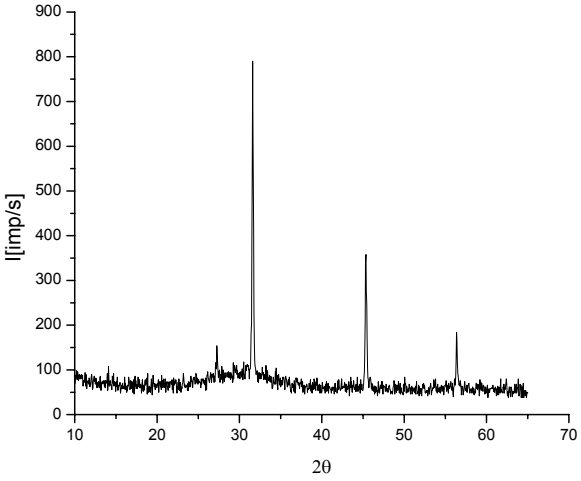

Fig. 3 – The X-ray diffractogram of iron phosphate.

Matrices that simulate the conditioning matrix of the radioactive waste were analyzed through XRD obtaining the specific X-ray diffractograms. In these X-ray diffractograms can be noticed the presence of some new compounds which appear after the chemical reactions between the Portland cement and iron precipitates.

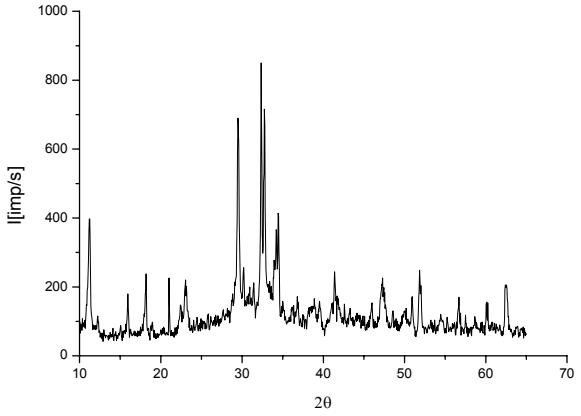

Fig. 4 – The X-ray diffractogram of cement - iron hydroxide.

In the X-ray diffractogram no. 4, can be noticed that the peaks characteristic of the hydrated cement compounds do not disappear, they presenting a very small decreasing of intensity of the lines specific to these compounds ($Ca(OH)_2$, tricalcium hydrosulfataluminate – $Ca_3Al_2O_6 \cdot 3CaSO_4 \cdot 31H_2O$, calcium hydroaluminate – $Ca_4Al_2O_7 \cdot 13H_2O$ and calcium hydrosilicates like tobermorite gel – $Ca_2SiO_4 \cdot H_2O$). In this X-ray diffractogram appeared new compounds during the hardening of cement paste as a consequence of the chemical reactions between iron hydroxide and the hydrated cement compounds: calcium iron oxide – β-$Ca_4Fe_{14}O_{25}$ (2θ: 34.55; 34.21; 33.30; 29.92), calcium iron silicate – $Ca_3Fe_2(SiO_4)_3$ (2θ: 33; 29.59; 36.45; 20.8), calcium aluminium iron oxide – $Ca_4Al_2Fe_2O_{10}$ (2θ: 34.09; 32.31; 47.34; 33.56). These compounds belonging to the hydrated cement present an important role concerning the hardening structure of the cement and the mechanical strength of the concrete.

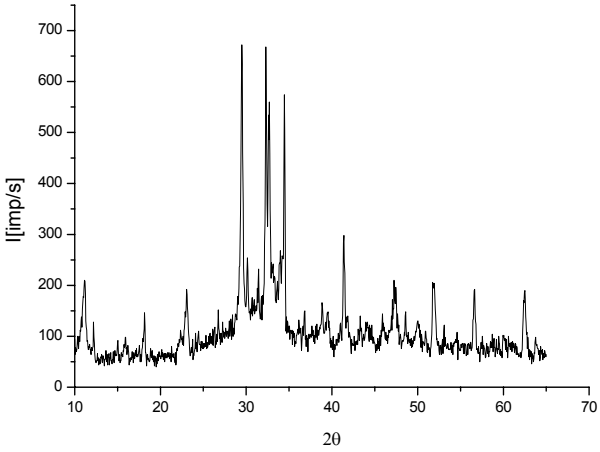

Fig. 5 – The X-ray diffractogram of cement - iron phosphate.

The X-ray diffractogram no. 5, emphasizes the existence of some new compounds which appear after the chemical reactions between the cement and iron precipitate namely: phosphate hydroxide double of iron and calcium – $Ca_2Fe(PO_4)_2(OH) \cdot 1½H_2O$ (its diffraction angle being: 29.2; 32.8; 34.6; 25.6). Beside these new compounds, lower quantities of iron hydrate orthophosphate - $FePO_4 \cdot 2H_2O$ unreactioned, can be identified. It is also emphasize the important presence of compounds from the hydrated cement, but presenting a diminution of the Röentgen interferences intensities specific to these compounds.

One can notice that, in the x-ray diffractograms the iron precipitates don't have important changes concerning the hydration compounds of the hydrated cement (the iron precipitates influence just a little the structural properties of the concrete).

4. CONCLUSIONS

The analyses of the simulated radioactive waste processing products by X-rays diffraction proved that, despite of the investigated systems complexity, the main phases could be identified.

This study allowed the identification of the compounds that appear after the interaction between the cement and the iron precipitates.

The new results obtained concerning the embedding of the iron compounds in cement offered large possibilities for a detailed characterization of the mechanism during the cementation process.

The XRD proved to be useful in the establishing of the composition and structure of the iron compounds used in the chemical treatment of the radioactive waste.

In the future these data will be the reference data for structural and mechanical characterization of the long term behaviour of these matrices kept in condition simulating the final disposal.

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