Effect of Gamma Radiation on the Morphology of Concrete in Radioactive Waste Disposal Site

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Cement is an important material in radioactive waste management. It is used as a solidifying agent for the concentrated wastes resulting from the treatment process. The solidification process results in immobilized wastes. To protect the human and the environment for long periods of time, the solidified waste forms should withstand the operation and storage conditions. Hence, the cement blocks should have proper mechanical and chemical properties. Moreover, the effect of radiation on the blocks should be studied to assure the retention of radionuclides by the cement matrix under radiation fields. To carry out the study, cement blocks were irradiated by Gamma radiation at doses 40, 120 and 240 KGy. The morphology of the blocks was studied before and after irradiation using X-ray Diffraction Patterns (XRD), and Scanning Electron Microscopy (SEM). The results of morphology studies are presented. The morphology studies indicated an improvement in the fixation of radionuclides on the cement matrix after irradiation.

Keywords: Gamma radiation, XRD, SEM, Cement blocks and disposal site

Introduction

Cementation is one of the most common methods of radioactive waste management, as waste immobilization matrix, engineering barriers or structural material in repositories. In each case, the cement has performed as required for the period of the service life in the installation. This period can range from hundreds to thousands of years; it depends on the characteristics of the waste to be disposed [1]. Concrete is macroscopically consisting of two components: cement paste and aggregate. Cement paste includes hydration products of Portland cement. Cement reacts with water to form hydration products. Unhydrated cement involves five constituents of which alite ($3CaO \cdot SiO_2$) and belite ($2CaO \cdot SiO_2$) are responsible for the strength of the cement block. Both of them form(C-SH), which have a complex internal pore structure with a high specific surface area [2].

Large amounts of water subsist in the cement in different conditions. They can be divided into three kinds according to the manner in which the water is bound to the hydration products. Free water subsists in pores, and it has a similar behavior to bulk water [2].

From the chemical reaction, water is bound strongly with hydration products. The description of water chemical bound with the hydration products is still under discussion. The dehydration

at 105°C under CO_2-free conditions is normally used to differentiate between chemical bound and non-evaporable water [3]. Both of gel water and capillary water are dehydrated below 105°C as evaporable water [4].Also there is an access of water contained in cement by immersing the cement blocks in distilled water to simulate water infiltration from the surrounding environment causing the penetration of harmful ions into the cement blocks, and leaching of cement blocks compounds [5-10]. So after the cement blocks are irradiated, two reactions occur as a clue to gamma radiation

a- Reaction between gamma rays and water
Under gamma radiation, the pore water present in cement blocks undergoes radiolysis and there are some reactive products that can be produced such as electrons, hydroxyl radicals and hydrogen peroxide. The products of radiolysis will interact with cement blocks components and its hydration products to form large numbers of compounds [11-13].

b- Reaction between gamma rays and cement blocks components
Interaction of gamma rays with cement blocks can lead to the photoelectric effects, Compton scattering, or pair production, which may be the reason for ejection of electrons ejected and the occasional involvement of positrons. The produced or ejected electrons collide with cement blocks compounds to eject more electrons, so that the number of ejected electrons (secondary electrons) increases until the energies of the secondary electrons become lower than the ionization energies of the cement blocks compounds. When the mass of the secondary electrons is very low, electrons do not directly eject atoms composing the cement blocks. Gamma radiation has a very little effect on the solid cement blocks, which consist of rather isotropic, ionic and metallic bonds [2].
Gamma rays affect cement blocks through electronic excitations. When the secondary electrons collide with cement blocks electronic excitations occur. At the excited states, the electrons lose their excess electronic energies to the vibrational energies of atoms composing the cement blocks producing a damage of anisotropic chemical bonds such as covalent bonds. Siliceous minerals are decomposed by gamma rays because the Si-O bond is covalent [14]. Water existing in

cement blocks, as one of the main components, is decomposed by the effect of radiolysis into hydrogen, oxygen and hydrogen peroxide [15].
The present work aims to investigate the effect of gamma radiation on the cement morphology and the immobilization of elements in the cement blocks. Scanning electron microscopy and XRD are good tools to study the influence of gamma radiation on cement microstructure and mineralogy of each component in non-irradiated and irradiated concretes.

Materials and Methods
A-Preparations of cement blocks
The cement material is mixed with different elements to form blocks. All experiments used cement blocks with water to cement ratio 0.6. The mixture (cement and solution (water+ salts)) is stirred for 1 minute and casted in cubic moulds of dimensions 0.8 cm× 0.8 cm× 0.8 cm. The blocks are removed after one day and left for curing time28 days. The cement blocks are exposed to gamma rays with different doses; 40, 120, and 240 KGy.

  A- Methods:
    a- Leaching tests:

The tests were carried out on cement blocks containing Sr, Fe, Co individually and a mixture of them. The used concentrations are 0.01, 0.02, 0.1, and 0.15 M/L, respectively. the tests were carried out as the follows:

1. The cement blocks were immersed in 300 ml of distilled water.
2. Leachate is collected and key elements are determined after 90 days using ICP.
3. The cement blocks are crushed (non irradiated and irradiated cement blocks).
4. The samples were examined using Energy Dispersive X-Ray Spectroscopy (EDS) (Oxford ISIS attached to Scanning Electron Microscope (SEM) Jeol 5400).
5. The samples analysis by X-Ray Diffraction (XRD) patterns were recorded by using PHILIPS X-ray unit (PW 1830), with diffractometer (PW 3710/31), scintillation counter (PW

2563/00).Samples were irradiated with monochromatized Cu Kα radiation (n=1.542 Å) and analyzed between 2 and 60° (2θ). The voltage and current used were 30 kV and 30 mA.

Results and Discussion

A- Chemical analysis of leachate

The chemical analysis was performed for the key elements (Na, Ca, Al, and Si) of the cement in the non irradiated and irradiated cement blocks by ICP tool. This analysis shows the effect of radiation on the release of concerned ions from the cement blocks.

Table (1) illustrates the chemical analysis of leachate for non-irradiated and irradiated cement blocks. The results indicate that there is a decrease in the release of most of ions such as Na, Si, and Al, and an increase in the Ca ions under radiation. This may be attributed, as observed in all the samples, to a depletion of Portlandite and an increase of Calcite quantity in the surface of the specimens. This process, called carbonation, can be explained by the reaction of Portlandite with the carbon dioxide present in the atmosphere, as shown in the equation below [1]

$$Ca(OH)_2 + CO_2 \longleftrightarrow CaCO_3 + H_2O \quad Eq.(1)$$
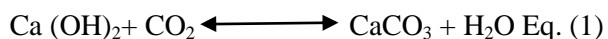
This calcite formation was less pronounced in the specimen's core. It probably occurs due to the fact that the calcite can block the cement pores and prevent the carbon dioxide penetration into the inner part of the specimen [1]. There is also a decrease in the release of the concerned ions from the cement blocks, and this may be due to the effect of radiation, which blocks the cement pores and immobilizes the concerned ions in the cement blocks.

The results indicate that the carbonation leads to immobilization of heavy-metals in cementitious blocks [16-21]. A wide review on the carbonation of waste immobilization was given by Fernandez Bertos et al. [17]. Carbonation of cement waste blocks modifies the microstructure, and may inhibit the leaching of elements from cement blocks. Therefore, carbonation may result in the precipitation of **Ca^{++}** and formation of metal-silicate complexes [17]. Carbonation has double effects on of them on heavy metals from either hydroxy carbonate or carbonate precipitates and the other one on calcium silicates. Additionally,

the decrease of pH reduces metal mobility for some elements was briefly discussed by R.S. Zaky et al [22]. Carbonation of waste seems to be a best process for immobilization of elements in cement blocks. However, the behavior may be different depending on the type of waste. So, for different types of waste and different cement materials, additional experiments should be performed.

A- Scanning Electron Microscopy (SEM):

Figure (1) shows cement blocks irradiated at different radiation doses. The results show that non irradiated cement blocks surface has very tiny pores. The gamma rays lead to changes in cement structure, creating new crystals, (needle ($CaCO_3$)) in all the different doses. This may be explained as resulting from the reaction of calcium hydroxide (CH) with CO_2causing changes of chemo-mechanical in the microstructure [16]. The reaction of Carbon Dioxide with dissolved (CH) may precipitate sparingly soluble Calcium Carbonate in the cement blocks pore space [23-25] as shown in Eq. (1).

Carbonation of calcium hydroxide includes three steps [24]: (1) dissolution of (CH); (2) absorption of $CO_2$and formation of Co_3^{+2} ions; and (3) chemical reaction and precipitation.

Calcium carbonate results from the chemical reaction of carbon dioxide with calcium hydroxide [26]. In the first step of carbonation, carbon dioxide diffusion through the carbonated layer (second step), is controlling step for carbonation of calcium hydroxide [23, 27]. Although carbon dioxide diffusivity is considerably higher in gas filled cement blocks pores, compared to cement blocks water filled pores, the presence of moisture is essential for the reaction of carbon dioxide with calcium hydroxide [28]. In the limiting step of the carbonation process the changes result as the rate of calcium hydroxide carbonation decreases due to the formation of calcium carbonate thin layer on the surface of CH crystals [25, 27, 22, 29-31]. (Ca$(CO_3)_2$) crystals form at the calcium hydroxide surface random on Figure (1, a-d). Finally, the cement blocks surface covers due to the nucleation sites growing and coalescing [29]. This is made possible by the small surface areas of portlandite crystals as compared to calcium-silicate hydrates [32]. Figure (2) shows SEM of cement blocks containing Sr and irradiated with different doses. The results illustrate the effect of gamma ray on the morphology structure of the cement

blocks. In case of non-irradiated cement block, the surface of cement blocks shows Sr^{+2} incorporation into the hydrated cement resulting in a poor crystalline structure. For the different doses 40, 120 and 240 KGy the structure of cement is changed into crystalline state. This may be due to the generation of hydrogen gas under radiation, and the partial reaction of calcium sulphoaluminate particles with surrounding formed strontium aluminate. In these cement blocks ettringite is detected as smaller but needle shaped crystals; the presence of $SrAl_2O_4$ inhibits the formation of ettringite crystals [33]. Also, as a result of carbonation, the cement blocks may undergo changes in the porosity of cement blocks. These changes may lead to a decrease in the porosity for the different doses [17, 20, 34-40]. The dissolution of cement phases lead to the changes in the Porosity. Carbonation of cement leads to an increase in the volume and precipitation of calcium carbonate in the cement pore.

So, the decrease of cement blocks pore volume is associated with CaCO3 precipitation. Precipitation of calcium carbonates takes place in smaller cement pores. It leads to a shift in the cement blocks pore size distribution curve towards smaller cement pore diameters and total volume of cement pores per gram of cement blocks [41]. On the other side, the cement blocks pore structure may be associated with the formation of additional silica gel due to the decomposition of C-S-H [55]. Additionally, apparently cement reacts in a similar way, the carbonation delays the formation of bilite $(2CaO \cdot SiO_2)$: Rimmelé et al. [17] noticed that the cement blocks porosity decreases by radiation. In fact, the C-S-H carbonation is the key factors in the variation of cement blocks porosity. This was reported by some authors [42].

Table (1) The chemical analysis of leachate for non-irradiated and irradiated cement blocks after 90 days

Cement block	Na (mg/ml)	Ca (mg/ml)	Si (mg/ml)	Al (mg/ml)	Fe (mg/ml)	Sr (mg/ml)	Co (mg/ml)
Cement+ water Non irradiated	11,25	4.00	35.00	3.500	0.001	0.000	0.000
Cement+SrCl2 0.15 M/L Non irradiated	7.427	61.00	26.0033	3.00	0.000	2.50	0.000
Cement+FeCl3 0.15M/L Non irradiated	6.40	23.00	23.00	3.00	0.005	0.000	0.000
Cement+ CoCl2 0.15M/L Non irradiated	7.45	26.00	26.00	4.00	0.000	0.000	0.037
Cement+ mixture 0.15 M/L Non irradiated	6.75	27.00	26.00	3.00	0.010	2.78	0.035
Cement + water 40 KGy	2.924	19.606	27.875	0000	0000	0.000	0.000
Cement+SrCl2 0.15 M/L 40 KGy	3.152	12.055	16.560	0.1044	0.000	1.1255	0.000
Cement+FeCl3 0.15 M/L 40 KGy	2.592	19.523	21.308	0.000	0.000	0.000	0.000
Cement+CoCl2 0.15M/L 40 KGy	1.699	20.889	12.020	0.007	0.000	0.000	0.004
Cement + mixture 0.15 M/L 40 KGy	3.651	21.612	23.658	0000	0.000	0.9153	0.040
Cement + water 120KGy	2.896	22.141	24.623	0000	0000	0.000	0.000
Cement + SrCl2 0.15 M/L 120 KGy	2.020	18.926	9.967	0.035	0.000	1.3381	0.000
Cement+FeCl3 0.15 M/L 120 KGy	3.011	17.635	11.125	0.0191	0.000	0.000	0.000
Cement + CoCl2 0.15M/L 120 KGy	2.155	23.320	13.032	0.009	0.000	0.000	0.042
Cement + mixture 0.15 M/L 120 KGy	5.000	30.982	35.000	0.0017	0000	1.6236	0.040
Cement + water 240 KGy	2.961	14.454	16.031	0.024	0000	0.000	0.000
Cement + SrCl2 0.15 M/L 240 KGy	2.475	14.263	5.930	0.061	0.000	1.4495	0.000
Cement + FeCl3 0.15 M/L 240 KGy	1.602	24.187	11.651	0.0197	0.000	0.000	0.000
Cement+CoCl2 0.15M/L 240 KGy	1.698	20.898	11.581	0.017	0.000	0.000	0.003
Cement+mixture 0.15 M/L 240 KGy	4.010	16.73	26.054	0.090	0000	1.313	0.004

a-0 KGy

b- 40 KGy

c-120 KGy

d- 240 KGy

Fig. (1): The SEM of cement blocks irradiated at different doses

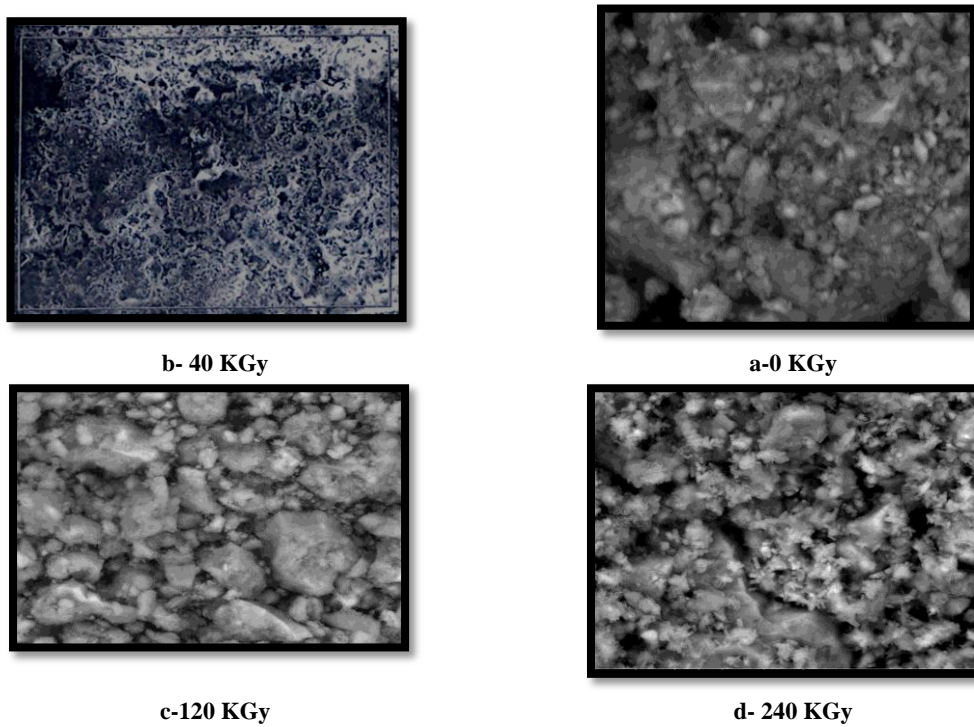b- 40 KGy

a-0 KGy

c-120 KGy

d- 240 KGy
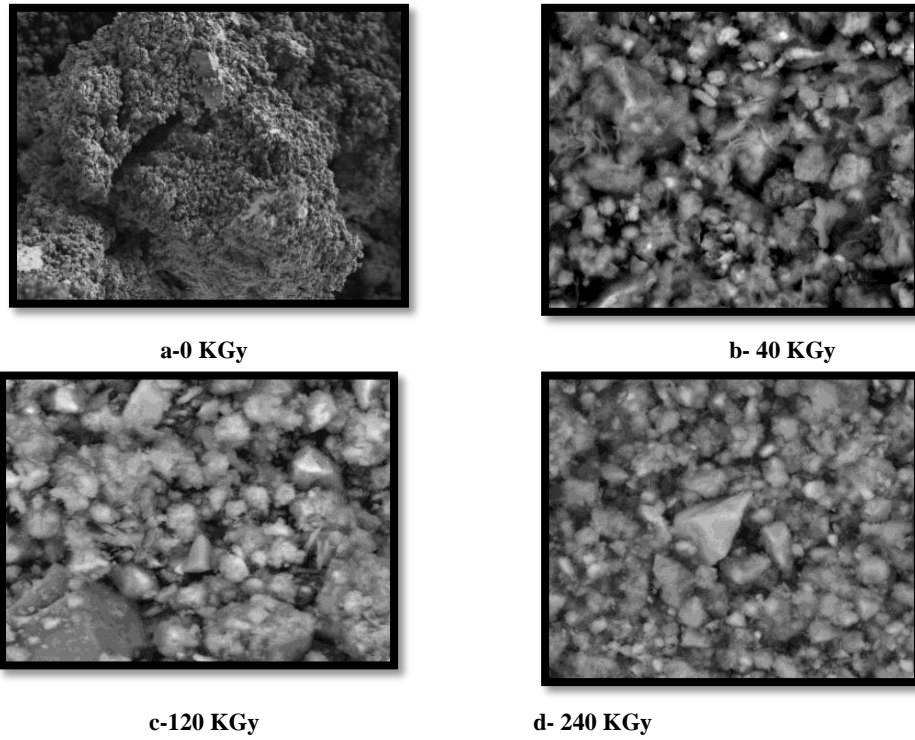
Fig. (2): The SEM of cement blocks containing Sr irradiated at different doses

Figure (3) illustrates SEM of cement blocks containing Fe and irradiated at different doses. The results demonstrate that for the non-irradiated cement, the surface is covered by Fe^{+2}ions. It can be observed that the hydration of cement may be modified by Fe^{+2}ions due to coating the cement grains [18]. For irradiated cement blocks there are crystal and some needle shape ($CaCO_3$) appearing in the morphology of cement under irradiation at different doses. This may be due to immobilization of Fe ions on the surface of cement resulting in blocking the pores of the cement as confirmed by in the chemical analysis.

The reaction can be illustrated by forming calcium carbonate due to carbonation. It has a very low leaching rate and solubility thus leading to block the cement pores, at least in the first stage of carbonation [17, 19]. Houst and Wittmann [43] noted that uncarbonated cement blocks have a high absorption capacity compared to the carbonated cement blocks. Ngala and Page [38] found that the transport properties of the elements have a large effect by the carbonation.

Figure (4) illustrates SEM of cement blocks containing Co and irradiated at different doses. The results demonstrate that in case of non-irradiated cement, there is a precipitation of Co^{+2}. Under radiation, the structure is changed into a crystalline state and the needle shape appears due to the effect of the gamma rays on the morphology of cement, which can significantly improve the immobilization of Co ions and most of the elements on the cement blocks by carbonation. This relates to the decrease of porosity of cement blocks and possibly of structural changes of the C-S-H gel as the main binding component in cement [44].

Figure (5) illustrates SEM of cement blocks containing mixture of salts and irradiated at different doses. The surface of cement blocks in case of non-irradiated cement after addition of a mixture of (Sr^{+2}, Fe^{+3}, and Co^{+2}) salts. The results indicate the precipitation of mixture of salts on cement. This phenomenon reveals a new bulky structure on the surface of cement with the tiny pores. Under radiation, the structure of cement changes. The pores may be blocked and the crystalline state and the needle shape of the calcium carbonate appear. Ions are immobilized on the cement surface.

Figure (6) illustrates XRD of cement blocks irradiated at different doses. The results indicate that there is a decrease in the number and size of unhydrated cement particles. Carbonation of cement blocks results from the reactions of (C_3S) and (C_2S) with Carbon Dioxide. These reactions result in formation of $CaCO_3$ and silica gel, as follows [21, 33]:

$$3CaO \cdot SiO_2 + 3CO_2 + nH_2O \rightarrow SiO_2 + nH_2O + 3CaCO_3 \quad (3)$$

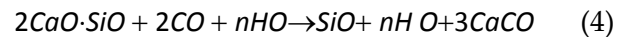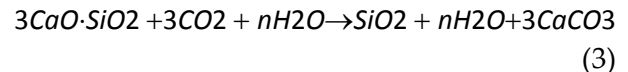$$2CaO \cdot SiO + 2CO + nHO \rightarrow SiO + nH\,O + 3CaCO \quad (4)$$

Figure (7) illustrates XRD of cement blocks containing Sr and irradiated at different doses. The results show that under radiation there is an increase in the intensity of some peaks and a decrease in others, some peaks are broadened, and new peaks appear. It may be due to carbonation.

Figure (8) illustrates XRD of cement blocks containing Fe and irradiated at different doses. The results demonstrate that the precipitation of Fe ions on the surface of cement. In case of irradiated cement blocks there are new peaks appear and others disappear; the intensity of the peaks increases.

Figure (9) illustrates XRD of cement blocks containing Co and irradiated at different doses. The results indicate an appreciable change in diffraction intensity under radiation, and new peaks appeared. Also the results show a decrease in the intensity and in the number of peaks.

Figure (10) illustrates XRD of cement blocks containing mixture of salts and irradiated at different doses. The results show a decrease in the intensity and number of the peaks. There is a shift in the basal spacing of the cement. This can be attributed to the energy transferred from the gamma rays to the molecules of water and the cement components. The energy transfer leads to water hydrolysis resulting in hydrogen, oxygen and hydrogen peroxide [15]. Also the energy transfer leads to damage in the weak chemical bond (covalent bonds) between silicon and oxygen. Si-O bond is covalent [45]. The hydrogen, oxygen and hydrogen peroxide formations and damage of silicon-oxygen bond are manifested in the intensity decrease and the number of peaks, also,there is a shifting in basal spacing.
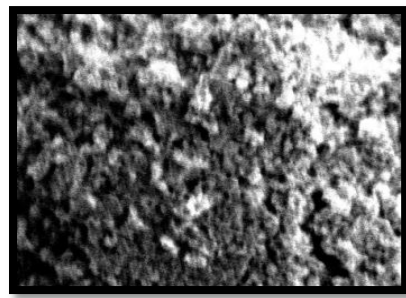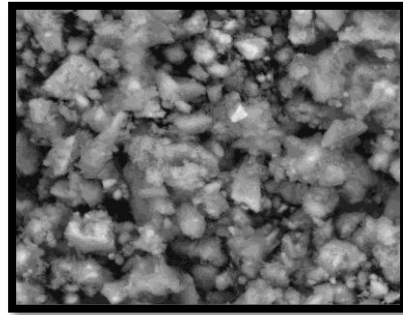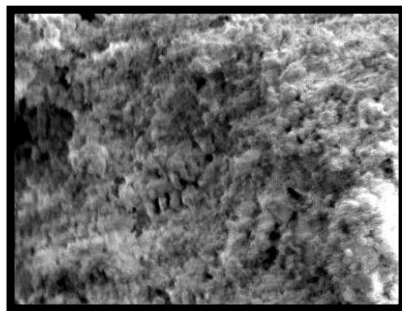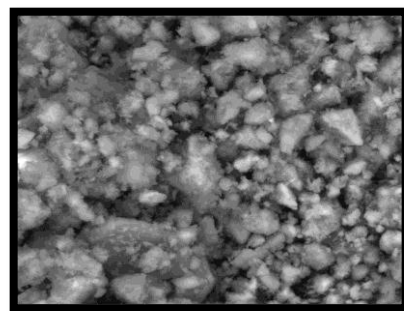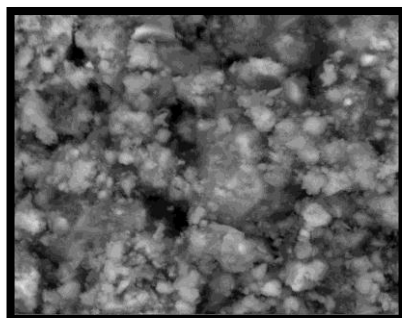
a-0 KGy
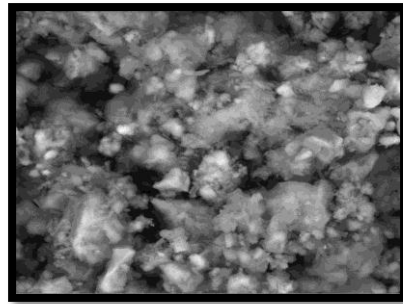
b- 40 KGy
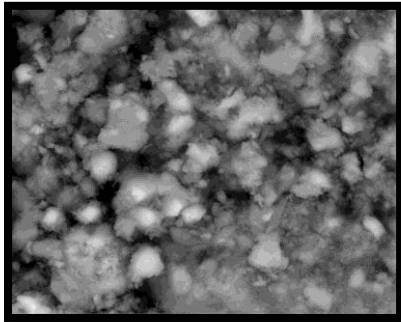
c-120 KGy

d- 240 KGy

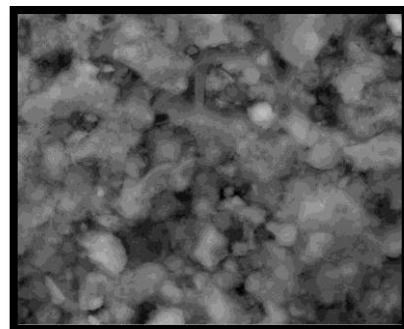**Fig. (3): The SEM of cement blocks containing Fe irradiated at different doses**

a- 0 KGy

b- 40 KGy

c-120 KGy

d- 240 KGy

Fig. (4): The SEM of cement blocks containing Co irradiated at different doses

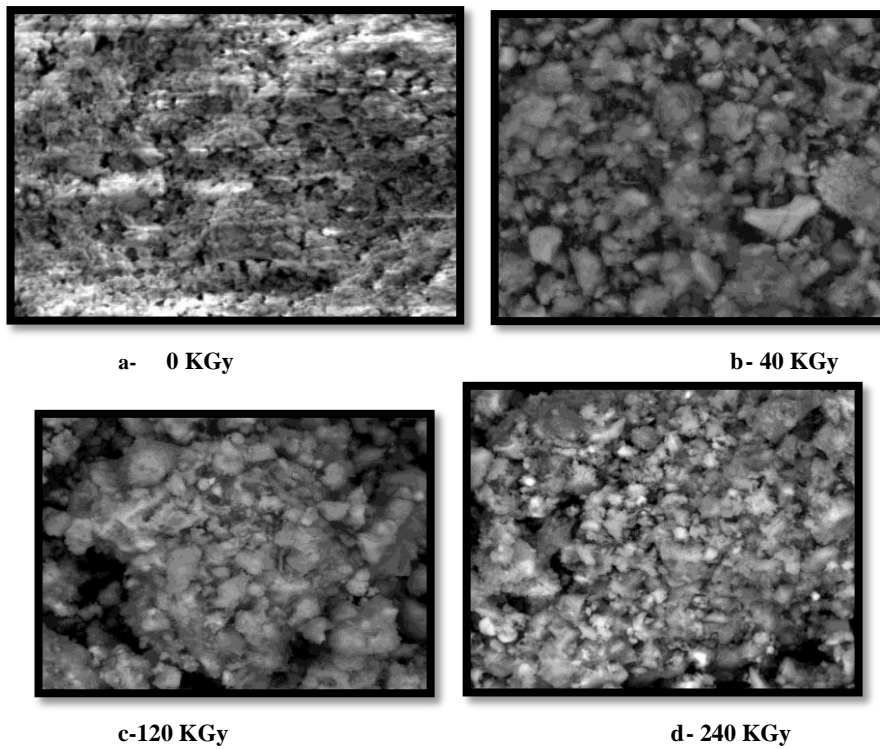a- 0 KGy
b- 40 KGy

c-120 KGy
d- 240 KGy

Fig. (5): The SEM of cement blocks containing mixture of salts and irradiated at different doses
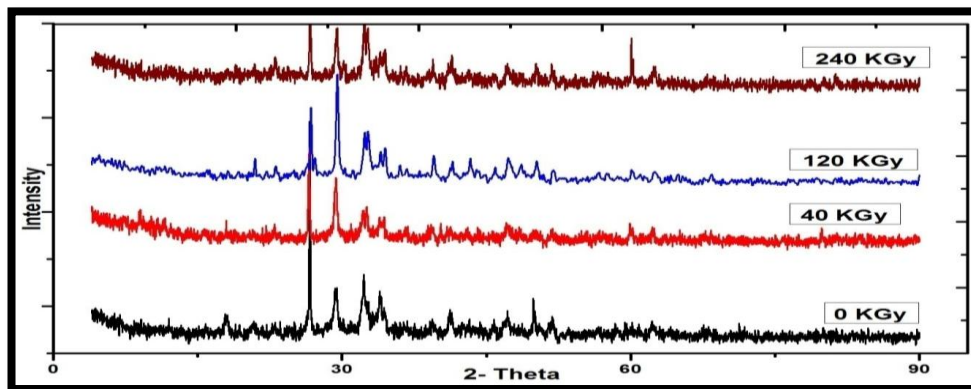

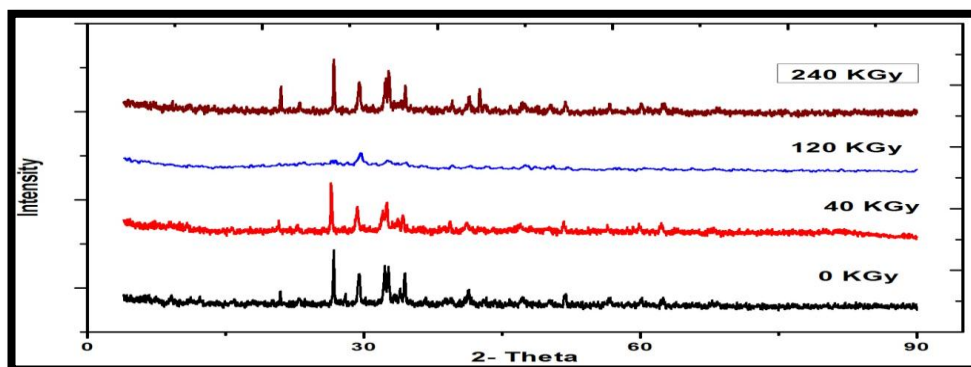Fig. (6): The XRD of cement blocks irradiated at different doses

Fig. (7): The XRD of cement blocks containing Sr irradiated at different doses
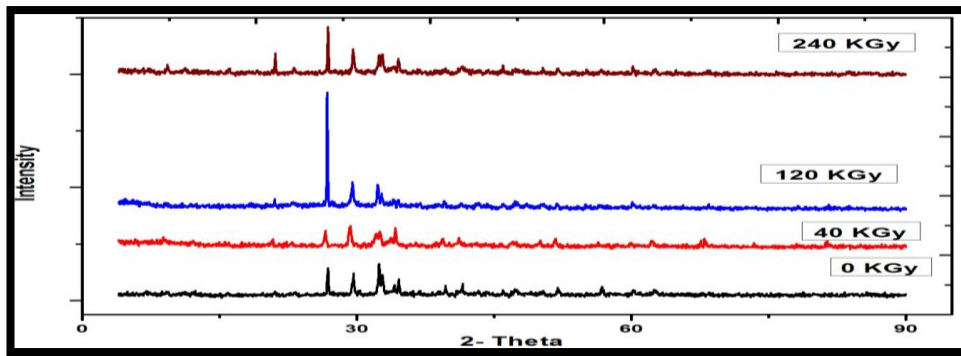
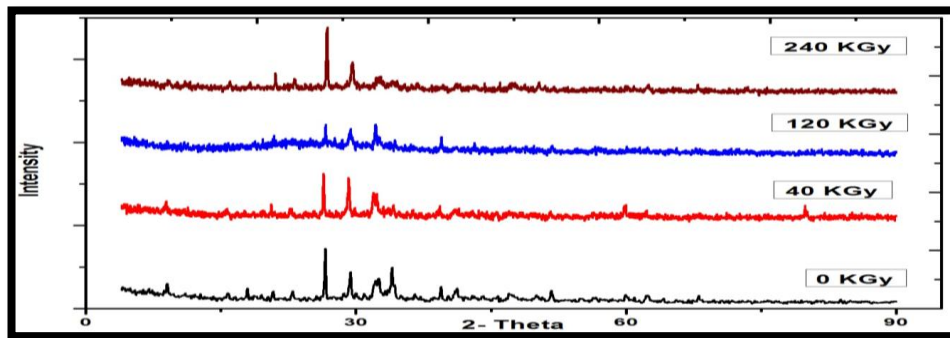**Fig. (8): The XRD of cement blocks containing Fe irradiated at different doses**

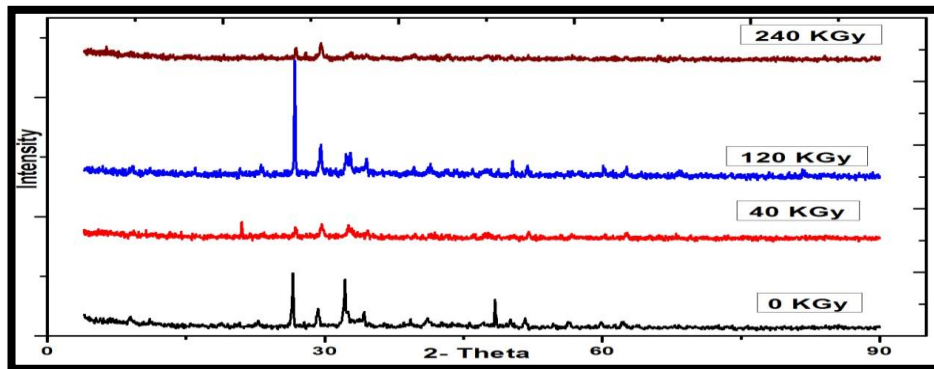**Fig. (9): The XRD of cement blocks containing Co irradiated at different doses**

Fig. (10): The XRD of cement blocks containing mixture of salts and irradiated at different doses

Conclusions

The results of the present work show that the ratios of calcium hydroxide (Ca (OH)$_2$) and calcite (CaCO$_3$) are directly affected by irradiation. In the environment of a repository for radioactive waste, the carbonation reaction can be influenced by the presence of bicarbonate ions in the groundwater, or due to the presence of other factors (presence of sulfate and chloride, temperature difference, pressure, etc.).

The results of the chemical analysis of leachate indicate that there is a decrease in the release of the key elements under gamma radiation except for calcium.

The results of the SEM clarify the effect of radiation on the pure cement structure, crystals and pores change. This may be due to carbonation.

The XRD examination of pure cement indicates a decrease in the number and size of hydrated cement particles carbonation of cement blocks which may be result from the reaction of C$_3$s and C$_2$s with CO$_2$.

In case of Sr and Fe additives, the results due to gamma radiation show an increase in the intensity of some peaks and a decrease in other peaks as well as the appearance of new peaks. In case of Co and mixture there is a decrease in the intensity and number of peaks.

Further studies need to be carried out to evaluate the chemistry and mineralogy of the cementitious materials in the repository environment. Furthermore, more analysis on the specimens exposed to the irradiation needs to be conducted, for instance, thermogravimetric analysis and imaging analysis.

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