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Effect of different media on some parameters in a simulated disposal site

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Abstract

The present work studies the effect of chemical reaction on the migration behavior of radionuclides from a disposal site. The study considers the release from the cement blocks which will be investigated by the leaching tests, and the variation of five parameters; percentage change in weight, pH, Reduction potential (ORP), Conductivity (COND), and Total Dissolved Solids (TDS). These parameters are recorded as a function of time for blocks prepared with different water to cement ratios. These parameters are indicators of the change in the chemical reaction of the different medium. The experimental study is considered for 90 days.

1. Introduction

Disposal is the emplacement of radioactive waste into a facility or a location with no intention of retrieving the waste. Disposal options are designed to contain the waste by means of passive engineered and natural features to isolate the waste from the accessible human environment to the extent necessitated to avoid associated hazard [1].

The safety of environment from a radioactive waste disposal site requires detailed knowledge about the possible release of radionuclides through the evaluation of safety performance of disposal. Mathematical models and computer codes are tools to evaluate the possible release rate of radionuclides from disposal site. Since the chemical reaction of radionuclides with the components of different media of the disposal site and with the surrounding environment is not considered in these mathematical models, the results obtained are significantly different from the real behavior of radionuclides. Therefore, the current study focuses on the effect of chemical reaction between different media (waste, cement, and soil) in the disposal system.

The study concentrates on two topics; the first is the release from the cement blocks which will be investigated by the leaching tests. The second is the migration of the released elements. This will be illustrated through studying the retention of the released elements by the soil in the hosting medium. The indicator parameters used to evaluate this study are; Reduction potential (RP), Conductivity (COND), and Total Dissolved Solids (TDS) as a function of time for blocks with different water to cement ratios.

2. MATERIALS AND METHODS

Cement blocks were prepared with different water (distilled water (pH=6)) to cement (Portland cement) ratios (0.5, 0.6, 0.65, and 0.7). Some Cement blocks were prepared by mixing Cement with different salts (Fe as $FeCl_3$ with concentrations $6.6*10^{-3}$ and $4.6*10^{-2}$ mole/L, Sr as $SrCl_2$, with concentrations $1*10^{-3}$ and $1*10^{-2}$ mole/L and Co is added as $CoCl_2$ with concentration $2.4*10^{-2}$ mole/L). The mixtures (Cement-salts) are poured into cubic molds with a volume of $1cm^3$, and cured for 28 days. X-Ray Diffraction (XRD) patterns are obtained by using PHILIPS X-ray unit (PW 1830), with diffractometer (PW 3710/31), and scintillation counter (PW 2563/00. Parameters such as pH, OPR, COND, and TDS are measured before and after 90 days using a digital pH-meter (Ultrameter ™, Myron L Company, USA) with an error of ± 0.01. The concentration of metals in the leachant is measured using Inductively Coupling Plasma (ICP) (Ultima 2 Jobin Yvon, France).

3.1. RESULTS AND DISCUSSIONS

3.1.1.XRD Results.

Figures (1, 2), show the XRD patterns of cement and hydrated cement for 28 days, respectively. Results show that the composition of cement powder and hydrated cement is similar. The reaction of water with cement as shown in the equations leads to reducing the basal spacing [17]:

$$C_3S + H_2O\ C_3S_2Hx\ \text{(Hydrated Gel)} + Ca(OH)_2 \qquad (1)$$

Primary Cementitious Product

$$Ca\ (OH)\ 2\ Ca^{++} + 2(OH)^- \qquad (2)$$

$$Ca^{++} + 2(OH)^- + SiO^2\ \text{(Soil Silica)}\ CSH \qquad (3)$$

Secondary Cementitious Product

$$Ca^{++} + 2(OH)^- + Al_2O_3\ \text{(Soil Alumina)}\ CAH \qquad (4)$$

Secondary Cementitious Product

Also, it has been observed from XRD peaks that there is a change in the intensity and the number for cement before hydration [18, 19].

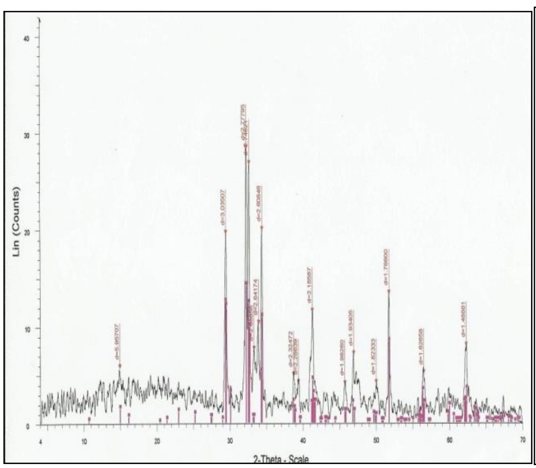

Fig.1. XRD Pattern of Cement

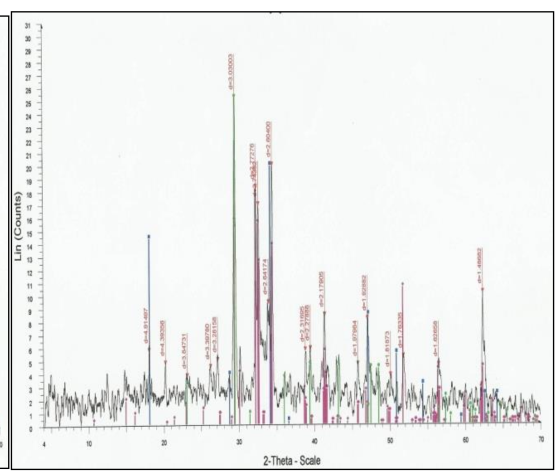

Fig. 2. XRD Pattern Hydrated Cement

The XRD patterns for solidified matrix containing Fe, Sr, Co, and mixture of salt are presented in Figures (3, 4, 5 and 6) respectively. It is shown that a slight shifting in basal spacing took place. Moreover, the change in diffraction intensity is appreciable. From Figure (3) it is clear there are new peaks appeared and some peaks are broadened. This can be explained by precipitation of Fe^{+2} ions on the surface of cement particles in the form of CSH gel (C-Fe-S-H) [19].

Figure (4) shows the XRD pattern of cement with $SrCl_2$ additive. It is clear that there is a decrease in the intensity and in the number of peaks.

In case of Co^{+2} and mixture of salt (Figures (5, 6)) there is a shifting in basal spacing, new peaks appeared and a decrease in the number of peaks due to the incorporation of these ions into the lattices of CSH gel [19].

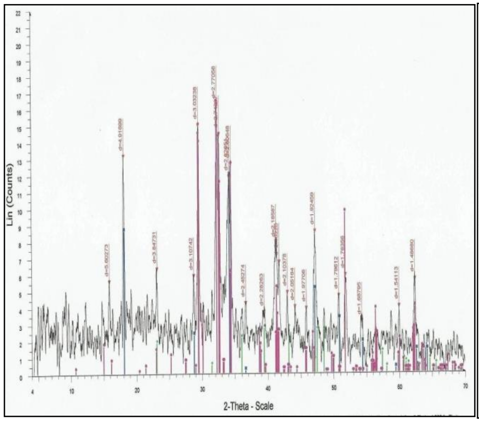

Fig 3: XRD Pattern Fe (II) Ions on Cement

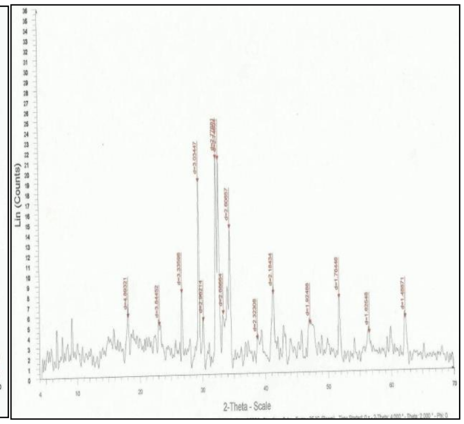

Fig 4: XRD Pattern Sr (II) Ions on Cement

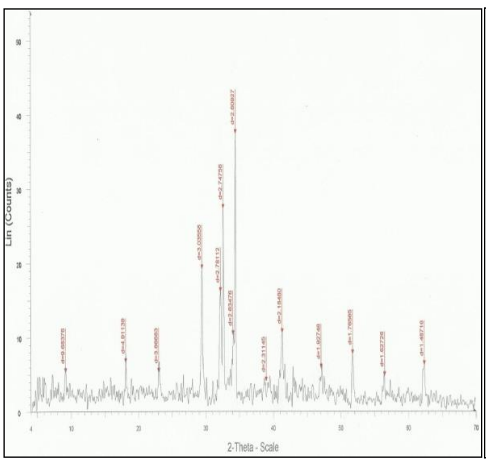

Fig 5: XRD Pattern Co (II) Ions on Cement

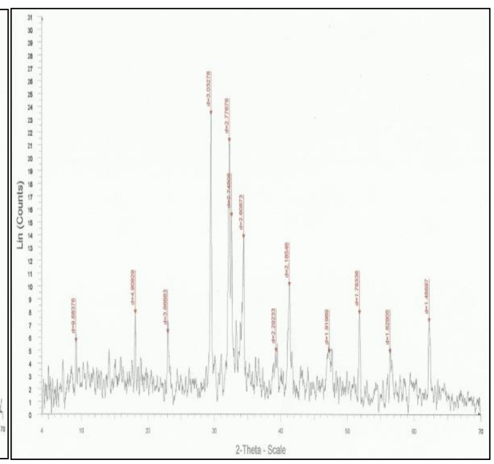

Fig 6: XRD Pattern Mixture of Salt on Cement

3.1.2. SEM Results

The images of hydrated cement, cement after addition of Fe^{2+}, Sr^{2+}, Co^{2+}, and mixture of salts (Fe, Sr, and Co) are presented in Figures (7.A–E). Figure (7.A) shows portlandite needle-shaped silicate crystals which are the main crystalline products in the hydration of cement.

Fig (7.B) indicates that the surface of cement particles is covered by Fe+2. It may be explained by the fact that the hydration of cement can be modified by heavy metals due to coating around cement grains [20]. Also the structure remains crystalline. Figure (7.C) shows Sr^{+2} incorporation into the hydrated cement results in a poor crystalline structure. Figure (7.D) shows the morphology of cement after precipitation of Co^{+2}. It is densely covered with portlandite or needle-shaped silicate crystals. Figure (7.E) shows the cement after precipitation metals salts of mixture. There is a clear indication for the precipitation of mixture of salt on cement. This phenomenon reveals a structure as a new bulky on the surface of cement. The mixture fixation on the cement is different from that of hydrated cement in the morphology.

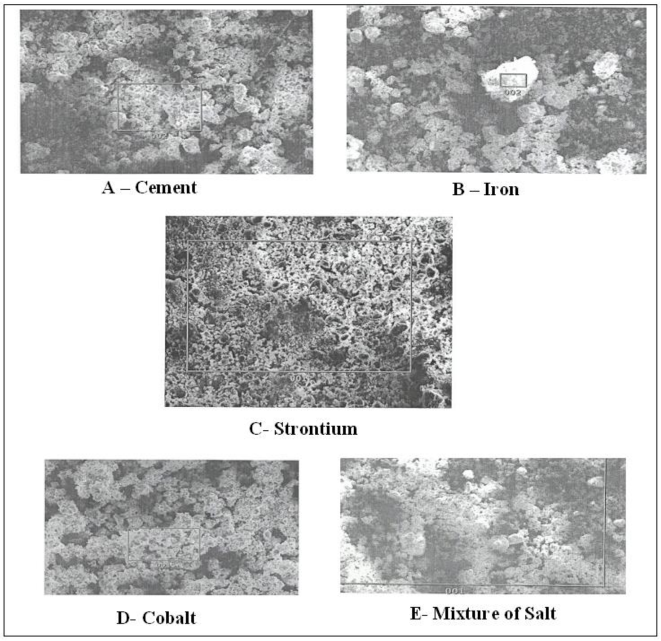

Fig (7.A–E): SEM Analyses

3.1.2. Leaching Test.

3.1.3.1. Leachability of Cement Blocks without Additives.

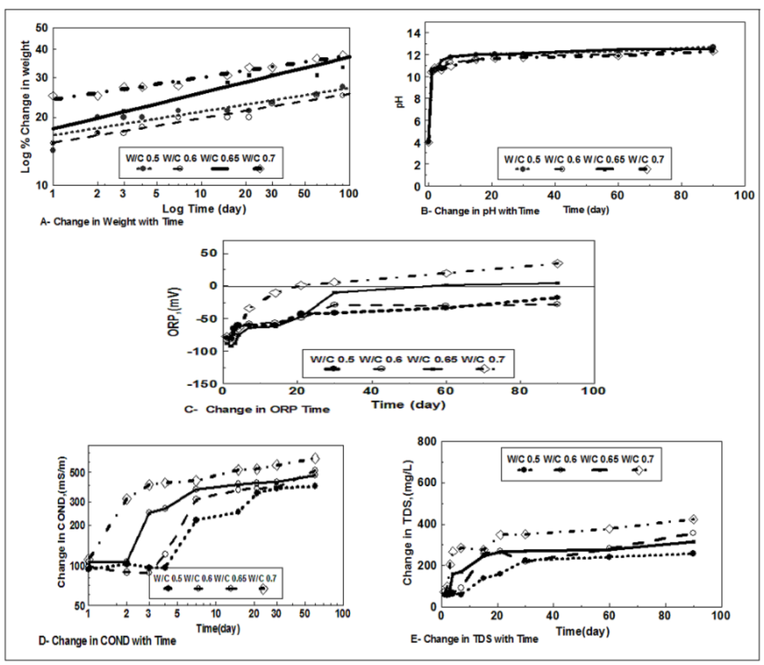

Fig 8: Effect of Leaching Process on Some Parameters.

A- Change in weight of Cement block with Time, B- Change in pH with Time, C- Change of OPR with Time, D-and E- Change in COND and TDS with Time.

Fig (8) illustrates the results of the leaching test for cement blocks without additives. The variation of the five parameters; % change in weight, pH, ORP, COND and TDS as a function of time for blocks with different water to cement ratio is shown.

Fig (8) illustrates the variation of the cement block weight with time. It is clear that the weight increases as the time increases. For the same period of the time, the weight increases as the W/C ratio increases. This can be attributed to the penetration of water through the pores of the blocks. It can also be said that as the W/C ratio increases the porosity of cement block increases. Penetration of water onto the pores is not a passive event but it indicates that some reactions take place. This is reflected on the change of the leachate characteristics (pH, ORP, COND and TDS). The general behavior of these parameters is an increasing function of time and of W/C ratio. This can be explained by the dissolution of one of the constituents of the cement [$Ca(OH)_2$] in the water which penetrates into the pores leading to the increase of the concentration of this compound in the leachate [21].

3.1.3.2. Leachability of Cement Blocks with Fe Additives.

Fig (9) shows the leaching results of cement blocks containing different concentrations of Ferric Chloride ($FeCl_3$); $6.16*10^{-3}$, and $4.6*10^{-2}$ mole/L. Figure (9,A), shows the increase of the cement blocks weight as the leaching time increases. For the two $FeCl_3$ concentrations, the effect of concentration on the weight is nearly negligible. The same behavior is realized for the pH, COND and TDS Figure (9, B, D, E). This indicates an increasing function of the time with a very slight effect of $FeCl_3$ concentration. The ORP change as a function of time Figure (9, C) shows an appreciable effect of the $FeCl_3$ concentration. For higher concentration the change of the ORP from negative values to positive values is higher for the higher concentration. This can be explained by the higher tendency for reaction in case of higher concentration than the lower concentrations [21].

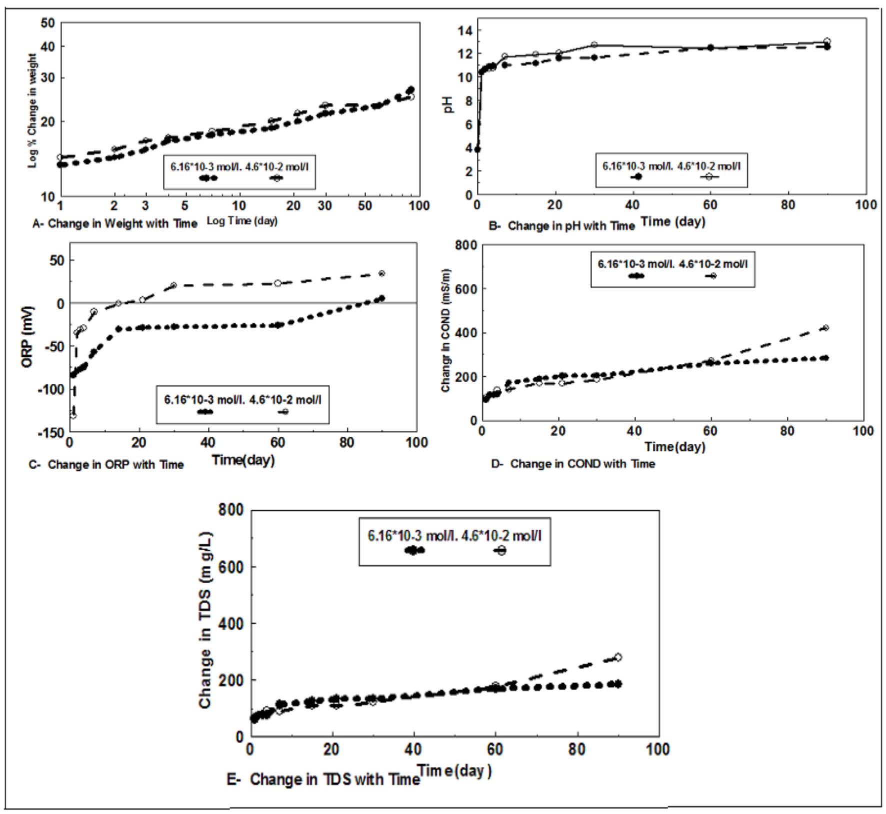

Fig 9: Effect of Leaching Process on Cement Blocks (W/C 0.5, mixed with $FeCl_3$ at Different Concentrations).

A - Change in Weight with Time, B- Change in pH with Time, C- Change OPR with Time,D and E- Change of COND and TDS with Time.

3.1.3.3. Leachability of Cement Blocks Containing Sr additives

Fig (10), illustrates the leachability of cement blocks containing different concentrations of $SrCl_2$; $1*10^{-3}$, and $1*10^{-2}$ mole/L on the same parameters.

From Figure (10, A) it is clear that the weight change is an increasing function of time as well as of $SrCl_2$ concentration. This can be explained by the release of Sr^{2+} ions into the solution which offers more pores filled by water. This also results in an increase in the values with the time in case of the higher concentration by the effect of Sr^{2+} ions and Ca^{2+} ions that released in the solution.

Concerning the change of the ORP with time, it goes from negative to positive values. The lower concentration shows the lower values than the higher concentration. This indicates that the higher concentration results in a higher release of free ions from the cement blocks into the solution. The same behavior is realized for both COND and TDS.

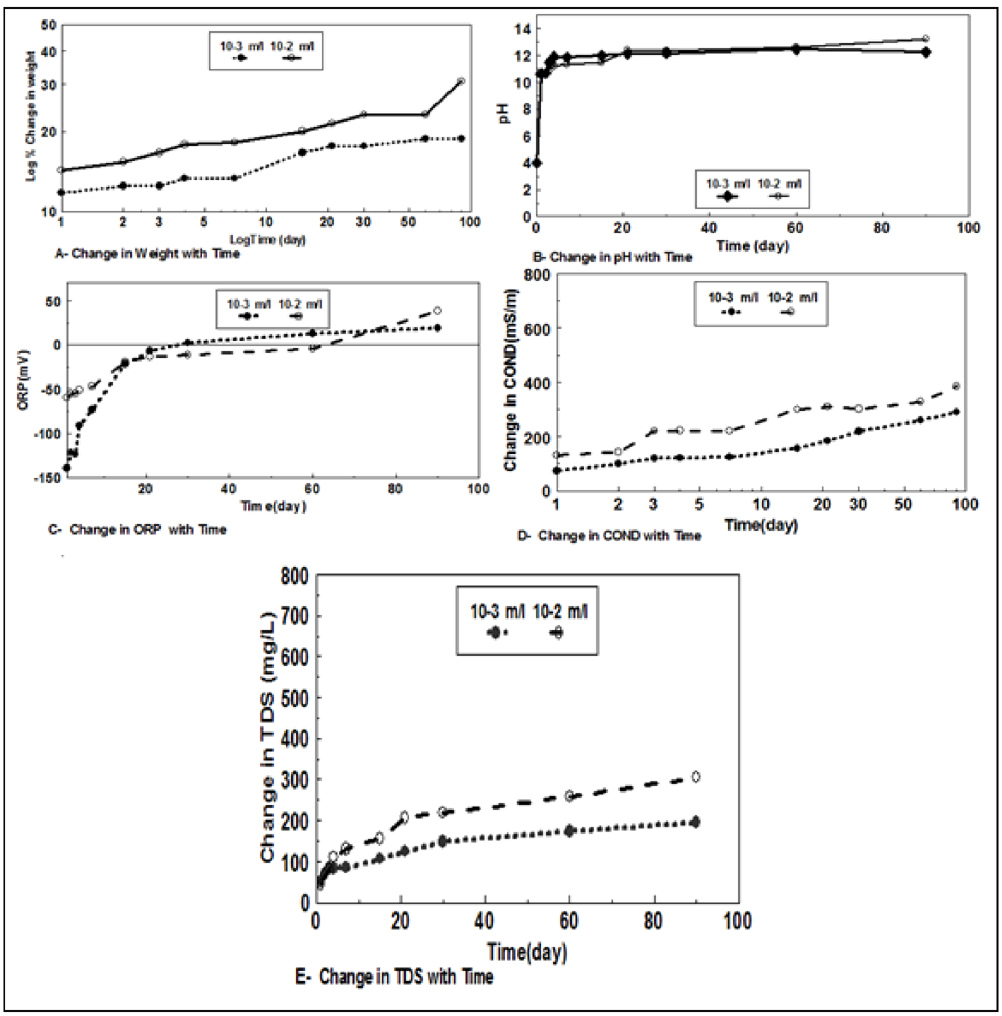

Fig 10: Effect of Leaching Process on Cement Blocks (W/C 0.5 and mixed with $SrCl_2$ with Different Concentrations). A- % Change in Weight with Time, B- Change in pH with Time, C-Change in OPR with Time, and D and E - Change in COND and TD with Time.

3.1.3.4. Leachability of Cement Blocks Containing Co Additives.

Fig (11) shows the leachabiltiy results of cement blocks containing $CoCl_2$ of concentration equals $2.4*10^{-2}$ mole/L. It can be shown that the increase in the weight reaches approximately 30% of the initial weight after the 100 days. This is the same case for all concentrations of $FeCl_3$ and the higher concentration of $SrCl_2$. The pH, ORP, COND and TDS are increasing functions with time but not similar in case of $FeCl_3$ and $SrCl_2$. This can be due to the co-precipitation of Cobalt into the pores which hinders the release of inorganic elements from cement blocks.

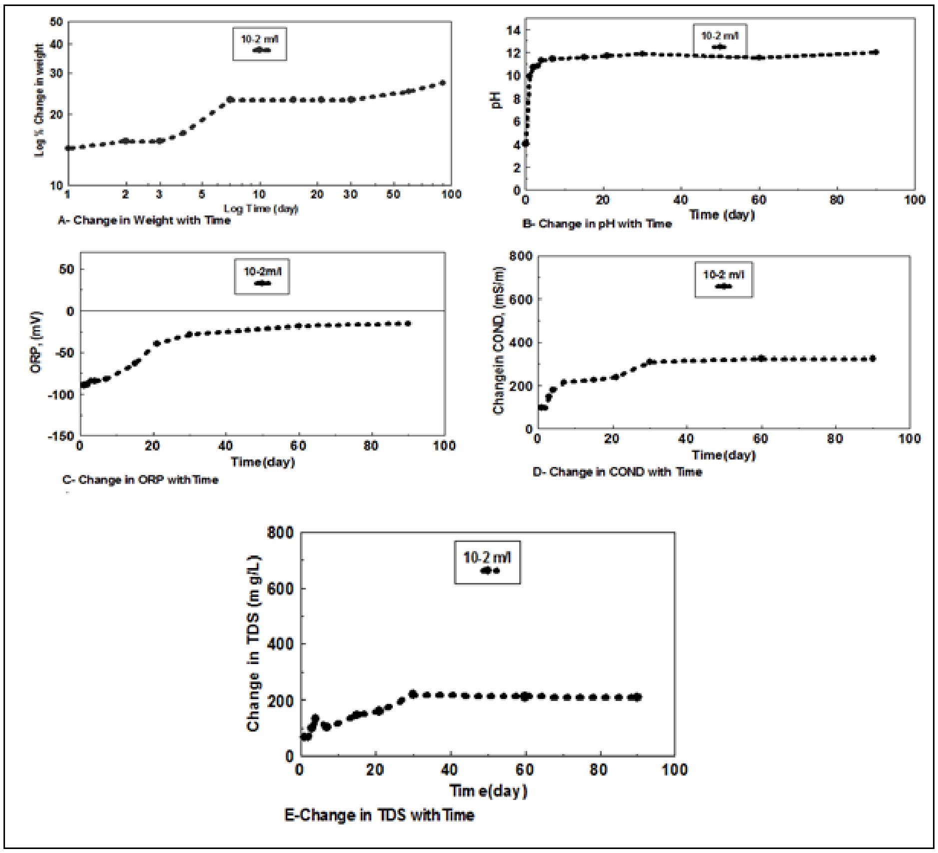

Fig 11: Effect of Leaching Process on Some Parameter Cement Blocks (W/C 0.5 and mixed with $CoCl_2$).

A- Change in Weight with time, B- Change in the pH in the Solution with Time, C- Change in OPR with Time, and D and E- Change in COND and TD Respectively with Time.

3.1.3.5. Leachability of Cement Blocks Containing a Mixture of Chlorides of Different Elements.

Fig (12) illustrates the results of the leaching process in the presence of a waste mixture containing; $4.6*10^{-2}$ mole/L $FeCl_3$, $1*10^{-2}$ mole/L $SrCl_2$, and $2.4*10^{-2}$ mole/L $CoCl_2$. As shown in the Figure (11), there is a continuous increase in weight with the time. pH values are an increasing function of time. This is attributed to the presence of traces of $Ca(OH)_2$, Fe ions and traces of Sr ions released from the cement blocks, pH reaches nearly 14.0. ORP increases with time from the negative to the positive values but lower than in case of $FeCl_3$ and $SrCl_2$ separately. Both of COND and TDS increase with time with higher values than in case of $FeCl_3$ and $SrCl_2$ separately.

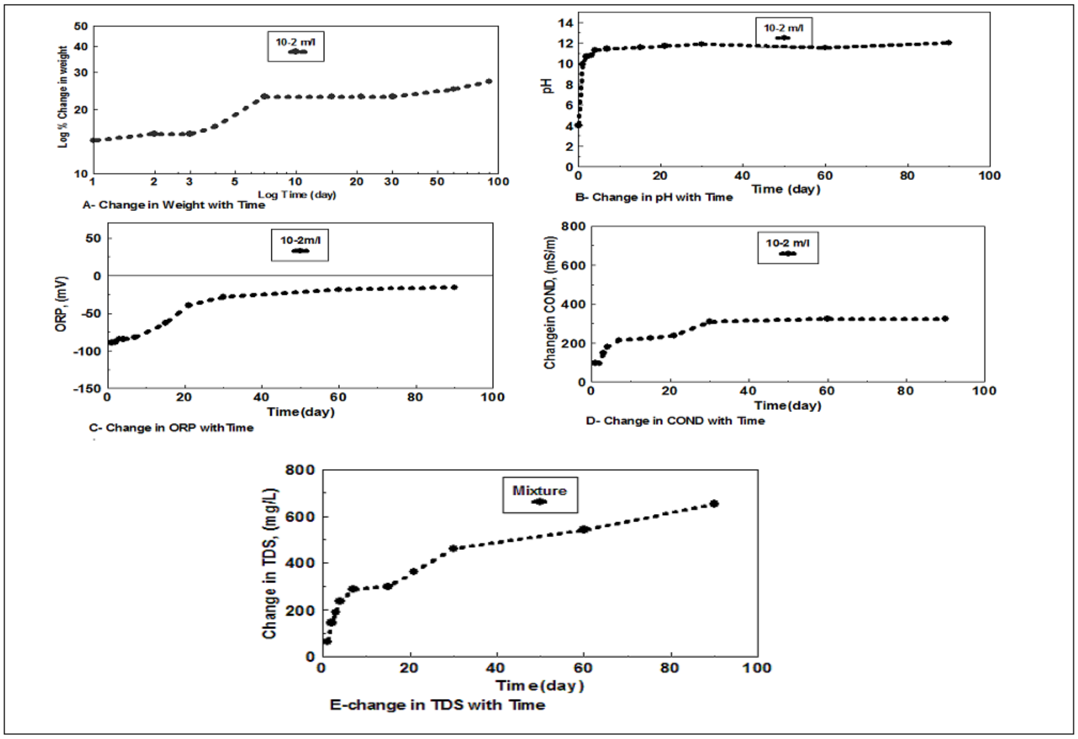

Fig 12: Effect of Leaching Process on Cement Blocks (W/C 0.5 and mixed with the three salts)

A- Change in Weight with Time, B- Change in pH with Time, C- Change in OPR with Time, and D and E- Change in COND and TDS with Time.

3.1.4. Chemical Analysis.

Table (2), lists the results of the chemical analysis of leachate from cement and sand clay after 21 days with different salts concentrations.

Table (2): Chemical Analysis of Salts in the Solution with Sand Clay and Cement Blocks.

Salt of	Initial Concentration (Con.) (mole/L) in Solution	Retained (Con.) in Soil (mole/L)	% (Con.) In Solution	Retained (Con.) in Cement (mole/L)	% (Con.) In Solution
Fe	4.6E-02	4.59E-02	0.001%	4.59E-02	0.001%
Sr	1.00E-02	5.421E-03	45.87%	7.49E-03	25.14%
Co	1.00E-02	9.99E-03	0.001%	9.99E-03	0.001%
Mixture					
Fe	4.6E-02	4.59E-02	0.001%	4.59E-02	0.001%
Sr	1.00E-02	8.63E-03	13.69%	8.66E-03	13.35%
Co	1.00E-02	9.983E-03	0.002%	1.0 E-02	0000

Understanding the long-term behavior of contaminants is of more importance in disposal site. The pervious results indicates that when water containing contaminants gets in contact with soil a part of the contaminants is retained by the soil and other part remains in the water. This phenomenon is quantified by the distribution coefficient (K_d).

The distribution coefficient (K_d) is the retention of salts on 1g of solid phase divided by the quantity of the same salt in 1 ml of liquid phase. K_d is an important parameter to understand the behavior of radionuclides in a media. It is difficult to take K_d values from literature (generic values). When this is the only alternative, it introduces a great deal of uncertainty. Therefore, the following experiments are used to determine the distribution coefficient of salts.

Fig (13) shows the retention of salts on soil and cement in case of the presence of a single salt in the solution and in case of using a mixture of salts. As shown, the retained concentration of salts on the soil and cement are similar in both cases of using a single or mixed salts except with Sr salt, which shows lower value on soil than that on cement (in case of a single salt). The comparison of the quantity retained of salts in case of a single and a mixture illustrates in Figure (14).

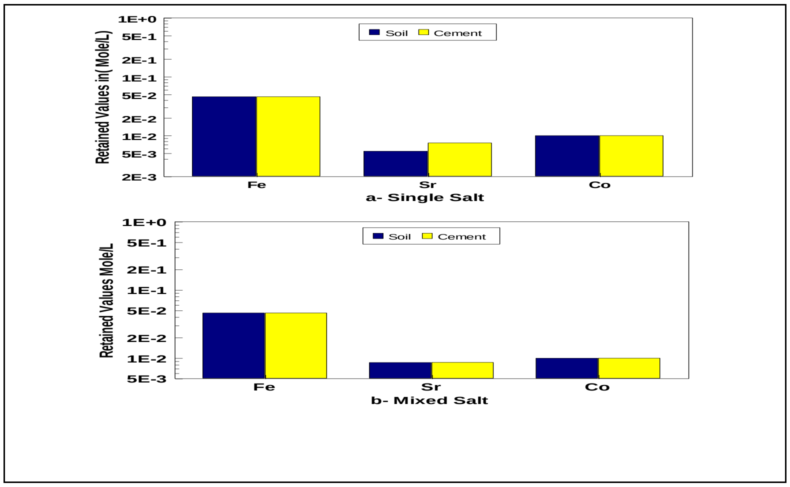

Fig 13: Comparison between the retention concentration of salts on the soil and cement.

a- Single Salt, b- Mixed Salt.

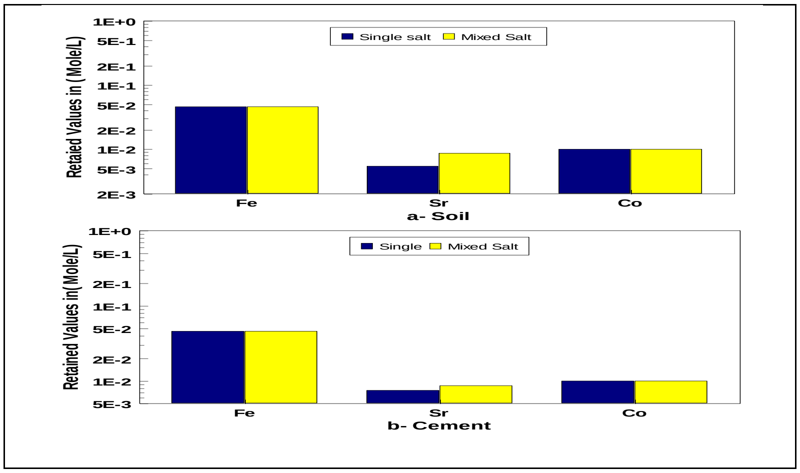

Fig 14: Comparison between the Retention concentration in case of single and mixed salt.

a- In Soil, b- In Cement.

4. CONCLUSIONS

Because all components of the disposal system are porous materials, the natural and engineered barriers are used to decrease the leakage of waste into the surrounding environment. The safety performance of disposal site is carried out through the safety assessment methodologies. Mathematical models and computer codes are the tools to evaluate the possible release rate of radionuclides from disposal site. Since the chemical reaction of radionuclides with different media of the disposal site the components of the system with the surrounding environment are not considering in these mathematical models. The results obtained are significantly different than the real behavior of radionuclides. Therefore, the current study focuses on the effect of chemical reactions between different media (waste, cement, and soil) in the disposal system by considering some parameters such as; pH, ORP, COND, and TDS.

XRD analysis indicates that the salts incorporated into the cement have a strong effect on the crystalline form. Additionally, SEM analyses provide very valuable insight onto the physical/chemical characterization of the microstructure and morphology of the solids. From the leaching processes, all cement blocks weight increase with time due to the absorption of water inside the pores and pH rises as a result of releasing Ca(OH)2 from cement blocks. Since the potential reduction depends on pH, an increase of ORP occurs with time for all cement blocks. Also both of the COND and TDS increase with time due to the release of inorganic elements from cement blocks. On the other hand, reactions of metals ions with soil are important in determining their effects on the environment. Accordingly, the results of soil reactions with leaching solution shows that the equilibrium of the reaction dependent on time and concentration of elements.

Finally, from experimental, the retention values of Fe and Co in case of single salt on soil have nearly the same values with cement. On the other hand, the retained quantity of Sr as a single salt is lower on soil than on cement. Meanwhile the retained values of mixed salts show nearly same values in both cases on soil and cement. Additionally, the value of distribution coefficient experimentally calculated is higher than the generic values. Except in the case of Sr, K_d is nearly the same value in both cases.

The chemical reaction occurring in the disposal site medium and the surrounding geosphere affects the migration behavior of radionuclide. The present study is considered as a first part to study some chemical indicators. Further studies will be followed.

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