# New trend for incorporation of cobalt and cesium radionuclides in natural and thermal activated bentonite cement blends

M. Abdel Geleel

National Centre for Nuclear Safety and Radiation control,
Atomic Energy Authority, Nasr City 11762, B.O Box 7551 Cairo, Egypt

mageleel2000@gmail.com

**Abstract:** The aim of this study is to provide regulatory bodies and the operators that generate and manage radioactive waste with some recommendations on how to meet the IAEA safety requirements for the solidification of radioactive waste. Safe management of radioactive waste includes treatment, solidification, storage and disposal. The incorporation of radioactive waste into Portland cement is the most widely used technique for its practical, technological and economical advantages. Bentonite had high adsorption capacity for cobalt and cesium but it decreases the compressive strength when incorporated into Portland cement. To improve the compressive strength and leaching behavior of final solid block, bentonite coated by acrylic acid and styrene before incorporation into Portland cement. The evaluation of mechanical integrity, chemical properties, radiation stability has been carried out under different experimental conditions. Bentonite additions to Portland cement in excess of approximately 15 wt. % causes significant decreases in the compressive strength of cemented waste form. Also, it is found that the best waste isolation, withought causing a loss in the mechanical strength, is obtained when the bentonite content in the cement is 10 wt% and it is reached to 25 wt.% by coated with acrylic acid and styrene. The compressive strength for Portland cement containing 10 wt. % T-bentonite was 67 MPa while T-bentonite coated by acrylic acid and styrene was 118 and 138 MPa respectively. Radiation dose to solidified cemented waste form in excess of 1.5 Mrad causes significant decreases in the mechanical stability, while at 1.5 Mrad the compressive strength increased to its maximum value. To assess the safety for disposal of radioactive waste-cement composition, the leaching of $^{60}Co$ and $^{137}Cs$ from a waste composite into a surrounding fluid has been studied. Leaching tests were carried out in accordance with a method recommended by the IAEA. [Nature and Science 2010;8(10):311-316]. (ISSN: 1545-0740).

**Key words:** Immobilization; Radioactive wastes; Portland cement; Bentonite; Mechanical properties.

## 1. Introduction

Each type of nuclear power plant is producing a nuclear waste stream of different salt concentration and composition. Therefore, cesium and cobalt salts are massively present in low and medium radioactive liquid wastes from pressurized water reactor. In order to prevent widespread dispersion of these radionuclides into the human environment, radioactive waste produced in nuclear facilities has been incorporated in several kinds of matrices(1-3). A significant number of works dealing with the immobilization of different radionuclides with cement and cement mixed with different additives have been carried out(4-10). In Egypt, radioactive liquid wastes are being immobilized in cement matrices, which must have adequate formulation to avoid the retarding effects that cesium and cobalt have on the hardening of ordinary Portland cement. Cement is porous, continuously hydrating material whose actual surface area greatly exceeds its geometric surface area. In leaching, the rate of dissolution varies as a function of phase chemistry and this dissolution exposes or enlarges pores; thus the leaching behavior must be related to pore structure and the composition of the pore solution. Although cement has several unfavorable characteristics as a solidifying material, i.e. low volume reduction and relatively high leachibility, it possesses many particle advantages: good mechanical characteristics, low cost, easy operation and radiation and thermal stability.

The objectives of immobilization of radioactive waste are to convert the waste into forms which are(11):

- Leaching resistant so that the release of radionuclides will be slow even though they may come into contact with flowing water;
- Mechanically, physically and chemically stable for handling, transport and disposal.

This paper is the continuation of the management process of radioactive liquid wastes that containing $^{60}Co$ and $^{137}Cs$. The previous work focus onto fixation of $^{60}Co$ and $^{137}Cs$ on natural and thermal activated bentonite.

## 2. Experiment

The cement used for incorporating bentonite loaded by Co-60 and Cs-137 radioactive waste was ordinary Portland cement (OPC) from National Cement Company at Helwan, Helwan, Egypt. Different matrices were prepared by mixing modified and activated clay with cement at a ratio ranging from 5 to 25 wt. % until homogenous paste is obtained. These mixture were prepared at water/cement ratio (w/c) 0.35 to determine the mechanical and chemical characteristics of these matrices. Specimens were cast in 5 cm diameter cylindrical polyethylene vials and 5 cm length. The vials were then capped to prevent evaporative water loss. Specimens were compression tested after curing for at least 60 days.

### 2.1. Compressive strength

Compressive strength testing was conducted as a measure of mechanical integrity. The compressive strength of ordinary Portland cement waste forms were tested in accordance with the ASTM method C 39-72, "Test for the compressive Strength of Cylindrial Concrete Specimens" (American Socity for Testing and Materials, C39-72 1975).

### 2.2 Leaching behavior

The leaching characteristics, which refer to the release of radionuclides from the solidified waste forms to aqueous environment, were reported using different percent of modified activated bentonite added to Ordinary Portland cement. Radioactive wastes containing Co-60 and Cs-137 were incorporated into different modified clay/cement ratios. Leaching experiments were carried out following Hesp's leaching test[12].

$(\sum a_n / A_o) / (F/V)$ versus square root of the total leachant renewal period $\sqrt{t_n}$

Where:

$a_n$ = radioactivity leached during the leachant renewal period n.

$A_o$ = radioactivity initially present in the specimen.

F = exposed surface area of the specimen ($cm^2$).

V = volume of the specimen ($cm^3$).

$T_n$ = duration (days) of the leachant renewal period.

Samples were suspended in a way that the whole surface area was exposed to the leaching solution. Ground water as leachant was obtained from Abu-Zaable well No. 202, which is one of the nearst grounds well to the suggested disposal site. The chemical analysis of the ground water is shown in table (1)[13].

**Table (1) Chemical analysis of ground water well No.202[13].**

| TDS* (mg/l) | pH | Soluble cations (ppm) | | | Soluble anions (ppm) | | | |
|---|---|---|---|---|---|---|---|---|
| | | $K^+$ | $Na^+$ | $Mg^+$ | $Ca^{++}$ | $Cl^-$ | $SO_4^-$ | $HCO_3^-$ |
| 1.05 | 7.2 | 23 | 149 | 13 | 74 | 137 | 317 | 272 |

***Total Dissolves Salts**

## 3. Result and Discussions

### 3.1. Compressive strength

Mechanical integrity of waste forms is an important consideration in the safe handling and transportation of radioactive waste prior to disposal. Waste form failure under load may result in cracking or friability leading to possible dispersion of activity. Waste form failure creates a larger effective surface area from which activity can be leached. Therefore, mechanical properties of waste forms are of concern within the disposal environment[14].

#### 3.1.1. Natural and thermal bentonite additive

The effect of different weight percent of natural and thermal bentonite on the compressive strength at different curing time are represented in Figures 1,2. These figure shows that the compressive strength depending on the weight percent of natural and thermal bentonite added to OPC. The compressive strength decreases from 67.4 MPa to 13.8 MPa and from 73.2 MPa to 32.3 MPa by increasing the weight percent of natural and thermal bentonite from 5 wt.% to 25 wt.%, respectively. This result could be attributed to the increase in the alkali metal concentrations in the prepared mixture at the expense of aluminosilicates, which could affect the whole integrity of the pastes[15]. On the other hand, the compressive strength increases with increasing setting time till t reached to certain time (28 days) it levels off.

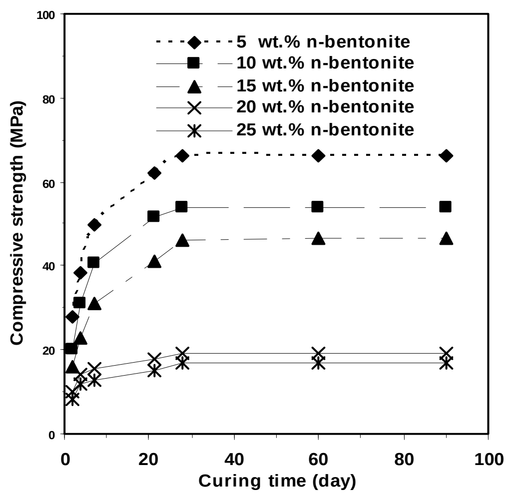


**Fig. (1) Effect of compressive strength on the curing time for different ratio of n-bentonite**

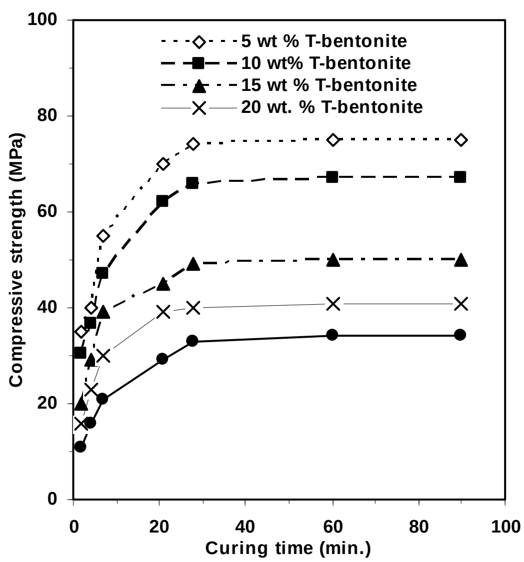


**Fig.(2) Effect of compressive strength on the curing time for different ratio of T-bentonite**

### 3.1.2. Effect of polymer coating

The effect of different weight percent of bentonite coated by acrylic acid and styrene on the compressive strength was examined and the obtained results are given in Figures 3,4. From these figures it is clear that the compressive strength increases from 73.5 MPa ( 5 wt.% T-bentonite without coating) to 128.7 and 149.2 MPa when it is coated by styrene and acrylic acid, respectively. On the other hand, when 5 wt.% n-bentonite coated by styrene and acrylic acid the compressive strength increases from 62.2 MPa (5 wt.% n-bentonite without coating) to 98.4 MPa and 131.1 MPa when it is coated with styrene and acrylicacid.

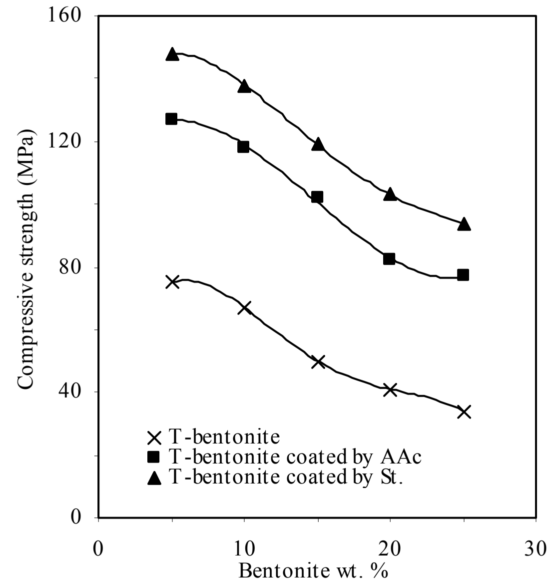


Fig.(3) Effect of weight percent on the compressive strength on T-bentonite coated by acrylic acid (AAc) and styrene (St).

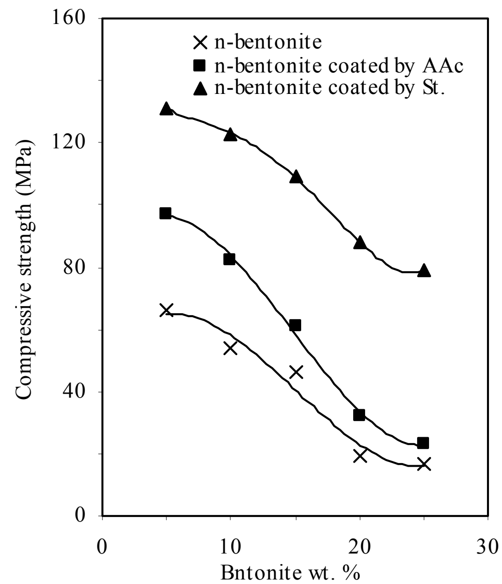


Fig.(4) Effect of weight percent on the compressive strength on n-bentonite coated by acrylic acid (AAc) and styrene (St).

### 3.1.3. Gamma Radiation dose

Ordinary Portland Cement is often used as a solidifying agent for radioactive wastes. One factor that needs to be assessed is the resistance of OPC to radiation that may be cause losses in mechanical strength. Gamma radiation from radioactive wastes is especially important because of its ability to deeply penetrate and degrade materials. The effect of gamma irradiation dose to the compressive strength of T-bentonite and n-bentonte is represented in figure 5. The compressive strength increases from 80.8 MPa to 86.7 MPa (in case of T-bentonite) and from 71.2 MPa to 77.8 MPa (in case of n-bentonite) with increasing the radiation dose from 1 to 1.5 Mrad then it is sharply decrease when exposed to irradiation dose more than 1.5 Mrad. This may be due to the deeply penetrate and degrade materials of OPC.

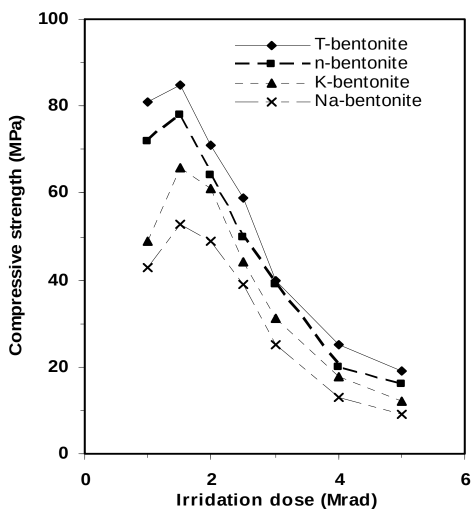


Fig. (5). Effect of irriadiation dose on the compressive strength of bentonite; 5 % wt. bentonite; 28 dayes curing time

### 3.2. Leaching behavior of Cs-137 and Co-60 radionuclides

The shallow land burial waste forms contain fairly high concentrations of short-lived radionuclides and very low concentrations of long-lived radionuclides. Various radionuclides and salts make chemical bondage with cement components, or they exist dispersively in the state of sole crystals in concrete[15]. When the cemented waste forms come in contact with water, the transfer of soluble materials from the waste to the surrounding water is caused by dissolution or chemical reaction with chemical components of water. In this study, the radionuclides chosen for the leach test are intended to represent the desorption (leaching) behavior of some of the typical radionuclides encountered in low-level solid waste forms. The variations of the cumulative leach fractions of $^{137}$Cs and $^{60}$Co radionuclides incorporated into natural and thermal bentonite coated by acrylic acid and styrene and mixed with OPC are depicted in Fig. 6-9. From these figures it is clear that; the leaching curves obtained have two distinct parts. The initial part shows a high leach rate and the second final part shows a low leach rate. The initially high release may be attributed to the surface activities which are easily washed when the sample comes in contact with leachant. On the other hand, the results showed that, the coating with acrylic acid and styrene decreased the leaching rate of both cesium and cobalt and this may be due to the acrylic acid and styrene are capable to reduce the volume of large pores and capillaries found in cement pastes. The magnitude of the cumulative leach fraction is an index for the release of the nuclide for the cement matrix. In both studied cases have highest values of cumulative leach fraction than cobalt radionuclides. The cumulative leach fractions are in the following order:

Bentonite > Bentonite coated with styrene > Bentonite coated with acrylic acid

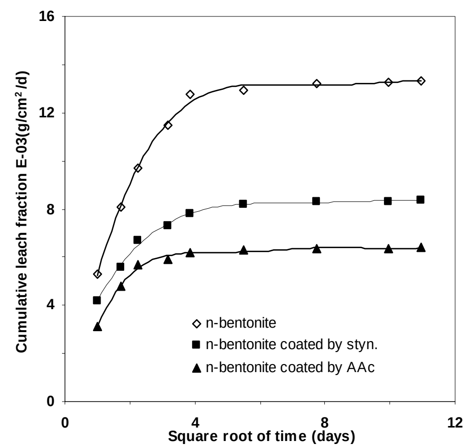


**Fig.6 Cumulative leach fraction of Cs- 137 versus square root of time in days in under ground water using n-bentonite, n-bentonite coated by styrene and n-bentonite coated by acrylic acid**

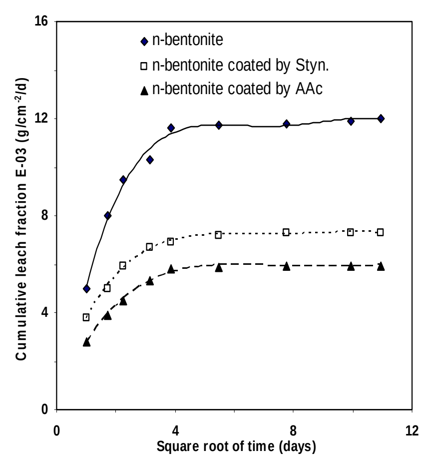


**Fig.7. Cumulative leach fraction of C0-60 versus square root of time in days in under ground water using n-bentonite, n-bentonite coated by styrene and n-bentonite coated by acrylic acid.**

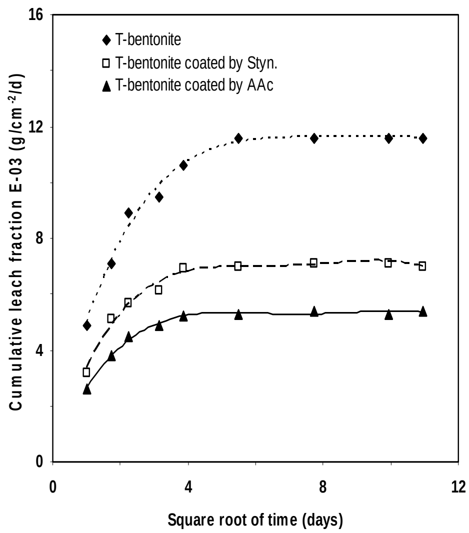


Fig.8. Cumulative leach fraction of Cs-137 versus square root of time in days in under ground water using T- bentonite, T-bentonite coated by styrene and T-bentonite coated by acrylic acid.

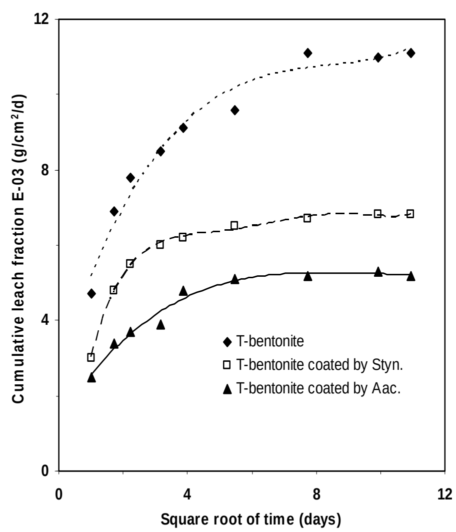


Fig.9. Cumulative leach fraction of Co-60 versus square root of time in days in under ground water using T-bentonite, T-bentonite coated by styrene and T-bentonite coated by acrylic acid.

## 4. Conclusion

The fixation of cesium and cobalt radionuclides on natural and thermal bentonite coated by acrylic acid and styrene then immobilized into OPC was investigated. The results showed that the best waste isolation, withought causing a loss in the mechanical strength, is obtained when the bentonite content in the cement is 10 wt.% and it is reached to 25 wt.% by coated with acrylic acid and styrene. The compressive strength for Portland cement containing 10 wt. % T-bentonite was 67 MPa while T-bentonite coated by acrylic acid and styrene was 118 and 138 MPa. The leachability test shows that the coating with acrylic acid and styrene decreased the leaching rate of both cesium and cobalt and this may be due to the acrylic acid and styrene are capable to reduce the volume of large pores and capillaries found in cement pastes.

## 5. Recommendation

From this study we can recommended that:

- Natural bentonite and thermal bentonite has high adsorption capacity for cobalt and cesium, thus we recommend use it instead of resin because resin have some problems when mixing with cement.
- In case of uses bentonite it should be coated with acrylic acid and styrene before immobilization into OPS to avoid the decreasing in the compressive strength.
- The leaching values are lower than bentonite without coating at the same time these values lower than safety requirement.

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