International Conference on HAZARDOUS WASTE : Sources, Effects and Management
12-16 December 1998, Cairo-Egypt

EG0000181

SD-11

Studies Involving Immobilization Of Hazardous Wastes In Cement –Ilmenite Matrix

By
A.M.El-Dakrory , M.S.Sayed and K. Adham
Hot Laboratories Center, Atomic Energy Authority
Cairo, Egypt.

ABSTRACT

Ilmenite was added to Ordinary Portland Cement to modify the characterisic properties of the matrix as density, compressive strength and thermal stability. Coal tar and radiocesium were solidified as hazardous wastes in cement-ilmenite matrix. The physical properties as density, sitting times and porosity were studied. The mechanical properties as compressive strength values and the chemical properties as leaching were measured.

Key Words: Cement, Ilmenite, Industrial waste, Coal tar, radioactive waste, Leaching properties, Economic studies.

INTRODUCTION

Cement is the material, which has the adhesive and cohesive properties necessary to bond the aggregates into a solid mass of adequate strength and durability. Ilmenite used in this work was taken from Abu Ghalaga mines in the Estern Desert of the ARE. Ilmenite has a specific gravity value of 4.694 $g.cm^{-3}$. Addition of illmenite to cement modifies the studied physical and mechanical properties of the used cement [(1)]. The wastes coal tar and radioactive cesium were fixed in cement –ilmenite matrix. Coal tar was a waste product, which obtained during manufacturing of the cocking industry. Coal tar usually contains much solid matter [(2)]. Coal tar contains less phenol, naphthalene and toluene insoluble matter [(3)]. Cs^{137} was used as example of radioactive waste, which may arise from many parts of nuclear fuel cycle and from the application of radioactive isotopes.

EXPERIMENTAL

Ordinary Portland cement was provided from Helwan Portland Cement Company, Cairo, Egypt. The composition percent of the used Portland cement was given in Table 1.

Table 1: The chemical composition of ordinary Portland cement

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3
61.0	21.0	4.74	4.00	2.50	0.60	2.43

Illmenite was provided from El-Nasr Phosphate Company, Cairo, Egypt. The chemical analysis is given in Table 2.

Table2: The chemical composition of ilmenite.

SiO_2	Al_2O_3	MgO	K_2O+Na_2O	TiO_2	Fe_2O_3	FeO	S	P
4.00	1.07	2.00	0.25	37.0	27.00	26.00	0.20	0.02

Coal tar is the waste generated in the production of Coke from El-Nasr Company for Coke and Chemicals. The chemical analysis is given in Table 3.

Table 3: The chemical analysis of coal tar.

Item	Daily rat(ton)	Composition of the waste	%
Coal tar deposits	10	-heavy tar content	20-30%
		-Insoluble matter in toluene	50-60%
		- ash content	7%
		-water content	7%
		-Ammonium salt	4%

^{137}Cs were used in the leaching experiments. The ground water used in the leaching experiments was obtained from Abu-Zaabal well (No.202) which is one of the nearest ground water well to Inshas nuclear site where the storage and disposal facilities for radioactive wastes are under construction. The chemical analysis of the ground water is given in Table 4.

Table 4: The chemical composition of the ground water.

T.D.S. (ppm)	pH	Soluble cations (ppm)				Soluble anions(ppm)		
1050	7.2	K^+	Na^+	Mg^+	Ca^+	Cl^-	SO_4^-	HCO_3^-
		23	149	13	74	137	317	272

EQUIPMENTS

-Thermogravimetric analysis system, TGA was used for all the samples. The analysis were carried out in nitrogen gas as inert atmosphere to prevent oxidation of the phenolic compounds. Heating of the sample from room temperature up to 800°C with heating rate 10°C/min was take place.

-Gamma spectrometer was used to measure the gamma energy emitted from ^{137}Cs used in the leaching experiments. The gamma spectrometer used has 2"x2" sodium iodide crystal activated with thalium. The multichannel analyzer used has 256 channels used for the gamma measurements of different radioactive ions.

-The mixer used has different speeds high and low to facilitate the complete mixing of the matrix material. The removable mixing bowl has a capacity of 4 liters.

-Vicat apparatus with different needles was used to determine some of the physical properties as sitting times of the studied samples.

-Load compression machine was used to study the compressive strength tests. It has a rigid frame assembly with type Wykeham France Eng. Model WF.

PREPARATION

The samples were prepared in the form of cubes of dimensions 7x7x7 cm^3 to study the compressive strength tests. Cubes of dimensions 2x2x2 cm^3 were prepared to study the leaching of the radiocesium from the matrix. Cylinders of 5 cm diameter and 1 cm height were prepared to study radiation sheild experiments of the studied matrix. The gamma rays emitted from 1.0 µCi cesium as a standard source which emites gamma energies at 662 Kev ($t_{½}$ =30.7 year). For the measurements of the linear absorption coefficient, the following relation was used:

$$A=A_0e^{-\mu x}$$

Where:

X = the thickness of the sample in cm,

A_o = the activities of gamma source before the sample,

A = the activities of gamma source after the sample,

μ = the linear gamma absorption coefficient, cm^{-1}.

The specimen thickness was increased in gradual steps towards the source. The linear absorption coefficient was determined from the slope of the semi-logarithm of the activity against thickness.

RESULTS AND DISCUSSIONS

Ilmenite was added to Ordinary Portland Cement to modify its charachteristic property and forming a heavy concrete matrix suitable for long term disposal of the radioactive waste [1]. Cement-15% ilmenite was used as a solid material in all the experiments. Coal tar was added with different percentages to the solidified matrix and Table 5 gives the changes of the physical properties by adding different percentages of coal tar.

Table 5:The physical properties of cement-15% ilmenite at different coal tar percents

Coal tar%	ρ (g/cm^3)	A%	P%	T_1(min)	T_2(min)
0	2.90	9.50	17	60	210
5	3.00	9.20	16	75	200
10	3.20	8.70	15	105	245
15	3.30	8.30	14	125	270

From this Table, it is observed that as the coal tar percentage increases the density value increase due to the coating of the cement particles by an oily layer which blocks the voids in cement and hence, increasing the density values. In the same time decreasing the absorption percent and porosity percent have been resulted. For the initial and final sitting times, it was observed that as the coal tar percentage increases the sitting times increase due to the coating of the cement-15% ilmenite particles with the oily layer from coal tar decreasing the contact between cement and water delaying the sitting times.

The compressive strength of all the samples were measured after 28 days to get certain accidental stress during the handling, storage or transportation for the final disposal Fig.(1).

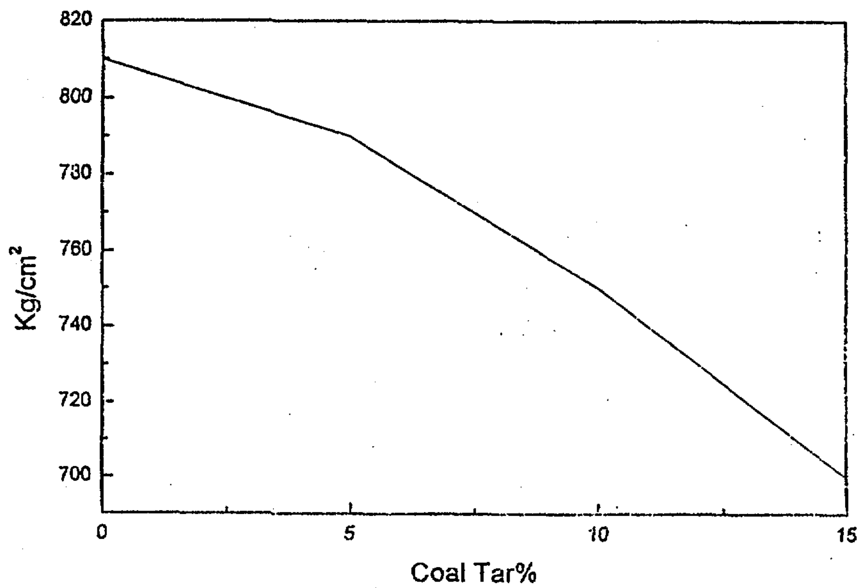

Fig. 1: Variation of the compressive strength values at different coal tar percentages.

From this Figure it is observed that as the coal tar percent increase the compressive strength value decreased. This can be explained by the coal tar coating of cement particles by an oily film which reduces the contact between cement and water particles leading to a decrease in the formation of gel and $Ca(OH)_2$. This consequently, reduces the bonding between the cement particles.

Fig. 2 determines the linear gamma absorption coefficient factor for cement-15% ilmenite at different percentages of coal tar. It is clear that the linear absorption coefficient (μ) increases as the coal tar content increases due to increasing the density values of the matrix material [4].

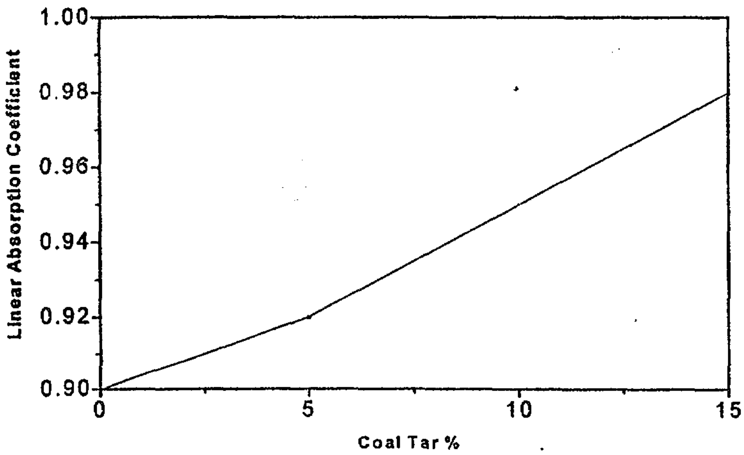

Fig.2: Variation of linear absorption coefficient with cement-15% Ilmenite at different coal tar percents.

Thermogravimetric analysis (TGA) for cement-15% ilmenite at different coal tar percentages was performed in Table 6. The samples were heated from room temperature up to 800°C in nitrogen atmosphere.

Table 6: Thermogravimetric analysis (TGA) of cement-15% ilmenite at different coal tar percentages

CT%	Weight loss %
0	7.074
5	7.583
10	8.241
15	8.924

The general behavior of the weight loss values were characterized by three zones according to the published cement hydration [5]

-The first zone was due to the release of water of hydration in the range from 30°C up to 120°C. This zone was rapid and with weight loss range about 0.9 mg.

-The second zone was ranged between 120°C and 400°C. This range was due to the degradation of the coal tar content. It is observed that as the coal tar percentage increases the weight loss value increases.

-The third zone was ranged from 400°C up to 800°C. This zone was characterized by an enhanced weight loss again according to the thermal reaction of coal tar at this high temperature. It was observed that at coal tar percentages more than 15% a sharp increase in the weight loss values was observed.

Incorporation of radioactive wastes into an inert matrix and lowering the release of this waste to the environment were the main object of this work. Leaching properties of radioactive cesium from cement-15% ilmenite at different coal tar percent were studied according to Hespe's method [6]. The whole area of the cubic samples was exposed to the leachant solution. The ground water from Abu-Zaabal well (No-202) was used as leachant solution. The results were expressed by plotting the cumulative leach fraction $[(\Sigma a_n/A_o)/(F/V)]$ versus the total leaching time(Σt_n) where:

A_o = Radioactivity initially in specimen,
F = Exposed surface area of the specimen,
V = Volume of the specimen (cm^3),
t_n = Duration in hours of leaching at renewal period n,
a_n = Radioactivity leached during the leaching process at renewal period.

Fig. 3 shows the leachability results of cement-15% ilmenite at different coal tar percentages. It is clear from this curve that all leaching results obtained show two distinct parts. An initial first part shows a high leach rate due to the surface contamination. The second part shows a slow diffusion process of the radiocesium up to 300 hours. The results of ^{137}Cs leaching from cement-15% ilmenite at different coal tar percentages show a decrease in the leaching factor as the coal tar percentage increases. This can be attributed to the blocking of the pores by a viscous coal tar, which hinders the access of the leaching water to the interior of the cement-15% ilmenite.

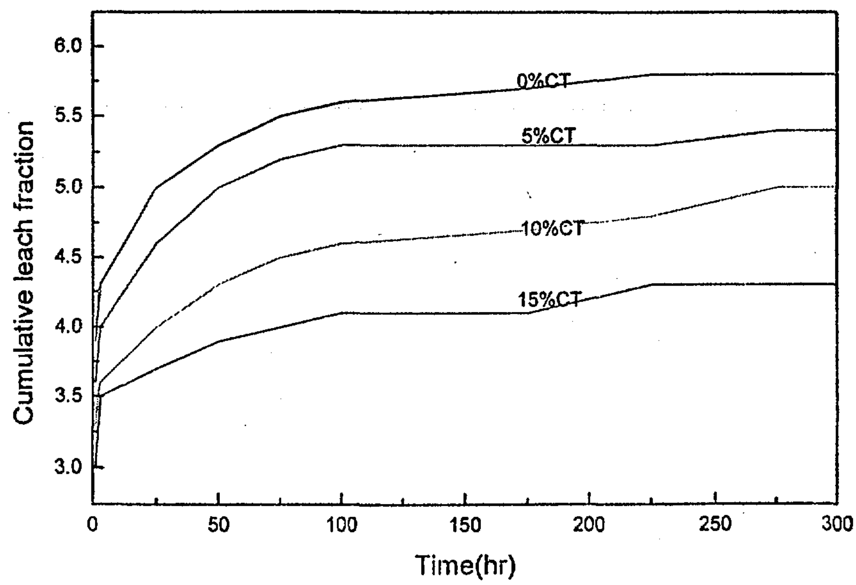

Fig. 3: Variation of cumulative leach fraction for ^{137}Cs versus total leaching time for cement-15% illmenite at different coal tar percentages.

Economic expense is the most important factor affecting the application of coal tar additives to cement-ilmenite in waste treatment

A cumulative table for the different characteristics of cement, cement-ilmenite and cement ilmenite at different coal tar percentages was given at Table 7.

Table 7: Cumulative Table for the different characteristics of cement, cement-illmenite and cement –illmenite at different coal tar percentages

Type	C	C-Il	5%CT	10%CT	15%CT
Density gm.cm^{-3}	1.95	2.90	3.00	3.20	3.30
Water absorption percent	13.4	9.5	9.2	8.7	8.3
Porosity percent	26	17	16	15	14
Compressive strength after 28 days Kg/cm^2	660	800	780	750	700
Cumulative leach fraction	10.8	5.10	5.5	5	4.9
Linear gamma absorption coefficient (μ cm^{-1}) for ^{137}Cs	0.72	0.92	0.93	0.95	0.98
Cost	252	227	218	210	200

In fact from the results above, one can conclude that the addition of 15% coal tar to ordinary portland cement in presence of 15% ilmenite affects the characteristic properties of the final solidified waste form toward the safety requirements, sufficient high density, suitable compressive strength and low leachability. So we recommended to solidify the coal tar in presence of radioactive wastes in cement-15%ilmenite as a matrix material for long term disposal.

REFERENCE

1- A.M. El-Dakrory "Assessment of some Additives to Cement Used for Radioactive Waste Immobilization" Ph.D. in Chemical engineering work, Faculty of Engineering –Cairo, Egypt, (1998).

2- V.E. Privalov and M.A. Stepanenko "State and improvement trends in coal tar processing" (Ukhin), Koks I Khimiya, no. 2, pp. 51-55, (1976)

3- N.S. Kipot and E.Ya. Stetsenko "Phenolic production in Ukranian carbonization plants", (Ukhin), Koks I Khimiya, no.5, pp. 31-34,(1976).

4- ASTM "Standard specification for aggregates for radiation shielding concrete", C- 637, (1992).

5- E.T. Stepkowska "Thermal mass changes of Portland Cement and Slag cement after water absorption" journal of thermal analysis, Vol. 42, pp.41-65, (1994).

6- E.D. Hespe's "International Atomic Energy Agency", Atomic Energy Review, Vol.9 (1), pp. 195. Vienna (1971).