LEACHING BEHAVIOUR OF WASTE FORM RESULTED BY RADIOACTIVE MAGNETITE EMBEDDING IN CEMENT BASED MATRICES

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Abstract

The management of contaminated magnetite is a very important problem both due to the presence of a large number of radionuclides, alpha and gamma emitters, as well as the quantity in which it is produced during the operation of a CANDU reactor but also the quantity found during decommissioning. In order to determine the behaviour of the final conditioned product, during disposal, immobilization experiments in cement of radioactive magnetite (containing ^{60}Co, ^{137}Cs, ^{152}Eu and ^{241}Am) have been performed. The obtained conditioned products were subjected to leaching tests for 400 days. It was found the global leaching rates for ^{137}Cs is within 4.37 and 6.6x10^{-4} cm/day, for ^{60}Co of 10^{-5} and 10^{-6} magnitude. No losses of ^{152}Eu and ^{241}Am have been found.

Keywords: *Radioactive magnetite, Conditioning, Cement matrix, Leaching tests*

Introduction

Magnetite (Fe_3O_4) is one of the most common corrosion product formed in the entire secondary circuit from CANDU type nuclear power plants (NPP), during the normal operation of the steam generator. The corrosion products are continuously transported to the generator.

In order to improve the heat transfer factor and to reduce the overall power production it is necessary to remove the magnetite deposits. For example, in some CANDU NPPs, as Cernavoda NPP, the magnetite removal from steam generators lead to an increase by 1.5-2% in productivity comparatively with the forecasted production level when this action is not done.

The magnetite deposits contains radionuclides and according to the results of the experimental tests for the verification of the radiological characterization methods [1] on real samples from Cernavoda NPP, the main radionuclides present in the contaminated magnetite are the following: ^{60}Co, ^{54}Mn, ^{94x}Nb, ^{125}Sb, ^{137}Cs, ^{239}Pu / ^{240}Pu, ^{238}Pu, ^{241}Am, ^{243}Cm/ ^{244}Cm; in very small quantities, are also present: ^{242}Cm, ^{95x}Nb, ^{51}Cr, ^{95}Zr, ^{113}Sn, ^{238}U, ^{235}U, ^{233}U / ^{234}U).

Accordingly, the contaminated magnetite management becomes a very important problem both due to the presence of a large number of radionuclides, alpha and gamma emitters, as well as to the quantity in which they are produced but also to the quantity found during decommissioning.

To select a conditioning method for radioactive magnetite, some experiments for conditioning magnetite in cement based matrix have been performed. The conditioned products have been tested by performing leaching tests aimed to obtain data regarding the leaching of radionuclides from the conditioning matrix and the behaviour of the product, if it comes in contact with water during the storage period. The results give us indications if the conditioned waste block corresponds to the requirements imposed for final storage.

In this paper, data regarding leaching behaviour of waste form resulted by radioactive magnetite embedding in cement are presented.

Radioactive magnetite embedding in cement matrix experiments

For conditioning the radioactive magnetite in cement matrix seven experiments [2] were performed. In these experiments, simulated radioactive magnetite (loaded with solution containing radionuclides of interest) with the following composition was used:
^{60}Co = 49.13 Bq/ml; ^{137}Cs = 86.24 Bq/ml;
^{152}Eu = 65.37 Bq/ml; ^{241}Am = 90.12 Bq/ml.

After the contacting period, loaded magnetite has been filtered, and, using the gamma spectrometry to determine the remained activity in the magnetite, the elutes were measured.

The radionuclides activities in contaminated magnetite used in experiments were determined as follows:
^{60}Co = 2.382x10^4 Bq/kg; ^{137}Cs = 3.557x10^4 Bq/kg;
^{152}Eu = 3.228 x10^4 Bq/kg; ^{241}Am = 4.501 x10^4 Bq/kg.

The magnetite, corresponding to the chosen embedding ratio, was added to the cement paste (Portland type 42.5R), in portions, and under continuous mixing; the recipes are presented in Table 1.

Table 1. Recipes for embedding radioactive magnetite in cement

Sample. No	Magnetite		Cement-water mixture			Total sample mass (magnetite + cement paste)	Embedding ratio of dry magnetite / cement
	Wet magnetite [g]	Dry magnetite [g]	Cement [g]	Water [g]	Cement paste mass used theoretically [g]	[g]	[%]
0 *	0	0	150.92	60.45	211.37	211.37	0
0d *	-	0	149.23	59.77	209.00	209.00	0
1	13.36	9.49	139.90	56.04	195.94	209.30	4.53
2	19.74	14.02	135.80	54.40	190.20	209.94	6.68
3	27.79	19.73	130.33	52.20	182.53	210.32	9.38
4	35.70	25.35	126.09	50.51	176.60	212.30	11.94
5	40.38	28.67	121.29	48.58	169.87	210.25	13.64
0c *	0	0	150.92	60.45	211.37	211.37	0
6	13.76	9.77	139.64	55.93	195.57	209.33	4.67
7	49.83	35.38	113.58	45.49	159.07	208.90	16.94

* samples 0 represents blank tests

Long-term leaching tests of cemented radioactive magnetite

The leaching tests have been started in 2019 [3]. The cement-radioactive magnetite mixture was poured into special metallic moulds. After drying and removal from mould, it was left for 30 days in wet atmosphere; the samples have been immersed in distilled water to be subjected to the leaching test. The testing temperature was the ambient temperature.

The main characteristics of the obtained samples are presented in Table 2.

Table 2. Characteristics of cement-radioactive magnetite samples subjected to the leaching test

Sample no.	Sample mass after 24 h decaf	Sample mass after 30 days removing from moulds	Dimensions h / l / L			Sample volume	Surface exposed	Incorporated radionuclides [Bq/sample]			
	[cm^3]	[cm^2]	[cm^3]			[cm^2]	[cm^3]	^{137}Cs	^{60}Co	^{152}Eu	^{241}Am
0 d *	188	105.6	3.3	4	8	143.20	500	0	0	0	0
1	184	96	3	4	8	136.00	500	475.23	318.30	431.26	601.37
2	184	92.8	2.9	4	8	133.60	500	702.18	470.30	637.2	888.55
3	192	99.2	3.1	4	8	138.40	500	988.53	662.09	897.05	1250.9
4	192	99.2	3.1	4	8	138.40	500	1269.9	850.55	1152.4	1606.9
5	185	105.6	3.3	4	8	143.20	500	1436.4	962.05	1303.4	1817.6
0 c *	193	107.5	4.3	5	5	136.00	500	0	0	0	0
6	192	102.5	4.1	5	5	132.00	500	489.46	327.83	444.17	619.37
7	194	97.5	3.9	5	5	128.00	500	1772.5	1187.2	1608.5	2243

* samples 0 represents blank tests

During the leaching period, the leaching waters have been analysed, the following parameters being of interest: radionuclides activity in leaching medium, pH and conductivity values and mass of the cement-radioactive magnetite products. Measurements have been performed in the 4th, 11th, 19th, 45th, 110th, 165th, 250th, 350th and 400th day, respectively.

Results and Discussions

As a visual observation, even after 400 leaching days, the samples are presented in form of hard blocks similar to the classic concrete, with small pores homogenous distributed.

The results of the measurements are presented in Tables 3 and 4, and also in Figs.1 and 2.

It can be noticed, in the first part of the leaching test, an increase of the conductivity values, and from the 110th day, a decrease of the values begun, such as in the 400th day values became ten times less than at the test starting. It is as well observed that the conductivity of the products containing magnetite, follow, in all cases and during the complete leaching period, the trajectory of the blank samples values (with no magnetite content).

The pH values are within the basic domain. Compared to the slightly fluctuating values of the conductivity, the pH variations are very low during the leaching period, for all samples, with values within a very narrow range. After the 110th day a higher decrease occurs, as expected considering a much longer period for almost 300 days. Despite all, the differences, even small, remain in the domain 11.5 -12.5, excepting the samples 3, 4 and 5 where the pH reaches 9 - 9.5.

Table 3. The conductivities [mS/cm] of the leaching waters of the cement-magnetite samples

Sample no.	day 1**	day 4	day 11	day 19	day 45	day 110	day 165	day 250	day 350	day 400
0 d *	0.01274	7.92	8.54	8.80	8.13	2.05	1.44	1.09	0.96	0.959
1	0.01274	4.14	8.26	9.18	8.33	1.85	0.89	1.03	2.21	2.140
2	0.01274	5.85	8.98	9.16	8.94	0.64	1.01	1.12	1.95	1.495
3	0.01274	7.79	8.45	8.97	7.59	0.59	0.50	0.62	0.78	0.810
4	0.01274	5.34	8.41	9.33	8.48	0.76	0.92	0.69	0.87	0.893
5	0.01274	3.51	8.44	9.55	9.19	0.83	0.79	0.67	0.86	0.887
0 c *	0.01274	6.80	8.28	8.96	8.27	0.55	0.48	0.63	0.83	0.886
6	0.01274	4.45	8.40	8.66	6.81	1.74	1.22	1.12	1.95	1.429
7	0.01274	4.14	8.32	8.63	6.84	1.43	1.06	1.24	1.74	1.628

* samples 0 represents blank tests; ** the conductivity of distilled water used for leaching tests

Table 4. pH of the leaching waters of cement-magnetite samples

Sample no.	day 1**	day 4	day 11	day 19	day 45	day 110	day 165	day 250	day 350	day 400
0 d *	5.94	12.50	12.53	12.51	12.43	11.86	11.69	11.55	10.54	9.34
1	5.94	12.25	12.46	12.56	12.41	11.84	11.42	11.46	11.92	11.91
2	5.94	12.40	12.44	12.57	12.43	11.16	11.51	11.57	11.84	11.73
3	5.94	12.51	12.37	12.57	12.34	11.07	9.28	9.05	9.47	9.22
4	5.94	12.26	12.40	12.57	12.41	11.26	11.42	9.95	9.22	9.13
5	5.94	12.11	12.40	12.56	12.36	11.34	11.23	9.20	9.54	9.18
0 c *	5.94	12.39	12.36	12.51	12.35	10.66	8.91	9.06	9.13	9.15
6	5.94	12.23	12.38	12.48	12.27	11.63	11.61	11.59	11.87	11.67
7	5.94	12.21	12.42	12.50	12.30	11.60	11.52	11.60	11.75	11.72

* samples 0 represents blank tests; ** pH of distilled water used for leaching tests

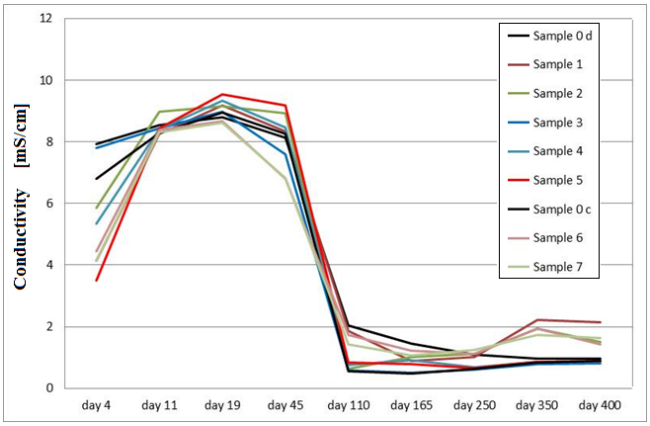


Fig.1. Variation of conductivities [mS/cm] of the leaching waters

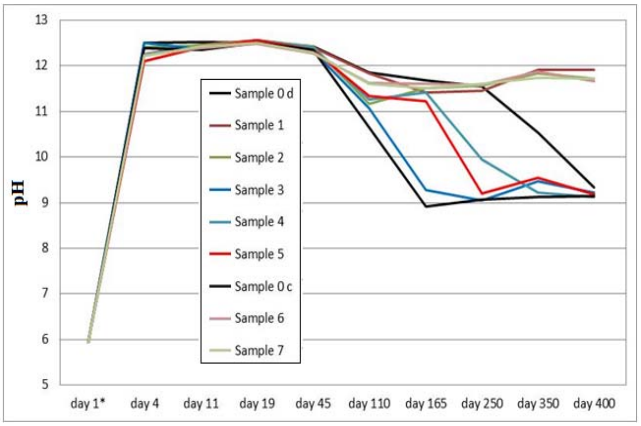


Fig.2. Variation of pH of the leaching waters

Leaching rates of ^{137}Cs, ^{60}Co, ^{152}Eu, ^{241}Am

Radionuclide losses in the leaching medium have been measured by gamma spectrometry.

The results of the leaching tests were calculated in the form of the leaching rate (R) which represents the mass or activity of an element extracted by the leaching water from the sample of the mass m_p in the time unit (days) and on the surface unit (cm^2) (see the equation below).

$$R = \frac{A_x}{A_0} \times \frac{m_p}{S \cdot t} \quad [g/cm^2\,day]$$

where:
A_x - X isotope activity extracted during time t [g]
A_0 - Initial activity of the X isotope in sample [g]
m_p - mass of the sample [g]
S - surface exposed to leaching [cm^2]
t - leaching time [days]
V_p - sample volume [cm^3]

Table 5 presents the values which characterize the loss of activity for the samples of cement-radioactive magnetite in leaching waters, and the leaching rates of radionuclides.

Table 5. ^{137}Cs losses from cement-radioactive magnetite products in leaching waters; ^{137}Cs leaching rates

	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**	**Sample 7**
^{137}Cs initially in sample	475.23	702.18	988.53	1269.90	1436.37	489.46	1772.52
^{137}Cs total leached [Bq]	151	177	288	329	462	166	478
^{137}Cs total leached [%]	31.83	25.14	29.12	25.89	32.16	34	26.99
^{137}Cs leaching rate [cm/day]	5.62E-04	4.37E-04	5.22E-04	4.64E-04	5.93E-04	6.60E-04	5.14E-04

The following should be mentioned:
- The leaching rates were determined in the following leaching days: 4, 11, 19, 45, 110, 165, 250, 350 and 400.
- The leaching waters analysis was carried out on samples of 25 ml. The volume taken was replaced by an equal volume of distilled water. Therefore, the analysis of the leaching activity, determined during the leaching test, was made in relation to the activity already existing in the leaching water at the time of measurements.
- In the 45th day, the leaching water was totally changed and remained unchanged until the end of leaching test (400th day).

^{137}Cs is the only radionuclide leached from the beginning of the leaching test and throughout the entire leaching period. In fact, it is known that cement does not represent a very good matrix in the case of Caesium. However, it's leached activity is low.

^{60}Co is found in the leaching water only in the 19th day, and only for the samples 1 and 4. Leached ^{60}Co in these particular cases are 1.57% and 0.87%, respectively. The leaching rates for ^{60}Co are 2.47×10^{-5} for sample 1 and 3.03×10^{-6} for sample 2.

There are no losses of ^{152}Eu and ^{241}Am, or the losses are below the detection limit of the equipment. The detection limit for ^{152}Eu is in the range 0.29 - 0.6 Bq/sample, and for ^{241}Am in the range 0.14 - 0.34 Bq/sample, respectively.

Mass variation of cement-radioactive magnetite products

The mass variation of the samples of cement-radioactive magnetite is an important criterion in the evaluation of waste products, when the experiences show a significant increase of the blocks due to the water absorption when they come in contact with it.

Product mass has been measured before the immersion in water, in the 45th and in the 400th leaching day, respectively.

The results are shown in Table 6. In Fig. 3, the graphical distribution of the mass variation values for the products is presented, analysed in relation to the quantity of cement and magnetite from the sample.

Table 6. Variation of the cement- magnetite samples mass after 45 days of immersion in water

	Sample 0 d	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 0 c**	**Sample 6**	**Sample 7**
Dry Magnetita [g]	0	9.49	14.02	19.73	25.35	28.67	0	9.77	35.38
Cement [g]	149.23	139.9	135.8	130.33	126.09	121.29	150.92	139.64	113.58
Sample mass before leaching (31 days after removing from moulds) **[g]**	188	184	184	192	192	185	193	192	194
Sample mass after 400 days of leaching [g]	202.96	199.11	199.06	206.11	205.33	198.58	205.48	204.66	205.56
Mass increase (after 400 days) **[%]**	7.44	7.67	7.64	6.92	6.57	6.89	6.15	6.27	5.72
Dimensions (h ; l ; L) initial/final [cm]	3.3/3.2	3/2.9	2.9/2.8	3.1/2.9	3.1/2.9	3.3/2.9	4.3/4	4.1/3.9	3.9/3.8
	4/4	4/3.9	4/3.9	4/4	4/4	4/4	5/5	5/5	5/5
	8/7.9	8/7.8	8/7.9	8/7.9	8/7.9	8/7.9	5/5	5/5	5/5

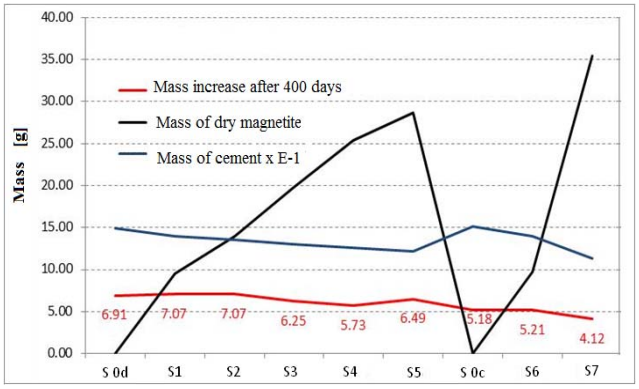


Fig.3. Variation of the conditioned products mass [g]

The increase in mass is due to the absorption of water by the cement layer.

From the graph, it can be observed that there is an increase of the products mass directly proportional to the cement mass. Meantime, the variation of the quantity of magnetite does not influence the mass of the products conditioned on contact with water.

The mass growth is relatively low, the obtained values being in a narrow range.

Conclusions

The paper aimed at performing cement immobilization tests of radioactive magnetite, leaching tests of conditioned products, to determine the behaviour of the magnetite and final products, respectively, under storage conditions.

During the leaching tests, the losses of radionuclides in the leaching water and variation of the leaching water parameters, pH and conductivity, aimed to be quantified.

The leaching experiments were performed on simulated magnetite samples (loaded with radioactive solution of ^{60}Co, ^{137}Cs, ^{152}Eu, ^{241}Am).

The following conclusions can be highlighted:

- The values of the global leaching rates were within 4.37 and 6.6x10^{-4} cm/day for ^{137}Cs. ^{60}Co was detected only in two samples, the leaching rates being of 2.47x10^{-5} and 3.03x10^{-6} cm/day, respectively. The leaching rates are low, considering, first of all, the generally high leachability of Caesium from cemented products;
- During the 400 days of leaching, no losses of ^{152}Eu or ^{241}Am were detected;
- During the considered leaching period it was observed an increase in mass of conditioned products of 5.72-7.67 %, after 400 days of contact with water;
- During the considered leaching period the pH values increase, reaching the basic domain;
- The conductivity increases by about 2 orders of magnitude in the first part of the leaching period. In the last part of the period, namely after the 110th day of leaching, a decreasing by one order of magnitude was noticed.
- No any correlation between the values of conductivity and the magnetite content was observed.

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