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RELEASE OF U(VI) FROM SPENT BIOSORBENT IMMOBILIZED IN CEMENT CONCRETE BLOCKS

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ABSTRACT

This paper deals with cementation as the method for the disposal of spent biosorbent, *Ganoderma lucidum* (a wood rotting macrofungi) after it is used for the removal of Uranium. Results on the uranium release during the curing of cement - concrete (CC) blocks indicated that placing the spent sorbent at the centre of the blocks during their casting yields better immobilization of uranium as compared to the homogeneous mixing of the spent sorbent with the cement. Short term leach tests indicated that the uranium release was negligible in simulated seawater, 1.8% in 0.2 N sodium carbonate and 6.0% in 0.2 N HCl. The latter two leachates were used to represent the extreme environmental conditions. It was observed that the presence of the spent biosorbent up to 5% by weight did not affect the compressive strength of CC blocks. Thus cementation technique is suitable for the immobilization of uranium loaded biosorbent for its ultimate disposal.

Introduction

Use of nuclear energy for the generation of electricity and other purposes is expected to increase and replace conventional energy sources in the future. However, this is inevitably associated with the production of ratioactive wastes from various stages of the nuclear circle. Among the liquid wastes, high level liquid wastes (HLW) are generated during the processing of spent fuel and contain fission products and long lived α-emitting radionucleides.(1) These are concentrated, immobilized in vitrified blocks and finally disposed of in stable geologic repositories several hundred meters below ground level. Low level liquid wastes (LLW) arising from uranium andthorium minining contain 1-100 mg/L of metal along with other mtallic cations such as Cu, Ni, Zn, Cr etc. and anions like HCO_3^-. (2) LLW production from nuclear reactors depend on the type of reactor and contain activated structural, moderator and coolant materials, fission products like Sr, Cs etc. as well as low concentrations of actinides arising from the fuel processing.(3)

Radionucleides from LLW are generally concentrated using ion exchange resins[4] and the spent resins are then embedded in cement concrete blocks for final disposal. Extensive studies have been conducted by Atkins et.al.[5] and Glasser[6] on the use of cement based composite material for radioactive waste immobilization with U(VI) as the model radoinucleide.

High cost of synthetic resins has focused the attention towards the development of alternative technologies for the concentration of radionucleides from LLW. Biosorption, sequestering of heavy metal ions by microorganisms, have been attracting wide attention for the removal and recovery of heavy metal ions.[7,8] It has been shown that some fungi, algae and bacteria exhibit a very high uranium uptake potential.[9-11] Investigations in our laboratory have shown that naturally occurring wood rotting macrofungi *Ganoderma lucidum* removes uranium from aqueous solutions very effectively and its capacity is higher than the generally used ion exchange resins.[12]

The present work deals with the solidification of uranium loaded biomass, *G.lucidum*, using cementation technique and short term leachability tests for uranium from cement/concrete blocks under different environmental conditions. The compressive strength was tested to determine the effect of immobilizing the biosorbent in these blocks.

Materials and Methods

Biosorbent: *Ganoderma lucidum* was sun dried, washed with distilled water and oven dried at 50°C before pulverizing to a geometric mean size of 347 μm (200 - 600 μm). This nonviable *G.lucidum* was used as biosorbent for all experiments.

Uranium Uptake: 100 gm biosorbent was suspended in 5 L of 3000 mg/L uranium solution (as uranyl nitrate) at pH 4.0. This suspension was agitated at 60 rpm and after an hour of contact time, biosorbent was separated by filtration. The filtrate was analyzed for U (VI) using arsenazo - III reagent as per the method described by Shumate.[13] Uranium laden *G.lucidum* was then dried at 50° C and was used as spent biosorbent for all immobilization experiments.

Concrete: A M20 (200 Kg/sq.cm) strength concrete mix was used for casting the blocks. Cement, fine and course aggregates were mixed in the ratio of 1:2:3. Six cubic blocks of 15 cm size were cast using 48Kg of the above mixture maintaining the cement to water ratio of 0.5 employing the standard procedure. Five different types of cement concrete (CC) blocks as given below were cast. (a) Normal blocks without biosorbent to be used as control, (b) Blocks with biosorbent uniformly distributed in the cement concrete mix, (c) Blocks in which the biosorbent was placed at the central region, (d) Blocks with spent biosorbent uniformly distributed in cement concrete mix, and (e) Blocks with spent biosorbent placed at the central portion of the cubes.

Preparation of the blocks containing the biosorbent at the centre was carried out as follows. The required amount of *G.lucidum* was placed in a small polyethylene bag having a number of holes to allow the leaching of uranium. Half of the cast mould was first filled with the mix followed by the placing of the biosorbent at the central region. The concrete mix was then poured to fill the rest of the mould and was vibrated carefully so as not to disturb the sac containing the biosorbent. Biosorbent to cement ratio was varied from 0.5 - 5.0% for these blocks while it was maintained at 1% for others. All the cubes were cured separately in tap water for 28 days as per standard procedure.[14] During this period, aliquots were taken for uranium determination.

Short term leach tests: The concrete blocks cast as per the above procedure were subjected to short term uranium leaching tests. The leachates used were 0.2 N HCl, 0.2 N Na_2CO_3 and simulated sea water (Table 1) which represent the wide range of environmental conditions. Two specimen blocks were placed in a container having 12 litres of leachate. Samples were withdrawn every day for uranium analysis. All cement concrete blocks, which were cast, were tested for their compressive strength using standard testing procedure.

Table 1
Composition of Simulated Sea Water

Constituent	Concentration g/L
NaCl	29.31
$MgCl_2$	3.99
$MgSO_4$	1.83
$CaSO_4$	1.34
K_2SO_4	0.85

Results and Discussion

Earlier work in our laboratory had shown that nonviable macrofungi, *G.lucidum,* is an effective biosorbent for the removal of uranium from aqueous solutions around the concentration range generally present in LLW.[12] Bound uranium can be recovered using carbonate as an eluant and the sorbent can be reused for many cycles.[12] Recovery of radionucleides from LLW, which are concentrated by ion exchange resins, is not generally practiced due to the following reasons. LLW contains many other fission products like Sr, Cs etc. along with actinides. These ions are also bound to resins and are likely to be eluted by the reagent. These cations have to be removed before uranium can be selectively recovered, which may not be economically viable. It has been shown that *G.lucidum* can also bind many heavy metal ions like Cu, Cd, Cs etc.[15] During elution, *G.lucidum* is also expected to release other cations as observed with ion exchange resins. Hence, the present study was directed on the feasibility of immobilizing the spent biosorbent in cement matrix for ultimate storage and disposal. Short term leachability tests were conducted using different leachates which simulate extreme environmental conditions during storage.

Leaching of uranium from CC blocks during curing:

Uranium uptake was determined to be 74 mg/g of biosorbent. The ratio of biosorbent/cement was maintained as 1% (13.5 gm spent biosorbent/block) for uniformly mixed block and was varied from 0.5 to 5% (6.75 - 67.5 gm sorbent/block) for others. Uranium leaching during curing was determined by placing 2 specimen blocks in 57 liters of tap water and analyzing an aliquot for U(VI) on the 7th and 28th days.

It was observed that 2.34 and 2.4% uranium was leached into the aqueous phase when the biosorbent was uniformly distributed. However it was undetectable from the blocks containing 5% sorbent when it was embedded at the centre. These results indicated that leaching of uranium from the blocks having homogeneously mixed sorbent is due to its presence at the surface of the block. Thus, embedding the spent biosorbent at the centre of the cement concrete block is a better mode of immobilization.

Leaching of uranium from cement concrete blocks by different leachates:

Ultimate disposal sites for CC blocks having the spent sorbent are either geological repositories or sea. It is thus essential to examine whether uranium is leached from the CC blocks when they are placed in such an aqueous environment. In this study, short term leachability tests for uranium were conducted under two extreme conditions using 0.2 N HCl and 0.3 N Na_2CO_3 as well as in simulated seawater. The results are presented in Figs. 1 -3.

It was observed that a higher release of U (VI) was observed in all three leachates from the blocks having homogeneous distribution of the biosorbent as compared to those in which sorbent

was placed in centre (Table 2). Maximum leaching of 6.0 % was observed in 0.2 N HCl and minimum was with sea water.

Uranium was undetectable in simulated sea water even when 3% by weight of spent biosorbent was centrally placed in the blocks, where as only 0.04% was leached into the aqueous phase when the sorbent concentration was increased to 5%. These results are presented in Table 2.

A simple mathematical model on the leachability data would facilitate to predict the rate and the mode of leaching of actinides.[16] The data from short term leach tests was fitted to the following equation

$$C/Co0 = \beta t^n$$

where C is the uranium released (mg) on any day; Co is the initial uranium sorbed onto *G.lucidum;* t is the time in days; β is the cumulative fraction of uranium released on 1st day, and n is the coefficient indicating the mode of leaching.

The results presented in Fig. 4 indicate that the above relationship holds good and the values of exponent, n, are given in Table 3. As can be seen from the Table, only in the case of homogeneously mixed system with sea water as leachate the value is 0.5, indicating that the release of U(VI) is governed by diffusion. In other cases, this could be due to mechanisms other than diffusion.

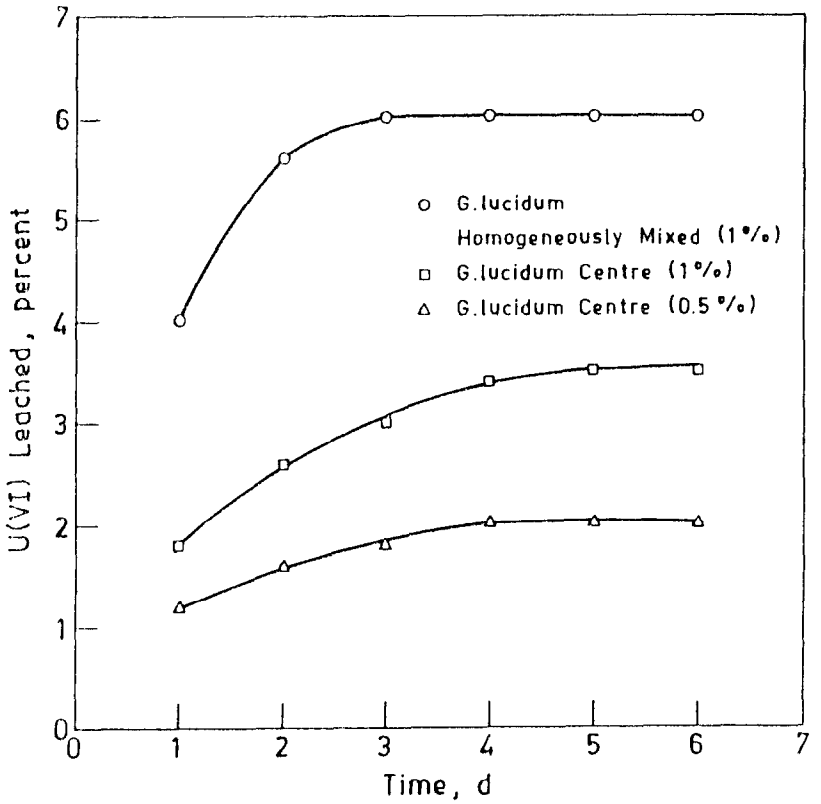


Fig.1
Release of U(VI) from C.C. Blocks in 0.2 N HCl

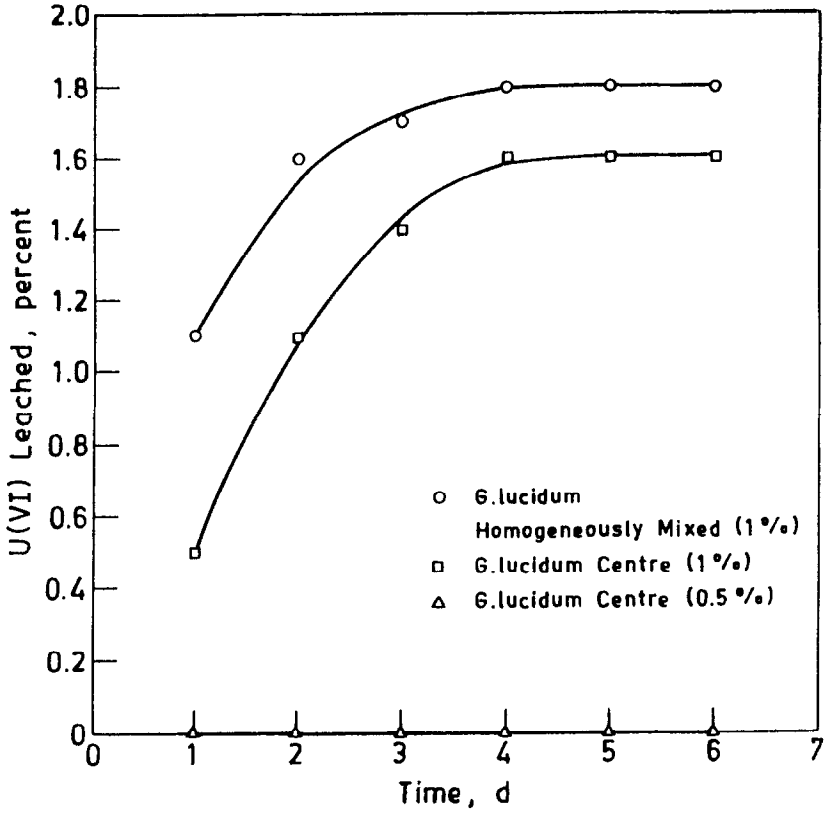


Fig. 2
Release of U(VI) from C.C. Block in 0.2 N NaCO

TABLE 2
Release of uranium from spent biosorbent immobilized on cement concrete blocks in different leachates

SL.No.	C.C block containing spent biosorbent	% of spent sorbent by weight of cement	Max. % uranium leached		
			0.2 N HCl	0.2 N Na_2CO_3	Simulated sea water
1	Uniformly mixed	1.0	6.0	1.8	0.39
2	Centrally placed	1.0	3.5	1.6	a
3	Centrally placed	0.5	2.0	ND	ND
4	Centrally placed	3.0	a	a	ND
5	Centrally placed	5.0	a	a	0.04

a - Leach tests were not performed
ND - Not dectectable

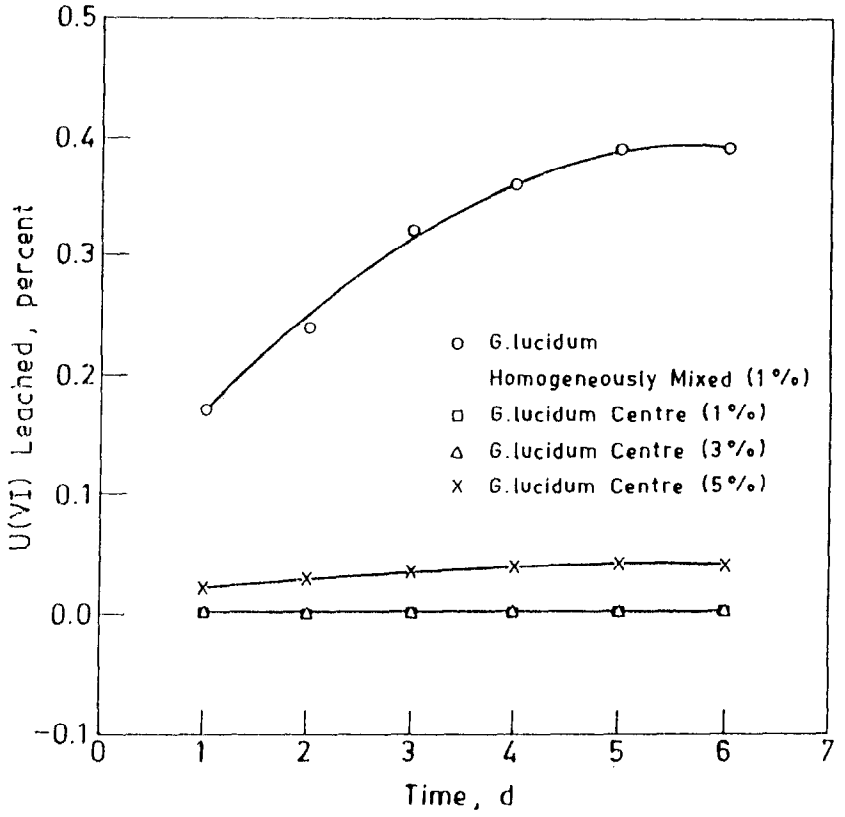


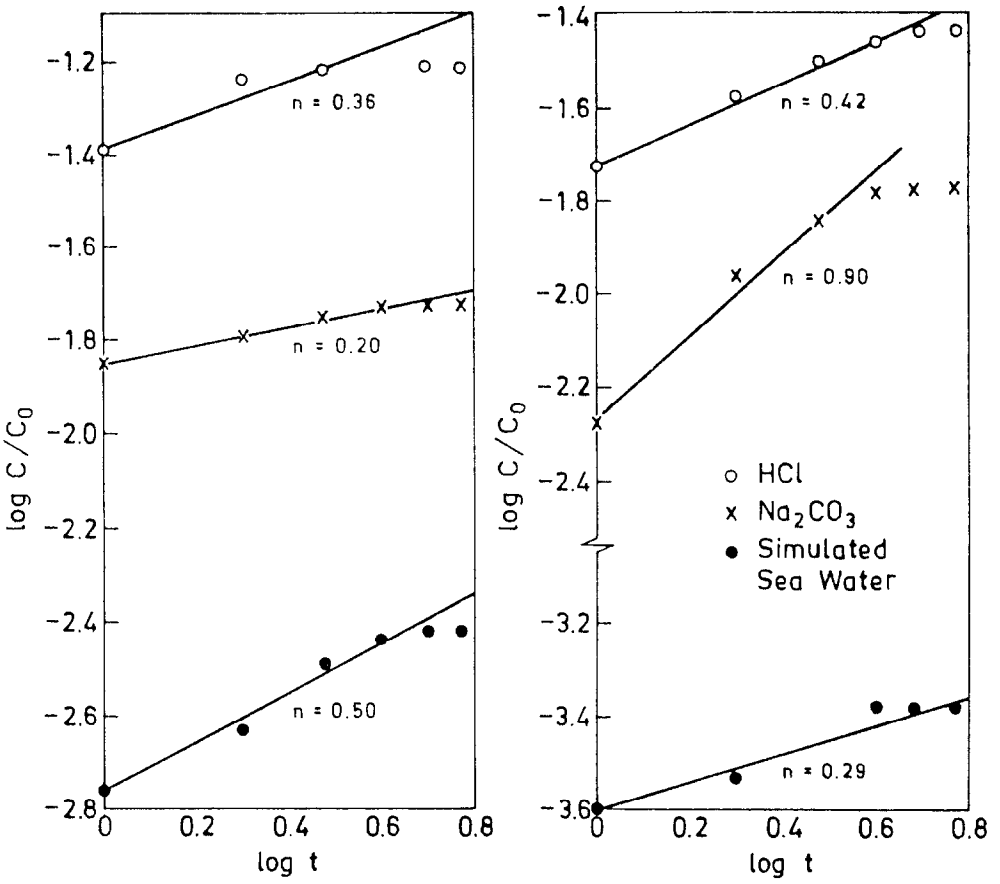
Fig.3
Release of U(VI) from C.C. Blocks in Simulated Sea Water

TABLE 3
Values of exponent n for different leachates

Sl. No.	C.C.block containing spent biosorbent	Value of exponent, n		
		0.2 N HCl	0.2 N Na_2CO_3	Simulated sea water
1	Uniformly mixed	0.36	0.20	0.50
2	Centrall placed	0.42	0.90	0.29

Compressive Strength:

Compressive strength, porosity and pore size distribution are the important factors in assessing the suitability of cementation as the method for the immobilization of U(VI) enriched biosorbent. In the present work, compressive strength of cement concrete blocks were determined after subjecting them to leachability tests. The data presented in Table 4 shows that the presence of biosorbent does not affect the compressive strength of the blocks.



(a) Homogeneously Mixed U(VI) Loaded G.lucidum.

(b) Centrally Placed U(VI) Loaded G.lucidum.

Fig.4
Cumulative Fraction Release of U(VI) from Cement Concrete Blocks

TABLE 4
Comparison of Compressive Strength of Different Types Of Blocks

Sl.No	C.C block containing spent Biosorbent	%Biosorbent by weight of cement	Compressive Strength (Kg/cm^2) Tap water	0.2 N HCl	0.2 N Na_2CO_3	Simulated sea water
1	Normal	0.0	191.1	-	-	-
2	Uniformly mixed	1.0	196.0	-	-	-
3	Uniformly mixed	1.0	190.5	-	-	-
4	Centrally placed	1.0	210.0	203	190	196
5	Centrally placed	5.0	195.0	-	-	-

Conclusions

Based on the results of the present study, following conclusions can be drawn.

1. Uranium release during curing is higher from cement concrete blocks in which sorbent is homogeneously mixed as compared to the blocks with the sorbents embedded at the centre.

2. Results of short term leachability studies indicate that uranium release in presence of HCl and Na_2CO_3 which represent extreme environmental conditions is only 3.5% and 1.4% when the sorbent is placed at the centre of the blocks.

3. Uranium release in simulated sea water was not detected up to 3% of sorbent in the cement concrete blocks.

4. Embedding the U(VI) loaded sorbent in CC block did not have any effect on its compressive strength.

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