

**CEMENT MATRIX FOR IMMOBILISATION OF SPENT ANIONIC RESINS IN
BORATE FORM ARISING FROM NUCLEAR POWER PLANTS**

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Abstract

In water cooled reactors boron is added as boric acid to control nuclear reactor power levels. The boric acid concentration in coolant/moderator water, is controlled by using strongly basic anionic resins in borate (H_2BO_3^-) form. The spent anionic resins in borate form contain ^{131}I odine, ^{99}Tc hnetium and ^{137}Cs esium activities.

Direct immobilisation of anionic resins in borate form in Ordinary Portland Cement (OPC) and Slag Cement was investigated using vermiculite, bentonite, calcium oxide and silica as admixtures. The cumulative fraction of ^{137}Cs esium leached and ^{137}Cs esium leach rate for slag cement matrix were 0.029 and $0.00064 \text{ g.cm}^2.\text{d}^{-1}$ respectively for 95 days of leaching. The volume reduction factor achieved by direct immobilisation of anionic resins in borate form was 0.48.

Immobilisation of pyrolysis residues from these resins in OPC matrix was also studied. Leaching of matrix blocks was carried out for 180 days in DM water to optimise the matrix formulation. The cumulative fraction of ^{137}Cs esium leached and ^{137}Cs esium leach rate were 0.076 and 0.00054 respectively for 180 days leaching. The volume reduction factor achieved by immobilisation of pyrolysis residues was 2.4 .

OPC is non compatible to cationic resins loaded with alkali in absence of specific admixtures. Hence cationic resins loaded with alkali and anionic resins in borate form can not be immobilised together.

Keywords

Borate resins

OPC

Slag cement

Leaching

Leach Index

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1. INTRODUCTION

Boron is used[1] to control nuclear reactor power levels because of its high neutron capture cross section. In water cooled reactors boron is added as boric acid. By increasing boric acid concentration in coolant of Pressurised Light Water Reactors (PWR) or moderator of Pressurised Heavy Water Reactor (PHWR) the nuclear power level can be decreased and vice versa. This operation involves use of strongly basic anionic resins in borate (H_2BO_3^-) form. Anionic resins remove ^{131}I and ^{99}Tc which are released to reactor water from failed fuel pins and exist as anionic species. Also the pore water of anionic resins are in equilibrium with the reactor water which contains ^{137}Cs . Spent anionic resins in borate form are discharged as radioactive solid wastes.

Currently spent borated anionic resins are immobilised [2,3] in polymer matrix. Considerable research has been carried out [4 to 9] to use cement matrix for immobilising anionic resins in borate form. Both Ordinary Portland cement (OPC) and Slag Cements have been investigated. Hence studies were initiated to optimise cement matrix formulations to incorporate borated anionic resins. The report discusses the findings of these studies.

2. COMPATIBILITY OF CEMENT MATRIX WITH ION EXCHANGE (IX) RESINS

Cement absorbs pore water from swollen IX resins which shrink in size while cement is setting. Water ingress in set cement matrix block leads to swelling of resins. This swelling pressure can disintegrate cement matrix. This problem is more severe with anionic resins due to their higher swelling compared to cationic resins.

Borate is known to retard [10] setting of cement. Long setting time puts constraint on plant throughput. $\text{Ca}(\text{OH})_2$ or CaO are used [10] to precipitate calcium borate which is sparingly soluble. The anion resins get converted to hydroxide form and CaBO_3 precipitate can be incorporated into cement matrix along with anionic resins.

Compatibility of cement matrix can be improved by using certain admixtures. Vermiculite is known[11] to adsorb ^{137}Cs irreversibly. Since ^{137}Cs is not chemically bound in borated resins, vermiculite is used as an admixture. Bentonite has tendency to swell on contact with water. The reaction between bentonite and CsOH produces [12] pollucite. Pollucite is a cesium mineral in which cesium ions are firmly immobilised. Hence bentonite was used as admixture to minimise water ingress and cesium leaching. Silica reacts with $\text{Ca}(\text{OH})_2$ generated

during hydration of cement. The additional calcium silicate hydrates formed decreases porosity and increases[13] strength of cement matrix. Hence precipitated silica or silica fumes are used. Copper hexacyanoferrate is[14] very efficient in sorption of $^{137}\text{Cesium}$ from alkaline medium present in pore water of cement matrix. Addition of potassium hexacyanoferrate and copper sulphate solutions while preparing cement matrix forms copper hexacyanoferrate insitu.

Some of these admixtures were used in combination while preparing cement matrix blocks using OPC and Slag Cement.

3. EXPERIMENTAL

3.1 Preparation of Simulated Spent IX Resins

Indigenously available nuclear grade cationic resins in H^+ form and anionic resins in hydroxide form were selected. INDION 223 grade cationic resins supplied by Ion Exchange India Limited were used. GA- 11 grade anionic resins were supplied by Doshi Ion Exchange and Chemicals Limited. The cationic and anionic resins had IX capacities of 1.8 and 0.9 equivalents/litre respectively. They were washed with demineralised water to remove organic and metallic impurities. The cationic resins were converted to Li^+ and K^+ forms by contacting with 1 M LiOH and 1 M KOH respectively. Addition of LiOH/KOH was continued till constant pH of around 8 was achieved. The resins were then washed to remove excess alkali and air-dried.

Stainless steel of 304 grade contains 71.5 % iron, 19 % chromium and 9.5 % nickel. In reactor water, iron and chromium are present in trivalent state and nickel in divalent state as corrosion products of stainless steel. These are loaded on cationic resins in the purification system. Concentrated solutions of AR grade iron, chromium and nickel nitrates were prepared and analysed by complexometry using EDTA. These were mixed in appropriate proportion to prepare simulated solution of corrosion products of stainless steel having 5 equivalents/litre concentration. It was assumed that 10 % of cation exchange capacity is used by corrosion products of stainless steel at the time of discharge of spent IX resins. One litre washed cationic resins in Li^+ and K^+ forms were taken with minimum quantity of excess water. Appropriate quantity of corrosion product solution was added along with $^{137}\text{Cesium}$ trace solution. The contents were allowed to equilibrate. The excess water was allowed to evaporate partially. One ml samples of the resin were transferred to counting vials and excess water was sucked out completely. The $^{137}\text{Cesium}$ loading was estimated by counting the samples on Na(Tl)I detector

coupled to single channel analyser. From analyses of 5 samples, average $^{137}\text{Cesium}$ loading was estimated.

Since H_3BO_3 is a weak acid, only first dissociation was considered for preparing anionic resins in borate form. To 1 litre of anionic resins in hydroxide form, excess H_3BO_3 added [9] and pH was adjusted to 8 by addition of alkali. Contents were allowed to equilibrate. The resins were washed to make free from borates. To the washed borated resins, $^{137}\text{Cesium}$ tracer solution was added and allowed to equilibrate with pore water of resins. The average $^{137}\text{Cesium}$ loading was estimated by method indicated above.

3.2 Immobilisation of IX Resins in OPC Matrix.

PWR and VVER type reactors use cationic resins in Li^+ or K^+ form. Hence their disposal in cement matrix along with borate resins was considered. Thirty ml of $^{137}\text{Cesium}$ loaded wet resins flooded with water were taken for making blocks. Matrix blocks containing $^{137}\text{Cesium}$ loaded anionic resins in borate form alone or along with $^{137}\text{Cesium}$ cationic resins in Li^+/K^+ form were prepared using OPC. After adding water and admixtures to the IX resins, the contents were stirred for 15 minute to allow admixtures to sorb $^{137}\text{Cesium}$. After adding cement the contents were mixed for additional 15 minutes and allowed to set in plastic containers.

From the size of the matrix block, the Volume Reduction Factor(VRF) achieved was estimated as-

$$\text{VRF} = \frac{\text{Volume of Resins Incorporated}}{\text{Volume of Matrix Block}}$$

The details of OPC matrix blocks compositions and VRFs are given in Table 1.

Table 1

Composition of Ordinary Portland Cement Matrix Blocks Prepared from Wet IX Resins

Weight of cement (OPC) - 50 gms

Waste - Gravity Dried $^{137}\text{Cesium}$ loaded Anionic Resin in Borate Form

Waste Loading = 600 ml Wet Resin / kg Cement

| Block Code | Waste Composition | Aqueous Phase/ Cement Ratio | Wt. % W.R.T Cement | | | $^{137}\text{Cesium}$ added ($\mu\text{Ci. g}^{-1}$) | VRF Achieved |
|------------|---|--------------------------------|--------------------|-----|--------|---|--------------|
| | | | Vermiculite | CaO | Silica | | |
| A | Anionic Resin in Borate Form | 0.2 | 0 | 8.8 | 8 | 1.440 | 0.51 |
| B | Anionic Resin in Borate Form | 0.2 | 8 | 8.8 | 0 | 1.616 | 0.46 |
| C | Cationic Resin in Li Form and Anionic Resin in Borate : 1:1 | 0.4* | 0 | 4.4 | 8 | 1.160 | 0.51 |
| D | Cationic Resin in Li Form and Anionic Resin in Borate : 1:1 | 0.4 * | 8 | 4.4 | 0 | 1.269 | 0.48 |
| E | Cationic Resin in K Form and Anionic Resin in Borate : 1:1 | 0.2 | 0 | 4.4 | 8 | 1.486 | 0.51 |
| F | Cationic Resin in K Form and Anionic Resin in Borate : 1:1 | 0.2 | 8 | 4.4 | 0 | 1.672 | 0.40 |

* For these blocks 2.7 M Aluminium nitrate solution was used [15] instead of water.

3.3 Immobilisation of IX Resins in Slag Cement Matrix.

Matrix blocks incorporating anionic resins in borate form were prepared using 'Commando' brand slag cement supplied by Indorama Cement Limited. ¹³⁷Cesium loaded wet resins were transferred to 100 BSS mesh sieve for gravity drying. Procedure indicated in 3.2 was followed for making the blocks. The details are given in Table 2 along with VRFs,

Table 2

Composition of Slag Cement Matrix Blocks Prepared from Wet IX Resins

Wt of Slag Cement - 51gms (50 % slag)

Waste - Gravity Dried ¹³⁷Cesium loaded Anionic Resin in Borate Form

Vermiculite - 8.8 % of Slag cement

Bentonite - 8.8 % of Slag Cement

Aqueous phase / cement Ratio - 0.58

| Code No | Waste Loading Wt % of Cement | K ₄ Fe(CN) ₆ (0.25 M) ml/100g of Slag Cement | CuSO ₄ (0.5 M) ml/100g of Slag Cement | ¹³⁷ Cesium added (iCi. g ⁻¹) | VRF Achieved |
|---------|------------------------------|--|--|---|--------------|
| G | 61.76 | 0 | 0 | 0.0751 | 0.40 |
| H | 79.41 | 0 | 0 | 0.0906 | 0.48 |
| I | 52.92 | 29.4 | 19.6 | 0.01077 | 0.40 |
| J | 79.41 | 29.4 | 19.6 | 0.1039 | 0.48 |
| K | 88.24 | 29.4 | 19.6 | 0.1026 | 0.52 |

3.4 Immobilisation Of Pyrolysis Residue From Anionic Resins In Borate Form In OPC Matrix.

¹³⁷Cesium loaded anionic resins in borate form and ¹³⁷Cesium loaded cationic resins in Li⁺/K⁺ forms were pyrolysed at 300°C in 100 ml batches. The pyrolysis residues were [16] 508, 513 and 279 gm/litre respectively for IX resins in Li⁺, K⁺ and borate forms. The residues were mixed and analysed for ¹³⁷Cesium activity content by counting 0.5 gram samples on Na(Tl)I detector coupled to single channel analyser. From analyses of 5 samples, average ¹³⁷Cesium loading was estimated.

Matrix blocks incorporating pyrolysis residues were prepared using OPC. Procedure indicated in 3.2 was followed for making the blocks. The details are given in Table 3 along with VRFs.

Table 3

Composition of Cement Matrix Blocks Prepared with Pyrolysis Residue from IX Resins

Waste Loading - 600 gms /Kg Cement , Wt of cement (OPC) - 50 gms

| Block Code | Residue From IX Resin | Aqueous Phase/ Cement Ratio | Wt % W.R.T Cement | | | ¹³⁷ Cesium added ($\mu\text{Ci. g}^{-1}$) | VRF Achieved |
|------------|---|--------------------------------|-------------------|-----|--------|---|--------------|
| | | | Vermiculite | CaO | Silica | | |
| L | Anionic Resin in Borate Form | 0.52 | 8 | 0 | 8 | 0.4635 | 2.4 |
| M | Anionic Resin in Borate Form | 0.56 | 8 | 8 | 8 | 0.4403 | 2.2 |
| N | Anionic Resin in Borate Form | 0.6 | 8 | 16 | 8 | 0.4194 | 2.0 |
| O | Anionic Resin in Borate Form | 0.6 | 8 | 24 | 8 | 0.4065 | 1.9 |
| P | Anionic Resin in Borate Form | 0.72 | 8 | 32 | 8 | 0.3774 | 1.8 |
| Q | Anionic Resin in Borate Form | 0.72 | 8 | 40 | 8 | 0.3669 | 1.7 |
| R | Cationic Resin in K Form and Anionic Resin in Borate : 1:1 | 0.6 | 8 | 4.4 | 8 | 0.0891 | 0.9 |
| S | Cationic Resin in Li Form and Anionic Resin in Borate : 1:1 | 0.6 * | 8 | 4.4 | 8 | 0.1850 | 0.9 |

* For these blocks 1.35 M Aluminium nitrate solution is used instead of water.

3.5 Leaching of Cement Matrix Blocks

OPC matrix blocks were cast and cured for 1 month in closed saturated humidity chamber before leaching. The slag cement matrix blocks were similarly cured for 3 months. For leaching, the ratio of volume of the matrix block to demineralised water leachant volume was maintained at 1 : 10. The leaching was carried out as per ANSI/ANS 16.1. 1986 procedure[17].

3.6 Estimation of Leach Rate and Leach Index

In many studies, the results of leaching tests are simply indicated as the fraction leached of the bulk activity under the respective experimental conditions. Under these conditions it is practically impossible to compare the leaching results obtained by various authors.

$$\text{Cumulative Fraction (CF) Leached} = \frac{A_n}{A_o}$$

Where

A_n : radioactivity leached during the n^{th} leaching period

A_n : Sum of all A_n from first leaching interval

A_o : radioactivity originally incorporated in the specimen

Another unit frequently used to denote leaching capability is the leaching rate (R) expressed in ($\text{g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$) . However, this indication is not unequivocal ; the following definitions are possible, of which the last one is the most common one :

$$R = \frac{\text{Activity of substance leached}}{\text{area} \times \text{time}} \quad (\text{activity leached} \cdot \text{cm}^{-2} \cdot \text{d}^{-1})$$

$$R = \frac{\text{Activity leached}}{(\text{Total Activity/grams of waste}) \times \text{area} \times \text{time}} \quad (\text{g waste} \cdot \text{cm}^{-2} \cdot \text{d}^{-1})$$

$$R = \frac{\text{Activity leached}}{(\text{Total Activity/grams of Matrix}) \times \text{area} \times \text{time}} \quad (\text{g matrix} \cdot \text{cm}^{-2} \cdot \text{d}^{-1})$$

The resulting figures would be different in each case.

The incremental leach rate R_n is defined as –

$$R_n = \frac{(A_n / A_o)}{t_n} \quad (\text{Fraction of activity leached} \cdot d^{-1})$$

Where R_n - Incremental leach rate in n^{th} time interval t_n

t_n : n^{th} time interval

S : Surface area of the specimen (cm^2)

V : Volume of specimen (cm^3)

If less than 20 % of activity incorporated is leached from uniform regular shaped solid matrix, the leaching behaviour approximates that of semi-infinite medium. Under these conditions effective diffusivity can be calculated from the mass transport equations. By

$$D = \frac{1}{6} [R_n]^2 \{V/S\}^2 T$$

Where

D – Effective diffusivity cm^2/s

$T = \text{Square of } \left[\frac{1}{2} \{ t_n - t_{n-1} \} \right]$ - mean time of leaching

Leachability Index (LI) defined as per ANSI/ANS 16.1. 1986[17] standard is defined as –

$$LI = \frac{1}{n} \left[\log(\hat{a}/D) \right]_n$$

Where \hat{a} is defined as constant $1 cm^2/s$ and D is effective diffusivity. The average value upto first decimal is reported as leachability index of matrix .

At the time of changing leachant, it was analysed for $^{137}\text{Cesium}$ activity to find fraction leached. The data generated was used to estimate cumulative fraction (CF) of $^{137}\text{Cesium}$ activity leached, leach rate in terms of $gm/cm^2/day$ and leach index.

The results are presented in Fig. 1 to 4 for OPC matrix blocks. The results are presented in Fig. 5 to 7 for slag cement matrix blocks. The results are presented in Fig. 8 to 15 for resin residue OPC matrix blocks.

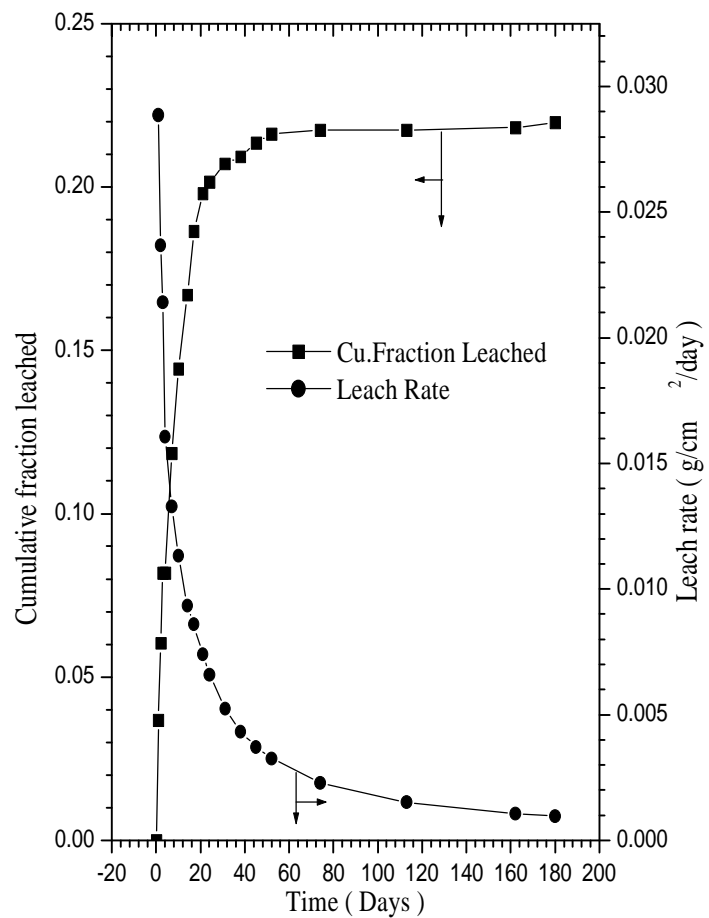


Fig.1 Cumulative fraction of ^{137}Cs leached and leach rate as function of time for OPC matrix block A

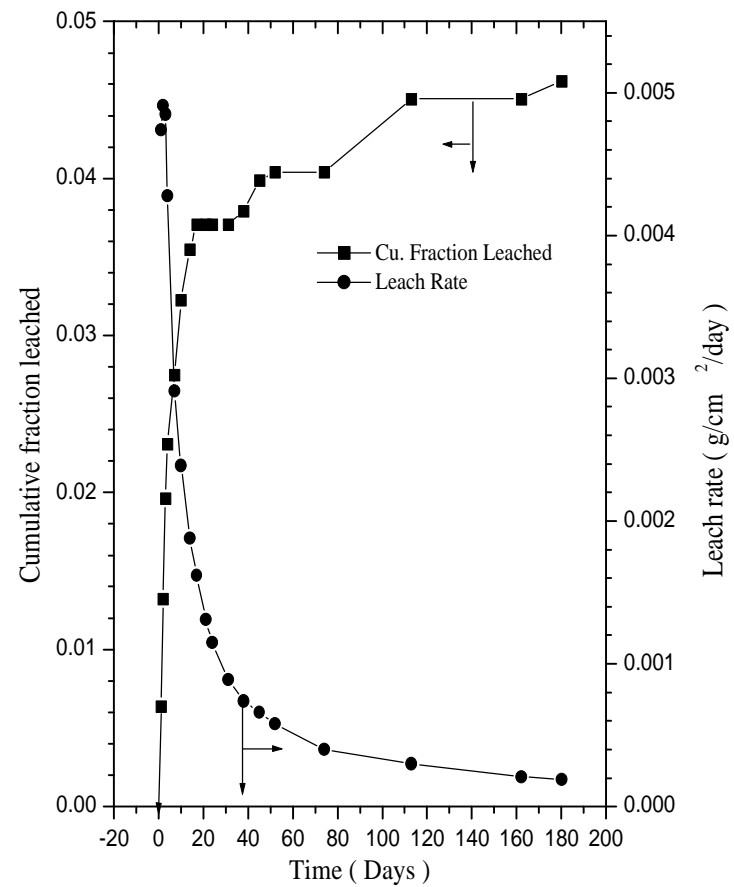


Fig.2 Cumulative fraction of ^{137}Cs leached and leach rate as function of time for OPC matrix block B

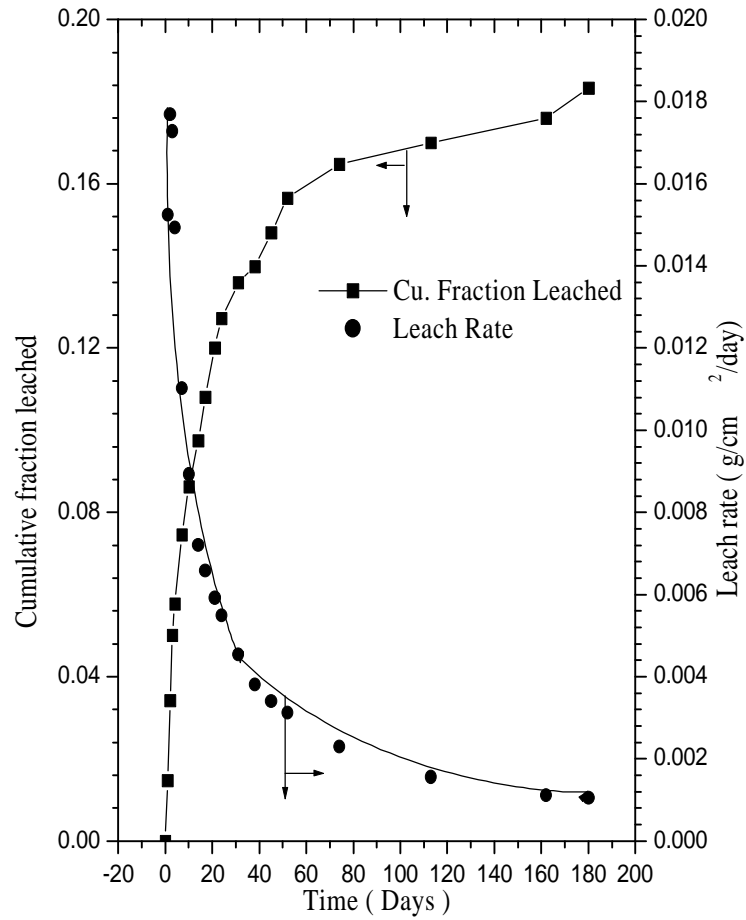


Fig.3 Cumulative fraction of ¹³⁷Cs leached and leach rate as function of time for OPC block C

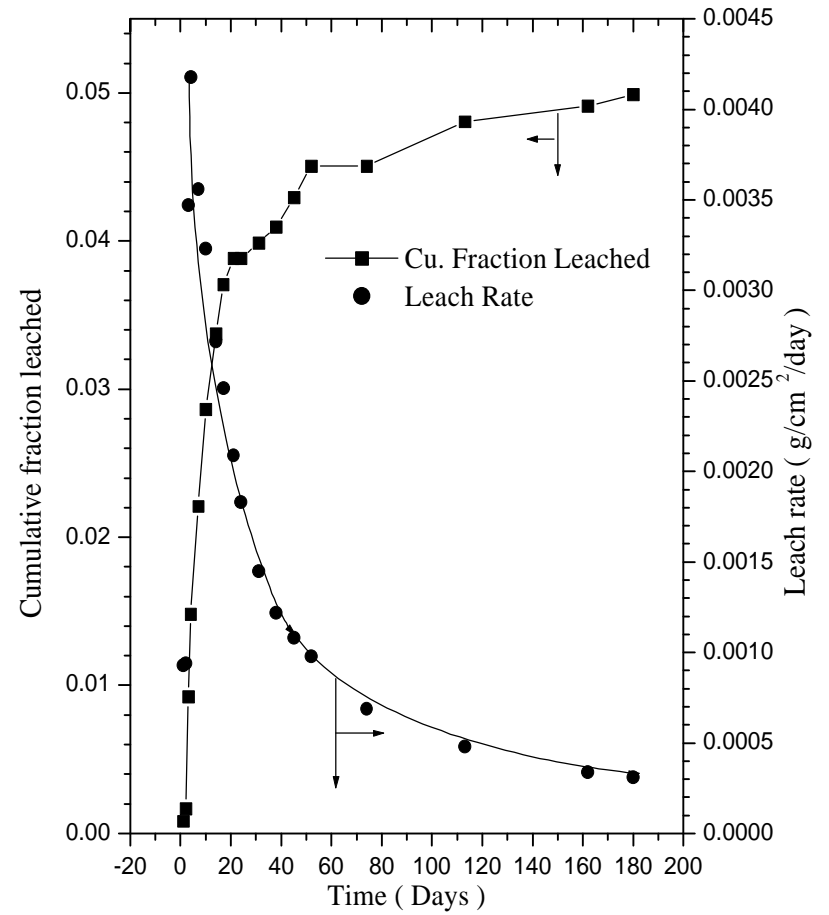


Fig.4 Cumulative fraction of ¹³⁷Cs leached and leach rate as function of time for OPC matrix block D

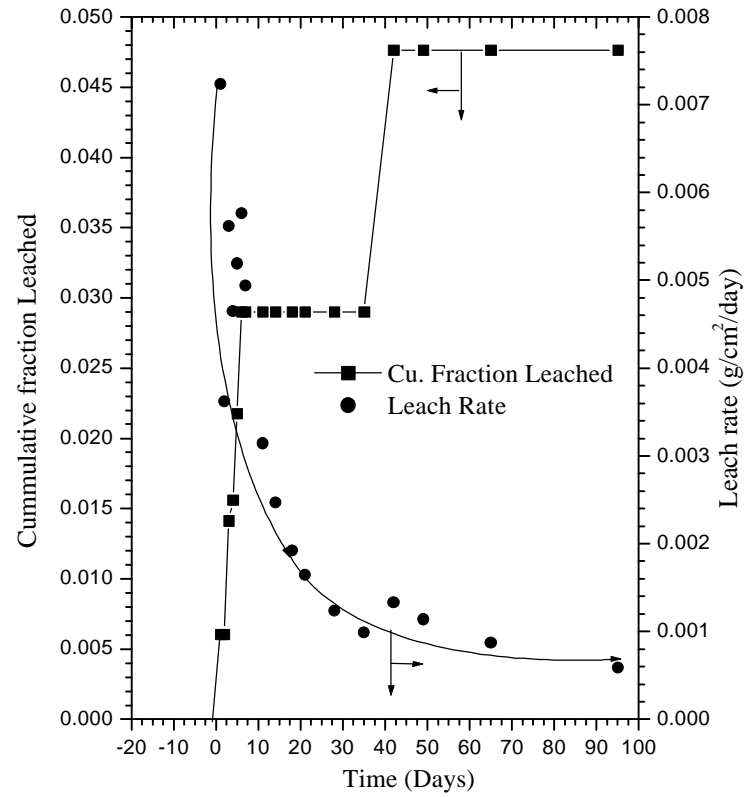


Fig.5 Cumulative fraction of ^{137}Cs leached and leach rate as function of time for slag cement matrix block G

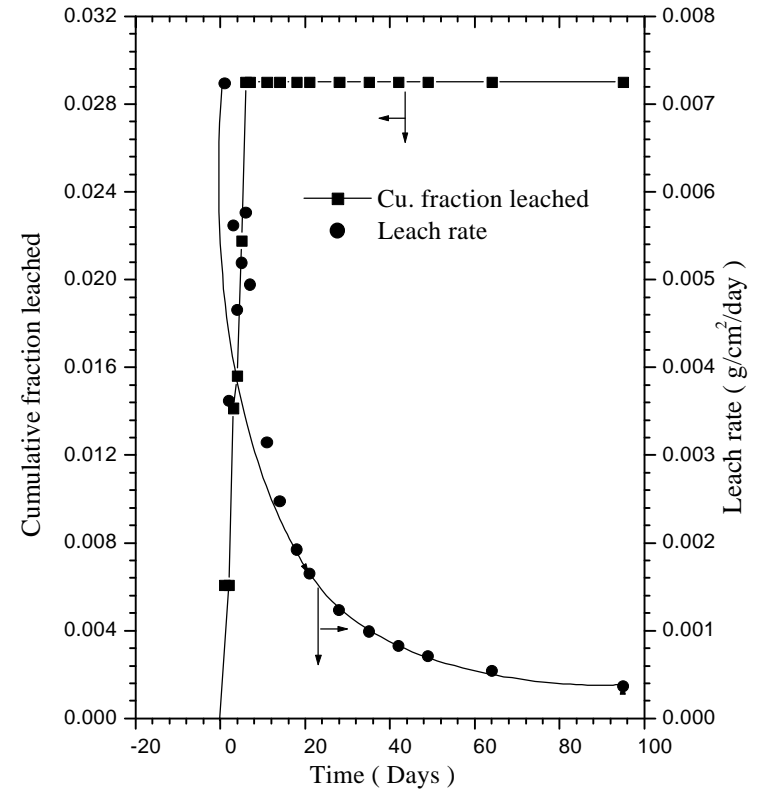


Fig.6 Cumulative fraction of ^{137}Cs leached and leach rate as function of time for slag cement matrix block H

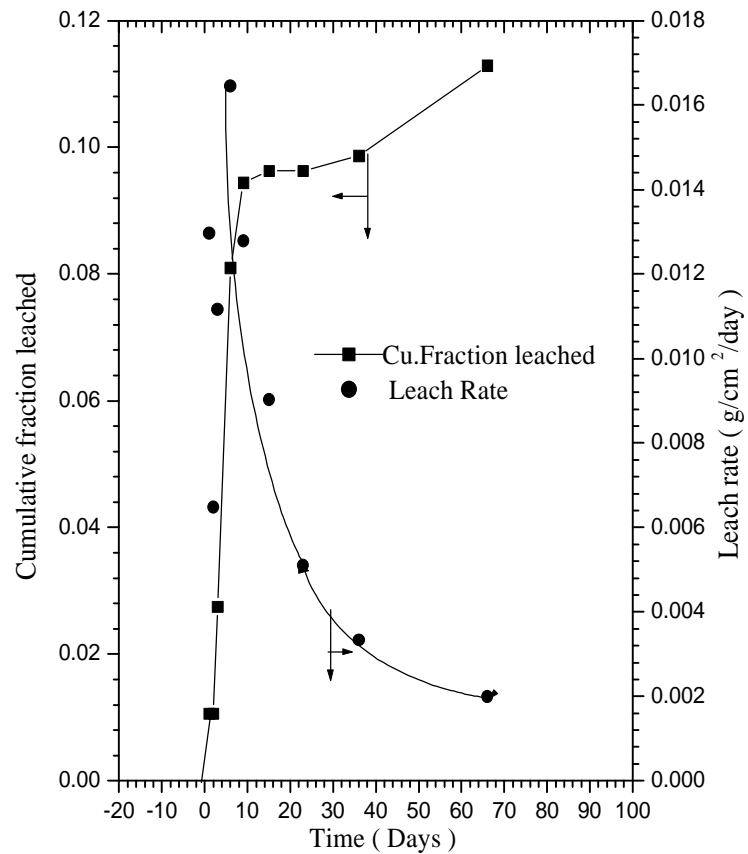


Fig.7 Cumulative fraction of ^{137}Cs leached and leach rate as function of time for slag cement matrix block I

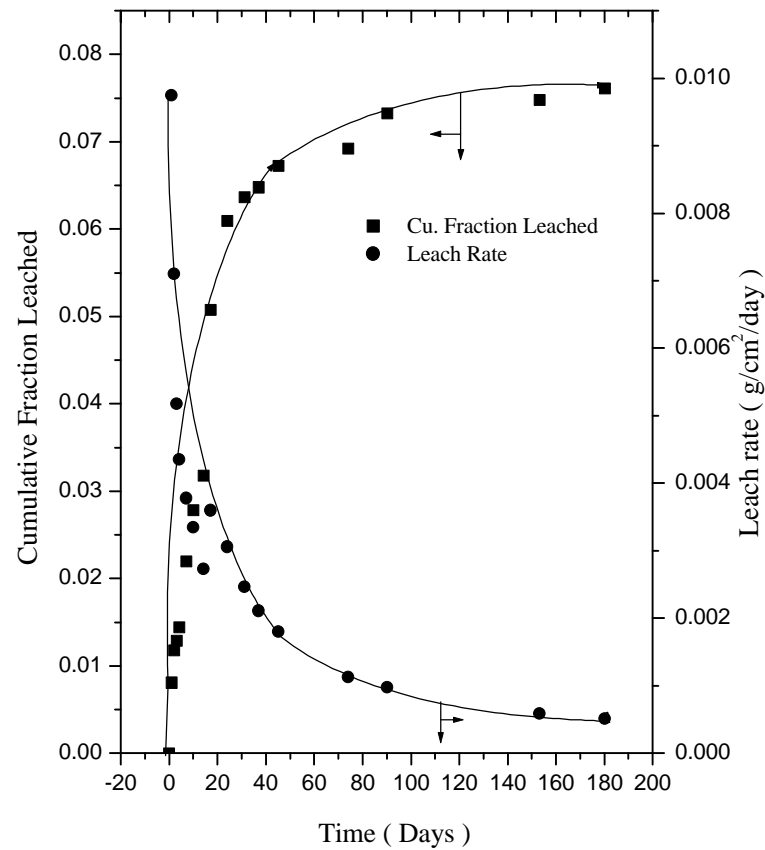


Fig.8 Cumulative fraction of ^{137}Cs leached and leach rate as function of time for OPC matrix block L

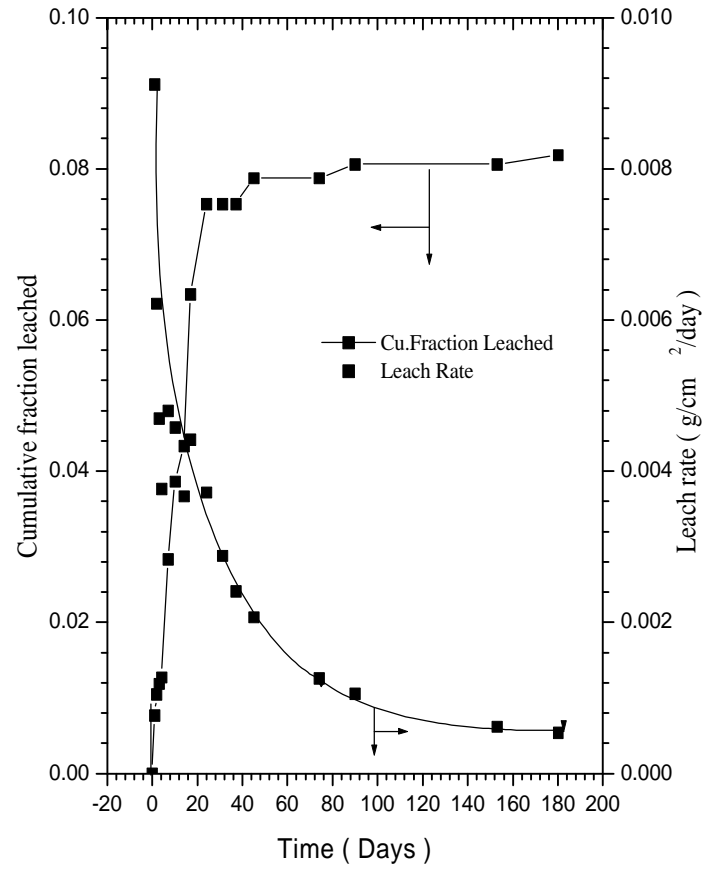


Fig.9 Cumulative fraction of ¹³⁷Cs leached and leach rate as function of time for OPC matrix block M

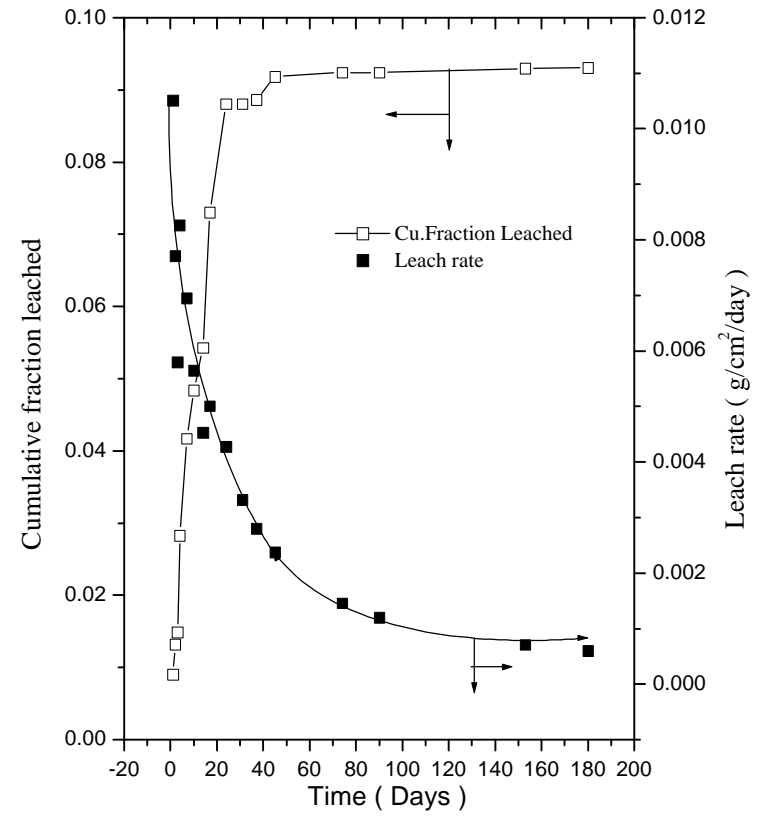


Fig.10 Cumulative fraction of ¹³⁷Cs leached and leach rate as function of time for OPC matrix block N

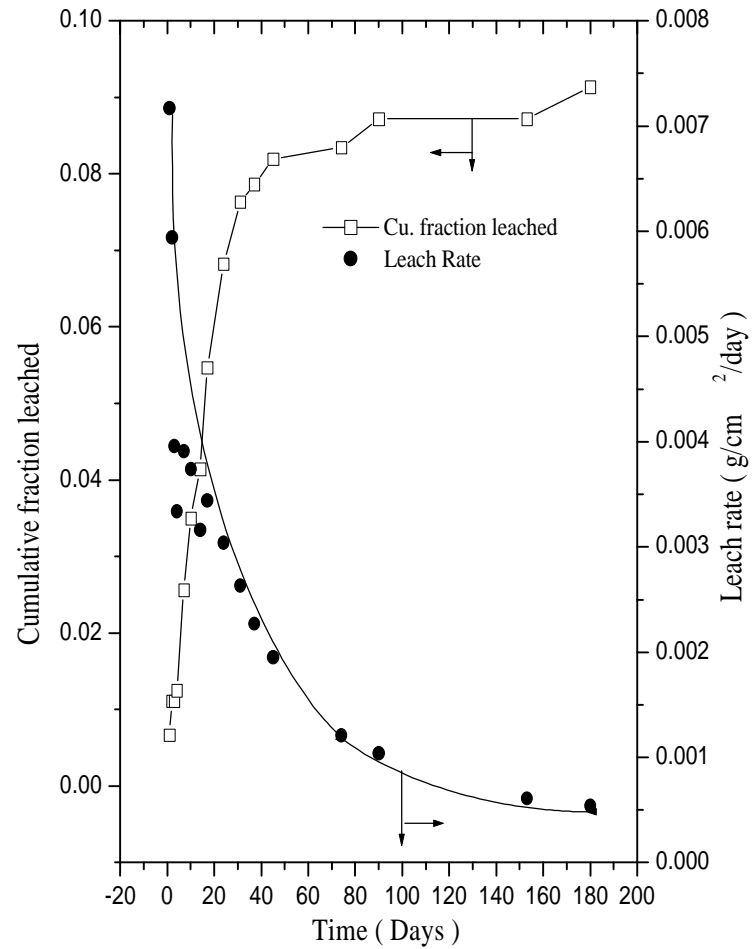


Fig.11 Cumulative fraction of ^{137}Cs leached and leach rate as function of time for OPC matrix block O

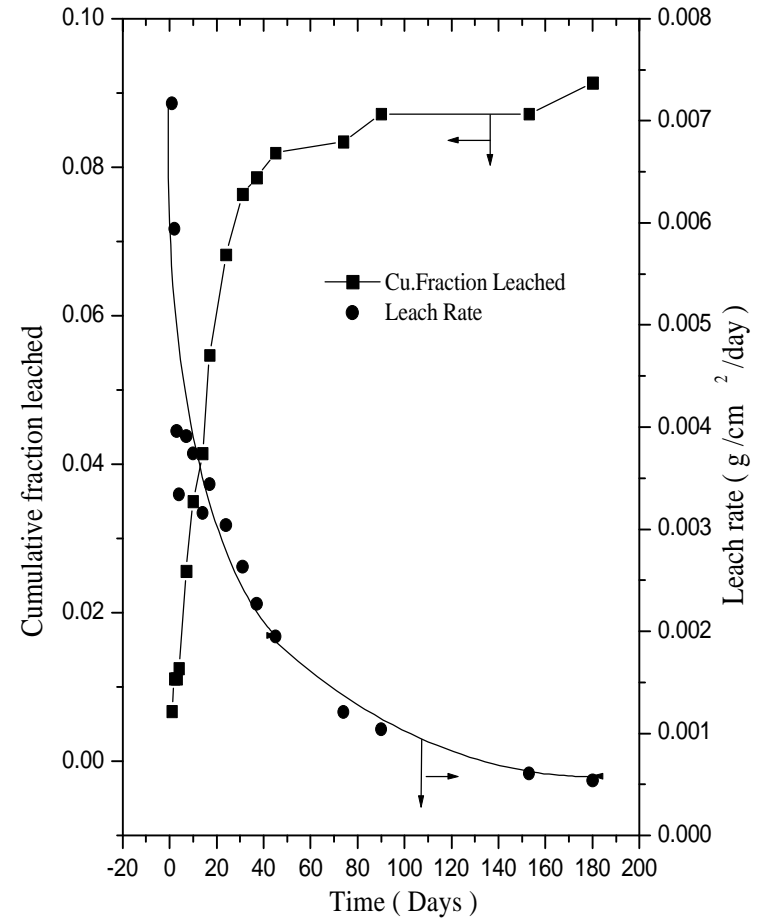


Fig.12 Cumulative fraction of ^{137}Cs leached and leach rate as function of time for OPC matrix block P

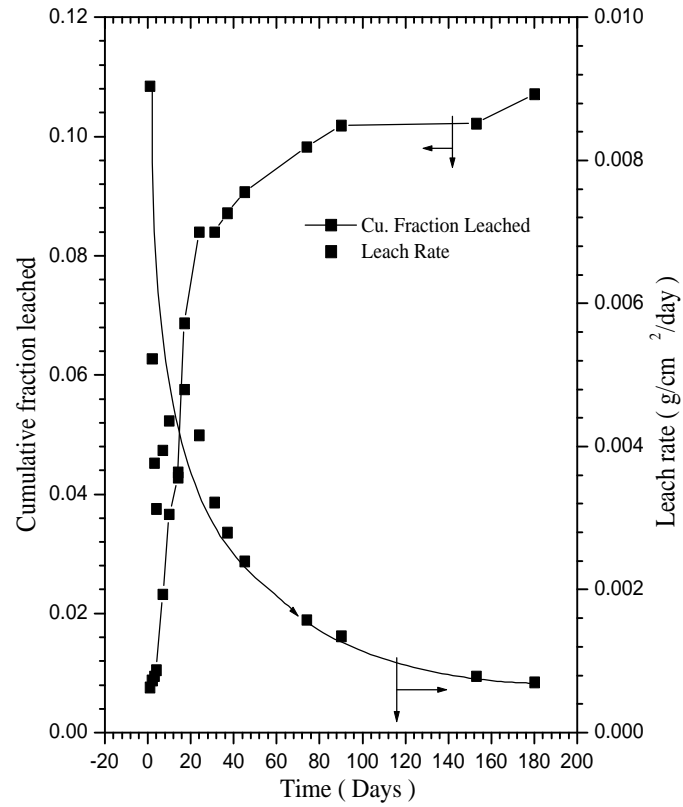


Fig.13 Cumulative fraction of ^{137}Cs leached and leach rate as function of time for OPC matrix block Q

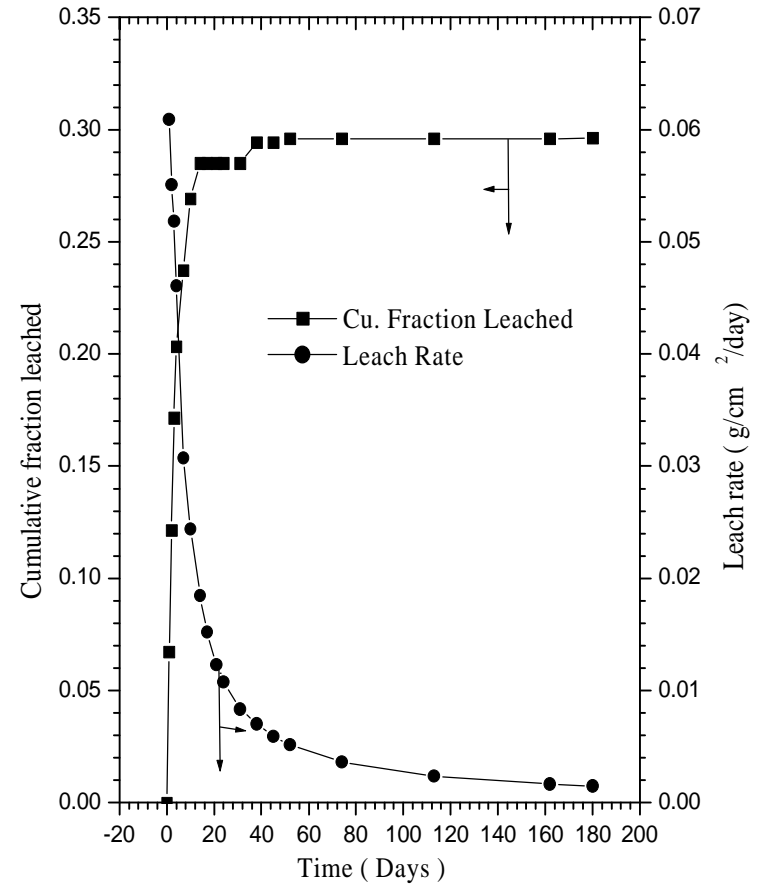


Fig.14 Cumulative fraction of ^{137}Cs leached and leach rate as function of time for OPC matrix block R

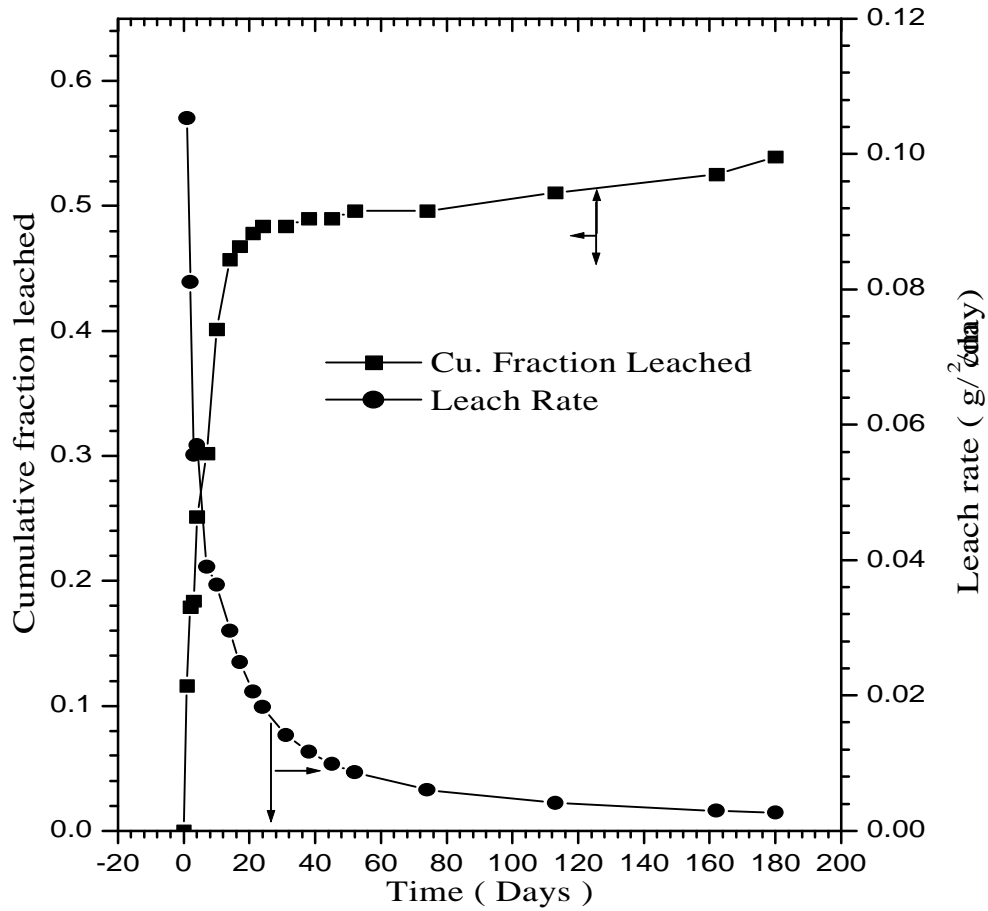


Fig.15 Cumulative fraction of ¹³⁷Cs leached and leach rate as function of time for OPC matrix block S

Table 4 gives Leach Index data of selected cement matrix blocks.

Table 4

Leach Indices of Selected Cement Matrix Blocks

| Block Code | Leach Index (LI) | Block Code | Leach Index (LI) |
|------------|------------------|------------|------------------|
| B | 9.9 | L | 9.8 |
| D | 9.8 | M | 10.2 |
| H | 8.6 | | |

4. RESULTS AND DISCUSSIONS

The swollen IX resins have specific gravity of 1.04. The swollen resins in flooded condition have inter-particle water whereas the gravity dried resins do not. For the OPC matrix blocks, resins were used under flooded conditions. Hence the water to cement ratio was lower at 0.2 to 0.4. For slag cement matrix blocks, IX resins were gravity dried and taken by weight. . Hence the water to cement ratio was higher at 0.4 to 0.58. Pyrolysis residues are dry solids with very low moisture content. The water to cement ratio in OPC matrix blocks containing pyrolysis residues was between 0.52 to 0.72. In all sets of matrix blocks, extra water added was just sufficient for maintaining required workability. Hence water/aqueous phase to cement ratio was not considered as factor affecting matrix characteristics.

Among the OPC matrix blocks indicated in Table 1, the OPC matrix blocks A and B incorporating anionic resins in borate form alone or along with cationic resins in Li⁺ form (blocks C and D) remained in perfect condition for 180 days of leaching. Comparison of leaching data presented in Fig 1 and 2 shows that the block B incorporating anionic resin in borate form was superior to block A. This is because the block B contained vermiculite as admixture in addition to CaO. The CF of ¹³⁷Cesium leached for block B was 0.046 and LR was 0.00019 g.cm².d⁻¹ in 180 days of leaching.

Comparison of Fig 3 and 4 indicated that block D showed lower CF and LR as compared to block C because of presence of vermiculite. The CF and LR values for block D were 0.05 and 0.00031 g.cm².d⁻¹ respectively for 180 days leaching. Comparisons of blocks A,B, C and D indicates that precipitated silica has no effect on CFs and LRs. The formulations of blocks B and D can be used for incorporating anionic resins in borated form alone or along with cationic resins in Li⁺ form respectively. As seen in Table 1, the VRFs for blocks B and D were 0.46 and 0.48 as against 0.5 achievable for polymer matrix. The leach indices of block B and D were 9.8 and 9.9 respectively which are comparable and satisfactory. OPC formulation of block D can be considered for immobilising anionic resins in borate form

The blocks E and F incorporating cationic resins in K⁺ form and anionic resins in borate form disintegrated on second day of leaching. This indicated the unsuitability of OPC matrix. Lithium and potassium are both alkali metals , hence properties of cationic resins did not contribute to disintegration of blocks E and F. Use of Aluminium nitrate in making blocks C and

D instead of water as in case of blocks E and F has improved integrity of matrix in blocks C and D because of formation of lithium aluminate[15]. This indicates that OPC is non compatible to cationic resins loaded with alkali in absence of specific admixtures. In another study [18], have observed that slag cement is compatible with alkali loaded cationic resins.

Slag cement matrix blocks G,H,I,J and K indicated in Table 2 were cured for 3 months instead of normal 1 month because, slag cement develops strength slowly and borates retard curing. Comparison of Fig 5 and 6 indicates that CF and LR are lower for block H than for block G in spite of higher loading of anionic resins in borate form. The CF and LR values for block H were 0.029 and $0.00036 \text{ g.cm}^2.\text{d}^{-1}$ respectively for 95 days of leaching. The extra quantity of anionic resins in borate form added in making block H has lowered the resin to bentonite ratio. Like IX resins, bentonite also shrinks in size due to loss of water during curing of cement matrix. In other study we have observed [18] that high bentonite content of matrix lowers compressive strength and increase CR and LR. The higher resin to bentonite ratio used in block G has increased its CF and LR.

Block I, J and K were prepared with $\text{K}_4\text{Fe}(\text{CN})_6$ and CuSO_4 solutions to incorporate copper hexacyanoferrate. Comparison of Fig. 7, 8 and 9 indicated that, Blocks I, having 52.92% loading of anionic resins in borate form, has no specific advantage of copper hexacyanoferrate addition. The slag cement matrix blocks J and K disintegrated in first week of leaching. This may be due to higher loading of anionic resins in borate form.

The VRFs of block H in Table 2 was 0.48 which compares very well with OPC matrix blocks B and D. Block H has high waste loading but because of bentonite swelling its VRF remained at 0.48. The leach index of block H was lower at 8.6 in comparison with 9.9 and 9.8 of blocks B and D respectively. These leach index values are based on 95 days leaching for block H and 180 leaching for blocks B and D. CF is directly proportional to square root of time whereas LR is inversely proportional to time. Since leach index is related to LR, it is likely to improve for block H as leaching progresses. Hence formulation of block H is preferred for immobilisation of anionic resins in borate form in slag cement matrix.

Pyrolysis of IX resins destroys its functional groups and polymer structure. The moisture content and swelling associated with IX resins are absent in pyrolysis residues. Borates remain as boric acid on the residue of anionic resins and alkali metals as hydroxides on the residue of cationic resins.

For incorporation of pyrolysis residue from anionic resins in borate form alone, CaO was added to precipitate CaBO_3 . Since $\text{CaO}/\text{Ca}(\text{OH})_2$ and boric acid are both sparingly soluble in water, formation of CaBO_3 may not be complete during mixing. CaO adds to volume of block decreasing its VRF. During cement hydration unreacted CaO becomes $\text{Ca}(\text{OH})_2$ which is one of the hydration product. It alters Ca/Si ratio of cement. Hence blocks L, M, N, O, P and Q were prepared with varying CaO content. As seen in Table 3, the VRF decreased with increasing CaO content. The comparison of Fig 10 to 15 indicates that there was gradual increase in CF and LR with increasing CaO content. The CFs for blocks L and M were 0.076 and 0.082 respectively. The LR values for blocks L and M were 0.00051 and 0.00054 respectively. Block L did not contain CaO. Hence there was no specific advantage of adding CaO to prepare OPC matrix blocks from pyrolysis residue of anionic resins in borate form. The leach indices of blocks L and M were 9.8 and 10.2 which are higher than any of the blocks incorporating anionic resins in borate form directly. The formulation of block L is most suited for this purpose.

The blocks R contained residues from cationic resins in Li^+ form and anionic resins in borate form. The block S contained residues from cationic resins in K^+ form and anionic resins in borate form. As seen in Figs 14 and 15, the CF values for R and S blocks were 0.3 and 0.54 respectively which are about an order of magnitude higher than for blocks L, M, N, O, P and Q. Similarly LR values were also higher by an order of magnitude. High alkali content was found to be detrimental for pyrolysis residue blocks. Hence pyrolysis residue of anionic resins in borate form needs to be separately immobilised. OPC matrix can be deployed for this purpose.

Pyrolysis of IX resins requires a dedicated set up having elaborate off gas treatment system. It involves additional pre-treatment step operating at 300°C . In absence of such facility, direct fixation of borated IX resins is preferred as their generations rates are low. The use of slag cement with 50 % slag content and vermiculite and bentonite as admixtures can give a good matrix.

5. CONCLUSIONS

Direct fixation of spent anionic resins in borate form is preferred as their generations rates and activity levels are low. The use of slag cement with 50 % slag content and vermiculite and bentonite as admixtures gave a good matrix. The cumulative fraction of 137 Cesium leached

was 0.029 and the $^{137}\text{Cesium}$ leach rate was $0.00064 \text{ g/cm}^2/\text{day}$ in 95 days for best slag cement formulation. OPC is non compatible to cationic resins loaded with alkali in absence of specific admixtures. Although OPC matrix blocks gave nearly same cumulative fraction leached and leach rate for $^{137}\text{Cesium}$ as slag cement matrix block, OPC requires separate treatment for cationic and anionic resins. Hence cationic resins loaded with alkali and anionic resins in borate form can not be immobilised together. The volume reduction factor achieved by direct immobilisation of anionic resins in borate form is around 0.48. The leach indices of the selected OPC and slag cement matrix blocks were above 8.6 which are satisfactory.

The cumulative fraction of $^{137}\text{Cesium}$ leached and $^{137}\text{Cesium}$ leach rate were 0.076 and 0.00054 respectively for 180 days leaching of OPC matrix block prepared after pyrolysing anionic resins in borate form. The pyrolysis of anionic resins as a pre-treatment step improved the volume reduction factor to 2.4. However pyrolysis of IX resins requires a dedicated set up having elaborate off gas treatment system to be operated at 300°C .

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