

Cation exchange applications of synthetic tobermorite for the immobilization and solidification of cesium and strontium in cement matrix

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Abstract. Immobilization and solidification of hazardous cations like Cs^{137} and Sr^{90} are required while handling the radioactive waste of nuclear power plants. Efforts are on to find a fail proof method of safe disposal of nuclear wastes. In this context, various materials like borosilicate glass, zeolites, cements and synthetic rocks have been tried by several workers. This communication deals with the synthesis, characterization, cesium uptake capacity and leaching behaviour of synthetic alumina-substituted calcium silicate hydroxy hydrate, which are close to that obtained for the natural mineral, 11 Å tobermorite. The synthetic mineral show cation selectivity for Cs^+ in presence of 500–1000 times concentrated solutions of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} and Sr^{2+} . Although the ordinary portland cement (OPC) which is often used in waste management operations alone holds negligible amounts of Cs^+ and Sr^{2+} , the addition of alumina-substituted tobermorite to OPC enhances the retention power of cement matrix by drastically lowering the leach rate of cations.

Keywords. Cesium; strontium; selectivity; alumina substituted tobermorite; cement matrix.

1. Introduction

Solidification is one of the key technologies for removing hazardous wastes. The technique consists of entrapping the waste within a solid matrix having high structural integrity, so that the risk of leaching from the waste body is reduced to minimum (Plecas *et al* 1992). Radioactive waste is an unavoidable by-product in nuclear energy production (Plecas *et al* 1985). After volume reduction and valuable component recovery, waste materials have to be conditioned by cement for transport, storage and disposal. Conditioning is the waste management step in which radioactive waste is immobilized and packed. The objectives of immobilization are to convert the wastes into forms which are (i) leach resistant and impermeable, so that the release of radionuclides will be slow even though flowing water may contact them and (ii) mechanically, physically and chemically stable for handling, transport and disposal (Plecas *et al* 1985, 1991a). Many different types of glass and ceramic waste-forms have been studied over a long period of time. Some of the waste forms considered include borosilicate, aluminosilicate, high silica and phosphate glasses, silicate-based glass-ceramic, titania-based crystalline ceramics, alumina-based ceramics, clay-based materials and various forms of cement and concrete. Waste forms have been examined in which the

radionuclides and other waste elements are incorporated directly into the waste form lattice on an atomic scale as solid solutions. In addition, the wastes are incorporated macroscopically into a separate matrix phase, which may be either metallic or non-metallic to form a composite material. Keeping above points in view, calcium silicate hydroxy hydrate (tobermorite) may successfully be used as an additive with ordinary portland cement to reduce the leach rate of cesium and strontium. It is well known that cement has many characteristics in its favour: (i) it is a readily available material which is widely used in civil engineering, (ii) the raw material is cheap and processing equipment can be based on conventional technology, and (iii) the resulting (cement + additive) blocks have good mechanical properties. They are noncombustible, radiation resistant, chemically stable and moderately resistant to the release of radionuclides (Plecas *et al* 1991b, c, 1995). Additives like vermiculite, fly ash, different types of slags, sodium silicate, polymer etc are incorporated at the manufacturing or application stage as property modifiers in improved blended cement formulations (Gandhi 1997).

2. Experimental

The material was synthesized from lime, silica and alumina by the hydrothermal method described elsewhere (Kalousek 1957; Shrivastava and Rashmi 1998). The

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product was characterized by chemical analysis and powder X-ray diffraction in the range $2\theta = 5-80$. The morphology of the specimen was also examined under electron microscope (Phillips 420 TEM). The cesium uptake experiment had been carried out as follows: 25 mg of sample was mixed with 75 mg of OPC, and this 1 : 3 ratio was maintained because on increasing the additive more than 33% the block starts losing their mechanical strength. The mixing of additive and OPC was conducted in dry state in mortar pestle followed by homogenization using ethanol. The mixture was then equilibrated with 25 ml of mixed aqueous solution containing 5×10^{-4} N Cs^+ and 0.1 N of M^{n+} (where $\text{M}^{n+} = \text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}$ and Sr^{2+}) ions, by using appropriate amounts of 0.0005 N $\text{CsCl} + 0.1$ N NaNO_3 , 0.0005 N $\text{CsCl} + 0.1$ N KNO_3 , 0.0005 N $\text{CsCl} + 0.1$ N $\text{Mg}(\text{NO}_3)_2$, 0.0005 N $\text{CsCl} + 0.1$ N $\text{Ca}(\text{NO}_3)_2$, 0.0005 N $\text{CsCl} + 0.1$ N $\text{Ba}(\text{NO}_3)_2$, 0.0005 N $\text{CsCl} + 0.1$ N $\text{Sr}(\text{NO}_3)_2$. pH of the mixed solution was about 7.15. The ionic strength for 1 : 1 and 1 : 2 ionic solutions were 0.1005 and 0.3005, respectively. Leach rate studies were performed using standard method (Hespe 1971). The general procedures adopted are given below.

(I) The 10, 20, 30 and 40% blocks each of similar dimensions (ht = 1.2 cm, r = 0.5 cm) were prepared by adding 90, 80, 70 and 60% of OPC to 14.4 wt% alumina-substituted tobermorite. The contents were thoroughly mixed in mortar pestle keeping total solid/water ratio = 0.6. This was later cured for 28 days in 100% relative humidity. The geometrical surface area of each cylindrical block was measured manually.

(II) Sealed polythene bottles were used as leachant containers.

(III) The leachant was 25 ml of distilled water at 25°C, renewed at each sampling. The sampling was done daily for the first week, weekly for three weeks and fortnightly for the rest of the period.

Cs^+ and Sr^{2+} analyses have been carried out on GBC 902D/B double beam atomic absorption spectrophotometer. Each experiment was performed in duplicate to record the final concentration change.

3. Results and discussion

X-ray powder pattern of the hydrothermally synthesized title phase $\text{Ca}_5(\text{OH})_2\text{Al}_x\text{Si}_{6-x}\text{O}_{16} \cdot 4\text{H}_2\text{O}$ matches in intensity and position with the JCPDS file (JCPDS 1989). It gives 22 reflections with 'd' values between 11.3 and 1.15 Å (figure 1). Figures 2 and 3 compare the lattice expansion of cesium exchanged phase with that of the synthetic alumina-substituted tobermorite. The powder pattern of the tobermorite loaded OPC shows largely a mixed pattern of crystalline and amorphous phase of both OPC and additive with lower intensity. The pattern of the mixture shows that the powder mix of OPC and tobermorite retains the tobermorite structure intact. However, the X-ray diffraction pattern of the blocks shows the presence of 'ettringite' along with highly disordered or even amorphous phases of other calcium silicate hydrates (Vlachou and Piau 1997, 1998). The scanning electron micrographs of the material show aggregate of lath like crystallites, which are 0.2–5.0 µm long and 0.2–1 µm wide (figure 4a). Cesium loaded tobermorite shows the change in shape of crystallites from plate like to lath like. The size of the crystal after cesium uptake remains same as seen in figure 4b. The typical lath like and plate like morphology of tobermorites is a function of the extent of Al-substitution and an inverse relationship between particle size and extent of Al-substitution has been confirmed (Komarneni and Tsuji 1989a).

Table 1 shows the data on selective uptake of the Cs^+ from mixed cationic solution. The cesium sorption properties of the material may be attributed to the crystallo-

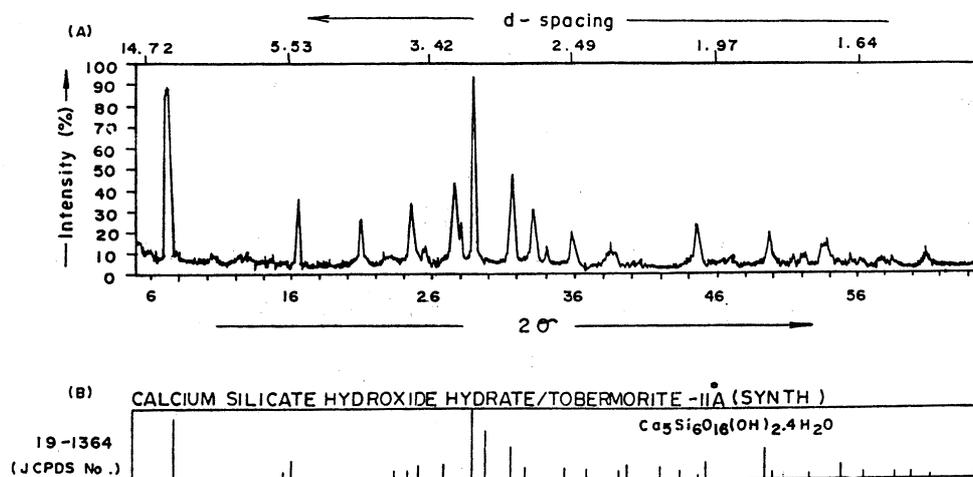


Figure 1. X-ray powder diffraction pattern of synthetic unsubstituted 11 Å tobermorite: (A) XRD pattern of synthetic sample and (B) JCPDS profile.

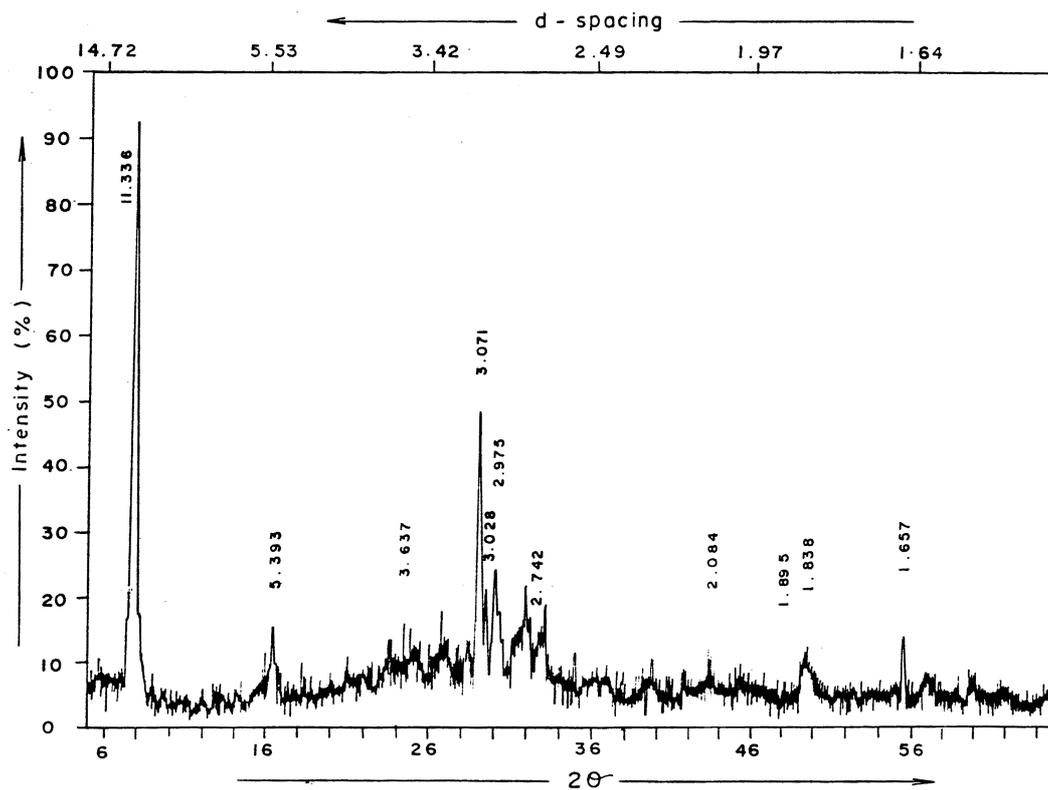


Figure 2. X-ray powder diffraction pattern of synthetic 10.0 mole% Al-substituted tobermorite.

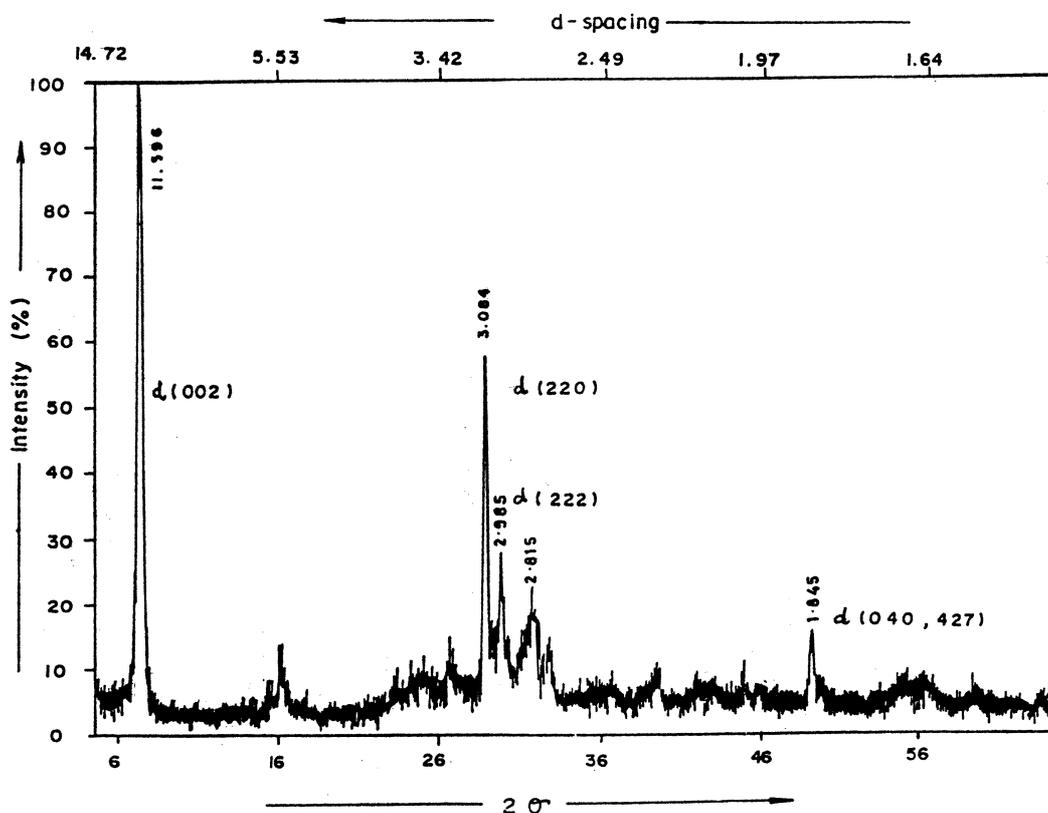


Figure 3. X-ray powder diffraction pattern of Cs⁺-exchanged 10.0% Al-substituted tobermorite.

chemical incorporation of cesium in layered lattice framework of tobermorite (Komarneni and Roy 1983). The cesium fixation in the layered lattice framework of the tobermorite is also confirmed by the expansion of d spacing from 11.336 to 11.596 Å. The uptake in tobermorite is partly due to the breaking of bonds from planar and edge surface sites of the layered lattice (Komarneni and Tsuji 1989a). It has also been observed that the Cs^+ removal decreases in the presence of larger cations like K^+ and Ba^{2+} whereas, in presence of other smaller cations like Na^+ , Ca^{2+} and Mg^{2+} the selective property of tobermorite is significantly retained (Komarneni and Tsuji 1989b; Shrivastava and Verma 1995b; Shrivastava *et al* 1995). The alkali metal ions have been found to lie in the sequence $\text{Li}^+ > \text{Na}^+ \gg \text{K}^+$ with respect to their tolerance of Cs^+ uptake onto synthetic tobermorite, indicating that K^+ causes the maximum hindrance in Cs^+ uptake. The blocking action appears to be a function of cation size. Similarly the selectivity sequence for alkaline earth metal ions exist as $\text{Mg}^{2+} > \text{Ca}^{2+} \gg \text{Ba}^{2+}$. The ion exchange remains selective for Cs^+ even in the presence of 500–1000 times

higher concentration of the competing metal ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} and Sr^{2+}).

Figure 5 shows the leaching curve obtained by plotting the cumulative leach fraction $(\Sigma An/A_0)/(S/V)$ vs leach time, t , where, ΣAn is the sum of the Cs^+ ($\mu\text{g}/\text{ml}$) released in all leaching periods up to time t , A_0 the initial Cs^+ ($\mu\text{g}/\text{ml}$) present in the block, V the volume of the block, S the surface area of the block and t the time (days). It is clear from figure 5 that, as compared to 100% OPC block,

Table 1. Selective sorption of Cs^+ onto 1:3 mixture of tobermorite + OPC in presence of strong solution of competing cations.

Ion pair [$\text{M}^{n+} + \text{Cs}^+$]	Initial Cs^+ ($\mu\text{g}/\text{ml}$)	Δ ($\mu\text{g}/\text{ml}$)	% Cs removal
Na + Cs	39.8	14.6	36.70
K + Cs	12.4	nil	nil
Mg + Cs	9.6	1.8	18.75
Ca + Cs	6.4	6.4	76.19
Ba + Cs	8.0	5.0	62.50
Sr + Cs	8.2	5.6	68.29

Wt. of exch. = 25 mg; wt. of OPC = 75 mg; vol. of soln. = 25 ml;

Normality of cations = 0.1 N M^{n+} + 0.0005 N Cs^+ [$\text{M}^{n+} = \text{Na}^+$, K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , and Sr^{2+}].

Equilibration time = 7 days, pH = 7.15.

Δ = Initial concn. Cs^+ , final concn. Cs^+ .

$$\% \text{ Cs removal} = \frac{\Delta \times 100}{\text{Initial Cs concn.}}$$

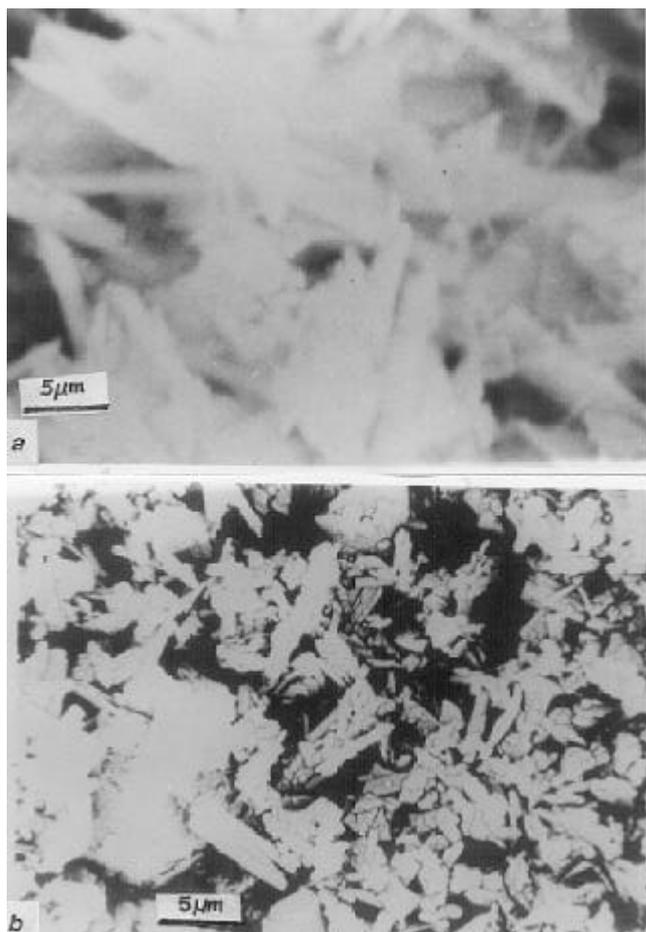


Figure 4. Scanning electron micrographs of **a.** alumina-substituted tobermorite and **b.** Cs loaded alumina-substituted tobermorite.

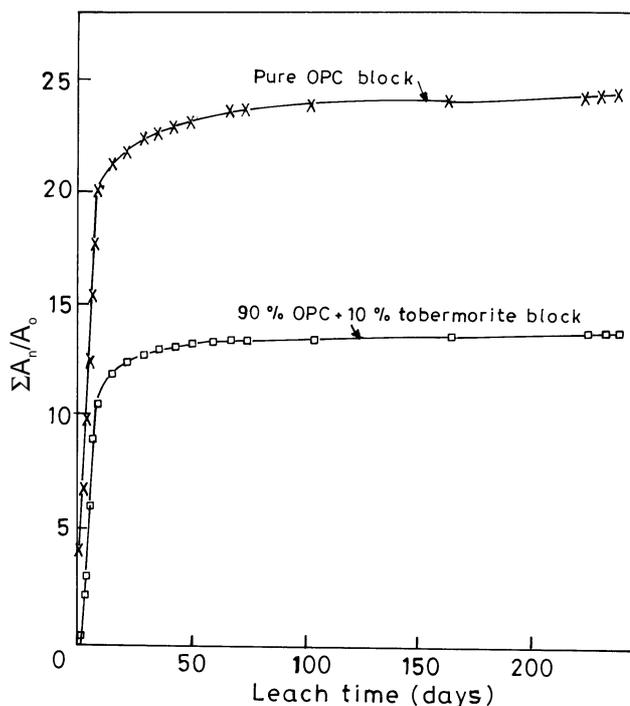


Figure 5. Cesium leach rate profile of 10% block of 14.4 wt% alumina-substituted tobermorite in ILW.

the block prepared by adding 10% tobermorite and mixing it with simulated intermediate level waste (ILW), the cumulative fraction leach rate decreases by a factor of 10, thus indicating that OPC mixed additive can be effectively used to separate Cs^+ from ILW (Shrivastava *et al* 1994). The composition of ILW simulate is as follows (g/l). $\text{Na}^+ = 114.17$, $\text{Fe}^{3+} = 0.025$, $\text{Al}^{3+} = 9.98$, $\text{OH}^- = 21.22$, $\text{NO}_2^- = 4.80$, $\text{NO}_3^- = 160.20$, $\text{CO}_3^{2-} = 6.24$, $\text{Cs}^+ = 0.01$, $\text{Sr}^{2+} = 0.01$, UO_2^{2+} in trace amounts (sp. gravity 1.19). The calculated quantities of corresponding water soluble salts were mixed to adjust the composition in g/l (Wattal *et al* 1989).

Figure 6 shows a comprehensive data profile obtained from five test blocks. The reference block contains only OPC whereas, the other four-test specimen are prepared from the additive and OPC in four different proportions (10, 20, 30 and 40). The mixing of the synthetic alumina-substituted calcium silicate hydroxy hydrate along with OPC increases its Sr^{2+} retention power while OPC alone shows poor uptake of Sr^{2+} . This is demonstrated by the study of leach rate data on the five different blocks. Leach rates (LR) were calculated using the Hespe formula:

$$\text{LR} = l.w/c.t.s.$$

where, l is the quantity of ion in leach solution ($\mu\text{g}/\text{ml}$), c the quantity of ion left in solid block ($\mu\text{g}/\text{ml}$), w the wt. of block (g), t the time of leach (days), and s the surface area of the test specimen (cm^2). Leach rates expressed as $\text{g cm}^{-2} \text{day}^{-1}$ on log scale were plotted against leach time in days. The entire leaching period can be broadly divided into three regions. Region I from 1 to 7 days, region II from 8 to 50 days and region III from 51 to 90 days. Region I shows the initial leaching within first 7 days, i.e. leaching from superficial surfaces of the block. Region II shows that after initial leaching within first seven days, there is a drastic reduction in release of Sr^{2+} ions from the blocks which is maintained over a longer period of time (50 days). In region III the leach rates are further lowered to 10^{-5} to $10^{-6} \text{ g/cm}^2 \text{ days}$. This trend continues up to 90 days. The leach behaviour of the blocks can be explained as a combination of the two processes: (i) surface wash-off mechanism and (ii) diffusion stage mechanism. Region I shows the maximum leaching of the Sr^{2+} ions because of surface wash-off process. In this process a rapid equilibrium is established between ionic species present in the surface pores of the portland cement block and ions in the leachant solution. When all the Sr^{2+} has been leached out from the surface of the block, the Sr^{2+} ions migrate by longer pathways from the bulk (Crawford *et al* 1985). It is this diffusion-controlled stage which determines the long term leaching behaviour of the block. The final analysis of the post leached blocks have shown that strontium content appears to be permanently fixed in cement matrix. Analysis of the post leached block shows that up to a maximum of 38.20 meq of $\text{Sr}^{2+}/100 \text{ g}$ could be fixed in

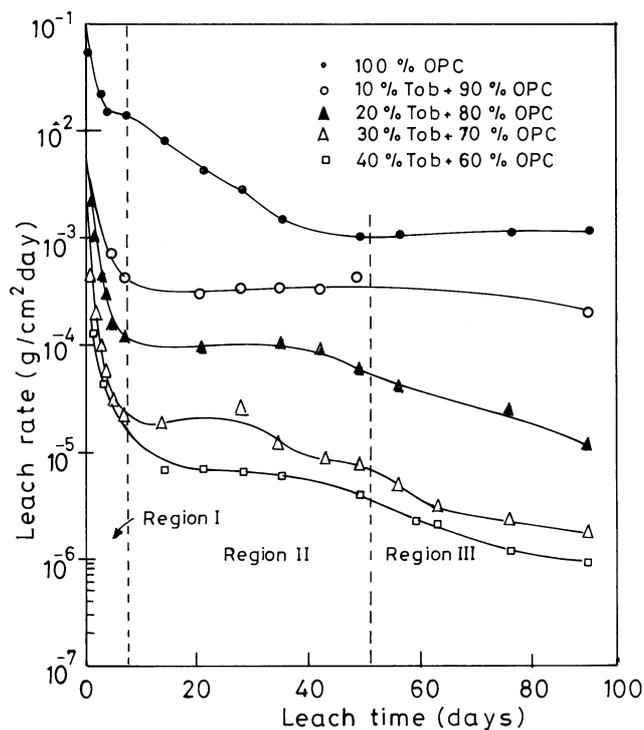


Figure 6. Leach rate profile of Sr^{2+} from OPC + 14.4 wt% alumina-substituted tobermorite.

the blocks. It may be concluded from the data that (i) the synthetic phase of alumina-substituted tobermorite could be used for decontamination of radioactive Cs and Sr containing waste effluent, (ii) the title phase acts as an additive to OPC without degrading its mechanical strength and other properties and (iii) that the long-term leach rate of cesium and strontium from OPC can be drastically reduced by addition of ≈ 14.4 wt.% of alumina substituted tobermorite in appropriate quantity.

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