

DESORPTION OF RADIOACTIVITY FROM THE NEARSHORE SEDIMENT

B. Patel, S. Patel, S. Pawar

Health Physics Division

Bhabha Atomic Research Centre, Trombay, Bombay 400 085

INTRODUCTION

The radioactive low level aqueous wastes originating from the fuel reprocessing facility at Trombay are being discharged after monitoring into the Bombay harbour (Fig.1). The present paper in continuation of our earlier publication (1), discusses the possible mechanism involved in the sorption-desorption of cesium-137, cerium-144 and ruthenium-106 from the sedimentary particles under environmental conditions.

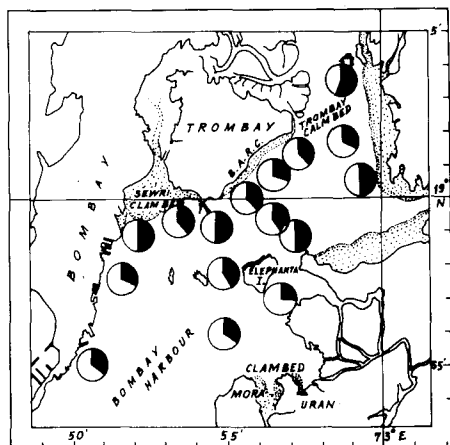
DISTRIBUTION OF RADIOACTIVITY IN THE BOMBAY HARBOUR SEDIMENT

In general, the concentration of cesium-137, cerium-144 and ruthenium-106 in the bed material was found dependant upon the ambient concentrations, which in turn were similarly dependant upon the release. The levels of radioactivity deposited were found to drop sharply with the distance from the discharge point. Thus the sedimentary radioactivity decreased by more than hundred times towards the mouth of the harbour, about 15-20 kms away from the discharge point and was beyond detection limit about 100 kms away.

During the present studies the absolute levels of all the three radionuclides in the surface sediment from the Trombay clam bed (Fig.1) were found to drop significantly with time (1971-76)-after reaching apparent peak concentrations in 1971-as is evident from Fig.2, which records the annual average concentration of the three nuclides. Similar drop, ranging from 50 to 70 % over a period of three years, in the sedimentary radioactivity was also observed over the entire 240 km² of the harbour bed as seen from Fig.1, which records the distribution pattern of cesium-137 in the bed material during 1971 and 1974. In the vertical profile of the bed also similar drop in the cesium activity, amounting to about 48-57%, was evident (Fig.3). It will be seen from the exponential decrease in the radioactivity (Fig.2),

that the effective sedimentary half life ($T_{eco}/2$) for cesium-137 works out to about 1.86 years, which is significantly shorter than its radiological half life (33

Fig.1: Bombay Harbour and environ showing the clam beds and percent cesium 137 activity retained or desorbed from the bed material in March 1974, as compared to that observed during March '71. The full circle represents the observed concentration during 1971 and the shaded as the fraction retained during 1974 at various stations.



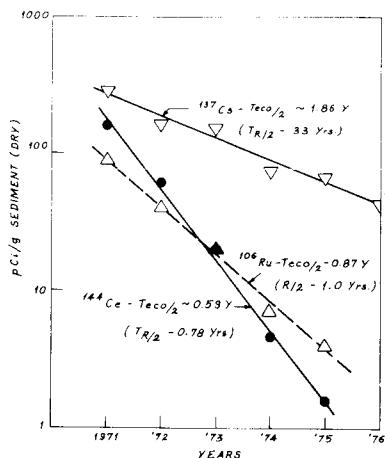


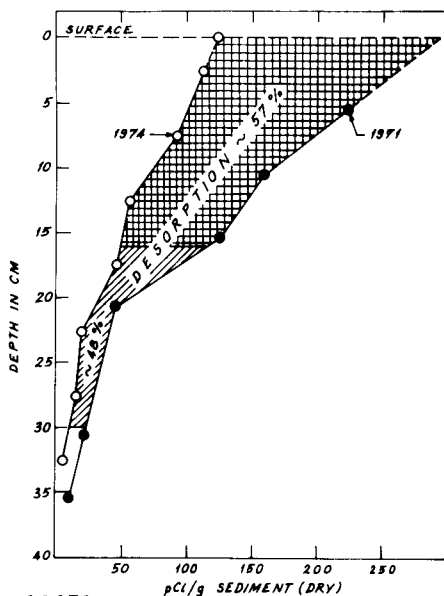
Fig. 2: Annual average distribution of cerium-144(●), ruthenium-106 (Δ), and cesium-137(▽) in the sediment from Trombay clam bed during 1971-76.

years). On the other hand, the effective sedimentary half life of ruthenium-106 and cerium-144 comes out as 0.87 and 0.59 years respectively, and are practically the same as their radiological half life (1.0 and 0.78 year). This clearly demonstrates the efficiency of the environment in the removal of cesium-137 from the sediment. The observed minor differences in case of ruthenium and cerium after allowing for their radiological decay could be due to the influx of fresh sediment rather than due to those causes which deplete radiocesium in the sediment. Assuming the sedimentary half lives of cerium and ruthenium to be meaningful and ruling out other parameters for the observed decrease in the sedimentary radioactivity, one could easily see that there is an influx of about 20% of fresh sediment. Allowing for this sedimentary influx, especially during monsoon run-offs, and the natural decay of cesium-137, the observed effective half life of the radionuclide should have been about 26 years instead of 1.86 years, as has been observed (Fig. 2). It is tempting to suggest that the environment or some physico-bio-chemical properties of one or more of its constituents is playing a significant role in bringing down the levels of cesium activity in the bed material, at a rate much faster than its natural decay.

MECHANISM OF SORPTION-DESORPTION

The observed drop in radioactivity of the sediment may well be due to biotic and abiotic environmental parameters. These include the removal of radioactivity by heterotrophic bacteria and/or through the ingestion

Fig. 3: Distribution of cesium-137 in vertical profile at a mid-stream station off the discharge zone in the Bombay harbour during March 1971 (●) and 1974 (○). Assuming the sedimentation rate of about 1 cm/year at the station, the profile for the year 1971 has been plotted with its surface layer about 3 cms deep with reference to the surface layer of 1971.



by benthic communities. The drop in activity to a certain extent, could also have been accentuated by the influx of fresh material and/or through the tidal currents leading to churning of the mobile layer of the sediment, which in turn may cause frictional detachment, and/or by the subsequent movement of the bed material from the area of higher or lower concentrations to the region under study. Notwithstanding these mechanisms, the desorption of some radionuclides (cobalt-60, zinc-65, cesium-137) from the sedimentary particles have been observed under laboratory conditions, with sufficient concentrations of radioactivity in the superincumbent sea water. Thus about 10% of cesium-137 was desorbed from the sediment- both original and one made free of organic matter- after 50 days of exposure and attaining peak sorption despite the presence of radioactivity in the medium (2).

The sorption mechanism of the radionuclides follow either isotopic exchange reaction with kinetics comparable to an ion-exchange type reaction or isotopic exchange through precipitation and dissolution reactions or a mixture of precipitation and ion-exchange reactions with formation of compounds. The sorption of cerium and ruthenium radionuclides is found through precipitation and formation of compounds, whereas that of cesium has been observed through an ion-exchange type of reaction either with potassium or magnesium or sodium (3). The sorption-desorption of various radionuclides also depend upon the crystal structure and the physico-chemical characteristics of the sedimentary particles and of the nuclides. The Bombay harbour sediment has a large quantity of clay mineral, especially illite (32-34%), the major exchangeable ion of which is potassium. It has high organic (3%) and iron-contents (7.5%), with a specific surface of 187-188 m²/g and the base exchange capacity of 46-47 meq./100 g. These characteristics of the sediment have been found to allow a ready sorption of the cesium radionuclides, the half-uptake time to reach an apparent equilibrium state being only 0.4 day (1,3). The rates of sorption of cerium-144 and ruthenium-106 have been found relatively slow though these nuclides have higher sorption distribution coefficient (10⁴-10⁵) than has cesium-137 (10³, 1). Further the cesium sorption is found suppressed at higher salinity due to increased concentration of the exchangeable ions (K⁺, Na⁺, Mg⁺⁺), which are known to reduce the binding sites of cesium on the clay (4). In the laboratory experiments, the desorption of cesium isotopes was found dependant upon the salinity, Fig. 3. The maximum desorption (40%) occurred at normal harbour salinity (38 ‰) and the minimum at the lowest salinity (9.5 ‰) studied, after 10 days of mechanical shaking. Thus the cesium desorption was found directly proportional to the exchangeable co-ion concentration. The salinity dependance of sorption-desorption of radiocesium further shows that with the influx of fresh water during monsoon (June-September), the retention of cesium by the sediment is relatively better than during the rest of the year. These observations incidentally explain our earlier findings that there was little change in the sedimentary radioactivity during and after monsoon, when the salinity was observed to go as far down as about 4-8 ‰ in the harbour (1).

The sediment on treatment with ammonium acetate pH 7.0, ammonium acetate/acetic acid (1:1) pH 5.4 and 5% EDTA pH 7.0, was found to desorb about 15-15, 22-26 and 15-24% radiocesium respectively within

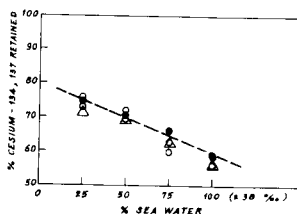


Fig. 4: Effect of salinity on desorption of cesium-134, 137 in the sediment from Bombay harbour (●- ^{137}Cs) & Tarapur (○- ^{137}Cs , Δ - ^{134}Cs) after ten days of shaking under laboratory condition.

The failure to observe the desorption of cerium and ruthenium radionuclides in the laboratory experiments may well be due to their extremely low concentrations in the sediment samples from the environment (Fig. 1). The desorption of these nuclides was not expected, since these are sorbed through complex reactions involving ion-exchange, precipitation and formation of compounds (5), which are difficult to solubilize at sea water pH. However, both the nuclides could be complexed (22-77%) with EDTA (6). The cesium radioactivity, on the other hand, could be easily desorbed or exchanged through the same ion-exchange mechanism working in either direction, when washed with sea water free of radioactivity or with very little cesium activity at sea water pH and at normal concentrations of exchangeable co-ions (K/Na/Mg). The former situation is expected when the sediment is transported from the contaminated to non-contaminated zones along the coast and later when the radioactivity discharges are extremely low/stabilized.

In general, our field and laboratory observations on the desorption - particularly of cesium - under depleted environmental conditions are contrary to those observed by others through laboratory experiments alone. We find that cesium sorbed on the marine sediment is readily desorbed under favourable environmental conditions, including the transportation of the sediment from the discharge zone to non-contaminated areas. This needs to be confirmed in other coastal environments, where fairly long residence time for cesium radionuclides has been predicted. This has recently become more imperative because of possible increased discharge of radioactive wastes in the coastal zones. The fact that the environment can decontaminate itself, as has been observed here, offers a possibility to revise the present levels of maximum permissible discharges especially those in which radiocesium dominates.

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