



A CRITICAL REVIEW OF SELECTIVE ABSORBERS FOR RADIOACTIVE AND HAZARDOUS SPECIES

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Abstract

Selective removal of radioactive and hazardous species has been a fertile research area for several years. However, for commercial application sorbers need to possess satisfactory properties beyond selectivity and these are reviewed. The benefits of selectivity itself need to be set against the limits for liquid discharges and categorisation of solid wastes. Two examples are given to illustrate the aspects described.

Many current and potential applications of selective adsorbers are to process streams which were not designed for waste management, but consideration of this at the planning stage as now occurs in the nuclear industry can lead to economic benefit.

1. INTRODUCTION

Selective removal of radioactive and hazardous species has been a fertile research area for several years and has also provided a potential application for research from earlier years on complex formation which initially had only a curiosity value. In many instances, the nature of waste streams (liquid) or waste materials (solid) has been determined in advance of legislation now applying to discharge or disposal. These situations often present particularly challenging clean-up problems. Process development might be very different when waste requirements are incorporated at the design stage.

Selective absorbers for a particular element or species can be considered against several properties such as:

- (i) distribution ratio or selectivity
- (ii) reversibility
- (iii) absorber stability (radiation, chemical)
- (iv) absorber form
- (v) cost and supply

However it is important first to consider some target levels which treated liquid and solid wastes must meet, so as to have a perspective on the extent of decontamination which may be required. Unfortunately, different countries define standards in rather different ways. To some extent this reflects the difficulty in defining a publicly acceptable or scientifically justifiable concentration. The sensitivity of measuring or monitoring devices is also pertinent.

This review begins with an initial brief discussion of some legislation, to give a feel for the extent of treatment which may be required. It then goes on to discuss in general terms, with some specific examples, absorber properties, as broken down above. Two examples are then given to illustrate some of the aspects described.

2. LEGISLATIVE BACKGROUND - RADIOACTIVITY

2.1. LIQUID DISCHARGES

Historically in the United Kingdom, major nuclear installations such as power stations, reprocessing facilities and prototype reactors were generally constructed on coastal sites where the sea offered a ready means of dilution of liquid discharges. Countries with less significant or no coastal boundaries that have developed nuclear power facilities, have often sited such facilities on rivers or lakes.

Again historically in the United Kingdom, radioactive liquid discharge limits were considered in relation to the critical group, those people whose lifestyle predisposed them to the largest exposure to discharged radioactivity by known pathways. This type of logical but narrow assessment allowed very substantial discharges from establishments such as Windscale in the 1970s. Gradually the focus for liquid discharge authorisations moved from what was considered necessary to what could be achieved. Concepts such as ALARP (As Low As Reasonably Practicable), ALARA (As Low As Reasonable Achievable) were favoured, paralleled by the perhaps slightly less onerous BATNEEC (Best Available Technology Not Entailing Excessive Cost) for non-radioactive waste applications. Some have questioned the real value of expenditure to meet or stay well below current authorisations compared with the benefits of direct expenditure on human and environmental problems.

2.2. SOLID WASTES

The regulations vary in different countries, and IAEA have recently issued a safety guide which discusses possible approaches to the classification of radioactive waste [1].

There is often a desire to define a level below which radioactive material need not be controlled, but this is not always achieved although several countries have exemption levels, and in some cases specific substances, unconnected with the nuclear industry may be exempt. The level exemption levels for nuclear waste are of the order of kBq/kg.

At the other end of the radioactive waste scale comes high level waste which is characterised primarily by its continued high heat generation. The vitrified fission products from reprocessing operations come into this category, but long stored thermal reactor fuel would probably not.

Solid wastes with intermediate characteristics are distinguished in some countries, e.g. USA, Spain, Italy, on the basis of half-life and in others simply on the basis of total activity, although a distinction is usually made between alpha and beta/gamma activity. In the UK, waste with <12 MBq/kg beta/gamma and <4 MBq/kg alpha is classified as low level waste, LLW, and waste with higher levels but not classified as heat generating is classified as intermediate level waste, ILW.

Thus very roughly LLW spans a factor of 10000 in activity between the exempt and ILW limits, and the activity span covered by ILW will also be several orders of magnitude. This perspective is important in considering the merits of selective absorbers.

3. ABSORBER SELECTIVITY OR DISTRIBUTION RATIO

There are different ways of expressing how effectively an absorber removes a desired nuclide, often depending on the process objective.

3.1. DISTRIBUTION RATIO

If it is simply required to remove activity from solution e.g. by contacting with a solid, the distribution ratio is often used. This is an experimentally measured quantity defined, for a solid sorber in contact with a solution containing species A, as

$$\text{final concentration of A on sorber} / \text{final concentration of A in solution}$$

Since the concentration of A on the sorber is measured as amount or activity per unit mass, and the concentration in solution by amount or activity per unit volume, the units of the distribution ratio are volume/mass, e.g. m³.kg⁻¹. The distribution ratio as mentioned above is an experimentally measured quantity, and it may depend on the concentration of A and the solution properties (e.g. ionic strength), as well as on sorber surface to volume ratio.

This quantity is often used to describe sorption on natural materials.

3.2. SELECTIVITY

Under circumstances where it is desired to remove one, usually active, chemical species A in presence of another often chemically similar but inactive species B, a quantity called the selectivity is often used, defined as

$$(\text{concn of } A \text{ on sorber} / \text{concn of } B \text{ on sorber}) / (\text{concn of } A \text{ in solution} / \text{concn of } B \text{ in solution})$$

This quantity is dimensionless.

For example, it is useful to describe the efficiency of removal of caesium in the presence of relatively large amounts of sodium, and strontium from large concentrations of calcium or magnesium, cobalt from iron.

3.3. DECONTAMINATION FACTOR

On some occasions, the term decontamination factor is used. This generally expresses the ratio of contamination level before treatment to that after treatment, and the quantity is dimensionless. It is a useful quantity when considering removal of activity from solids and in treating solutions e.g. by precipitation or flocculation.

3.4. DISCUSSION

The different ways of expressing the ability of sorbers to take activity out of solution, outlined above, do not lead to simple numerical generalisations, and can sometimes make literature comparisons difficult.

TABLE 1. EXAMPLES OF DISTRIBUTION RATIOS (R_D), SELECTIVITY (X) AND DECONTAMINATION FACTORS (DF).

Nuclide	Sorber	R_D (mL/g)	X	DF	Comment
Pu	Charcoal	150			
	Silico-titanates	>2000			
	Alumina	3000			
	Argillite	>10000			
Cs	Zeolite	10^5		40,000	
	Lewatit DN		100		in presence of sodium
	Resorcinol - formaldehyde resin	3×10^4			
	$K_2CoFe(CN)_6$ Silico-titanates MAG*SEP _{SM} / clinoptilolite	>103	> 10^4		100 ppm Cs ⁺ in 5 M Na ⁺ Application to milk Ref. 10
Sr	Synthetic Chabazite	4000			in 0.5 M NaNO ₃
	" "	250			in 0.5 M Ca (NO ₃) ₂

This can be seen from examples given in Table I. It is obviously useful to assess both the decontamination factor and the selectivity desired in choosing a suitable sorber.

Thus to remove caesium from milk in the region around Chernobyl to give an activity below the intervention level of 370 Bq/L ^{137}Cs requires only a modest decontamination factor of about 10 (e.g. [2]), but a suitable process needs to leave the milk otherwise unchanged, i.e. without removal of other nutritionally important constituents and without addition of undesirable, though non-active, contaminants.

In other instances, the extent of decontamination required would lead to very inefficient use of sorber in a one stage process, thus prompting consideration of multistep processing. For this to be successful the initial sorption process or processes must be reversible, and this is discussed below. (Reversibility is also important if the cost of the sorber or its other attributes makes disposal undesirable - see later).

4. SORPTION REVERSIBILITY

The criteria for satisfactory sorption reversibility usually include relatively rapid kinetics to give reasonable cycle times, no degradation of sorber in the desorption cycle, no detrimental addition of chemicals to the process stream containing desorbed material.

Many natural absorbers, though having good sorption characteristics, are not amenable to straightforward reversion of the sorption process. This is well illustrated by inadvertently contaminated soils which hold activity strongly, resist activity dispersion by leaching, and now require decontamination as part of remediation programmes. Sorbed species may be recovered by treatment with strong chemicals, such as concentrated acids, but this often brings host materials into solution, complicating further processing, and preventing re-use of sorber.

To date the most suitable sorbers for regeneration and re-use are generally those which have been specially designed for this purpose and where the sorption process is well characterised. The few suitable natural materials include zeolites, such as clinoptilolite.

Ion exchange processes are often rapidly reversible, the desorption being achieved by exposure to a high concentration of a species which is probably less selectively sorbed. This method inevitably introduces an additional ion burden into the desorbed stream, which may or may not complicate further treatment.

The removal of activity by complex formation can, with careful design, sometimes be reversed semi-quantitatively, i.e. without the need to add a large excess of reagent, and also benignly, i.e. by simple pH changes or perhaps change in solution oxidation potential.

5. ABSORBER STABILITY

Satisfactory sorbers need to withstand the sorption process conditions, and consideration also needs to be given to behaviour during subsequent storage and processing for disposal.

5.1. SORBER STABILITY IN SORPTION PROCESS

Solutions from which it is desired to remove activity or trace elements may sometimes be strongly acid or fairly strongly alkaline. Aluminosilicates, which can be very effective for activity removal by ion exchange, are not stable indefinitely in alkaline solutions above about pH10.5. If such materials are to be used for caesium removal from alkaline solutions, the solution pH must be brought down beforehand, e.g. with carbon dioxide as used by British Nuclear Fuels Ltd in the SIXEP plant at Sellafield. Alternatively alkali-tolerant synthetic organic resins can be used to remove caesium from alkaline solutions, as practised by Nuclear Electric (See Section 8).

Sorbers with very high capacity and/or high selectivity may be subject to high radiation doses by dose accumulation if the sorber is recycled, potentially limiting extent of re-use. If the sorber is not reused, but

stored with its retained activity pending final processing for disposal, some consideration needs to be given to any changes in suitability for consolidation or encapsulation. However lifetime doses can be simulated fairly rapidly and this aspect of sorber stability checked.

There may be some aspects of sorber stability which affect both storage and disposal safety issues. One could mention combustion characteristics of organic resins which may be relevant to consideration of external hazards, and possible microbial degradation organic resins.

6. ABSORBER FORM

To achieve efficient use of absorber and rapid processing it is desirable to have a large absorber surface area to solution volume, effectively good absorber mixing. It is also necessary to separate the absorber readily and this tends to favour solid absorbers for use with solutions, although solvent extraction is a classic method and used in conventional reprocessing technology.

A very common form of solid liquid interaction is that achieved by passing the liquid through a bed of the solid. This achieves good use of absorber capacity, and is particularly convenient if the sorber is regenerated and reused, i.e. discharge of sorber is infrequent. In such flow processes particle size is important to avoid high pressures/low flow rates. Beds are however less suited to instances where the liquid to sorber volume ratio is very large, and to instances where the liquid is an intermediary for the transfer of activity from another solid such as soil. Composite sorbers have been manufactured with specific properties. Thus sorbers incorporating magnetic particles allow ready recovery of sorber after dispersion in a liquid [3]. Another example of a composite sorber combines the selective advantages of inorganic sorbers with the controllable physical properties of synthetic resin particles [4]. Examples of sorber form are given in Table II.

TABLE 2. EXAMPLES OF DIFFERENT ADSORBER FORM TYPE

Natural Materials	Coal Clays Coconut Husks Shell
Inorganic	$K_2CoFe(CN)_6$ Silicotitanates Synthetic Zeolites
Organic Resins	Weak Acid Strong Acid Chelating
Composite	Organic/Inorganic Magnetic/Inorganic Magnetic/Organic

7. ABSORBER COST AND SUPPLY

The cost effectiveness of an absorber depends in large part on the difference between disposal costs before and after treatment, compared with the treatment cost.

For example, there are cases where treatment results in 'free release' of a large volume of liquid or solid material, and a relatively small quantity of waste which requires protected disposal. In other instances treatment produces little free release material, but alters or splits the waste classifications. (As a gross example of this, fuel reprocessing produces a range of waste categories from irradiated fuel which, if disposed of directly, would probably fall in an intermediate category.) The benefit of concentration of activity depends

Operations	
Option (1)	Option (2)
Box and bury	Soil washing
Recovery	Recovery
Packaging	Processing
Disposal of final volume	Disposal of reduced final volume

Capital costs
 Operational costs
 Waste costs
 (Decommissioning)

Breakeven cost between approach (1) and (2) occurs when:
 Process Cost (2) = Disposal Cost (1) - Disposal Cost (2).
 If the disposal costs are high or the difference in the final disposal volumes is large then the processing option becomes economic.

FIG. 1. Outline cost benefit analysis.

on disposal costs which are often not known. Volume reduction, i.e. concentration, may be offset by the need for shielding or enhanced interim storage arrangements, e.g. cooling.

An example of a simple cost benefit analysis is shown in Figure 1.

In planning for processes which will operate over protracted timescales, manufacturing scale and security of supply of sorber material are factors which have to be addressed.

8. CAESIUM REMOVAL FROM MAGNOX FUEL STORAGE PONDS

The history of removal of caesium from cooling pond water in which uranium metal fuel from the first generation of civil nuclear reactors in the UK illustrates several of the general points made above.

The UK Magnox reactors have magnesium clad uranium metal fuel elements. It was intended that after discharge the fuel elements would be stored briefly (100days) in cooling ponds on station sites to allow iodine and heat to decay prior to transport to Sellafield for reprocessing. Station fuel ponds were originally not provided with caesium removal facilities since the expectation was that although magnesium was vulnerable to aqueous corrosion, clad penetration would be avoided by a short residence time.

However a combination of factors resulted in fuel having to be held in station ponds for longer than intended, with the result that clad was locally penetrated by pitting corrosion exposing uranium metal which also corroded in water releasing caesium. The corrosion of magnesium could be inhibited by making the pond water alkaline, but this complicated caesium activity removal, which was judged necessary to ensure that discharge limits could be met. First the pH increase introduced a large sodium ion burden into the pond water, requiring an absorber which was highly selective for caesium, and second the absorber needed to tolerate the alkaline conditions. This latter constraint essentially ruled out aluminosilicate sorbers which have an attractive selectivity for caesium over sodium. Finally a phenol formaldehyde methylene sulphonc acid resin was adopted, sold as Lewatit DN.

The Lewatit DN was to be used to exhaustion, and then disposed of. At the time sea dumping of radioactive waste was an annual event in several European countries. There was an activity limit, and the main other criterion was that the package would sink. Safety assessments assumed immediate release of all activity as soon as the package reached the sea floor. This was the 'dilute and disperse' approach. If sea dumping ceased, it was recognised that waste would have to be surface stored and then land disposed, and treatment options for the Lewatit resin were examined against what was described as the 'concentrate and contain' philosophy.

At exhaustion after passage of pond water, the active sites on the Lewatit DN were mainly occupied by sodium, since although the selectivity for caesium over sodium was a factor of 100, the sodium to caesium ratio in solution was several orders of magnitude higher than this. Resin regeneration and secondary sorption was attractive, but as discussed in Section 4, it was desirable to avoid the introduction of further competing cations in the regeneration step. Ammonium carbonate was therefore proposed as a regenerant [5] as there had already been some experience with this material [6] which can be removed from the regenerant solution by heating and recovered for re-use.

The activity of caesium on the resin at initial exhaustion may be roughly estimated assuming the resin capacity is 1 mequiv per g, the selectivity for caesium is 100, the pond water has a sodium content of 5 mequ Na/litre and a caesium activity in the pond water of 50 kBq/L. This leads to an initial activity on the resin of 1 MBq/g of resin or 1 GBq/kg. Thus referring back to Section 2.2., on this estimate, the waste would be classified as intermediate level within the UK classification. A resin regeneration and second absorption using the same selectivity would increase the loading by a further factor of 100 to 100 GBq/kg, and a third to 10 TBq/kg. Even the last figure would probably still be ILW, and therefore the cost benefit of concentrating activity on the resin depends on how disposal costs for ILW will be weighted with regard to volume as against activity. Until the ground rules are clear, investment in volume reduction and activity concentration in this example is of doubtful value.

British Nuclear Fuels Ltd, BNFL, also need to remove caesium from pond water at the Sellafield site and they do this in the SIXEP plant. However they use a once through water flow at around pH 11 in the pond complex, and bring the pH down to neutral by passing in carbon dioxide before caesium removal. This allows them to use a naturally occurring clay with high selectivity, good capacity, and long term stability (clinoptilolite) for caesium removal.

A further point can be mentioned. To further inhibit magnesium corrosion during transport of Magnox fuel from station sites to Sellafield, fluoride ion is added to the transport flask water to give a 1000 ppm concentration. When the procedure was first introduced by the electricity generators, potassium fluoride was used since this was much more soluble than sodium fluoride. However when BNFL introduced their caesium removal facility they required that sodium fluoride be used because the potassium adversely affected sorber usage, the sorber being less selective for caesium in the presence of potassium.

9. SELENIUM REMOVAL FOR WATER PURIFICATION

Although most of this review has been concerned with radioactive sorption, similar approaches are valuable in selecting materials and processes for removal of non-radioactive but hazardous species. As an illustration, water treatment for removal of selenium will be considered.

Oil refinery effluent plus drinking water project.

Some groundwaters potentially suitable as drinking water have selenium levels significantly higher than the WHO recommended limit of 0.010 $\mu\text{g/L}$ (10ppb) such that DFs of 10^3 - 10^4 would be needed to achieve recommended levels. In another instance, oil refinery effluents in the San Francisco Bay area have an average concentration of 200 ppb, whereas new EPA guidelines will require levels of < 50 ppb, a relatively small DF.

Both situations have common features:

- (i) large volumes of water to be treated
- (ii) very small amounts of material at very low concentration to be removed
- (iii) maybe high anion concentrations present
- (iv) economics dictate a rapid sorption process
- (v) economics dictate sorber must be represented
- (vi) a solid selenium product for recycling or protracted storage is advantageous

Selenium can exist in several oxidation states. That most commonly occurring in natural aqueous systems open to the atmosphere is Se (iv) as the selenite anion SeO_3^{2-} . This is well known to sorb readily unlike Se (vi) as the selenate anion SeO_4^{2-} . Elemental selenium is insoluble in water. Change in oxidation state thus offers, in principle, one means of removing sorbed selenium.

Selenium removal as selenite has been investigated using readily available chemically stable, but non-specific, sorbents such as alumina [7]. An alternative approach using highly selective functional resins has been developed [8]: rapid collection of selenium (iv) by the use of bismuthiol II as a terfunctional reagent and a commonly used ion exchange resin has been demonstrated. A proposal has also been made to adapt the reagents to the MAG*SEPSM technology. Selenium was separated at the elution stage as the red elemental form. Oxidation of selenite to selenate as a means of desorption is another theoretical possibility. The oxidation of selenite to selenate at a MnO_2 surface has, however, been shown to be rather slow [9]. Thus the optimisation of selenium removal at low level from effluents and naturally occurring waters is still in progress.

10. SUMMARY AND CONCLUSIONS

Many current and potential applications of selective absorbers are to process streams which were not designed for waste management. When waste management is considered at the planning stage, or advantage is taken of previous experience, there can be considerable economic benefit. Different applications produce different constraints on choice of sorber and the important sorber properties have been summarised. Although to date in this review emphasis has been placed on radioactive species, the principles are also applicable to selective sorption of non-radioactive hazardous species. Because of major progress in control of waste, particularly from modern nuclear reactors, it is probably in the hazardous waste area that the major challenges remain.

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