

Sorption properties of oxides VI. Silver ion impregnated mixed oxides

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Abstract. Hydrous bismuth-thorium mixed oxide coprecipitated with silver ion is shown to be a useful sorbent for the removal of I^- from alkaline solutions. Required capacity of the sorbent for I^- could be achieved by controlling the amount of Ag^+ in the mixed oxide.

Keywords. Sorption; hydrous bismuth-thorium mixed oxides; Ag^+ impregnation iodide ion; alkaline solution.

1. Introduction

In reactor systems, the spent fuel after removal from the core is cooled in a water pool. The water is kept alkaline to minimise corrosion. During cooling, iodine present in the fuel slowly leaks out from defective fuel rods and on solubilisation in the cooling water, this active iodine appears as I^- . The cooling water is usually circulated both to maintain the temperature of the spent fuel pool as well as to purify it by ion exchange from soluble fission products, like iodine. But it is well-known that organic ion exchangers, especially anion exchangers, suffer from radiation and temperature instability (Egrov and Novikov 1967; Hall *et al* 1969). It will, therefore, be useful if suitable inorganic sorbents are developed for this purpose. It has been shown (Venkataramani *et al* 1979) that hydrous bismuth-thorium mixed oxide is capable of sorbing anions from alkaline solutions and hence this particular oxide was taken up for further investigations.

In purification systems for the removal of gaseous iodine, it is customary to impregnate the adsorber with Ag^+ to improve the efficiency (Anon 1973). To improve the efficiency of hydrous bismuth-thorium (Bi-Th) mixed oxide for the sorption of I^- , it was impregnated with Ag^+ and the resultant product investigated.

2. Experimental

2.1. Preparation of the mixed oxides

2.1a. *Loading Ag^+ on to the Bi-Th mixed oxide*: Bi-Th mixed oxide was prepared in the same way as described earlier (Venkataramani *et al* 1979) using NH_4OH for precipitation. Bi to Th ratio in the initial mixture was 4 : 1. Ag^+ was loaded on to the mixed oxide by equilibrating 5 g of Bi-Th mixed oxide with 500 ml of 0.1 M $AgNO_3$ solution for 24 hr. Sorption of Ag^+ by Bi-Th mixed oxide was only to an extent of 0.08 meq/g.

2.1b. *Preparation of Ag^+ coprecipitated Bi-Th mixed oxide* : In order to increase the amount of Ag^+ in the mixed oxide to enhance the sorption of halide ions, Ag^+ was added (in the form of $AgNO_3$ solution) to the initial solution containing the mixture of Bi(III) and Th(IV) salts in the concentration ratio 4 : 1. The Bi-Th-Ag mixed oxide was coprecipitated using 1 M NaOH (NaOH, and not NH_4OH , was used in order to precipitate Ag^+).

2.2. Determination of Ag^+ present in the mixed oxide

To estimate the amount of Ag^+ present in the final mixed oxide, 0.5 g of the oxide of a particular composition was contacted for 24 hr in a mechanical shaker, with 25 ml of 6 M HNO_3 . The oxide dissolved completely and the Ag^+ present in the equilibrated solution was estimated using standardised KCNS solution.

2.3. Leaching of Ag^+ from the mixed oxide

In order to estimate the Ag^+ leaching out when Bi-Th-Ag mixed oxide is contacted with distilled water, 2 g of each of the coprecipitated mixed oxide was contacted with 50 ml of distilled water for 24 hr in a mechanical shaker at room temperature. The Ag^+ present in the equilibrated water was estimated using standardised KCNS solution.

2.4. Sorption experiments

Mixed oxide (0.5 g) was contacted with 25 ml of 0.1 M NaX (X = Cl, Br) or 0.1 M KI for 24 hr in a mechanical shaker. The halide content of the equilibrated solution was determined by Volhard's method of back titration. To study the sorption of I^- from alkaline media, 0.05 M KI in 10^{-5} and 10^{-4} M NaOH were used as testing solutions. Both, Bi-Th mixed oxide loaded with Ag^+ (to an extent of 0.08 meq/g) as well as Bi-Th-Ag mixed oxide were used for the investigation.

3. Results and discussion

In the case of a hydrous mixed oxide, involving two metal ions, the difference between the charges of the metal ions chosen introduces a net charge into the coprecipitated oxide matrix, and this excess charge imparts to the mixed oxide an intrinsic sorption characteristic which is independent of the pH of the solution. For Bi-Th mixed, as a result of coprecipitation, an excess positive charge is

introduced and it functions as an anion exchanger. It was shown earlier (Venkataramani *et al* 1979) that for the formation of a true mixed oxide, the ionic radii of the metal ions chosen should be as close as possible (within $\pm 10\%$). Also, it was shown (Venkataramani *et al* 1979) that the sorption ability of the final product depends on the nature of the constituent oxides.

The anion sorption ability of the Bi-Th mixed oxide has been attributed to the more basic nature of not only the mixed oxide but also the constituent oxides, namely, hydrous bismuth and thorium oxides (Venkataramani *et al* 1979). It has also been shown earlier (Venkataramani *et al* 1978), that oxides prepared using NH_4OH sorb cations poorly. Hence, the poor sorption of Bi-Th mixed oxide for Ag^+ (only 0.08 meq/g) is to be expected. The intention of loading Ag^+ on to Bi-Th mixed oxide was to enhance its ability to sorb more halide ions. As the sorption of Ag^+ on Bi-Th mixed oxide was itself poor, no improvement in the sorption behaviour of the mixed oxide was observed as a result of Ag^+ loading (table 1, columns 1 and 2). This approach is, therefore, not suited for improving the sorption capacity of the mixed oxide for iodide ion.

As an alternative, Ag^+ was introduced into the mixed oxide matrix in the preparation step itself.

The leaching of Ag^+ from Bi-Th-Ag mixed oxide when contacted with water is given in table 2. Although the amount of Ag^+ leached out showed a maximum when Ag^+ present in the mixed oxide is around 0.7 meq per g, the per cent of Ag^+ present in the mixed oxide leaching out showed a decrease with increase in Ag^+ content of the mixed oxide (table 2).

Table 1. Sorption of halide ions on Bi-Th mixed oxides (Bi/Th = 4)

Test solution	Sorption capacity, meq/g							
	Bi-Th mixed oxide ^a		Bi-Th-Ag coprecipitated oxide ^c					
	Pure oxide	Ag^+ loaded oxide ^b	Ag^+ present in the mixed oxide, meq/g					
			0.0	0.15	0.29	0.57	0.72	1.38
0.1 M NaCl	1.07	0.91	0.16	0.40	0.46	0.70	1.0	1.68
0.1 M NaBr	1.04	0.90	0.12	0.54	0.72	0.84	1.26	1.76
0.1 M KI	0.94	1.05	0.17	0.37	0.50	0.79	0.89	1.46
0.05 M KI	1.0	1.01	0.16	0.32	0.45	0.77	0.82	1.46
0.05 M KI + 10^{-5} M NaOH	0.98	1.05	0.15	0.35	0.47	0.77	0.88	1.51
0.05 M KI + 10^{-4} M NaOH	0.96	0.89	0.19	0.32	0.47	0.77	0.89	1.54
0.05 M KI + 10^{-3} M NaOH	0.92	0.90
0.05 M KI + 10^{-2}	0.47	0.49

^a Mixed oxide precipitated using NH_4OH .

^b Ag^+ loading on the mixed oxide = 0.08 meq Ag^+ /g of oxide.

^c Precipitation effected using NaOH.

Table 2. Leaching of Ag^+ from Ag^+ -coprecipitated Bi-Th mixed oxides (Bi/Th = 4)

Ag ⁺ -Coppted into the mixed oxide (meq/g)	Ag ⁺ -leached into solution in 24 hr (meq/g/50 ml)	Per cent of Ag ⁺ present in the mixed oxide leached
0.15	0.027	18.0
0.29	0.024	9.3
0.57	0.041	7.2
0.72	0.044	6.1
1.38	0.024	1.7

It is likely that Ag^+ is not tightly bound in the oxide matrix at lower concentrations and hence the observed higher leaching tendency. At higher Ag^+ concentration, the leaching from the mixed oxide is considerably reduced and one would expect a negligible leaching when the mixed oxide is contacted with a solution containing halide ion. Thus, the Ag^+ leaching from the Ag^+ -coprecipitated mixed oxide is not a serious one.

Sorption of halide ions from neutral salt solution on Ag^+ -coprecipitated mixed oxides is given in table 1 (columns 3 to 8). As the pure Bi-Th mixed oxide was prepared using NaOH, its poor anion sorption capacity (table 1, column 3) is to be expected (Venkataramani *et al* 1978). However, with increasing amount of Ag^+ present in the final product, the sorption of halide ions increased (table 1, columns 4 to 8). A plot of the sorption capacity of the Bi-Th-Ag mixed oxide from 0.1 M NaX (X = Cl, Br) or 0.1 M KI solution, against the amount of Ag^+ present in the final mixed oxide, gave straight lines for all the three halide ions investigated and from the slopes of these straight lines, the amount of halide ions sorbed per meq of Ag^+ present in the mixed oxide could be calculated. For chloride ion it was 1.11 meq Cl^-/meq of Ag^+ present in the mixed oxide, for bromide ion it was 1.07 meq Br^-/meq Ag^+ and for iodide ion it was 0.91 meq I^-/meq Ag^+ . This provides a guideline for controlling the amount of Ag^+ to be coprecipitated with the mixed oxide to get a required capacity for the halide ions.

The sorption capacities of the Ag^+ -coprecipitated mixed oxides for iodide ion from alkaline solutions are also sufficiently high (table 1, columns 4 to 8). The capacities of the Ag^+ -coprecipitated mixed oxides for halide ions from neutral solutions and iodide ion from alkaline solutions compare favourably with those of the strong base anion exchange resins (e.g. Dowex 1 \times 4 in OH^- form) (table 3).

Results thus indicate that among the two possible ways by which the sorption capacity of Bi-Th mixed oxide for halide ions could be improved by Ag^+ -impregnation, the first, namely, loading of Ag^+ on to Bi-Th mixed oxide, has the limitation in that, owing to the more basic character of the Bi-Th mixed oxide, higher loading of Ag^+ is not possible and as a consequence no significant improvement in sorption capacity can be achieved (as a result of Ag^+ loading). On the other hand, by the second method, namely, coprecipitating Ag^+ along with Bi(III) and

Table 3. Sorption of halide ions on Dowex 1 × 4 in OH⁻ form (50–100 BSS mesh)

Halide ion	Test solution	Sorption capacity meq/g
Cl ⁻	0.1 M NaCl	2.02
Br ⁻	0.1 M NaBr	2.07
I ⁻	0.1 M KI	2.54
I ⁻	0.05 M KI + 10 ⁻⁵ M NaOH	2.07
I ⁻	0.05 M KI + 10 ⁻⁴ M NaOH	2.04
I ⁻	0.05 M KI + 10 ⁻³ M NaOH	2.07
I ⁻	0.05 M KI + 10 ⁻² M NaOH	1.94

Th(IV) in the preparatory stage, it is possible to fix Ag⁺ in the mixed oxide matrix and provide a non-leachable sorption site for the halide ions present in the solution. Moreover, the second method has the added advantage in that, the capacity of the final product could be suitably varied by introducing known amounts of Ag⁺ with the mixed oxide.

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