

Sorption properties of oxides II. Sorption of certain corrosion product cations on hydrous zirconium oxide, thorium oxide and magnetite

B VENKATARAMANI, K S VENKATESWARLU,
J SHANKAR and L H BAETSLE*

Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085
*Chemistry Department, SCK-CEN, 2400 Mol. Belgium

MS received 26 December 1977; Revised 16 October 1978

Abstract. Performance of hydrous ZrO_2 , ThO_2 and magnetite in a column upto $90^\circ C$ has been evaluated with reference to the sorption of Cr^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} on them. The general trend in sorption was found to be $Cr^{3+} > Fe^{3+} > Mn^{2+} > Co^{2+}$. The sorption of individual ions on these oxides from a mixture of the four ions was also studied at $90^\circ C$, by varying different parameters like the amount of sorbent, concentration of the ions, flow rates and pH of the medium. The results indicate that the rate of sorption is rather low. All the oxides showed good sorption in alkaline media. Hydrous ZrO_2 exhibits, in general, better sorption characteristic as compared to hydrous ThO_2 and magnetite.

Keywords. Sorption; zirconium oxide; thorium oxide; magnetite; transition metal ions; temperature dependence; Langmuir adsorption isotherm; pH effect; column characteristic.

1. Introduction

Inorganic ion exchangers, because of their thermal stability, are attractive alternatives to organic exchangers for the removal of corrosion products from nuclear reactor coolant water, giving the possibility that the clean-up process becomes more efficient. In the present study three oxides, hydrous zirconium oxide (ZrO_2), hydrous thorium oxide (ThO_2) and magnetite, have been evaluated for their performance upto $90^\circ C$ in a column for the removal of four commonly encountered corrosion product cations, Cr^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} .

2. Experimental

2.1. Preparation of the oxides

ZrO_2 and ThO_2 were prepared by adding either 1M NH_4OH or 1M $NaOH$ to a well stirred solution of 0.2 M $ZrOCl_2$ in HCl and 0.15 M $Th(NO_3)_4$ in HNO_3 , respectively. Magnetite was prepared by mixing 0.1 M $FeCl_3$ in HCl and 0.05 M $FeSO_4$ in dilute H_2SO_4 and precipitating with 1M NH_4OH . All precipitations were effected with

the initial salt solutions heated to 70°C. The precipitates were digested at this temperature for 2 hr left in contact with the mother liquor for 2 days and were later filtered, washed well with distilled water until free of alkali and dried at 50°C. The dried products were broken in water, washed, filtered and dried again at 50°C. The dried material was ground and sieved. The oxides were designated ZrO₂(NaOH), ZrO₂(NH₄OH), ThO₂(NH₄OH), ThO₂(NaOH), the alkali used for precipitation being indicated in the parentheses. Oxides used for batch experiments had a particle size of -100 BSS mesh, whereas for column operations it was 50-100 BSS mesh.

It was observed (Venkataramani *et al* 1978a) that when NH₄OH was used for precipitating the FeCl₃ and FeSO₄ mixture, the final product was essentially magnetite, even though not very crystalline. It was also observed that the final product remained the same both in composition as well as in their sorption properties when the precipitation was effected either at room temperature (25°C) or at 70°C (Venkataramani 1974).

2.2. Effect of drying temperature on sorption

As the inorganic sorbents are likely to be used at temperatures of about 300°C in reactor water purification systems, it is of interest to know their sorption behaviour when fired at higher temperatures.

Known amounts of the oxides originally dried at 50°C were heated for 24 hr in an oven maintained at a definite temperature between 50° and 300°C. These were later cooled in a desiccator and weighed to calculate the weight loss (table 1). Sorption of Cu²⁺ on the fired materials was determined by equilibrating 0.5 g of the oxides with 25 ml of 0.1 M CuSO₄ solution for 24 hr. Cu²⁺ was estimated iodimetrically. All batch experiments were done at 25°C, by constantly shaking the solid-solution mixture. It was found that contacting for 24 hr was enough to give a steady state value.

ZrO₂(NaOH) fired at different temperatures was tested for its sorption behaviour at 90°C on a column. Through 1 g of the oxide 100 ml of CoCl₂ solution containing

Table 1. Effect of firing different oxides on the weight loss and on the sorption of Cu²⁺ and Co²⁺

Temperature of firing of °C	ZrO ₂ (NH ₄ OH)		ZrO ₂ (NaOH)		ThO ₂ (NH ₄ OH)		Magnetite	
	% wt. loss	Amount of Cu ²⁺ sorbed* × 10 ³ µg/g	% wt. loss	Amount of Co ²⁺ sorbed** µg/g	% wt. loss	Amount of Cu ²⁺ sorbed* × 10 ³ µg/g	% wt. loss	Amount of Cu ²⁺ sorbed* × 10 ³ µg/g
50	—	50.9	—	98	—	19.1	—	12.8
110	10.1	35.1	15.6	98	2.0	12.8	0.4	9.2
160	18.5	28.7	—	—	5.0	3.1	0.8	9.5
210	20.6	28.7	21.7	98	9.0	—	2.3	9.5
260	19.1	23.5	24.7	97	9.3	—	2.4	6.5
300	—	—	24.1	95	—	—	—	—

*Batch equilibration technique, at room temperature, using 6.4 × 10³ µg/ml CuSO₄ solution.

**Column experiments at 90°C using 1 µg/ml CoCl₂ solution.

1 $\mu\text{g Co}^{2+}/\text{ml}$ and traced with ^{58}Co was passed at flow rate of 50 ml/hr. The amount of Co^{2+} sorbed was calculated from a knowledge of the total Co^{2+} in the influent and the effluent.

2.3. Choice of material for column operation

Preliminary batch experiments were conducted on the sorption of Cr^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} on the different oxides so as to choose an appropriate material for column operation, using 0.25 g of the oxide and 25 ml of the test solution, containing the metal salts of appropriate concentration ($\text{Cr}(\text{NO}_3)_3$, MnCl_2 , $\text{Fe}(\text{NO}_3)_3$, and CoCl_2 were used) and equilibrating them for 24 hr. Sorption experiments were conducted in the concentration range 25 to 250 μg in 25 ml of the particular metal ion. Sorption was followed by tracing the salt solutions with ^{51}Cr , ^{54}Mn , ^{59}Fe and ^{58}Co , and measuring the γ -activity of a known aliquot of the solution using a scintillation counter before and after equilibration.

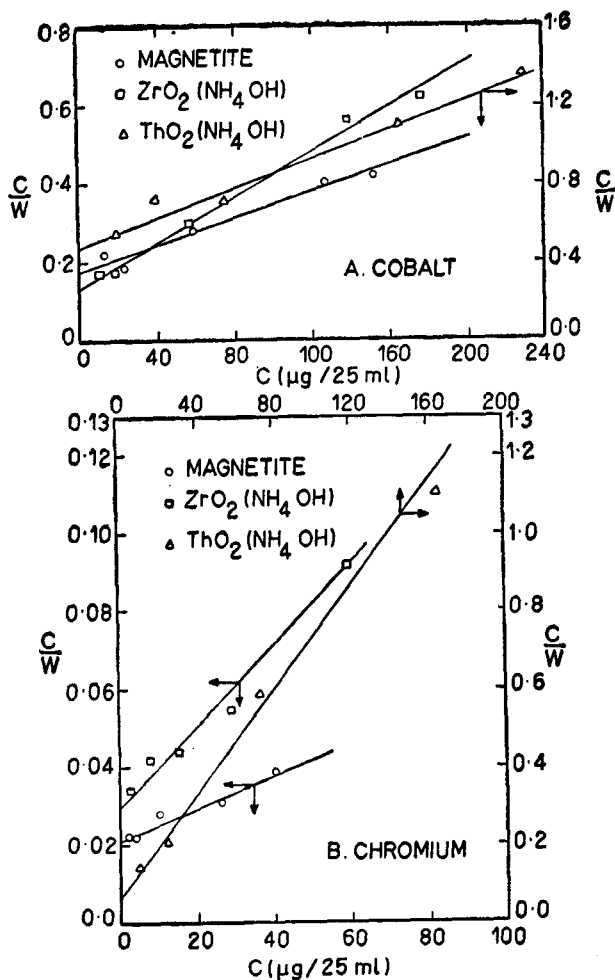


Figure 1. Sorption of cobalt and chromium on oxides—Langmuir plots

Table 2. Saturation capacities of Cr³⁺, Mn²⁺, Fe³⁺ and Co²⁺ ions on oxides

Ions	Capacity, $\mu\text{g/g}$		
	ZrO ₂ (NH ₄ OH)	ThO ₂ (NH ₄ OH)	Magnetite
Cr ³⁺	860	150	2270
Mn ²⁺	510	310	1220
Fe ³⁺	1120	1160	1600
Co ²⁺	350	100	430

Table 3. Sorption of Cr³⁺, Mn²⁺, Fe³⁺ and Co²⁺ on ZrO₂ (NH₄OH) and ZrO₂ (NaOH)

Amount added $\mu\text{g/g}$	Amount sorbed, $\mu\text{g/g}$			
	Cr ³⁺	Mn ²⁺	Fe ³⁺	Co ²⁺
ZrO ₂ (NH ₄ OH)				
100	89	86	91	58
200	168	159	195	107
400	337	270	391	182
800	677	407	698	246
1000	769	484	969	298
ZrO ₂ (NaOH)				
100	98	97	53	98
200	152	193	91	194
400	336	389	290	385
800	713	776	629	785
1000	900	971	924	980

The sorption data were analysed by the Langmuir adsorption isotherm (Mishra 1968)

$$c/w = c/B + 1/aB, \quad (1)$$

where c is the equilibrium concentration, w is the amount adsorbed per g at the particular equilibrium concentration c , B is the saturation capacity per g and a is a constant associated with the heat of adsorption. A plot of c/w against c would be expected to be linear, if the treatment is valid and the reciprocal of the slope would give the saturation capacity. Representative Langmuir plots showing conformity of the data collected on Cr³⁺ and Co²⁺ sorption with eq. (1) are given in figure 1, for the three oxides. The saturation capacities for ZrO₂ (NH₄OH), ThO₂ (NH₄OH) and magnetite are listed in table 2. The NaOH preparations had higher adsorption and hence small values for c . Consequently c/w vs c plots had points which were very close to the Y -axis and a straight line could not be drawn through those crowded points. Even if drawn, calculation of slopes would have been erroneous and misleading. However, sorption data for ZrO₂(NaOH) and ZrO₂(NH₄OH) are given in table 3, for comparison purposes.

2.4. Experimental set-up for studies at high temperatures

The set-up consisted of a jacketed glass column of 13 mm diameter, fitted with a sintered glass disc. Water from a thermostat was circulated through the jacket and the temperature of the thermostat was regulated at a particular temperature. The temperature of the thermostat and that of the solution in the column were the same and hence the temperature of the thermostat was taken as the temperature of the run. The column was loaded with the oxide at room temperature (25°C); it was later brought to the temperature of interest. The test solution was taken in a separating funnel fitted to the column. One gram of $ZrO_2(NaOH)$, $ThO_2(NaOH)$ and magnetite occupied a volume of 1.4, 1.0 and 1.6 cm^3 , respectively, while 5 g of these oxides occupied a volume of 5.2, 3.2 and 7.4 cm^3 , respectively, when filled in the column. The non-proportionate differences in wet volumes for 1 g and 5 g could be due to loose and a little tighter packing respectively, but care was taken to ensure that no air was trapped in-between the packed column of the oxides. Flow was regulated at 50 ml/hr and 100 ml/hr.

Stock solutions containing 100 $\mu g/ml$ of a particular ion were prepared from Anala R $Cr(NO_3)_3$, $MnCl_2$, $Fe(NO_3)_3$, and $CoCl_2$. They were then suitably diluted to give the required concentration in the final mixture.

2.5. Sorption of ions as a function of temperature

One gram of the oxide was loaded on to the jacketed columns and was maintained at the specified temperature (25, 50, 75 and 95°C). 200 ml of the solution of a particular

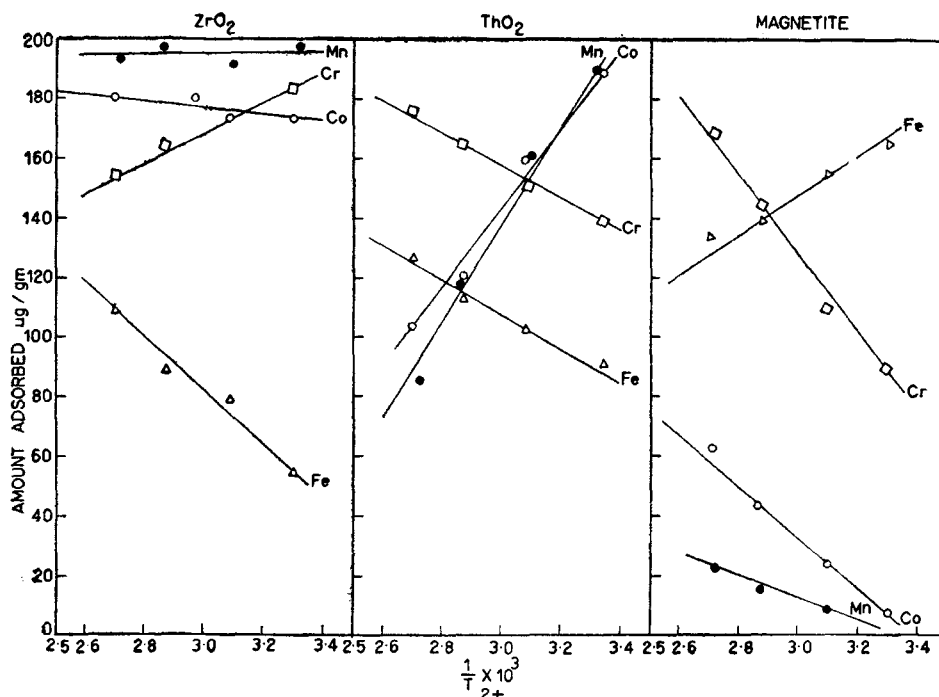


Figure 2. Sorption of Cr^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} on oxides at different temperatures

ion of concentration $1 \mu\text{g/ml}$ and traced suitably was passed through the oxide at a flow rate of 50 ml/hr . Plots of the amount of ion sorbed vs $1/T$ (where T is the absolute temperature) on the three oxides and for the four ions are given in figure 2.

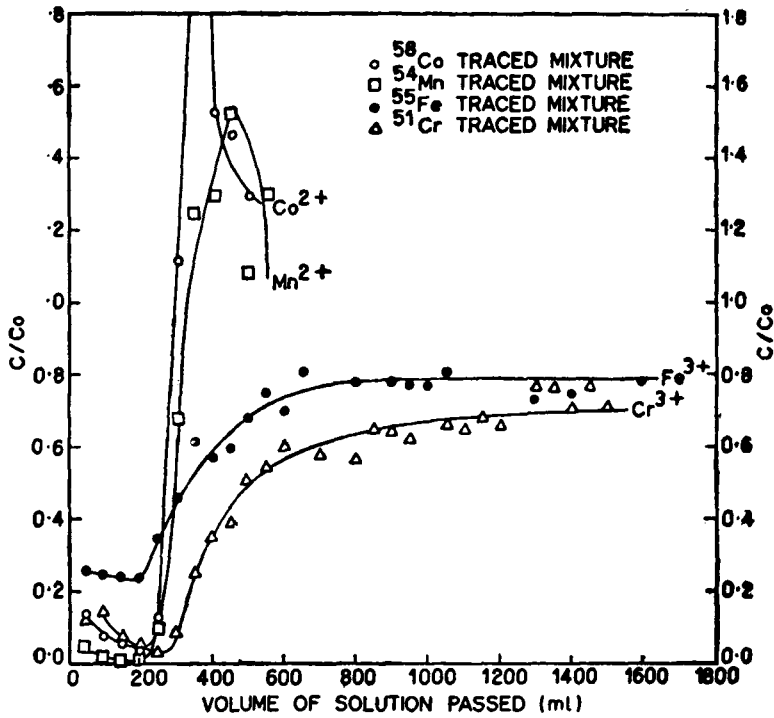


Figure 3. Sorption of Cr, Mn, Fe and Co on Zirconium oxide at 90°C

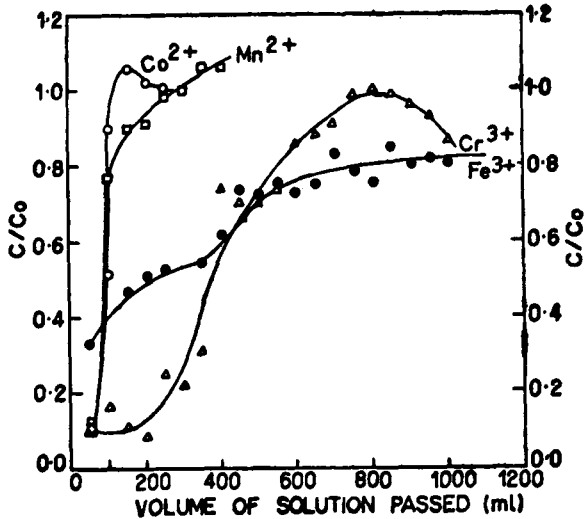


Figure 4. Sorption of Cr, Mn, Fe and Co on thorium oxide at 90°C

2.6. Sorption of ions on oxides from a mixture of transition metal ions at 90°C from neutral solutions (pH ~ 6)

Ions were mixed in equal amounts so that the mixture contained 1 $\mu\text{g}/\text{ml}$ of each ion (that is a total concentration of 4 μg of cation per ml in the final solution). The mixture was traced with one isotope at a time to follow the sorption. Through 1 g of the oxide, the solution mixture was passed at a flow rate of 50 ml/hr till the breakthrough for the traced ion occurred. Figures 3, 4, 5 show the different curves obtained for ZrO_2 , ThO_2 and magnetite, for the four cations. The area under the curve upto an effluent volume of 1000 ml for ThO_2 and 1600 ml for ZrO_2 and magnetite give the amount of the traced ion present in the effluent. From a knowledge of the amount of the traced ion passed (1000 μg through ThO_2 and 1600 μg each through ZrO_2 and magnetite), and the amount left in the effluent (not sorbed), the percentage sorption values were calculated and are listed in table 4.

2.7. Sorption of Mn^{2+} and Co^{2+} under different conditions from neutral solutions (pH ~ 6)

The sorption behaviour of Mn^{2+} and Co^{2+} present in a mixture of the four cations on the three oxides was tested by varying the concentration of the ions in the mixture

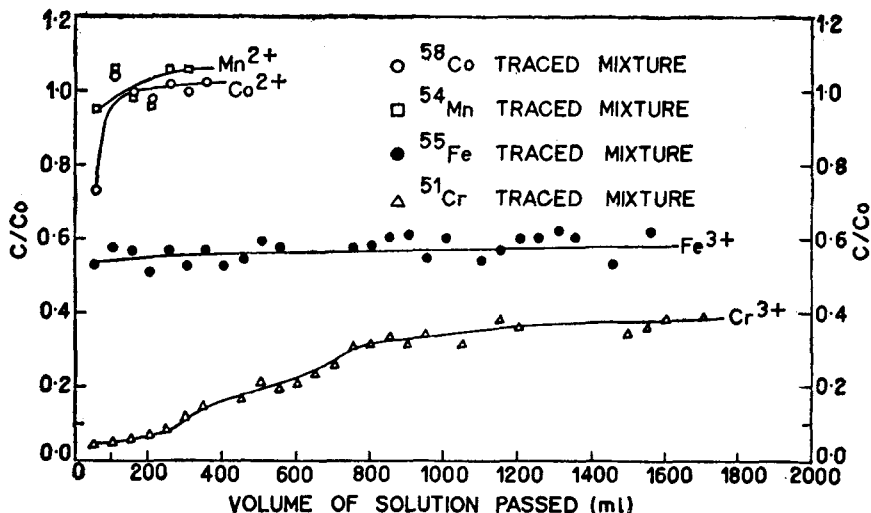


Figure 5. Sorption of Cr, Mn, Fe and Co on magnetite at 90°C

Table 4. Sorption of ions on oxides from a mixture of ions at 90°C under flow conditions

Oxide	Influent		% sorption of the traced ion/g				Net efficiency of the oxide
	Total amount of ions present in mixture (μg)	Amount of traced ion present in mixture (μg)	Cr^{3+}	Fe^{3+}	Mn^{2+}	Co^{2+}	
$\text{ZrO}_2(\text{NaOH})$	6400	1600	51	35	16	14	29%
$\text{ThO}_2(\text{NaOH})$	4000	1000	35	34	7	5	20%
Magnetite	6400	1600	74	43	0	0.8	30%

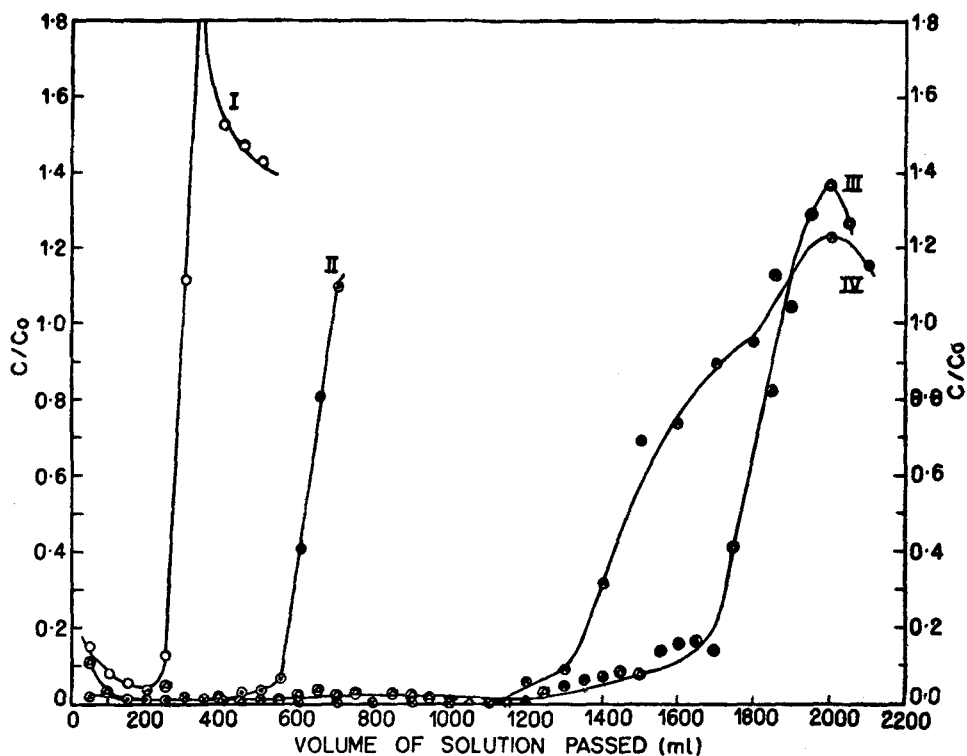


Figure 6. Sorption of ^{68}Co traced mixture on zirconium oxide at 90°C under different conditions. 1. Amount of sorbent (g). 2. Concentration of Co^{2+} or Mn^{2+} ($\mu\text{g}/\text{ml}$). 3. Flow rate (ml/hr)

Curve No. I: Amount—1; concentration—1; flow rate—50.

Curve No. II: Amount—5; concentration—1; flow rate 50.

Curve No. III: Amount—5; concentration—0.1; flow rate—50.

Curve No. IV: Amount—5; concentration—0.1; flow rate—100.

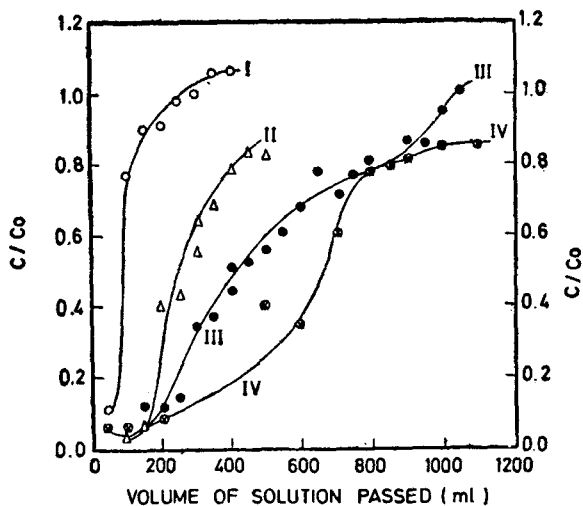


Figure 7. Sorption of ^{64}Mn traced mixture on thorium oxide at 90°C under different conditions (Legend for I to IV is given in figure 6)

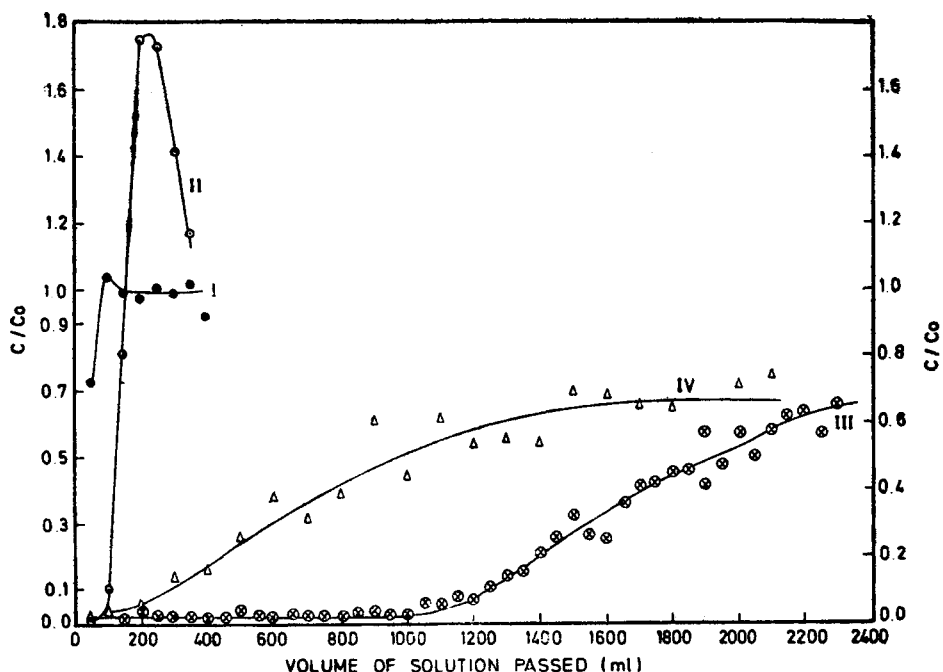


Figure 8. Sorption of ^{56}Co traced mixture on magnetite at 90°C under different conditions (Legend for I to IV is given in figure 6)

($1\ \mu\text{g}/\text{ml}$ and $0.1\ \mu\text{g}/\text{ml}$ of each of the ions (Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+}) in the final solution), the flow rate ($50\ \text{ml}/\text{hr}$ and $100\ \text{ml}/\text{hr}$) and the amount of the oxide ($1\ \text{g}$ and $5\ \text{g}$). The column operation were performed at 90°C and the sorption was followed by tracing the mixture with either ^{54}Mn or ^{56}Co at a time.

Some typical curves for the sorption behaviour for $\text{ZrO}_2(\text{NaOH})$, $\text{ThO}_2(\text{NaOH})$ and magnetite are given in figures 6, 7, 8. The following parameters were either measured or calculated from the curves: (i) the bed volume; (ii) the breakthrough volume (here it is defined as the volume when $C/C_0=0.95$; C =the number of counts of the effluent at a particular time per 100 sec per 5 ml; and C_0 is the number of counts of the initial solution per 100 sec per 5 ml; C/C_0 thus gives the fraction of the initial activity present in the effluent at a particular time), (iii) the total amount of Mn^{2+} or Co^{2+} passed till the breakthrough; (iv) the amount of Mn^{2+} or Co^{2+} sorbed till the breakthrough and (v) the percentage sorption of Mn^{2+} or Co^{2+} . These values are listed in tables 5 and 6.

2.8. Sorption tests using alkaline solutions at 90°C

To minimise corrosion, the coolant water in pressurised water reactors is maintained at a pH of 9.5 to 10.5 with LiOH. Sorption tests were, therefore, performed under alkaline conditions also. Test solutions contained a mixture of the four cations at a concentration of $0.1\ \mu\text{g}/\text{ml}$ each, and LiOH concentration was maintained at 8.5×10^{-5} (pH ~ 10) and was traced with either ^{54}Mn or ^{56}Co . Five grams of the oxide was initially pre-conditioned with 700 ml $8.5 \times 10^{-5}\ \text{M}$ LiOH at room temperature. The

Table 5. Sorption of ^{54}Mn traced mixture on oxides at 90°C

Run	Total concentration of ions ($\mu\text{g/ml}$)	Amount of the oxide (g)	Bed Vol. (ml)	Flow rate (ml/h)	Total volume of solution passed (ml)	Total amount of ^{54}Mn sorbed (μg)	Amount of ^{54}Mn sorbed per g ($\mu\text{g/g}$)	% sorption	Breakthrough volume (ml) at $\frac{C}{C_0} = 0.95$	No. of column volume passed with 95% sorption = Col. 10 = Col. 4
ZrO₂ (NaOH)										
1	4	1	1.4	50	300	249	249	83	250	176
2	4	5	5.2	50	1000	741	148	74	650	137
3	0.4	5	5.2	50	1750	134	27	76	1650	306
4	0.4	5	5.2	100	1800	129	26	72	1050	243
ThO₂ (NaOH)										
1	4	1	1.0	50	250	67	67	26	50	51
2	4	5	3.2	50	500	279	56	56	150	46
3	0.4	5	3.2	50	1050	52	10	50	200	66
4	0.4	5	3.2	100	1100	52	10	48	200	62
Magnetite										
1	4	1	1.6	50	—	—	—	—	—	—
2	4	5	7.4	50	150	40	8	26	50	7
3	0.4	2	3.1	50	550	43	22	78	250	91
4	0.4	2	3.1	100	700	41	21	58	100	30

Table 6. Sorption of ^{58}Co traced mixture on oxides at 90°C

Run	Total concentration of ions ($\mu\text{g/ml}$)	Amount of the oxide (g)	Bed volume (ml)	Flow rate (ml/hr)	Total volume of solution passed (ml)	Total amount of ^{58}Co sorbed (μg)	Amount of ^{58}Co sorbed/g ($\mu\text{g/g}$)	% sorption	Breakthrough volume at $\frac{C}{C_0} = 0.95$	No. of column volumes passed with 95% sorption = $\frac{\text{Col. 10}}{\text{Col. 4}}$
ZrO₂(NaOH)										
1	4	1	1.4	50	250	222	222	89	200	151
2	4	5	5.2	50	700	573	115	82	550	112
3	0.4	5	5.2	50	1850	170	34	94	1500	225
4	0.4	5	5.2	100	2000	156	31	78	1300	232
ThO₂(NaOH)										
1	4	1	1.0	50	100	47	47	47	50	51
2	4	5	3.2	50	300	168	34	56	150	44
3	0.4	5	3.2	50	950	73	15	77	150	44
4	0.4	5	3.2	100	900	51	10	57	200	58
Magnetite										
1	4	1	1.6	50	100	13	13	13	—	—
2	4	5	7.4	50	1500	103	21	69	100	14
3	0.4	5	7.4	50	2300	182	36	79	1200	154
4	0.4	5	7.4	100	2100	212	22	53	200	28

test solution was later passed through the oxide column maintained at 90°C at a flow rate of 50 ml/hr.

3. Results and discussion

3.1. *Effect of methods of preparation and drying temperature on sorption*

Due to loss of both interstitial and chemically bound water, the sorption capacity is reduced on firing the oxides to higher temperatures (table 1). It has been observed earlier (Venkataramani *et al* 1978b) that an oxide prepared using NaOH is liable to contain more—OH groups in the matrix as compare to the one prepared using NH_4OH . Consequently the cation sorption capacity of the NaOH preparation will be more (table 3) and also the weight loss due to heating at higher temperatures will be more in the case of NaOH preparation (table 1), as can be seen from the data on ZrO_2 (NH_4OH) and $\text{Zr}_2(\text{NaOH})$. At lower concentrations and at 90°C the sorption is not, however, much altered on firing ZrO_2 (NaOH) as can be seen from table 1 for Co^{2+} sorption. Because of their higher sorption, the NaOH preparation of ZrO_2 and ThO_2 , was used for further studies.

3.2. *Temperature dependence of sorption*

The temperature dependence of sorption of the four cation on the oxides is a little complicated (figure 2) and cannot be explained as due to one factor alone.

In the case of ZrO_2 , sorption of Mn^{2+} and Co^{2+} was not very much affected by temperature. The sorption of Cr^{3+} decreased with increase in temperature, while that of Fe^{3+} increased. The sorption of Mn^{2+} and Co^{2+} on ThO_2 decreased sharply with increase in temperature. The sorption of Cr^{3+} increased with an increase in temperature. While the sorption of Cr^{3+} , Mn^{2+} and Co^{2+} on magnetite increased with increase in temperature, that of Fe^{3+} decreased with temperature.

The increased sorption of Cr^{3+} and Fe^{3+} on oxides with temperature could be due to the fact that hydrolysis increases with temperature and as a result of this sorption also increases. The increased sorption of UO_2^{2+} on crystalline zirconium phosphate (Vesely *et al* 1968) with temperature has been shown to be associated with the formation of uranyl phosphate. It is likely that at higher temperatures, an initial step of sorption of hydrolysed products of Fe^{3+} and Cr^{3+} on the oxide followed by the formation of the respective oxides, could be a mechanism operative in the case of trivalent ion sorption on these oxides. But this mechanism does not explain the decrease in the sorption with temperature of Cr^{3+} on ZrO_2 and that of Fe^{3+} on magnetite. The high flow rate conditions under which these experiments were performed could be a reason for such a behaviour. It is quite interesting to note that the strong common ion effect (that is, the preferential sorption of Fe^{3+} on magnetite) (Venkataramani *et al* 1978a) does not seem to play a specific role here.

The decrease in sorption with increase in temperature is a common feature observed with other inorganic ion exchangers also. An interesting feature is the fact that the Co^{2+} sorption on magnetite increased with temperature while Tewari *et al* (1972) have reported a negative temperature coefficient for the same. The material prepared by Tewari *et al* were quite different both from the point of view of preparation method

and capacity (Venkataramani *et al* 1978a; Tewari *et al* 1972) and also the sorption experiments were performed by batch techniques. Thus the results are not strictly comparable.

3.3. Sorption behaviour of the four cations in the mixture

From figures 3, 4, 5 it can be seen that, while the breakthrough for Mn^{2+} and Co^{2+} are sharp, that for Cr^{3+} and Fe^{3+} are not. An equilibrium sorption is reached in the case of Cr^{3+} and Fe^{3+} sorption on the oxides. In the pH range under investigation (between 5 and 6), Cr^{3+} and Fe^{3+} would be more hydrolysed than Mn^{2+} and Co^{2+} and this would increase with increase in temperature also (see § 3.2). It is, therefore, quite possible that hydrolysed products of Cr^{3+} and Fe^{3+} are sorbed on the oxides—initially by a fast 'filtration' step followed by a slow sorption process (and hence the attainment of an equilibrium sorption value). Initially, Mn^{2+} and Co^{2+} are sorbed efficiently on ZrO_2 and ThO_2 , but saturation is also reached quickly. On passing more of the mixture, the highly sorbing Cr^{3+} and Fe^{3+} displace the already sorbed Mn^{2+} and Co^{2+} and the later two ions start appearing in the effluent.

The amount of the individual ions sorbed from the mixture were calculated and is listed in table 4. In general, the sorption decreased in the order: $Cr^{3+} > Fe^{3+} > Mn^{2+} > Co^{2+}$. This was also the order found by batch equilibration method (table 3). From the total amount of all the ions passed (6400 μg for ZrO_2 and magnetite and 4000 μg in the case of ThO_2) and the total amount of all the ions (Cr, Fe, Mn, Co) sorbed, a net efficiency was calculated: 20% for ThO_2 , 29% for ZrO_2 and 30% magnetite. Needless to add, a major contribution was from the trivalent ions.

A decrease in the influent concentration, increase in the amount of the oxide or increase in the pH of the influent solution will certainly increase the sorption efficiency of the trivalent ions. It was, therefore, of interest to select Mn^{2+} and Co^{2+} for further study, because of their comparatively poorer sorption.

3.4. Sorption behaviour of Mn^{2+} and Co^{2+} under different conditions (pH ~ 6)

Tables 5 and 6 and figures 6, 7 and 8 summarise the results obtained on the sorption of Mn^{2+} and Co^{2+} on the oxides under different conditions and at 90°C.

In general, it was observed that when the concentration was reduced from 1 $\mu g/ml$ to 0.1 $\mu g/ml$, the breakthrough was not sharp. However, more column volumes of the solution mixture could be passed through the oxide column before a breakthrough occurred, by increasing the amount of the oxide and by reducing the concentration of the ions in the mixture. But the increase in the number of bed volumes passed before the breakthrough was neither proportional to the increase in the amount of the sorbent nor to the decrease in the concentration of the cations in the mixture. Again, the increase in the number of bed volumes passed before the breakthrough decreased when the flow rate was doubled.

The degree of column utilization, defined as,

$$\text{degree of column utilization} = \frac{\text{breakthrough volume}}{\text{total volume passed till the breakthrough}}$$

should increase when the amount of the sorbent is increased or when the concentration of the ion being sorbed is decreased, if the sorption equilibrium is favourable.

Such an increase is observed in the present case (column No. 11 of tables 5 and 6), but they are not proportional to the reduction in the influent concentration and increase in the amount of the oxide. The values also drop down when the flow is increased (See 4th run in tables 5 and 6). It is well known (Helfferich 1962) that the sharp boundaries in breakthrough curves are most strongly affected by low rate of ion exchange (or sorption). It is likely that the rate of sorption is so slow that the time of contact under the high flow condition is insufficient for the sorption equilibrium to be established. This is more so in the case ThO_2 .

ZrO_2 exhibits, in general, better sorption characteristics as compared to ThO_2 and magnetite.

3.5. Sorption of Mn^{2+} and Co^{2+} from alkaline solutions

When 7.5 l of ^{54}Mn or ^{58}Co traced mixtures in alkaline medium ($\text{pH} \sim 10$) was passed through 5 g of the oxides at 90°C , all the oxides showed 95–99% sorption upto 6.0l and then slowly decreased to 75%. The good sorption exhibited by oxides in alkaline medium is to be expected. In alkaline media the oxides behave as cation exchangers (Venkataramani et al 1978b); and the transition metal ions are hydrolysed or probably exist in the form of colloidal hydroxides. These factors, both working in the positive direction, enhance sorption.

Results indicate that the oxides investigated do show promise as corrosion product sorbers from alkaline solutions at higher temperature and warrants further studies at still elevated temperatures.

Acknowledgements

One of the authors (BV) is grateful for the award of the scholarship under the Indo-Belgium Nuclear Cooperation Programme. The authors also wish to thank Dr M D Karkhanavala, Chemistry Division, BARC, for his keen interest during the course of this work.

References

- Mishra D N 1968 *J. Colloid Interfacial Sci.* **28** 24
- Tewari P H, Campbell A B and Lee W 1972 *Can J. Chem.* **50** 1642
- Venkataramani B 1974 *Studies on Inorganic Ion-Exchangers-Adsorption properties of oxides*. Ph.D., Thesis, University of Bombay, Bombay
- Venkataramani B, Venkateswarlu K S and Shankar J 1978a *J. Colloid Interfacial Sci.* **67** 187
- Venkataramani B, Venkateswarlu K S and Shankar J 1978b *Proc. Indian Acad. Sci.* **A87**
- Vesely V, Ruvarac A and Sedlakova L 1968 *J. Inorg. Nucl. Chem.* **30** 1101