# Sorption properties of oxides I. Hydrous thorium oxide

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**Abstract.** Sorption properties of hydrous thorium oxide depend very much on the preparatory conditions. The sorption of alkali metal ions from alkaline solutions gives rise to a sequence: $Li^+ > Na^+ > K^+ > Cs^+ > NH_4^+$ and that for transition metal ion: $Cu^{2+} > Co^{2+} > Ni^{2+}$. A sequence for the sorption capacities for the anions: $CrO_4^{2-} > Cl^- > NO_3^- > Br^- > CNS^-$ has also been established. Results indicate that hydrous thorium oxide is both a weakly acidic and weakly basic amphoteric exchanger.

**Keywords.** Sorption; hydrous thorium oxide; alkali metals; anions; Langmuir adsorption.

## 1. Introduction

Ion exchange properties of hydrous oxides have attracted great attention during the past two decades (Amphlett 1964; Fuller 1971). Still very few attempts have been made to study the ion exchange properties of hydrous thorium oxide ($ThO_2$) (Anderson 1958; Nancollas and Paterson 1961; Heitner-Wirguin and Albu Yaron 1965, 1966). Hydrous $ThO_2$ is an amphoteric oxide exhibiting both anion and cation exchange properties. The basis of exchange is due to the presence and pH-dependent dissociation of surface hydroxyl groups. In the present study the cation and anion sorption properties of hydrous $ThO_2$ are reported.

## 2. Experimental

### 2.1. *Preparation of the oxides*

$ThO_2$ was prepared by adding excess of either 1M NaOH or 1M $NH_4OH$ to a well stirred solution of 0·2M $Th(NO_3)_4$ in 1M $HNO_3$ either at room temperature or at 70°C. The precipitate was digested well (or digested at 70°C for 1 hr in the case of preparation under hot condition), left with the mother liquor overnight, filtered, washed well free of alkali with distilled water and was then air dried. The air dried product was broken in distilled water, washed, filtered and air dried again.

The samples were designated $ThO_2(NH_4 \cdot C)$ and $ThO_2$ $(NH_4 \cdot H)$ indicating that $NH_4OH$ was used for precipitation and that it was effected under cold (room temperature) (C) or hot (H) condition. Likewise $ThO_2(Na \cdot C)$ and $ThO_2$ $(Na \cdot H)$ refer to the NaOH preparation. All sorption experiments were carried out with materials of —100 BSS mesh size.

## 2.2. *Sorption experiments*

The uptake of $Cu^{2+}$ and $CrO_4^{2-}$ on the four $ThO_2$ preparations ($ThO_2$ (NaC), $ThO_2$ (NaH), $ThO_2(NH_4.C)$ and $ThO_2$ ($NH_4.H$) was studied by equilibrating 0·5 g of the oxide with 25 ml of either 0·1M $CuSO_4$ or 0·1M $K_2CrO_4$ for 24 hr at 25°C and analysing the $Cu^{2+}$ and $CrO_4^{2-}$ iodimetrically. Table 1 lists the sorption capacities of the oxides.

Sorption of alkali metal ions on $ThO_2(Na·C)$ was studied by equilibrating 0·5 g of the oxide with 25 ml 0·1M (MeOH+MeCl) for 24 hr (where Me=Li, Na, K, Cs and $NH_4$) at 25°C. The $OH^-$ concentration of the solution after filtration, was determined by titrating with standard HCl.

Under the experimental conditions, in the presence of alkali, the following reaction operates on an oxide surface:

$$(- OH)_s \ \rightleftarrows \ (-O^-)_s + H^+, \tag{1}$$

$$(-OH)_s + Me^+ + OH^- \ \rightarrow \ (-OMe)_s + H_2O \tag{2}$$

where $(-OH)_s$ represents one of the hydroxyl groups on the surface, and $Me^+$ is the exchanging metal ion present in the solution, and in this instance it is the alkali metal ion. The decrease in the $OH^-$ ion concentration can, therefore, be taken as a measure of the sorption capacity of alkali metal ions. Table 2 lists the sorption of alkali metal ions at different $OH^-$ concentration on $ThO_2$ (Na·C).

Sorption of transition metal ions ($Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$) on $ThO_2(Na·C)$ from neutral solutions was studied as a function of the concentration of the respective cation. 0·5 g of the oxide was equilibrated with constant shaking with 25 ml of the salt solution ($CuSO_4$, $NiSO_4$ and $CoCl_2$) of appropriate concentration for 24 hr at 25°C, $Cu^{2+}$ was estimated iodimetrically, while $Ni^{2+}$ and $Co^{2+}$ were estimated by titrating against

**Table 1.** Sorption of $Cu^{2+}$ and $CrO_4^{2-}$ on different $ThO_2$ preparations.

| Oxide | Capacity, meq/g | |
|---|---|---|
| | $Cu^{2+}$ | $CrO_4^{2-}$ |
| $ThO_2$ (Na,C) | 1·20 | 0·36 |
| $ThO_2$ (Na,H) | 0·80 | 0·40 |
| $ThO_3$ (NH₄,C) | 0·42 | 2·30 |
| $ThO_2$ (NH₄,H) | 0·34 | 2·10 |

**Table 2.** Sorption of alkali metal ions on $ThO_2$ (Na,C).

| Alkali concentration (N) | Capacity, meq/g | | | | |
|---|---|---|---|---|---|
| | $Li^+$ | $Na^+$ | $K^+$ | $Cs^+$ | $NH_4^+$ |
| 0·04 | 0·79 | 0·75 | 0·66 | 0·69 | 0·23 |
| 0·06 | 0·96 | 0·87 | 0·82 | 0·81 | 0·32 |
| 0·08 | 1·07 | 0·96 | 0·94 | 0·90 | 0·40 |
| 0·10 | 1·15 | 1·03 | 1·04 | 0·96 | 0·46 |

EDTA using EBT as indicator. It was observed that equilibrating for 24 hr was enough to give a steady state value.

Sorption of anions ($CrO_4^{2-}$, $Cl^-$, $NO_3^-$, $Br^-$ and $CNS^-$) on $ThO_2$ ($NH_4 \cdot C$) from neutral solutions was studied as a function of the concentration of the respective anions, by equilibrating with constant shaking 0·5 g of the oxide with 25 ml of the respective salt solutions ($K_2CrO_4$, NaCl, $NaNO_3$, NaBr and KCNS) of appropriate concentration for 24 hr at 25°C. The anions were estimated by the usual techniques.

The sorption isotherms for transition metal ions and anions on the $ThO_2$ samples were smooth and could be analysed by the Langumir adsorption isotherm (Mishra 1968).

$$c/w = c/B + 1/aB \qquad (3)$$

where $c$ is the equilibrium concentration in solution, $w$ is the amount of adsorbate per unit amount of the adsorbent for a given concentration, $B$ is the saturation amount
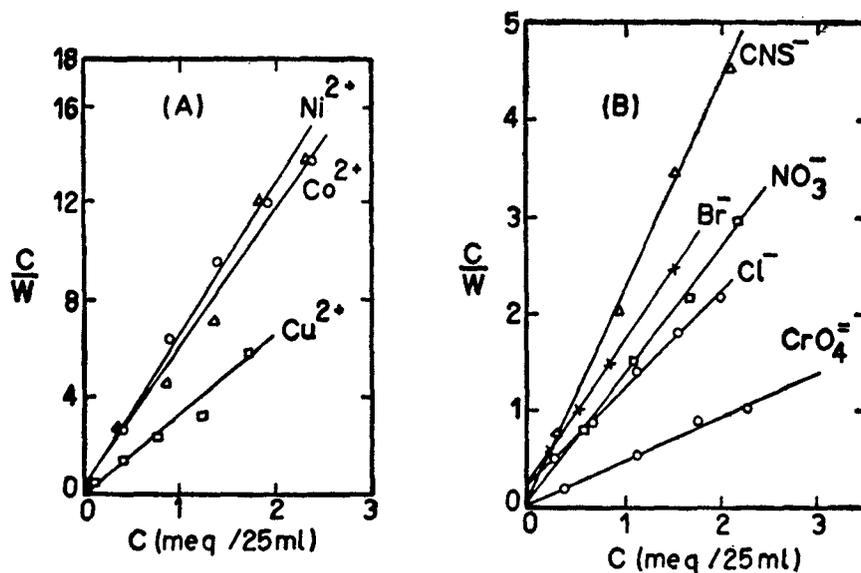


**Figure 1.** Sorption of anions and cations on hydrous thorium oxide—Langumir plots (A) $ThO_2$ (Na·C); (B) $ThO_2$ ($NH_4 \cdot C$).

**Table 3.** Sorption of transition metal ions and anions on $ThO_2$.

| Ions | Saturation capacity, meq/g | |
|---|---|---|
| | $ThO_2$ (Na,C) | $ThO_2$ ($NH_4$,C) |
| $Cu^{2+}$ | 1·23 | ... |
| $Co^{2+}$ | 0·21 | ... |
| $Ni^{2+}$ | 0·16 | ... |
| $CrO_4^{2-}$ | ... | 2·15 |
| $Cl^-$ | ... | 1·04 |
| $NO_3^-$ | ... | 0·75 |
| $Br^-$ | ... | 0·67 |
| $CNS^-$ | ... | 0·45 |

of the adsorbate per unit amount of the adsorbent, and $a$ is a constant related to 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. Langumir plots showing conformity of the data collected on the transition metal ions and anion sorption with eq. (3) is given in figure 1, and the saturation capacity values are tabulated in table 3.

The saturation capacity values obtained from Langumir plots represent the sorption values averaged over a concentration range (in the present case upto 0·1M of the particular ion). This value is likely to be different from the sorption values recorded at any one concentration. The apparent discrepancy in the sorption values quoted, for example, in tables 1 and 2 for chromate ion reflect this aspect.

## 3. Results and discussion

X-ray analysis of the hydrous $ThO_2$ samples showed that they were amorphous. Infrared spectra (Venkataramani 1974) revealed the presence of two types of water: interstitial water and chemically bound water. Thermogravimetric analysis of $ThO_2$ ($NH_4 \cdot C$) indicated a break around 300°C and plateau after 500°C. The steady weight loss upto 300°C probably corresponds to the loss of interstitial water (1·2 moles) and the loss in weight after the break upto the plateau at 500°C could be due to the loss of chemically bound water or the condensation of hydroxyl groups (3 moles). Similar observations have been reported by other workers (Nancollas and Paterson 1961; Heitner-Wirguin and Albu Yaron 1966). The present values correspond very closely to the empirical formula $ThO(OH)_2 \cdot nH_2O$, proposed by Heitner-Wirguin and Albu Yaron (1966).

Table 1 shows the sorption of $Cu^{2+}$ and $CrO_4^{2-}$ on the four preparations of $ThO_2$. The oxide prepared using $NH_4OH$ had a higher capacity for anions while the one prepared using $NaOH$ had a higher capacity for cation. Chernykh and Boichinova (1971) observed that adsorption of transition metal ions on hydrous $ZrO_2$ precipitated with $NaOH$ was twice as high as that precipitated with $NH_4OH$. Both these observations must be related to the structure of the oxides. As these oxides were amorphous, the explanation is sought through the mechanism of the formation of hydrous oxides by precipitation techniques.

It is known that $Th^{4+}$ is present as a hydrolysed complex ion such as $[Th(OH)_3Th]_n^{n+4}$ in solution (Kraus 1965). When precipitation is brought about by the addition of alkali, the anions co-ordinated to the thorium ion are slowly replaced by $OH^-$ ions and a precipitate of hydrous $ThO_2$ results. Randomness in the structure of the oxide would be favoured by rapid polymerisation such as might result from a sudden increase in pH (Clearfield 1964). The hydrous oxide prepared by precipitation with a base is believed to have this random structure and is consequently amorphous. Also, under conditions of rapid polymerisation some of the anions which are electrostatically associated with the polymer groups are trapped within the polymer matrix producing a neutral substrate before the stoichiometric ratio of the metal to hydroxide is attained. The amount of anion retained by the precipitate is pH dependent, decreasing as the final pH of the precipitation increases (Clearfield 1964). Crystalline hydrous oxides are considered to be hydrated oxo-hydroxides, $[MO_b (OH)_{4-2b} \cdot x H_2O]$, where $M = Zr$, Th, etc. The value of $b$ is variable and

depends upon the condition of preparation. The base precipitated hydrous oxide differs from the crystalline product in that it has a much smaller value of *b*.

Based on the foregoing discussion, one can conclude that, an oxide precipitated using $NH_4OH$ is liable to entertain more anions than the one which is precipitated with NaOH, because of the differences in alkalinity and the final pH of precipitation of the two alkalis. The anions trapped in the polymer are perhaps exchangable in nature and thus they behave like basic salts. Probably it is this property that makes $ThO_2(NH_4 \cdot C)$ sorb more anions and $ThO_2(Na \cdot C)$ more cations.

It has been shown (Clearfield 1964) that the number of $OH^-$ groups in the hydrous oxides are reduced on refluxing or heating and the value of *b* increases. Heating the precipitate removes the trapped anions too and hence anion capacity is also likely to reduce. This may probably be the reason for the observed decrease in the cation and anion sorption by $ThO_2(Na \cdot H)$ and $ThO_2(NH_4,H)$, preparation, respectively (table 1).

It is possible that some $Na^+$ ions are present in the initially prepared material, $ThO_2(Na \cdot C)$. The sorption values for the alkali metal ions given in table 2 do not show any specific effect of the presence of $Na^+$ ions in the initially prepared material, $ThO_2(Na,C)$. As far as the transition metal ions (Cu, Co, Ni) are concerned, the sorption values are compared amongst themselves (table 3) and $Na^+$ ion present, if any, in $ThO_2(Na \cdot C)$, is only a common ion, for all the three ions (Cu, Co, Ni) being compared.

Table 2 lists the sorption of alkali metal ions at different alkali concentrations and a sorption series for the alkali metal ions could be written as:
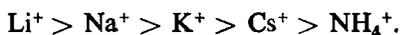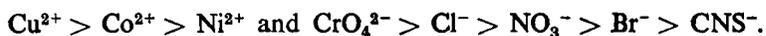
$$Li^+ > Na^+ > K^+ > Cs^+ > NH_4^+.$$

Table 3 lists the sorption of transition metal ions and anions on $ThO_2$ preparations from which the following affinity series could be deduced.

$$Cu^{2+} > Co^{2+} > Ni^{2+} \text{ and } CrO_4^{2-} > Cl^- > NO_3^- > Br^- > CNS^-.$$

The decrease in the affinity of alkali metal ions with increase in the ionic radii of the metal ions and also the affinity series for the monovalent anions could be explained well on the basis of the effective field strength theory of Eisenman (1962) and Sherry (1969) and Reichenberg (1966). $ThO_2$ behaves like a matrix with high field strength, where the electrostatic interaction between the exchanging ion and the exchanging sites (the surface hydroxyl groups) is more predominant over the hydration of the exchanging ions. Weakly basic anion exchangers and weakly acidic cation exchangers exhibit such a behaviour. The high capacity for divalent ion is quite understandable (electro selectivity).

A sorption series for transition metal ions similar to the one observed for $ThO_2$ (Na·C) has also been reported for other oxides (Fuller 1971). This series parallels the stability constants of the respective cations, more especially their hydrolysis reaction (Martell and Sillen 1964).

$$Me^{2+} + H_2O \rightleftharpoons Me(OH)^+ + H^+ \tag{4}$$
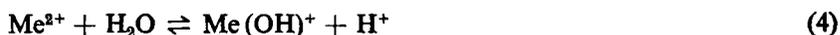
where $Me^{2+}$ is a transition metal ion. The series observed also follows the sequence for the solubilities of the respective hydroxides (Faitknecht and Schlindler 1963).

There seems to be, thus, a close relation between the strength of the metal oxygen bond and the sorbability.

In an independent investigation (Venkataramani 1974), mixed oxides of Th(IV) containing Co(II) or Ni(II) were prepared in order to improve the sorption properties of $ThO_2$ and the sorption of $Cu^{2+}$ on these oxides were studied. It was observed that $Co^{2+}$ or $Ni^{2+}$ initially in solid was completely replaced by $Cu^{2+}$ in solution. The sorption behaviour could, thus, be related to the solubilities of the respective hydroxides. An observation similar to this was reported by Phillips and Kraus (1965) for transition metal sulphides, where the sorption of a metal ion was interpreted in terms of the solubilities of the respective sulphides. In the light of the observation on transition metal hydrous oxides (Venkataramani 1974), the sorption sequence observed for Cu, Co, and Ni on hydrous $ThO_2$ in the present investigation can be interpreted as arising out of the bond formation between the transition metal ion and the surface oxygen of the $ThO_2$. The transition metal ion that forms a stronger bond with surface oxygen is sorbed better.

## Acknowledgement

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