

CHROM. 5025

Zirconium tellurate, an inorganic ion exchanger

In contrast to organic ion-exchange resins, inorganic ion-exchangers are highly stable under high temperatures and high doses of radiation. As a result, inorganic ion-exchangers have the potentiality of being used in the recovery of highly radioactive fission products. During the last decade different inorganic compounds, specially the zirconium salts, have been investigated as ion-exchange materials^{1,2}. Very little information is available regarding the ion-exchange properties of zirconium tellurate³. The composition and some ion-exchange properties of this compound are reported in this paper.

Experimental

Preparation. The sample was prepared by refluxing solutions of zirconyl chloride and sodium tellurate in 1.0 *M* hydrochloric acid. 400 ml of a 0.45 *M* sodium tellurate solution were placed in a refluxing assembly and refluxed for about 1 h before 330 ml of a 0.2 *M* zirconyl chloride solution were added dropwise at the rate of about 5 ml/min. There was instant precipitation as the two solutions were mixed. The system was refluxed for 40 h. The precipitate was separated by centrifugation and was washed with distilled water and dried at 50–60° until it broke into coarse particles. These particles were converted to the H⁺ form by treating with a 1.0 *N* hydrochloric acid solution until there was no Na⁺ in the effluent. The granules were again dried at 50–60° and sieved to different mesh sizes. The particles of mesh size 72–120 BSS were used in all the experiments unless otherwise mentioned.

Analysis. Analysis with respect to the ratio of Te/Zr was made in an indirect way by using known amounts of zirconium and tellurium while precipitating and then estimating the excess tellurium. Tellurium was determined by a gravimetric method⁴ involving reduction of the tellurate ion to the tellurium element. To study the thermogravimetric behaviour of the sample, thermograms were obtained using a Stanton Thermobalance.

Exchange capacity and pH titration. The total exchange capacity of the sample was determined by batch method in strongly alkaline solution. 1.0 g of the solid was first equilibrated with 25 ml of distilled water to which 25 ml of strong NaOH or KOH solution were added and equilibrated. The strength of NaOH in contact with the solid was 1.3 *N* and that of KOH was 0.63 *N*. The amount of H⁺ released was determined by estimating the amount of alkali neutralized. During this experiment and the pH titration described below, due precaution was taken to keep the system free from atmospheric carbon dioxide.

To study the mode of dissociation of the exchangeable H⁺ 1.0 g of the solid was equilibrated by shaking at room temperature (28°) with 50 ml of a 2.0 *M* NaCl solution and the equilibrium pH was recorded. After that a known amount of standard NaOH solution was added with time and the constant pH was recorded after each addition. The pH reading was taken to be constant when the variation was <0.01 pH scale per 30 min. It took several minutes to several hours to get equilibrium readings. A similar operation was repeated with KCl and KOH and also with LiCl and NaOH. This experiment was carried out with a Beckmann Electroscan TM30P. The electrode

system was earlier calibrated using standard buffer solutions, and the pH reading was corrected according to the calibration curve.

Results and discussion

Supernatant liquid of the ZrTe precipitate gave a negative test for zirconium but a positive test for tellurium. This indicates that during precipitation tellurium was in excess. According to the analysis the molar ratio of Te/Zr in the reported sample was found to be 1.13. Fig. 1 shows the thermogram of the zirconium tellurate in particle as well as powdered form. If the composition corresponding to the constant weight at the temperature 700–900° is assumed to be $\text{ZrO}_2 \cdot \text{TeO}_3$, then the calculated composition of the product reported in this paper becomes $\text{ZrO}_2 \cdot \text{TeO}_3 \cdot 5\text{H}_2\text{O}$ which is identical to the composition $\text{ZrOTeO}_4 \cdot 7\text{H}_2\text{O}$ reported by MONTIGNIE⁵. The excess two molecules of water in the latter case could be due to absorbed moisture.

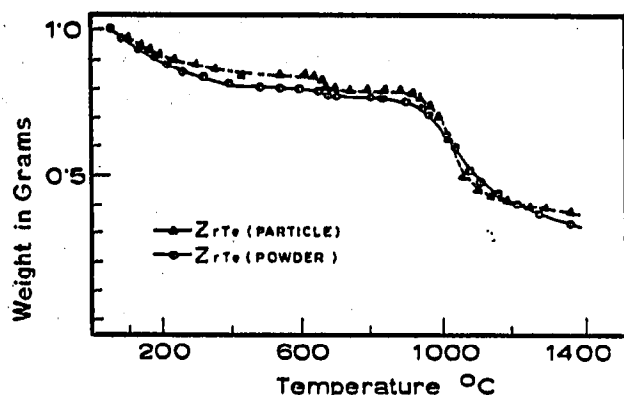


Fig. 1. Thermograms for ZrTe samples.

While the work reported in this paper was carried out ZSINKA *et al.*³ presented a report on zirconium tellurate inorganic ion exchanger and proposed its formula to be $\text{ZrO}(\text{HTeO}_4) \cdot n\text{H}_2\text{O}$ and concluded an analogy between phosphates and tellurates of zirconium. However, it is to be noted that the above formula cannot explain the electroneutrality of the compound if, as proposed by the authors, the univalent (HTeO_4^-) be functional group because the cationic ZrO group is supposed to be a divalent one and because it is not clear whether $n\text{H}_2\text{O}$ in any form has chemical bonding with the $\text{ZrO}(\text{HTeO}_4)$ matrix. They have considered the compound as a salt of *o*-telluric acid whose formula they have taken as $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ but this is discarded by others⁶. The latest formula of the *o*-telluric acid is H_6TeO_6 and it forms monoclinic salts like KH_5TeO_6 and $\text{Li}_2\text{H}_4\text{TeO}_6$ and a few salts, Ag_6TeO_6 being one of them, in which more than two protons of the acid are replaced⁷.

Until recently all the zirconium phosphates would be generally represented as zirconyl phosphates¹. Recently using soluble zirconyl salt and phosphoric acid CLEARFIELD AND STYNE⁸ prepared gelatinous zirconium phosphate which on refluxing with an excess of phosphoric acid yielded crystalline zirconium phosphate and by X-ray and thermogravimetric analysis established the formula $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$.

Considering the above facts it is likely that the molecular formula of the compound reported in this paper is $\text{Zr}(\text{H}_2\text{TeO}_6) \cdot 4\text{H}_2\text{O}$. Based on this formula all the experimental results can be best explained. The formula is in agreement with observed

Te/Zr ratio of about 1. Approximately 18% weight loss at 100–500° indicates the splitting out of the equivalent of four moles of water. About 4.5% weight loss at 650–700° is likely the loss of one mole of water of constitution because of the condensation of $Zr(H_2TeO_6)$ to $Zr(TeO_6) \cdot H_2O$. The continuous weight loss starting at about 900° may be due to the decomposition of $ZrTeO_6$ into ZrO_2 and TeO_3 followed by evaporation of TeO_3 . The difference observed between the particle and the powder forms of the sample is likely due to excess adsorption of moisture by the powder.

According to the composition of the compound proposed above the total capacity should be 2 moles per mole and there should be two plateaus in the pH titration curves.

TABLE I
EXCHANGE CAPACITY AT ROOM TEMP. (28°)

Ions	Total capacity (mequiv/g)	Approx. capacity up to pH 12 ^a (mequiv/g)
Li ⁺	—	2.8
Na ⁺	4.7	2.8
K ⁺	4.4	2.6

^a Calculated from the titration curves.

The observed total capacities as shown in Table I are 4.4 and 4.7 mequiv./g which on calculation according to the proposed formula result in the capacities 1.8 and 1.9 mole/mole for K⁺ and Na⁺, respectively. These values are quite in agreement with theoretical values. The pH titration curves shown in Fig. 2 have no sharp plateaux. Some difference in the titration curves may be due to different metal ions. The approximate capacities up to pH 12, as calculated from the titration curves, are 1.0 to 1.1 mole/mole for Li⁺, Na⁺ and K⁺. These values are in agreement with those reported by ZSINKA *et al.*³. Thus it appears that in the pH range from 2.5 to 12 only about 50% of the H⁺ are exchanged while the rest of the H⁺ exchange only in strongly

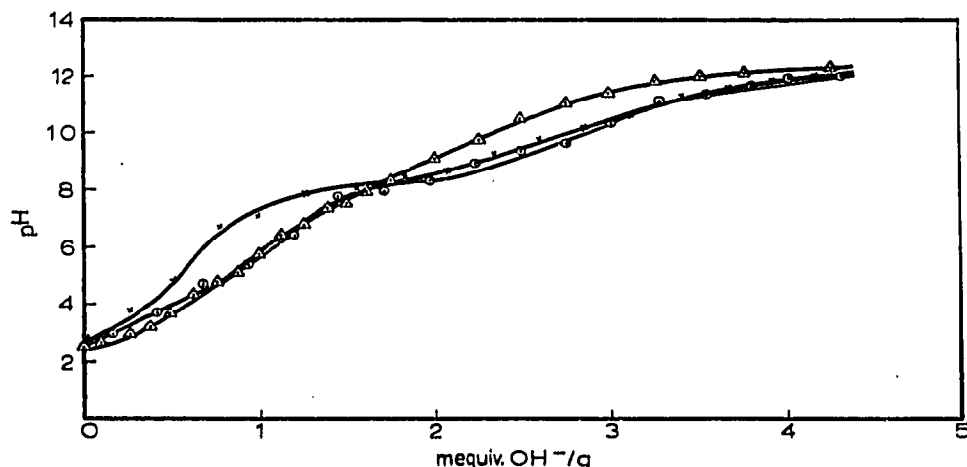


Fig. 2. Titration curves of Zr-tellurate with different salts and alkalis. \odot , NaCl + NaOH; \times , LiCl + NaOH; \triangle , KCl + KOH.

alkaline medium. Further investigations for evaluating the distribution of different ions, specially of those which constitute the fission products, are receiving attention.

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The use of Teflon film in quantitative analysis by enclosed-strip paper electrophoresis

The separation and determination of the valence states of iron

The enclosed-strip method of paper electrophoresis has been used widely as a qualitative tool for the identification of unknown compounds, for the separation of mixtures and for the study of complexes, but it seems rarely to have been applied to quantitative work, probably for the following reason. The insulating films most commonly used for enclosure of the paper strips consist of polyethylene or Mylar [poly(ethylene terephthalate)] and when wet papers are removed from the apparatus after electrophoresis, traces of the impregnating electrolytes often adhere as droplets to the films, making quantitative recovery of the experimental compounds difficult. It is now shown that the method is readily adaptable to quantitative analysis if a film of Teflon (polytetrafluoroethylene) is used as the insulating envelope. The hydrophobic nature of Teflon allows the paper strips to retain aqueous electrolytes completely when they are parted from the film after electrophoresis. Mixtures of iron(II)

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