

## SORPTION OF IODIDE IONS ON FERRIC OXIDE

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The effect of the crystal structure, shape, and dispersity of the ferric oxide particles on the kinetics and extent of the iodide ion sorption was investigated. The dependences of the sorption on the pH and on the liquid-to-solid ratio as well as the sorption isotherm were determined. The reversibility of the sorption of the iodide ions on ferric oxide and the occurrence of a single species of the iodine sorbed were established.

Soil is capable of retention of radioiodine and generally all iodine through a number of different mechanisms, in which the mineral as well as the organic soil constituents are involved. The final effect is a resultant of many factors, acting frequently in opposite directions. The experiments performed with real soils indicate or model the actual relations in the biosphere, their significance for the study of the nature of the reactions occurring is, however, limited, since they do not enable us to explain the observed facts uniquely. For this reason it is convenient to simplify the system under study by employing appropriate model sorbents, the choice of which must be based on the soil composition. In fact, the results obtained on an artificial product should not be applied mechanically to its natural counterpart, on the other hand, however, in this manner the effects of the various factors can be studied separately, apart from the other ones.

From the complex chemical analysis of soils performed by employing instrumental neutron activation analysis<sup>1</sup> and from their mineral structure<sup>2</sup> it follows that iron compounds play an important part in the mineral soil component. Of the various iron compounds the oxides are among the most significant, as they can appreciably affect the sorption processes in the soils and sediments through their oxidation-reduction reactions, as observed in the case of phosphate ions<sup>3</sup>.

For the study of the sorption behaviour of iodide ions from aqueous solutions, ferric oxide was chosen, being characteristic of the aerobic conditions of natural systems and being present as such or in the hydrate form in soils as a component of the so-called secondary minerals. Attention has been paid in this work also to the effect of the crystal structure, shape, and dispersity of the ferric oxide particles on the iodide retention.

According to some papers, iodide virtually does not sorb on hydrated ferric oxide<sup>4</sup>, the sorption capacity increases, however, considerably if activated by silver.<sup>5</sup>

## EXPERIMENTAL

Natural ferric oxide is not sufficiently pure, the studies were therefore performed with synthetic samples obtained from the Research Institute for Sound and Picture in Prague (it serves as the ferromagnetic material for the preparation of the magnetic signal record carriers). Three ferric oxide samples were employed — one of the  $\alpha$ - $\text{Fe}_2\text{O}_3$  type and two  $\gamma$ - $\text{Fe}_2\text{O}_3$  samples differing in shape and dimensions; they were supplemented by a sample of synthetic goethite  $\text{FeO}(\text{OH})$ . The technique of the preparation and the chemical and physicochemical properties have been reported<sup>6,7</sup>. The elementary particles of the  $\gamma$ - $\text{Fe}_2\text{O}_3$  samples were cubic or needle shape, structurally identical as proved by X-ray diffraction analysis. The chemical composition of the cubic ferric oxide was as follows: total iron 69.5%,  $\text{Fe}^{2+}$  0.17%,  $\text{SO}_4^{2-}$  0.03%, humidity 0.27%, losses on annealing up to 850°C 0.28%; density  $4.827 \text{ g cm}^{-3}$ . The needle-shaped oxide displayed higher annealing losses (about 1%) and higher sulfate content ( $\sim 0.7\%$ ). All the oxide samples employed were virtually monodisperse isometric particles. The particle size was estimated from the X-ray diffraction and determined along with the particle shape and distribution from electron microscope photographs. The average particle size of the cubic  $\gamma$ - $\text{Fe}_2\text{O}_3$  sample was determined to be  $0.103 \mu\text{m}$  (ranging from  $0.06$  to  $0.17 \mu\text{m}$ ), the average length of the needle samples was  $0.23 \mu\text{m}$ , the length-to-width ratio 7:1, the particles of the remaining samples had virtually the same dimensions as the needle  $\gamma$ - $\text{Fe}_2\text{O}_3$  sample, because they constitute a genetic series. The specific surface areas, determined by the thermal desorption method according to Nelson and Eggertsen<sup>8</sup>, were 10, 21, and  $29 \text{ m}^2 \text{ g}^{-1}$  for the cubic and needle  $\gamma$ - $\text{Fe}_2\text{O}_3$  and for  $\alpha$ - $\text{Fe}_2\text{O}_3$ , respectively; for  $\text{FeO}(\text{OH})$  the value has not been determined. The surface of the cubic  $\gamma$ - $\text{Fe}_2\text{O}_3$  particles was rather smooth and pore-free, whereas the electron microscope photographs of the needle  $\gamma$ - $\text{Fe}_2\text{O}_3$  particles revealed rough surface with large pits.

All the chemicals used for the preparation of the oxides and of all the solutions were reagent grade purity. The sorption of the iodide ions was studied by using radioactive tracer  $\text{K}^{131}\text{I}$  (carrier-free preparation of Soviet provenance); only such  $^{131}\text{I}^-$  solutions were employed that did not exhibit any other chemical form of radioiodine when checked by thin layer chromatography<sup>9</sup>. Differences between the analytical concentrations of the various  $\text{K}^{131}\text{I}$  preparations were eliminated by using  $10^{-9} \text{ M}$  labelled potassium iodide solutions, unless stated otherwise. The partition of the radionuclide between the solid and the liquid phases was examined in equilibrium conditions. The solution, volume  $V$ , was agitated with a weighed amount ( $m$ ) of the  $\text{Fe}_2\text{O}_3$  sample for a preselected time. The pH values of the solutions were adjusted by means of citrate buffers; the ionic strength was the same in all cases,  $\mu = 0.1$ . The phases were separated by centrifugation. From the radioactivity measured before and after the sorption, the relative sorption  $y = [\text{A}]/[\text{A}]_{\text{tot}}$  was determined; here  $[\text{A}]$  is the amount of the iodide sorbed on  $\text{Fe}_2\text{O}_3$ ,  $[\text{A}]_{\text{tot}}$  is the total iodide concentration in the system. The values of the distribution coefficient  $K_d$  were also calculated, defined as the amount of the iodide sorbed on 1 g of  $\text{Fe}_2\text{O}_3$  divided by the amount remaining in 1 ml of the solution. The sorbent was in contact with the solution for a time  $\Delta t$ . The radioactivity of the evaporation residues from the aqueous phase was measured by GM tubes, the pH values of the solutions were determined by means of an instrument PHM 26c (Radiometer, Copenhagen, Denmark) using a glass electrode G 200 B and a saturated calomel electrode K 100 of the same manufacturer. The pH values given pertain to the equilibrium solutions, *i.e.* after the sorption.

## RESULTS AND DISCUSSION

Sorption of ions by insoluble metal hydroxides and hydrated metal oxides is being explained in terms of various mechanisms, most commonly by the relation between the charge of the precipitate surface and that of the ions sorbed, or by the ion exchange between the dissociated hydroxyl groups of the sorbent and the ions in the solution. According to both mechanisms, anions are sorbed preferentially in the acidic region, whereas a high pH enables the sorption of cations. In a neutral medium the sorption of both cations and anions is found experimentally. According to some authors, the second mechanism can more easily and convincingly account for all the phenomena observed during the sorption of cations as well as anions on insoluble hydroxides or hydrated oxides, because the dissociation of the hydroxyl groups can proceed in two ways according to the pH:  $M-OH \rightleftharpoons M^+ + OH^-$  or  $M-OH \rightleftharpoons M-O^- + H^+$ . The results of the present work support this view.

The time course of the iodide ion sorption on ferric oxide (Fig. 1) indicates that the trapping proceeds in two stages: after an apparent fast start the sorption slows down until an equilibrium state is established. How fast this state is attained depends on the amount of the solid in the system — the equilibrium is approached more rapidly

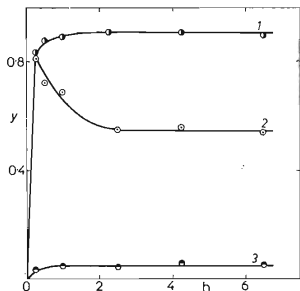


FIG. 1

## Kinetics of Sorption of Iodide Ions on Ferric Oxide

$c_{I^-} = 2 \cdot 10^{-10} \text{ mol l}^{-1}$ ,  $V/m = 25 \text{ ml} \cdot \text{g}^{-1}$ ; 1 pH 3.1,  $\gamma\text{-Fe}_2\text{O}_3$ , needle-shaped, nonhydrated; 2 pH 0.85,  $\gamma\text{-Fe}_2\text{O}_3$ , needle-shaped, nonhydrated; 3 pH 5.1,  $\alpha\text{-Fe}_2\text{O}_3$ , without hydration and with hydration for 5 days.

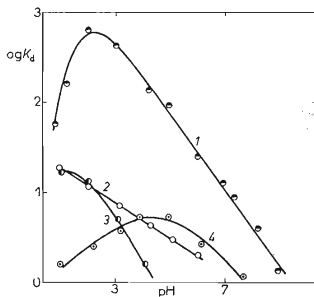


FIG. 2

## Sorption of Iodide Ions in Dependence on the pH

$c_{I^-} = 2 \cdot 10^{-10} \text{ mol l}^{-1}$ , hydration for 1 day,  $\Delta t$  5 h,  $V/m = 25 \text{ ml g}^{-1}$ ; 1  $\gamma\text{-Fe}_2\text{O}_3$ , needle-shaped; 2  $\alpha\text{-Fe}_2\text{O}_3$ ; 3  $\gamma\text{-Fe}_2\text{O}_3$ , cubic shape; 4  $\text{FeO}(\text{OH})$ .

if a higher sorbent amount is applied. Under vigorous shaking the equilibrium on hydrated samples is reached in less than 2 h, on nonhydrated samples in a time up to 3 h. In some instances, particularly during sorption of iodide on nonhydrated oxides from acidic solutions, anomalous shapes of the kinetic dependence can occur (Fig. 1, curve 2), which are usually a complex resultant of several consecutive or simultaneous processes, particularly electrostatic adsorption of the iodide ions from the solution on the oppositely charged surface of the solid, the aforesaid ion exchange, surface dissolution of the oxide with the sorbed iodide by the acid, or the effect of the macroconcentrations of the other anions present in the system. Ferric oxides that had been prior hydrated in water or in the buffer did not exhibit such anomalies. A long-time examination of the sorption was performed with the solutions pH 3.1 and 0.85. In the former case a true equilibrium state was attained, thus the amount of the iodide sorbed on  $\gamma\text{-Fe}_2\text{O}_3$  remained unchanged even after 720 hours' contact of the sorbent with the solution. In systems pH 0.85, however, a steady decrease of the relative sorption was observed, only negligible at the beginning but quite apparent after 150 h; this phenomenon, as well as the poorer reproducibility of the results obtained with this series of experiments, was obviously due to the proved dissolution of the sorbent.

The principal dependence to be investigated is, naturally, that of the iodide ion sorption on the pH. The shapes of these dependences are shown in Fig. 2 for the three  $\text{Fe}_2\text{O}_3$  samples as well as for  $\text{FeO}(\text{OH})$ ; a wide pH range has been examined although obviously the limiting conditions do not occur in the natural processes. The lower sorption occurring at the lowest pH has been discussed above. This also accounts for the fact that  $\text{Br}^-$  and  $\text{I}^-$  ions can be separated from one another on a column packed with ferric oxide as the adsorbent, if nitric or hydrochloric acid is used as the eluting agent<sup>10</sup>. As the pH increases, the sorbed amount of the iodide ions reaches a maximum and then decreases gradually. The  $\log K_d$  values plotted against the pH afford straight lines whose slopes are dependent on the crystal structure of the ferric oxide, its particle shape, dispersity, and particularly surface quality have an effect on the efficiency of the sorption.

From the microelectrophoretic measurements the zero charge point<sup>11</sup> of the  $\gamma\text{-Fe}_2\text{O}_3$  particle was found at pH 3.8, with a rapid increase of the positive surface charge towards lower pH values and a very mild rise of the negative charge towards higher pH values up to the neutral region; only above pH 7 the particles gain an appreciable negative charge. As can be seen from Fig. 2, the iodide ion sorption on ferric oxide proceeds also in the basic region, hence also on the negatively charged particles, which does not comply with the concept of the ion exchange in the secondary double layer. From this it follows that the electrostatic mechanism is not responsible for the sorption itself, it rather indicates the circumstances in which the ion approaches the sorbent surface.

The efficiency of the iodide ion sorption on  $\gamma\text{-Fe}_2\text{O}_3$  (needle form) in dependence on the liquid-to-solid ratio is shown in Fig. 3. The shapes of the dependences allow to determine the optimum experimental conditions for the application of hydrated ferric oxide as the scavenger during the decontamination of aqueous solutions containing iodine radionuclides.

For an explanation of the sorption mechanism, use is being made of the sorption isotherms. This dependence for the optimum conditions of the sorption is shown in Fig. 4. The sorbed amount of the iodide grows gradually with the increasing iodide concentration in the solution. The limiting value of the sorbed amount was not attained. The sorption was found to obey the Freundlich relation in the case of the  $\alpha$  oxide form, but not in the case of the  $\gamma$  form. The results of the determination are also presented as plots of  $K_d$  versus the equilibrium iodide concentration in the solution (Fig. 4, curves 4, 5). The  $\gamma$  form is seen to be effective for microquantities and

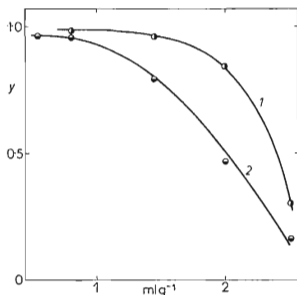


FIG. 3

Dependence of the Sorption of Iodide Ions on the Logarithm of Liquid-to-Solid Ratio  
 $c_1 = 2 \cdot 10^{-10} \text{ mol l}^{-1}$ ;  $V = \text{const.}$ ;  $\gamma\text{-Fe}_2\text{O}_3$  needle-shaped,  $\Delta t$  5 h; 1 pH 2.0, 2 pH 4.9.

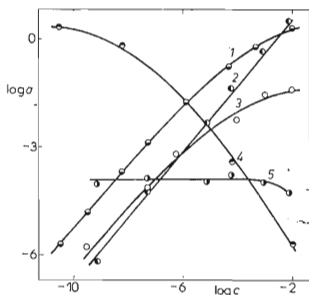


FIG. 4

Sorption Isotherm for the Sorption of Iodide Ions on Ferric Oxide and Dependence of the Distribution Coefficient on the Anion Concentration

$a$  Sorbed amount of the anion, mmol per g sorbent;  $c$  equilibrium concentration of the anion in the solution,  $\text{mol l}^{-1}$ ; hydration for 1 day;  $\Delta t$  5 h;  $V/m = 25 \text{ ml g}^{-1}$ ; 1 pH 2,  $\gamma\text{-Fe}_2\text{O}_3$ , needle-shaped; 2 pH 2,  $\alpha\text{-Fe}_2\text{O}_3$ ; 3 pH 4.9,  $\gamma\text{-Fe}_2\text{O}_3$ , needle-shaped; 4 dependence of  $K_d$  for the conditions of the curve 1; 5 dependence of  $K_d$  for the conditions of the curve 2.

very low concentrations of the iodide ions, the  $K_d$  values drop rapidly with the increasing concentration. In the case of the  $\alpha$  form,  $K_d$  is low and virtually constant over the whole concentration region examined. According to the sorbed quantities of the iodide anion, the sorption of this ion cannot proceed in the secondary double layer only; the latter can only take a limited part in the sorption.

The reversibility of the iodide ion trapping by ferric oxide was examined by applying the method of multiple desorption with equal solution volumes, as worked out and with some cations tested experimentally by Gromov<sup>12</sup>. The existence of different physicochemical species of the nuclide sorbed is revealed by the occurrence of a number of constants of proportionality between the amount of the nuclide remaining on the sorbent and its equilibrium concentration in the solution. The process of desorption of iodide ion microquantities from ferric oxide is plotted in Fig. 5. The series of experiments were chosen so as to reveal both the effect of the pH and that of the  $V/m$  ratio, the volumes as well as the pH values of the desorption solutions being the same as in the solutions from which the ions had been sorbed. The solutions were exchanged ten times, each of them being allowed to be in contact with the sorbent for 2.5 h under vigorous shaking; this was according to the kinetic study sufficient for the equilibrium state in the systems in question to establish. The results indicate that the process of sorption of iodide ions on ferric oxide is a perfectly reversible process, there being no strong bonding between the nuclide and the sorbent formed even partly. As the dependences in Fig. 5 show, the  $K_d$  values remain constant in all cases during all the ten desorption cycles, which gives an experimental evidence of the iodine being sorbed on ferric oxide in a single form. The  $K_d$  values calculated from the sorption and desorption experiments are not quite identical; those derived from the desorption are always somewhat lower. This can be explained taking into

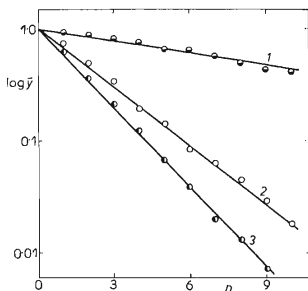


FIG. 5

Desorption of Iodide Ions from Ferric Oxide

$\bar{y}$  Relative amount of the anion remaining on the sorbent;  $n$  number of the desorption stages;  $c_1 = 2 \cdot 10^{-10} \text{ mol l}^{-1}$ ;  $\gamma\text{-Fe}_2\text{O}_3$  needle-shaped; citrate buffer;  $\Delta t$  2.5 h; 1 pH 2.0,  $V/m = 6.25 \text{ ml g}^{-1}$ ; 2 pH 4.9,  $V/m = 6.25 \text{ ml g}^{-1}$ ; 3 pH 2.0,  $V/m = 100 \text{ ml g}^{-1}$ .

account that the relation for the multiple desorption has been only derived for the case of a simple exchange sorption process, while in the case under study the electrostatic properties of the ferric oxide particles are involved too.

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