

removal of the grid; aggregation could occur during the final drying of the film of liquid.

Although the validity of the specimens has been checked by comparison with haemacytometer counts, the latter cannot be used to give the required results directly. The haemacytometer gives the total number of particles in the liquid dispersion, and once it has been verified that substantially the same numbers of particles of differing sizes are preserved on the specimen films, the electron microscope can be used to measure the size distribution with some confidence.

The most important feature of the results is that the ratios of the numbers of particles of different sizes is preserved, since two effects could alter this ratio in opposite directions. The smaller particles are the more difficult to centrifuge onto the film, but the larger ones have the greater tendency to become detached after impact on the film. These effects could conceivably cancel out, but the good correlation of the absolute numbers shows that this is not the case.

The choice of latex particles for this investigation was governed by their availability in monodisperse form with a range of mean particle sizes. It cannot be assumed that the same results would be obtained for

dispersions of different types, and it may be considered advisable to check specimens of any system under study by comparison with haemacytometer counts. However, only a limited check should be necessary, in each case, in view of the principle established.

Acknowledgements

The authors are grateful to Dr. J. N. Shaw, University of Bristol, for the polystyrene latices and to the Department of Scientific & Industrial Research for a scholarship to one of us (W.D.C.).

Summary

Particle size distribution data have been determined by electron microscopy for dispersions containing known mixtures of monodisperse polystyrene latices of diameters in the range 0.08–0.4 μ and particle concentrations of 10^6 – 10^8 particles ml^{-1} , and good agreement was found for grid specimens prepared by centrifugation.

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Heterogeneous Exchange of Precipitates

V. Exchange between an Aqueous Ferric Chloride Solution and Ferric (Hydr)oxides Differently Treated after the Precipitation*)

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With 5 figures

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1. Introduction

Investigating the heterogeneous exchange of ferric ion between an aqueous ferric chloride solution and some differently prepared solid ferric (hydr)oxides, we found various courses of the exchange process, evidently related to the properties of the solid phase.

The problem should be considered therefore from two points of view: the relation of

heterogeneous exchange to some already known characteristics of the solid phase, and some properties of the ferric (hydr)oxide system.

1.1. Heterogeneous Exchange

The heterogeneous exchange consists of a number of different processes. In the case of consecutive processes (such as diffusion inside the liquid phase – usually well stirred, boundary reaction and selfdiffusion inside the solid phase), selfdiffusion, being in general the slowest process, governs the

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course of heterogeneous exchange (1). If some other processes on the solid phase occur simultaneously with selfdiffusion, the selfdiffusion process and selfdiffusion coefficient can be investigated when other interfering processes are finished or reduced to a negligibly small role [fig. 3 in (2)], e. g. after "ageing" of the precipitate by standing in the mother liquor, heating, boiling, roasting, melting, smoothing, or for well developed crystals (2, 3, 4, 5, 6, 7, 8).

The (self)diffusion inside the solid phase is related to the disorder and vacancies in the crystal lattice, the exchange being faster for a low ordered lattice than for a high ordered one (9, 3, 10), which was also observed in some solids with structurally conditioned defects [e. g. double-layer structure consisting of an ordered main layer and a (partly) disordered interstitial layer (9)]. The structural change, related to lattice defects, can influence the mechanism of exchange governing process also [boundary reaction in amorphous precipitate with an imperfect lattice, and selfdiffusion in the precipitate after removal of lattice defects by heating (10)].

The "ageing" of a precipitate, by allowing it to stand in the mother liquor (11) at room or elevated temperature or by some special treatment [e. g. (10)], often introduces processes which can be considered as two kinds of recrystallization:

a) recrystallization inside the particles or some of the lattice layers [the ordering of the lattice being brought about by diminishing the lattice defects, see fig. 6 in (14)],

b) recrystallization in the sense of *Ostwald's* ripening (some of the particles grow, others dissolve). A much lower exchange rate for older (or "aged") systems than for the fresh one indicates that recrystallization has taken place [p. 38 in (12), (13)].

The curve of fraction exchange or a suitably related function, plotted vs. time, consists generally of two parts: a relatively fast part attributed to the boundary reaction, and the following slower part due to (self)diffusion in the solid. If required conditions are fulfilled, the plot of fraction exchange or a suitably related function vs. square root of exchange time shows that the first part representing boundary reaction is generally curved, while the following part standing for (self)diffusion is linear [1, 15, 7, 8, 3, 6; one system has been reported, in which the "boundary reaction" part was also linear, owing to the diffusion within a

surface layer, and followed by a slower diffusion within the lattice (4)].

The heterogeneous exchange of ferric ion between the liquid phase and solid ferric oxide has been investigated. A rapid surface exchange, used to calculate the specific surface, and the following slow exchange process have been observed (16). The equilibrium between "solid" and "colloidal" ferric oxide in the solution (17), the diffusion coefficient and activation energy for iron (18, 19, 20) and tritium (7), and exchange and diffusion for oxygen (21, 22) in iron oxides have been investigated by various methods. The heterogeneous exchange of ferrous ion between the solution and solid Fe_3O_4 has been described, the surface reaction and slower diffusion observed, and diffusion coefficient and activation energy calculated (23).

1.2. Ferric (Hydr)oxide

If a solution of ferric ions is mixed with a base, an "amorphous" precipitate is formed, consisting of very small particles, "amorphous" for X-rays, but showing relatively sharp electron diffraction pattern of the $\alpha - \text{Fe}_2\text{O}_3$ (24). [It is of interest to mention that *Suzuki* (28) found an analogously prepared precipitate showing a $\gamma - \text{FeOOH}$ diffraction pattern - probably owing to the not identical conditions - which, after boiling, changed into the $\alpha - \text{Fe}_2\text{O}_3$]. Depending on the conditions, the "ageing" of a freshly formed "amorphous" precipitate introduces some changes of the system. The change of crystallographic structure (29) and the transformation of the "true" ferric hydroxide $\text{Fe}(\text{OH})_3$ into $\alpha - \text{Fe}_2\text{O}_3$ by condensation of hydroxyl groups and formation of water have been reported (25). The growth of the particles was indicated by sharp X-ray diffraction pattern (24) and observed in photographs from an electron microscope [26, 28, formation of particles $\text{K} - \text{Fe}_2\text{O}_3$ (27)]. We observed earlier (30, 31) that fresh positive "amorphous" ferric (hydr)oxide precipitate, formed near the equivalency on the precipitation curve of the system $\text{FeCl}_3 + \text{NaOH}$, was not stable. Evidently sensitive to an excess of ferric ions and pH , the previously formed precipitate dissolved slowly [α on figs. 7 and 8 in (30), fig. 4 G and H in (31)].

The mentioned properties of ferric (hydr)oxide could explain some phenomena of heterogeneous exchange reported in this paper.

2. Experimental

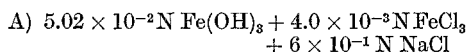
All systems were investigated at the room temperature.

2.1. Preparation of the Systems

The solutions were prepared from the analytical grade substances and bidistilled water.

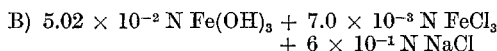
2.1.1. "Amorphous" ferric (hydr)oxide

Two systems, A and B, were prepared and investigated.



(at the beginning of the experiment).

Into a stirred solution ($5.02 \times 10^{-2} \text{ N NaOH} + 6 \times 10^{-1} \text{ N NaCl}$), solution of FeCl_3 was slowly added so that finally the concentration of $4.92 \times 10^{-2} \text{ N FeCl}_3$ was obtained. The negatively charged solid phase of ferric hydroxide was formed, $p_{\text{H}} = 8$ (30, 31). After 17 hours, FeCl_3 solution was added, and the increase of the concentration was $5 \times 10^{-3} \text{ N FeCl}_3$. The system contained positively charged solid phase, $p_{\text{H}} = 3.3$ (30, 31). After labelling by $^{59}\text{FeCl}_3$ solution, the ferric chloride concentration in the liquid phase increased by $4 \times 10^{-4} \text{ N}$. $nL + nS = 5.46 \times 10^{-2}$ (the sum of gram-equivalents of ferric ions in the liquid (nL) and in the solid phase (nS) per liter of the system; one third of the atomic weight of Fe was taken as the equivalent weight). The NaCl component had been added previously to coagulate the colloidal ferric hydroxide.



(at the beginning of the experiment).

The negatively charged solid phase of ferric hydroxide was prepared as described under A by the reaction $5.02 \times 10^{-2} \text{ N NaOH} + 6 \times 10^{-1} \text{ N NaCl} + 4.92 \times 10^{-2} \text{ N FeCl}_3$. After 17 hours FeCl_3 solution was added to increase the concentration by $8 \times 10^{-3} \text{ N FeCl}_3$, and the system contained positively charged solid phase, $p_{\text{H}} = 3.3$ (30, 31). After labelling by $^{59}\text{FeCl}_3$ solution, the ferric chloride concentration in the liquid phase increased by $4 \times 10^{-4} \text{ N}$.

$$nL + nS = 5.76 \times 10^{-2}.$$

2.1.2. Ferric oxide obtained by drying an "amorphous" ferric (hydr)oxide in the air (165 °C, 4.5 hours)

Into a stirred solution $1.3 \times 10^{-1} \text{ N FeCl}_3$ a solution $2.6 \times 10^{-1} \text{ N NH}_4\text{OH}$ was added in excess ($p_{\text{H}} = 9.3$). The obtained "amorphous" precipitate was washed with water, dried in the air at 165 °C for 4.5 hours, crushed, and put into aqueous ferric chloride solution.

The composition of the system (at the beginning of the experiment):

$$nS = 5.9 \times 10^{-2}, nL = 8.5 \times 10^{-3},$$

$$nL + nS = 6.75 \times 10^{-2}.$$

2.1.3. Ferric oxide obtained by boiling an "amorphous" ferric (hydr)oxide in water (100 °C, 4.5 hours)

The "amorphous" ferric hydroxide, prepared as that in chapter 2.1.2., was boiled under reflux condenser for 4.5 hours. After cooling, an aqueous ferric chloride solution was added to the solid phase.

The composition of the system (at the beginning of the experiment):

$$nS = 4.95 \times 10^{-2}, nL = 8.5 \times 10^{-3},$$

$$nL + nS = 5.8 \times 10^{-2}.$$

2.2. Preparation of Labelling $^{59}\text{FeCl}_3$ Solution

Fe_2O_3 p. a. "Merck" was irradiated by neutrons in the "A" Reactor of the Institute "Boris Kidrič" in Vinča. The radioactive sample $^{59}\text{Fe}_2\text{O}_3$ was dissolved in conc. HCl p. a. "Merck", and the solution $3.66 \text{ N } ^{59}\text{FeCl}_3$ in a HCl medium was obtained.

By irradiation of the Fe_2O_3 by neutrons, two kinds of radioactive nuclides, ^{59}Fe and ^{54}Mn (^{54}Mn without isotopic carrier), were obtained.

2.3. Investigation of the Heterogeneous Exchange and the Instruments

The system consisted of the solid phase ferric (hydr)oxide and ferric ions in the liquid phase. Immediately after the preparation, the system was divided into portions of 100 ml, and, after certain time intervals, the portions of the system of corresponding "age" were labelled by the addition of 10λ radioactive $3.66 \text{ N } ^{59}\text{FeCl}_3$ solution in a HCl medium (the "age" of the system is the time interval from the preparation of the system to the moment the system was labelled). After certain "exchange time" (the time interval from the moment of labelling the portions of the system to the moment the sample was taken out), the liquid phase was separated from the solid phase, the counting rate and ferric ion concentration of the liquid phase determined, and the specific ^{59}Fe radioactivity of the liquid phase calculated.

The liquid phase was separated from the solid by a Servall centrifuge (4500 g for "amorphous" hydroxide and 28800 g for the other systems for 40–60 minutes) and a clear or negligibly turbid supernatant liquid was obtained.

The counting rate was determined by EKCO Electronic Scintillation Counter (Well type NaI, activated Tl, crystal). $(A_t)_{\text{Fe}}$ represents the counting rate of 2 ml of the liquid phase of the sample, $(A_0)_{\text{Fe}}$ the counting rate of 2 ml of the system, when the same volume (10 λ) of radioactive solution was added into the same volume (100 ml) H_2O . The value $(A_t/A_0)_{\text{Fe}}$ was used for the relative ^{59}Fe radioactivity (the relative counting rate) of the liquid phase. The error from ^{59}Fe decay was eliminated, because $(A_0)_{\text{Fe}}$ was determined immediately before each $(A_t)_{\text{Fe}}$ (practically at the same time). The counting rate was corrected for background.

The p_{H} measurements were carried out by a Beckman instrument with a glass electrode.

The concentration of ferric ion was determined colorimetrically (with a Klett-Summerson photoelectric colorimeter or a Lange's Universal-Kolorimeter), HCl was used for reagent and light absorption determined in transmittance region at 420 $m\mu$).

X-ray analysis of the solid phase was made by a Philips Debye-camera, $\varnothing = 57.3 \text{ mm}$, CoK α radiation, 30 kV, 11 mA¹).

2.4. The Fraction Exchange F_I and F_{II}

The simple formula for fraction exchange, according to p. 8 (12) is represented by

$$F = (\beta_0^L - \beta_t^L) / (\beta_0^L - \beta_\infty^L) \quad [1]$$

(β^L represents the specific radioactivity of the liquid phase, the subscript letters correspond to the exchange time). If the inactive (i. e. not labelled) solid dissolved during the experiment (e. g. "amorphous" ferric

¹) We are indebted to Miss B. Prodić of the "Rudjer Bošković" Institute and Dr. A. Bezjak of "Jucema" for the X-ray analysis.

(hydr)oxide, chapter 2.1.1), the decrease of the specific radioactivity of the liquid phase is produced by two quite different processes: a) heterogeneous exchange, b) the dissolution of the (inactive) solid phase. The dissolution of the solid phase is not related to heterogeneous exchange, and eq. [1] can give erroneous results and essentially wrong conclusions if strictly applied. In order to calculate the real fraction exchange, we introduced some corrections, and, being too large for this paper, they are presented in a following paper (32). The exchange fraction F_I in fig. 2 was obtained by the corrected formula.

In other systems investigated (chapter 2.1.2. and 2.1.3.), the concentration of ferric ion in the previously labelled liquid phase decreased, and the solid phase was formed during the experiment. The specific radioactivities of the liquid and of the solid phase were equal during the formation of the solid phase, and that process introduced no change of βL value. Eq. [1] gives the correct value for fraction exchange, and the results are represented by F_{II} in figs. 3 and 4.

The values obtained by formulae F_I and F_{II} for corresponding cases can be compared with each other in the same sense, as can be the values obtained by the simple formula F for systems of different composition, but without composition change during the experiment.

2.5. $(A_t/A_0)_{Fe}$ Value

In order to investigate heterogeneous exchange for ferric ion, it is necessary to know the counting rate originating from ^{59}Fe . During the experiment with "amorphous" ferric (hydr)oxide, the radioactivity of ^{54}Mn , introduced into the system by labelling, was negligibly small if compared to ^{59}Fe radioactivity. During the experiments with other ferric oxide systems, the ratio of ^{54}Mn radioactivity to ^{59}Fe radioactivity increased, according to their half-life values (47 days for ^{59}Fe , 310 days for ^{54}Mn). It was necessary to discriminate the counting rate originating from ^{59}Fe from the total counting rate originating from both ^{59}Fe and ^{54}Mn . Some of the samples were analysed by the γ -ray analyser (256 channels, made at "Rudjer Bošković" Institute, Zagreb), and the radioactivity of ^{59}Fe (γ -ray energy peaks at 1.10 and 1.30 MeV) was discriminated from ^{54}Mn radioactivity (γ -ray energy peak at 0.85 MeV). The analysis by γ -ray spectra of these samples showed that the whole radioactivity of ^{54}Mn (error 10%) remained in the liquid phase of the fresh system as well as of the oldest system (age 7.2 days), after the shortest exchange time interval as well as after the longest time interval. We concluded therefore that in all the systems investigated the whole ^{54}Mn radioactivity remained in the liquid phase, $(A_t/A_0)_{Mn} = 1$.

In this way it was possible to calculate the relative counting rate $(A_t/A_0)_{Fe}$ for ^{59}Fe in the liquid phase for all the systems investigated from the corresponding $(A_t)_{Count}/(A_0)_{Count}$ value. $(A_t)_{Count}$ and $(A_0)_{Count}$ represent the total counting rate obtained by scintillation counter, originating from both ^{59}Fe and ^{54}Mn radioactivity for corresponding exchange time $t = t$ or $t = 0$ resp. If $\log (A_0)_{Count}$ values are plotted vs. T (time related to the data the counting rate was determined), fig. 1 is obtained. The values Δ_D , Δ_E , Δ_F represent the difference $\log [(A_0)_{Count}]_T - \log [(A_0)_{Fe}]_T$, giving the value $[(A_0)_{Mn}]_T/[(A_0)_{Fe}]_T$ for corresponding time T . Applying the equations for ^{59}Fe and ^{54}Mn decay, the value $[(A_0)_{Mn}]_T/[(A_0)_{Fe}]_T$ can be determined for any time T . From the relations $[(A_t)_{Count}]_T = [(A_t)_{Fe}]_T + [(A_t)_{Mn}]_T$ and $[(A_0)_{Count}]_T = [(A_0)_{Fe}]_T + [(A_0)_{Mn}]_T$, the value $(A_t/A_0)_{Fe}$ was calculated, supposing that $(A_t/A_0)_{Mn} = 1$, as mentioned previously.

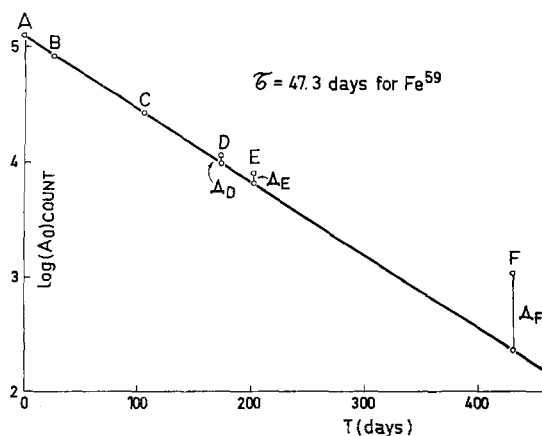


Fig. 1. $\log (A_0)_{Count}$ plotted vs. time (days). $(A_0)_{Count} = (A_0)_{Fe} + (A_0)_{Mn}$ for radioactive nuclides ^{59}Fe and ^{54}Mn

3. Results

The results are shown in fig. 2 for "amorphous" ferric (hydr)oxide (1), in fig. 3 for

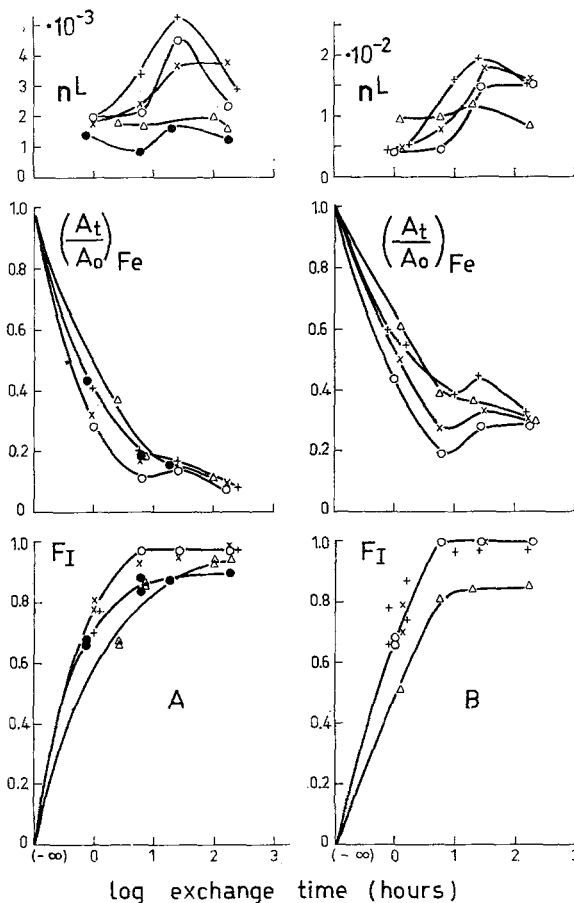


Fig. 2. "Amorphous" ferric (hydr)oxide [system (1)]. The fraction exchange F_I , the relative radioactivity $(A_t/A_0)_{Fe}$ for ^{59}Fe and the normality nL of ferric ion in the liquid phase plotted vs. log exchange time (hours) for systems A and B. Age of the system: 5 minutes (\circ), 6 hours (\times), 25 hours ($+$), 7 days (Δ), 3 weeks (\bullet)

ferric oxide (2) obtained by drying a freshly prepared precipitate in the air, and in fig. 4 for ferric oxide (3) obtained by boiling the fresh precipitate in water.

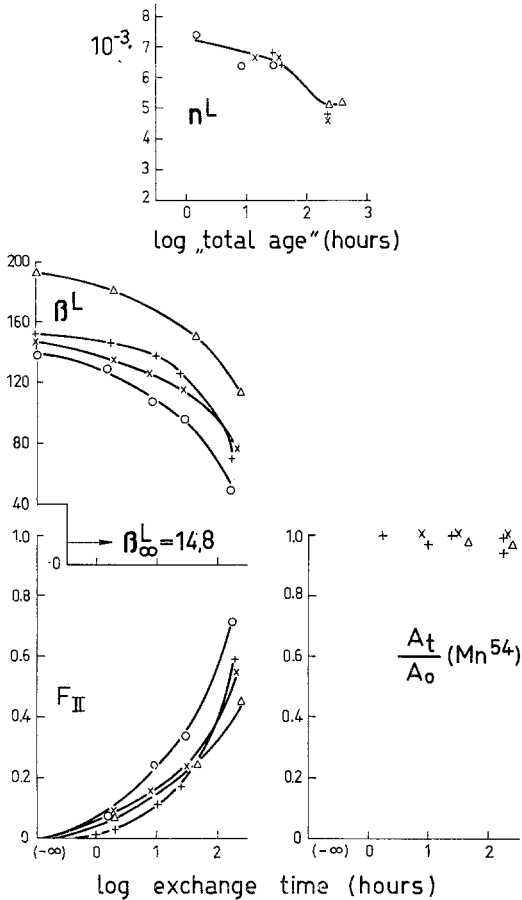


Fig. 3. Ferric oxide obtained by drying an "amorphous" ferric (hydr)oxide in the air [system (2)]. The fraction exchange F_{II} and the specific radioactivity β^L of ferric ion in the liquid phase plotted vs. log exchange time (hours), the relative radioactivity $(A_t/A_0)_{Mn}$ of ^{54}Mn in the liquid phase plotted vs. log exchange time (hours), and the normality n^L of ferric ion in the liquid phase plotted vs. log "total" age (hours) of the system. Age of the system: 25 minutes (\circ), 6.5 hours (\times), 27.5 hours ($+$), 7.2 days (Δ)

The heterogeneous exchange for the system (1) is indicated by a decrease of radioactivity of the liquid phase [$(A_t/A_0)_{Fe}$ in fig. 2], for the system (2) by a decrease of specific radioactivity of the liquid phase (β^L in fig. 3), and for the system (3) a low or no exchange is indicated by corresponding small or no β^L decrease (fig. 4). The heterogeneous exchange in the mentioned systems was accompanied by different simultaneous processes [the dissolution of the inactive solid ferric (hydr)oxide - n^L in fig. 2 - for

system (1), and the formation of the solid phase from the ferric ions labelled in the liquid phase - n^L in fig. 3 and fig. 4 - for the systems (2) and (3)].

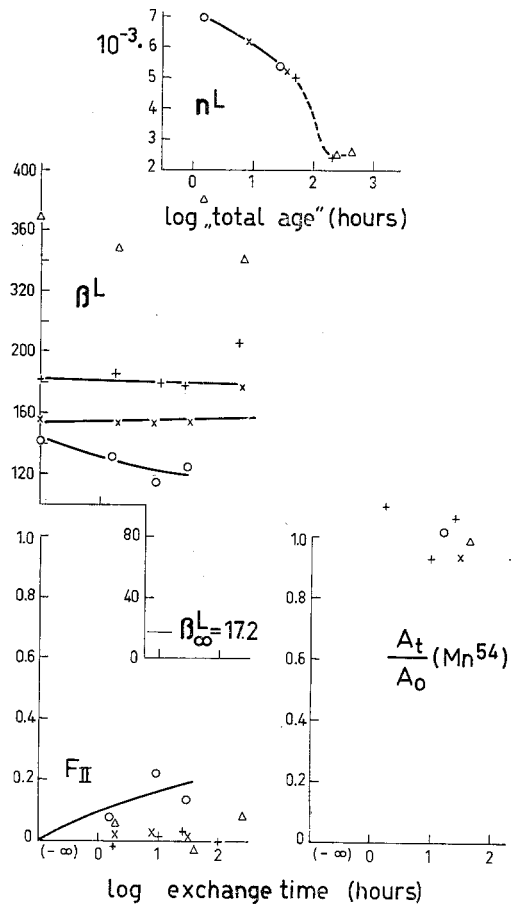


Fig. 4. Ferric oxide obtained by boiling an "amorphous" ferric (hydr)oxide in water [system (3)]. The fraction exchange F_{II} and the specific radioactivity β^L of ferric ion in the liquid phase plotted vs. log exchange time (hours), the relative radioactivity $(A_t/A_0)_{Mn}$ of ^{54}Mn in the liquid phase plotted vs. log exchange time (hours), and the normality n^L of ferric ion in the liquid phase plotted vs. log "total" age (hours) of the system. Age of the system: 30 minutes (\circ), 6.5 hours (\times), 27.5 hours ($+$), 7.2 days (Δ)

In order to compare the course of heterogeneous exchange for all the systems investigated, the fraction exchange, calculated for the corresponding case [F_I and F_{II} , see paper (32)], is represented in fig. 2, 3, and 4, showing that the rate of heterogeneous exchange decreased by the sequence: system (1), system (2), system (3), and was slower in an old ("aged") system than in the fresh one.

The ^{54}Mn nuclides without isotopic carrier, introduced by labelling into the liquid phase

of the system, remained in the liquid phase of the systems (2) and (3), $(A_t/A_0)_{Mn} = 1$ (the results in fig. 3 and 4 are scattered within experimental error). In the system (1), the ^{54}Mn radioactivity, introduced by labelling, was negligibly small, and counting rate results for ^{59}Fe were not disturbed (all counting rate results $\log(A_0)_{\text{count}}$ plotted vs. time were placed on a good straight line with a gradient corresponding to the half-life for ^{59}Fe).

The p_H value during the experiment was 2.5–3.5 for the systems investigated.

The X-ray analysis for the system (1–A) was made 1.7 years after its preparation and showed $\alpha\text{-FeOOH}$; for the system (2) 10 months after the preparation showing a mixture of $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-FeOOH}$; for the system (3) 10 months after the preparation showing $\alpha\text{-Fe}_2\text{O}_3$ with a small admixture of $\alpha\text{-FeOOH}$.

It is necessary to mention that, after a certain time interval, the n^L value for the system (1) decreased, owing to the slow hydrolysis and formation of $\beta\text{-FeOOH}$ [fig. 5 in (33), (34)], but the fraction exchange had already reached the value $F_I = 1$ (n^L and F_I in fig. 2).

The "total" age of the system (n^L curve in figs. 3 and 4) represents the sum of the age at the moment of labelling and the exchange time.

4. Discussion

If figs. 2, 3, and 4 are compared and the observed phenomena considered, some characteristics of our freshly formed "amorphous" precipitate and some changes, connected with the treatment of the solid phase after the precipitation, are evident.

4.1. Our "amorphous" ferric (hydr)oxide corresponded to the previously described positively charged precipitate of the system $\text{FeCl}_3 + \text{NaOH}$ near the equivalency on the precipitation curve, where the previously formed solid phase dissolved slowly, evidently owing to the sensitivity of the system to ferric ions in excess and p_H .

Considering the results of fig. 2, we can conclude:

a) The process of heterogeneous exchange as well as of the dissolution of the solid phase was initiated by the addition of the labelling solution $^{59}\text{FeCl}_3$ in a HCl medium. If the fraction exchange F_I curves in fig. 2 for the systems of different age are compared, the differences are relatively small. The fact, that the fraction exchange reached the value

$F_I \approx 1$ after a few hours (F_I for "age" 5 min. in fig. 2) and that after 3 weeks the intensity of the heterogeneous exchange was almost the same (F_I for "age" 3 weeks in fig. 2), indicates that it was not a continuous process, but a process initiated by the labelling of the system.

b) The recrystallization of the solid phase was the process initiated by addition of $^{59}\text{FeCl}_3$ in a HCl medium and was governing the course of heterogeneous exchange (it is not probable that the addition of the labelling solution would initiate a process of selfdiffusion inside the solid phase). Some of the particles dissolved, the others grew building radioactive (^{59}Fe) $^{3+}$ ions from liquid phase into their crystal lattice. The increase of the concentration of the liquid phase (n^L) indicates that the dissolution of some particles was faster than the growth of the others.

It seems that the mentioned phenomenon (recrystallization of the solid phase initiated by FeCl_3 in an acid medium) is characteristic of our "amorphous" ferric (hydr)oxide.

4.2. The role of treatment of the solid phase becomes evident if the curves for fraction exchange in figs. 2, 3, and 4 are compared. The rate of heterogeneous exchange decreased in the sequence: "amorphous" ferric (hydr)oxide (1), ferric oxide (2) obtained by drying in the air, ferric oxide (3) obtained by boiling in water.

Our "amorphous" precipitate (fig. 2) showed a specific phenomenon of initiated recrystallization. The precipitate dried in the air (fig. 3) showed no recrystallization during the exchange process, but the self-diffusion in the solid phase is indicated by linear relationship of value

$$1 - (\beta L)_t / (\beta L)_0 = F_{II} \cdot (n^S)_0 / (n^L + n^S)$$

plotted vs. square root of exchange time (fig. 5) [$(n^S)_0$ represents the n^S value at the moment the liquid phase of the system was labelled]. The first curved part, preceding the straight line, has to be attributed to the boundary reaction.

The fraction exchange values for boiled precipitate are too low and scattered, and it is not possible to detect the process governing heterogeneous exchange.

We can conclude that the previously described treatment introduced a structural change of primarily formed "amorphous" precipitate, a recrystallization in the sense of lattice ordering and particle growth inside the aggregates of small primarily

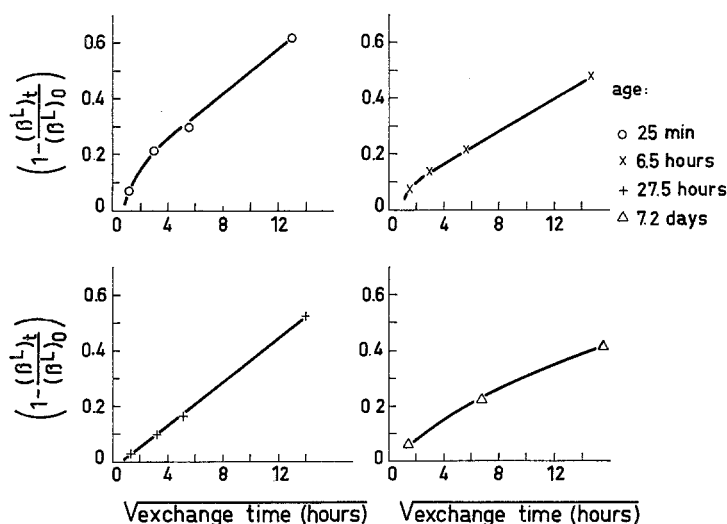


Fig. 5. Ferric oxide obtained by drying an "amorphous" ferric (hydr)oxide in the air [system (2)]. The value $[1 - (\beta L)_t / (\beta L)_0]$ for ferric ion plotted vs. square root of exchange time (hours). Age of the system: 25 minutes (\circ), 6.5 hours (\times), 27.5 hours ($+$), 7.2 days (\triangle)

formed particles, before the precipitate had been brought in contact with ferric ion solution and labelled. The fact that the boiled precipitate showed the effect of being "better recrystallized" (a slower heterogeneous exchange, fig. 4, corresponds to a better ordered lattice and larger particles) than the precipitate dried during the same time interval, could be plausibly explained. It is to be supposed that the particle growth and lattice ordering was going on through the liquid phase, and more successfully if the precipitate was boiled; if the precipitate dried in the air, the water gradually escaped and finally stopped the process.

It is interesting that *Schulman, Pontrelli* and *Brescia* (17) have reported that no dynamic equilibrium exists between solid ferric oxide and its corresponding colloidal dispersed particles, and that the colloidal ferric oxide under these conditions does not exchange with dissolved ferric iron (the experiment described in (17b), last section on p. 19). We have found that the treatment of the solid phase plays an important role in heterogeneous exchange, and we accept the author's conclusion, according to the authors' text, "under these conditions" [the colloidal solution, prepared by the authors (17), was dialysed].

4.3. We have discussed the phenomena observed from the point of view of the colloidal state and the degree of lattice order of the solid phase, and we think that these factors can play an important role. But it is to be emphasized, that other factors, such as the crystallographic structure of the solid phase, the change of the "true" ferric hydroxide $\text{Fe}(\text{OH})_3$ into ferric oxide (25),

and the composition of the solution (ferric complexes), could also be significant. This should be investigated before a final conclusion is made.

Summary

The heterogeneous exchange of ferric ion between a labelled aqueous ferric chloride solution and some differently prepared ferric (hydr)oxides [(1) a freshly formed "amorphous" ferric (hydr)oxide, (2) ferric oxide obtained by drying the freshly formed precipitate in the air at 165°C for 4.5 hours, (3) ferric oxide obtained by boiling the freshly formed precipitate in water at 100°C for 4.5 hours] was investigated at room temperature.

The exchange rate decreased in the sequence: (1), (2), (3), that sequence being attributed to the recrystallization of the solid phase in the sense of lattice ordering and particle growth, related to the treatment of freshly formed precipitate before the solid was put in contact with the ferric chloride and labelled.

System (1) corresponded to a positively charged precipitate near the equivalency of the system $\text{FeCl}_3 + \text{NaOH}$, and the exchange was governed by a rapid recrystallization (particle growth), initiated by labelling $^{59}\text{FeCl}_3$ solution in an acid (HCl) medium. In the system (2) selfdiffusion is indicated as the exchange governing process.

The radionuclide ^{54}Mn , being present without isotopic carrier in labelling $^{59}\text{FeCl}_3$ solution and introduced into the liquid phase, remained in the liquid phase of systems (2) and (3).

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Heterogeneous Exchange of Precipitates

VI. Exchange of Ferric Ion between an Aqueous Ferric Chloride Solution and Colloidal Beta Ferric Oxide Monohydrate Obtained by Slow Hydrolysis*)

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1. Introduction

A preceding paper (1) reported on heterogeneous exchange of ferric ion between the liquid phase of an aqueous ferric chloride solution and the solid phase of ferric (hydr)-oxide. An „amorphous“ precipitate, formed by relatively fast mixing of the components and consisting of small instable particles, showed some characteristics which were influenced by the subsequent treatment of the precipitate (1). It seemed to be of interest to investigate an analogous system, where the solid phase was produced without any oversaturation effects.

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In this paper we report on a system, where the colloidal β -FeOOH, produced by slow hydrolysis of an aqueous ferric chloride solution (2, 3), was chosen as the solid phase.

2. Experimental

An aqueous 3.0×10^{-1} N ferric chloride solution, containing 3.0×10^{-3} NHCl, was boiled for 5 hours under reflux. A yellow colloidal precipitate was formed. After cooling to room temperature, the system was labelled, and the heterogeneous exchange was investigated at room temperature. $n^L = 2.1 \times 10^{-1}$ (remained constant [$\pm 4\%$] during the experiment), $n^L + n^S = 3.0 \times 10^{-1}$.

The method of investigation and the instruments were described previously (1). In order to calculate the fraction exchange, the simple formula (p. 8 in [4]) was used, because the n^L value was constant during the experiment (5).