

Coprecipitation of Fission Products on Ferric Hydroxide

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Coprecipitation of fission products with ferric hydroxide was studied. Two techniques for precipitation of the hydroxide were adopted, those are, precipitation from homogeneous solution and a conventional one. Effects of pH of solutions were also studied.

Cations, such as alkali earths and rare earths, coprecipitate more with a precipitate obtained at a high pH than with one precipitated at a low pH. On the other hand, ruthenium and anions behave converse.

It can be concluded that the conventional precipitation process is more effective for the removal of fission products from a solution. The coprecipitation of mixed fission product, cooled for about three years, was above 80%.

INTRODUCTION

Various precipitates such as ferric hydroxide, aluminium hydroxide, and calcium phosphate have been used as scavengers in radiochemical separation and as decontaminating agents in radioactive waste treatments. In most cases, precipitate was produced by a conventional method, that is, for example, the pH of a solution containing ferric iron or aluminium is enhanced by the addition of sodium or ammonium hydroxide solution. In such a method, the pH of a solution is partially increased, so the chemical and physical forms of precipitates would not be kept uniform.

Recently, several methods of precipitation from homogeneous solution have been developed and many efforts have been made to get purer precipitates¹⁻⁴⁾. Many of them are made by gradually rising of pH and some are made by destruction of complex. MacNevin *et al.*⁵⁾ suggested the possibility about the usefulness of precipitation of ferric hydroxide from homogeneous solution. They found that EDTA-Fe (III) complex is destructed with hydrogen peroxide in an adequate solution. But, they have not made quantitative study.

In this paper, quantitative study was made on the precipitation of ferric hydroxide using a similar procedure to that of MacNevin. An influence of pH on the coprecipitation in homogeneous solution was studied; the pH was kept constant at various values during the formation of precipitates by the use of buffer solutions. And radioactive nuclides used in the experiment were ⁹⁰Sr, ⁹⁰Y, ⁹⁵Zr-⁹⁵Nb, ¹³⁷Cs, ¹⁴⁰Ba, ¹⁴⁰La, ¹⁰⁶Ru-¹⁰⁶Rh, ¹⁴⁴Ce-¹⁴⁴Pr, (which are main nuclides contained in fission products), and a mixture of fission products.

A conventional precipitation method was also examined, in which coprecipitation

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capacity of ferric hydroxide for strontium was studied using stable strontium as carrier.

APPARATUS AND REAGENTS

Ammonium chloride, ferric nitrate, disodium salt of EDTA and hydrogen peroxide were of reagent grade. Strontium-90, ^{137}Cs , ^{140}Ba - ^{140}La , ^{144}Ce - ^{144}Pr , and fission product were obtained from the Oak Ridge National Laboratory. Yttrium-90 was prepared by radiocolloid method from ^{90}Sr - ^{90}Y mixture, ^{140}La and ^{140}Ba were separated by paper chromatography, and ^{95}Zr - ^{95}Nb and ^{106}Ru - ^{106}Rh were prepared from fission product by ion exchange method.

It was verified that all radioactive nuclides were radiochemically pure by the ranges of β ray in aluminium plates.

Measurements of radioactivities were done by a Metro EIT Scaler with G.M. counter (TEN. G. M.-132, window thickness $1.95\text{mg}/\text{cm}^2$).

Beckman spectrophotometer type DU was used for the spectrophotometric determination of iron, and Beckman model H glass electrode pH meter was used for the pH measurements.

EXPERIMENTAL

1. Coprecipitation of Fission Products

1.1. Precipitation from homogeneous solution. Solution containing 1mg of ferric iron, 0.0223m.mole of EDTA-2Na, 2.2gr of NH_4Cl were prepared, the pH was adjusted with HCl or NH_4OH to 8.3, 7.0, 6.3, or 5.5, and diluted to 10 ml.

After addition of 0.5 to 3.0ml of 28% H_2O_2 , the solutions were diluted to 15ml with water. On addition of H_2O_2 , pH of the solutions decreased a little owing to the acidic property of H_2O_2 solution. In the solution, Fe(III) is believed to form

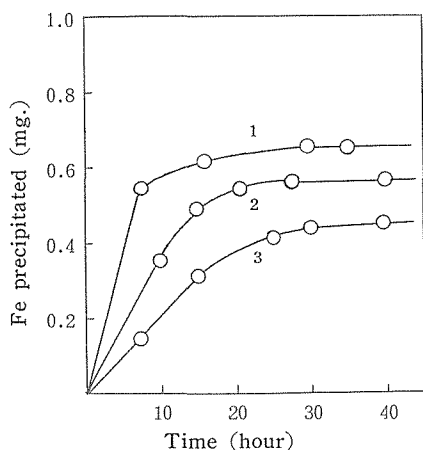


Fig. 1.

1. pH : 8.18, H_2O_2 3ml
2. pH : 8.20, H_2O_2 2ml
3. pH : 8.30, H_2O_2 1ml

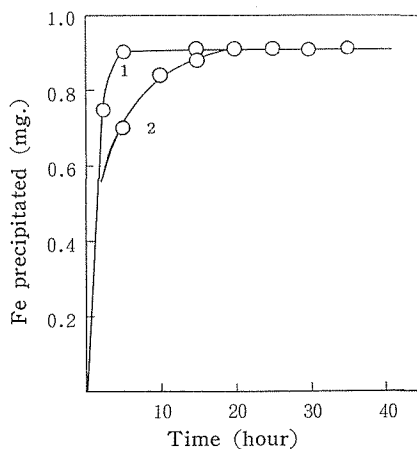


Fig. 2.

1. pH : 6.80, H_2O_2 2ml
2. pH : 6.95, H_2O_2 0.5ml

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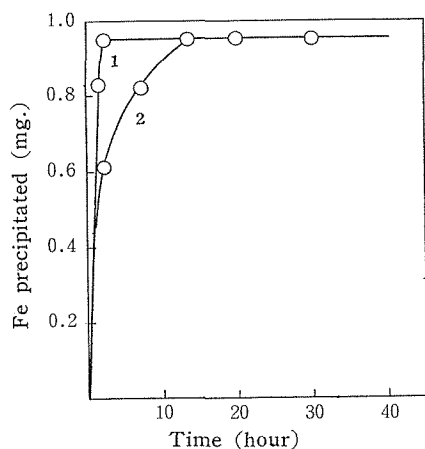


Fig. 3.

- 1. pH : 5.85, H₂O₂ 1ml
- 2. pH : 6.05, H₂O₂ 0.5ml

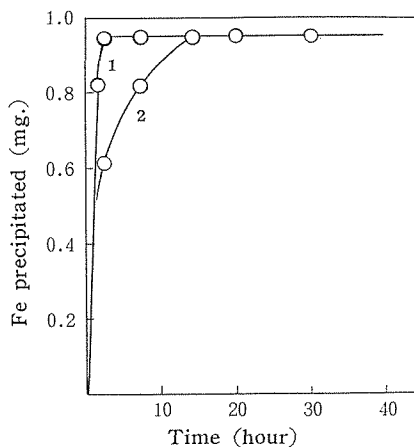


Fig. 4.

- 1. pH : 3.70, H₂O₂ 1ml
- 2. pH : 4.80, H₂O₂ 0.5ml

Figs. 1~4. Rate of precipitation of ferric hydroxide from homogeneous solution.

a complex with EDTA and H₂O₂ which develops violet colour. On standing, the coloration decreases gently and Fe(OH)₃ precipitates gradually owing to the decomposition of the Fe(III)-EDTA complex with hydrogen peroxide. However, it was observed that the precipitation of iron was inhibited by the use of ammonium acetate instead of ammonium chloride as a buffer agent.

Amounts of Fe(III) precipitated were measured by spectrophotometric method⁶⁾ at various intervals of time after addition of H₂O₂; precipitates, which were filtered with No. G4 glass filter and washed with 1% NH₄Cl solution, were dissolved in 25ml of 3N HCl, and absorbance of the solution was measured at 340m μ .

The results are shown in Figs. 1-4.

From these results, following conditions for the coprecipitation experiment were chosen. In Table 1, the precipitation conditions and the results obtained are shown.

Table 1. Precipitation conditions employed in precipitation from homogeneous solution.

Initial pH of Solutions	Volume of H ₂ O ₂ added (ml)	Standing Time (hour)	Amount of Fe Precipitated (mg)	Observation of Precipitates	
				Colour	form
8.18	3	20	0.67	Light yellowish brown	Fine powder
6.95	0.5	20	0.90	Brown	Colloidal
6.05	0.5	20	0.92	Light brown	Powder
4.60	0.5	20	0.93	Light brown	Powder

1. 2. Precipitation of ferric hydroxide by ammonia. Solutions examined here had the same composition used in the homogeneous solution except for the absence of EDTA-2Na. Ferric hydroxide was precipitated by the addition of concentrated ammonia.

1. 3. Coprecipitation of radioactive nuclides. In the series of the experiments

on the coprecipitation of radioactive nuclides on $\text{Fe}(\text{OH})_3$, which were precipitated either from homogeneous solution or by ammonia, the following procedure was taken.

One millilitre of carrier free radioactive solution was added to the sample solutions mentioned above. After thoroughly mixing 1ml of the solution was pipetted out into a stainless steel planchet. Then H_2O_2 or NH_4OH was added and after standing for 20 hours, the precipitate was filtered, and 1ml of filtrate was pipetted out into another counting dish.

Activities of the two planchets were measured with G.M. counter and the coprecipitation of radioactive substances was calculated. In this measurement, activities were corrected for those of daughters, if necessary.

The results obtained, especially the coprecipitation of radioactive nuclides are shown in Table 2.

Table 2. Coprecipitation of radionuclides.

Initial pH of Solutions	Coprecipitation of nuclides (%)								
	^{137}Cs	^{89}Sr	^{140}Ba	^{90}Y	^{95}Zr - ^{95}Nb	^{140}La	^{144}Ce - ^{144}Pr	^{106}Ru	Fission Product
*8.18	0	17.6	78.0	97.1	90.3	97.8	90.8	13.5	87.8
*6.95	0	14.3	40.4	95.2	82.9	97.8	97.2	20.8	89.7
*6.05	0	14.1	40.3	95.0	85.7	98.2	96.1	39.8	89.8
*4.60	0	11.8	40.1	96.7	80.2	87.3	88.3	44.7	88.9
**8.0-9.5	0	34.7	68.4	98.4	97.9	99.7	99.4	—	93.1
***8.0-9.5	0	74.5	78.4	99.3	98.2	100.0	99.5	49.0	96.2

* Precipitation from homogeneous solution.

** Ammonia Precipitation from the solution in which 2.2mg of NH_4Cl is present.

*** Ammonia Precipitation from the solution in which NH_4Cl is absent.

1. 4. Discussion. As the amounts of ferric hydroxide precipitated depend upon the pH and the composition of the solution and the influence of the decomposition products of EDTA are little known, the direct comparison of the coprecipitation percentages is hardly possible. Nevertheless, the tendency of the coprecipitation can be grasped, because nuclides coprecipitated are in tracer quantity and the surface of the precipitate is not saturated with the nuclide.

Rare earths coprecipitate above 80% in all cases and tend to perfect coprecipitation with increasing of pH. It is assumed that formation of radiocolloid is the other cause of increase of coprecipitation.

Coprecipitation of alkaline earths is much dependent on the pH of the solution, and alkaline metal (Cs) coprecipitates little. The latter seems to suggest that the excess of ammonium ion replaces cesium ion in tracer quantity. This is deduced from the results of a conventional precipitation method in which coprecipitation of alkaline earths in the presence of 2.2gr of NH_4Cl is smaller than in the absence. Ruthenium shows the tendency to coprecipitate more at higher pH in homogeneous solution. Although the differences of amounts of precipitates might lead to this results, the following experiments support this conclusion. Ruthenium was copre-

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coprecipitated heterogeneously from the solution of which the pH were adjusted at 3, 4, 8 and 10. The results are shown in Table 3.

Table 3. Coprecipitation of ruthenium by ammonia precipitation.

pH	3	4	8	10
Coprecipitated (%)	60.0	58.6	49.0	46.8

It goes without saying that majority of cesium and a portion of alkaline earths or ruthenium can be removed from the solution on treatment of fission products with ferric hydroxide.

2. On the coprecipitation Capacity of Ferric Hydroxide for Strontium

It has been found in the previous experiment that several tens of a percent of alkaline earths coprecipitate on ferric hydroxide from the solution. In this study, it was the purpose to know how much strontium could be carried with ferric hydroxide.

2. 1. Procedure. Fifteen ml of 0.067*N* HCl solution containing FeCl₃ (1mg Fe) and ⁹⁰Sr-⁹⁰Y mixture in radioactive equilibrium (if necessary, 1 to 10⁻¹⁰m. mole of SrCl₂ is added as carrier) was taken in an Erlenmyer flask. Nitrogen gas was bubbled through for about ten minutes to remove dissolved carbon dioxide in the solution. Soon after 0.1ml of concentrated ammonium hydroxide free from carbonate was added, a rubber stopper was adapted in order to shut off air. After vigorous shaking, the solution was allowed to stand for an hour. The pH of the solution was from 8.5 to 9.5.

The solution was filtered and 1ml of the filtrate was pipetted out into a counting dish, dried under an infrared lamp and the radioactivity was measured. At the same time, the activity of the original solution was similarly measured. The coprecipitation percentage was calculated as the ratio of both activities in the solution before and after the precipitation.

Activities of ⁹⁰Y were corrected as follows ; planchet were mounted on the second shelf of the measuring stand and activities of both components (⁹⁰Sr and ⁹⁰Y) were measured. Then in order to shelter the β ray of ⁹⁰Sr, 220mg/cm² aluminium absorber was placed on the first shelf, which corresponds to the half thickness of ⁹⁰Y. Twice of the counting rate measured with absorber was subtracted from the former, thus net counting rate of ⁹⁰Sr was obtained.

2. 2. Results and discussion. Fig.5 shows the relation between strontium concentration and coprecipitation percentages. It is found that coprecipitation of strontium retains constancy up to 10⁻⁴ m.mole of Sr added but abruptly decreases at the amount over 10⁻³ m.mole of strontium.

This relation can be rewritten as Fig. 6, that is Freundlich's adsorption isotherm. In this figure, it is obvious that, in these experimental conditions, the amount of strontium carried by ferric hydroxide (containing 1mg Fe) approaches saturation at the concentration of strontium over 0.067 m.mole.

Ferric hydroxide is frequently used as scavenger, however, it must be borne in mind that the use of small amount of strontium will not be useful as a hold back

carrier as indicated by the experimental results of Sr, because considerable loss of activity will arise.

In the present study, the atomic ratio of strontium to iron in the precipitates becomes 1/10 at the maximum.

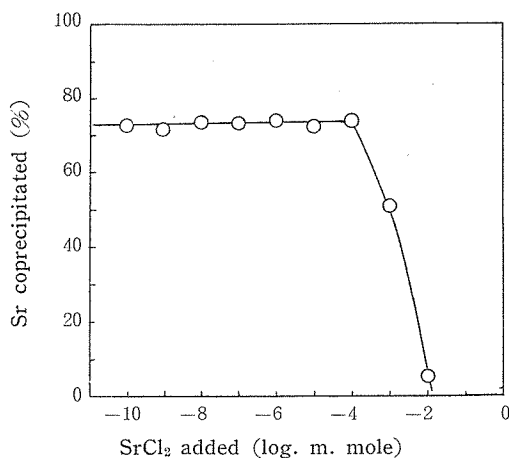


Fig 5. Coprecipitation of strontium at various concentration.

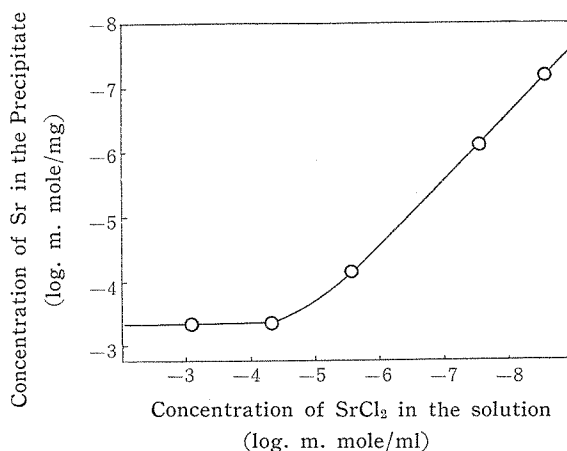


Fig. 6. Relation between concentration of strontium in the solution and in the precipitate.

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