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APPEARANCE AND STABILITY OF HYDROLYZED $Fe(ClO_4)_3$ SOLUTIONS*

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Abstract—$Fe(ClO_4)_3$ solutions of different concentration and acidity were studied to search for the factors governing their appearance and stability during aging and to elucidate the mechanisms for the formation of amorphous and crystalline iron(III) hydroxides from slow hydrolysis. It was found that dilute solutions (0·001M or lower) rapidly hydrolyzed to clear sols after a brief induction period. With an increase in iron(III) concentration, one could notice gradual increases in the induction period, turbidity and particle size. Thus, solutions 0·006M to 0·01M in iron(III) developed into dense, cloudy, yellow suspensions impervious to light. The polymeric iron(III) species in the aged 0·02M solution were primarily large particles that settled under gravity, resulting in a suspension of low turbidity. It was also observed that in dilute solutions, the initial polymerization product was amorphous iron(III) hydroxide which yielded X-ray diffraction peaks for FeOOH only after prolonged aging or not at all. In 0·01 and 0·02M solutions, however, crystalline FeOOH was the major product from the very beginning of polymerization. The results suggest that the initial degree of supersaturation with respect to amorphous iron(III) hydroxide is the key factor governing particle size distribution, which in turn governs the appearance, stability and crystallinity of the hydrolyzed product during aging.

The addition of $HClO_4$ to dilute $Fe(ClO_4)_3$ solutions decreased, whereas the addition of NaOH to concentrated solutions increased, the degree of supersaturation and, thus, induced changes in induction period, appearance, stability and crystallinity of the hydrolyzed product accordingly.

INTRODUCTION

IT HAS long been recognized that when an iron(III) salt is dissolved in water, the initial reaction products are true solutions containing monomeric and possibly dimeric species. Nevertheless, except in a strongly acidic medium, the initial reaction products will undergo a further relatively slow hydrolysis during aging. The secondary hydrolysis products are known to contain colloidal particles or suspended solids and may vary greatly in appearance and stability. At one extreme, the products are clear sols that are stable for many years. At the other extreme, the products are large, well crystallized FeOOH particles that settle under gravity. The difficulty of reproducible preparation has been repeatedly emphasized in the literature (Mellor, 1935; Lamb and Jacques, 1938). It has been pointed out by Goodwin and Grover (1900) and by Heymann (1928) that the appearance and stability of hydrolyzed iron(III) solutions are very sensitive to iron(III) concentration, degree of acidity and temperature but the detailed conditions and the mechanisms leading to such differences have not been reported. The striking differences in appearance and stability led some workers (Feitknecht and Michaelis, 1962; Spiro *et al.*, 1966) to assume that brown sols, turbid suspensions and precipitates are formed through different mechanisms.

Although the secondary slow hydrolysis is fundamental to the understanding of many earth science problems, it has received little attention among chemists since the work of Lamb and Jacques (1938). Most of the studies of iron(III) hydrolysis during the past three decades have been confined to the initial hydrolysis in a strongly acidic medium. This report presents a systematic study of the effects of iron(III) concentration and acidity on the formation of clear sols, turbid suspensions and precipitates resulting from the secondary slow hydrolysis. The results are interpreted in terms of a nucleation hypothesis recently reported (Hsu and Ragone, 1972; Hsu, 1972). According to this hypothesis, the initial number of nuclei for polymerization relative to the concentration of non-colloidal iron(III) species, likely monomeric, is the

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key factor governing particle size distribution which, in turn, governs the color, turbidity and stability during aging.

METHODS

Preparation of sample solutions. Sample solutions were prepared by diluting a stock 0·5M $Fe(ClO_4)_3$ solution to the desired concentration and keeping it at 23°C. The stock 0·5 M solution was prepared by dissolving G. F. Smith reagent-grade yellow hydrate crystals in water without further purification. For studying the effect of acidity, predetermined amounts of 0·1 N $HClO_4$ or NaOH were added to a 0·5 M $Fe(ClO_4)_3$ solution before dilution. The rate of NaOH addition and the order of mixing must be identical each time in order to observe reproducible results. In this study, samples were prepared by adding 0·1 N NaOH, drop by drop, to 40 or 80 ml of 0·5 M $Fe(ClO_4)_3$ at a rate of 5 ml per min under vigorous stirring and then diluting to 1 l.

Turbidity. Turbidity was measured with a Hach Turbidimeter, Model 2100.

Oxalate-extractable iron(III) hydroxide. Polymeric iron(III) hydroxide was first precipitated with Na_2SO_4 as with the method of its determination (Hsu and Ragone, 1972). The precipitate was separated from the supernatant solution by centrifugation and was then dispersed in 50 ml of oxalate–oxalic acid of pH 3 (Schwertmann, 1962) for 2 hr, recentrifuged, washed with 50 ml of 0·01 N Na_2SO_4 and then dissolved in 3 ml of 6 N HCl at 60°C in a water bath. The oxalate-extractable iron(III) hydroxide was obtained by subtracting the residual iron(III) from total iron(III) hydroxide which was determined separately.

H^+ concentration. Solution pH was measured with a Beckman Research pH meter, using a NaCl calomel electrode as reference (Mulay and Selwood, 1955). The concentration of H^+ in solution was calculated using an $HClO_4$-pH calibration curve. It was found necessary to use a NaCl calomel electrode for concentrated $Fe(ClO_4)_3$ solutions (0.04 M or above). The emf readings were found to be erratic when a regular KCl calomel electrode was used as reference.

Other determinations. Total polymeric iron(III) hydroxide was separated from solution by adding an appropriate amount of Na_2SO_4. Large particles that settle under gravity were separated from suspension by centrifuging the sample aliquot with an International Centrifuge, Size 2, at 2,000 r.p.m. (approximately 1,000 G) for 30 min. Particle size was estimated with Millipore filtration, using a filtering centrifuge tube. The fraction of iron(III) that slowly reacts with SCN^- was estimated from the rate of Fe–SCN color development. The $[Fe^{3+}][OH^-]^3$ concentration product was calculated by assuming noncolloidal iron(III) species to be primarily monomeric, following Lamb and Jacques' (1938) model of Fe^{3+} hydrolysis and using their hydrolysis constants. The details of the above determinations were given in an earlier report (Hsu and Ragone, 1972). The specimen for X-ray diffraction was prepared by collecting the hydrolyzed product on Millipore filter paper of desired pore size. For clear sols, a sample aliquot was dialyzed in ammoniated water of pH 8 for 2 days to induce coagulation prior to Millipore filtration (Hsu, 1972).

RESULTS

Effect of iron(III) concentration

Hydrolysis and induction period. $Fe(ClO_4)_3$ solutions of different concentrations ranging from 0·0002 to 0·1 M were investigated. A slow secondary hydrolysis, as indicated by the amount of H^+ released, was observed in all solutions up to 0·02 M in iron(III) following an induction period (Fig. 1, Table 1). The higher the iron(III) concentration, the longer the induction period. The induction periods for the 0·0002 and 0·0005 M solutions are 2 and 10 min, respectively (not shown in the figure). Because of these brief induction periods, their initial H^+/Fe^{3+} ratios were only approximately estimated to be 1·05 and 1·1, respectively. In contrast, the induction period for the 0·02 M solution was 4 months. No change in pH was observed in solutions 0·04–0·1 M in iron(III) up to at least 15 months.

It is also shown in Fig. 1 that the time required for equilibration greatly increased with an increase in iron(III) concentration. For the four most dilute solutions, the change in pH became unnoticeable after approximately 1 day (0·0002 M), 10 days (0·0005 M), 30 days (0·001 M) and 300 days (0·002 M), respectively, but the exact equilibration time is difficult to determine because experimental uncertainty exceeds the real pH change as solutions approach equilibrium. Similar results were reported by Goodwin and Grover (1900), Heymann (1928) and Lamb and Jacques (1938) among others but those earlier studies were confined to dilute solutions and short periods of aging.

Formation of polymeric iron(III) hydroxide. Comparison of Fig. 2 with Fig. 1 shows that the secondary hydrolysis was accompanied by formation of polymeric iron(III) hydroxide. In the three most dilute solutions, considerable amounts of polymeric iron(III) hydroxide were observed only several hours after preparation, and eventually

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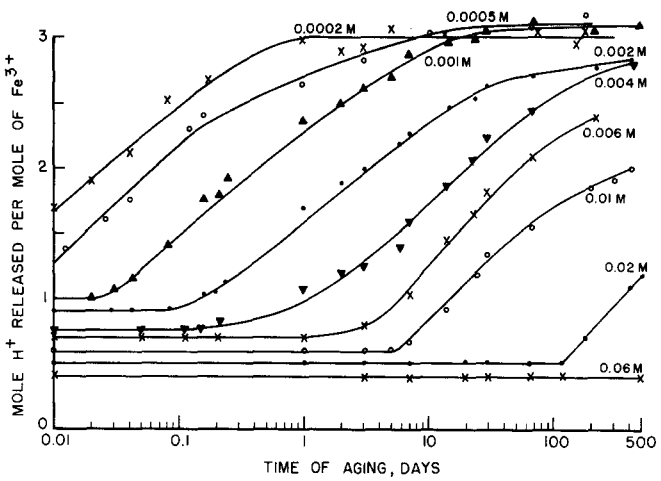


Fig. 1. Progress of hydrolysis of $Fe(ClO_4)_3$ solutions of varying concentrations.

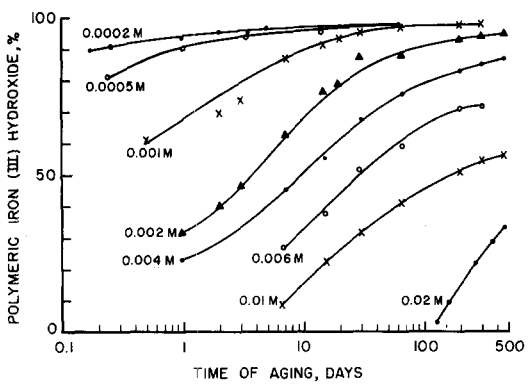


Fig. 2. Formation of polymeric iron(III) hydroxide in $Fe(ClO_4)_3$ solutions of different concentrations.

some 97 per cent of the iron(III) became polymeric iron (III) hydroxide, as determined by Na_2SO_4 precipitation. It is our experience that in solutions highly supersaturated with respect to amorphous iron(III) hydroxide, part of the monomeric iron(III) species may be rapidly polymerized during the Na_2SO_4 treatment and also precipitated. Because of this possibility, the rapid polymerization of $Fe(OH)_3$ in fresh, dilute solutions was further ascertained on the basis of the rate of Fe–SCN color development. It is known that monomeric iron(III) species react with SCN^- instantaneously (Hsu and Ragone, 1972). Therefore, the fraction of iron(III) that slowly reacts with SCN^- may be considered to be the minimum amount of polymeric iron(III) hydroxide. On the basis of this reasoning, $Fe(OH)_3$ polymerization was detectable in the 0·0002 M solution only 5 min after preparation and in the 0·001 M solution, 1 hr after preparation. The Na_2SO_4 precipitable fraction of iron(III) was always higher than the fraction that slowly reacts with SCN^-, but the differences were small after 4 hr for the 0·0002 M solution and after 12 hr for the 0·001 M solution (data not shown). Only results, from these two methods, that differed by less than 10 per cent were considered to be acceptable and were reported in Fig. 2.

The results of Millipore filtration indicate that particle size* increased with increased iron(III) concentration (data not shown). Consequently, the large particles that settled under gravity were found only in solutions of moderate iron(III) concentration; the quantity increased with increased iron(III) concentration (Table 1). In 0·02 M solution, 94 per cent of the polymeric iron(III) hydroxide was large enough to settle under gravity at the end of 10 months.

Appearance and stability. The hydrolyzed products of different concentrations were very different in appearance and stability after prolonged aging (Table 1). The three most dilute solutions were initially colorless but gradually darkened in color as the secondary hydrolysis began and then rapidly developed to a yellow (0·0002 M), light brown (0·0005 M) or brown (0·001 M) colloidal sol a few hours after preparation. When an aged, clear,

*The results of Millipore filtration are useful for illustrating the relative magnitude of particle size distribution, provided that all measurements are made under identical conditions such as the volume of sample aliquot, the concentration of iron and the conditions of centrifugation. This technique, however, does not give the exact dimension of particles, and is not useful for any quantitiative interpretation.

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Table 1. Characteristics of aged $Fe(ClO_4)_3$ solutions of different concentrations

Iron(III) conc., M	pH		Induction period	Appearance*	Polymeric iron(III) hydroxide*			
	Init.	10 month			Total†	FeOOH ppt‡	Oxalate extractable‡	Initial $[Fe^{3+}][OH^-]^3 \times 10^{39}$
0·0002	3·52	3·26	2 min	Clear, yellow sol	92·0	nil	76·0	1,690
0·0005	3·32	2·85	10 min	Clear, light brown sol	97·7	nil	45·0	644
0·001	3·21	2·64	40 min	Clear, brown sol	97·5	nil	23·8	279
0·002	2·92	2·33	2 hr	Slightly turbid, brown suspension	93·5	nil	18·9	142
0·004	2·65	2·02	5 hr	Moderately turbid, brown suspension	85·0	5·5	14·0	74·7
0·006	2·50	1·85	1 day	Very turbid, yellow susp., impervious to light	71·4	25·4	11·7	50·5
0·01	2·32	1·75	5 days	Very turbid, yellow susp., impervious to light	53·5	44·8	8·5	27·9
0·02	2·07	1·74	4 month	Slightly turbid, yellow suspension	23·0	94·0	nil	15·4
0·04	1·84	1·86		Clear, pale yellow solution				10·0
0·06	1·63	1·64		Clear, yellow solution				4·94
0·1	1·42	1·44		Clear, yellow solution				1·74

*Determined after 10 months of aging.
†Percent total iron(III).
‡Percent total polymeric iron(III) hydroxide.

brown (0·001 M) sol was diluted to 0·0002 M, it changed to a yellow sol immediately after dilution while its polymeric iron(III) hydroxide content remained unchanged. This suggests that the different colors shown by these three samples were due only to the concentration of polymeric iron(III) hydroxide. All three of these hydrolyzed products were clear to the naked eye. The turbidity for 0·0002 M solution was less than 0·1 JTU during the entire period of this study. The turbidity readings for the 0·0005 M and 0·001 M solutions rapidly increased to 0·2 JTU in 4 hr and 1·2 JTU in 12 hr, respectively, and no significant change during aging was observed. With further increase in iron(III) concentration, the color of the hydrolyzed products gradually changed from brown to orange to yellow, with a concurrent increase in turbidity. For example, the 0·006 and 0·01 M solutions became dense, cloudy yellow suspensions impervious to light, with considerable amounts of settled precipitate. The precipitate separated from the liquid phase was yellow with slightly orange color. The 0·02 M solution, following a 4-month induction period, rapidly developed into a dense, cloudy yellow suspension. The turbidity then decreased with 94 per cent of the polymeric iron(III) hydroxide particles having settled to the bottom of the container. The precipitate was yellow. Those solutions 0·04 M or higher with respect to iron(III) remained clear up to the end of this study.

Nature of iron(III) hydroxide. Goethite or a mixture of goethite and lepidocrocite was observed in all samples in the concentration range from 0·001 to 0·02 M after prolonged aging, but the crystallinity decreased with decreased iron(III) concentration (Fig. 3). The aged 0·001 M solution, after dialysis for 2 days in ammoniated water of pH 8, yielded a precipitate which gave several broad X-ray diffraction peaks resembling the pattern for goethite. The polymeric iron(III) hydroxide in these two most dilute solutions (0·0002 and 0·0005 M), however, is amorphous to X-ray diffraction and highly extractable with oxalate solution (Table 1).

The hydrolysis products reported above were characterized only at the end of aging. In order to gain insight into the process of crystallization, new

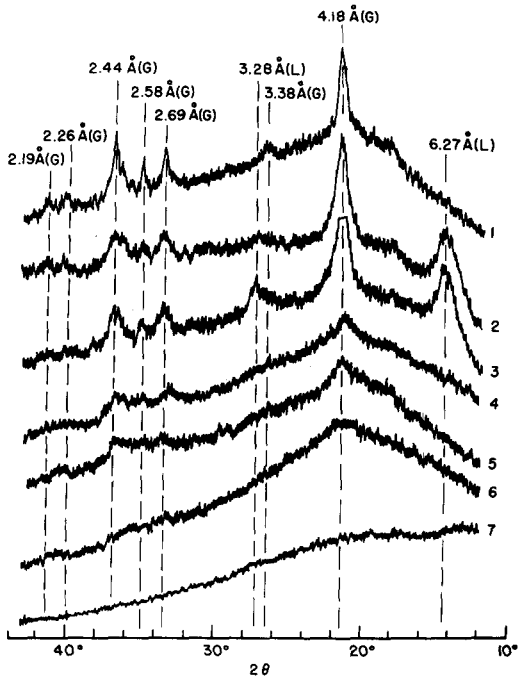


Fig. 3. X-ray diffraction patterns of hydrolyzed products collected from $Fe(ClO_4)_3$ solutions after 10 months of aging. G = goethite; L = lepidocrocite.

1. 0·02 M
2. 0·01 M
3. 0·006 M
4. 0·004 M
5. 0·002 M
6. 0·001 M
7. 0·0005 M

samples of two representative solutions, 0·01 and 0·001 M in iron(III), were prepared and periodically analyzed for their mineralogical composition and oxalate-extractable iron(III) hydroxide at close intervals for total aging periods up to 4 months. It was found that the polymeric iron(III) hydroxide in the 0·01 M solution yielded X-ray diffraction peaks for goethite only 5 days after it became turbid. Although the total polymeric iron(III) hydroxide increased from 45·1 ppm after 10 days to 305 ppm after 4 months, the oxalate-extractable iron(III) accounts for only a small fraction of this total throughout the aging process (Table 2). Also, polymeric iron(III) hydroxide was exclusively retained by the 650 nm Millipore filter from the very beginning, similar to the results reported earlier (Hsu and Ragone, 1972). These circumstances suggest that the increase in polymeric iron(III) hydroxide is exclusively crystalline FeOOH during aging. In contrast, the hydrolyzed species in the 0·001 M solution, after being dialyzed in ammoniated water of pH 8, was amorphous to X-ray diffraction up to at least 2 months and yielded broad FeOOH diffraction peaks only after prolonged aging.* Neverthe-

*Broad FeOOH peaks were observed in all aged samples (7 months or older), but the exact time for the first appearance of crystalline FeOOH is difficult to determine. With the method of specimen preparation used in this study, the reproducibility of X-ray diffraction is satisfactory for both well crystallized FeOOH and amorphous precipitates, but not satisfactory for poorly crystallized precipitates.

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Table 2. Changes in total and oxalate-extractable polymeric iron(III) hydroxide, in ppm Fe, of two $Fe(ClO_4)_3$ solutions during aging

Polymeric iron(III) hydroxide	Time of aging (days) 1	2	10	15	30	60	120
				0·01 M $Fe(ClO_4)_3$			
Total			45·1	90·0	162·0	253·4	305·2
Oxalate extractable			15·1	15·7	14·5	13·0	25·0
				0·001 M $Fe(ClO_4)_3$			
Total	34·4	39·0	47·5	49·5	53·5	54·5	54·0
Oxalate extractable	20·9	18·5	14·5	12·0	11·0	11·5	10·5

less, the hydrolyzed species became fairly resistant to oxalate extraction after 30 days. This situation suggests that the sample is a suspension of submicron crystals, even though it remained clear to the naked eye, with a turbidity less than 2 JTU.

It will be shown later in the Discussion that all but one of these solutions are supersaturated with respect to iron(III) hydroxide, and that the degree of supersaturation decreases with increased iron(III) concentration. The different appearance and stability displayed by different solutions are attributed to these differences in degree of supersaturation. To investigate this hypothesis, two other experiments were conducted. In one experiment, acid was added to dilute iron(III) solutions to reduce the supersaturation. In the other, NaOH was added to concentrated solutions to increase supersaturation. The results are presented in the following two sections.

Effect of acid addition

In this experiment, three series of solutions, 0·0002, 0·0005 and 0·001 M in iron(III) respectively, were investigated. In each series, varying amounts of $HClO_4$ were added to give different degrees of acidity. The addition of acid prolonged the induction period, changed the clear sol to a turbid suspension and to large particles that settled under gravity, increased the resistance to oxalate extraction, and changed the precipitate from amorphous to well crystallized FeOOH. These changes followed the same trend as was seen with increased iron(III) concentration. The results for the 0·0005 M solutions are summarized in Table 3.

Effect of base addition

Two series of solutions, 0·02 and 0·04 M in iron (III) respectively, were investigated. In each series, various amounts of 0·1 N NaOH were added to obtain NaOH/Fe mole ratios ranging from 0 to 1. Addition of NaOH induced changes in induction period, stability and process of crystallization, following the same trend as was seen with decreasing iron(III) concentration. The results for the 0·04 M samples are shown in Table 4. It should be pointed out that the clear brown sols prepared in this experiment eventually became turbid after 6 months for the solution with NaOH/Fe = 0·5, and after 10 months for the solution with NaOH/Fe = 1. Nevertheless, the clear sols prepared by spontaneous hydrolysis of dilute $Fe(ClO_4)_3$ solutions were stable for many years. This difference probably is related to the concentration of polymeric iron(III) hydroxide.

This experiment is in essence an extension of an earlier report (Hsu and Ragone, 1972). The present work investigated samples of higher iron(III) concentration and wider range of NaOH/Fe ratio. Consequently, a series of hydrolyzed products of appearance, stability and crystallinity varying from one extreme to another were obseerved.

DISCUSSION

The results indicate that the appearance and stability of hydrolyzed iron(III) solutions are sensitive to iron(III) concentration and acidity level in preparation and are closely related to the duration of the induction period prior to the secondary hydrolysis. In general, clear sols formed when the induction period was less than 1 hr. With longer induction period, the hydrolyzed products were invariably turbid suspensions, and the longer the induction period, the higher the turbidity. With an induction period of 2 months or longer, the hydrolyzed products were mainly large particles that settled under gravity. These observations are in good accord with the hypothesis that the initial number of nuclei relative to the concentration of monomeric iron(III) species is the key factor governing the appearance and stability of hydrolyzed iron(III) solutions during aging (Hsu and Ragone, 1972; Hsu 1972).

For convenience in discussion, the hypothesis proposed in two earlier reports is summarized as follows: when dissolving an iron(III) salt in water,

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Table 3. Characteristics of acidified 0·0005 M $Fe(ClO_4)_3$ solution

$HClO_4$/Fe. Mole ratio	pH Init.	pH 5 months	Induction period	Appearance*	Polymeric iron(III) hydroxide* Total†	FeOOH ppt‡	Oxalate extractable‡	X-ray diff. (FeOOH)	Initial $[Fe^{3+}][OH^-]^3 \times 10^{39}$
0·0	3·32	2·85	10 min	Clear, light-brown sol	97·4	nil	49·5	Amorp.	644
1·0	3·05	2·73	2 hr	Slightly turbid, light-brown suspension	96·2	nil	36·6	Broad peaks	141
2·0	2·89	2·63	5 days	Moderately turbid, yellow suspension	94·3	13·7	16·3	Well-defined peaks	55·2
2·5	2·81	2·62	25 days	Moderately turbid yellow suspension	73·2	40·2	12·2	Well-defined peaks	40·0
3·0	2·75	2·62	3 months	Slightly turbid, yellow suspension	60·0	91·5	4·5	Well-defined peaks	24·5
4·0	2·67	2·65		Clear, colorless solution					18·1

*Determined 5 months after preparation.
†Percent total iron(III).
‡Percent polymeric iron(III) hydroxide.

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Table 4. Characteristics of partially neutralized 0·04 M ($Fe(ClO_4)_3$ solutions

NaOH/Fe Mole ratio	pH Init.	pH 7 months	Induction period	Appearance†	Polymeric iron(III) hydroxide† Total‡	FeOOH ppt.§	Oxalate extractabfie§	X-ray diff. (FeOOH)	Initial $[Fe^{3+}][OH^-]^3 \times 10^{39}$
0	1·89	1·90		Clear, light yellow solution					10·0
0·025	1·91	1·65	4 months	Slightly turbid, yellow suspension	17·8	95·7	nil	Well-defined peaks	11·5
0·1	2·01	1·61	1 month	Very turbid, yellow suspension	19·4	72·7	2·8	Well-defined peaks	21·6
0·2	2·08	1·56	3 days	Moderately turbid, yellow-brown suspension	29·7	14·8	16·7	Well-defined peaks	35·9
0·5	2·21*	1·58	< 1 hr*	Slightly turbid, brown suspension	40·0	2·0	60·0	Broad peaks	80·0
1·0	2·30*	1·66	< 1 hr*	Clear, brown sol	58·3	nil	83·5	Amorp.	133·0

*Secondary hydrolysis began before the dropwise addition of NaOH was complete. The initial pH was estimated in a separate preparation by mixing NaOH and $Fe(ClO_4)_3$ solution rapidly and measuring solution pH immediately after preparation.

†Determined 7 months after preparation.

‡Percent total iron(III).

§Percent total polymeric iron(III) hydroxide.

the products of primary hydrolysis are monomeric $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe(OH)_3$, which rapidly alter from one form to another. The process of secondary hydrolysis begins with the condensation of monomeric $Fe(OH)_3$ to polymeric $Fe_n(OH)_{3n}$. This latter species may act as nuclei for continuing condensation of other monomeric $Fe(OH)_3$ molecules (Lamb and Jacques, 1938). During prolonged aging, the fresh amorphous $Fe_n(OH)_{3n}$ gradually dehydrates to the less soluble $Fe_nO_x(OH)_{3n-2x}$ of varying composition and eventually to $Fe_n(OOH)_n$ (Glemser and Rieck, 1958; Schindler *et al.*, 1963). This crystallization process then perpetuates further hydrolysis and polymerization. The initial number of nuclei for polymerization relative to the concentration of monomeric iron(III) species is the key factor governing particle size distribution which, in turn, governs the appearance and stability during aging. In the first report on this subject (Hsu and Ragone, 1972), clear brown sols were prepared by adding $NaHCO_3$ to 0·01 M $Fe(ClO_4)_3$ solutions ($NaHCO_3$/Fe mole ratio = 1 or 2), which resulted in a large number of nuclei initially. In the second report (Hsu, 1972), hydrolyzed products of different appearance and stability were prepared by adding varying amounts of a clear brown sol as nuclei to acidified $Fe(ClO_4)_3$ solutions. The results in the current report can be interpreted by the same mechanism, but the initial number of nuclei is governed by the degree of supersaturation.

Following Lamb and Jacques' model of Fe^{3+} hydrolysis, the concentration of free Fe^{3+} in each solution can be calculated using the equation

$$[Fe_{tot.}] = [Fe^{3+}]\left(1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2} + \frac{k_1k_2k_3}{[H^+]^3}\right)$$

where $k_1 = 2{\cdot}5 \times 10^{-3}$; $k_2 = 2 \times 10^{-5}$ and $k_3 = 4 \times 10^{-7}$. From the concentration of free Fe^{3+} so obtained and the OH^- concentration (determined), the $[Fe^{3+}][OH^-]^3$ concentration product for each solution can be calculated (Table 1). By assuming the solubility product of amorphous iron(III) hydroxide* to be $2{\cdot}5 \times 10^{-39}$ (Biedermann and Schindler, 1957), it can be seen from Table 1 that all but one of these solutions were supersaturated with respect to amorphous iron(III) hydroxide, and that the degree of supersaturation decreased with increase of iron(III) concentration. The three most dilute solutions were so highly supersaturated that a large number of nuclei formed at the beginning of polymerization. Much of the iron(III) polymerized to amorphous $Fe_n(OH)_{3n}$ shortly after preparation, leaving a small fraction of monomeric iron(III) species available for continuing hydrolysis and particle growth. Consequently, the equilibration times were brief and particles were small, giving rise to the formation of clear colloidal sols. During aging, the initial amorphous $Fe_n(OH)_{3n}$ gradually dehydrated, through $Fe_nO_x(OH)_{3n-2x}$ of varying composition, eventually to $Fe_n(OOH)_n$. The products remained amorphous to X-ray diffraction or yielded only broad diffraction peaks because of their small particle size even after the complete dehydration of $Fe_n(OH)_{3n}$ to $Fe_n(OOH)_n$. It has been shown that many so-called X-ray amorphous iron(III) hydroxide gels were actually suspensions of crystals of extremely small size (Atkinson *et al.*, 1968; Giessen, 1966; Towe and Bradley, 1967). The brief induction period was apparently attributed to the high degree of supersaturation (Kolthoff *et al.*, 1969).

With a gradual increase in iron(III) concentration, the degree of supersaturation gradually decreased, accounting for a longer induction period and a larger fraction of monomeric iron(III) ions available for continuing hydrolysis and particle growth. This situation favors a longer equilibration time and larger particle size, giving rise to the formation of suspensions of a wide range of turbidities. The 0·02 M solution was only slightly supersaturated with respect to amorphous iron(III) hydroxide. The amount of amorphous iron(III) hydroxide, if any, should always have been very small, whereas abundant monomeric iron(III) species were available for continuing hydrolysis and particle growth. Therefore, this solution required a long time to attain equilibrium, and crystalline FeOOH particles of large size were the dominant product from the beginning of polymerization.

The addition of $HClO_4$ to dilute $Fe(ClO_4)_3$ solutions simply lowered the degree of supersaturation (Table 3) and consequently induced changes in induction period, particle size, appearance and stability of hydrolyzed solutions, following the same trend as the increase of iron(III) concentration. On the other hand, the addition of NaOH to concentrated iron(III) solution increased the degree of

*The solubility product of amorphous iron(III) hydroxide was also reported to be 1×10^{-37} (Lamb and Jacques, 1938). This writer now believes that the solubility product of amorphous iron(III) hydroxide may cover a wide range rather than a point, because of its varying composition. A scrutiny of their methods of calculation suggests that Lamb and Jacques' data more likely represent fresh precipitate of $Fe_n(OH)_{3n}$ composition whereas Biedermann and Schindler's data more likely represent the precipitate after brief aging with part of its *ol*-linkages converted to *oxo*-linkages. The investigation on this subject is in progress.

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supersaturation (Table 4) and induced changes in induction period, appearance and stability following the same trend as decreasing iron(III) concentration. The addition of NaOH also caused an irreversible formation of iron(III) hydroxide nuclei at the beginning and thus accelerated the process of secondary hydrolysis (Hsu and Ragone, 1972). The latter possibility is evident when the results for the low NaOH/Fe samples are compared. For example, a pure 0·04 M solution was stable for at least 15 months. With NaOH/Fe ratio = 0·025 in preparation, however, the secondary hydrolysis took place in 4 months after preparation. The initial pH values of these two samples were nearly the same and, thus, the difference in supersaturation was too small to be considered.

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Résumé – Des solutions de Fe $(ClO_4)_3$ de concentrations et acidités différentes ont été utilisées pour étudier les facteurs gouvernant leur aspect et leur stabilité lors du vieillissement et pour élucider les mécanismes de formation des hydroxydes de fer(III) amorphes et cristallins par hydrolyse lente. On a trouvé que les solutions diluées (0,001 M ou moins) s'hydrolysent rapidement en sols clairs après une courte période d'induction. Quand la concentration en fer(III) augmente, on peut noter une augmentation graduelle de la période d'induction, de la turbidité et de la taille des particules. Ainsi, des solutions de 0,006 M à 0,01 M en fer(III) développent des suspensions jaunes, denses, floconneuses et opaques. Les espèces polymérisées du fer(III) dans la solution 0,02 M vieillie sont d'abord de grandes particules qui se déposent par gravité, ce qui donne une suspension de faible turbidité. On a observé également qu'en solutions diluées, le produit de la polymérisation initiale est un hydroxyde amorphe de fer(III) qui ne donne les pics de diffraction *X* de Fe OOH qu'après un vieillissement prolongé seulement. Il peut ne pas les donner du tout. En solutions 0,01 et 0,02 M cependant, Fe OOH cristallisé est le produit principal juste au début de la polymérisation. Ces résultats suggèrent que le degré initial de sursaturation par rapport à l'hydroxyde amorphe de Fe(III) est le facteur clé qui détermine la distribution granulométrique, qui à son tour détermine elle-même l'aspect, la stabilité et la cristallinité du produit hydrolysé lors du vieillissement.

L'addition de $HClO_4$ à des solutions diluées de Fe $(ClO_4)_3$ diminue le degré de sursaturation alors que l'addition de NaOH à des solutions concentrées l'augmente; ces deux réactifs induisent donc ainsi des changements dans la période d'induction, dans l'aspect, la stabilité et la cristallinité du produit hydrolysé.

Kurzreferat—$Fe(ClO_4)_3$-Lösungen unterschiedlicher Konzentration und Acidität werden untersucht, um die Faktoren zu erforschen, die ihr Aussehen und ihre Stabilität während des Alterns bestimmen, und um die Mechanismen der Bildung von amorphen und kristallinen Eisen(III)–Hydroxiden durch langsame Hydrolyse aufzuklären. Es wurde gefunden, daß verdünnte Lösungen (0,001 m oder niedriger) nach einer kurzen Anlaufzeit schnell zu klaren Solen hydrolysieren. Mit Anstieg der Eisen(III)–

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Konzentration ließ sich eine allmähliche Zunahme der Anlaufzeit, der Trübung und der Teilchengröße feststellen. Eisen(III)-Lösungen mit einer Molarität von 0,006–0,01 entwickelten sich daher zu dichten, wolkigen, gelben Suspensionen, die lichtundurchlässig waren. Die polymeren Eisen(III)-Arten in der gealterten 0,02 *m*-Lösung bestanden vorwiegend aus großen Teilchen, die unter dem Einfluß der Schwerkraft sedimentierten und eine Suspension geringer Trübung ergaben. Auch konnte beobachtet werden, daß in verdünnten Lösungen das anfängliche Polymerisationsprodukt aus amorphem Eisen(III)-Hydroxid bestand, das – wenn überhaupt – nur nach langer Alterungszeit Röntgenbeugungspeaks für FeOOH ergab. In 0,01 und 0,02 m-Lösungen war dagegen kristallines FeOOH vom Beginn der Polymerisation an das vorherrschende Produkt. Die Ergebnisse lassen vermuten, daß der anfängliche Grad der Übersättigung bezüglich des amorphen Eisen(III)-Hydroxids der Schlüsselfaktor ist, der die Teilchengrößenverteilung steuert, die ihrerseits das Aussehen, die Stabilität und Kristallinität des hydrolysierten Produktes während der Alterung bestimmt.

Die Zugabe von $HClO_4$ zu verdünnten $Fe(ClO_4)_3$-Lösungen vermindert den Grad der Übersättigung – während die Zugabe von NaOH zu konzentrierten Lösungen ihn erhöht – und rief daher enstprechende Veränderungen in der Anlaufzeit, dem Aussehen, der Stabilität und Kristallinität der hydrolysierten Produkte hervor.

Резюме — Исследуются растворы $Fe(ClO_4)_3$ различной концентрации и кислотности для определения факторов регулирующих их внешний вид и устойчивость при подвержении старению и для пролития света на механизмы образования некристаллической и кристаллической гидроокиси железа(3) при медленном гидролизе. Нашли, что после недолгой индукции разбавленные растворы (0,001 М или ниже) быстро гидролизировались в прозрачные твердые частицы. По мере повышения концентрации железа(3), замечалось постепенное возрастание периода индукции, более сильное помутнение и увеличение размера частиц. Таким образом, растворы от 0,006 до 0,001 М железа(3) превращались в густые, желтые светонепроницаемые суспензии. Полимерное железо(3) из раствора подвергавшегося старению образовало главным образом крупные частицы оседавшие под силой тяжести и в результате получалась довольно ясная суспензия. Также заметили, что при разбавленных растворах исходным продуктом полимеризации являлась аморфная гидроокись железа(3), дававшая пиковую рентгенограмму только для FeOOH после долгого подвержения старению или совсем ее не дававшая. В растворах 0,01 и 0,02 М, однако, кристаллический FeOOH является главным продуктом с самого начала полимеризации. По результатам можно предполагать, что первоначальная степень насыщения аморфной гидроокиси железа(3) является главным фактором влияюшим на размеры частиц, которые в свою очередь влияют на внешний вид, устойчивость и кристалличность гидрализованного продукта во время подвержения старению.

Разбавление растворов $Fe(ClO_4)_3$ добавлением $HClO_4$ понижает пересыщение, в то время как добавление NaOH к концентрированным растворам повышает степень перенасыщения и, таким образом, ведет к изменениям во времени индукции, внешнего вида, устойчивости и кристалличности гидролизированного продукта, соответственно.

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