BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3306—3307 (1970)

On the Precipitation of Siderite and Magnetite from Homogeneous Solutions as Observed by Means of Visual Autoclaving

Tominosuke KATSURAI* and Masayuki UDA

Pilot Laboratory, Hiratsuka-Kanagawa and The Institute of Physical and Chemical Research, Yamato-machi, Saitama

(Received June 11, 1970)

Visual autoclaving was worked out for the purpose of following the hydrothermal changes which take place during the course of autoclaving.[1] The method is useful not only in the sense seeing is believing, but it also makes it possible for us to observe the change taking place in a homogeneous solution above 100°C.[2] Precipitation from homogeneous solutions has been extensively studied in the field of analytical chemistry for obtaining compact, easily filtrable precipitates. However, it seems that the studies were restricted to temperatures below 100°C. We would like to describe the results which we obtained with homogeneous ferrous and ferrous-ferric solutions. The solutions were subjected to visual autoclaving in the presence of urea, and the structures of the resulting precipitates were confirmed by means of X-ray diffraction. Commercial reagents of the best grade were used in the experiments. The results were found to be of interest in relation to mineral synthesis.

Formation of Siderite. Preparation of pure siderite is known to be difficult. However, we found that it can be obtained by autoclaving a solution of ferrous ammonium sulfate in the presence of urea. A solution containing ferrous ammonium sulfate (0.1M) and urea (0.4M) was used. A white bulky precipitate appears at 150°C. It begins to coagulate at 170°C and at 200°C becomes compact. This snow-white precipitate contains a small amount of dark magnetic particles which can easily be removed by a magnet. It was found that the white precipitate is siderite ($FeCO_3$) and the dark particles magnetite. The magnetite is derived from the ferric compound contained in ferrous ammonium sulfate in a small amount as an impurity. This can be illustrated by the formation of magnetite from a ferrous-ferric solution in the presence of urea.

Formation of Magnetite. The following solutions (a) and (b) were subjected to autoclaving at 200°C for 1 hr. For the sake of comparison, a ferrous-ferric solution (c) was also studied.

Solution (a): 0.05M in $FeSO_4 \cdot (NH_4)_2SO_4$, 0.1M in $FeCl_3$ and 1M in $CO(NH_2)_2$. A brown precipitate

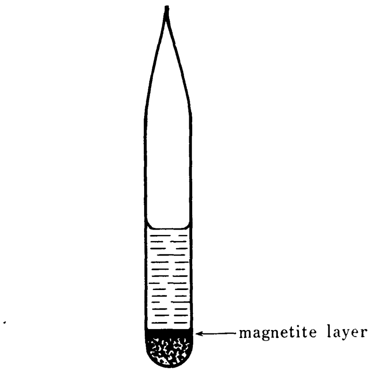

Fig. 1. Formation of magnetite.

---

* Present address: The Chemical Society of Japan, Kanda Surugadai, Chiyoda-ku, Tokyo.

[1] For the technique of autoclaving, *cf.* T. Katsurai and K. Sone, *Kolloid-Z.*, **163**, 70 (1959); T. Katsurai, *ibid.*, **170**, 57 (1960).

[2] T. Katsurai, *Kolloid-Z. Z. Polym.*, **204**, 126 (1965).

Table 1

No.		Composition of solution	Autoclaving product
1		0.1M in $FeSO_4\cdot(NH_4)_2SO_4$ 0.4M in $CO(NH_2)_2$	Siderite ($FeCO_3$) Magnetite (Fe_3O_4), small amount
2	(a)	0.05M in $FeSO_4\cdot(NH_4)_2SO_4$ 0.1M in $FeCl_3$ 1M in $CO(NH_2)_2$	Magnetite (Fe_3O_4) $\left.\begin{array}{l}\text{Siderite (FeCO}_3\text{)}\\ \alpha\text{-FeO}\cdot\text{OH}\end{array}\right\}$ small amount Hematite (α-Fe_2O_3), trace
	(b)	0.2M in $FeSO_4\cdot(NH_4)_2SO_4$ 0.04M in $FeCl_3$ 1M in $CO(NH_2)_2$	Magnetite (Fe_3O_4) Siderite ($FeCO_3$), small amount
	(c)	0.05M in $FeSO_4\cdot(NH_4)_2SO_4$ 0.1M in $FeCl_3$	Hematite (α-Fe_2O_3)

is formed at about 100°C. It turns to brick red at 150°C. The upper liquid turns colorless at 160°C. The surface of the precipitate turns black above 170°C. The black layer thickens with the rise of temperature. The principal constituent of the autoclaving product is magnetite. Siderite, αFeO·OH and a trace of hematite are found as minor constituents.

Solution (b): 0.2M in $FeSO_4\cdot(NH_4)_2SO_4$, 0.04M in $FeCl_3$ and 1M in $CO(NH_2)_2$. The process of the formation of magnetite could be demonstrated more clearly than for (a). At 100°C a brown precipitate is formed and the upper liquid phase becomes turbid. With temperature rise up to 140°C, the precipitate turns brick red and the contact surface of precipitate with the liquid phase begins to blacken. The thickness of the black layer gradually increases in a downward direction (Fig. 1). At 170°C two distinct phases are formed, *viz*., an almost colorless, clear upper liquid phase and a compact, black precipitate. The gradual formation of magnetite in two steps, *viz*., formation of hematite and that of magnetite by the interaction between hematite and the ferrous ion in solution, could be followed.

Solution (c): 0.05M in $FeSO_4\cdot(NH_4)_2SO_4$ and 0.1M in $FeCl_3$. In contrast to cases (a) and (b), hematite only and no magnetite was obtained. The same formation of hematite as in the autoclaving of $FeCl_3$ solution only takes place.3) This is in line with the previous results in which no magnetite was formed by the autoclaving of the solutions containing various pairs of ferrous and ferric salts.4) For the sake of illustration, the results are summarized in a table (Table 1).

---

3) T. Katsurai and T. Watanabe, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **13**, 89 (1930).

4) T. Katsurai, T. Okubo and H. Mikawa, *Kolloid-Z.*, **154**, 56 (1957).