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著者	GOTO Tae, IKEDA Masako
journal or publication title	Tohoku journal of agricultural research
volume	13
number	3
page range	287-292
year	1962-10-06
URL	http://hdl.handle.net/10097/29399

STUDIES ON THE BEHAVIOR OF METALS IN COLLOIDAL
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BEHAVIOR OF IRON IN STARCH PASTE BY
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By

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(Received, May 31, 1962)

In the preceding report (1) the conjugation of iron and starch paste, and the action of starch paste in inhibiting the hydrolysis of iron solution was described. In the present work, the changes of iron in starch paste due to ascorbic acid was examined. A mixed solution of starch, iron, and ascorbic acid was submitted to ultracentrifugation and the residual rate of iron in its supernatant was examined with the use of ^{55}Fe . The residual rate of starch was also examined with a part of this supernatant.

Experimental Method

1. Sample and Reagents

Starch suspension: A suspension of potato starch (J.P.) in concentrations of 0.01, 0.1 and 1 per cents.

Ferric chloride solution: A solution containing ^{55}Fe in a concentration of 1 mg Fe/100 ml (same as in the previous work (1))

Ascorbic acid solution: Crystalline *l*-ascorbic acid solution in concentrations of 2, 4, 10, 20, 40, and 100 mg/ml.

Reagents for analysis of starch. (HCl, NaOH, Fehling's solution, $\text{Fe}_2(\text{SO}_4)_3$, KMnO_4)

2. Apparatus

2π Gas-flow Counter

Ultracentrifuge (same as in Part II (1))

3. Experimental Procedure

(1) Changes in the Residual Rate of ^{55}Fe according to the Mixing Iron

Examination of the method of mixing iron: Solutions tested were as follows:

(a) Iron solution added to starch suspension, the mixture was boiled for 15 minutes, cooled, and ascorbic acid was added to make a concentration of 2 mg/100 ml.

(b) Starch suspension was boiled for 15 minutes, cooled, iron solution was added, followed by ascorbic acid to make a concentration of 2 mg/100 ml.

(c) Iron solution was boiled for 15 minutes, cooled, and ascorbic acid was added to make a concentration of 2 mg/100 ml.

(d) Ascorbic acid was added to iron solution to make a concentration of 2 mg/100 ml.

(e) Iron solution and ascorbic acid (2 mg/100 ml) was added to starch suspension.

Each of these solutions was adjusted to final pH 3.8 and submitted to ultracentrifugation for one hour at 40,000 revolutions. Radioactivity of the residual ^{55}Fe in its supernatant was measured by the 2π gas-flow counter in the same manner as described in Part I of this series (2). The residual amount of starch in the supernatant was also determined.

(2) Variation in the Residual Rate of ^{55}Fe according to the Concentration of Ascorbic acid

The experiments were the same as in the foregoing (1) except that the concentration of ascorbic acid was varied to 2, 4, 10, 20, 40, and 100 mg/ml.

Result

(1) Variation in the Residual Rate of ^{55}Fe by the Addition of Iron

The results of the experiments carried out as in (1) are summarized in Table 1.

Table 1. Variation in the residual rate of ^{55}Fe by the addition of iron and the residual rate of starch

Sample solution	Starch concn. (%)	Residual rate of ^{55}Fe (%)				Residual rate of starch (%)			
		0	0.01	0.1	1	0	0.01	0.1	1
a	—	—	17	35	80	—	68	74	80
b	—	—	57	75	92	—	70	65	52
c	10								
d	75								
e	—	—	70	62	45	—	0	0	0

As will be seen from this table, the residual rate of ^{55}Fe increased with increasing concentration of starch if iron was added after boiling and cooling

the starch suspension and then by the addition of ascorbic acid. The residual rate of ^{55}Fe was especially great when iron was added after boiling. The residual rate of starch increased with increasing concentration of starch when iron was added before boiling but the rate decreased inversely with increasing concentration of starch if iron was added after boiling.

In the control iron solution not containing starch, the residual rate of ^{55}Fe in the supernatant was 10 per cent when boiled but 75 per cent when the iron solution was not boiled. The residual rate of ^{55}Fe in the supernatant of a mixture of starch and iron solution was smaller than that in the iron solution alone, not containing starch, and the residual rate decreased with increasing concentration of starch. In all these cases, starch was not found in the supernatant. These facts are shown in Fig. 1.

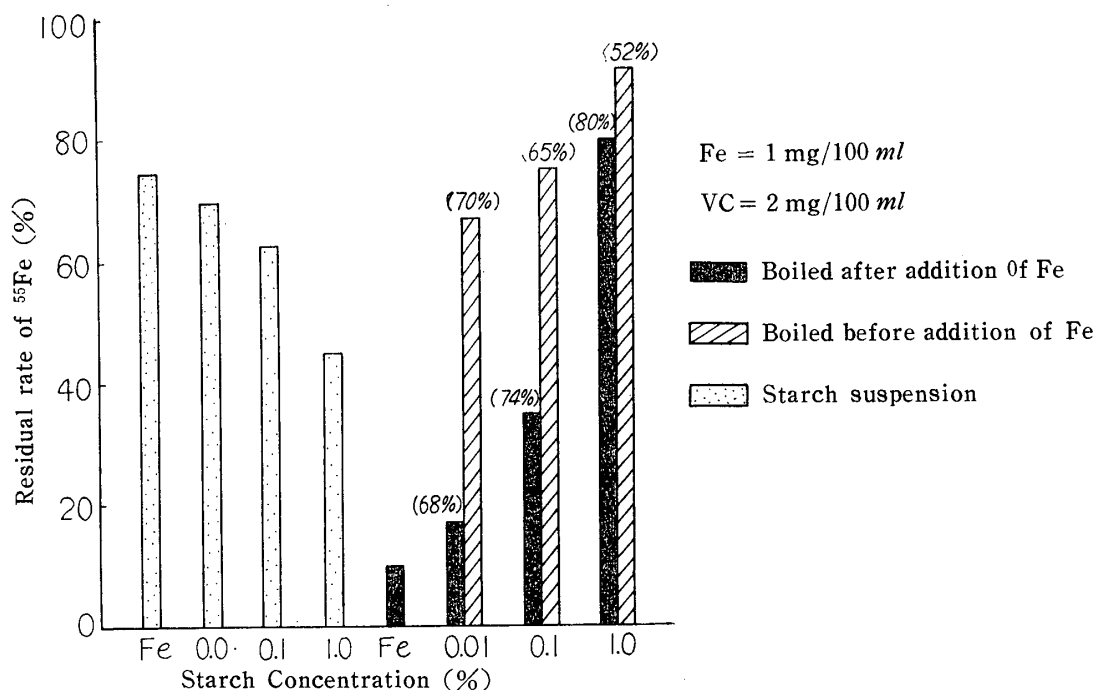


Fig. 1. Residual rate of ^{55}Fe in starch paste by the manner of addition of iron.

(2) Variation in the Residual Rate of ^{55}Fe according to the Concentration of Ascorbic acid

The residual rate of ^{55}Fe in the supernatant was examined as in the foregoing cases with solutions of starch suspension added with iron solution before or after boiling and ascorbic acid to make a concentration of 2, 4, 10, 20, 40, or 100 mg/100 ml. The results of these experiments are summarized in Table 2.

As will be seen from Table 2, the residual rate of ^{55}Fe according to the manner of addition of iron was the same as in the case of ascorbic acid concentration of 2 mg/100 ml as in (1), at all the concentrations of ascorbic acid

Table 2. Residual rate of ^{55}Fe and ascorbic acid concentration

Sample solution	Concn. of ascorbic acid (mg/100 ml)	Residual rate of ^{55}Fe (%)			
		Starch concn. (%)			
		0	0.01	0.1	1
a	2	—	20	43	85
	4		20	46	84
	10		24	50	86
	20		32	58	91
	40		35	68	92
	100		39	78	90
b	2	—	65	76	91
	4		66	79	91
	10		70	80	93
	20		70	80	97
	40		69	80	98
	100		70	75	90
c	2	14			
	4	16			
	10	15			
	20	17			
	40	19			
	100	20			
d	2	70			
	1	69			
	40	73			
	20	75			
	40	75			
	100	74			
e	2	—	66		42
	4		66		44
	10		70		48
	20		72		50
	40		71		50
	100		71		51

tested. The residual rate of ^{55}Fe was a little higher in (a) solution with a starch concentration of 0.1 per cent and ascorbic acid concentration of 100 mg/100 ml. In (a) solution, where iron was added before boiling the starch suspension and then boiled, cooled, and ascorbic acid added, the residual rate of ^{55}Fe tended to increase with increasing concentration of ascorbic acid, especially in the solution with starch concentration of 0.1 per cent. In (b) solution, where iron was added after boiling the starch suspension and ascorbic acid mixed in it, there was no great difference in the residual rate of ^{55}Fe in the supernatant according to the concentration of ascorbic acid. In the control iron solution (c) containing ascorbic acid and the starch suspension (d) containing iron and ascorbic acid, the residual rate of ^{55}Fe was the same as in (b) solution. These facts are shown in Fig. 2.

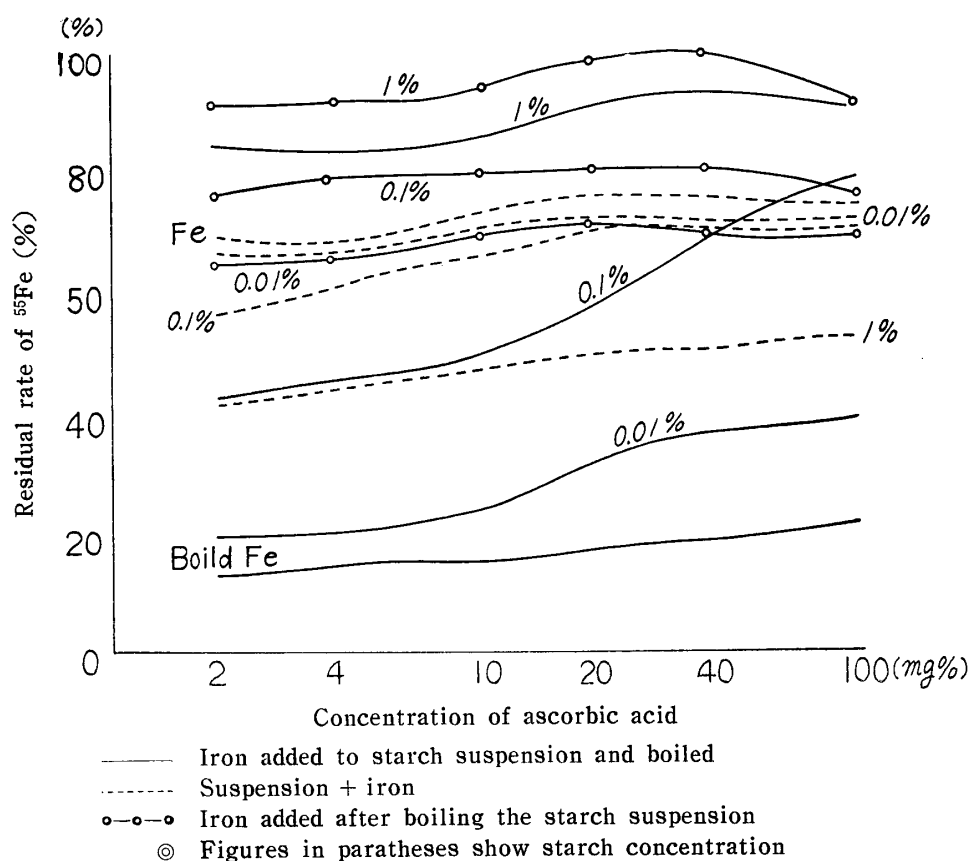


Fig. 2. Variation of residual rate of ^{55}Fe in starch paste according to ascorbic acid concentration (Fe 1 mg/100 ml)

Conclusion and Consideration

The behavior of iron in starch paste was examined by the variation of iron, using radioactive iron-55, by the effect of ascorbic acid. From the manner of mixing iron in starch paste and by varying the concentration of ascorbic acid, the following facts were found.

When iron solution is added to starch suspension, either before or after boiling, then ascorbic acid added to it, and the mixture submitted to ultracentrifugation, the residual rate of ^{55}Fe in its supernatant is smaller by the addition of iron before boiling than after boiling, though this residual rate increases with increasing concentration of starch in both cases. In the control iron solution without starch, the residual rate of ^{55}Fe is the smallest when the iron solution is boiled, while the rate is very great when the iron solution is not boiled. The rate was about the same when iron was added to 0.01 per cent starch suspension after boiling and cooling.

These tendencies are the same at all concentrations of ascorbic acid tested but the residual rate of ^{55}Fe in the supernatant increases with increasing concentration of ascorbic acid in the starch suspension added with iron before boiling and in the control iron solution after boiling.

From these facts, the following considerations are made.

Ferric chloride solution undergoes hydrolysis to form ferric hydroxide and this hydrolysis is especially promoted in the boiled ferric chloride solution, resulting in the small residual rate of ^{55}Fe in the supernatant. The addition of ascorbic acid causes reduction of trivalent iron to bivalent iron, which stops hydrolysis and this results in the larger residual rate of ^{55}Fe in the supernatant. The smaller residual rate of ^{55}Fe by the increasing concentration of starch when starch suspension is present is due to co-precipitation of iron with starch granules, as was pointed out in Part II of this series. (1)

In the case of a starch suspension mixed with iron solution and boiled, the residual rate of ^{55}Fe and starch increase with increasing concentration of starch and this is probably due to the greater conjugation of starch and iron, and inhibition of hydrolysis of ferric chloride by starch, as was also the case reported in Part II. (1) The increased residual rate of ^{55}Fe with increasing concentration of ascorbic acid, as in boiled solution of iron, may be due to the reduction of once hydrolyzed iron by the increase of ascorbic acid. When the residual rate of ^{55}Fe increased markedly, there may have been a complex formation between iron and ascorbic acid.

When iron is added to starch suspension after boiling and cooling, the residual rate of ^{55}Fe increases with increasing concentration of starch with inverse decrease of residual rate of starch in the supernatant. This may be due to the small amount of hydrolyzed iron in the absence of heating of ferric chloride. On the other hand, the viscosity of starch paste falls by the addition of iron and the quantity of starch deposited increases with increasing concentration of starch, resulting in the smaller residual rate of starch in the supernatant.

Summary

Ferric chloride solution was added to potato starch suspension, either before or after boiling, ascorbic acid was added to it in various concentrations, the mixture was submitted to ultracentrifugation, and the residual iron and starch in the supernatant were examined. These experiments revealed the behavior of iron in the starch paste reduced by ascorbic acid, inhibition of the hydrolysis of iron by starch paste, conjugation of starch and iron coprecipitation of iron with starch granules, and the role of iron in viscosity of starch.

References

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