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## PROPERTIES OF POTATO STARCH SATURATED WITH FERRIC SALTS

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Key words: starch, ferric salts, iron content, viscosity of starch pastes, enzymatic degradation

Starch saturated with ferric salts and containing 7-80 mg Fe/100 g of dry matter was examined. Viscosity of 0.25% pastes produced from starches containing higher than that of the control samples. This starch was characterized by lowered susceptibility to enzymatic degradation carried out with use of  $\alpha$ -amylase and glucoamylase.

Potato starch, owing to phosphoric acid linked with carbohydrate chains by esters, has the properties of an ion-exchanger [19, 22]. These properties were utilized in the preparation of hydrogen starch [11, 21] and of the so-called cationic starches, i.e. starches where the radicals of phosphoric acid are saturated with cations of one type [10, 12, 18, 21]. For the complete saturation of phosphoric acid radical with a defined cation, it is necessary to rinse starch with a mixture of the solutions of salts and hydroxide of this cation [20]. This method is applied in obtaining starches saturated with mono- and divalent cations, the hydroxides of which are soluble in water [10, 12].

We may find in literature relatively numerous data on starches saturated to a lower or higher degree with sodium, potassium, calcium and magnesium cations [2, 9, 10, 12, 16, 18]. Only few literature references present properties of starches saturated with other cations, such as the ammonium group [13, 16], barium [9, 16], lithium, zinc and aluminium [16] or copper [18]. There are no data concerning starch saturated with ferrum ions.

Iron is one of the indispensable components of human nutrition. Due to the shortage of this element, especially in the diet of civilized societies, enrichment of food with iron or its mineral compounds or organic combinations, is applied [6]. In spite of the fact that starch present in the

diet lowers the assimilation ability of iron added to food [1], technical reasons cause that most frequently, bread and flour products are enriched with iron [6]. Hence, the possibility arises to enrich these products with a supplement of potato starch after its saturation with ferric cations.

The conducted studies of starch rinsed from potato tubers with water containing an admixture of ferric salt [7] and of starch saturated in excess with ferric salts [8] revealed differences in certain properties in comparison with the control starch.

The aim of the present study was to determine the changes in properties of potato starch induced by its saturation with ferric salts, and to examine the influence of the method for starch saturation with these salts on its properties.

## METHODS

Potato starch (from the starch mill) was rinsed with distilled water or with 1/10 M hydrochloric acid and then with 1/30, 1/300 and 1/3000 M solution of ferric chloride or ferric citrate in a 1:5 ratio in relation to starch amount. The control samples were not saturated with ferric salts. All samples were rinsed with distilled water till a decay of colour reaction for presence of iron with ammonium rhodanate (in case of hydrogen starch — of chloride with silver nitrate) and were dried at about 20°C.

Changes in properties of the obtained samples were determined by comparison with the control starch samples. The differences in their properties, depending on the rinsing of starch with water or acid, on the type of ferric salt used and concentration of its solution were examined as well. For this purpose, the following properties of the obtained starch were determined:

- moisture by drying at 50° and 105°C,
- pH of suspension at weight ratio of starch and water 1:5 [14],
- iron content after dry mineralization, by the method of atomic absorption spectrophotometry [15],
- viscosity of 0.25% pastes with the use of Ostwald viscosimeter [17],
- viscosity of 7% starch pastes, measured in the range of temperatures 50 → 80 → 20°C, using a rotary viscosimeter Rotovisko RV 3, with a special agitator [23] at 600 r.p.m.
- susceptibility to enzymatic degradation using 10 cm<sup>3</sup> of paste corresponding to 25 mg of dry starch, 1 cm<sup>3</sup> of the solution of enzymatic preparation and 5 cm<sup>3</sup> buffer, in the following conditions of analysis [4]:
  - 1)  $\alpha$ -amylase (preparation BAN L-120 of Novo company, with concentration 0.15% in reaction mixture (pH = 7.0; phosphate buffer), temperature 37°, time 30 min.,

2) glucoamylase (preparation AMG L-150 of Novo company, with concentration 0.01% in reaction mixture (pH = 4.8; acetate buffer), temperature 37°C, time 30 min.

The susceptibility of starch to enzymatic degradation was determined by the use of paste prepared in the same way as paste used for the determinations of viscosity in Ostwald viscosimeter [17] and again repeated after additional holding of paste in a boiling water bath for 30 min.

The effect of enzyme activity was determined on the basis of quantities of reducing substances produced, according to the method of enzymatic activity determination [5], applying centrifugation (2000 r.p.m.) instead of filtration.

The obtained results were subjected to statistical calculations—analysis of variance and the correlation and regression calculus with choice of the optimal subset.

## DISCUSSION OF THE RESULTS

Together with the increase of concentrations of the solutions used for saturation of starch, the content of iron in starch was increased from 3 to 82 mg Fe in 100 g of dry matter (Fig. 1). The quantities of iron in starch

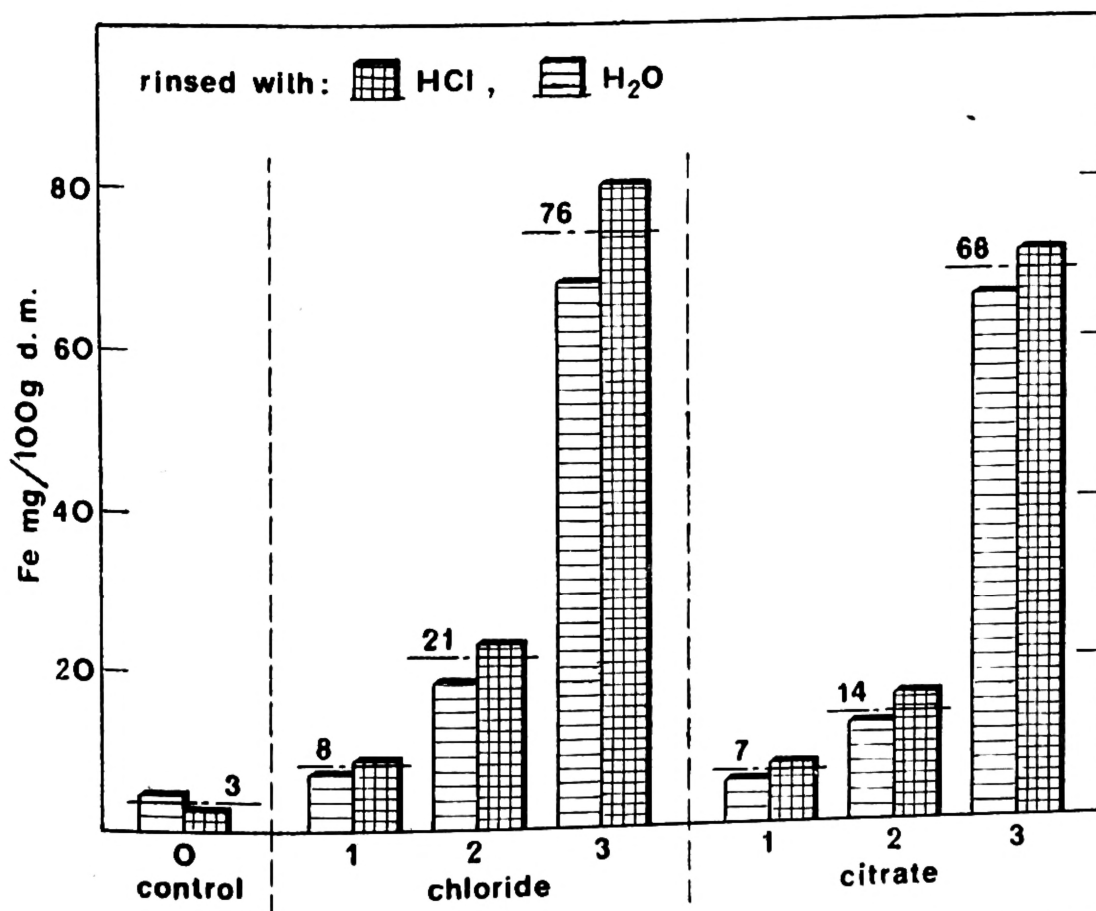


Fig. 1. Content of iron in starch rinsed with water or hydrochloric acid and saturated with solutions of ferric chloride or ferric citrate in three concentrations concentration: 1 —  $\frac{1}{3000}$  M, 2 —  $\frac{1}{300}$  M, 3 —  $\frac{1}{30}$  M, --- medium

obtained with the use of a solution having the lowest concentration, did not differ significantly from the control samples. In starch saturated with chloride significantly higher quantities of iron were found than when using citrate. No significant differences were found between the content of iron in starch rinsed with hydrochloric acid and with water before its saturation with iron. The level of phosphorus in starch was 65.6 mg/100 g of dry matter, i.e., saturation of phosphoric acid radicals with iron reached 100%. This indicates that starch displayed the properties of a two-basic amylophosphoric acid in spite of the acid and neutral reaction of saturating solutions. This could be caused by high affinity of iron in relation to starch, or the binding of iron with starch was not limited to combination with phosphoric acid [3].

Fig. 2 presents pH values of starch saturated with ferric salts depending on the concentration of the solution used. In case of starch saturated with iron after its previous rinsing with hydrochloric acid, the increase of concentration in saturating solution caused a rise in pH from 3.4 to 4.4.

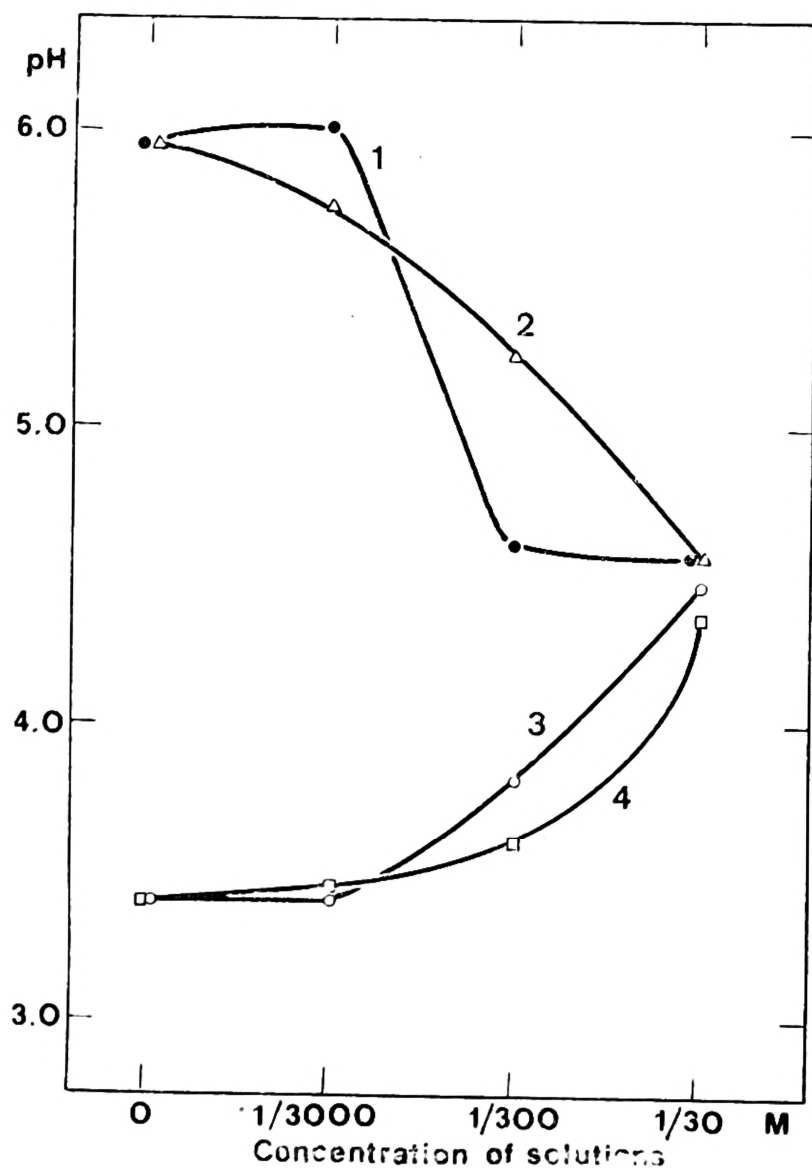


Fig. 2. pH value of starch rinsed with water or hydrochloric acid and saturated solutions of ferric chloride or ferric citrate in three concentrations

rinsed with: H<sub>2</sub>O { 1 — chloride , HCl { 3 — chloride  
 2 — citrate , 4 — citrate

The pH of starch rinsed with water before saturation with iron was decreased from 6.0 to 4.5 together with the rise in concentration of the saturating solution.

Viscosity of 0.25% pastes prepared from the "ferric" starch was directly proportional to pH of starch — the correlation coefficients were: for samples saturated with iron after rinsing of starch with acid  $r = 0.8362$  and for the samples saturated after rinsing with water  $r = 0.8749$ .

Simultaneously the viscosity of pastes was correlated with the iron content in starch. The performed statistical calculations demonstrated that iron content in starch has a decisive influence on the viscosity of starch pastes. Together with the increase of iron content in starch, the viscosity of pastes was lowered in case of samples saturated after rinsing of starch with water ( $r = -0.9550$ ) and was increased in case of samples rinsed with acid before their saturation with iron ( $r = 0.8776$ ) (Fig. 3). Additional

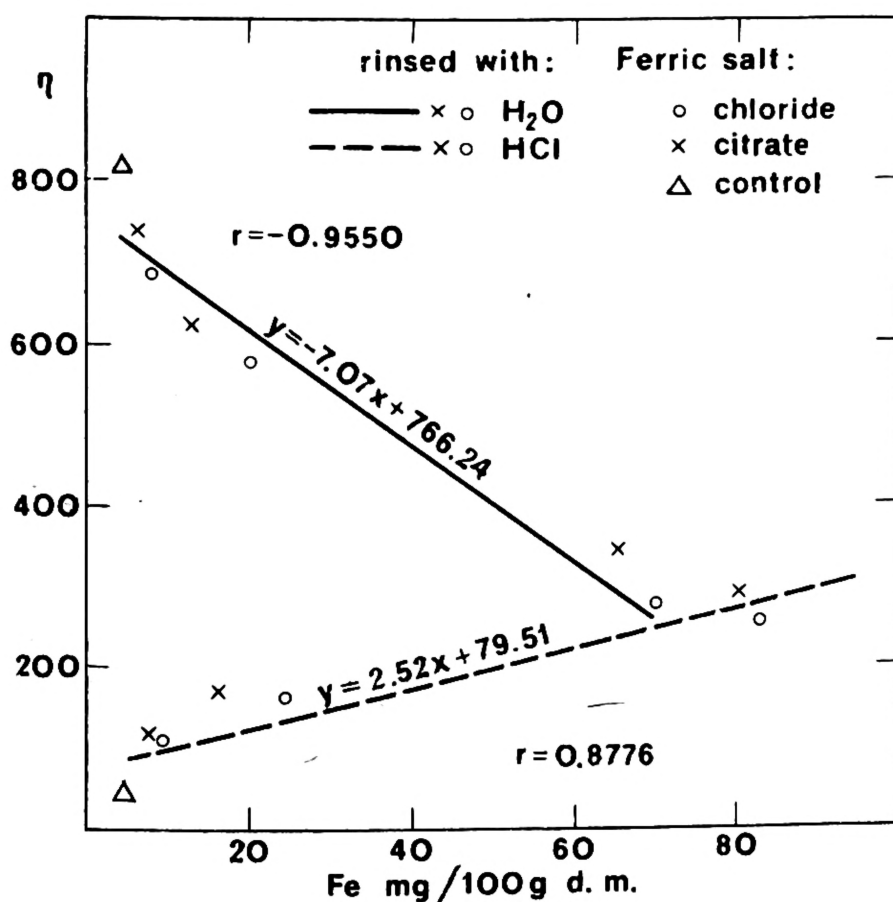


Fig. 3. Influence of iron content in starch rinsed with water or hydrochloric acid and saturated with ferric salts solutions on relative viscosity (reduced value) of 0.25% starch pastes

tests were made to explain whether the low viscosity of pastes produced from starches saturated with iron resulted from a partial autohydrolysis of starch during preparation of paste due to their low pH values. It was found that viscosity of 0.25% pastes from "ferric" starch at pH = 4.5 (sample saturated with 1/30 M ferric chloride after rinsing with water) prepared on water and phosphate buffer with pH = 7.0 was the same.

Lowering of viscosity of pastes together with the rise of iron content in starch remains in accordance with data concerning the decrease of

viscosity of pastes by starch-saturating multivalent cations [16]. The samples of starch rinsed with hydrochloric acid and saturated with diluted solution of ferric salts, that is, containing small iron quantities, produced pastes with a low viscosity, similar to that of pastes produced from hydrogen starch (Fig. 3). In samples saturated with solutions containing higher concentrations of ferric salts, hydrogen ions were replaced with ferric cations to a higher degree. This explains the higher viscosities of pastes made from these samples.

Figs. 4 and 5 present the characteristic of gelatinization of starch

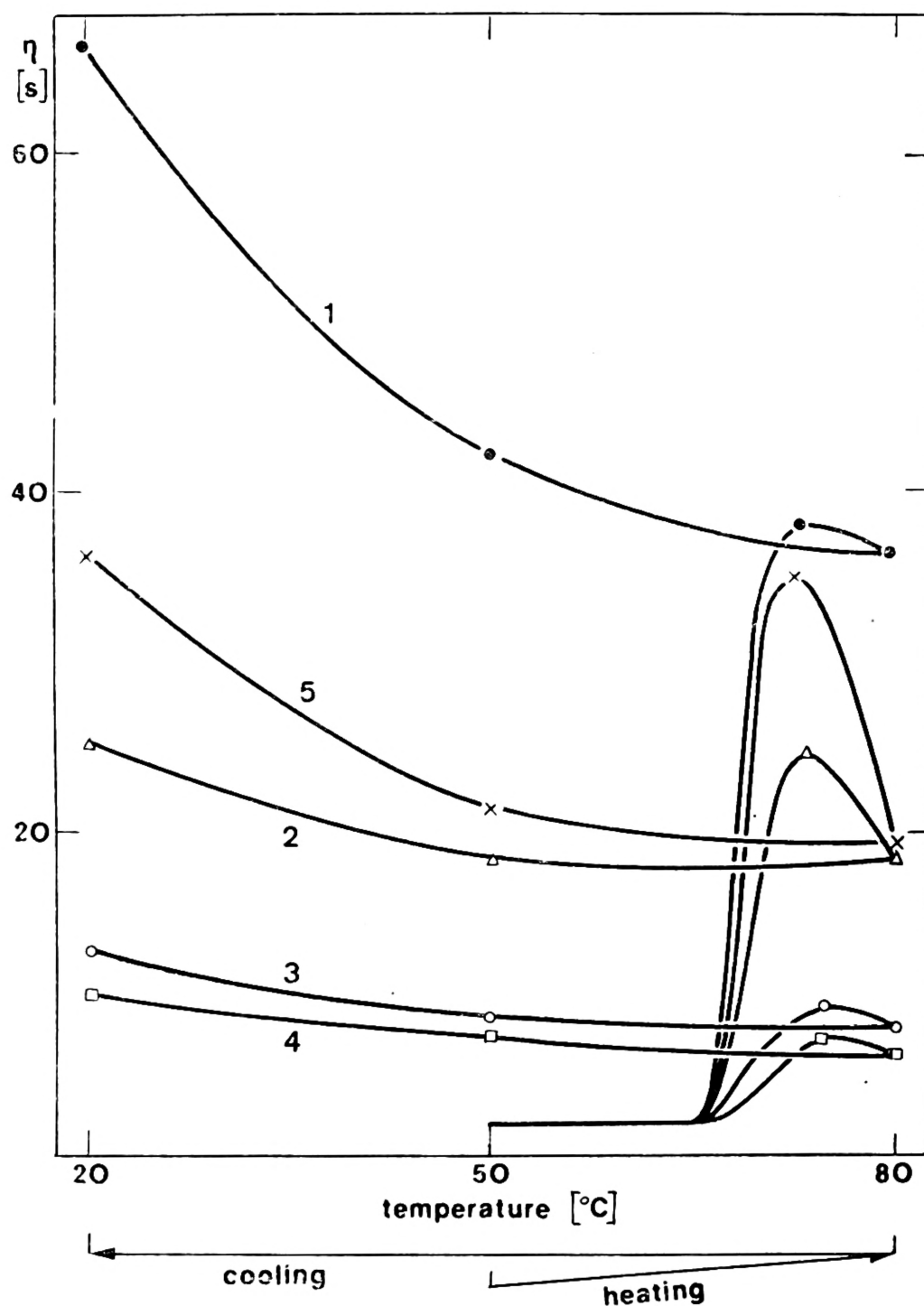


Fig. 4. Changes of viscosity of 7% pastes from starch rinsed with hydrochloric acid and saturated with ferric chloride. Measurements at temp. 50 → 80 → 20°C  
 chloride concentration: 1 —  $\frac{1}{30}$  M, 2 —  $\frac{1}{300}$  M, 3 —  $\frac{1}{3000}$  M, 4 — control (H — starch),  
 5 — control (washed with H<sub>2</sub>O)

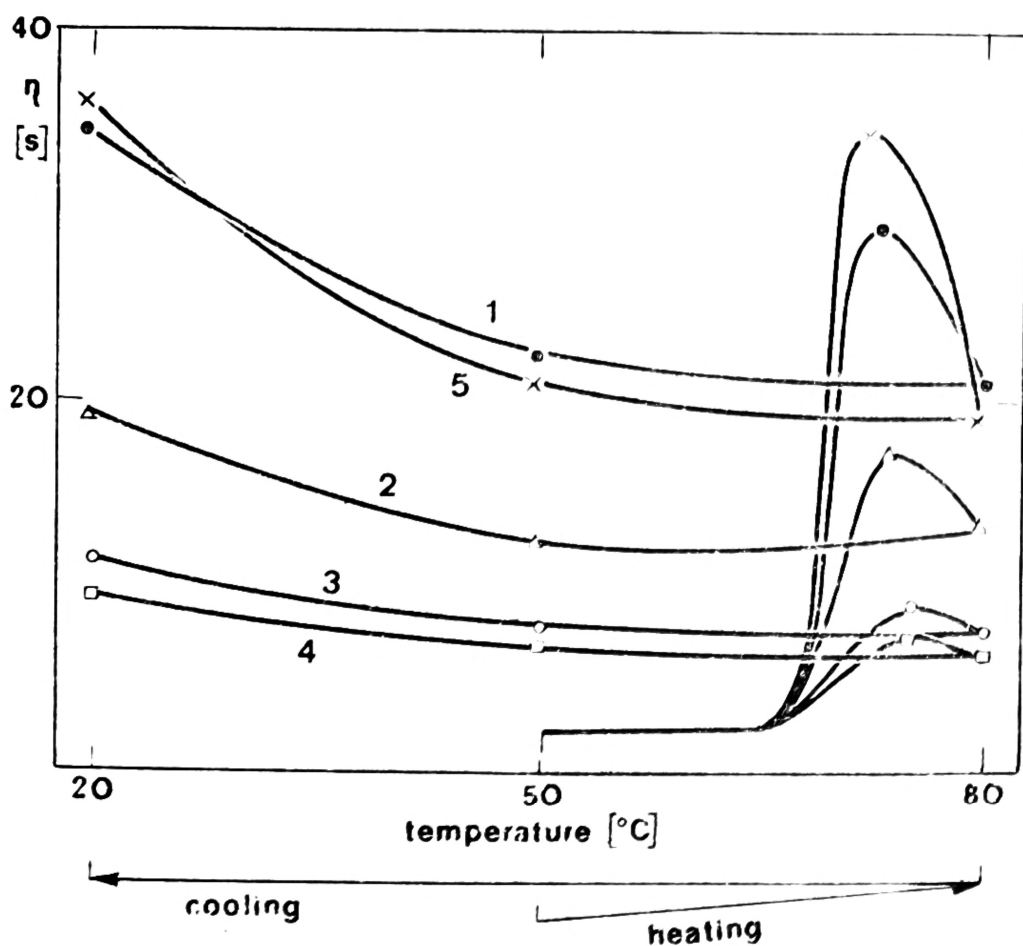


Fig. 5. Changes of viscosity of 7% pastes from starch rinsed with hydrochloric acid and saturated with ferric citrate. Measurement at temp. 50 → 80 → 20°C  
 citrate concentration: 1 —  $\frac{1}{30}$  M, 2 —  $\frac{1}{300}$  M, 3 —  $\frac{1}{3000}$  M, 4 — control (H — starch),  
 5 — control (washed with H<sub>2</sub>O)

rinsed with hydrochloric acid and then saturated with solutions of chloride (Fig. 4) and ferric citrate (Fig. 5).

As it results from the diagram, viscosity of 7% pastes prepared from starches saturated with ferric salts in concentrations 1/30 and 1/300 M, measured in the range of temperature 50 → 80 → 20°C was statistically significantly higher than that of starch non-saturated with iron (hydrogen starch). This may be explained by the replacement of hydrogen ions with ferric cations, preventing the autohydrolysis of starch saturated with ferric chloride was higher than that of starch saturated with citrate.

Fig. 6 shows changes in viscosity of 7% pastes prepared from starch saturated with 1/30 M solution of ferric chloride, hydrogen starch and the control starch, measured during cooling (temp. 80 → 20°C). Starches saturated with ferric chloride (both the sample rinsed previously with acid and the one rinsed with water) containing 70-80 mg Fe/100 g of dry matter, produced pastes with considerably higher viscosity than in case of control starch (especially higher than hydrogen starch). This seems to contradict the data concerning viscosity of 0.25% pastes from which it resulted that iron had an influence on the decrease of viscosity (Fig. 3). However, in earlier work, viscosities of cooled 10% pastes made from

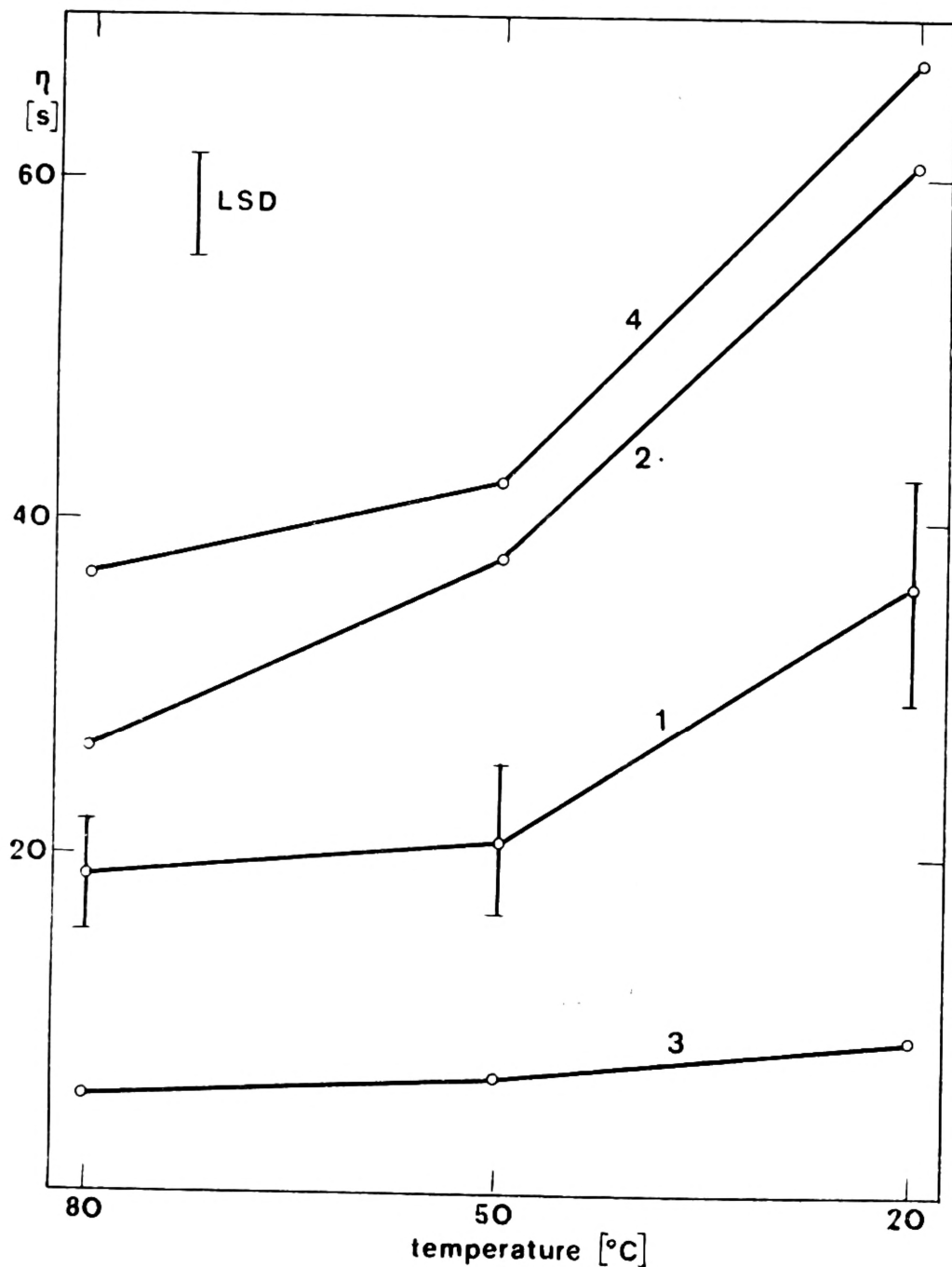


Fig. 6. Changes of viscosity of 7% pastes from starch rinsed with water or hydrochloric acid and saturated with 1/30 M ferric chloride — measured during cooling (temp. 80 → 20°C)

rinsed with H<sub>2</sub>O: 1 — control, 2 —  $\frac{1}{30}$  M FeCl<sub>3</sub>

rinsed with HCl: 3 — control (H — starch), 4 —  $\frac{1}{30}$  M FeCl<sub>3</sub>

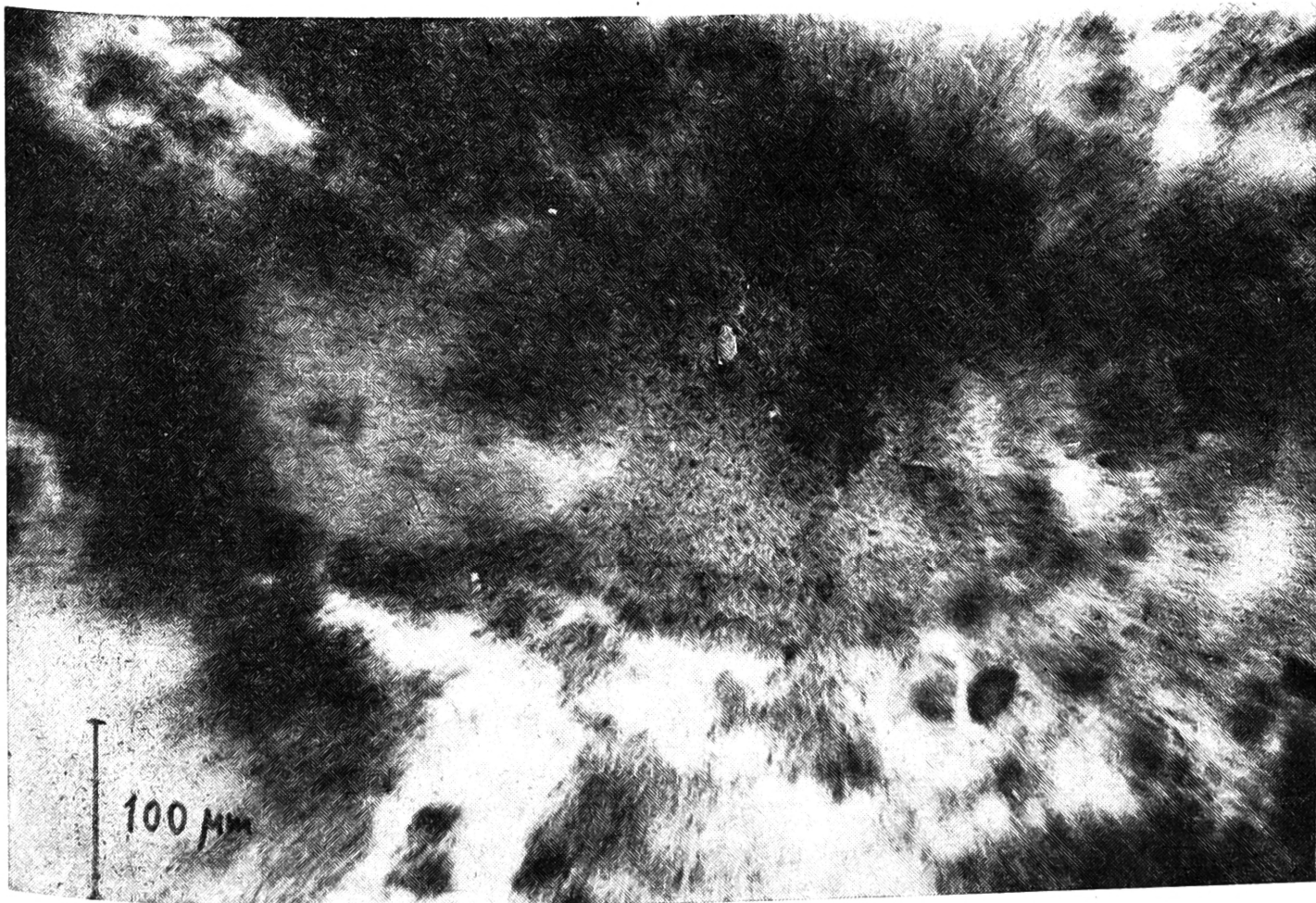
starch rinsed from potato tubes with water containing ferrous chloride were higher than those from the control starch [7].

Photographs of microscopic preparations of starch made from starch saturated with 1/30 M solution of ferric chloride and from the control starch (preparations were treated with iodone solution in potassium iodide), were performed. Under the microscope, paste from the control starch revealed a relatively uniform structure with small fragments of gelatinized granules of starch (Photo 1). Paste made from starch saturated with iron was mostly composed of unbroken "gel bags" (Photo 2). It would results from it that iron bond with phosphoric acid of amylopec-





Fot. 1. Paste from control starch



Fot. 2. Paste from starch saturated with 1/30 M ferric chloride

tin, appearing in the outer layer of granules, formed links between the chains of various molecules, making thus fragmentation of "gel bags" difficult. Some authors observed during microscopic examinations that starch-saturating iron appeared precisely in the top layers of the granules [3].

Lower viscosity of diluted (e.g. 0.25%) pastes in comparison with the control ones could be caused by the smaller than rated concentration of those pastes due to unpenetration of a certain amount of starch substance to the solution as a result of incomplete fragmentation of "gel bags" of "ferric" starch. In case of pastes with high concentration (the range of concentration 5-10% was examined) made from "ferric" starch, most probably the non-destroyed "gel bags" were compactly packed and as

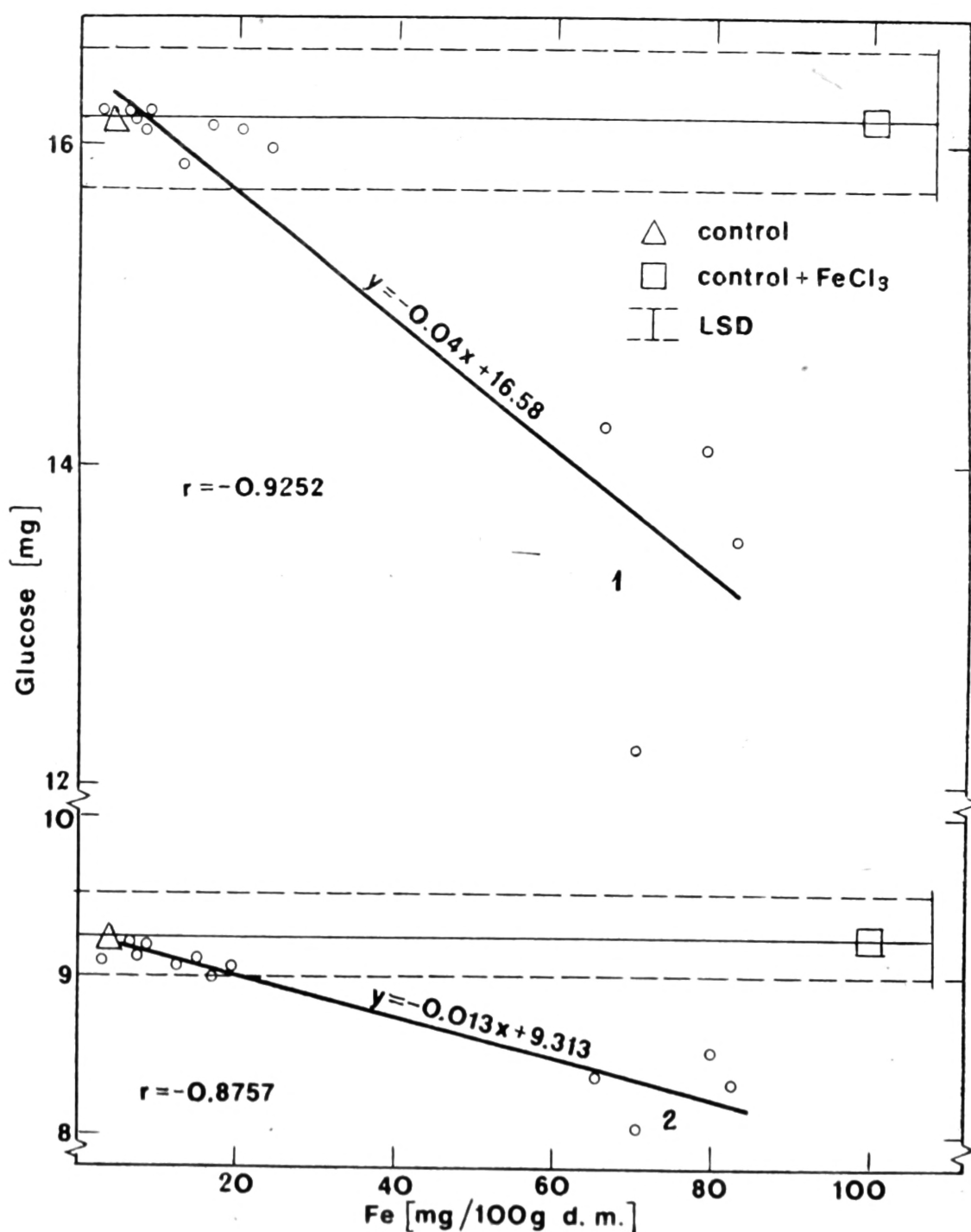


Fig. 7. Effect of iron content in starch saturated with ferric salts on enzymatic degradation of starch (LSD — Least Significant Difference) 1 — glucoamylase, 2 — α-amylase

a result of it an elastic mass with firm structure, high viscosity and high consistency, such as that obtained in the conducted experiments, was formed.

Fig. 7 shows the influence of iron contained in starch on its susceptibility to the action of  $\alpha$ -amylase and glucoamylase. As it can be seen from the diagrams, starch saturated with ferric salts, was subjected to enzymatic degradation to a smaller degree than the control starch. Coefficients of correlation between the susceptibility of starch to enzymatic degradation and the content of iron were as follows: for  $\alpha$ -amylase  $r = -0.8757$  and for glucoamylase  $r = -0.9252$ . In case of an iron content in starch equal to 60-80 mg Fe in 100 g dry matter, a significantly lower degradation of starch as a result of the examined enzymes' effect was noticed in comparison with the control samples. Similar results were obtained in an earlier work where starch saturated with an excess of iron was subjected to degradation affected by  $\alpha$ -amylase, diastase and glucoamylase [8] to a smaller degree than the control starch.

The lowered susceptibility of "ferric" starch to degradation caused by amylolytic enzymes cannot be explained by the toxic effect of iron present in starch upon these enzymes. In the additional determinations of susceptibility of starch to the examined enzymes, applying control pastes with a supplement of ferric chloride in quantities corresponding to 100 mg of Fe in 100 g of dry matter, the obtained results did not differ from the results of the control samples (Fig. 7).

Starch saturated with iron was resistant to the complete gelatinization of granules (Photo 2) as a result of which it was less subjected to enzymatic degradation. In connection with this fact, the effect of starch saccharification was determined, using pastes after holding them in boiling water bath for an additional 30 minutes. On the basis of the results summarized in Table 1, it was established that the additional boiling of starch pastes caused an intensification of the enzymes' effect in case of enzyme-resistant starch samples containing 60-80 mg Fe in 100 g starch. However, even the additional boiling of pastes did not cause an enzymatic degradation of starch with high content of iron to degree met in other samples. We may suppose therefore that starch-saturating iron made the complete degradation of "gel bags" difficult and that the applied heat treatment of paste was insufficient. It is also probable that iron present in starch, when forming links between the chains of various molecules of starch, makes the action of amylolytic enzymes on starch, difficult.

## CONCLUSIONS

1. Starch saturated with 1/30, 1/300 or 1/3000 M solutions of chloride or ferric citrate contained iron in quantities amounting to 80 mg Fe/100 g

dry matter. These quantities increased together with the rise in concentration of the saturating solution; they were higher in case of chloride than ferric citrate and did not depend on the previous rinsing of starch with water or 1/10 M hydrochloric acid.

2. Simultaneously with the increase of iron content in starch viscosity of 0.25% pastes decreased in case of samples rinsed with water and increased in case of starch rinsed with hydrochloric acid — before saturation with ferric salts.

Table 1. Influence of extra heating of pastes from starch saturated with ferric salts on enzymatic degradation of starch (mg of glucose)

Enzyme	Starch pastes	Concentration of solutions of ferric salts (M)				
		0	1/3000	1/300	1/30	LSD
$\alpha$ -amylase	normal	9.3	9.2	9.1	8.4	0.2
	heated	9.3	9.2	9.2	8.8	
gluco-amylase	normal	16.3	16.3	16.1	13.6	0.3
	heated	16.3	16.3	16.2	14.4	

LSD — Least Significant Difference

3. Viscosity of 7% pastes prepared from starch rinsed with hydrochloric acid and saturated with chloride or ferric citrate was higher within the range of temperature 50 → 80 → 20°C than in the case of pastes made from starch non-saturated with ferric salts and it increased together with the rise in concentration of the saturating solution.

4. Viscosity of 7% pastes prepared from starch rinsed with water or hydrochloric acid and saturated with 1/30 M solution of ferric chloride was higher than that of the control starch.

5. Starch containing 60-80 mg Fe in 100 g dry matter was characterized by a lowered susceptibility to degradation by  $\alpha$ -amylase and glucoamylase. The same took place after the additional boiling of pastes from this starch, causing a rise of its susceptibility to enzymatic degradation.

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## WŁAŚCIWOŚCI SKROBI ZIEMNIACZANEJ WYSYCANEJ SOLAMI ŻELAZA

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### Streszczenie

Skrobię ziemniaczaną wysycano solami żelaza po jej uprzednim przemyciu 1/10 M kwasem solnym lub wodą destylowaną. Do wysycania skrobi stosowano 1/30, 1/300 i 1/3000 M roztwory chlorku lub cytrynianu żelazowego. Następnie próby przemycano wodą destylowaną do zaniku reakcji barwnej na obecność żelaza i suszono w temp. ok. 20°C. Próbami kontrolnymi były próby skrobi nie wysycanej solami żelaza.

W otrzymywanych próbach oznaczano zawartość żelaza, lepkość 0,25% kleików skrobiowych, lepkość 7% past skrobiowych mierzoną w zakresie temp. 50 → 80 → 20°C oraz podatność skrobi na rozkład enzymatyczny za pomocą α-amylazy i glukoamylazy.

Stwierdzono, że wraz ze wzrostem stężenia roztworów wysycających wzrastała zawartość żelaza w skrobi, dochodząc do 80 mg Fe w 100 g suchej masy (rys. 1). W miarę zwiększania stężeń użytych roztworów pH prób wysyconych solami żelaza wzrastało z 3,4 do 4,4 w przypadku skrobi przemytej uprzednio kwasem solnym i obniżało się z 6,0 do 4,5 — w przypadku skrobi przemytej wodą (rys. 2). Stwierdzono dodatnią korelację między pH badanych prób a lepkością sporządzonych z nich 0,25% kleików. Na lepkość tych kleików decydujący wpływ miało jednak żelazo zawarte w skrobi. W miarę wzrostu zawartości żelaza w skrobi lepkość malała — w przypadku prób przemytych wodą przed wysycaniem ich solami żelaza, a wzrastała w przypadku prób przemytych kwasem solnym (rys. 3).

Skrobia przemyta kwasem solnym, a następnie wysycana solami żelaza tworzyła 7% pasty o wyższej lepkości niż nie wysycana (rys. 4 i 5); 7% pasty sporządzone

ze skrobi wysycanej 1/30 M roztworem chlorku żelazowego wykazywało znacznie wyższą lepkość mierzoną w zakresie temp. 80-20°C od past kontrolnych (rys. 6). W paście ze skrobi kontrolnej widoczne były pod mikroskopem nieliczne fragmenty gałeczek skrobiowych na tle skleikowanej substancji skrobiowej (fot. 1). Pasta ze skrobi wysycanej żelazem składała się w większości z nierozzerwanych woreczków żelowych (fot. 2).

Skrobia wysycona żelazem charakteryzowała się obniżoną podatnością na działanie  $\alpha$ -amylazy i glukoamylazy (rys. 7). Dodatkowe gotowanie kleików z tej skrobi powiększało efekt działania enzymów, lecz nie doprowadzało do rozkładu skrobi w takim stopniu jak w przypadku prób kontrolnych (tab.).