INTERACTION OF FERROUS SULFATE WITH POTASSIUM BROMATE AND IODATE IN BREW AND DOUGH SYSTEMS

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ABSTRACT

The proposed higher enrichment level of 3800 mg iron to be added by the baker to 100 lb of flour and the use of ferrous sulfate as the preferred iron source require examination of the possible reaction between ferrous sulfate and bromate and iodate in brew and dough systems. Such a reaction is thermodynamically possible and field reports have indicated a loss of the oxidant effect with this level of iron. The reaction of bromate and iodate with ferrous sulfate in no-flour and 30% flour brews and in sponge doughs has been measured by an amperometric procedure. Bromate reacted with ferrous sulfate in brew systems but not in sponge doughs. Iodate did not react with ferrous sulfate although it did react with flour or other brew components. Baking tests confirmed the loss of oxidant in continuous bread processes.

The Federal Register of October 15, 1973, proposed new standards of identity for enriched flour, bread, rolls, and enriched self-rising flour. The proposal increased the levels of thiamine, riboflavin, niacin, and iron and was to go into effect April 15, 1974. Because of objections to the iron level, further hearings on this issue were held in April, the results of which are not yet known.

In the interim period, the baking industry and enrichment suppliers were working out an enrichment tablet formulation which would meet the proposed iron level of 25 mg of iron per lb of bread. The level chosen varied from 3600 to 3800 mg of iron per 100 lb of flour.

Nutritional studies on the form in which iron should be added to bread indicate that ferrous sulfate is generally a more assimilable form of iron than is ferric orthophosphate. For this reason, in the last few years the manufacturers of enrichment wafers and mixtures for bakery use have converted almost universally to ferrous sulfate as the preferred iron source.

Since ferrous sulfate is a reducing agent and potassium bromate and iodate are oxidizing agents, one would predict that they would react with a loss of oxidant and formation of ferric compounds. Evidently, this possibility was not sufficiently considered when the change in iron level was being discussed since Brooke (1) stated there would be no problem.

During the early part of 1974, bakeries began to try out the new higher iron level derived from ferrous sulfate. Immediately, instances of production problems such as poorer volume, lack of dough strength, and longer proof time came to our attention. All of these results are consistent with a loss of the required oxidant effect. The problem was more severe in continuous breadmaking systems than in sponge-dough systems.

The objective of the work reported in this paper was to explore the quantitative relation between bromate and/or iodate and ferrous sulfate in brew and dough systems and to show what happens under actual pilot baking conditions.

TABLE I
Laboratory Brew Formula[a]

Ingredient	No-Flour Brew g	% Based on Total Flour[b]
Water, distilled	2000.00	59.7
Sucrose	268.68	8.02
Salt	64.00	1.91
CMF[c]	15.20	0.45
Yeast, compressed	91.26	2.72
Calcium propionate	5.06	0.15
Potassium bromate (when added)	0.1842	55 ppm
Potassium iodate (when added)	0.03685	11 ppm
Ferrous sulfate, dried (when added)	0.999[d]	

[a]Procedure: Brew set at 88°F. All ingredients except oxidant, iron, and yeast blended together and then these three ingredients added. Brew stirred gently for entire brew period. Samples were removed as needed for oxidant analyses.
[b]Total flour weight = 3350 g.
[c]Proprietary name for yeast food containing $CaSO_4 \cdot 2H_2O$, $CaH_4(PO_4)_2 \cdot H_2O$, NaCl, corn starch, $(NH_4)_2SO_4$.
[d]Equals 3800 mg Fe/100 lb flour.

TABLE II
Laboratory Sponge-Dough Formula[a]

Ingredient	% Based on Flour	
	Sponge	Dough
Flour	65	35
Water	40	23
Yeast, compressed	2.5	...
Arkady	0.5	...
Salt	0.5	2.2
Dry malt	0.5	...
Sucrose	...	8.45
Shortening	...	2.8

[a]Sponge time: 4 hr at 90°F.; floor time: 30 min; proof time: 70 min.

MATERIALS AND METHODS

Ingredients

Flour: Southwestern patent flour, 12.5% protein, bleached, with 5 ppm of bromate added at mill.

Ferrous sulfate: Dried, 28.1% iron content.

Determination of Bromate and Iodate

The amperometric method of Cunningham and Anderson (2) was followed although better results were obtained if the reagents were added in the order of sulfuric acid, potassium iodide solution, and thiosulfate followed by titration with potassium iodate. A Simpson Model 2100 D.C. Micro Ammeter with full-scale μA ranges of 0–10, 0–50, and 0–250 was used to measure the current changes during the titration. The current was plotted *vs.* ml 0.001 N KIO_3 and the resulting end point determined graphically as described by Cunningham and Anderson (2).

For determination of oxidant in brews, 100 g of brew was weighed into a 250-ml centrifuge bottle. Ten ml of $ZnSO_4$ solution (120.25 g $ZnSO_4 \cdot 7H_2O$/ 1000 ml) was added and swirled to mix, and 10 ml of NaOH solution (32.5 g NaOH/ 1000 ml) was added and swirled to mix. This was allowed to stand 5 min and was then

TABLE III
Amflow No-Flour Brew Formula and Procedure

Ingredient		% (Based on Total Flour)
Brew stage		
Water		70.0
Dextrose hydrate		7.5
Salt		2.4
CMF		0.5
Calcium sulfate (gypsum)		0.25
Whey solids		0.50
Calcium propionate		0.16
Yeast		2.75
Potassium bromate, 50 ppm		
Potassium iodate, 10 ppm		
Ferrous sulfate, dried, 3800 mg Fe/ 100 lb flour		
Dough stage		
Flour		100.0
Liquid shortening (PG7N)		3.69
Procedure		
Brew set at:	No-flour, 83.5°F; flour, 90°F	
Brew time:	2 hr	
Dough temp:	103°–104°F	
Mixer rpm:	290	
Proof box temp:	106°/100°F	
Baking temp:	485°F for 15 min	
Scaling weight:	13.5 oz	
Pan size:	Top in: 9 1/8 × 4 3/8 in.	
	Bottom out: 8 1/2 × 3 3/4 in.	
	Depth: 3 in.	

centrifuged 5 min at about 2500 rpm. An appropriate aliquot was pipetted into a 100-ml beaker and diluted to 50 ml with distilled water. An amount of bromate and/or iodate was determined by amperometric procedure as described above.

For determination of bromate and iodate in doughs, the method was as follows: A 20-g dough sample was taken and blended with 80 g distilled water in an Osterizer blender, deproteinized with $ZnSO_4$ and NaOH, centrifuged, and the oxidant determined in an aliquot.

Laboratory Brew and Sponge-Dough Formulas

The no-flour brew formula is shown in Table I. The odd percentages are the result of reducing an actual bakery formula to laboratory size. For the flour brew, 1005 g of flour (30% of total flour) was added to this formula. The brews were not carried through to the dough stage. The sponge-dough formula is shown in Table II.

Continuous Bread Processing

To confirm the analytical tests on the changes in bromate level in brews and doughs, tests were run in our Amflow Pilot Plant unit as described in our previous work (3,4). The basic no-flour Amflow formula and procedure, again based on an actual production formula, are shown in Table III. A control was run with only the oxidants added at set; the second test was made with both oxidants and ferrous sulfate added at set. Samples for oxidant analysis were taken at appropriate intervals and analyzed amperometrically for residual oxidants. After proofing to a constant height of 3/8 in. over the top of the pan, some of the pans were dropped from a height of 1-3/4 in. to test the stability of the dough. After this drop test, all of the doughs were baked in a standard reel oven. After cooling, loaf volume was measured by rapeseed displacement.

The same formula and procedure were used for the 30% flour brew formula except that 30% of the flour was added to the brew and 70% added at the incorporator along with the brew and shortening.

TABLE IV
Reaction of Potassium Bromate with Iron Compounds in Laboratory Brew Systems

	Added Bromate Remaining, %[a]		
	Brew time, hr		
Level and Type of Iron	**0**	**1**	**2**
No-flour brew			
None	100	100	100
Ferrous sulfate[b]	100	35	10
Ferric orthophosphate[b]	100	100	100
Ferrous sulfate[c]	100	75	50
Flour brew (30%)			
None	100	95	95
Ferrous sulfate[b]	100	5	0

[a]All brews contained 55 ppm of potassium bromate.
[b]Equivalent to 3800 mg of Fe per 100 lb flour.
[c]Equivalent to 900 mg of Fe per 100 lb flour.

RESULTS AND DISCUSSION

The results obtained in the laboratory brew formula with 55 ppm of potassium bromate are shown in Table IV. When no iron compounds were added, the potassium bromate showed no change in either no-flour or flour brews. Addition of ferrous sulfate at the proposed level of 3800 mg of iron, which is equal to 25 mg of iron per lb of bread (assuming a yield of 152 lb of bread from 100 lb of flour), results in a rapid loss of bromate. The loss of bromate in the no-flour brew was 90% after 2 hr. The rate of decrease was much more rapid in the flour brew and there was only 5% left after 1 hr and none after 2 hr. As might be expected, there was no loss of bromate when using ferric orthophosphate.

The reaction with potassium iodate is somewhat different than with potassium bromate, as shown in Table V. In the no-flour brew, the iodate decreases at a rate which seems independent of the presence of either ferrous or ferric salts so that at the end of 2 hr there is about 35–55% iodate remaining. In the flour brew the decrease is much more rapid so that after about 1 hr all of the iodate is gone.

The data obtained with a laboratory sponge-dough system with potassium bromate are shown in Table VI. There is a gradual decrease in the bromate level during sponge fermentation which seems rather independent of the amount of ferrous sulfate present. It should be noted that there is a significant loss in the sponge. In the dough there is only a slight loss after 2 hr which encompasses the normal floor, makeup, and proof times.

Amflow Baking Tests

Our laboratory brews showed distinct losses of bromate in the presence of ferrous sulfate. To illustrate the practical importance of this loss, tests were carried out in an Amflow Pilot Unit. The baking results for both a no-flour and a flour brew are shown in Table VII and the data for residual bromate in Table VIII.

The results of the baking test were in excellent agreement with the laboratory results. In no-flour brews the proof time with added ferrous sulfate was 5 min longer and the dropped loaves showed a loss of 17% in volume, whereas the loaf without iron showed a loss in volume of only 3%.

The results were even more marked in the 30% flour brew. The dough with ferrous sulfate had very poor gas retention and after 46 min longer proof time, it appeared that it would never reach a normal proof height in a reasonable time so proofing was stopped and the dough baked. The resulting loaf volume was 27% less in volume than the loaf without added ferrous sulfate. The drop test had very little effect since the dough already had such a poor volume.

The percentage of added bromate at each stage of the brew and dough shows the same course of reaction as observed in laboratory brews. In this case, both bromate and iodate were present so the oxidant level was calculated as bromate. In the no-flour brew, the oxidant level remained essentially constant in the brews without iron and decreased rapidly with iron. There was practically no bromate left in the dough. In flour brews without iron, the oxidant decrease was somewhat greater than had been observed in the laboratory brews; with iron the decrease was very rapid.

TABLE V
Reaction of Potassium Iodate with Iron Compounds in Laboratory Brew Systems[a]

Level and Type of Iron	Added Iodate Remaining, % Brew time, hr 0	1	2
No-flour brew			
None	100	75	45
Ferrous sulfate	100	80	55
Ferric orthophosphate	100	75	35
Flour brew (30%)			
None	100	0	...
Ferrous sulfate	100	10	...

[a]All brews contained 11 ppm of potassium iodate and equivalent of 3800 mg of Fe per 100 lb of flour.

TABLE VI
Reaction of Potassium Bromate with Ferrous Sulfate in Sponge-Dough

	Added Bromate Remaining, %[a]						
	Sponge Time hr					Dough Time hr	
Level of Ferrous Sulfate	0	1	2	3	4	0	2
None	100	75	65	75	...	100	90
Current[b]	100	95	55	50	50	...	...
Proposed[c]	100	75	90	70	65	100	90

[a]Sponge contained 15 ppm potassium bromate.
[b]Equal to 900 mg Fe per 100 lb flour.
[c]Equal to 3800 mg Fe per 100 lb flour.

TABLE VII
Amflow Bread-Baking Tests

Level of Ferrous Sulfate	Proof Time min	Loaf Volume, cc[a] Dropped No	Yes
No-flour brew			
None	53	1960	1900
Proposed[b]	58	2085	1720
Flour brew (30%)			
None	62	1900	1880
Proposed[b]	108[c]	1385	1335

[a]Average of four loaves.
[b]Equivalent to 3800 mg of Fe per 100 lb flour.
[c]Dough had only reached 1/2 in. below top of pan when proofing was stopped.

GENERAL DISCUSSION

As has been conclusively demonstrated, there is a definite reaction between iron in the form of ferrous sulfate and bromate and iodate in brew systems when both are added at set which results in a loss of the oxidants and in poor gas retention, a longer proof time, and generally poorer bread quality.

Whether high levels of ferrous salts are suitable for use in bread-baking along with oxidants was not adequately considered when changes in the Bread Standards were proposed. Thermodynamically (5) the following reactions are possible:

$$6\ Fe^{++} + BrO_3^- + 6\ H^+ = 6\ Fe^{+++} + Br^- + 3H_2O \qquad E_o = 0.67$$

$$6\ Fe^{++} + IO_3^- + 6\ H^+ = 6\ Fe^{+++} + I^- + 3H_2O \qquad E_o = 0.43$$

In both cases the oxidation-reduction potential is positive, the free energy is negative, and thus the reaction is possible. A reaction is possible but kinetic factors may prevent experimental attainment. Our work shows that the brew systems provide the necessary factors to make the reaction go.

It is interesting to calculate the amount of ferrous sulfate which can be oxidized by various amounts of bromate and iodate. Table IX shows the milliequivalents of potassium bromate and iodate equal to various ppm of oxidant up to the maximum of the Bread Standards. Under the present iron

TABLE VIII
Residual Oxidant as Bromate

Time	No-Flour Brew		30% Flour Brew	
	No Fe %	With Fe %	No Fe %	With Fe %
Brew Stage				
Initial	100	46	110	35
1 hr	100	28	94	12
2 hr	100	13	86	8
Dough Stage				
Initial	...	...	80	10
1 hr	73	0	60	10
2 hr	...	...	...	10

TABLE IX
Equivalent Amounts of Oxidizing Agents

Amount of Oxidant			
ppm	mg/100 lb flour	$KBrO_3$ meq	KIO_3 meq
1	45.36	1.63	1.27
10	453.6	16.29	12.72
15	680.4	24.44	19.07
20	907.2	35.59	25.43
40	1814.4	65.17	50.87
60	2721.6	97.76	76.30
75	3402.0	122.20	95.37

levels, current enrichment wafers provide 900 mg of iron equal to 16.1 meq of iron; the new proposed wafers would supply 3800 mg of iron or 68.0 meq of iron. The present iron level could potentially react with 10 ppm of bromate and the new level with 41.7 ppm of bromate. Thus, one can see why it was easy to blame a loss of 10 ppm of bromate as a varying flour bromate requirement, but the loss becomes quite serious when 42 ppm is lost.

The most logical way out of this dilemma is to delay the reaction as long as possible. Enrichment is generally added at the time of setting a brew; thus, the oxidants should be added at the end of fermentation, as was done in the original Wallace and Tiernan process via a separate metering pump directly into the incorporator. Even adding at transfer will provide an appreciable time for reaction before a 1 hr brew is used up.

It is generally agreed (6,7) that ferrous sulfate is the most assimilable and preferred iron source for bread enrichment. The absorption of iron from various plant and animal foods (6) is generally rather low and thus the Recommended Daily Allowance of 18 mg is based on the assumption that only 10% of the dietary iron is absorbed by all population categories.

Even though the tests adding various iron compounds to bread (7) did show ferrous sulfate best, these tests were run in sponge-dough bread where the oxidant is at a relatively low level. No references could be found to any nutritional tests with continuous process bread where the iron should be in the ferric state since there is more than enough oxidant to oxidize the iron present at the current enrichment level. Little attention has been paid to the actual valence of iron in bread. Leichter and Joslyn (8) showed that the iron present in bread is largely in the ferric state. If this is so, what is the significance of adding ferrous iron to bread?

Another important factor that seems to have been overlooked is the fact that most continuous bread formulas usually contain monocalcium phosphate as one of the brew ingredients. The two formulas used in this work contained 0.45 to 0.5% CMF which contained 25% monocalcium phosphate monohydrate ($MCP \cdot H_2O$). Both ferrous and ferric ions theoretically can react with the MCP to form ferrous phosphate $Fe_3(PO_4)_2$, ferric phosphate, $FePO_4$, or other complex ions. Addition of 3.8 g of iron per 100 lb of flour could react with 8.57 g of $MCP \cdot H_2O$ if in the ferric state and 5.72 g if in the ferrous state. Both iron phosphates are practically insoluble in water but soluble in acid. CMF used at a 0.5% level would contribute 56.7 g of $MCP \cdot H_2O$ so there would be more than enough to react completely with the iron in either valence. If, as indicated by our work and Leichter and Joslyn (8), the iron is indeed all in the ferric state at least with the current iron level, then ferric orthophosphate could be formed *in situ* in the brew or later. It would seem that the advantages of using ferrous sulfate would be lost and ferric orthophosphate could be added, thus eliminating the problem of losing the bromate or iodate by reaction with ferrous sulfate.

No matter what iron level is finally accepted for bread enrichment, selection of an acceptable iron salt cannot be based only on nutritional demands but on the chemistry of the total breadmaking system.

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