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INVESTIGATION OF CALCIUM SULFATE'S CONTRIBUTION TO CHEMICAL OFF FLAVOR IN BAKED ITEMS

by
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14. ABSTRACT This report documents research performed at the U.S. Army Natick Soldier Research, Development and Engineering Center (NSRDEC), between October 2007 and June 2008, to determine if calcium sulfate, an additive in many shelf-stable bread items, was responsible for a persistent off-flavor in military ration bread products. Current formulations for the Meals, Ready to Eat™ (MRE™) bread and the Filled French Toast (FFT) bread jacket, which contain calcium sulfate, were produced along with a variable substituting calcium carbonate for calcium sulfate and a variable with no calcium additive. These variables were stored for 6 months at 100 °F. The NSRDEC Consumer Research Team conducted technical and consumer panels at time 0, 3 and 6 months. The sensory panels focused on assessing the aroma, flavor, and overall taste quality of the MRE bread and FFT variables as well as the level of perceived off-note intensity in aroma and flavor. Final analysis of the data indicated no strongly significant difference in overall acceptability of the baked items and does not merit a suggestion for elimination of the calcium sulfate from the formulations at this time. However, it should be noted that the variables containing calcium sulfate exhibited the greatest off-note intensities and the variable with no calcium treatment was consistently acceptable. Due to the close proximity of the data trend toward significance, it may be worthwhile to determine with further studies if any calcium additive is needed. If shelf life and texture are not adversely effected it may prove to be a cost savings to eliminate calcium sulfate from the formulas.					
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SPOIL	QUALITY	FOOD STORAGE	FOOD PRESERVATION		
AROMA	STORAGE	ACCEPTABILITY	SENSES(PHYSIOLOGY)		
BAKED	SAMPLING	SENSORY PANELS	MRE(MEALS READY-TO-EAT)		
BREAD	SHELF LIFE	MILITARY RATIONS			
PANELS	FORMULAS	CALCIUM SULFATE			
FLAVOR	BAKED GOODS	CALCIUM CARBONATE			
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PREFACE

This report summarizes research conducted at the U.S. Army Natick Soldier Research Development and Engineering Center (NSRDEC), between October 2007 and June 2008, to determine if calcium sulfate was responsible for a persistent off-flavor in military ration bread products. It was funded under the Continuous Process Improvement, (CPI) Program (project number CPI2007CFD).

The authors wish to acknowledge and express thanks to Ms. Claire Lee, microbiologist, Combat Feeding Directorate, for conducting microbiological analysis on study samples to assure safety of consumption and to the Consumer Research/Cognitive Science (CR/CS) Team, Warfighter Science, Technology and Applied Research Directorate for conducting technical and consumer panels and analyses.

INVESTIGATION OF CALCIUM SULFATE'S CONTRIBUTION TO CHEMICAL OFF FLAVOR IN BAKED ITEMS

1. INTRODUCTION

This report presents the results and findings of research performed at the U.S. Army Natick Soldier Research, Development and Engineering Center (NSRDEC) between October 2007 and June 2008 to determine if calcium sulfate, an additive in many shelf-stable bread items, was responsible for a persistent off-flavor in a selection of military ration products. This effort was funded under the NSRDEC Continuous Process Improvement (CPI) Program.

There is a persistent chemical off-flavor that develops during storage of baked items such as Meals, Ready to Eat™ (MRE™) bread, Shelf Stable Sandwiches (SSS), and Filled French Toast (FFT). Each product has a slightly different dough formulation, but functional ingredients such as shortening, dough conditioners, mold inhibitors, etc., are at similar levels. To date, attempts to discover and eliminate the cause of the off-flavor have been unsuccessful, but it has been speculated that one or a combination of these functional ingredients may be responsible. During a production test of FFT, the commercial vendor substituted calcium carbonate for calcium sulfate, and the resultant product did not seem to exhibit the characteristic chemical off-flavor. Due to this outcome, the following further information was acquired, which lent support to the theory that calcium sulfate could contribute to chemical off-flavors in baked items:

- 1) Dr. Debi Rogers of the American Institute of Baking (AIB) stated, in an interview with B. L. Strouts, that calcium sulfate is more reactive than calcium carbonate and could lead to rancidity/off-flavor issues [1].
- 2) Additionally, Specialty Minerals Company conducted a calcium enrichment study in conjunction with Rutgers University. Results of this study in regards to calcium sulfate are as follows:
 - Release of the sulfite ion from calcium sulfate may be causing a bitter, acidic taste [2].
 - Greater solubility of CaSO_4 contributes to more intense negative effects on bread taste, appearance, and shelf stability [2].

Based on the additional information regarding calcium, it was determined that, although apparent results in the FFT with calcium carbonate may have been product-specific, there was merit in further investigation of this compound's effect on military shelf-stable baked goods.

2. MATERIALS AND METHODS

2.1 Product Formulas

The MRE™ bread and the FFT bread jacket were chosen as representative products to illustrate any possible effect of calcium sulfate on the overall flavor of these highly acceptable baked products. Three variables per each representative product were produced in-house. The variables included 1) A – Control, the current formulation, containing 0.25% calcium sulfate; 2) B – Calcium Carbonate, containing 0.25% calcium carbonate in place of calcium sulfate; and 3) C – No Calcium Additive. See Tables 1 and 2 for the MRE™ and FFT formulations, respectively.

Table 1. MRE™ Bread Formula Variables

Ingredients	A – Control Calcium Sulfate (%)	B – Calcium Carbonate (%)	C – No Calcium Additive (%)
Flour, bread	52.15	52.15	52.28
Water	28.67	28.67	28.74
Shortening	8.53	8.53	8.55
Glycerol	6.36	6.36	6.38
Yeast (instant dry)	0.90	0.90	0.90
Salt	1.29	1.29	1.29
Sucrose ester	1.00	1.00	1.00
Sodium carboxymethylcellulose	0.75	0.75	0.75
Calcium sulfate	0.25	0.0	0.0
Calcium carbonate	0.0	0.25	0.0
Sorbic acid (encapsulated)	0.10	0.10	0.10

Table 2. FFT Bread Jacket Formula Variables

Ingredients	A - Control Calcium Sulfate (%)	B – Calcium Carbonate (%)	C – No Calcium Additive (%)
Flour, bread	46.49	46.49	46.60
Water	25.19	25.19	25.24
Shortening	7.81	7.81	7.83
Glycerol	4.63	4.63	4.64
Yeast (instant dry)	1.84	1.84	1.85
Salt	1.16	1.16	1.17
Sucrose ester	0.74	0.74	0.75
Gum arabic	0.46	0.46	0.46
Calcium sulfate	0.23	0.0	0.0
Calcium carbonate	0.0	0.23	0.0
Xanthan gum	0.23	0.23	0.23
Sorbic acid (encapsulated)	0.09	0.09	0.09
Maple flavor flakes	5.98	5.98	6.00
Cinnamon flavor flakes	4.65	4.65	4.66
French Toast Flavor # 1466	0.48	0.48	0.48
Yellow Lake # 5	0.01	0.01	0.01

2.2 Processing and Packaging

The MRE™ bread variables and the FFT bread jacket variables were processed and packaged almost identically. The only difference was that the MRE™ variables were baked for approximately 3 min longer than the FFT variables.

Both types of bread variables were made using the straight dough method. The dough was mixed to development and allowed to relax for 10 min. The dough was divided manually into 65 g balls, then pressed into small loaf pan trays. The filled trays were placed in a proof box (Hobart, Troy, OH) at 90 °F and 85% RH for 1 h. The bread dough was then baked in a convection oven (Hobart, Troy, OH) at 350 °F, the MRE™ for approximately 16 min and the FFT for approximately 13 min. The samples were cooled to between 80 °F and 120 °F and were packaged individually in multi-laminate pouches with a 100 cc oxygen scavenger (Multisorb Technologies, Buffalo, NY) in each pouch.

2.3 Storage and Microbiological Analysis

After production, all products were stored for 6 months at 100 °F and withdrawn after 3 months and after 6 months. The samples underwent microbiological analysis to confirm their safety for human consumption by the Combat Feeding Directorate (CFD) microbiology lab at each

evaluation point before they were given to the Consumer Research/Cognitive Science (CR/CS) Team for sensory analysis. Microbiological analysis included total plate count, yeast, mold, *Escherichia coli*, and *Staphylococcus aureus* testing. All products were deemed to be microbiologically safe for consumption.

2.4 Sensory Analysis

The CR/CS Team conducted technical and consumer sensory evaluations on all six variables at time 0 and after 3 and 6 months of storage at 100 °F. The basic focus of the sensory analysis was to assess the level of intensity/differences of off-flavors, specifically chemical off-flavors, in the bread products. Technical panels were administered to trained sensory panelists using the 9-point Quality scale to assess the overall aroma and flavor quality. The 9-point Quality scale is based on the Hedonic scale developed by David Peryam and colleagues in the early 1950s at the Quartermaster Food and Container Institute of the U.S. Armed Forces [3]. “The scale was quickly adapted by industry and is now the most widely used scale for measuring food acceptability” [3]. The difference between the Quality and Hedonic scales is what they measure and is reflected in the verbal anchors. The Hedonic scale measures acceptability based on how much a product is liked. Verbal anchors may range from extremely dislike to like extremely. Alternatively, the Quality scale, measures acceptability based on the apparent quality of a food product. The Quality scale currently used at NSRDEC for technical panels assigns a verbal anchor to successive integers 1 through 9 corresponding to “extremely poor” through “excellent” assessments. The off-note intensity was also assessed by a trained technical panel utilizing a basic 0-to-15-point sliding line scale. The panelists were instructed to record the level of perceived off-note intensity in the product by sliding the arrow to a point along the scale that represented the degree of off-note character from 0 (none) to 15 (maximum perceivable). The consumer panelists rated samples using the Labeled Affective Magnitude (LAM) scale, which assesses relative degree of liking/disliking. The scale runs from - 100 (highest imaginable degree of dislike) backward to 0 and forward to + 100 (highest imaginable degree of like). The LAM scale is frequently utilized for consumer panels because it has proven more sensitive in assessing relative like or dislike as compared to a basic Hedonic assessment. Unlike the technical panels, which try to identify the character of products, the consumer panels using the LAM scale try to identify how much products are liked or disliked. The LAM scale allows ratio comparisons (e.g., a score of 50 vs. 25, meaning the first is liked twice as much as the second).

3. RESULTS AND DISCUSSION

The differences in scores for all parameters were generally small. Figure 1 illustrates aroma and flavor quality ratings at time 0 (no storage). The ratings for both aroma and flavor correlate with one another in that the breads with calcium carbonate were rated slightly higher than controls with calcium sulfate. However, samples without calcium additives were rated just as highly as those with calcium carbonate, which indicates that calcium does not negatively or positively affect aroma or flavor.

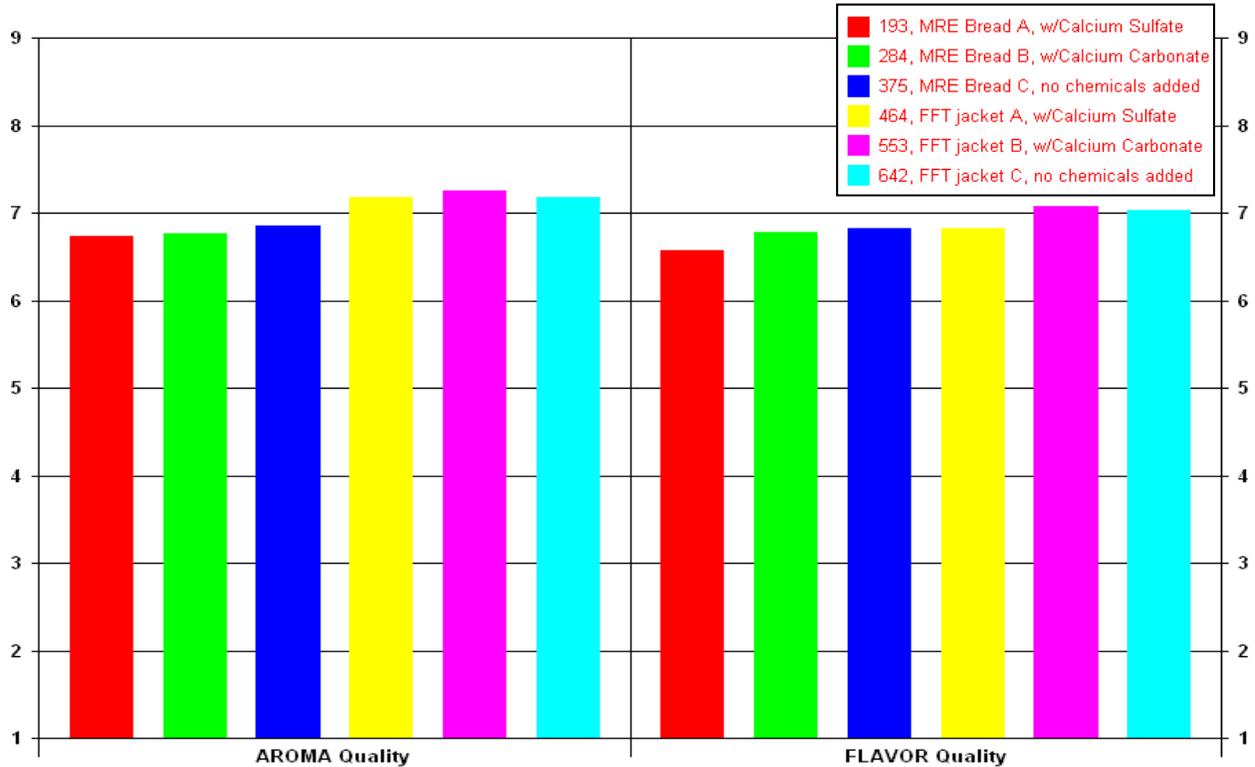


Figure 1. Quality Ratings for MRE™ and FFT Breads at Time 0

Figure 2 illustrates quality ratings after 3 months of storage at 100 °F. The aroma and flavor ratings for the variables containing calcium sulfate decreased more than the bread variables containing calcium carbonate or no additive. Similar to the results for the time 0 items, the 3 month aroma and flavor ratings for the breads with calcium carbonate and without any calcium additive were comparable.

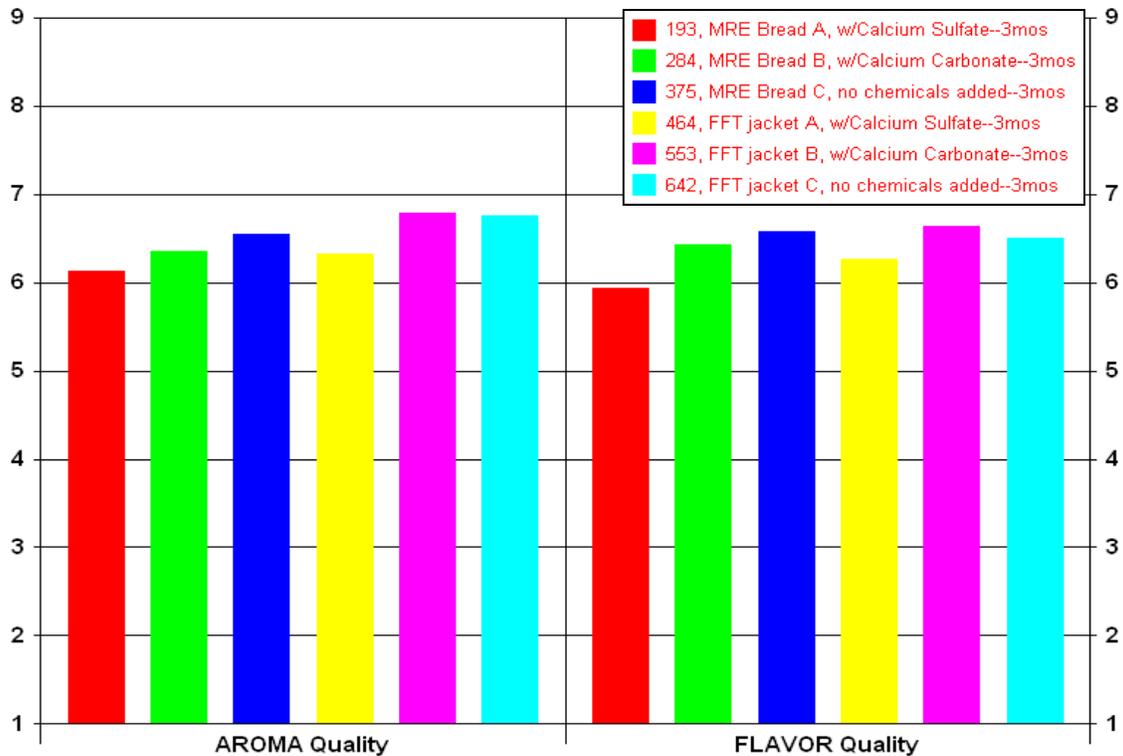


Figure 2. Quality Ratings for MRE™ and FFT Breads Stored for 3 Months at 100 °F

Figure 3 shows the quality ratings for aroma and flavor for all three storage periods, at 100 °F. All three products scored well over the extended period in that no product rating fell below 5, which is considered to be an unacceptable score for military rations. After 3 months of storage there was very little difference in flavor and aroma degradation between the variables, and quality ratings remained near or above 6. Results show that the addition of neither calcium sulfate nor calcium carbonate causes off-flavors significant enough to cause a failure of military acceptance tests, i.e., a score of 5 or below (≤ 5). However, results do suggest that breads containing calcium sulfate exhibit slightly more degradation in quality for flavor and aroma than breads containing calcium carbonate.

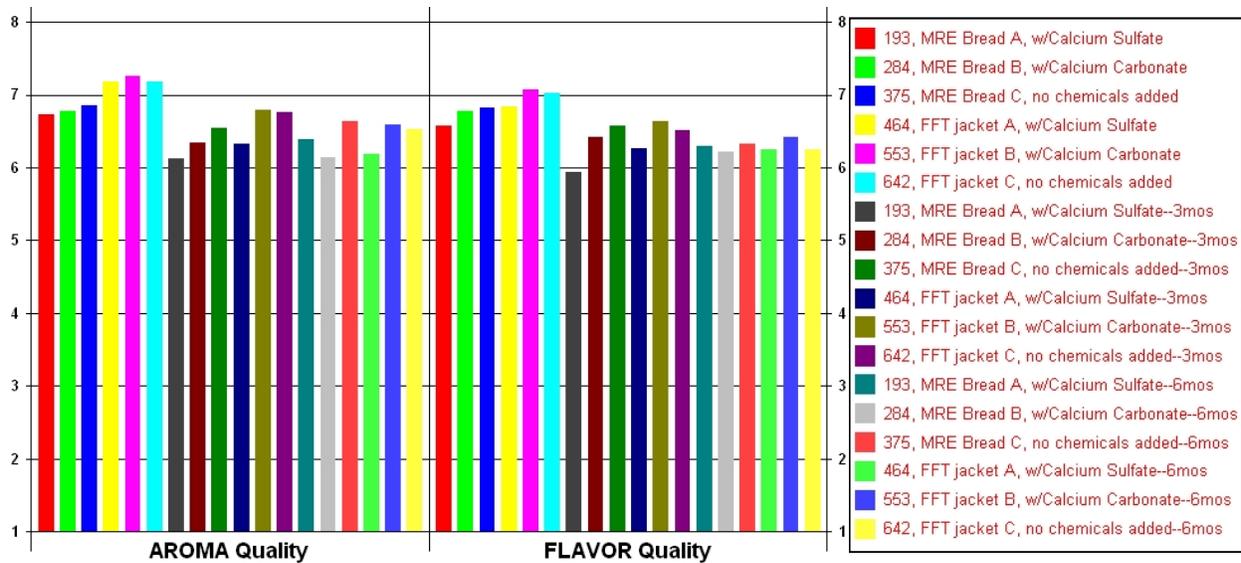


Figure 3. Quality Ratings for MRE™ and FFT Breads Stored for 0, 3, and 6 Months at 100 °F

Figure 4 shows that products containing calcium sulfate had a slightly higher off-note intensity than products containing either calcium carbonate or no calcium additive. This effect can be seen at an even greater magnitude after 3 months of storage (Figure 5). However, that effect was only seen for the FFT off-note flavor after 6 months (Figure 6, which includes all ratings at each storage interval). In fact, the FFT off-note aroma rating and both of the MRE off-note ratings for calcium sulfate were lower than those for calcium carbonate after 6 months, and they were lower than the no additive variable for FFT off-note aroma.

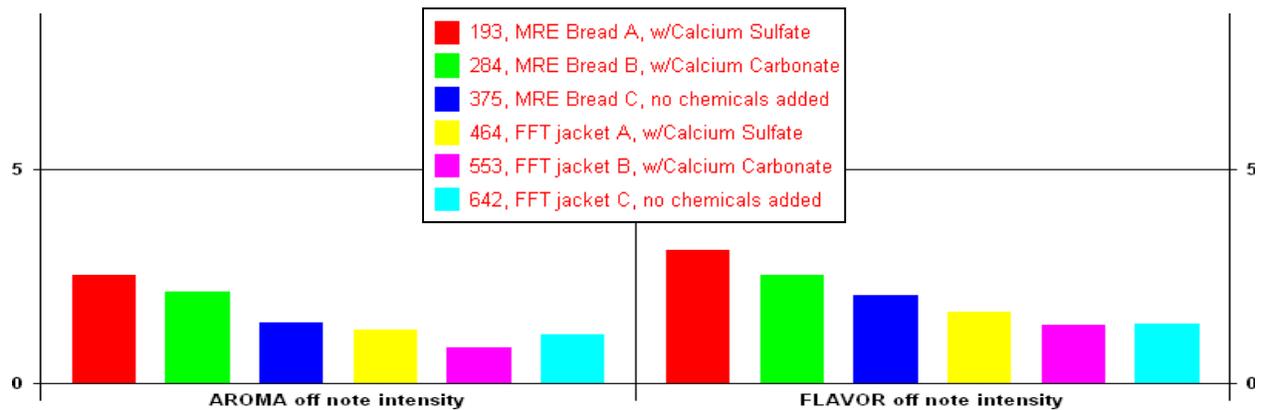


Figure 4. Off-Note Intensities for MRE™ and FFT Breads at Time 0

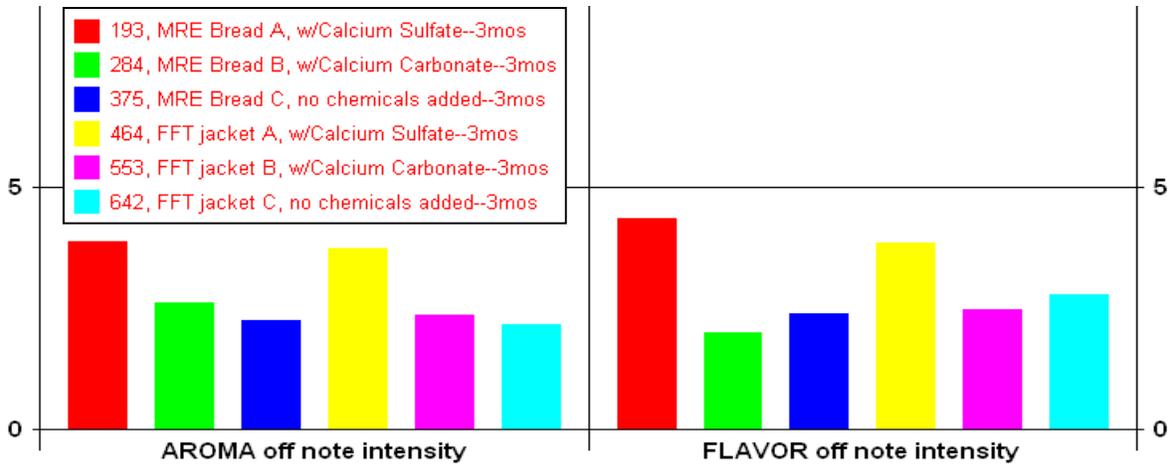


Figure 5. Off-Note Intensities for MRE™ and FFT Breads Stored for 3 Months at 100 °F

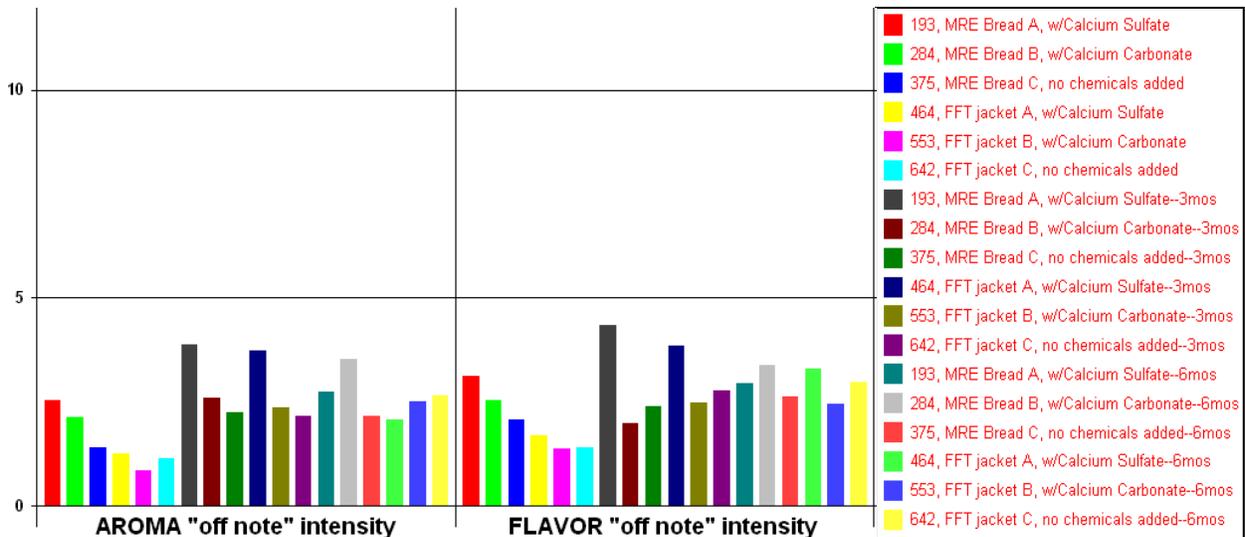


Figure 6. Off-Note Intensities for MRE™ and FFT Breads Stored for 0, 3, and 6 Months at 100 °F

Figures 7, 8, and 9 show the consumer panel ratings using the LAM scale, which assesses the relative degree of liking/disliking and allows for ratio comparisons. These figures show that all the ratings were “likes”. There was no significant difference in the degree of like between FFT variables at time 0 (Figure 7), and the MRE™ bread containing calcium carbonate was liked slightly more than the calcium sulfate control. After 3 months of storage at 100 °F (Figure 8), the degree of like for the MRE bread dropped considerably, by approximately 50%; however, the ratings between variables were still comparable to time 0 products. FFT bread showed a lesser degree of change and was comparable to time 0 samples, though the calcium carbonate declined the most and the calcium sulfate slightly more than no additive. Analysis of all three storage intervals (Figure 9) shows that the greatest change in LAM scores for the samples occurred between time 0 and 3 months and that the scores remained constant between 3 and 6 months. Figure 9 also shows that MRE bread degraded significantly more after 3 months than the FFT.

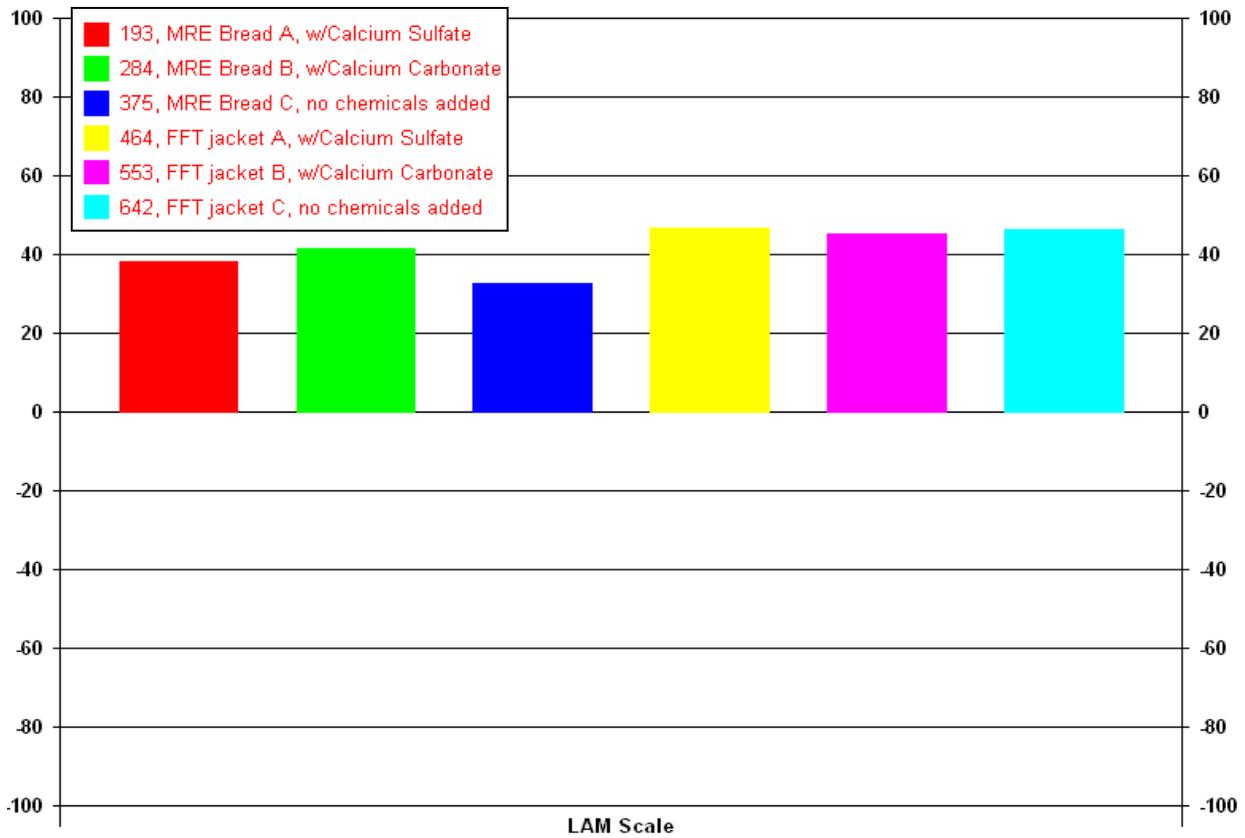


Figure 7. LAM Scores for MRE™ and FFT Breads at Time 0

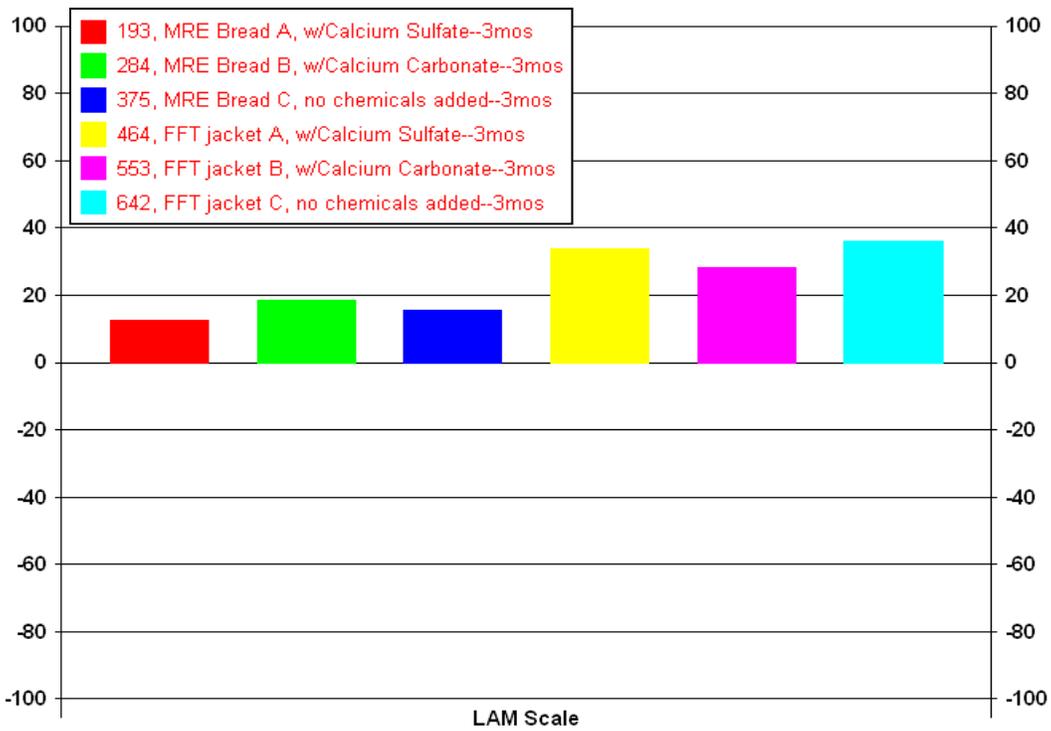


Figure 8. LAM Scores for MRE™ and FFT Breads Stored for 3 Months at 100 °F

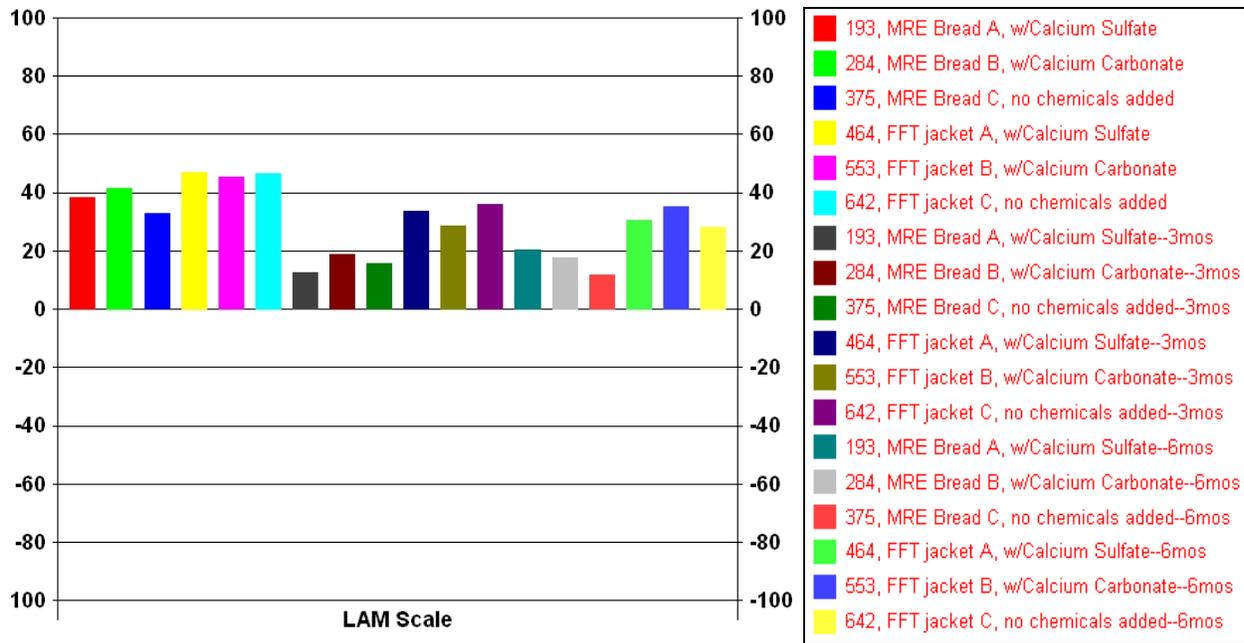


Figure 9. LAM Scores for MRE™ and FFT Breads Stored for 0, 3, and 6 Months at 100 °F

Table 3 contains summary rankings of scores from all samples and test conditions; the lowest average total ranking for each food item within each storage interval is bolded. Both consumer and technical panel scores ranked and combined yield a mixed message. A similar pattern was seen in the actual scores—3 months appeared clear, but the 6 month scores did not continue the trend. The issue of determining significance between means becomes a moot point because trends are too unpredictable, differences too small, and/or variances too wide to make any clear statements about the sensory value of one treatment over another.

Table 3. Summary Rankings of Scores from All Samples and Test Conditions

Storage time:	0 months						3 months at 100 °F						6 months at 100 °F					
Bread type:	MRE			FFT			MRE			FFT			MRE			FFT		
Chemical additive:	CaSO ₄	CaCO ₃	None	CaSO ₄	CaCO ₃	None	CaSO ₄	CaCO ₃	None	CaSO ₄	CaCO ₃	None	CaSO ₄	CaCO ₃	None	CaSO ₄	CaCO ₃	None
Consumer Rankings	2	1	3	1	3	2	3	1	2	2	3	1	1	2	3	2	1	3
Flavor (tech) rankings	3	2	1	3	1	2	3	2	1	3	1	2	2	3	1	2.5	1	2.5
Aroma (tech) rankings	3	2	1	2.5	1	2.5	3	2	1	3	1	2	2	3	1	3	1	2
Flavor "off-note" (tech) rankings	3	2	1	3	1	2	3	1	2	3	1	2	2	3	1	3	1	2
Aroma "off-note" (tech) rankings	3	2	1	3	1	2	3	2	1	3	2	1	2	3	1	1	2	3
Total ranking average	2.8	1.8	1.4	2.5	1.4	2.1	3.0	1.6	1.4	2.8	1.6	1.6	1.8	2.8	1.4	2.3	1.2	2.5

Ranking key: best to worst = 1 to 3

Bolded total rankings: lowest average total ranking for the bread type within the storage interval

CaSO₄ = calcium sulfate

CaCO₃ = calcium carbonate

4. CONCLUSIONS

Final analysis of the data indicates no relevant differences occurred in the overall acceptability of the baked items due to changes in aroma, flavor, and level of off-note intensity over time. The differences among the three treatments within each product at each evaluation point are small, and changes in sensory properties are subtle and inconsistent. However, it is apparent that aroma and flavor degrade and off-note intensity ratings increase over storage time, especially after 3 months.

One way to present the decision making model is in a simple ranked summary sheet (Table 3). A general conclusion is that the calcium sulfate treatment renders the lowest quality product, especially in regard to levels of off-note intensity during every evaluation point with one exception in the MRE™ bread sample after 6 months of storage. Specifically, the highest levels of off-notes were perceived in the calcium sulfate containing variables. This finding, along with the consistent acceptability of Variable C, suggest that it may be worthwhile to study further whether any calcium additive is needed in the formulation of the aforementioned baked products. No clear sensory benefit is evident in this study from the use of calcium sulfate or calcium carbonate. However, this recommendation is based upon non-weighted categories. Therefore, due to the inconclusive results from this study, it may be prudent to conduct a future study that uses both a larger study population and weighted categories. Then, if subsequent tests determine that shelf life and texture are not adversely affected by the lack of calcium fortification, cost savings may be realized by elimination of calcium sulfate from the formulas.

This document reports research undertaken at the U.S. Army Natick Soldier Research, Development and Engineering Center, Natick, MA, and has been assigned No. NATICK/TR- 13/037 in a series of reports approved for publication.

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