PROPERTIES OF MINERALS USED IN CEREAL FORTIFICATION (Section 6 in MI's Fortification Handbook)

The different essential minerals fall in one of the following classifications that depend on their concentration in the body and dietary requirement. This difference in the quantity needed has a major impact on cost and other aspects of mineral fortification.

- Major elements - calcium, phosphorus, sodium, potassium, chloride and magnesium.
- Elements needed in small amounts - iron and zinc.
- Trace elements needed in tiny amounts - includes iodine, copper and selenium.

For a more comprehensive source on mineral fortification consult *The Mineral Fortification of Foods* (Hurrell 1999)

Iron

There is a great need to increase the level of absorbable dietary iron due to the extremely high incidence of iron deficiency anemia (IDA) in many countries. Iron has the greatest complexity and produces more problems in fortification than any other micronutrient. Creating an effective iron fortification program for cereals can be very challenging. Iron is included in all the cereal fortification programs in the world to date (see Table 5.2). Despite lingering questions on its effectiveness, it would not be wise to exclude it from cereal fortification programs in countries with high levels of IDA.

Because of the importance and difficulty in iron fortification, a number of good publications have already been made on this topic, which can be consulted for additional information. A major concern is which iron source to use. Guidelines on iron in cereal fortification programs have been prepared by SUSTAIN (SUSTAIN 2001), WHO (Allen 2003) and PAHO (PAHO 2002) that can be consulted. The key recommendations of WHO are given in Table 6.1.

Table 6.1 Suitable Iron Fortificants for Cereals

According to WHO Guidelines

Cereal Product	*Fortificant*
Low extraction (white) wheat flour or degermed maize meal or flour	Ferrous sulfate, dried (bakery flour only) Ferrous fumarate Electrolytic iron (2X amount)* Encapsulated ferrous sulfate
High extraction wheat flour, maize meal or flour, corn masa flour	NaFeEDTA Ferrous fumarate (2X amount) Encapsulated ferrous sulfate (2X amount) Encapsulated ferrous fumarate (2X amount)
Pasta or semolina	Ferrous sulfate, dried

* If X is the amount of iron that would be normally added in an ideal situation (e.g. 30 ppm), 2X means that twice that amount of iron should be used (e.g. 60 ppm) to account for a lower bioavailability, either due to the nature of the added iron source or the absorption inhibiting properties of the food to be fortified

The main criteria in choosing an iron source are bioavailability, effect on product quality and cost.

Bioavailability

Bioavailability, or the degree, to which the body can utilize or absorb a particular mineral source, is a particularly important factor with iron since it varies greatly with different iron sources. Ferrous sulfate and ferrous fumarate are considered to have good bioavailability while that of the elemental (reduced) iron powders is believed to be lower. There are many factors in the meal, diet and the way the food is processed that will affect the ability of people to absorb different forms of iron. There is ongoing research on the bioavailability of the different forms of iron from different products made from wheat flour and maize that will hopefully provide answers on which type of iron is best to use.

Organoleptic changes

Ferrous sulfate is a pro-oxidant that can accelerate rancidity development in unsaturated lipids. Because flour contains small amount of fats, the addition of ferrous sulfate can reduce its acceptable shelf life. This is not normally a problem with flour that is used within a month after milling, such as flour for commercial bakeries (bakery flour), but it can cause unacceptable flavor developments in household flour after months of storage. Reduced elemental iron is considered safe in any type of flour, even those requiring extended storage periods and flours of higher extractions and therefore higher levels of fat.

Iron fortificants that can be added to flour without causing adverse sensory changes in one situation do not necessarily work with the same food product in another situation. One example is ferrous sulfate, which is added as a fortificant to wheat in Chile but could not be used for this purpose in Central America. This may have been due to differences in climate, type and extraction of the wheat flour, or the quality of the ferrous sulfate purchased from different suppliers.

The extent to which fat oxidation has occurred in cereal flours can be determined by measuring hexanal (2,4-dimethy-2-pentene) levels with gas chromatography. This can be used as a rapid estimate (within hours) of the propensity of a flour going rancid by comparing a fortified to an unfortified flour (Bovell-Benjamin 1999). Others have preferred to use more long term storage of cereal products in cans at 37°C for 4 months, followed by measurement of pentane in the headspace (Hurrell 1989). Both chemical detection methods agree well with taste panel evaluations of rancidity. Trained sensory evaluation panels should determine if there are changes in texture, flavor, color or aroma in the fortified food compared to an unfortified control food, as a result of processing or storage (including simulated shelf-life conditions), and during food preparation (Bovell-Benjamin 2000). The amount of detectable rancidity correlates closely with pentane and hexanal production, which can increase ten fold.

Color

A potential problem with iron fortification is development of unwanted color. These include a green or bluish color when free iron interacts with cereals and a gray color when it interacts with chocolate or cocoa. Dried ferrous sulfate is a light tan powder and adds no color to flour, but it can react with other compounds and ingredients (i.e. bananas) to cause noticeable color changes in dough. Ferrous sulfate added to maize meal can cause undesirable blue or green colors in cooked products made from maize meal. Encapsulated forms of ferrous sulfate are recommended for maize. Large particle size ferrous sulfate can cause black spots on bread crust. Hydrated ferrous sulfate is blue-green in color and will cause color problems in the fortified flour and bread. As a result, hydrated ferrous sulfate should never be used in flour fortification.

Ferrous fumarate is dark red in color and can be noticed in white flour or white maize meal if used at high levels. It is not as soluble or reactive in dough as is ferrous sulfate. Elemental iron powders are black in color. They add no color to maize meal or wheat flour but have a slight darkening effect, which is considered acceptable. They produce no known color reactions in dough.

The color of fortified flour and baked products can be assessed by both visual and instrumental methods. The latter are very sensitive to small changes that are not visually noticeable. The potential of an iron fortificant to cause color changes can sometimes be assessed by the “blue banana test”, in which the iron fortificant is added to a hot cereal porridge mixed with puréed bananas. Soluble iron compounds such as ferrous sulfate will rapidly turn the porridge a deep blue.

Cost

The relative cost of the different iron sources are shown in Tables 5.1 and 7.1. The cheapest form of iron to add is elemental reduced iron followed by ferrous sulfate and then ferrous fumarate.

Sources of iron

Encapsulated iron salt

There are coated forms of ferrous sulfate and ferrous fumarate available. The encapsulates used include hydrogenated vegetable oils, mono- and diglycerides, maltodextrins, and ethyl cellulose. The best products have a fat coating that protects them from chemically reacting with unsaturated fats in the flour or meal, but which will melt on baking and/or be degraded by lipases in the gut so that the ferrous salt is available for absorption. These products may have a large particle size causing them to be removed from flour during final (rebolt) sifting. The products are fairly expensive, costing 4 to 8 times that of the uncoated product on an equal iron basis. But preliminary studies have shown them to be well absorbed, even with high extraction flour, and costs may drop if their use becomes more prevalent.

Iron EDTA

A proposed solution to the problem of phytic acid inhibiting the bioavailability of added iron (discussed in Section 3) is to use iron-EDTA (ferric sodium edetate) (INACG 1998). The iron in this compound is chelated with EDTA, a commonly used food additive. This prevents the iron from being bound to phytic acid making it more easily absorbed by the body. In the human gut the iron is released from the EDTA allowing it to be absorbed. There is little advantage in using EDTA in low extraction white flour used in a yeast-leavened breadmaking process since the final level of phytic acid is very low. However, there does appear to be good justification to use it in high extraction flours, such as *atta* used in South Asian counties to make unleavened *chapattis*. The main drawbacks with iron-EDTA are it's much higher cost compared to the other iron sources and its tendency to cause color changes in some foods, but unlike other soluble iron compounds it does not promote lipid oxidation in stored cereals.

Elemental iron powders

These powders, called *reduced iron* or *ferrum reductum*, are the most common iron sources used in cereal fortification because they have the least detrimental effect on product quality and shelf-life and the lowest cost. There are five types commercially available, shown in the following table, which differ in their method of manufacture and physical properties, which in turn affects their bioavailability. The current thinking is that electrolytic, carbonyl reduced and hydrogen reduced forms have about half the bioavailability of ferrous sulfate, so they should be used at twice the level to achieve the same effect, a strategy that was first adopted by WHO/EMRO for flour fortification in the Middle East. Other forms of elemental iron powders, or forms with large particle size (> 44 microns) should not be used.

Table 6.2 Types of Elemental Iron Powders used in Fortification

Elemental iron product type	***Use in fortification***	***Cost***	***Bioavailability***[1]
Hydrogen reduced	Common	Low	Medium
Carbon monoxide reduced	Seldom	Low	Poor
Atomized	Common	Low	Uncertain
Electrolytically reduced	Occasional	High	Good
Carbonyl reduced	Never	Very High	Uncertain

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[1] Studies are being conducted by SUSTAIN (www.sustaintech.org) to better assess the bioavailability of these products.

Magnets and metal detectors

All the elemental iron powders are attracted to a magnet, whereas the iron salts are not. Many mills and bakeries use magnets to remove tramp iron from the flour in order to prevent equipment damage and maintain food safety. There is sometimes a concern that the magnets will remove elemental iron powders when added in a fortification program. Ferrous sulfate and ferrous fumarate will not be attracted to a magnet, so there is no problem in having a magnet in the line when these two iron salts are used.

There are three types of magnets in common use: iron, ceramic and rare earth. Only the rare earth magnet, the strongest and most expensive, can pull reduced iron out of flour. The iron magnet type is the cheapest and the weakest. Ceramic types fall in between these two other types of magnets and are the most common in mills but the rare earth types are generally used in new equipment. When using a magnet with flour that has been fortified with reduced iron, the problem is not that the magnet will remove the iron from the flour but that the magnet will become clogged with iron causing it to lose its effectiveness in removing tramp iron. This problem can be solved by a self-cleaning magnet or by directing the flour at the magnet surface so that it continually cleans it of reduced iron.

There is no evidence of separation of any of the enrichment components added to flour on a continuous basis at the flour mill, during transport and storage, at the bakery and in the final bread. Studies (Fortmann 1974) on flour passing by a magnet show no difference in iron content before and after the magnet. There was also no evidence of flour streaking, which might be expected if large clumps of reduced iron were falling off the magnet. Alternatively, to ensure uniformity and minimize separation, sieves can be used in conjunction with magnets. Reduced iron has a very small particle size (<325 mesh) and will easily go through the finest rebold or final sifter (100 mesh), which will remove, all tramp iron or any ferrous or nonferrous metals of a large enough size to be dangerous. A mill can then use magnets at the start of the milling process before the iron is added, and rely on the final screen to remove any tramp metal.

Food manufacturers often use metal detectors to ensure that no large clumps of iron are in the final food product. These detectors may respond slightly to elemental iron powder added to the flour, but they can be calibrated so that they ignore the added iron and still detect larger iron particles that would be noticeable or possibly harmful to the consumer.

Zinc

While zinc deficiencies are not as obvious and measurable as IDA, they often accompany those of iron. Zinc and iron are similar in their dietary requirements, their levels in cereals and having their absorption inhibited by phytic acid, so any dietary deficiency in iron usually means there will be one for zinc as well. Based on estimates of zinc intake and bioavailability from FAO’s food balance data, it is estimated that about 20% of the world is at risk of zinc deficiency. Zinc only started to be included in cereal fortification programs in the 1990s after recognizing this situation and the serious problem with its deficiency, particularly in children, where it can result in stunting and increased risk of disease. It is now being added to wheat flour in Mexico, South Africa, Central Asia and Indonesia, and to maize meal in South Africa and Mexico. The levels added are typically 20 to 30 ppm zinc, or restoration levels.

Zinc Source

Unlike the iron sources used in cereal enrichment, all of the zinc sources are white in color, so inherent color is not a problem. There is a potential problem in some of the more soluble sources causing color changes in certain food ingredients, such as chocolate. All zinc salts have undesirable flavors. For example, zinc oxide has a bitter taste while zinc sulfate is very astringent. It does not appear that these inherent flavors carry over to the fortified foods at the levels used in fortification. As with ferrous sulfate, there is both a dried and hydrated form of zinc sulfate. The hydrated form is reported to cause problems with caking, giving a preference to the dried form.

Perhaps the most important difference in the zinc sources is their solubility, since it relates to both bioavailability and effects on food quality. Zinc oxide is insoluble in water, but soluble in dilute acid. This implies it will be inert in dry foods but should be available for absorption following exposure to stomach acid. Zinc acetate, zinc gluconate and zinc sulfate are soluble in water and the chloride is very soluble.

Zinc oxide is the most commonly used zinc source in the fortification of cereal-based foods, followed by zinc sulfate and, to a very limited extent, zinc gluconate. Zinc sulfate is specified for use in the blended foods corn soy blend (CSB) and wheat soy blend (WSB) produced for the U.S. Food for Peace Program. It is also used in similar weaning or complementary foods made throughout the world. Zinc acetate and zinc gluconate find use only in dietary supplements and some weaning foods. There is a wide range in the cost. The least expensive source is zinc oxide, costing approximately one-third that of zinc sulfate, the next cheapest source.

Bioavailability of zinc sources

The absorption of zinc from foods is similar to that of iron. Approximately 15% of a zinc fortificant will be absorbed on average. This percentage will be lower from high phytate foods such as whole maize (closer to 5-10%), and higher from refined or low phytate cereals (10 to 40%) (Sandstrom 1989, Sandstrom 1997). One study on bread (Ranhotra 1977) showed little difference in absorption in rats of the different sources. Absorption of zinc carbonate was poor, but absorption of zinc oxide was nearly as good as the more soluble forms. Zinc absorption from the oxide is as good as from zinc sulphate when used to fortify tortillas in Mexico (Diaz 2001), or low- or high-phytate wheat-based meals in the United States (Lopez de Romana 2002), presumably because it is soluble in gastric acid. Zinc absorption from the oxide may be poor in individuals with low stomach acid secretion. In healthy, well-nourished adults in the United States, zinc absorption from the sulfate or oxide added to a low-phytate bread meal was about 14%, compared to around 6% when either fortificant was added to a higher-phytate wheat porridge meal(Lopez de Romana 2003). Studies in Turkey (Saldamli 1996) reported that bread fortified with zinc acetate had acceptable quality and was effective in preventing zinc deficiency in children.

Effect on product quality

A number of studies have shown zinc fortification to have few detrimental effects on flour, bread and noodle quality, even at levels several times higher than that normally used (Ranhotra 1977, Kilic 1998, Lopez de Romana 2002).

Selenium

Selenium functions as a component of enzymes involved in antioxidant protection and thyroid hormone metabolism. Selenium deficiency (Keshan and Urov diseases) is rare and found mainly in areas where the soil is very low in selenium. This includes regions in China, Siberia, Finland and New Zealand. Finland has tried adding selenium to fertilizers where it increased selenium levels in milk, meat and cereals within six months (Aro 1995). Asian wheat tend to have lower selenium content than that in North America, which has higher soil selenium levels. The greatest interest in selenium fortification of flour is in Asia and countries in the former Soviet Union for that reason, as well as the belief that selenium helps provide protection against radiation damage, such as occurred after the Chernobyl nuclear disaster.

Salt has been fortified with sodium selenite (15 mg/kg) since 1983 in regions of endemic selenium deficiency in China. Sodium selenate is the most common form used in food fortification. It has been added to infant formula and sports drinks. Sodium selenate is colorless, less soluble in water, and more stable than the selenite, especially in the presence of copper and iron. There are high selenium forms of inactive yeast available that could be used to fortify baked products.

When tested in milk-based infant formulas, more selenium was absorbed than the selenate (97% vs, 73%) but more was excreted in the urine (36% vs. 10%), so the net retention of selenium was similar from both Sources (Van Dael 2002). Most cooking procedures cause relatively little loss of selenium from foods.

No country currently fortifies flour or any cereal staple with selenium, but there has been some interest in doing so, particularly in Russia. The very small amounts (0.1 to 0.2 ppm) of selenium that would be required to provide a major portion of the RDA would not be expected to have a detrimental effect on the color, baking properties or consumer acceptance of wheat flour. The cost of adding selenium is very low.

Calcium

Calcium is essential for the formation of bones and teeth and is important in maintaining a healthy skeleton. Calcium also helps regulate the acid-base balance of the body, the heartbeat, and the irritability of the neuro-muscular system (tetany). Inadequate calcium consumption is associated with risk of bone fracture and osteoporosis (bone softening) but is not the only cause of these conditions, which are most prevalent in elderly women.

There is a clear need for additional calcium in many populations, particularly in developing countries that have limited intakes of milk and dairy products, the primary dietary source of calcium in most diets. Wheat and maize are very poor sources of calcium, as shown in Tables 3.8 and 3.9. Most of the calcium provided by cereal foods comes from the calcium containing ingredients that are added to bread and biscuits as functional ingredients, such as calcium propionate, calcium phosphates and whey. These ingredients are not normally added to bread in developing countries, however.

Dried, nixtamalized maize flour, called *masa flour*, used to make tortillas is a common product in Mexico and Central America. This product has high calcium content due to the addition of calcium carbonate in the nixtamalation process, so there is no need for additional calcium. *Self-rising flour* also contains high levels of calcium due to the addition of the chemical leavening ingredients. All other cereal products are very low in calcium.

History of calcium fortification

Calcium has a long history of being added to flour and bread, originally as ground bone meal but now as calcium salts. During the Second World War the UK Government decreed that the milling industry should produce flour milled to an 85% extraction to conserve wheat supplies. The Medical Research Council recommended that calcium carbonate be added to this flour to counteract the effect of phytic acid. In 1942 the UK government ordered the addition of calcium carbonate at the rate of 156 mg per 100 g of flour, which was increased to 235-390 mg per 100 g of flour in 1946. As Newfoundland was part of the UK in 1942, the mandatory addition of calcium to wheat flour was in effect. When Newfoundland joined the Canada in 1948, wheat flour continued to be fortified with calcium, while in the rest of Canada calcium fortification was voluntary. Many other Commonwealth countries including India, Pakistan, Kenya, Uganda, and Nigeria adopted the UK flour fortification regulations that included calcium on a voluntary basis. While a number of other countries permit the addition of calcium to flour (see Table 5.2 for voluntary standards), no country requires it. However, because of the positive marketing and cost advantages, some millers find it advantageous to fortify some of their flour brands with calcium without being required to.

Calcium sources -The main calcium sources used in cereal fortification are calcium sulphate (gypsum) and calcium carbonate (limestone). Both are white and bland in flavour. Calcium sulphate is produced from mined gypsum by a precipitation process and is available either as the dihydrate with 23% calcium or the anhydrous form with higher calcium content (27%) but generally a higher price as well. Calcium carbonate used in cereal fortification is normally made by grinding limestone mined from very pure deposits. There is a considerable variation in the particle sizes available, from very fine to coarse. Manufacturers can recommend which of their products is best for flour fortification. All the calcium sources are added as is and can experience packing and flow problems if too fine a product.

There are many other calcium salts (such as calcium phosphates, calcium lactate and calcium citrate) that are used to fortify different types of foods, but they are much more expensive and offer no real additional benefits over the sulphate and carbonate in cereal fortification. They may differ somewhat in bioavailability, but that is not considered as critical an issue with calcium as it is with iron. Tricalcium phosphate is currently used to fortify complementary blended foods (CSB and WSB) since it provides both phosphorus and calcium, and is believed to help prevent infestation of the food on storage. Neither of these is particularly important with flour or maize fortification. While the body needs a balanced intake of both calcium and phosphorus, cereals already contain a high level of phosphorus, as shown in Table 3.8, so it is not necessary to add more.

Methods and economics of calcium fortification - Because of the large bulk of the calcium source that needs to be added, it is not normally included in the fortification premix and its addition is done separately from the rest of the fortification. The amount of calcium sulphate that needs to be added to flour to meet the U.S. optional standard of 2.1 g/kg is 8.7 kg/MT, which is 58 times greater than a normal fortification premix addition rate of 150 g/MT. As a result, it would make no economic sense to combine these, so a separate feeder with a higher capacity will be required if calcium is to be added.

The ingredient cost of adding calcium is about $1 per metric ton of fortified flour, but it could be higher depending on the local availability of the calcium compounds. This would appear to make it expensive compared to the rest of the micronutrients (see table 7.1), but that is misleading since the calcium source replaces an equal amount of flour, which effectively lowers the cost. If the cost of the replaced flour is higher than the cost of the added calcium, the ingredient cost to the miller can even be negative, meaning the mill can actually save money by adding calcium. This savings is possible but not likely in most countries. The value of the flour to the miller ranges from $150 to $250 per MT while the cost of the calcium source can range from $125 to $300 per MT, with shipping and tariffs largely accounting for difference. The cost of adding calcium can be calculated by the formula:

$C = P + A\ (C_c - C_f)/1000$
Where:
C = Cost of calcium fortification in $/MT of fortified flour
P = processing cost (~0.10 $/MT of flour)
A = calcium source addition rate in kg/MT
Cf = cost or value of wheat flour in $/MT
Cc = cost of calcium source in $/MT

Calcium fortification has no effect on the color or taste of flour or bread, even at the high levels used. Calcium carbonate has a slight pH raising and buffering action on flour. Added calcium is generally believed to be beneficial for yeast-leavened bread baking. Calcium fortification will greatly increase the flour's ash content, making ash levels unusable as a way of measuring flour quality or extraction.

Iodine

Iodine fortification is usually reserved for salt. There are no countries that currently require iodine to be added to flour. However, there can be situations where salt iodization is not adequate and additional measures are needed to prevent the occurrence of IDD. If flour or maize meal is being fortified in these countries, iodine can be included for hardly any additional cost.

Iodates function as oxidative bread improvers and have been added to flour and bread dough for that reason, typically at levels up to 15 ppm, which is ten times the amounts that would be added for nutritional reasons. An addition of 10 ppm calcium iodate would add 412 ug of iodine per 100 grams of bread or 110% of the RDA for iodine per slice serving size.

Bread is normally made with 2% salt on a flour basis. This has been reduced in recent years due to concerns on high sodium levels, but it normally stays above 1.5%. If the salt is iodized to U.S. standards of 77 mg/kg, 2% salt addition would add 96 ug/100g iodine to bread or 25% of the RDA per serving, assuming no loss during baking. That would make bread an important source of iodine. However, if non-iodized salt is used in baking, as may often be the case, this source of iodine is lost.

Iodized bread has been used in some countries. This can be achieved either by adding special iodized bakers' salt, as done in the Netherlands, or deliberately adding iodine to bread, the preferred source being calcium iodate. The level of iodine fortification suggested is 0.2 to 0.4 ppm iodine, which would put it in line with the levels of other micronutrients added. At this addition, it would be insufficient to have either a safety problem or much of an oxidative improving effect, and would add very little cost to the premix.

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