

## **A STUDY ON ELEMENTAL IRONS AND IRON COMPOUNDS FOR FOOD FORTIFICATION**

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### **INTRODUCTION**

Iron deficiency has become a major global health problem that was ranked 7<sup>th</sup> among the preventable risks for disease, disability and death by World Health Organization. Iron deficiency causes anemia, which can have widespread effects in terms of retarding growth, impairing IQ, tiredness and lowering body resistance to infection. It is estimated two billion people or one-third of the world's population is anemic, in which approximately 50% of all anemia cases are due to iron deficiency and most of them are found in infants, children and adult women [1]. Strategies to combat anemia include short-term solution with medication and using iron supplement, and long-term approach with increasing iron intake through food fortification. The food-based approaches are important sustainable strategies for preventing iron deficiency.

### **Iron sources for food fortifications**

The basic requirements on iron fortificants include 1) soluble to provide good bioavailability; 2) stable during storage and food processing to resist oxidation from moisture and heat; and 3) inexpensive and capacity available to be able for large-scale applications. Based on current experience and practice, the iron sources used as fortificants can be divided into two large groups: elemental irons and iron compounds.

Elemental irons have three common types available: reduced iron, electrolytic iron and carbonyl iron that can provide more than 97%Fe per unit. Iron compounds mainly include ferrous sulfate, iron chelates and other iron salts that usually have iron content from 14% to 37% dependent on their chemical formula. Here elemental iron can provide 3 to 5 times more unit iron than iron compounds regardless their bioavailability.

Commercial practices and scientific studies [2] have found iron compound such as ferrous sulfate and NaFeEDTA has poor stability during storage and food processing due to the nature of easy oxidation. This oxidation can create discoloration as well as undesirable odor and flavors in food products. Elemental irons, however, were found to have long shelf life for storage and good oxidation resistance during food processing because they start from a zero oxidation state.

Finally, elemental irons are more cost-effective iron fortificants when compared to iron compounds. For example, iron compounds are usually 2 to 20 times or more expensive than reduced irons. When considering key components such as unite iron content, stability and cost-efficiency, elemental irons are superior to iron compounds. Because of these advantages, elemental irons have been given primary consideration for large-scale food fortifications from past to present.

## Commercial elemental iron manufacturing methods

Commercial Iron powders are generally manufactured using either mechanical or chemical methods. Water-atomization of molten iron or alloy is a primary mechanical manufacturing method today. Chemical methods include reduction, electrolytic and carbonyl processes, with chemical reduction of iron oxides being the least expensive, large-scale manufacturing method. Figure 1 illustrates the different types of commercial iron powder manufacturing methods and Figure 2 demonstrates the particle morphology of powders made from these processes. Unlike iron compounds that can be identified by chemical formula, elemental irons have various physical shapes and chemical purity dependent on manufactured methods and processes that create significant difference in physical and chemical characteristics.

The atomized iron powder is produced with disintegrating molten iron stream into fine droplets by high velocity water jets. The atomized iron powder has a solid and irregular particle structure.

The reduced iron powders are mainly produced by two major chemical reduction processes. One uses carbon monoxide and the other uses hydrogen as the reducing agent. The raw material used in the reduction methods is iron oxides either high-grade iron ore or selected mill-scale, which are reduced continuously at 1000~1200°C for 5 to 10 hours. The particles of reduced iron powder are irregularly porous shaped, and therefore are referred as sponge iron powder. Overall, the hydrogen-reduced iron powder has a sponge-like microstructure with very fine porosity compared to carbon-reduced iron powder.

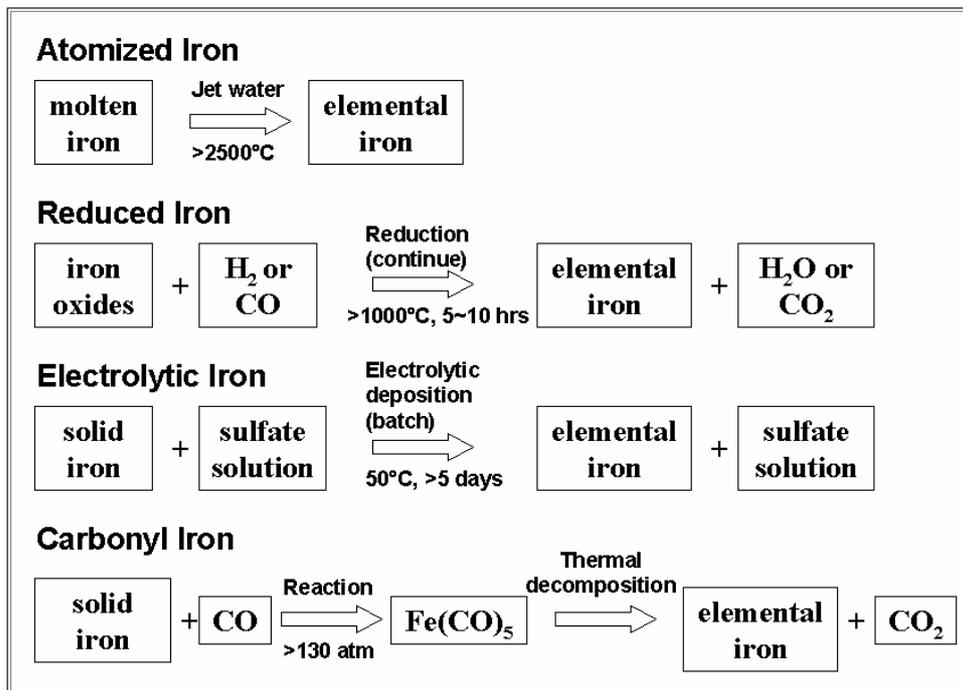


Figure 1 Manufacturing methods of commercial elemental iron powders

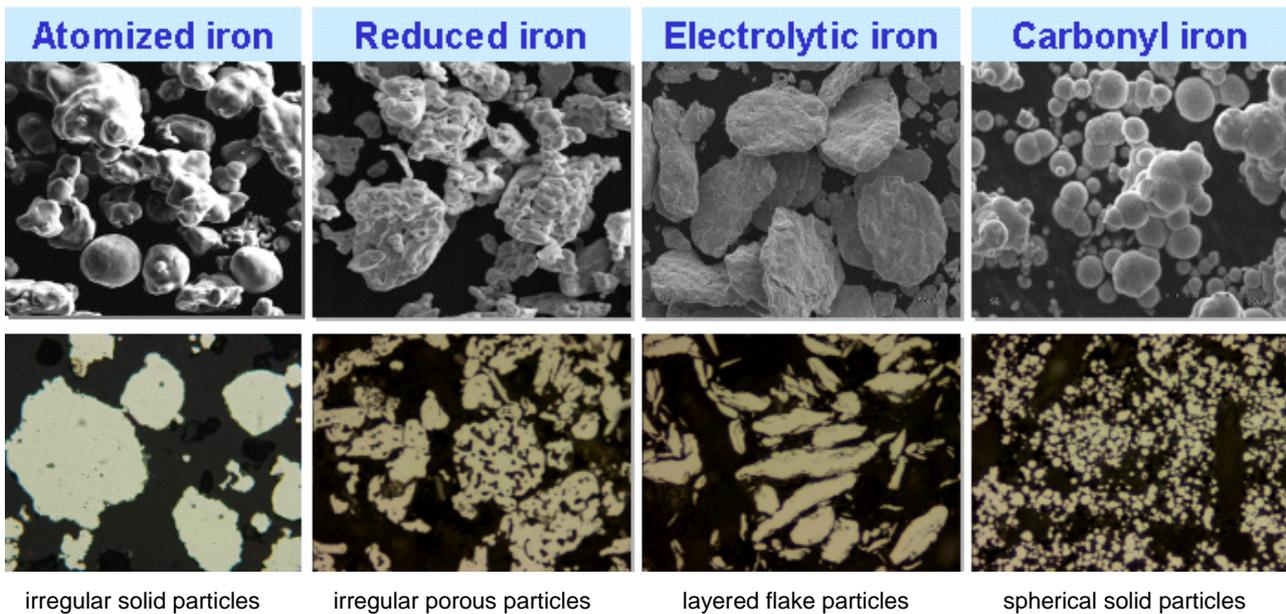


Figure 2 Particle morphology of elemental iron powders manufactured by different processes

The electrolytic iron powder is produced by electrolytic deposition from ferrous sulfate solution at 50°C with a 5-day batch process so that this type of manufacturing method has low productivity and limited capacity. Ideally, the electrolytic iron powder is a layered solid particle with a flake shape. Since the electrolytic deposits (usually they are 45x45x0.5 cm plates) have to be ground into required particle size, final milling technology often determines the particle morphology and powder quality that relate to fortification performance. Therefore, not all electrolytic irons have equal bioavailability.

Carbonyl iron powder is produced by thermal decomposition of iron carbonyl molecules  $[\text{Fe}(\text{CO})_5]$  which are formed at >130atm from a reaction between reduced iron and CO gas. As compared to reduced and electrolytic iron, this is a high cost process with very limited capacity. The carbonyl iron powder consists of small solid particles (1~10  $\mu\text{m}$ ) with near true spherical shape.

Among the commercial elemental irons for food fortification, reduced irons are the most cost-effective iron and the only elemental iron source that has capacity to meet large-scale applications. As a result, reduced irons have the largest market share in food fortifications today.

### Issues on food fortification with elemental irons

It is well known that food fortification with iron is the best long-term approach in reducing iron deficiency and has been successfully practiced in developed countries for more than 60 years. Elemental irons and iron compounds are widely used as the iron sources for food fortification. However, available evidence on nutrition responses of iron from these iron sources, especially from elemental irons, are limited and conflicting due to variety of iron sources.

Past studies on bioavailability of elemental irons have shown relative biological values (RBV) to ferrous sulfate ranging from 5% to 148% in human studies. In what seems to be a paradox of solubility vs. RBV, these studies have reported the less soluble hydrogen-reduced iron in dilute HCl

acid to have a higher RBV values than the much more soluble carbonyl iron, which consistently tested to have low RBV values [3].

In addition to the possible contradiction of solubility vs. RBV, few publications investigate the physical and chemical changes of iron fortificants in food matrix after food processing such as heating. In fact, thermodynamic reactions and interactions between iron and the food matrix do occur, so that, the results obtained from model and animal studies may not correspond well with human studies [3].

Furthermore, conventional elemental irons, especially reduced irons, are initially a form of byproduct that was not designed specifically for food fortification. With the better understanding of requirements for food fortification, today iron powder manufacturers are able to modify their process and powder characteristics to design an elemental iron suitable for food applications.

This study investigates all commercial elemental irons used today, including a newly developed reduced iron powder, with regard to their purity, particle morphology and surface area. Solubility tests are performed on the powders in order to predict their relative bioavailability to ferrous sulfate. Finally, the oxidation mechanism of iron fortificants is explored. The purpose is to provide better understanding on the nature of elemental irons.

## **MATERIALS AND METHODS**

### **Elemental iron powders**

8 commercial elemental iron powders that represented the characteristics of all iron powders manufactured today were selected for this study. They cover atomized, C-reduced, H-reduced, electrolytic and carbonyl iron powders produced by different manufacturing process. In addition, a newly developed reduced iron that is designed specifically for food fortification was also included.

### **Analysis methods**

Chemical composition analysis was performed based on FCC specifications [4] to determine the assay of iron, percentage of acid-insoluble, and the content of As, Pb, Hg.

Particle size of the elemental iron powders was measured by combining sieve analysis with laser particle size analysis (Sympatec, Germany).

Specific surface area of iron powders was determined by BET method with nitrogen gas absorption.

Particle morphology was observed with a scanning electron microscope (SEM) and cross-sections of powder particles were observed under an optical microscope.

Dissolution rate was measured by adding 50mg of iron powder into 250 ml diluted HCl solution (0.1N or pH1.0) after consistent stirring (150rpm) at 37°C for 30min. ICP analysis was performed to determine the amount of iron dissolved in solution.

The oxidation states of iron powder and iron compound were analyzed with a potentiometric method to determine the content of total iron, metallic iron and ferrous ions ( $\text{Fe}^{2+}$ ), after the powder was heated at various temperatures for 60 min in humidity atmosphere. H-reduced iron powder and ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was used for comparison.

## RESULTS AND DISCUSSIONS

### Chemical composition of elemental irons

When elemental iron powder is sold as a food grade, it must meet with the requirements of Food Chemical Codex (FCC), especially the low levels of toxic trace elements such as As, Pb and Hg. Most of conventional atomized iron cannot be used as food grade due to the high levels of toxic trace elements. Table 1 presented the chemical analysis results of commercial elemental irons based on FCC requirements. There are different FCC requirements dependent on the types of elemental irons, which reflect the nature of application and manufacturing capability. As compared to conventional reduced iron, on the other hand, the newly developed reduced iron has much purer chemistry that is identical to electrolytic iron.

Table 1 Typical chemical compositions of elemental irons and the FCC requirements

Elemental iron		Fe-total,%	Acid-insoluble,%	As, ppm	Pb, ppm	Hg, ppm
Reduced iron	FCC	>96	<1.25	<8	<10	<5
Conventional	typical	>97	0.47			
<b>New developed</b>	<b>typical</b>	<b>&gt;98</b>	<b>0.19</b>	<b>1.0</b>	<b>&lt;1.0</b>	<b>&lt;0.25</b>
Electrolytic iron	FCC	>97	<0.2	<3	<4	<2
	typical	>98	0.06			
Carbonyl iron	FCC	>98	<0.2	<3	<4	<2
	typical	>99	0.04			

### Particle size and surface area

As FCC specified, all commercial elemental irons are practically prepared in a fine particle size, in which they are 100% less than 100 mesh (150 $\mu$ m) and the fine fraction of -325mesh (-45 $\mu$ m) must be more than 95%. Table 2 shows the mean particle size ( $D_{50}$ ) and the percentage of particles smaller than 500mesh (25 $\mu$ m) of elemental irons as well as their specific surface area. For reduced and electrolytic irons, their mean particle size ranged from 25 to 33 $\mu$ m while carbonyl iron has the smallest particle size ( $D_{50}$ =9 $\mu$ m). In general, the finer the particle size is, the larger the specific surface area is. However, it is not always true for iron powders with a sponge-like microstructure. As mentioned before, the iron powder produced by hydrogen reduction contains extremely high porosity with fine pores while iron powder produced using carbon reduction has far fewer but much larger pores. Therefore, the H-reduced iron powder has much higher surface area than the C-reduced iron powder. The atomized iron has the least surface area due to its solid particle structure. With modified particle structure, the newly developed reduced iron has the highest surface area among all elemental irons even though its particle size is much coarser than carbonyl iron.

Obviously, particle size alone does not fully explain differences in bioavailability of the iron powders because they are manufactured by different methods [5]. Surface area is a suitable parameter that

can reflect the solubility of iron powders. The iron powder with high surface area will be expected to have better solubility and therefore better bioavailability.

Table 2 particle size and surface area of elemental irons

Elemental iron	D <sub>50</sub> <sup>*</sup> , μm	%-25 μm <sup>**</sup>	BET SSA <sup>***</sup> , m <sup>2</sup> /kg
atomized iron	35	15	50
Reduced iron			
C-reduced	33	20	110
Reduced	30	29	230
H-reduced iron	25	49	330
<b>New developed</b>	<b>29</b>	<b>28</b>	<b>560</b>
Electrolytic iron			
grade A (A-131)	28	44	400
grade B	25	32	290
Carbonyl iron			
grade A	8	90	540
grade B	9	88	490

\*with laser particle size analyzer; \*\*with sieve analysis; \*\*\* BET specific surface area

### Dissolution rate and relative bioavailability (RBV)

Table 3 presented the solubility results of elemental irons and their relative bioavailability in rat and human studies compared to ferrous sulfate. As expected, the dissolution rate of elemental irons corresponds well with their surface area. The atomized iron has the least solubility due to its small surface area. At the same time, dissolution rate in dilute HCl acid (pH1.0) are significantly different depended on the iron sources: carbonyl (94~95%) > electrolytic (50~74%) > reduced (28~39%) except the newly developed reduced iron. Due to its high surface area, the newly developed reduced iron presented a high dissolution rate that is even more soluble than the electrolytic iron. Rat tests performed by USDA indicated the dissolution rate corresponds with the RBV to ferrous sulfate [4]. However, recent human studies performed by the same research group have shown that the relative bioavailability was 50% for reduced iron and 85% for electrolytic iron, which have shown 24% and 54% of RBV in rat studies respectively [6]. It is clear that the rat studies gave much less estimation of RBV than human studies for elemental irons. Nonetheless, the new generation reduced iron is expected to have identical or higher bioavailability to electrolytic iron since it has much purer chemistry and higher surface area compared to conventional reduced irons.

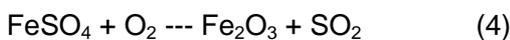
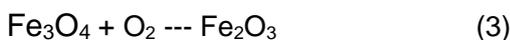
Table 3 Dissolution rate of elemental irons and their RBV to FeSO<sub>4</sub> in rat and human studies

Elemental iron	BET SSA	Dissolution	RBV-rat*	RBV-human*
Atomized iron	50	19		
Reduced iron				
C-reduced	110	28	21	50
Reduced	230	35	24	
H-reduced	330	39	42	
<b>New developed</b>	<b>560</b>	<b>75</b>		
Electrolytic iron				
grade A (A-131)	400	74	54	85
grade B	290	50	46	
Carbonyl iron				
grade A	540	95		
grade B	490	94	64	

\*References [5], [6]

### Oxidation of iron fortificants

The rat and human studies showed significant different RBV of elemental irons to ferrous sulfate. According to the studies, the rat tests used uncooked meals while the human tests used cooked meals. This indicates that an oxidation reaction may happen to the iron fortificants when they were cooked. It is well known that elemental iron and ferrous sulfate will be oxidized with the following chemical reactions in the presence of oxygen and moisture. Heating will accelerate the reactions.



For elemental iron, it oxidizes gradually from zero electron state to higher electron states (reactions 1 to 3) depending on the oxidation conditions. However, FeSO<sub>4</sub> will oxidize directly from the ferrous (Fe<sup>2+</sup>) state to the ferric (Fe<sup>3+</sup>) state (reaction 4). It is known that FeO can be easily dissolved in a diluted acid while Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> can only dissolve in strong acid, as shown in Table 4. The Fe<sub>3</sub>O<sub>4</sub> is more soluble than the Fe<sub>2</sub>O<sub>3</sub> because it is a mixture of FeO and Fe<sub>2</sub>O<sub>3</sub>.

Table 4 Dissolution rates of iron oxides in various HCl solution

Iron oxide	HCl Concentration		
	0.1N	0.5N	1.0N
Fe <sub>3</sub> O <sub>4</sub>	6.0	30.0	96.0
Fe <sub>2</sub> O <sub>3</sub>	4.0	6.0	94.0

Conditions: 0.5g iron oxide added in 100ml HCl solution at 25°C and stirred for 60 min.

Table 5 demonstrates the oxidation behaviors of a H-reduced iron and FeSO<sub>4</sub>+7H<sub>2</sub>O in a humidity atmosphere when they were heated. Although the oxidation rate of both reduced iron and ferrous sulfate increased as the temperature was raised, the oxidation of reduced iron was minimal (3.4% at 200°C) while the ferrous sulfate oxidized rapidly (70% at 200°C). Recent studies found that baking process promoted the oxidation of FeSO<sub>4</sub> so that it significantly reduced its bioavailability [7]. Therefore, further research is required to clarify the oxidation mechanism of different iron fortificants during food processing (heat treatment) including the interactions with different food matrix before selecting one of them as a reference or standard.

Table 5 Oxidation rate of reduced iron and ferrous sulfate when heated in humidity atmosphere

Temperature °C	H-reduced iron				FeSO <sub>4</sub> +7H <sub>2</sub> O		
	%Fe-total	%Fe-met	%Fe <sup>2+</sup>	%oxidized	%Fe-total	%Fe <sup>2+</sup>	%oxidized
25	97.8	96.5	1.3	1.3	20.8	20.8	0.0
150	97.7	95.6	2.1	2.1	31.8	19.5	38.7
175	97.8	95.2	2.6	2.6	32.1	14.1	56.1
<b>200</b>	<b>98.0</b>	<b>94.6</b>	<b>3.4</b>	<b>3.4</b>	<b>32.2</b>	<b>9.6</b>	<b>70.2</b>
225	97.7	94.5	3.2	3.2	32.3	9.2	71.5
250	97.7	93.4	4.3	4.3	32.4	5.1	84.3

## CONCLUSIONS

Although elemental irons and iron compounds are widely used as the iron sources for food fortification, available evidence on nutrition responses of iron from these iron sources, especially from elemental irons, are limited and conflicting due to variety of iron sources and lack of thermodynamic studies in food fortification. Further research is required to clarify the oxidation mechanism of different iron fortificants during food processing including the interactions with different food matrices.

Commercial practices indicate that elemental irons are superior to iron compounds in the key components such as unit iron content, stability and cost-efficiency. Reduced irons are the most cost-effective iron and the only elemental iron source that has capacity to meet large-scale food applications. The new generation reduced iron has much purer chemistry and higher surface area compared to conventional reduced irons and thus it is expected to have identical bioavailability to electrolytic iron.

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