

PHYSICAL CHARACTERIZATION OF POLYMETALLIX™  
NANOSCALE IRON

FOR

POLYFLON  
A DIVISION OF CRANE CO.

PERFORMED BY

THE WHITMAN COMPANIES, INC.

AND

LEHIGH UNIVERSITY

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**TITLE**

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# PHYSICAL CHARACTERIZATION OF POLYMETALLIX™ NANOSCALE IRON

## 1.0 EXECUTIVE SUMMARY

On behalf of the Polyflon Division of Crane Co., Dr. Wei-xian Zhang's research group performed a physical characterization of three (3) samples of PolyMetallix™ nanoscale iron particles from unique process lots. Six parameters including the particle size distribution, particle morphology, moisture content, specific surface area, surface (zeta) potential, and equilibrium oxidation-reduction potential (ORP) and pH. These parameters provided a representative list of physical characteristics by which to predict relative reactivity and evaluate process representativeness.

The PolyMetallix™ iron was generally spherical in shape. It exhibited a large specific surface area of 38-54 m<sup>2</sup>/g indicating the likelihood of substantial reactivity despite large median particle sizes on the order of several hundred nanometers. In this context, reactivity is expressed relative to commercially available microscale iron powders typically utilized in permeable reactive barrier installations. The data generated herein suggest that the reactivity of the PolyMetallix™ iron should be in line with other nanoscale irons tested in our laboratory. However, since no contaminant degradation experiments were performed as part of this undertaking, we cannot quantify the reactivity potential of the PolyMetallix™ iron. We strongly suggest that Polyflon and Crane conduct well-designed batch and column contaminant degradability tests to better define process kinetics, identify potential degradation intermediates/products, and facilitate development of solid product comparisons with competing iron products.

## 2.0 INTRODUCTION

### 2.1 Overview

On March 15, 2004, Polyflon shipped samples from three (3) separate lots of PolyMetallix™ iron to Dr. Wei-xian Zhang's laboratory at Lehigh University for physical characterization testing. The rationale for testing multiple lots is to develop a sense of the batch-to-batch variability which may exist in connection with Polyflon's manufacturing process. Given the interest in nanoscale iron as a potential remediation tool and the fact that few commercial manufacturers of the material exist, it is imperative that a relatively simple procedure be developed to help characterize its physical capabilities. The parameters included in this work are particularly relevant to not only basic characterization and classification efforts but are also germane to end users in the remediation community. As is the case with any "first-

effort”, this work is clearly an evergreen process and refinements to the scope and content are both welcomed and expected.

## 2.2 Objectives

The specific objectives for this physical characterization effort were to:

- (1) Develop a meaningful set of parameters by which to evaluate and compare the reactivity and capabilities of the PolyMetallix™ nanoiron particles.
- (2) Work with Polyflon and Crane personnel to incorporate this data in creative and effective marketing/technical information that support the PolyMetallix™ product line.
- (3) Using this data as a basis, to develop a streamlined yet applications-oriented design for bench-scale studies using one or more target reference contaminants (e.g. trichloroethene and perchlorate) to evaluate the degradation potential of the PolyMetallix™ product.

In keeping with recent developments in the peer-reviewed research, six basic physical parameters were selected for inclusion in this initial characterization effort. These included the particle size distribution (PSD), particle morphology, moisture content, BET specific surface area, surface potential, and equilibrium ORP/pH. A brief explanation of the importance of these parameters is summarized in the descriptions as follows:

- Particle Size Distribution (PSD) – provides the quantitative distribution of sizes for nanoparticle clusters and aggregates and an indirect approximation of reactivity and subsurface transport potential.
- Particle Morphology – a qualitative depiction of particle shape and to some degree, an indication of the extent of cluster and/or aggregate formation.
- Moisture Content – a quantitative measure of the percent water content of the manufactured nanoiron particles. This is an important parameter in determining the accurate dosing requirements and in proper calculation of the reactive capacity of the iron surface.
- BET Specific Surface Area – provides the quantitative area of the iron surface per gram available for surface association and reaction. This parameter is directly linked to reactivity; the more reactive surface available, the greater the reactivity.

- Surface Potential – provides a quantitative measure of the extent of surface charge on the iron particles. This parameter is important in assessing the aggregation probability of a given iron and its relative affinity for native aquifer solids. By extension, the surface potential can provide an indication of the relative ease by which the iron can migrate in the subsurface.
- Equilibrium ORP/pH – a quantitative measure of the solution oxidation-reduction potential and pH at equilibrium resulting largely from reactions between adsorbed water and the iron surface. This is an indirect measure of the surface reactivity of the iron.

### **2.3 Role of Lehigh University**

Since 1996, Dr. Wei-xian Zhang's research group at Lehigh University has focused on the development and testing of nanoscale metals for the remediation of contaminated soils and ground water. Thus far, Lehigh has investigated the efficacy of nanoscale iron and bimetals on more than seventy (70) different environmental contaminants from a wide variety of chemical classes including chlorinated aliphatic and aromatic hydrocarbons, polychlorinated biphenyls (PCBs), nitroaromatics, perchlorate, and toxic metals such as hexavalent chromium. Lehigh has conducted numerous bench-scale batch studies to evaluate reactivity and process kinetics issues. Moreover, two in-depth field demonstrations were conducted in 2000 (manufacturing site in Trenton, NJ) and 2003 (manufacturing site near Raleigh, NC). Zhang's group has also been very involved in the characterization of nanoiron and bimetals particularly insofar as inferences to reactivity is concerned. The Zhang group is among the vanguard of research groups working to develop the nanoscale metal technology as an environmental remediation technology.

This work has been published in several prestigious peer-reviewed journals including *Environmental Science & Technology*, the *Journal of Environmental Engineering*, *Civil Engineering*, *Catalysis Today*, and *Industrial & Engineering Chemistry Research*, among others. In addition to this publication record, the Zhang group is frequently represented at major regional, national, and international conferences presenting various aspects of their current research.

### **3.0 EXPERIMENTAL OVERVIEW AND METHODOLOGIES USED**

The experimental procedures used in this characterization effort are discussed in the order in which they were introduced in Section 1.2. The instrumentation used and a very brief description of the experimental procedure are included for each parameter. A detailed treatment of the methodologies used is beyond the scope of this discussion.

### **3.1 Particle Size Distribution (PSD)**

A Dispersion Technologies DT 1200 Acoustic and Electroacoustic Spectrometer was used to characterize the PSD for each of the three PolyMetallix™ samples. A representative aliquot of sample is introduced into the sample chamber and the instrument is readied for operation. The instrument operates by transmitting sound pulses through the aqueous sample. The attenuation of these pulses is measured over a wide range of ultrasonic frequencies. The particle size can be deduced by the instrument using software that incorporates an extensive database of acoustic attenuation in concentrated polydisperse systems.

### **3.2 Particle Morphology**

Photomicrographic images of the dried nanoparticle clusters and aggregates were obtained using a Phillips EM 400 T Transmission Electron Microscope (TEM). A small representative sample of the nanoiron is placed on slide plates and gently dried overnight by a stream of nitrogen gas. The dried sample plate is then inserted into the microscope which is subsequently readied for operation. Four images were obtained for each sample.

### **3.3 Moisture Content**

The average moisture content in percent water (% H<sub>2</sub>O) was measured using a Mettler-Toledo HB43 moisture analyzer. A small mass of water wet iron is introduced into the sample compartment and the instrument is readied for analysis.

### **3.4 BET Specific Surface Area**

BET refers to the Brunauer-Emmett-Teller isotherm and is the basis for determining the extent of nitrogen gas adsorption on a given surface. The surface area is measured using a Micromeritics ASAP 2010 Chemisorption Analyzer. Representative iron samples were pre-dried at room temperature (22±0.5 °C) in a vacuum desiccator and degassed at 90 °C for 1 hour and then at 200 °C for 4 hours.

The basics of BET adsorption are well known in the literature and are as follows. The iron sample is contained within an evacuated sample tube cooled to cryogenic temperature. It is then exposed to nitrogen gas at a series of precisely controlled pressures. With each incremental pressure increase, the number of nitrogen molecules on the surface increases. The pressure at which adsorption equilibrium occurs is measured and the Universal Gas Law can be used to determine the quantity of gas adsorbed. As adsorption proceeds, the thickness of the adsorbed

nitrogen film increases with surficial micropores being filled before macropores. The process continues until the point of bulk condensation of the nitrogen and then the reverse sequence of desorption occurs. The systematic sorption and desorption of nitrogen provides a wealth of information on the surface characteristics of the iron.

### **3.5 Surface Potential**

The Dispersion Technologies DT 1200 Acoustic and Electroacoustic Spectrometer was used to measure the zeta ( $\zeta$ ) potential of the iron surface. According to classical colloidal stability theory, a charged particle contains a double-layer which can be perturbed by an applied field. Using this instrument, the double layer around the iron clusters is perturbed by an applied acoustic wave, causing the formation of a temporary dipole moment (e.g. force associated with a separation of charge). A receiving antenna immersed in the sample measures the extent of the summed dipole moments in terms of a residual potential in millivolts (mV).

### **3.6 Equilibrium ORP/pH**

A sample of the nanoiron was placed in a beaker containing deionized water under well mixed conditions at room temperature and ambient pressure. The pH and ORP was tracked continuously by immersed combination electrodes for pH and ORP (Ag/AgCl) respectively. Equilibrium pH and ORP values are generally attained with a few minutes under these conditions. Adsorbed water is readily reduced by zero valent iron producing hydrogen gas and hydroxide as products. Hence, one of the classical signatures of aqueous zero valent iron-mediated reactions is an increase in solution pH and a dramatic decline in solution ORP.

## **4.0 NARRATIVE INTERPRETATION OF RESULTS**

A summary of the quantitative data is presented herein in Section 4.0. The subsequent subsections provide an interpretation of the data's significance and meaning with respect to the stated objectives. Table 1 summarizes the equilibrium ORP/pH data and the results from the electroacoustic spectrometer. Table 2 summarizes the moisture content results, particle morphology data, and the results from the BET specific surface area determinations. The complete dataset is included in Section 5.0.

### **4.1 Particle Size Distribution (PSD)**

As indicated in Table 1 and in Figure series 4.1, the median particle size of the PolyMetallix iron ranged from 306-1,131 nanometers (nm). PolyMetallix™ sample #2 exhibited the smallest median size range with the majority (>90 %) of the particles between 100 nm and

1 micrometer ( $\mu\text{m}$ ). Similarly, the majority of PolyMetallix™ sample #1 was between 200 nm and 3  $\mu\text{m}$ . In contrast, the majority of the PolyMetallix™ sample #3 exhibited particle sizes between 100 nm and 10  $\mu\text{m}$ , a much broader particle size range than with PolyMetallix™ #1 and #2. The rationale for the disparity in the PSD data for PolyMetallix™ sample #3 is not known. No specifics associated with the manufacturing process for the PolyMetallix iron have been provided to Whitman but it is likely that the differences with sample #3 involved either different reaction conditions or possibly a difference in any stabilization agent(s) used in the process. It may also reflect the possibility that the synthetic scheme is still undergoing process changes and has not been rigorously optimized.

This data, coupled with the particle morphology images (addressed below in Section 4.2), suggests that the PolyMetallix iron tested undergoes aggregation fairly easily and that the iron clusters were generally in the upper nanoscale size range. The relatively large size of the PolyMetallix clusters and aggregates could translate into somewhat reduced mobility in the subsurface. On the other hand, iron clusters and aggregates of this size are well-suited to attacking contaminant source areas or matrices of relatively low permeability.

**Table 1**  
**Summary of Relevant Results from Characterization of PolyMetallix™ Iron**

	<b>Iron Dose (g/L)</b>	<b>pH</b>	<b>ORP (mV)</b>	<b><math>\zeta</math> (mV)</b>	<b>PSM (<math>\mu\text{m}</math>)</b>
<b>Sample #1</b>	5.5	8.89	-450.9	+35.70	0.588
<b>Sample #2</b>	5.0	8.86	-462.2	+38.03	0.306
<b>Sample #3</b>	8.1	8.88	-507.8	+52.89	1.131

#### **4.2 Particle Morphology**

Photomicrographic images of the three samples are provided in Section 5.0 as Figure series 5.2, Images #1-1 through #3-4. As mentioned earlier, four images were obtained for each sample of PolyMetallix™ iron.

Generally speaking, the iron can be described as spherical clusters or aggregates with some evidence of fine dendritic-type structures clearly visible on some of the images. It is not clear what the origin of these structures is. Interestingly, the images with finer resolution (those with size reference bars of 100 nm or smaller) appear to depict “bud-like” chains of nanoiron clusters. There is a significant spherical quality to the clusters which may contribute to the relatively large specific surface area observed (described in greater detail in Section 4.4). These results are

encouraging as some nanoiron samples evaluated at Lehigh have exhibited very angular morphologies which may be detrimental insofar as subsurface migration potential is concerned.

### 4.3 Moisture Content

The average moisture content for PolyMetallix™ sample #1 was 40.61%. Thus, water-wet filtered nanoiron contains significant residual water content. This moisture content is in line with the residual moisture contained within the various lines of nanoiron produced at Lehigh and with other samples of nanoiron tested at Lehigh. Dry nanoscale iron particles are unstable in the presence of air and, practically speaking, are far too reactive for use in an environmental remediation context. Thus, some minimum residual moisture on the order of 20-30% or more is desirable. The moisture content data should be factored into bench scale and field scale pilot tests to enable proper determination of iron degradation capacity data and dose optimizations.

### 4.4 BET Specific Surface Area

The specific surface area measurements ranged from  $37.471 \pm 0.299$  square meters per gram ( $\text{m}^2/\text{g}$ ) for PolyMetallix™ sample #3 to  $58.461 \pm 0.473 \text{ m}^2/\text{g}$  for sample #2. A summary of the condensed data appears in Table 2. The raw BET output files and isotherm plots can be found in Section 5.0 as Figure series 5.3.

As expected, the trend of specific surface area results is inversely proportional to the median particle size. These values were higher than anticipated given the relatively large median size of the particles. The high specific surface areas may, to some degree, result from the relatively large number of “bud-like” clusters observed. In any case, this parameter is linked to reactivity in the sense that the nanoiron-catalyzed degradation reactions are surface mediated. Hence, the larger the available surface area, the greater the potential reactivity. The range of specific surface areas reported herein are very large in comparison to available microscale irons ( $<1 \text{ m}^2/\text{g}$ ) and are in line with the other nanoscale irons evaluated by Lehigh.

**Table 2**  
**Summary of BET Specific Surface Area for the PolyMetallix™ Iron Samples**

	<b>BET Specific Surface Area (<math>\text{m}^2/\text{g}</math>)</b>
<b>PolyMetallix™ Sample #1</b>	$52.964 \pm 0.416$
<b>PolyMetallix™ Sample #2</b>	$58.461 \pm 0.473$
<b>PolyMetallix™ Sample #3</b>	$37.471 \pm 0.299$

## 4.5 Surface Potential

The measured zeta potential ( $\zeta$ ) at the iron surface ranged from +35.70 to +52.89 millivolts (mV). The values for each of the three PolyMetallix™ iron samples are shown in Table 1. The existence of a slightly positive surface charge can be inferred at the nanoiron surface.

In an aqueous environment, iron surfaces typically develop formations of iron oxides and hydroxides which, at neutral pH, tend to develop an overall negative surface charge. Thus, the positive surface charge may result from certain amendments used in the manufacturing process or in product storage. The slightly positive surface positive charge could be problematic in that electrostatic attraction with the natural aquifer solids, which tend to be negatively charged, could result in reduced subsurface mobility. All issues being equal, it would be preferred for the nanoiron to possess a net negative surface charge to discourage aggregation and enhance repulsion towards the natural aquifer materials.

## 4.6 Equilibrium pH/ORP

The equilibrium pH values for aqueous slurries containing 5.0 – 8.1 grams per liter (g/L) of PolyMetallix™ iron ranged from 8.86 – 8.89 standard pH units indicating that the pH maxima reached is not particularly sensitive to iron loading. The ORP values ranged from –450.9 to –507.8 mV. In general, these results are right in line with the data for other nanoscale iron samples tested by Lehigh. As mentioned previously, these data are significant in that they provide a measure of the general reactivity of the iron. In this case, the reactant (or reductate) is water. The practical importance of these data are that equilibrium pH values in the 9-10 range or above can be expected to result in decreased iron reactivity over time due to precipitation of various iron oxides and hydroxides which tend to blind off the reactive sites. As far as the ORP results are concerned, all three PolyMetallix samples produced equilibrium ORP data indicating strongly reducing solution conditions. This is critical not only in that it demonstrates the reducing power of the iron but also in that maintained highly negative redox conditions are essential to the growth and proliferation of anaerobic microorganisms capable of degrading contaminant concentrations.

## 4.7 Summary

A suite of six (6) parameters was developed to serve as the working baseline by which to characterize the PolyMetallix™ nanoscale iron manufactured by Polyflon. These parameters include the particle size distribution, particle morphology, moisture content, specific surface area (BET), surface (zeta) potential, and equilibrium pH/ORP. This list is meant to be evergreen with Polyflon adding or deleting parameters as needed. One additional parameter, which was not

performed as part of this characterization effort, involves a litmus-type reactivity test using one or standard environmental contaminants. This type of degradability test will be included in the scope of the bench-scale feasibility study to be proposed by Whitman and Lehigh University.

Overall, the three samples of PolyMetallix™ nanoiron exhibited a relatively large median particle size on the order of several hundred nanometers. Specific surface area values were quite substantial ranging from 38-54 m<sup>2</sup>/g and two or more orders of magnitude larger than commercially available microscale iron powders. This is significant in that specific surface area can be closely correlated to reactivity for surface-mediated reactions like those involving iron. Photomicrographs suggested that the PolyMetallix™ iron samples tested showed appreciable clustering and aggregation and that the particles were largely spherical. Equilibrium pH and ORP results were comparable to other nanoiron samples tested at Lehigh.

Each of these parameters should be included in technical and product marketing materials to help familiarize potential clientele with the basic characteristics of the material. If determined with some frequency, some or all of these parameters could also form the core of an internal manufacturing quality assurance/quality control (QA/QC) for the PolyMetallix™ product line.

## **5.0 APPENDIX – COMPLETE DATASET**

Figure Series 5.1. Particle Size Distribution Data

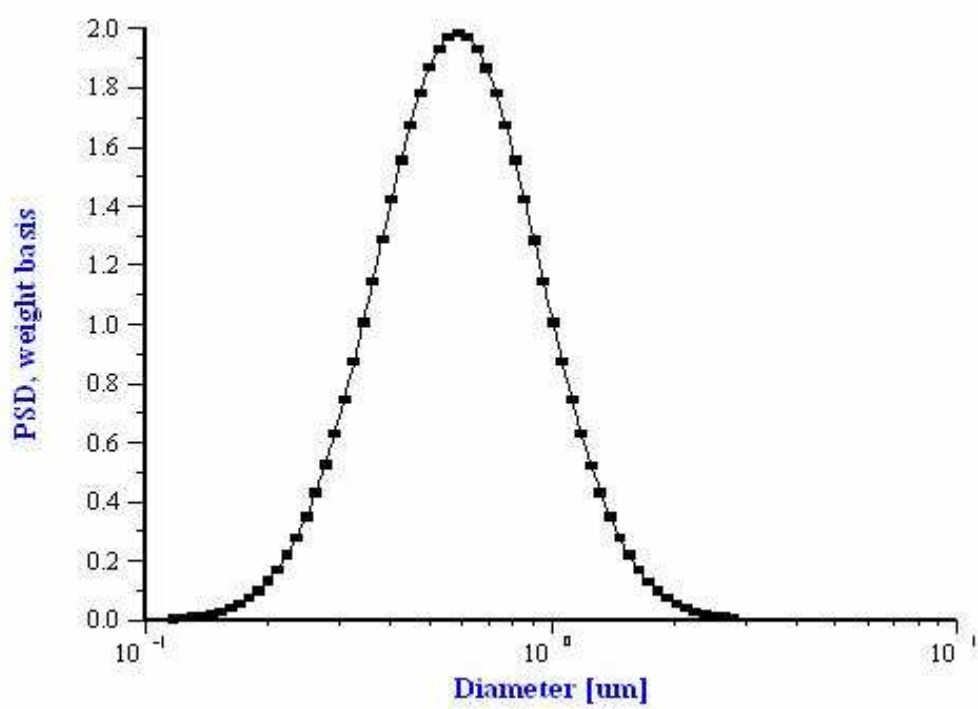


Figure Series 5.1.a. PSD of PolyMetallix™ Iron Sample #1

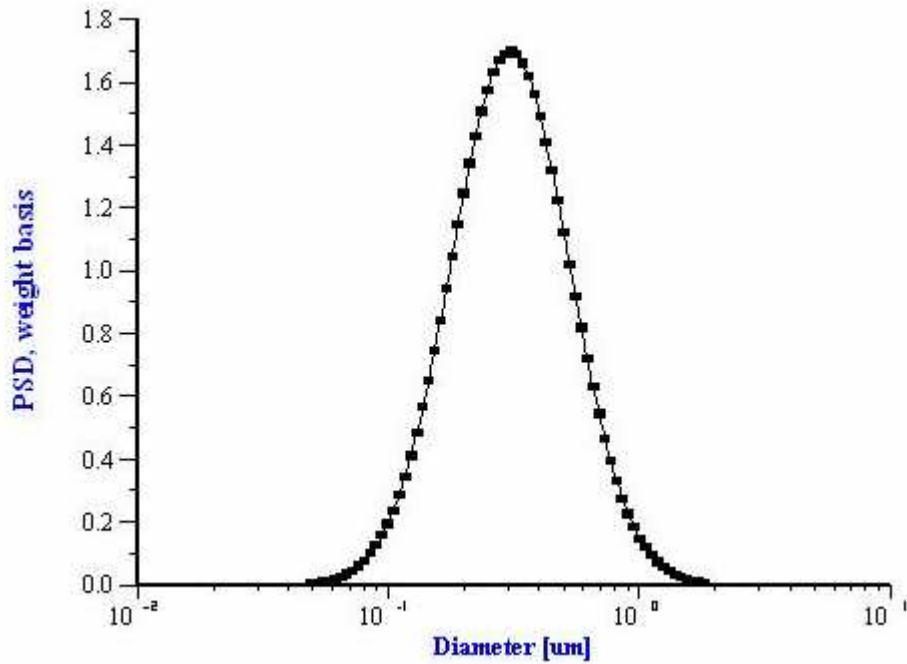


Figure Series 5.1.b. PSD of PolyMetallix™ Iron Sample #2

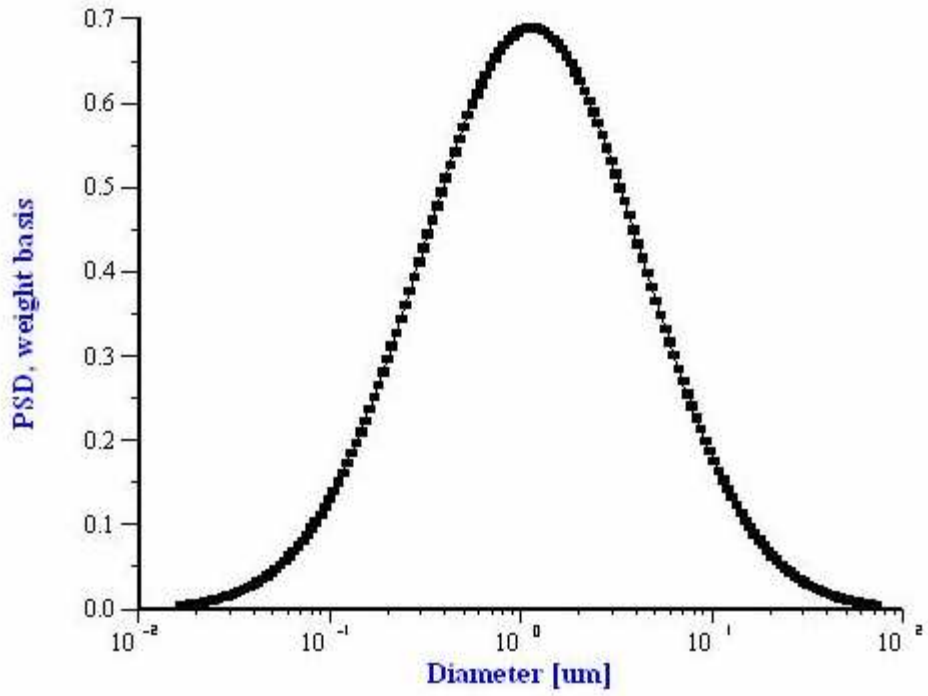


Figure Series 5.1.c. PSD of PolyMetallix™ Iron Sample #3

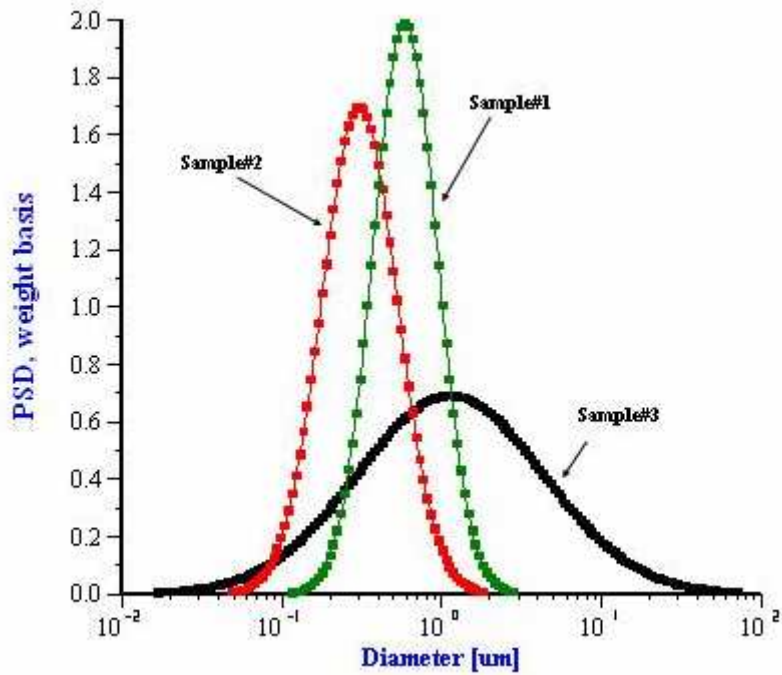


Figure Series 5.1.d. PSD Comparison for PolyMetallix™ Iron Samples

## **Figure Series 5.2. TEM Photomicrographs**

The original images of the nanoiron surface are contained in this sub-section on the following pages. Four (4) images with varying size scales were obtained and are denoted using the following format: #1-1 refers to PolyMetallix™ sample 1, image 1, etc.

### **Figure Series 5.3. BET Specific Surface Area Data**

The following pages contain the raw data and adsorption isotherm plots for BET specific surface area determinations of the three PolyMetallix™ samples.