

# Mill Scale-Steam Reforming: A Novel and Inexpensive Route of Hydrogen Generation

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## Abstract

*Mill-scale wastes from steel industry have been successfully reduced to pure metallic iron via hydrogen and carbothermic reduction. Use of high temperature and H<sub>2</sub> gas has been eliminated by a novel solution-based room temperature reduction technique whereby nanoscale iron powder is produced. This new scheme totally obviates the issue of sintering of the iron/iron oxide and hence the deactivation during the cyclic operation of metal-steam reforming. Some of the preliminary results of this investigation are discussed.*

## Introduction

Hydrogen, though not a fundamental energy source, has been touted to be the ideal energy-carrying fuel for fuel cells, particularly the PEMFCs. However, it is not as abundant a commodity in nature as oxygen and nitrogen and must be derived from other natural occurring resources. The question of its storage and supply arises only after it is produced in large enough quantity so as to cater to the fuel cell need. In the light of the serious economic constraints and safety concerns associated with production, storage and supply of gaseous hydrogen, one ought to find ways and means of generating, storing, transporting and supplying hydrogen to the end use port - in more reversible, much simpler and far safer ways.

An economically viable and environment friendly method of generating hydrogen is by the reaction of certain metals with steam, also appropriately called 'steam-metal reforming'. For example, the reaction,



which occurs around 600°C, has long been known and has recently been described as one of the ways of generating hydrogen [1-3]; the reverse reaction could be viewed as a hydrogen storage scheme. The theoretical amount of hydrogen being stored is 4.8% by weight which corresponds to ca. 4211 L H<sub>2</sub>/L Fe at STP. However, the kinetic of metal oxidation (forward) and oxide reduction (reverse) in a cyclic fashion has to be significantly improved, in order to mitigate sintering and coarsening of iron and iron oxide particles during repeated redox cycles.

We report an effective technique of producing hydrogen by using the so-called 'mill-scale' waste from steel industry, as an iron source in a way consistent with the criteria listed above: environment, availability and price. The mill-scale is a hard brittle coating of several distinct layers of iron oxides formed during the processing of steel. It is magnetic in nature (Fe<sub>3</sub>O<sub>4</sub> predominantly) with iron content ranging between 66 to 88%.

A perceived design for the generation of hydrogen via metal-steam reforming consists of the following. Iron derived from mill-scale is packed into cartridges and loaded on the vehicles. Addition of water into the pre-heated cartridges would produce pure humidified hydrogen that could be supplied directly to PEMFC on the vehicles. The cartridges with corresponding oxides after water decomposition are exchanged for the new ones packed with fresh metal at local gas stations where the oxide is again reduced to ready-to-use active metal.

Thus, the process of hydrogen generation from steel industry's waste in an efficient and cyclic fashion consists of: (a) conversion of magnetite to elemental iron, (b) Fe-steam reaction and, (c) reduction of the spent iron oxide into active elemental iron for next cycle.

We have recently carried out a systematic and thorough investigation on steel waste material to establish the feasibility of hydrogen production and recycling of the oxide on a laboratory scale. It was found that the mill-scale samples from different vendors could be quantitatively (~100%) reduced to elemental iron, both via H<sub>2</sub> and carbothermic reduction (mill-scale: activated C = 1:3 mole/mole). With an objective to eliminate the use of high temperature and H<sub>2</sub> gas, a solution-based technique has been devised resulting in the formation of nanoscale elemental iron particles from mill-scale powder at room temperature, which could be used directly in metal-steam reforming process to produce H<sub>2</sub>. Metal-steam reforming experiments carried out using active iron powder derived from mill-scale magnetite waste showed that near stoichiometric conversion (99%) of water into hydrogen was obtained. This paper discusses the methodology and the results of the investigations carried out in our laboratory.

## **Experimental**

### Sample processing

Five mill-scale samples were obtained from three different vendors: North American Steel (KY), Midrex (NC) and Nucor-Yamato (AR). They are labeled as pickled, sludge rinse and entry loop (NAS), Midrex (MR) and Nucor-Yamato (NY). All the five mill scale samples were attrition-milled in 2-propanol and sieved through 325 mesh (average particle size ≤ 45 μm) prior to any processing or characterization.

### Sample reduction

Hydrogen reduction was performed in high purity dry H<sub>2</sub> at 1173K for 8 h. The total pressure of the gas flowing through the fixed bed of the mill scale was maintained at ~101 KPa. For the carbothermic reduction, the processed mill-scale powders were mixed with activated carbon in 1:3 molar ratio, ball-milled, dried and pelletized after adding polyvinyl alcohol (PVA) as a binder to aid compaction. The carbothermic reaction carried out at 1373K for 4 h, using nitrogen as a blanket gas can be represented as:



### Metal-steam Reforming reaction

Metal-steam reforming was conducted in a stainless steel tubular reactor (inner diameter ~0.68 inch). A thermocouple placed in sample's proximity monitored the temperature. Helium was used as an inert background during the temperature ramp to 873 K. After the sample attained the final temperature, a 50:50 v/v mixture of steam (water preheated to 673 K) and He was introduced while maintaining the total pressure ~101 KPa. The reaction was allowed to run until no hydrogen formation was detected in the mass spectrometer attached to the reactor at the exit end.

### Characterization

Chemical analysis of the as-received mill scale samples was done by X-ray fluorescence (XRF) technique. Magnetic measurements were carried out by Mössbauer spectroscopy while X-ray powder diffraction patterns were collected at room temperature on a

Philips powder diffractometer (PW 3050/60 X'pert Pro), using monochromatic  $\text{CuK}\alpha_1$  radiations ( $\lambda = 1.54056 \text{ \AA}$ ). Morphology of the samples before and after reduction and steam reforming were examined by a Philips scanning electron microscope (XL30 FEG). The morphology and crystal structure of the nano iron particles were studied by transmission electron microscopy (JEOL 3010) operated at 300 kV together with selected area electron diffraction (SAED). Hydrogen formation was quantified by quadrupole mass spectrometer (QMS 200, Pfeiffer Vacuum Omnistar).

## Results and Discussion

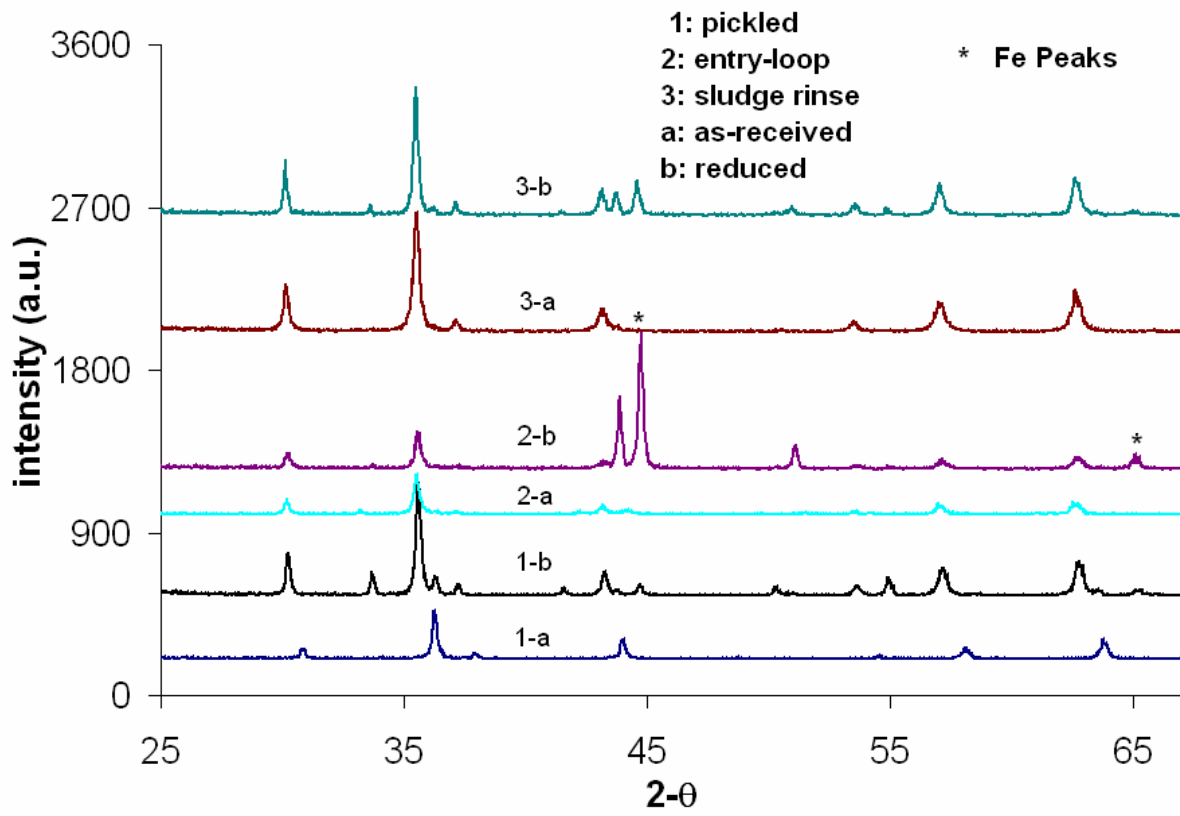
Table 1 shows the XRF analyses of the as-received mill scale samples from various vendors. Two of the three samples from North American Steel were predominantly rich in Cr (52 to 67% by weight), while the third sample contained about 18% Cr and 8% Ni by weight. The samples from Midrex and Nucor-Yamato contained 93-94 wt% Fe but no Cr or Ni.

**Table 1.** XRF analyses of the mill scale samples used in this study.

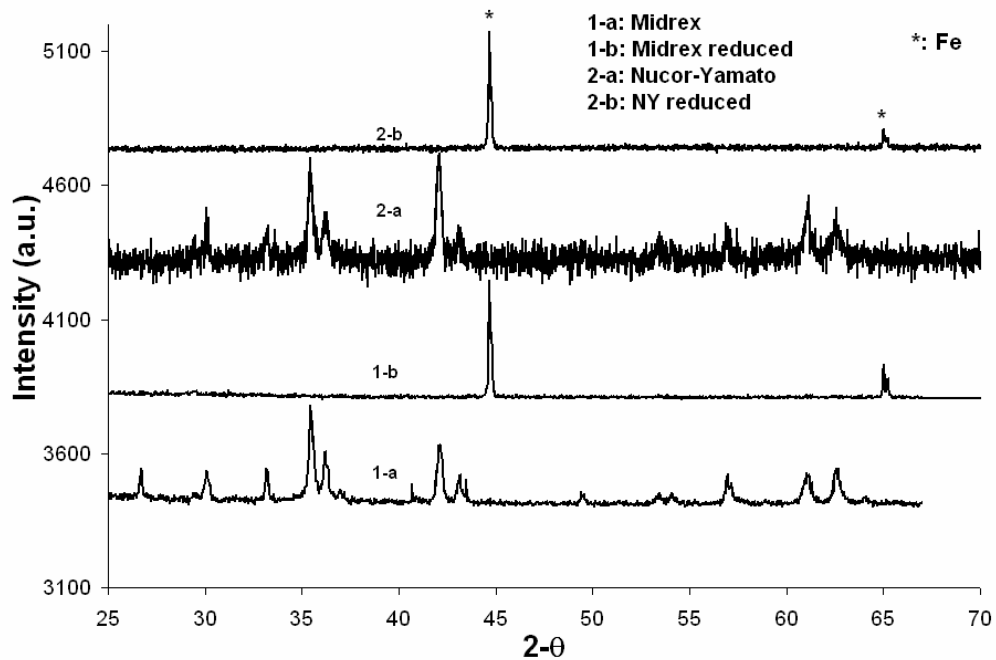
M	Mass %				
	Pickled	Sludge	Entry	Midrex	Nucor-Yamato
Fe	29.13	42.3	70.42	93.92	92.91
Cr	66.57	51.59	18.11	0.16	0.168
Mn	2.75	2.49	1.4	1.19	1.3
Ni	0.178	0.872	8.24	0.232	0.189
Ca	-	0.128	-	1.33	3.14
Si	0.332	0.267	0.357	1.49	1.05
Mo	0.282	1.3	0.53	-	-
Cu	-	0.337	0.366	0.608	0.515
V	0.412	0.259	-	-	-
Mg	-	-	-	0.209	-
Al	-	-	-	0.421	0.209

The presence of impurities (especially Cr) in significant amounts has serious implications on the environmental aspects of the process. If these mill-scales were to be used for hydrogen production, one has to isolate Fe which means disposing nickel and hexavalent chromium, the latter being a known health hazard in water system. Preliminary reduction experiments failed to generate elemental iron from NAS samples (since Ni and Cr-ferrites are difficult to breakdown), as revealed by the XRD (Fig. 1) and gravimetry. Hence, they were not used in subsequent experiments. On the other hand, hydrogen and carbothermic reduction of Midrex and Nucor-Yamato samples resulted in complete conversion of the scales into elemental iron. Figure 2 shows the XRD signatures of as-received and reduced samples from Midrex and Nucor-Yamato, which corroborates the above statement. Gravimetric analyses of the samples before and after reduction gave an average weight loss of 27.5 wt% (hydrogen reduction) and 27 wt% (carbothermic reduction) for the Midrex and Nucor-Yamato samples,

respectively, which agrees very well with the theoretical value of 27.64 wt% for the  $\text{Fe}_3\text{O}_4$  to Fe reduction.

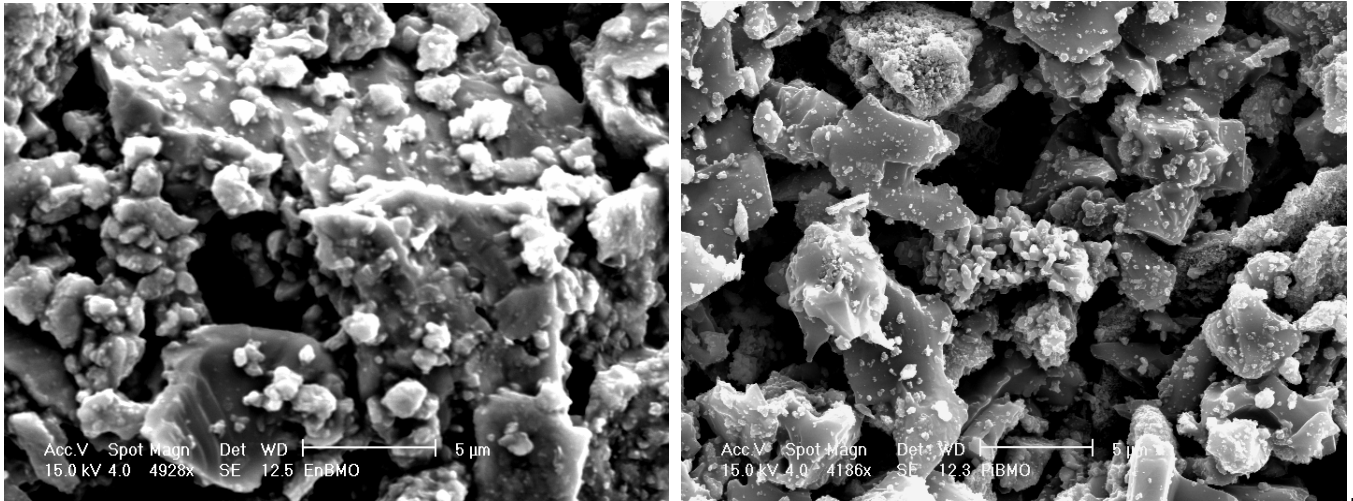


**Fig 1.** XRD spectra of the as-received and reduced mill-scale samples from NAS.



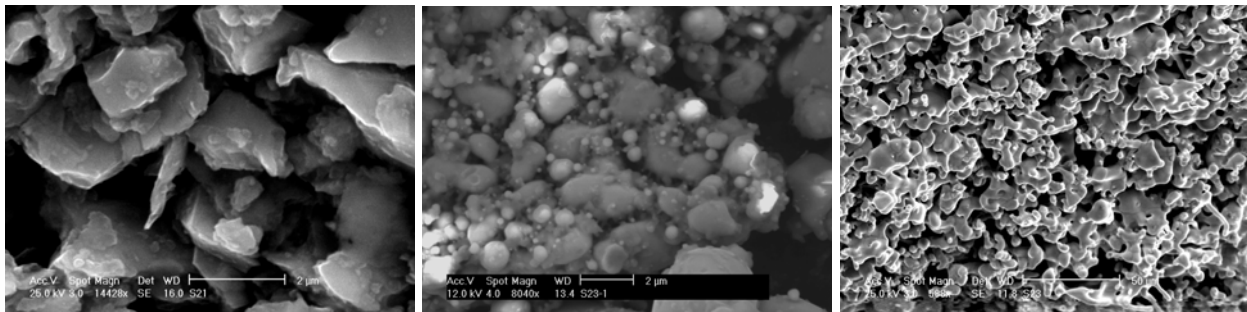
**Fig 2.** XRD patterns of the as-received and reduced Midrex and Nucor-Yamato samples.

The particle size and morphology of the entry loop sample is compared with that of the pickled sample in Fig. 3.

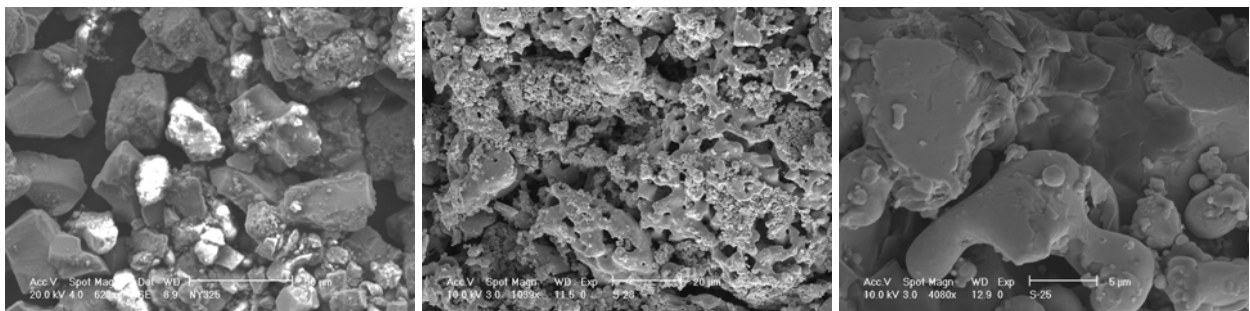


**Fig 3.** SEM micrographs of entry loop (left) and pickled (right) samples from NAS.

Figure 4 and 5 show the micro structural features of Midrex and Nucor-Yamato samples before and after reduction, respectively.

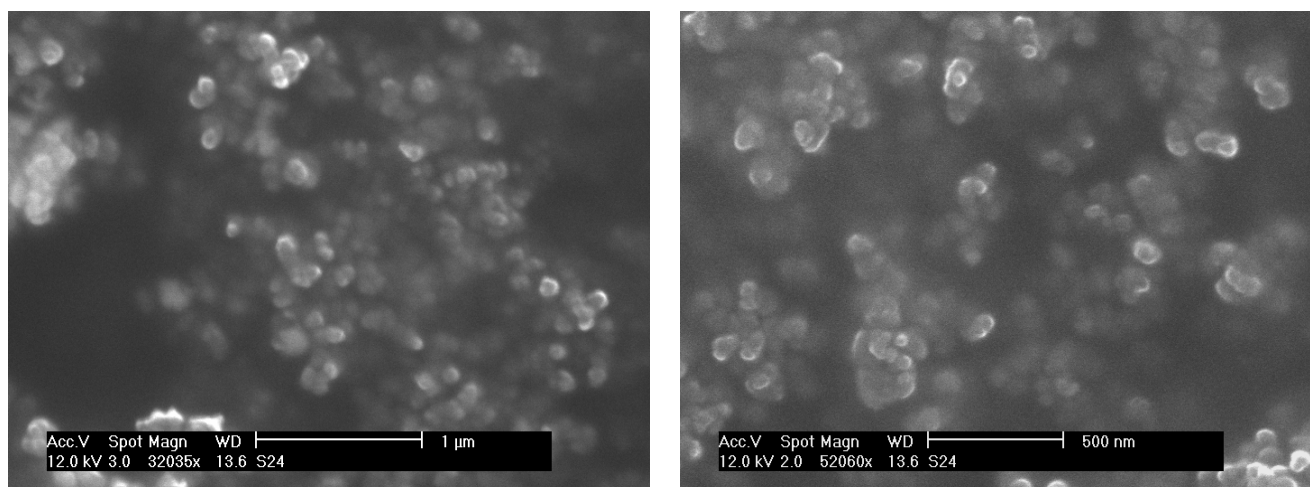


**Fig 4.** SEM micrographs of Midrex sample: attrition milled (left), after H<sub>2</sub>-reduction (center) and after carbothermic reduction (right).

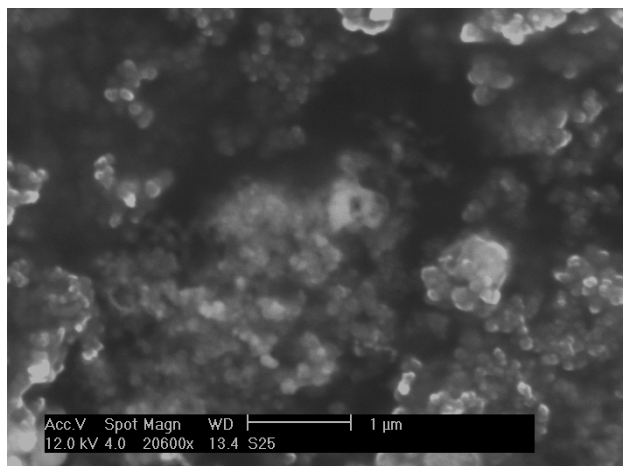


**Fig 5.** SEM micrographs of Nucor-Yamato sample: attrition milled (left), after H<sub>2</sub>-reduction (center) and after carbothermic reduction (right).

As mentioned earlier, regeneration of elemental iron from the spent oxide via hydrogen or carbothermic reduction is an energy-intensive process and hence undesirable in a commercial setting. To obviate these commercial predicaments the Midrex and Nucor-Yamato samples were dissolved in aqua regia and treated with aqueous sodium borohydride solution in the presence of sodium hydroxide as pH stabilizer (pH ~6.8) This resulted in immediate precipitation of nanoscale iron particles – a clear advantage over the agglomeration seen during hydrogen and carbothermic reduction. Figure 6 and 7 shows the SEM of the so-formed iron particles from Midrex and Nucor-Yamato samples, respectively. Figure 8 shows the TEM images of the nanoscale iron particles from Midrex, while Fig. 9 shows the SAED pattern of the nanoscale iron. The diffraction rings denote the (110), (200) and (211) planes of the body centered cubic iron.



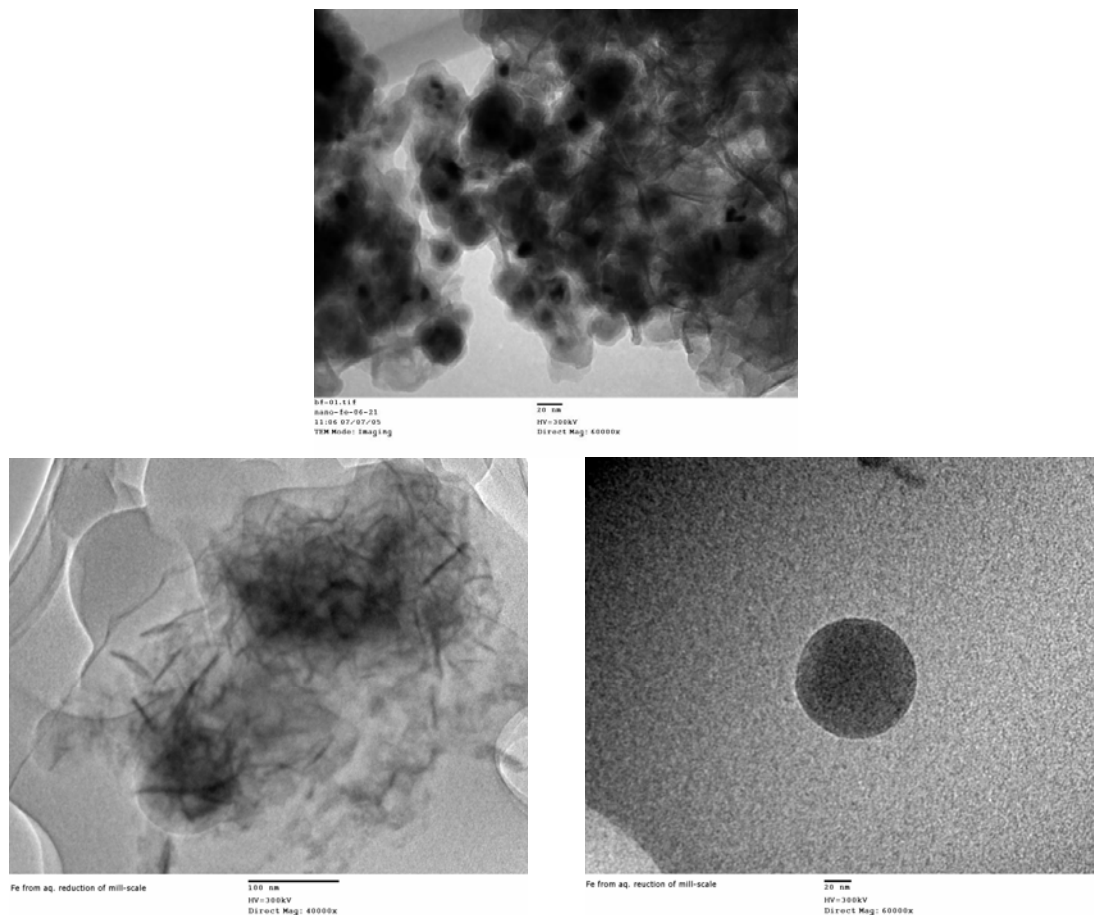
**Fig. 6.** SEM micrographs of solution-derived iron nanoparticles from Midrex sample.



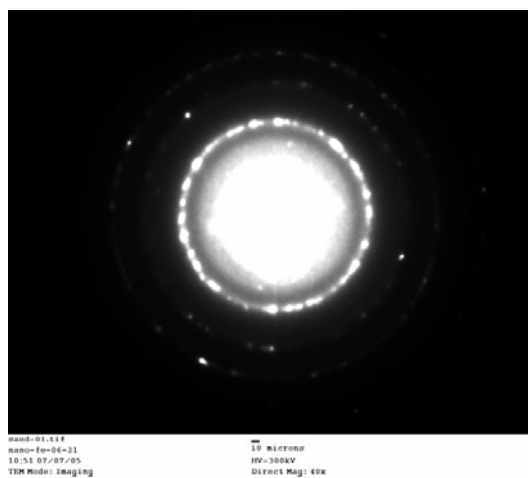
**Fig. 7.** SEM features of solution-derived iron nanoparticles from Nucor-Yamato.

Figure 10 shows the metal-steam reforming (MSR) carried out on carbothermically and H<sub>2</sub> reduced NY sample and on the nano iron obtained by room temperature aqueous reduction, under identical conditions. It can be clearly seen that a higher activity with regard to hydrogen formation by MSR is evident when solution derived nano Fe was used as compared to that by

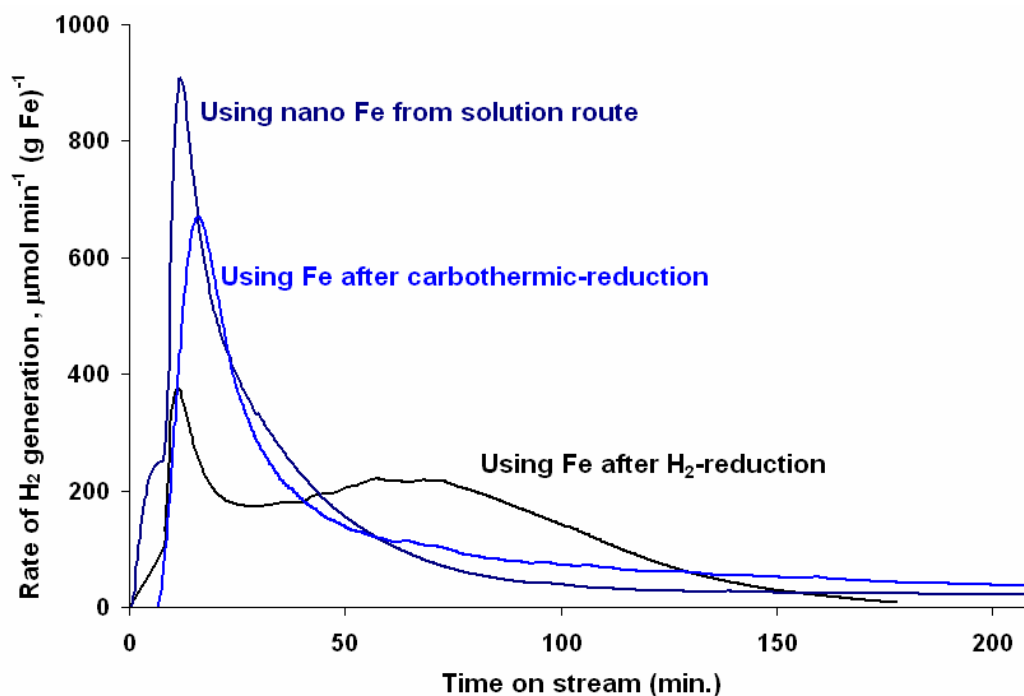
other two techniques, for 90% conversion. The magnetite formed as a result of MSR reaction can be easily dissolved in mineral acids from which high activity nano iron is again recovered without the loss of its activity towards the subsequent cycles of steam-reforming reaction.



**Fig. 8.** TEM images of iron particles obtained from steel industry waste by room temperature processing. Scale bar: 20 nm (top and right) and 100 nm (left).



**Fig. 9.** Selective area electron diffraction (SAED) pattern of the nano iron.



**Fig. 10.** Amount of hydrogen formation vs. time from Nucor-Yamato samples.

## Conclusions

Metal-steam reforming using iron is a safe and economically viable method of hydrogen generation from inexpensive raw materials for PEMFC utilization. An attractive and inexpensive source of iron is the waste from the steel industry in the form of magnetite, provided it can be reduced to metallic iron. In this work, two of the five mill-scale samples from commercial vendors were quantitatively reduced to iron via hydrogen, and carbothermic processes at high temperatures. A novel solution-based technique using aqueous sodium borohydride as the reductant, yielded nano iron with an average particle size of ~40 nm. Optimization of the latter process also obviated the formation of sodium borate as a by-product and hence the need for its separation. The hydrogen production via metal-steam reforming reaction represented by Eq. (1) shows that the nano iron possesses a higher propensity of reaction with steam than that derived via either of the high temperature reduction processes adopted here, under identical experimental conditions. Furthermore, the spent oxide can be quantitatively recycled to yield highly active nanoscale metallic iron again by an acid dissolution route without the loss of its reactivity, thereby maintaining the hydrogen generation capacity of the starting material over several cycles.

## References

1. K. Otsuka, T. Kaburagi, C. Yamada and S. Takenaka, *J. Power Sources*, **122** (2003) 111-121.
2. S. Takenaka, T. Kaburagi, C. Yamada, K. Nomura and K. Otsuka, *J. Catal.* **228** (2004) 66-74.
3. D.M.D. Santos and M.D. Mauro, *Scand. J. Metall.* **33** (2004) 229-235.