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Conversion of steel mill waste into nanoscale zerovalent iron (nZVI) particles for hydrogen generation via metal-steam reforming

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ABSTRACT

The proton exchange membrane fuel cells (PEMFCs) are the most preferred and efficient energy conversion devices for automotive applications but demand high purity hydrogen which comes at a premium price. The currently pursued hydrogen generation methods suffer from issues such as, low efficiency, high cost, environmental non-benignity, and, in some cases, commercial non-viability. Many of these drawbacks can be overcome by resorting to metal-steam reforming using iron from steel industry’s mill-scale waste. A novel solution-based room temperature technique using sodium borohydride (NaBH₄) as the reducing agent has been developed that produces highly active nanoscale (30–40 nm) iron particles. A slightly modified version of this technique using a surfactant and water–oil microemulsion resulted in the formation of 5 nm spherical Fe particles. By using hydrazine as an inexpensive and more stable (compared to NaBH₄) reductant, body centered cubic iron particles with edge dimensions ~5 nm were obtained under mild solvothermal conditions in ethanol. The nanoscale zerovalent iron (nZVI) powder showed improved kinetics and greater propensity for hydrogen generation.

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1. Introduction

Hydrogen, though not a primary energy source, has been considered to be the ideal energy-carrying medium for fuel cells, particularly the proton exchange membrane fuel cells (PEMFCs) that are of interest to the automobile industry worldwide due to some distinct advantages such as quick start up, rapid response to varying loads, high power density, low temperature of operation and higher level of technical readiness [1]. However, the PEM fuel cells require hydrogen of highest purity which is either difficult to come by, or comes at a premium price if one starts with fossil fuels. In the light of the serious economic constraints and safety concerns associated with hydrogen in the context of a truly global hydrogen economy, one needs to find ways and means of generating, storing, transporting and supplying hydrogen to the end users. Interestingly, the question of its storage and supply arises only after it is produced in large enough quantity so as to cater to the need of its use on the national and global scale.

Metal-steam reforming using iron is a safe and economically viable method of hydrogen generation from inexpensive raw materials. The use of iron and iron waste for hydrogen generation via metal-steam reforming is known. The hydrogen production using a metal-steam reforming reaction is represented by:

\[ 3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2. \] (1)
The reverse reaction could be viewed as a hydrogen storage scheme. The theoretical amount of hydrogen being stored is 4.8 wt% which corresponds to ca. 4211 L H₂/L Fe at standard temperature and pressure. In a practically viable design, the elemental iron is packed into cartridges which are loaded on the vehicle; if desired, the elemental iron cartridges may be preheated. Addition of steam to the pre-heated cartridges produces pure humidified hydrogen which could then be supplied directly to PEMFC on the vehicle. After the conversion of water into hydrogen, the cartridges with the spent iron oxide are exchanged for the new ones packed with fresh elemental iron. The spent iron oxide is again converted into ready-to-use active metal. Thus, the process of H₂ generation via MSR in an efficient and cyclic fashion consists of: (a) iron-steam reaction and, (b) reduction of the spent iron oxide into active elemental iron for the next cycle.

However, the task of making this process technologically viable and sustainable is challenging. Most importantly, the kinetic of metal oxidation (forward) and oxide reduction (reverse) as per reaction (1) ought to be significantly improved, in order to mitigate sintering and coarsening of iron and iron oxide particles during repetitive hydrogen generation-oxide conversion cycles.

With this goal, we have developed an effective technique of producing H₂ by using the so-called ‘mill-scale’ from steel industry, as an iron source, in a way that is consistent with the most sought-after criteria: environment, availability and price. An attractive and inexpensive source of iron is the waste from the steel industry in the form of magnetite, provided magnetite can be reduced to metallic iron. Mill-scale is a porous, hard and brittle coating of several distinct layers of iron oxides (predominantly Fe₃O₄) formed during the fabrication of steel structures. It is magnetic in nature with iron content up to as high as 93%. Prior to sale or use, the steel structures must be cleaned of this oxide scale. Most of the steel mill-scale waste usually ends up in landfills. A purer commercial form of this oxide in combination with nickel and zinc oxide is used in making soft magnets that are essential components of all the audio-visual components. The currently known art, however, requires a great deal of energy in the practice of making iron from the steel industry waste, as it necessitates employing high temperatures.

It can be envisioned that all process parameters and experimental conditions remaining identical, the reaction involving nanoscale iron would possess and exhibit higher propensity of reaction with steam according to Eq. (1) than the micron-scale or coarser Fe derived via either of the high temperature processes, namely, hydrogen reduction or carbothermic reduction [1–6]. Such processes are not efficient ways of producing iron from the oxide as they are energy-intensive. Moreover, the use of high temperatures results in the formation of coarse iron that is not as active or ‘potent’ and is unlikely to yield hydrogen as per the theoretical prediction owing to the limitation of gas-solid reaction via diffusion. In addition, one of them requires precious H₂ while the second process generates carbon dioxide gas (stoichiometrically, 2 mol for every three atoms of iron produced). Thus, the regeneration of elemental iron from the spent oxide via hydrogen reduction is unattractive in a commercial setting and makes the recovery of iron from steel waste more expensive than disposing such waste into a landfill. The carbothermic reduction, which produces micron size iron particles by a high temperature energy-intensive process, also leads to the generation of carbon dioxide gas thus defeating the sustainability aspect.

In the present work, novel solution-based reduction techniques were developed whereby the mill-scale is converted into highly active nanoscale iron powder. The spent oxide after the metal-steam reaction (1) could also be quantitatively recycled to yield highly active nanoscale metallic iron again, without the loss of its reactivity; thus, the hydrogen generation capacity of the same material over several cycles is maintained. Moreover, the method totally obviates the issue of sintering and coarsening of the iron/iron oxide that is a direct result of high temperature use. Consequently, the possibility of deactivation during the cyclic operation of metal-steam reforming becomes a non-issue.

The methodology employed to obtain value-added high activity nanoscale zerovalent iron (nZVI) powder from the mill-scale waste, and its use to produce hydrogen via metal-steam reaction is discussed in this paper.

2. Experimental technique

2.1. Materials and processing

Mill-scale samples procured from Midrex Technologies Inc. (North Carolina) and Nucor-Yamato Steel Company (Arkansas) were used in this study. The crude samples were ball milled followed by attrition milling in 2-propanol and sieved through 325 mesh (average particle size ~45 μm) prior to any processing or characterization. The details of hydrogen and carbon reduction of the mill-scale (that are undesirable in a commercial setting for the above-mentioned reasons) have been reported elsewhere [7,8]. To obviate these predicaments, solution-based procedures were developed. In a typical experiment, 6 g of the Midrex (MR) or Nucor-Yamato (NY) samples were first digested in 200 ml aqua regia. The undissolved non-magnetic impurities were removed by centrifugation and the clear yellow solution was made up to 250 ml with distilled water. In one case, this acid solution was treated with aqueous sodium borohydride (NaBH₄, Alfa-Aesar) solution in the presence of sodium hydroxide as pH stabilizer [9,10]. This resulted in immediate formation of nanoscale iron particles (30–40 nm)—a clear advantage over the agglomeration observed during hydrogen and carbothermic reduction.

In order to reduce the size of the nanoscale iron particles further, the borohydride reduction method was slightly modified by utilizing a combination of surfactant and co-surfactant. Water-in-oil (W/O) microemulsions also known as reverse micelle solutions are transparent, isotropic and thermodynamically stable liquid media and have been shown to offer adequate, versatile and simple method for synthesizing nanosized particles [11]. In these systems, fine microdroplets of an aqueous phase are trapped within the assemblies of surfactant molecules dispersed in a continuous oil phase. The surfactant-stabilized microcavities (typically of...
the order of 10 nm) provide a confinement effect that limits nucleation, growth and agglomeration of particles.

In a typical reverse micelle reaction technique adopted in the present work, cetyltrimethylammonium bromide (CTAB) was used as the cationic surfactant while butanol served as the co-surfactant and octane was used as the non-aqueous oil phase. All the reagents were high purity chemicals from Alfa-Aesar. The molar ratio of water to surfactant ($\omega = [H_2O]/[CTAB]$) was varied between 20 and 1000 to optimize the complete conversion of the ferric ($Fe^{3+}$) ion in the solution into zerovalent iron ($Fe^0$). In a typical run, 9 ml of the ferric-ion solution of the mill-scale powder (30.5 g mill-scale/1000 ml acid solution) diluted with 130 ml of DI water were mixed with 6.45 g of CTAB, 50 ml butanol and 100 ml octane, and homogenized by gentle and constant swirling by a magnetic stirrer. A freshly prepared solution containing 4.5 g of sodium borohydride in 13 ml DI water was slowly added to the above mixture with occasional shaking whereupon a black precipitate of strongly magnetic iron particles formed instantaneously. A molar ratio $\omega = [H_2O]/[CTAB] \approx 400$ was found to be the most optimum for the desired results. Such a high molar ratio of water to the surfactant (compared to 20 used by other investigators [12] who have essentially used commercial ferric chloride as the precursor) could possibly be due to rather high concentration of the acid associated with the mill-scale solution in the present case. The metal particles formed via the reverse micelle reduction of mill-scale by the modified borohydride reduction were $\sim 5 \text{ nm}$ in size.

Though both the original and the modified borohydride methods of reduction of mill-scale waste to zerovalent nano-iron have advantages, they are not economically feasible options as the reductant by itself is deemed hydrogen storage material and is quite expensive. Moreover, its aqueous options as the reductant by itself is deemed hydrogen storage material and is quite expensive. Moreover, its aqueous solutions are rather unstable. Therefore, in a second method, iron nanoparticles were prepared by a simple solvothermal process using hydrazine monohydrate as an inexpensive and more stable reducing agent [13]. Preliminary experiments were carried out with commercial $FeCl_3 \cdot 6H_2O$ (Alfa-Aesar, ACS min 97%) in order to first establish and optimize the experimental conditions and procedural protocols for the mill-scale reduction. In a typical experiment, 4 g of $FeCl_3 \cdot 6H_2O$ were dissolved in 20 ml absolute ethanol. Sodium hydroxide pellets (5 g) were added and the mixture was stirred for 2 h. To this, 15 ml of hydrazine monohydrate (99%+, Alfa-Aesar) were added and the mixture was transferred to a 1-L capacity stainless steel autoclave vessel (AutoClave Engineers, PA) whose internal wall was vacuum dried at 60°C. All the reagents were high purity chemicals from Alfa-Aesar, and the precipitate centrifuged and then thirty ml of the mill-scale solution was precipitated with sodium hydroxide and the precipitate centrifuged and vacuum dried at 60°C for 8 h followed by solvothermal reduction with 150 ml hydrazine monohydrate and at 50 atm initial $N_2$ pressure. This produced 4 g of nZVI. The autoclave temperature was maintained at 100°C in all the runs.

2.2. Metal-steam reforming reaction

The metal-steam reforming experiments were carried out in a cylindrical quartz reactor (OD = 1-in; ID = 0.78-in) at 600°C in a Lindberg/Blue (NC) tubular furnace with a PID controller. Hydrogen gas was used as an inert background during the temperature ramp. After the sample attained the desired temperature, a 50:50 (v/v) mixture of steam (water preheated to 400°C) and He was introduced into the reactor at ambient (1 atm) pressure. The reaction was allowed to run until no hydrogen signal was detected in the gas chromatograph unit attached to the reactor at the outlet.

2.3. Characterization

Chemical analysis of the as-received mill-scale samples was done by X-ray fluorescence (XRF) technique [7,8]. X-ray powder diffraction patterns on the raw, reduced and post-MSR samples were collected at room temperature on a Philips diffractometer (PW 3050/60 X’pert Pro), using monochromatic CuK$_\alpha$ radiations ($\lambda = 1.54056 \text{ Å}$) and Ni filter. 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 nanoscale iron particles were studied by transmission electron microscopy (TEM) (JEOL 3010) operated at 300 kV equipped with selected area electron diffraction (SAED) and the energy dispersive spectroscopy (EDS). The samples for TEM analyses were prepared by ultrasonication of a very dilute suspension of the nZVI particles in acetone for 5 min followed by placing a drop onto a copper TEM grid and drying by evaporation in ambient air. Hydrogen yield in the MSR reaction was quantified by a Shimadzu GC-2010 unit fitted with a molecular sieve 5A PLOT capillary column (30 m × 0.32 mm) and a Pulsed Discharge Helium Ionization Detector (PDHID) detector. Class-VP software was used for the peak analysis and quantification.
3. Results and discussion

Reduction of the mill-scale waste to nanoscale iron by sodium borohydride route has a number of distinct advantages over the conventional techniques, viz., (1) the reduction process is not energy-intensive, (2) no harmful/toxic gases are released and (3) it provides a mean of maintaining the material active over several cycles for hydrogen generation via MSR, thus avoiding sintering and deactivation of metal (Fe) or the metal oxide (Fe3O4) between consecutive runs.

Fig. 1 shows the SEM images of solution-derived iron nanoparticles from the MR and NY mill-scale samples, respectively, while the TEM images of the nZVI derived by sodium borohydride reduction of the Midrex sample are shown in Fig. 2.

As can be seen, the borohydride reduction leads to the formation of zerovalent iron particles that are about 40 nm in size. The powder XRD pattern collected on these particles is shown in Fig. 3 which confirms that the product of solution route reduction of mill-scale waste is indeed elemental iron possessing body-centered cubic (bcc) phase structure [14].

The TEM images of the iron particles obtained via microemulsion-based borohydride reduction (with \( \omega = 400 \)) of the mill-scale solution are shown in Fig. 4. While the individual nanoscale iron particle is about 5 nm in size, due to their strong magnetic character, the particles tend to form agglomerates that are 15–25 nm in size. The EDS spectrum collected on these particles shows that they are phase pure iron particles without any oxide impurity (Fig. 5); other peaks belong to copper from the grid used to prepare the TEM specimen. The XRD pattern of the microemulsion-derived iron nanoparticles was identical to that shown in Fig. 3 and hence is not reproduced here.

The solvothermal process using hydrazine as the reducing agent described by Xiaomin et al. [13] for the one-step synthesis of nanoscale iron was also used by Li et al. [12] for nickel. It has been found that the use of hydrazine as a reductant is particularly advantageous as it leads to the complete reduction of Ni2+ ions in solution to Ni0, as compared to the formation of Ni–B, Ni3B or Ni2B or Ni–P nanoparticles with sodium borohydride or hypophosphite [15,16]. In the context of the present work, use of
hydrazine provides the following additional and relevant advantages:

1. precise control of size (subject to processing conditions) and shape of nanoparticles,
2. the ultimate chemical state is zerovalent metallic species and not an intermetallic,
3. the process is greener as no noxious fumes or chemicals are emitted whose disposal could pose a challenge of problem; the only byproduct is nitrogen as the hydrogen is utilized in the reduction scheme,
4. the process is less energy-consuming because the reaction is carried out in an autoclave (closed system) under moderately high pressure and mild temperature, and
5. hydrazine is chemically more stable and cheaper, compared to sodium borohydride, and the process can be scaled up easily for large-scale production.

The phase composition of the product was characterized by XRD and a typical pattern of the sample obtained using commercial FeCl$_3$·6H$_2$O as the iron precursor at 5 atm N$_2$ pressure is shown in Fig. 6a.

It can be readily seen that the diffraction signature is identical to the one shown in Fig. 3. The most prominent diffraction peaks at 2$\theta$ = 44.69, 65.03 and 82.3 could again be indexed as those corresponding to the (110), (200) and (211) planes, respectively, of the phase pure $\alpha$-Fe (bcc); no iron oxides or hydroxides were detected. The strong and sharp peaks revealed that the iron powder synthesized via hydrazine reduction under solvothermal conditions was highly crystalline.

Fig. 7 shows the TEM images of the iron sample obtained by the reduction of commercial FeCl$_3$·6H$_2$O with hydrazine. The particle shows cubic morphology with the crystal edge lengths falling in two distinct size domains: one covering...
the range 300–450 nm and the other a much narrower ~30–40 nm.

The fact that these nanoparticles consist of elemental iron, is corroborated by the TEM-EDS signature shown in Fig. 8, which again is identical to the one obtained with the nano-iron derived from the mill-scale sample via microemulsion technique (Fig. 5).

Fig. 9 shows the TEM images of the nZVI particles obtained from the hydrazine reduction of a small batch of mill-scale under solvothermal conditions (100 °C/5 atm). The average size of the nZVI is around 5 nm; this is very significant from

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**Fig. 5 – EDS signature of the nanoscale iron with microscopic features shown in Fig. 4.**

**Fig. 6 – XRD patterns of the nanoscale iron obtained by solvothermal process (experimental duration: 10 h) using: (a) FeCl₃ · 6H₂O, and (b) smaller batch of the mill-scale precursor at 100 °C and initial nitrogen pressure of 5 atm.**

**Fig. 7 – TEM images of the iron particles obtained by solvothermal reduction of ferric chloride solution; scale bar: 100 nm (top) and 20 nm (bottom).**
pressures of 5 and 10 atm N2 are shown in Fig. 10a and b, hydroxide slurry reduced by hydrazine at the ambient prevailing in the conditions employed here), at high temperature, in strongly alkaline solutions (such as those prevailing in the conditions employed here), at high temperature; in order to overcome this limitation and to realize successful conversion of the mill-scale waste into nano Fe on a large-scale, an alternative route was established. In this case, ferric hydroxide (precipitated from precursor solution with sodium hydroxide, centrifuged and vacuum dried) was used as the feed in the solvothermal reaction.

The XRD patterns obtained on the 0.5 g batch ferric hydroxide slurry reduced by hydrazine at the ambient pressures of 5 and 10 atm N2 are shown in Fig. 10a and b, respectively. In the first case, the product was identified as a mixture of Fe3O4 and Fe whereas in the second case, pure α-Fe was obtained; this is clearly related to the high N2 pressure in the later case. Similar trend was observed when 2.5 g batch of the ferric hydroxide were autoclaved with hydrazine at N2 pressures of 10, 40 and 60 atm. XRD showed mixture of Fe3O4 and Fe in the first two cases (Fig. 10c and d) whereas pure α-Fe was obtained in the third case (Fig. 10e). As is evident, the diffraction peaks become sharper and more defined as the initial N2 pressure increases which aids higher crystallization. These results can be explained as follows. The pH of the solution plays an important role too in aiding the reduction of Fe3+ ion by hydrazine. This can be deduced from the values of the standard electrode potential for the reactions in acidic and alkali solution:

\[
\begin{align*}
N_2H_4 & \leftrightarrow N_2 + 4H^+ + 4e^- \quad \text{(acidic; } E' = -0.23 \text{ V}), \\
N_2H_4 + 4OH^- & \leftrightarrow N_2 + 4H_2O + 4e^- \quad \text{(alkaline; } E' = -1.15 \text{ V}).
\end{align*}
\]

\[
N_2H_4 + 3N_2H_4 \leftrightarrow 4Fe + 12H_2O + 3N_2.
\]

or,

\[
4Fe^{3+} + 12OH^- \leftrightarrow 3N_2H_4 + 4FeO + 12H_2O + 3N_2; \quad E' = +0.36 \text{ V}.
\]

The positive value of the standard electrode potential indicates that theoretically, reduction of Fe(III) to Fe(0) with hydrazine is feasible. However, as discussed above, when the reaction is conducted in an open system (ambient pressure ~1 atm) keeping other conditions same, the predicted reduction does not proceed and consequently no iron could be produced. It is likely that the spontaneous disproportionation of hydrazine in strong alkaline solution supersedes the reduction, as given by

\[
3N_2H_4 = 4NH_3 + N_2; \quad E' = +1.05 \text{ V}.
\]

Even when conducted under closed-system conditions, up to certain threshold pressure (~5 atm for 0.5 g and 40 atm for 2.5 g batches, respectively), a phase mixture of Fe3O4 and α-Fe was obtained. This could be related to the fact that with steady rise in the reaction temperature, there is a concomitant increase in pressure as well, suggesting the likelihood of reactions (4) and (6) occurring concurrently. Initially, reaction (6) dominates and a condition of relative high pressure is
established within the autoclave by the gas mixture generated in situ. When the pressure build-up reaches and then exceeds a given threshold, it begins to restrain and even reverse the direction of reaction (6), thus allowing the desired reaction (4) to proceed. With time, reaction (6) is further constrained while reaction (4) gradually and steadily preponderates, causing the reduction of Fe(III) ions to go to completion. However, if the pressure build-up is not decisively high enough, both reactions compete, yielding a mixture of Fe$_3$O$_4$ and Fe.

To substantiate the above-mentioned speculation, pressure build-up in the autoclave vessel (which is equipped with an online chart recorder to register instantaneously the temperature and pressure values throughout the operation) was constantly monitored in each case. As mentioned above, pure nZVI formed when 0.5 and 2.5 g batches of Fe(OH)$_3$ were autoclaved under 10 and 60 atm initial N$_2$ pressure, respectively. Under these conditions, real-time monitoring showed that the pressure within the vessel rose steadily and reached a steady value of ~14 and ~75 atm, respectively. Under these high pressure conditions, the undesired reaction (6) is restrained while reaction (4) is dominant, causing the complete reduction of Fe(III) to Fe(0). The XRD signatures shown in Fig. 10b and e corroborate the formation of nZVI from these two batches.

In an attempt to scale-up the nZVI production further (4 g batch; from 7.85 g Fe(OH)$_3$ either from (i) commercial Fe(III) chloride precursor or, (ii) 130 ml of the mill-scale acid solution and, using 150 ml of hydrazine monohydrate), it was required to initiate the operation of the autoclave at 60 atm initial N$_2$ pressure and the steady-state pressure reached ~109 atm.

In the course of these studies it was also found that the process economics could be greatly improved by eliminating the vacuum drying stage and mere neutralization of the acid content of the solution with NaOH followed by centrifugal extraction of the precipitate [Fe(OH)$_3$] would suffice. For example, 13.5 g of Fe(OH)$_3$ was obtained from 250 ml of the mill-scale solution (30.5 g mill-scale/1000 ml acid solution) and with adequate amount of NaOH. The precipitate was centrifuged (but not vacuum dried). Seventy-five ml of hydrazine monohydrate and 60 atm initial N$_2$ pressure was needed to yield 7.5 g of nZVI. Experiments are currently underway to examine if complete conversion to nZVI can be achieved under milder pressure conditions by using blanket gases (such as He or Ar) instead of N$_2$.

Fig. 11 compares the hydrogen yield from metal-steam reforming reaction carried out at 600 °C by using elemental iron obtained via a number of reduction techniques employed in this work: namely, using hydrogen, carbothermic, sodium borohydride and hydrazine. For a ready appreciation of the relative propensity of various iron samples for hydrogen generation via metal-steam reforming reaction vis-à-vis the schemes employed for their recovery from the mill-scale waste, representative microstructural features are also included. The correlation between the particle size and kinetic profile of hydrogen generation is quite evident. Even though the amount of hydrogen generated per gram of iron sample (given by the area under the respective curve) is nearly the same within the precision limits of such measurements by gas chromatography, the mode of hydrogen generation is very characteristic of the morphological features of the iron used. For instance, the fastest hydrogen release kinetics were
observed with the cubic 5 nm nZVI derived from solvothermal hydrazine reduction route, followed by those with 40 nm nZVI particles obtained via sodium borohydride reduction at room temperature. In both these cases, about 90% of hydrogen was released within the first 10–15 min of the MSR initiation. In comparison, the effect of larger grain size (micro versus nano) of iron particles derived via high temperature hydrogen and carbothermic (high temperature), and borohydride and hydrazine (low temperature).

It is worth pointing that the initial MSR reaction carried out in a quartz reactor using stainless steel filter as the sample holder, yielded more H₂ than predicted theoretically (Eq. (1)) compared to the case where iron powder was kept in an alumina crucible. This is shown in Fig. 12.

This anomaly can be explained by taking into account the fact that the steel reactor also participated in the MSR reaction. Therefore, in all the subsequent runs, the steam reforming was carried out by placing the iron sample in an alumina crucible which was contained in a quartz reactor with quartz wool plugs. The data shown in this paper pertain to the experiments conducted under those conditions. That the MSR reaction was based on a classical solid–gas diffusion-controlled mechanism, became evident from the relative shapes of the hydrogen release curves (akin to those shown in Fig. 11 but not shown here); the kinetics for 90% hydrogen attractive, as the magnetite formed after the steam reforming can be recycled to generate fresh batch of active nano-iron particles for subsequent MSR cycles again.

Fig. 10 – XRD patterns of the samples obtained by solvothermal process from mill-scale via precipitation route using: 0.5 g batch at 5 atm (a) and 10 atm N₂ pressure (b); 2.5 g batch at 10 atm (c); 40 atm (d) and (e) 60 atm N₂ pressure.

Fig. 11 – Comparison of hydrogen yield from MSR reaction at 600 °C and the mode of hydrogen release using iron from mill-scale after reduction by hydrogen and carbothermic (high temperature), and borohydride and hydrazine (low temperature).

Fig. 12 – Effect of the reactor material on the H₂ yield from MSR at 600 °C using nZVI.
generation were found to be faster for powder samples than for the pellets.

The TEM and high-resolution TEM images of the post-MSR samples, where the NBH-derived nZVI powder was used, are shown in Fig. 13a and b, respectively. One can notice slight increase in the particle size due possibly to the conversion of iron (Fe: bcc) into magnetite (Fe₃O₄: spinel) and some sintering. The XRD pattern of the post-reformed sample is shown in Fig. 13c, which conforms to that of magnetite, Fe₃O₄ (ICDD 79-0418) in its entirety.

As highlighted above, the ambient sodium borohydride and the solvothermal hydrazine reduction techniques employed in this work, have certain distinct advantages of producing highly active nanoscale iron from a precursor that comes from an industrial waste. They are, however, still somewhat disadvantageous in a commercial setting for the generation of hydrogen via metal-steam reforming due mainly to: (i) the high cost of the reducing agents, and (ii) the overall energy balance when the entire life cycle of the process is taken into account. This is due to the fact that the manufacturing of the two reducing agents themselves involves the use of hydrogen or hydrogen-bearing sources as the raw materials. Synthesis of sodium borohydride and hydrazine both, is an energy-intensive process, which could lower the energy efficiency of the whole cycle. For example, hydrazine hydrate is produced commercially by a number of techniques, viz., the Raschig process, the ketazine process, and the peroxyde process all of which require ammonia as the raw material [17,18], which in turn is made by the catalytic combination of hydrogen with nitrogen. This, in turn, increases the overall energy input of the entire process. Consequently, the cost of the unit process also goes up despite the fact that the mill-scale waste is rather inexpensive (almost free). The energetics and conversion cost could become attractive if a regenerable non-hydrogen reductant becomes viable. Hydrogen generation via metal steam-steam reforming would become more meaningful.

Work is currently in progress to find alternative reductants that are capable of reducing Fe³⁺ to nZVI without the above caveat, thereby making the process economically feasible.

4. Conclusions

By using a solution route we have obtained high purity nano-iron particles of average size ~40 nm at room temperature and ambient pressure with sodium borohydride as the reducing agent. By using a slightly modified process (with CTAB as surfactant, butanol as cosurfactant and octane as the oil phase), the particle size was reduced to ~5 nm. In another case, by using hydrazine as an alternate reductant and solvothermal conditions (100 °C/5 atm), bcc iron particles ~5 nm in size were obtained. This is a significant achievement in that hydrazine is more stable and much less expensive reductant compared to sodium borohydride, and the solvothermal process is easily scalable. The performance of nanoscale ZVI in the metal-steam reforming experiments was superior to that of iron derived from the reduction of the mill-scale samples by means of hydrogen and/or carbon at elevated temperatures. Thus, large particle size, reduced surface area and agglomeration become non-issue in the case of solution route of generating elemental iron of higher catalytic activity. Hydrogen generation via metal-steam reforming using nanoscale iron derived from mill-scale waste would become a benign proposition both in its energy intensiveness and the overall economics of the process, if and when an alternative non-hydrogen bearing regenerable reductant becomes viable. This work is in progress.
REFERENCES

[14] ICDD card # 6-0696.