2160 *Chem. Mater.* **2001,** *13,* 2160−2168

Chemical Synthesis, Processing, and Characterization of Nanostructured Fe−B for the Magnetically Assisted Chemical Separation of Hazardous Waste

P. Fulmer, M. Manivel Raja, and A. Manthiram*

Materials Science and Engineering Program, ETC 9.104,
The University of Texas at Austin, Austin, Texas 78712

Received January 5, 2001. Revised Manuscript Received March 26, 2001

Nanostructured Fe−B alloys have been synthesized by reducing aqueous $FeCl_2$ with potassium borohydride both in the presence and in the absence of an applied magnetic field and investigated for the separation of hazardous waste in the magnetically assisted chemical separation (MACS) process. Linear chain and discrete particle microstructures of Fe−B are obtained depending on the reaction conditions. The Fe−B samples exhibit a saturation magnetization as high as 190 emu/g after annealing in a 90%Ar−10%H_2 atmosphere at 400 °C. The Fe−B magnetic materials are then encapsulated within a uniform polyacrylamide matrix using a solution-based technique developed in this study. With an optimum surfactant concentration, homogeneous Fe−B/polyacrylamide composite materials could be readily prepared. The particle size of the composite could be controlled by varying the monomer concentration during the polymerization. Laboratory level testing with a surrogate species (cobalt ions) indicates that these materials are highly suitable for the MACS process. For example, partitioning coefficient values greater than 6000 and 8200 mL/g are obtained at pH = 6.5 for the composites based on Fe−B chain and particle microstructure, respectively.

Introduction

The development of advanced nuclear weapons by the United States government during the past 50 years has led to the storage of millions of gallons of radioactive and hazardous byproducts in underground storage tanks at various sites across the country. With the end of the Cold War era, the Department of Energy (DOE) has shifted its attention toward reducing the total volume of such wastes and developing more effective procedures for long-term storage. The long-term objective of the DOE programs is the development of appropriate remediation processes to reduce the potential risk posed by underground tank wastes.[1] However, traditional laboratory techniques such as liquid−liquid (solvent) extraction and ion-exchange chromatography[2] lack both the selectivity and efficiency that would be required for implementation in a large-scale waste remediation facility. As a result, much attention is being directed toward the development of new methodologies that offer high efficiency and excellent selectivity while still presenting a cost-effective and feasible option for DOE sites having numerous underground storage tanks.

In response to the growing need for a feasible actinide separation process, researchers at the Argonne National Laboratory have developed the Magnetically Assisted Chemical Separation (MACS) process. The MACS process utilizes ferromagnetic composite materials for the separation of actinides from the waste tanks at DOE sites.[3−7] Before being used for the separation process, selective organic extractants such as octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) derivatives[8−10] are coated onto the composite material. The coated microparticles are then added directly to the contents of the waste tank. The organic extractant chelates with the radioactive and hazardous species contained within the tank while still being absorbed onto the polymer surface of the composite material. The loaded microparticles are then recovered through the application of an external field to the waste tank or through the direct immersion of a permanent magnet into the tank.

The recovered microparticles may be disposed of as high-level waste while the remaining liquid can be treated as low-level waste. Alternatively, the contami-

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* To whom correspondence should be addressed.

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10.1021/cm010014j CCC: $20.00 © 2001 American Chemical Society
Published on Web 05/12/2001

nated coating can be stripped from the microparticles. In doing so, the total volume of high-level waste will be significantly reduced even further, and the microparticles can then be recycled through the application of an additional organic coating.[11] However, the microparticles currently employed for the MACS process were originally designed for immunological assays. These particles, which are marketed under the trade name MagaCharc by Cortex Biochem, Inc., consist of a 1:1:1 mass ratio of Fe_3O_4 (magnetic), a cross-linked polyacrylamide, and Norit SX-Ultra charcoal.[12] MagaCharc has a particle size distribution of 0.1−25 μm and has a saturation magnetization, M_s, value of ≈16 emu/g.[4] Moreover, electron microscopy studies have shown that MagaCharc and other commercially available magnetic composite materials contain a significant fraction of magnetic particles that are not completely bound to the polymer matrix.[11] As the micron-size particles currently employed for the MACS process were originally designed for other purposes, the MACS process may not be fully optimized. The full potential of the MACS process may be realized by employing materials with smaller particle sizes. However, the reduction in particle size may result in a lower magnetization per particle. In turn, this may prevent the loaded particles from being readily retrieved from the waste tank. This problem can be circumvented by employing alloys with a higher magnetization per unit volume. In this regard, Fe and Fe-based alloys are attractive as they have a higher magnetization per unit volume than Fe_3O_4.

Generally, a solution-based synthesis route is used to obtain small particle size. For example, nanometer-size iron particles consisting of some boron (Fe−B particles) are known to be easily prepared through a borohydride reduction of the corresponding metal salt solutions.[13−17] However, the literature data on borohydride reduction show a maximum saturation magnetization value of 160 emu/g for Fe−B,[13−15] which is quite low relative to the theoretical value of 218 emu/g for pure Fe. So the first objective of this paper is to investigate systematically the influence of synthesis conditions of the borohydride reduction on the microstructure and magnetic properties of Fe−B alloys and develop Fe−B alloys with high saturation magnetization.

To be employed for the MACS process, the nanosize magnetic alloys must be encapsulated within a polyacrylamide matrix. However, the literature contains no techniques available for accomplishing this task. Therefore, the second objective of this investigation is to develop a solution-based technique to encapsulate the nanosize alloys within a uniform polyacrylamide matrix. The magnetic composite material resulting from this process will have submicron dimensions and a higher magnetization per unit volume than the commercially available MagaCharc particles currently employed for the MACS process. The third objective is to test the magnetic composite materials prepared here in a MACS process using a surrogate species. Toward this task, the composite materials are coated with an organic extractant (Cyanex-272) and tested in a MACS process for the removal of cobalt ions from aqueous solution.

Experimental Section

The Fe−B alloys (particles and chains) were prepared with a laboratory-made T-form reactor and electromagnet apparatus shown in Figure 1. Required amounts of KBH_4 and $FeCl_2 \cdot 4H_2O$ salts were dissolved in deionized water and equal volumes of the reactants were placed inside the syringes. The solutions were then slowly fed through the Tygon tubing, and the reduction reaction occurred stoichiometrically inside the T-form reactor in the absence and presence of an applied magnetic field (3000 Oe). The alloys were then subjected to an annealing treatment in a flow of 10%H_2−90%Ar to cleanse the oxidized surfaces. The magnetic materials were then coated with a cross-linked polyacrylamide by adding a known mass of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), to a beaker containing 50 mL of a nonaqueous solvent, *N*,*N*′-dimethylformamide (DMF), and 0.2 g of Fe−B alloy. This mixture was placed in a sonicator for 10 min to aid the dispersion of Fe−B in the solvent. Appropriate quantities of acrylamide and the cross-linking agent (*N*,*N*′-methylenebisacrylamide) were then dissolved in the dispersed solution. After transferring the dispersed solution to a three-neck round-bottom flask equipped with a nitrogen inlet and a magnetic stir bar, a small amount (50 mg) of the free radical initiator (potassium persulfate) was added. A flow of nitrogen was passed through the flask as a warm water bath surrounded the round-bottom flask to promote the polymerization. After being stirred for 2.5 h, the solution was filtered and washed three times with ethanol. The samples were characterized before and after polymer coating by X-ray powder diffraction, Hitachi-4500 scanning electron microscopy (SEM), and SQUID magnetic measurements at 5 K.

To prepare the composite material for the MACS process, the Fe−B/polymer composite material was coated with an organic extractant (Cyanex-272). The Cyanex-272 was obtained in 80% purity as a gift from Cytec Industries, Inc. The Fe−B/polymer composite material (0.2 g) was placed in a Teflon beaker containing 4 mL of ethanol and 0.23 g of Cyanex-272. The Teflon beaker was placed in a sonicator for 10 min to aid the dispersion of the composite material in the viscous solution of the extractant in ethanol. The ethanol was then allowed to evaporate, leaving the extractant-coated composite material in the Teflon beaker. The MACS process was carried out as follows. A known mass of the extractant-coated particles was added to 50 mL of a 2 mg/L Co^{2+} aqueous solution prepared by dissolving cobalt acetate tetrahydrate in deionized water. The pH of the solution was adjusted as required, and the particles were stirred in the cobalt solution for 20 min. The loaded particles were removed from the aqueous solution by placing the reaction vessel between the poles of an electromagnet and carefully decanting the solution from the loaded particles.

Results and Discussion

Synthesis and Characterization of Fe−B Alloys. The Fe−B samples were prepared in the presence and absence of an applied magnetic field to obtain linear chain and discrete particle microstructures. The linear Fe−B chains were prepared by mixing equal volumes of 0.1 M $FeCl_2$ and 0.1 M KBH_4 solutions in the T-form reactor in the presence of an applied magnetic field of 3000 Oe. Discrete Fe−B particles were prepared by mixing equal volumes of 0.1 M $FeCl_2$ and 2.0 M KBH_4 solutions in the T-form reactor in the absence of a magnetic field.

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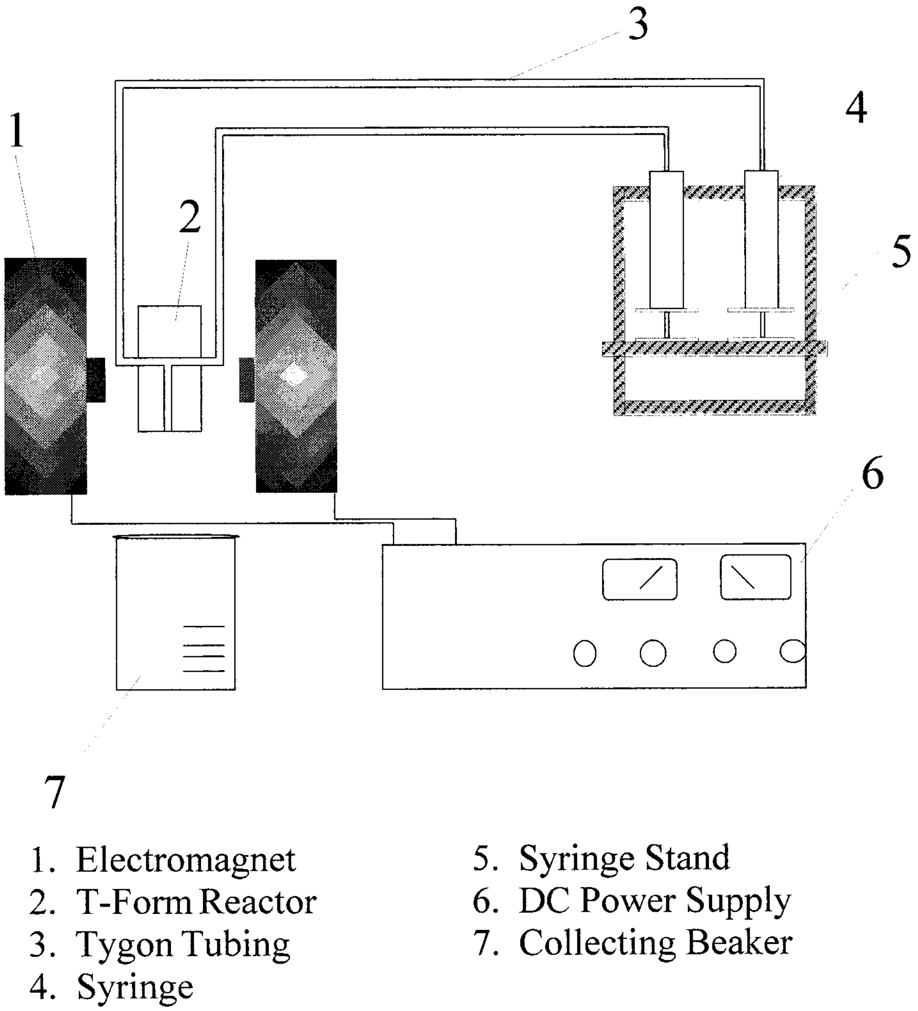

Figure 1. Schematic of the T-form reactor used for the synthesis of Fe−B chains and particles.

After the heat treatment to clean the surface, all samples were characterized by X-ray diffraction, TEM, and SQUID magnetometer measurement. X-ray data show reflections corresponding to BCC Fe with no indication of any oxide phase. Figure 2 shows the TEM photographs of both the samples. It shows that the sample prepared in a magnetic field consists of linear chains composed of spherical particles of 50−60 nm in size whereas the sample prepared in the absence of a magnetic field consists of discrete particles of ≈25 nm in size. The sample with the chain microstructure was found to exhibit a saturation magnetization value of 190 emu/g (Figure 3), which is higher than that previously reported in the literature[13−17] for Fe−B samples prepared by the borohydride reduction method. The slightly lower magnetization compared to the theoretical value of 218 emu/g for Fe is due to the presence of some B in the sample as indicated by chemical analysis (inductively coupled plasma analysis). The sample with the discrete particle microstructure was found to have a saturation magnetization value of 136 emu/g.

Processing of Fe−B Alloys for Use in the MACS Process. The Fe−B alloys synthesized must be encapsulated within a uniform polyacrylamide matrix prior to the MACS process. As there are no techniques available in the literature for accomplishing this task, a comprehensive investigation was required to develop a solution-based polymerization technique. The two selected microstructures (linear chain and discrete particles) were encapsulated within a polymer matrix using the procedure described in the Experimental Section. A nonaqueous solvent, *N,N′*-dimethylformamide (DMF), was chosen as the medium because preliminary experiments using an aqueous medium caused oxidation of the Fe−B during the course of the polymerization. Such oxidation significantly reduces the overall magnetic moment of the resulting Fe−B/polymer composite material. With the objective of developing a variety of magnetic composite materials for the MACS process, both the particle and the chain microstructures were extensively investigated. To maximize the surface area of the Fe−B during the polymerization of acrylamide, the Fe−B particles or chains were dispersed in solution using a cationic surfactant, cetyltrimethylammonium bromide (CTAB).

(a) Optimization of Surfactant Concentration. To determine the precise influence of the surfactant concentration, experiments were carried out using various CTAB concentrations from 0.001 to 1.0 M with a fixed monomer concentration of 0.05 M. SEM micrographs of representative Fe−B/polymer composite materials prepared with Fe−B chains are shown in Figure 4. With low CTAB concentrations, a nonuniform polymer coating is evident in addition to a large degree of agglomeration. Very high surfactant concentrations lead to composite materials in which the particle or chain

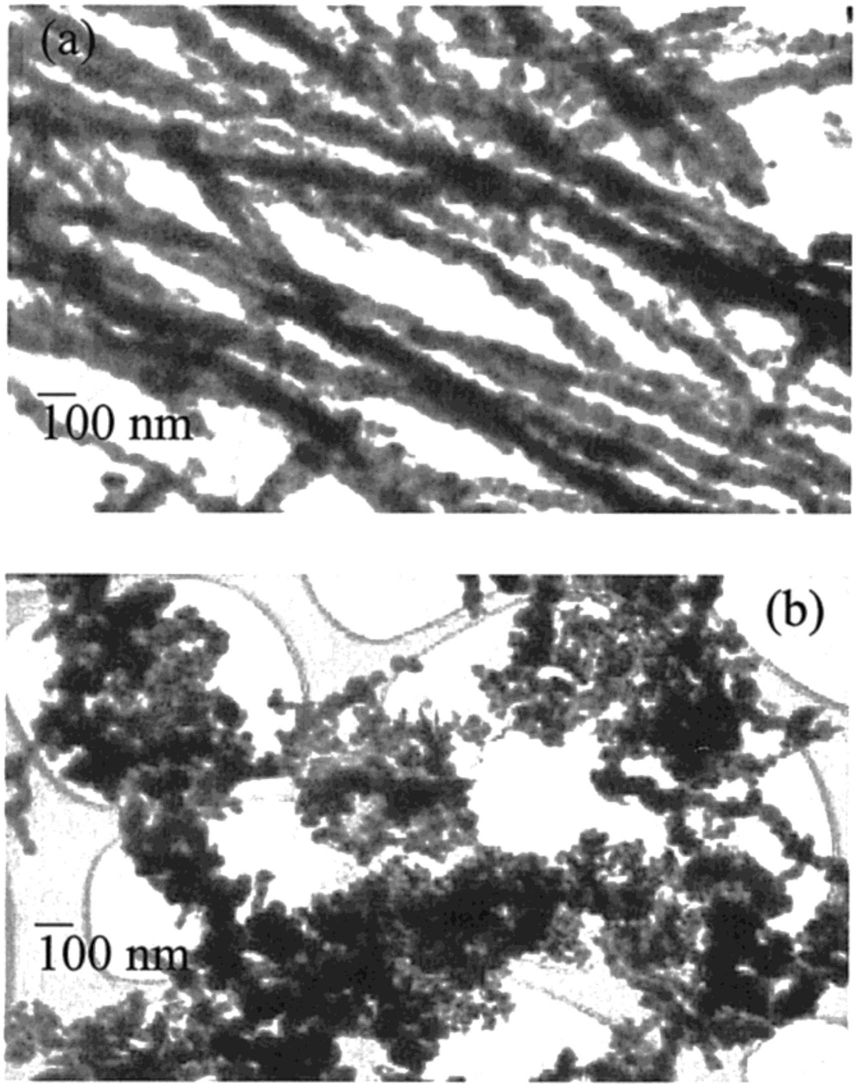

Figure 2. TEM micrographs of Fe−B alloys prepared in the T-form reactor: (a) in the presence of an applied magnetic field of 3000 Oe and (b) in the absence of a magnetic field.

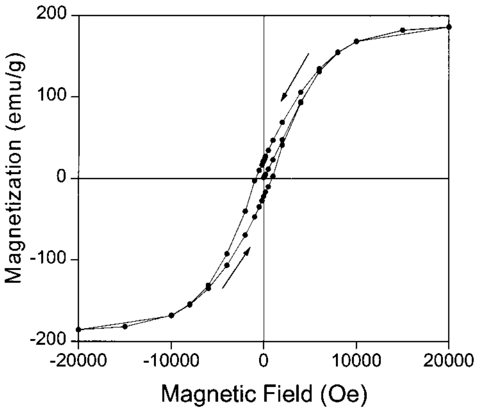

Figure 3. Magnetic hysteresis loop for Fe−B chain microstructure that was prepared with 0.1 M iron chloride and 0.1 M borohydride in the presence of an applied magnetic field (3000 Oe).

microstructure is obscured by the formation of nonuniform entities, which suggests that the excess surfactant is becoming trapped within the polymer matrix. Interestingly, a surfactant concentration of 0.1 M leads to a more homogeneous composite material as seen in Figure 4b. The particle size of the Fe−B chains is 65 nm before polymerization. It is evident from the SEM photographs that the particle size—the width of the chain structure—is significantly increased after the polymerization. This suggests that the Fe−B chains are encapsulated within the polymer matrix during the course of the polymerization reaction. A detailed investigation of this assumption is presented below.

(b) Synthesis of Fe−B/Polyacrylamide Composite Materials. As mentioned earlier, both the Fe−B chains and discrete particles were encapsulated within the polyacrylamide matrix. With an optimum surfactant concentration of 0.1 M, the monomer concentration was varied from 0.01 to 2.0 M to determine if the monomer concentration would allow for control of particle size after the polymerization. Figure 5 shows the X-ray diffraction patterns of the Fe−B/polymer composites prepared with Fe−B chains and various concentrations of monomer. The X-ray data reveal that the intensity of the diffraction peaks corresponding to BCC Fe decreases as the mass fraction of polymer in the composite material increases. More importantly, the diffraction patterns do not contain reflections corresponding to the oxide phase, indicating that the use of a nonaqueous solvent does indeed prevent oxidation.

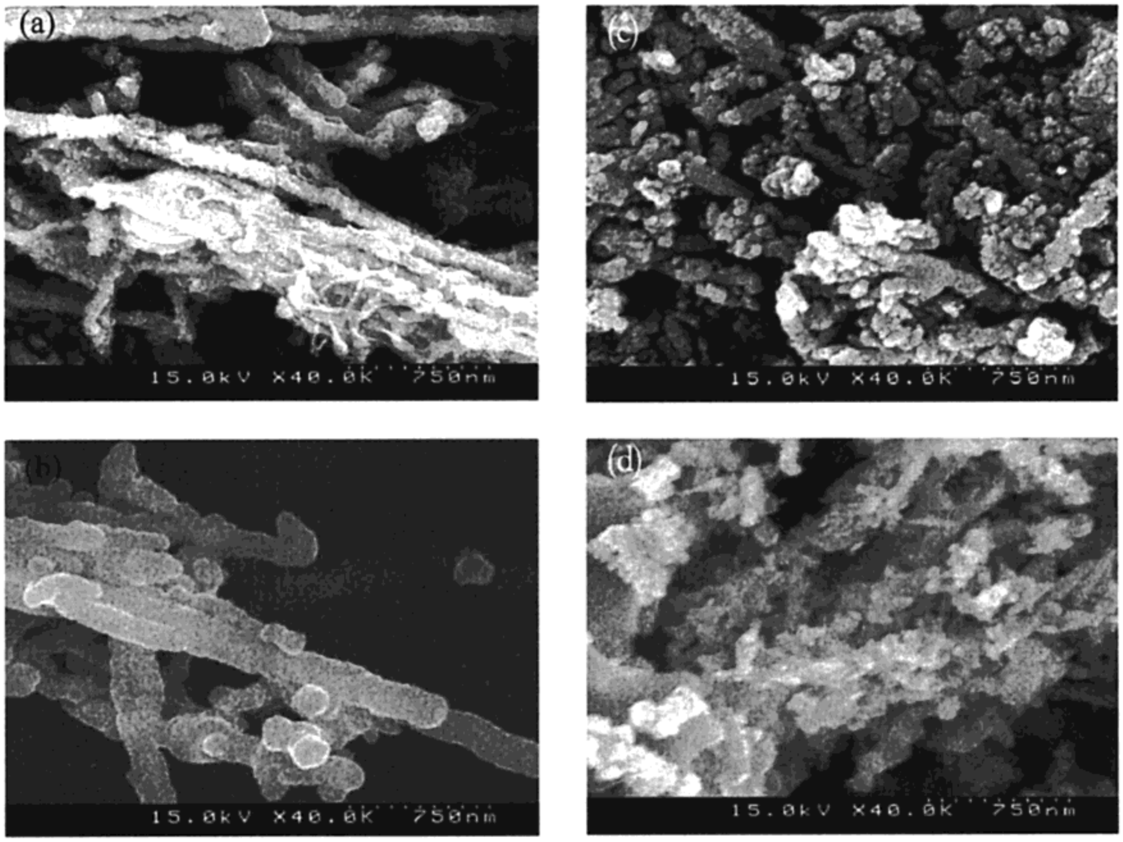

Figure 4. SEM micrographs of Fe–B chain/polymer composite materials prepared using 0.05 M monomer solution and with (a) 0.001 M, (b) 0.1 M, (c) 0.5 M, and (d) 1.0 M CTAB (surfactant) concentrations.

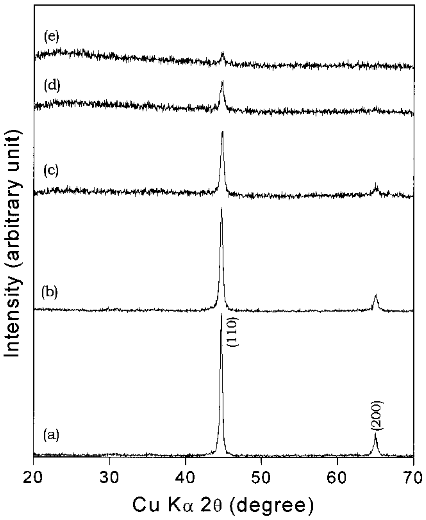

Figure 5. X-ray powder diffraction patterns of Fe–B chain/polymer composite materials prepared with 0.1 M CTAB and monomer concentrations of (a) 0.01 M, (b) 0.025 M, (c) 0.07 M, (d) 1.0 M, and (e) 2.0 M.

High-resolution SEM micrographs of representative Fe–B chain/polyacrylamide composite materials are shown in Figure 6. With very low monomer concentrations (0.01–0.5 M), chain microstructures with increased diameters are formed. With monomer concentrations greater than 0.5 M, large polymer particles obscuring the underlying microstructure of the magnetic material are formed. The influence of the monomer concentration on the particle size of the resulting composite material is shown in Figure 7. The particle size refers to the width of the chain structure, if it is not obscured by the formation of large polymer particles and the diameter of the polymer particles if the chain structure is obscured. As seen in Figure 7, the particle size can be varied from 80 nm to ≈2 μm by controlling the monomer concentration during the reaction.

The SEM micrographs of Fe–B particle/polyacrylamide composite materials are shown in Figure 8. For composite materials prepared with low monomer concentrations, the micrographs show that the particles are highly agglomerated. As these spherical Fe–B particles have nanosize dimensions, this agglomeration is difficult to prevent. High monomer concentrations yield particles with diameters of ≈350 nm. The variation of the particle size of the Fe–B particle/polymer composite material with the monomer concentration is also shown in Figure 7. The particle size increases from 50 to 350 nm as the monomer concentration increases from 0.01 to 1 M and remains constant around 350 nm for monomer concentrations of 1–2 M.

(c) Evidence of Polymer Coating on Fe–B Chains. In the previous sections, it was noted that the width of the chain structure after the polymerization increased significantly. Although the increased width of the chain structure suggests that the Fe–B chains are encapsulated within a polymer matrix, further experiments were designed to prove this assumption. Accordingly, the Fe–B/polymer composite materials were examined in the SEM without applying a chrome coating as seen in Figure 9. The contrast and brightness levels in this photograph were adjusted beyond normal limits to obtain a relatively clear image as charging was readily evident when normal levels of contrast and brightness were used. In this micrograph, the underlying Fe–B

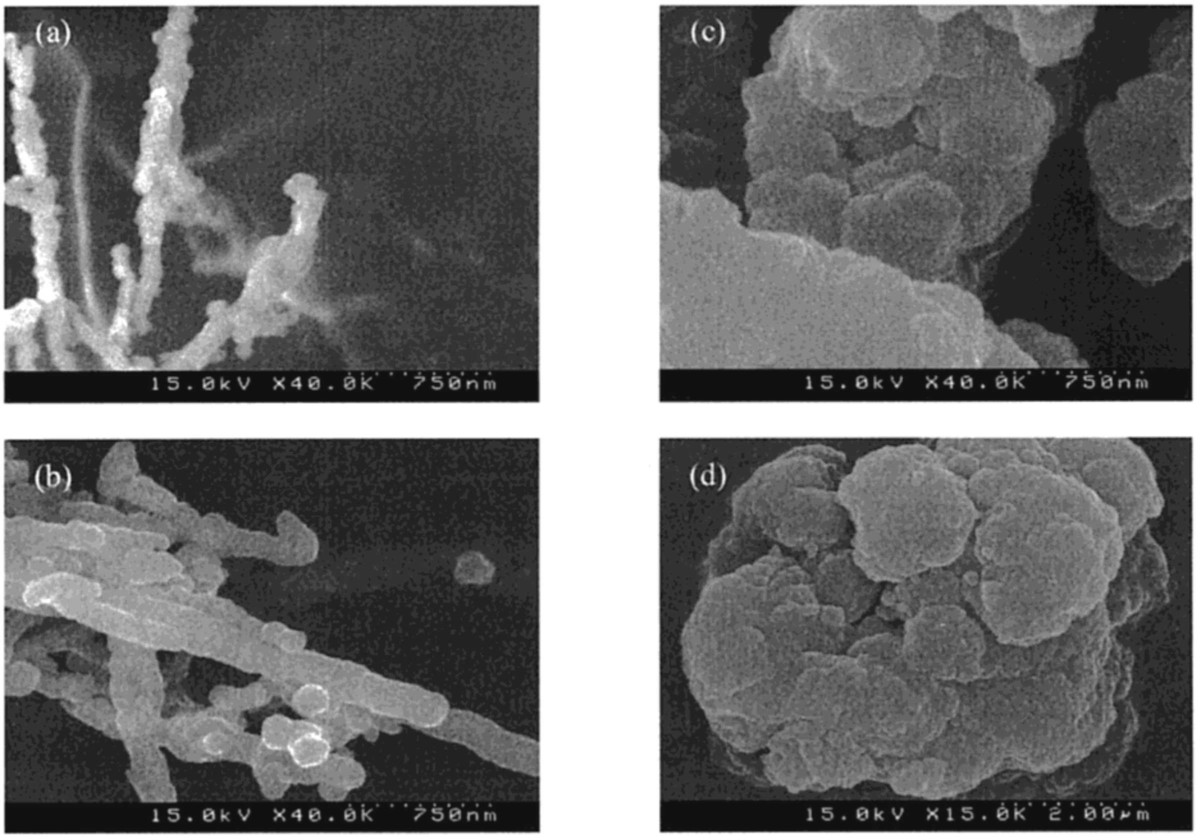

Figure 6. SEM micrographs of Fe–B chain/polymer composite materials prepared using 0.1 M CTAB (surfactant) and with (a) 0.01 M, (b) 0.05 M, (c) 0.7 M, and (d) 2.0 M monomer concentrations.

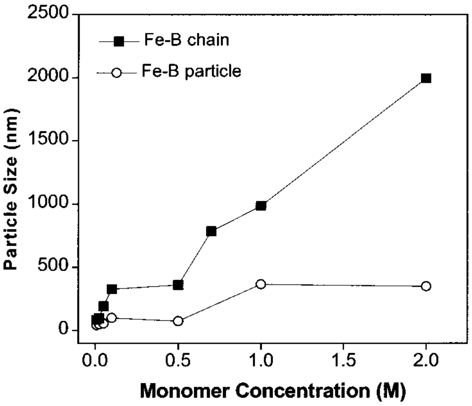

Figure 7. Variation of the particle size of Fe–B/polymer composite with monomer concentration used during the synthesis of Fe–B chain/polymer and Fe–B particle/polymer composites. A constant CTAB (surfactant) concentration of 0.1 M was used.

chain structures are clearly visible as the white regions, while the darker regions represent the polymer surrounding the chain structure. These experiments indicate that the chain structures are encapsulated within the polymer matrix.

If the Fe–B chains are completely encapsulated within the polymer matrix, then it follows logically that the polymer matrix should prevent atmospheric oxidation of the Fe–B alloy. With this objective, the Fe–B chain/polymer composite material seen in Figure 9 was exposed to an ambient atmosphere for 30 days and examined by magnetic measurements. It was found to have a M_s value of 94 emu/g, which is close to the value (97 emu/g) found for a similar sample that was stored in a vacuum desiccator during this time period of 30 days. The negligible difference in the M_s value before and after the exposure period further proves that the Fe–B is indeed encapsulated within the polymer matrix and protected from oxidation.

Magnetic Properties of Fe–B/Polyacrylamide Composite Materials. The magnetic properties of the Fe–B/polyacrylamide composite materials are given in Figure 10. The M_s values are most strongly influenced by the monomer concentration. For the samples prepared with the Fe–B chains, the M_s value of the composite material decreases steadily from 140 to 2 emu/g as the monomer concentration increases from 0.01 to 2.0 M. The M_r values also follow a similar trend as they decrease from 20 to 0.5 emu/g with increasing monomer concentration. The H_c values increase slightly from 600 to 700 Oe as the monomer concentration increases from 0.01 to 0.1 M and thereafter remain fairly constant at 720 Oe.

For the samples prepared with the Fe–B particles, the M_s value remains fairly constant at 110 emu/g from a monomer concentration of 0.01 to 0.1 M. With monomer concentrations greater than 0.1 M, the M_s value decreases sharply to $\approx$2 emu/g. The M_r values follow similar trends as they decrease from 20 to 1 emu/g with increasing monomer concentration. The H_c values initially increase from 600 to 700 Oe as the monomer concentration increases to 0.5 M and thereafter remain fairly constant at 750 Oe with increasing monomer concentrations.

Testing of the Fe–B/Polyacrylamide Composite Materials in the MACS Process Using Surrogate Species. Solvent extraction is a common laboratory technique used for the removal of a species from

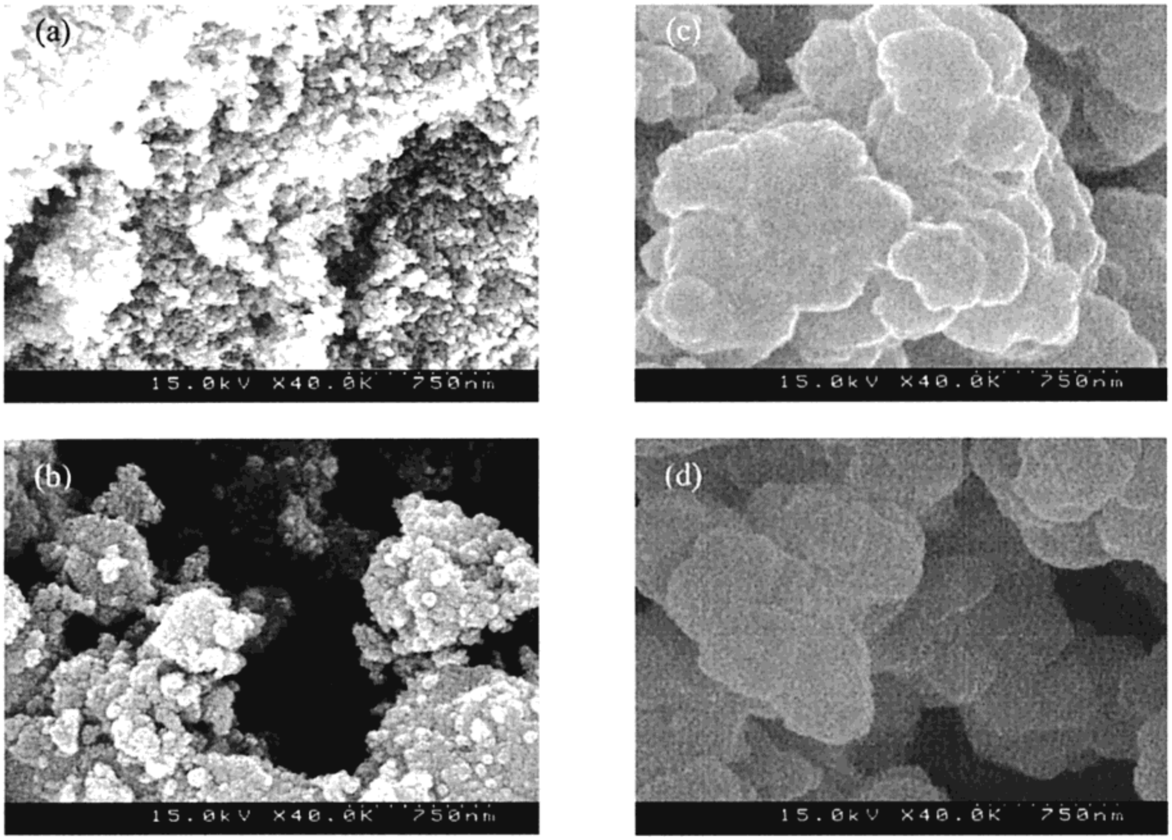

Figure 8. SEM micrographs of Fe−B particle/polymer composite materials prepared using 0.1 M CTAB (surfactant) solution and with (a) 0.01 M, (b) 0.5 M, (c) 1.0 M, and (d) 2.0 M monomer concentrations.

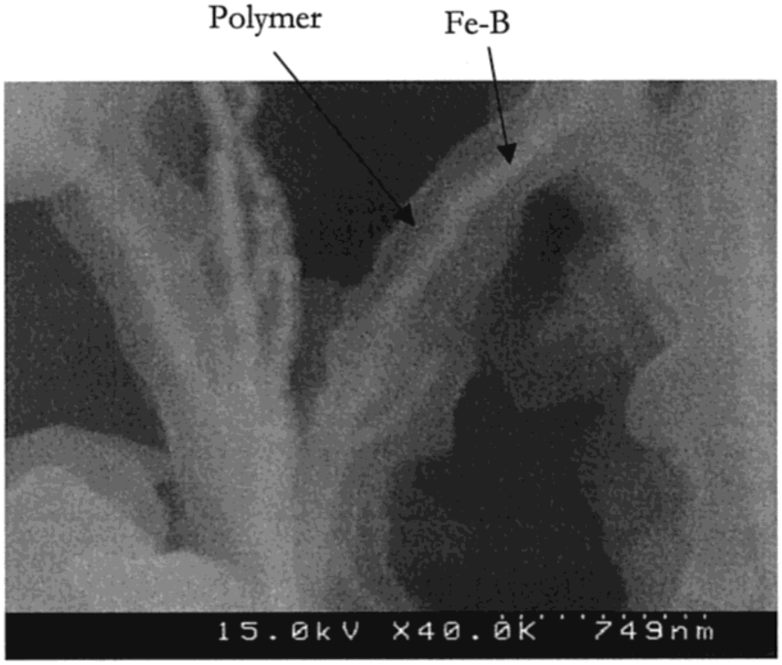

Figure 9. SEM micrograph of an Fe−B chain/polymer composite material that was imaged without a chrome sputter coating. The Fe−B chains are visible as the white regions, while the surrounding polymer is present as a darker region.

aqueous solution. The efficiency of the extraction process is determined by evaluating the concentration C of the desired species in the aqueous phase and in the organic phase. In doing so, the distribution coefficient D can be readily obtained as

$$D = C_{\text{organic}}/C_{\text{aqueous}} \tag{1}$$

where C_{organic} is the concentration of the species in the organic phase and C_{aqueous} is the concentration of the species in the aqueous phase. As the methodology of the MACS process is quite different from that of a solvent extraction procedure, a new parameter must be defined to properly evaluate the efficiency of the MACS process. This parameter, defined as the partitioning coefficient

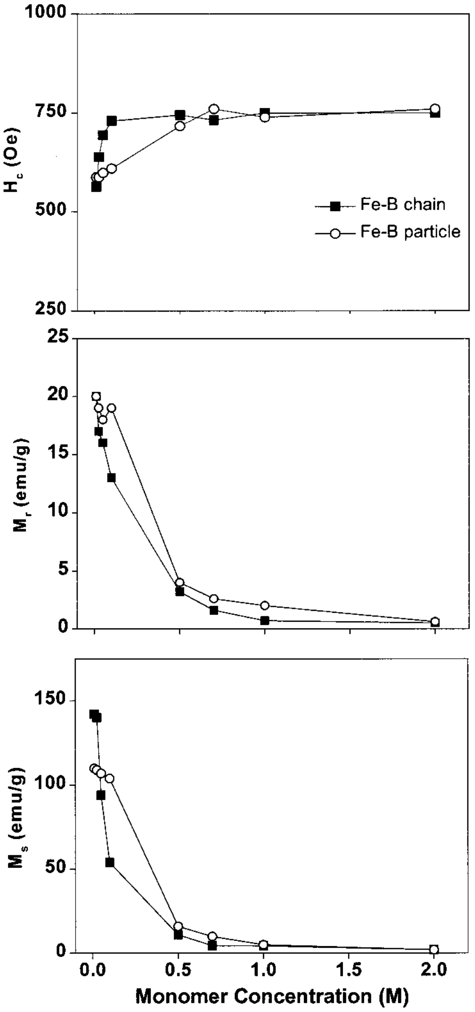

Figure 10. Variations of the saturation magnetization (M_s), remanent magnetization (M_r), and coercive field (H_c) values of the Fe–B/polymer composites with monomer concentration used in the synthesis of Fe–B chain/polymer and Fe–B particle/polymer composites. The error bars in M_s and M_r values are approximately ±1 emu/g and that in H_c is ±5 Oe.

K_d, is a measure of the ability of the microparticles to extract a species from a fixed volume of solution,[11]

$$K_d = [(C_{\text{initial}} - C_{\text{final}})V_s]/[(C_{\text{final}})M_p] \qquad (2)$$

where K_d is the partitioning coefficient (mL/g), C_{initial} is the initial concentration of the species to be extracted in the solution, C_{final} is the final concentration of the species in the solution after the MACS process, and V_s is the volume of solution (mL) in contact with coated particles of mass M_p (g). Although the composite materials synthesized in this investigation were designed for the separation of actinide species from radioactive and hazardous waste,[3–6] such experiments are not feasible at the university level. Therefore, other experiments were designed to test the efficiency of these materials with surrogate species. Specifically, the extraction of Co^{2+} ions with Cyanex-272 was investigated. Researchers at the Argonne National Laboratory have also used MagaCharc in conjunction with Cyanex-272 for the extraction of cobalt and nickel ions from aqueous media.[11]

The ability of Cyanex-272 to extract cations from aqueous solution is highly dependent upon the pH of the solution. The following reaction has been proposed in the literature in this regard,[18]

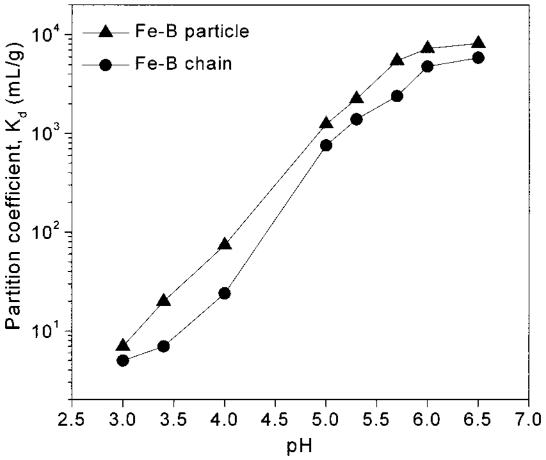

Figure 11. Variations of the partition coefficient with pH of the partition medium in the MACS process for the separation of cobalt ions from aqueous solution. Data are shown for composites prepared with Fe–B chains and particles. The error bar in K_d values at pH ≥ 5 is ≈50 mL/g.

$$[M^{2+}] + m[HA]_2 \rightarrow [MH_{2m-2}A_{2m}] + 2[H^+] \qquad (3)$$

where M^{2+} is the cationic species to be extracted from solution, $(HA)_2$ is the dimeric species of Cyanex-272, and m is a parameter related to the nature of the species to be extracted. For the extraction of Co^{2+} ions from aqueous solution, experimental results have indicated that $m = 2$.[18]

The composite material chosen for testing was prepared with the optimum surfactant concentration of 0.1 M and a monomer concentration of 0.7 M. The composite material was coated with Cyanex-272 as described in the Experimental Section. The pH of the partitioning medium was varied from 3.0 to 6.5 to determine the influence of the pH on the extraction of cobalt ions from aqueous solution. The results of these experiments are presented in Figure 11. The partitioning coefficient K_d increases from 7 to 8200 mL/g for the composite prepared with Fe–B particles and from 4 to 6000 mL/g for the sample prepared with Fe–B chains as the pH increases from 3.0 to 6.5, illustrating the strong influence of the pH of the partitioning medium on the K_d values. The K_d values are higher than that obtained for the commercially available Fe_3O_4-based composite[11] because of the smaller particle size. For the MACS process to be industrially feasible, K_d values above 1000 mL/g must be obtained. The above results indicate that the composite materials synthesized in this study are indeed suitable for the MACS process.

As mentioned in the Experimental Section, the Cyanex-272 used in this study was obtained as a gift sample in ≈80% purity. In all of the experiments described above, the Cyanex-272 was used in its 80% purity. To determine if the impurities in the Cyanex-272 were negatively influencing the partitioning coefficients, experiments were carried out using purified Cyanex-272. Conventional solvent extraction techniques were employed for the purification of Cyanex-272 with

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hexane and water as the organic and aqueous phases, respectively.

When the purified Cyanex-272 was employed during the extractant coating process, significant changes were observed. When Fe−B/polymer composite masses of <0.2 g were used in the coating procedure, the coated particles did not dry. Therefore, experiments were carried out by coating various masses of Fe−B/polymer composite (0.2−0.3 g) with 4 mL of ethanol containing 0.23 g of purified Cyanex-272. The results are rather striking when compared to those previously discussed. Partitioning coefficient values of ≈1500 mL/g are obtained at pH = 5.3 when composite masses of 0.23−0.28 g are employed in the coating process. However, a partitioning coefficient of 3200 mL/g is obtained when 0.3 g of composite is coated with the purified Cyanex solution. These results show that a simple purification of the Cyanex-272 can have a dramatic influence on the partitioning behavior of the composite materials developed in this study.

Conclusions

Nanostructured Fe−B having chain and particle microstructures have been synthesized by reducing ferrous chloride with borohydride in the presence and absence of an applied magnetic field. The Fe−B samples thus obtained exhibit higher saturation magnetization (190 emu/g) than previously reported in the literature.[13−17] The Fe−B samples have been encapsulated within a polyacrylamide matrix using a solution-based polymerization technique developed in this study. With an optimum surfactant concentration (0.1 M), agglomeration of the Fe−B could be minimized during the polymerization. By variation of the monomer concentration, the particle size of the Fe−B/polyacrylamide composite material could be varied from 80 nm to 2 μm. These composite materials, after being coated with an organic extractant (Cyanex-272), have been investigated for the separation of a surrogate species (cobalt ions) in the MACS process. The smaller particle size of the Fe−B/polyacrylamide composites with a higher saturation magnetization compared to the commercially available Fe_3O_4-based composite material leads to higher efficiency in the MACS process. The composite materials developed in this study thus have a great potential for application in the MACS process.

Acknowledgment. This work was partially supported by the Amarillo National Resource Center (ANRC), Amarillo, TX.

CM010014J