Recent advances and future perspectives of nanosized zero-valent iron for extraction of heavy elements from metallurgical sludges

I Yu Mikhailov, V V Levina, E A Kolesnikov, K O Chuprunov, A A Gusev, A Yu Godymchuk, D V Kuznetsov

National University of Science and Technology “MISiS”, 4 Leninsky prospect, Moscow, 119049, Russia

E-mail: ivan.mikhailov@misis.ru

Abstract. Advanced oxidation processes with nanosized zero-valent iron have presented great potential in wastewater treatment technology and now experience both increasing popularity and reliable technical improvements. Besides wastewater treatment, there is another promising application for an emerging technology of iron nanoparticles – as Fenton-like catalyst for extraction of valuable elements from poor and secondary raw materials such as metallurgical sludges. In present research, we carried out a set of experiments with emphasis on the physicochemical mechanisms and their relationship to the performance. In particular, we examined complex acidic – hydrogen peroxide leaching of zinc from blast furnace sludge with nanosized zero-valent iron as Fenton-like catalyst. Results of the experiments showed promising potential for subsequent application in extraction of heavy and rare-earth elements.

1. Introduction

Ongoing development of state-of-art technologies and production is the increasing trend of modern industry. Essential role of heavy and rare-earth elements in magnets, batteries, catalysts, metallurgy, ceramics and other applications leads to rapidly increasing consumption. That makes search of new and reliable sources of rare-earth elements one of most important strategic issues [1-2]. Industrial wastes are promising secondary source of hard and rare-earth elements. For example, valuable information on the presence of rare-earth oxides in flux powders used in the continuous steel casting as well as in slags and sludges resulting from the smelting of rare-earth-containing iron ores was presented by various researchers [3-10].

On the other hand technologies and methods for effective recovery are still an issue due to presence of goal elements in hard soluble phases, requiring high oxidation-reduction potential besides of high concentrations of acids. To promote the oxidation conditions, so-called Fenton-like process is widely used [11]. Nanosized zero-valent iron (nZVI) has shown significant results as highly reactive Fenton-like catalyst for production of hydroxyl radicals [12]. High values of specific surface area makes it more reliable compared to other sources of ferrous ions for Fenton reaction [13].

A significant example of large scale industries generating valuable heavy and rare-earth elements is ferrous metallurgy. During conventional steel-making process, a various types of dusts and sludges are formed. Traditionally one of the most problematic metallurgical wastes is blast furnace sludge, which is basically produced during wet scrubbing of top furnace gas. In Europe alone, annual production
of solid blast furnace sludge exceeds as high as 500 000 tons. Blast furnace sludge is mostly not suitable for direct recycling in blast furnace process due to zinc content, higher than 0.5 % by mass: during the metallurgical process, zinc partially condensates at the upper levels of blast furnace, which creates huge risks of damage to refractory coatings of the furnace. On the other hand, continuous tightening of environmental laws make such waste unacceptable for landfilling due to moderately high content of hard metals and alkalis, that may cause environment and public health risks [14]. Various types of sludges generated during steel production are shown in table 1.

**Table 1. Types of sludge waste generated by steel plants [15]**

| Waste               | Source        | Production (kg/t of metal) |
|---------------------|---------------|---------------------------|
| Coke sludge         | Coke oven     | -                         |
| Blast furnace sludge| Blast furnace | 25-30                     |
| Sintering plant sludge | Sintering plant | -                       |
| LD sludge           | Steel melting | 15-17                     |
| ACP/GCP sludge      | Steel melting | -                         |
| Carbide sludge      | Acetylene plant | -                    |
| Mill sludge         | Rolling mills  | 10-12                     |
| Water treatment sludge | Water treatment plant | -       |

As is shown above (table 1) blast furnace sludge is also generated in the highest quantities compared to other sludges from steel plants. Besides zinc, blast furnace sludge and slug could also contain lanthanum (La), cerium (Ce), praseodymium (Pr), yttrium (Y), europium (Er), dysprosium (Dy), neodymium (Nd) and indium (In) [16-18].

In this study we focused on the effect of nZVI additions on complex leaching of zinc and indium from blast furnace sludge in presence of 0.4 M sulfuric acid and hydrogen peroxide at various concentrations.

2. Materials and methods

In present study we used a sample of air-stable nZVI, synthesized by chemical precipitation and metal recovery in continuous hydrogen flow with subsequent passivation in technical grade nitrogen, as described in [19]. nZVI sample was characterized by BET adsorption (Quantachrome Nova 1200e instrument) and TEM (JEOL JEM-2000 EX with accelerating voltage of 100 kV).

In order to prepare nZVI sample for TEM analysis, small quantity of nZVI (below 10^{-8} kg) was added to 50 ml of 98% ethanol and thoroughly mixed using ultrasonic irradiation (Hielscher UP400S) for approximately 1 min. Then, a few drops of nZVI suspension were added on a carbon grid. Finally, prepared grid was dried under N_2 (nitrogen) atmosphere at room temperature for 15 min.

Particle size was calculated (assuming that all particles have spherical morphology) as follows:

\[
d_{SSA} = \frac{\rho}{6 \cdot S}
\]

where \( \rho \) – density, kg/m^3 and \( S \) – specific surface area, m^2/kg.

As mentioned above, as an example of possible source of valuable elements, we used a sample of blast-furnace sludge, provided by Cherepovetsky metallurgical plant of JSC “Severstal” (Vologda
region, Russia). Before experiments, sample of blast furnace sludge was dried at room temperature and carefully homogenized using agate mortar.

All leaching experiments were carried with the solid-liquid (S/L) ratio of 1:10, in opened 300 ml quartz flask with cooling jacket. Constant temperature 20 °C during all experiments was maintained using Lauda RE420 thermostat. To achieve different initial pH and ORP levels, sulfuric acid and hydrogen peroxide solutions with concentrations 0.4 M and 0.1, 0.05, 0.01, 0.005 M were used, respectively. Amount of nZVI addition was 1 g/dm$^3$ for all experiments. Mixing was carried out using Heidolph RZR-1 mechanical stirrer at continuous rate 500 RPM.

After treatment, leachates were separated from nZVI using 0.22 μm nylon membrane (Millipore), heated for 15 min at 60 °C in 1 M nitric acid to prevent possible precipitation and analyzed by ICP-AES (Thermo Scientific iCAP 6300 Radial View).

3. Results and discussions

Results for specific surface area measurement of nZVI sample are shown in table 2. TEM image of synthesized sample is presented in figure 1.

| Sample | Material | Specific surface area, m$^2$/g | Calculated particle size, nm |
|--------|---------|-------------------------------|-----------------------------|
| 1      | nZVI    | 13.9±1                        | 55                          |

![Figure 1. TEM image of the air-stable nZVI](image_url)

Specific surface area for nZVI sample (table 1) correlates with diameter estimated from TEM image (fig. 1). It should be noted that iron nanoparticles have thin protective oxide shell that prevents air and water oxidation without significant loss of reactive properties.

Typical and sample element compositions of blast furnace sludge obtained by ICP-AES are shown in table 3. As it could be seen, sample contains significant amounts of Fe, Zn, Al, Pb, Si, alkali metals and about 0.008 % of In. Such amount of In makes blast furnace sludge a promising secondary source upon condition of its effective recovery into solution.
Table 3. Typical [14, 18] and sample element compositions of blast furnace sludge

| Component | Typical (%) | Sample (%) |
|-----------|-------------|------------|
| Fe        | 21-32       | 36.7       |
| Zn        | 1.0-3.2     | 3.38       |
| In        | 0.0017      | 0.008      |
| Pb        | 0.3-1.2     | 0.22       |
| Cr        | ≤ 0.024     | 0.02       |
| Al        | -           | 0.39       |
| Cu        | -           | <0.01      |
| Ni        | -           | <0.01      |
| Mg        | <2          | 1.23       |
| Ca        | <13         | 3.13       |
| Si        | -           | 2.13       |
| Mn        | -           | 0.11       |
| Loss on ignition | - | 36.4 |

Possible Fenton-like reactions, taking place during the leaching of blast furnace sludge are presented in table 4. Conventional Fenton process includes reactions #1-9. In presence of nZVI as catalyst and source of ferrous ions, Fenton-like process includes also reactions #10-12. High reactivity of nZVI ensures fast dissolution and formation of extremely oxidative hydroxyl radicals.

Table 4. Possible chemical reactions during Fenton-like process

| # | Reaction | Source |
|---|----------|--------|
| 1 | \( \text{H}_2\text{O}_2 \rightarrow 2\text{OH}^* \) |       |
| 2 | \( \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^* + \text{OH}^- \) |       |
| 3 | \( \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^* + \text{H}^+ \) |       |
| 4 | \( \text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \) |       |
| 5 | \( \text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \) | [20]  |
| 6 | \( \text{OH}^- + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- \) |       |
| 7 | \( \text{Fe}^{3+} + \text{HO}_2^* \rightarrow \text{Fe}^{2+} + \text{O}_2\text{H}^+ \) |       |
| 8 | \( \text{Fe}^{2+} + \text{HO}_2^* + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \) |       |
| 9 | \( 2\text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \) |       |
| 10 | \( \text{Fe}^0 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \) |       |
| 11 | \( \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \) | [21]  |
| 12 | \( \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe} (\text{IV}) + \text{H}_2\text{O} \) |       |

Results of the leaching experiments in presence of nZVI additions are shown in figure 2. As could be seen, addition of nZVI provides a significant catalytic effect on the process, which particularly noticeable at a concentration of \( \text{H}_2\text{O}_2 \) equal to 0.05 and 0.1 M. Thus, more than 70 % of Zn and 65 % of In are dissolved after treatment with 0.1 M of \( \text{H}_2\text{O}_2 \). It should be noted that further investigations are required for kinetics and mechanisms of Zn and In leaching processes.
Taking into account possible reactions (table 4) it is clear that decreasing of \( \text{H}_2\text{O}_2 \) concentration should lead to appropriate decrease of metals extraction due to decrease of oxidation-reduction potential. But for most of concentrations observed slow fall in In and especially Zn dissolution. We assume that effect takes place due to Fenton process: continuous production of water radicals allows to maintain necessary oxidative conditions for extraction.

Figure 2. A: Dissolution degrees of zinc (Zn), B: dissolution degrees of indium (In)

4. Conclusions
The presented research focused on effect of nanosized zero-valent iron showed that Fenton-like process has a great potential in extraction of heavy and rare-earth elements from secondary sources such as blast furnace sludge.

Additions of nZVI lead to promotion of oxidative conditions and therefore more effective extraction of metals into solution. Achieved dissolution degrees observed during experiments makes Fenton-assisted leaching with nZVI as Fenton catalyst a possible solution for other applications in the field of extraction valuable rare-earth elements form poor ores and sludge wastes.

Acknowledgements
Authors gratefully acknowledge the Federal Program for Research and Development of Russian Federation (Ministry of Science and Education of Russian Federation, project 0RFMEFI57514X0102) for financial support.

References
[1] Binnemans K, Jones P T, Blanpain B, Van Gerven T, Yang Y, Walton A and Buchert M 2013 J. Clean. Prod. 51 1
[2] Binnemans K, Jones P T, Blanpain B, Van Gerven T and Pontikes Y 2015 J. Clean. Prod. 99 17
[3] Zheng X P, Lin H K 1994 Miner. Eng. 7 1495
[4] Anacleto N M, Lee H G and Hayes P C 1993 ISIJ Int. 33 549
[5] Derevyankin V A, Gasik M I, Anelok L I, Porotnikova T P and Vukelich S B 1981 Izv. Vyssh. Uchebn. Zaveden. Tsveten. Met. 5 84
[6] Derevyankin V A, Porotnikova T P, Kocherova E K and Yumasheva I V 1981 Izv. Vyssh. Uchebn. Zaveden. Tsveten. Met. 5 119
[7] Fang X, Hu L, Tan R, Wang Z Process for utilizing waste smelting dregs of rare-earth ferrosilicon. Patent of China CN1302910A Published July 11 2001 (in Chinese)
[8] Jia Y L, Dong Y C and Qin Z Z 1995 J. Rare Earth. 3 133
[9] Lin H K and Zheng X P 1997 Miner. Metall. Proc. 14 18
[10] Yang X H, Long H, Cheng G G, Wu C C and Wu B 2011 J. Rare Earth 29 1079
[11] Babuponnusami A and Muthukumar K 2014 J. Env. Chem. Eng. 2 557
[12] Crane R, Scott T B 2012 J. Hazard. Mater. 211-212 112
[13] Liang J, Komarov S, Hayashi N and Kasai E 2007 Ultrason. Sonochem. 14 201
[14] Van Herck P, Vandecasteele C, Swennen R and Mortier R 2000 Environ. Sci. Technol. 34 3802
[15] Das B, Prakash S, Reddy P S R and Misra V N 2007 Resour. Conserv. Recycl. 50 40
[16] Das B, Prakash S, Biswal S K, Reddy P S R, Mohapatra B K and Tripathy H K 2002 Utilization of solid waste materials generated at steel plants by physical beneficiation technique: report submitted to Ministry of Steel, India (Bhubaneswar: Govt. of India Regional Research Laboratory (CSIR)) p 1
[17] Bandara H M D, Mantell M A, Darcy J W and Emmert M H 2015 Energ. Technol. 3 118
[18] Shen X, Li L, Wu Z, Lü H and Lü J 2013 Metall. Mater. Trans. B 44 1324
[19] Mikhailov I, Mandal A R, Kotov S and Kuznetsov D 2013 Adv. Electrochem. 1 83
[20] Umar M, Aziz H A and Yusoff M S 2010 Waste Manag. 30 2113
[21] Xu L and Wang J 2011 J. Hazard. Mater. 186 256