

Recycle of valuable products from oily cold rolling mill sludge

Bo Liu¹⁾, Shen-gen Zhang¹⁾, Jian-jun Tian¹⁾, De-an Pan¹⁾, Yang Liu¹⁾, and Alex A. Volinsky²⁾

1) Institute for Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China

2) Department of Mechanical Engineering, University of South Florida, Tampa 33620, USA

(Received: 8 January 2013; revised: 6 February 2013; accepted: 13 February 2013)

Abstract: Oily cold rolling mill (CRM) sludge contains lots of iron and alloying elements along with plenty of hazardous organic components, which makes it as an attractive secondary source and an environmental contaminant at the same time. The compound methods of “vacuum distillation + oxidizing roasting” and “vacuum distillation + hydrogen reduction” were employed for the recycle of oily cold rolling mill sludge. First, the sludge was dynamically vacuum distilled in a rotating furnace at 50 r/min and 600°C for 3 h, which removed almost hazardous organic components, obtaining 89.2wt% ferrous resultant. Then, high purity ferric oxide powders (99.2wt%) and reduced iron powders (98.9wt%) were obtained when the distillation residues were oxidized and reduced, respectively. The distillation oil can be used for fuel or chemical feedstock, and the distillation gases can be collected and reused as a fuel.

Keywords: cold rolling mills; sludge; recycling; distillation; oxidation; hydrogen reduction

1. Introduction

Oily cold rolling mill (CRM) sludge is a kind of by-product of steel making in the process of cold rolled strip production and is basically composed of metallic iron and iron oxides (70wt%-90wt%) with variable oil and grease (7wt%-20wt%). Since the sludge contains lots of iron and alloying elements along with plenty of hazardous organic components, it is considered as both an attractive secondary source and an environmental contaminant. Nowadays, the sludge is mainly reutilized as a raw material in secondary smelt furnaces [1-3]. Its direct reuse in sintering may lead to some problems, since the high oil content of sludge results in the increased emission of volatile organic compounds, including dioxins. This can bring trouble in waste gas purification systems, e.g., glow fires in electrostatic precipitators. The sludge needs to be pretreated before it is reused. Piling up for a long time and landfill are the main pretreatment of the sludge due to economic considerations. Continuous harm for the landfill and leaching of some small concentration of heavy metals into soil and ground water threatens the environment and highlights the need for more effective methods of waste disposal and the efficient utilization of the sludge.

To avoid environmental pollution, waste oil in oily

CRM sludge must be separated before the utilization of valuable components. At present, numerous routes have been employed to remove oil from industrial solid wastes, including landfill, incineration, aqueous surfactant washing [4-5], supercritical extraction [6], biological treatment [7], etc. Landfill is a cheap and straightforward treatment for oily sludge. However, the simple landfill of oily CRM sludge can not only reduce the service life of landfill sites but also create a risk of contamination, particularly for ground water. Incineration is a valuable means of waste disposal with the advantage of reducing the waste volume efficiently. However, incineration may cause environmental pollution. Incineration and landfill methods are challenged by increasingly strict regulations. Biological treatment of organic pollutants is a promising, reliable, simple, and inexpensive technology compared with chemical and physical processes. However, it is reported as being very difficult or non practical, because it takes a relatively long time to treat, and the oil removal rate is low. As mentioned above, no technology currently has reached a satisfactory solution from the views of environment, efficiency, and economy.

Distillation technology, which has obvious superiority in separation efficiency, scope of applications, and innocuous processing, has also been commonly used in the

Corresponding author: Shen-gen Zhang E-mail: zhangshengen@mater.ustb.edu.cn

treatment of harmful substances, such as petroleum refinery wastewater [8], spent pickling solutions from steel processing [9], harmful ions in the solution [10-11], biosludge [12], and spent nuclear fuel [13]. Compared with other distillation methods, vacuum distillation has several advantages in oil separation processing because of the short residence time of organic vapor in reactors, which reduces the occurrence and intensity of secondary reactions. Value-added and expanded applications of the recycled oily CRM sludge, based on the green recycling of organic wastes, still pose a major problem for iron and steel industries or environmental protection agencies. There are few reports about compound techniques for oily CRM sludge recycling. In this paper, two new processes of “vacuum distillation + oxidizing roasting” and “vacuum distillation + hydrogen reduction” were proposed and utilized for processing oily CRM sludge, offering an effective way of recovering oily CRM sludge. Experimental conditions were carefully studied to obtain the optimal results.

2. Experimental

2.1. Oily CRM sludge material

Oily CRM sludge used in the experiment was obtained from Baosteel Group Corporation in Shanghai, China. Table 1 shows that the oily CRM sludge sample predominantly contains Fe (70.6wt%), oil and moisture (18.2wt%), and small amounts of Ni, Mn, Cr, Si, and V.

Table 1. Chemical analysis results of the oily CRM sludge dried by air

Fe	Ni	Mn	Cr	Si	V	Oil	Moisture	Other
70.6	0.049	0.18	0.065	0.058	0.024	17.4	0.8	10.82

2.2. Recovery process

In this study, the new compound methods of “vacuum distillation + oxidizing roasting” and “vacuum distillation + hydrogen reduction” were used, as shown in Fig. 1. First, the sludge was distilled in a rotary furnace under vacuum. Oxidizing roasting and hydrogen reduction were employed to treat the obtained distillation. After oxidizing roasting and hydrogen reduction, the iron oxide powders and reduced iron powders were obtained.

2.3. Methods

2.3.1. Vacuum distillation

A vacuum distillation system for the oily CRM sludge processing, which consisted of a rotary furnace, a vacuum pump, a condensing unit, a tail gas absorption device, a gas collector, etc., was employed, as shown in Fig. 2. The sludge was initially placed in the rotary furnace. The reactor's pressure was pumped down to lower than 0.1 Pa before heating, and the condensing unit remained at room temperature. The rotary furnace was heated to the design temperature at a rate of 10°C/min, while the rotating

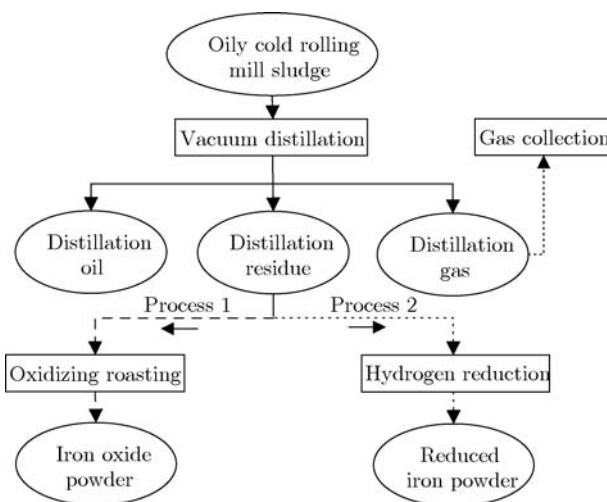


Fig. 1. Processing scheme for recycling the oily CRM sludge.

speed was fixed at 50 r/min. When the furnace chamber reached the design temperature, it was held at this temperature for several hours to separate organic components as much as possible. Then, distillation volatiles entered the condensing unit. Most of distillation volatiles were condensed and formed distillation oils. The rest of distillation volatiles that were not condensed went into the tail absorption device (alkali solution as an absorbent). A small amount of tail gas was finally collected by the gas collector.

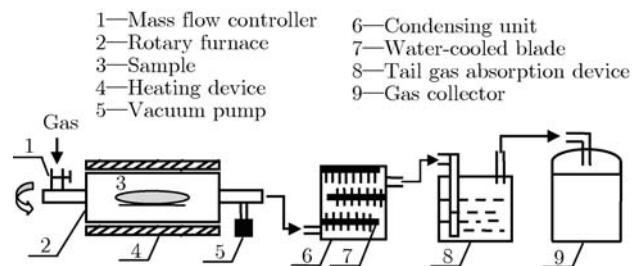


Fig. 2. Schematic diagram of experimental apparatus.

2.3.2. Oxidizing roasting

After vacuum distillation, the vacuum pump was closed, and air was fed into the rotary furnace. Then, the rotary furnace was heated to the design temperature at a rate of 10°C/min, while the rotating speed was fixed at 50 r/min. When the furnace chamber reached the design temperature, it was held at this temperature for several hours to oxidize iron components into ferric oxide (Fe_2O_3) as much as possible. Finally, magnetic separation was carried out to remove small amounts of nonferromagnetic impurities.

2.3.3. Hydrogen reduction

After vacuum distillation, the vacuum pump was closed, and hydrogen was fed into the rotary furnace. Then, the rotary furnace was heated to the design temper-

ature at a rate of 10°C/min. When the furnace chamber reached the design temperature, it was held at this temperature for several hours to reduce iron component powders as much as possible. Finally, magnetic separation was carried out to remove small amounts of nonferromagnetic impurities.

2.4. Characterization techniques

X-ray diffraction (XRD) analysis was performed using a Philips APD-10 X-ray diffractometer with Cu K α radiation, 40 kV voltage, and 150 mA current at 10°/min scanning rate from 10° to 100°. Thermogravimetry and differential scanning calorimetry (TG-DSC) (NETZSCH STA 409 C/CD, Germany) of the oily CRM sludge was carried out at a heating rate of 10°C/min in Ar. To know the composition of distillation oils, the types of functional groups present in distillation oils were determined by Fourier transform infrared spectroscopy (FT-IR) analysis using Nicolet Nexus-470. Particle size distribution of the obtained iron oxide red sample was determined using a laser particle size analyzer (Seishin LMS-30). Chemical analysis of the obtained iron oxide red and reduced iron powders was performed according to GB/T 1863–2008 and GB/T 4136–94 (China Industrial Standard), respectively.

3. Results and discussion

3.1. Vacuum distillation

To investigate the distillation process of the oily CRM sludge, thermal analysis (TG-DSC) was carried out, and the results are shown in Fig. 3. The TG curve can be roughly divided into three regions, 92.5–243.2°C, 243.2–400°C, and 400–454.1°C. In the 92.5–243.2°C range, the weight loss of the sample is about 4% due to water evaporation. When the temperature rises to 243.2–400°C, part of the oil is distilled, increasing the slope of the TG curve. In this temperature range, the weight loss of the sample is about 5%. As the temperature continues to rise above

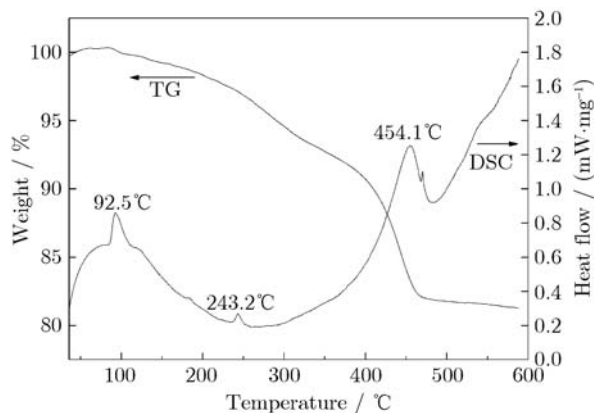


Fig. 3. TG-DSC curves of the oily CRM sludge in argon.

400°C, the weight loss increases faster, compared with the two prior stages, indicating that the oil with high distillation temperature in the oily CRM sludge begins to be distilled. The TG curve becomes flat above 450°C.

To study the effects of distillation temperature and holding time, a series of experiments were performed under vacuum at different distillation temperature from 450°C to 700°C for different holding time from 1 h to 3 h, when the rotation speed was set at 50 r/min. Oil removal results from different processes are shown in Fig. 4. The organic residue of the oily CRM sludge drops to 0.16wt% when it is heated at 600°C. Compared with the sample distilled at 600°C, the sample distilled at 700°C has the slightly lower residual oil content. However, a higher distillation temperature can increase the occurrence and intensity of organic residue reactions. In view of this, the optimal parameters of organic residue removal were the distillation temperature of 600°C and the holding time of 3 h.

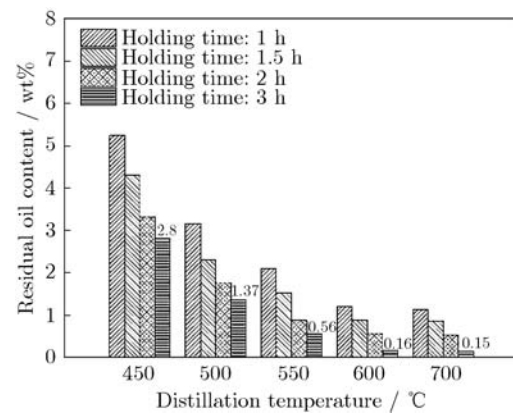


Fig. 4. Efficiency comparison of different treatment process.

Table 2 shows the product yields of the oily CRM sludge at the optimal parameters. Solid and liquid distillation yields were determined in each experiment by weighing each material obtained, while the gas yields were calculated by the difference. The equations used for calculating the distillation yields are the following.

$$\text{Solid yield} = \frac{\text{Weight of solid residue}}{\text{Weight of oily CRM sludge}} \times 100\% \quad (1)$$

$$\text{Liquid yield} = \frac{\text{Weight of distillation oil and water}}{\text{Weight of oily CRM sludge}} \times 100\% \quad (2)$$

$$\text{Gas yield} = 1 - \text{solid yield} - \text{liquid yield} \quad (3)$$

Table 2. Distillation yields of the oily CRM sludge distilled at 600°C for 3 h

wt%		
Solid yield	Liquid yield	Gas yield
82.3	15.6	2.1

As seen in Table 2, the oily CRM sludge was composed of 82.3wt% solid residue, 15.6wt% oil (containing a small amount of water), and 2.1wt% gas when it was distilled at 600°C for 3 h. Fig. 5 shows the X-ray diffraction pattern of the distillation residue. Fe, FeO, and Fe₂O₃ are the major constituents of the distillation residue.

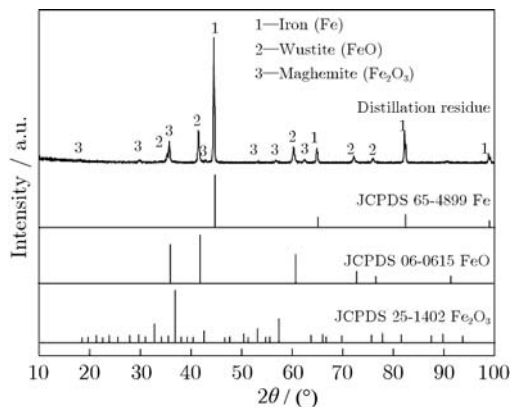


Fig. 5. XRD patterns of the distillation residue.

To know the composition of distillation oils, the types of functional groups present in distillation oils were determined by FT-IR analysis, as shown in Fig. 6. The band assignments of distillation oils are shown in Table 3. The spectra of distillation oils contain a large peak between 3500 cm⁻¹ and 3300 cm⁻¹, associated with O–H stretches

in either alcohols or phenols. Two peaks between 3000 cm⁻¹ and 2800 cm⁻¹ can be associated with methylene groups. The absence of absorbance peaks between 1725 cm⁻¹ and 1700 cm⁻¹ may indicate the presence of aromatic carboxylic acids or α/β unsaturated carboxylic acids. The peaks between 1650 cm⁻¹ and 1420 cm⁻¹ can be associated with aromatic C=C stretches, and the peaks appearing at 966 cm⁻¹ and 721 cm⁻¹ are associated with C–H out-of-plane deformation vibrations in benzene rings. The bands between 1390 cm⁻¹ and 1220 cm⁻¹ are always present when the phenols are analyzed, although they can also be associated with other functional groups.

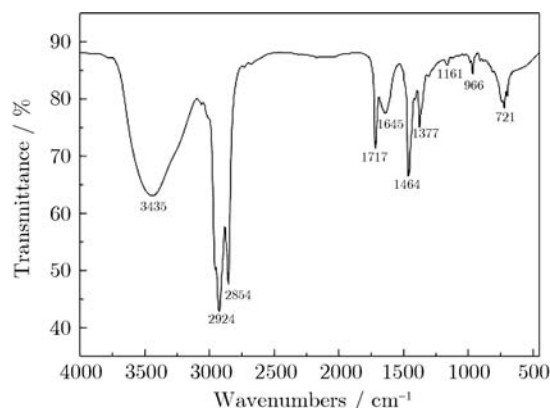


Fig. 6. FT-IR spectrum of the oils produced by distilling the oily CRM sludge.

Table 3. Band assignments of the FT-IR spectrum

Band number / cm ⁻¹	Assignment
3435	O–H stretching vibration in hydroxyl group
2924, 2854	C–H stretching vibration in methylene groups
1717	C=O stretching vibration in saturated aliphatic carboxylic acid
1645, 1464	C=C stretching vibration in aromatics group
1377	O–H stretching vibration in phenols or phenol derivatives
1161,	C–O stretching vibration in alcohol (R–OH) group
966, 721	C–H stretching vibration in aromatic group

The FT-IR analysis results indicated that most of distillation oils consisted of saturated aliphatic carboxylic acid and substituted phenols. Therefore, the distillation oil can be used as fuel or chemical feedstock for further processing. The distillation gases contained the uncondensed oil gas and a small amount of other substances generated from the organic residue reaction in the distillation process, such as CO and CO₂. Since such gases had a high combustion value, these distillation gases could be collected for use as fuel.

3.2. Oxidizing roasting

Iron oxide red is nontoxicity, chemical stability, durable, and inexpensive. It is widely used in various industrial products, e.g., pigments and absorbents in the pa-

per industry, lacquers, or plastics [14-15]. In addition, iron oxide red is also the main raw material for ferrite magnetic materials [16]. The use of iron wastes in iron oxide red preparation is an important subject not only from the environmental protection standpoint but also with respect to the recovery of valuable materials. There are many methods reported for the preparation of iron oxide red by using iron wastes, e.g., dry methods [17] and wet methods [18-19]. Compared with other iron wastes, the distillation residue has high iron content in the form of oxides and metal with low impurities. Thus, oxidizing roasting is an optional follow-up treatment for the distillation residue.

First, the vacuum pump was closed, and air was fed into the rotary furnace at 10 L/min flow rate. When the rotating speed was fixed at 50 r/min, the rotary furnace

was heated to different temperatures (700, 750, 800, and 850°C) at a rate of 10°C/min and oxidized for different times (1, 1.5, 2, and 2.5 h). Then, these oxidized powders obtained at different conditions were milled in a ball mill for 2 h. The effects of roasting temperature and holding time on the oxidation degree of the oil CRM sludge are shown in Fig. 7. In Fig. 7, the oxidation rate of the oil CRM sludge is more than 99% when the oxidation temperature is above 800°C and the holding time exceeds 2 h.

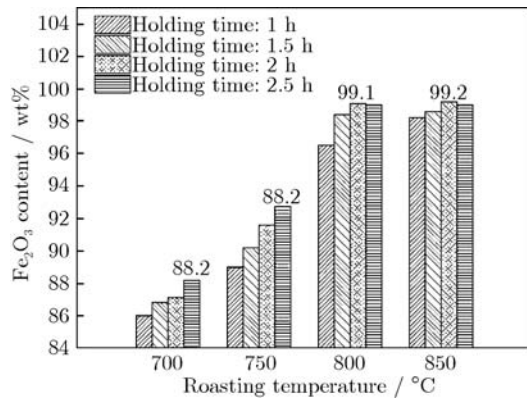


Fig. 7. Effects of annealing temperature and time on the Fe_2O_3 content of the oil CRM sludge.

Characteristics of the iron oxide red product (phase, sizes, and the main content) prepared under the above optimal conditions were determined by XRD, laser particle size distribution, and titration. The results show that the content of Fe_2O_3 is 99.1wt%. Fig. 8 shows the XRD pattern of the iron oxide red product. It indicates the highly crystalline character of iron oxide red, and it matches well with the standard $\alpha\text{-Fe}_2\text{O}_3$ (hematite) reflections. Fig. 9 shows the size distribution of the iron oxide red product. The average particle size of the obtained iron oxide red is 2.139 μm .

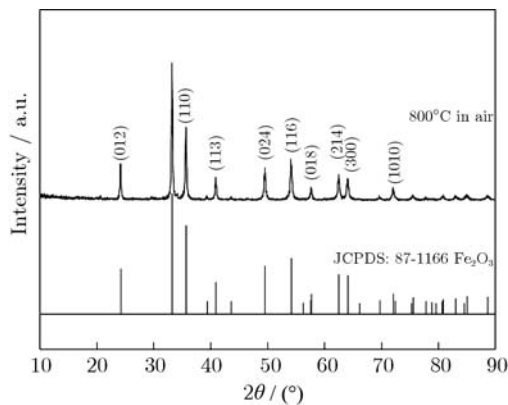


Fig. 8. XRD pattern of CRM sludge powders obtained at the optimal processing conditions.

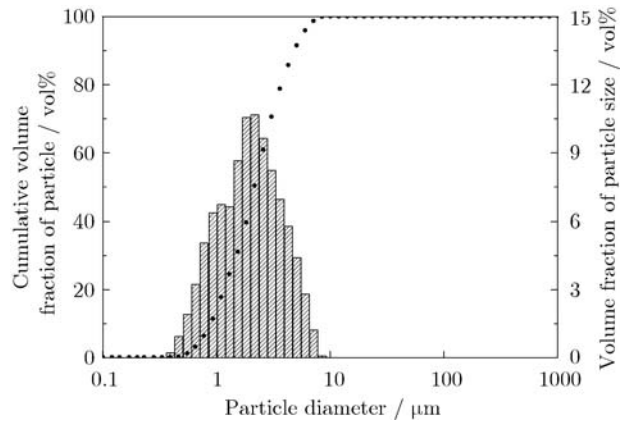


Fig. 9. Particle size distribution of iron oxide red obtained at the optimal processing conditions.

The quality of the obtained iron oxide red can meet the first rank criterion of GB/T 1863–2008 (China Industrial Standard). These powders can be used as pigments or other purposes.

3.3. Hydrogen reduction

Reduced iron powders are one of the most widely used raw materials in the powder metallurgy industry. Considering high total iron content and low impurities content in the distillation residue, hydrogen reduction is the other optional follow-up treatment for the distillation residue in this study.

First, the vacuum pump was closed and hydrogen was fed into the rotary furnace at a flow rate of 0.4 L/min after vacuum distillation. The rotary furnace was heated to different temperatures (800, 850, 900, 950, and 1000°C) at a rate of 10°C/min and reduced for 2 h. The effect of reduction temperature on the total iron content in the distillation residue is shown in Fig. 10. The total iron content in the distillation residue is more than 99wt% when the reduction temperature is higher than 950°C.

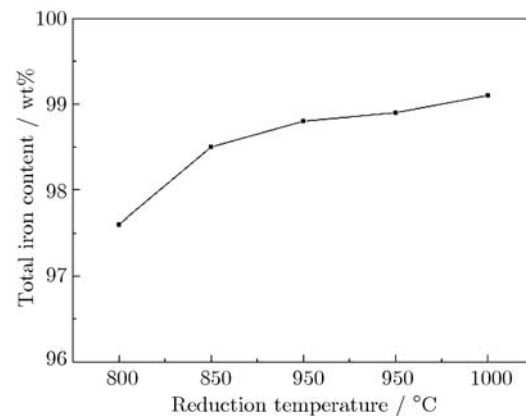


Fig. 10. Reduction temperature effect on the total iron content of the distillation residue.

4. Conclusions

(1) Vacuum distillation results indicate that the organic residue of the oily CRM sludge decreases to 0.16wt% at 600°C, and the drum of the rotating furnace is rotated at 50 r/min for 3 h. Under these conditions, the oily CRM sludge distillation is composed of an average of 89.2wt% residue, 8.6wt% oil, and 2.2wt% gas.

(2) Oxidizing roasting results indicate that iron oxide powders of 99.2wt% in purity are obtained when the distillation residues are oxidized at 850°C for 3 h in flowing air.

(3) Hydrogen reduction results indicate that reduced iron powders with the total iron content of 98.9wt% are obtained when the distillation residues are reduced at 950°C for 2 h in hydrogen.

(4) The distillation oil can be used as fuel or chemical feedstock for further processing, and the distillation gases can be collected for fuel.

(5) This clean and nonpollution technology can offer a new way to recycle valuable materials from the oily CRM sludge and prevent environmental pollution effectively.

Acknowledgements

This work was financially supported by the National Key Technology R&D Program (Nos. 2012BAC02B01, 2012BAC12B05, 2011BAE13B07, and 2011BAC10B02), the National High-Tech Research and Development Program of China (No. 2012AA063202), the National Natural Science Foundation of China (Nos. 51174247 and 51004011), the Science and Technology Program of Guangdong Province, China (No. 2010A030200003), and the Ph.D. Programs Foundation of the Ministry of Education of China (No. 2010000612003).

References

- [1] V.I. Shatokha, O.O. Gogenko, and S.M. Kripak, Utilising of the oiled rolling mills scale in iron ore sintering process, *Resour. Conserv. Recycl.*, 55(2011), No. 4, p. 435.
- [2] B. Das, S. Prakash, P.S.R. Reddy, and V.N. Misra, An overview of utilization of slag and sludge from steel industries, *Resour. Conserv. Recycl.*, 50(2007), No. 1, p. 40.
- [3] J.W. Park, J.C. Ahn, H. Song, K. Park, and H.S. Shin, J. Ahn, Reduction characteristics of oily hot rolling mill sludge by direct reduced iron method, *Resour. Conserv. Recycl.*, 34(2002), No. 2, p. 129.
- [4] J.I. Chang, J.J. Lin, J.S. Huang, and Y.M. Chang, Recycling oil and steel from grinding swarf, *Resour. Conserv. Recycl.*, 49(2006), No. 2, p. 191.
- [5] B. Ruffino and M.C. Zanetti, Recycling of steel from grinding scraps: Reclamation plant design and cost analysis, *Resour. Conserv. Recycl.*, 52(2008), No. 11, p. 1315.
- [6] B.C. Cui, F.Y. Cui, G.L. Jing, S.L. Xu, W.J. Huo, and S.Z. Liu, Oxidation of oily sludge in supercritical water, *J. Hazard. Mater.*, 165(2009), No. 1-3, p. 511.
- [7] B. Mrayyan and M.N. Battikhi, Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge, *J. Hazard. Mater.*, 120(2005), No. 1-3, p. 127.
- [8] L. Yan, H.Z. Ma, B. Wang, W. Mao, and Y.S. Chen, Advanced purification of petroleum refinery wastewater by catalytic vacuum distillation, *J. Hazard. Mater.*, 178(2010), No. 1-3, p. 1120.
- [9] M. Regel-Rosocka, A review on methods of regeneration of spent pickling solutions from steel processing, *J. Hazard. Mater.*, 177(2010), No. 1-3, p. 57.
- [10] D.Y. Hou, J. Wang, X.C. Sun, Z.K. Luan, C.W. Zhao, and X.J. Ren, Boron removal from aqueous solution by direct contact membrane distillation, *J. Hazard. Mater.*, 177(2010), No. 1-3, p. 613.
- [11] D. Qu, J. Wang, D.Y. Hou, Z.K. Luan, B. Fan, and C.W. Zhao, Experimental study of arsenic removal by direct contact membrane distillation, *J. Hazard. Mater.*, 163(2009), No. 2-3, p. 874.
- [12] K.H. Lin, H.T. Hsu, Y.W. Ko, Z.X. Shieh, and H.L. Chiang, Pyrolytic product characteristics of biosludge from the wastewater treatment plant of a petrochemical industry, *J. Hazard. Mater.*, 171(2009), No. 1-3, p. 208.
- [13] H.C. Eun, H.C. Yang, Y.Z. Cho, H.S. Lee, and I.T. Kim, Vacuum distillation of a mixture of LiCl-KCl eutectic salts and RE oxidative precipitates and a dechlorination and oxidation of RE oxychlorides, *J. Hazard. Mater.*, 160(2008), No. 2-3, p. 634.
- [14] G. Montes-Hernandez, J. Pironon, and F. Villieras, Synthesis of a red iron oxide/montmorillonite pigment in a CO₂-rich brine solution, *J. Colloid Interface Sci.*, 303(2006), No. 2, p. 472.
- [15] N. Kijima, M. Yoshinaga, J. Awaka, and J. Akimoto, Microwave synthesis, characterization, and electrochemical properties of α -Fe₂O₃ nanoparticles, *Solid State Ionics.*, 192(2011), No. 1, p. 293.
- [16] R.C. Pullar, Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics, *Prog. Mater. Sci.*, 57(2012), No. 7, p. 1191.
- [17] M.A. Legodi and D. de Waal, The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste, *Dyes Pigm.*, 74(2007), No. 1, p. 161.
- [18] D.X. Li, G.L. Gao, F.L. Meng, and C. Ji, Preparation of nano-iron oxide red pigment powders by use of cyanided tailings, *J. Hazard. Mater.*, 155(2008), No. 1-2, p. 369.
- [19] Y.J. Zheng and Z.C. Liu, Preparation of monodispersed micaceous iron oxide pigment from pyrite cinders, *Powder Technol.*, 207(2011), No. 1-3, p. 335.