

REDUCTION BEHAVIOR OF IRON IN THE RED MUD

S. Eray ^a, E. Keskinilic ^{b,*}, Y.A. Topkaya ^c, A. Geveci ^c

^a Agri Ibrahim Cecen University, Agri, Turkey

^b Atilim University, Department of Metallurgical and Materials Engineering,
Ankara, Turkey

^c Middle East Technical University, Department of Metallurgical and Materials Engineering,
Ankara, Turkey

(Received 27 February 2021; accepted 01 August 2021)

Abstract

Red mud or bauxite residue contains significant quantities of industrial metals such as Fe, Al, and Ti, as well as rare earth elements such as Sc, Ce, and La. The authors performed a laboratory-scale project dealing with stepwise recovery of valuable elements from two bauxite residues, namely Iranian red mud (IRM) and Turkish red mud (TRM). The first stage involved the recovery of iron which was present in large quantities in red mud. Two different methods were investigated for this purpose: 1) solid state reduction followed by wet magnetic separation and 2) smelting. In the scope of this paper, some results of pyrometallurgical part of this project are presented. According to solid-state reduction experiments, it was found that more excess coal was needed for IRM (35%) than for TRM (15%) to maximize iron reduction. Temperature had significant effect on the reduction process and metallization increased from about 70% to about 95% when the temperature was raised from 1000 to 1200°C. Metallization degree was reported to be slightly higher for IRM (96.2%) than for TRM (94.1%). The results demonstrated that a high degree of iron metallization can be achieved regardless of the chemical and mineralogical composition of the bauxite residue sample.

Keywords: Red mud; Iron; Solid-state reduction

1. Introduction

Red mud is a waste, or more correctly, a by-product obtained from the Bayer process during alumina production from bauxite ores. Roughly speaking, quantity of red mud generated is at least the same amount of alumina produced [1]. Generally, bauxite residue is stored in large red mud dams, not only causing a significant amount of land loss but also creating a problem for pollution of water resources and environment [2, 3] mainly due to its high basicity (pH 10-12.5). This situation has caused great economic losses and has become one of the serious problems of the aluminum industry.

Red mud contains a significant amount of industrial metals [4, 5] such as iron, aluminum, and titanium, as well as precious metals such as scandium, cerium, vanadium, and other rare earth elements. Of these economically valuable elements, iron is the most abundant element in the red mud. In the processing chain of the red mud, recovery of iron in the first stage is important in two ways. It decreases the amount of the product that should be processed

during the next stages for recovery of other elements. It also reduces the likelihood that iron will interact with other elements in later stages, especially if hydrometallurgical methods are to be employed to recover rare earths.

There are primarily two methods for iron recovery: 1. Solid state reduction, which is generally followed by magnetic separation and 2. Smelting. Solid state reduction can be conducted as:

- Carbothermic reduction using a certain type of carbon source [6], conventional process for pig iron making;
- Reduction roasting, using certain additive(s) in addition to a carbon source [7-13];
- Gaseous reduction using H₂ and/or CO or certain gas mixtures [14-17]; and
- Microwave heating applications [18-20].

Keskinilic et al. [21] reviewed those examples, so more details can be found in the related literature. The authors have performed a laboratory-scale project dealing with stepwise recovery of valuable elements from red mud. The first part of the project was related to recovery of iron from bauxite residue using

*Corresponding author: ender.keskinilic@atilim.edu.tr



pyrometallurgy, both by solid-state reduction and by smelting. In the scope of this paper, some results about solid-state reduction part of the work are therefore presented. The experiments were carried out in parallel on two red mud samples of completely different composition and mineralogy. The aim was to examine whether the methods are applicable for red mud samples of different characteristics.

2. Experimental

2.1. Raw Materials

Two bauxite residues were supplied from two different aluminum plants. The first sample was obtained from Seydisehir Eti Aluminum Co, Turkey. The second sample was taken from Iran Alumina Co. founded in Khorasan, Iran. In the present paper, Seydisehir red mud is abbreviated as TRM (Turkish Red Mud) and Khorasan red mud is shortened as IRM (Iranian Red Mud). The wet as-received red mud samples agglomerated upon drying. The dried sample was passed through a 75 μm sieve. Agglomerates remaining on the sieve were ground in a mortar and again passed through the sieve. The process was repeated until the entire sample passed through the sieve. Chemical and mineralogical analyses of the samples were determined by ICP and XRD, respectively.

In the experiments, coal obtained from Ukraine was used as a reductant. In order to achieve a homogeneous mixture with red mud, the coal was crushed and finely ground to -75 μm in a disc grinder. Chemical composition of the reductant coal is given in Table 1.

Table 1. Chemical composition of the reductant coal (wt.%)

Carbon	S	Ash	Moisture	Volatile matter
76.06	0.33	4.2	1.77	17.64

2.2. Reduction Experiments

Reduction experiments were conducted in a vertical tube furnace. Experimental setup is shown in Figure 1a. In all experiments, the furnace reaction tube was first flushed with nitrogen at 100 ml/min for 30 minutes. Then, the gas flow rate was reduced and kept constant at 50 ml/min throughout the experiment. A setup composed of a gas manometer, capillary tube and a column of a liquid (water) was used to regulate the gas flow rate (Figure 1-b). The flow of gas was controlled by adjusting the height of the liquid in the column.

To perform the reduction experiments, thoroughly mixed red mud + coal mixture of 50 g was poured into the cylindrical alumina crucible and then squeezed with a mallet. Effects of coal amount and temperature on iron metallization were investigated. Iron metallization (hereinafter referred to as metallization) was calculated as follows:

$$\text{Metallization} = \frac{\text{Weight of metallic Fe in the reduced sample (g)}}{\text{Total weight of iron in the red mud (g)}} \times 100 \quad (1)$$

Stoichiometric amount of coal and excess coal (in the range of 5 to 55%) were used to study the effect of reductant. Reduction experiments were conducted between 1000 and 1200°C. The crucible together with the ingredients was charged to the furnace at room temperature and heated to the desired temperature with a rate of 7°C/min. The furnace was kept at the desired temperature for 40 min and then it was cooled down again at the same rate. All heating-waiting-cooling steps were performed under nitrogen atmosphere, as indicated before. The sample was taken out when the furnace reached room temperature.

2.3. Characterization of the Reduced Samples

The partially sintered samples obtained from

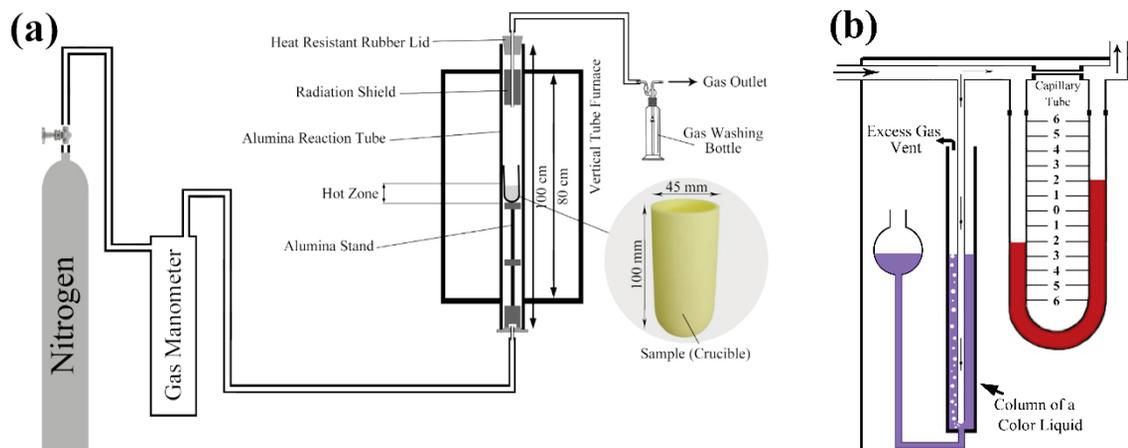


Figure 1. (a) Schematic diagram of the experimental setup, (b) a close-up of the gas manometer

reduction experiments were ground using a disc grinder. Mineralogical composition of the samples was determined by X-ray diffraction (XRD) analysis. It was done with Cu radiation ($K\alpha$ (\AA)=1.54 \AA) (40 kV and 40 mA). Spectra were acquired from 5 to 70° 2 θ at a scanning rate of 0.02° s⁻¹. The fixed mode with 1° divergence slit was used during the test. The ICDD database was used to index the diffraction pattern. Chemical analyzes of the samples were determined by XRF method in accordance with TS EN 15309 standard. In addition, metallic iron content of the reduced samples was determined by the extraction of the metallic phases with bromine-methanol solution and the measurement of the dissolved metals using atomic absorption spectrometry (AAS). The procedure of the analysis could be summarized as follows:

- 1 g of reduced sample was weighed and poured into a 100 ml Erlenmeyer flask,
- 50 ml of bromine-methanol solution (5 vol.%) was added to the flask and mixed with a magnetic stirrer for 1 hour,
- The solution was passed through a filter paper and collected in a 1000 ml beaker,
- 25 ml of sulfuric acid solution (20 vol.%) was added on the filtered solution,
- The solution was boiled to evaporate all the bromine and methanol leaving behind a solid residue. During boiling, 1 ml of hydrogen peroxide was added to the solution,
- 200 ml of distilled water and 25 ml of HCl were added and boiled for 30 minutes to completely dissolve the residue,
- The final solution obtained was passed through a filter paper (grade 1) and collected in 500 ml volumetric flask. Distilled water was added to fill the 500 ml flask, and
- Solution was analyzed for iron using AAS [22].

3. Results and Discussion

3.1. Chemical Composition of the Red Mud Samples

The major constituents of Turkish and Iranian red muds are presented in Table 2. The main difference between the two red mud samples appears to be due to their Fe₂O₃, Na₂O, and CaO contents. Turkish red mud had higher Fe₂O₃ and Na₂O content, while Iranian red mud contained much higher proportions of CaO (12 times larger). The lower Fe₂O₃ content of the Iranian red mud sample was evident from its light brown color as compared to the reddish brown color of the Turkish sample (Figure 2). The different composition of the red mud made it possible to examine the effect of chemical composition on the reduction process as explained in the following sections.

Table 2. Chemical composition of Turkish and Iranian red muds (wt.%)

Sample Name	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	Na ₂ O	TiO ₂	MgO	CaO	K ₂ O	LOI
Turkish Red Mud (TRM)	38.65	19.30	12.10	10.60	4.65	3.15	1.75	0.40	8.20
Iranian Red Mud (IRM)	23.35	16.45	14.70	3.55	4.00	1.25	21.00	0.45	14.10



Figure 2. Photograph of the red mud samples distinguishing the difference in color

3.2. Mineralogy of the Red Mud Samples

The XRD patterns of the as-received red mud samples are shown in Figure 3. It can be seen that Iranian bauxite residue has more complex mineralogy. This is mostly attributed to its high CaO content (Table 2). Both red muds contain Ca containing phase and cancrinite. However, Ca-rich phases calcite and katoite were also detected in Iranian red mud due to its high CaO content.

Formation of sodium containing aluminosilicates was another important finding of mineralogical analysis mainly due to presence of high amounts of Al, Si, and Na in both samples. Again according to XRD findings, iron to be recovered in both bauxite residues was reported as in the form of hematite (Fe₂O₃). Therefore, stoichiometric coal calculations were made for solid-state reduction reaction considering the reaction between carbon and hematite. Rutile as a Ti-bearing mineral was detected in the TRM, but no titanium-containing phases were detected in the IRM. This might be attributed to possible overlapping of the peaks of hematite and ilmenite (FeTiO₃), the possible Ti-containing mineral other than rutile.

Red muds contain a considerable amount of Al-bearing minerals, often as hydroxides. Examination of the XRD results revealed that katoite, cancrinite, kaolinite, and diaspor were the main Al-bearing minerals in the IRM. On the other hand, cancrinite and gibbsite were the Al-bearing minerals in the TRM.

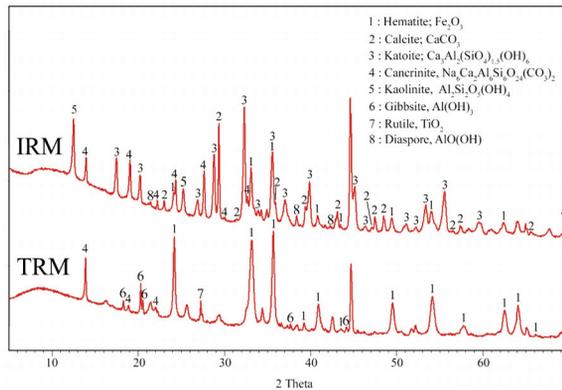


Figure 3. XRD patterns of the as-received red mud samples

3.3. The Effect of Coal Amount on Metallization

The effect of coal amount on metallization was investigated with the experiments performed at 1000°C. As indicated before, the degree of metallization in reduced samples was determined using bromine-methanol analysis. Metallization values obtained from Turkish and Iranian red muds are shown in Figure 4.

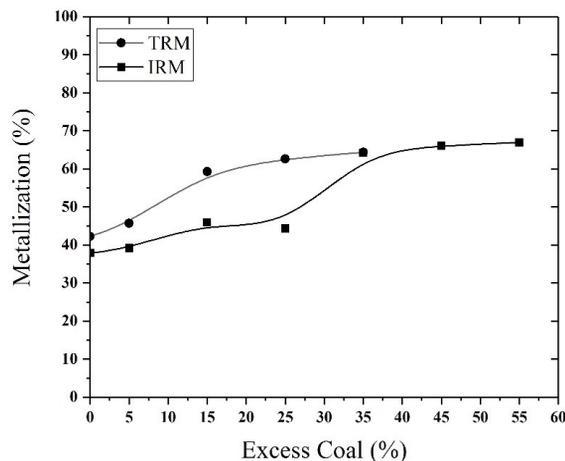


Figure 4. Variation of metallization with excess coal

Metallization for Turkish red mud was reported to increase significantly until 15% excess coal, the rate of increase was sluggish beyond this value. On the contrary, metallization for Iranian red mud was found to rise till 35% excess coal usage. Higher excess coal amounts were also tried for Iranian red mud but no meaningful change in metallization was observed. Therefore, for both bauxite residues, ~70% metallization was obtained from the runs investigating the effect of coal amount and this was achieved with lower amount of coal usage for TRM. The beneficial effect of increased carbon content was also reported in a study [23] using blast furnace sludge as a carbon

source. The same study, however, reported the dissimilar results for graphite, i.e. adverse effect of increased graphite on metallization.

3.4. Remaining Carbon in Reduced Samples

As mentioned in the previous sections, coal was added to the mixture at stoichiometric amount and also at 5-55% in excess of the stoichiometric amount. Coal was added at ratios higher than the stoichiometric amount to improve the kinetics of the reduction reactions, however, some part of the added coal remained unreacted. The remaining carbon content of the samples after reduction was analyzed in LECO brand and SC-144DR model carbon-sulfur analyzer. The carbon contents of the reduced samples are shown in Figure 5 a. It can be seen that the unreacted carbon ratio also increased with the increase of initial coal addition. This result was consistent with literature [23]. Figure 5 b shows the same data in terms of percentage of reacted coal which was calculated as below:

$$\text{Reacted Coal (\%)} = \frac{\text{Carbon input (g)} - \text{Remaining Carbon (g)}}{\text{Carbon input (g)}} \times 100 \quad (2)$$

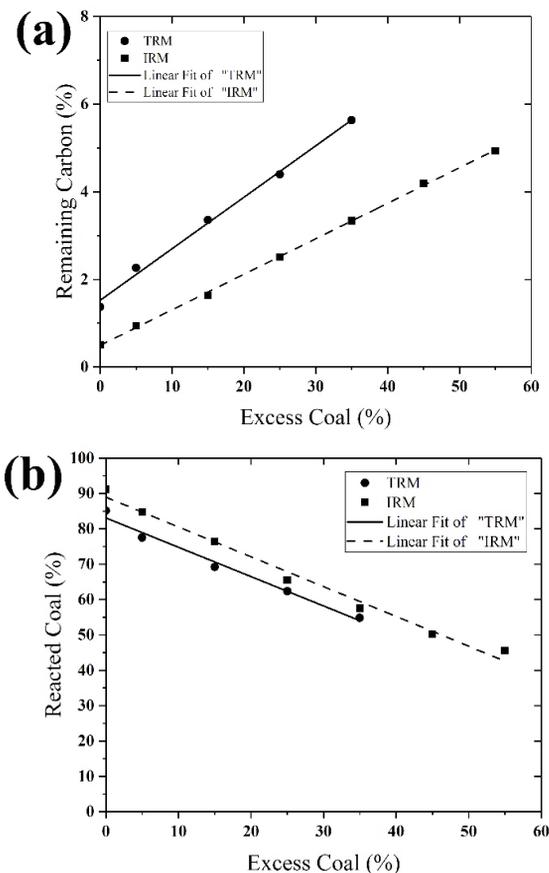


Figure 5. (a) Carbon content of the reduced samples, (b) reacted coal percentage

3.5. The Effect of Temperature on Metallization

The effect of temperature on metallization was studied with the reduction experiments performed at 1000, 1100, and 1200°C. As found from the coal amount studies explained above, 15 and 35% excess coal was respectively used for Turkish and Iranian red mud samples. The results of the bromine-methanol analysis are presented in Figure 6 a for the reduced samples which were coarsely ground in the disc grinder.

For both bauxite residues, an increase of temperature from 1000°C to 1100°C resulted in an increase in metallization. However, further increase of temperature to 1200°C caused a decrease in metallization, which was not in accordance with the expectations considering the thermodynamics and kinetics. This unexpected behavior was linked to partial sintering of the reduced sample at 1200°C causing harder final structure, which was more resistant to grinding. Consequently, poor grinding performance caused some metallic particles locked in the matrix without liberation and so the bromine-

methanol analysis gave lower metallization results. Therefore, considering the importance of grinding time all the samples were subjected to bromine-methanol analysis again after 72 hours grinding operation. From the results, the variation of metallization with temperature was repeated and presented in Figure 6 b. As it can be seen from the figure, although IRM showed slightly better reducibility results, both red muds displayed similar metallization behavior as the temperature increased. Metallization was reported to increase with temperature and the highest values of ~95% were obtained at 1200°C (For TRM and IRM, the values were 94.1% and 96.2%, respectively).

Higher extent of metallization for IRM despite its lower iron content may be explained by the formation of phases with low melting point. As noted above, reduced IRM samples were more difficult to crush than reduced TRM samples, indicating that more liquid phases were formed during reduction. Formation of the liquid phases may have facilitated the diffusion process and contributed to the kinetics of the reduction reactions.

Effect of the temperature on the metallization degree of red mud was investigated by other researchers. In a study [23] graphite and blast furnace sludge were used as the reductant. The metallization degrees were reported to be 80-85% for graphite and 75-80% for blast furnace sludge at 1200 °C temperature. For 1500 °C, the metallization degrees were found to be lower by a few percentages which was attributed to higher oxidation extents at this temperature. Depending on the experimental conditions and mineralogy of the red mud samples, metallization degrees from 50 to over 90% were reported in the literature [18, 24-26].

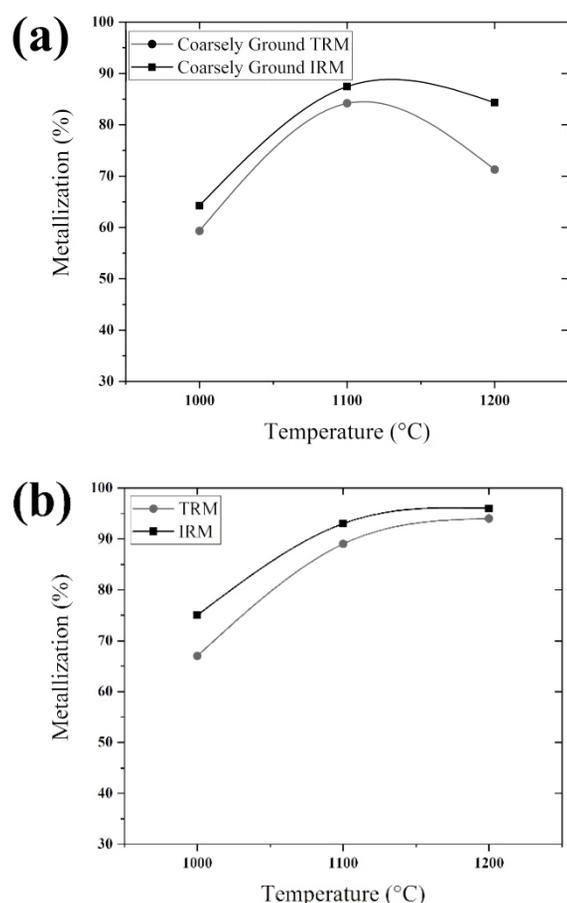


Figure 6. Variation of metallization with temperature for (a) coarsely ground reduced samples, (b) 72 hour-ground reduced samples

3.6. Mineralogy of Reduced Red Mud Samples

The XRD analysis of TRM and IRM samples reduced at 1100°C is shown in Figure 7. The XRD results confirm the high iron metallization. No iron-containing compounds were detected in the reduced IRM, while only weak characteristic peaks of Fe_3O_4 were detected in the reduced TRM. The reduced IRM sample also consisted of two different phases rich in calcium; gehlenite and nepheline. These results were in agreement with the chemical analysis of the as received red mud sample which was rich in CaO. According to the literature [19], however, gehlenite could be also formed in the reduced red mud samples with much lower CaO percentages (5-7%). When the reduced TRM sample was examined, nepheline was the second important compound following iron. Some of the titanium combined with calcium oxide to form perovskite, while the rest formed brookite. In both samples, aluminum and silicon oxides combined to

form a common phase, but no common phase was detected between them and oxide of titanium.

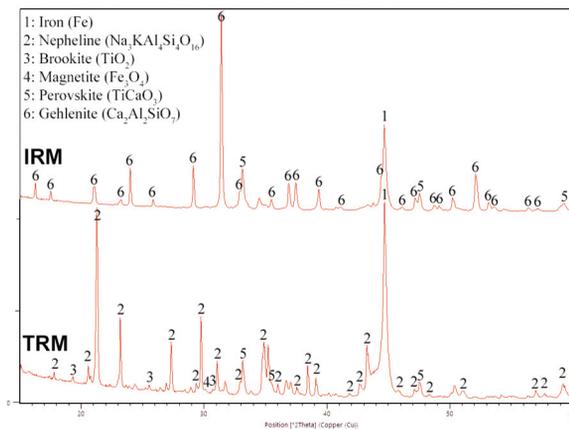


Figure 7. XRD patterns of the red mud samples reduced at 1100°C

4. Conclusions

In this study, reduction behavior of iron in the red mud was studied. Two chemically and mineralogically different red mud samples were used in the experiments. The first sample was obtained from Seydisehir Eti Aluminum Co, Turkey. The second sample was taken from Iran Alumina Co. founded in Khorasan, Iran. Although the two samples were chemically different, iron was present as hematite in both samples. Coal was used to reduce the iron oxide to metallic iron. It was found that more excess coal (i.e. coal/iron oxide weight ratio) was needed for IRM (35%) than for TRM (15%) to maximize reduction. Temperature had significant effect on the reduction process and metallization increased from about 70% to about 95% when the temperature was raised from 1000 to 1200°C. Metallization degree was found to be slightly higher for IRM (96.2%) than for TRM (94.1%). The results proved that a high degree of iron metallization can be achieved regardless of the chemical and mineralogical composition of the red mud sample.

Acknowledgements

The authors would like to thank the Scientific and Technological Research Council of Turkey (TUBITAK) for the financial support given under Project No: 117M185. The authors also wish to express their thanks to Eti Aluminum Co. and Iran Alumina Co. for supplying the red mud samples.

References

[1] M. Shamsuddin, JOM, 38 (2) (1986) 24-31.

- [2] W.M. Mayes, I.T. Burke, H.I. Gomez, Á.D. Anton, M. Molnár, V. Feigl, É. Ujaczki, J. Sustainable Metall., 2 (2016) 332-343.
- [3] S.N. Das, R.S. Thakur, H.S. Ray, Environmental and Waste Management, NML Jamshedpur, Jamshedpur, 1998, p.11-16.
- [4] Y. Liu, R. Naidu, Waste Manage. (Oxford), 34 (2014) 2662-2673.
- [5] Z. Liu, H. Li, Hydrometallurgy, 155 (2015) 29-43.
- [6] G. Qiu, Y. Liu, T. Jiang, Y. Hu, J. Cent. South Univ., 2 (2) (1995) 27-31.
- [7] W. Liu, J. Yang J, B. Xiao, J. Hazard. Mater., 161 (2009) 474-478.
- [8] D. Zhu, T. Chun, J. Pan, Z. He, J. Iron. Steel Res. Int., 19 (8) (2012) 1-5.
- [9] M.J. Rao, J.Q. Zhuang, G.H. Li, Proc. TMS Light Metals Symposium, TMS2013, 3-7 March 2013, San Antonio, Texas, USA, 2013, p. 125-130.
- [10] G. Li, M. Liu, M. Rao, T. Jiang, J. Zhuang, Y. Zhang, J. Hazard. Mater., 280 (2014) 774-780.
- [11] T.J. Chun, D.Q. Zhu, J. Pan, Z. He, Can. Metall. Q., 53 (2) (2014) 183-189.
- [12] T. Chun, D. Li, Z. Di, H. Long, L. Tang, F. Li, Y. Li, J. South. Afr. Inst. Min. Metall., 117 (2017) 361-364.
- [13] P.I. Grudinskii, V.G. Dyubanov, D.V. Zinoveev, M.V. Zheleznyi, Russ. Metall., 11 (2018) 1020-1026.
- [14] M. Samouhos, M. Taxiarchou, G. Pilatos, P.E. Tsakiridis, E. Devlin, M. Pissas, Miner. Eng., 105 (2017) 36-43.
- [15] Y. Man, J. Feng, Powder Technol., 301 (2016) 674-678.
- [16] S. Gostu, B. Mishra, G.P. Martins, Proc. TMS Light Metals Symposium, TMS2017, 26 February-2 March 2017, San Diego, California, USA, 2017, p. 67-73.
- [17] Y. Li, S. Yuan, Y. Han, S. Zhang, P. Gao, J. Min. Metall. Sect. B-Metall., 54 (3) (2018) 393-399.
- [18] M. Samouhos, M. Taxiarchou, P.E. Tsakiridis, K. Potiriadis, J. Hazard. Mater., 254-255 (2013) 193-205.
- [19] S. Agrawal, V. Rayapudi, N. Dhawan, J. Sustainable Metall., 4 (2018) 427-436.
- [20] S. Agrawal, V. Rayapudi, N. Dhawan, Miner. Eng., 132 (2019) 202-210.
- [21] E. Keskinilic, S. Pournaderi, A. Geveci, Y.A. Topkaya, Proc. 11th International Symposium on High-Temperature Metallurgical Processing, TMS2020, 23-27 February 2020, San Diego, California, USA, 2020, p. 511-519.
- [22] K. Kison, J. E. Dickeson, C. B. Belcher, Anal. Chim. Acta, 41 (1968) 107-112.
- [23] D. Mombelli, S. Barella, A. Gruttadauria, C. Mapelli, Appl. Sci.-Basel, 9 (22) (2019) 4902.
- [24] Y. Guo, J. Gao, H. Xu, K. Zhao, X. Shi, J. Iron. Steel Res. Int., 20 (5) (2013) 24-27.
- [25] M. Rao, J. Zhuang, G. Li, J. Zeng, T. Jiang, in Light Metals 2013 (B.A. Sadler), The Minerals, Metals & Materials Series, Springer, Cham., 2016, p.125-130.
- [26] P. Li, Z. Liu, H. Yan, Y. He, IOP Conf. Ser.: Earth Environ. Sci, 252 (2019) 042037.



PONAŠANJE GVOŽĐA U CRVENOM MULJU PRILIKOM POSTUPKA REDUKCIJE

S. Eray ^a, E. Keskinilic ^{b,*}, Y.A. Topkaya ^c, A. Geveci ^c

^a Univerzitet Ari Ibrahim Čečen, Agri, Turska

^b Univerzitet Atilim, Fakultet za metalurško inženjerstvo i materijale, Ankara, Turska

^c Tehnički univerzitet Bliskog istoka, Fakultet za metalurško inženjerstvo i materijale, Ankara, Turska

Apstrakt

Crveni mulj ili ostatak prerade boksita sadrži značajne količine industrijskih metala poput Fe, Al i Ti, kao i retko-zemljanih elemenata Sc, Ce i La. Autori su izveli laboratorijski projekat koji se bavio postepenim izvlačenjem vrednih elemenata iz dva različita ostatka prerade boksita, taloga iranskog crvenog mulja (IRM) i turskog crvenog mulja (TRM). Prva faza je uključivala izvlačenje gvožđa koje je bilo prisutno u crvenom mulju u velikim količinama. Korišćene su dve različite metode: 1) redukcija u čvrstom stanju i magnetna separacija u vlažnoj sredini i 2) topljenje. U okviru ovog rada prikazan je deo rezultata dobijenih tokom izvođenja pirometalurškog dela ovog projekta. Eksperimenti redukcije u čvrstom stanju su pokazali da je za iranski crveni mulj potrebno upotrebiti više uglja (35%) nego za turski crveni mulj (15%) da bi se povećala redukcija gvožđa. Temperatura je imala značajan uticaj na postupak redukcije i metalizacija se povećala sa oko 70% na oko 95% kada je temperatura povišena sa 1000 na 1200°C. Zabeleženo je da je stepen metalizacije bio nešto veći za IRM (96,2%) nego za TRM (94,1%). Rezultati su pokazali da se visok stepen metalizacije gvožđa može postići bez obzira na hemijski i mineraloški sastav uzorka ostatka prerade boksita.

Ključne reči: Crveni mulj; Gvožđe; Redukcija u čvrstom stanju

