Communication

Use of Industrial Waste (Al-Dross, Red Mud, Mill Scale) as Fluxing Agents in the Sulfurization of Fe-Ni-Cu-Co Alloy by Carbothermic Reduction of Calcium Sulfate

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The use of industrial waste [mill scale (MS), red mud (RM), Al-dross (AD)] as fluxing agents in the sulfurization of Fe-Ni-Cu-Co alloy to matte (Fe-Ni-Cu-Co-S) by carbothermic reduction of $CaSO_4$ was investigated at 1673 K (1400 °C). The sulfurization efficiency (SE) was 76 (± 2) pct at RM or AD single fluxing. However, SE drastically increased to approximately 89 pct at a '5AD + 5MS' combination, which was equivalent to reagent-grade chemical '$5Al_2O_3 + 5Fe_2O_3$' fluxing (SE = 88 pct). The present results can be used to improve the cost-effective recovery of rare metals (Ni and Co) from deep sea manganese nodules.

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Manganese nodules have been investigated as an alternative source of rare metals (or critical metals) such as nickel and cobalt. The composition of manganese nodules is listed in Table I.[1,2] One effective method to extract these rare metals from manganese nodules is the reductive smelting—sulfurization (alloy-to-matte conversion)—hydrometallurgy (RSH) combinatorial process.[1,2] Details of the RSH process have been presented in previous articles.[1–3] The Fe-Ni-Cu-Co alloy, which is produced by electric arc furnace (EAF) smelting, is very difficult to crush and leach because of the high energy required for grinding and the low leaching rate caused by the high iron content.[4]

To resolve these problems, the sulfurization step, *viz*. conversion of the Fe-Ni-Cu-Co alloy to the Fe-Ni-Cu-Co-S matte phase, is necessary in the RSH process.[3–5] Elemental sulfur has been added to the molten alloy in the conventional matte-making (sulfurization) method.[3–5] However, because the conversion efficiency is relatively low and the cost of pure sulfur is high, we recently proposed that dehydrated waste gypsum ($CaSO_4$) can be a good alternative sulfur source (in conjunction with appropriate amounts of carbon as a reducing agent) for the conversion of alloy to the matte phase.[3–5] It was also confirmed in our previous study that the addition of Al_2O_3-Fe_2O_3 flux (reagent-grade chemicals) was very effective in the sulfurization process because the intermediate reaction product, *i.e.*, calcium ferrite slag, has a relatively low melting point and thus accelerates the sulfurization reaction.[3]

Alternatively, many researchers have investigated the potential utilization (or valorization) of industrial waste, such as mill scale [MS], red mud [RM], and Al-dross [AD], to create high-added value and reduce environmental problems.[6–13] Therefore, in the present study, we tried to experimentally confirm the feasibility of direct use of industrial wastes as inexpensive fluxing agents to promote the sulfurization efficiency in the matte-making process because these wastes contain useful oxides such as Fe_2O_3 and Al_2O_3.

The experimental apparatus, procedure, and conditions are described in detail in our previous article.[3] We carried out metal-slag-gas three-phase equilibration experiments using a vertical electric resistance furnace at 1673 K (1400 °C) under conditions of $p(O_2) = 1.0 \times 10$ 10 atm and $p(SO_2) = 1.0 \times 10^{-3}$ atm, which was confirmed from a CO-CO_2-SO_2-Ar gas mixture. The impurities in the gas mixture were removed by passage through a purification system. The 17.5Fe-43.5Ni-33.2Cu-5.6Co (mass pct) alloy (produced by the smelting reduction of a manganese nodule in an EAF),[3] reagent-grade $CaSO_4$ (S source), solid carbon (reducing agent), and three kinds of industrial waste (fluxing agents: mill scale, red mud, and Al-dross) were loaded in a fused alumina crucible [outer diameter (OD): 35 mm, inner diameter (ID): 30 mm, height (HT): 50 mm], which was held in a porous alumina holder (OD: 45 mm, ID: 40 mm, HT: 60 mm). The crucible assembly was connected to a molybdenum wire. The composition of the industrial wastes used in the present study is listed in Table II.

After equilibration was attained, the sample was quickly extracted from the hot zone of the furnace and directly quenched by dipping into brine. The slag and metal samples were carefully separated from the crucible. The slag samples were crushed to fine powder and filtered using a stainless steel sieve for chemical analysis. The sulfur content in the samples was determined using a combustion analyzer (CS-800, LECO). Furthermore,

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the slag phase was analyzed using X-ray fluorescence spectroscopy (XRF; ZSX Primus II, Rigaku) and an X-ray diffractometer (XRD; D/MAX-2500PC, Rigaku) to confirm the chemical composition and mineral phase formed during the experiments, respectively.

Before performing the experiments, morphology and crystallographic analyses were performed using XRD and SEM-EDS methods. The mineral phases in each material identified by XRD analysis are shown in Figure 1. Metallic Al and corundum phase (Al_2O_3) in conjunction with a spinel phase ($[Mg,Mn]Al_2O_4$) were identified in Al-dross. Hematite (Fe_2O_3) was the major phase in red mud, while quartz (SiO_2) and wollastonite ($CaSiO_3$) phases also appeared. There were various valences of iron, *i.e.*, hematite, magnetite, and wüstite, in the steel plant mill scale.

Backscattered electron SEM images of Al-dross combined with EDS mapping for the major elements (Al, Si, Mg, and O) are shown in Figure 2. Fine metallic Al particles with different sizes ranging from approximately 10 to 100 μm are dispersed in Al-dross, of which the average diameter of 15 μm was analyzed using an automatic image analyzing software. Furthermore, Al_2O_3 matrix containing small amounts of SiO_2 and MgO constitutes the bulk of the Al-dross.

However, there is a more complicated structure of red mud, as shown in Figure 3. Fe_2O_3 and SiO_2 are distinctly confirmed in red mud by SEM-EDS and XRD analyses. Additionally, other minor phases, such as Al_2O_3, (Ca,Mg)O, and $(Na,K)AlSiO_4$, were also identified, representing a very complicated and diverse composition of red mud as shown in Table II. Alternatively, Qin and Wu[14] reported that there were more complicated phases such as $CaTiO_3$, $FeTiO_3$, $K(Na,K)_3Al_4Si_4O_{16}$ and $Al_2Ca_2FeSi_3H_4O_{14}$ in red mud by XRD analysis. Thus, it is not easy to conclude which phase is the most dominant in red mud; that is dependent on the location and original mineral sources.

The mill scale supplied from the steel plant was mainly composed of various forms of iron oxide and irregular shapes of iron oxide particles are observed in Figure 4. Based on the basic information described above, we will discuss the effect of each industrial waste material as a fluxing agent on the sulfurization efficiency of the Fe-Ni-Cu-Co alloy produced from an EAF smelting of manganese nodules.

The influence of the addition of waste on the sulfurization efficiency of Fe-No-Cu-Co alloy at 1673 K (1400 °C) is shown in Figure 5. The sulfurization efficiency, SE (η_{sulf}), was defined by Eq. [1] in our previous article.[14]

$$\text{Sulfurization Efficiency, } \eta_{\text{sulf}}\ (\text{pct}) = \frac{[\text{pct S}]^{\text{Alloy}}}{[\text{pct S}]_{\text{sat}}^{\text{Matte}}(=27\ \text{pct})} \times 100. \qquad [1]$$

Here, the saturation sulfur content to maintain the matte phase was approximately 27 pct at 1673 K (1400 °C), which was calculated by FactSage™ software in a previous study.[3] The gypsum equivalent ($G_{eq} = 1.0$) and carbon equivalent ($C_{eq} = 1.0$) represent the theoretical amount of $CaSO_4$ required for complete sulfurization and the theoretical molar amount of carbon for complete reduction of $CaSiO_4$ based on Eq. [2], respectively. Values of $G_{eq} = 1.7$ and $C_{eq} = 0.7$ for the effective sulfurization by carbothermic reduction of $CaSO_4$ were obtained in our previous experiments.[3] The effect of carbon addition on sulfurization efficiency was understood based on the following reactions.[3]

$$CaSO_4(s) + 4C(s) = CaS(s) + 4CO(g), \qquad [2a]$$

$$\Delta G^\circ = -653{,}950\ \text{J/mol at 1673 K (1400 °C)}. \qquad [2b]$$

Furthermore, it was proposed that CO gas produced by Eq. [2a] indirectly reduced $CaSiO_4$ by producing CaS as well as CaO with gaseous species such as CO_2 and SO_2 *via* Eqs. [3] and [4]. The Boudouard reaction (Eq. [5]) also contributed to producing CO gas.

$$CaSO_4(s) + 4CO(g) = CaS(s) + 4CO_2(g) \qquad [3a]$$

$$\Delta G^\circ = -172{,}840\ \text{J/mol at 1673 K (1400 °C)} \qquad [3b]$$

Table I. Composition of Manganese Nodules (Mass Percent)[1]

Component	Mn	Fe	Ni	Cu	Co	Si	Al	Ca	Mg
Content	19.8–23.4	6.0–12.0	0.6–0.9	0.3–0.8	0.1–0.4	8.3–16.3	2.7–3.1	1.8–2.0	1.5–1.8
Component	Ti	K	Na	Zn	Mo	Sr	V	Zr	
Content	0.4–0.7	0.7–1.3	2.0–2.2	0.06–0.10	0.04–0.05	0.04–0.09	0.03–0.06	0.03–0.06	

Table II. Composition of Mill Scale, Al-Dross, and Red Mud Used in Present Study (Mass Percent)

	M-Al	M-Fe	FeO	Fe_2O_3	SiO_2	CaO	MgO	Al_2O_3	MnO	TiO_2	Na_2O	Others*
Mill scale	—	0.2	64.2	33.9	0.5	0.6	0.1	0.1	0.2	—	—	0.2
Al-dross	28.6	—	1.4	—	12.4	1.4	6.0	47.8	0.2	—	—	2.2
Red mud	—	—	—	37.6	10.1	6.1	0.4	23.3	0.1	8.0	5.4	9.0

*Cr_2O_3, P_2O_5, ZnO, PbO, K_2O, C, and S.

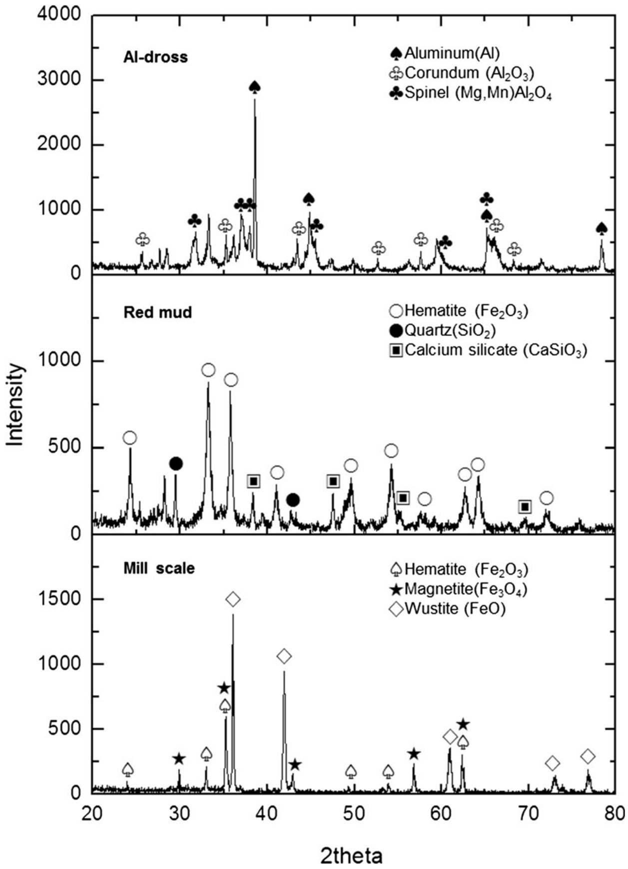

Fig. 1—X-ray diffraction patterns of Al-dross, red mud, and mill scale.

$$CaSO_4(s) + CO(g) = CaO(s) + CO_2(g) + SO_2(g) \qquad [4a]$$

$$\Delta G^\circ = -83{,}290 \text{ J/mol at } 1673 \text{ K } (1400\,^\circ\text{C}) \qquad [4b]$$

$$C(s) + CO_2(g) = 2CO(g) \qquad [5a]$$

$$\Delta G^\circ = -120{,}300 \text{ J/mol at } 1673 \text{ K } (1400\,^\circ\text{C}) \qquad [5b]$$

The sulfurization efficiency (SE) at 10 to 15 pct red mud fluxing and 10 pct Al-dross fluxing was approximately 74 to 78 pct as shown in Figure 5. However, SE increased to approximately 89 pct at '5 pct Al-dross + 5 pct mill scale' fluxing. Hence, combinatorial fluxing with Al-dross and mill scale was cost-effective and the most efficient compared to the single addition of each waste material. Iron oxide in the mill scale promoted the decomposition of $CaSO_4$ due to the formation of the CaO-Fe_tO based slag system. In a previous study,[3] we calculated the liquidus surface of CaO-SiO_2, CaO-Al_2O_3, and CaO-Fe_tO binary systems by FactSage™ software and concluded that the CaO-Fe_tO system exhibits much lower liquidus than other systems, resulting in an acceleration of the sulfurization process. Several authors also reported that the Fe_tO is a suitable catalyst for $CaSO_4$ decomposition.[15–17]

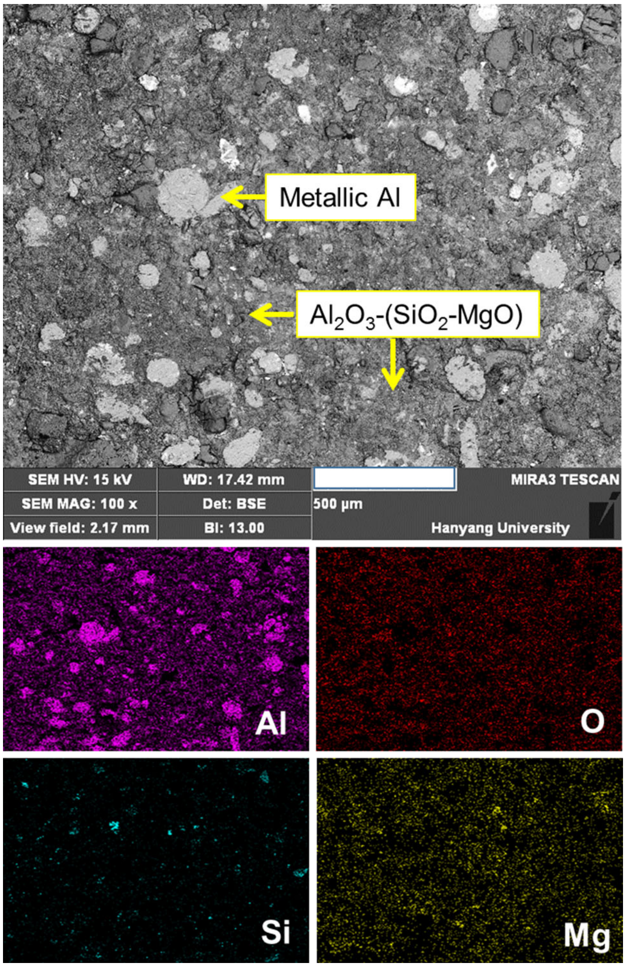

Fig. 2—Backscattered SEM images of Al-dross combined with EDS element mapping.

In addition, it is noteworthy in Figure 5 that the addition of industrial wastes for the sulfurization (matte-making) process exhibits a similar or higher efficiency compared to the fluxing efficiency with reagent-grade chemicals. Specifically, the addition of 10 pct Al-dross (SE = 77 pct) is superior to 10 pct pure Al_2O_3 fluxing (SE = 56 pct) due to the existence of various kinds of impurity oxides in Al-dross such as SiO_2 and MgO. The wide variation of slag composition in the multi-component system could provide lower liquidus, resulting in the promotion of sulfurization efficiency. Moreover, combinatorial fluxing with 5 pct Al-dross and 5 pct mill scale exhibits a similar SE (= 89 pct) compared to the SE (= 88 pct) with reagent-grade chemicals, *viz*. 5 pct Al_2O_3 and 5 pct Fe_2O_3.

The precipitation behavior of solid compounds in the slag during the sulfurization reaction was characterized by XRD analysis as shown in Figure 6. CaS and Ca_2SiO_4 compounds were commonly precipitated when red mud and Al-dross were added separately, whereas only CaS was precipitated when Al-dross and mill scale were added as a fluxing agent. Based on our previous

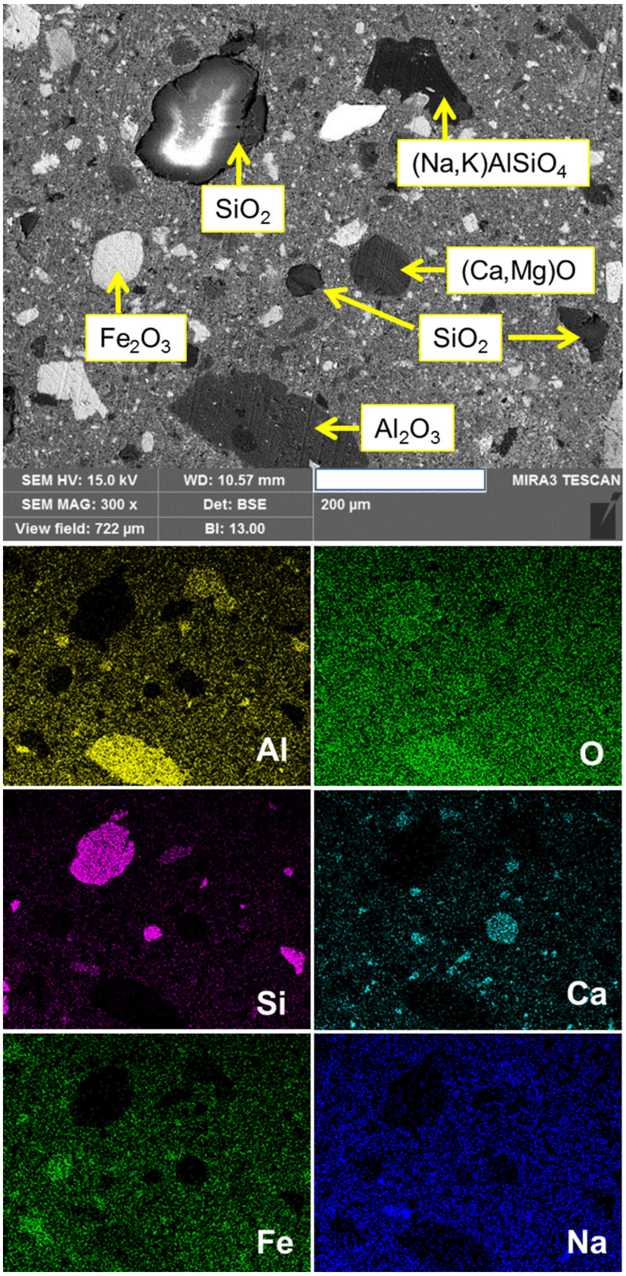

Fig. 3—Backscattered SEM image of red mud combined with EDS element mapping.

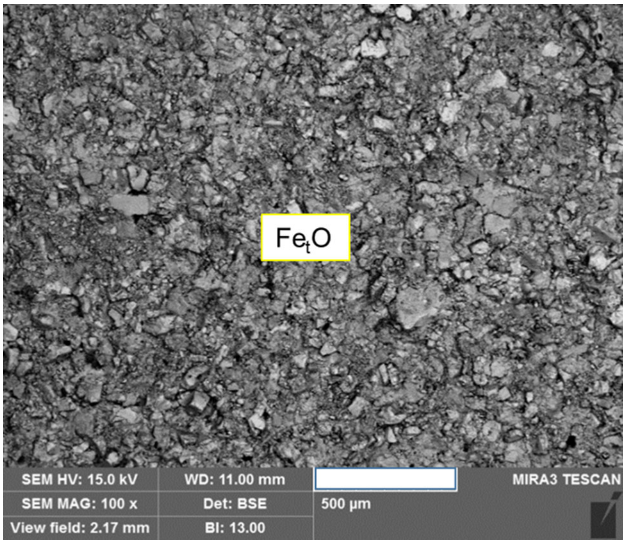

Fig. 4—Backscattered SEM image of mill scale.

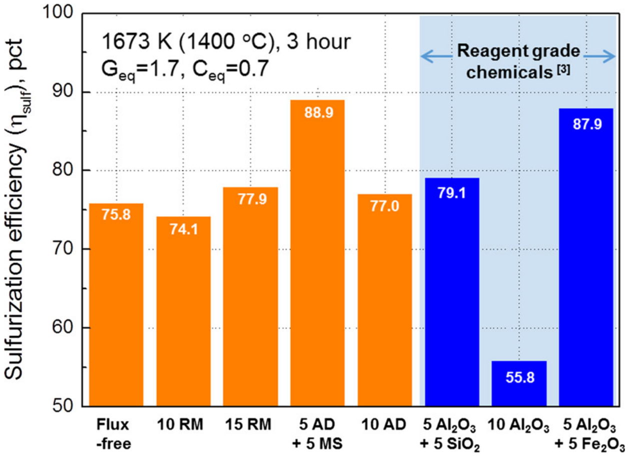

Fig. 5—Fluxing effect of industrial wastes on the sulfurization efficiency of Fe-Ni-Cu-Co alloy at 1673 K (1400 °C). Numbers on the *x*-axis represent mass pct of each flux (*RM* red mud, *AD* Al-dross, *MS* mill scale). The experimental results using reagent-grade chemicals were taken from Ref. [3].

findings,[3] CaS is mostly induced by Eqs. [2] and/or [3], and there is an additional thermodynamic driving force of the following reaction to produce CaO as given in Eq. [6].

$$3CaSO_4(s) + CaS(s) = 4CaO(s) + 4SO_2(g) \qquad [6a]$$

$$\Delta G^\circ = -160{,}300\ \mathrm{J/mol\ at\ 1673\ K\ (1400\ ^\circ C)} \qquad [6b]$$

Specifically, Ca_2SiO_4 was precipitated by the reaction between CaO and SiO_2; the latter was supplied from red mud and Al-dross. Precipitation of Ca_2SiO_4 increases the melting point and thus decreases the fluidity of slag, resulting in a retardation of the sulfurization reaction.[3] In addition, MS is a steel mill by-product, mainly wüstite (FeO$\cong$66 pct) rather than magnetite and hematite (Fe_3O_4 + $Fe_2O_3$$\cong$34 pct). Thus, it is not easy to precipitate $Ca_2Fe_2O_5$ when MS is used compared to the use of reagent-grade Fe_2O_3 because of the lower melting point of FeO than Fe_2O_3. Therefore, it is suggested that low melting point slag with a calcium ferrite-based composition was formed, resulting in promotion of the sulfurization reaction without precipitation of the $Ca_2Fe_2O_5$ compound.

In summary, we considered the sulfurization (matte-making) process using several industrial wastes such as mill scale, red mud, and Al-dross as fluxing agents. It was experimentally confirmed that the addition of industrial waste for the sulfurization process leads to similar or higher sulfurization efficiency than

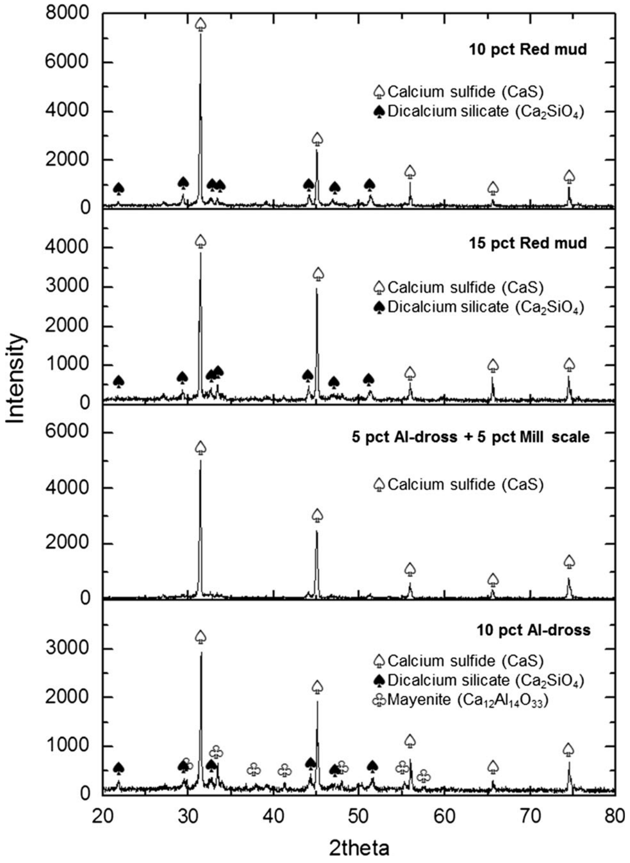

Fig. 6—X-ray diffraction pattern of slag samples after carbothermic reduction of $CaSO_4$ and the sulfurization process fluxed by red mud, Al-dross, and mill scale.

the use of reagent-grade chemicals as a fluxing agent. Specifically, combinatorial fluxing with appropriate amounts of Al-dross and mill scale exhibited a superior sulfurization efficiency compared to fluxing with a single component because of the formation of a calcium ferrite system, which has a relatively low melting point. Consequently, the present results can be utilized in the cost-effective sulfurization of the Fe-Ni-Cu-Co alloy to Fe-Ni-Cu-Co-S matte using cheap industrial waste.

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REFERENCES

1. C.W. Nam, B.S. Kim, and K.H. Park: *Kor. Soc. Geosyst. Eng.*, 2003, vol. 40, pp. 191–97.
2. K.H. Park, D. Mohapatra, H.I. Kim, and X. Guo: *Sep. Purif. Technol.*, 2007, vol. 56, pp. 303–10.
3. E.H. Jeong, C.W. Nam, K.H. Park, and J.H. Park: *Metall. Mater. Trans. B*, 2016, vol. 47B, pp. 1103–12.
4. K.H. Park, C.W. Nam, J.S. Chang, S.C. Ahan, and H.I. Kim: *J. Kor. Inst. Resour. Recycl.*, 2008, vol. 17, pp. 51–58.
5. K.H. Park and C.W. Nam: *Trends Met. Mater. Eng.*, 2002, vol. 15, pp. 15–23.
6. Z. Wang, D. Pinson, S. Chew, B.J. Monaghan, M.I. Pownceby, N.A.S. Webster, H. Rogers, and G. Zhang: *Metall. Mater. Trans. B*, 2016, pp. 1–13.
7. M.C. Bagatini, V. Zymla, E. Osorio, and A.C.F. Vilela: *ISIJ Int.*, 2011, vol. 51, pp. 1072–79.
8. G. Bantsis, M. Betsiou, A. Bourliva, T. Yioultsis, and C. Sikalidis: *Ceram. Int.*, 2012, vol. 38, pp. 721–29.
9. J. Hong, J. Wang, H. Chen, B. Sun, J. Li, and C. Chen: *Trans. Nonferros Met. Soc. China*, 2010, vol. 20, pp. 2155–61.
10. E.M.M. Ewais, N.M. Khalil, M.S. Amin, Y.M.Z. Ahmed, and M.A. Barakat: *Ceram. Int.*, 2009, vol. 35, pp. 3381–88.
11. Y. Pontikes and G.N. Angelopoulos: *Resour. Conserv. Recycl.*, 2013, vol. 73, pp. 53–63.
12. G. Lazzaro, M. Eltrudis, and F. Pranovi: *Resour. Conserv. Recycl.*, 1994, vol. 10, pp. 153–59.
13. V.I. Shatokha, O.O. Gogenko, and S.M. Kripak: *Resour. Conserv. Recycl.*, 2011, vol. 55, pp. 435–40.
14. S. Qin and B. Wu: *Green Chem.*, 2011, vol. 13, pp. 2423–27.
15. www.factsage.com. Accessed May 2015.
16. E.M. van der Merwe, C.A. Strydom, and J.H. Potgieter: *Thermochim. Acta.*, 1999, vols. 340–341, pp. 431–37.
17. I Gruncharov, Y Pelovski, G Bechev, I Dombalov, and P Kirilov: *J. Therm. Anal.*, 1988, vol. 33, pp. 597–602.