Metallurgy and materials

Metalurgia e materiais

Replacement of fluorspar in the desulfurization of hot metal

http://dx.doi.org/10.1590/0370-44672017710039

Arthur Silva Bahiense Moreira
Mestrando
Universidade Federal de Ouro Preto – UFOP
REDEMAT - Rede Temática em Engenharia de Materiais
Ouro Preto – Minas Gerais - Brasil
arthur.sbm@hotmail.com

Carlos Antônio Silva
Professor-Titular
Universidade Federal de Ouro Preto – UFOP
Escola de Minas
Departamento de Engenharia Metalúrgica
Ouro Preto – Minas Gerais - Brasil
casilva@em.ufop.br

Itavahn Alves Silva
Professor-Associado
Universidade Federal de Ouro Preto – UFOP
Escola de Minas
Departamento de Engenharia Metalúrgica
Ouro Preto – Minas Gerais - Brasil
itavahnufop@yahoo.com.br

Abstract

In the steel industry, lime is used as a desulfurizing agent and fluorspar as flux in the hot metal desulfurization process. However there are environmental concerns regarding the use of fluorspar, even when its harmful effects are not fully known. In order to reduce such risks and also to anticipate possible future restrictions, which could undermine the sustainability of steel production, it is proposed to replace the fluorspar for alternative materials in the composition of the desulfurizing lime based mixture. For this purpose new mixtures using aluminum dross, ilmenite, sodalite and ulexite were tested, comparing them with a reference mixture containing fluorspar. The impact of these mixtures on the refractories commonly used in hot metal pretreatment was also checked, since this is an important cost parameter for the steel industries. The laboratory tests showed ulexite as a feasible substitute since the lime (84.03%) – ulexite (10.97%) – graphite (5%) mixture presented the highest desulfurization ratio and low refractory wear (less than the standard fluorspar mixture). The sodalite mixture was the worst by comparison. The ilmenite and aluminum dross mixtures showed similar behavior when compared to the fluorspar mixture.

Keywords: fluorspar, replacement, desulfurization.

1. Introduction

Fluorspar is a common raw material used at ironmaking and steelmaking facilities. Although it is a powerful fluxing agent, its benefits are to be weighed against health and environmental concerns. Fluor can be lost from industrial slags due to the reaction $2CaF_{2\ (slag)} + SiO_{2\ (slag)} \rightarrow SiF_{4\ (g)} + 2CaO_{\ (slag)}$. Depending on temperature and slag composition compound such as NaF(g), KF(g) and (SiF_4), AlF_3, CaF_2, BF_3 can be emitted, Figure 1.

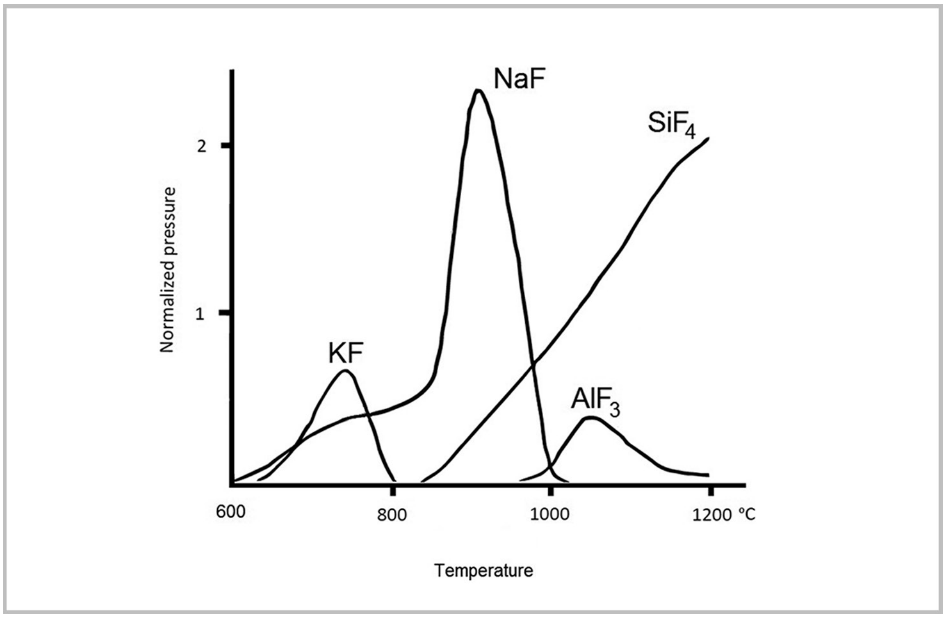

Figure 1
Evolution of fluoride compounds from mould powder under vacuum conditions. (adapted from Zaitsev, 1994)

Other reasons for fluorspar substitution is refractory wear and availability (it is becoming scarce). According to VOLKMANN (2002), sodalite nepheline has been evaluated for fluorspar substitution in BOF operations. Using a 1:1 replacement, a ratio of 88.8% de-P was achieved for fluorspar and 88.1% for sodalite nepheline. Furthermore, at ladle metallurgy, de-S ratio didn't change. Refractory wear due to sodalite was evaluated under laboratory conditions and deemed to be smaller than that of fluorspar. KEUM *et al* (2007) conducted de-S experiments under laboratory conditions in order to assess the performance of some lime mixtures, Table 1. B_2O_3 was suggested as a possible replacement for fluorspar.

Type	Composition (%)				Results	
	CaO	C	CaF_2	B_2O_3	de-S rate (%)	Ks (cm^{-1})
5F	90	5	5	-	82.1	0.014
5C	95	5	-	-	60.6	0.007
10C	90	10	-	-	74.4	0.009
5C-5B	90	5	-	5	81.9	0.0125
5C-10B	85	5	-	10	76.4	0.01
5C-15B	80	5	-	15	81.6	0.013

Table 1
lime-flux mixtures for hot metal de-S.

AMINI *et al* (2004) report studies of fluorspar replacement by a mineral of the feldspar group (nepheline syenite) and ilmenite at steelmaking shops. Slags of similar rheological behaviors can be built. Nepheline was suggested as a proper fluxing agent, Table 2.

Slag	initial	30 min	60 min
Standard	15.27	21.55	23.76
+ 10% fluorspar	11.32	13.9	17.04
+ 10% nepheline	18.76	23.31	26.39
+ 10% ilmenite	29.49	30.89	30.04

Table 2
Lime dissolution using
fluorspar replacements, in wt%.

In regard to hot metal pretreatment, it has been suggested using soda ash additions. CHOI *et al* (2001), NIEKERK and DIPPENAAR (1993) report de-S using $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Na_2O$ slags at 1350°C. Reasonable degrees of de-S can be achieved but alkaline losses by evaporation/chemical reactions can pose metallurgical and environmental restrictions.

As can be seen most of the references regarding fluorspar replacement, they are related to steelmaking (not the scope of this article and where the thermodynamic environment is less favorable). AGUIAR *et al* (2011, 2012) did some work on the utilization of marble cutting residues and fluorspar for hot metal desulfurization; their main drive was related to environmental concerns. SILVA *et al* (2012) investigated the replacement of fluorspar by sodalite in calcium carbide mixtures for hot metal desulfurization. A less common approach is to investigate lime based mixtures used for hot metal pretreatment. Lime is an important reagent due to its unique combination of price and availability.

PEZZIN *et al* (2016) studied the replacement of fluorspar by sodalite nepheline in lime based mixtures and marble waste based mixtures. They tested some mixtures, see Table 3, for de-S efficiency of a hot metal at 1400°C. The laboratory results have shown the addition of sodalite nepheline decreases the de-S efficiency; in addition it has been observed that most of the reaction occurred in the first 10 minutes.

Mixture	Composition (wt%)						$(S_i - S_f) / S_i$ x 100
	CaO	Na_2O	CaF_2	Al_2O_3	MgO	SiO_2	
lime +10% fluorspar	87.4	-	8.7	0.6	-	2.8	97.1
lime +5% fluorspar	92.5	-	4.7	0.42	-	2.49	96.4
marble waste +10% fluorspar	66.3	-	4.04	-	23.9	5.75	90.3
marble waste +5% fluorspar	67.8	-	1.95	-	24.4	5.77	86.2
lime + 5% nepheline	92.7	0.7	-	1.5	-	4.9	85.9
lime +5% fluorspar +3%SiO_2	89.35	-	4.7	0.42	-	5.5	85.2
lime +10% fluorspar +3%SiO_2	84.12	-	9.13	0.62	-	5.8	85.2
marble waste +5% nepheline	67.8	0.29	-	0.51	24.5	6.86	81.4
marble waste +10% nepheline	66.2	0.61	-	1.06	23.8	8.03	78.6
lime + 10% nepheline	87.3	1.3	-	2.8	-	7.62	74.6

Table 3
de-S efficiency using
sodalite nepheline and fluorspar.

Thus replacement of fluorspar at hot metal pretreatment facilities, mainly regarding de-S purposes, is still a challenge. This work reports laboratory results dealing with lime mixtures containing ilmenite, sodalite, aluminum dross and ulexite for de-S at the Kanbara reactor. At the same shops, a lime fluorspar mixture is the standard agent; thus it is taken as a basis of comparison.

A brief information regarding price, world production and reserves of the fluxes tested in these experiments is shown in Table 4. Where this information is not readily available due to marketing reasons, a similar mineral or material, such as alumina instead of aluminum dross, borate minerals in place of ulexite and nepheline syenite instead of sodalite syenite, is taken into consideration for comparison purposes. It is apparent that in some cases a market needs to be developed, if the new technology is adopted.

Table 4
Price, production and reserves in 2016.

Item	Fluorspar	Alumina	Borates (i)	Nepheline Syenite	ilmenite
Average price (US$/t)	270 (a)	360 (c)	550 (e) 494 (j)	73 (f)	150 (g)
World production (t x 1000)	6,400	118.000	9.400	23,000	-
World reserves (t x 1000)	260,000 (b)	28,000,000 (d)	380,000	-	7,400,000 (h)

(a) U.S. export price, acid grade, filtercake, yearend; (b) Measured as 100% calcium fluoride; (c) For U.S. imports, Free Alongside Ship; (d) Bauxite reserves; (e) mineral imports at port of exportation; (f) feldspar, marketable production; (g) U.S. Producer price index, yearend; (h) Yearend operating capacity; (i) borate minerals, such as colemanite, kernite, tincal and ulexite; (j) calcined ulexite used in this work, Free On Board at Suzano (Brazil), US$/R$=3.3833 (2016 average).
Adapted from USGS (2017) and MARTINS (2017).

2. Materials and methodology

Raw materials

The chemical composition of hot metal and raw materials is shown in Table 5 and 6.

Table 5
Hot metal composition, wt%.

Fe	C	Si	Mn	P	S	Cu	Ti	Cr
94.19	5.005	0.275	0.385	0.065	0.025	0.004	0.0255	0.026

Table 6
Raw materials composition, wt%

Material	SiO_2	CaO	MgO	TiO_2	Fe_2O_3	FeO	Na_2O	K_2O	P	S	Al_2O_3	CaF_2	Metallic Al	Mn	B_2O_3	CO_2
Al dross	18.8	2.49	1.81	-----	3.15	------	1.25	0.26	-----	0.04	37.72	-----	31.68	---	---	---
Fluorspar	6.88	2.35	-----	------	0.8	------	------	------	0.04	0.01	1.5	83.6	---	---	---	---
Ilmenite	15.1	---	-----	29.4	44.58	2.52	0.88	0.06	0.07	0.01	2.11	-----	---	1.4	---	---
Sodalite	54.5	----	2.06	0.4	4.26	-----	6.58	1.37	-----	0.08	22.17	------	---	---	---	---
Ulexite	---	---	---	---	---	---	---	---	---	---	---	---	---	---	48.49	---
lime (slag formation)	0.51	92.62	0.30	---	0.21	---	---	---	0.05	0.04	0.08	---	---	---	---	6.18
lime (de-S)	0.22	90.8	0.13	---	0.07	---	---	---	0.05	0.06	0.04	---	---	---	---	8.58

Mistures

Four de-S mixtures, containing ilmenite, sodalite, aluminum dross and ulexite, were designed with the goal of fully replacing the fluorspar and roughly keeping lime participation (75~85%). All the mixtures and their compositions are shown in Tables 7 and 8.

Table 7
de-S mixtures (wt%).

Name	Mixture
Al dross	90% lime + 10% Al dross
Fluorspar (standard)	94% lime + 6% fluorspar
Ilmenite	93% lime + 6.41% ilmenite + 0.59 graphite
Sodalite	93% lime + 7% sodalite
Ulexite	84.03% lime + 10.97% ulexite + 5% graphite

Oxides	Al dross	Fluorspar	Ilmenite	Sodalite	Ulexite
SiO_2	2.07	0.62	1.17	4.02	0.19
CaO	81.98	85.50	84.45	84.45	76.31
MgO	0.298	0.12	0.12	0.27	0.11
TiO_2	-	-	1.88	0.03	-
Fe_2O_3	0.38	0.12	2.92	0.36	0.06
FeO	-	-	0.162	-	-
Na_2O	0.13	-	0.06	0.46	-
K_2O	0.026	-	-	0.096	-
P	0.058	0.052	0.054	0.049	0.045
S	0.054	0.053	0.053	0.057	0.047
Al_2O_3	3.808	0.128	0.172	1.589	0.034
CaF2	-	5.016	-	-	-
Metallic Al	3.17	-	-	-	-
Mn	-	-	0.088	-	-
B_2O_3	-	-	-	-	5.319
CO_2	7.72	8.07	-	7.98	7.21
C	-	-	0.006	-	0.050

Table 8
de-S mixture chemical compositions (wt%).

De-S experiments

In order to reflect industrial conditions a slag/metal ratio of 7.5kg of reagent/ton of hot metal was charged to an electrical resistance furnace, Figure 2.

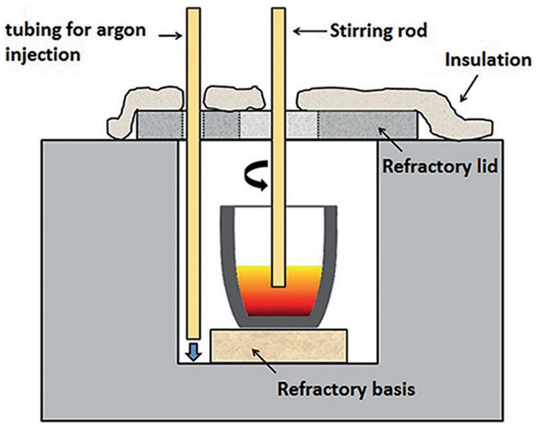

Figure 2
de-S furnace schematics.

The furnace inside was continuously purged with argon at 10~15 lpm flow rate. Agitation was provided by a stirring rod rotating at 800 rpm. A previously dried and pre-heated reagent mixture was added on the top of the metal bath; samples were collected at the beginning of the experiments, 10, 20 and 30 minutes; and temperature was controlled at 1420 ± 5°C. In addition, small amounts of each mixture were pressed into cylinders (3mm high, 5mm diameter) and placed in a furnace at 1400^{o}C during 30 minutes; heating rate was about 8K/s and the furnace was continuously purged with dry nitrogen. The specimens were then taken to an Automatized Mineralogical Analyzer (TIMA of Tescan, Nanolab-Redemat).

Slag attack experiments

Four typical refractory bricks were tested for slag corrosion. An octagonal arrangement made of these bricks composed a crucible where a load of metal was melted. After temperature stabilization, the mixture was added to the bath top and the refractory wear was measured after 30 minutes contact, at the slag line, wall, impeller (according to Figure 4).

3. Results and discussion

A glimpse of the mineralogical analysis results is shown at Figure 3 for the Ilmenite reagent. Labelled as Calcite is a 44.6% oxygen, 1.39% aluminum, 54.1 % calcium phase; unclassified is a phase with roughly 33% oxygen, 1.9% aluminum, 33% calcium, 28.8% titanium and 3.48% iron; peroviskite as a phase containing 33.37% oxygen, 2.05% aluminum, 27.9% calcium, 30.87% titanium and 5.81% iron. All other phases are below the 0.5% level.

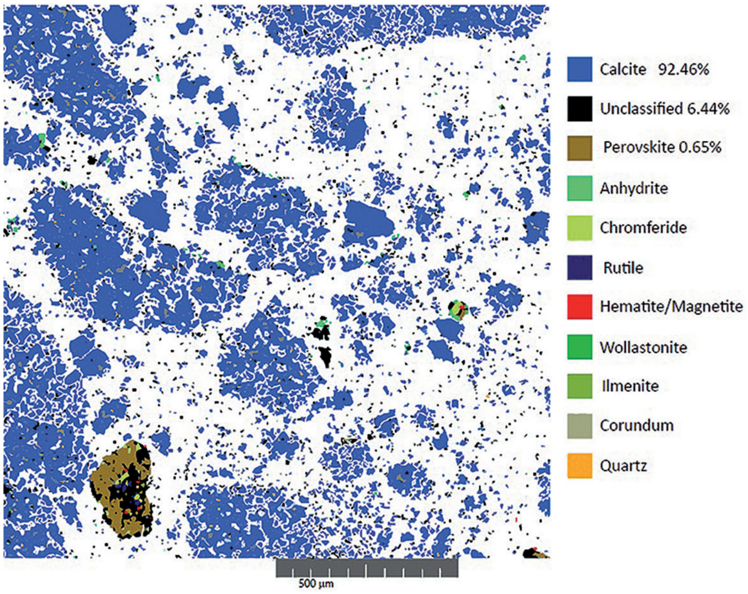

Figure 3
Ilmenite reagent after heat treatment at 1400°C during 30 minutes according to TIMA scanning microscopy analysis.

The objective was to assess the formation of liquid phases and it can be seen that most of this reagent is untouched lime. The same was found for the other mixtures. This result was anticipated by module PHLAMECH of CEQCSI software (an ArcelorMittal's in-house software); accordingly a dry slag would be produced with exception being made for the fluorspar containing mixture, with 6.87% liquid phase. As a suggestion, the de-S process at Kanbara reactor can be deemed as kinetically controlled, since calcium oxide (with its characteristically high sulfur capacity) is the dominant phase and less than 10% of calcium oxide is converted to calcium sulfide in the process. Accordingly CEQCSI software forecasts a remarkable degree of de-S (metal sulfur levels at equilibrium below 2 ppm). This software seeks the minimum of the Gibbs free energy of a chemical system under the mass balance constraints. The Gibbs free energy of the system is the sum of the Gibbs free energy of the constituting phases. Therefore CEQCSI employs some thermodynamic models to describe the different phases: steel, slag, gas, solids, etc. For slag, it uses the Generalized Central Atom model (GCA), which is based on the quasichemical approach. Under equilibria Sulfur and other solutes are distributed within the phases in such way to equalize their chemical potential.

Refractory wear by slag attack for components at critical spots (impact region of ladle and torpedo car, ladle slag line, wall and KR's impeller) is shown in Figure 4. As can be seen, fluorspar potentially brings about the highest level of slag corrosion. Aluminum dross mixture can be especially corrosive to wall refractory and impeller. Sodalite, Ilmenite and Ulexite mixtures seem promising since the slag attack is comparatively lower. The results regarding fluorspar and sodalite are in accordance with those from VOLKMANN (2002), although his experiments showed a difference not so pronounced as in the present study.

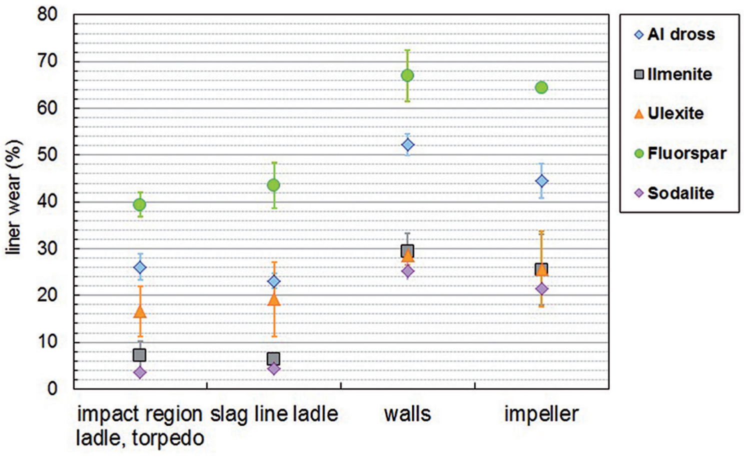

Figure 4
Refractory expected wear by slag attack.

Average values for metal composition and degree of desulfurization are shown at Table 9 and Figure 5. Data for fluorspar are averages of three runs. All mixtures can lead to Sulfur removal, as predicted by thermodynamic calculations and mineralogical analysis. Ulexite, one of the less corrosive options seems highly feasible as a hot metal desulfurization reagent additive. Desulfurization with ulexite can be even better than with standard fluorspar mixtures, following the same trend presented by KEUM et al (2007). The sodalite mixture is the worst by comparison. This contrast between fluorspar and sodalite was not observed by VOLKMAN. However, it is important to mention that VOLKMAN's work was done for steel (metallurgy ladle process) with a fluorspar replacement ratio of 1:1, while in the present work de-S was studied for hotmetal. Here, the replacement ratio was almost the same, 6:7 (fluorspar:sodalite). The others, fluorspar, ilmenite and aluminum dross mixtures show similar behavior. Results from PEZZIN (2016) are not directly comparable since the mixtures components are different.

experiment	Sample	%C	%S	100x(S_0 - S) / S_0
Fluorspar (1)	Initial	4.86	0.034	0.00
	10 min	4.81	0.020	41.18
	20 min	4.90	0.020	41.18
	30 min	4.70	0.017	50.00
Fluorspar (2)	Initial	4.76	0.029	0.00
	10 min	4.75	0.012	58.62
	20 min	4.76	0.008	77.65
	30 min	4.80	0.008	73.79
Fluorspar (3)	Initial	4.88	0.035	0.00
	10 min	4.85	0.024	31.43
	20 min	4.91	0.025	26.47
	30 min	4.81	0.024	31.43
Aluminum dross	Initial	4.68	0.027	0.00
	10 min	4.69	0.02	25.93
	20 min	4.76	0.018	47.06
	30 min	4.80	0.014	48.15
ilmenite	initial	4.62	0.032	0.00
	10 min	4.65	0.025	21.88
	20 min	-	-	-
	30 min	4.60	0.024	25.00
sodalite	initial	4.77	0.026	0.00
	10 min	4.79	0.024	7.69
	20 min	4.79	0.022	35.29
	30 min	4.76	0.018	30.77
ulexite	initial	4.81	0.030	0.00
	10 min	4.82	0.019	36.67
	20 min	4.86	0.012	64.71
	30 min	4.82	0.008	73.33

Table 9
Evolution of carbon and sulfur contents during de-S experiments.

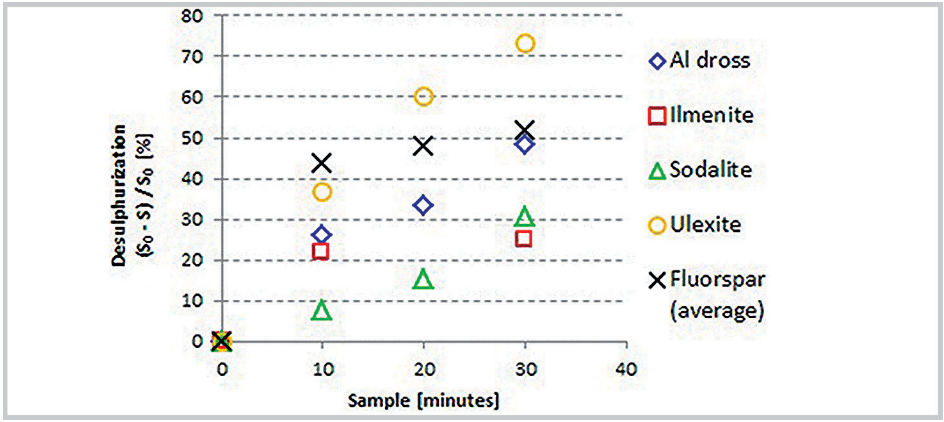

Figure 5
Desulfurization results for some specific mixtures.

Results from these experiments are important since they suggest options for fluorspar removal. Disposal of heavily under-reacted (~90% of free lime) desulfurization agent can pose an environment challenge. Thus finding reactants with better de-S performance than the standard fluorspar mixture is also important.

4. Conclusions

- Thermodynamic calculations suggested that any of the tested mixtures could be used for de-S purposes;
- No significant liquid phase formation was anticipated for any of the tested mixtures, even for the standard fluorspar mixture;
- Mineralogical analysis made apparent the presence of a large amount of unreacted lime;
- The lime (84.03%) ulexite (10.97%) graphite (5%) mixture presented the highest desulfurization performance and low refractory wear (less than half of refractory wear experimented with the fluorspar mixture). The ilmenite and aluminum dross mixtures showed similar de-S behavior as compared to the fluorspar mixture. The sodalite mixture was the worst by comparison.

References

AGUIAR, F. N. ***Utilização de resíduo de mármore como dessulfurante de ferro-gusa.*** Vitória: Instituto Federal de Educação, Ciência e Tecnologia do Espírito Santo, 2011. (Master Thesis).

AGUIAR, F. N., GRILLO, F. F., TENORIO, J. A. S., OLIVEIRA, J. R. Hot metal desulfurization by marble waste and fluorspar. ***Rem: Rev. Esc. Minas,*** Ouro Preto, v. 65, n. 2, p. 233-240, 2012.

AMINI, H., OSTROVSKI, S. O., BRUNGS, M. A study of dissolution of dense lime in molten slags under static conditions. In: INTERNATIONAL CONFERENCE ON MOLTEN SLAGS FLUXES AND SALTS, 7. Cape Town, South Africa, p. 595-599, 2004.

CHOI, J. Y., KIM, D. J., LEE, H. G. Reaction kinetics of desulfurization of molten pig iron using CaO-SiO2-Al2O3-Na2O Slag Systems. ***ISIJ International,*** v. 41, n. 3, p. 216-224, 2001.

KEUM, C. H., SEO, S. M., CHOI, J. H., PARK, J. M., HONG, J. K. Fluorspar-free desulfurization flux in hot metal pretreatment at kwangyang works, Posco. In: IAS STEELMAKING CONFERENCE, 16. Rosario, Argentina, p. 183-188, 2007.

MARTINS, V. Produquímica [personal message]. Message received by <arthur.moreira@arcelormittal.com.br> at 31 oct. 2017.

NIEKERK, V. W. H., DIPPENAAR, R. J. Thermodynamic aspects of Na_2O and CaF_2 containing lime-based slags used for desulphurization of hot-metal. ***ISIJ International,*** v. 33, n. 1, p. 59-65, 1993.

PEZZIN, R. O., SOARES, S. G., OLIVEIRA, H. C. C., OLIVEIRA, S. M. R. D., GRILLO, F. F., JUNCA, E., OLIVEIRA, J. R. Determinação da Iinfluência da composição das misturas dessulfurantes de ferro-gusa usando a termodinâmica computacional. In: STEELMAKING SEMINAR INTERNATIONAL, 47. Rio de Janeiro, p.684-692, 2016.

SILVA, M. A. ***Avaliação da utilização de agentes dessulfurantes à base de carbureto de cálcio contendo sodalita em substituição à fluorita em carro-torpedo.*** Belo Horizonte: Universidade Federal de Minas Gerais, 2012. (Master Thesis).

USGS – U.S Geological Survey. Available at: <https://minerals.usgs.gov/minerals/pubs/mcs/>. Accessed 26 oct. 2017.

VOLKMANN, A. Utilização da sodalita-nefelínica em substituição à fluorita na Aciaria da Usiminas. In: SEMINÁRIO DE FUSÃO, REFINO E SOLIDIFICAÇÃO DOS METAIS, 33. Santos, p.151-160, 2002.

ZAITSEV, A. I., LEITES, A. V., LITVINA, A. D., MOGUTNOV, B. M. ***Steel research,*** v. 65, p. 368-374, 1994.

Received: 3 November 2017 - Accepted: 23 January 2018.