

STUDY OF INDIGENOUS FLUORSPAR AS METALLURGICAL FLUX

Zeeshan Al Hameed¹, Junaid Saleem^{2*}, Syed Sajid Hussain¹, Ahsan Abdul Ghani², Hira Lal²

ABSTRACT

The mineral reservoirs of Pakistan have an enormous amount of Fluorspar. Approximately 1 million ton reservoir of Fluorspar was reported previously and is mostly exploitable. Also, around one third of its usage is in the form of metallurgical flux, a key slag fluidizer in steel industry as it increases the fluidity of slag in the ladle furnace. However, it needs to undergo beneficiation process to get it concentrated before being added into the furnace. In this study, we report, for the first time in Pakistan, that the indigenous Fluorspar can directly be used as a metallurgical flux without any beneficiation process as it is rich in Fluorite and also contains small amount of other compounds that are required to be fed as part of slag. Specifically, it contains only trace amount of apatite as compared to global Fluorspar. The composition of indigenous Fluorspar was compared with standard specifications and a detailed characterization was carried out including chemical, mineralogical, and spectroscopic analysis. Further, indigenous Fluorspar was applied as flux in the ladle refining operation of a local steel mill of Pakistan and results were stated on the basis of degree of desulphurization and different basicity indexes.

KEYWORDS: Fluorspar, metallurgical flux, slag, Fluorite

INTRODUCTION

Fluorite is one of the industrial minerals with commercial name as Fluorspar and chemical formula as CaF_2 . One-third of the Fluorite's production is 'metaspar' or metallurgical grade Fluorspar which contains approximately 80% CaF_2 . Fluorspar is generally produced in three different grades: acid grade, metallurgical grade, and acid & metallurgical grade. Interestingly most of the Fluorite mines have similar problem i.e. presence of apatite, which makes it inappropriate to be directly used in steel sector¹. Fluorite obtained from these mines is subjected to the beneficiation process to get it concentrated and then utilized in steel industry. After beneficiation the concentrates are generally produced in powder forms which are not suitable for metallurgical operations².

China is by far the biggest producer of Fluorspar and cover almost 62% of the world's total Fluorspar production^{3,4}. Pakistan, on the other hand, has Fluorite mines in two of its provinces namely Baluchistan and Khyber Pakhtunkhwa (KPK). In Baluchistan, Kalat district; Maran and pad Maran have reservoirs of low to medium grade Fluorite⁵, while in KPK, Kohat basin, Sulaiman basin, and Khyber Hazara zone have Fluorite deposits. Recently, huge deposits were discovered in KPK province⁶.

Although considerable research has so far been conducted on Pakistani Fluorite⁶⁻¹², the focus was mainly placed to its geological studies. In this study, characterization of indigenous Fluorspar has been performed by means of chemical, mineralogical, & spectroscopic investigations. Furthermore, its industrial application as metallurgical Fluorspar has also been validated.

MATERIAL AND METHODS

Three different materials have been investigated in this study; Fluorspar, Slag formed by CaO which fluidized by indigenous Fluorspar during the ladle refining process. The Fluorspar, mined from Lora Lai collected from local supplier, Slag samples collected before & after addition of Fluorspar and lime (CaO) in ladle furnace and at the same time steel sample were also drawn to check its sulfur content.

Chemical Composition

The chemical composition of Fluorspar & slag has been determined by Wet chemical method & XRF spectrometer (Axios max, PANalytical, Netherlands). Moisture has been determined at 105°C in lab oven. The C & S both were analyzed by combustion rapid analyzer (Leco CS444, USA) in Fluorspar and Slag samples. The composition of steel grade under process has been analyzed by optical emission spark spectrometer (OES,

¹ Department of Quality Assurance, Peoples Steel Mills Ltd., Karachi, Pakistan.

^{2*} Department of Chemical Engineering, University of Karachi, Karachi, Pakistan.

ARL, and Switzerland).

Mineralogical Study

The mineralogical characterization of indigenous Fluorspar has been carried out by X-Rays Diffractometer (XPRT-PRO, PANalytical, Netherlands) with Cu tube; 2 Theta angle with start Position 10.00°, End position 79.995° and step size 0.01°

Infrared Spectroscopy

The IR spectra was obtained by using Fourier Transform Infrared spectroscopy (FTIR, Shimadzu, Germany) to investigate the presence of bonds of different functional groups ; OH, C-O, Ca-F and C=O, Si-O & P-O at particular frequencies.

RESULT & DISCUSSION

Characterization studies of indigenous Fluorspar

The chemical composition of Fluorite sample based on Wet chemical method is mentioned in Table 1. CaF₂ has been analyzed by wet chemical method, S by Leco-CS444

Table 1: Chemical analyses of indigenous Fluorspar¹³

	CaF ₂	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	R ₂ O ₃	P ₂ O ₅	S
Samples (%) Requirement	84.31	5.46	2.8	0.9	0.13	1.03	0.012	0.15
	Min 80	Max 8	Max 3	-	-	Max 3.5	trace	Max0.3

and remaining compounds by XRF spectrometer. The XRF and Leco- CS444 calibrated by certified reference material BCS 392 (Fluorspar). The accuracy of XRF and Leco CS-444 is tabulated in Table 2. The chemical composition of indigenous Fluorspar is found as per required specification of metallurgical grade (Grade 3) Fluorspar. This standard was developed by Ore & raw material sectional committee, SMSC 16 under the Bureau of Indian standards¹³. It is important to mention that phosphorous content is very low (less than 0.1%) in the indigenous Fluorspar which makes this type of Fluorspar useful to be directly used in steel plant without any beneficiation process to remove phosphorous.

The XRD pattern of indigenous Fluorspar is mentioned in Figure 1 while the peak list is mentioned in Table 3. The peak list was obtained by XRD and searched and matched by power diffraction file (PDF) pattern by software and revealed the presence of CaF₂, SiO₂ and Fe content of indigenous Fluorspar. It is evident that all of Fluorine available in the sample is in the form of single phase of CaF₂.

No other fluorine compounds are present in the sample. Further that Phosphorus peak is not visible which confirms the absence of apatite (Phosphorous content) in

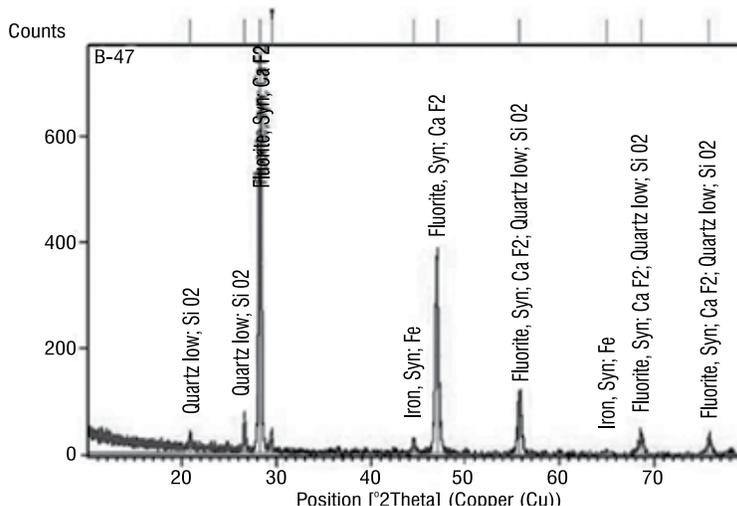


Figure 1: XRD analysis of indigenous Fluorspar

Table 2: The accuracy and precision of the equipments used in experiments

Element	Accuracy	Precision	Equipment
Si	98.35%	0.001	XRF
Al	98.11%	0.001	XRF
Fe	99.1%	0.002	XRF
P	99.35%	0.0008	XRF
S	99.995%	0.00003	Leco
C	99.993%	0.000003	Leco

Table 3: XRD peak list of indigenous Fluorspar

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing	Rel. Int.[%]
20.84984	27.77963	0.47232	4.26057	3.83
26.65899	63.13157	0.27552	3.34389	8.7
28.23372	726.032	0.0984	3.16087	100
29.44394	32.96217	0.31488	3.03365	4.54
29.44394	32.96217	0.31488	3.03365	4.54
44.52279	23.70047	0.31488	2.03503	3.26
47.03336	370.7361	0.3936	1.9321	51.06
55.68906	100.4607	0.35424	1.65057	13.84
64.95895	5.109705	0.47232	1.43564	0.7
68.604	35.12172	0.3936	1.36799	4.84
75.8407	30.27708	0.47232	1.25444	4.17

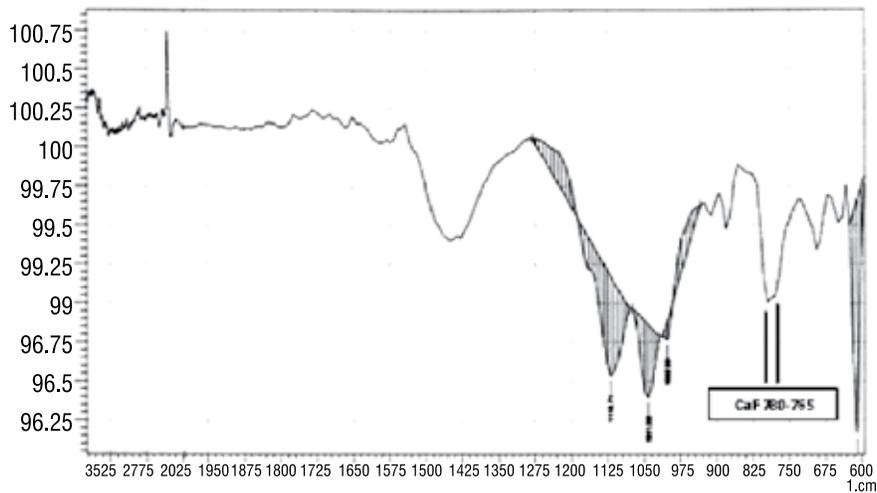
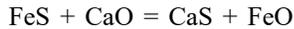


Figure 2: IR spectra of Fluorite sample by FTIR

the indigenous Fluorspar. The IR spectra of the sample obtained by FTIR has further strengthen the claim of CaF₂ presence by Ca-F stretching peak between 765 cm⁻¹ to 780 cm⁻¹ (shown in the Figure 2). It also resembles to the standard IR spectrum of Fluorite¹⁴. The presence of a band at 1460 cm⁻¹ in Figure 4b and 5b indicates that sodium carbonate species are present A band present at 1460 cm-1 indicates calcium carbonate presence in the Fluorspar while Peaks between 1080-to-1100 cm-1 may be due to strong vibrations of Si-O bands and the peak at 1550 cm-1 is due to H-O-H bending.

Characterization of slag formed for De-sulphurization

The sulphur (S) removal from molten steel during steel making is very important step because S limits are almost defined in every steel grade. S content in steels plays a vital role for machining capabilities of steels in the end products. Lime is the better desulphurizer and make following reaction with dissolved sulphur of molten metal and transfer it into the slag:



Once the lime saturation in the slag achieved, no more de-sulphurization is possible. At this point, Fluorspar is added into the slag to increase fluidity of the slag and hence lime solubility increases which results in more de-sulphurization. The experiment has been conducted to verify indigenous Fluorspar as a metallurgical flux without beneficiation. Low carbon steel grade has been chosen to demonstrate the slag forming with lime and fluidity effect of Fluorspar in the thick slag. Molten steel was transferred from Electric Arc Furnace to the Ladle furnace along with some slag. This molten steel & slag was collected, marked (Sample 1) and analyzed by spark spectrometer (ARL, Switzerland) and CS rapid analyzer (Leco, USA) respectively. After 15 min, lime was added to form slag and continuously purging of Nitrogen gas (N₂) for homogenization. Another sample of molten metal and slag, each was drawn and marked as Sample 2. When the slag became thick and the melter seemed that no more sulphur is removing then some indigenous Fluorspar has been added into the ladle and after 15 minutes of purging another sample of metal and slag was drawn separately and marked as sample 3. The ‘S’ content of metal and Slag as well as degree of desulphurization (η_s) is mentioned in Table 4.

Table 4: ‘S’ content in steel and slag & degree of desulphurization

		S% in Slag	S% in Steel	η _s
LAS	Phase 1		0.026	
	Phase 2	0.29	0.02	23.08%
	Phase 3	0.45	0.0087	66.54%
MCS	Phase 1		0.0319	
	Phase 2	0.1192	0.0291	8.78%
	Phase 3	0.1868	0.023	27.90%
HCS	Phase 1		0.0387	
	Phase 2	0.1334	0.0293	24.29%
	Phase 3	0.173	0.0254	34.37%
LCS	Phase 1		0.0146	
	Phase 2	0.177	0.0138	5.48%
	Phase 3	0.224	0.0052	64.38%

Where: $\eta_s (\text{From Metal}) = \frac{[S]_i - [S]_t}{[S]_i}$ and

[S]_i = Initial sulphur content in steel

[S]_t = After addition sulphur content in steel

η_s = Degree of Desulphurization [15]

LAS= low alloy steel; MCS= medium carbon steel; HCS= high carbon steel; LCS= low carbon steel

A cumulative plot between degrees of desulphurization in phase-2 and phase-3 is drawn in Figure 3. Moreover the η_s was initially Low in phase-2 when slag became thick and further desulphurization was not possible then Fluorspar added (Phase-3) and η_s drastically increased up to 66.54 %. An inverse relationship has also been verified by plotting the scatter diagram between S% in steel and S% in slag among different phases of experiment as shown in Figure 4, it is evident that S% is decreasing in the metal whereas increasing in the slag, as the process proceeds from phase-2 to phase-3. An almost linear but inverse relationship between S% in steel and S% in slag is also evident for all four steel grades (LAS, MCS, and HCS 7 LCS).

Investigation of slag parameters

The complete chemical composition of slags by XRF spectrometer is mentioned in Table 5.

The slag parameters in terms of basicity and Mannesmann’s index was calculated by chemical composition of slags and listed up in Table 6. The slag basicity B1 shows basic nature of slags and after addition of CaF₂ the basicity increased and also doubled, it means more CaO/CaS is transferred into slag. The slag basicity B5 is decreasing and near minimum basicity ratio of 1.5¹⁶. Furthermore the MM index is varying with the degree of desulphurization as shown in Figure 5.

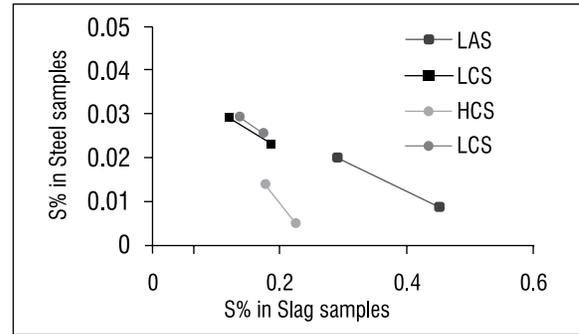


Figure 4: Scatter diagram of S% in steel and slag

Table 5: Complete Chemical composition of slags

Chemicals %	Slag (only CaO)	Slag(CaF ₂ added)
SiO ₂	11.278	15.166
Al ₂ O	10.135	10.69
CaO	4.625	13.08
MgO	29.84	21.41
P ₂ O ₅	0.079	0.022
S	0.29	0.45
FeO	35.049	13.398
MnO	1.884	20.942

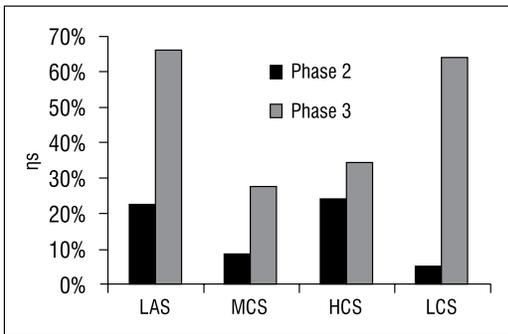


Figure 3: Impact of η_s in different steel grade

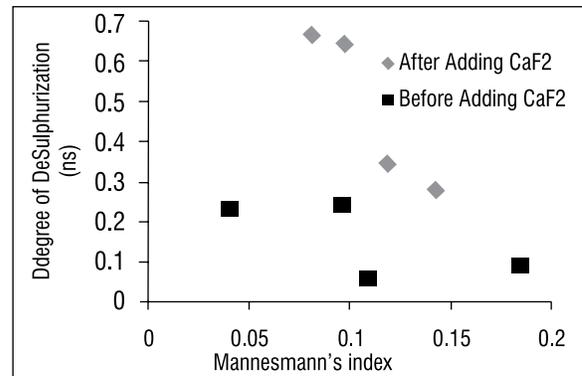


Figure 5: The relationship diagram of η_s and MM index before and after addition of CaF₂

Table 6: Slag parameters where B1 (basicity) = (CaO/SiO₂), B5 (basicity) = (CaO+MgO)/(SiO₂ + Al₂O₃)

		Slag Parameters			MM
		B1	B5	ηs	
LAS	Before (CaO)	0.410	1.610	23.08%	0.040
	After (CaF ₂)	0.862	1.334	66.54%	0.081
MCS	Before (CaO)	1.445	1.700	8.78%	0.184
	After (CaF ₂)	1.520	1.725	27.90%	0.143
HCS	Before (CaO)	2.662	1.204	24.29%	0.096
	After (CaF ₂)	2.134	1.441	34.37%	0.118
LCS	Before (CaO)	3.531	1.146	5.48%	0.109
	After (CaF ₂)	2.966	1.251	64.38%	0.098

CONCLUSIONS

The characterization of indigenous Fluorspar has been carried out by means of its chemical, mineralogical and molecular properties to verify its suitability as a metallurgical flux in local steel industries. Furthermore, its application as flux has also been studied in a local steel plant by using indigenous Fluorspar as a flux (fluidizer) at ladle furnace refining of low alloy steel. The following findings may be enlisted from achieved results:

The chemical composition of indigenous Fluorspar found as per metallurgical grade (Type 3). It may be directly used as metallurgical flux in steel industry without any beneficiation process which is essentially required by most of the world Fluorite reservoirs.

Mineralogical and molecular studies are evident that organic species are not present in indigenous Fluorspar. Also, phosphate content is found to be very low which otherwise may cause alteration in the composition of molten metal in ladle furnace refining operation.

The characterization of steel sample and slag sample revealed that there is a vital impact of indigenous Fluorspar on the degree of de-sulphurization and its addition during ladle refining increases the degree of desulphurization from 23.08% to 66.56%.

The slag basicity investigation reveals that the basicity B1 of slag is improved from 0.41 to 0.86 which indicates the increase in saturation of lime (CaO) in the slag. However, Basicity B5 is slightly reduced from 1.61 to 1.33 while the optimum value of B5 is generally considered as 1.5.

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