

Co-processing of Spent Pot Liner Generated in Aluminum Industry



Ulhas Parlikar

Director MRAI & Global Consultant



Cement Kiln Co-processing is an ideal option for gainful management of SPL Carbon & Refractory



Aluminium
Smelters



SPL Carbon & Refractory

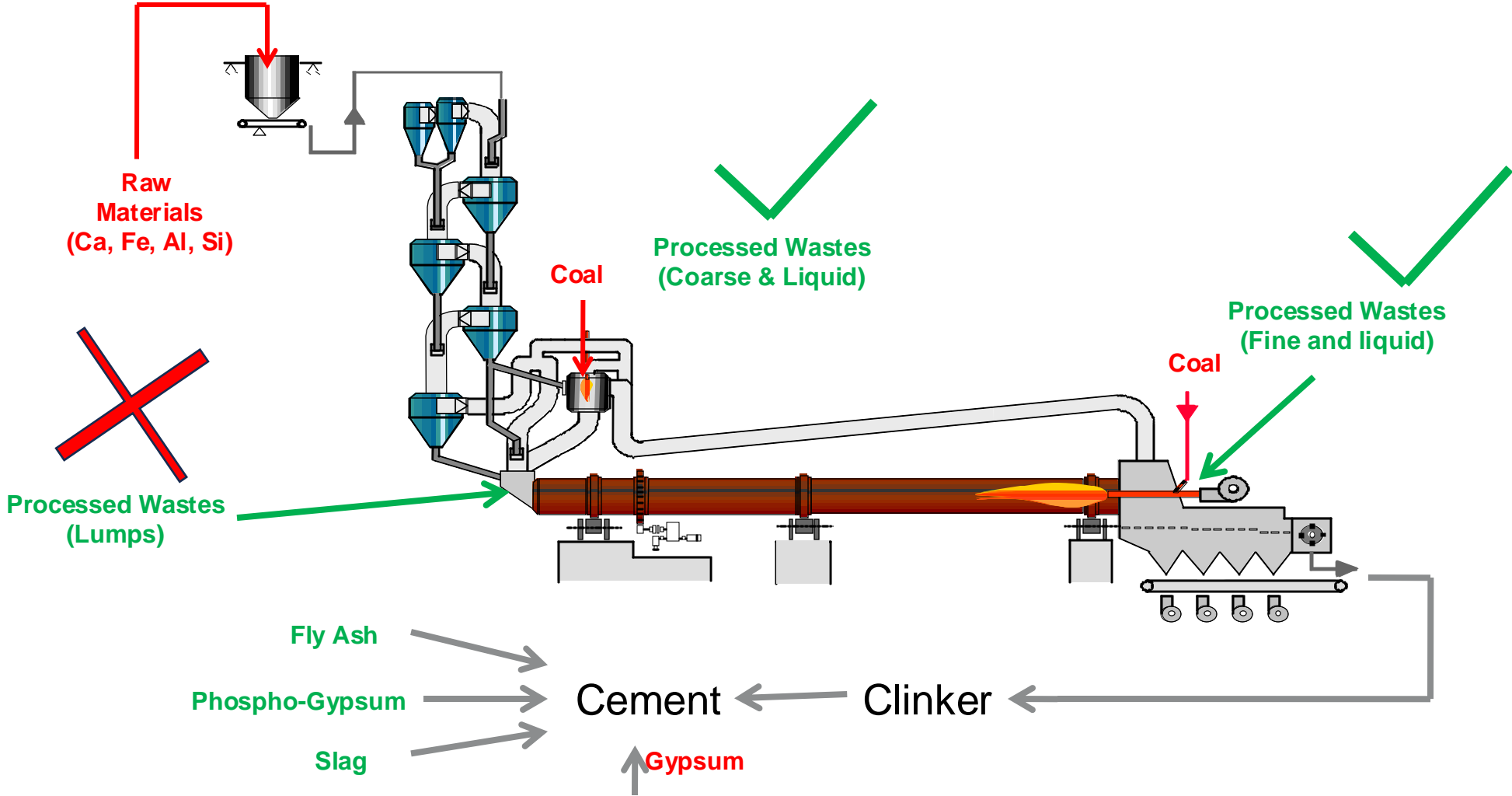


Cement Plant

- Carbon content in SPL gets utilised as source of energy
- Oxides present in refractory portion get utilised as Raw materials
- Fluorine present in SPL gets utilised as Mineraliser to reduce the liquification temperature
- CN present in SPL gets disposed in an environmentally sound manner
- Co-processing of SPL provides an excellent option to contribute to the cause of circular economy rather than sending the same to the landfills.



Where should we feed SPL for its gainful Co-processing



Requirements for feeding SPL into the Cement Kiln

- **How much SPL should be dosed into the kiln?**

- The desired level is 0.2% to 0.3% Fluorine / Ton of Clinker
- The maximum level should be 0.3% / Ton of clinker
- Depending upon the Fluorine content in the SPL, the SPL dosage rate is desired to be adjusted.

- **What should be the size of SPL?**

- The desired size is as fine as feasible so that it effectively reacts with the raw mix in the kiln.
- Ideally, ground SPL is most desired. However, handling the SPL that is ground to fine size is a potentially dangerous proposition from the point of view of exposure of operators to the Cyanide liberations and fluorine leaching into the environment.
- Reaction of SPL in the form of chunks or pieces > 20 mm is very slow and hence, the possibility of unreacted SPL coming out of kiln along with clinker is a potentially very high.
- The acceptable size from safety and ease of reaction that seems to be working well is <10 mm and preferably <5 mm.



Pre-Processing of SPL Chunks into Crushed SPL

SPL Chunks



Crushing Facility



Crushed SPL



Concerns of Cement plants to undertake SPL Pre-processing & Co-processing

- SPL is harder to crush than normal coal.
 - Requires dedicated and rugged equipment.
 - Consumes higher Energy
- SPL needs to be crushed to Finer size for co-processing
 - It may lead to the SPL having larger surface area
 - Prone to get exposed to moisture in air
 - Likelihood of release of Fluorine into water and soil
 - Release of poisonous Cyanides .

The Fluorine leachability & Cyanide release during the handling and coprocessing of SPL are the major cause of concerns from environment and safety considerations.



Safe management of Cyanides present in SPL Carbon and Refractory Portions

- The Cyanide is present in SPL Carbon and Refractory portions in following forms.
 - Sodium Cyanide NaCN
 - Sodium Ferro-Cyanide $\text{Na}_4\text{Fe}(\text{CN})_6$
 - Sodium Ferri-Cyanide $\text{Na}_3\text{Fe}(\text{CN})_6$
- To determine the severity of this cyanide contamination and find an appropriate methodology to handle them in a safe manner, a study on the leachability of the cyanide from SPL at different pH conditions was undertaken.
- Based on these evaluations, the conclusions drawn were presented in the paper published in IBAAS 2023.



Study Protocol

- (1) Random spot lumps of SPL Carbon (Black) and SPL Refractory (Grey/white) from the storage site of Vedanta Aluminum Ltd. located at Jharsuguda were taken sent by courier to the laboratory of TTCWMA located at Navi Mumbai.
- (2) The laboratory grounded the entire sample and made it uniform by quartering and coning method to 10% of entire sample.
- (3) The total cyanide content present in the SPL Carbon and SPL Refractory samples was evaluated at the laboratory of TTCWMA using standard testing procedures as Blank or Zero status sample
- (4) Leachability study was carried out as per the prescribed procedure (EPA 1311 and EPA9010, 9014) at different pH conditions in the range of 4 to 9.
- (5) Total cyanide content was determined using standard testing procedure in the different pH extracts collected while undertaking the leachability study.



Cyanide Content in SPL Carbon & Refractory Portion

Sample Name	Total Cyanide mg/kg	Total Cyanide (Duplicate) mg / kg
SPL Carbon	241	250
SPL Refractory	70	90



Leachability of the SPL Carbon Portion

Leachability of Cyanide from Carbon portion of SPL		
pH Buffer Solution	Cyanide - (mg/l)	Duplicate Cyanide - (mg/l)
@pH 4.0	1.88	1.75
@pH 5.0	22.50	21.00
@pH 7.0	22.50	21.50
@pH 8.0	20.00	21.00
@pH 9.0	22.50	22.00



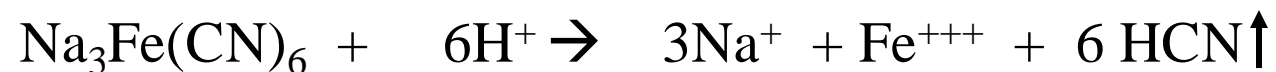
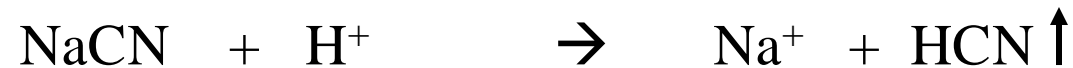
Leachability of the SPL Refractory Portion

Leachability of Cyanide from Refractory portion of the SPL		
pH Buffer Solution	Cyanide - (mg/kg)	Duplicate Cyanide - (mg/kg)
@pH 4.0	0.03	0.03
@pH 5.0	1.75	1.50
@pH 7.0	4.00	3.75
@pH 8.0	3.50	3.75
@pH 9.0	3.00	2.75



Results & Discussions

- The cyanide content in SPL Carbon is about 240 - 250 mg / Kg
- The Cyanide content in SPL refractory portion is 70-90 mg / kg.
- Leachability of Cyanide is observed to be less in acidic pH of 4 to 5 compared to that in pH 5 to 9.
- Leachability of Cyanide is observed to be high in neutral and basic pH of 7 to 9.
- Lesser leachability in acidic pH is attributable to following reactions.



Gainful management of Fluorides present in SPL Carbon and Refractory Portions

- The Fluoride is present in SPL Carbon and Refractory portions in following forms.
 - Sodium Fluoride NaF
 - Sodium Aluminium Fluoride $\text{Na}_3\text{Al}(\text{F})_6$
 - Calcium Fluoride CaF_2
- To determine the severity of this Fluoride contamination and find an appropriate methodology to handle them in a safe manner, a study on the leachability of the Fluoride from SPL at different pH conditions was undertaken.
- Based on these evaluations, the conclusions drawn were presented in the paper published in IBAAS 2024.



Study Protocol on Leachability of Fluorine at different pH conditions

- (1) Random spot lumps of SPL Carbon (Black) and SPL Refractory (Grey/white) from the storage site of Vedanta Aluminum Ltd. located at Jharsuguda were sent to the laboratory of TTCWMA located at Navi Mumbai.
- (2) The laboratory grounded the entire sample and made it uniform by quartering and coning method to 10% of entire sample.
- (3) The total Fluoride content present in the SPL Carbon and SPL Refractory samples was evaluated at the laboratory of TTCWMA using standard testing procedures.
- (4) Leachability study was carried out as per the prescribed procedure (EPA 1311 and EPA9010, 9014) at different pH conditions in the range of 4 to 9.
- (5) Total Fluoride content was determined using standard testing procedure in the different pH extracts collected while undertaking the leachability study.



Fluoride Content in SPL Carbon & Refractory Portion

Table - 1

Sample Name	Total Fluoride %	Total Fluoride (Duplicate) %
SPL Carbon	4.36	3.6
SPL Refractory	2.5	2.19



Leachability of Fluorine from the SPL Carbon Portion Table - 2

Leachability of Fluorine from Carbon portion of SPL		
pH Buffer Solution	Fluorine - (mg/l)	Duplicate Fluorine - (mg/l)
@pH 4.0	359	446
@pH 5.0	468	690
@pH 7.0	944	1060
@pH 8.0	758	780
@pH 9.0	969	690



Leachability of Fluorine from the SPL Refractory Portion Table - 3

Leachability of Fluorine from Refractory portion of the SPL		
pH Buffer Solution	Fluorine - (mg/l)	Duplicate Fluorine - (mg/l)
@pH 4.0	574	574
@pH 5.0	168	156
@pH 7.0	202	156
@pH 8.0	417	398
@pH 9.0	477	369



Results & Discussions

- The results of the analysis depicted in Table 2 to Table 3 indicate following.
- Fluoride content leachability in acidic pH of 4 is low in Carbon Fraction and increases with increasing pH reaching highest at neutral pH and then reduces in the alkaline conditions.
- Fluoride content leachability in acidic pH of 4 is highest in Refractory Fraction and then reduces reaching lowest at neutral pH and then increases with increase in alkaline pH.



Conclusions

- The leachability of Fluoride occurs to a reasonable extent at acidic, neutral & basic conditions.
- The extent of leachability of Fluoride at different pH conditions varies from both materials.
- The Fluoride analysis from Leachability study indicates that the chemical nature of fluoride in Carbon & Refractory fractions is different.
- Apparently, the extent of presence of different fluorides such as NaF , Na_3AlF_6 and CaF_2 at different depths appear to be varying and the leachability of the same varies according to the same.
- Hence, from storage and handling perspective, it is important that contact of water / moisture with both fractions, as is the case with Cyanide contamination, needs to be avoided for both Carbon and Refractory fractions of SPL. This will ensure that there is no leaching of Fluoride from the them.
- Cement plants / other entities storing, handling and processing carbon and refractory portions of SPL need to ensure that the operations are carried out in covered shed and in dry environment to avoid the leachable Fluorine getting into the environment.



Thanks!



Ulhas Parlikar

Board Director – MRAI

Global Consultant

(Waste Management, Circular Economy,
Policy Advocacy & Co-processing)

ulhas.parlikar@gmail.com

+91 99675 81975

