Spent Pot Liner Utilization in Cement Industry  Steel  Industry

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Author’s vision towards Sustainable India

Creation/amendments & enforcement of policy framework for efficient Waste Handling Management System in the country, which would go a long way in enhancing not only the percentage level of Thermal Substitution Rate in the Cement Industry but would also be helpful in addressing a few major concerns of the Govt. considerably such as:

- Protecting the environment through bringing down the emissions Level & establishing circular economy model in Industries.
- Reducing the use of fossil fuel by encouraging more usage of AFR
- Generating downstream employment opportunities
- Industrial wastes reduction by generators and usage by Co-processor in the country should be linked with PAT scheme by establishing three category reduction/recycle/reuse aligned with of E-certs.
Cement plants have lion’s share in creating a blueprint for sustainable development in India’s bright future through co-processing.

• Co-processing: It is a secure form of waste management that recovers the energy and mineral content of waste for beneficial utilization of waste, to save conventional energy resources and product additives in manufacturing processes.
• Rigorous on-site supervision of co-processing experts help to ensure maximum benefit of cement company, community and environment.
• Co-processing is an efficient waste management stream which minimizes the requirement of waste materials to be dumped in landfill area or incinerated at high temperature while reducing impact on environment.
India’s sustainability vision-Benefit of Co-processing

Cement Industry - Kiln: one solution to multiple aspects:

• COMPANIES: Complete thermal destruction of waste reduces need for onsite waste storage, reduces liability, reduces risk to corporate reputation and enhances regulatory compliance efforts particularly with respect to hazardous waste.

• COMMUNITIES: Less waste going to nearby landfills, preserves energy resources for future generations along with jobs created in co-processing industry.

• ENVIRONMENT: Fewer natural resources are taken from the earth, lower CO2 emission for a facility that use co-processed waste as fuel, reduces emissions of methane from landfills, less material in landfill helps to reduce chances of pollution in soil or water.

• CO-PROCESSING is a secure form of waste management that utilizes the energy and mineral components from waste for beneficial use in production. It conserves fossil fuels and natural mineral resources, while safely destroying materials that would otherwise go to landfills or incinerators.

• CO-PROCESSING of waste is a complex, precise procedure that requires advanced engineering expertise.
India’s sustainability vision—Contd...

HOW CO-PROCESSING WORKS?

Once waste material reaches in plant facilities, technicians conduct further analysis in laboratories and pretreat the waste if required. Solid wastes are shredded to uniform size to yield maximum energy creation. Solids are sometimes blended with liquid waste, creating a relatively dry material that stabilizes the liquids and allows them to be utilized more easily. The waste is then safely and securely co-processed, often by using it as a fuel source in cement kiln with vision of reduction in TSR. With Operating temperatures of kiln around 1370 degrees Celsius, the kilns provide complete thermal destruction, recovering the energy and mineral components within the waste. An added benefit is that no additional waste is produced during the process.

WHY CO-PROCESSING IS SAFE

Co-processing is a safe and effective waste disposal technique because of three unique reasons:

The very high operating temperatures of the kiln break the long-chain hydrocarbons in the waste, reducing it back to its basic elements.

The wastes experience long residence times inside the kiln, allowing adequate time to break down even the most complex chemical compounds.

When co-processing in cement kilns, fine limestone dust captures heavy metals; those materials are kept out of the atmosphere and safely, fully incorporated into the product.
WHY CO-PROCESSING IS BETTER THAN LANDFILLS OR INCINERATION?

- **Landfills** pose potential soil and groundwater contamination issues if they are not properly constructed and maintained, and they occupy valuable real estate that could be used for other purposes.
- **Incinerators** do dispose of solid wastes, but they do nothing to capture heavy metals such as mercury, lead and others which can be of risk to the human population, even in small concentrations.
- **Incinerators** also generate fly ash and bottom ash which must be disposed off, typically a toxic waste landfill, which creates the potential for soil or water contamination.
- **Co-processing** achieves complete thermal destruction of waste, and when applied to the cement industry, can capture mineral components, which are safely incorporated into the final product.
- **Co-processing** also reduces the need for on-site waste storage, reducing liability and enhancing regulatory compliance efforts.
• Spent Pot Liner (SPL) is a by-product generated when the carbon and refractory lining of an aluminium electrolytic cell, known as a pot, reaches the end of its useful life. Life of Aluminium Smelter pot is 2000-3000 days and generation of SPL per pot is around 60-85 MT varies as per design linked with Potline amperage.

• SPL has been classified as Hazardous Waste mainly due to: Toxic fluoride and cyanide compounds that are leachable in water, Corrosive - exhibiting high pH due to alkali metals and oxides and Reactive with water which may produce inflammable & toxic gases.

• The waste consists of 2 parts viz. first cut (carbon cathode) and second cut (refractory).

• SPL typically contains 70% by weight of carbon and 30% by weight of refractory portion.

• Specific generation of SPL is 15-25 kg/ton of Aluminium produced which is significant outcome of Pot design & Operational practices.
Section View of Electrolytic Cell
Section View of Cathode and Bottom Lining

SPL-- Cathode lining- 1st cut (Carbon Portion)

SPL--Refractory lining- 2nd cut (Refractory portion)
Section of lining of an aluminium pot during its dismantling (light line enhances carbon blocks)
SPL- Indian Scenario

Annual Aluminium Production in Indian currently; 3.3 MTPA with capacity installation at 4.1 MTPA

SPL Availability in Aluminium plants:

- NALCO- 4500-5000 TPA (Quantity of SPL lying at Smelter Plant: approx 65000 MT)
- BALCO-8000-8500 TPA
- VEDANTA (VAL)- 14000-15000 TPA
- HINDALCO, Renukoot- 5500-6000TPA
- Hirakud-4000 TPA
- Aditya- 3500- 4000 TPA
- MAHAN-3500 - 4000 TPA (Total HINDALCO- 18000 TPA)

Total availability in India- 43000 TPA (In HINDALCO, Renukoot Plant- SPL is being reprocessed in cryolite recovery plant. In that case, the tentative Availability of SPL = 40000 MT/annum
Gross Calorific Value (GCV) of SPL is around 3200-3400 kcal/kg
Odisha and Chhattisgarh produces 80% of Aluminium in India and none of these states have incineration facility.
Secured Landfill practice as per CPCB guidelines is commonly adopted by Aluminium plants.

SPL co processing trial at ACL Bhatapara completed on 15.04.16 as per MOU signed between HOLCIM & BALCO. ACL received the bulk permission of 3200 MT/Yr last FY.

Ultradech Hirmi Works got permission of 2880 MT/Year SPL co-processing from BALCO for 5 years (Dated:11.08.16). Execution started.

In HINDALCO, Renukoot Plant- SPL is being reprocessed in cryolite recovery plant.

Some Quantity is being converted to Mineral fuel by Green Energy Sambalpur and Subhra Chemicals, who are authorized reprocessor at Odisha.

Agreement with TSDF being finalized by some smelters.
Global Practices for SPL handling

ALBA:
Waste refractory bricks are crushed and used as a substitute for alumina to obtain a flat horizontal cathode shell surface prior to the start of laying insulation bricks for pot re-lining. At Alba, 60,000 cubic metres of spent pot lining (SPL) waste that had been generated over the past years were subjected to physical segregation into four fractions namely steel, carbon blocks, refractory and insulation bricks, and the fine fractions which cannot be segregated. All the steel was sold to a steel recycling furnace adjacent to Alba. The carbon and refractory portions are now being recycled in ways that have been approved by the environmental authorities, and which generate a financial return, to the extent that Alba alone has saved over US$1 million in the process.

ALCOA:
The multiple benefit of recycling SPL is both to eliminate landfill and extract the energy from it. Alcoa Fjardaál has a goal to recycle 100% of SPL generated in the smelter.

EGA
Spent pot lining (“SPL”) and carbon dust, both being forms of process waste generated in the reduction process, are recycled within the cement industry in UAE.

RUSAL:
Spent potlining (SPL) trial taken for utilization. The behavior of cyanide and fluoride under high temperature treatment has been investigated. On the basis of this laboratory investigation, the possibilities for SPL utilization in red brick manufacturing, cement industry and thermal power stations are evaluated.
Major Challenges for the disposal of SPL through Co-processing

- **Hardness and Crushability**: Very hard to crush. Bond index of lime stone is 13-15 and of SPL is around 39-42 BHI (lime crusher not feasible).
- **Process and maintenance impact**: abrasive, high and variable content of sodium and fluorine and high ignition temperature of the carbon fraction.
- **Chemical Properties and Handling**: Possibility of the formation of Toxic and inflammable gases such as Hydrogen Ammonia and Cyanogen when in contact with moisture. Transportation and feeding is to be done in a tactful manner, so that the material does not get wet.
- **Homogenization**: Essential to ensure homogenization of the material before use. Mainly the alkali and fluoride content can vary strongly. Segregation of aluminium metal, carbon material and refractory material needs to be done.
- **Storage**: Any storage under open sky or without sealed paved ground is prohibited
- **Safety**: Important at all levels of handling SPL from generator end to user end.
Major Challenges for the disposal of SPL through Co-processing – contd.

- **Permitting Process**: Permitting Scenario for the disposal of SPL from CPCB is a very lengthy procedure.
- **Willingness to pay for co-processing / Proper disposal of SPL**: Most of the Aluminium smelters are not willing to pay even the minimum tipping fees for disposal of SPL.
- **Continuous availability** of raw material is also an issue.
- **Disposal through Un-organized sector**: Need to find a permanent solution for the safe and environment friendly disposal of SPL.
- **Waste Quantification and National Database for SPL**: The Cement Industry in India does not have a reliable quantification of the total amount of SPL which is available for disposal, including current generation as well as stocks lying in SLF or within plant premises, hence it's difficult to do a reliable cost benefit analysis on the long term disposal of SPL through cement manufacturing.
- **Lack of directives**: from the regulatory authorities for safe and environmental friendly disposal of Untreated SPL.
Opportunities for SPL Co-processing in India

India is the second largest Cement producer in the world after China with achieved production of around 280 million metric tons in 2017

- Opportunities and availability of Cement Kilns for SPL disposal through co-processing is not a constraint.
- SPL (1st cut and 2nd cut) to be used as fuel supplement with raw materials additives properties.
- SPL contain ~ 11-15% fluoride, fluoride is mineralizer and substitute fluorspar.
- SPL contain ~ 60-70% carbon, calorific value ranges from 3200-3400 kCal.
- SPL contains ~ 10-15% sodium, can be beneficial if operating with high sulfur containing fuels.
- Recycling is an attractive and proven option; Best may be for Cement & Steel Industry
- Co-processing in cement has already been established as the proven and most reliable option for disposal of SPL, Cement plant in Europe, Australia, Latin America are regularly using SPL as part of their Alternative fuel usage strategy.
No. of Large Cement Plants in India – 188
Production in 2017–280 MTPA
Coal Consumption – 56-58 MTPA
Tentative SPL Generation in India – 40000 MT/Annum
SPL Co-processing Requirement (3.4 MTPA of Al production in India) = 0.069% of Coal used
Future Co-processing Requirement (As per 4.7 MTPA of Al production in India) = 0.096% of Coal used
General Chemical Analysis : SPL

For first cut material GCV varies from 3200 to 4000 Kcal/Kg & HGI is 39 units

Table 1: Chemical composition of SPL

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<thead>
<tr>
<th>SN</th>
<th>Particular</th>
<th>% Composition</th>
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<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>SiO₂</td>
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<tr>
<td>3</td>
<td>Al₂O₃</td>
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<td>4</td>
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<td>6</td>
<td>MgO</td>
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<tr>
<td>7</td>
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<td>8</td>
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<tr>
<td>9</td>
<td>Fluoride</td>
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</tr>
<tr>
<td>10</td>
<td>Aluminium Carbide &amp; Nitride</td>
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<tr>
<td>11</td>
<td>Cyanide</td>
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Lab Scale Analysis : SPL

- Heat Treatment of SPL

<table>
<thead>
<tr>
<th>SN</th>
<th>Oxide Composition</th>
<th>Raw Mix (%)</th>
<th>Coal Ash (%)</th>
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<tr>
<td>2.</td>
<td>SiO₂</td>
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<td>62.5</td>
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<td>3.</td>
<td>Al₂O₃</td>
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<td>4.</td>
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<td>5.</td>
<td>CaO</td>
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<td>1.0</td>
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<tr>
<td>6.</td>
<td>MgO</td>
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<td>0.6</td>
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<tr>
<td>7.</td>
<td>Na₂O</td>
<td>0.15</td>
<td>0.5</td>
</tr>
<tr>
<td>8.</td>
<td>K₂O</td>
<td>0.85</td>
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<td>12.</td>
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- Laboratory Clinkerization - Oxide Composition of Kiln feed & Coal Ash

<table>
<thead>
<tr>
<th>Temperature (℃)</th>
<th>Temperature (℃)</th>
<th>Weight Loss (%)</th>
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</thead>
<tbody>
<tr>
<td>1.</td>
<td>200</td>
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<tr>
<td>2.</td>
<td>400</td>
<td>13.90</td>
</tr>
<tr>
<td>3.</td>
<td>600</td>
<td>23.70</td>
</tr>
<tr>
<td>4.</td>
<td>800</td>
<td>25.60</td>
</tr>
<tr>
<td>5.</td>
<td>900</td>
<td>27.20</td>
</tr>
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</table>
Advantages of SPL

The benefits of using SPL or SPL derivatives in cement kilns as an alternate fuel and raw material (AFR) have essentially consist of the following:

First cut SPL contains sufficient carbon that it can be burnt as fuel and therefore reduce the consumption of primary fuel in the kiln.

It has been found that fluoride is beneficial for reducing clinkering temperature by fluxing action (from 1450 deg C to 1350 deg C). Due to the presence of large quantities of lime and limestone within the kiln, virtually all gaseous fluoride is scrubbed from the kiln exhaust and fixed in the clinker as fluorspar (CaF2).

Ammonia and cyanide from the SPL act to reduce nitrous oxide (NOX) emissions from the cement kiln by up to one-third, via the following reactions:

Cyanide: 4HCN + 2NO2 + 3O2 → 2H2O + 4CO2 + 3N2
Ammonia: 4NH3 + 2NO2 + O2 → 3N2 + 6H2O;

4NH3 + 6NO → 5N2 + 6H2O.

Refractory materials (silica, alumina) in the first and second cut SPL can substitute for these components in the cement kiln raw materials.
### Table 2: Oxide Composition of Clinker Prepared with SPL

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Chemical composition (%)</th>
<th>Chemical Composition of Clinker (%) with</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SPL</td>
<td>Raw Mix</td>
</tr>
<tr>
<td>LOI</td>
<td>27.20</td>
<td>35.06</td>
</tr>
<tr>
<td>SiO₂</td>
<td>9.20</td>
<td>13.15</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.30</td>
<td>3.27</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.60</td>
<td>2.25</td>
</tr>
<tr>
<td>CaO</td>
<td>trace</td>
<td>42.94</td>
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<tr>
<td>MgO</td>
<td>trace</td>
<td>1.20</td>
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<tr>
<td>Na₂O</td>
<td>14.30</td>
<td>0.15</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.25</td>
<td>0.85</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>F</td>
<td>12.00</td>
<td>-</td>
</tr>
<tr>
<td>Al carbide &amp; nitrite</td>
<td>6.50</td>
<td>-</td>
</tr>
<tr>
<td>Cyanide</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>C₃S</td>
<td>39.48</td>
<td>40.30</td>
</tr>
<tr>
<td>C₂S</td>
<td>33.72</td>
<td>31.78</td>
</tr>
<tr>
<td>C₃A</td>
<td>9.43</td>
<td>9.48</td>
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<tr>
<td>C₃AF</td>
<td>11.08</td>
<td>11.08</td>
</tr>
<tr>
<td>Liquid</td>
<td>29.16</td>
<td>29.29</td>
</tr>
<tr>
<td>Free CaO</td>
<td>1.90</td>
<td>1.40</td>
</tr>
</tbody>
</table>
The variation of free lime in clinker with varying dosage of SPL is given fig.1 which shows that free lime decreases with increasing SPL percentage. The Lowest free lime is found in presence of 2% SPL. 

The decrease in free lime is attributed to mineralizing effect of SPL. It is well established that fluorine acts as mineralizer in clinkerization which reduces clinkering temperature and facilitates the oxides combination. 

The fluoride present in SPL acted as mineralizer while burnt with cement raw mix and mineralizing effect was increases with increasing percentage of fluoride. 

The increase of C3S content in clinker with increasing addition of SPL confirmed its mineralizing effect (Fig.2). 

The fluorine content was determined in clinker increases with increasing SPL (Table-2) which indicates the absorption/entrainment of fluorine in clinker mineral phases.
SPL Trial outcome in Cement plant-Summary

- The prepared clinker showed decrease in free lime in presence of SPL.
- The fluorine present in SPL acts as mineralizer and reduces the free lime in clinker substantially.
- The fluorine detected in clinker confirmed its assimilation as well as mineralizing effect and increases the C S content in clinker.
- Dust & Nox concentration was observed to be low during SPL co processing
- SO2 concentration was found to be varying within permissible range of pre co processing & post Co processing
- HCL was absent in emission during study (Reporting Limit-1.5 mg/Nm3)
- HF was below detection limit in results (Reporting limit-0.5mg/Nm3)
- TOC (Total Organic carbon) emission was showing decreasing trend from pre to post co processing
- Cyanide – Analyte was not detected in any of the sample collected during study. Cyanide was below detection limit (Reporting limit-0.2 µg/Nm3)
- Hydrocarbon concentration was showing decreasing trend during co processing
1. The carbonaceous content of SPL is well burnt at higher temperature and provides additional heat to the system. The results show that up to 2.0% SPL can be strategically used as raw mix component without affecting the quality of clinker.

2. The utilization of SPL in cement manufacturing not only offers saving of fuel and conventional raw material depletion but also provides solution to environmental problem created by disposal of SPL in plant area.

3. SPL a national Challenge & being hazardous waste should be looked through holistic view rather as a business opportunity to make money. In Indian context, with new thought coming in advocacy that SPL material having good calorific value must be used for the saving of natural resources to avoid its fast depletion rather wasting its fuel value through landfilling.

4. As per authors view, it must be put in CTO conditions for related industry to close the loop by using waste of one industry as resource for another as a governance within periphery of 200-300 Kms.

5. Regulators must promote such industrial tie up promptly to attain better carbon footprints in such industry through PAT Scheme with some percentage of hazardous waste utilization in plants through compliance of CTO terms & conditions.
Visible Gains of SPL Usage – Cement Plants

In Global perspective, due to heat value & fluoride contents in SPL has given following gains in Cement Plants;

*Approximately 5% saving by substituting primary fuel inputs due to carbon value utilization from SPL into the cement kiln.*

SPL should be fed through separate weighed system to fuel input stream.

*Approximately 5% saving on primary fuel input by achieving equivalent clinker properties at reduced temperature.* Due to fluxing property of fluorides present in SPL, it lowers the clinker temperature by 100 degree C

However, this effect is dependent on the sodium content of the clinker raw materials and how much additional sodium can be tolerated with the SPL addition. The sodium limit may prevent addition of sufficient fluoride to see this fluxing effect; The intake of spent anode butts will result in further, considerable savings on the energy input from primary fuel.

*Study suggests total energy saving potential of about 10% for a cement kiln using SPL with 55% carbon content in the first cut material.*
Pioneer/Path finder Plants for SPL Co Processing

Cement Australia – Fisherman’s Landing Plant (Queensland):
SPL derivative from the Comalco COMTOR SPL treatment plant at Boyne Smelter Limited Gladstone.
Ongoing since July 2004;

Blue Circle southern cement (BCSC) – Waurn Ponds Plant (Victoria): SPL derivative “Hi-Cal 50” from the Regain SPL treatment facility at Alcoa Aluminium Point Henry smelter Geelong.
Ongoing since January 1998;

Adelaide Brighton Cement Birkenhead Plant (South Australia): SPL derivative from Regain pilot plant at Tomago Aluminium Newcastle. Trial period 2001-2003;

• As nation is poised for inclusive growth, industries should work together to reduce use of natural resources by adopting “Reuse – Recycle – Reduce” philosophy.
• SPL and Other wastes of industries should be mapped and Cement industries should be guided with new policy frame works & advantages in PAT scheme through E-certs
• SPL usage can reduce COP of cement making by adding value in TSR & reduce use of natural resources for future generations.
• Cement / Steel and Aluminium industry should join hands and work out a ‘win – win’ solution. A part of the savings out of SPL usage by Cement industry may be shared with aluminum industry to make the SPL utilization a viable solution.
• Being a responsible citizen of India, Storage of SPL is not a viable solution due to scarcity of storage space and threat to land and water contamination.
THANK YOU!