SPL UTILIZATION IN CEMENT & STEEL INDUSTRY

Technical Report

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1. Introduction

This technical report is created to provide general information on processing of SPL. There are a number of ways including direct charging in cement kilns as fuel substitute or feed mix received after detoxification process can be used in various Steel & clay bricks manufacturing. This technical report would shed light on SPL usage in Indian Industrial scenario and creating awareness about its positivity with complete corporate responsibilities in line with environmental norms. There are more aspects reviewed such as transportation and technical aspects that come with the implementation of each selected option.

SPL (Spent Pot Liner) : The Aluminium reduction Cell or “Pot” contains a lining of Refractory Carbon blocks & bricks that contain Molten Cryolite and metal pool in around 960 degree Centigrade temperature. During pot under production ageing causes worn off lining material along with impregnation with chemical compounds. Once the refractory & carbon reaches to end of life, pot is taken out from Production & lining material is removed as Spent Pot liner .In its raw form, Spent Pot liner varies in size from fine dust to lumps of up to one meter. Its typically made up of a wide range of minerals & chemical compositions because the different materials in the pot liner are mixed together during removal from shut down pot.

2. Base Case: Recycling of SPL in a Cement Kiln

Other than disposal in a landfill this option is today the most widely used option by aluminium producers worldwide. In this option we also consider the potential inclusion of spent carbon butts with the shipment of SPL. The primary reason for the cement producer to process the SPL is the heating value from the contained carbon. By adding the spent butts the heating value increases substantially which makes it even more attractive for a cement producer to take SPL.

2.1 Production of cement

Cement clinker is produced via calcining of wet, semi-dry or dry solids counter-current to hot gas flow in a rotary kiln. The raw materials for manufacture of cement clinker are alumino silicates and iron oxides (from clays and shales) and calcium carbonate (from limestone).

After blending and milling, the raw materials are added to the kiln counter-current to the flow of hot gases from the burner, thereby being preheated and dried as they pass down-wards through the cyclone preheater tower. The day reactions which occur within the kiln to form clinker (the precursor to cement and the combination of lime (CaO) from the limestone, and silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) from the clays and other additives, including ash from coal if this is used as fuel in the kiln. These components react to form the complex compounds forming the clinker – tricalcium and dicalcium silicates, tricalcium aluminate and tetra-calcium alumino-ferrite. This reaction typically proceeds at 1450^0C. After cooling, the clinker is ground with gypsum to form Portland cement.

Cement kilns are energy-intensive, consuming from 3.2 Gj/tone of clinker for a dry process with suspension (cyclone) preheater to 5.5 Gj/tone for a wet process.

2.2 Use of SPL or Derivatives (outcome after Detoxification) in Cement kilns

SPL or its derivatives can be introduced into a cement kiln via either of the following.

- Injected as a powder alongside pulverized coal via the kiln burner (first cut SPL only);
- Injected pneumatically into the pre-heater end of the kiln (both first and second cut SPL).

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

1. First cut SPL contains sufficient carbon that it can be burnt as fuel and therefore reduce the consumption of primary fuel in the kiln.
2. It has been found that fluoride is beneficial for reducing clinkering temperature by fluxing action (from 1450^0C to 1350^0C). 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 (CaF_2).

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

- Cyanide: $4HCN + 2NO_2 + 3O_2$ -- $2H_2O + 4CO_2 + 3N_2$
- Ammonia: $4NH_3 + 2NO_2 + O_2$ -- $3N_2 + 6H_2O$;
  $4NH_3 + 6NO$ -- $5N_2 + 6H_2O$.

4. Refractory materials (silica, alumina) in the first and second cut SPL can substitute for these components in the cement kiln raw materials.

However, despite the above benefits to its use as AFR in a cement kiln, there is a limit to the rate at which SPL can be used in the clinkering process due to its sodium content. Sodium is problematic for product quality, and will attack the kiln refractory lining. At one Brazilian cement plant where SPL is processed, new **less porous refractory lining** had to be installed in the kiln to accommodate the co-processing of SPL sodium. Blue Circle Southern Cement (BCSC) in Australia have achieved a 12 month kiln refractory life which is close to the industry standard of 15-16 months, despite using an SPL – derivative in their kiln at Waurn Ponds. Up to **3wt% SPL** in clinker has been used in some cases without exceeding clinker sodium specifications or having a detrimental effect on kiln refractories.

However, consistent sodium content in the SPL or SPL derivative is essential to avoid problems with off-specification clinker. The same for the high fluoride content that increase set times of the cement after pouring.

Based on the typical SPL compositions and a conservative sodium limit of 0.25% by weight for clinker, the estimated cement kiln capacity required to wholly dispose of the SPL (both first and second cut) as generated is 300,000 tonne per year (resulting in approximately 2% by weight of SPL in the clinker). **Blue Circle Southern Cement (BCSC)** can tolerate up to 0.7%wt sodium in clinker, however the tolerable addition rate of SPL –derived sodium must be considered on a case-by-case basis to variation in sodium levels in raw materials for cement kilns around the world.

2.3 The fuel savings expected from using SPL at this substitution rate are :

- Approximately 5% saving by reducing energy input from primary fuel by 160 MJ/tonne of clinker;
- Approximately 5% saving by lowering the clinker temperature by 100^0C. 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.

This suggests **a total energy saving of about 10%** for a cement kiln using SPL with 55% carbon content in the first cut material. This is consistent with trials of as SPL derivative at Adelaide

Brighton Cement's Birkenhead kiln in South Australia (2001-2003) wherein fuel savings of about 9% were reported (SPL only).

It is more likely that only first cut SPL will be attractive to cement kilns as an alternative fuel due to its higher carbon content than second cut material. A cement kiln of 110,000 jtpa capacity would be required to consume only the first cut SPL generated.

SPL will most likely require a certain minimum level of pre-treatment before it can be accepted for use in a cement kiln, namely:

- Grinding to a suitable size (< ¼ inch in US plants for injection into the cement kiln. Carbon from the SPL is mainly graphitic and much harder than coal. Thus SPL causes increased wear if it must be pulverized to fuel via the cement kiln's coal milling plant. Pre-milled SPL is therefore preferred for introduction into cement kilns. The BCSC specification is for 90% < 90 micron sizing for SPL derivatives;
- Mixing with other materials to enhance its calorific value (e.g. spent anode carbon dust, coal tar pitch). Increasing the SPL fuel value without increasing its sodium content allows the cement kiln to realize greater energy cost savings by using this material as an AFR.

2.4 Precedent for Using SPL in Cement Plants

SPL and SPL derivatives have been used in cement kilns as alternate fuel and raw materials (AFR) over a number of years. Trials and continuing processing of treated SPL have been completed in Australia:

- 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 (Sough Australia): SPL derivative from Regain pilot plant at Tomago Aluminium Newcastle. Trial period 2001-2003;
- Cement Australia – Railton Plant (Tasmania): SPL from Comalco Bell Bay. Trial November 2006.

Information available in the public domain indicates that the Cement Australia Gladstone and BCSC Waurn Ponds plants are currently the only cement kilns in Australia consuming pre-treated SPL on an ongoing basis. Comalco Bell Bay Propose to send all freshly generated SPL from their smelter to the Cement Australia Railton kiln in the future.

SPL is processed in cement kilns by Alcoa at two locations in Brazil, enabled by a 1998 decision by the Brazilian government to license certain cement manufacturers to use SPL in their clinker kilns. Alumar Sao Luis sends 13,000 TPA SPL to the Cimento Poty Ltd cement plant in Sobral where it is injected pneumatically into the base of the preheater tower. At Pocos de Caldas approximately 8,000 TPA SPL is disposed of in this manner.

3. Advantages/Disadvantages of SPL;

Advantages:

- Both first and second cut are processed in the cement kiln;
- SPL is fully detoxified in the kiln process. Residual emissions are well below acceptable limits;
- The carbon content lowers the requirement for normal fuel, which typically is coal. This off sets costs for fuel;
- The fluoride content increase the flux and thus lowers the melting temperature of clinker. The kiln can operate at a slightly lower temperature and thus reduces the net fuel consumption and the net GHG intensity;
- This use of SPL has many good sustainable aspects. There is also much experience becoming available to the cement producers.

Disadvantages:

- The sodium content of the SPL can be an issue and some cement plants cannot take SPL for this reason;
- The composition of SPL varies considerably. It is hard for the plant operators to balance the intake of the materials. Using raw SPL requires a good safety margin to deal with its variability;
- The fluoride can also have an unacceptable impact on clinker chemistry and ultimate set time;
- This option still requires transportation of a hazardous material between sites and sometimes over considerable distances.

4. Sustainability of using SPL in cement kilns

The option of disposing of SPL either pre-treated or un-treated depends on a number of factors to be sustainable in the long term:

1. Government legislation in the country of treatment/disposal to enable the use of SPL or its derivatives in cement kilns.

2. Recognition by the public and other stakeholders that this is a mutually beneficial method by which two industries can gain benefit: “one industry’s waste is another industry’s resource”.

3. Ongoing demand for cement clinker. Since cement is the second most widely utilized resource in the world (behind water), it is almost impossible to imagine that the cement kiln process will

Cease to be an outlet of sufficient capacity for the treatment of SPL, although the development of concrete substitutes in the future may reduce the cement market to some extent.

Table 1 : Global Sustainability review on SPL

TEST QUESTION	FOR THIS OPTION	SCORE
(1) This options, how does it improve on existing methods of disposal or processing of SPL? And how does it replace any other methods?	Both first and second cut are ground and added to the clinker production process in the kiln. Cyanides are destroyed and fluoride immobilized. Emissions are kept at a minimum. The fluoride is beneficial by lowering the melting point of clinker. The carbon replaces a fraction of the normal fuel and reduces the GHG intensity.	4
(2) Can this improvement be quantified or measured?	Yes. On the basis that both first and second cut are used, 100% of the SPL is reused in the clinker material. Metals are recycled.	5
(3) Are alternative materials or energy sources used that over-all, from a life cycle point of view, make this method better or worse?	The use of SPL saves on regular fuel used in the cement kiln, which in 54% of the cases is coal. The fluorides lead to lower melting temperatures and save on fuel intake. This lowers the energy intensity and directly leads to lower GHG intensities. The sodium may be a problem for cement producers. An-other challenges is the variability in the SPL composition. This is another challenge for the operators. Transportation over a substantial distance is involved that requires fuel and leads to incremental GHG allocations.	4
(4) How does this method eliminate wastes and if new wastes are created, are these easier or more difficult to deal with?	It eliminates virtually all wastes. It does, however, still require to transport a hazardous waste over road, by ship or by rail.	4
(5) Is this method reducing the long term impact on environment for other generations that follow Us?	The SPL is fully recycled. Provided the cement meets all criteria then all future liabilities are taken away from the SPL. The use of SPL in cement is a practice from the last 5 to 10 years. Long term effects beyond 30 to 50 years are not known yet.	4

5. Conclusion

SPL a national Challenge & being hazardous waste should be looked through holistic view rather as a business opportunity to make money. There are several aspects to consider in determining the cost of treating SPL or its derivatives in cement or Steel industries. 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. 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. Regulators must promote such industrial tie up promptly to attain better carbon foot prints is such industry through PAT Scheme.

Cost Related Global Inputs:

1. The cost of safely transporting the treated SPL – still classified as a hazardous waste, but not a dangerous good-from smelter to a receptive cement kiln or Steel making Furnaces.
2. The liability insurance costs for transporting SPL off-site, to cover spillages during transport.
3. The cost of a receiving, storage and kiln injection/feed system at the cement plant site, to allow the SPL to be added to the kiln at a known and monitored rate. Given that this will generally be < 1 – 2 tph, the cost of such a system will largely be governed by the quantity of storage required at the cement plant to cover the time between SPL shipments from a smelter. As an example, the cost for installing a receiving system (SPL delivered by 27 tonne possolanic tankers), 1500 M3 storage silo and pneumatic injection system at the Ci-mento Potty cement kiln in Brazil was USD 0.3 Million (excl. crushing plant) in 2001. Scaling for Indian operations the cost would be approximately the same in current dollars. The cost of the SPL injection facility at BCSC Waurn Ponds – comprising a 50 tonne silo, and variable speed screw feeder delivering material into the calciner end of the kiln was < AUD 1 Million in 1998. In today's costs this would be around USD 0.5 Million. In the US, Alcoa spent up to 3 million USD to make two cement plants ready to process their SPL.