CO-PROCESSING AT CEMENT PLANT OF SPENT POTLINING FROM THE ALUMINUM INDUSTRY

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Keywords: SPL, Coprocessing, Waste Recycling

Abstract

In line with the concept of Sustainable Development, the Aluminum Consortium of Maranhão – [Consórcio de Alumínio do Maranhão – ALUMAR] in partnership with Cimento Poty S/A, in their respective environmental management strategies incorporate the unending search for recycling and coprocessing of all their waste, in such a way as to add value to the end products and not to compromise the environment. Accordingly, ALUMAR along with Cimento Poty S/A implemented coprocessing of SPL- Spent Potlining, from the aluminum industry, in rotary clinker kilns, on the basis of CONAMA resolution N$^{\underline{0}}$ 264 of 1999, from the National Environmental Council [Conselho Nacional de Meio Ambiente – CONAMA]. Due to its physicochemical characteristics, the addition of SPL as secondary raw material and secondary fuel, entail economic benefits for cement production and safely eliminates a waste considered class I by standard ABNT-NBR 10004 of the Brazilian Technical Standards Association [Associação Brasileira de Normas Técnicas].
The purpose of the present study is to present the main stages in the process of generation, characterization, and coprocessing of SPL in cement industries, as well as, its economic benefits and environmental aspects.

Introduction

Use of SPL at cement plants, bearing in mind that is carbonaceous fraction is on the order of 20 to 60% by mass, with average heating value of 1,200 Kcal/kg, and the refractory fraction on the order of 35% to 75%, give the SPL the approximate characteristics of a secondary fuel and of a secondary raw material.
Some elements in the composition of SPL are very useful to the cement industry. Fluorine, for example, plays an important role due its ability to augment the rate of clinker formation. Substances that have this feature are called fluxes or mineralizers. Fluxes reduce the temperature of formation of the liquid phase and raise the total phase content. Other compounds present in SPL like Fe_2O_3, Al_2O_3, MgO, and alkalis act as fluxes in the Portland clinker system.
Mineralizers, in turn, are substances that accelerate solid-state reactions such as, for example, decarbonation of $CaCO_3$, however some of them are effective only at higher temperatures, at which there is liquid phase in the system. Besides accelerating solid-rate reactions, they cam promote reactions in the liquid phase or at the solid-liquid interface, without changing the temperature of formation and the amount of the liquid phase.
The possibility also exists of replacing the clay with the refractory portion of the SPL. The refractory materials present in SPL consist basically of alumina and silica, with some smaller amounts of metallic aluminum. The advantage of this replacement would be based on the fact that the refractory portion of the SPL has lower moisture compared to clay.

Production of Aluminum and Generation of SPL

In the process for production of aluminum, performed in electrolytic pots, alumina is reduced to metallic aluminum by electrolysis in a cryolitic bath. This is called the Hall-Heroult process. The main functions of the electrolyte are to lower the melting of alumina, making possible electrolytic decomposition into metallic aluminum at lower temperatures (around 950 ^{0}C) and guaranteeing the physical separation of the aluminum produced at the cathode and of the oxides of carbon formed at the anode. The most important component of the electrolyte is the cryolite, or complex of aluminum fluoride and sodium (Na_3AlF_6). Other elements may be added to the electrolytic bath to modify its physicochemical properties and, thus, to improve operating efficiency and energy consumption.
Aluminum fluoride, calcium fluoride, and sodium carbonate are widely used to keep the Ratio (ratio between Sodium Fluoride – NaF and Aluminum Fluoride – AlF_3) and, consequently, the temperature desired in the process, stable.
During the reduction process in new pots, a portion of the electrolyte is absorbed by the carbon layer, which becomes saturated in the first 90 days of operations. In the aluminum production process, ALUMAR uses Prebake electrolytic pots, in which the anodes are prebaked before being used in the pots.
Over the useful life of the pot, which is approximately 2,500 days at ALUMAR, the layer of carbonaceous material (cathode) and the layer of refractory that line the pot are impregnated with the cryolite electrolytic solution, exposes the metal surface of the pot (frame) to the aluminum bath.
When it is necessary to disconnect the pot due to the exposure of the metal surface of the pot or of the busbar of the cathode to the bath, or due to advanced age through scheduled disconnection due to the natural wear of the cathode, replacement of the lining is necessary and, consequently, spent potlining is generated.
The rate of generation of SPL at ALUMAR is approximately 7Kg/tAl at present. Significant advances in lining technology, process engineering, and pot operation have contributed to lowering this rate over the year, based on the increase in the useful life of the electrolytic pots.

SPL Processing Stage – ALUMAR

The material generated in the pots and stockpiled in the sheds, blend of first and second-cut, is sent to the area for selection/segregation (metal parts) and for separation of course from fine material. Coarse SPL in then broken to approximately 10'' and is then mixed with fine SPL.
This mixture feeds magnetic separator where separation of the ferrous metal portion from the SPL takes place. After the

separation process, the metallic parts are sending to the steel plants to co-processing.
The SPL then passes through the secondary crusher where it is reduced to 1-1/4'' and it is then sent to the second magnetic separator. The SPL is then screened to guarantee the granulometry of the material to be sent to the mill according to the following table:

Table I. Average SPL Granulometry

325 Mesh	250 Mesh	100 Mesh
63.2 ± 13	48.30 ± 11	18.31 ± 7.80

After crushing, selection is done using the aero-separator where the fines at the desired specification are sent to stockpiling (where sampling for later physicochemical analysis takes place) while the coarse fraction returns to the grinding process.
The SPL stored in the silo is transferred to the silo truck at the filling station. All dust generated in this process is collected using an exhaust system and returned to the storage silo. The truck is then weighed and sent to Cimento Poty.

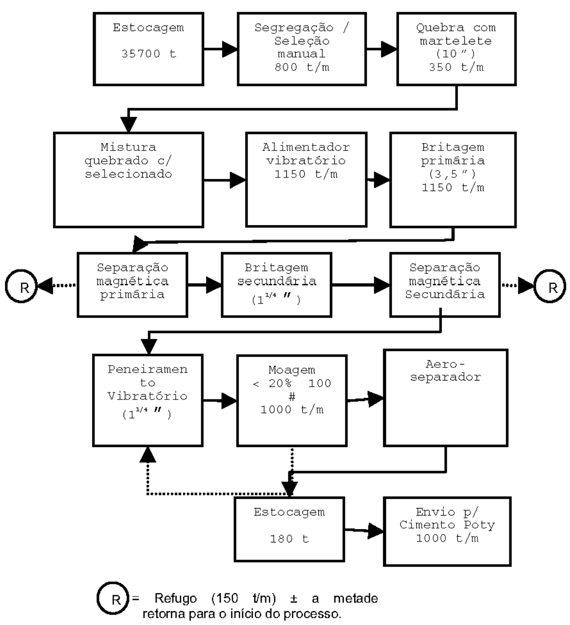


Figure 1. Flowchart of SPL Coprocessing at ALUMAR

Characterization of Spent Potlining - SPL

Spent potlining is the main solid waste generated in the aluminum industry. Table II. gives the average composition of SPL at ALUMAR considering the blend of first and second-cut

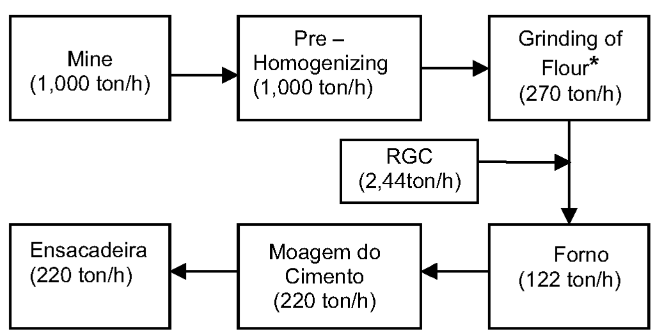
Table II. Average SPL Composition

Compound	Typical Content (%W/W)
Carbon	18.5
Sodium	17.9
Aluminum	14.6
Fluoride	19
Calcium	1.7
Magnesium	0.6
Iron	2.5
Potassium	0.39
Cyanide	0.02
Heating Value	1,200Kcal/Kg

The sample under study underwent the test recognized by the Brazilian Association of Technical Standards –ABNT, method 1005, Leaching of Wastes and method "NBR 1006 – Solubilization of Wastes.
In the leaching test of SPL sample, the fluoride content exceeded the limit set by "NBR 10004 – Classification of Wastes". According to NBR 10004, item 4.1.4 –b, a waste is characterized as toxic if its leached extract contains any of contaminants as concentration greater than the values appearing in listing N$^{\underline{o}}$ 7 of the mentioned standard.
In the solubilization tests various elements exceeded the limits of NBR 10004: Arsenic (As), Iron (Fe), Sodium (Na), Nitrates (N), Fluoride (F^-) and Cyanides (CN^-), which makes SPL a class I waste.

Production Process at Cimento Poty S/A

Cimento Poty S/A produces Portland cement. Based on standard ASTM C 150, Portland cement is a hydraulic binder, obtained from the grinding of clinker (a product obtained from the burning of a mixture of raw materials containing silica, aluminum, and iron oxide such as limestone and clay, at a temperature of approximately 1450 ^{0}C), which essentially consists of hydraulic calcium silicates, normally containing one or more forms of calcium silicates as additive (ASTM C 150, 2002).
Clinker, the most important component in cement, is obtained from the mixture of limestone, clay, and mineralizes or compositions corrector, like bauxite or iron ore, which, when subjected to high temperatures, sinter, forming nodules 5 to 25 mm in diameter. The stages in the production process at Cimento Poty S/A consist basically of: Mining, Pre-homogenizing, grinding of the "flour"*, clinkering, grinding of the cement, and bagging. Figure II. shows the overall mass balance for production



* Flour = Limestone + Clay, notation used in the cement industry
Figure 2. Mass Balance for Production at Cimento Poty S/A

Limestone Mine: The limestone is extracted using explosives. Detonated ore is transported to a hammer mill (primary crusher) to reduce the granulometry. The crushed limestone is stored in piles and later transported by buckets to the plant.
Pre-Homogenizing: The unit has a pre-homogenizing shed able to form 2 piles of material of 20,000 each for the purpose of homogenizing the crushed limestone. Removal from this pile is

done using a bucket that carries the pre-homogenized material to the limestone silo.

"Flour" Grinding: The cement plant has two flour mills, one using balls and the other rolls. After grinding, the flour is homogenized in two silos on top of the flour-storage silos.

Clinkering: The thermo-chemical reactions that will form the clinker take place in this stage. The "flour" is removed from the silos and transported to a weighing silo and then take to the feed point of 6 stages tower. The flour falls through the tower, where heat exchange occurs with the gases coming from the combustions and decarbonation reaction, using a cyclone process.

At the kiln intake there is a precalciner with 4 burners, the purpose of which is to lower the degree of decarbonation of the kiln, the dimensions of the kiln, heat and refractory consumption. There is a main burner at the head of the kiln. The material reaches a temperature of approximately 1450 ^{0}C in the clinkering reaction.

On leaving the kiln the clinker enters a cooler that operates with a flow of air coming from fans. The heat resulting from cooling (tertiary air), return (to) the cyclone tower where it is used to lower fuel consumption as much as possible. After cooling, the clinker is transported by buckets to the storage silos, with capacities of 15,000 and 35,000 tons.

Off gases from the cooler continue to an electrostatic precipitator that retains the dust, releasing only the gases to the atmosphere.

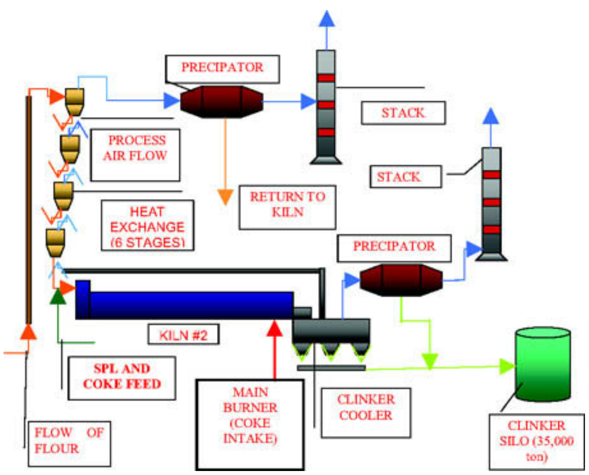


Figure 3. Schematic Flowchart for Kiln II

SPL Addition System

During the test period, SPL feed was done using big-bags that were poured into a screw feeder that directed the material to the kiln. Presently the SPL addition system used at Cimento Poty S/A is pneumatic, where the greatest gain was the elimination of possible contacts by employees involved with the unloading of the big-bags, and fugitive emissions of SPL to the environment.

Cimento Poty S/A invested about US$ 300,000 to implement the pneumatic system to guarantee, besides the points listed above, greater control of the addition of SPL to the clinker kiln.

Presently all transport of SPL is done using silo trucks with a capacity of 27 tons and it rigorously obeys Brazilian Legislation for transportation of hazardous cargoes, as well as the SPL Management Guideline of Alcoa – Spent Potlining Management Standards and Guideline, which imposes technical conditions for transport, handling, and storage of SPL so as not to generate conditions harmful to health, to employees safety, and to the environment. Figure 4 shows a simplified layout of the pneumatic transport system used at Cimento Poty S/A

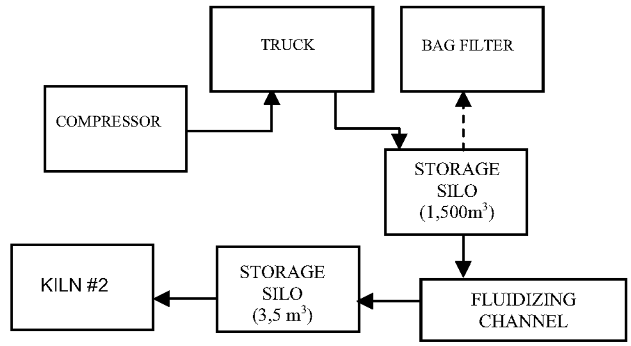


Figure 4. Simplified Layout of the Pneumatic Transport System

Applicable Environmental Legislation

The National Environmental Council of Brazil – CONAMA, in the use of the responsibilities conferred on it, considering the need for defining specific procedures, criteria, and technical aspects for environmental permitting of coprocessing of wastes in rotary clinker kilns for cement production, published resolution number 264 on 26 August 1999.

Overall, the environmental permitting process described in this resolution comprises sis stages:

II – Burning Feasibility Study – BFS [EVQ – Estudo de Viabilidade de Queima in Portuguese];
III – White Test Plan;
III – White Test Report;
IV – Burn Test Plan;
V – Burn Test Report;
VI – Risk Analysis

Of the basic criteria for the use of wastes the resolution considers, for purposes of coprocessing in clinker-production kilns, wastes able to be used as replacement for raw material and/or for fuel, provided that the process conditions ensure adherence to the technical requirements and to the parameters set in the present resolution in question, verified on the basis of the practical results of the proposed burn test plan.

Environmental Control and Results of Atmospheric Emissions

As part of the environmental permitting, for the coprocessing of SPL, in the year 2000 Cimento Poty S/A conducted emissions tests to verify the adequacy of the levels of emissions versus the limits set by CONAMA Resolution N$^{\underline{0}}$ 264/1999. Thus, tests were conducted without SPL processing (White Test) and with SPL (Black Test), so that the actual impacts of coprocessing on the levels of atmospheric emissions could be evaluated. The results are described in table 3.

Table III. Limits set by CONAMA Resolution N⁰ 264 of 1999

Parameters	White Test (corrected to 7% O_2, dry basis)	Burn Test (corrected to 7% O_2, dry basis)	Legal Limits (corrected to 7% de O_2, dry basis)
Hydrochloric Acid (HCl)	0.34 Kg/h	0.09 Kg/h	1.8 Kg/h
Hydrochloric Acid (HF)	< 0.03 mg/Nm³	< 0.04 mg/Nm³	5.0 mg/Nm³
CO (Carbon Monoxide)	156 ppmv	<98.9 ppmv	100 ppmv
Particulate Matter (corrected to 11%, dry basis)	267 mg/Nm³	35.3 mg/Nm³	70 mg/Nm³
THC (expressed as propane)	< 0.1 ppmv	3.0 ppmv	20 ppmv
Mercury (Hg)	< 0.002 mg/Nm³	< 0.001 mg/Nm³	0.05 mg/Nm³
Lead (Pb)	<0.005 g/Nm³	<0.0019 mg/Nm³	0.35 mg/Nm³
Thallium (Tl)	< 0.035mg/Nm³	< 0.0019 mg/Nm³	0.10 mg/Nm³
Tálio (Tl)	< 0.005 mg/Nm³	< 0.0019 mg/Nm³	0.10 mg/Nm³
(As+Be+Co+Ni+Se+Te)*	0.51 mg/Nm³	0.02 mg/Nm³	1.4 mg/Nm³
(As+Be+Co+Cr+Cu+Mn+Ni+Pb+Sb+Se+Sn+Te+Zn)*	4.73 mg/Nm³	0.150 mg/Nm³	7.0 mg/Nm³

* Metals monitored: As (arsenic), Be (beryllium), Co (cobalt), Ni (nickel), Se (selenium), Te (tellurium), Cr (chrome) Cu (copper), Mn (manganese), Sb (antimony), Sn (antimony) e Zn (zinc)

Results were considered satisfactory overall. Because of the process control that coprocessing requires, some parameters even improved versus the White Test. This improvement in the process control is one of the gains recorded after the start of coprocessing of SPL at Cimento Poty S/A.
The value for particulate matter exceeded the standard set in the White Test. Various steps were taken to correct a problem that was localized in nature and that did note permanently compromise coprocessing. Accordingly, maintenance actions on the electrostatic precipitator of kiln 2 were intensified to promote improvement in efficiency of the treatment system. The outcome of the action plan was seen in the burn test, where the value obtained for emissions of particulate matter was better than that in the white test.
In accordance with section VIII, article 28, item II of CONAMA Resolution N⁰ 264/1999, the limit of 100 ppmv may be exceeded, for CO, as long as values measured for THC do no exceed 20 ppmv, in terms of hourly average, and that the upper limit for CO of 500 ppmv, corrected to 7% O_2 (dry basis), is not exceeded at any instant.
The results of the analyses of atmospheric emissions in the kiln II process stack at Cimento Poty S/A, show that SPL coprocessing consistently meets the limits set by the applicable resolution. Table 4 shows the results over the years.

Table IV. Levels of atmospheric emissions over the years with SPL coprocessing, compared to the limits in CONAMA Resolution N⁰ 264 of 1999

Parameters	2001 (corrected to 7% O_2, dry basis)	2002 (corrected to 7% O_2, dry basis)	2003 (corrected to 7% O_2, dry basis)	Legal Limits (corrected to 7% O_2, dry basis)
Hydrochloric Acid (HCl)	0.020 Kg/h	0.145 Kg/h	0.106 Kg/h	1.8 Kg/h
Hydrochloric Acid (HF)	0.034 mg/Nm³	0058 mg/Nm³	0037 mg/Nm³	50 mg/Nm³
CO (Carbon Monoxide)	95 ppmv	<989 ppmv	2002 ppmv	100 ppmv
Particulate Matter	4188 mg/Nm³	2516 mg/Nm³	324 mg/Nm³	70 mg/Nm³
THC (expressed as propane)	001 ppmv	231 ppmv	1031 ppmv	20 ppmv
Mercury (Hg)	0000061 mg/Nm³	< 0001 mg/Nm³	0005 mg/Nm³	005 mg/Nm³
Lead (Pb)	0034 mg/Nm³	0011 mg/Nm³	00471 mg/Nm³	035 mg/Nm³
Thallium (Tl)	0.014 mg/Nm³	0.035 mg/Nm³	<0,0075 mg/Nm³	0.10 mg/Nm³
(As+Be+Co+Ni+Se+Te)	< 0.00009 mg/Nm³	< 0.0016 mg/Nm³	< 0.0075 mg/Nm³	0.10 mg/Nm³
(As+Be+Co+Cr+Cu+Mn+Ni+Pb+Sb+Se+Sn+Te+Zn)	0.019 mg/Nm³	0.0338 mg/Nm³	0.0656 mg/Nm³	1.4 mg/Nm³
Hydrochloric Acid (HCl)	0.039 mg/Nm³	<0.017 mg/Nm³	<0.015 mg/Nm³	Não Aplicável
Hydrochloric Acid (HF)	6.52 mg/Nm³	0.345 mg/Nm³	0.3341 mg/Nm³	7.0 mg/Nm³

One of the reactions proposed for the destruction of the cyanide in high-temperature processes is hydrolysis and later oxidation:

$$2CN^{-} + H_2O + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 2NO + 2OH^{-} \quad (1)$$

Evaluation of the Characteristics of the Cement and Clinker

To evaluate possible impacts of SPL coprocessing on the characteristics of the cement, leaching, solubilization, and heavy-metals tests were conducted on samples of cement and clinker processed without SPL and samples of the same materials processed with SPL.
Contents of metals in the clinker produced using SPL do no differ significantly from those obtained in clinker produced without SPL. No limit set by NBR 10004 was exceeded in the leaching tests. The solubilization tests verified that the constituents that exceeded the limits of NBR 10004 are the same in clinkers and cements produced with SPL and without the use of SPL. The only exceptions were fluorine, the limit for which was exceeded in the clinker and cement produced with SPL, and mercury, for clinker processed with SPL, but it is important to note that the classification of all the materials analyzed did not change with the use of SPL. It was observed that 99.9% of fluoride was chemically fixed by the cement.

Advantages of Coprocessing - Environmental and Non-Financial Aspects

Elimination of an Environmental Liability

Elimination of an environmental liability can be considered the main advantage of SPL coprocessing. Since the start of operation of the plant, all SPL generated by ALUMAR was always stockpiled on closed lots designed to properly stockpile this waste. Figure 5 show the forecast for coprocessing off the SPL liability, with the estimate that in 2008 the amount recycled will be equal to the amount generated.

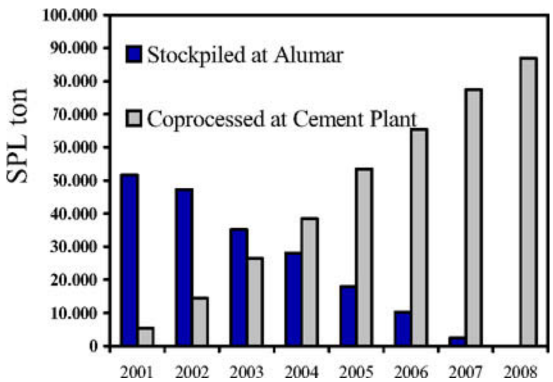


Figure 5. Estimated disposal of SPL liability with estimated rate of recycling of 1,000 ton/month

Reduced NO_x Generation

With the reduction in the operating temperature of the clinker kiln at Cimento Poty S/A there was a proportionate reduction in NO_x generated in the kiln. NO_x is monitored continually as indicator of kiln temperature. The greater the temperature inside the kiln the greater the concentration of NO_x formed by the oxidation reaction of free N_2 (nitrogen) in the air with excess O_2 (oxygen) in the kiln. Since the NO_x formation reaction is endothermic (it consumes energy/heat to react) the drop in the temperature implies a shift in the chemical reaction to the right side resulting in decrease in the formation of NO_x as shown in the reaction described below.

$$\frac{1}{2}N_2 + \frac{x}{2}O_2 \underset{\Delta}{\longleftrightarrow} NO_x \tag{2}$$

Before the use of SPL the fluctuation in NO_x concentration was 800 – 900 ppm at the kiln outlet. After the start of coprocessing the average dropped to 500 – 600 ppm.

Improved Environmental Control

One of the most important conditions for permitting of a process for SPL coprocessing is the guarantee of environmental control for the facility. Accordingly it is necessary to harmonize with the requirements of CONAMA Resolution N$^{\underline{0}}$ 264/1999. To meet the cited Resolution and to improve control of the process, Cimento Poty S/A purchased a continuous gas analyzer to monitor emissions from the stack for kiln II. The investment was approximately US$ 150,000 and the parameters analyzed are: Oxygen (O_2), Carbon Monoxide (CO), Oxides of Nitrogen (NO_x), Total Hydrocarbons (THC). Monitoring of particulate matter was already done using opacimeters installed on the stack, but, in any case, there was a need intensify maintenance to guarantee reliability of the equipment.

Greater Social Involvement

As part of the permitting process at Cimento Poty S/A the method for SPL coprocessing, as well as its relevant point and advantages, it was submitted to the authorities, the environmental, agency, and the local population (Sobral, State of Ceará), so that coprocessing enjoyed the consensus of everyone.

After authorization, by the environmental agency, Cimento Poty S/A developed an Environmental Education Plan whose main goal is to involve the local community in activities and projects that seek the Sustainable Development of the Region. Accordingly, the Environmental Education Plan of Cimento Poty S/A includes projects for planting and recovery of stripped areas, implementation of selective sampling, talks on safety on the job, in transit, and health.

Besides community involvement overall, there was greater closeness and greater technical support with the state environmental agency.

Advantages of Coprocessing - Economic Aspects

Besides the advantage of eliminating the environmental liability, as described above, SPL coprocessing has economic advantages in the cement production process, due to its physicochemical characteristics that allow greater production efficiency in clinker kilns.

Reduce Thermal Load – Energy Saving

For the productive process, the main advantage from the use of SPL, incorporated into the raw material, is reduction in the thermal load in the piping of the clinker kiln. This is due to fluxing property of the fluoride, found in the SPL composition, which lowers the melting point in the clinkering process. The reduction observed in the process at Cimento Poty S/A was approximately 80 ^{0}C (from 1450 ^{0}C to 1370 ^{0}C).

With the drop in temperature it was noted that the heat consumption of the kiln dropped on average 10 Kcal/Kg of clinker produced. For an average daily coke consumption of 280 ton/day, this represents approximate savings of 3.7 tons/day.

Consumption of Lower-Cost Raw Material

Another economic gain that can listed was making if feasible for Cimento Poty S/A to consume coke with high sulfur content, a cheaper fuel, without negatively influence the level SO_2 emissions, monitored on the stack for the clinkering process. With the lower temperature, part of the sulfur is incorporated into the clinker instead of oxidized. Average SO_3 composition in the clinker, before coprocessing, was approximately 1.6% by mass. After the use of SPL this value was 2.0%. Before the use of SPL the coke used had between 4 and 5% sulfur in the composition; presently the average sulfur content in the coke is 7%, forecast to reach 10% with the replacement by fluid coke, as fuel, in the clinkering process. The reaction for absorption of SO_3 in the clinker can be described in two stages:

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3 \tag{3}$$

$$SO_3 + CaO \longrightarrow CaSO_4 \tag{4}$$

The use of high-sulfur-content fuels, like petcoke, can supply the need for SO_3 in the mineralization of the clinker. Even with the increase in the coke's sulfur content, glue formation was not observed in the ducts as a consequence in the rise in concentration of alkalis in the kiln atmosphere.

Greater Stability in the Process

With the use of SPL improvement in the stability of the process was also observed. The fluxing element, fluoride, functions as a catalyst acting in the reaction for the formation of minerals among a CaO and SiO_2, Al_2O_3 and Fe_2O_3, avoiding the formation of undesirable free CaO. The presence of free CaO reduces the mechanical strength of the clinker due to reduction in the percentage of formation of minerals (mainly C_3S – $3CaO.SiO_2$, tricalcium silicate).

When there is a high concentration of free CaO in the kiln it is necessary to reduce production in the kiln to re-establish process equilibrium.

Knowing the theory of attack on the kiln refractory due to the increase in alkalis found in the SPL, Cimento Poty worked proactively with the supplier to develop a new refractory the withstood the new process conditions. The porosity of the refractory used before the use of SPL fluctuated between 16 and 20%. The current range of fluctuation is 12.5 to 15.5%.

Besides porosity, room-temperature compression strength also improved. The compression index for the previous refractory was 45 to 90 MPa (mega Pascal) and for the brick developed it is 70 to 110. The height of the firebrick was changed, increasing 10%.

All these changes did not alter the refractoriness of the brick, which remained 1760 ^{0}C. Service life, under normal process conditions, went from 6 to 10 month.

Saving in Raw Material

On of the main parameter monitored in the quality of the cement is SO_3 content. The specification to be achieved is 3% by mass of the product. Generally, in the cement production process at Cimento Poty S/A, the clinker produced has on average 1.6% SO_3 in the composition and it is necessary to add gypsum to correct the product. With the use of coke with higher sulfur content, and with the fixing through the reduction in temperature, the average SO_3 in the clinker rose to 2.0%. Thus, the amount of gypsum necessary to correct the clinker dropped. On average 5%gypsum was added in relation to the cement. After the use of SPL the addition o f gypsum dropped to 3.5%.

Remarks Relevant to SPL Coprocessing

Increase in "Setting" time

Setting time may be defined as time for stiffening of the product. Depending on the needs of the client, this parameter is extremely important. Some clients prefer cement with longer setting time due to the long distances between the place of preparation of the cement and the site of use. In other cases, shorter setting times are required mainly in the construction of large structures. After the use of SPL the fluctuation in the setting time of the cement of Cimento Poty S/A rose about 1h to 1:30h. Figure 6 shows the behavior of setting time and compression strength as a function of fluoride content.

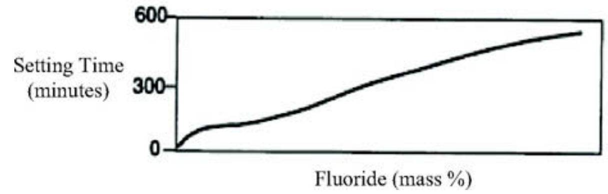


Figure 6. Fluctuation in Setting Time and Compression Strength as a Function of the Fluctuation in Fluoride

Increase in alkaline Equivalent

The increase in alkalis in the clinker can entail loss of final compression strength of the cement at 28 days. The percentage of sodium with SPL rose from 0.25 to 0.50, thus the Alkaline Equivalent, percentage of K_2O*0.638+ %Na_2O, rose from 0.90 to 1.1%. However Cimento Poty S/A increased the saturation of the flour (ratio between CaO and oxides of metals) from 98% to 101%, thus C_3S, responsible for the strength of the cement, rose from 68% to 73%. With this change in process at Cimento Poty S/A, it continued with the same value for mechanical compression strength of 36 MPa.

Maintenance of Piping

Based on the high abrasiveness of the SPL, an increased was noted in the number of maintenance interventions in the pneumatic transport system. The observations include holes in piping, mainly at joints. The pneumatic transport system is made entirely of carbon steel. Cimento Poty has built concrete boxes lining the piping on the curves, but the development of another material that better adapts to the material transported is necessary.

Conclusion

SPL coprocessing in the cement industry has clearly shown how the management of industrial wastes can make a waste considered class I into a secondary fuel and partially replace raw material. As shown previously the SPL added significant and important values to the clinkering process at Cimento Poty S/A. Some examples of financial values can be cited like: the purchase of cheaper input (fuel), savings in raw material, and greater stability in the process.

Besides economic values, coprocessing also brought non-financial values like bringing together of the production process, of the local community, and of the state environmental agency, through the Environmental Education Program established as a requirement for the operating permit. Moreover, it made environmental control more rigorous and reduced the generation of NO_x.

From the environmental point of view, it was observed that there was no significant change in atmospheric emissions levels. Even with the increase in the SPL feed rate, fluoride emissions, for example, remained well below the limit imposed by applicable environmental legislation, and cyanide emissions reached almost negligible concentrations.

It is also extremely important to emphasize how adequate knowledge of coprocessing can prevent some possible negative aspects that SPL coprocessing could entail. Note, by way of example, development of a new refractory that minimized attack by alkalis, and consequently an increase in service life from 6 to 10 months. The increase in the saturation of the clinker was another change that prevented the loss of final mechanical compression strength at 28 days. Strength was maintained at 36 MPa while the theory demonstrated that if there were no intervention the quality of the cement would be compromised.

References

- BRASIL, Ministério do Meio Ambiente, Conselho Nacional do Meio Ambiente, CONAMA, Resolução N ^{0} 264 de 26.08.1999

- ABNT NBR 10.004, Associação Brasileira de Normas Técnicas (ABNT). "NBR 10.0004 Resíduos Sólidos – Classificação", Rio de Janeiro, 1987

- ASTM C150, "Standard Specification for Portland Cement", Anual Book of ASTM Standards 4, volume 04.01; 1983

- IPT – Instituto de Pesquisa e Tecnología, "Relatório N$^{\underline{0}}$ 69691 – "Levantamento do Estado da Arte e Possibilidade do uso de SPL no coprocessamento de clínquer Portland", (not published paper), 2000

- Alcoa Aluminio S. A – "Spent Potlining Management Standards and Guidelines", (not published paper), 2000

- Centurione, Sérgio; Kihara, Yushiro; Maringolo, Vagner; Munhoz, Flávio A. da Cunha; Pecchio, Marcelo, "Avaliação do Grau de Mineralização do Clínquer", Associação Brasileira de Cimento Portland, 5$^{\underline{0}}$ Congresso Brasileiro de Cimento, 1999.

- Companhia Cearense de Cimento Portland – CCCP, "Relatório de Caracterização química, ensaios e lixiviação e solubilização de Coque de Petróleo e Residuo" (not published paper), 2000

- Companhia Cearense de Cimento Portland – CCCP, Relatório de Amostragem de Chaminé", (not publisher paped), 2000

- Companhia Cearense de Cimento Portland – CCCP; "Relatório de Amostragem de Chaminé", (not published paper), 2001

- Companhia Cearense de Cimento Portland – CCCP, "Relatório do Teste de Queima para Aumentar a Adição do Resíduo Revestimento Gasto de Cubas RGC Proveniente da Alumar-São Luís no Forno de Cimento W2 da Cimento Poty S/A – Unidade Sobral", (not published paper), 2003

- Companhia Cearense de Cimento Portland – CCCP, "Relatório de Amostragem de Chaminé", 2002