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Effectiveness of cement-based systems for stabilization and solidification of spent pot liner inorganic fraction

B.I. Silveira*, A.E.M. Dantas, J.E.M. Blasques, R.K.P. Santos

Chemical Engineering Department, Federal University of Pará, Pará, Brazil

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Abstract

Approximately 7000 t of spent pot liner (SPL) wastes are generated annually from activities associated with Alumínio Brasileiro S.A. (ALBRAS) plant located at Barcarena, Pará state, Brazil. The inorganic fraction of SPL contains high level of toxic compounds like cyanide and fluoride; its safe disposal has been the subject of serious discussions in Brazil. This study evaluated the option of a cement-based stabilization/solidification system as an effective means for safe disposal of SPL inorganic fraction in the field. The studies were carried out with concrete hexagonal blocks manufactured with a constant mass of 10% (w/w) of waste, 20% (w/w) of cement, and varied percentages of water, coarse aggregate, sand, and additives. The concrete matrices porosity and compressive strength were controlled by using microsilica (MS) and superplaticizer (SP). The results showed an average pH values for the SPL inorganic fraction and fragmented blocks of 10.2 and 11.1, respectively. Mixing the waste with concrete ingredients the solidification/stabilization effectiveness for the leachable cyanides and fluorides were of 59.33 and 57.95%, respectively. The results showed that the water/cement (W/C) ratio reduction through superplasticizer addition improved the compressive strength and the required value of 35 MPa was reached with blocks manufactured with 10 and 15% (weight of cement) of microsilica, after 28 days of curing time.

Keywords: Stabilization/solidification; Fluoride; Cyanide; Spent pot liner; Solid waste

1. Introduction

Cement-based solidification/stabilization is a process in which inorganic reagents react with certain waste components and/or among themselves to form chemically stable solids which are capable of developing mechanical resistance. The major inorganic reagent is

* Corresponding author. Fax: +55-91-211-1291.
E-mail address: inacio@ufpa.br (B.I. Silveira).

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portland cement, which upon addition of water produces a hardened paste. This paste binds together aggregates and other substances to form concrete and stabilize wastes [1,2]. This technology is currently being used to treat a wide variety of wastes containing contaminants as metals, organics, organo-metallics, soluble salts, etc. [1,3,4] and showed to be effective in reducing the mobility of cyanide and soluble fluoride salts, when a bottom ash spent pot liner (SPL) waste was mixed with soil, binder, and water [5].

SPL is a solid waste generated by the aluminum industry during the reduction of alumina to aluminum metal in electrolytic cells. This waste has a composition highly variable (e.g. cyanides, fluorides, organics and metals), but the components of greatest concern environmentally are cyanides and soluble fluoride salts [6]. In Brazil, aluminum industries generate about 35,000 t of SPL a year, seven of which are generated by Alumínio Brasileiro S.A. (ALBRAS) industry, located at Barcarena, Pará state. ALBRAS has stored the SPL in controlled deposits, but it is conscious that in the long term needs solutions environmentally more viable. Seeking a reduction in the quantity of this waste, the SPL generated in each cell was separated into two fractions: one fraction, about 25 t, contained the majority of the carbonaceous material, while the other, about 28 t, consisted primarily of inorganic components. The characterization of the SPL inorganic fraction showed a relatively low cyanide content [7], what stimulated the ideas of recycling of this fraction as part of the raw material in the concrete manufacturing.

There are many factors that affect the concrete matrix structure, such as the quality and quantity of cement, water, aggregates, additives, curing time, etc. all of them thoroughly studied [1,2,8–15]. The stabilization/solidification of cyanides and fluorides contained in the SPL inorganic fraction depends on the concrete structure and must be studied before using this waste as part of raw material in civil construction industry.

The purpose of this work was to evaluate the effectiveness of concrete matrices, prepared with different mix proportions, in stabilizing and solidifying hazardous constituents, leachable cyanides and fluorides, contained in the SPL inorganic fraction.

From published data about concrete preparation with material commonly used in the region [15], a concrete composition was selected so that a high compressive strength and low permeability matrices could be manufactured. The concrete effectiveness in immobilizing/solidifying the hazardous waste constituents and the compressive strength were controlled through the addition of microsilica (MS) and superplasticizer (SP) to the mixture.

The studies were carried out with concrete hexagonal blocks manufactured with a constant values of 10% (w/w) of SPL inorganic fraction, 20% (w/w) of cement, varied percentages of water, coarse aggregate, and sand, and with different proportions of additives. The total leached cyanide and fluoride and compressive strength results were used to evaluate the concrete matrices performance.

2. Materials and methods

2.1. Sampling and sample preparation

The waste to be studied was arranged in piles and the material was collected by simple random sampling [16–18]. The waste mass collected was fragmented and homogenized,

random sampling again was used. This material was taken to laboratory and was prepared for analysis according to extraction procedure requirements.

2.2. pH measurement

Solid sample pH was measured by electrometric procedure according to the EPA Method 9.045C [19], where 20 g of solid sample was placed in a 50 ml beaker, added 20 ml of reagent water, and at $25 \pm 1\,^{\circ}C$ stirred the suspension for 5 min. The solid waste suspension was let stand for about 15 min, filtered off aqueous phase, and measured the pH.

2.3. Total and leachable cyanides

Total cyanide extraction was performed according to the procedure established by EPA SW 846 Method 9.010B [20] with a solid sample size of 10 g and a distillation time of 1 h and 15 min. Leachable cyanides were determined using EPA SW 846 Method 9.013 [21], where a representative aliquot of 25 g of solid sample was placed in a 1000 ml bottle, added 500 ml of water and 5 ml of 50% (w/v) of NaOH aqueous solution, and at room temperature stirred the suspension for 16 h. The pH of the extract was monitored and maintained above 12 throughout the extraction step and subsequent filtration. After filtration, the extract was submitted to a distillation as established by EPA SW 846 Method 9.010B [20], and the distilled cyanides were evaluated using a selective ion electrode method, Orion Model 94-06 [22].

2.4. Total and leachable fluorides

Total fluoride extraction was done by alkaline fusion, where 0.5 g of the solid waste was mixed with 15 ml of 10% (w/w) $Ca(OH)_2$ solution and heated until completely dry. To this mixture was added 3 g of solid NaOH and heated to $800\,^{\circ}C$ for 30 min. After cooling, 40 ml of distilled water were added, heated gently until complete dissolution. Then 40 ml more of distilled water were added and distilled [23,24]. Leachable fluorides were determined using ASTM Method D3987-85 [25], where a representative aliquot of 70 g of solid sample was placed in a 2000 ml container, added 1400 ml of water, and at room temperature stirred the suspension for 18 h. After filtration the extract was submitted to a distillation procedure as established by the standard methods [26] and the distilled fluorides evaluation carried out through the ion selective electrode method, instrument Orion Model 96-09 [27].

2.5. Preparation of concrete blocks

Concrete hexagonal blocks, measuring 15 cm side, 8 cm thickness, and about 17 kg of weight, were prepared following the civil construction standard procedures, i.e. (i) concrete dosage: based on the literature recommendations [8–15], it was selected the amount of cement, water, coarse aggregates and sand to be used. This selection took into account the low permeability of the concrete matrix and the blocks compressive strength of 35 MPa, as required by Brazilian Standards [28]; (ii) mixing the components in a cement mixer

Table 1
Composition of the mixtures used to manufacture the concrete blocks

Batch numbre	Water (% w/w)	Sand (% w/w)	Coarse aggregate (% w/w)	Water/cement ratio	SP (% by weight of cement)	MS (% by weight of cement)
1	10.00	25.64	34.36	0.50	0	0
2	9.00	18.30	42.70	0.45	0	0
3	8.00	17.70	44.30	0.40	1.5	0
4	7.00	16.70	46.30	0.35	2.5	0
5	8.22	18.58	43.20	0.41	2.0	5.0
6	8.22	18.58	43.20	0.41	2.0	10.0
7	8.22	18.58	43.20	0.41	2.0	15.0

until homogenization; (iii) molding and condensing the mixture in a metallic mold; and (iv) curing the blocks for 28 days. In the concrete dosage the following materials were used: (i-1): Portland Cement CPI32, produced by "Nassau Cimentos do Brasil S.A.", and composed of (%): SiO_2, 20.10; Al_2O_3, 4.99; Fe_2O_3, 2.95; CaO, 64.63; MgO, 3.39; SO_3, 3.05; insoluble matter, 0.89. (i-2): coarse aggregates commonly used in the region, with a size distribution that varied from 0.5 to 1 cm, 3 to 4% (w/w) of which under 0.5 cm, a moisture content that varied from 1 to 2%, and a dried sand, considered as a medium size distribution in the commercial standard. (i-3): distilled water, the studies were conducted with blocks prepared in seven batches, whose percentages of water, cement, coarse aggregate, sand and additives are showed in Table 1. In all batches was used a constant value of 10% (w/w) of SPL inorganic fraction, and 20% (w/w) of cement. To meet the stabilization/solidification requirements for soluble salts and the compressive strength of 35 MPa a superplasticizer (SP) and microsilica (MS) were added to the concrete mixture, both viewing the water/cement ratio (W/C) and matrix permeability reduction and the compressive strength increase. These products were kindly supplied by Sika Co.

2.6. Blocks compressive strength and cyanide and fluoride analysis

Once ready, the blocks were removed from the molds, and left curing at room temperature for 28 days. For all batches, blocks with a curing time of 7 and 28 days were submitted to a compressive strength tests as established by Brazilian Standards [28]. One block of each batch, with a curing time of 28 days, was fragmented, homogenized, and prepared according to the extraction procedure requirements for cyanide and fluoride analysis.

3. Results

In Table 2 are presented the pH values of the SPL inorganic fraction, the leaching liquid used for cyanides extraction (US EPA 9013 Method), and the aqueous medium used for fluorides extraction (ASTM 3987 Method) from SPL inorganic fraction.

Table 2 also shows the results of the SPL inorganic fraction total cyanides and fluorides, total leached cyanides and fluorides extracted in basic conditions (US EPA 9.013 Method) and in aqueous medium (ASTM 3987 Method).

Table 2
Contents of total cyanides and fluorides in the SPL inorganic fraction, and total leached cyanides and fluorides for extracts obtained in basic conditions (US EPA 9.013 Method) and in aqueous medium (ASTM 3987 Method)

Test	pH	Total cyanides (mg/kg)	Total fluorides (mg/kg)
Solid waste (SPL inorganic fraction)	10.2	598.72	92,500.00
Extract (US EPA 9013 Method)	>12	342.94	67,591.53
Extract (ASTM 3987 Method)	10.2–10.6	290.75	33,095.13

Table 3
Changes of the pH for fragmented blocks (US EPA 9.045C Method) and for leaching liquid used for fluorides extraction in aqueous medium (ASTM 3987 Method)

Batch number	pH (USEPA 9045)	Leaching in aqueous medium (ASTM 3987)	
		Initial pH	Final pH
1	11.0	11.0	11.50
2	10.5	10.5	11.40
3	11.0	11.0	11.76
4	11.5	11.5	11.90
5	11.0	11.0	11.76
6	11.5	11.5	11.96
7	11.0	11.0	11.94

Table 3 shows the changes of the pH for fragmented blocks (US EPA 9.045C Method) and for leaching liquid used for fluorides extraction from the fragmented blocks in aqueous medium (ASTM 3987 Method).

Table 4 shows the results of the leachable cyanides (US EPA 9.013 Method) and fluorides (ASTM 3987 Method) concentrations for fragmented concrete blocks prepared according to the composition shown in Table 1, after 28 days of curing time. This table also shows the cyanide and fluoride solidification/stabilization effectiveness by different concrete matrices.

Table 4
Behavior of the leachable cyanides (US EPA 9.013 Method) and fluorides (ASTM 3987 Method) concentrations for fragmented concrete blocks prepared according to the composition showed in Table 1, after 28 days of curing time

Batch number	Leached cyanides (mg/kg)	Effectiveness of cyanide S/S (%)	Leached fluorides (mg/kg)	Effectiveness of fluoride S/S (%)
1	19.404	43.42	1391.66	57.95
2	24.126	29.65	1959.86	40.78
3	15.228	55.60	2001.46	39.52
4	16.182	52.82	1930.16	41.68
5	13.948	59.33	1882.76	43.11
6	20.684	39.70	2581.46	22.00
7	20.106	41.38	2078.16	37.21

Table 5
Changes in compressive strengths for concrete blocks prepared with mixtures of compositions showed in Table 1 and curing times of 7–28 days

Batch number	Compressive strength (MPa)	
	Curing time 7 days	Curing time 28 days
1	11.90	15.80
2	18.88	20.80
3	20.33	24.39
4	N/A	N/A
5	16.30	30.75
6	29.70	37.64
7	29.61	37.87

N/A: not available.

In Table 5 are presented the results of the changes in the compressive strengths for concrete blocks prepared with mixtures of compositions showed in Table 1 and curing times of 7–28 days.

4. Discussion and conclusions

The pH results (Tables 2 and 3), showed that the SPL inorganic fraction and fragmented concrete blocks prepared with different compositions are highly alkaline, with a value of 10.2 and an average value, after 28 days of curing time, of 11.1, respectively. The leaching liquid pH for cyanides extraction, as much for the solid waste, as for the fragmented blocks, as required by US EPA 9013 Method, was maintained above 12, and for fluorides extraction following ASTM 3987 Method varied from 10.2 to 10.6 for the solid waste and from 10.5 to 11.96 for the fragmented blocks.

Table 2 results showed that in the extraction test conditions, only part of the waste cyanides and fluorides was leached, regardless of extraction liquid pH. The total leached cyanides and fluorides values obtained at pH > 12 are higher than those obtained in aqueous medium, where there was no pH correction. For the fluorides, this can be explained by the increase of the solubility with the increase of the extraction liquid pH, but with respect to the cyanides we believe that this difference is much more related to the losses of cyanides to the environment in lower pH than the increase of the solubility in higher pH values.

Table 4 results showed that mixing 10% (w/w) of SPL inorganic fraction, with total leached cyanide of 342.94 mg/kg, with cement, water, coarse aggregate, sand, and additives to manufacture concrete blocks, after 28 days of curing time, fragmented blocks total leached cyanide changed from 13.948 mg/kg for batch 5 to 24.126 mg/kg for batch 2, what represents a cyanide S/S effectiveness of 29.65% for the batch 2 and 59.33% for the batch 5. Similarly, mixing 10% (w/w) of the SPL inorganic fraction, total leached fluorides of 33,095.13 mg/kg, with other components to manufacture concrete blocks, after curing and blocks fragmentation, the fluorides mobility was substantially reduced, with a fluoride S/S effectiveness of 22.00% for the batch 6 and 57.95% for the batch 1. This table results also showed that a change in the W/C from 0.5 to 0.35 (see Table 1) did not reduce the leachable

fluorides mobility, that was better stabilized/solidified by concrete matrices prepared with $W/C = 0.5$. This can be explained by considering that in matrices without microsilica and with higher water content, the soluble fluoride can react more easily with calcium hydroxide given off by the cement hydration and form insoluble calcium fluoride, which is not detected by leaching tests.

The water/cement ratio changes through the addition of different superplasticizer contents (see Table 1) almost did not influence the total leachable cyanides S/S, but when 2% (by weight of cement) of superplasticizer were combined with 5% (by weight of cement) of microsilica there was a significant cyanide immobilization of 59.33% for the batch 5. In part, this can be explained by considering that the microsilica is a mineral composed of ultrafine, amorphous glassy spheres of silicon dioxide (SiO_2), produced during the manufacture of silicon or ferrosilicon, and the ultrafine spheres fill the gaps between the cement grains, refining the voids in the fresh concrete. Besides, microsilica is a pozzolan, what means that it reacts with the calcium hydroxide given off by the cement hydration and forms more of the calcium silicate hydrates that bind concrete together. Due to the very fine size of the microsilica particles, the crystalline structure formed by this reaction is also very fine and fills the void spaces within the matrix. This densifies the whole concrete structure, resulting in increased strength and significant reductions in permeability.

Table 5 results showed that the water/cement ratio reduction through superplasticizer addition improved the compressive strength, and the Brazilian Standards of 35 MPa was reached in the batches 6 and 7, with addition of 10 and 15% (by weight of cement) of microsilica, respectively, after 28 days of curing time.

From the results of this work it can be concluded that mixing SPL inorganic fraction with other ingredients to manufacture concrete blocks following civil construction standards, cyanides and fluorides mobility was substantially reduced, and the S/S effectiveness for the leachable cyanides and fluorides were 59.33 and 57.95%, respectively. For the waste recycling these values are not so impressive considering the treatment standards for hazardous wastes proposed by US EPA [29], but in practice they could be better because the concrete blocks fragmentation, as required by leaching test procedures, broken the concrete matrices monolithic effects [1]. Also, it can be concluded that was possible to manufacture concrete hexagonal blocks that supported a compressive strength of 35 MPa using a percentage of 10% (w/w) of SPL inorganic fraction as part of the raw material.

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